

# 1 The Macromolecule

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Collaborators: *None*

- 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.
  - 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 it 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  $C_\infty$  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  $\ell_A$  and  $N_B$  steps of Kuhn length  $\ell_B$ . 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  $\ell_k$  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  $R$ .
5. (25 pts) Consider monomers which interact via the following pairwise interaction potential, which is called a square well interaction:

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

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