Modeling of weak polyelectrolyte hydrogels under compression.

Implications for water desalination.

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Intro

figures/step2.png

- Hydrogels for desalination
- Forward osmosis
- Various stimuli: thermo-, pH-, electric-, magnetic-, light-indused gel collapse
- Manfred Wilhelm and Yu Chi experiment

Fengler, C., Arens, L., Horn, H., Wilhelm, M. (2020). **Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation.** Macromolecular Materials and Engineering

Yu, C., Wang, Y., Lang, X., Fan, S. (2016). **A Method for Seawater Desalination via Squeezing**

The model of a polyelectrolyte gel.

Langevin dynamics.

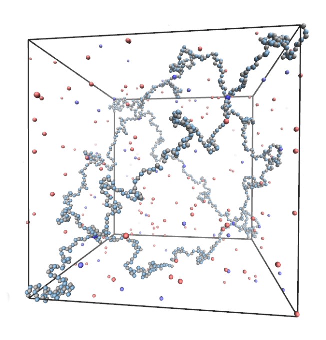


Figure 1: The snapshot of the hydrogel model for Langevin dynamics

- Diamond network of point particles
- Lennard–Jones interaction

$$V_{LJ}(r) = \begin{cases} 4\varepsilon \left(\left(\frac{\sigma}{r-r_c} \right)^{12} - \left(\frac{\sigma}{r-r_c} \right)^{6} \right) & , \ r < r_c \\ 0 & , \ r > r_c \end{cases}$$

- FENE potential

$$V_{FENE}(r) = -\frac{1}{2}\Theta \Delta r_{max}^2 \ln \left[1 - \left(\frac{r - r_0}{\Delta r_{max}} \right)^2 \right]$$

- Electrostatic interaction

$$V_{EL} = l_B k_B T \cdot \frac{q_1 q_2}{r}$$

Grand-reaction ensemble.

$$\mathrm{HA} \overset{K}{\leftrightarrows} \mathrm{A}^- + \mathrm{H}^+$$

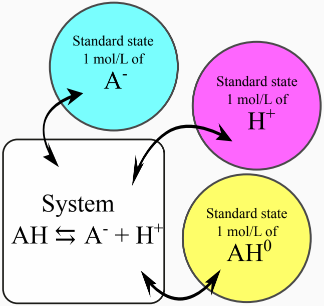
$$K = \mu^\ominus_{\mathrm{H}^+} + \mu^\ominus_{\mathrm{A}^-} - \mu^\ominus_{\mathrm{HA}}$$

$$\emptyset \leftrightarrows \mathrm{Na}^+ + \mathrm{Cl}^-$$

$$K = \mu_{\mathrm{Na}^+} + \mu_{\mathrm{Cl}^-}$$

$$\emptyset \leftrightarrows \mathrm{Ca}^{2+} + 2\mathrm{Cl}^-$$

$$K = 2\mu_{\mathrm{Ca}^{2+}} + \mu_{\mathrm{Cl}^-}$$



$$\boxed{\Delta\Omega = k_B T \ln\left(K^\xi \prod_i V^{\nu_i \xi} \frac{N_i!}{(N_i + \nu_i \xi)!}\right) + \Delta E}$$

Simulation protocol.

1. `Choose randomly: LMD or RE.`

2. `Simulate the chosen, collecting 50 samples of:`

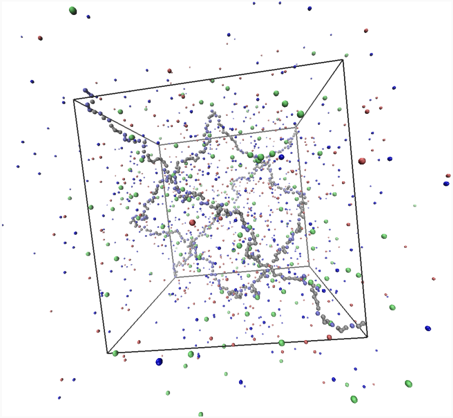
LMD: pressure, P, and $\{R_e\}$	RE: number of ionized segments, N_{A^-}	RE: number of salt ions, N_{Na^+}, N_{Cl^-}, $N_{\mathrm{Ca}^{2+}}$

   `Check the autocorrelation of each samples array.`
   `Pearson coefficient must be < 0.2.`

3. `Repeat collecting at least 100 averages from each process.`

Results

Seawater model solution



$$c_{\mathrm{Cl}^-} = 0.54 \text{ mol/l}$$
of negative ions

$$c_{\mathrm{Na}^+} = 0.47 \text{ mol/l}$$
of positive ions

$$c_{\mathrm{Ca}^{2+}} = 0.063 \text{ mol/l}$$
of positive divalent ions

$$c_{\mathrm{Na}^+} \simeq 0.87 \cdot c_{\mathrm{Cl}^-}$$
$$c_{\mathrm{Ca}^{2+}} \simeq 0.117 \cdot c_{\mathrm{Cl}^-}$$

$$\mu_{\mathrm{Na}^+} = \mu_{\mathrm{Cl}^-} - 0.139kT$$
$$\mu_{\mathrm{Ca}^{2+}} = \mu_{\mathrm{Cl}^-} - 2.03kT$$

Compression of hydrogel.

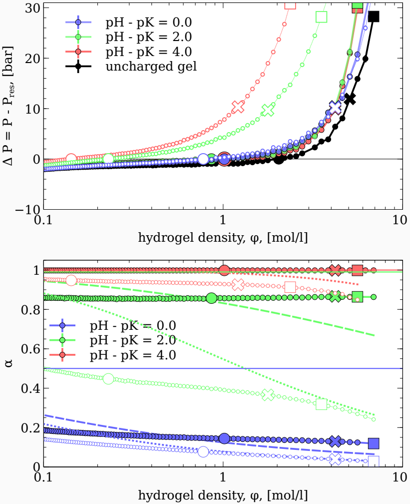
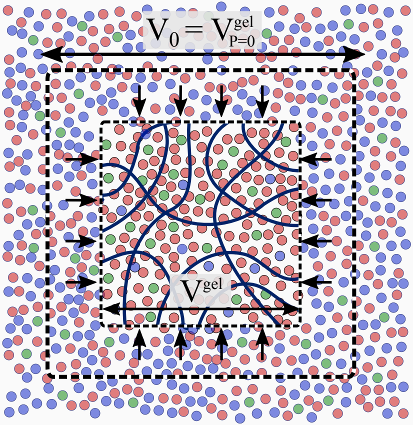


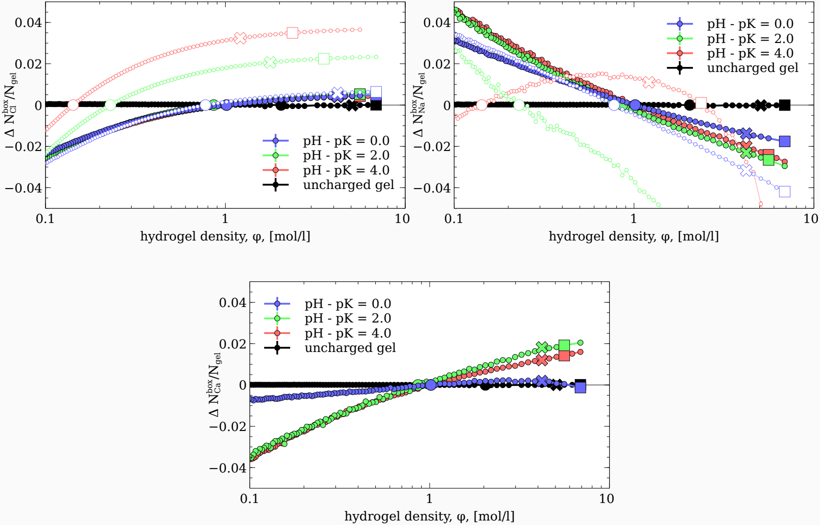
Figure 2: Compression of hydrogel in equilibrium with the bath of salinity $c_\mathrm{s} = c_{\mathrm{Cl}^-} = 0.007$ mol/l

Desalination effect.



- The gel is compressed from the initial volume, V_0 to a volume V^{gel}.
- And exchanges small ions with a reservoir solution.

Desalination and/or ion exchange.



Mean field model of hydrophobic weak polyelectrolyte gel.

- The gel is **regular network.** big enogh to treat it is homogeneous medium
- Affine deformation approximation $R \sim V^{1/3}$
- weak hydrophobic polyacid, pK = 6, chi = 2.0

Ionization equilibrium

figures/grand_reaction_model_noCa.png

$$\boxed{\mathrm{pA^- + H_3O^+ \leftrightarrows pAH}}$$

Rud, O., Borisov, O., Kosovan, P. (2018).
Thermodynamic model for a reversible desalination cycle using weak polyelectrolyte hydrogels. Desalination, 442, 32–43.

The desalination cycle.

figures/step1.png

(a) step 1

figures/step2.png

(b) step 2

figures/step4.png

figures/step3.png

The desalination cycle.

figures/cycle_PV_chi0.pdf

(a) $\chi = 0$

figures/cycle_PV_chi2.pdf

(b) $\chi = 2$

Questions?

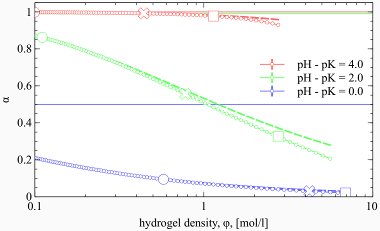
Monovalent salt. “No electrostatics” vs “Mean field theory”.

$$\frac{\alpha}{1-\alpha}10^{\mathrm{p}K-\mathrm{pH}} = \sqrt{1+\left(\frac{\alpha c_\mathrm{p}}{2c_\mathrm{s}}\right)^2} - \frac{\alpha c_\mathrm{p}}{2c_\mathrm{s}}$$

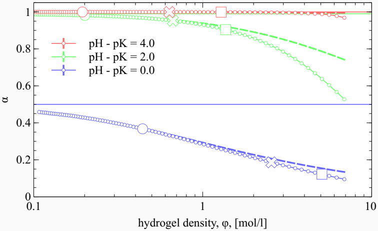
Together with electroneutrality condition it translates to

$$-\frac{\alpha^3 c_\mathrm{p}}{c_\mathrm{s}} + \alpha^2\left(\frac{c_\mathrm{p}}{c_\mathrm{s}} + \Theta - \frac{1}{\Theta}\right) + \frac{2\alpha}{\Theta} - \frac{1}{\Theta} = 0$$

where $\Theta = 10^{\mathrm{p}K-\mathrm{pH}}$.



(e) low salinity, $c_s = 0.007$ mol/l



(f) high salinity, $c_s = 0.209$ mol/l