

# Gibbs ensemble for polyelectrolyte hydrogel

Michail Laktionov<sup>a,b</sup>, Oleg V. Rud<sup>a</sup>, Lucie Nova<sup>a</sup>, Filip Uhlik<sup>a</sup>

<sup>a</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, Praha 2 128 00, Czech Republic

<sup>b</sup>Institute of Macromolecular Compounds of Russian Academy of Sciences, 199004, Bolshoy pr. 31, Saint-Petersburg, Russia

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## Abstract

By this article we model compression of polyelectrolyte hydrogel in equilibrium with small volume of salty aqueous solution. We show that the change of the hydrogel volume affects the salinity of the solution. The decrease of the gel volume decreases the solution and vice versa the swelling of the gel increases the surrounding solution. This effect can be employed for water desalination ...

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## 1. Theory behind the simulation

Figure 1 presents a diamond-like polymer network inserted in a simple cubic simulation box of volume  $V_{\text{box}}$  with periodic boundaries. The network consists of 16 linear polyelectrolyte chains, each chain comprising 30 monomer units. Each unit is able to change its ionization state from charged to neutral and vice versa according to the ionization equilibrium. The mobile ions ( $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$ ) are present in certain amount such that they fulfill the electroneutrality condition.

We model the network in equilibrium with the bulk of aqueous solution. In order to keep the equilibrium conditions we consider three processes to occur:

1. the thermal movement of all segments in simulation box (Langevin dynamics);
2. the transfer of ions between two vessels;
3. the change of ratio between volumes of the two vessels emulating the piston applying certain pressure to one of the vessels;

All three processes occur simultaneously in real systems, however, we simulate them alternating each other in stop-run mode in a random order.

### 1.1. Langevin dynamics

We use three types of interactions, *i. e.* bonded interactions, short-range non-bonded interactions and electrostatic interactions.

We use Finite extension nonlinear elastic (FENE) potential Equation 1 to account for the bonding interactions.

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

where  $K$  is the magnitude of symmetric interaction between two segments,  $\Delta r_{\max}$  is the maximal stretching length of the bond and  $r_0$  is the equilibrium bond length. In our simulations we set  $K = 10k_{\text{B}}T/\sigma^2$ ,  $\Delta r_{\max} = 2\sigma$  and  $r_0 = 1.0\sigma$  [?].

We model the non-bonded interactions using truncated Lennard-Jones interaction potential. This potential imposes strong repulsion between all particles at short distances:

$$V_{\text{LJ}}(r) = \begin{cases} 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) & \text{if } r < r_{\text{cut}}, \\ 0 & \text{elsewhere} \end{cases}, \quad (2)$$

remove  $\text{Ca}^{2+}$   
ions from  
snapshot

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Email address: michail.laktionov@natur.cuni.cz (Michail Laktionov)  
URL: <http://www.physchem.cz/> (Michail Laktionov)

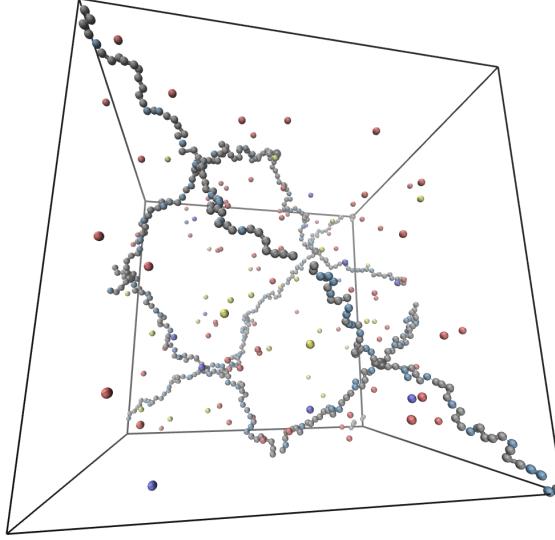


Figure 1: Diamond-like network in the simulation box. Color code represents the individual ion types (red:  $\text{Na}^+$ , blue:  $\text{Cl}^-$ , yellow:  $\text{Ca}^{2+}$ ) and the hydrogel (gray: neutral segment (AH), cyan: charged segment ( $\text{A}^-$ )).

where  $r$  is the interparticle distance,  $\sigma = 0.35\text{nm}$  is the characteristic size of the particles,  $\varepsilon$  is the depth of the potential well in  $k_B T$  units and  $r_{\text{cut}}$  is the cut-off distance beyond which the potential is set zero.

We model the long range electrostatic interactions by the Coulomb potential:

$$V_{\text{EL}} = l_B k_B T \frac{q_1 q_2}{r}, \quad (3)$$

where  $l_B$  is Bjerrum length. We set  $l_B = 2\sigma = 0.7\text{nm}$  which corresponds to water at  $T = 300\text{K}$ .

We use Langevin thermostat, *i. e.* we add two additional terms to force in equation of motion

$$f_i = -\gamma v_i(t) + \sqrt{2\gamma k_B T} \eta_i(t), \quad (4)$$

where the first term correspond to constant friction with  $\gamma$  being a friction coefficient, and the second one corresponds to random thermal force with  $\eta_i$  being a normally distributed random number (see for details [?]).

## 2. Sampling in the Gibbs ensemble

All thermal moves are frozen during the sampling of the ion pairs exchange. The system represents the ensemble with constant number of particles distributed between two vessels (I) and (II).

In the following paragraph we derive the criteria for sampling of the ion exchange equilibrium.

*Gibbs canonical ensemble.* Let us first consider the total free energy of both vessels assuming that we have only particles of a single type:

$$F = (E_I - TS_I) + (E_{II} - TS_{II}) \quad (5)$$

where  $E$  is internal energy,  $T$  — temperature,  $S$  — entropy.

The entropy  $S$  is given by the Boltzmann formula [?]:

$$S = k_B \ln \frac{V^N}{N!} \quad (6)$$

where  $N$  is a number of particles in corresponding vessel. This formula accounts for two contributions:

1. the combinatorial entropy  $S_c = -k_B \ln N!$  which reflects the freedom of choice among  $N$  particles

2. the mixing entropy  $S_m = k_B N \ln V$  which reflects the freedom to place the chosen particle randomly within the simulation box.

$V$  is the unitless volume, *i. e.* the volume measured in units of  $\sigma^3$ . Thus Equation 5 turns to

$$F = E_I - k_B T \ln \frac{V_I^{N_I}}{N_I!} + E_{II} - k_B T \ln \frac{V_{II}^{N_{II}}}{N_{II}!} \quad (7)$$

When a single particle transferred from the vessel (I) to the vessel (II) the free energy in vessel (I) changes

$$\Delta F_I = \Delta E_I + k_B T \ln \frac{V_I^{N_I}}{N_I!} - k_B T \ln \frac{V_I^{N_I-1}}{(N_I-1)!} = \Delta E_I + k_B T \ln \frac{V_I}{N_I} \quad (8)$$

whwhereas the free energy change in (II) vessel is

$$\Delta F_{II} = \Delta E_{II} + k_B T \ln \frac{V_{II}^{N_{II}}}{N_{II}!} - k_B T \ln \frac{V_{II}^{N_{II}+1}}{(N_{II}+1)!} = \Delta E_{II} + k_B T \ln \frac{N_{II}+1}{V_{II}} \quad (9)$$

Thus the total change of free energy will be

$$\Delta F = \Delta E_I + \Delta E_{II} + k_B T \ln \frac{V_I}{V_{II}} \frac{N_{II}+1}{N_I} \quad (10)$$

Introducing  $\xi = \pm 1$ , which reflects the direction of movement of particle,  $\xi = +1$  if the particles moves from vessel (I) to vessel (II), and  $\xi = -1$  if the particles moves backwards, then the previous formula transfers to

$$\Delta F = \Delta E_{tot} + k_B T \xi \ln \frac{V_I}{V_{II}} \frac{N_{II} + \theta(\xi)}{N_I + \theta(-\xi)} \quad (11)$$

where  $\theta(x)$  is the Heaviside function.

In order to keep electroneutrality of the system we transfer particles by electroneutral pairs. Accounting for two types of particles which are moved all the time together the previous formula translates to the following

$$\Delta F = \Delta E_{tot} + k_B T \xi \left( \ln \frac{V_I}{V_{II}} \frac{N_{II}^{Na^+} + \theta(\xi)}{N_I^{Na^+} + \theta(-\xi)} + \ln \frac{V_I}{V_{II}} \frac{N_{II}^{Cl^-} + \theta(\xi)}{N_I^{Cl^-} + \theta(-\xi)} \right) \quad (12)$$

or

$$\Delta F = \Delta E_{tot} + k_B T \xi \ln \left( \left( \frac{V_I}{V_{II}} \right)^2 \prod_i \frac{N_{II}^i + \theta(\xi)}{N_I^i + \theta(-\xi)} \right) \quad (13)$$

where  $i$  runs over the ion types  $i \in \{Na^+, Cl^-\}$ .

In order to simulate an ensemble composed of two vessels exchanging particles with each other we need to perform the following Monte Carlo procedure [? ? ?]

1. we propose the new configuration of the system by removing ion pair from one vessel and inserting it to another
2. we accept the new configuration if

$$\mathcal{R}^\xi < e^{\Delta F / k_B T} \quad (14)$$

where  $\mathcal{R}$  is uniformly distributed random number in range between 0 and 1.

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