Phase transition in hydrophobic weak polyelectrolyte gel. A computer simulation study.

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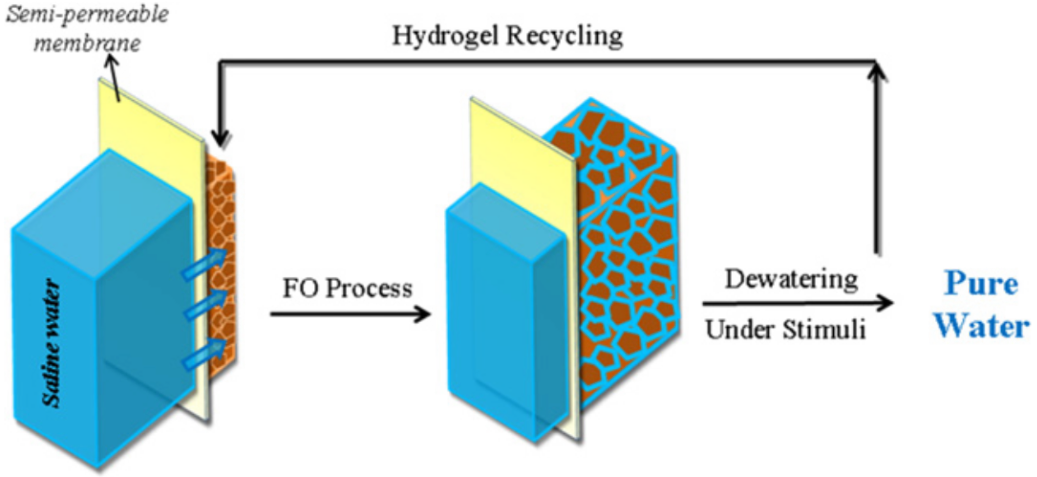
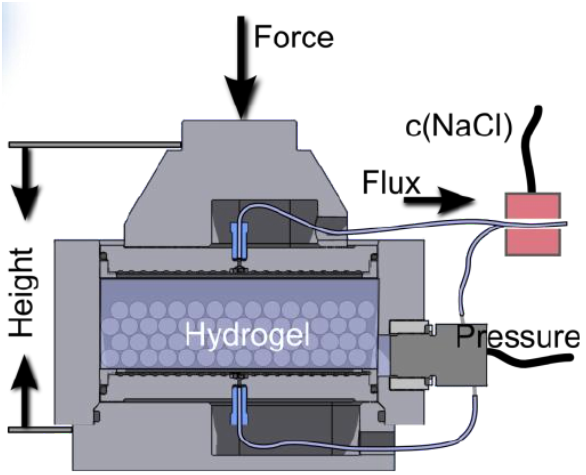
Introduction.

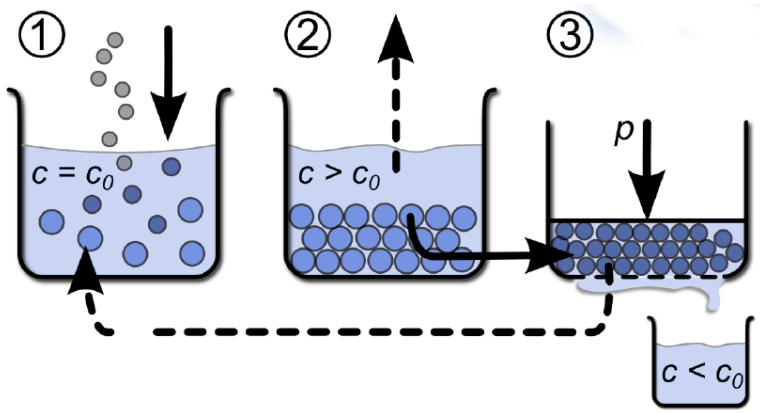
- Hydrogels for desalination
- Forward osmosis
- Various stimuli: thermo-, pH-, electric-, magnetic-, light-indused gel collapse



Dan Li a,c , et al. (2013). **Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance**. Water Research

Introduction. Prof. Wilhelm experiment.





Fengler, C., et al (2020). **Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation.** Macromolecular Materials and Engineering

Mean field analytical model.

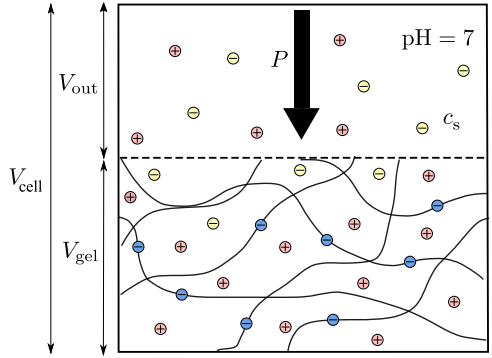


Figure 1: The hydrogel in equilibrium with a bath of aqueous solution

- Free energy of a hydrogel chain

$$F = F_{conf} + F_{int} + F_{ion}$$

- Conformational entropy

$$F_{\text{conf}} = \frac{3}{2}\frac{R^2/(b^2N) - 1}{1 - R^2/(b^2N^2)} - \frac{3}{2}\ln\left(\frac{R^2}{b^2N}\right)$$

- Steric interactions

$$F_{\text{int}} = \frac{N}{c_{\text{p}}}\left[(1 - c_{\text{p}})\ln(1 - c_{\text{p}}) - \chi c_{\text{p}}^2\right]$$

$$F_{ion} = \frac{N}{c_{\text{p}}}\sum_i \left(c_i^{in}\ln\frac{c_i^{in}}{c_i^{out}} + c_i^{out} - c_i^{in}\right)$$

Mean field analytical model. Donnan potential.

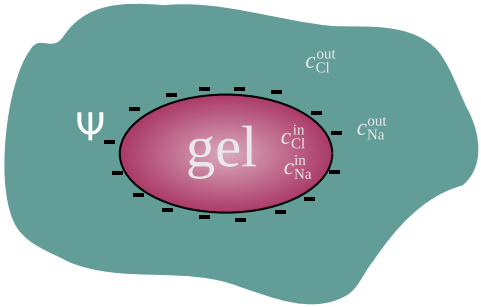


Figure 2: Electrostatic potentioal of the particle surface is a driving force of ion partitioning

- Donnan electrostatic potential, ψ

$$e^{\psi} = \xi = \frac{c_{H^+}^{out}}{c_{H^+}^{in}} = \frac{c_{Na^+}^{out}}{c_{Na^+}^{in}} = \frac{c_{Cl^-}^{in}}{c_{Cl^-}^{out}} = \frac{c_{OH^-}^{in}}{c_{OH^-}^{out}}$$

- Local electroneutrality condition

$$\alpha c_p + c_{Cl^-}^{in} + c_{OH^-}^{in} = c_{Na^+}^{in} + c_{H^+}^{in}$$

$$\xi(c_p, c_s) = \sqrt{1 + \left(\frac{\alpha c_p}{2c_s}\right)^2} \pm \frac{\alpha c_p}{2c_s}$$

Mean field analytical model. pH sensitive hydrogel.

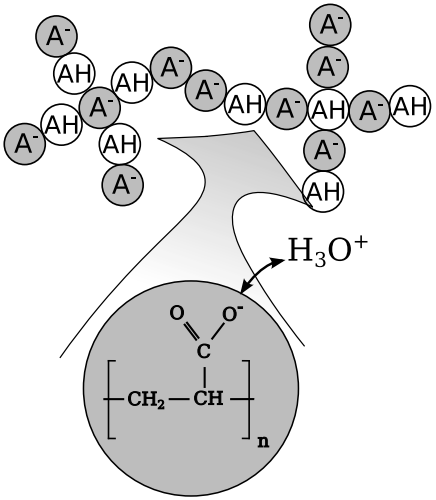


Figure 3: Each bead of hydrogel is acidic. It changes its charge depending on pH.

- ionization reaction

$$\mathrm{pAH} \overset{K}{\rightleftharpoons} \mathrm{pA^-} + \mathrm{H^+}$$

- ionization equilibrium

$$\frac{\alpha}{1-\alpha} = \frac{c^{in}_{\mathrm{H^+}}}{K} = \frac{c^{out}_{\mathrm{H^+}}}{K}\frac{c^{in}_{\mathrm{H^+}}}{c^{out}_{\mathrm{H^+}}} = 10^{pK-pH}\xi^{-1}$$

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

- Free energy ionization term

$$F_\alpha = \alpha N\left(\ln\alpha + \ln(1-\alpha) + \ln c^{in}_{\mathrm{H^+}} - \ln K\right)$$

Mean field analytical model. Equation of state.

$$F(c_p, c_s) = F_{conf}(c_p) + F_{int}(c_p, \chi) + F_{ion}(c_p, c_s) + F_{\alpha}(c_p, c_s, pK)$$

pK and χ are the parameters of the model

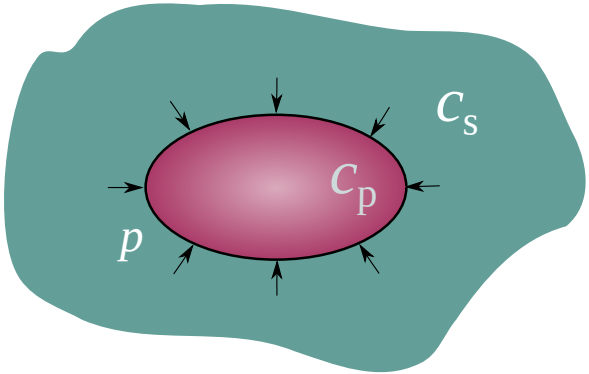
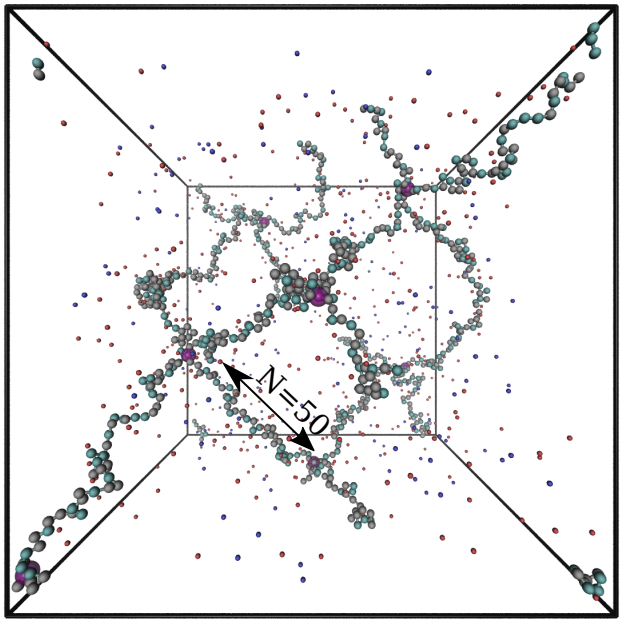


Figure 4: Gel particle under compression in equilibrium with aqueous solution of salinity c_s

Partial pressure of the gel network

$$\left(\frac{\partial F}{\partial V}\right)_{c_s} = -p$$

MCMD model. Langevin Molecular Dynamics (LMD).



The snapshot of the hydrogel model for Langevin dynamics

- Diamond network of point particles
- Lennard–Jones interaction

$$V_{\mathrm{LJ}}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], & \text{if } r < r_{\mathrm{cutoff}} \\ 0, & \text{elsewhere} \end{cases}$$

σ = 0.35 nm

- FENE potential

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

Δr_{max}= 2σ

- Electrostatic interaction

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

MCMD model. Grand reaction ensemble

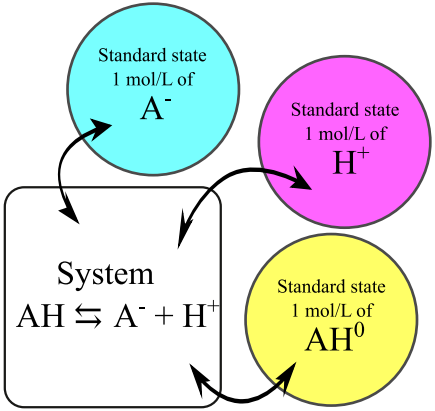
System free energy

$$\Omega = E - TS + \sum_i \left(\mu_i - \mu_i^{\ominus}\right) N_i$$

Reactions

$$\mathrm{HA} \overset{K}{\leftrightarrows} \mathrm{A^-} + \mathrm{H^+} \qquad K = \mu^{\ominus}_{\mathrm{H^+}} + \mu^{\ominus}_{\mathrm{A^-}} - \mu^{\ominus}_{\mathrm{HA}}$$

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



The change of system free energy during a reaction step

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

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

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

MCMD model. Simulation protocol

1. Choose randomly: LMD or RE.

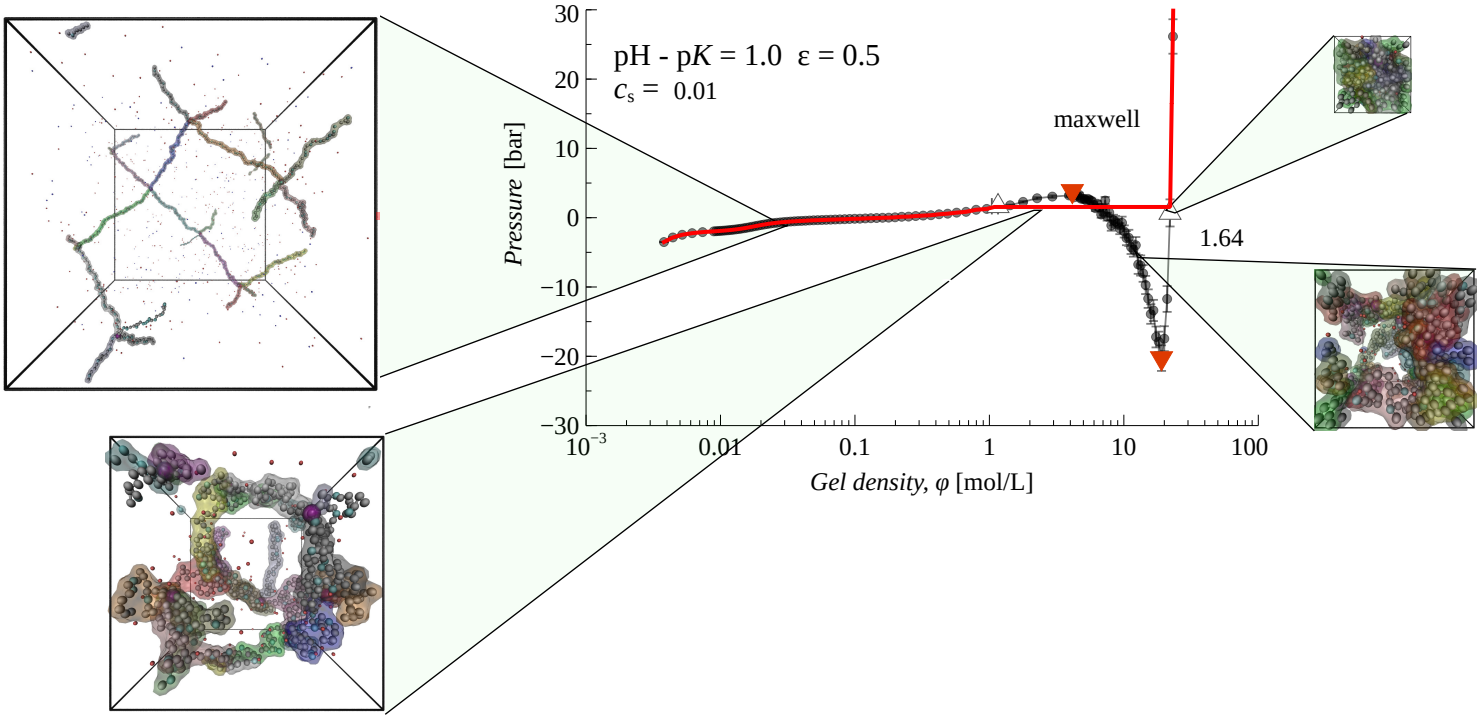
2. Simulate the chosen, collecting 50 samples of:

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

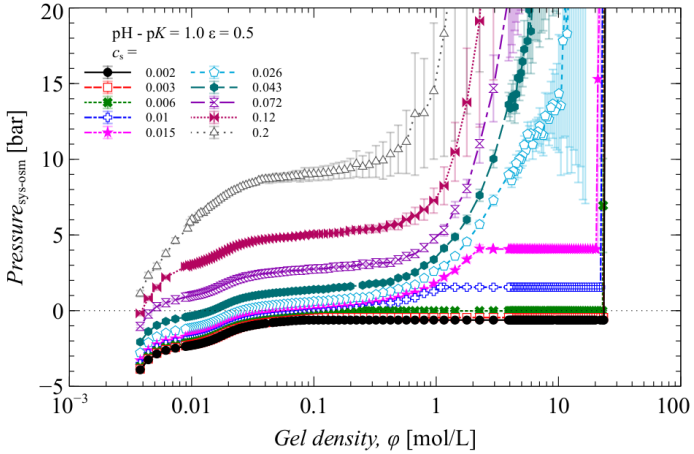
   Check the autocorrelation of each samples array.
   Pearson coefficient must be < 0.2.

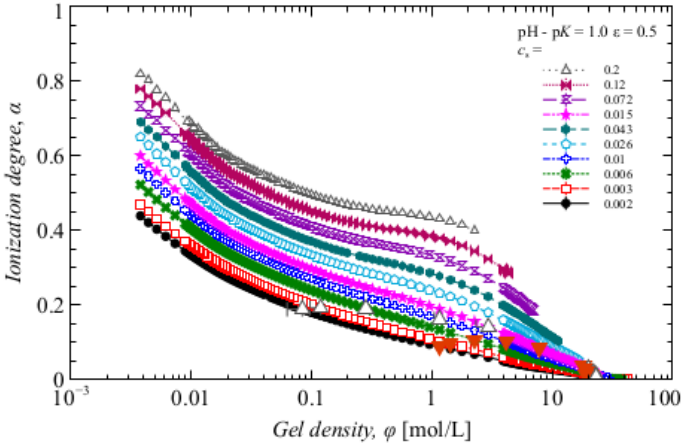
3. Repeat collecting at least 100 averages from each process.

Results. Compression of the gel.



Results. Various salinity.





Results. Fitting MCMD data by analythical theory.

$\mathrm{pH} - \mathrm{p}K = 1.0$

$\varepsilon = 0.5$

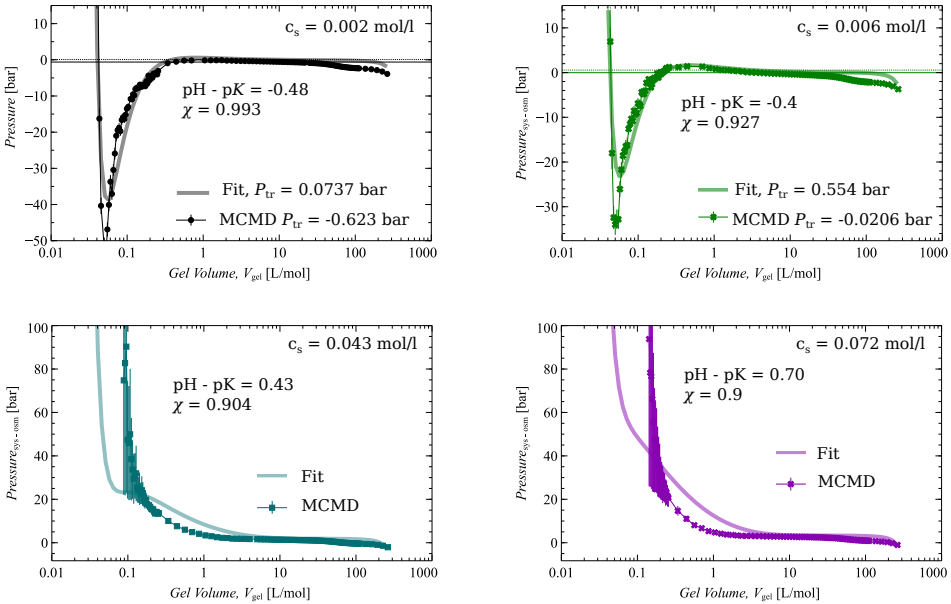
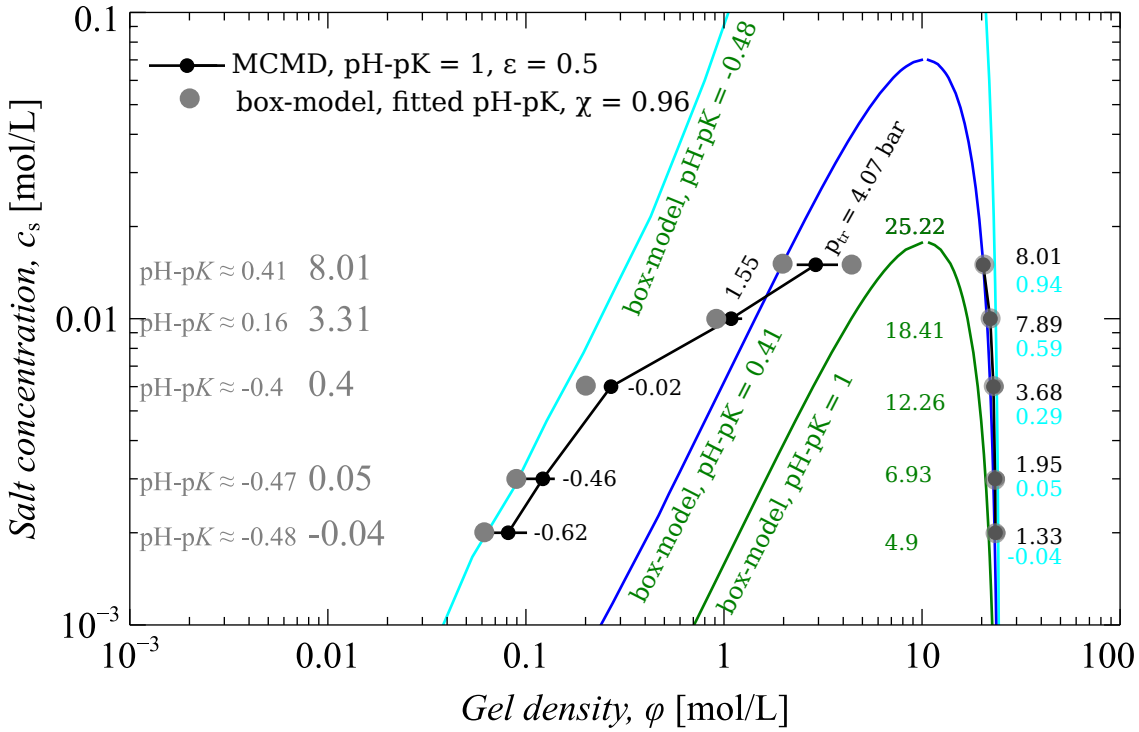


Figure 4: Results of thebootstrap fit of pressure-extension curves of gels with p$K = 6.0$ and the same hydrophobicity $\varepsilon = 0.5$ and at different salt concentration: (a) $c_s = 0.002$, (b) $c_s = 0.003$, (c) $c_s = 0.006$, (d) $c_s = 0.01$, (e) $c_s = 0.015$, (f) $c_s = 0.026$, (g) $c_s = 0.043$, (h) $c_s = 0.072$. The result of the fitting is an approximate value of χ parameter written in the legend.

Results. Phase diagram c_s - φ.



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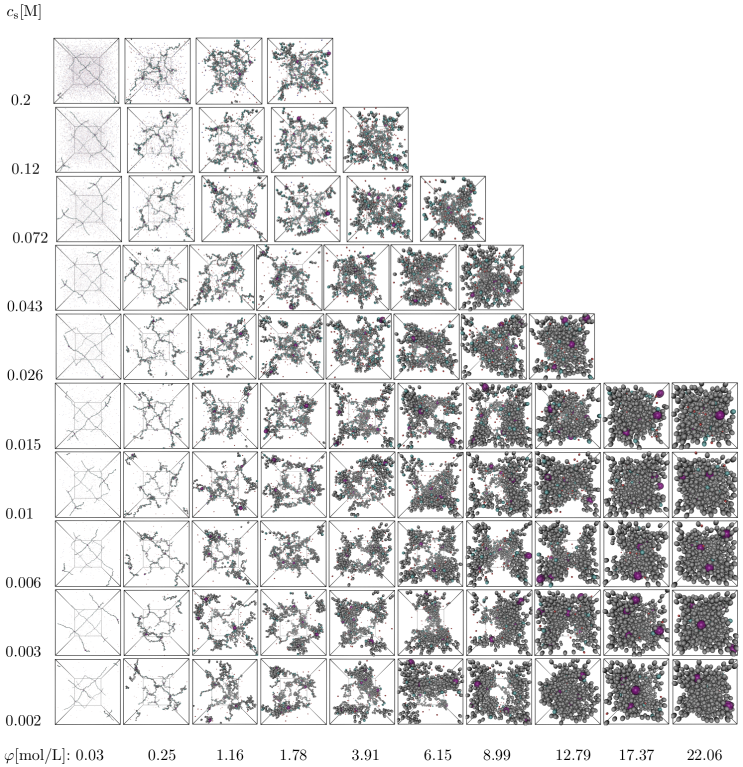

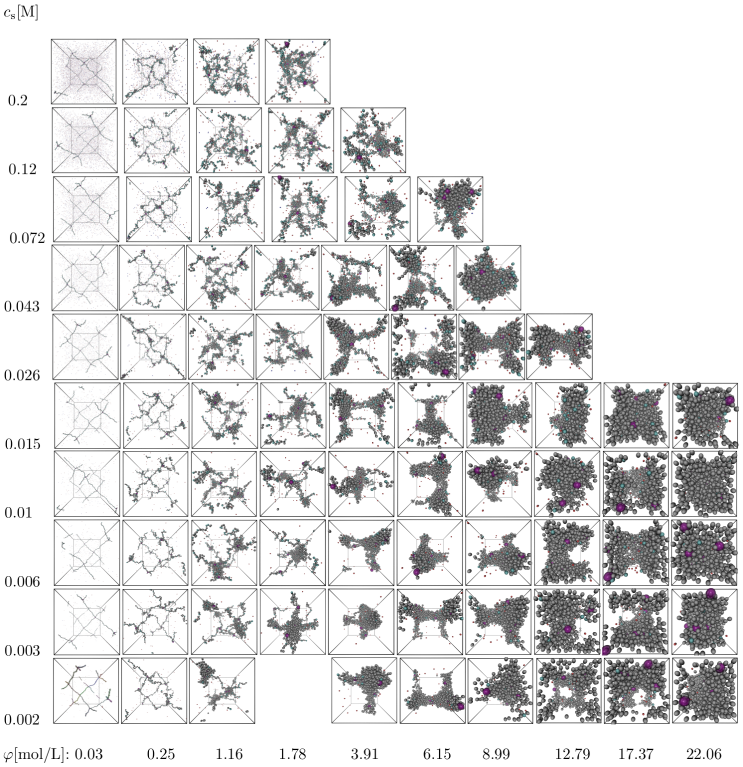

Conclusions.

- The compression of *hydrophobic weak polyelectrolyte* a gel initiates the phase transition showing up in a step-wise change of the gel density.
- The change of the gel density happens at a certain constant pressure, P_{tr}, which value is defined by c_s, pK and χ.
- P_{tr} increases with a decrease of pK and with an increase of c_s.
- The collapse of the gel is accompanied by its discharge, allowing all the neutralising ions to escape from the gel.

Oleg,do not forget to acknowledge friends