

Scientific paper

Attraction Between Like-Charged Surfaces: Effect of Counterion Dimerization

Jurij Reščič^{1,*} and Klemen Bohinc²¹ Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia² Faculty of Health Sciences, University of Ljubljana, Ljubljana, Slovenia

* Corresponding author: E-mail: jurij.rescic@fkt.uni-lj.si

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

A force between two equally charged surfaces depends on the composition of intervening solution. While the force is always repulsive for monovalent counterions, multivalent counterions turn the interaction into the attractive one. An example of the attraction between like charged surfaces is the aggregation of colloidal particles mediated by multivalent counterions with spatially separated charges. A model system represents the colloids by equally charged planar surfaces. In our consideration the intervening salt-free solution is composed of rod-like dimmers. Some of dimmers can be disconnected to monovalent ions. This model system was solved using the Monte Carlo (MC) simulations and the Poisson-Boltzmann (PB) theory, which was extended to deal with rigid complex ions. The study was made by varying a range of parameters including the surface charge density and the ratio of the number of monovalent counterions to the number of all counterions. The calculated pressure shows that with increasing surface charge density the lower fraction of dimeric counterions is needed to induce attractive force between surfaces. A good agreement between the MC simulations and the theoretical results was obtained.

Keywords: Poisson-Boltzmann, colloid, attraction, charged planar slit, bridging, rod-like ion

1. Introduction

Aqueous solutions containing charged colloidal particles and small ions represent a cornerstone of biological systems and biotechnological applications. Typical examples of charged colloidal particles include proteins, micelles, lamellar liquid crystals, and silica. These particles are significantly larger than small ions which justifies the choice of a model where intervening solution is placed between two equally charged planar surfaces. The intervening solution contains simple monovalent charge-neutralizing counterions and also monovalent coions, if salt is present. Even salt-free colloidal systems are stable as predicted by the DLVO theory.^{1,2} However, replacing monovalent ions with divalent ones gives rise to the effective attractive force between colloidal particles, which was observed for both planar geometry^{3,4} and also for isotropic systems containing spherical colloids.⁵ Presence of effective attraction between colloidal particles is required for a system to undergo phase separation.^{6,7,8}

Attraction between equally charged particles is additionally enhanced in both magnitude and range if polycentric multivalent ions are present. It has long been known that oppositely charged short polyions cause aggregation of colloidal particles by bridging mechanism.⁹ This was later demonstrated by simulation studies^{10,11} and supported by theoretical approaches.¹² Complex multivalent ions with spatially separated charge are also common in biological systems. Short polyamines spermine and spermidine, which play an important role in DNA packaging, are such an example.^{13,14}

It is therefore of crucial importance to understand the mechanism and circumstances when the effective attractive Coulomb electrostatic interactions between macroions emerge.

Traditional approach to study electrolyte solutions is the Poisson-Boltzmann theory, which treats small ions as point charges. The Poisson-Boltzmann theory neglects correlations between small counterions, which limit its validity toward low concentrations, small surface charge

density and monovalent ions. This theory was recently extended to allow for treatment of rigid multivalent ions with spatially separated charge distribution.^{15,16} The simplest situation of rigid multivalent ions is that of rod-like ions where the charges are connected by a stiff rod of given length. The fixed separation of charges within the rods introduces the intra-ionic correlations into the Poisson-Boltzmann theory. This extended theory can predict attraction between like-charged plates. The detailed considerations have shown that the introduced intra-ionic correlations cause the bridging between the charged plates. The theory was generalized to systems with polydisperse rod lengths and arbitrary charge distribution along the rods. Also the influence of added salt was considered.¹⁷

On the other hand, the MC computer simulations are powerful and exact tool for solving model systems. With MC simulations we can test the theoretical predictions and consider the cases which could not be covered by the theory. We showed that for sufficiently long rods there is a very good agreement between the extended Poisson-Boltzmann theory and MC simulations.^{18,19} Kim et al.²⁰ have confirmed that the bridging configuration contribute to the attraction between like charged plates.

The attractive force between like charged surfaces was also experimentally observed. The first observation of attraction between two highly negatively charged clays was reported for CaCl_2 solution.^{21,22,23}

In this article we study a system of two like charged plates in the solution of divalent rod-like and monovalent counterions. We utilize both the extended Poisson-Boltzmann theory and canonical Monte Carlo computer simulations to study the effect of increased fraction of rigid divalent counterions with spatially separated charges on the force between equally charged plates.

2. Model and Methods

An aqueous salt-free colloidal solution where colloidal particles are much larger than counterions, can be modeled as a planar gap between two equally and uniformly charged surfaces and filled with charge-neutralizing intervening solution containing positive point like counterions as illustrated in Figure 1.

The counterions can be either divalent in a form of a rigid dimer with the bulk concentration n_0 either monovalent with the bulk concentrations m_0 . The planar surfaces are negatively charged with the surface charge density σ . The length of rod-like counterions is equal to l . Each rod-like ion has two charges each located at one end of the rod.

2. 1. Poisson-Boltzmann Theory

We introduce a Cartesian coordinate system whose x axis is oriented perpendicular to the charged surfaces. They are located at $x = 0$ and $x = D$. Due to sufficiently

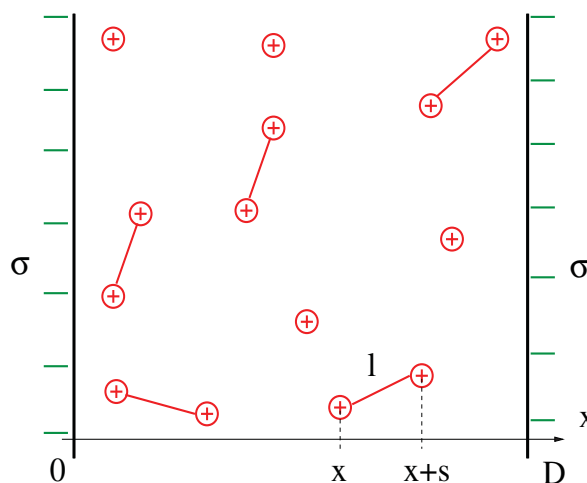


Figure 1: Schematic illustration of two like-charged planar surfaces, located at $x = 0$ and $x = D$ with σ denoting the surface charge density. The surfaces are immersed in an electrolyte solution that contains a mixture of divalent rod-like and monovalent point-like counterions. Rod-like ions have two charges at the ending of the rods. This illustration is connected to the theoretical description.

large planar surfaces and the translational invariance of the system along y and z directions, we can describe the systems with functions depending only on the x coordinate. See Fig. 1 for an illustration of the system.

The overall charge neutrality of the system requires

$$\int_0^D 2n(x) dx + \int_0^D m(x) dx = \frac{2|\sigma|}{e}, \quad (1)$$

where e is the elementary charge. The first term in Eq. 1 represents the number of positive charges of rod-like counterions between the charged surfaces. As shown in Fig. 1, along the x axis the reference charges of rod-like counterions are located at x and the second charges at $x + s$. Central quantity to describe location and orientation of rod-like counterions is the ionic distribution function $n(x,s)$. The number density of reference charges at position x is

$$n(x) = \frac{1}{2l} \int_{-l}^l n(x,s) ds, \quad (2)$$

where we integrate over all possible projections s . The second term in Eq. 1 represents the number of monovalent counterions between the charged surfaces, which is calculated via integral of the number density of monovalent counterions $m(x)$. Eq. 1 ensures that the number of positive elementary charges in the solution is equal to the number of elementary charges on the surfaces.

The electrostatic free energy of the system, F , measured per unit area A and expressed in units of the thermal energy $k_B T$ (here k_B is Boltzmann's constant and T is the absolute temperature) can be expressed as

$$\frac{F}{Ak_B T} = \frac{1}{8\pi l_B} \int_{-\infty}^{\infty} dx \Psi'(x)^2 + \int_{-\infty}^{\infty} dx \langle n(x, s) \ln n(x, s) v_n - n(x, s) \rangle + \int_{-\infty}^{\infty} dx [m(x) \ln m(x) v_m - m(x)] + \lambda \left[\int_{-\infty}^{\infty} dx [2 \langle n(x, s) \rangle + m(x)] - \frac{2|\sigma|}{e} \right] + \int_{-\infty}^{\infty} dx [\langle n(x, s) U(x, s) \rangle] \quad (3)$$

where v_i is the effective volume of counterions and Ψ is the reduced electrostatic potential. The prime in $\Psi'(x)$ denotes the first derivative with respect to the coordinate x . The Bjerrum length in water at a room temperature is $l_B = 0.714 \text{ nm}$. The first term in Eq. 3 corresponds to mean electrostatic field energy, the second term includes the orientational and positional entropic contribution of rod-like counterions to the free energy and the third term includes the translational entropic contribution of monovalent counterions to the free energy. $\langle \dots \rangle = 1/2l \int_{-l}^l \dots ds$ denotes the averaging over all possible rotations of rod-like counterions. The fourth term in Eq. 3 ensures the electro-neutrality of the whole system and λ is the Lagrange multiplier. This free energy is given on mean field level where the intra-ionic correlations are accounted for. The steric interactions of rods with the charged surfaces are taken into account via the external non-electrostatic potential $U(x, s)$.

The presence of rod-like and monovalent point-like counterions implies the volume charge density

$$\rho(x) = e \langle n(x, s) + n(x - s, s) \rangle + e m(x), \quad (4)$$

where the first term collects all charges of the rod-like counterions, i.e. the reference charges located at x and second charges whose reference charges are located at x . The last term collects all charges of monovalent ions.

In thermal equilibrium the free energy adopts a minimum. The functional minimization of the free energy F leads to the modified Boltzmann distributions

$$n(x) = \frac{1}{v_n} \left\langle e^{-\Psi(x) - \Psi(x+s) - 2\lambda - U(x, s)} \right\rangle, \quad (5)$$

and

$$m(x) = \frac{1}{v_m} e^{-\Psi(x) - \lambda}. \quad (6)$$

Insertion of Eqs. (5) and (6) into volume charge density $\rho(x)$ (Eq. 4) and then into the Poisson's equation $\Psi''(x) = -4\pi l_B \rho(x)/e$ results in the integral differential equation

$$\Psi''(x) = -4\pi l_B \left[\frac{2}{v_n} \left\langle e^{-\Psi(x) - \Psi(x+s) - 2\lambda - U(x, s)} \right\rangle + \frac{1}{v_m} e^{-\Psi(x) - \lambda} \right] \quad (7)$$

This integral differential equation can be solved numerically subject to the following two boundary conditions

$$\Psi'(0) = +4\pi l_B |\sigma| / e, \quad (8)$$

and

$$\Psi'(D) = -4\pi l_B |\sigma| / e, \quad (9)$$

where we recall that σ denotes the surface charge density on each of the two planar surfaces.

The parameters v_i are searched for in order to satisfy the ratio between the number of monovalent counterions and all charges in the solution

$$\eta = \frac{\int_0^D m(x) dx}{\int_0^D [m(x) + 2n(x)] dx} \quad (10)$$

For the external non-electrostatic potential we chose

$$U(x, s) = \begin{cases} 0 & \text{if } x > 0 \ \& \ x+s > 0 \ \& \ x < D \ \& \ x+s < D. \\ \infty & \text{otherwise} \end{cases} \quad (11)$$

2. 2. Monte Carlo Computer Simulation

Canonical Monte Carlo simulations were performed using the integrated Monte Carlo / Molecular Dynamic / Brownian dynamic simulation package Molsim,²⁴ following the standard Metropolis scheme. Total 3000 elementary charges in monomeric and dimeric form were placed randomly into the Monte Carlo simulation box. The size of the MC box was calculated according to the chosen surface charge density to achieve electroneutrality.

Since all mobile ions are of the same sign, it is possible to use point like ions as in the PB theory. A rigid dimer is a particle consisting of two »atoms« and is moved in the MC box as a single entity with two interaction sites, preserving its internal structure.

A trial move consists of both random displacements for both types of particles; for dimeric counterions a trial move also includes a random rotation. When a dimeric counterion is moved, an interaction energy difference emerging from both interaction sites is calculated and used as in the case of monomeric counterions. Displacement parameters were chosen to obtain approximately 50% acceptance rate. 60,000 attempted moves per particle were used for equilibration followed by 200,000 attempted moves during production runs. Interparticle interactions were calculated as described elsewhere.²⁵ Long range corrections due to ionic distribution outside the MC

box are found to be small and were therefore not used in present simulations.¹⁹ To calculate single particle distributions, the x-axis was always divided into 200 bins. The standard deviation of values in histograms was less than 0.2% for each separate bin in all cases.

3. Results and Discussion

For a model system both structural and thermodynamic parameters are evaluated. We performed calculations for two different values of surface charge density, -0.05 C/m^2 and -0.10 C/m^2 . The length of divalent rod-like ions is fixed to $l = 4 \text{ nm}$ in all cases. Variation in the distance between two plates, D , corresponds to variation in concentration, and was between 2 and 10 nm.

Figs. 2 and 3 show single particle distributions of both types of counterions as a function of the distance from the left charged plate. The profiles are calculated for two different surface charge densities and four different parameters η . Generally, the concentration of counterions decreases with increasing distance from the left charged

plate. At the midplane the concentration reaches a minimum and then further increases when approaching the right plate. As one should expect, positively charged counterions accumulate near negatively charged surfaces, and are depleted from the inner part of the slit. Density profiles are similar for both types of counterions. Comparison between Fig. 2 and 3 reveal that the accumulation of both types of counterions is more pronounced at a higher surface charge density. If the fraction of monomeric counterions is larger than the fraction of their dimeric counterparts, its profile has larger values throughout the slit's width. The theoretical results agree (full and dashed lines) with the results of MC simulations (stars and squares).

The osmotic pressure exerted by rod-like and monovalent counterions on two equally charged surfaces can be calculated from the contact theorem, first derived by Henderson *et al.*²⁶ and used in systems with dimeric ions:²⁷

$$\frac{P}{kT} = 2n(0) + m(0) - \frac{\sigma^2 2\pi l_B}{e^2}, \quad (12)$$

where $n(0)$ is the concentration of reference charges of

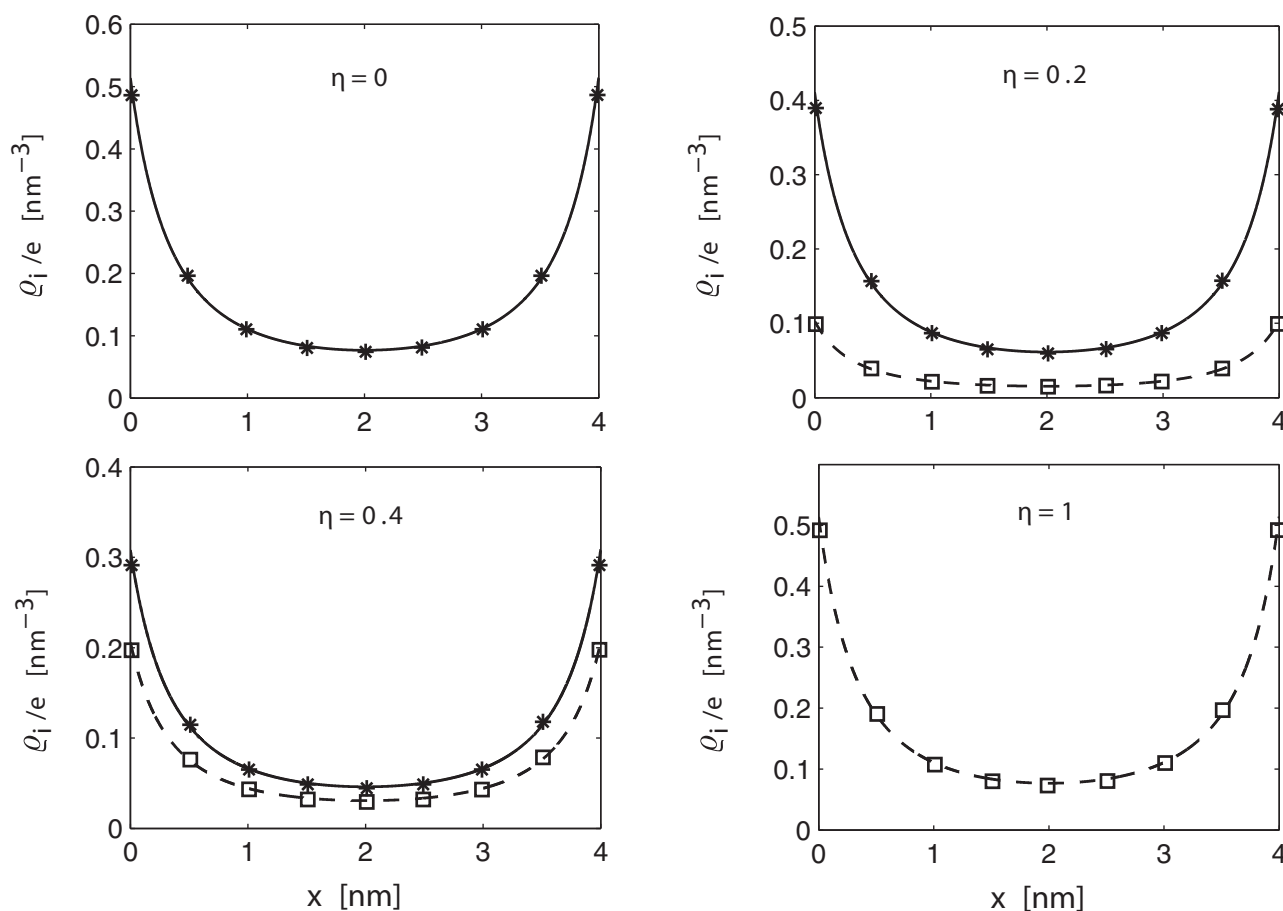


Figure 2: Concentration profiles of rod-like counterions (full lines) and monovalent point-like counterions (dashed lines) for four different parameters η . Full and dashed lines are the theoretical results whereas the stars and squares are the results of MC simulations. The model parameters are $l = 4 \text{ nm}$, $D = 4 \text{ nm}$ and $\sigma = -0.05 \text{ C/m}^2$.

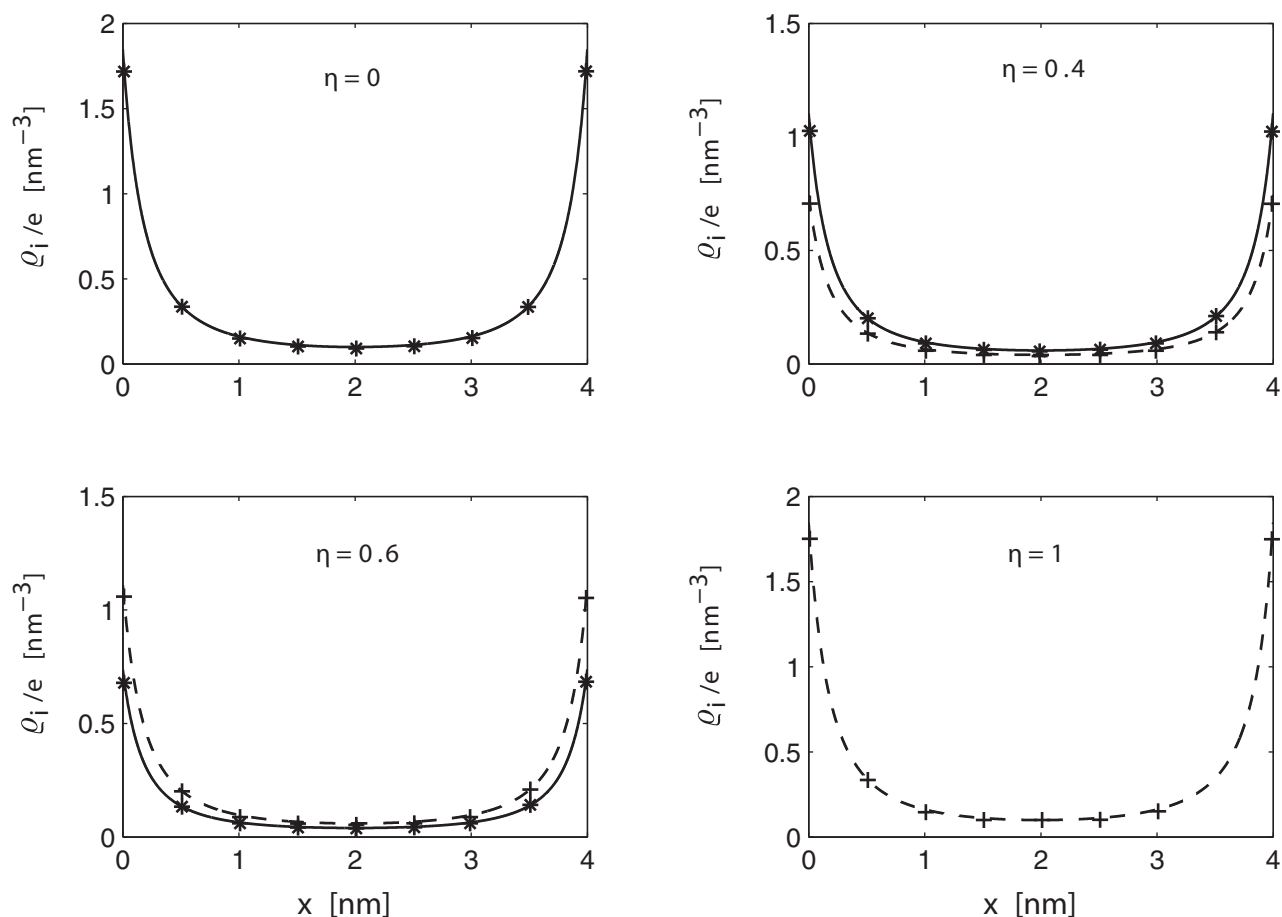


Figure 3: Concentration profiles of rod-like counterions (full lines) and monovalent point-like counterions (dashed lines) for different parameters η . Full and dashed lines are the theoretical results whereas the stars and squares are the results of MC simulations. The model parameters are $l = 4$ nm, $D = 4$ nm and $\sigma = -0.1$ C/m².

rod-like counterions at the charged surface and $m(0)$ is the concentration of monovalent counterions at the charged surface. Figs. 4 and 5 show the pressure as a function of the distance between the charged surfaces for three different parameters η and for two surface charge densities. The pressure p first decreases with increasing distance D and then crosses the abscissa. Let's note that the energetically most favorable situation is at the pressure equal to zero. From Figs. 4 and 5 we see that the most favorable distance D between the charged surfaces is approximately equal to the length of divalent ions. This corresponds to the bridging, where the rod-like ions are oriented perpendicular to the charge surfaces. The rod-like ions connect left and right surfaces. After the pressure passes the abscissa the pressure continues to decrease, reaches a minimum and then further converges to zero. For sufficiently large fraction of monovalent counterions to all counterions the pressure monotonously decreases with increasing distance between the plates. The interaction between the like charged plates is always repulsive.

However, only a thorough inspection of density profiles' contact values, required for pressure evaluation, reveals

its subtle yet nonuniform variation with increasing distance between two charged plates. Pressure is for monovalent counterions positive for all D regardless of surface charge density, σ . For point-like divalent counterions it was demonstrated that they induce an attractive force between plates, thus indicating a possible phase separation.^{3,4} In the work of Guldbrand *et al.*³ was shown that pointlike divalent counterions induce attraction between two plates at surface charge density larger than ~ 0.1 C/m². Our data (Fig. 6) show very weak attraction at the same surface charge density, which conforms to the results from the literature.³

Short divalent counterions are therefore also expected to give rise to attractive force; however, a question at which fraction this happens, is addressed in this study. At $\sigma = -0.1$ C/m² the fraction of monomers at which the attractive interaction vanishes, is about 70%. At $\sigma = -0.05$ C/m² this fraction is roughly two times lower, which leads to the conclusion that equal number of dimeric counterions per unit area is needed to induce attraction between plates.

If the rod length is zero, a rod-like ion becomes an ordinary point-like divalent ion. A Poisson-Boltzmann

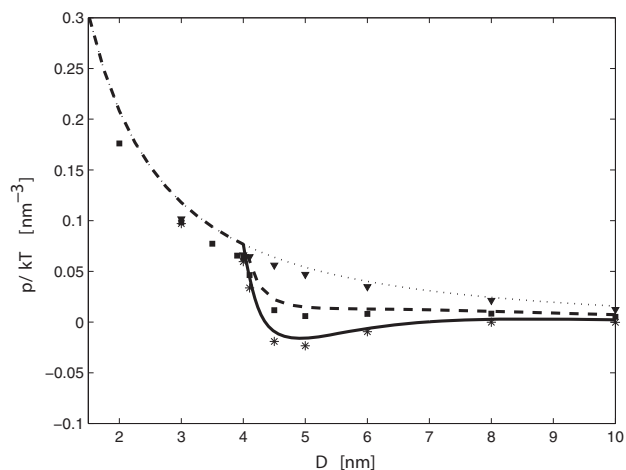


Figure 4: Pressure p as a function of the plate separation D for three different parameters: $\eta = 0$ (full line; stars), $\eta = 0.4$ (dashed line; squares) and $\eta = 1$ (dotted line; triangles). The lines are the theoretical predictions whereas the symbols correspond to MC simulations. The model parameters are $l = 4 \text{ nm}$ and $\sigma = -0.05 \text{ C/m}^2$.

study of salt-free polyelectrolyte solution containing mixture of mono and divalent counterions only also show nonlinear dependence of osmotic coefficient on the fraction of monovalent counterions.²⁸

Monovalent pointlike counterions are unable to induce attraction³ and introducing excluded volume further weakens electrostatic interactions. This also holds for dumbbells, especially if they are monovalent. Generally, the ion valency, shape of ions and surface charge density influence the interaction between like-charged surfaces.

A recent theoretical study²⁹ involving only charge-neutralizing chains of different stiffness confined between

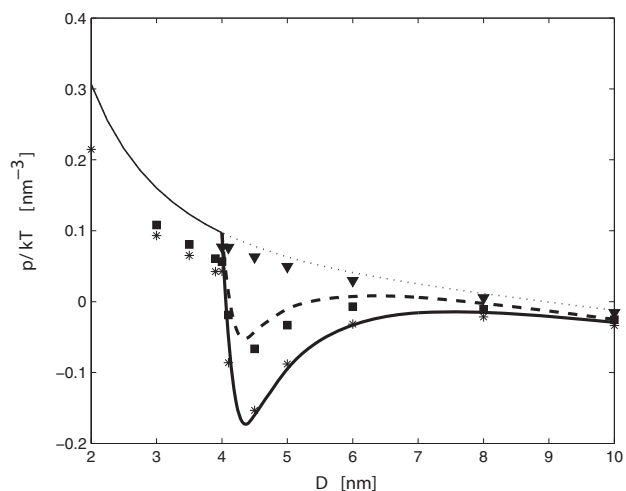


Figure 5: Pressure p as a function of the plate separation D for three different parameters: $\eta = 0$ (full line; stars), $\eta = 0.4$ (dashed line; squares) and $\eta = 1$ (dotted line; triangles). The lines are the theoretical predictions whereas the symbols correspond to MC simulations. The model parameters are $l = 4 \text{ nm}$ and $\sigma = -0.1 \text{ C/m}^2$.

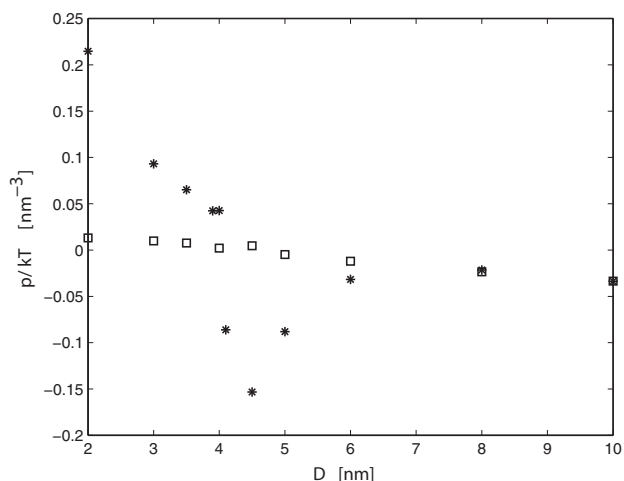


Figure 6: Pressure p as a function of the plate separation D for rod-like counterions of length $l = 4 \text{ nm}$ (stars) and point-like divalent counterions (squares). The model parameter is $\sigma = -0.1 \text{ C/m}^2$.

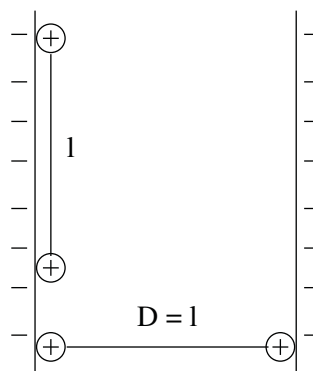
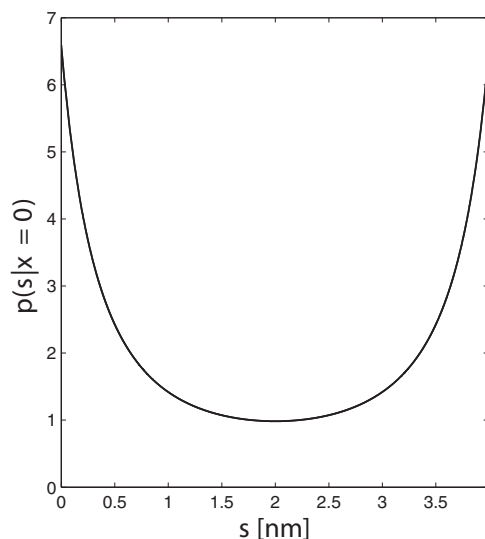


Figure 7: Top: Conditional probability density $P(s|x = 0)$ as a function of the projection S of the rod-like counterions with respect to x -axis. The surface charge density is $\sigma = -0.05 \text{ C/m}^2$ whereas the distance between the plates is $D = 4 \text{ nm}$. The reference charges are located at $x = 0$, the length of ions is $l = 4 \text{ nm}$. Bottom: schematic presentation of the most probable orientations of the rod-like ions. The distance between the surfaces is $D = l$.

two uniformly charged plates also displays similar pressure dependence on the separation between plates.

To better understand the structure of the intervening solution when attraction between the two equally and uniformly charged plates takes place, orientation of rigid rod-like ions was evaluated during calculations. Fig. 7 shows the conditional probability density $p(s|x=0)$ as a function of the projection s of the rod-like counterions with respect to the x -axis. The reference charges are located at the left charged plate at $x = 0$. Here we consider the case $D = l$. The conditional probability density first decreases with increasing projection s . It reaches a minimum and then further increases with increasing s . The situation is schematically presented in Fig. 7 (right panel). At high surface charge densities both orientations are more pronounced and other orientations are less pronounced.³⁰ Surprisingly, the conditional probability density was found to be almost insensitive on the parameter η . These results help us to understand the bridging mechanism. Namely, we have two most probable orientations of rod-like counterions: i) parallel and ii) perpendicular to the charged surface. Those rod-like counterions which are oriented perpendicular to the charged surfaces connect both charged surface – they bridge left and right charged surfaces.

4. Conclusions

In this study we considered a model system of two like charged plates embedded in a salt-free solution composed of a mixture of divalent rod-like and monovalent counterions. The system was solved with both the extended Poisson-Boltzmann theory and the canonical Monte Carlo computer simulations. Results show that attractive force between equally charged plates start to appear at a certain fraction of divalent rod-like counterions. At larger surface charge density smaller fraction of rod-like counterions is needed to turn the repulsive force between the plates into the attractive one. Rod-like ions which are oriented perpendicular to the plates gives rise to the bridging and thus contribute most to the effective attraction. It should be emphasized that theoretical predictions agree very well with computer simulation data for all parameters used in the present work.

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Povzetek

Sila, ki deluje na dve vzporedni in enako nabiti plošči, je odvisna od sestave raztopine elektrolita, ki zapolnjuje vmesni prostor. Če so v raztopini prisotni samo monovalentni protioni, je sila vedno odbojna, medtem ko v primeru dvovalentnih ionov pri dovolj veliki gostoti naboja postane privlačna. Krajši večvalentni ioni s prostorsko ločenim nabojem povzročijo agregacijo koloidnih delcev. V tem članku nam koloidno suspenzijo predstavlja enakomerno nabita reža, v kateri se nahajajo tako točkasti monovalentni kot tudi paličasti divalentni protioni. Modelni sistem smo obravnavali s kanoonično Monte Carlo simulacijo ter z razširjeno Poisson-Boltzmannovo teorijo, ki lahko obravnava paličaste ione. Raziskali smo vpliva površinske gostote naboja na stenah reže ter deleža paličastih protionov na strukturne in termodinamske lastnosti modelnega sistema. Rezultati kažejo, da je pri bolj nabitih površinah potreben manjši delež paličastih dvovalentnih protionov za nastanek privlačne sile med nabitima površinama. Prav tako smo ugotovili, da se rezultati razširjene Poisson – Boltzmannove teorije in Monte Carlo simulacij zelo dobro ujemajo med seboj.