Supporting Information

Electric double layer interaction between dissimilar charge-conserved conducting plates

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Details of the derivation of key results in the main text are given in this document.

TWO PLATES

Consider two dissimilar charge conserved constant potential (CCCP) parallel plates labeled "L" (left) and "R" (right), with thickness t_L and t_R at a separation, l as illustrated in Figure 1. They are immersed in a 1:1 electrolyte of bulk molar concentration c_B (M/L) or bulk ion number density, n_B (m^{-3}) = $10^3\, N_A\, c_B$, where N_A is Avogadro's number. The one-dimensional Debye-Hückel equation for the electrostatic potential, $\phi(z)$ at position z is: $d^2\phi/dz^2 - \kappa^2\phi = 0$, with the usual inverse Debye length $\kappa = (2\, n_B\, q^2/\varepsilon\varepsilon_o\, k_B T)^{1/2}$ where q the elementary charge, ε and ε_o the permittivity of the solution and of free space, k_B the Boltzmann constant and T the absolute temperature. The solution of the Debye-Hückel equation for the potential in different parts of the electrolyte is

$$\phi(z) = \psi_L(l)\exp(\kappa[z + t_L]), \qquad -\infty < z \le -t_L \tag{1a}$$

$$\phi(z) = \psi_L(l)\frac{\sinh(\kappa[l - z])}{\sinh(\kappa l)} + \psi_R(l)\frac{\sinh(\kappa z)}{\sinh(\kappa l)}, \qquad 0 \le z \le l \tag{1b}$$

$$\phi(z) = \psi_R(l)\exp(-\kappa(z - [l + t_R])), \qquad l + t_R \le z < \infty \tag{1c}$$

The surface charge densities $\sigma_{L<}$, $\sigma_{L>}$ are on plate L are (see Figure 1 for definition):

$$\sigma_{L>}(l) = -\varepsilon\,\varepsilon_o\left[\frac{d\phi}{dz}\right]_{z=0} = -\varepsilon\,\varepsilon_o\kappa\left[-\psi_L(l)\frac{\cosh(\kappa l)}{\sinh(\kappa l)} + \psi_R(l)\frac{1}{\sinh(\kappa l)}\right] \tag{2a}$$

$$\sigma_{L<}(l) = \varepsilon\,\varepsilon_o\left[\frac{d\phi}{dz}\right]_{z=-t_L} = \varepsilon\,\varepsilon_o\kappa\,\psi_L(l) \tag{2b}$$

and the surface charge densities $\sigma_{R<}$ and $\sigma_{R>}$ on plate R are:

$$\sigma_{R<}(l) = \varepsilon\,\varepsilon_o\left[\frac{d\phi}{dz}\right]_{z=l} = \varepsilon\,\varepsilon_o\kappa\left[-\psi_L(l)\frac{1}{\sinh(\kappa l)} + \psi_R(l)\frac{\cosh(\kappa l)}{\sinh(\kappa l)}\right] \tag{3a}$$

(3b)

$$\sigma_{R>}(l) = -\varepsilon\,\varepsilon_o \left[\frac{d\phi}{dz}\right]_{z=l+t_R} = \varepsilon\,\varepsilon_o \kappa\,\psi_R(l)$$

At large separations ($l \to \infty$), the surface charge density ($\sigma_L(\infty)$, $\sigma_R(\infty)$) or the surface potential ($\psi_L(\infty)$,$\psi_R(\infty)$) of each plate is specified and are related by $\sigma(\infty) = (\kappa/\varepsilon\varepsilon_o)\psi(\infty)$. The charge conservation condition for each plate at any separation is: $\sigma_<(l) + \sigma_>(l) = 2\,\sigma(\infty)$ and has to be applied for each plate to determine the variations of its surface potentials with separation, l.

Doing so for plate L gives

$$-\left[-\psi_L(l)\frac{\cosh(\kappa l)}{\sinh(\kappa l)} + \psi_R(l)\frac{1}{\sinh(\kappa l)}\right] + \psi_L(l) = 2\,\psi_L(\infty) \tag{4}$$

and for plate R gives

$$\left[-\psi_L(l)\frac{1}{\sinh(\kappa l)} + \psi_R(l)\frac{\cosh(\kappa l)}{\sinh(\kappa l)}\right] + \psi_R(l) = 2\,\psi_R(\infty) \tag{5}$$

These equations can be solved for $\psi_L(l)$ and $\psi_R(l)$:

$$\psi_L(l) = \psi_L(\infty) + \psi_R(\infty)\,e^{-\kappa l} \tag{6a}$$

$$\psi_R(l) = \psi_R(\infty) + \psi_L(\infty)\,e^{-\kappa l} \tag{6b}$$

The surface charge densities on the surfaces of plate L and R follows from eq 2 and 3

$$\sigma_{L>}(l) = \varepsilon\, \varepsilon_o \kappa\, [\psi_L(\infty) - \psi_R(\infty)\, e^{-\kappa l}] \tag{7a}$$

$$\sigma_{L<}(l) = \varepsilon\, \varepsilon_o \kappa\, [\psi_L(\infty) + \psi_R(\infty)\, e^{-\kappa l}] \tag{7b}$$

$$\sigma_{R<}(l) = \varepsilon\, \varepsilon_o \kappa\, [\psi_R(\infty) - \psi_L(\infty)\, e^{-\kappa l}] \tag{7c}$$

$$\sigma_{R>}(l) = \varepsilon\, \varepsilon_o \kappa\, [\psi_R(\infty) + \psi_L(\infty)\, e^{-\kappa l}] \tag{7d}$$

THREE PLATES

Consider a 3-plate system: "*L*" (left), "*M*" (middle) and "*R*" (right), at separations *l* and *r* between them as illustrate in Figure 2. The solution of the Debye-Hückel equation for the electrostatic potential in the four regions of the electrolyte is: (see Figure 2 for the definition of various symbols)

$$\phi(z) = \psi_L(l,r)\exp(\kappa[z + t_L]), \qquad -\infty < z \le -t_L$$

$$\phi(z) = \psi_L(l,r)\frac{\sinh(\kappa[l - z])}{\sinh(\kappa l)} + \psi_M(l,r)\frac{\sinh(\kappa z)}{\sinh(\kappa l)}, \qquad 0 \le z \le l$$

(8)

$$\phi(z) = \psi_M(l,r)\frac{\sinh(\kappa[r - x])}{\sinh(\kappa r)} + \psi_R(l,r)\frac{\sinh(\kappa x)}{\sinh(\kappa r)}, \qquad 0 \le x \le r$$

$$\phi(z) = \psi_R(l, r)\exp(-\kappa y)\,, \qquad y \geq 0$$

where we have defined $x \equiv z - (l + t_M)$, $y \equiv z - (l + t_M + r + t_R)$.

We impose the charge conservation condition on each plate: $\sigma_<(l) + \sigma_>(l) = 2\,\sigma(\infty)$ to determine the surface potentials of the 3 plates: $\psi_L(l, r)$, $\psi_M(l, r)$ and $\psi_R(l, r)$ as functions of on the plate spacing l and r.

Doing so for plate L gives, suppressing the dependence on (l, r)

$$-\left[-\psi_L \frac{\cosh(\kappa l)}{\sinh(\kappa l)} + \psi_M \frac{1}{\sinh(\kappa l)}\right] + \psi_L = 2\,\psi_L(\infty) \tag{9}$$

for plate M gives, suppressing the dependence on (l, r)

$$\left[-\psi_L \frac{1}{\sinh(\kappa l)} + \psi_M \frac{\cosh(\kappa l)}{\sinh(\kappa l)}\right] - \left[-\psi_R \frac{1}{\sinh(\kappa r)} + \psi_M \frac{\cosh(\kappa r)}{\sinh(\kappa r)}\right] = 2\,\psi_M(\infty) \tag{10}$$

and for plate R gives, suppressing the dependence on (l, r)

$$\left[-\psi_M \frac{1}{\sinh(\kappa r)} + \psi_R \frac{\cosh(\kappa r)}{\sinh(\kappa r)}\right] + \psi_R = 2\,\psi_R(\infty) \tag{11}$$

Eqs 9-11 can be solved for $\psi_L(l, r)$, $\psi_M(l, r)$ and $\psi_R(l, r)$ in terms of the surface potentials: $\psi_L(\infty)$, $\psi_M(\infty)$, $\psi_R(\infty)$ on each plate when they are far apart

$$\psi_L(l,r) = \psi_L(\infty) + [\psi_M(\infty) + \psi_R(\infty)\, e^{-\kappa r}]\, e^{-\kappa l} \tag{12a}$$

$$\psi_M(l,r) = \psi_M(\infty) + \psi_L(\infty)\, e^{-\kappa l} + \psi_R(\infty)\, e^{-\kappa r} \tag{12b}$$

$$\psi_R(l,r) = \psi_R(\infty) + [\psi_M(\infty) + \psi_L(\infty)\, e^{-\kappa l}]\, e^{-\kappa r} \tag{12c}$$

REMARKS

In applying the CCCP boundary condition, the charge conservation conditions will determine the values of the unknown surface potentials of the plates in terms of the surface potential (or equivalently the surface charge) of the plates at infinite separation and the spacing between the particles. This is the *global* nature of the CCCP boundary condition.