[pex25] Ionized colloidal surface: diffuse layer of counter-ions and co-ions

Consider a flat, positively charged colloidal surface. The liquid dispersion medium is an electrolyte, containing equal average number densities, n_0, of positively charge co-ion and negatively charged counter-ions. The electric field outside the colloid (at $x > 0$) will be screened by a differential, $n_-(x) - n_+(x) > 0$, in the density of counter-ions over the density of co-ions. The thermodynamic equilibrium state thus stabilized by the electrostatic forces between the colloidal surface and the mobile ions in the dispersion medium is governed by the Poisson equation,

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

where $\psi(x)$ is the electrostatic potential, $\epsilon \doteq \epsilon_r\epsilon_0$ is the permittivity of the liquid,

$$\rho(x) = q\big[n_+(x) - n_-(x)\big],$$

is the charge density with empirical constant q. The number densities, in turn, depend on the potential via the familiar Boltzmann exponentials,

$$n_\pm(x) = n_0 \exp\left(\mp\frac{q\psi(x)}{k_BT}\right).$$

(a) Show that the electrostatic potential thus satisfies the differential equation,

$$\frac{d^2\psi}{dx^2} = \frac{2qn_0}{\epsilon}\sinh\left(\frac{q\psi(x)}{k_BT}\right).$$

Introduce scaled quantities $\bar{\psi}(\bar{x}) \doteq \psi(x)/\psi_0$, $\bar{x} \doteq x/x_D$, to infer the universal (i.e. non-parametric) differential equation, $\bar{\psi}'' = \sinh(\bar{\psi})$, for the function $\bar{\psi}(\bar{x})$. Identify ψ_0 and x_D in terms of q, n_0, ϵ, k_BT. The characteristic length scale x_D is known as the Debye screening length.
(b) Search for a numerical solution $\bar{\psi}(\bar{x})$ with boundary value $\bar{\psi}(0) = 1$ that is monotonically decreasing and approaches $\psi(\infty) = 0$. Plot that solution for $0 < \bar{x} < 5$. In a separate panel, plot scaled versions of the densities, $n_+(x)$, $n_-(x)$, and $\rho(x)$, inferred from that solution.
(c) Compare the numerical solution from (b) with the Debye-Hückel solution $\bar{\psi}_{DH}(\bar{x}) = e^{-\bar{x}}$ of the linearized differential equation. Plot $\bar{\psi}_{DH}(\bar{x}) - \bar{\psi}(\bar{x})$ for $0 < \bar{x} < 5$. Comment on your findings.

Solution: