

Interactions Between Charged Macroions Mediated by Molecules with Rod-Like Charged Structures

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A short review of recent theoretical advances in studies of the interaction between highly charged systems embedded in a solution of rod-like molecules is presented. The system is theoretically described by the functional density theory, where the correlations within the rod-like molecules are accounted for. We show that for sufficiently long molecules and large surface charge densities, an attractive force between like-charged surfaces arises due to the spatially distributed charges within the molecules. The added salt has an influence on the condition for the attractive force between like-charged surfaces. The theoretical results are compared with Monte Carlo simulations. Many phenomena motivate the study of the interaction between like-charged surfaces (DNA condensation, virus aggregation, yeast flocculation, cohesion of cement paste).

Key words: *Electrical double layer, biomaterials and biological interfaces*

Introduction

In biology, chemistry and technology, there are many phenomena which motivate the study of electrostatic interactions between charged macroions in a solution.^{1,2} Usually, the macroions appear as charged surfaces of charged lipid membranes, DNA, colloids, actin molecules, proteins, viruses and even cells. The embedded solution can contain salt and also multivalent ions. They are represented by multivalent metal ions, charged micelles, dendrimers, polyelectrolytes including polyamines, and DNA. These ions influence the electrostatic interaction between charged macroions. Generally, we need to have multivalent ions in order to induce an attractive force between like-charged macroions. Here we mention a few examples. The divalent diamine ions induce the aggregation of rod-like M13 viruses.³ Multivalent ions mediate network formation in actin solutions.⁴ The condensation of DNA is induced by the presence of multivalent counterions.^{5,6} Positively charged colloidal particles^{7,8} complex with DNA. Even the cohesion of cement paste is controlled by divalent calcium counterions.⁹ The destabilization of charged colloidal suspensions was studied in the presence of polyelectrolytes and oligomers.¹⁰

Here we mention a few experimental works related to our subject of interactions between charged objects. Experimentally, the swelling of the lamellar liquid crystalline phase within the solution composed of monovalent or divalent ions¹¹ was considered. It was shown that replacing monovalent counterions with divalent ones drastically decreases swelling of lamellar phases.¹² The attractive interaction between bilayers in the presence of divalent calcium ions has been obtained.¹³ The short range attractions between equally charged mica or clay surfaces in the solution of divalent

ions have been detected in direct surface force measurements and atomic force microscopy.¹⁴

Such system could not be described by the mean field Poisson-Boltzmann (PB) theory where the correlations between ions are neglected. This theory is valid only in the presence of small mobile ions in the aqueous solution, which has high dielectric constant $\epsilon = 80$. Ions often dissociate in solution and become mobile. The reason is the reduced cation-anion attraction because of high dielectric constant. For a given charge distribution of ions within the system, the electrostatic potential is obtained from Poisson's equation. Mobile ions, however, migrate toward regions of favorable potential. That is, the volume charge density adjusts according to the electrostatic potential. The volume charge density is composed of contributions from counterions and coions $\rho = e(n_+ - n_-)$, where n_+ is the concentration of counterions, n_- is the concentration of coions and e is the elementary charge. Both concentrations follow the Boltzmann distributions $n_+ = n_0 \exp(-\Psi)$ and $n_- = n_0 \exp(\Psi)$, where Ψ is the reduced electrostatic potential, and n_0 equals the bulk concentration of cations and anions if a salt reservoir is present. Inserting volume charge density into Poisson's equation yields the classical PB equation for a symmetric 1 : 1 electrolyte¹

$$\Delta \Psi = 8 \pi l_B n_0 \sinh \Psi \quad (1)$$

where l_B is the Bjerrum length. The Bjerrum length in water at room temperature is $l_B = 0.714$ nm.

In the case of only counterions, the volume charge density is $\rho = e n_+$, where $n_+ = n_0 \exp(-\Psi)$ and PB equation is^{15,16}

$$\Delta \Psi = -(4 \pi l_B / \nu) \exp(-\Psi) \quad (2)$$

The parameter ν follows from the condition of overall electro-neutrality of the system. The boundary conditions for equations (1) and (2) are given at both charged surfaces.

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Many theories go beyond the classical PB theory. The real ions are neither point-like nor can the solvent be regarded as passive and featureless. An extension of PB theory was made including ion correlations, charge images and finite ion size. Many theories have been developed in order to include correlations: modified PB theory,^{17,18} liquid state theories such as hypernetted-chain theories,¹⁹ loop expansions,²⁰ variational approximations²¹ and density functional theories.^{22,23} In the limit of strong electrostatic coupling these theories break down and a strong coupling expansion theory can be introduced.^{24,25} Recently, an approximative field theory has been developed that covers the weak, intermediate, and the strong coupling regimes.^{26,27}

The attractive interaction between like-charged macroions has also been confirmed by Monte Carlo (MC) simulations. *Guldbrand et al.*²⁸ were the first to confirm the existence of attraction between similarly charged surfaces immersed in a solution composed of divalent ions in the limit of high surface charge density. These and other MC simulations^{29,30} demonstrated that attractive interactions between similarly charged surfaces may arise for sufficiently high surface charge densities, low temperatures, low relative permittivity, or polyvalent counterions. Recent MC simulations have provided that the existence of attractive interaction between like-charged surfaces is strongly conditioned by the finite size of ions.³¹

The molecules in a solution which mediate interactions between macroions usually have an internal structure, with individually separated charges and possibly with additional internal degrees of freedom. *Bohinc et al.*^{32–35} demonstrated that intra-ionic correlations induced by the fixed distance within a particular rod-like ion are enough to change repulsive into attractive interactions between like charged surfaces. In this study, the rod-like ions carry a single elementary charge on each end. The free energy has a minimum when the counterions are oriented perpendicularly to the like-charged surfaces, thus connecting them. MC simulations showed good agreement with the theoretical predictions.^{34–37} The study of the system was later extended to the intermediate and strong coupling regimes, where the inter-ionic correlations alone can lead to an attraction between the surfaces.^{38–39} The theory was also generalized to systems with polydisperse rod lengths and arbitrary charge distribution along the rods.

In this review article we examine the interaction between two like-charged macromolecules which are represented by charged planar surfaces. The only interactions between the rod-like ions are the electrostatic interactions. We search for the conditions for attractive interactions. We examine the appearance of attractive interactions between like-charged surfaces due to the internal structure of multivalent ions.

Theory

We study the interaction between two macroions, which are represented as two planar surfaces, separated by a distance D , which carry a uniform negative surface charge density σ . Between these surfaces is an aqueous solution containing charged, multivalent, rod-like ions. Each rod-like ion carries two identical positive charges e . The charges are separated by a fixed distance l . All charges are restricted to lie between

the surfaces. A schematic diagram of the system is provided in Fig. 1. We distinguish two cases: I) rod-like counterions and coions (Fig. 1, right) and II) only counterions (Fig. 1, left).

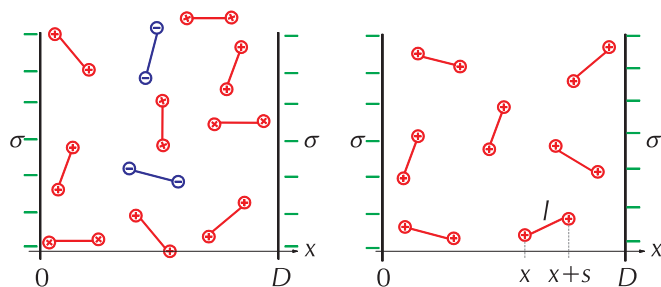


Fig. 1 – Schematic presentation of two like-charged planar surfaces, located at $x = 0$ i $x = D$, with σ denoting the surface charge density. Each surface has a surface area A . The surfaces are immersed in an electrolyte solution that contains positively and negatively charged rod-like ions (left). Only rod-like counterions are present in a solution between two charged surfaces (right).

Slika 1 – Shematski prikaz dviju nabijenih ravnih ploha koje se nalaze na $x = 0$ i $x = D$, gdje σ označava površinsku gustoću naboja. Površina plohe iznosi A . Plohe su uronjene u otopinu elektrolita koja sadrži pozitivno i negativno nabijene štapičaste ione (lijevo). Na slici desno u otopini su prisutni samo štapičasti protuioni.

We define our Cartesian coordinate system such that the y -axis and z -axis are parallel to the surfaces, and the x -axis is perpendicular to both surfaces. The origin is located on the left surface.

All quantities of the system vary only along the x -axis, the normal direction between the two charged surfaces. We assume that there is no electric field behind each of the two charged planar surfaces (which is appropriate if inside the macroions the dielectric constant is much smaller than in the aqueous region between the surfaces). Rod-like ions are characterized by positional and orientational degrees of freedom. We describe them by referring to one of the two charges of each ion as a reference charge, denoting the local concentration of all the reference charges by $n(x)$. The location of the second charge of a given ion is then specified by the conditional probability density $p(s|x)$, denoting the probability to find the second charge at position $x + s$ if the first resides at x . Thus the ion distribution function is defined as joint probability $n(x,s) = n(x) p(s|x)$. Integration over all possible orientations gives

$$n(x) = [1/(2l)] \int_{-l}^l n(x,s) ds \quad (3)$$

The free energy F in terms of thermal energy $k_B T$ and surface area A can be written as

$$F / (Ak_B T) = [1/(8\pi l_B)] \int_{-\infty}^{\infty} dx \Psi'^2(x) + \int_{-\infty}^{\infty} dx [1/(2l)] \int_{-l}^l ds n(x,s) [\ln n(x,s)v - 1 - U(x,s)], \quad (4)$$

where v is the effective volume of rod-like counterions and Ψ is the reduced electrostatic potential. The prime in $\Psi'(x)$ denotes the first derivative with respect to the argument x . The first term in Eq. 4 corresponds to mean electrostatic field energy, whereas the second term includes the orienta-

tional and positional entropic contribution of rod-like counterions. The steric interaction of rods with the charged surfaces is taken into account via the external non-electrostatic potential $U(x,s)$. The electroneutrality of the whole system demands

$$\sigma A = \int_0^D n(x) dx.$$

In thermal equilibrium, the free energy F adopts a minimum with respect to the ion distribution function. The functional minimization leads to the modified Boltzmann distribution function

$$n(x,s) = (1/v) \exp[-\Psi(x) - \Psi(x+s) - U(x,s)]. \quad (5)$$

Upon insertion of the ion distribution function (5) into Poisson's equation results in the integral differential equation

$$\Psi''(x) = -8\pi l_B / (v \cdot 2l) \int_{\alpha(x)}^{\beta(x)} ds \exp[-\Psi(x) - \Psi(x+s)]. \quad (6)$$

where $\alpha(x) = \max[-l, -x]$ and $\beta(x) = \min[l, D - x]$.

Integral differential equation (6) is subject to two boundary conditions at each surface

$$\Psi'(0) = -4\pi l_B \sigma / e \quad \Psi'(D) = +4\pi l_B \sigma / e. \quad (7)$$

Eq. (7) is equivalent to the electro-neutrality of the system. In the case of a system of rod-like counterions and coions the integral differential equation becomes

$$\Psi''(x) = [16\pi l_B n_0 / (2l)] \int_{\alpha(x)}^{\beta(x)} ds \sinh[\Psi(x) + \Psi(x+s)]. \quad (8)$$

Results

Integral differential equations (6) and (8) have no analytical solutions. The following analysis is based on the numerical solution of integral differential equations (6) and (8).

First we study the properties of divalent rod-like counterions confined between two like-charged surfaces separated by a distance D . Fig. 2 presents the concentration of reference charges $n(x)$ as a function of the distance from the left charged surface x for three different lengths l of rod-like ions.³⁵ The inset of Fig. 2 shows the reduced electrostatic potential $\Psi(x)$ as a function of the distance x from the charged surface. Theoretical results are compared against Monte Carlo data. The right part of Fig. 2 shows the results for only rod-like counterions, whereas the left part of Fig. 2 shows the results for rod-like counterions and co-ions.

The concentration of reference charges of rod-like counterions decreases with increasing distance from the charged surface. The discontinuous derivative of concentration of reference charges $n(x)$ at $x = l$ and $x = D - l$ are the result of the orientational restriction of counterions close to the charged surface. For sufficiently long divalent rod-like counterions, the comparison between the density functional theory and the Monte Carlo simulations gives good agreement. The non-continuous derivative of the concentration $n(x)$ at $x = l$ and $x = D - l$ is also obtained by Monte Carlo simulations.³⁵

We proceed with the electrostatic free energy. The minimized expressions for the electrostatic potential and ionic distribution function are inserted back into the free energy (4). Fig. 3 shows the equilibrium free energy as a function of the separation between the charged surfaces for two dif-

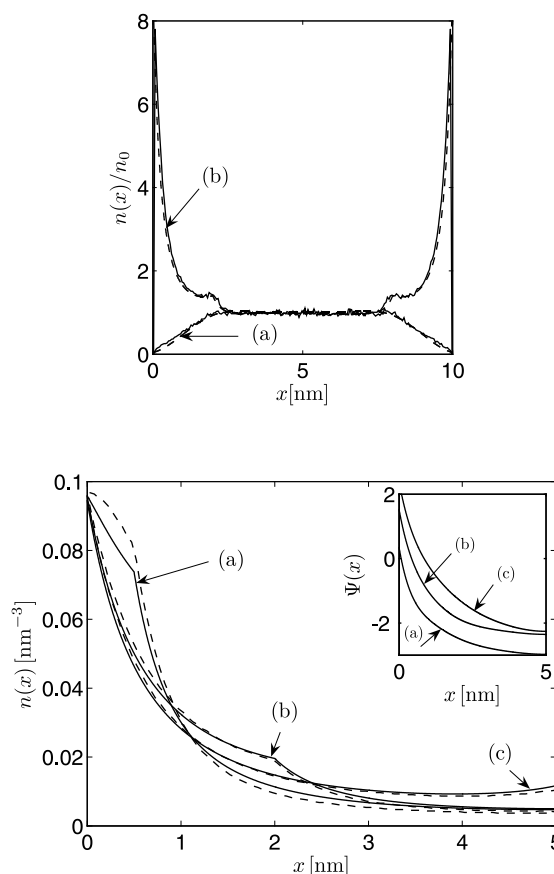


Fig. 2 – Down: Concentration of reference charges $n(x)$ as a function of x . The different curves correspond to different lengths of divalent rod-like counterion $l = 0.5$ nm (a), $l = 2$ nm (b) and $l = 5$ nm (c). Full lines display the theoretical approach whereas dashed lines display results of MC simulations. The inset shows reduced electrostatic potential $\Psi(x)$ as a function of x . The model parameters are $D = 10$ nm, $Z = 1$ and $\sigma = 0.333$ C m⁻². Up: Counterions and coions are present. Dashed lines display the theoretical approach, whereas full lines display results of MC simulation. The model parameters are: the length of the rod-like ions $l = 2$ nm, their bulk concentration $n_0 = 0.1$ mol l⁻¹ and surface charge density $\sigma = 0.036$ C m⁻². Reprinted with permission from ref.³⁵ Copyright 2009. *J. Phys. A*.

Slika 2 – Dolje: koncentracija referentnih naboja $n(x)$ kao funkcija od x . Različite krivulje odgovaraju različitim duljinama dvovalentnih štapičastih protuiona $l = 0.5$ nm (a), $l = 2$ nm (b) i $l = 5$ nm (c). Pune linije prikazuju teorijski pristup, dok isprekidane linije prikazuju rezultate MC simulacija. Umetak pokazuje reducirani elektrostatski potencijal $\Psi(x)$ kao funkciju od x . Parametri modela: $D = 10$ nm, $Z = 1$ i $\sigma = 0,333$ C m⁻². Gore: prisutni su protuioni i koioni. Isprekidane linije prikazuju teorijski pristup, dok pune linije prikazuju rezultate MC simulacija. Parametri modela su: duljina štapičastih iona $l = 2$ nm, koncentracija $n_0 = 0,1$ mol l⁻¹ i gustoća površinskog naboja $\sigma = 0,036$ C m⁻². Preneseno uz dozvolu iz lit.³⁵ Autorska prava 2009. *J. Phys. A*.

ferent lengths of ions. The free energy first decreases with increasing distance D , reaches a minimum and then further increases with increasing distance D to a plateau value. The minimum in the free energy appears at the distances which are approximately equal to the length of rod-like ions.^{34,40}

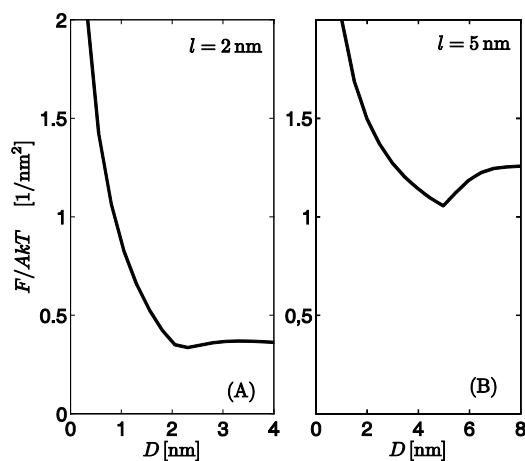


Fig. 3 – Free energy F as a function of the distance between the charged surfaces D . Only counterions are included. The full curves correspond to theoretical calculations. The model parameter is $\sigma = 0.1 \text{ C m}^{-2}$. The length of ions is $l = 2 \text{ nm}$ (A) and $l = 5 \text{ nm}$ (B). Reprinted with permission from ref.^{34,35}

Slika 3 – Slobodna energija F kao funkcija udaljenosti D među nabijenim plohama. Uključeni su samo protuioni. Pune krivulje odgovaraju teorijskim proračunima. Parametar modela $\sigma = 0,1 \text{ C m}^{-2}$. Duljina iona je $l = 2 \text{ nm}$ (A) i $l = 5 \text{ nm}$ (B). Preneseno uz dozvolu iz lit.^{34,35}

Discussion

In summary, we have considered a density functional theory for rod-like ions of arbitrary length, subject to an additional non-electrostatic external potential, which takes into account steric restrictions with the charged surface. The two interacting, like-charged, planar macroions reveal the possibility of attractive interactions, introduced entirely by correlations within the rod-like ions.

The free energy analysis shows that for sufficiently long ions and sufficiently large surface charge density, the theory can predict an attractive force between like-charged surfaces. The analysis of the orientational distributions of rod-like ions shows that the rod-like ions are oriented either parallel or normal to the macroions. It is the latter case that signifies the bridging transition (Fig. 4).

The parallel and perpendicular orientations indicate the tendency for positive part of rod-like ions to be in contact with the negatively charged surfaces. For high surface charge densities both preferred orientations are even pronounced. The counterions oriented perpendicular to the charged surfaces connect both surfaces and act as a bridge between equally charged surfaces. This bridging mechanism of rod-like charged counterions is responsible for the attractive interaction between like-charged surfaces.^{41,42} DNA packing *in vivo* is not only ion-dependent but is also governed by proteins. Proteins possess positively charged domains allowing nonspecific interactions with DNA.

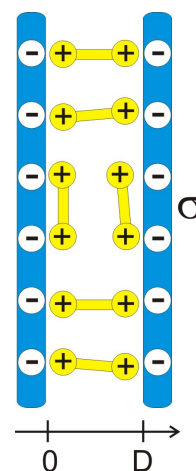


Fig. 4 – Illustration of bridging between two charged surfaces induced by rod-like counterions. Reprinted with permission from ref.⁶

Slika 4 – Prikaz premoščivanja između dvije nabijene površine štapičastih protuiona. Preneseno uz dozvolu iz lit.⁶

This type of interaction may be understood with the help of a simplified model of two negatively charged surfaces (DNA molecules) in a solution of positively-charged rod-like particles (proteins).

List of symbols and abbreviations

Popis simbola i kratica

- A – surface area
– površina
- D – distance between like-charged surfaces
– udaljenost među nabijenim površinama
- e – elementary charge
– elementarni naboj
- F – free energy
– slobodna energija
- l – distance between charges in rod-like ion
– udaljenost među nabojima u štapičastoj molekuli
- l_B – Bjerrum length
– Bjerrumova duljina
- n_- – coion concentration
– koncentracija koiona
- n_+ – counterion concentration
– koncentracija protuiona
- n_0 – bulk concentration of cations and anions
– koncentracija kationa i aniona u masi otopine
- p – probability density
– gustoća vjerojatnosti
- s – x -axis projection of l
– projekcija l na x -os
- T – thermodynamic temperature
– termodinamička temperatura
- U – external non-equilibrium potential
– vanjski neravnotežni potencijal
- Z – charge number
– nabojni broj
- ϵ – dielectric constant
– dielektrična konstanta

ν	– parameter – parametar
ρ	– volume charge density – obujamska gustoća naboja
σ	– surface charge density – površinska gustoća naboja
Ψ	– reduced electrostatic potential – reducirani elektrostatski potencijal
MC	– Monte Carlo method – Monte-Carlo-metoda
PB	– Poisson-Boltzmann

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SAŽETAK

Međudjelovanje nabijenih makroiona putem štapićastih nabijenih molekula

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Predstavljen je kratak pregled nedavnih teorijskih dostignuća u istraživanju međudjelovanja nabijenih sustava u otopini štapićastih molekula. Sustav je opisan teorijom funkcionala gustoće uzevši u obzir odnose među štapićastim molekulama. Pokazano je da se u slučaju dovoljno dugačkih molekula i velike površinske gustoće naboja javlja privlačna sila između nabijenih ploha zbog prostornog rasporeda naboja u molekulama. Dodatak soli utječe na privlačnu silu među nabijenim plohami. Teorijski rezultati uspoređeni su sa simulacijama Monte-Carlo. Mnoge pojave potiču proučavanje međudjelovanja nabijenih površina (kondenzacija DNA, agregacija virusa, flokulacija kvasca, povezivanje cementne paste).

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