Debye length cannot be interpreted as screening or shielding length

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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 ($\rho_e$) 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’ ($\lambda_D$) is wrong, too.

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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 [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 $\lambda_D$ [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 $\rho_e$. According to the old formula, the integral of $\rho_e$ i.e. the ‘net’ charge in fluid depends upon its temperature $T$, through $\lambda_D$. 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 $\rho_e$, addressing the conservation issue. We noticed that some works assigned values to electrostatic potential ($\psi$) 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 $\psi$ 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 different boundaries cannot be assigned independent values [1–8], interfacial chemistry, solutions, colloids and plasmas and many associated phenomena [17–23], etc.

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; $\rho_e$ varies essentially along the shortest side, the x-direction, say [7]. PBE, in its linear form, can be solved to obtain $\rho_e$ as a function of $x$. Now, $\rho_e$ also involves a parameter $\kappa (\equiv \lambda_D^{-1})$ 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 $\kappa$ appears in $\rho_e$ 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 $\kappa$. It can be checked using old formula [7, 8] that $Q_0$ contains $\kappa$ 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 $\kappa$, 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:

$$\psi(+a) - \psi(-a) = V$$

(1)

We must use it, as $\rho_e$ 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 ($d^2 \psi / dx^2 = -\rho_e/\epsilon$; $\epsilon$ is permittivity),

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

(2)

We assign constant value to $Q_0$ explicitly (free of $\kappa$), solve PBE for $\psi$, hence obtain $\rho_e$,

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

(3)

Where $\rho_0 \equiv \kappa e \zeta/a^2$; $\zeta(>0)$ is a suitable scale for $\psi$ that must not be confused with so called ‘zeta-potential’ [11]; we normalized $\lambda_D$ by ‘$a$’ so that $\kappa$ 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...
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; \(\lambda_D\) 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 \(\lambda_D\), 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 \(\lambda_D\) cannot estimate both. Finally, if the fluid is neutral everywhere, there is no ionic layer at all, although we can get finite \(\lambda_0\).

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’.

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\[\text{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 \(Q_0 > 0\).}\]

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I. SUPPLEMENTARY MATERIAL

A. Old \(Q_o\) depends upon \(\kappa\)

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

\[
Q_0 = \int_{-a}^{+a} \rho_{e,old}(x)dx = \frac{C\kappa^2}{\cosh(\kappa)} \int_{-a}^{+a} \cosh(\kappa x/a)dx = \frac{C\kappa^2}{\cosh(\kappa)} \left[ \frac{\sinh(\kappa x/a)}{k/a} \right]_{-a}^{+a} = \frac{C\kappa^2}{\cosh(\kappa)} \frac{2\sinh(\kappa)}{k/a} = C2a\kappa \tanh(\kappa) \tag{S2}
\]

Therefore \(Q_0\) depends upon \(\kappa\) in old formulation.

B. Derivation of new formula

Here we solve PBE and obtain correct formula for \(\rho_e\) 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.

\[
\eta = x/a; \quad \psi^* = \psi/\zeta \tag{S3}
\]

Note that \(\eta\) varies between \(-1\) and \(+1\) as \(x\) varies between \(-a\) and \(+a\). We can derive a relationship between \(\rho_e\) and \(\psi\) as follows: the number density distributions of \(\pm ve\) ions separately follow Boltzmann distribution: \(n^\pm = n_0 \exp(\mp ez\psi/(k_BT))\). Where, \(n_0\) is mean of number density 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 \(\alpha\), we can write \(\exp(\pm \alpha) \approx 1 \pm \alpha\). Similarly, when \(ez\psi/(k_BT) \ll 1\),

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

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 \(\rho_e\) as,

\[
\rho_e = ez^+n^+ + ez^-n^-
\]

\[
= ez(n^+ - n^-)
\]

\[
= -\left[ \frac{2n_0e^2z^2}{k_BT} \right] \psi \quad \text{(Using eq. (S4))}
\]

\[
= -e\left[ \frac{2n_0e^2z^2}{k_BT} \right] \psi
\]

\[
= -\left[ \frac{e}{\lambda_D^2} \right] \psi \quad \text{Where,} \quad \lambda_D = \left[ \frac{2n_0z^2e^2}{k_BT} \right]^{-1/2} \tag{S5}
\]

\[
= -\left( \frac{\kappa^2\zeta}{a^2} \right) \psi^* \quad \text{Where,} \quad \kappa \equiv a/\lambda_D \tag{S6}
\]

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

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

\(\lambda_D\) is called the Debye length scale. Now, \(\psi\) and \(\rho_e\) 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):

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

\[
\frac{d^2\psi^*}{d\eta^2} \left( \frac{\zeta}{a^2} \right) = -\frac{\rho_0}{\epsilon} \rho_e^* = -\left( \frac{\kappa^2\zeta}{a^2\epsilon} \right) \rho_e^* \tag{S10}
\]

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

\[
\int_{-a}^{+a} \rho_e d\eta = \frac{1}{\rho_0} \int_{-1}^{+1} \rho_e d\eta = Q_0/\rho_0 \equiv q_0 \tag{S11}
\]

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

\[
\frac{d\psi^*}{d\eta} \bigg|_{\eta=+1} - \frac{d\psi^*}{d\eta} \bigg|_{\eta=-1} = -q_0k^2 \tag{S12}
\]

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 \(A, B\)),

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

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

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

\[
\frac{d\psi^*}{d\eta} \bigg|_{\eta=-1} = \kappa[A \exp(-\kappa) - B \exp(\kappa)] \tag{S17}
\]
Subtracting eq. (S17) from eq. (S16), and using eq. (S12) we get,

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

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

$$\psi^*|_{\eta=+1} = A \exp(\kappa) + B \exp(-\kappa)$$  \hspace{1cm} (S19)
$$\psi^*|_{\eta=-1} = A \exp(-\kappa) + B \exp(\kappa)$$  \hspace{1cm} (S20)

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

$$A - B = \frac{\delta}{2 \sinh(\kappa)}$$  \hspace{1cm} (S21)

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

$$A = \frac{1}{4 \sinh(\kappa)} [\delta - q_0 \kappa]$$  \hspace{1cm} (S22)
$$B = -\frac{1}{4 \sinh(\kappa)} [\delta + q_0 \kappa]$$  \hspace{1cm} (S23)

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

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

From eq. (S7) we get,

$$\rho^*_e = \frac{1}{2 \sinh(\kappa)} [q_0 \kappa \cosh(\kappa \eta) - \delta \sinh(\kappa \eta)]$$  \hspace{1cm} (S25)

Finally, we return to the original variables,

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