

Linearized Poisson Boltzmann theory in cylindrical geometry

Klemen Bohinc^{a,b}, Aleš Iglič^a, Tomaž Slivnik^a

^a Laboratory of Physics, Faculty of Electrical Engineering, Tržaška 25, SI-1000 Ljubljana, Slovenia

^b College for Health Studies, University of Ljubljana, Poljanska cesta 26a, 1000 Ljubljana, Slovenia

E-pošta: klemen.bohinc@fe.uni-lj.si

Abstract. The linearized Poisson-Boltzmann theory was applied to the system of a charged cylindrical surface in contact with an electrolyte solution composed of monovalent counter- and co-ions. An analytical solution for the spatial dependence of the electric potential and the concentration of counter and co-ions inside the charged tube was obtained.

Key words: electric potential, cylindrical geometry

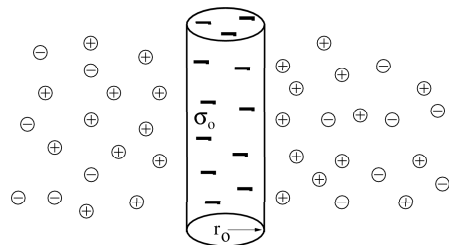


Figure 2. Schematic presentation of a cylindrical electric double layer outside the tube with radius r_o and surface charge density σ_o . The counterions are accumulated near the charged surface while the coions are depleted from the charged surface.

1 Introduction

In some biological systems, the walls of membrane nanotubes are charged and in contact with the electrolyte solution. Due to the electric charge of the nanotube wall, counterions of the electrolyte are accumulated near the charged wall while coions of the electrolyte are depleted from the region near the wall. At inner (Fig. 1) and outer (Fig. 2) surfaces of the charged tube the electric double layers of cylindrical geometry are therefore formed [1; 2].

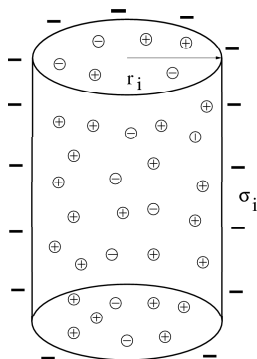


Figure 1. Schematic presentation of a cylindrical electric double layer inside the tube with radius r_i and surface charge density σ_i . The counterions are accumulated near the charged surface while the coions are depleted from the charged surface.

The constituents of the biological membranes may carry ionized or polar groups [2]. The ionized groups contribute to the surface charge density of the inner and outer surfaces of the membrane nanotube. The examples of such membrane molecules with charged groups are lipids, glycolipids, or proteins. The molecules which are bound to or absorbed onto the membrane surface may also contribute to the surface charge density of nanotube surfaces [3]. A widely used description of the electric double layer is given by the Poisson-Boltzmann (PB) theory [4; 5; 6] in which the ions are treated as point charges in a dielectric continuum enclosed by a uniformly charged surface. For monovalent salt, the predictions of the PB theory are found to agree well with experiments and simulations [7]. A quite useful approximation to the PB theory is the linearized PB theory (LPB) [8], where the electrostatic energy is assumed to be small compared to the thermal energy.

In the present paper we consider the charged micro or nano tube in contact with an electrolyte solution composed of counterions and coions. We study the inner charged surface of the tube in a contact with the inner electrolyte solution and the outer charged surface of the tube in a contact with the outer electrolyte solution. The potential and the concentration profiles are calculated.

2 Theory

We consider the charged tube in contact with a solution of symmetric monovalent electrolyte. The electric double layer inside nanotube (concave case) and outside nanotube (convex case) are studied. r_i is the radius of the inner tube, while r_o is the radius of the outer tube. The length l of the tube is assumed to be much larger than the radius. The system of the outer surface and outer electrolyte solution is electrically neutral. Also the system of the inner surface and inner electrolyte solution is electrically neutral.

If the electrostatic energy is small compared to the thermal energy, $|e\Phi/kT| \ll 1$, where Φ is the electrostatic potential, then the linearized Poisson Boltzmann (LPB) equation can be used

$$\Delta \Psi = \kappa^2 \Psi \quad (1)$$

where $\Psi = \frac{e_0 \Phi}{kT}$ is the reduced electrostatic potential and $\kappa^{-1} = \sqrt{\frac{\epsilon \epsilon_0 kT}{2n_d N_A e_0^2}}$ is the Debye length, ϵ is the dielectric constant of the solution, ϵ_0 is the permittivity of vacuum, T is the temperature and k is the Boltzmann constant, N_A is the Avogadro number, n_d is the bulk counterion concentration, e_0 is the elementary charge, Δ is the Laplace operator and r is the radial coordinate.

In the case of uniformly charged and very long cylinder the three-dimensional problem reduces to one-dimensional problem, i.e. the differential equation (1) for the potential becomes

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\Psi(r)}{dr} \right) = \kappa^2 \Psi(r) \quad (2)$$

Multiplying Eq. (2) by r^2 and performing the derivation we get

$$r^2 \Psi''(r) + r \Psi'(r) - \kappa^2 r^2 \Psi(r) = 0, \quad (3)$$

where the symbol ' denotes derivation with respect to the radial coordinate r .

The solution of differential Eq. (2) is [9]

$$\Psi(r) = A I_0(\kappa r) + B K_0(\kappa r) \quad (4)$$

where I_0 and K_0 are the modified Bessel functions of order 0. The constants A and B are determined by boundary conditions.

In a **convex** case the outer charged surface of the tube with the radius r_o is in a contact with the outer electrolyte solution. The boundary conditions outside the tube are

$$\frac{d\Psi(r)}{dr} \Big|_{r \rightarrow \infty} = 0 \quad (5)$$

$$\frac{d\Psi(r)}{dr} \Big|_{r=r_o} = -\frac{\sigma_o e_0}{\epsilon \epsilon_0 kT} \quad (6)$$

where σ_o is the surface charge density of the outer surface of the tube. The first boundary condition (Eq. 5) gives $A = 0$, while from the second boundary condition (Eq. 6) the constant B was calculated. The electrostatic potential outside the tube is [7]

$$\Psi(r) = \frac{\sigma_o e_0}{kT \epsilon \epsilon_0 \kappa_o} \frac{K_0(\kappa_o r)}{K_1(\kappa_o r_o)}, \quad (7)$$

where $\kappa_o = \sqrt{\frac{2n_d^o N_A e_0^2}{\epsilon \epsilon_0 kT}}$, n_d^o is the electrolyte strength far from the charged tube and K_1 is the modified Bessel function of order 1.

Inside the tube we consider electric double layer being in contact with the **concave** surface of radius r_i , where the inner part of the tube is in contact with the electrolyte solution. The boundary conditions inside the tube are

$$\frac{d\Psi(r)}{dr} \Big|_{r=0} = 0 \quad (8)$$

$$\frac{d\Psi(r)}{dr} \Big|_{r=r_i} = \frac{\sigma_i e_0}{\epsilon \epsilon_0 kT} \quad (9)$$

where σ_i is the surface charge density of the inner surface of the tube. The first boundary condition (Eq. 5) gives $B = 0$, while from the second boundary condition (Eq. 6) the constant A was calculated. The electrostatic potential inside the tube becomes

$$\Psi(r) = \frac{\sigma_i e_0}{kT \epsilon \epsilon_0 \kappa_i} \frac{I_0(\kappa_i r)}{I_1(\kappa_i r_i)}, \quad (10)$$

where $\kappa_i = \sqrt{\frac{2n_d^i N_A e_0^2}{\epsilon \epsilon_0 kT}}$, n_d^i is the electrolyte strength along the axis of the tube and I_1 is the modified Bessel function of order 1.

The concentration of counterions n_{ct} is given by the Boltzmann distribution

$$n_{ct} = n_d e^{-\Psi(r)}, \quad (11)$$

where n_d is the bulk concentration of counterions. In the LPB theory the exponent in Eq. (11) is expanded in electrostatic potential up to the first order. The concentration of counterions outside the charged tube n_{ct}^o thus becomes

$$n_{ct}^o = n_d^o (1 - \Psi(r)). \quad (12)$$

Inserting Eq. (7) into Eq. (12) we obtain

$$n_{ct}^o = n_d^o \left(1 - \frac{\sigma_o}{\sqrt{n_d^o N_A}} \sqrt{\frac{1}{2kT \epsilon \epsilon_0}} \frac{K_0(\kappa_o r)}{K_1(\kappa_o r_o)} \right). \quad (13)$$

Within LPB the concentration of counterions inside the charged tube n_{ct}^i is

$$n_{ct}^i = n_d^i(1 - \Psi(r)), \quad (14)$$

inserting Eq. (10) into Eq. (14) we obtain

$$n_{ct}^i = n_d^i \left(1 - \frac{\sigma_i}{\sqrt{n_d^i N_A}} \sqrt{\frac{1}{2kT\epsilon\epsilon_0}} \frac{I_0(\kappa_i r)}{I_1(\kappa_i r)} \right). \quad (15)$$

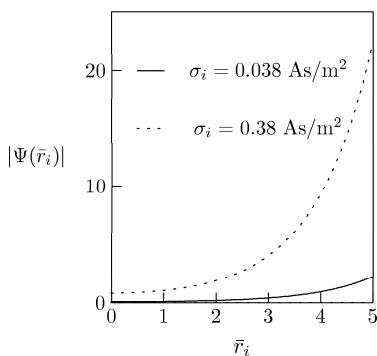


Figure 3. Reduced electric potential $|\Psi(\bar{r}_i)|$ inside the charged surface for two different surface charge densities σ_i and $n_d^i = 0.1\text{mol/l}$. We use dimensionless spatial coordinates $\bar{r}_i = \kappa_i r$.

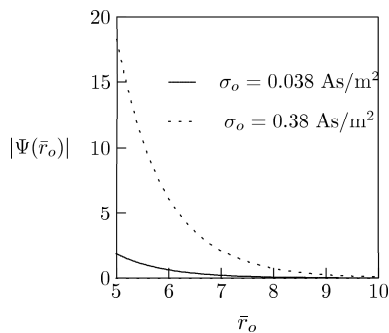


Figure 4. Reduced electric potential $|\Psi(\bar{r}_o)|$ outside the charged surface for two different surface charge densities σ_o and $n_d^o = 0.1\text{mol/l}$. We use dimensionless spatial coordinates $\bar{r}_o = \kappa_o r$.

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3 Results and Discussion

Figs. 3 and 4 show the reduced potential inside and outside the charged tube, respectively. The linearized PB theory was used. The electric potential decreases with the increasing distance from the charged surface. In centre of the tube and far from the tube the

electrostatic potential converges to 0. The absolute value of the potential increases with the increasing surface charge density.

The LPB theory is justified for the dimensionless ions and the reduced potential $|\Psi|$ smaller than 1. This corresponds to the potential $\Phi = 25\text{mV}$ at room temperature. Our calculations show that the maximal reduced potential is equal to 2 for surface charge density $\sigma_m = 0.038\text{As/m}^2$ and bulk concentrations $n_d^m = 0.1\text{mol/l}$. This is nearly the limit of the validity of LPB. For smaller σ_m and n_d^m the linearized Poisson-Boltzmann theory can be applied.

We assumed a permittivity of 78.5 for the solution. Large ion concentration near the charged surface reduces the permittivity of the solution near the charged surface. This change of the permittivity near the charged surface will lead in a minor correction of our calculation.

The length of the tube was much greater than the radius of the tube. This improves the statistics of the system and neglects the role of the edges of the tube. We also assumed large radius of the tube compared to the Debye length. This assumption avoids overlapping of concave double layers of opposite surfaces of the charged tube [10; 11].

In summary, our model of the cylindrical double layer is based on the LPB theory. The convex and concave electric double layer in cylindrical geometry is studied. The analytical solution for the electrostatic potential and the counterion concentration inside the tube are obtained. We show that the absolute value of the electrostatic potential as well as the counterion concentration decrease with the increasing distance from the charged surface.

References

- [1] Israelachvili J N (1997) Intermolecular and surface forces. Academic Press, London, 1997.
- [2] S. McLaughlin, Ann. Rev. Biophys. Chem. 18 (1989) 113-136.
- [3] G. Cevc, Biochim Biophys Acta 1031-3 (1990) 311-382.
- [4] M.G. Gouy, J. Phys. Radium (Paris) 9 (1910) 457-468.
- [5] D.L. Chapman, Philos. Mag. 6 (1913) 475-481.
- [6] F. Oosawa, Polyelectrolytes, Marcel Dekker, New York, 1970.
- [7] D.F. Evans, H. Wennerström, The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet, VCH Publishers, New York (1994).
- [8] E.J. Verwey and J.Th.G. Overbeek, Theory of Stability of Lyophobic Colloids, Elsevier Publishing Company, New York (1948) 22-30.
- [9] J. D. Jackson, *Classical Electrodynamics*, John Wiley, New York, 1998.
- [10] D. Bratko, A. Luzar, S.H. Chen, J. Chem. Phys. 89 (1988) 545-550.
- [11] K. Bohinc, J. Gimsa, V. Kralj-Iglič, T. Slivnik, A. Iglič, Bioelectrochem. 67 (2005) 91-99.