3.942 (Polymer Physics) Problem Sets

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Contents

1 The Macromolecule

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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.
   b) Calculate the weight average molecular weight of this distribution.
   c) What is the polydispersity index of this distribution?
   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?

2. (25 pts) The root mean squared end-to-end distance $\langle R^2 \rangle^{1/2}$ of a poly(methyl methacrylate) (PMMA) molecule ($M_W = 10^7$ 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?
   b) Estimate C_∞ for this polymer.
   c) Estimate the Kuhn length and number of Kuhn segments for this polymer.
   d) Estimate the persistence length for this polymer.
   e) Is this PMMA a "flexible," "semi-flexible," or "rod-like" 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).
   b) Will your answer in (a) change if the chain has a random distribution of monomers A and B? Explain why or why not.

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.

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

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

   a) Calculate the excluded volume B.
   b) Simplify your expression for B by assuming $\varepsilon/k_\mathrm{B}T \ll 1$. *Hint*: Expand the exponential.
   c) Using your answer in (b), determine the Theta temperature for this system.