Electrostatics of soft charged interfaces with pH-dependent charge density: Effect of consideration of appropriate hydrogen ion concentration distribution – Supplemental Material

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I. DERIVATION AND SOLUTION OF GOVERNING EQUATIONS FOR UNIFORM DISTRIBUTION OF POLYELECTROLYTE CHARGEABLE SITES (PCS) WITHIN THE PEL

The free energy can be expressed as:

$$F = \int f\left[\psi, n_{\pm}, n_{H^+}, n_{OH^-}\right] d^3\mathbf{r}, \tag{1}$$

where f is the free energy density, expressed as:

$$\begin{aligned} f =& -\frac{\epsilon_0\epsilon_r}{2}|\nabla\psi|^2 + e\psi\left(n_+ - n_-\right) + e\psi(n_{H^+} - n_{OH^-}) - en_{A^-}\psi \\ &+k_BT\left[n_+\left(\ln\left(\frac{n_+}{n_{+,\infty}}\right)-1\right) + n_-\left(\ln\left(\frac{n_-}{n_{-,\infty}}\right)-1\right) + n_{H^+}\left(\ln\left(\frac{n_{H^+}}{n_{H^+,\infty}}\right)-1\right) + n_{OH^-}\left(\ln\left(\frac{n_{OH^-}}{n_{OH^-,\infty}}\right)-1\right)\right] \\ &\qquad [\text{for} \quad -h \le y \le -h+d], \\ f =& -\frac{\epsilon_0\epsilon_r}{2}|\nabla\psi|^2 + e\psi\left(n_+ - n_-\right) + e\psi(n_{H^+} - n_{OH^-}) \\ &+k_BT\left[n_+\left(\ln\left(\frac{n_+}{n_{+,\infty}}\right)-1\right) + n_-\left(\ln\left(\frac{n_-}{n_{-,\infty}}\right)-1\right) + n_{H^+}\left(\ln\left(\frac{n_{H^+}}{n_{H^+,\infty}}\right)-1\right) + n_{OH^-}\left(\ln\left(\frac{n_{OH^-}}{n_{OH^-,\infty}}\right)-1\right)\right]. \\ &\qquad [\text{for} \quad -h+d \le y \le 0] \end{aligned} \tag{2}$$

Here n_{A^-} is the number density of the *PEL ions*, which can be related to the local hydrogen ion concentration through the following equation of state (this equation of state comes from the reaction equilibrium condition, see [1]):

$$n_{A^-} = \frac{K'_a\gamma}{K'_a + n_{H^+}}, \tag{3}$$

where $K'_a = 10^3 N_A K_a$ [N_A is the Avogadro number, K_a (having units of $moles/liter$) is the ionization constant of the acid dissociating to produce A^- ions (or *PEL ions*)] and γ is the maximum density of the PCS (in units of $1/m^3$). Also in eq.(2), ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the medium (assumed identical for the media both inside and outside the PEL, e is the electronic charge, k_BT is the thermal energy, n_i and $n_{i,\infty}$ are the number density and the bulk number density of ion i ($i = \pm,\ H^+,\ OH^-$). Also both the PEL ions and the electrolyte ions are assumed to be monovalent.

In order to obtain the equilibrium conditions, we next minimize eq.(2) [after using eq.(3) to replace n_{A^-} in terms of n_{H^+} in eq.(2)] with respect to ψ, n_+, n_-, n_{H^+}, n_{OH^-}.

Minimizing with respect to ψ yields:

$$\begin{aligned} &\frac{\delta F}{\delta\psi} = 0 \Rightarrow \frac{\partial f}{\partial\psi} - \frac{d}{dy}\left(\frac{\partial f}{\partial\psi'}\right) \Rightarrow \frac{d^2\psi}{dy^2} = \frac{-e(n_+ - n_-) + e\frac{K'_a\gamma}{K'_a+n_{H^+}} - e\left(n_{H^+} - n_{OH^-}\right)}{\epsilon_0\epsilon_r} \\ &\qquad [\text{for} \quad -h \le y \le -h+d], \\ &\frac{\delta F}{\delta\psi} = 0 \Rightarrow \frac{\partial f}{\partial\psi} - \frac{d}{dy}\left(\frac{\partial f}{\partial\psi'}\right) \Rightarrow \frac{d^2\psi}{dy^2} = \frac{-e(n_+ - n_-) - e\left(n_{H^+} - n_{OH^-}\right)}{\epsilon_0\epsilon_r} \quad [\text{for} \quad -h+d \le y \le 0]. \end{aligned} \tag{4}$$

Minimizing with respect to $n_{\pm}$ yields:

$$\frac{\delta F}{\delta n_{\pm}} = 0 \Rightarrow n_{\pm} = \left(n_{\pm,\infty}\right)\exp\left(\mp\frac{e\psi}{k_BT}\right) \qquad [\text{for} \ \ y \ge -h]. \tag{5}$$

Minimizing with respect to n_{OH^-} yields:

$$\frac{\delta F}{\delta n_{OH^-}} = 0 \Rightarrow n_{OH^-} = \left(n_{OH^-,\infty}\right)\exp\left(\frac{e\psi}{k_BT}\right) \qquad [\text{for} \ \ y \ge -h]. \tag{6}$$

Minimizing with respect to n_{H^+} yields:

$$\begin{aligned} &\frac{\delta F}{\delta n_{H^+}} = 0 \Rightarrow n_{H^+} = \left(n_{H^+,\infty}\right)\exp\left[-\frac{e\psi}{k_BT}\left(1 + \frac{K'_a\gamma}{\left(K'_a + n_{H^+}\right)^2}\right)\right] \quad [\text{for} \quad -h \le y \le -h+d], \\ &\frac{\delta F}{\delta n_{H^+}} = 0 \Rightarrow n_{H^+} = \left(n_{H^+,\infty}\right)\exp\left(-\frac{e\psi}{k_BT}\right) \qquad [\text{for} \quad -h+d \le y \le 0]. \end{aligned} \tag{7}$$

Using eqn.(5,6,7) in eqn.(4), we shall get:

$$\frac{d^2\psi}{dy^2} = \frac{e}{\epsilon_0\epsilon_r}\left[2n_\infty \sinh\left(\frac{ez\psi}{k_BT}\right) + n_{OH^-,\infty}\exp\left(\frac{e\psi}{k_BT}\right) - n_{H^+} + \frac{K_a'\gamma}{K_a' + n_{H^+}}\right] \qquad [\text{for} \quad -h \le y \le -h+d],$$
$$\frac{d^2\psi}{dy^2} = \frac{e}{\epsilon_0\epsilon_r}\left[2n_\infty \sinh\left(\frac{ez\psi}{k_BT}\right) + n_{OH^-,\infty}\exp\left(\frac{e\psi}{k_BT}\right) - n_{H^+,\infty}\exp\left(-\frac{e\psi}{k_BT}\right)\right] \qquad [\text{for} \quad -h+d \le y \le 0]. \quad (8)$$

Please note that since n_{H^+} variation is not explicit in ψ in the region $-h \le y \le -h+d$ [see the first part of eq.(7)], the first part of eq.(8) is not explicit in ψ. Therefore, we shall need to solve ψ and n_{H^+} simultaneously from eqs.(7,8). The corresponding boundary conditions will be:

$$\left(\frac{d\psi}{dy}\right)_{y=0} = 0, \quad (\psi)_{y=(-h+d)^+} = (\psi)_{y=(-h+d)^-}, \quad \left(\frac{d\psi}{dy}\right)_{y=(-h+d)^+} = \left(\frac{d\psi}{dy}\right)_{y=(-h+d)^-}, \quad \left(\frac{d\psi}{dy}\right)_{y=-h} = 0. \quad (9)$$

We shall first express eqs.(7,8,9) in dimensionless forms as:

$$\bar{\psi} = -\frac{\ln\left(\frac{\bar{n}_{H^+}}{\bar{n}_{H^+,\infty}}\right)}{1 + \frac{\bar{K}_a'\bar{\gamma}}{\left(\bar{K}_a' + \bar{n}_{H^+}\right)^2}} \quad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}],$$
$$\bar{\psi} = -\ln\left(\frac{\bar{n}_{H^+}}{\bar{n}_{H^+,\infty}}\right) \quad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0], \quad (10)$$

$$\frac{d^2\bar{\psi}}{d\bar{y}^2} = \frac{1}{\bar{\lambda}^2}\left[\sinh\bar{\psi} + \frac{\bar{n}_{OH^-,\infty}}{2}\exp(\bar{\psi}) - \frac{\bar{n}_{H^+}}{2} + \frac{1}{2}\frac{\bar{K}_a'\bar{\gamma}}{\bar{K}_a' + \bar{n}_{H^+}}\right] \qquad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}],$$
$$\frac{d^2\bar{\psi}}{d\bar{y}^2} = \frac{1}{\bar{\lambda}^2}\left[\sinh\bar{\psi} + \frac{\bar{n}_{OH^-,\infty}}{2}\exp(\bar{\psi}) - \frac{\bar{n}_{H^+,\infty}}{2}\exp(-\bar{\psi})\right] \qquad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0], \quad (11)$$

and

$$\left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=0} = 0, \quad (\bar{\psi})_{\bar{y}=(-1+\bar{d})^+} = (\bar{\psi})_{\bar{y}=(-1+\bar{d})^-}, \quad \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^+} = \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^-}, \quad \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=-1} = 0, \quad (12)$$

where $\bar{y} = y/h$, $\bar{\lambda} = \lambda/h$ ($\lambda = \sqrt{\frac{\epsilon_0\epsilon_r k_BT}{2n_\infty e^2}}$ is the EDL thickness), $\bar{d} = d/h$, $\bar{\psi} = e\psi/(k_BT)$, $\bar{n}_{H^+} = n_{H^+}/n_\infty$, $\bar{n}_{OH^-} = n_{OH^-}/n_\infty$, $\bar{n}_{H^+,\infty} = n_{H^+,\infty}/n_\infty$, $\bar{n}_{OH^-,\infty} = n_{OH^-,\infty}/n_\infty$, $\bar{K}_a' = K_a'/n_\infty$, and $\bar{\gamma} = \gamma/n_\infty$.

In order to solve the coupled equations [eqs.(10,11)], we first eliminate $\bar{\psi}$ and obtain the governing equation and the boundary conditions solely in terms of $\bar{n}_{H^+}$. The resulting equations are:

$$\frac{d^2\bar{n}_{H^+}}{d\bar{y}^2} = \frac{\frac{P_1}{Q} - 2\frac{P'Q'}{Q^2} - \frac{PQ_1}{Q^2} + 2\frac{P(Q')^2}{Q^3} - Q_3}{\frac{PQ_2}{Q^2} - \frac{P_2}{Q}} \qquad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}],$$
$$\frac{d^2\bar{n}_{H^+}}{d\bar{y}^2} = \left(\frac{1}{\bar{n}_{H^+}}\right)\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)^2 - \left(\frac{1+\bar{n}_{OH^-,\infty}}{2\bar{\lambda}^2}\right)\bar{n}_{H^+,\infty} + \left(\frac{1+\bar{n}_{H^+,\infty}}{2\bar{\lambda}^2}\right)\frac{\bar{n}_{H^+}^2}{\bar{n}_{H^+,\infty}} \qquad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0], \quad (13)$$

where

$$P = -\ln\left(\frac{\bar{n}_{H^+}}{\bar{n}_{H^+,\infty}}\right), \quad (14)$$

$$P' = \frac{dP}{d\bar{y}} = -\frac{1}{\bar{n}_{H^+}}\frac{d\bar{n}_{H^+}}{d\bar{y}}, \quad (15)$$

$$P_1 = \left(\frac{1}{\bar{n}_{H^+}}\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)^2, \quad (16)$$

$$P_2 = -\frac{1}{\bar{n}_{H^+}}, \tag{17}$$

$$Q = 1 + \frac{\bar{K}_a'\bar{\gamma}}{\left(\bar{K}_a' + \bar{n}_{H^+}\right)^2}, \tag{18}$$

$$Q' = \frac{dQ}{d\bar{y}} = -2\frac{\bar{K}_a'\bar{\gamma}}{\left(\bar{K}_a' + \bar{n}_{H^+}\right)^3}\frac{d\bar{n}_{H^+}}{d\bar{y}}, \tag{19}$$

$$Q_1 = 6\frac{\bar{K}_a'\bar{\gamma}}{\left(\bar{K}_a' + \bar{n}_{H^+}\right)^4}\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)^2, \tag{20}$$

$$Q_2 = -2\frac{\bar{K}_a'\bar{\gamma}}{\left(\bar{K}_a' + \bar{n}_{H^+}\right)^3}, \tag{21}$$

and

$$Q_3 = \frac{1}{\bar{\lambda}^2}\left[\sinh\left(\frac{P}{Q}\right) + \frac{\bar{n}_{OH^-,\infty}}{2}\exp\left(\frac{P}{Q}\right) - \frac{\bar{n}_{H^+}}{2} + \frac{1}{2}\frac{\bar{K}_a'\bar{\gamma}}{\bar{K}_a' + \bar{n}_{H^+}}\right]. \tag{22}$$

Finally the boundary conditions [see eq.(12)] can now be expressed in terms of $\bar{n}_{H^+}$ as:

$$\begin{aligned}
&\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=0} = 0 && \text{[Resulting from the condition } \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=0} = 0\text{]},\\
&\left(\frac{P}{Q}\right)_{\bar{y}=(-1+\bar{d})^+} = (P)_{\bar{y}=(-1+\bar{d})^-} && \text{[Resulting from the condition } (\bar{\psi})_{\bar{y}=(-1+\bar{d})^+} = (\bar{\psi})_{\bar{y}=(-1+\bar{d})^-}\text{]},\\
&\left(\frac{P'Q - PQ'}{Q^2}\right)_{\bar{y}=(-1+\bar{d})^+} = (P')_{\bar{y}=(-1+\bar{d})^-} && \text{[Resulting from the condition } \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^+} = \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^-}\text{]},\\
&\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=-1} = 0 && \text{[Resulting from the condition } \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=-1} = 0\text{]}.
\end{aligned} \tag{23}$$

Eq.(13) can be solved in presence of the boundary conditions specified in eq.(23). From the 2nd and 3rd conditions of eq.(23), it is easy to note this solution will produce discontinuity in the value and the slope of $\bar{n}_{H^+}$ at the PEL-electrolyte interface (i.e., $\bar{y} = -1 + \bar{d}$).

II. DERIVATION AND SOLUTION OF GOVERNING EQUATIONS FOR NON-UNIFORM DISTRIBUTION OF POLYELECTROLYTE CHARGEABLE SITES (PCS) WITHIN THE PEL

It is evident that the procedure illustrated above cannot ensure continuities in the value and in the gradient of both $\bar{\psi}$ and $\bar{n}_{H^+}$ simultaneously. This unphysical condition results from the electrostatic contribution of the PEL charges and the fact that the corresponding charge density is a function of the local hydrogen ion concentration. To be more specific, this unphysical condition occurs because the relationship between $\bar{\psi}$ and $\bar{n}_{H^+}$ at the PEL-electrolyte interface (i.e., the dimensionless location $\bar{y} = -1 + \bar{d}$) differs depending on whether the interface is approached from the PEL side or from the electrolyte side. This happens since the PEL is assumed to consist of uniform depth dependent distribution of the chargeable sites. To counter this, here we shall consider a non-uniform distribution of chargeable sites (within the PEL), described by a dimensionless function $\varphi(y)$, which in turn will ensure continuities of both the value as well as the gradient of both $\bar{\psi}$ and $\bar{n}_{H^+}$ at the PEL-electrolyte interface, and at the same time ensure no flux of hydrogen ions at the PEL-solid interface (i.e., the dimensionless location $\bar{y} = -1$). Also $\varphi(y)$ must satisfy the constraint of the total number of chargeable sites on a given polyelectrolyte. Considering this number as N_p and assuming that σ is the area corresponding to a single polyelectrolyte chain and a is the chain thickness, we can write:

$$\frac{\sigma}{a^3}\int_{-h}^{-h+d}\varphi(y)dy = N_p. \tag{24}$$

Please note that for the case of uniform distribution of chargeable sites, $N_p = \sigma d/a^3$.
In this scenario of the non-uniform density of the chargeable sites, the free energy density can be expressed as:

$$
\begin{aligned}
f= & -\frac{\epsilon_0\epsilon_r}{2}|\nabla\psi|^2 + ez\psi\left(n_+ - n_-\right) + e\psi(n_{H^+} - n_{OH^-}) - e\varphi(y)n_{A^-}\psi \\
& +k_BT\left[n_+\left(\ln\left(\frac{n_+}{n_{+,\infty}}\right)-1\right) + n_-\left(\ln\left(\frac{n_-}{n_{-,\infty}}\right)-1\right) + n_{H^+}\left(\ln\left(\frac{n_{H^+}}{n_{H^+,\infty}}\right)-1\right) + n_{OH^-}\left(\ln\left(\frac{n_{OH^-}}{n_{OH^-,\infty}}\right)-1\right)\right] \\
& +\alpha\left[N_p - \frac{\sigma}{a^3}\int_{-h}^{-h+d}\varphi(y)dy\right] \qquad [\text{for} \quad -h \le y \le -h+d], \\
f = & -\frac{\epsilon_0\epsilon_r}{2}|\nabla\psi|^2 + ez\psi\left(n_+ - n_-\right) + e\psi(n_{H^+} - n_{OH^-}) \\
& +k_BT\left[n_+\left(\ln\left(\frac{n_+}{n_{+,\infty}}\right)-1\right) + n_-\left(\ln\left(\frac{n_-}{n_{-,\infty}}\right)-1\right) + n_{H^+}\left(\ln\left(\frac{n_{H^+}}{n_{H^+,\infty}}\right)-1\right) + n_{OH^-}\left(\ln\left(\frac{n_{OH^-}}{n_{OH^-,\infty}}\right)-1\right)\right] \\
& \qquad [\text{for} \quad -h+d \le y \le 0], \qquad (25)
\end{aligned}
$$

where α is the Lagrange multiplier and n_{A^-} is provided by eq.(3).
To obtain the equilibrium condition, we shall minimize eq.(25) with respect to ψ, n_+, n_-, n_{H^+}, n_{OH^-} and $\varphi(y)$.

Minimizing with respect to ψ gives

$$
\begin{aligned}
&\frac{\delta F}{\delta\psi} = 0 \Rightarrow \frac{\partial f}{\partial\psi} - \frac{d}{dy}\left(\frac{\partial f}{\partial\psi'}\right) \Rightarrow \frac{d^2\psi}{dy^2} = \frac{-e(n_+ - n_-) + e\varphi(y)\frac{K_a'\gamma}{K_a'+n_{H^+}} - e\left(n_{H^+} - n_{OH^-}\right)}{\epsilon_0\epsilon_r} \\
&\qquad [\text{for} \quad -h \le y \le -h+d], \\
&\frac{\delta F}{\delta\psi} = 0 \Rightarrow \frac{\partial f}{\partial\psi} - \frac{d}{dy}\left(\frac{\partial f}{\partial\psi'}\right) \Rightarrow \frac{d^2\psi}{dy^2} = \frac{-e(n_+ - n_-) - e\left(n_{H^+} - n_{OH^-}\right)}{\epsilon_0\epsilon_r} \qquad [\text{for} \quad -h+d \le y \le 0]. \qquad (26)
\end{aligned}
$$

Minimizing with respect to $n_\pm$ gives:

$$
\frac{\delta F}{\delta n_\pm} = 0 \Rightarrow n_\pm = (n_{\pm,\infty})\exp\left(\mp\frac{e\psi}{k_BT}\right) \qquad [\text{for} \quad y \ge -h]. \qquad (27)
$$

Minimizing with respect to n_{OH^-} yields:

$$
\frac{\delta F}{\delta n_{OH^-}} = 0 \Rightarrow n_{OH^-} = \left(n_{OH^-,\infty}\right)\exp\left(\frac{e\psi}{k_BT}\right) \qquad [\text{for} \quad y \ge -h]. \qquad (28)
$$

Minimizing with respect to n_{H^+} yields:

$$
\begin{aligned}
&\frac{\delta F}{\delta n_{H^+}} = 0 \Rightarrow n_{H^+} = \left(n_{H^+,\infty}\right)\exp\left[-\frac{e\psi}{k_BT}\left(1+\varphi(y)\frac{K_a'\gamma}{\left(K_a'+n_{H^+}\right)^2}\right)\right] \qquad [\text{for} \quad -h \le y \le -h+d] \\
&\frac{\delta F}{\delta n_{H^+}} = 0 \Rightarrow n_{H^+} = \left(n_{H^+,\infty}\right)\exp\left(-\frac{e\psi}{k_BT}\right) \qquad [\text{for} \quad -h+d \le y \le 0] \qquad (29)
\end{aligned}
$$

Minimizing with respect to φ yields:

$$
\alpha = -\frac{ea^3\psi}{\sigma d}\frac{K_a'\gamma}{K_a'+n_{H^+}}. \qquad (30)
$$

Eq.(30) clearly shows that by minimizing with respect to $\varphi(y)$, we can only get a condition dictating the Lagrange multiplier, and not the functional form of $\varphi(y)$. Solution procedure to obtain $\varphi(y)$, in this light, will be discussed later. Below we first discuss obtaining the governing differential equations [which are dependent on $\varphi(y)$] that dictate the problem.

Using eqs.(27,28,29) in eq.(26) as well as the condition expressed in eq.(29) we shall get the governing equations in dimensionless forms as [$\varphi(y)$, which is dimensionless, is henceforth considered to be a function of $\bar{y}$]

$$
\begin{aligned}
&\bar{\psi} = -\frac{\ln\left(\frac{\bar{n}_{H^+}}{\bar{n}_{H^+,\infty}}\right)}{1+\frac{\bar{K}_a'\bar{\gamma}\varphi(\bar{y})}{\left(\bar{K}_a'+\bar{n}_{H^+}\right)^2}} \qquad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}], \\
&\bar{\psi} = -\ln\left(\frac{\bar{n}_{H^+}}{\bar{n}_{H^+,\infty}}\right) \qquad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0]. \qquad (31)
\end{aligned}
$$

and

$$\frac{d^2\bar{\psi}}{d\bar{y}^2} = \frac{1}{\bar{\lambda}^2}\left[\sinh\bar{\psi} + \frac{\bar{n}_{OH^-,\infty}}{2}\exp(\bar{\psi}) - \frac{\bar{n}_{H^+}}{2} + \frac{1}{2}\frac{\bar{K}'_a\bar{\gamma}\varphi(\bar{y})}{\bar{K}'_a + \bar{n}_{H^+}}\right] \quad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}],$$
$$\frac{d^2\bar{\psi}}{d\bar{y}^2} = \frac{1}{\bar{\lambda}^2}\left[\sinh\bar{\psi} + \frac{\bar{n}_{OH^-,\infty}}{2}\exp(\bar{\psi}) - \frac{\bar{n}_{H^+,\infty}}{2}\exp(-\bar{\psi})\right] \quad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0] \tag{32}$$

The boundary conditions for eqs.(31,32) are the ones expressed in eq.(12). Just like the previous case, here too we shall first eliminate $\bar{\psi}$ and obtain the boundary conditions solely in terms of n_{H^+}. The resulting equations are:

$$\frac{d^2\bar{n}_{H^+}}{d\bar{y}^2} = \frac{\frac{P_1}{R} - 2\frac{P'R'}{R^2} - \frac{PR_1}{R^2} + 2\frac{P(R')^2}{R^3} - R_3}{\frac{PR_2}{R^2} - \frac{P_2}{R}} \quad [\text{for} \quad -1 \le \bar{y} \le -1+\bar{d}],$$
$$\frac{d^2\bar{n}_{H^+}}{d\bar{y}^2} = \left(\frac{1}{\bar{n}_{H^+}}\right)\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)^2 - \left(\frac{1+\bar{n}_{OH^-,\infty}}{2\bar{\lambda}^2}\right)\bar{n}_{H^+,\infty} + \left(\frac{1+\bar{n}_{H^+,\infty}}{2\bar{\lambda}^2}\right)\frac{\bar{n}^2_{H^+}}{\bar{n}_{H^+,\infty}} \quad [\text{for} \quad -1+\bar{d} \le \bar{y} \le 0], \tag{33}$$

where P, P', P_1 and P_2 are defined by eqs.(14,15,16,17) and

$$R = 1 + \frac{\bar{K}'_a\bar{\gamma}\varphi(\bar{y})}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^2}, \tag{34}$$

$$R' = \frac{dR}{d\bar{y}} = -2\frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^3}\frac{d\bar{n}_{H^+}}{d\bar{y}}\varphi(\bar{y}) + \frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^2}\varphi'(\bar{y}), \tag{35}$$

$$R_1 = 6\frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^4}\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)^2\varphi(\bar{y}) - 4\frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^3}\frac{d\bar{n}_{H^+}}{d\bar{y}}\varphi'(\bar{y}) + \frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^2}\varphi''(\bar{y}), \tag{36}$$

$$R_2 = -2\frac{\bar{K}'_a\bar{\gamma}}{\left(\bar{K}'_a + \bar{n}_{H^+}\right)^3}\varphi(\bar{y}), \tag{37}$$

$$R_3 = \frac{1}{\bar{\lambda}^2}\left[\sinh\left(\frac{P}{R}\right) + \frac{\bar{n}_{OH^-,\infty}}{2}\exp\left(\frac{P}{R}\right) - \frac{\bar{n}_{H^+}}{2} + \frac{1}{2}\frac{\bar{K}'_a\bar{\gamma}\varphi(\bar{y})}{\bar{K}'_a + \bar{n}_{H^+}}\right], \tag{38}$$

$$\varphi'(\bar{y}) = \frac{d\varphi}{d\bar{y}}, \qquad \varphi''(\bar{y}) = \frac{d^2\varphi}{d\bar{y}^2}. \tag{39}$$

Finally the boundary conditions [see eq.(12)] can now be expressed in terms of $\bar{n}_{H^+}$ as:

$$\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=0} = 0 \qquad \left[\textit{Resulting from condition}\ \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=0} = 0\right],$$
$$\left(\frac{P}{R}\right)_{\bar{y}=(-1+\bar{d})^+} = (P)_{\bar{y}=(-1+\bar{d})^-} \qquad \left[\textit{Resulting from condition}\ (\bar{\psi})_{\bar{y}=(-1+\bar{d})^+} = (\bar{\psi})_{\bar{y}=(-1+\bar{d})^-}\right],$$
$$\left(\frac{P'R - PR'}{R^2}\right)_{\bar{y}=(-1+\bar{d})^+} = (P')_{\bar{y}=(-1+\bar{d})^-} \qquad \left[\textit{Resulting from condition}\left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^+} = \left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^-}\right],$$
$$(P'R - PR')_{\bar{y}=-1} = 0 \qquad \left[\textit{Resulting from condition}\left(\frac{d\bar{\psi}}{d\bar{y}}\right)_{\bar{y}=-1} = 0\right]. \tag{40}$$

In addition to the first condition of eq.(40), we must have such a distribution of $\varphi(\bar{y})$ that will ensure the following:

$$\begin{aligned}
(\bar{n}_{H^+})_{\bar{y}=(-1+\bar{d})^+} &= (\bar{n}_{H^+})_{\bar{y}=(-1+\bar{d})^-} && \left[\textit{from the condition } \left(\frac{P}{R}\right)_{\bar{y}=(-1+\bar{d})^+} = (P)_{\bar{y}=(-1+\bar{d})^-}\right] \\
\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^+} &= \left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=(-1+\bar{d})^-} && \left[\textit{from the condition } \left(\frac{P'R-PR'}{R^2}\right)_{\bar{y}=(-1+\bar{d})^+} = (P')_{\bar{y}=(-1+\bar{d})^-}\right] \\
\left(\frac{d\bar{n}_{H^+}}{d\bar{y}}\right)_{\bar{y}=-1} &= 0 && \left[\textit{from the condition } (P'R-PR')_{\bar{y}=-1} = 0\right] \qquad (41)
\end{aligned}$$

Using eqs.(14,15,34,35), each of the conditions of eq.(41) can be ensured by employing the following conditions on $\varphi(\bar{y})$:

$$[\varphi(\bar{y})]_{\bar{y}=-1+\bar{d}} = 0 \quad \text{[This ensures the 1st condition of eq.(41)],} \qquad (42)$$

$$\left[\frac{d\varphi(\bar{y})}{d\bar{y}}\right]_{\bar{y}=-1+\bar{d}} = 0 \quad \text{[This ensures the 2nd condition of eq.(41)],} \qquad (43)$$

$$\left[\frac{d\varphi(\bar{y})}{d\bar{y}}\right]_{\bar{y}=-1} = 0 \quad \text{[This ensures the 3rd condition of eq.(41)],} \qquad (44)$$

As we have seen minimization of the free energy functional does not produce any specific functional form of $\varphi(\bar{y})$. Therefore, $\varphi(\bar{y})$ can be any function as long as it satisfies eqs.(24,42,43,44) simultaneously. The simplest possible form of $\varphi(\bar{y})$ that satisfies these four conditions will be a cubic function, expressed as:

$$\varphi(\bar{y}) = \beta\left(\bar{y}+1-\bar{d}\right)^2\left(\bar{y}+1+\frac{\bar{d}}{2}\right) \qquad (45)$$

where $\beta = \frac{4N_p a^3 h^3}{\sigma d^4}$ is a new parameter.

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[1] Das, S. Explicit interrelationship between Donnan and surface potentials and explicit quantification of capacitance of charged soft interfaces with pH-dependent charge density. *Colloid. Surf. A* **2014**, *462*, 69–74.