Homework 5
February 17, 2025
Polymer Physics

Chain persistence in polyelectrolytes (l_p) is governed by the charge spacing on the chain (a or b), the Debye screening length (λ_D), the Bejerrum length (l_B), and the bare persistence length in the absence of charge (l_0). The Odijk-Skolnick-Fixman (OSF) Model predicts the dependence of polyelectrolyte persistence length on these parameters and the counter ion concentration, $l_e = l_o + l_e$ where $l_{p,e} = \dfrac{l_b}{4}\left(\dfrac{1}{\kappa b}\right)^2$ and $\kappa = 1/l_D$. Li X, Wang Y, Sun C, Zhao Y, Lu W, Fang Y *Collapse-reexpansion conformational transition of alginate under non-specific ion conditions* Food Hydrocolloids **160** 110744 (2025) use AFM to measure the persistence length of alginate as a function of counter ion concentration. Alginate is a polysaccharide composed of mannuronate (M-blocks) and guluronate (G-blocks) units that is obtained from seaweed and is used in biomedicine, and food. The chain is a block-copolymer with M, G and MG blocks. The polyelectrolyte is negatively charged due to carboxyl groups on the six membered main chain rings common to cellulose, starch and other polysaccharides.
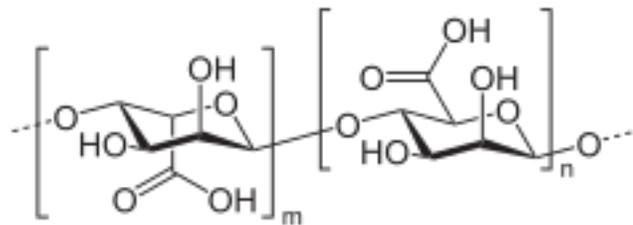
The addition of bivalent Ca^{+2} salts leads to the formation of an egg-carton structure with specific organizational interactions but other monovalent cations and some bivalent cations show non-specific interactions (mean field behavior). Li studies Na^+, Mg^{+2} and K^+. The study uses a Swiss program, FiberApp, to calculate the persistence length from the AFM micrographs.

a) Li's analysis is based on chain concentrations below the overlap concentration. Li claims that the samples are 100 times more dilute than the overlap concentration. Glance at Figures 1, 2 and 3 and decide if this is above or below chain overlap. (Remember that you are looking at a 2D image of a 3D sample.) On the second page of the supplemental to Li's paper at the bottom of the page the equation he used to calculate c* is given. Does this equation have the correct units for concentration? Does it make sense? Do you expect the overlap concentration to change with salt concentration? Would that be a problem?

b) It appears that Li calculates the persistence length from a single micrograph for each condition prepared through a complicated drying process with silane surface treatment of a mica surface to ensure adhesion of the alginate to the mica. Comment on the problems you can see in this method to determine persistence length. (For instance, is a cast monolayer adhering to a treated mica surface likely to distort the chains, the changes that Li obtains from the FiberApp program are not visible to the naked eye in any of the

micrographs that he shows, that is the micrographs could be reordered and it wouldn't impact the paper, what is a sufficient sample size to get an accurate persistence length, does he observe chain end effects (calculate the number of Kuhn units in his chains, I get 50 units), why are there no error bars in Figure 4, does he have a sufficient number of samples, you can probably can come up with several more issues).

c) Explain the Odijk-Skolnick-Fixman (OSF) theory and its prediction for the counter ion contribution to chain persistence and the prediction for counter ion condensation. Do Li's results agree with this theory? (Define the Manning number, Bjerrum length, Debye screening length, charge density along chain, electrostatic persistence length.)

d) Explain why the polyelectrolyte chain first collapses and then expands as counter ion concentration is increased, Figure 4. What is the Zeta potential and how is it determined, Figures S6 in the supplemental? How does this plot coupled with Figure 4 support your explanation for why collapse and reexpansion occurs?

e) In Figure 7, why does $\lambda_{Mg+2} > \lambda_{K+1} > \lambda_{Na+1}$ in chain collapse but $\lambda_{Mg+2} < \lambda_{K+1} < \lambda_{Na+1}$ in chain reexpansion? Why is λ always positive?