

Gibbs ensemble for polyelectrolyte hydrogel

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Abstract

Recently polyelectrolyte hydrogels have been proposed as draw agents for reverse osmosis desalination techniques. Indeed, 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. By this article, we present our recent theoretical 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.

Introduction

Water desalination technologies.

1. There are two basic approaches to separating water from salt. The first approach is to use thermal means to effect a phase change of the water (to vapor or solid), physically separate the new phase from the remaining salt solution, and then recover the thermal energy for reuse as the separated water reverts to liquid form. Distillation processes were the first desalination processes to be conducted on a large commercial scale and account for a large portion of the world's desalination capacity. In addition to the thermal component, distillation processes often include vacuum components to increase evaporation at lower temperatures.
2. The second approach to desalination is to physically separate the components, generally with a membrane, as they move in response to an externally applied gradient. The two major processes of this type are reverse osmosis (RO), and electrodialysis (ED). In RO, water passes through a membrane that is impermeable to the solute in response to a chemical potential gradient achieved through pressurization. In ED, ions in solution migrate through anion and cation selective membranes in response to an electric field. Both of these processes have been commercialized on a large scale. The flow through capacitor also uses an electric field to collect and separate dissolved ions from water.
3. Distillation is easy cheap technology but it is characterized by relatively high energy costs, compared to RO. On the contrary, RO uses expensive osmotic membranes and requires a very huge pressures to apply, but in terms of energy losses it works close to the thermodynamical limit. That is, theoretically it may consume per one transferred

from fresh water to salty water ion pair only the energy which equals to the difference of chemical potentials of that ions in fresh and salty water. The drawback of this method is that the osmotic pressure of ions in seawater may reach up to 100 bar, and this is the pressure which needs to be applied to osmotic membrane let the water to pass through it. This imposes certain requirements on the mechanical properties of the reverse osmosis setup.

4. The new emerging membrane technology is forward osmosis (FO).¹ In FO, a concentrated draw solution with a lower water chemical potential and a more diluted feed solution with a higher water chemical potential are separated by a membrane that rejects the salt but allows the passage of water. The water permeation from feed solution to draw solution is a spontaneous process driven by the chemical potential gradient . The draw agent is a²

Hydrogels for desalination.

1. Recently in desalination technology; hydrogels have been proposed as draw agents for FO. Hydrogels have the ability to absorb water across FO membrane as a result of their swelling pressure. Their insoluble cross-linked network enables dewatering under the influence of stimuli (thermal and/or mechanical).^{3,4} For example, Zhang *et al.*⁴ proposed the use of hydrogel made of thermoresponsive polyelectrolyte (copolymer of PNIPAM and polyacrylic acid). As polyelectrolyte these particles have good affinity to water and as being sensitive to heating they allow dewatering. Razmjou *et al.*³ proposed to combine such gel with magnetic nanoparticles, which allowed for direct magnetic field-induced heating.
2. Meanwhile, Zhao has reported that the swelling pressure is not the same as the osmotic pressure of a traditional solution⁵ . Zhao concluded that it is unreasonable to use “forward osmosis” in hydrogel absorbing water because the chemical residues present

in hydrogels are responsible for their water-absorption properties and not osmotic pressure. However, Wang et al. argued that hydrogels are essentially draw agents for FO because the network structure of a polymer hydrogel is an osmotic membrane from a thermodynamics perspective.⁶

3. Recently the new alternative to conventional desalination methods was proposed by prof. Manfred Wilhelm.⁷ Their method
4. The key feature of the gel employed in this study was the ability of the gel to absorb a huge amount of water. At the same time if the gel is made of polyelectrolyte it is able to reject ions.

Physics of the desalination process.

1. Roughly speaking the maximum entropy principle requires the density of charges to be moreless the same throughout the system medium. Therefore since the gel has its own charges and its own counterions neutralizing the gel charges, the density of mobile ions in the gel appear to be smaller than the density of ions outside the gel. Thus, providing that the gel counterions are kept in the gel squeezing the gel may release the solution of lower salinity then the gel was initially equilibrated with.
2. The motivation of this study was to simulate the process of desalination using polyelectrolyte hydrogel.

The target of our study is to model the thermodynamic equilibrium between the two boxes and to show how the compression of the gel affects the ion density in the outside solution

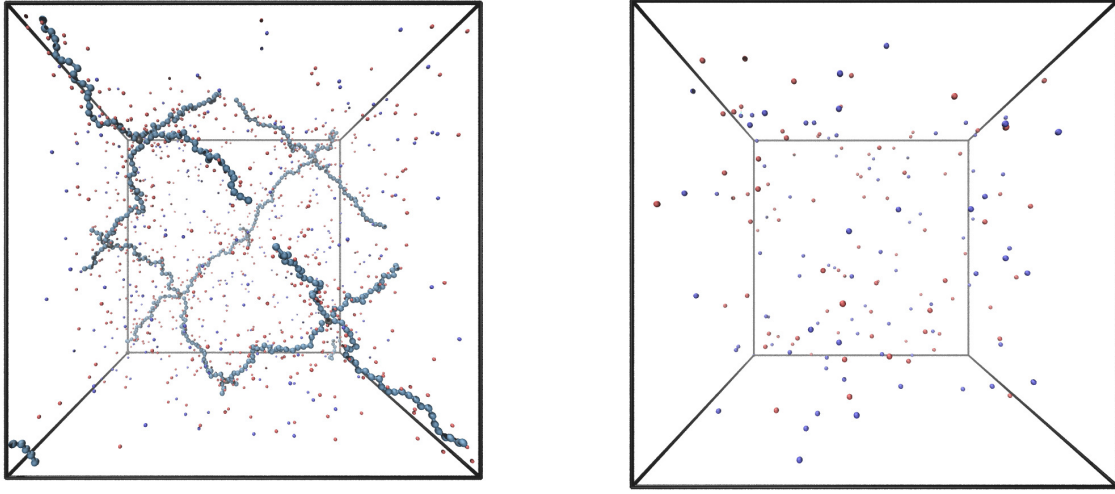


Figure 1: Diamond-like network in the simulation box. Color code represents the individual ion types (red: Na^+ , blue: Cl^- , yellow: Ca^{2+}) and the hydrogel (gray: neutral segment (AH), cyan: charged segment (A^-)). .

Theory behind the simulation

Model

We model the gel as a diamond-like polymer network, which consists of 16 linear polyelectrolyte chains, each chain comprising 30 monomer units. Each unit carries an electric charge equal to the charge of electron, $-e$. Except network the first box contains mobile ions, Na^+ and Cl^- , in such amounts that the total charge of the box is zero.

Simulation

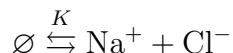
The goal of this study is to simulate the process of water desalination by means of compression. In order to do it we simulate the gel in two ensembles.

1. The first is so called *open system*, when the simulation gel freely exchanges ions with a big amount of aqueous solution.
2. And in *closed system*, when the gel is in equilibrium with a finite volume of aqueous

solution, so that the total amount of salt ions .

The compression of the gel in the open system does not affect the surrounding salinity, thus the chemical potential of ions remains constant $\mu_{\text{Na}^+} = \mu_{\text{Cl}^-} = \text{Const}$. On the contrary, what remains constant in the closed system is total number of ions, that are contained in the gel and in the external volume, $N_{\text{Na}^+} = \text{Const}$ and $N_{\text{Cl}^-} = \text{Const}$.

Open system. We simulate the first ensemble using the grand reaction method.^{7,8} This method is a hybrid of molecular dynamics (MD) and Monte Carlo (MC). The whole simulation is represents a chain of subsimulations of MD and MC following each other. The MD simulation is a standard Langevin dynamics⁹ which models the mechanical movement of all the system particles. Whereas MC simulates the thermodynamic equilibrium with reservoir, which exchanges ions with the simulation box. The insertion (and deletion) of ion pairs is considered as a reaction of creation (annihilation) of an ion pair



with corresponding reaction constant, which is defined by chemical potential of ions, $K = \exp(\mu_{\text{Na}^+} + \mu_{\text{Cl}^-})$.

Closed system. The similar scheme we use to simulate the gel in closed system. Again the procedure represents a chain of subsequent MD and MC simulation, but now we run the molecular dynamics in two simulation boxes simultaneously. The first box of the volume V^{gel} contains the gel with ions, and the second box, V^{out} — contains only ions of certain density, c_s . These two boxes are represented in Figure 1. The total volume of both boxes is kept constant, $V = V_{\text{gel}} + V_{\text{out}}$, so the compression of the gel implies the increase of the out volume.

The thermodynamic equilibrium, that is exchange of the ion pairs between the boxes, is done using MC procedure in a way similar to described in.[?]

Algorithm. In general the simulation algorithm looks the following:

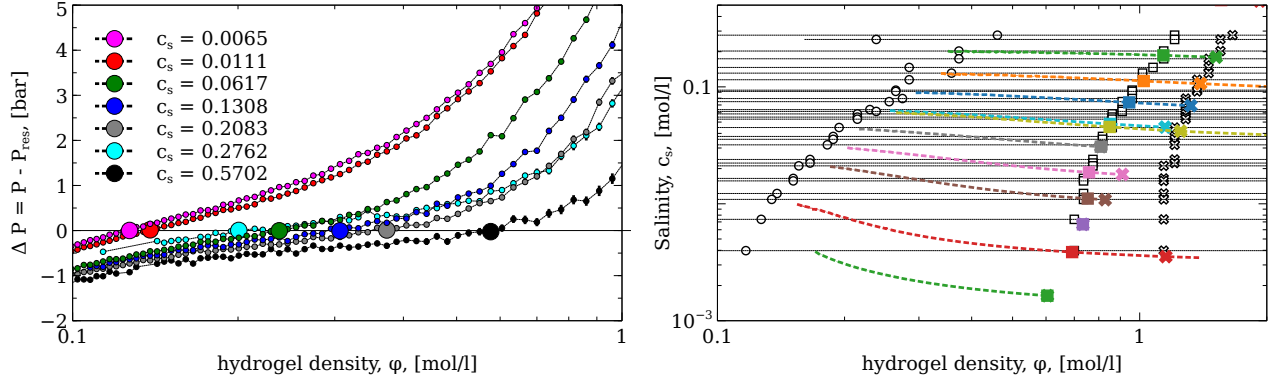
1. simulate molecular dynamics in both boxes in parallel; collect the observable sample arrays: pressure and end-to-end distances, P and R_e ;
2. perform Monte-Carlo procedure simulating ion pair exchange; collect the observables sample arrays: number of ions in both boxes, $N_{\text{Na}^+}^I$, $N_{\text{Cl}^-}^I$, $N_{\text{Na}^+}^{II}$ and $N_{\text{Cl}^-}^{II}$;
3. repeat the procedure until the desired length of sample arrays is reached.

Results

Compression in open system. First we run a set of simulations modeling the compression of the gel in open system, *i. e.* in equilibrium with big bath of certain salinity. Figure 2a shows how the gel partial pressure depends on the density of the gel segments, φ . The partial pressure of the gel is that pressure which needs to be applied in mechanical equilibrium to compress the hydrogel and achieve a specific density, φ . Several curves on the plot correspond to different salinities of the reservoir c_s . By big circles marked the states where the applied to the gel pressure is zero, that is the so called free swelling equilibrium states. These states are characterized by the values of the gel density, φ_0 , and the corresponding molar volume of the gel, $V_0^{\text{gel}} = \frac{1}{\varphi_0}$. It is seen already from this figure that the increase of salinity shifts the free swelling equilibrium states towards higher densities. In other words, increase of salinity shrinks the gel. This is well known effect, typical for all the strong polyelectrolytes and caused by the screening of electrostatic interactions by ions¹⁰ and by the condition of electroneutrality of the hydrogel media.¹¹

Compression in closed system. We use the free swelling equilibrium states as the initial ones for simulation of the gel in closed system. So we compress the gel starting from the volume V_0^{gel} and zero pressure until the pressure reaches 10 bar. We compress it in a box of the same volume V_0^{gel} , *i. e.* the volume of outside solution increases starting from zero

as much as the volume of the gel decreases, such that the total volume remains constant $V^{\text{tot}} = V^{\text{gel}} + V^{\text{out}}$. Since the amount of external solution is small, the compression of the gel affects its salinity, which is depicted on Figure 2b.



(a) The compression of the gel in grand canonical ensemble for different salinities. The crosssection of the curves with x-axis indicate the free selling equilibrium. The states, which are close to pressure of 5 bar and 10 bar, using the corresponding indices '5' and '10'.

(b) Salinity vs gel density

Figure 2: Compression of the gel in open and in closed system.

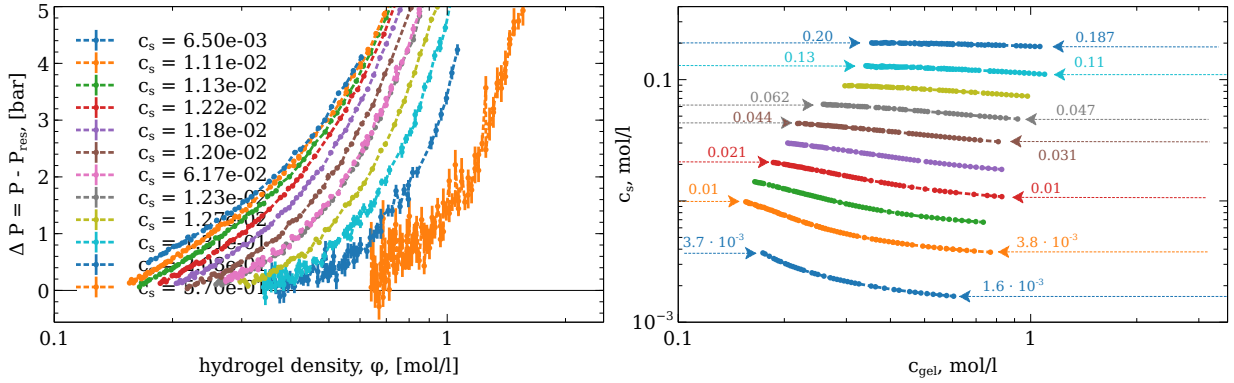


Figure 3: (a) The pressure extension curve of the gel. (b) The dependence of the salinity of the outside bath, during the hydrogel compression. The numbers reflect the initial and final salt concentration of the external solution. HERE MUST BE A PANEL ILLUSTRATING THE EFFICIENCY OF THE STAIRCASE, HOW MANY LITRES OF WATER FOR HOW MUCH ENERGY

Acknowledgments

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