

# Electric Triple Layer Theory

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## Abstract

I correct hundred years old theory of charge distribution within an electrolytic solution surrounded by charged walls. Existing theory always implies excess amount of counter-ions (having polarity unlike walls) everywhere in the solution domain; so it cannot handle a solution that possesses excess ions of other type (co-ions) or is electrically neutral as a whole. Here, in the corrected distribution, counter-ions dominate near the walls, while the rest of the domain is allowed to be dominated by co-ions; the algebraic sum gives the net charge present, which can be of any sign and magnitude that makes theory quite general. This clarifies and raises many important concepts: a novel concept of ‘Electric Triple Layer’ (ETL) replaces ‘Electric Double Layer’ (EDL) theory; widths of electric layers can be calculated accurately instead of estimating by Debye length scale etc.

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Analysis of charge density distribution ( $\rho_e$ ) within an electrolytic solution confined by charged walls is very important in the study of electrokinetics and colloid science. Many scientists like Helmholtz, Smoluchowski, Debye, Gouy, Chapman etc. developed the theory since a very long time [1, 2]. In recent days it attracted considerable attention due to its applicability in various novel microfluidic devices that are used in different fields like micro-pumping and micro-mixing [3–5], lab-on-a-chip [5, 6], chemical separation and analysis [7], bio-technology, bio-medical drug delivery, etc. [8–10]. Processes at small scales are difficult to understand because of experimental difficulties and the non-intuitiveness due to dominant surface effects. In this regard, a precisely formulated theory could prove very useful in describing, analyzing and predicting new phenomena. However, the widely used formula of  $\rho_e$  is incomplete, because the derivation did not take care of charge conservation principle properly.

When exposed to solution, the charged wall attracts counter-ions and repels co-ions, hence, the counter-ions appear excess in number near the wall region and that must be accompanied by the absence of same number of them in other regions. In particular, at equilibrium, a solution that is electrically neutral as whole (i.e. the net charge,  $Q_0$  over a domain cross-section is zero), must have regions with excess co-ions to satisfy principle of conservation of charge. However, the existing theory always predicts an excess number of counter-ions everywhere in the solution and clearly cannot handle the cases  $Q_0 = 0$ , or excess co-ions. In this paper I have achieved the correct formula using fundamental considerations, that removes above discrepancies.

It is well known that, electrostatic potential  $\psi$  is defined to within an additive constant, i.e. adding an arbitrary constant ‘ $C$ ’ to  $\psi$  does not change the physics [11–13]. Now, in order to derive  $\rho_e$  as a spatial function, the earlier works, in an intermediate step, derived a relation between  $\rho_e$  and  $\psi$ , [14, 15]. This demands ‘ $C$ ’ to be fixed to a definite value, because for a given problem,  $Q_0$  is constant, and the integral of  $\rho_e$  must be consistent with it. This crucial point was overlooked in the old theory. I write the corrected distribution  $\rho_{e,Corr.}$  as a sum of old distribution  $\rho_{e,Old}$  and another term containing ‘ $C$ ’. I integrate  $\rho_{e,Corr.}$  using old expression of  $\rho_{e,Old}$ , and equate it to  $Q_0$ , which is assumed to be known, and that fixes ‘ $C$ ’ in terms of solution/geometrical parameters and  $Q_0$ . The graph of  $\rho_{e,Old}$  (plotted along the domain cross-section) never crosses the abscissa (see Fig. 1); when ‘ $C$ ’ is fixed properly, old graph gets a uniform translation to give the graph of  $\rho_{e,Corr.}$  (see Fig. 1(a) and Fig. 2) that

could subtend both positive and negative areas, the algebraic sum of the areas is precisely equal to  $Q_0$ , which in turn, can be assigned any magnitude and sign, and hence the theory can handle both types of solution polarities and a neutral solution.

Consider a rectangular domain of width  $2a \ll \text{length}$ , containing solution;  $y$ -axis is aligned with long, vertical domain-axis,  $x$ -axis is horizontal and along shorter domain axis. Long, charged walls are at  $x = \pm a$ . For simplicity, concept of ‘Stern layer’ [16, 17] is avoided without sacrificing the main idea. The fluid has uniform material properties: permittivity  $\epsilon$ , viscosity  $\mu$  etc. Define non-dimensional distance,  $\eta \equiv x/a$  [18].

The initial steps for the derivation of  $\rho_{e,Corr}$  are similar to that of  $\rho_{e,Old}$ ; I briefly mention a few old formulae below, see Refs. [14, 15]. Whenever any expression is found with suffix ‘Old’, it means it will have a corrected version with suffix ‘Corr’.

The number density distributions of  $\pm ve$  ions separately follow Boltzmann distribution that can be linearized [19] for small values of arguments in the exponential (see Ref. [9]):  $n_{Old}^{\pm} = n_0 \exp[\mp(ez\psi)/(k_B T)] \approx n_0[1 \mp(ez\psi)/(k_B T)]$ , 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. The Debye length scale is defined as  $\lambda_D \equiv [(2n_0 z^2 e^2)/(\epsilon k_B T)]^{-1/2}$ . An important non-dimensional parameter is  $\kappa \equiv a/\lambda_D$ .

$\rho_{e,Old}$  and  $\psi$  are related [20]:  $\rho_{e,Old} = -(\epsilon\kappa^2/a^2)\psi$ . Also,  $\psi$  and  $\rho_{e,Old}$  can be expressed as functions of  $\eta$ :  $\psi = \zeta \cosh(\kappa\eta)/\cosh(\kappa)$  and  $\rho_{e,Old} = -(\epsilon\kappa^2\zeta/a^2) \cosh(\kappa\eta)/\cosh(\kappa)$ , where  $\zeta$  comes from the boundary conditions  $\psi|_{\eta=\pm 1} = \zeta$ , see Refs. [14, 15].

One remark:  $\psi|_{\eta=0} = \zeta/\cosh(\kappa) \neq 0$ , so it is not clear where the datum of  $\psi$  (i.e. where  $\psi = 0$ ) was fixed in the earlier works. I define  $\zeta^* \equiv \psi|_{\eta=\pm 1} - \psi|_{\eta=0} = \zeta - \psi|_{\eta=0}$ . Clearly,  $\zeta^*$  is measurable and physically meaningful, and  $\zeta$  may be written in terms of it.

Now, hyperbolic cosine function is strictly positive, so  $\rho_{e,Old}$  never changes sign and is  $\mp ve$  for  $\pm ve$  values of  $\zeta$ , hence, implies an excess amount of counter-ions everywhere in the solution, and  $Q_0 (= \int_{-1}^+ \rho_e d\eta)$  always has this polarity; see Fig. 1, here I plot  $\rho_{e,Old}/\rho_0$  vs  $\eta$ , where  $\rho_0 \equiv |(\epsilon\kappa^2\zeta/a^2)|$ .

The shortcoming of the formula was evident and it became a topic of debate whether the fluid domain should be electrically neutral as a whole or not; [5, 7, 15, 17] say, near the wall the solution has a net charge due to the domination of counter-ions, while the bulk is neutral (that means  $Q_0$  is nonzero ); on the other hand [1] says, the debate is resolved

in favour of electro-neutrality ( $Q_0 = 0$ ). So, the electro-neutrality issue was handled with intuitive reasoning, without proper theoretical justification.

Some researchers tried to find some systems that indeed contain net charges in the solution, together with an explanation that the wall may adsorb ions from solution, acquire a net charge on surface, leaving equal number of counter-ions in solution and thus supports the theoretical prediction (although ‘qualitatively’) [5, 10, 15, 17, 21]. However, derivation of  $\rho_e$  is not sophisticated enough to anticipate such chemical interaction between wall and solution; it never prohibits a charged wall that does not at all exchange ions with solution and hence a neutral solution must remain neutral as a whole when exposed to that wall. So, modification of the old formulae became a necessity that I describe below.

When  $\psi$  is replaced by  $\psi + C$  in  $\rho_{e,Old}$ , I call it  $\rho_{e,Corr}$ ,

$$\rho_{e,Corr} = \rho_{e,Old} - \frac{\epsilon\kappa^2}{a^2}C = -\frac{\epsilon\kappa^2\zeta}{a^2} \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} - \frac{\epsilon\kappa^2}{a^2}C \quad (1)$$

Now, I fix ‘ $C$ ’ by the condition  $\int_{-1}^+ \rho_{e,Corr} d\eta = Q_0$ , where  $Q_0$  is assumed to be known; I

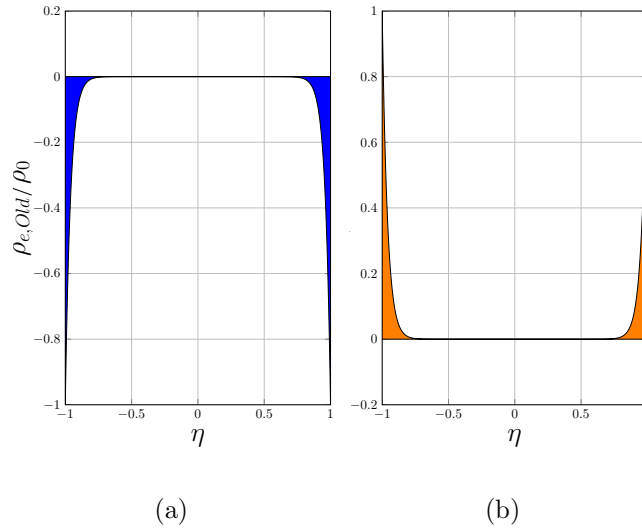


FIG. 1. Charge density distribution along the domain cross-section, in an electrolytic solution, enclosed by charged walls, according to **EDL** theory. The graph never crosses abscissa; counter-ions dominate everywhere; incompatible with cases where the solution is electrically neutral as a whole, or has excess co-ions. (a) For positively charged wall. (b) For negatively charged wall. In each case  $\kappa = 25$ .

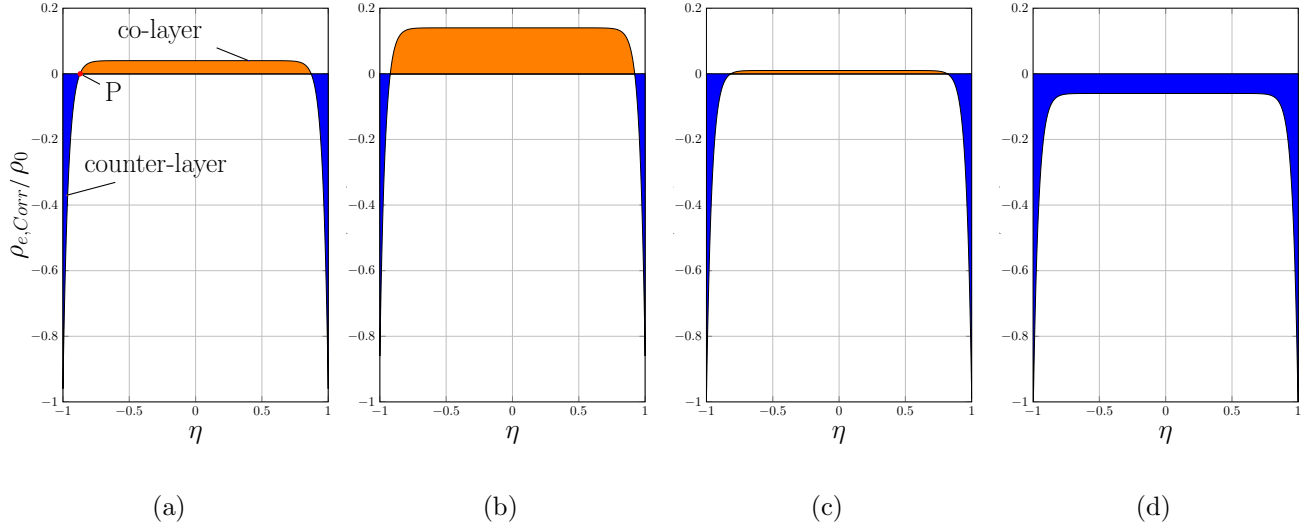


FIG. 2. Charge density distribution along the domain cross-section, in an electrolytic solution enclosed by *positively charged* walls, according to **ETL** theory. Counter-ion dominated layer forms near wall; point ‘P’ is electrically neutral where the graph crosses abscissa, and a co-ion dominated layer forms away from wall (except when number of counter-ions is much greater than co-ions). The algebraic sum of areas represents net charge  $Q_0$  in solution, which can be of any sign and magnitude. (a):  $Q_0 = 0$  (b):  $Q_0 > 0$  (c):  $Q_0 < 0$  (d):  $Q_0 \ll 0$  (no co-layer). In each case  $\kappa = 25$ .

get,

$$C = - \left[ \frac{\tanh(\kappa)}{\kappa} \zeta + \left( \frac{a^2}{\epsilon \kappa^2} \right) \left( \frac{Q_0}{2} \right) \right] \quad (2)$$

‘ $C$ ’ depends upon various parameters describing geometry and solution properties, and it is not zero even for an electrically neutral solution (in old theory, it implicitly assumed zero value). Hence,

$$\rho_{e,Corr} = \left( \frac{\epsilon \kappa^2 \zeta}{a^2} \right) \left[ \frac{\tanh(\kappa)}{\kappa} - \frac{\cosh(\kappa \eta)}{\cosh(\kappa)} \right] + \left( \frac{Q_0}{2} \right) \quad (3)$$

The graph of  $\rho_{e,Corr}$  is obtained from that of  $\rho_{e,Old}$ , (see Eq. 1, Fig. 1(a) and Fig. 2), with a uniform translation due to ‘ $C$ ’. Unlike before, the translated graph may change sign and hence can subtend both positive and negative areas under it. The translation is of precisely that amount, which makes the algebraic sum of the areas equal to  $Q_0$ . We can assign any number and sign to  $Q_0$ ; I plot  $\rho_{e,Corr}$  in Fig. 2 for different cases: Fig. 2(a):  $Q_0 = 0$ , Fig. 2(b):  $Q_0 > 0$ , Fig. 2(c):  $Q_0 < 0$ , and Fig. 2(d):  $Q_0 \ll 0$ . The point ‘P’, where the graph crosses the  $\eta$ -axis (at  $\eta = \eta_p$ , say) is electrically neutral and can be called ‘neutral point’. We have

three distinct kinds of electric layers, layer-1: a layer of wall surface charge, layer-2: adjacent to a wall a layer having net polarity opposite to that of wall (counter-layer) and layer-3: far away from wall, near the longer domain-axis, a layer having polarity same to that of wall (co-layer). The aggregate can be called Electric Triple Layer or ETL. Unlike this, the old Electric Double Layer (EDL) theory contains two electric layers: the layer of wall charge and the layer of counter-ions.

The error in the previous theory occurred because it implicitly assumed excess counter-ions at the very beginning. With  $\psi = \zeta \cosh(\kappa\eta)/\cosh(\kappa)$ , the pair of number density distribution functions  $n_{Old}^\pm$  behave differently, one increases (corresponds to counter-ions) while the other decreases (corresponds to co-ions) with  $|\eta|$ ; this increasing function always lies above the other, hence has greater area i.e. counter-ions are excess in number, see Fig. 3(a), that I plot for  $\kappa = 4$ ,  $\zeta > 0$  and  $|\zeta ez/k_B T| = 0.2$ .

Adding constant ‘C’ (given by Eq. 2) to  $\psi$  in  $n_{Old}^\pm$ , I arrive at,

$$n_{Corr}^\pm = n_0 \left[ 1 \mp \frac{ez}{k_B T} \psi \right] \pm \frac{n_0 ez}{k_B T} \left[ \frac{\tanh(\kappa)}{\kappa} \zeta + \left( \frac{a^2}{\epsilon \kappa^2} \right) \frac{Q_0}{2} \right] \quad (4)$$

For  $Q_0 = 0$ , I plot the graphs of  $n_{Corr}^\pm$  in Fig. 3(b); the two graphs may cross each other and one graph may lie above and below the other in different parts of the domain, hence

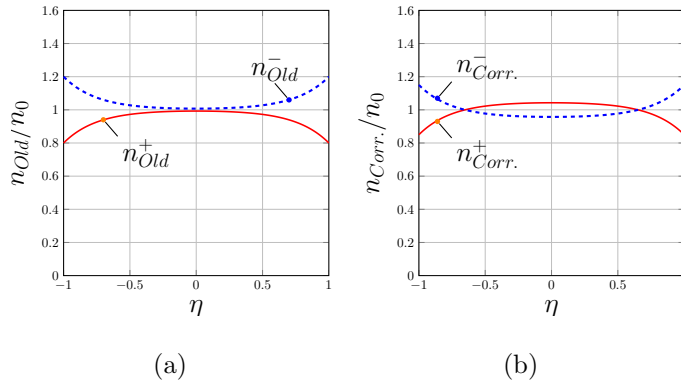


FIG. 3. Number density distribution along domain cross-section, for counter-ions and co-ions in an electrolytic solution, enclosed by *positively charged* walls. Area under a graph represents total number of corresponding ion. (a) according to **EDL** theory, counter-ion graph always lies above co-ion graph, implies excess counter-ions. (b) according to **ETL** theory, two graphs can cross each other; they subtend equal areas if net charge  $Q_0 = 0$ . In each case  $\kappa = 4$

it is possible that their areas are equal, which is necessary for  $Q_0 = 0$ . The corrected pair coincide with the old pair for  $C = 0$  i.e.  $Q_0 = -2\epsilon\kappa \tanh(\kappa)\zeta/a^2$ , and the old analysis can handle a net charge of that amount only, out of infinite possibilities.

In the old theory, charged layer was thought to occupy only a fraction of the fluid domain and its extent was estimated using Debye length scale  $\lambda_D$ . In new ETL theory, the spatial extents of different electrical layers in the fluid domain can be calculated accurately (although numerically) by solving for the neutral point ‘P’, i.e. solving the equation  $\rho_{e,Corr} = 0$  for  $\eta$ , for a given set of parameter values. In a 3-D rectangular domain, the collection of all neutral points forms a plane that can be called ‘neutral plane’; for a channel of arbitrary geometry there corresponds a neutral surface.

For a given solution concentration (i.e. constant  $\lambda_D$ ), when the domain width is increased, the parameter  $\kappa$  increases; I plot  $\rho_{e,Corr}$ . (see Eq. 3), in Fig. 4 for different values of  $\kappa$ . When  $\kappa$  increases, the counter-layer (adjacent to wall) becomes narrower but deeper, while co-layer (far from wall) becomes wider but shallower ; if the width of the domain is so large that we take it as infinite, charge density is visible only in the counter-layer, while co-layer amplitude almost vanishes. It happens because, if a quantity (here, it is  $\rho_e$ ), integrated over an infinite domain results a finite number (here, the net charge in co-layer is finite), that quantity (i.e.  $\rho_e$ ) must be infinitesimal every where (discrete spikes are mathematically possible, but this possibility is neglected here). Hence, for a wide domain, the presence of the co-layer is likely to be undetected. The same argument applies when one analyzes the ion distribution around a charged wall that bounds a semi-infinite domain [22].

However, for very narrow domains,  $\rho_e$  in co-layer is integrated over a very small distance and hence its amplitude may be appreciable.

In summary, I have generalized the theory of charge distribution in an electrolytic solution enclosed by charged walls; it can handle a solution that is electrically neutral as a whole, or can have a net charge of any kind of polarity, that was not possible with the old theory. I have achieved this by adding a suitable constant term to electrostatic potential in existing formulae, to make distribution consistent with the net charge present in the solution. The net charge can be assigned any value or sign explicitly unlike before. A novel theory of *Electric Triple Layer* emerges, replaces Electric Double Layer theory by adding the concept of a third possible electric layer, dominated by co-ions; spatial extents of electric layers can be calculated accurately.

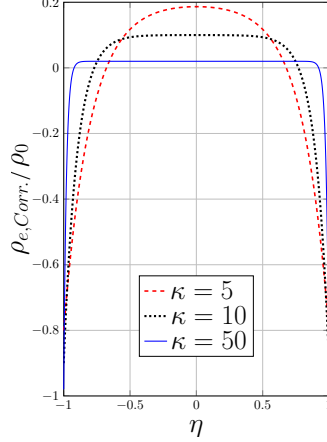


FIG. 4. Variation of corrected charge density distribution with parameter  $\kappa$ , in an electrolytic solution, which is electrically neutral as a whole, enclosed by *positively charged* walls. Amplitude of co-layer (see Fig. 2(a)) decreases as  $\kappa$  increases. For very large  $\kappa$ , co-layer is hard to detect; it corresponds where the domain thickness is large.

I conclude by saying, this work puts theoretical electrokinetics and colloid science on a firm foundation by filling up certain gaps and would be invaluable for future research works in these fields and many inter-disciplinary areas. A large volume of works needs to be modified using ETL theory.

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