Electric Force Between Charged Plates II [pln72]

Parallel plates immersed in electrolyte solution:

The number densities of $n_\pm(x)$ of mobile ions assume equal values n_0 far away from the plates, thus satisfying charge neutrality.

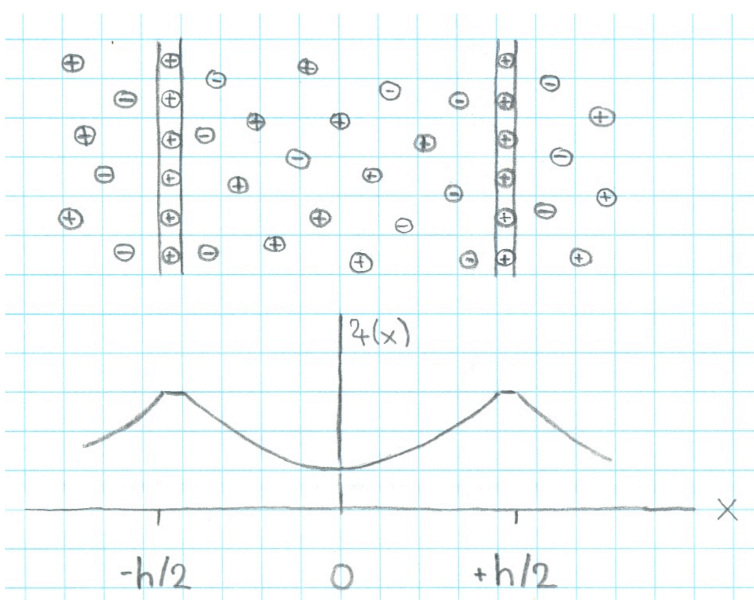
In the region $-h/2 < x < +h/2$ the counter-ions are being pulled toward one or the other plate whereas the co-ions are being pushed away from either plate and, in part, out of the region between the plates. The electric field $E(x)$ between the plates is directed inward with decreasing strength toward the center ($x = 0$), where it vanishes.

The electric potential $\psi(x)$ assumes reflection-symmetric profile as sketched. The charge density $\rho_e(x)$ is related to the potential $\psi(x)$ via the Poisson equation,

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\epsilon}\,\rho_e(x), \tag{1}$$

making it negative throughout the region but more so near the plates than at the center.

The presence of the electolyte has the effect of weakening the repulsive force between the plates as analyzed in the following.



The force per unit area has an electrostatic contribution and an osmotic contribution: $f = f_{\rm el} + f_{\rm os}$.

The *osmotic force* (per unit area) is caused by the inhomogeneous ionic densities in the region between the plates:

$$f_{\rm os}(x) = \Delta\pi(x) = k_{\rm B}T\sum_{\pm}\Delta n_{\pm}(x), \quad \Delta n_{\pm}(x) = n_0\big[e^{\mp\beta e_0\psi(x)} - 1\big]. \tag{2}$$

The *electrostatic force* (per unit area) is calculated as the Coulomb force between charges to the left and to the right of a fictitious plane at position x between the plates. We use the same strategy as in [pln71] for plates with charge densities $\sigma = \rho dx$:

$$\begin{aligned} f_{\rm el}(x) &= \frac{1}{2\epsilon}\int_{-h/2}^{x} dx_1\,\rho_e(x_1)\int_{x}^{+h/2} dx_2\,\rho(x_2) \\ &= \frac{\epsilon}{2}\int_{-h/2}^{x} dx_1\,\frac{d^2\psi}{dx_1^2}\int_{x}^{+h/2} dx_2\,\frac{d^2\psi}{dx_2^2} = -\frac{\epsilon}{2}\left(\frac{d\psi}{dx}\right)^2 + \text{const.} \end{aligned} \tag{3}$$

The total force,

$$f = f_{\rm os}(x) + f_{\rm el}(x) = k_{\rm B}T\sum_{\pm}\Delta n_{\pm}(x) - \frac{\epsilon}{2}\left(\frac{d\psi}{dx}\right)^2, \tag{4}$$

is independent of x, $df/dx = 0$, by virtue of the fact that the potential $\psi(x)$ must satisfy the Poisson-Boltzmann equation,

$$\epsilon\frac{d^2\psi}{dx^2} = -e_0\big[n_+(x) - n_-(x)\big], \quad n_{\pm}(x) = n_0\,e^{\mp\beta e_0\psi(x)}. \tag{5}$$

The force f is thus most conveniently calculated for $x = 0$ where $d\psi/dx = 0$ for symmetry reason. Here we have

$$f_{\rm int} \doteq f(0) = k_{\rm B}Tn_0\big[e^{-\beta e_0\psi(0)} + e^{\beta e_0\psi(0)} - 2\big]. \tag{6}$$

We find the potential $\psi(x)$ via the linearized Poisson-Boltzmann equation,

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0, \quad \kappa^2 = \frac{2e_0^2 n_0}{k_{\rm B}T\epsilon}, \tag{7}$$

with the physical boundary conditions,

$$\left.\frac{d\psi}{dx}\right|_{\pm h/2} = \pm\frac{\sigma}{\epsilon}, \tag{8}$$

where σ is the charge density on each plate.

Resulting (symmetric) profile of electric potential between the plates:

$$\psi(x) = \frac{\cosh(\kappa x)}{\epsilon\kappa \sinh(\kappa h/2)}. \tag{9}$$

Substitution of (9) into (6) with the exponential expanded yields

$$f_{int} = \frac{1}{2}\epsilon\kappa^2[\psi(0)]^2 = \frac{\sigma^2}{2\epsilon \sinh^2(\kappa h/2)}. \tag{10}$$

With plate separation h increasing, the force f_{int} weakens exponentially fast on the scale of the Debye screening length κ^{-1}.

[adapted from Doi 2013]