# The Dirichlet and the Neumann boundary conditions may not produce equivalent solutions to the same electrostatic problem

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Electrostatic problems are widely solved using two types of boundary conditions (BC), namely, the Dirichlet condition (DC) and Neumann condition (NC). The DC specifies values of electrostatic potential ($\psi$), while the NC specifies values of $\nabla\psi$ at the boundaries. Here we show that DC and NC may not produce equivalent solutions to a given problem; we demonstrate it with a particular problem: 1-D linearized Poisson-Boltzmann equation (PBE), which has been regularly used to find the distribution of ionic charges within electrolyte solutions. Our findings are immediately applicable to many other problems in electrostatics.

**Key words:** Poisson-Boltzmann equation, Debye length, Dirichlet, Neumann

**This paper is being uploaded to vixra.org , in the previous version, the reference (Ninham and Parsegian, 1971) did not show up properly, we correct it here.**

## 1. INTRODUCTION

A large number of problems in electrostatics involve solving the Poisson's equation (PES): $\nabla^2\psi = -\rho_e/\epsilon$ to obtain $\psi$ as a spatial function [1], where, $\rho_e$ is the charge-density distribution of the *free* charges, $\epsilon$ is the permittivity of the medium. PES is widely solved using two types of BCs, namely, DC and NC, please see Ref. [2](Sec (1.9), pp. 37). However, it is not clear whether DC and NC produces the same solution to a given equation or not; the author is unaware of any work that resolves this issue. Here, we will show that DC and NC do not produce equivalent solutions in general.

When the positions of all the charges are known i.e. $\rho_e$ is known beforehand, it is relatively easier to find $\psi$. However, when the exact form of $\rho_e$ is unknown, it is not very straight forward to find $\psi$, but, it may be possible to model $\rho_e$ in these cases using available information from the system. The Poisson-Boltzmann (PB) model is one such model that is relevant to the distribution of free ions within electrolyte solutions [3–5]. The PB model expresses $\rho_e$ as a function of $\psi$ itself using the electrolyte-solution properties. This leads to the PBE, which is a non-linear function of $\psi$ in general, but, can be reduced to a simpler linear equation in some special cases [5, 6]. PBE is usually solved with DC [7, 8] or NC [9, 10]; for symmetric problems one can exploit the symmetry instead of specifiyeing relevant values at all the boundaries e.g. please see equations (5) and (6) in Ref. [11], the pair is actually equivalent to NC.

To demonstrate our idea of the non-equivalence of DC and NC, we will take the help of a 1-D linearized PBE; the idea is immediately applicable to other problems.

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## 2. ANALYSIS AND CONCLUSION

We consider a 1-D problem in a rectangular domain like in Ref. [7], where $\rho_e$ varies essentially in the $x$ direction, between right ($R$) and left ($L$) boundaries at $\pm a$. The linearized PBE is given by:

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi \tag{1}$$

Where $\kappa$ is a parameter; $\lambda_D \equiv \kappa^{-1}$ is known as 'Debye length' [7]. To solve Eq. (1) we first use the DC:

$$\psi(x = +a) = \zeta_R^D \ ; \ \psi(x = -a) = \zeta_L^D \tag{2}$$

The suffixes $R$ and $L$ in $\zeta$ correspond to 'Right' and 'Left', while the superscript $D$ corresponds to the DC. Solving Eq. (1) using Eq. (2) we get,

$$\psi_D = \zeta_R^D \left[\frac{\sinh\{\kappa(x+a)\}}{\sinh(2\kappa a)}\right] - \zeta_L^D \left[\frac{\sinh\{\kappa(x-a)\}}{\sinh(2\kappa a)}\right] \tag{3}$$

Eq. (3) is the same as equation (1) in Refs. [12, 13] with some difference in notations; please see appendix (B) in the present paper for the derivation. The correctness of Eq. (3) can be checked (see appendix (B) ) by considering a particular symmetric case: $\zeta_R^D = \zeta_L^D = \zeta$, to get

$$\psi_{D_0} = \zeta\frac{\cosh(\kappa x)}{\cosh(\kappa a)} \tag{4}$$

We used a suffix $D_0$ here. Please compare Eq. (4) with equation (4) in Ref. [7]; the little difference is due to different scaling.

Differentiating Eq. (3) we get:

$$\frac{d\psi_D}{dx} = \kappa\zeta_R^D\left[\frac{\cosh\{\kappa(x+a)\}}{\sinh(2\kappa a)}\right] - \kappa\zeta_L^D\left[\frac{\cosh\{\kappa(x-a)\}}{\sinh(2\kappa a)}\right] \tag{5}$$

Using Eq. (5) we define the quantities $\mu^D$:

$$\mu_R^D \equiv \left.\frac{d\psi_D}{dx}\right|_{x=+a} = \frac{\kappa}{\sinh(2\kappa a)}\left[\cosh(2\kappa a)\zeta_R^D - \zeta_L^D\right] \tag{6}$$

$$\mu_L^D \equiv \left.\frac{d\psi_D}{dx}\right|_{x=-a} = \frac{\kappa}{\sinh(2\kappa a)}\left[\zeta_R^D - \cosh(2\kappa a)\zeta_L^D\right] \tag{7}$$

We write Eq. (6) and Eq. (7) in a compact matrix form:

$$\begin{pmatrix}\mu_R^D\\ \mu_L^D\end{pmatrix} = \frac{\kappa}{\sinh(2\kappa a)}\begin{pmatrix}\cosh(2\kappa a) & -1\\ 1 & -\cosh(2\kappa a)\end{pmatrix}\begin{pmatrix}\zeta_R^D\\ \zeta_L^D\end{pmatrix} \tag{8}$$

The above square matrix is invertible, because its determinant, $\Delta \equiv -\cosh^2(2\kappa a) + 1 \equiv -\sinh^2(2\kappa a) \neq 0$ ($\because \kappa a \neq 0$); therefore the ordered pair $(\zeta_R^D, \zeta_L^D)$ has a one-to-one correspondence with the ordered pair $(\mu_R^D, \mu_L^D)$ i.e. if we specify values of one pair, that determines the other pair *uniquely.* We invert the matrix and write,

$$\begin{pmatrix}\zeta_R^D\\ \zeta_L^D\end{pmatrix} = \frac{1}{\kappa\sinh(2\kappa a)}\begin{pmatrix}\cosh(2\kappa a) & -1\\ 1 & -\cosh(2\kappa a)\end{pmatrix}\begin{pmatrix}\mu_R^D\\ \mu_L^D\end{pmatrix} \tag{9}$$

Now, we will solve the PBE with NC:

$$\left.\frac{d\psi}{dx}\right|_{x=+a} = \mu_R^N \;;\; \left.\frac{d\psi}{dx}\right|_{x=-a} = \mu_L^N \tag{10}$$

Solving Eq. (1) using Eq. (10) we get:

$$\psi_N = \frac{\mu_R^N}{\kappa}\left[\frac{\cosh\{\kappa(x+a)\}}{\sinh(2\kappa a)}\right] - \frac{\mu_L^N}{\kappa}\left[\frac{\cosh\{\kappa(x-a)\}}{\sinh(2\kappa a)}\right] \tag{11}$$

The correctness of Eq. (11) can be checked easily, please see appendix (A).

Using Eq. (11) we define the quantities $\zeta^N$:

$$\zeta_R^N \equiv \psi_N(+a) = \frac{1}{\kappa\sinh(2\kappa a)}\left[\cosh(2\kappa a)\mu_R^N - \mu_L^N\right] \tag{12}$$

$$\zeta_L^N \equiv \psi_N(-a) = \frac{1}{\kappa\sinh(2\kappa a)}\left[\mu_R^N - \cosh(2\kappa a)\mu_L^N\right] \tag{13}$$

We write Eq. (12) and Eq. (13) together in a compact matrix form:

$$\begin{pmatrix}\zeta_R^N\\ \zeta_L^N\end{pmatrix} = \frac{1}{\kappa\sinh(2\kappa a)}\begin{pmatrix}\cosh(2\kappa a) & -1\\ 1 & -\cosh(2\kappa a)\end{pmatrix}\begin{pmatrix}\mu_R^N\\ \mu_L^N\end{pmatrix} \tag{14}$$

Eq. (14) can be inverted to get,

$$\begin{pmatrix}\mu_R^N\\ \mu_L^N\end{pmatrix} = \frac{\kappa}{\sinh(2\kappa a)}\begin{pmatrix}\cosh(2\kappa a) & -1\\ 1 & -\cosh(2\kappa a)\end{pmatrix}\begin{pmatrix}\zeta_R^N\\ \zeta_L^N\end{pmatrix} \tag{15}$$

The similarity between the Eq. (9) and Eq. (14) is evident. However they are actually different that we describe below; we also describe the difference between Eq. (8) and Eq. (15) that looks similar, too.

Let, we are given a 1-D system as described in the beginning of Sec. (2), with known values of the parameters $\kappa$ and $a$. Suppose we measured the values of $\psi$ and $d\psi/dx$ at two boundaries to obtain the two ordered pairs $(\zeta_R^D, \zeta_L^D)$ and $(\mu_R^N, \mu_L^N)$. When the pair $(\zeta_R^D, \zeta_L^D)$ is used as BC to solve the PBE it is called DC and we obtain $\psi_D(x)$ given by Eq. (3). We take spatial derivative of $\psi_D(x)$ and evaluate $d\psi_D/dx$ at boundaries to obtain $(\mu_R^D, \mu_L^D)$. However, this pair may not coincide with the experimentally obtained $(\mu_R^N, \mu_L^N)$, because, $\psi_D(x)$ may not be accurate enough due to various limitations of the Poisson-Boltzmann (PB) model. Similarly, when experimentally obtained $(\mu_R^N, \mu_L^N)$ is used as BC to solve the PBE, it is called NC, we obtain $\psi_N(x)$ given by Eq. (11). We evaluate $\psi_N(x)$ at two boundaries to get the pair $(\zeta_R^N, \zeta_L^N)$ that may not coincide with the experimentally obtained pair $(\zeta_R^D, \zeta_L^D)$.

*Summary:* We showed that the DC and NC do not produce equivalent solutions to the PBE. The idea is immediately applicable to other problems in electrostatics. The consequences should be very important to many branches of physical, chemical and biological sciences.

### Appendix A: Description with simple symmetric cases:

In Ref. [9], A. Ajdari solved the PBE with NC, for the simple symmetric case; he used $\mu_R^N = \sigma^0/\epsilon$, and $\mu_L^N = -\sigma^0/\epsilon$, with different notations ($z \to x$, $h \to a$); but, we will stick to our convention. In this special case, we use the symbol $\psi_{N_0}$ instead of $\psi_N$; using these particular values in Eq. (11), and using the identities $\cosh(X+Y) + \cosh(X-Y) \equiv 2\cosh X\cosh Y$, and $\sinh 2X \equiv 2\sinh X\cosh X$, we get:

$$\psi_{N_0} = \left[\frac{\sigma^0}{\epsilon\kappa}\right]\frac{\cosh(\kappa x)}{\sinh(\kappa a)} \tag{A1}$$

The formula of $\psi_{N_0}$ given by Eq. (A1) is the same as in Ref. [9], which checks the correctness of Eq. (11). We use Eq. (14) in this particular case:

$$\begin{pmatrix}\zeta_R^N\\ \zeta_L^N\end{pmatrix} = \frac{\sigma^0}{\epsilon\kappa\sinh(2\kappa a)}\begin{pmatrix}\cosh(2\kappa a) & -1\\ 1 & -\cosh(2\kappa a)\end{pmatrix}\begin{pmatrix}1\\ -1\end{pmatrix} \tag{A2}$$

From Eq. (A2), using the identity $1 + \cosh(2\kappa a) \equiv 2\cosh^2(\kappa a)$, we get:

$$\zeta^{N_0} \equiv \zeta_R^N = \zeta_L^N = \frac{\sigma^0\cosh(\kappa a)}{\epsilon\kappa\sinh(\kappa a)} \tag{A3}$$

$$\Rightarrow \frac{\sigma^0}{\epsilon\kappa} = \zeta^{N_0}\tanh(\kappa a) \tag{A4}$$

Using Eq. (A4) in Eq. (A1) we get:

$$\psi_{N_0} = \zeta^{N_0} \frac{\cosh(\kappa x)}{\cosh(\kappa a)} \tag{A5}$$

Please note the similarity between Eq. (A5) and Eq. (4) of the present paper (i.e. equation (4) in Ref. [7]); however, these two equations are not the same; $\zeta$ may be obtained as a result of measurement, but $\zeta^{N_0}$ is a derived quantitiy, it is not a measured quantity, one measures something else and uses a model to calculate $\zeta^{N_0}$, which may not match with the experimental values.

## Appendix B: Solution of PBE with DC

$$\text{The PBE:} \quad \frac{d^2\psi}{dx^2} = \kappa^2 \psi \tag{B1}$$

$$\text{Two DCs:} \quad \psi(x = +a) = \zeta_R \tag{B2}$$

$$\psi(x = -a) = \zeta_L \tag{B3}$$

The general solution to PBE i.e. Eq. (B1) is given by,

$$\psi = A \exp(+\kappa x) + B \exp(-\kappa x) \tag{B4}$$

Using Eq. (B2) and Eq. (B3) in Eq. (B4) we get,

$$\psi(+a) = \zeta_R = A \exp(+\kappa a) + B \exp(-\kappa a) \tag{B5}$$

$$\psi(-a) = \zeta_L = A \exp(-\kappa a) + B \exp(+\kappa a) \tag{B6}$$

From Eq. (B5) and Eq. (B6) we get,

$$\zeta_R \exp(-\kappa a) = A + B \exp(-2\kappa a) \tag{B7}$$

$$\zeta_L \exp(+\kappa a) = A + B \exp(+2\kappa a) \tag{B8}$$

Subtracting Eq. (B7) from Eq. (B8) we get,

$$B = \frac{\zeta_L \exp(+\kappa a) - \zeta_R \exp(-\kappa a)}{2 \sinh(2\kappa a)} \tag{B9}$$

Again, From Eq. (B5) and Eq. (B6) we get,

$$\zeta_R \exp(+\kappa a) = A \exp(+2\kappa a) + B \tag{B10}$$

$$\zeta_L \exp(-\kappa a) = A \exp(-2\kappa a) + B \tag{B11}$$

Subtracting Eq. (B11) from Eq. (B10) we get,

$$A = \frac{\zeta_R \exp(+\kappa a) - \zeta_L \exp(-\kappa a)}{2 \sinh(2\kappa a)} \tag{B12}$$

Using expressions for $A$ and $B$ given by Eq. (B12) and Eq. (B9), in Eq. (B4), then rearranging terms, we get,

$$\psi = \zeta_R \left[ \frac{\sinh\{\kappa(x + a)\}}{\sinh(2\kappa a)} \right] - \zeta_L \left[ \frac{\sinh\{\kappa(x - a)\}}{\sinh(2\kappa a)} \right] \tag{B13}$$

It can be checked that for the special case, $\zeta_R = \zeta_L = \zeta$; Eq. (B13) will reduce to equaion (4) given in Ref. [7]. For the special case, $\zeta_R = \zeta_L = \zeta$; Eq. (B13) should reduce to equaion (4) given in Ref. [7]. Let's check it; we need the following identities:

$$\sinh(X + Y) - \sinh(X - Y) = 2 \cosh X \sinh Y \tag{B14}$$

$$\sinh(2X) = 2 \sinh X \cosh X \tag{B15}$$

Eq. (B13) simplifies to,

$$\begin{aligned} \psi &= \frac{\zeta}{\sin(2\kappa a)} [\sinh(\kappa x + \kappa a) - \sinh(\kappa x - \kappa a)] \\ &= \zeta \frac{2 \cosh(\kappa x) \sinh(\kappa a)}{2 \sinh(\kappa a) \cosh(\kappa a)} \end{aligned} \tag{B16}$$

$$\therefore \psi = \zeta \frac{\cosh(\kappa x)}{\cosh(\kappa a)} \tag{B17}$$

Please note the little difference between Eq. (B17) and equation (4) in Ref.[7] is due to the scaling of the variables (e.g. $\bar{x} \equiv x/a$).

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