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Linearized Poisson-Boltzmann Equation for Zwitterions

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The Poisson-Boltzmann equation for double-charged macromolecules (zwitterions) is obtained from very basic assumptions. The final linearized equation is solved for two cases of general interest: spherical and cylindrical symmetries.

Keywords: LPB equation, polyelectrolytes, zwitterions

INTRODUCTION

The study of electrically charged systems is of enormous interest, both theoretically and technologically speaking, because many collective phenomena, as well as energy storage methodologies, are based on the behavior of highly charged particles. In spite of the important development of theoretical approaches to describe point-like electrical charges, there exists very scarce literature related to the fundamental theory of charged macromolecules. Besides the fundamental relevance of those systems, the practical applications of charged macromolecules, as the so-called Polyelectrolytes, demand a theoretical

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framework to explain some of the fascinating phenomena of those materials [1–5].

Indeed, the term Polyelectrolyte (PEL) is employed for describing polymer systems consisting of a macroion, that is macromolecule carrying covalently bound anionic or cationic groups, and low-molecular counterions, securing electroneutrality. Examples of an anionic and a cationic PEL and a polyampholyte (special case of polyelectrolyte carrying both anionic and cationic groups covalently bound to the macromolecule) are schematically represented in Figure 1. A macroion (or polyion) is a highly charged structure. If the macroion, that is, a macromolecule carrying the ionic sites, has charge $Q = Ze$ then, in solution there exist Z counterions. Typically, the solvent also contains a salt, so the total number of counterions is Z plus the number of corresponding ions from the salt.

One class of PEL widely studied are those consisting of slender, rod-like particles. For such systems, the idealized model is an infinite cylinder of radius a and uniform linear charge density with counterions and coions treated theoretically as point particles. This approach, however, neglects several effects as the interaction between macroions, the flexibility degrees of freedom of the

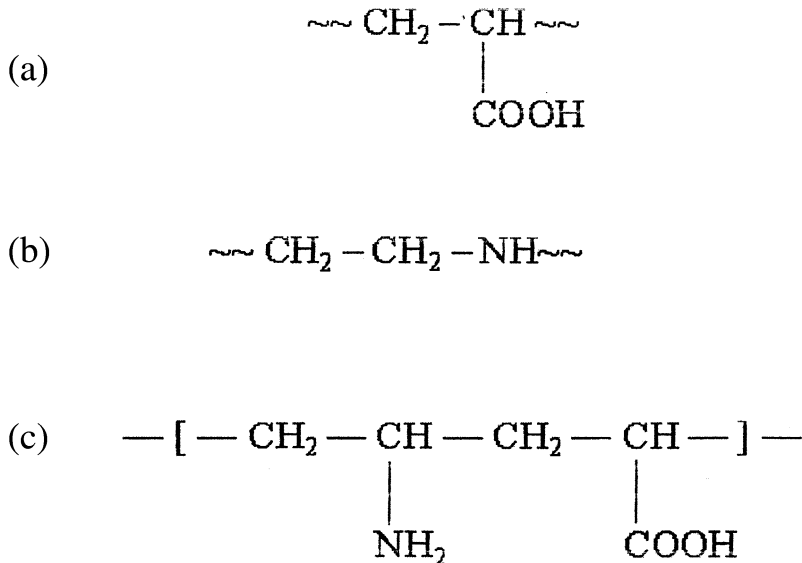


FIGURE 1 Examples of: (a) anionic polyelectrolyte, poly(acrylic acid); (b) cationic, poly(ethylene imine); and (c) polyampholyte, poly(aminocarboxylic acids).

macroion, finite size effects, to name but a few of the limitations of the available models.

The Poisson-Boltzmann (PB) equation is the main mathematical tool for studying the behavior of ionic solutions [1–4]. Its main advantages are its simplicity, which allows analytical solutions in simple cases, and its surprisingly good agreement with experiments. In its simple form, the linearized Poisson-Boltzmann (LPB) leads to the Debye-Hückel expression, thus providing a simple description of screening effects in terms of the Debye-Hückel screening length [5–6]. The success of the PB approach is quite impressive in view of the various strong approximations that are included in its derivation: it is a mean field approach that totally neglects correlations and all specific (non-electrostatic) interactions between the ions, including the ionic size.

Nevertheless, despite the success of the PB approach in describing a wide range of systems, it has been known for a long time to have some limitations in several important cases: phase transition of electrolyte solution, the adsorption of charged ions to highly charged surfaces, and the attractive interactions that can be observed between equally charged surfaces in the presence of multivalent counterions. Consequently, there have been numerous attempts to improve on the standard PB equation [7–9].

It has been accepted that PB equation is of fundamental importance for the theoretical study of low-molecular electrolytes as such as polyelectrolytes. The PB equation is based on a mean field potential, as mentioned. Actually, the PB theory is only quantitatively correct for ion concentrations less than 10 mM. The validity of PB theory is in question for large concentration of ions with the help of the LPB equation [5] (the linearization of the Boltzmann term can be avoided) and the theory still remains a mean field approach.

The so-called zwitterionic polymers are important copolymers carrying, on some of their monomeric units, small lateral chains where cations and anions are covalently bonded. A zwitterion is a macromolecule with both cationic and anionic sites [10–13] and in some cases maintain the zwitterionic end group in the propagation [14], as in poly-(4-Vinylpyridine) salts. The importance of zwitterions can be understood by recalling that aminoacids are zwitterions at physiological pH conditions. In addition to the theoretical interest of these polymers, there exist important applications and very scarce theory has been developed toward the understanding of the fundamental statistical mechanics of these systems. Accordingly, the present article shall extend the standard approach for zwitterionic polymers, aiming to provide a general theoretical framework for analyzing charged macromolecules.

THE LINEARIZED POISSON-BOLTZMANN EQUATION FOR ZWITTERIONS (LPBZ)

Begin from the Poisson equation

$$\nabla^2 \Psi_r = -\frac{4\pi\rho}{\epsilon\epsilon_0} \quad (1)$$

where Ψ_r is the electrostatic potential, ρ is the charge distribution, ϵ is the bulk dielectric constant, and ϵ_0 is the medium dielectric constant. If the distribution of the ionic sites around a central ionic site can be described by the Boltzmann distribution, in terms of the bulk concentration of ionic sites, there is a mean field approach of the charge distribution as:

$$\rho_r = \sum_i n_i^0 z_i e \exp\left(-\frac{z_i e \Psi_r}{kT}\right) \quad (2)$$

with r the distance from the central ionic site and where the summation includes all ionic species, z_i is the valence of the i th species, e is the elementary charge, n_i^0 is the corresponding bulk concentration, k is the Boltzmann constant and T the temperature. Figure 2 shows schematically the spatial arrangements of a typical zwitterion (Poly-(4-vinylpyridine-sulpho propyl betaine)), P4VP-SPB, where the cationic and anionic sites are shown. Figure 3 shows a representation of zwitterionic polymer chains, where ionic sites, randomly distributed, are shown.

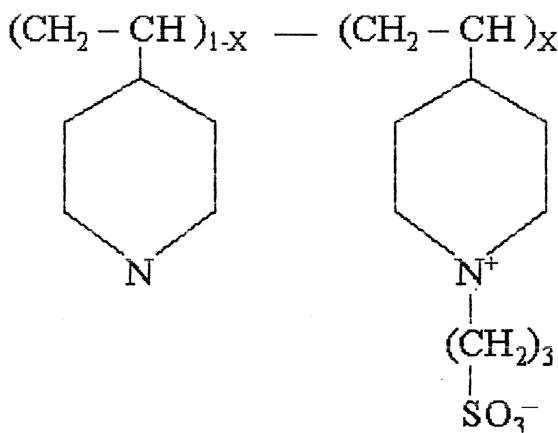


FIGURE 2 The Poly(4-vinylpyridine-sulpho propyl betaine), P4VP-SPB.

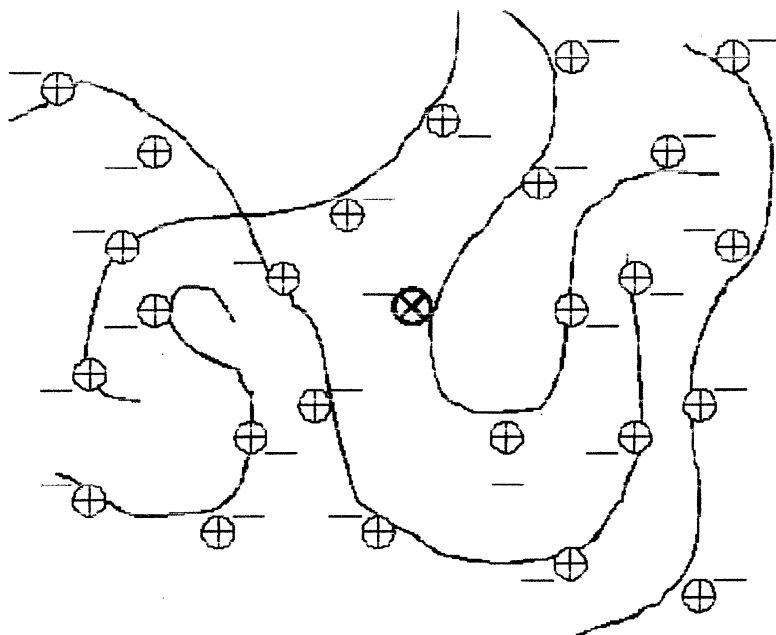


FIGURE 3 Representation of polymeric chains with ionic sites randomly distributed. The central ionic site \otimes is shown.

Consider a system with only one type of cationic and anionic sites, such as *P4VP-SPB*. Thus the distribution of ionic sites is described, from Equation 2, by

$$\rho_r = n_+^{(0)} z_+ e \exp\left(-\frac{z_+ e \Psi_r}{kT}\right) + n_-^{(0)} z_- e \exp\left(-\frac{z_- e \Psi_r}{kT}\right) \quad (3)$$

where z_+ and z_- are the valences of the cationic and anionic species respectively, and $n_+^{(0)}$ and $n_-^{(0)}$ are the corresponding bulk concentrations.

$$\rho_r = n^{(0)} z e \left[\exp\left(-\frac{z e \Psi_r}{kT}\right) - \exp\left(+\frac{z e \Psi_r}{kT}\right) \right] \quad (4)$$

where, for the *P4VP-SPB* case, $z = z_+ = z_-$ and $n^{(0)} = n_+^{(0)} = n_-^{(0)}$ was taken. These exponentials were expanded up to the linear term in Ψ_r (this is correct for weakly interacting potentials).

$$\rho_r = n^{(0)} z e \left\{ \left[1 - \frac{z e \Psi_r}{kT} + \frac{(z e \Psi_r / kT)^2}{2!} - \dots \right] - \left[1 + \frac{z e \Psi_r}{kT} + \frac{(z e \Psi_r / kT)^2}{2!} + \dots \right] \right\}$$

and, by retaining only the linear terms

$$\begin{aligned}\rho_r &\cong n^{(0)}ze\left(-\frac{2ze\Psi_r}{kT}\right) \\ \rho_r &\cong -2n^{(0)}z^2e^2\frac{\Psi_r}{kT}\end{aligned}\quad (5)$$

the *Linearized Boltzmann Equation for Zwitterions (LBZ)* was obtained.

Assuming that the electrostatic potential Ψ_r satisfies Eq. 1, Eq. 5 leads to

$$\begin{aligned}\nabla^2\Psi_r &= -\frac{4\pi(-2n^{(0)}z^2e^2(\Psi_r/kT))}{\varepsilon\varepsilon_0} \\ \nabla^2\Psi_r &= \lambda_M^2\Psi_r\end{aligned}\quad (6)$$

where $\lambda_M = (8\pi z^2 e^2 n^{(0)} / \varepsilon \varepsilon_0 kT)^{1/2}$ is a characteristic length scale of the system. Notice that Eq. 6 is just a generalization of the Debye-Hückel equation for zwitterions.

Solution of LPBZ Equation in Spherical Coordinates

The LPBZ equation in spherical coordinates is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi_r}{dr} \right) = \lambda_M^2 \Psi_r \quad (7)$$

$$\frac{1}{r^2} \left(r^2 \frac{d^2\Psi_r}{dr^2} + 2r \frac{d\Psi_r}{dr} \right) = \lambda_M^2 \Psi_r$$

$$\frac{d^2\Psi_r}{dr^2} + \frac{2}{r} \frac{d\Psi_r}{dr} - \lambda_M^2 \Psi_r = 0 \quad (8)$$

by setting $\Psi_r = u(r)/r$, where $u(r)$ is a function of r ; Eq. 8 takes the form

$$\frac{d^2u(r)}{dr^2} - \lambda_M^2 u = 0 \quad (9)$$

with solutions of the form

$$u(r) = A \exp(-\lambda_M r) \quad (10)$$

A is an arbitrary constant.

Finally

$$\Psi_r = \frac{A \exp(-\lambda_M r)}{r} \quad (11)$$

Notice that Eq. 11 is the typical expression for the LPB equation for polyelectrolytes, as has been reported in the literature [15].

The Debye-Hückel Parameter for Zwitterions in Spherical Coordinates

If the exponential of Eq. 11 is expanded into

$$\Psi_r = \frac{A}{r} \left[1 - \lambda_M r + \frac{(-\lambda_M r)^2}{2!} + \dots \right] \tag{12}$$

and by taking only the linear term

$$\Psi_r = A \left(\frac{1}{r} - \lambda_M \right) \tag{13}$$

$$\Psi_r = \Psi_{site} + \Psi_M \tag{14}$$

Here, $\Psi_{site} = A/r$ is the potential at a distance r from the ionic site under consideration and $\Psi_M = -A\lambda_M$ can be regarded as an interaction parameter, controlled by λ_M . This is the equivalent to the Debye-Hückel theory for polyelectrolytes.

Solution of LPBZ Equation in Cylindrical Coordinates

To express Eq. 6 in cylindrical coordinates, the idealized geometrical model of coaxial cylinder can be used, Figure 4, with a dielectric region inside. The inner cylinder of radius a and uniform linear charge density and the external cylinder of radius b and uniform linear charge density of opposite signs (cationic and anionic sites are treated as point particles) allow the neglect of the edge effects by taking the length of chains to be practically infinite, as compared to the ions dimensions.

If the cylinder shells are considered as potential surfaces and $L \gg \rho$

$$\Psi = \Psi(\rho, \varphi)$$

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \Psi}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 \Psi}{\partial \varphi^2} = 0 \tag{15}$$

$\Psi = R(r)Q(\varphi)$ can be proposed

$$\frac{Q}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial R}{\partial \rho} \right) + \frac{R}{\rho^2} \frac{\partial^2 Q}{\partial \varphi^2} = 0$$

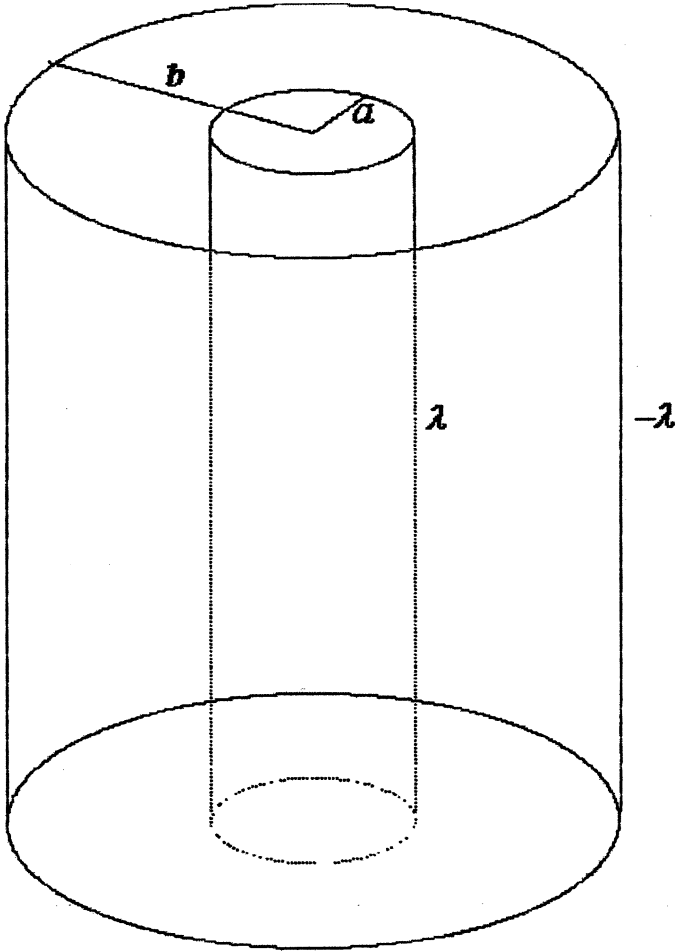


FIGURE 4 Idealized geometrical model of the system type coaxial cylinder.

multiplying by (ρ^2/RQ)

$$\frac{\rho}{R} \frac{d}{d\rho} \left(\rho \frac{dR}{d\rho} \right) + \frac{1}{Q} \frac{d^2 Q}{d\varphi^2} = 0$$

$$\frac{1}{Q} \frac{d^2 Q}{d\varphi^2} = -n^2$$

$$\frac{d^2 Q}{d\varphi^2} + n^2 Q = 0 \quad (16)$$

with solutions $Q(\varphi) = A \sin(n\varphi) + B \cos(n\varphi)$

$$\frac{\rho}{R} \frac{d}{d\rho} \left(\rho \frac{dR}{d\rho} \right) = n^2$$

$$\rho^2 \frac{d^2 R}{d\rho^2} + \rho \frac{dR}{d\rho} - n^2 = 0 \tag{17}$$

with solutions $R(\rho) = \rho^n + \rho^{-n}$

For $n = 0$, Eq. 16 is

$$\frac{d^2 Q}{d\varphi^2} = 0$$

$$\frac{dQ}{d\varphi} = B_0$$

$$Q = A_0 + B_0 \varphi$$

If we want φ to be single-valued, then $B = 0$, and

$$Q(\varphi) = A \sin(n\varphi) \tag{18}$$

Eq. 17 is, for $n = 0$,

$$\frac{\rho}{R} \frac{d}{d\rho} \left(\rho \frac{dR}{d\rho} \right) = 0$$

$$\frac{d}{d\rho} \left(\rho \frac{dR}{d\rho} \right) = 0$$

$$\rho \frac{dR}{d\rho} = D_0$$

$$\frac{dR}{d\rho} = \frac{D_0}{\rho}$$

$$R = C_0 + D_0 \ln \rho \tag{19}$$

So, from Eqs. 18 and 19

$$\Psi(\rho, \varphi) = \sum_n A_n \sin(n\varphi) (C_n \rho^n + D_n \rho^{-n}) + D_0 \ln \frac{\rho}{\rho_0} \tag{20}$$

where $C_0 = -\ln \rho_0$, and absorbs A_0 .

With boundary conditions

$$\Psi(a, \varphi) = V_a$$

$$\Psi(b, \varphi) = V_b$$

For $\rho = a$ we have, from Eq. 20,

$$\begin{aligned} \Psi(a, \varphi) &= \sum_n A_n \sin(n\varphi)(C_n a^n + D_n a^{-n}) + D_0 \ln \frac{a}{\rho_0} = V_a \\ C_n a^n + D_n a^{-n} &= 0 \quad \text{and} \quad D_0 \ln \frac{a}{\rho_0} = V_a \\ D_n &= -C_n a^{2n} \\ \Psi(\rho, \varphi) &= \sum_n A_n \sin(n\varphi) C_n (\rho^n + a^{2n} \rho^{-n}) + D_0 \ln \frac{\rho}{\rho_0} \\ \Psi(\rho, \varphi) &= \sum_n E_n \sin(n\varphi) (\rho^n + a^{2n} \rho^{-n}) + D_0 \ln \frac{\rho}{\rho_0} \Psi, \end{aligned} \tag{21}$$

where $E_n = A_n C_n$.

And for $\rho = b$,

$$\begin{aligned} \Psi(b, \varphi) &= \sum_n E_n \sin(n\varphi)(b^n + a^{2n} b^{-n}) + D_0 \ln \frac{b}{\rho_0} = V_b \\ \Psi(b, \varphi) &= \sum_n E_n \sin(n\varphi)(b^n + a^{2n} b^{-n}) + D_0 \ln \frac{b}{\rho_0} \left(\frac{V_a}{D_0 \ln(a/\rho_0)} \right) = V_b \\ \Psi(b, \varphi) &= \sum_n E_n \sin(n\varphi) \left(\frac{b^{2n} + a^{2n}}{b^n} \right) + V_a \ln \frac{b}{a} = V_b \tag{22} \\ \sum_n E_n \sin(n\varphi) \left(\frac{b^{2n} + a^{2n}}{b^n} \right) &= V_b - V_a \ln \frac{b}{a} \\ \sum_n E_n \sin(n\varphi) \left(\frac{b^{2n} + a^{2n}}{b^n} \right) &= V_0 \end{aligned}$$

where $V_0 = V_b - V_a \ln(b/a)$,

$$\begin{aligned} \int d\varphi \sin(n'\varphi) \sum_n E_n \sin(n\varphi) \left(\frac{b^{2n} + a^{2n}}{b^n} \right) &= \int d\varphi \sin(n'\varphi) V_0 \\ \sum_n E_n \left(\frac{b^{2n} + a^{2n}}{b^n} \right) \delta(n, n') &= \int d\varphi \sin(n'\varphi) V_0 \\ E_{n'} \left(\frac{b^{2n'} + a^{2n'}}{b^{n'}} \right) &= \int d\varphi \sin(n'\varphi) V_0 \end{aligned}$$

$$E_{n'} = \left(\frac{b^{n'}}{b^{2n'} + a^{2n'}} \right) \int d\varphi \sin(n'\varphi) V_0 \quad (23)$$

CONCLUDING REMARKS

The Poisson-Boltzmann theory was extended for zwitterions, by assuming a rod-like structure of the corresponding molecular chains. A generalization of the Debye-Hückel equation for zwitterions was obtained, as well as the linearized Poisson-Boltzmann equation for zwitterions.

Two relevant symmetries were considered for solving the equations obtained. In spherical coordinates, interestingly, the solution of the LBPZ leads to the Debye-Hückel expression, thus providing a simple description of interaction effects in terms of the characteristic length scale of the system, λ_M . In the case of cylindrical coordinates, an explicit expression was obtained for the potential Ψ as a function of φ .

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