Debye length cannot be interpreted as screening or shielding length

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(Dated: February 6, 2015)

We show the existing solution of Poisson-Boltzmann equation (PBE) to violate charge conservation principle, and then derive the correct formula for charge density distribution (ρ_e) in a fluid. We replaced unphysical old boundary conditions with some conditions that have never been used. Our result demonstrates that PBE cannot explain the formation of 'Electric Double Layer' (EDL); it follows that the present physical interpretation of 'Debye length' (λ_D) is wrong, too.

Presence of free electric charges in fluids and plasmas controls many natural and man-made processes, ranging from sub-nanometer to astronomical scales, e.g. nanotechnology and microfluidics with their various applications [1–8], interfacial chemistry, solutions, colloids and electrokinetics [1, 5, 6, 9–16], laboratory/astrophysical plasmas and many associated phenomena [17–23], etc.

The ubiquitous parameter λ_D [1–23] appeared almost hundred years back [24] in order to solve PBE [6, 7, 11] that gives us very simple analytical formula [7, 8] for ρ_e. According to the old formula, the integral of ρ_e i.e. the 'net' charge in fluid depends upon its temperature T, through λ_D. This clearly violates charge conservation principle, because change in T cannot alter the charge content of a closed system [25]. Here we derive the correct formula for ρ_e, addressing the conservation issue. We noticed that some works assigned values to electrostatic potential (ψ) at boundaries in an absolute sense [7, 8]; but, the potential of a single point is meaningless unless we specify a reference point. Here we use the potential difference between two points, which is measurable [25, 26]. Also, we found that the derivatives of ψ at different boundaries cannot be assigned independent values unlike done before [15]. Our result demonstrates a remarkable fact against the present understanding that EDL phenomena [3, 5, 9–11, 14, 16], that we observe at solid-fluid interfaces, cannot be described by PBE; λ_D looses its interpretation as the 'screening' or 'shielding' length [1–6, 8, 12, 14, 17, 19, 22].

A simple 1-D analysis often gives us considerable insights about the processes. Here we analyze a fluid domain of rectangular cross-section; its width '$2a$' is very small compared to length and height; ρ_e varies essentially along the shortest side, the x-direction, say [7]. PBE, in its linear form, can be solved to obtain ρ_e as a function of x. Now, ρ_e also involves a parameter κ ($\equiv \lambda_D^{-1}$) that depends upon several quantities e.g. temperature: $\kappa \propto T^{-1/2}$. Consider some fluid whose temperature can vary, but that does not exchange particles with surroundings. Variation of T redistributes charges and hence κ appears in ρ_e as a parameter. However, the total amount of charges does not change with T, and hence the quantity $Q_0 \equiv \int_{-a}^{+a} \rho_e dx$ cannot contain κ. It can be checked using old formula [7, 8] that Q_0 contains κ and hence violates charge conservation principle, please see Supplementary Material (SM).

Our earlier 'electric triple layer' (ETL) theory [27, 28] made Q_0 independent of κ, but, we abandoned it, because it does not satisfy Poisson's equation in electrostatics. Here, we derive the correct formula below, see SM for details. We need two conditions to solve PBE ($d^2\psi/dx^2 = \kappa^2\psi$). The first one assumes that we know the potential difference V between walls:

$$\psi(+a) - \psi(-a) = V \tag{1}$$

We must use it, as ρ_e must depend upon V, hence we cannot use two independent conditions for $d\psi/dx$ [15]. The second condition comes from integrating Poisson's equation ($d^2\psi/dx^2 = -\rho_e/\epsilon$; ϵ is permittivity),

$$\left.\frac{d\psi}{dx}\right|_{x=+a} - \left.\frac{d\psi}{dx}\right|_{x=-a} = -\frac{Q_0}{\epsilon} \tag{2}$$

We assign constant value to Q_0 explicitly (free of κ), solve PBE for ψ, hence obtain ρ_e,

$$\frac{\rho_e}{\rho_0} = \frac{1}{2\sinh(\kappa)}\left[\kappa\left(\frac{Q_0}{\rho_0}\right)\cosh\left(\frac{\kappa x}{a}\right) - \left(\frac{V}{\zeta}\right)\sinh\left(\frac{\kappa x}{a}\right)\right] \tag{3}$$

Where $\rho_0 \equiv \epsilon\kappa^2\zeta/a^2$; $\zeta(>0)$ is a suitable scale for ψ that must not be confused with so called 'zeta-potential' [11]; we normalized λ_D by 'a' so that κ is dimensionless.

Many interesting conclusions follow from eq. (3). If the walls are at same potential ($V = 0$), and the fluid is neutral as a whole ($Q_0 = 0$), then the solution is neutral everywhere. If we add some extra charges of a given sign (say, $+ve$), they accumulate mostly near the walls (Fig. 1(A)). Raising the potential of the right wall ($V > 0$) causes an additional electric field directed from higher

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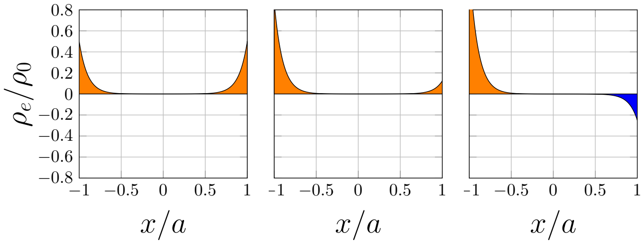

(A) (B) (C)

Figure 1. Charge density distribution within a fluid, bounded by walls. $\kappa = 10$; $Q_0/\rho_0 = 0.1$. (a) $V/\zeta = 0$; excess charges accumulate near walls. (b) $V/\zeta = 0.75$; an applied voltage makes distribution asymmetrical. (c) $V/\zeta = 1.5$; strong voltage segregates negative charges even if $Q_0 > 0$.

to lower potential; charges re-distribute (Fig. 1(B)) to develop an opposing field. Even if $Q_0 > 0$, it is possible to segregate negative charges if V is sufficiently high (Fig. 1(C)). Non-trivial distributions exist even for neutral fluids (if $V \neq 0$) that could not be captured before.

According to EDL theory, a charged wall, when exposed to a fluid, attracts counter-ions (oppositely charged ions) and eventually it gets 'screened' or 'shielded' by a layer of counter-ions i.e. the presence of the wall-charges cannot be felt beyond that layer; λ_D is interpreted as an estimate for the thickness of that layer. However, eq. (3) does not say anything about the sign of wall-charges. We get the same V with various wall-charge configurations. For example, let $V > 0$; firstly, the right and left wall may contain positive and negative charges respectively; secondly, both contains positive charges, but the right has higher charge density; thirdly, both contains negative charges, but the right has less charge density, etc. In all the cases we have same charge distribution in the fluid for a given Q_0. Hence, PBE cannot describe the formation of EDL, which requires the wall and Q_0 to be of 'opposite' signs. If wall is neutral or has charge of same sign as Q_0, there is no question of 'screening'. Also, for a given λ_D, the widths of ionic layers at two walls may be quite different due to an applied voltage (see Fig. 1(B) and Fig. 1(C)); obviously, the same λ_D cannot estimate both. Finally, if the fluid is neutral everywhere, there is no ionic layer at all, although we can get finite λ_D.

In summary, we found that the solution of Poisson-Boltzmann equation violates charge conservation principle; we consequently correct it using proper boundary conditions. It necessitates reviewing two important physical concepts: 'electric double layer' and 'Debye length'.

Anthony Leggett and Wolfgang Ketterle pointed out my earlier formulation to violate Poisson's equation, which helped me correcting the formula. Soujanna Sarkar helped me with writting. Sujata and Abhijit Sarkar, and, Utfulla and Sandhya Chakraborty provided financial support.

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I. SUPPLEMENTARY MATERIAL

A. Old Q_o depends upon κ

Some old works (S. Chakraborty and D. Paul, 2006) used the same geometry that we use here and obtained the expression for ρ_e given by,

$$\rho_{e,old}(x) = C\kappa^2 \left[\frac{\cosh(\kappa x/a)}{\cosh(\kappa)}\right] \tag{S1}$$

Where, C is a constant, which depends upon several parameters excluding κ.

$$\begin{aligned} Q_0 &\equiv \int_{-a}^{+a} \rho_{e,old}(x)dx \\ &= \frac{C\kappa^2}{\cosh(\kappa)} \int_{-a}^{+a} \cosh(\kappa x/a)dx \\ &= \frac{C\kappa^2}{\cosh(\kappa)} \left| \frac{\sinh(\kappa x/a)}{k/a} \right|_{-a}^{+a} \\ &= \frac{C\kappa^2}{\cosh(\kappa)} \frac{2\sinh(\kappa)}{k/a} \\ &= C2a\kappa \tanh(\kappa) \end{aligned} \tag{S2}$$

Therefore Q_0 depends upon κ in old formulation.

B. Derivation of new formula

Here we solve PBE and obtain correct formula for ρ_e in detail. For completeness, we first derive PBE, in its non-dimensional form. Initial part of the derivation may be found in old works. We make different quantities non-dimensional right from the beginning.

$$\eta \equiv x/a; \quad \psi^* \equiv \psi/\zeta \tag{S3}$$

Note that η varies between -1 and $+1$ as x varies between $-a$ and $+a$. We can derive a relationship between ρ_e and ψ as follows: the number density distributions of $\pm ve$ ions separately follow Boltzmann distribution: $n^{\pm} = n_0 \exp\left(\mp ez\psi/(k_B T)\right)$. Where, n_0 is mean of number densities of $\pm ve$ ions; for a symmetric electrolyte $z = |z_{\pm}|$, where $z_{\pm}$ are valences of $\pm ve$ ions; e, k_B and T are elementary charge, Boltzmann constant and absolute temperature respectively. Now, for a small real number α, we can write $\exp(\pm\alpha) \approx 1 \pm \alpha$. Similarly, when $ez\psi/(k_B T) \ll 1$,

$$n^{\pm} \approx n_0 \left[1 \mp \frac{ez\psi}{k_B T}\right] \tag{S4}$$

Now, there are $n^{\pm}$ number of $\pm ve$ ions per unit volume; a $\pm ve$ ion of valency $z^{\pm}$ carries a charge $ez^{\pm}$ i.e. $\pm ez$, hence we get the net charge per unit volume ρ_e as,

$$\begin{aligned} \rho_e &= ez^+ n^+ + ez^- n^- \\ &= ez(n^+ - n^-) \\ &= -\left[\frac{2n_0 e^2 z^2}{k_B T}\right]\psi \quad \text{(Using eq. (S4))} \\ &= -\epsilon \left[\frac{2n_0 e^2 z^2}{\epsilon k_B T}\right]\psi \\ &= -\left[\frac{\epsilon}{\lambda_D^2}\right]\psi \ \text{ Where, } \lambda_D \equiv \left[\frac{2n_0 z^2 e^2}{\epsilon k_B T}\right]^{-1/2} && \text{(S5)} \\ &= -\left[\frac{\epsilon}{a^2}\left(\frac{a^2}{\lambda_D^2}\right)\right]\zeta\left(\frac{\psi}{\zeta}\right) \\ &= -\left[\frac{\epsilon\kappa^2\zeta}{a^2}\right]\psi^* \ \text{ Where, } \kappa \equiv a/\lambda_D && \text{(S6)} \end{aligned}$$

$$\therefore \rho_e^* = -\psi^* \tag{S7}$$

$$\text{Where, } \rho_e^* \equiv \rho_e/\rho_0 \ \text{ with } \ \rho_0 \equiv \left(\epsilon\kappa^2\zeta/a^2\right) \tag{S8}$$

λ_D is called the Debye length scale. Now, ψ and ρ_e are also related by Poisson's equation (PE) in electrostatics; using eq. (S3) and eq. (S8) we first make PE non-dimensional (for 1-D):

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\epsilon} \tag{S9}$$

$$\frac{d^2\psi^*}{d\eta^2}\left(\frac{\zeta}{a^2}\right) = -\frac{\rho_0}{\epsilon}\rho_e^* = -\left(\frac{\epsilon\kappa^2\zeta}{a^2\epsilon}\right)\rho_e^*$$

$$\Rightarrow \frac{d^2\psi^*}{d\eta^2} = -\kappa^2\rho_e^* \tag{S10}$$

If Q_0 be the net charge present in fluid (in a cross-section, per unit axial length),

$$\int_{-1}^{+1} \rho_e^* d\eta = \frac{1}{\rho_0}\int_{-1}^{+1} \rho_e d\eta = \frac{Q_0}{\rho_0} \equiv q_0 \tag{S11}$$

Integrating both sides of eq. (S10) w.r.t η and using eq. (S11),

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=+1} - \left.\frac{d\psi^*}{d\eta}\right|_{\eta=-1} = -q_0\kappa^2 \tag{S12}$$

Now, eq. (S7) and eq. (S10) gives PBE:

$$\frac{d^2\psi^*}{d\eta^2} = \kappa^2\psi^* \tag{S13}$$

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

$$\psi^* = A\exp(\kappa\eta) + B\exp(-\kappa\eta) \tag{S14}$$

$$\Rightarrow \frac{d\psi^*}{d\eta} = \kappa[A\exp(\kappa\eta) - B\exp(-\kappa\eta)] \tag{S15}$$

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=+1} = \kappa[A\exp(\kappa) - B\exp(-\kappa)] \tag{S16}$$

$$\left.\frac{d\psi^*}{d\eta}\right|_{\eta=-1} = \kappa[A\exp(-\kappa) - B\exp(\kappa)] \tag{S17}$$

Subtracting eq. (S17) from eq. (S16), and using eq. (S12) we get,

$$A + B = -\frac{1}{2}\frac{q_0\kappa}{\sinh(\kappa)} \tag{S18}$$

Let, V be the potential difference between walls at $\eta = +1$ and $\eta = -1$; define $\delta \equiv V/\zeta$. From eq. (S14),

$$\psi^*|_{\eta=+1} = A\exp(\kappa) + B\exp(-\kappa) \tag{S19}$$

$$\psi^*|_{\eta=-1} = A\exp(-\kappa) + B\exp(\kappa) \tag{S20}$$

Subtracting eq. (S20) from eq. (S19) we get,

$$A - B = \frac{\delta}{2\sinh(\kappa)} \tag{S21}$$

From eq. (S18) and eq. (S21) we solve for A and B,

$$A = \frac{1}{4\sinh(\kappa)}[\delta - q_0\kappa] \tag{S22}$$

$$B = -\frac{1}{4\sinh(\kappa)}[\delta + q_0\kappa] \tag{S23}$$

Using eq. (S22), eq. (S23), eq. (S14), and rearranging terms,

$$\psi^* = \frac{1}{2\sinh(\kappa)}\left[\delta\sinh(\kappa\eta) - q_0\kappa\cosh(\kappa\eta)\right] \tag{S24}$$

From eq. (S7) we get,

$$\rho_e^* = \frac{1}{2\sinh(\kappa)}\left[q_0\kappa\cosh(\kappa\eta) - \delta\sinh(\kappa\eta)\right] \tag{S25}$$

Finally, we return to the original variables,

$$\frac{\rho_e}{\rho_0} = \frac{1}{2\sinh(\kappa)}\left[\kappa\left(\frac{Q_0}{\rho_0}\right)\cosh\left(\frac{\kappa x}{a}\right) - \left(\frac{V}{\zeta}\right)\sinh\left(\frac{\kappa x}{a}\right)\right] \tag{S26}$$