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Charged cylindrical surfaces: effect of finite ion size

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Abstract

A simple statistical mechanical approach is applied to calculate the profile of the density of the number of particles and the profile of the electrostatic potential of an electric double layer formed by a charged cylindrical surface in contact with electrolyte solution. The finite size of particles constituting the electrolyte solution is considered by including the excluded volume effect within the lattice statistics while the electrostatic interactions are considered by means of the mean electrostatic field. It is shown that the excluded volume effect decreases the density of the number of counterions and increases the electrostatic potential near the charged cylindrical surface. The effect is more pronounced for high area densities of charge of the charged surface and for larger counterions. Further, it is shown that the ratio between the density of the number of the counterions near the charged cylindrical surface and the density of the number of counterions far from the charged surface reaches a plateau at large linear charge densities for ions of finite size, while no plateau is reached for dimensionless ions. The effective thickness of the electric double layer in cylindrical geometry is introduced. It is shown that the effective thickness increases with increasing counterion size while its dependence on the area density of charge of the charged surface exhibits a minimum. The theoretical approach presented in this work can be used for description of the electrostatics of the thin cylindrical structures in biological systems such as DNA, protein macromolecules and charged micro and nano tubes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electric double layer; Canonical ensemble; Excluded volume effect; Counterion condensation; Cylindrical structures in biological systems

1. Introduction

The distribution of the ions in the electrolyte solution in the vicinity of a charged object is mainly determined by the competition between the interactions within the system and the entropy of the particles that constitute the solution. As a result, in thermodynamic equilibrium the counterions are accumulated close to the charged object and the coions are depleted from this region. A diffuse electric double layer is created [1–3]. A well known example of the planar electric double layer is a planar layer of phospholipid molecules with charged headgroups in contact with the electrolyte solution [3]. A spherical electric double layer may be formed around a colloidal particle [4], while the cylindrical electric double layer may be formed around a charged polymer molecule (polyelectrolyte) [5–8]. The structure of the counterion–coion atmosphere around the charged polymer molecule importantly influences its internal electrostatic stability. For example, in the case of deoxyribonucleic acid (DNA) molecules, the conformational changes resulting from the interaction between the DNA molecule and ions in the surrounding electrolyte solution depend on the distribution of the counterion–coion charges around the phosphate groups, in the helical grooves, and around the base pairs. These interactions affect also the flexibility and curvature properties of the DNA molecules. The cylindrical electric double layer may be also created in the system composed of charged cylindrical parts of the cell membrane or in the cylindrically shaped phospholipid bilayer structures, which are in contact with the electrolyte solution. It was recently suggested that the electrostatic interactions may significantly influence the bending properties of such structures under physiological conditions [9].

Since the first description of the flat electric double layer by Gouy [1] and Chapman [2] the description of the electric double layer has been extended also to the cylindrical geometry. The Poisson–Boltzmann (PB) differential equation for the mean electrostatic potential around the charged cylindrical surface was solved [4]. The concept of the condensation of the counterions near the charged surface was introduced in cylindrical geometry by Imai and Oosawa

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[5,6]. The counterion condensation was later thoroughly studied by Manning [7,10]. The counterion distribution around the charged cylindrical surface was treated in terms of the linear charge density parameter $\xi = l_B/b$, where $l_B = e_0{}^2/4\pi\varepsilon\varepsilon_0 kT$ is the Bjerrum length, b is the cylinder length containing one unit of charge, e_0 is the elementary charge, ε is the permittivity of the solution, ε_0 is the permittivity of the free space, k is the Boltzmann constant and T is the temperature. Manning [10] found that in the case of highly charged polyelectrolytes ($\xi > 1/z_i$), the fraction $[1 - 1/(z_i\xi)]$ of the charge on the charged cylindrical surface is completely neutralized by the counterions of the valency z_i that condense onto the charged cylindrical surface. It was shown for polyelectrolyte solutions [11] that in the limit of infinite dilution the solution of the Poisson–Boltzmann (PB) equation leads to the Manning condensation. Stigter [12] compared the Manning condensation with the PB theory using the free energy test. He showed that the PB theory gives the lowest free energy and hence the most stable ion distribution.

The description of the electric double layer by the PB theory has been improved by considering the molecular Hamiltonian models that take into account direct interactions between the charges in the system and solvent structure and interactions. Approximate theories have been developed, such as the modified Poisson–Boltzmann (MPB) theory [13–16], generic density functional theories [17] and integral equation theories [18–20]. Theoretical results have been compared with the results of the Monte-Carlo simulations [14–16,21]. The description of the planar electric double layer within the PB theory has been upgraded by considering the effect of the finite size of the ions [22–24] and used for description of various systems [25–28]. The importance of the steric effects was supported by the results of the experiments involving large trivalent tungstic ions [29].

In this work we used the PB theory that was upgraded by considering the effect of finite size of ions [23] for the description of the cylindrical electric double layer. We improved the derivation of the consistently related expressions for the equilibrium free energy of the system, the ion and solvent distribution functions and the differential equation for the electric potential [23] by using the method of undetermined multipliers within the canonical statistics. The effective thickness of the electric double layer in the cylindrical geometry is introduced. The influence of the size of the counterions is studied.

2. Theory

2.1. Minimization of the free energy

We imagine a charged cylindrical surface of the radius r_0, length l and line charge density λ. The line charge density can be connected to the surface charge density of the charged cylindrical surface σ by the equation $\sigma = \lambda/2\pi r_0$. The length l of the charged cylindrical surface is assumed to be much larger than r_0. The charged surface is coaxially enclosed in a cylindrical cell of the radius R, which is filled with the electrolyte solution composed of solvent molecules and M species of ions. At the distance R from the center of the charged cylindrical surface the effect of this surface is negligible. The system is described by the mean electrostatic field while the finite size of the particles in the solution is considered by means of the excluded volume effect.

The volume of the whole system is the sum of the volumes occupied by the ions and the solvent molecules. Within this description each particle in the solution occupies one and only one site of a finite volume. A lattice with an adjustable lattice constant a is introduced (Fig. 1), all sites of this lattice being occupied. The density of the number of the lattice sites in the system n_s can be expressed as $n_s = 1/V_s$, where V_s is the volume of a three-dimensional lattice site. The lattice sites may have different forms (Fig. 1), however, we take that they have equal volumes V_s. The corresponding lattice constant is $a = V_s{}^{1/3}$, so that

$$n_s = \frac{1}{a^3}. \tag{1}$$

Further, it is taken that the particles may approach the charged surface only to the distance $a/2$. Hence, the density of the number of the particles is defined in the interval $[r_0 + a/2, R]$, while the electric field strength is defined in the interval $[r_0, R]$. However, in the interval $[r_0, r_0 + a/2]$, the electric field strength attains a constant value.

In deriving the expression for the free energy of the system F subject to the local thermodynamic equilibrium, the methods of statistical mechanics are used (Appendix A). The free energy of the system F is obtained by starting from the energies of the individual particles and treating the particles as independent and indistinguishable (Eq. (A.10))

$$F = W^{\mathrm{el}} + kT \int_{r_0+a/2}^{R} \left(\sum_{j=0}^{M} n_j(r) \ln \frac{n_j(r)}{n_s q_j^0} \right) 2\pi r l \mathrm{d}r, \tag{2}$$

where

$$W^{\mathrm{el}} = \frac{1}{2}\epsilon\epsilon_0 E_0^2 (\pi(r_0 + a/2)^2 - \pi r_0^2) l + \frac{1}{2}\epsilon\epsilon_0 \int_{r_0+a/2}^{R} E^2(r) 2\pi r l \mathrm{d}r, \tag{3}$$

is the energy of the electrostatic field, $E(r)$ is the electric field strength, E_0 is the electric field strength near the cylindrical charged surface and n_j is the density of the number of particles of the j-th species. The index $j = 0$ denotes the solvent molecules while $j = 1, 2, \ldots, M$ denotes ions of the j-th species. Further, $q_j{}^0$ is the partition function of the particle of the j-th species subject to no electrostatic variable. The integrations are performed over the extension of the system in the radial direction (r), $2\pi r l \mathrm{d}r$ being the volume element. Because of the cylindrical geometry there

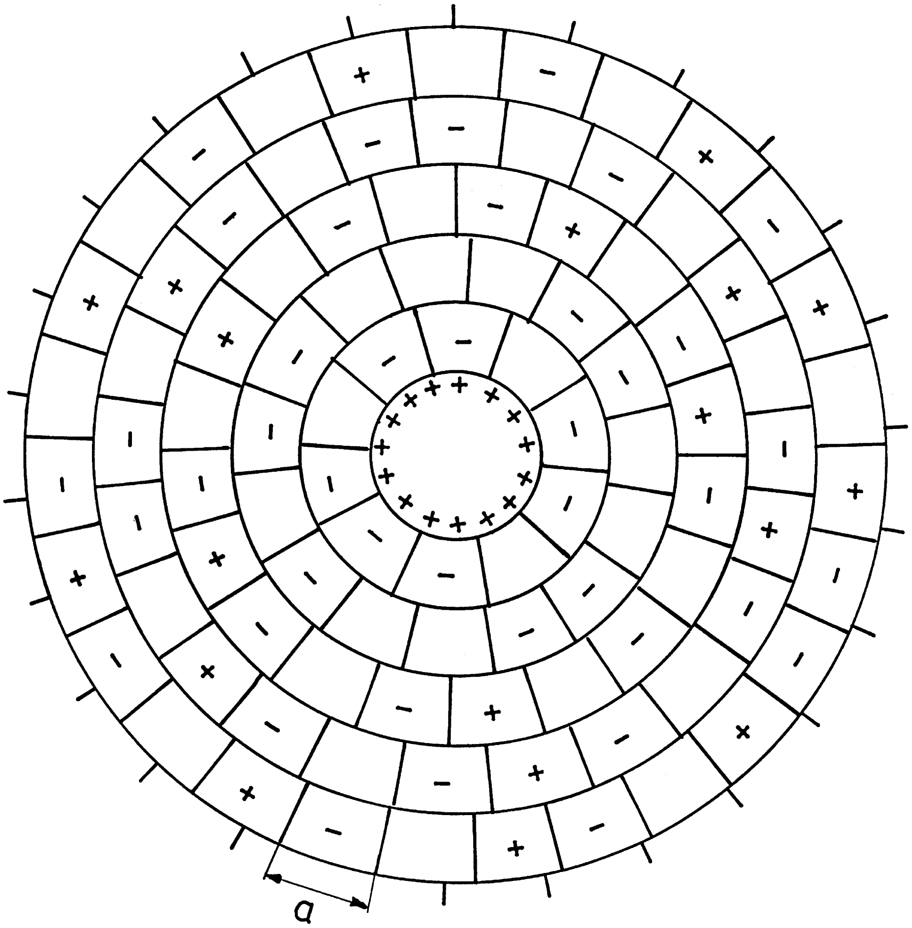

Fig. 1. Schematic presentation of the electric double layer for a positively charged cylindrical surface. The anions are accumulated near the charged cylindrical surface while the cations are depleted from this region. The electrolyte solution is presented within the lattice model.

is a nonzero contribution to the electrostatic field only in the radial direction.

The particle distribution functions n_j, $j=0, 1,\ldots, M$ and the electric field strength are in general not known. In the following, the explicit expressions for the functions $n_j(x)$, $j=0, 1,\ldots, M$ and $E(r)$ are obtained by using the condition for the free energy to be at its minimum in the thermodynamic equilibrium of the whole system. The free energy can be expressed by means of a function L, which depends on the electric field strength $E(r)$ and on the densities of all species of the particles (represented by $\mathbf{n}_j(r)=(n_0, n_1,\ldots, n_M)$),

$$F = \int_{r_0+a/2}^{R} L(E(r),\mathbf{n}_j(r))2\pi r l \mathrm{d}r + \frac{1}{2}\epsilon\epsilon_0 E_0^2(\pi(r_0+a/2)^2 - \pi r_0^2)l, \tag{4}$$

where

$$L(E(r),\mathbf{n}_j(r)) = \frac{1}{2}\epsilon\epsilon_0 E^2(r) + kT\left(\sum_{j=0}^{M} n_j(r)\ln\frac{n_j(r)}{n_s q_j^0}\right). \tag{5}$$

We simulated the size of the counterions by the choice of the lattice constant a, which enters the above functional through Eq. (1).

The condition for the global equilibrium

$$\delta F = 0, \tag{6}$$

is subject to a global constraint requiring that

- the total number of the particles of each species is constant

$$\int_{r_0+a/2}^{R} (n_j(r) - \Lambda_j)2\pi r l \mathrm{d}r = 0, \quad j = 0,1,2,\ldots,M, \tag{7}$$

where Λ_j is a constant, and two local constraints requiring

- the validity of the Gauss law at any r

$$\epsilon\epsilon_0 \frac{1}{r}\frac{\partial(rE(r))}{\partial r} - e_0\sum_{j=1}^{M} v_j n_j(r) = 0, \tag{8}$$

- and that all of the lattice sites are occupied

$$n_{\mathrm{s}} - \sum_{j=0}^{M} n_j(r) = 0. \tag{9}$$

The valency of the ion of the j-th species is denoted by v_j, $j = 1, 2, \ldots, M$.

To find the extremum of functional (4) by taking into account constraints (7)–(9), the method of undetermined multipliers is used. The function $L^*(r)$ is constructed,

$$\begin{aligned} L^*\left(E(r),\mathbf{n}_j(r),\frac{\partial E(r)}{\partial r},\eta_1(r),\eta_2(r)\right) &= L(E(r),\mathbf{n}_j(r)) + \sum_{j=0}^{M} \lambda_j (n_j(r) - \Lambda_j) \\ &\quad - \eta_1(r)\left(\epsilon\epsilon_0 \frac{1}{r}\frac{\partial(rE(r))}{\partial r} - e_0 \sum_{j=1}^{M} v_j n_j(r)\right) \\ &\quad + \eta_2(r)\left(n_{\mathrm{s}} - \sum_{j=0}^{M} n_j(r)\right), \end{aligned} \tag{10}$$

and examined for the extrema. Here, λ_j, $j = 0, 1, \ldots, M$ are the global Lagrange multipliers, while $\eta_1(r)$ and $\eta_2(r)$ are the local Lagrange multipliers. The variation is performed by solving a system of Euler equations

$$\frac{\partial L^*}{\partial E} - \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\partial L^*}{\partial\left(\frac{\partial E}{\partial r}\right)}\right) = 0, \tag{11}$$

$$\frac{\partial L^*}{\partial n_j} = 0, \quad j = 0,1,2,\ldots,M. \tag{12}$$

Far away from the charged cylindrical surface (at the distance R from the center of the charged cylindrical surface), the electrostatic field vanishes

$$\left.\frac{\mathrm{d}\Phi}{\mathrm{d}r}\right|_R = 0, \tag{13}$$

which means that the electrostatic potential $\Phi(R)$ is constant. We chose

$$\Phi(R) = 0. \tag{14}$$

Eqs. (11) and (12) and conditions (13) and (14) give after some calculation the particle distribution functions

$$n_j(r) = \frac{n_{\mathrm{s}}(n_{jR}/n_{0R})\exp(-v_j e_0 \Phi(r)/kT)}{1 + \sum_{i=1}^{M} (n_{iR}/n_{0R})\exp(-v_i e_0 \Phi(r)/kT)}$$

$$j = 0,1,2,\ldots,M \tag{15}$$

and the differential equation for $\Phi(r)$

$$\frac{\mathrm{d}^2\Phi(r)}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r} = \frac{-e_0 n_{\mathrm{s}}\left(\sum_{i=1}^{M} v_i (n_{iR}/n_{0R})\exp(-v_i e_0 \Phi(r)/kT)\right)}{\epsilon\epsilon_0\left(1 + \sum_{i=1}^{M} (n_{iR}/n_{0R})\exp(-v_i e_0 \Phi(r)/kT)\right)}, \tag{16}$$

where n_{jR} is the density of the number of particles of the j-th species at $r = R$. The local Lagrange multipliers are

$$\eta_1(r) = \Phi(r), \tag{17}$$

$$\eta_2(r) = kT\left(\ln\frac{n_j}{n_{\mathrm{s}} q_j^0} + 1 + \frac{\lambda_j}{kT}\right) + e_0 v_j \Phi(r). \tag{18}$$

The local Lagrange multiplier $\eta_1(r)$ is the electrostatic potential (Eq. (17)).

In order to obtain the explicit dependencies of n_j, $j = 0, 1, \ldots, M$ and Φ on the distance r, the differential Eq. (16) is solved numerically. The condition

$$\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r}\Big|_{r_0+a/2} = -\frac{2kT\xi}{r_0 e_0}, \tag{19}$$

where $\xi = \sigma r_0 e_0 / 2\epsilon\epsilon_0 kT$ and condition (14) are taken into account.

2.2. A case of the univalent electrolyte

The solution under consideration consists of the solvent molecules, univalent counterions and univalent coions. Far from the charged cylindrical surface the density of the number of counterions and the density of the number of coions are equal and are denoted by n_R, while the density of the number of the solvent molecules is denoted by n_{0R}.

We take positively charged cylindrical surface ($\sigma > 0$). The valency of counterions is $v_{\mathrm{ct}} = -1$, while the valency of coions is $v_{\mathrm{co}} = 1$. The mean electrostatic potential is obtained by solving the differential equation that follows from expression (16)

$$\frac{\mathrm{d}^2\Phi(r)}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r} = \frac{2e_0 n_{\mathrm{s}} n_R}{\epsilon\epsilon_0 n_{0R}} \frac{\sinh(e_0\Phi(r)/kT)}{\left(1 + \frac{2n_R}{n_{0R}}\cosh(e_0\Phi(r)/kT)\right)}, \tag{20}$$

subject to the boundary conditions (14) and (19).

According to Eq. (15), the respective densities of the number of counterions and coions are

$$n_{\mathrm{ct}} = \frac{n_{\mathrm{s}} n_R \exp(e_0 \Phi(r)/kT)}{n_{0R}\left(1 + \frac{2n_R}{n_{0R}}\cosh(e_0\Phi(r)/kT)\right)}, \tag{21}$$

$$n_{\mathrm{co}} = \frac{n_{\mathrm{s}} n_R \exp(-e_0 \Phi(r)/kT)}{n_{0R}\left(1 + \frac{2n_R}{n_{0R}}\cosh(e_0\Phi(r)/kT)\right)}. \tag{22}$$

To study the counterion distribution, we solved Eq. (20) and determined the distribution function given by Eq. (21). The solution of Eq. (20) is obtained numerically by using the fourth order Runge–Kutta method starting at $r = R$.

Fig. 2A shows the densities of the number of the counterions and the coions, n_{ct} and n_{co}, respectively, in dependence on the radial distance (r) while Fig. 2B shows the electrostatic potential $e_0\Phi/kT$ in dependence on r. The results obtained by considering a finite lattice constant a and the results of the PB theory are given. In the vicinity of the charged cylindrical surface the density of the number of counterions is affected by the lattice constant, while far from the charged cylindrical surface the density of the counterions is insensitive to the lattice constant. We consider a symmetric univalent electrolyte $v_{\mathrm{ct}} = -1$ and $v_{\mathrm{co}} = 1$. In the limit of vanishing a the density of the number of counterions n_{ct} calculated within the presented model including steric effects converges towards the corresponding density of the number of counterions obtained by the PB theory. For large values of a the density of the number of counterions near the charged cylindrical surface reaches a plateau (not shown). The plateau is not so pronounced as in the case of planar electric double layer.

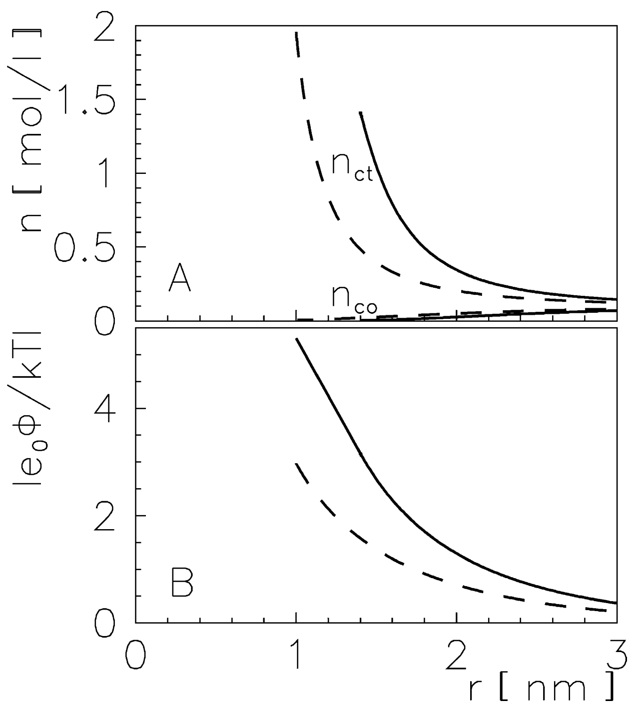

Fig. 2. (A) The density of the number of the counterions (n_{ct}) and the density of the number of coions (n_{co}) (full lines) and (B) the electrostatic potential $e_0\Phi/kT$ (full line) in dependence on the radial coordinate (r). The results of the PB theory (broken lines) are also shown. The model parameters are $a = 0.8$ nm, $\epsilon = 78.5$, $T = 310$ K, $n_{\mathrm{R}} = 0.1$ mol/l, $r_0 = 1$ nm and $\xi = 2.7$.

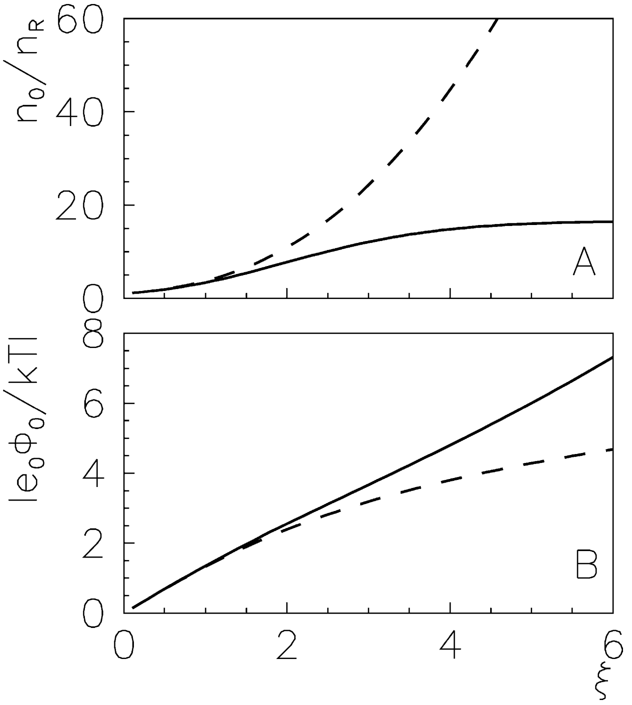

Fig. 3. (A) The ratio between the density of the number of counterions at a distance of the closest approach to the charged cylindrical surface and the bulk density of the number of counterions n_0/n_R (full line) and (B) the electrostatic potential at a distance of the closest approach to the charged cylindrical surface $e_0\Phi_0/kT$ (full line) as a function of the linear charge density parameter ξ of the charged cylindrical surface. The broken lines represent the respective results of the PB theory. The model parameters are $a = 1$ nm, $\epsilon = 78.5$, $T = 310$ K, $n_{\mathrm{R}} = 0.1$ mol/l and $r_0 = 1$ nm.

Fig. 3A presents the calculated ratio between the density of the number of the counterions at a distance of the closest approach to the charged cylindrical surface ($n_0 = n_{\mathrm{ct}}(r_0 + a/2)$) and the density of the number of counterions far from the charged surface n_R, in dependence on the linear charge density parameter ξ. The corresponding results calculated by using the PB theory are also shown, where it is taken that $n_0 = n_{\mathrm{ct}}(r_0)$. The discrepancy between the results obtained by considering a finite lattice constant a and the results of the PB theory increases with increasing parameter ξ. At high values of the parameter ξ the ratio n_0/n_R obtained by considering a finite lattice constant approaches the ratio between the density of the number of lattice sites and the density of the number of counterions far from the charged surface (n_{s}/n_0). The corresponding ratio n_0/n_R in PB theory increases without limit with increasing parameter ξ. Fig. 3B presents the electrostatic potential at a distance of the closest approach to the charged cylindrical surface ($\Phi_0 = \Phi(r_0 + a/2)$ in dependence on the linear charge density parameter ξ. The corresponding results calculated by using the PB theory are also shown where it is taken that $\Phi_0 = \Phi(r_0)$. At small values of the parameter ξ the electrostatic potential near the charged cylindrical surface for finite lattice constant coincides with the corresponding results of the PB theory, while the discrepancy between the two curves increases with increasing parameter ξ, the value of Φ_0 being larger for finite lattice constant.

The ratio n_0/r_R and the electrostatic potential Φ_0 are compared to the respective limit cases where r_0 is very large, representing the planar electric double layer (Fig. 4A,B). For the limit case, we solved the differential equation for the electric potential in the flat geometry [30]. The results are calibrated to the same surface charge density σ. Fig. 4A shows the calculated ratio n_0/r_R while Fig. 4B shows the electrostatic potential Φ_0 as a function of the parameter r_0. With increasing r_0, the results of the cylindrical geometry converge to the respective results of the planar geometry.

The screening of the electrostatic field by the counterions that accumulate close to the charged cylindrical surface can be represented by the effective thickness of the electric double layer [30]. In cylindrical geometry the effective thickness of the electric double layer is defined as

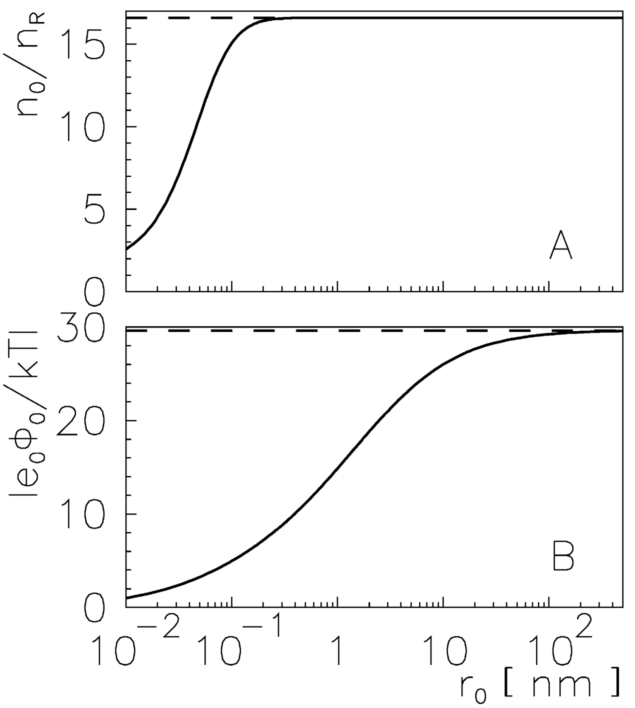

Fig. 4. (A) The ratio between the density of the number of counterions at a distance of the closest approach to the charged cylindrical surface and the bulk density of the number of counterions (n_0/n_R) (full line) and (B) the electrostatic potential at a distance of the closest approach of the charged cylindrical surface $e_0\Phi_0/kT$ (full line) as a function of the radius of the charged cylindrical surface r_0. For comparison, the respective results for the planar geometry are given (broken lines). The model parameters are $a = 1$ nm, $\sigma = 0.4$ As/m^2, $\epsilon = 78.5$ and $T = 310$ K.

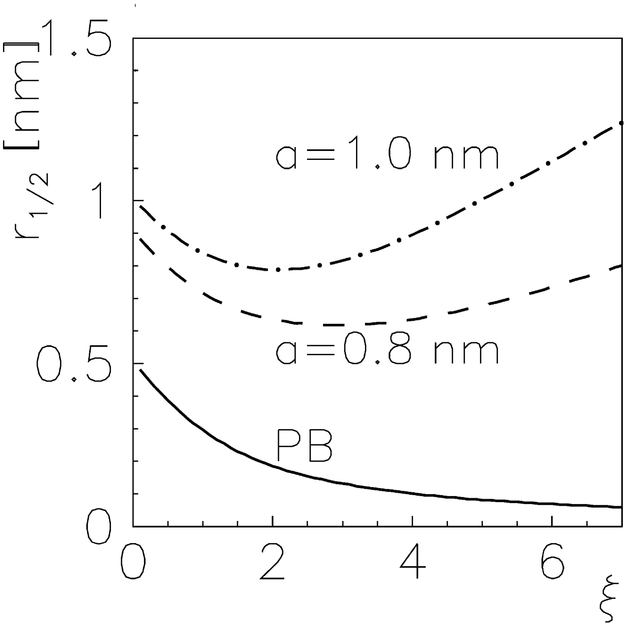

Fig. 5. The effective thickness of the electric double layer represented in cylindrical geometry by the parameter $r_{1/2}$ in dependence of the linear charge density parameter ξ for two different lattice constants a. The result of the PB theory is also shown. The model parameters are $\epsilon = 78.5$, $T = 310$ K, $n_R = 0.1$ mol/l and $r_0 = 1$ nm.

$$n_{ct}(r_0 + r_{1/2}) - n_R = \frac{1}{2}(n_{ct}(r_0 + a/2) - n_R). \tag{23}$$

Eq. (23) assumes that at the distance $r_{1/2}$ from the charged cylindrical surface, the density of the number of the counterions (calculated relative to its value far from the charged cylindrical surface) drops to half of its value at the closest approach to the charged cylindrical surface. Fig. 5 shows the parameter $r_{1/2}$ in dependence on the dimensionless linear charge density parameter ξ. Two choices of the lattice constant a are considered. It can be seen in Fig. 5 that the effective thickness of the electric double layer containing counterions of a finite size first decreases, then reaches a minimum and then increases as a function of increasing parameter ξ. The corresponding results of the PB theory show a monotonous decrease of $r_{1/2}$ with increasing ξ.

3. Discussion and conclusion

Starting with the energies of individual particles, we obtained expressions for the equilibrium particle distribution functions and the differential equation for the electrostatic potential in cylindrical geometry. We considered the finite size of particles by including the excluded volume effect.

Close to the charged cylindrical surface, the density of the number of counterions is very high (Fig. 2A) while the corresponding density of the number of coions attains the values which are at least two orders of magnitude smaller. Therefore, in this region, the contribution of the counterions to the excluded volume effect is considerable while the contribution of the coions to the excluded volume effect is negligible. The calculated density of the number of counterions near the charged surface obtained by using the PB theory is higher than the corresponding value calculated by taking into account the excluded volume effect (Fig. 3A). The differences between the respective ion densities and the differences between the respective electrostatic potentials can be attributed to the steric effect of counterions and solvent molecules in a small region in the vicinity of the charged cylindrical surface (Fig. 3A,B). However, in the cylindrical electric double layer this effect is less pronounced than in the planar electric double layer [30] since the decrease of the electric field strength with increasing r is stronger in cylindrical geometry. In the cylindrical geometry the electric field strength decreases in the free space as $1/r$ while the corresponding electric field in the planar geometry is constant.

There is a difference in the qualitative behaviour of the dependence of the ratio (n_0/n_R) on the parameter ξ when calculated by using the PB theory and by considering the finite size of ions (a nonzero lattice constant). For $a>0$, the dependence of the n_0/n_R on ξ reaches a plateau for large values of the parameter ξ (Fig. 3A). In contrast, the corresponding result of the PB theory shows a monotonous increase of the ratio (n_0/n_R) with increasing ξ. A similar effect of the finite size of ions was obtained in the planar geometry [31]. Recently, these results were supported by the experimental data [29].

The ratio n_0/n_R in the cylindrical geometry is lower than the corresponding ratio in the planar geometry. The same is true for the potential $|\Phi_0|$. For large r_0 the results obtained in the cylindrical geometry coincide with the results obtained in the planar geometry (Fig. 4A,B). It can be seen in Fig. 4B that regarding n_0/n_R the regime of the flat electric double layer is for the data used reached already for radii as small as ~ 1 nm.

The thickness of the electric double layer in the cylindrical geometry is described by the characteristic length $r_{1/2}$, i.e. the distance from the charged surface where the excess of the counterions drops to half of its value at the distance of the closest approach to the charged cylindrical surface (Eq. (23)). Within the presented theory including steric effects, the thickness of the diffuse layer $r_{1/2}$ is always larger than within the PB theory. When finite size of ions is considered, the shielding of the electric field of the charged surface is less effective than in the PB theory where there is no limit regarding to the number density of counterions. For small parameters ξ the effective thickness of the electric double layer is decreasing with increasing ξ (Fig. 5) in both models as the surface bearing higher charge attracts in its vicinity larger number of counterions. Consequently, the screening is more effective. If we further increase the parameter ξ, the influence of the excluded volume effect increases with increasing ξ. The effective thickness $r_{1/2}$ after reaching its minimum, begins to increase with increasing ξ. This is the result of the fact that the excluded volume imposes an upper limit on the density of the number of counterions. There is no upper limit of the density of the number of ions in the PB theory and the effective thickness in the PB theory decreases monotonously with ξ. No minimum is reached (Fig. 5).

In our model we do not take into account the direct ion–ion interactions. It was established [4,19], that for 1-1 electrolyte (that was studied in this work) the effect of the direct interactions is negligible. However, this effect could be important in the case of multivalent ions [4,18].

The force between two identical parallel charged rods predicted by the PB theory was found to be repulsive at all distances for all surface charge densities [4]. By including the short range ion–ion interactions, the attractive forces between identical parallel charged rods were obtained at certain conditions such as in the limit of high electrolyte concentrations in the case of multivalent counterions and/or low bulk dielectric constant. Therefore, it would be interesting in the future to study the influence of the ion size on the force between two charged cylindrical structures in electrolyte solution.

To conclude, we showed that the effect of finite ion size on the density of the number of counterions and on the electrostatic field near the charged cylindrical surface is considerable also in the cylindrical geometry although it is weaker than in the flat geometry.

Appendix A. Free enery of the electrolyte solution in contact with the charged cylindrical surface

Assuming local thermodynamic equilibrium and taking into account energies of the individual particles in the solution, the expression for the free energy within the mean field approximation is derived.

We divide the system into cells of volume $V^c = 2\pi r l \Delta r$, where Δr is the dimension of the cell in the r direction. We assume that Δr is small comparing to the distance over which macroscopic properties change essentially. In the cell we have N_j ions of the j-th species, $j = 1, 2, \ldots, M$, and N_0 solvent molecules. The finite size of particles is introduced by means of the excluded volume effect. A lattice is introduced with all sites occupied: the particles are distributed over N_s^c lattice sites of equal volume

$$\sum_{j=0}^{M} N_j = N_s^c. \tag{A.1}$$

Any cell is open with respect to heat, and closed with respect to matter. The cell is characterized by the volume V^c, the temperature T and the number of the particles of all species N_j, $j = 0, 1, 2, \ldots, M$.

A particle in the cell is described by using the statistical mechanical approach. The canonical partition function $q_{m_j j}$ of the m_j-th particle of the j-th species is

$$q_{m_j j} = \sum_i \exp(-\epsilon_{m_j ji}/kT),$$
$$m_j = 1,2,\ldots,N_j,\ j = 0,1,\ldots,M, \tag{A.2}$$

where $\epsilon_{m_j ji} = K_{m_j ji} + e_j(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\mathrm{ref}})$ is the energy state of the m_j-th particle, which consists of the electrostatic potential energy of the charged particles situated at $\mathbf{r}_{m_j j}$, $e_j(\Phi(\mathbf{r}_{m_j j}) - \Phi_{\mathrm{ref}})$, and other contributions $K_{m_j ji}$ to the energy; $\Phi(\mathbf{r}_{m_j j})$ is the potential of the electric field, e_j is the charge of the ion of the j-th species, k is the Boltzmann constant and i is the index that runs through all possible energy states $K_{m_j ji}$ of the m_j-th particle. The electrostatic potential energy of the ion is calculated relative to the potential energy of the reference system in which the ions are infinitely far apart, so that the electrostatic field in this case vanishes and its potential is constant. For the reference potential we chose $\Phi_{\mathrm{ref}} = 0$.

We assume that the electrostatic field in the system does not influence the contributions to the energy $K_{m_j ji}$. Therefore, by inserting $\epsilon_{m_j ji} = K_{m_j ji} + e_j\Phi(\mathbf{r}_{m_j j})$ into Eq. (A.2) and summing over all energy states of ions, the electrostatic potential energy can be written before the sum,

$$q_{m_j j} = q^0_{m_j j}\exp(-e_j\Phi(\boldsymbol{r}_{m_j j})/kT), \tag{A.3}$$

where $q^0_{m_j j} = \sum_i \exp(-K_{m_j ji}/kT)$, $m_j = 1,2,\ldots,N_j$, $j = 1,2,\ldots,M$.

The solution in the chosen cell is a system with constant volume V^{c}, constant temperature T and constant number of ions and solvent molecules. It is assumed that the particle–particle correlations are described by the mean electrostatic field and by the excluded volume effect so that the particles in the cell are explicitly considered to be independent.

The particles of the j-th species are also considered to be equal with respect to all energy states $K_{m_j ji}$

$$q^0_{m_j j} = q^0_j,\quad m_j = 1,2,\ldots,N_j,\quad j = 0,1,\ldots,M, \tag{A.4}$$

where q^0_j is the particle partition function subject to non-electrostatic interactions. It is assumed that the solution in the cell is in thermodynamic equilibrium. Taking into account all possible nonequivalent distributions of particles in the cell, the canonical partition function of the cell Q^{c} can be written as

$$Q^{\mathrm{c}} = \exp\left(-\frac{\Delta W^{\mathrm{el}}}{kT}\right)\left(\prod_{j=0}^{M}(q^0_j)^{N_j}\right)\frac{N^{\mathrm{c}}_{\mathrm{s}}!}{\left(\prod_{j=0}^{M} N_j!\right)}, \tag{A.5}$$

where

$$\Delta W^{\mathrm{el}} = \sum_k e_k\Phi(\mathbf{r}_k). \tag{A.6}$$

The summation is performed over all ions in the cell.

The expression for the free energy of the solution in the cell can be obtained by the statistical mechanical relation $\Delta F = -kT\ln Q^{\mathrm{c}}$,

$$\Delta F = \Delta W^{\mathrm{el}} + kT\left(\sum_{j=0}^{M} n_j \ln\frac{n_j}{n_{\mathrm{s}}q^0_j}\right)2\pi rl\Delta r. \tag{A.7}$$

The Stirling approximation for large N_j was used while the density of the number of particles of the j-th species $n_j, j = 0, 1,\ldots, M$ and the density of the number of sites n_{s} were introduced

$$N_j = n_j 2\pi rl\Delta r \quad \text{and} \quad N^{\mathrm{c}}_{\mathrm{s}} = n_{\mathrm{s}}2\pi rl\Delta r. \tag{A.8}$$

Eq. (A.7) represents the free energy of the chosen cell. To obtain the free energy of the whole system, we sum the contributions of all the cells. This summation can be expressed by the integration over the extension of the system in the radial direction. The expression for the electrostatic potential energy of the system is calculated by taking into account that the potential at the site of a given ion is created by all other ions and the charged cylindrical surface. We consider that the ions in the solution are distributed with volume charge density $\varrho_{\mathrm{e}}(\mathbf{r})$ so that expression (A.6) can be transformed into

$$W^{\mathrm{el}} = \frac{1}{2}\epsilon\epsilon_0\int_{r_0}^{R} E^2(r)2\pi rl\mathrm{d}r. \tag{A.9}$$

Here ϵ is the permittivity of the solution, ϵ_0 is the influence constant, E is the electric field strength and E_0 is the electric field strength near the cylindrical charged surface. The electric field strength is constant in the region $[r_0, r_0 + a/2]$ and is determined by Eq. (19). Therefore, the integral in Eq. (A.9) is divided into two parts.

For the free energy of the whole system, subject to the local thermodynamic equilibrium, we finally get

$$\begin{aligned} F = {} & \frac{1}{2}\epsilon\epsilon_0 E_0^2(\pi(r_0 + a/2)^2 - \pi r_0^2)l \\ & + \frac{1}{2}\epsilon\epsilon_0\int_{r_0+a/2}^{R} E^2(r)2\pi rl\mathrm{d}r \\ & + kT\int_{r_0+a/2}^{R}\left(\sum_{j=0}^{M} n_j(r)\ln\frac{n_j(r)}{n_{\mathrm{s}}q^0_j}\right)2\pi rl\mathrm{d}r. \end{aligned} \tag{A.10}$$

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