3.942 (Polymer Physics) Problem Sets

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1   The Macromolecule

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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.

$$M_{\mathrm{n}} = M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i}$$
$$= M_0 \cdot \frac{100 \cdot 10 + 1000 \cdot 100 + 10\,000 \cdot 10}{10 + 100 + 10}$$
$$\boxed{M_{\mathrm{n}} = 1675 M_0}$$

☐

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

Answer.

$$M_{\mathrm{w}} = M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i}$$
$$= M_0 \cdot \frac{100^2 \cdot 10 + 1000^2 \cdot 100 + 10\,000^2 \cdot 10}{100 \cdot 10 + 1000 \cdot 100 + 10\,000 \cdot 10}$$
$$\boxed{M_{\mathrm{w}} \approx 5473 M_0}$$

☐

c) What is the polydispersity index of this distribution?

Answer.

$$Đ = \frac{M_{\mathrm{w}}}{M_{\mathrm{n}}}$$
$$\approx \frac{5473 M_0}{1675 M_0}$$
$$\boxed{Đ \approx 3.27}$$

☐

d) If you randomly chose a monomer in the solution, what is the chance that is 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,

$$a = \frac{l_k}{2}$$
$$= \frac{1.59}{2}$$
$$\boxed{a \approx 0.795\,\text{nm}}$$

□

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

Answer. Since the chain length is $R_{\text{max}} = 25\,122\,\text{nm}$ 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 $\boxed{\text{flexible}}$ 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

$$\langle R^2 \rangle = \left\langle \sum_{i=1}^{N_A+N_B} \mathbf{l}_i \cdot \sum_{j=1}^{N_A+N_B} \mathbf{l}_j \right\rangle$$

$$= \sum_{i=1}^{N_A+N_B} \sum_{j=1}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle$$

$$= \sum_{i=1}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \underbrace{\sum_{i=1}^{N_A+N_B} \sum_{\substack{j=1 \\ j \neq i}}^{N_A+N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle}_{0}$$

$$= \sum_{i=1}^{N_A} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=N_A+1}^{N_B} \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle$$

$$\boxed{\langle R^2 \rangle = N_A \ell_A^2 + N_B \ell_B^2}$$

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 $\boxed{\text{not}}$ 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

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

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

$$0 = \frac{\partial F}{\partial R}$$

$$= k_{\mathrm{B}}T\left(-\frac{aN^2}{R^3} + \frac{2R}{N\ell_k^2}\right)$$

$$\frac{aN^2}{R^3} = \frac{2R}{N\ell_k^2}$$

$$\frac{aN^3\ell_k^2}{2} = R^4$$

$$\boxed{R \approx a^{1/4}N^{3/4}\ell_k^{1/2}}$$

$\square$

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

$$U = \infty \qquad\qquad\qquad\qquad\qquad\qquad (r < b)$$
$$U = -\varepsilon \qquad\qquad\qquad\qquad\qquad\quad (b \leq r \leq \lambda b)$$
$$U = 0 \qquad\qquad\qquad\qquad\qquad\qquad (r > \lambda b)$$

a) Calculate the excluded volume B.

Answer. The excluded volume B is given by

$$B = -4\pi\int_0^\infty r^2\left[\exp\left(-\frac{U(r)}{k_{\mathrm{B}}T}\right) - 1\right]\mathrm{d}r$$

$$= -4\pi\left\{\int_0^b r^2[-1]\,\mathrm{d}r + \int_b^{\lambda b} r^2\left[\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) - 1\right]\mathrm{d}r + \int_{\lambda b}^\infty r^2[0]\,\mathrm{d}r\right\}$$

$$= -4\pi\left\{-\int_0^b r^2\,\mathrm{d}r + \left[\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) - 1\right]\int_b^{\lambda b} r^2\,\mathrm{d}r + 0\right\}$$

$$= -4\pi\left\{-\frac{b^3}{3} + \left[\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) - 1\right]\cdot\frac{b^3}{3}(\lambda^3 - 1)\right\}$$

$$= \frac{4}{3}\pi b^3\left\{1 - \left[\lambda^3\cdot\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) - \exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) - \lambda^3 + 1\right]\right\}$$

$$= \frac{4}{3}\pi b^3\left[-\lambda^3\cdot\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) + \exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) + \lambda^3\right]$$

$$\boxed{B = \frac{4}{3}\pi b^3\left[(1 - \lambda^3)\exp\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right) + \lambda^3\right]}$$

$\square$

b) Simplify your expression for B by assuming $\varepsilon/k_{\mathrm{B}}T \ll 1$. *Hint*: Expand the exponential.

Answer. The Taylor series expansion for e^x is

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

Given that $x = \varepsilon/k_{\mathrm{B}}T$ 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 $\mathrm{e}^x \approx 1 + x$ for small x. Applying this line of reasoning to the result from part (a) and simplifying then yields

$$B = \frac{4}{3}\pi b^3 \left[(1 - \lambda^3)\left(1 + \frac{\varepsilon}{k_{\mathrm{B}}T}\right) + \lambda^3 \right]$$

$$= \frac{4}{3}\pi b^3 \left[\left(1 + \frac{\varepsilon}{k_{\mathrm{B}}T} - \lambda^3 - \lambda^3 \cdot \frac{\varepsilon}{k_{\mathrm{B}}T}\right) + \lambda^3 \right]$$

$$= \frac{4}{3}\pi b^3 \left[1 + \frac{\varepsilon}{k_{\mathrm{B}}T} - \lambda^3 \cdot \frac{\varepsilon}{k_{\mathrm{B}}T} \right]$$

$$\boxed{B = \frac{4}{3}\pi b^3 \left[1 + (1 - \lambda^3)\frac{\varepsilon}{k_{\mathrm{B}}T} \right]}$$

$\square$

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

$$0 = \frac{4}{3}\pi b^3 \left[1 + (1 - \lambda^3)\frac{\varepsilon}{k_{\mathrm{B}}T} \right]$$

$$-1 = (1 - \lambda^3)\frac{\varepsilon}{k_{\mathrm{B}}T}$$

$$\boxed{T = \frac{\varepsilon}{k_{\mathrm{B}}}(\lambda^3 - 1)}$$

$\square$

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.

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

$$\frac{\partial^2 \Delta G_{\mathrm{mix}}}{\partial \phi_1^2} = 0$$

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

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) $N_1 = N_2 = 1$.
   ii) $N_1 = 1$ and $N_2 = 1000$.
   iii) $N_1 = N_2 = 1000$.
   iv) $N_1 = 10$ and $N_2 = 1000$.

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

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 polymer-polymer blend. Show your work.

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

b) Show explicitly that Flory's χ parameter is always positive for nonpolar moleucles 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.

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

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 $10^5 \, \mathrm{g/mol}$ and polybutadiene is $10^4 \, \mathrm{g/mol}$. 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.

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 $\delta_{PDMS} = 14.9\,\text{MPa}^{1/2}$ and which will dissolve polystyrene ($\delta_{PS} = 18.7\,\text{MPa}^{1/2}$) at room temperature.

Solvent	n-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

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.

   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?

   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;

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

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.

   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.

   c) What is the scaling of the brush height with degree of polymerization in the dense brush regime from Q4b(ii)?