Solutions to problem set 7

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 g/mol / (44 g/mol) = 23 and for 100 kDa PEG we have N = 100,000 g/mol / (44 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 Å $\approx$ 9 nm for 1 kDa PEG and $L_C \approx$ 900 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 Å $\approx$ 1.9 nm for the 1 kDa PEG and R_{ee} = 19 nm.

d) Using that $R_g = R_{ee}/\sqrt{6} = b \cdot \sqrt{N}/\sqrt{6}$, we find $R_g \approx$ 0.8 nm and $R_g \approx$ 8 nm for 1 and 100 kDa PEG, respectively.

e) Measuring M_w in Da (or equivalently g/mol), we find

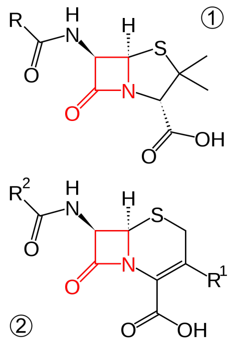
$$R_g = \frac{1}{\sqrt{6}} b \cdot \sqrt{N} = \frac{1}{\sqrt{6}} b \cdot \sqrt{\frac{M_w}{44}} = \frac{1}{\sqrt{6}} 4\text{Å} \cdot \sqrt{\frac{M_w}{44}} \approx 0.25 N^{0.5}\text{Å}$$

f) Comparing to the result of Devanand and Selser (*Macromolecules*, 1991), the two expressions are quite similar. They find a prefactor of 0.215 Å, while we find 0.25 Å, which is only a relatively small deviation, given that our assumption of b = 4 Å 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 $\pm$ 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.

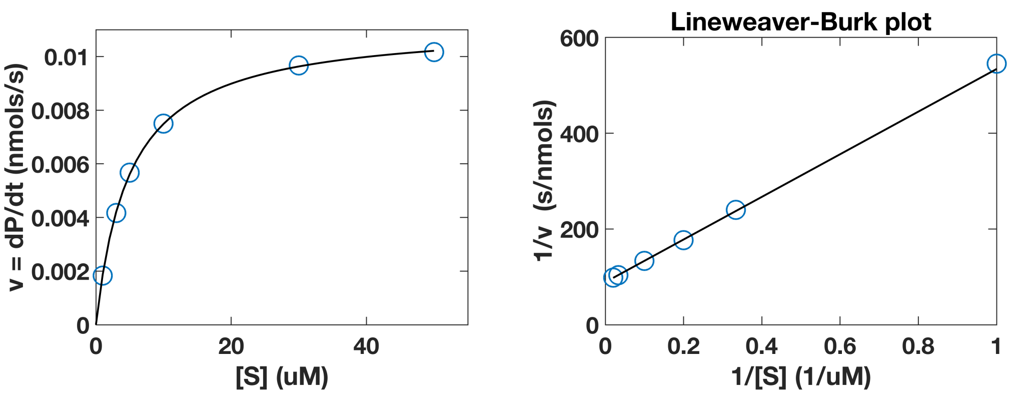
Problem 2

Michaelis-Menten for survival 1.

As a background, it is worth mentioning that the β-lactam antibiotics, which include penicillins (see figure, top) and cephalosporins (see figure, bottom) are the most widely used group of antibiotics. They work by inhibiting cell wall biosynthesis in the bacterial organism. Currently, resistance to β-lactam antibiotics is a major concern.



a) Plotting the data provided for the hydrolysis of penicillin by β-lactamase (see plot below), the activity appears to follow Michaelis-Menten kinetics. In particular, the data fall on a straight line in the Lineweaver-Burk plot. The blue line is a best fit of the Michaelis-Menten model.



b) From the Michaelis-Menten fit (see graph above), we find $v_{max} = 0.011$ nmols/s and $K_M = 5\ \mu$M. Note that you can also convert to M instead of working in mols; similarly, you can work in min^{-1} instead of s^{-1}.

c) To determine the turnover frequency k_{cat}, we use $k_{cat} = v_{max}/E_{total}$ where E_{total} is the enzyme concentration. If you work in mols, you simply need to compute the amount of enzyme, namely 1 ng / 29600 Da = 1 ng / (29600 g/ml) = $3.38 \cdot 10^{-5}$ nmols and k_{cat} = (0.0112 nmols/s) / ($3.38 \cdot 10^{-5}$ nmols) = 331 s^{-1}.
From this, you can also compute $k_{cat}/K_M = 6.6 \cdot 10^7$ M^{-1} s^{-1}, which indicates a fast and efficient enzyme, though it is still about one order-of-magnitude less than what one would expect for a diffusion limited enzyme.

Problem 3

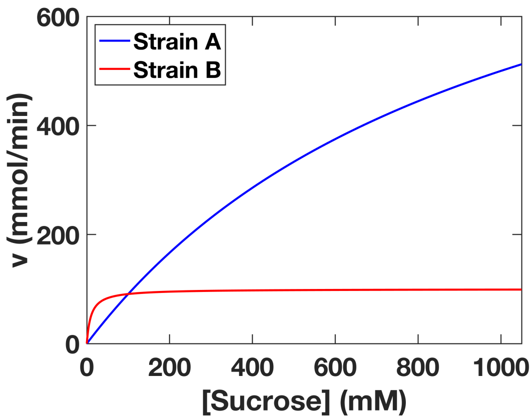
Michaelis-Menten for survival 2. The Michaelis-Menten rate is given by

$$V = V_{max} \cdot \frac{[S]}{K_M + [S]} \tag{1}$$

a) Using the values given in the table and the Michaelis-Menten equation above, we find:

Condition	Strain A	Strain B	Result
	V in mmol/min	V in mmol/min	
10 mM sucrose	9.9	50	B grows faster
100 mM sucrose	90.9	90.9	A and B grow equally fast
1000 mM sucrose	500	99	A grows faster

b) Transport rates as a function of the substrate sucrose:



c) Soil has likely a relatively low concentration of sucrose, while the environment in an ice cream shop has a high concentration of sucrose. Strain A, which grows very well under high sucrose conditions, would likely be found in the ice cream shop. Strain B grows faster than Strain A under low sucrose conditions and is, therefore, more likely to be found in the soil sample. This assume that sucrose uptake is growth limiting and that the strains have been well adapted to the different environments.