Water desalination using polyelectrolyte hydrogel.

Gibbs ensemble modelling.

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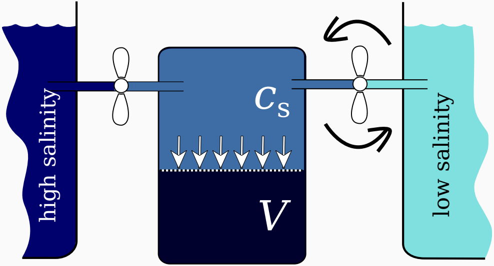
Intro

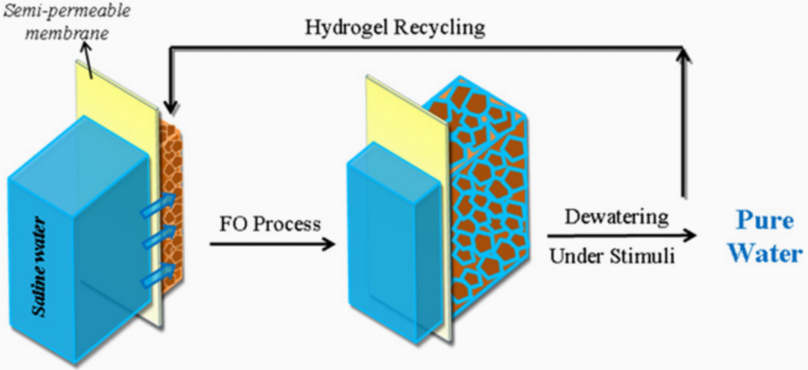
Introduction. Desalination.

1. Distillation
2. Reverse osmosis
3. Forward osmosis

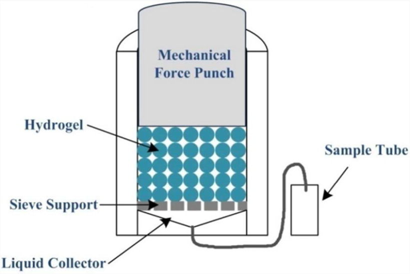


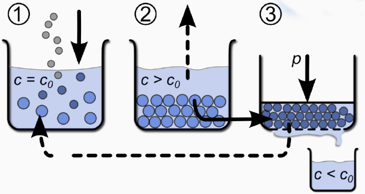
Introduction. Forward osmsis.

1. Hydrogels for desalination
2. Forward osmosis
3. Various stimuli: thermo-, pH-, electric-, magnetic-, light-indused gel shrinkage



Introduction. Manfred Wilhelm experiment



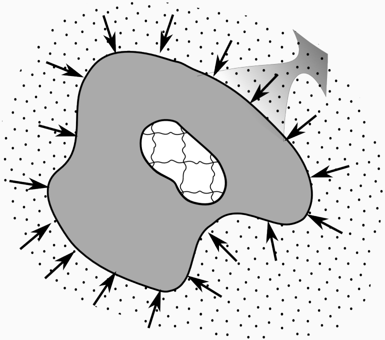


Fengler, C., Arens, L., Horn, H., Wilhelm, M. (2020). **Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation.** Macromolecular Materials and Engineering

Yu, C., Wang, Y., Lang, X., Fan, S. (2016). **A Method for Seawater Desalination via Squeezing Ionic Hydrogels.** Environmental Science and Technology

The model of a polyelectrolyte gel.

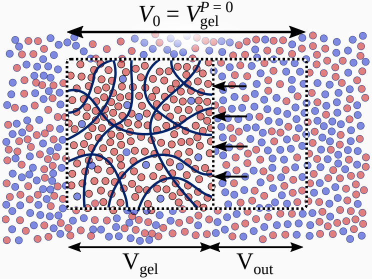
Model of the gel



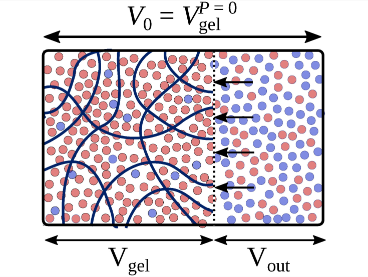
- The gel is a particle of mAcro size
- In aqueous solution
- Infinite network of polymer chains
- Each bead is charged

- The gel itself is a membrane
- Donnan equilibrium $c_s^2 = c_{Na}^{in} \cdot c_{Cl}^{in}$
- The compression of hydrogel affects the ionic composition of supernatant

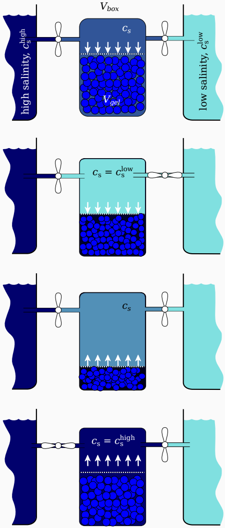
Model of the gel. Two ensembles.



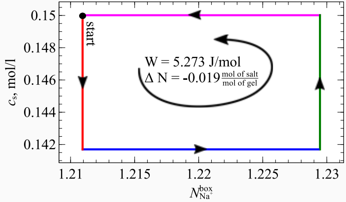
Open system
(grand-cannonical ensemble)

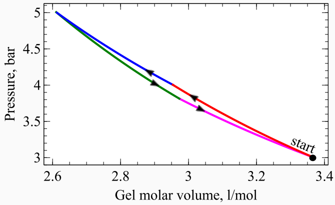


Closed system
(Gibbs ensemble)



1. A fully reversible desalination cycle
2. Analogy with Carnot cycle





Rud, et al. (2018).

Grand-cannonical ensemble.

The free energy of the grand-canonical ensemble exchanging ion pair with the bath

$$\boxed{\Omega = E - TS + \mu N}$$

The entropy S expands via Boltzmann formula

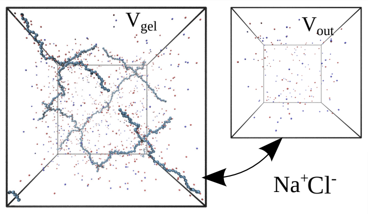
$$S = k_B \ln \frac{V^N}{N!}$$

The change of free energy associated with a single particle exchange is

$$\boxed{\Delta\Omega = k_B T \xi \ln V \left(N + \theta(\xi)\right) + \xi\mu + \Delta E}$$

`accept if` $\mathcal{R}^{\xi} < e^{\Delta\Omega / k_B T}$

Gibbs ensemble.



The free energy of the grand-canonical ensemble for single particle type

$$\boxed{\Omega = E_1 + E_2 - TS}$$

$$S = k_B \ln \frac{V_1^{N_1}}{N_1!} \frac{V_2^{N_2}}{N_2!} \tag{1}$$

The change of free energy associated with a single particle exchange is

$$\boxed{\Delta\Omega = k_B T \xi \ln \left(\frac{V_1}{V_2} \frac{N_2 + \theta(-\xi)}{N_1 + \theta(\xi)} \right) + \Delta E_1 + \Delta E_2}$$

`accept if` $\mathcal{R}^{\xi} < e^{\Delta\Omega / k_B T}$

Langevin dynamics.

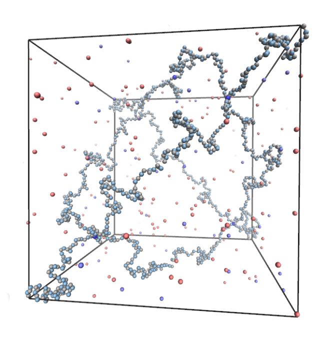


Figure 1: The snapshot of the hydrogel model for Langevin dynamics

- 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

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

Simulation protocol.

1. Choose randomly: LMD, or EX.

2. Simulate the chosen, collecting 50 samples of:

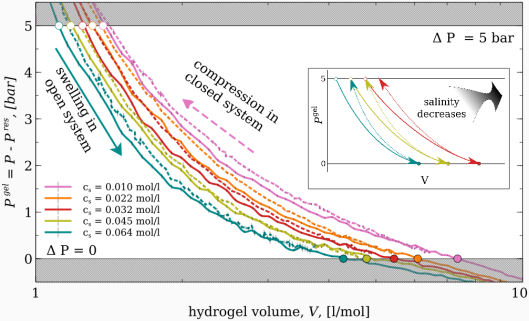
LMD: pressure, P, and $\{R_e\}$	EX: number of salt ions, N_{Na^+} and N_{Cl^-}

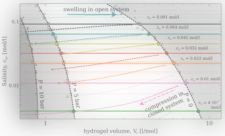
   Check the autocorrelation of each samples array. Pearson coefficient must be < 0.2.

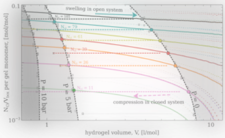
3. Repeat collecting at least 200 averages from each process.

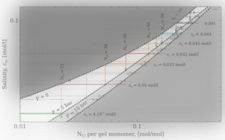
Results

Desalination in $\{P, V\}$ coordinates.

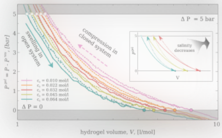


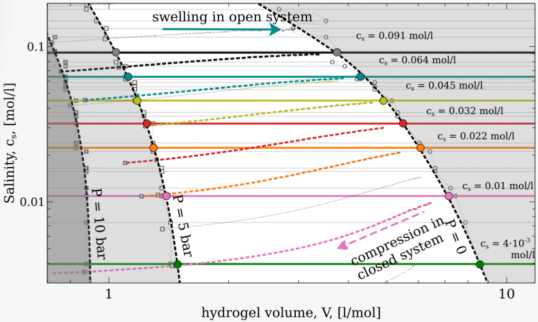


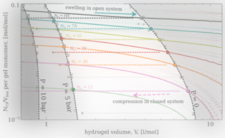


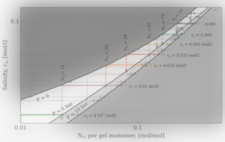


Desalination in $\{c_s, V\}$ coordinates.

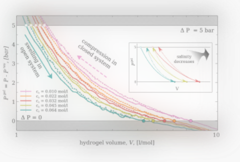


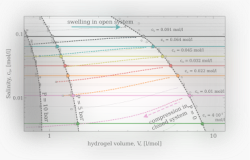


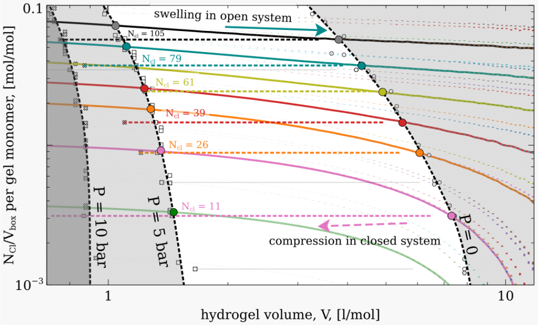


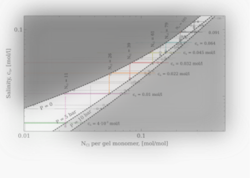


Desalination in $\{N, V\}$ coordinates.

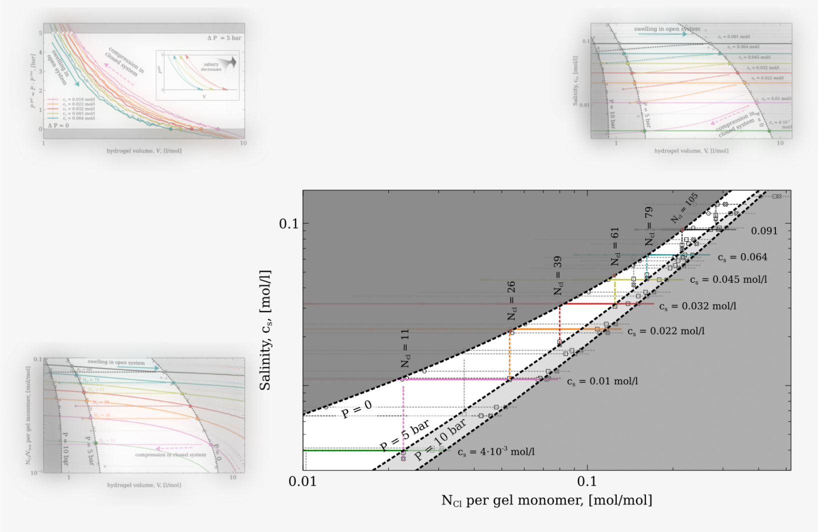








Desalination in $\{c_{\mathrm{s}}, N\}$ coordinates.



Conclusion

Summary

1. monovalent ions
   1.1 ionization of the hydrogel is suppressed as compared to predictions for monomeric acid, due
      - to the Donnan partitioning of H + ions;
      - to the electrostatic repulsion between charges of the gel.
   1.2 the decrease of ionisation degree is much less significant than previously estimated using mean-feld models.
   1.3 decreasing the ionization of the gel upon compression may completely reverse the desalination effect forcing the gel to release counterions upon compression instead of absorbing them.
2. with divalent ions
   2.1 the electrostatics is almost completelly screened
   2.2 alpha does not change versus compression
   2.3 The compression of gel in presence of divalent ions works as ion exchanger of Ca ion by Na

Questions are welcome.

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