Problem Set 9 – Microhydrodynamics & fluctuations

Problem 1: Diffusiophoretic mobility caused by a charged solute

Consider a charged sphere of radius a with a constant zeta potential ζ in equilibrium. The sphere is suspended in a fluid with a 1:1 salt dissolved in it, with number densities $n_{\pm}(\mathbf{r})$. We consider a thin electric double layer where $\kappa a \gg 1$, with κ^{-1} being the Debye screening length. We are interested in the diffusiophoreric velocity $\mathbf{U}$ when we apply an bulk concentration gradient ∇n^{∞} that is sufficiently small such that chemiphoretic effects are decoupled from induced electrophoretic effects. The electric double layer is described by a boundary layer located at $a < r < a^*$.

(a) Write down the electrokinetic equations describing this system and the relevant boundary conditions. Make a distinction between the system inside the boundary layer and outside of it. Here, you are allowed to neglect ion advection (low Péclet number).

(b) Explain why for $r > a^*$, we have that $n_+(\mathbf{r}) = n_-(\mathbf{r}) = n(\mathbf{r})$. What are the expressions for the ionic charge current $e(\mathbf{j}_+ - \mathbf{j}_-)$ and the osmotic current $\mathbf{j}_+ + \mathbf{j}_-$ for $r > a^*$? From your result, derive an expression for $n^* = n|_{r=a^*}$.

(c) Show that the electrostatic potential for $r > a^*$ is given by

$$\mathbf{E} = \frac{k_\mathrm{B}T}{e}\alpha\nabla\ln n,$$

and derive an expression for α. What is $\mathbf{E}(\mathbf{r})$ for $r = a^*$ and in which direction does it point?

(d) Now we consider the problem inside the boundary layer. Decompose the electrostatic potential as $\psi = \psi^{\mathrm{eq}} + \Phi$, where ψ^{eq} only depends on the normal coordinate and Φ only on the transverse coordinates. In this case the pressure can be decomposed as $p = p_\mathrm{b} + \Pi$, with p_b the bulk pressure and Π the osmotic pressure coming from the ions. Show that for $r = a^*$

$$\Pi|_{r=a^*} = 2k_\mathrm{B}Tn^*\left[\cosh\left(\frac{e\psi^{\mathrm{eq}}}{k_\mathrm{B}T}\right) - 1\right]. \tag{1}$$

Hint: Consider the normal component of the linear momentum balance.

(e) The problem naturally decomposes in a part driven by osmotic pressure (chemiphoresis, CP) and a contribution coming from Φ (electrophoresis, EP) . By linearity of the problem, we can treat both seperately and decompose $\mathbf{v}$ in the boundary layer as $\mathbf{v} = \mathbf{v}_\mathrm{CP} + \mathbf{v}_\mathrm{EP}$. Derive an expression for $\mathbf{v}_\mathrm{CP}|_{r=a^*}$ by setting $\mathbf{E} = 0$ in the transverse momentum balance .

(f) By setting $\Pi = 0$ in the transverse momentum equation derive an expression for $\mathbf{v}_\mathrm{EP}|_{r=a^*}$.

(g) Derive from (e) and (f) an expression for the slip velocity, and by matching to the bulk fluid, show that the diffusiophoretic mobility is given by $\mathbf{U} = \mathcal{M}\nabla\ln n^{\infty}$, where

$$\mathcal{M} = \frac{\varepsilon}{\eta}\left(\frac{k_\mathrm{B}T}{e}\right)^2\left[\frac{\alpha e\zeta}{k_\mathrm{B}T} + 4\ln\cosh\left(\frac{e\zeta}{k_\mathrm{B}T}\right)\right].$$

(h) In which direct does the particle move as a function of α and ζ?