

Solutions to problem set 6

Problem 1

Polyethylene glycol (PEG) as a freely-jointed chain.

- a) Each chemical repeat unit has a molecular mass (or “formula weight”) of 16 Da + 2 x 14 Da = 44 Da.
Therefore, for 1 kDa PEG we have $N = 1000 \text{ g/mol} / (44 \text{ g/mol}) = 23$ and for 100 kDa PEG we have $N = 100,000 \text{ g/mol} / (44 \text{ g/mol}) \approx 2270$.
- b) The maximum length (i.e. the contour length) of the chains is given by $L_C = N \cdot b = 92 \text{ \AA} \approx 9 \text{ nm}$ for 1 kDa PEG and $L_C \approx 900 \text{ nm}$ for 100 kDa PEG.
- c) The root mean squared end-to-end distance is given by $R_{ee} = b \cdot \sqrt{N} = 19.2 \text{ \AA} \approx 1.9 \text{ nm}$ for the 1 kDa PEG and $R_{ee} = 19 \text{ nm}$.
- d) Using that $R_g = R_{ee}/\sqrt{6} = b \cdot \sqrt{N}/\sqrt{6}$, we find $R_g \approx 0.8 \text{ nm}$ and $R_g \approx 8 \text{ nm}$ for 1 and 100 kDa PEG, respectively.
- e) Measuring M_w in Da (or equivalently g/mol), we find

$$R_g = \frac{1}{\sqrt{6}} b \cdot \sqrt{N} = \frac{1}{\sqrt{6}} b \cdot \sqrt{\frac{M_w}{44}} = \frac{1}{\sqrt{6}} 4 \text{ \AA} \cdot \sqrt{\frac{M_w}{44}} \approx 0.25 M_w^{0.5} \text{ \AA}$$

- f) Comparing to the result of Devanand and Selser (*Macromolecules*, 1991), the two expressions are quite similar. They find a prefactor of 0.215 \AA , while we find 0.25 \AA , which is only a relatively small deviation, given that our assumption of $b = 4 \text{ \AA}$ was somewhat *ad hoc*. More interestingly, the scaling exponent is slightly, but statistically significantly, different. The FJC finds an exponent of $1/2 = 0.5$, which is the typical scaling of the root-mean-squared-distance of Gaussian chains or random walks in general. The exponent of 0.583 ± 0.031 of Devanand and Selser is larger. Introducing excluded volume, due to the fact that two segments of the chain can not occupy the same space, gives rise to scaling exponents > 0.5 . In fact, a famous argument due to Flory gives a scaling exponent of $3/5 = 0.6$ for a random chain with excluded volume, which is within experimental error of empirical finding of Devanand and Selser.

Problem 2

Diffusion-limited reactions.

- a) In the diffusion-limited case we assume that diffusion is slow and that the monomer addition rate, $k_{on}[A_1]$, is very fast, so that almost as soon as a gap opens up, a monomer will 'drop in'. This means that $p(x)$ must drop almost to 0 above δ . If we integrate

$$0 = p(x) \frac{d}{dt} \sum_{n=0}^{\infty} P_n(t) \quad (1)$$

$$= -\frac{dj}{dx} - k_{on}A_1[p(x)H(x-\delta) - p(x+\delta)] + k_{off}[p(x-\delta) - p(x)] \cdot [1 - P_0(t)]$$

from δ to ∞ , we get

$$0 = j(\delta) - j(\infty) + k_{on}A_1 \int_{2\delta}^{\infty} p(x) \cdot dx - k_{on}A_1p_\delta + k_{off} - k_{off}p_\delta \quad (2)$$

$$= j(\delta) - \frac{dn_{av}}{dt} - k_{off}p_\delta$$

The second term, $j(\infty)$, vanishes according to earlier discussions in class, the third term vanishes because the probability that the gap reaches a size of 2δ is extremely small by the assumption that the monomer addition rate is very high, and the fourth and fifth terms together are the negative of the elongation rate. The last term cannot be ignored, even though in the diffusion limit p_δ is 0. This is because if the association rate is very high, then the dissociation rate must also be very high; otherwise, the equilibrium constant would be vanishingly small. Because $k_{off}p_\delta$ is not necessarily small, we write $k_{off} = K_c k_{on}$ in which case

$$k_{off}p_\delta = \frac{K_c k_{on} A_1 p_\delta}{A_1} = \frac{K_c}{A_1} \left(\frac{dn_{av}}{dt} + k_{off} \right)$$

using $\frac{dn_{av}}{dt} = k_{on}[A_1]p_\delta - k_{off}$. Substituting this into equation (1) and rearranging gives

$$\frac{dn_{av}}{dt} = \frac{j(\delta)}{1 + K_c/[A_1]} - \frac{K_c/[A_1]}{1 + K_c/[A_1]}$$

- b) If we assume that $[A_1] \gg K_c$ and that the off-rate constant is negligible, then the growth rate equals the flux (the rate at which a gap opens up). These two assumptions are reasonable if the actin monomer concentration is $\approx 30\mu M$, about 300 times greater than the critical concentration, and $k_{off} = 1.4s^{-1}$.