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Impact of added salt on the characteristics of electric double layer composed of charged nanoparticles

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A B S T R A C T

We consider a mixture of large spherical nanoparticles with the charge distributed over the surface and point-like ions embedded in an aqueous solution between two similarly-charged surfaces. The finite size of nanoparticles is included via a lattice gas entropy. The electrostatic energy takes into account exact charge distribution on the nanoparticles surface. For this system the Euler-Lagrange equations are derived and solved numerically. The results show a big impact of nanoparticle's size on the concentration profiles and characteristics of electric double layer. The theoretical model predicts an attractive interaction between like charged surfaces for large enough nanoparticles with large enough charge and the addition of point-like salt ions decreases the range of attraction.

1. Introduction

Forces between charged structures in solutions are of magnificent significance in medico-biological, chemical and technological systems. In biology important macroions are peptides, proteins, lipid membranes, and DNA as well as living bacteria and viruses. Polyelectrolytes, colloids, gels, micellar structures and nanoparticles (NPs) are present in chemical systems. Metal oxides, clays, mica, semiconductors, and glass are typical representatives of technological systems [1–4].

Charged surfaces possess non-mobile surface charge groups. On contrary ions are mobile within the aqueous solution. Ions with the charge sign opposite to the surface are attracted by the surface and named counterions. Ions of the same charge sign as the surface are separated from the surface and are named coions. Counterions and lesser extent coions in the surrounding of charged surface build a diffusive electric double layer [5].

The standard theory describing electric double layer is the Poisson-Boltzmann theory (PB) [6], where ionic compounds interact through a Coulombic type of the potential. All other types of interaction are not taken into account. After Poisson-Boltzmann also steric effects and correlations were considered [7–10]. But still the aqueous solution was represented as a matter of a known dielectric constant. Bikerman took into account the entropy of the ionic compounds within a lattice. The Carnahan-Starling introduced hard spheres. Other theoretic approaches

were prepared to more adequately describe the electric double layer [11–13].

Many molecules and ions in aqueous solution have their charge locally distributed. In recent studies the exact spatial charge distribution was considered. The existing theories were generalized by introducing rod- and sphere-like particles with spatially distributed charge [14–17]. The electrostatic part of the free energy (FE) for these systems includes the charge distribution in rod- and sphere-like particles. The entropic part of the FE is composed of orientational and translational parts of each individual mobile rod- and sphere-like particles. Inter- and intra-ionic correlations for these systems were considered [18].

Charge macroions in aqueous solution interact between each other. In vacuum similarly-charged surfaces (SCSs) repel each other whereas in aqueous solution attractive interactions are possible. Attractive interactions can be induced via inter- and intra-ionic correlations [19,20]. Due to the neglect of charge-charge correlations the mean-field theory [8] is not able to induce attractive interaction between SCSs. Field-theoretic approaches include charge-charge correlations and the force between like charged macroions can be attractive [19].

In this study we describe uniformly charged spherical NPs (charged hard spheres whose surfaces are uniformly charged) in terms of the density functional theory. The finite size of NPs is included via a lattice gas entropy. These NPs and point-like ionic compounds are placed between SCSs. Correlations between NPs are not taken into account but the connectivity of the charged groups within each NP enables intra-

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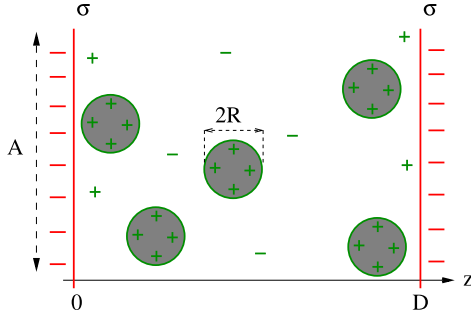


Fig. 1. Two planar negatively charged surfaces embedded in an aqueous solution composed of NPs and point-like ionic compounds. NPs are composed of positive charges and have the diameter $2R$. The SCD is denoted by σ , whereas the surface separation is D .

ionic correlations. The calculus of variations of the full FE results into the Euler-Lagrange equations which were numerically solved.

2. Theory

We consider two planar negatively SCSs placed into an aqueous solution composed of positively charged spherical NPs and small ionic compounds. Each planar surface of surface area A possesses a charge q and which corresponds to the surface charge density (SCD) $\sigma = q/A$. The surface distance is D . The schematic presentation of the system is shown in Fig. 1

The charge parameter of NPs

$$\lambda = z/(2R) \quad (1)$$

relates their valency z and radius R . NPs have the opposite sign of the charge as the charged surface and are attracted by the surface. The ionic compounds are point-like, counterions have valency $z_+ = 1$ and are attracted by the surfaces whereas the coions have the valency $z_- = -1$ and are repelled by the surfaces. Close to the charged surface a diffusive electric double layer of NPs and ionic compounds arises.

We introduce bulk concentrations of NPs n_0 , cations m_{0+} and anions m_{0-} , respectively. The electric field strength E is zero in the bulk of the solution and the bulk concentrations satisfy

$$zn_0 + z_+m_{0+} + z_-m_{0-} = 0 \quad (2)$$

The ratio between bulk concentrations of NPs and cations is

$$\frac{n_0}{m_{0+}} = K \quad (3)$$

The calculation is made in the Cartesian coordinate system in which the system's characteristics are dependent only on the distance to the interface, which we measure along the z -axis of the coordinate system. The symmetry of the system makes possible to describe the system by z -dependent functions.

The full FE $F = F^{el} + F^{ent}$ of the system can be written as a sum of the electrostatic part [21]

$$\frac{F^{el}}{k_B T A} = \int_0^D dz \left[\frac{E(z)^2}{8\pi l_B} \right] \quad (4)$$

and the entropic contribution [22]

$$\begin{aligned} \frac{F^{ent}}{k_B T A} = \int_0^D dz \left[m_+(z) \ln v_+ m_+(z) - m_+(z) + m_-(z) \ln v_- m_-(z) \right. \\ \left. - m_-(z) + n(z) \ln v n(z) + \frac{1}{v} (1 - v n(z)) \ln (1 - v n(z)) \right]. \end{aligned} \quad (5)$$

k_B denotes the Boltzmann's constant. The absolute temperature is T . l_B corresponds to the Bjerrum length whereas l_D is the Debye length. The reduced electric field strength is denoted by E . The concentration profile of NPs is denoted by n , whereas the concentration profiles of small counterions and coions are respectively denoted by m_+ and m_- . The corresponding volumes of NPs, cations and coions are v , v_+ and v_- . Eqs. (4) and (5) can be written in a form $\int_0^D \mathcal{L}$, where $\mathcal{L}$ is the Lagrangian.

Euler-Lagrange equations $\mathcal{L}_u - \nabla \mathcal{L}_{u'} = 0$, where u corresponds to m_+ , m_- , n or E and ∇ means the derivation with respect to z , are

$$m'_+(z) = z_+ E(z) m_+(z), z \in [0, L] \quad (6)$$

$$m'_-(z) = z_- E(z) m_-(z), z \in [0, L] \quad (7)$$

$$n'(z) = n(z)(1 - v n(z)) \lambda \int_{z-R}^{z+R} E(u) du, z \in [0, L] \quad (8)$$

$$E'(z) \frac{1}{4\pi l_B} = \lambda \int_{z-R}^{z+R} n(s) ds + z_+ m_+(z) + z_- m_-(z), z \in [0, L] \quad (9)$$

Boundary conditions

$$E(0) = 4\pi l_B / a \quad E(D) = -4\pi l_B / a \quad (10)$$

where a is the surface area of one elementary charge.

3. Numerical implementation

We solve Euler-Lagrange equations with boundary conditions by a finite difference method. The discretization of the interval $[0, D]$ was made with a step size h . Values at grid points have been used to estimate the first derivative in the middle point between grid points, e.g.,

$$m'_+ \left(ih + \frac{h}{2} \right) = \frac{m_+((i+1)h) - m_+(ih)}{h}, \quad (11)$$

with i positive integer. The electric field in between 2 grid points has been approximated with the mean value, i.e.,

$$E \left(ih + \frac{h}{2} \right) = \frac{E((i+1)h) + E(ih)}{2}. \quad (12)$$

We estimate the integrals by the trapezoidal rule.

Equations were solved by MATLAB, using the build-in function *fsolve*.

4. Results and discussion

Fig. 2 shows concentration profiles of charged NPs between two parallel surfaces for two different D . The NPs are positively charged whereas the surfaces are negatively charged. The ionic compound of monovalent ions is added. The SCD is $\sigma = 0.065$ C/m². The NP's diameter is 28 nm. The valency is $z = 1$. The bulk ionic compound concentration is 1 mM. Due to excluded volume the particles can not penetrate behind the surface. Concentration profiles exhibit a pronounced concentration of NPs in the surrounding of the charged surface. The NP's concentration close to the both surfaces (at $z = R$ and $z = D - R$) is maximal and subsequently decreases to their concentration in the mid-plane of the system. Oscillations of the concentration profiles can appear for larger plate separations. Similar results were found in the case of only spherical NPs without salt [23].

Fig. 3 represents the reduced concentration profiles $n(z)/n_0$ of positively charged spherical particles between two negatively charged surfaces. Calculations were made for three different radii of the spheres: 0.5 nm, 2 nm and 5 nm. The steric restriction with the surface was taken into account. The concentration profile between 0 and R as well as between $D - R$ and D is zero. The concentration of NPs at the contact is larger for larger NPs. The surface area under the curves needs to be the same and is connected to the fact that the system is electro neutral.

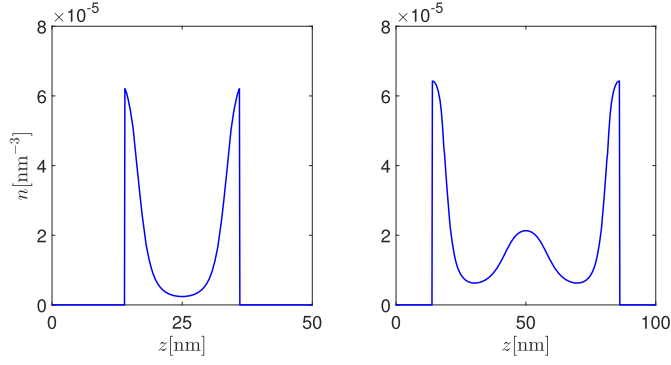


Fig. 2. Concentration profiles $n(z)$ of positively charged spherical NPs. Calculations were made for two different surface separations: $D=50$ nm (left) and $D=100$ nm (right). The radius of NPs is 14 nm. The parameters are $\sigma = 0.065$ C/m², $z = 1$ and $l_B = 0.7$ nm. The bulk concentration of ionic compound is 1 mM.

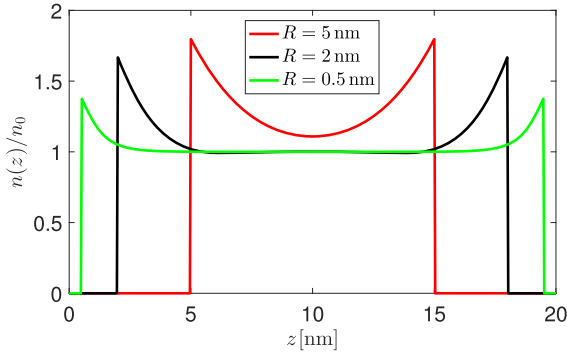


Fig. 3. Concentration profiles $n(z)$ of positively charged spherical NPs. The two negatively charged surfaces are separated $D=20$ nm. The radii of spheres are 0.5 nm, 2 nm and 5 nm. The valency is $z = 1$. The bulk concentration of spherical NPs is 0.1 mol/l. The surface area per elementary charge is $a = 60$ nm².

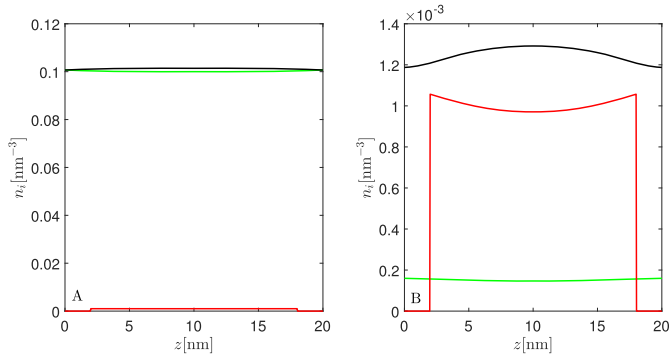


Fig. 4. Concentration profiles of charged spherical particles (red curves) and monovalent ionic compound (black and green curves). The surfaces are separated by $D=20$ nm. The radius of particles is 2 nm and $\lambda = 0.35$ /nm. Surface area per one elementary charge $a = 60$ nm². $l_B = 0.7$ nm. The bulk concentration of spherical NPs is 10^{-3} nm⁻³; The bulk counterions of counterions are (A) 10^{-1} nm⁻³ and (B) 10^{-6} nm⁻³.

Similar results were found in the case of only spherical NPs without salt [23].

Fig. 4 shows the profile concentrations of positively charged spherical particles. The aqueous solution includes also positively and negatively charged ionic compound. The concentration of spherical particles is getting lower with the distance from the surface. The radius of particles is 2 nm. In the mid-plane of the aqueous solution the minimal concentration of particles is reached. The concentration of the positive

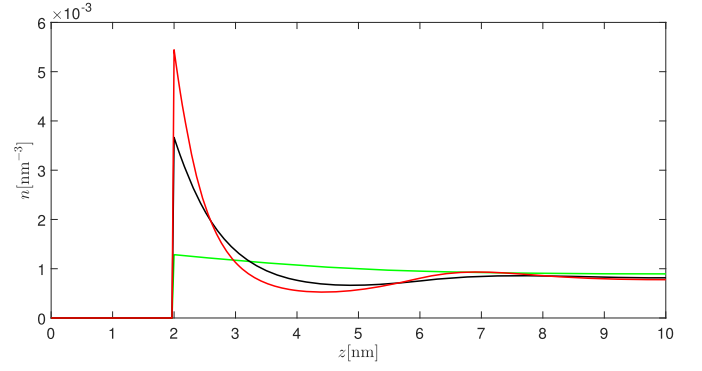


Fig. 5. Concentration profiles of spherical NPs. The separation between the surfaces is $D=20$ nm. The radius of particles is 2 nm. $l_B = 0.7$ nm. Surface area per one elementary charge $a = 15$ nm². $\lambda = 1$ /nm (green), 6 (black) and 10 (red curve). Bulk concentration of particles and ionic compound 0.001 nm⁻³.

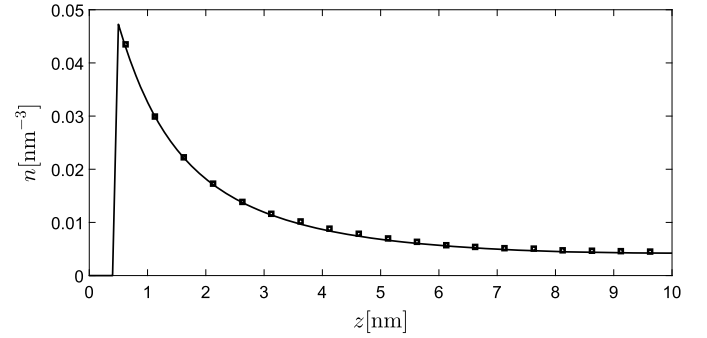


Fig. 6. Concentration profile of spherical NPs. Theory (line), MC simulations (dots). The separation between the surfaces is $D=20$ nm. The radius of particles is 0.5 nm. $l_B = 0.7$ nm. Surface area per one elementary charge $a = 10$ nm². $\lambda = 1$ /nm. Bulk concentration of particles and ionic compound 0.001 nm⁻³ [24].

ionic compound is close to the charged surface larger than its mid-plane value. On contrary the concentration of the negative ionic compound ions is close to the charged surface smaller than their mid-plane value. The concentration profiles strongly depend on the bulk concentrations (compare Fig. 4 A and B). Screening of small counterions can change the concentration profile of nanoparticles substantially.

Fig. 5 depicts the concentration profiles of NPs for different parameters $\lambda = 1$ /nm (green), 6 (black) and 10 (red curve). The comparison with MC simulations is given (Fig. 6). The concentration of particles is decreasing as a function of the surface separation. Small oscillations in the profiles can be observed. The oscillations are related to the structure of the NPs. Namely, the width of oscillation is in the order of NPs size. The comparison of the theory shows a good agreement with Monte Carlo simulation [24,25].

Recently, the phenomenon of charge reversal of the cumulative surface charge density attracted an interest [26]. This effect was also confirmed by the first work related to rod-like ions with spatial charge distribution [27].

The lateral pressure between both surfaces is given by the derivation of the full FE

$$P = -k_B T \frac{dF/(Ak_B T)}{dD}. \quad (13)$$

The lateral pressure P can be presented as a function of D . The pressure $P = 0$ means the minimum of the FE. This indicates the attractive force between two SCSS.

Fig. 7 shows the pressure as a function of D for three different salt concentrations. At lower salt concentration the pressure is decreasing with increasing D . At $D \sim 3R$ the pressure crosses the abscissa. This point marks the minimum in the free energy. With the further increase of the

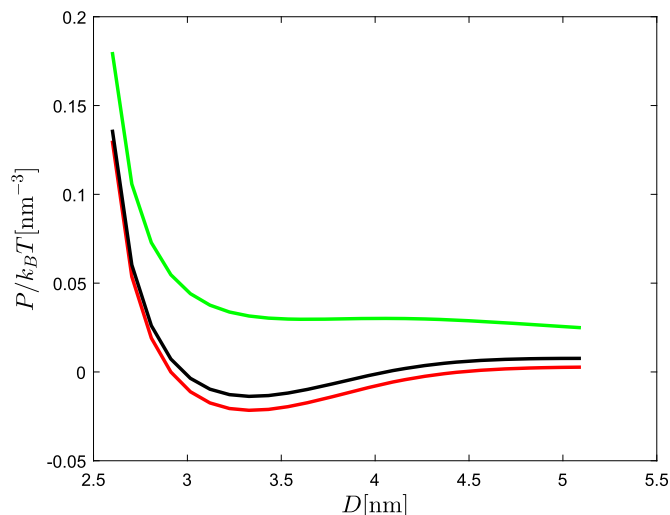


Fig. 7. Pressure as a function of the separation between the charged surfaces D . Model parameters: $R = 1$ nm $a = 5$ nm², $l_B = 0.7$ nm. The bulk concentrations of salt are 10^{-3} nm⁻³ (red curve), 10^{-2} nm⁻³ (black curve) and 10^{-1} nm⁻³ (green curve).

separation D the pressure is decreasing and reaching a minimum. At very large plate separations the pressure is increasing to zero value. The reason for the attractive interaction is the ability of spheres to link left and right surfaces. Therefore the minimum is reached at separations in the order of the sphere diameter. At higher salt concentration the pressure is only decreasing with increasing D to zero value a large D . Namely at higher salt concentrations small ions are able to screen the negative charge on both surfaces. The effective charge is decreased and spheres are not able to intermediate attractive interaction.

The attractive interaction between like charged surfaces is the result of the charge connectivity within the spherical nanoparticles. Part of the sphere is close to one oppositely charged surface whereas the opposite part of the sphere is close to the other charged surfaces.

5. Conclusions

In this study we considered NPs placed between two parallel charged surfaces. NPs are embedded into an electrolyte solution of small mobile ions. The consistent theory was developed and the equations were solved numerically. The results show the pronounced NP's concentration in the surrounding of surfaces. For small salt concentration spherical NPs can generate an attractive force between similarly charged surfaces. The addition of salt can cause that the attractive force gets lost. Namely, small counterions strongly attracted by the charged surfaces screen the charged surfaces and spherical nanoparticles embedded between weakly charged surfaces are not able to intermediate attractive interactions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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