

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 diffusiophoretic 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

$$\mathbf{E} = -\frac{k_B T}{e} \alpha \nabla \ln n,$$

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 $\psi = \psi^{\text{eq}} + \Phi$, 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 $p = p_b + \Pi$, with p_b the bulk pressure and Π the osmotic pressure coming from the ions. Show that for $r = a^*$

$$\Pi|_{r=a^*} = 2k_B T n^* \left[\cosh\left(\frac{e\psi^{\text{eq}}}{k_B T}\right) - 1 \right]. \quad (1)$$

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 separately and decompose \mathbf{v} in the boundary layer as $\mathbf{v} = \mathbf{v}_{\text{CP}} + \mathbf{v}_{\text{EP}}$. Derive an expression for $\mathbf{v}_{\text{CP}}|_{r=a^*}$ by setting $\mathbf{E} = 0$ in the transverse momentum balance.
- (f) By setting $\Pi = 0$ in the transverse momentum equation derive an expression for $\mathbf{v}_{\text{EP}}|_{r=a^*}$.
- (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

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

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