

Solution to Poisson Boltzmann equation in semi-infinite and cylindrical geometries

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(Dated: November 6, 2015)

Linearized Poisson-Boltzmann equation (PBE) gives us simple expressions for charge density distribution (ρ_e) within fluids or plasma. A recent work of this author shows that the old boundary conditions (BC), which are usually used to solve PBE, have serious defects. The old solutions turned out to be non-unique, and violates charge conservation principle in some cases. There we also derived the correct formula of ρ_e for a finite, rectangular geometry, using appropriate BCs. Here we consider some other types of geometries and obtain formula of ρ_e , which may be useful to analyse different experimental conditions.

I. INTRODUCTION

Linearized PBE has been used since a long time, almost a century [1], to obtain distribution of free electric charges within ionic solutions or plasma. It has applications in various fields ranging from nanofluidics-microfluidics [2, 3] to astrophysics [4, 5], covering radio-science [6], surface chemistry [7], colloid science [8], laboratory plasma/ thermo-nuclear fusion devices [9, 10], bio-science [11, 12] etc. However, a recent work of this author [13] shows that the Dirichlet or Neumann type BCs that are usually used to solve the PBE, have serious defects, as they produce non-unique solutions. The Dirichlet condition leads to violation of charge conservation principle. We have been able to remove those defects by using different BCs to obtain ρ_e . There we analyzed a 1-D problem using a ‘finite’ and ‘rectangular’ geometry to demonstrate the essential ideas. Here, we derive the formula of ρ_e for some other geometries. Firstly, we do an 1-D analysis for a cylindrical geometry; we consider two sub-cases, one with an annular cross-section, and the other with a circular cross-section. Secondly, we do an 1-D analysis for a rectangular, semi-infinite domain, where the fluid is bounded by a single plane and the fluid extends to infinity along the direction normal to that plane. After this, we give an ‘alternative’ derivation to the distribution formula for a finite rectangular domain that we have derived for the first time in Ref. [14]; a minute correction was done in Ref. [15].

II. CYLINDRICAL GEOMETRY

See Ref. [16] for some formulae that we used here.

For a cylindrical geometry, the position of a point is specified with (R, θ, z) , see Ref. [17]. The meaning of most of the other symbols can be found in Ref. ([14]), any exception will be notified. We analyse a straight domain of length L , with annular and circular cross-sections

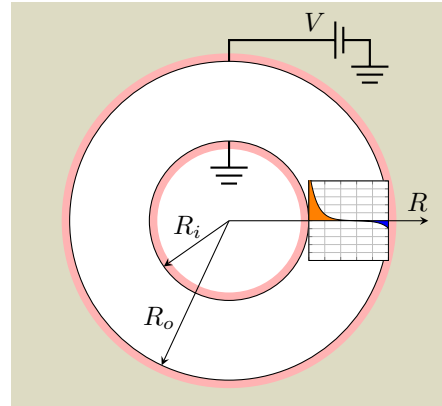


FIG. 1. (Color online) Ionic solution within a cylindrical geometry of annular cross-section. Two circular boundaries have a potential difference. A typical plot that shows how charge density varies in the radial direction, is embedded to show the domain of our interest, see Fig. (2)

respectively. We consider only axi-symmetric problems i.e independent of θ . When L is much greater compared to the radius, the problems become independent of z as well, except some end-effects. Hence, the problems depend only on the radial coordinate R . We use some suitable scales ‘ a ’ and ‘ ζ ’ (both are positive) for distance and electrostatic potential (ψ) respectively. Let’s define a few quantities:

$$r \equiv \frac{R}{a}; \quad \kappa \equiv \left[\frac{\lambda_D}{a} \right]^{-1}; \quad \psi^* \equiv \frac{\psi}{\zeta}; \quad \rho_0 \equiv \frac{\epsilon \kappa^2 \zeta}{a^2}; \quad \rho_e^* \equiv \frac{\rho_e}{\rho_0} \quad (1)$$

Where, λ_D is the ‘Debye length’, ϵ is the permittivity of the fluid.

A. Cylindrical geometry of annular cross-section

Here the domain is bounded by two concentric right cylinders, see Fig. (1); the ‘inner’ and ‘outer’ radii are R_i and R_o , normalized as: $r_i \equiv R_i/a$; $r_o \equiv R_o/a$; the annular ends are also walls.

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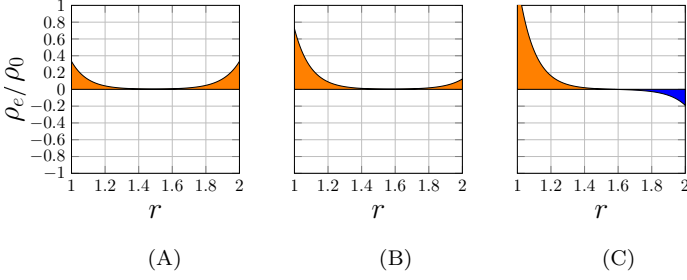


FIG. 2. (Color online) Charge density distribution within a fluid, bounded by two concentric cylinders. $\kappa = 10.0$; $q_0 = 0.1$. (a) $v = 0$; excess charges accumulate near boundaries. (b) $v = 0.6$; an applied voltage redistributes charges. (c) $v = 1.5$; strong voltage segregates negative charges even if $q_0 > 0$. Compare this figure with that in Ref. [13]

We start with a formula that we derived in Ref. [14] (within its Supplementary Material).

$$\therefore \rho_e^* = -\psi^* \quad (2)$$

We will define some useful quantities, which will be useful later. The net charge present in the total domain i.e. Q_{TOT} is given by $\iiint \rho_e dV$, where $dV = R dR d\theta dz$. If ρ_e depends only upon R , we have,

$$Q_{TOT} = \int_0^L dz \int_0^{2\pi} d\theta \int_{R_i}^{R_o} \rho_e R dR = 2\pi L \int_{R_i}^{R_o} \rho_e R dR \quad (3)$$

We define a quantity Q_{1c} , then using Eq. (1) we write its non-dimensional form q_{1c} ; the subscript ‘1c’ means an 1-D problem in cylindrical geometry.

$$Q_{1c} \equiv \frac{Q_{TOT}}{2\pi L} = \int_{R_i}^{R_o} \rho_e R dR = \rho_0 a^2 \int_{r_i}^{r_o} \rho_e^* r dr \quad (4)$$

$$q_{1c} \equiv \frac{Q_{1c}}{(\rho_0 a^2)} = \int_{r_i}^{r_o} \rho_e^* r dr \quad (5)$$

Q_{1c} is the net charge present in the fluid within an angular sector of unit radian, per unit axial length. Q_{1c} has dimension ‘charge per length’ e.g. *Coulomb · meter*⁻¹, unlike in the 1-D problem for a rectangular domain, where it had dimension *Coulomb · meter*⁻² (see Ref. [15]).

Now, ψ and ρ_e are also related by Poisson’s equation in electrostatics (PES), which is given by,

$$\nabla^2 \psi = -\frac{\rho_e}{\epsilon} \quad (6)$$

For a cylindrical geometry, ∇^2 is given by,

$$\nabla^2 \equiv \frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial}{\partial R} \right) + \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \quad (7)$$

In the special case, where ψ varies only in the ‘radial’ direction, the PES reduces to,

$$\frac{1}{R} \frac{d}{dR} \left(R \frac{d\psi}{dR} \right) = -\frac{\rho_e}{\epsilon} \quad (8)$$

using Eq. (1) we first make PES non-dimensional:

$$\begin{aligned} \frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi^*}{dr} \right) \left(\frac{\zeta}{a^2} \right) &= -\frac{\rho_0}{\epsilon} \rho_e^* = -\left(\frac{\epsilon \kappa^2 \zeta}{a^2 \epsilon} \right) \rho_e^* \\ \Rightarrow \frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi^*}{dr} \right) &= -\kappa^2 \rho_e^* \end{aligned} \quad (9)$$

Using Eq. (2) in Eq. (9) we get non-dimensional PBE in 1-D cylindrical (radial) coordinates:

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi^*}{dr} \right) = \kappa^2 \psi^* \quad (10)$$

Its general solution (see Ref. [16]), with arbitrary constants A and B , is given by,

$$\psi^* = AI_0(\kappa r) + BK_0(\kappa r) \quad (11)$$

Where, I_0 and K_0 are modified Bessel functions of order 0. We need two conditions to fix A and B . We get one condition by integrating PES i.e. Eq. (9) and using Eq. (5),

$$\begin{aligned} \int_{r_i}^{r_o} \left[\frac{1}{r} \frac{d}{dr} \left(r \frac{d\psi^*}{dr} \right) \right] r dr &= -\kappa^2 \int_{r_i}^{r_o} \rho_e^* r dr \\ \Rightarrow \left(r \frac{d\psi^*}{dr} \right) \Big|_{r=r_o} - \left(r \frac{d\psi^*}{dr} \right) \Big|_{r=r_i} &= -q_{1c} \kappa^2 \end{aligned} \quad (12)$$

We assume the potential difference (scaled with ζ) between outer and inner curved boundaries i.e. ‘ v ’ to be known,

$$\psi^*(r_o) - \psi^*(r_i) = v \quad (13)$$

We solve PBE i.e. Eq. (10) using two conditions given by Eq. (12) and Eq. (13). We use the following formulae, see Ref. [18, 19]:

$$\frac{dI_0(\xi)}{d\xi} = I_1(\xi); \quad \frac{dK_0(\xi)}{d\xi} = -K_1(\xi) \quad (14)$$

From Eq. (11) we get,

$$\begin{aligned} \frac{d\psi^*}{dr} &= A \frac{dI_0(\kappa r)}{dr} + B \frac{dK_0(\kappa r)}{dr} \\ &= \kappa [AI_1(\kappa r) - BK_1(\kappa r)] \end{aligned} \quad (15)$$

From Eq. (12) and Eq. (15) we get,

Where,

$$\begin{aligned} r_o \kappa [AI_1(\kappa r_o) - BK_1(\kappa r_o)] - r_i \kappa [AI_1(\kappa r_i) - BK_1(\kappa r_i)] &= -q_{1c} \kappa^2 \\ \Rightarrow [r_o I_1(\kappa r_o) - r_i I_1(\kappa r_i)] A - [r_o K_1(\kappa r_o) - r_i K_1(\kappa r_i)] B &= -q_{1c} \kappa \end{aligned} \quad (16)$$

From Eq. (11) and Eq. (13) we get,

$$\begin{aligned} [AI_0(\kappa r_o) + BK_0(\kappa r_o)] - [AI_0(\kappa r_i) + BK_0(\kappa r_i)] &= v \\ \Rightarrow [I_0(\kappa r_o) - I_0(\kappa r_i)] A + [K_0(\kappa r_o) - K_0(\kappa r_i)] B &= v \end{aligned} \quad (17)$$

We write Eq. (16) and Eq. (17) together in a compact, matrix form:

$$\begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} d_1 \\ d_2 \end{pmatrix} \quad (18)$$

$$C_{11} \equiv [r_o I_1(\kappa r_o) - r_i I_1(\kappa r_i)] \quad (19)$$

$$C_{12} \equiv (-1) \times [r_o K_1(\kappa r_o) - r_i K_1(\kappa r_i)] \quad (20)$$

$$C_{21} \equiv [I_0(\kappa r_o) - I_0(\kappa r_i)] \quad (21)$$

$$C_{22} \equiv [K_0(\kappa r_o) - K_0(\kappa r_i)] \quad (22)$$

$$d_1 \equiv -q_{1c} \kappa \quad (23)$$

$$d_2 \equiv v \quad (24)$$

The determinant Δ of the above 2×2 matrix is given by,

$$\Delta \equiv C_{11} \cdot C_{22} - C_{12} \cdot C_{21} \quad (25)$$

Finally we write A and B in terms of known quantities,

$$A = (d_1 \cdot C_{22} - d_2 \cdot C_{12}) / \Delta \quad (26)$$

$$B = (-d_1 \cdot C_{21} + d_2 \cdot C_{11}) / \Delta \quad (27)$$

We plug in the expressions of A and B given by Eq. (26) and Eq. (27) in Eq. (11) and rearrange terms; then we use Eq. (23), Eq. (24); finally we use Eq. (2) i.e. $\rho_e^* = -\psi^*$,

$$\begin{aligned} \psi^* &= \frac{(d_1 \cdot C_{22} - d_2 \cdot C_{12})}{\Delta} I_0(\kappa r) + \frac{(-d_1 \cdot C_{21} + d_2 \cdot C_{11})}{\Delta} K_0(\kappa r) \\ &= \frac{1}{\Delta} [d_1 \{C_{22} I_0(\kappa r) - C_{21} K_0(\kappa r)\} - d_2 \{C_{12} I_0(\kappa r) - C_{11} K_0(\kappa r)\}] \\ &= \frac{(-1)}{\Delta} [q_{1c} \kappa \{C_{22} I_0(\kappa r) - C_{21} K_0(\kappa r)\} + v \{C_{12} I_0(\kappa r) - C_{11} K_0(\kappa r)\}] \end{aligned} \quad (28)$$

$$\boxed{\therefore \rho_e^* = \frac{1}{\Delta} [q_{1c} \kappa \{C_{22} I_0(\kappa r) - C_{21} K_0(\kappa r)\} + v \{C_{12} I_0(\kappa r) - C_{11} K_0(\kappa r)\}]} \quad (29)$$

Using Eq. (29) we plot ρ_e^* vs r in Fig. (2) for the range $[1 \leq r \leq 2]$ i.e. we took $a = R_i$ and $R_o = 2R_i$, so that $r_i = 1$, and $r_o = 2$. The explanation of the plots goes along the same line as the rectangular geometry (Ref. [13]); if there is a net amount of charge in the domain, the charges accumulate near the two boundaries. An applied voltage redistributes the charges; positive and negative charges move towards the walls of lower and higher potentials respectively. A strong voltage can segregate two types of charges.

B. Cylindrical geometry of circular cross-section

Here we derive the formula of ρ_e for a right cylindrical domain of ‘circular’ cross-section, unlike the ‘annular’ one. The general solution to the PBE is given by Eq. (11). The function $K_0(\kappa r)$ blows up as $r \rightarrow 0$. Hence, in order to prevent ψ^* from blowing up as $r \rightarrow 0$, we must set

$B = 0$. We get,

$$\psi^* = AI_0(\kappa r) \quad (30)$$

For the special case $r_i = 0$, we write ${}^0q_{1c}$ instead of q_{1c} . Using Eq. (2) in Eq. (5), with $r_i = 0$, we get,

$$\int_0^{r_o} \psi^* r dr = -{}^0q_{1c} \quad (31)$$

Using Eq. (30) we get,

$$\begin{aligned} \int_0^{r_o} \psi^* r dr &= A \int_0^{r_o} I_0(\kappa r) dr \\ &= A \frac{r I_1(\kappa r)}{\kappa} \Big|_0^{r_o} \\ &= A \frac{r_o I_1(\kappa r_o)}{\kappa} = -{}^0 q_{1c} \\ \Rightarrow A &= -\frac{{}^0 q_{1c} \kappa}{r_o I_1(\kappa r_o)} \end{aligned} \quad (32)$$

$$\Rightarrow \psi^* = -\frac{{}^0 q_{1c} \kappa}{r_o I_1(\kappa r_o)} I_0(\kappa r) \quad (33)$$

Using Eq. (2) we finally have the formula for ρ_e^* ,

$$\boxed{\rho_e^* = \frac{{}^0 q_{1c} \kappa}{r_o I_1(\kappa r_o)} I_0(\kappa r)} \quad (34)$$

III. SEMI INFINITE RECTANGULAR GEOMETRY

Let's consider a plane, which, in its one side, bounds an infinite ocean of ionic solution. Here ρ_e varies only in the direction normal to the plane (x -direction); we set the origin on the plane so that x varies from 0 to ∞ . The general solution is the same as given in Ref. [13] (see the supplementary materials in that reference), however, the arbitrary constants of integration are fixed with different conditions. The non-dimensional PBE is $d^2 \psi^* / d\eta^2 = \kappa^2 \psi^*$; its general solution is given by:

$$\psi^* = A \exp(\kappa \eta) + B \exp(-\kappa \eta) \quad (35)$$

We must set 'A' to zero to prevent the solution to blow up when $\eta \rightarrow \infty$. Hence, using Eq. (2) we get

$$\begin{aligned} \rho_e^* &= -B \exp(-\kappa \eta) \quad (36) \\ \Rightarrow \int_0^\infty \rho_e^* d\eta &= -B \int_0^\infty \exp(-\kappa \eta) d\eta \\ &= -B \left(\frac{\exp(-\kappa \eta)}{-\kappa} \Big|_0^\infty \right) \\ &= -B \left(\frac{0 - 1}{-\kappa} \right) = -\frac{B}{\kappa} \end{aligned} \quad (37)$$

Let's define the following quantities (the subscript '1r' means 1-D and rectangular; left-superscript ' ∞ ' means infinite domain):

$${}^\infty Q_{1r} \equiv \int_0^\infty \rho_e dx \quad (38)$$

$${}^\infty q_{1r} \equiv \int_0^\infty \rho_e^* d\eta = \frac{1}{\rho_0 a} \int_0^\infty \rho_e dx = \frac{{}^\infty Q_{1r}}{(\rho_0 a)} \quad (39)$$

Please note the difference between Eq. (5) and Eq. (39); the dimensions of Q_{1c} and ${}^\infty Q_{1r}$ are different in two cases. We get,

$$B = -({}^\infty q_{1r} \kappa) \quad (40)$$

Finally we write the formula of ψ^* and ρ_e^* :

$$\psi^* = -({}^\infty q_{1r} \kappa) \exp(-\kappa \eta) \quad (41)$$

$$\boxed{\rho_e^* = ({}^\infty q_{1r} \kappa) \exp(-\kappa \eta)} \quad (42)$$

$$\boxed{\rho_e = \left(\frac{{}^\infty Q_{1r} \kappa}{a} \right) \exp(-\kappa x / a)} \quad (43)$$

Let's write the formula for the potential at boundary:

$$\psi_0^* \equiv \psi^*|_{\eta=0} = -{}^\infty q_{1r} \kappa \quad (44)$$

IV. FINITE RECTANGULAR GEOMETRY: AN ALTERNATIVE DERIVATION

For a finite, rectangular geometry we derived the formula of ρ_e in Ref. [13, 14], where ρ_e varies between two boundaries at $x = \pm a$ i.e. $\eta = \pm 1$; a minute correction of the formula can be found in Ref. [15]. Here we derive the same formula in a different way. We use a different symbol Q_{1r} instead of Q_0 . For the scaled potential difference (V/ζ) between boundaries we use the symbol v instead of δ .

$$Q_{1r} \equiv \int_{-a}^{+a} \rho_e dx \quad (45)$$

From Eq. (38) and Eq. (45) we see that ${}^\infty Q_{1r}$ and Q_{1r} differs only in the limits of integration. Integrating Eq. (2) we get,

$$\begin{aligned} \int_{-1}^{+1} \psi^* d\eta &= - \int_{-1}^{+1} \rho_e^* d\eta = - \int_{-a}^{+a} \frac{\rho_e}{\rho_0} d \left(\frac{x}{a} \right) \\ &= -\frac{1}{(\rho_0 a)} \int_{-a}^{+a} \rho_e dx = -\frac{Q_{1r}}{(\rho_0 a)} \\ \Rightarrow \int_{-1}^{+1} \psi^* d\eta &= -q_{1r} \end{aligned} \quad (46)$$

$$\text{Where, } q_{1r} \equiv \frac{Q_{1r}}{(\rho_0 a)} \quad (47)$$

We use Eq. (46) as one condition to solve PBE; the other condition is given by,

$$\psi^*(+1) - \psi^*(-1) = v \quad (48)$$

Integrating the general solution to the PBE i.e. Eq. (35) and then using Eq. (46) we get,

$$\begin{aligned} \int_{-1}^{+1} \psi^* d\eta &= A \left[\frac{\exp(+\kappa) - \exp(-\kappa)}{\kappa} \right] + B \left[\frac{\exp(-\kappa) - \exp(\kappa)}{-\kappa} \right] \\ &= [A + B] \frac{2 \sinh(\kappa)}{\kappa} = -q_{1r} \end{aligned} \quad (49)$$

Using Eq. (35) and Eq. (48) we get,

$$\begin{aligned} [A \exp(\kappa) + B \exp(-\kappa)] - [A \exp(-\kappa) + B \exp(\kappa)] &= v \\ \Rightarrow A [\exp(\kappa) - \exp(-\kappa)] - B [\exp(\kappa) - \exp(-\kappa)] &= v \\ \Rightarrow [A - B] 2 \sinh(\kappa) &= v \end{aligned} \quad (50)$$

From Eq. (49) and Eq. (50) we get,

$$A + B = -\frac{q_{1r}\kappa}{2 \sinh(\kappa)} \quad (51)$$

$$A - B = \frac{v}{2 \sinh(\kappa)} \quad (52)$$

From the above two equations we solve for A and B ,

$$A = \frac{[v - q_{1r}\kappa]}{4 \sinh(\kappa)}; \quad B = -\frac{[v + q_{1r}\kappa]}{4 \sinh(\kappa)} \quad (53)$$

Plugging in these expressions for A and B in Eq. (35), and rearranging terms we get the required expression for ψ^* ; then, using Eq. (2) we get the formula of ρ^* ; then we return to the dimensional variables:

$$\psi^* = \frac{1}{2 \sinh(\kappa)} [v \cdot \sinh(\kappa\eta) - (q_{1r}\kappa) \cdot \cosh(\kappa\eta)] \quad (54)$$

$$\rho_e^* = \frac{1}{2 \sinh(\kappa)} [(q_{1r}\kappa) \cdot \cosh(\kappa\eta) - v \cdot \sinh(\kappa\eta)] \quad (55)$$

$$\rho_e = \frac{\rho_0}{2 \sinh(\kappa)} \left[\kappa \left(\frac{Q_{1r}}{\rho_0 a} \right) \cosh \left(\frac{\kappa x}{a} \right) - \left(\frac{V}{\zeta} \right) \sinh \left(\frac{\kappa x}{a} \right) \right] \quad (56)$$

V. ACKNOWLEDGEMENT

This paper is a continuation of the work that I started at IISER-Kolkata; thanks for their hospitality. Thanks to Abhijit Sarkar, Sujata Sarkar and my parents for their financial supports. Thanks to Indian Association for the Cultivation of Science; I used their library facilities.

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