

Poisson Boltzmann equation cannot be solved using Dirichlet boundary condition

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The Poisson-Boltzmann equation (PBE) gives us very simple formula for charge density distribution (ρ_e) within ionic solutions. PBE is widely solved by specifying values to electrostatic potential (ψ) at different boundaries; this type of boundary condition (BC) is known as Dirichlet condition (DC). Here we show that DC cannot be used to solve the PBE, because it leads to unphysical consequences. For example, when we change the reference for ψ , the functional forms of ψ and ρ_e change in non-trivial ways i.e. it changes the physics, which is not acceptable. Our result should have far reaching effects on many branches of physical, chemical and biological sciences.

Key words: Poisson-Boltzmann, Debye length, Dirichlet

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1. INTRODUCTION

Distribution of free charges within liquids is important for the understanding of various physical, chemical and biological processes, [1–4]. The linearized PBE, that appeared almost 100 years back [5], has been serving as an important tool to find the charge distribution theoretically. Assigning values to ψ at the boundaries i.e. the DC is widely used to solve the PBE, [6, 7]. However, we found some serious fundamental problems associated with this. When ψ is measured w.r.t. different reference points that should not alter ψ by more than an additive constant, please see Refs. [8, 9]. Here we show that when PBE is solved with DC to derive the spatial distribution for ψ , the function ψ changes non-uniformly when we measure it w.r.t. different reference points. It follows that the charge density distribution ρ_e also gets changed with the origin; even the total charge in the domain gets changed, which clearly violate physical principles. It is an example where the mathematical correctness of a solution does not imply its physical correctness. We describe the details below.

2. ANALYSIS AND CONCLUSION

Let's introduce a few notations. Here we analyze a 1-D problem, see Ref. [6] for details; the fluid domain is of rectangular cross-section; its width '2a' is very small compared to its length 'L' and height 'H'; ρ_e varies essentially along the shortest side, the x -direction, say. The net charge present in the total domain is given by $Q_T = \iiint \rho_e dx dy dz = LH \int_{-a}^{+a} \rho_e dx$. We define,

$Q_0 \equiv \int_{-a}^{+a} \rho_e dx = Q_T/(LH)$; it is a measurable quantity, having unit *Coulomb · meter*⁻².

The PBE is given by $d^2\psi/dx^2 = \kappa^2\psi$; where $(1/\kappa)$ is called the Debye length [6]. We solve PBE with DCs [$\psi(x = +a) = \zeta_R$ and $\psi(x = -a) = \zeta_L$] to get [10],

$$\begin{aligned} \psi(x) &= \zeta_R \left[\frac{\sinh\{\kappa(x+a)\}}{\sinh(2\kappa a)} \right] - \zeta_L \left[\frac{\sinh\{\kappa(x-a)\}}{\sinh(2\kappa a)} \right] \\ &= \zeta_R f_+(x) - \zeta_L f_-(x) \end{aligned} \quad (1)$$

Where, $f_{\pm}(x) \equiv \sinh\{\kappa(x \pm a)\}/\sinh(2\kappa a)$. We consider a problem, where, for given values of κ and a , a potential difference V is maintained between the right (R) and the left (L) boundaries. We analyze the problem with two different reference points (for ψ) \mathcal{O} and \mathcal{O}^\dagger ; the potential of \mathcal{O}^\dagger is higher than that of \mathcal{O} by an amount δ^* . At the boundaries, if ψ takes values ζ_R and ζ_L w.r.t. \mathcal{O} , then its values w.r.t. \mathcal{O}^\dagger will be $(\zeta_R - \delta^*)$ and $(\zeta_L - \delta^*)$ respectively; the choice of different origins does not change the potential difference between the boundaries, which is given by $V = \zeta_R - \zeta_L$ in both cases.

When \mathcal{O} is chosen as the reference, the potential distribution is given by Eq. (1). When \mathcal{O}^\dagger is chosen as reference the distribution is given by,

$$\psi^\dagger(x) = (\zeta_R - \delta^*)f_+(x) - (\zeta_L - \delta^*)f_-(x) \quad (2)$$

Let's see how $\psi(x)$, $\rho_e(x)$ and Q_0 are affected when we move from \mathcal{O} to \mathcal{O}^\dagger to measure ψ . Subtracting Eq. (1) from Eq. (2) we get,

$$\begin{aligned} \Delta\psi(x) &\equiv \psi^\dagger(x) - \psi(x) = -\delta^* [f_+(x) - f_-(x)] \\ &= -[2\delta^* \sinh(\kappa a)] \cosh(\kappa x) \end{aligned} \quad (3)$$

According to Eq. (3), $\Delta\psi$ is not a constant, but a function of x whenever \mathcal{O} and \mathcal{O}^\dagger are at different potentials (i.e. $\delta^* \neq 0$). The charge distribution $\rho_e(x)$ also changes with the origin since $\rho_e(x) \propto \psi(x)$, see Ref. [6].

The total charge in the system also changes with the reference: using Eq. (3), we calculate: $\Delta Q_0 \equiv \int_{-a}^{+a} [\rho_e^\dagger(x) - \rho_e(x)] dx \propto \int_{-a}^{+a} [\psi^\dagger(x) - \psi(x)] dx = -[2\delta^* \sinh(\kappa a)] \int_{-a}^{+a} \cosh(\kappa x) dx$. The function $\cosh(\kappa x)$, being the sum of two exponential functions, is strictly

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positive, so its integral is positive, too. Therefore, when $\delta^* \neq 0$, we have $\Delta Q_0 \neq 0$. The above facts are not consistent with the physics, because the physics should not depend whether we measure ψ w.r.t. \mathcal{O} or \mathcal{O}^\dagger . Hence, DCs produce unphysical solution.

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