Problem set 6
(Hand in by July 6)

Problem 1

Polyethylene glycol (PEG) as a freely-jointed chain. PEG is a polymer that is often used in biophysical and biochemical applications. It consists of N repeating units of the formula $(\mathrm{O{-}CH_2{-}CH_2})_N$. We will assume that it can be modeled as a freely-jointed chain in which we assume the chemical repeat unit to be the segment length with a length $b = 4$ Å .

a) How many repeat units (i.e. what is N) for a 1000 g/mol and for a 100,000 g/mol PEG polymer chain?

b) What is the maximum length (i.e. the contour length) of the chains?

c) What are the root mean squared end-to-end distances?

d) What are the radii of gyration R_g? Hint: For a FJC the relationship between the root-mean-squared end-to-end distance R_{ee} and the radius of gyration R_g is $R_{ee} = \sqrt{\langle \vec{r}_{ee}^{\,2} \rangle} = \sqrt{6} \cdot R_g$.

e) Derive a general formula for the R_g of PEG as a function of molecular weight M_w (in g/mol or Daltons) using the assumptions above.

f) Devanand and Selser (*Macromolecules*, 1991) used light scattering to determine the R_g of different molecular weight PEG chains. They fitted their experimental data with a power law and found an empirical formula given by

$$R_g = 0.215\ M_w^{0.583 \pm 0.031}\ \text{Å}$$

Compare your results from the previous part to their formula. How well do they agree? Can you think of a reason for any observed differences?

Problem 2

Diffusion-limited Reactions. In class, we have discussed how the Brownian ratchet model can account for the polymerization speed of the cytoskeleton proteins actin and tubulin. We have also discussed how polymerization reactions can be **reaction-limited** or **diffusion-limited** and have derived the polymerization rate in the reaction-limited case to $v = \delta \frac{dn_{av}}{dt} = \delta \left(k_{on} [A_1] e^{-\frac{F\delta}{kT}} - k_{off} \right)$.
We will now turn our attention to the case of a diffusion-limited reaction.

a) Derive that the elongation rate in the diffusion-limited reaction case equals

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

with K_c being the critical monomer concentration, $[A_1]$ the monomer concentration of actin in a cell (30 micromolar) and j the flux (rate of gap opening).
Hint: Remember from class that we obtained for the reaction-diffusion reaction of the Brownian ratchet model:

$$0 = p(x)\frac{d}{dt}\sum_{n=0}^{\infty} P_n(t) = -\frac{dj}{dx} - k_{on}A_1[p(x)H(x-\delta) - p(x+\delta)] + k_{off}[p(x-\delta) - p(x)]\cdot[1 - P_0(t)]].$$

Integrate this from δ to ∞ to get started.

b) What form does the growth rate take on in the case of $[A_1] >> K_c$? Is this a reasonable assumption in the cell?