

Physical Solution of Poisson-Boltzmann Equation

Rajib Chakraborty*

89/3 Tanupukur Road,

Dhakuria, Calcutta 700 031,

West Bengal, India

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Abstract

We correct the solution of Poisson-Boltzmann equation regarding charge distribution in an electrolytic solution bounded by walls. Considering charge conservation principle properly, we show that the gradient of electrostatic potential at different walls are strictly related, and cannot be assigned independent values, unlike old theory. It clarifies some cause and effect ideas: distribution turns out to be independent of the initial polarity of walls; the accumulated charges in liquid usually induce opposite polarity on the wall surface, forms ‘Electric Double Layer’ (EDL), contrary to the common belief that a charged wall attracts counter-ions to form EDL. Distribution depends only on the potential difference between walls and the net charge present in the solution, apart from Debye length.

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* mecrajib@gmail.com

Let's find the charge density distribution ρ_e within an electrolytic solution bounded by walls. A rectangular geometry, with very small width '2a' compared to its length and height, makes it essentially a simple 1-D problem [1]; although keeps important physics we are interested in. Here, ρ_e varies only along the direction of the shortest side of domain, say in x -direction. Let's define a few parameters,

$$\kappa \equiv a/\lambda_D; \quad \eta \equiv x/a; \quad \psi^* \equiv \psi/\zeta \quad (1)$$

Where, λ_D is Debye length; ψ is electrostatic potential and ζ is a suitable scale for it ($\zeta > 0$).

Now, ρ_e and ψ are related through Boltzmann distribution [1, 2]

$$\rho_e = -\frac{\epsilon\kappa^2}{a^2}\psi = -\left[\frac{\epsilon\kappa^2\zeta}{a^2}\right]\psi^* \quad (2)$$

$$\Rightarrow \rho_e^* = -\psi^* \quad (3)$$

$$\text{Where, } \rho^* \equiv \rho_e/\rho_0, \text{ and } \rho_0 \equiv (\epsilon\kappa^2\zeta/a^2) \quad (4)$$

ψ and ρ_e are also related by Poisson's equation; for 1-D:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\epsilon} \quad (5)$$

$$\text{(using Eq. 1 and Eq. 4)} \quad \frac{d^2\psi^*}{d\eta^2} = -\kappa^2\rho_e^* \quad (6)$$

If Q_0 is the net charge present in liquid, in a cross-section,

$$\int_{-1}^{+1} \rho_e^* d\eta = \frac{1}{\rho_0} \int_{-1}^{+1} \rho_e d\eta = \frac{Q_0}{\rho_0} \equiv q_0 \quad (7)$$

Integrating both sides of Eq. 6 w.r.t η and using Eq. 7,

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=+1} - \left.\frac{d\psi^*}{d\eta}\right|_{\eta=-1} = -q_0\kappa^2 \quad (8)$$

Hence, we cannot assign independent values to $d\psi^*/d\eta$ at two walls, which was done earlier [3] and is not acceptable. Eq. 3 and Eq. 6 gives Poisson-Boltzmann equation,

$$\frac{d^2\psi^*}{d\eta^2} = \kappa^2\psi^* \quad (9)$$

It's general solution is (with arbitrary constants A, B),

$$\psi^* = A \exp(\kappa\eta) + B \exp(-\kappa\eta) \quad (10)$$

$$\Rightarrow \frac{d\psi^*}{d\eta} = \kappa[A \exp(\kappa\eta) - B \exp(-\kappa\eta)] \quad (11)$$

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=+1} = \kappa[A \exp(\kappa) - B \exp(-\kappa)] \quad (12)$$

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=-1} = \kappa[A \exp(-\kappa) - B \exp(\kappa)] \quad (13)$$

Subtracting Eq. 13 from Eq. 12, and using Eq. 8 we get,

$$A + B = -\frac{1}{2} \frac{q_0 \kappa}{\sinh(\kappa)} \quad (14)$$

Let, δ be the potential difference between walls at $\eta = +1$ and $\eta = -1$. From Eq. 10,

$$\psi^*|_{\eta=+1} = A \exp(\kappa) + B \exp(-\kappa) \quad (15)$$

$$\psi^*|_{\eta=-1} = A \exp(-\kappa) + B \exp(\kappa) \quad (16)$$

Subtracting Eq. 16 from Eq. 15 we get,

$$A - B = \frac{\delta}{2 \sinh(\kappa)} \quad (17)$$

From Eq. 14 and Eq. 17 we solve for A and B ,

$$A = \frac{1}{4 \sinh(\kappa)} [\delta - q_0 \kappa] \quad (18)$$

$$B = -\frac{1}{4 \sinh(\kappa)} [\delta + q_0 \kappa] \quad (19)$$

Using Eq. 18, Eq. 19, Eq. 10, and rearranging terms,

$$\psi^* = \frac{1}{2 \sinh(\kappa)} [\delta \sinh(\kappa \eta) - q_0 \kappa \cosh(\kappa \eta)] \quad (20)$$

From Eq. 3 we get,

$$\rho_e^* = \frac{1}{2 \sinh(\kappa)} [q_0 \kappa \cosh(\kappa \eta) - \delta \sinh(\kappa \eta)] \quad (21)$$

From Eq. 21 we can see many interesting things that are described below.

If the walls are at the same potential i.e. $\delta = 0$, and also the solution is neutral as a whole i.e. $q_0 = 0$, then the solution is neutral everywhere.

Suppose $\delta = 0$. If liquid contains a net charge, say, for definiteness $q_0 > 0$, the excess charges accumulate mostly near the walls (see Fig. 1(a)) and it does not depend on the initial polarity of the walls i.e. before walls come into contact with liquid. The accumulated charge in liquid must induce opposite charge of necessary amount on the wall surface, if it was already not present. It is contrary to the common belief that a charged surface, when exposed to a solution, induces counter-ions near it; actually this belief led this author to attempt forming erroneous ‘Electric Triple Layer (ETL) theory’ [4], that says when a neutral solution exposed to a charged wall, the counter-ions form layer near walls leaving behind co-ion abundant layer away from wall. But, for electrostatics, ψ^* can attain minima

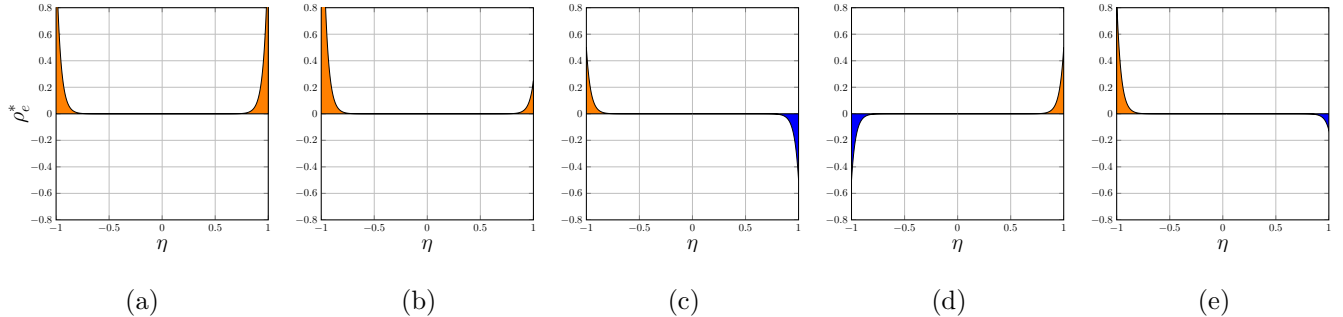


FIG. 1. Charge density distribution ρ_e^* (normalized) along the domain cross-section, in an electrolytic solution enclosed by walls; potential difference between right and left walls is δ ; the net charge in the cross-section is q_0 (normalized). For each case, inverse of scaled Debye length $\kappa = 25$. (a): $q_0 = 0.1$ and $\delta = 0$. (b): $q_0 = 0.1$ and $\delta = 2$. (c): $q_0 = 0$ and $\delta = 1$ (d): $q_0 = 0$ and $\delta = -1$ (e): $q_0 = 0.03$ and $\delta = 2$

or maxima only at boundaries, not inside domain [5], so formation of co-ion abundant layer away from the wall is not possible according to Poisson-Boltzmann model. For $\delta > 0$, the charges re-distribute (Fig. 1(b)); higher potential at right wall pushes some $+ve$ charges towards left.

Suppose $q_0 = 0$ and $\delta > 0$. We see from Fig. 1(c) $+ve$ ($-ve$) charges accumulate near the wall of lower (higher) potential (eventually induces opposite polarity on the walls). Reversing sign of δ reverses distribution (Fig. 1(d)). From Fig. 1(e), we see, even for $q_0 > 0$, some $-ve$ charges accumulate at one wall, because $\delta \neq 0$. Before their exposure to solution, two surfaces can contain same type of charges but have potential difference due to difference in charge density, but when brought in contact with the solution, they acquire different polarities because $\delta \neq 0$. We see that when $\delta \neq 0$, charge separation occurs even if $q_0 = 0$. Where ρ^* changes sign, $d\psi^*/d\eta = 0$, but it is not an extrema, but a point of inflection; $d^2\psi^*/d\eta^2 = 0$, too.

In some physical systems, the solution acquires a net charge by chemical interaction with the wall, or as a result of adsorption of ions by walls [6–9]. In this case wall automatically acquires a polarity opposite to that of q_0 .

If we add some neutral salt to solution, it changes concentration and hence changes κ , but q_0 should not change if there is no further adsorption by walls. It can be checked from Eq. 21 that $\int_{-1}^{+1} \rho_e^* d\eta$ produces q_0 indeed i.e. it does not change with κ . But in old theories

[1], the integral of ρ_e i.e the net charge in liquid turned out to be depend upon κ ; it means when we add neutral solution the net charge changes, it clearly violates the principle of conservation of charge, which got corrected in this work.

Now, see from Eq. 20, $\psi^*|_{\eta=0} = -q_0\kappa/(2\sinh(\kappa))$, which is not zero in general. It is well known that adding a constant to ψ^* should not change the physics [10–12]. But, from Eq. 3 we see that, in the Poisson-Boltzmann model, ψ^* is related to a definite quantity ρ_e^* , which cannot vary for a given problem. So, ψ^* gets fixed at all the points in a way that is consistent with Eq. 7; we cannot change ψ^* further by adding constant, without changing the physics.

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