Hydrogels in charged solvents

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Hydrogels are charged polymer-networks

Hydrogels can swell tremendously in aqueous solutions

Swelling behavior can be influenced by external parameters

- Pressure
- pH
- Concentration of electrolytes
Johannes Höpfner at KIT was investigating the desalination capacity of Hydrogels.

Poly-acrylic-acid

Idea:

- Swelling Hydrogel in salty water solution
- extract Hydrogel from salt solution
- Deswell/Compress Hydrogel and squeeze out the incorporated water

**Figure 1:** Experimental setup, taken from [1]
Experimental Results

- The process is reversible
- Desalination capacity per cycle is up to 35% [1]
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*Figure 2:* Salt concentration of the extracted water, taken from [1].
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**Open Questions**

- How does the desalination work on the microscopic level
- What influences the desalination capacity
  - Crosslinking density
  - Charge density

**Figure 2:** Salt concentration of the extracted water, taken from [1].
Simulation setup

- Tetrafunctional polymer-network with 16 chains and 8 nodes and equally spaced charged on the chains
- Periodic boundary conditions
- Explicit counterions
- Langevin thermostat $\rightarrow$ Brownian dynamics
- Simulation in (NVT) and ($\mu$VT) ensemble as well as testing those together with the “npt-isotropic” barostat in ESPResSo
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Translation of experiment to computer simulation

1. Determine chemical potential and pressure in salt solution
2. Determine equilibrium swelling and internal salt concentration at a certain external salt concentration $c_s \rightarrow$ fixed external chemical potential
   - equilibrium conditions $p = p_{\text{salt}}(c_s)$ and
   - $\mu_i = \mu_i^*$
Figure 3: Snapshot of the simulated system
Simulation in the grand canonical ensemble

- Using the (NVT) ensemble simulation ESPResSo already provides
- Adding particle exchange with external reservoir → Monte Carlo steps
- Acceptance probability according to [2]

\[
\text{acc}(N \rightarrow N + 1) = \min \left( 1, \frac{V}{\Lambda^3(N+1)} \exp \left( -\beta \left( -\mu_{\text{out}} + \Delta U \right) \right) \right) \quad (1)
\]

\[
\text{acc}(N \rightarrow N - 1) = \min \left( 1, \frac{\Lambda^3 N}{V} \exp \left( -\beta \left( \mu_{\text{out}} + \Delta U \right) \right) \right) \quad (2)
\]
Simulation Setup

Simulation in the grand canonical ensemble

\[ acc(N \rightarrow N + 1) = \min \left( 1, \frac{V}{\Lambda^3(N + 1)} \exp \left( -\beta (-\mu_{\text{out}} + \Delta U) \right) \right) \] (1)

\[ acc(N \rightarrow N - 1) = \min \left( 1, \frac{\Lambda^3 N}{V} \exp \left( -\beta (\mu_{\text{out}} + \Delta U) \right) \right) \] (2)

- Elimination of \( \Lambda \)
- with \( \mu_{\text{out}} = \mu_{\text{out}}^{\text{ex}} + k_B T \ln(\rho_{\text{out}} \Lambda^3) \)

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Simulation in the grand canonical ensemble

\[ acc(N \rightarrow N + 1) = \min \left( 1, \frac{V}{\Lambda^3(N + 1)} \exp(-\beta(-\mu_{\text{out}} + \Delta U)) \right) \] (1)

\[ acc(N \rightarrow N - 1) = \min \left( 1, \frac{\Lambda^3 N}{V} \exp(-\beta(\mu_{\text{out}} + \Delta U)) \right) \] (2)

Rewritten acceptance rates

\[ acc(N \rightarrow N + 1) = \min \left( 1, \frac{1}{\rho_{\text{in}}} \exp(-\beta(-\mu_{\text{out}}^{\text{ex}} - 1/\beta \ln \rho_{\text{out}} + \Delta U)) \right) \] (3)

\[ acc(N \rightarrow N - 1) = \min \left( 1, \rho_{\text{in}} \exp(-\beta(\mu_{\text{out}}^{\text{ex}} + 1/\beta \ln \rho_{\text{out}} + \Delta U)) \right) \] (4)
Figure 4: Chemical potential obtained with for Bjerrum-length equal 2 together with a fit of the extended Debye-Hückel model and experimental activity coefficients measurements done by Truesdell [3].
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\[ \mu_{DB} = -\frac{\sqrt{2\pi} \lambda_{b}^{\frac{3}{2}} \sqrt{\rho}}{1 + 8\pi a^{*} \sqrt{\rho}} \]
Check of the Grand canonical Algorithm:

Running the simulation with an empty box, no hydrogel and measure the salt density

- outside density: $10^{-3}$
- $\mu_{ex}$ obtained from Widom particle insertion

![Figure 5: Empty box test.](image)
Check of the Grand canonical Algorithm: Running the simulation with an empty box, no hydrogel and measure the salt density

- outside density: $2.7e - 3$
- $\mu_{ex}$ obtained from Widom particle insertion

**Figure 5:** Development of the salt concentration inside a hydrogel ($N=79 \ f=1/4 \ c_s = 0.1\text{mol/L} \approx 2.7e - 3$)
Determining the pressure dependence on Volume for a given external salt solution

![Graph showing the relationship between internal pressure and box length with error bars and trend line.](image)

**Figure 6:** Total pressure dependence on volume for a salt solution with concentration 0.2mol/L.
Philipse et. al derived an equation for colloid system in contact with an infinite reservoir of salt [4].

\[
\frac{\varrho_-}{\varrho_{\text{ext}}} = -\frac{\varrho_c}{2\varrho_{\text{ext}}} + \sqrt{1 + \left(\frac{\varrho_c}{2\varrho_{\text{ext}}}\right)^2},
\] (6)

- \(\varrho_-\) is the salt concentration in the hydrogel
- \(\varrho_c = \frac{mNf}{V_{\text{hg}}}\), \(m\) is the number of polymer chains and \(N\) the number of monomers per chain, \(f\) is the charge fraction of the hydrogel
Osmotic Donnan Model

- Combining Donnan theory for the salt partitioning with an equation for the pressure balance
  - Equation of state

Equation of state

\[ mN_f V_{hg} + \varrho - \varrho = \varrho + (7) \]

\[ \varrho_{ext}^2 = \varrho - \varrho + (8) \]

\[ (\varrho + \varrho - 1) N_b^2 R e_k B T + p_{ext} = 2 \varrho_{ext} k_B T (9) \]
Osmotic Donnan Model

- Combining Donnan theory for the salt partitioning with an equation for the pressure balance
  - Equation of state
- Minimal model: the chains in the hydrogel behave as ideal gaussian chains

\[ p_{\text{in}} = p_{\text{out}} \]
\[ p_{\text{in}}^{\text{osm}} + p_{\text{elastic}} + p_{\text{extern}} = p_{\text{salt}}^{\text{osm}} \]
Osmotic Donnan Model

- Combining Donnan theory for the salt partitioning with an equation for the pressure balance
  - Equation of state
- Minimal model: the chains in the hydrogel behave as ideal gaussian chains

\[(i):\quad \frac{mNf}{V_{hg}} + \rho_\text{--} = \rho_+\] (7)

\[(ii):\quad \rho_\text{ext}^2 = \rho_\text{--} - \rho_+\] (8)

\[(iii):\quad \left(\rho_+ + \rho_\text{--} - \frac{1}{N b^2 R_e}\right) k_B T + p_\text{ext} = 2\rho_\text{ext} k_B T\] (9)
Figure 7: Dependence of the equilibrium swelling degree on the salt concentration of the external reservoir. The dashed lines are the predictions of the osmotic Donnan model.
Results

Donnan theory

\[ \frac{\varrho_-}{\varrho_{\text{ext}}} = -\frac{\varrho_c}{2\varrho_{\text{ext}}} + \sqrt{1 + \left(\frac{\varrho_c}{2\varrho_{\text{ext}}}\right)^2}, \quad (10) \]

Figure 8: Testing the Donnan prediction for the salt partitioning against the simulation for two intermediately high salt concentrations: left: 0.01 mol/L, right: 0.1 mol/L.
**Figure 9:** Testing the Donnan prediction for salt partitioning for $c_s = 0.37 \text{mol/L}$ (left) and $0.2 \text{ mol/L}$ with randomly placed charges on the hydrogel with $N=59 \ f=1/4$. 
Donnan theory in the limit of no electrostatics ($\lambda_B = 0$)

Figure 10: Comparison of the partitioning prediction of Donnan and simulation data for $c = 0.2\text{mol/L}$.
Simulation in $\mu pT$

Figure 11: Pressure versus volume for the $N=59 \ f=1/4$ hydrogel. The circles indicate the start configurations for testing simulations in ($\mu pT$).

Above
Below

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Results

Simulation in $\mu pT$

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Figure 11: Left: The final volumes that were obtained using the ($\mu pT$) ensemble simulation for the two different start configurations. Right: The salt density inside the hydrogels for the simulations in ($\mu pT$).
Conclusions

- The equilibrium swelling for hydrogels in various external salt concentrations could be determined.
- The Osmotic Donnan model and the simulations qualitatively agree.
- The Donnan theory for the salt partitioning show increasing deviations for increasing charge fractions of the hydrogel.
  - The linear charge density on the hydrogel chains breaks the assumption of homogeneity.
- This seems to remain true even for very high salt concentrations (strong screening of the electrostatics) and randomly placed charges on the hydrogel backbone.
- In the case of no electrostatics (the salt behaves almost as ideal gas) the Donnan theory and the simulations fully agree.
- The barostat in combination with the grand canonical ensemble does not work to predict the equilibrium swelling volume.
Improvement of the “Donnan”–model
  - Poisson-Boltzmann Cell model to treat the elastic properties in an electrolyte solution

Track down the origin of the deviations

Having a closer look at the distribution of ions around the chains in the hydrogel
A novel approach for the desalination of seawater by means of reusable poly(acrylic acid) hydrogels and mechanical force. 

*Understanding Molecular Simulation*. 

Activity coefficients of aqueous sodium chloride from 15° to 50°c measured with a glass electrode. 

The donnan equilibrium: I. on the thermodynamic foundation of the donnan equation of state. 