

3.942 (Polymer Physics) Problem Sets

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October 29, 2025

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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.

$$\begin{aligned} M_n &= M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i} \\ &= M_0 \cdot \frac{100 \cdot 10 + 1000 \cdot 100 + 10\,000 \cdot 10}{10 + 100 + 10} \end{aligned}$$

$$\boxed{M_n = 1675M_0}$$

□

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

Answer.

$$\begin{aligned} M_w &= M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i} \\ &= M_0 \cdot \frac{100^2 \cdot 10 + 1000^2 \cdot 100 + 10\,000^2 \cdot 10}{100 \cdot 10 + 1000 \cdot 100 + 10\,000 \cdot 10} \end{aligned}$$

$$\boxed{M_w \approx 5473M_0}$$

□

c) What is the polydispersity index of this distribution?

Answer.

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

$$\boxed{D \approx 3.27}$$

□

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

$$\frac{10\,000 \cdot n_{10\,000}}{\sum_i i n_i} = w_{10\,000} = \frac{10\,000 \cdot 10}{100 \cdot 10 + 1000 \cdot 100 + 10\,000 \cdot 10} = \boxed{49.8\%}$$

□

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,

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

$$\boxed{N \approx 99880}$$

□

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

$$C_\infty = \frac{\langle R^2 \rangle}{nl^2}$$

$$= \frac{(200)^2}{(199760)(0.154)^2}$$

$$\boxed{C_\infty \approx 8.44}$$

□

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

$$R_{\max} = nl \cos(70.5/2) = (199760)(0.154 \text{ nm}) \cos(70.5/2) \approx 25\,122 \text{ nm}$$

Thus, the Kuhn length l_k is

$$l_k = \frac{\langle R^2 \rangle}{R_{\max}}$$

$$= \frac{(200)^2}{25122}$$

$$\boxed{l_k \approx 1.59 \text{ nm}}$$

It follows that the number N_k of Kuhn steps is

$$N_k = \frac{R_{\max}}{l_k}$$

$$= \frac{25122}{1.59}$$

$$\boxed{N_k \approx 15800}$$

□

- d) Estimate the persistence length for this polymer.

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

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

□

- 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

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

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

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

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

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

□

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

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

□

- b) Simplify your expression for B by assuming $\varepsilon/k_{\text{B}}T \ll 1$. *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 $x = \varepsilon/k_{\text{B}}T$ 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

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

□

- 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

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

□

2 Solution Thermodynamics

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Collaborator(s): None

Total grade: **Corrected**

- 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

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

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

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

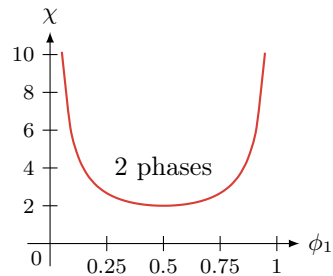
$$\boxed{\chi = \frac{1}{2} \left(\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} \right)}$$

□

- 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) $N_1 = N_2 = 1$.

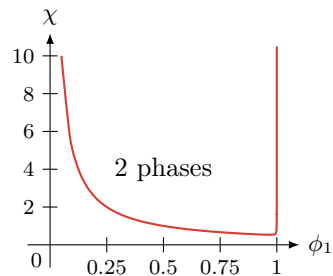
Answer.



□

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

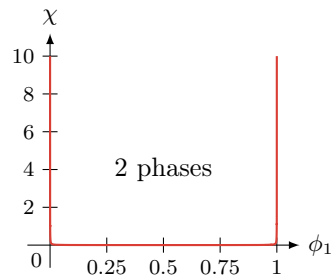
Answer.



□

- iii) $N_1 = N_2 = 1000$.

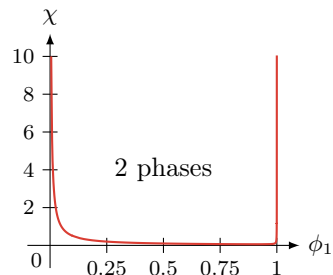
Answer.



□

- 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 a regular solution of two small molecules. Since the components are chemically similar, we obtain a symmetric graph. The critical point falls at $\chi_c = 2$, so super high temperatures are not necessary to guarantee mixing.

In case (ii), demixing is much more likely the more species 1 we have. Thus, we have an asymmetric graph. Indeed, full mixing is only possible if we either have very little of the polymeric component 2, or if the temperature is very high. This is because when we have polymers in solution at $c < c^*$, the molecules tend to coil up in localized areas, leading to out-of-equilibrium concentration domains throughout the solution. Unless we add enough thermal energy to access mostly elongated polymers, we will not be able to distribute the concentration of monomers evenly in the solution. Mathematically, this behavior is also consistent with the greater entropy gain for the system when ϕ_1 is increased from zero as the $\phi_1/N_1 = \phi_1/1$ prefactor is larger than the $\phi_2/N_2 = \phi_2/1000$ prefactor.

From case (iii), we can see that it is very hard to form a polymer blend at any concentration. Here, 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 one 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. \square

- 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

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

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. Note that an alternative way to derive the above expression is by noting that the critical concentration occurs at the bottom of the spinodal, and thus we could solve $0 = \partial\chi/\partial\phi_1$. 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

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

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

$$\phi_{1,c} = \frac{\sqrt{1}}{\sqrt{1} + \sqrt{1}}$$

$$\boxed{\phi_{1,c}(N_1 = N_2 = 1) = 0.5}$$

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

$$\boxed{\chi_c(N_1 = N_2 = 1) = 2}$$

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

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

$$\boxed{\phi_{1,c}(N_1 = 1 < N_2) = \frac{\sqrt{N_2}}{1 + \sqrt{N_2}}}$$

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

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

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

$$\phi_{1,c} = \frac{\sqrt{N}}{\sqrt{N} + \sqrt{N}}$$

$$\boxed{\phi_{1,c}(N_1 = 1 < N_2) = 0.5}$$

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

$$\boxed{\chi_c(N_1 = 1 < N_2) = \frac{2}{N}}$$

□

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. We have from class that

$$\begin{aligned}\chi &= \frac{v_0}{k_{\text{B}}T} (\delta_1 - \delta_2)^2 \\ &\approx \frac{(6.02 \times 10^{23} \text{ mol}^{-1})(100 \text{ \AA}^3)(18.7 \text{ MPa}^{1/2} - 16.2 \text{ MPa}^{1/2})^2}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \\ &= \frac{(6.02 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(6.25 \times 10^6 \text{ Pa})}{2476.38 \text{ J mol}^{-1}} \\ \chi &\approx 0.152\end{aligned}$$

□

- 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,

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

It follows that

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

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. □

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

Answer. Recall from Q1e that

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

We are interested in the specific case of high molecular mass polymers ($N_2 \rightarrow \infty$) dissolving in a solvent ($N_1 = 1$). Thus, taking these limits in the above equation, the χ value below which *any* high MW polymer will dissolve in a solvent must be

$$\begin{aligned} \chi_c &= \frac{1}{2} \left(\frac{1}{\sqrt{1}} + \frac{1}{\sqrt{\infty}} \right)^2 \\ &= \frac{1}{2} (1 + 0)^2 \\ \chi_c &= \frac{1}{2} \end{aligned}$$

□

- 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,

$$A = \chi T \approx (0.152)(298 \text{ K}) \approx 45.3 \text{ K}$$

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

$$N_{\text{PS}} = \frac{10^5}{104.15} \approx 1000 \qquad N_{\text{PB}} = \frac{10^4}{54.09} \approx 200$$

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

$$\begin{aligned} T_c &= \frac{A}{\chi_c} \\ &= \frac{2A}{\left(N_{\text{PS}}^{-1/2} + N_{\text{PB}}^{-1/2} \right)^2} \\ &= \frac{2(45.3 \text{ K})}{\left(1000^{-1/2} + 200^{-1/2} \right)^2} \\ T_c &\approx 9000 \text{ K} \end{aligned}$$

□

- 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 ($\text{MPa}^{1/2}$)	15.1	16.8	18.6	19.0	20.3

Answer. From Q3a, $\chi_c \rightarrow 1/2^+$ 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. Additionally, note that the units in the above table are such that if we plug the numbers in directly, everything will cancel. Let's begin.

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

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{HpH})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{HpH}})^2 \\ &= 0.34 + \frac{195.9 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 15.1 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2} \end{aligned}$$

and hence PDMS dissolves in *n*-heptane.

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

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{HpH})}{RT} (\delta_{\text{PS}} - \delta_{\text{HpH}})^2 \\ &= 0.34 + \frac{195.9 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (18.7 \text{ MPa}^{1/2} - 15.1 \text{ MPa}^{1/2})^2 \\ \chi &\approx 1.4 > \frac{1}{2} \end{aligned}$$

and hence PS does not dissolve in *n*-heptane.

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

$$\begin{aligned} \chi &= 0.34 + \frac{V_m(\text{CyH})}{RT} (\delta_{\text{PDMS}} - \delta_{\text{CyH}})^2 \\ &= 0.34 + \frac{108.5 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}} (14.9 \text{ MPa}^{1/2} - 16.8 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.50 \approx \frac{1}{2} \end{aligned}$$

and hence PDMS may dissolve in cyclohexane (within error).

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{CyH})}{RT}(\delta_{\text{PS}} - \delta_{\text{CyH}})^2 \\ &= 0.34 + \frac{108.5 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(18.7 \text{ MPa}^{1/2} - 16.8 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.50 \approx \frac{1}{2}\end{aligned}$$

and hence PS may dissolve in cyclohexane (within error).

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{PhH})}{RT}(\delta_{\text{PDMS}} - \delta_{\text{PhH}})^2 \\ &= 0.34 + \frac{29.4 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(14.9 \text{ MPa}^{1/2} - 18.6 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.50 \approx \frac{1}{2}\end{aligned}$$

and hence PDMS may dissolve in benzene (within error).

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{PhH})}{RT}(\delta_{\text{PS}} - \delta_{\text{PhH}})^2 \\ &= 0.34 + \frac{29.4 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(18.7 \text{ MPa}^{1/2} - 18.6 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence PS dissolves in benzene.

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{CHCl}_3)}{RT}(\delta_{\text{PDMS}} - \delta_{\text{CHCl}_3})^2 \\ &= 0.34 + \frac{80.7 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(14.9 \text{ MPa}^{1/2} - 19.0 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.89 > \frac{1}{2}\end{aligned}$$

and hence PDMS does not dissolve in chloroform.

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{CHCl}_3)}{RT}(\delta_{\text{PS}} - \delta_{\text{CHCl}_3})^2 \\ &= 0.34 + \frac{80.7 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(18.7 \text{ MPa}^{1/2} - 19.0 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.34 \leq \frac{1}{2}\end{aligned}$$

and hence PS dissolves in chloroform.

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{Ace})}{RT}(\delta_{\text{PDMS}} - \delta_{\text{Ace}})^2 \\ &= 0.34 + \frac{74.0 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(14.9 \text{ MPa}^{1/2} - 20.3 \text{ MPa}^{1/2})^2 \\ \chi &\approx 1.2 > \frac{1}{2}\end{aligned}$$

and hence PDMS does not dissolve in acetone.

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

$$\begin{aligned}\chi &= 0.34 + \frac{V_m(\text{Ace})}{RT}(\delta_{\text{PS}} - \delta_{\text{Ace}})^2 \\ &= 0.34 + \frac{74.0 \text{ cm}^3 \text{ mol}^{-1}}{2476.38 \text{ J mol}^{-1}}(18.7 \text{ MPa}^{1/2} - 20.3 \text{ MPa}^{1/2})^2 \\ \chi &\approx 0.42 \leq \frac{1}{2}\end{aligned}$$

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 coil up 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 less interaction energy between the two phases when everything is straight because only a few unlike monomers are near each other. Thus, these forces compete with each other and seek a happy medium. □

- 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?

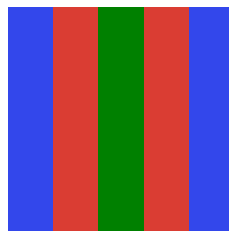
Answer. I think the morphology of choice will be parallel cylinders in an almost hexagonal grid, with each junction in the grid being the center of a star polymer. This would allow each cylinder to be composed of the like strands of three different molecules. \square

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

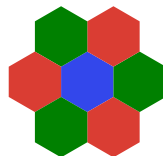
- i) A system where all the χ parameters are positive and equal and the degree of polymerization of each arm is sufficiently large so that microphase separation occurs;

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

For the ABC triblock copolymer, no particular component has a preference for any other component, so the system will relax to the configurations that minimize deformation of the chain. This will orient chains roughly parallel to each other and form lamellae.



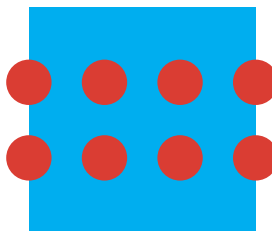
For the star polymer, as mentioned, we will form a kind of hexagonal lattice.



\square

- 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. (Indeed, the negative χ_{AC} parameter will lead the system to pay the deformation energy in order to maximize A-C contacts.) Thus, for both architectures, the expected morphology for a 33% distribution is cylinders, as follows. Note that the A/C blue/green mixed phase has been colored cyan.



\square

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. A grafted polymer system becomes a *brush* when the density of chains on the surface surpasses the density within a lone coil. Since the area of a coil goes as R_g^2 , the critical grafting density will be when there is 1 chain per every R_g^2 units of area on the surface, or when

$$\rho = \frac{1}{R_g^2}$$

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. \square

- 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. To answer this question, we will mimic the full analysis of the free energy change for diblock copolymers carried out in class. Let's begin.

Let State 1 denote n pure polymer chains in a melt, and let State 2 denote those n polymer chains bound to a surface of total area A . Recall from Q5a that for State 2 to be a brush, the density $\rho = n/A$ will have to be large enough for chains to overlap and stretch away from the surface. Note that even if there are more than n chains in the melt, the change in free energy is only dependent on the change in state of the n chains that make the transition to State 2, so we can well consider only these n chains to be our system under study. The change ΔG in free energy *per polymer chain* upon transitioning from State 1 to State 2 is

$$\Delta G = \Delta H - T(S_2 - S_1)$$

As in class, $S = -3k_B R^2/2Na^2$, where R is the end-to-end distance, N is the number of segments in the polymer chain, and a is the step length. Additionally, from the problem statement, $\Delta H = -\varepsilon$. We can think of this change in energy as analogous to the interfacial energy $\gamma_{AB}\Sigma$, and observe that there is no mixing energy because we only have one component in both states (it's just this component free, vs. this component bound to a surface). One additional complication is the excluded volume effects that occur when polymers become attached to the surface. From class, this adds an additional $k_B T v N^2/2HD^2$ term to the change in enthalpy, where v is the excluded volume, H is the average height to which the polymers extend away from the surface in State 2, and D is the average distance between polymer chains on the surface. Thus, we have

$$\begin{aligned} \Delta G &= -\varepsilon + \frac{k_B T v N^2}{2HD^2} - T \left[-\frac{3k_B H^2}{2Na^2} + \frac{3k_B (N^{1/2}a)^2}{2Na^2} \right] \\ &= -\varepsilon + \frac{k_B T}{2} \left(\frac{vN}{a^3} + \frac{3H^2}{Na^2} - 3 \right) \end{aligned}$$

Now the decrease in free energy for any individual chain will obviously be greatest when the chain only benefits from the sticking enthalpy and doesn't have to stretch away from it's entropically ideal conformation. However, this may not be best for the system, since this would limit the number of chains that can gain the sticking enthalpy *for the system*. Thus, before optimizing, we

need to switch to evaluating the free energy change of the whole system. It follows that the total change in free energy of the system (i.e., once all n chains have bonded to the surface) is

$$\Delta G_{\text{sys}} = -n\varepsilon + \frac{nk_{\text{B}}T}{2} \left(\frac{vN}{a^3} + \frac{3H^2}{Na^2} - 3 \right)$$

At this point, we have expressed the free energy change in terms of two variables: The number of chains n , and the height H . However, these variables are not independent of one another, since they are related through $n/A = \rho = H/Na^3$. Thus, we could express the above equation in terms of either n or H and optimize over that...or we could express the above equation in terms of the variable we're actually interested in (the optimal grafting density ρ), since it also happens to be related to both n and H ! Thus, let's change variables with the substitutions $H = \rho Na^3$ and $n = \rho A$.

$$\begin{aligned} \Delta G_{\text{sys}} &= -\rho A\varepsilon + \frac{\rho A k_{\text{B}}T}{2} \left[\frac{vN}{a^3} + \frac{3(\rho Na^3)^2}{Na^2} - 3 \right] \\ &= -\rho A\varepsilon + \frac{A k_{\text{B}}T}{2} \left(\frac{vN\rho}{a^3} + 3Na^4\rho^3 - 3\rho \right) \end{aligned}$$

It follows that the optimal grafting density is

$$\begin{aligned} 0 &= \frac{\partial \Delta G}{\partial \rho} \\ &= -A\varepsilon + \frac{A k_{\text{B}}T}{2} \left(\frac{vN}{a^3} + 9Na^4\rho^2 - 3 \right) \\ \frac{9}{2}k_{\text{B}}TNa^4\rho^2 &= \varepsilon - \frac{k_{\text{B}}TvN}{2a^3} + \frac{3k_{\text{B}}T}{2} \\ k_{\text{B}}TNa^4\rho^2 &\approx \varepsilon - \frac{k_{\text{B}}TvN}{a^3} \\ \rho &\approx \left(\frac{\varepsilon}{k_{\text{B}}TNa^4} - \frac{v}{a^7} \right)^{1/2} \end{aligned}$$

where from the third to the fourth line, we have made the approximation that we can ignore factors on the order of unity. \square

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

Answer. Substituting into the above, we have

$$\begin{aligned} \frac{H}{Na^3} &\approx \left(\frac{\varepsilon}{k_{\text{B}}TNa^4} - \frac{v}{a^7} \right)^{1/2} \\ H &\approx \left(\frac{Na^2\varepsilon}{k_{\text{B}}T} - \frac{vN^2}{a} \right)^{1/2} \end{aligned}$$

Thus, $\boxed{H \propto N^\nu \text{ for } \nu \in (0.5, 1).}$ \square

3 Dilute Solutions

Name: Steven Labalme

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Collaborator(s): Isa Pan, Jordan Gray

Total grade: 100/100

- 10/21: 1. (35 pts) Estimate, as a function of molecular weight, the characteristic diffusion time τ for a polymer in a solution of viscosity η , where τ is defined as

$$\tau = \frac{R^2}{D}$$

where R is the size of the polymer (function of N and l_k) and D is the diffusion coefficient (remember D is different for different coil models). Determine τ for polymer coils in a theta-solvent for...

- a) Freely-draining (Rouse-like) model;

Answer. Recall from class that in general,

$$R = N^\nu l_k \qquad D_t = \frac{k_B T}{f}$$

Additionally, in the specific case of a theta solvent and free-draining model, we have respectively that

$$\nu = \frac{1}{2} \qquad f = N\xi^*$$

Therefore,

$$\tau = \frac{(N^{1/2}l_k)^2}{k_B T / N\xi^*}$$

$$\tau = \frac{N^2 l_k^2 \xi^*}{k_B T}$$

□

- b) Non-draining (Zimm-like) model.

Answer. Everything from Q1a holds except that we are now in a non-draining regime, so $f \neq N\xi^*$ but rather

$$f = 6\pi\eta R_H$$

Additionally, we have in general that

$$R_H = \gamma R_g = \frac{\gamma R}{\sqrt{6}}$$

Therefore,

$$\tau = \frac{R^2}{k_B T / (6\pi\eta\gamma R / \sqrt{6})}$$

$$\tau = \frac{\sqrt{6}\pi N^{3/2} l_k^3 \eta \gamma}{k_B T}$$

□

- c) You are performing a GPC packed with beads with diameter $5\text{ }\mu\text{m}$. Estimate the time for a DNA molecule with $D = 0.01\text{ }\mu\text{m}^2/\text{s}$ to diffuse a distance equal to a bead diameter.

Answer. We want to find the time τ it takes for diffusion to displace a polymer with $D = 0.01\text{ }\mu\text{m}^2/\text{s}$ by $\Delta r = 5\text{ }\mu\text{m}$. Per class,

$$\begin{aligned}\langle \Delta r^2 \rangle &= 6D\tau \\ \tau &= \frac{(5\text{ }\mu\text{m})^2}{6(0.01\text{ }\mu\text{m}^2\text{ s}^{-1})} \\ \tau &\approx 417\text{ s}\end{aligned}$$

□

2. (30 pts) Ultracentrifugation is a means to separate polymers. The same is placed in a tube and spun quickly to exert a centrifugal force on the solution. Three main forces on a polymer molecule are

$$\begin{aligned}F_s &= m\omega^2 r && \text{(Sedimentation)} \\ F_b &= -m_0\omega^2 r && \text{(Buoyancy / Archimedes' Principle)} \\ F_d &= -\zeta U && \text{(Drag)}\end{aligned}$$

where m is the mass of a single polymer, ω is the angular speed of the centrifuge, r is the stator arm of the centrifuge, m_0 is the mass of fluid displaced by the polymer (given by $m_0 = m\rho v$), v is the partial specific volume of a polymer, ρ is the solvent density, ζ is the drag on the polymer, and U is the speed at which the polymer moves.

- a) Assuming the polymer has reached its terminal velocity (constant velocity, sum of forces equal zero), calculate the velocity U as a function of $\omega, r, v, \zeta, \rho, M, N_A$, where M is the molar mass of the polymer and N_A is Avogadro's number.

Answer. By the definition of molar mass,

$$M = mN_A$$

Thus, since the polymer has no net force acting on it, we have by Newton's second law that

$$\begin{aligned}0 &= F_s + F_b + F_d \\ &= m\omega^2 r - m_0\omega^2 r - \zeta U \\ &= \frac{M}{N_A} \cdot \omega^2 r - \frac{M}{N_A} \cdot \rho v \omega^2 r - \zeta U\end{aligned}$$

$$U = \frac{M\omega^2 r}{N_A \zeta} (1 - \rho v)$$

□

- b) Calculate how U scales with M for a flexible polymer in a theta solvent. *Hint:* Don't forget that $\zeta(M)$! Also, v is not a function of M .

Answer. For an impenetrable sphere (which is how a flexible polymer would behave in a theta solvent), we have from class that $\zeta \propto R_H \propto R_g \propto R \propto N^\nu$. Since $N \propto M$ and $\nu = 1/2$ in a theta solvent, it follows that $\zeta \propto M^{1/2}$. Thus, in the context of the above equation, $U \propto M/M^{1/2}$, or

$$U \propto M^{1/2}$$

□

3. (35 pts) This problem will explore viscometry of polymer solutions and data obtained from Lee and Tripathi (2005) in their microfluidic rheometer, discussed in Lecture 11.

- a) The authors measure an intrinsic viscosity of a polyethylene glycol solution to be 44.6 mL/g. The MW of the polymer is 35 000 g/mol. Estimate the radius of gyration of the molecule assuming a good solvent. Please use the experimental value of γ from the Lecture 10 slides.

Answer. From the Lecture 10 slides, $\gamma = 1.5$ for a linear, monodisperse polymer in a good solvent. PEG tends to be linear, hence that selection, and there is no other provided experimental γ value for a linear polymer, so I believe I have to assume it's monodisperse?? Thus, based on our theory from class,

$$\begin{aligned}\langle R_g^2 \rangle^{1/2} &= \sqrt[3]{\frac{3M[\eta]}{10\pi N_A \gamma^3}} \\ &= \sqrt[3]{\frac{3(35\,000\text{ g mol}^{-1})(44.6\text{ mL g}^{-1})}{10\pi(6.02 \times 10^{23}\text{ mol}^{-1})(1/1.5)^3}} \\ \boxed{\langle R_g^2 \rangle^{1/2} \approx 9.4\text{ nm}}\end{aligned}$$

□

- b) What is your estimate for the overlap concentration c^* for this polymer?

Answer. From class, we have that

$$\begin{aligned}c^* &= \frac{2.5}{[\eta]} \\ &= \frac{2.5}{44.6\text{ mL g}^{-1}} \\ \boxed{c^* \approx 5.6 \times 10^{-2}\text{ g/mL}}\end{aligned}$$

□

- c) Assuming the solvent has a viscosity of 1.1 Pa s, calculate the viscosity of the polymer solution at $c = c^*/2$.

Answer. From class, the approximation of η in terms of $[\eta]$ to one term is

$$\begin{aligned}\eta &= \eta_s (1 + c \cdot [\eta]) \\ &= (1.1\text{ Pa s}) \left[1 + \frac{1}{2}(0.056\text{ g mL}^{-1})(44.6\text{ mL g}^{-1}) \right] \\ \boxed{\eta = 2.5\text{ Pa s}}\end{aligned}$$

□

- d) The authors measured the intrinsic viscosity of the MW = 10 000 g/mol sample in water to be 11.9 mg/mL and in a water/methanol mixture to be 22.3 mg/mL. What can you conclude about the relative solvent quality of these solvents?

Answer. From class, intrinsic viscosity obeys the following proportionality.

$$[\eta] \propto M^{3\nu-1}$$

Thus, if the intrinsic viscosity is higher in the water/methanol mixture, ν must be higher for this solvent as well. Therefore, water/methanol is a better solvent than water. □

4 Networks

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- 10/30: 1. Rayleigh ratios (R_θ) were obtained at 25 °C for a series of solutions of a polystyrene sample in benzene, with a detector situated at various angles θ to the incident beam of unpolarized, monochromatic light with wavelength $\lambda = 546.1$ nm. The results of these measurements appear below.

Polystyrene concentration (g dm ⁻³)	10 ⁴ × R_θ /m ⁻¹ measured at $\theta =$			
	30°	60°	90°	120°
0.50	72.3	69.4	66.2	64.3
1.00	89.8	85.7	81.3	78.2
1.50	100.8	97.1	92.0	88.1
2.00	108.7	103.8	99.7	95.9

Under the conditions of the measurements, the Rayleigh ratio and the refractive index of benzene are 46.5×10^{-4} m⁻¹ and 1.502 respectively, and the refractive index increment for the polystyrene solutions is 1.08×10^{-4} m³/kg. The density of polystyrene is 1.05 g/cm³, the density of benzene is 0.8787 g/cm³, the molecular weight of benzene is 78.11 g/mol, and the molar volume of benzene can be approximated as its molecular weight divided by its density.

Using a Zimm plot, determine...

- The weight-average molar mass of the polystyrene sample.
 - The average radius of gyration, $\langle R_g^2 \rangle^{1/2}$ of the polystyrene molecules in benzene at 25 °C.
 - The second virial coefficient A_2 and χ for the polystyrene-benzene interaction at 25 °C.
2. a) Find the relation between the stress σ and the strain λ for a piece of ideal rubber undergoing biaxial extension. Assume the rubber has initial area A_0 and thickness d_0 , and let the final area be $A = \lambda^2 A_0$.
- b) Use the result from part (a) to calculate the relation between the pressure p of an ideal gas inside a balloon made from an ideal elastomer, expanded to a radius $R = \lambda R_0$, where R_0 is the initial radius. Use the following version of the **Young-Laplace equation** to relate the excess pressure Δp (inside the balloon minus outside) to the stress in the rubber, where d is the thickness of the balloon skin.
- $$\Delta p = \frac{2d\sigma}{R}$$
- Empirically, it often seems harder to “get started” blowing up a balloon, than to blow it up further beyond a certain point; explain this observation based on your result for p versus λ .
- c) Finally, suppose you have a balloon made of an ideal elastomer that is inflated to a reasonable size with an ideal gas at room temperature. If the temperature of the balloon plus gas system is then increased to 100 °C, will the balloon expand, contract, or stay the same size? Justify your answer.
3. Consider a cross-linked polyelectrolyte gel in a reservoir of water. Our goal is to understand the swelling behavior of this gel. A polyelectrolyte gel consists of a polymer where some (or all) monomers have ionizable functional groups that may or may not be charged. For each group that is charged, a corresponding counterion of opposite charge must exist to maintain overall charge neutrality. Calculations with charges are complicated, so for this problem we will consider a system composed of solvent, free particles (counterions), and polymers. The number of free particles is regulated by the degree of ionization f . Again, for the sake of the problem, ignore any actual charges and only consider the effect of the polyelectrolyte as giving rise to (uncharged) counterions in the system.

- In the absence of charges ($f = 0$), what is the thermodynamic condition that determines the equilibrium swelling ratio of the gel? Describe the qualitative competition between free energy terms in the context of Flory-Rehner theory.
- Now allowing for the possibility of charges ($f > 0$), write the Flory-Huggins free energy for this system. Remember that the polymer is a big cross-linked network with an enormous degree of polymerization N . Again, we are treating counterions like uncharged particles, so do not explicitly include Coulombic energies or other electrostatic interactions. *Hint:* You can imagine that the counterions act as a gas which exerts a hydrostatic pressure on the “walls” of the gel related to the number of counterions and the volume of the system by the ideal gas law.
- What is the chemical potential of the solvent in part (b) in terms of χ and f ?
- Construct a Flory-Rehner type theory to describe the swelling of this system, based on our description of Flory-Rehner theory in class.
- From your expression in part (d), identify which terms can be ignored and why. Show that the final perturbed dimension of the gel scales as

$$L \propto f^{1/2} N$$

where L is the swollen size of one side of the (isotropic) gel, and N is the degree of polymerization.

- We now are interested in using our polyelectrolyte gel as an actuator that can expand and contract in response to an electrical signal, recognizing that applying a voltage to the system will change the degree of dissociation f (Figure 1a).

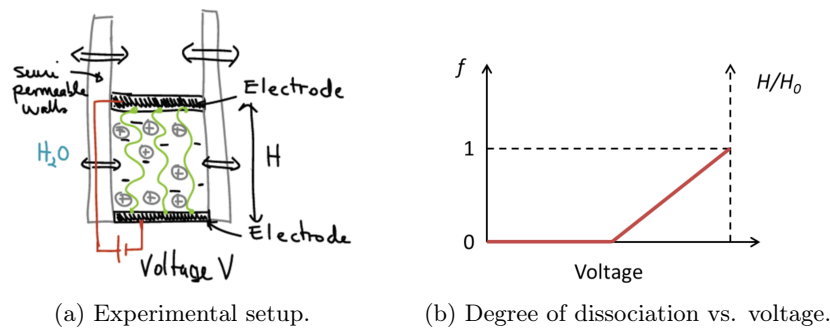


Figure 1: Polyelectrolyte gel as a piston.

The change in the number of dissociated ions is shown in Figure 1b. On the same graph, sketch the relative height H/H_0 of the piston as a function of the applied voltage, and derive a scaling law that relates the number of dissociated ions to the height H of the gel divided by the height H_0 of the gel in the absence of voltage. Assume the cross-sectional area of the gel is fixed at a value A by the walls of the apparatus.

References

Lee, J., & Tripathi, A. (2005). Intrinsic viscosity of polymers and biopolymers measured by microchip. *Analytical Chemistry*, 77(22), 7137–7147. <https://doi.org/10.1021/ac050932r>