Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modelling and experiment
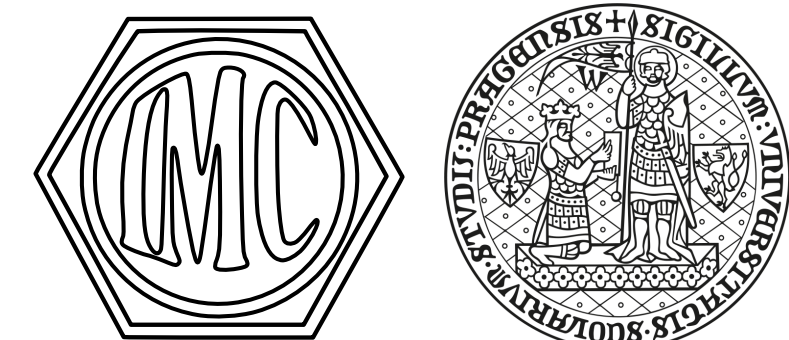
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Polyelectrolyte hydrogels have the ability to absorb a big amount of water across forward osmosis membrane as a result of their swelling pressure. The insoluble cross-linked network of the gel enables dewatering under the influence of stimuli (thermal and/or mechanical). On the other hand, the network structure of a polymer hydrogel, from a thermodynamic perspective, is already an osmotic membrane. So hydrogel microparticles may allow to completely avoid the osmotic membranes in forward osmosis and use microfiltration instead. Here we present our recent study of the use of polyelectrolyte hydrogel for water desalination. We modeled the thermodynamic equilibrium of coexistence of the gel and the aqueous salt solution in the so-called closed ensemble, in which the total amount of ions is assumed to be constant. We modeled the compression of the gel and the associated with that release of the solution. We have shown that the squeezed out solution has a little lower salinity than that the gel was equilibrated with. Also, we performed a set of simulations modeling the process of continuous decrease of water salinity up to freshwater concentrations.
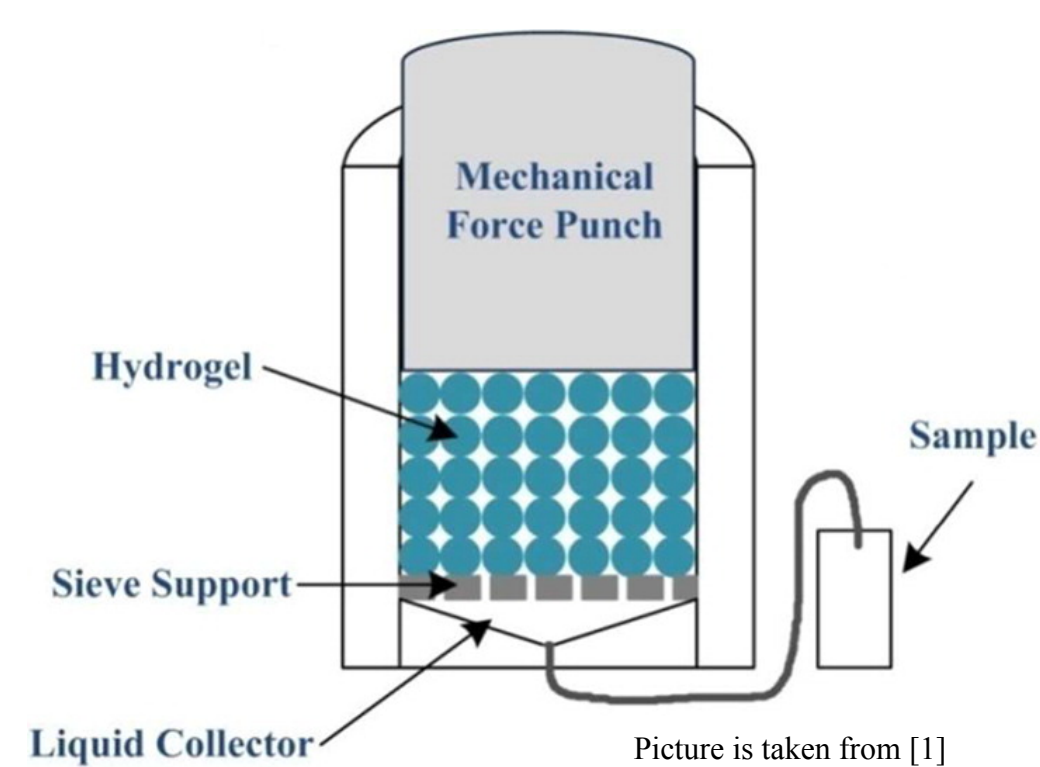
1. Hydrogels for desalination

1.1 Reverse osmosis
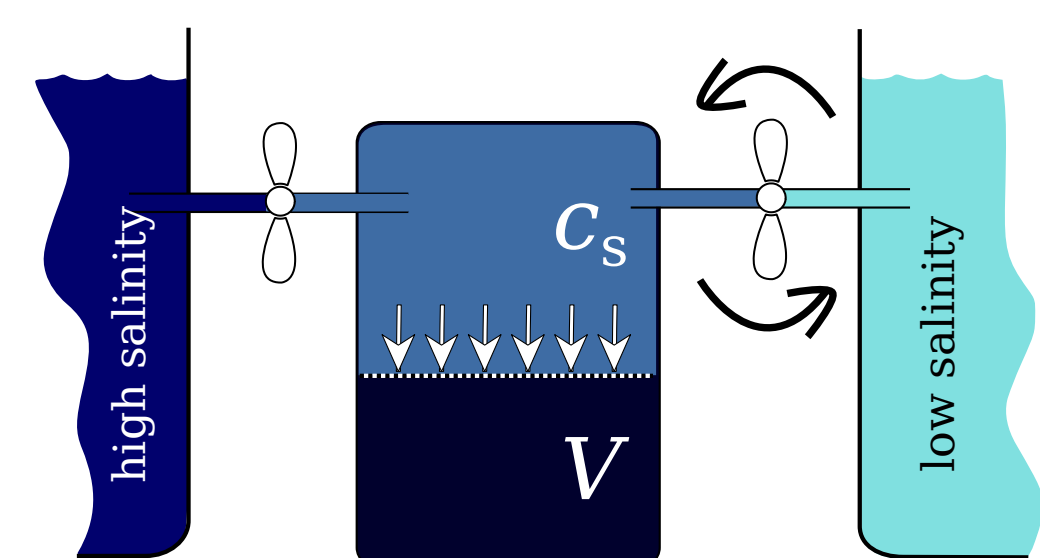
- Fully reversible, therefore works in ideal thermodynamic efficiency
- Membrane is expensive and sensitive to quality of feed water

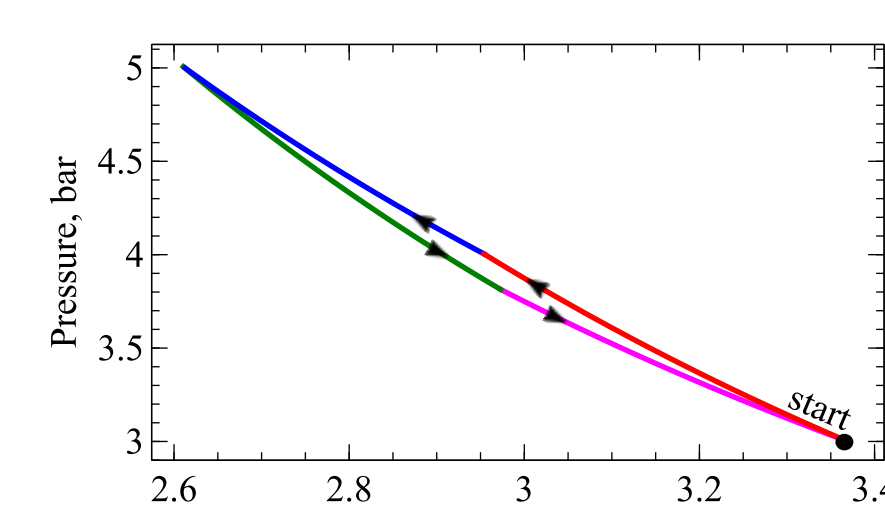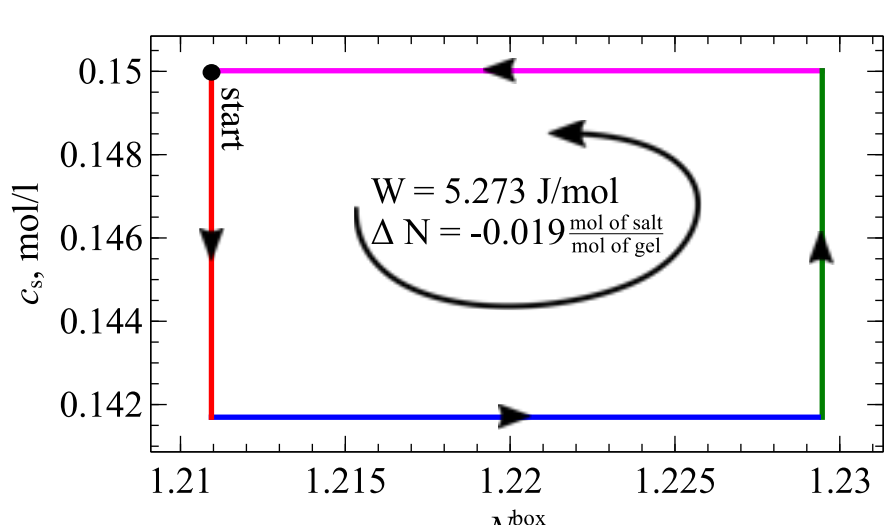### 1.2 The use of polyelectrolyte hydrogels

Picture is taken from [1]

- The idea [1, 2] is
  1. let the gel swell in salt solution
  2. squeeze the gel and collect the excluded brine
  3. repeat
- The approach is free from the use o osmotic membrane
- But contains an irreversible process

1.3 Reversible (Carnot) desalination cycle
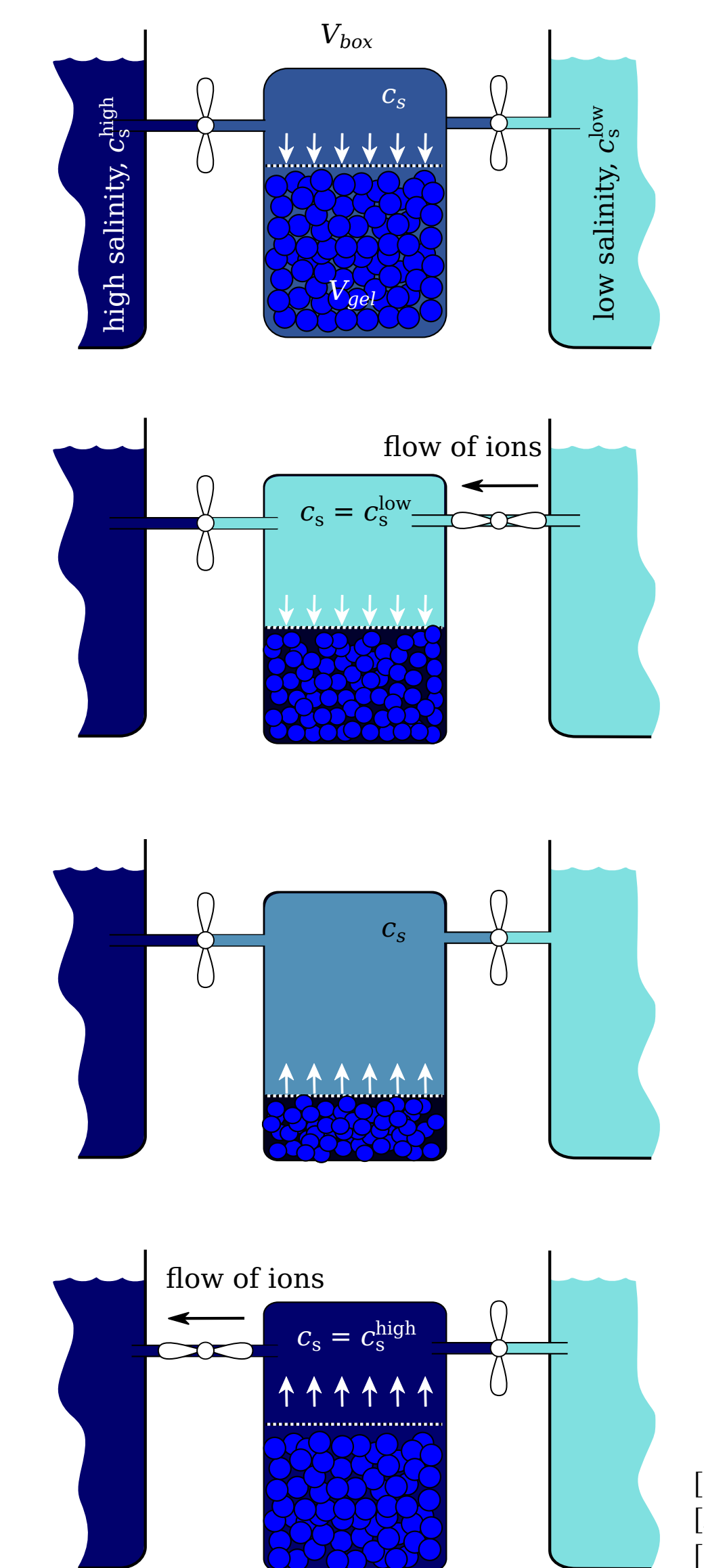
- A a fully reversible desalination cycle using polyelectrolyte hydrogels [3].
- The cycle is based on the analogy with the Carnot cycle for reversed heat engine

[1] Yu, C., et al. (2016). http://doi.org/10.1021/acs.est.6b03193
[2] Arens, et al. (2017). http://doi.org/10.1002/macp.201700237
[3] Rud, et al. (2018). http://doi.org/10.1016/j.desal.2018.05.002

2. The model of the gel

2.1 Diamond network

The model is a polyelectrolyte chains connected to a diamond lattice cell in periodic boundary conditions
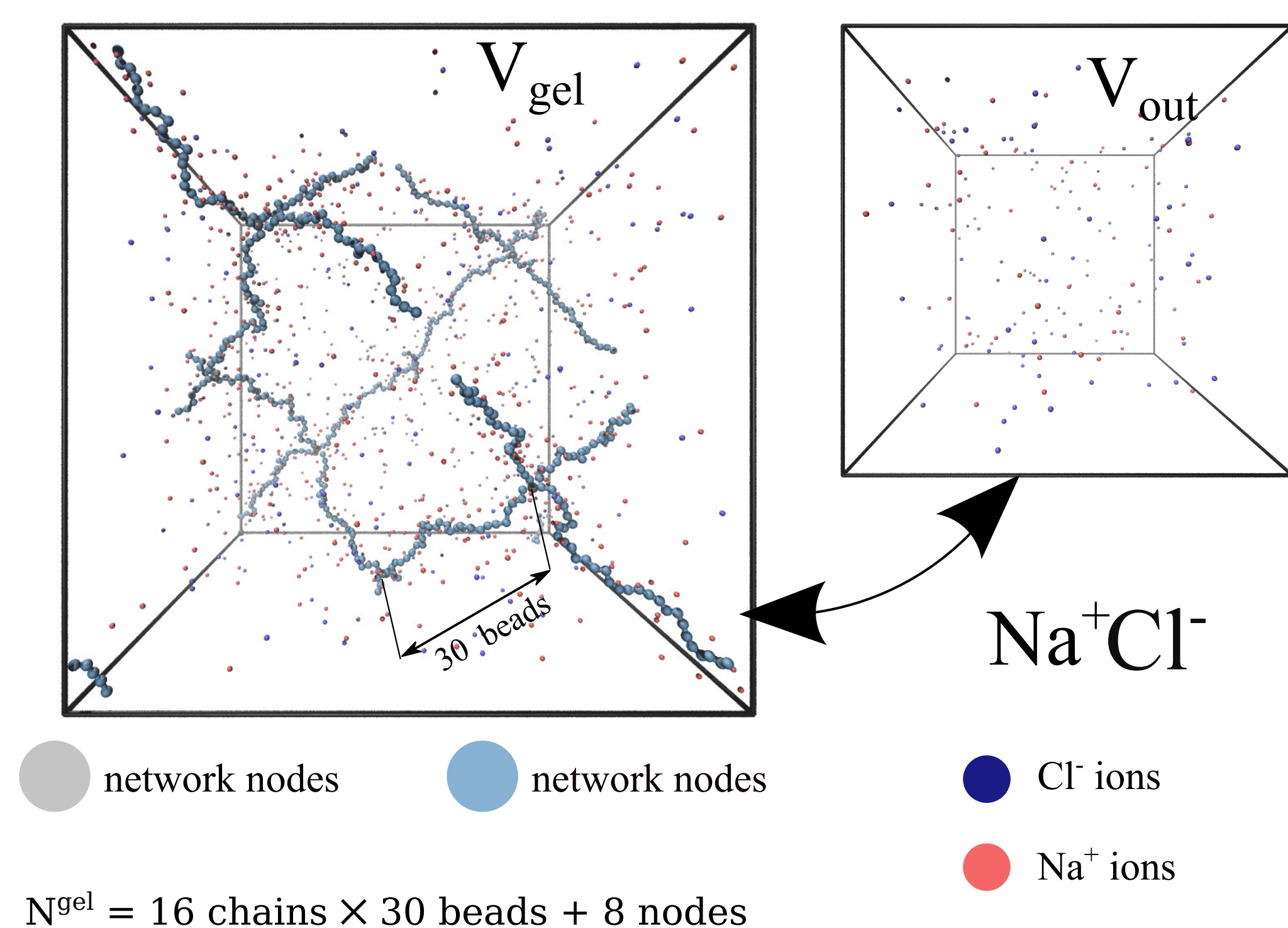
- network nodes
- network nodes
- Cl⁻ ions
- Na⁺ ions

N^{gel} = 16 chains × 30 beads + 8 nodes

2.2 Molecular dynamics (MD) simulation

- All the particles interact via Lennard-Jones potential

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$
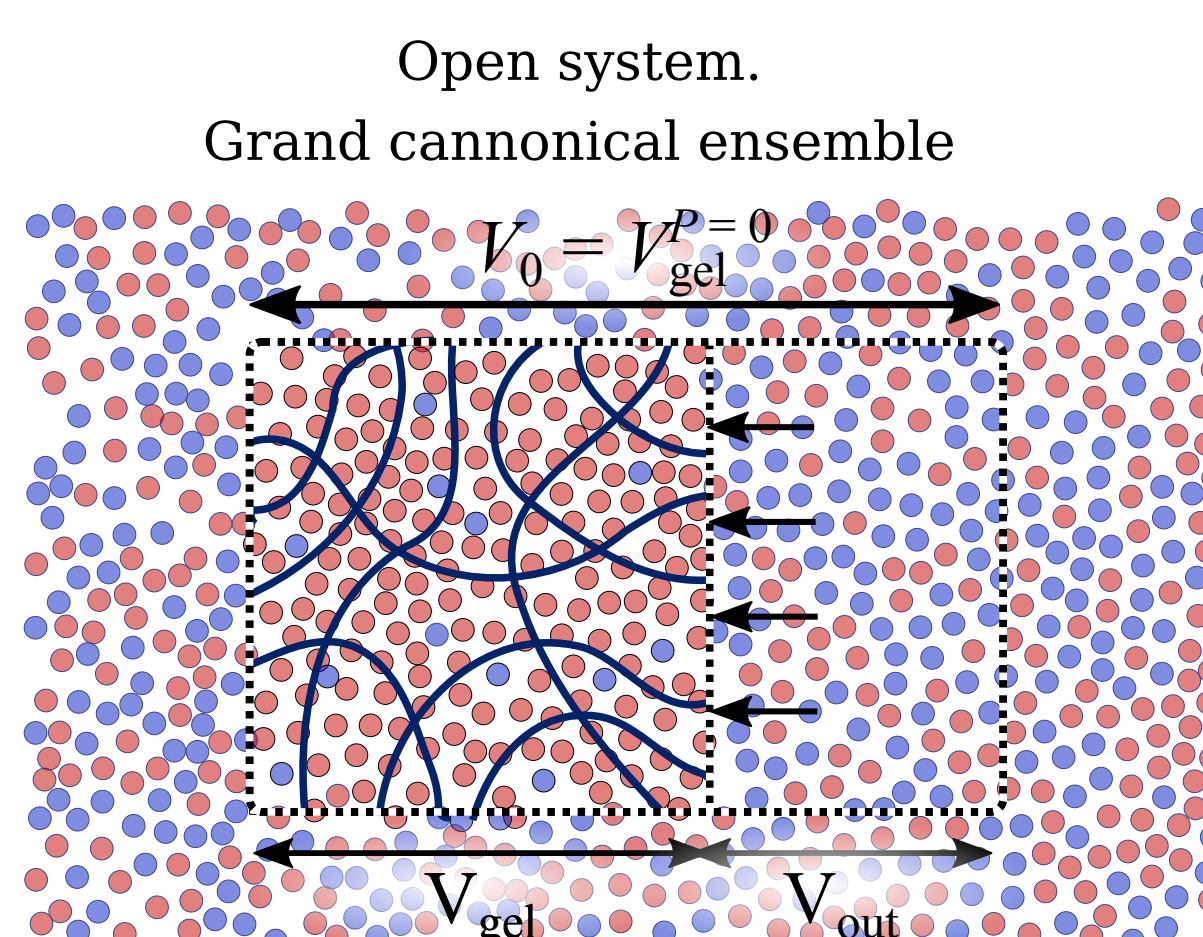
$\epsilon = k_B T$, $\sigma = 0.35$nm.

- The beads of gel network interact via FENE (finite extension nonlinear elastic) potential

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

$K = 10\epsilon$, $\Delta r_{max} = 2\sigma$, $r_0 = 0$

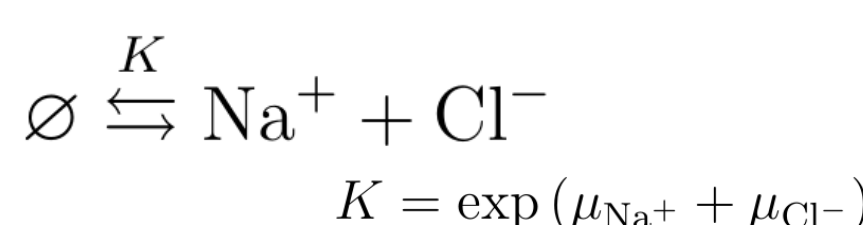- The electrically charged species interact via Coulomb potential.

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

$l_B = 2\sigma$ --- is Bjerrum length, $q_1, q_2 = e$
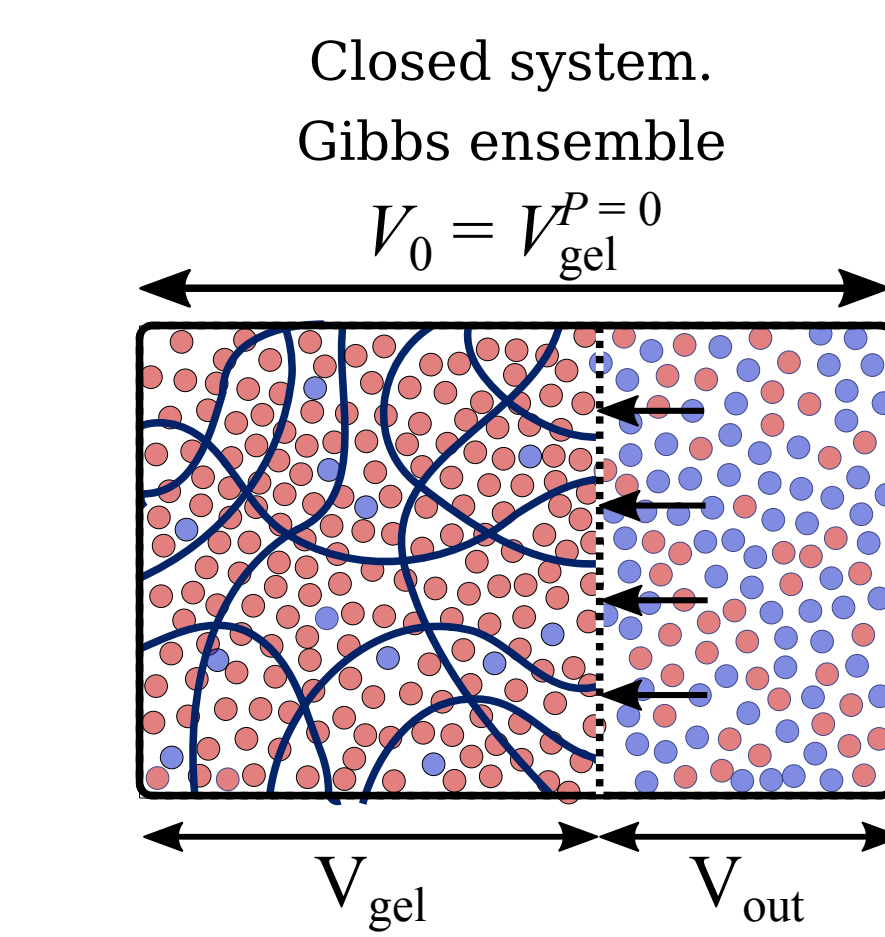
2.3 Monte Carlo (MC) sampling

Open system.
Grand cannonical ensemble
$V_0 = V_{gel}^{P=0}$

Closed system.
Gibbs ensemble
$V_0 = V_{gel}^{P=0}$

μ_{Na} = Const μ_{Cl} = Const

N_{Na} = Const N_{Cl} = Const

- perform a reaction with arbitrary ion pair

$$\varnothing \overset{K}{\rightleftharpoons} Na^+ + Cl^-$$

$K = \exp(\mu_{Na^+} + \mu_{Cl^-})$

- perform a move of an arbitrary ion pair

$$(Na^+ + Cl^-)^I \rightleftharpoons (Na^+ + Cl^-)^{II}$$
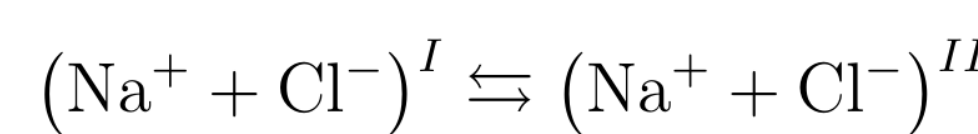
- accept new state if

$$rand(0,1] < K^\xi \prod_{i=Na,\,Cl} \left[\frac{N_i!}{(N_i + \xi)!} \right] \exp(-\beta\Delta E_{pot})$$

- accept new state if

$$rand(0,1] < \left(\frac{V^{II}}{V^I}\right)^\xi \prod_{i=Na,\,Cl} \frac{N_i^I!}{(N_i^I + \xi)!} \frac{N_i^{II}!}{(N_i^{II} + \xi)!} \exp(-\beta\Delta E_{pot})$$

3. Simulation of the desalination process
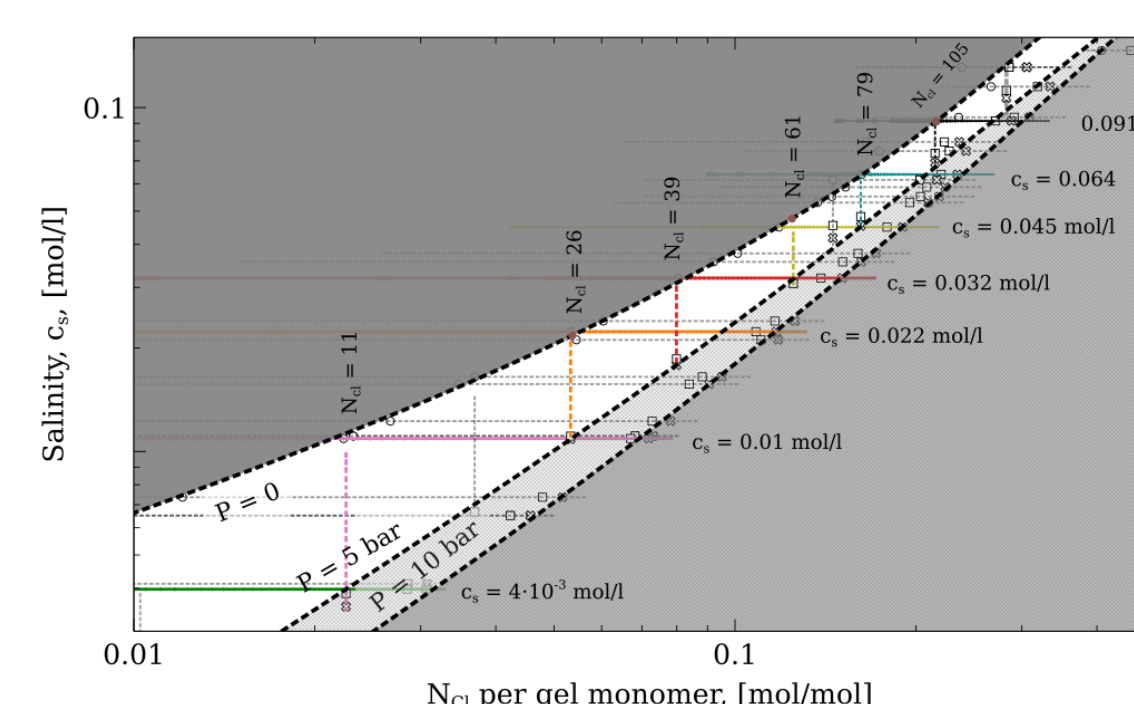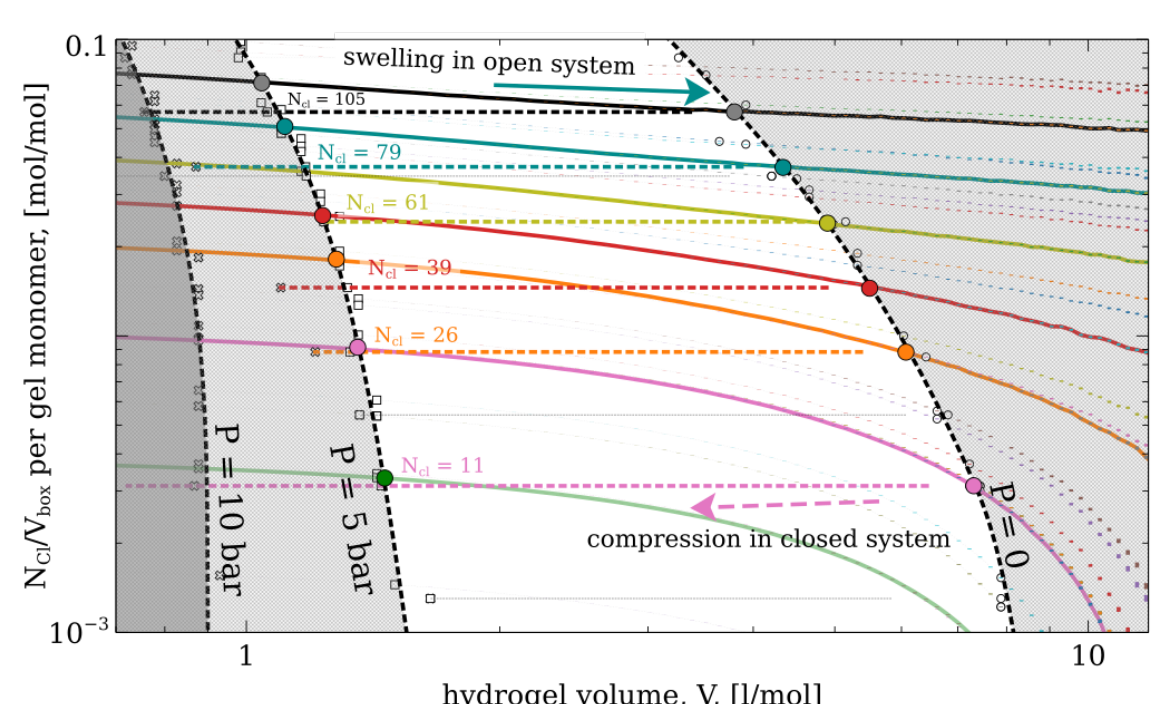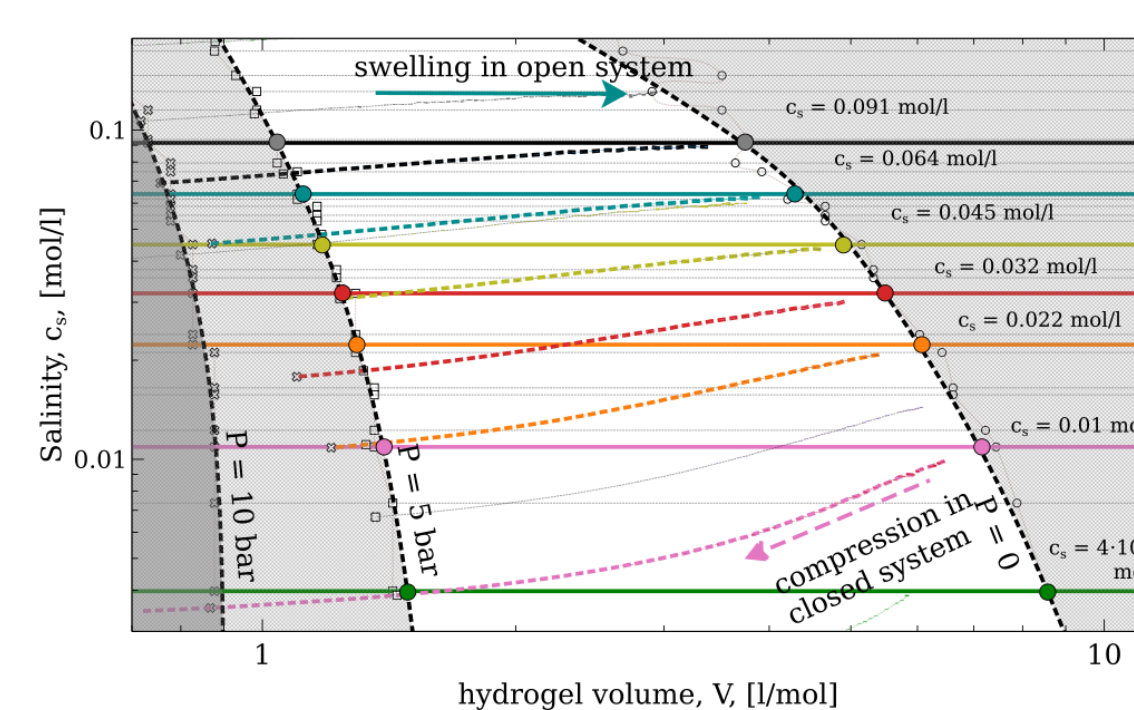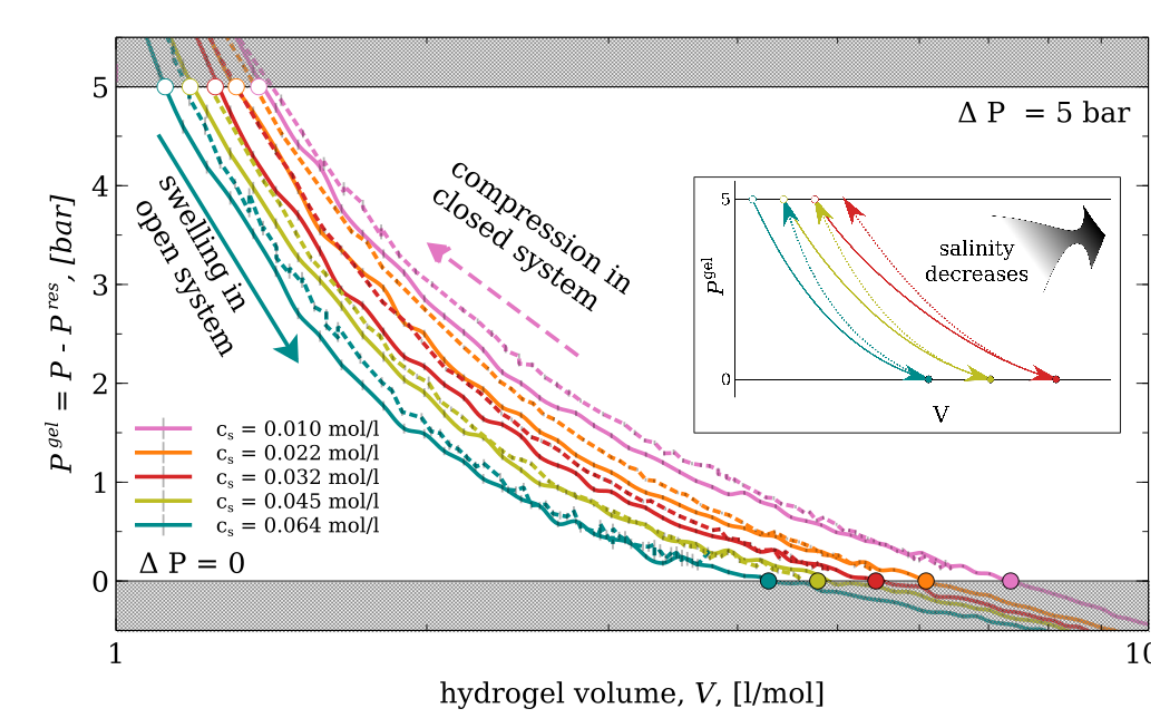
The estimation of the desalination efficiency

c_s^o, M	c_s^o, M	$N_{Cl^-}^{in}$	$N_{Cl^-}^{o}$	Δv, l	$|W|$, J/L	W^{id}, J/L
0.092		0.057 →	0.072	2.74	95.4	
0.089 →	0.074	0.057		2.72	109.1	
0.064		0.037 →	0.051	3.26	100.9	W^{id} = (52.9) R_w = 0.54
0.062 →	0.048	0.037		3.18	107.4	
0.045		0.024 →	0.036	3.82	100.7	
0.044 →	0.031	0.024		3.91	106.4	W^{id} = 58.2 R_w = 0.53
0.032		0.015 →	0.025	4.20	107.9	
0.030 →	0.019 (0.022)	0.015		4.17 (3.22)	115.6 (57.3)	W^{id} = 43.8 (41.0) R_w = 0.52 (0.80)
0.022		0.009 →	0.018 (0.015)	4.75 (3.76)	108.1 (68.5)	
0.021 →	0.011	0.009		4.71	110.8	W^{id} = 66.6 (22.0) R_w = 0.53 (0.80)
0.011		0.003 →	0.009	6.08	106.9	W^{id} = 60.7 R_w = 0.55
0.010 →	0.004	0.003		5.78	119.4	

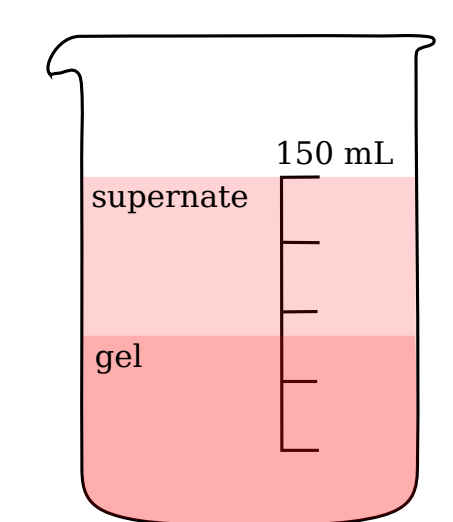## 3. Experimental part

1. Prepare three solutions of $c_s = 0.1, 0.05$ and 0.01 mol/L.
   Measure:
   (CND) the conductivity
   (CLP) potential pf Cl- ions

	0.1M	0.05M	0.01M
CND, µS/cm	10261 ±40.6	5547 ±12.1	1222.9 ±0.93
CLP, mg/L	3531 ±4.8	1829.9 ±1.41	345.9 ±0.21

2. equilibrate PAA gel in 150 mL of solution

0.3 g in 0.01M   69 mL
0.5 g in 0.05M   67 mL
0.75 g in 0.1M   70 mL

150 mL
supernate
gel

3. squeeze the gel in syringe to 45 mL

gel

4. collect the extract and measure CND and CLP in
   a) supernate phase
   b) in gel phase
   c) in extract
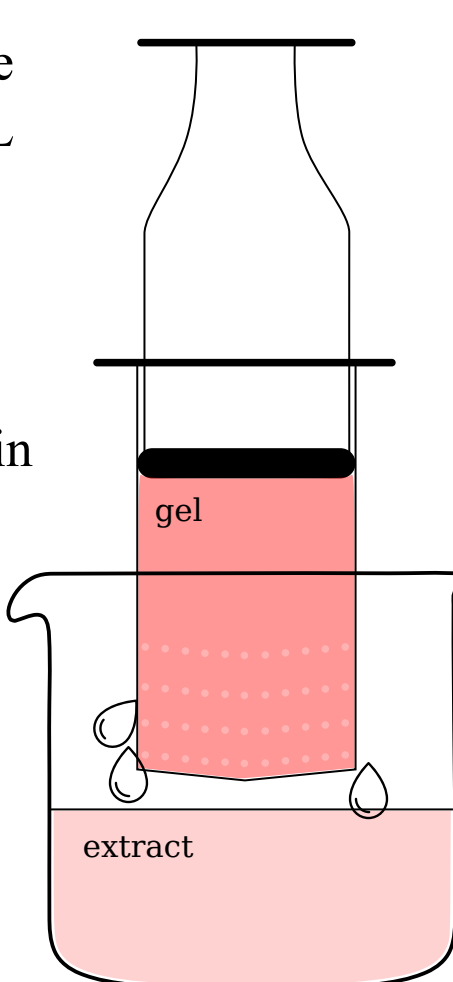
extract

c_s = 0.1 mol/L

	gel	sepernate	extract
CND µS/cm	11516 ±58.0	10980 ±58.1	9183 ±29.4
CLP mg/L	3564.9 ±3.28	3650.8 ±3.60	3411.7 ±2.57
c_s mol/L	1.01e-1 ±9.2e-5	1.03e-1 ±1.0e-4	9.62e-2 ±7.2e-5

c_s = 0.05 mol/L

	gel	sepernate	extract
CND µS/cm	6313 ±39.6	6001 ±14.7	5154 ±11.1
CLP mg/L	(1765)	1851 ±1.0	1540.9 ±1.03
c_s mol/L	(4.98e-2)	5.22e-2 ±2.9e-5	4.35e-2 ±2.9e-5

c_s = 0.01 mol/L

	gel	sepernate	extract
CND µS/cm	10261 ±40.6	5547 ±12.1	1222.9 ±0.93
CLP mg/L	359.5 ±0.37	378.8 ±0.37	352.1 ±0.36
c_s mol/L	1.01e-2 ±1.0e-5	1.07e-2 ±1.0e-5	9.93e-3 ±1.0e-5

References

[1] Yu, C., et al. (2016). http://doi.org/10.1021/acs.est.6b03193
[2] Arens, et al. (2017). http://doi.org/10.1002/macp.201700237
[3] Rud, et al. (2018). http://doi.org/10.1016/j.desal.2018.05.002
[4] Turner, et al. Molecular Simulation, 34(2), 119 (2008).
[5] J.M. Prausnitz, et al. (1999).