

Homework Assignment 4

Due date: 22.May.2024

In this homework assignment, we will study several problems related to the electrical double layer and electrokinetic phenomena.

Q1 Controlling Electroosmotic Flow by Gating

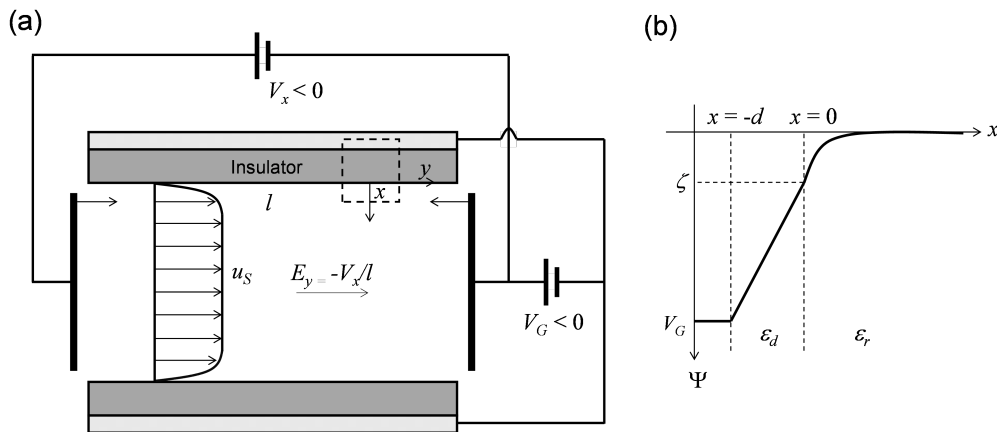


Figure 1: (a) The schematic illustration for an electroosmotic flow system that uses a gate electrode to control the zeta potential. (b) The electric potential distribution at the gate electrode – insulator – electrolyte solution (the dashed box in (a)).

In Lectures 10 and 12, we have shown that one can control the electric potential Ψ at an electrolyte solution- insulator interface in a more precise manner by applying a voltage on the additional “gate” electrode. Here let us see how it works. Consider the example of electroosmotic flow system shown in Fig. 1(a), by applying two voltage sources, V_x and V_G , one can control the lateral electric field, $E_x = -V_x/l$, where l is the length of the channel, as well as the surface potential at the electrolyte solution – insulator interface, ζ . The thickness of the insulator layer is d , and the relative dielectric constant for the insulator layer and the electrolyte solution is ϵ_d and ϵ_r , respectively. A binary electrolyte solution with $(z^+ : z^-)$ valence (note that z^+ can be not equal to z^-) is considered. We define the origin of the x coordinate at the electrolyte solution – insulator interface, as shown in Fig. 1(b).

1. Using the Debye-Hückel approximation, please derive the analytical expressions for $\zeta(V_G)$ and $u_s(V_G)$.
2. Using the same procedure for derivation of the G-C solution, followed by considering

the Gauss' law at an interface, please show that:

$$f(\zeta) = \text{sign}(\zeta) \sqrt{\frac{2\varepsilon_r k_B T}{\varepsilon_0}} \left[c_{+0} \exp\left(-\frac{-z_+ e \zeta}{k_B T}\right) + c_{-0} \exp\left(-\frac{-z_- e \zeta}{k_B T}\right) - (c_{+0} + c_{-0}) \right]^{1/2} - \varepsilon_d \frac{V_G - \zeta}{d} = 0 \quad (1)$$

3. The above equation has clearly suggested that one can control the zeta potential ζ by V_G . Please write a numerical function that solves Eq. (11) numerically, by using V_G as the input parameter.
4. Consider an aqueous, 1 mM NaCl solution at 298 K, and an Al_2O_3 insulator with $\varepsilon_d = 9$ and $d = 100$ nm, by applying an $E_x = 10$ V/cm, please use your numerical function in (3) to calculate ζ and u_S for $V_G = [0 \text{ V}; 1 \text{ V}; 50 \text{ V}]$. Compare the obtained profile with that using the expression derived in (1).

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Q2 Electroosmotic Flow in a Nanotube

As shown in Fig. 2, consider an infinitely long nanotube filled with electrolyte solution, and its diameter is comparable to the Debye screening length. Here we treat the nanotube as a perfect cylinder with the radius R in the cylindrical (r, z) coordinate, and the surface is negatively charged with the surface charge density σ_s . By applying an electric field along $+z$ direction, E_z , an electroosmotic flow (EOF) is induced, as we discussed in Lecture 14. When the flow is fully developed, the electric potential ψ , the positive (negative) ion concentration $c_+(c_-)$, and the fluid flow velocity u are all functions of r . The electrolyte is binary, univalent, and symmetric (1:1). Please answer the following questions:

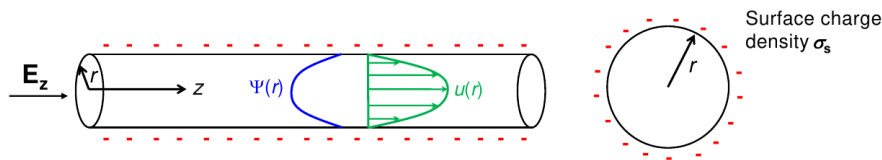


Figure 2: EOF in a nanotube; side (left) and cross-sectional (right) views. The electric potential ψ and the fluid flow velocity u profiles are sketched in blue and green curves, respectively.

1. Let $\psi(0) = 0$ and $c_+(0) = c_0$, one may write the Poisson Boltzmann equation (PBE) as follows:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi}{\partial r} \right) = -\frac{ec_0}{\varepsilon_r \varepsilon_0} \exp\left(-\frac{e\psi}{k_B T}\right) \quad (2)$$

You might have noticed that the right hand side (RHS) only has the cation contribution ($z_+ = +1$). Why can the anion ($z_- = -1$) contribution be neglected?

2. Using the Gauss law, please write down the PBE Boundary condition (BC) at $r = R$.
3. In the literature, it has been shown that the 1D PBE has an analytical solution given by:

$$\psi = \frac{k_B T}{e} \ln \left[\left(1 - \frac{1}{8} \left(\frac{r}{\kappa^{-1}} \right)^2 \right)^2 \right] \quad (3)$$

where $\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{c_0 e^2}}$ is the Debye screening length. Combining with the BC you obtained in Q1.2, please derive the relation of σ_s as a function of c_0 . Note that c_0 corresponds to the cation concentration at $r = 0$, so it is also an unknown. This is why we need three BCs, and the solution appears to fulfill the other two BCs, namely $\psi(0) = 0$ and $\frac{\partial \psi}{\partial r}(r = 0) = 0$.

4. From the equation (3), since $\sigma_s < 0$, please show that the maximum attainable concentration c_{\max} at $r = 0$, is $c_{\max} = \frac{8\epsilon_r \epsilon_0 k_B T}{e^2 R^2}$.
5. Following the derivation of DLVO theory in Lecture 13, when $E_z = 0$, the osmotic pressure P_{osmotic} , with the unit of force per unit area, and the electric force per unit volume F_{elec} , towards +r direction are given by:

$$\begin{aligned} P_{\text{osmotic}} &= k_B T (c_+ + c_-) \\ F_{\text{elec}} &= \left(-\frac{\partial \psi}{\partial r} \right) \rho \end{aligned} \quad (4)$$

Please derive the expressions for P_{osmotic} and F_{elec} , and as we did in the lecture, please show that:

$$\frac{\partial P_{\text{osmotic}}}{\partial r} - F_{\text{elec}} = 0 \quad (5)$$

What is the physical meaning of this equation?

6. As we demonstrated during the derivation of DLVO theory, one can imagine the solution would exert a radial pressure to the wall of nanotube at $r = R$, P_{wall} . Please derive the expression of P_{wall} . Following Q1.4, what is the maximum P_{wall} achievable? If the electrolyte is a water solution ($\epsilon_r = 80$) at room temperature (25°C), and the nanotube radius is 5 nm, what are the values of c_{\max} (in M) and the maximum P_{wall} (in atm)?
7. Following the derivation of EOF in Lecture 14, when an axial electric field E_z is applied, please write down the governing equation of the fluid flow velocity $u(r)$ together with BCs for the system considered here.
8. Accordingly, please solve $u(r)$ by putting the solution of $\psi(r)$ from equation (3) into the governing equation from Q1.7.
9. It appears that the maximum velocity u_{\max} , is at $r = 0$. Please plot u/u_{\max} as a function of r/R for $\kappa^{-1}/R = 0.36, 0.4, 0.5$, and 1.0. Please compare it with the Hagen–Poiseuille flow profile, i.e.,

$$\frac{u}{u_{\max}} = 1 - \left(\frac{r}{R} \right)^2 \quad (6)$$

What is your observation based the calculated curves?

Q3 Exact Solution of the Electric Potential between Two Charged Walls

In Lecture 13, we have considered the 1D profile of the electric potential ψ between two parallel, semi-infinite, charged walls with the surface potential ψ_0 , as shown in Figure 3. In the lecture, in order to determine the potential at the center between the walls, $\psi_{h/2}$, we have assumed the electric potential profile is additive, which might be problematic. Is it possible to determine the value of $\psi_{h/2}$ exactly by numerical methods? Consider a binary electrolyte solution with $(z_+ : z_-)$ valence (note that z_+ can be different from z_-), let us try the following procedure:

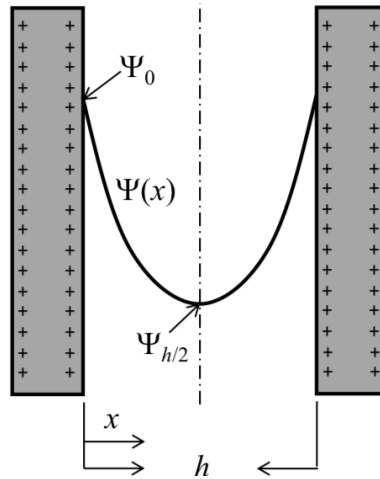


Figure 3: The electric potential profile between two charged walls in an electrolyte solution.

Shooting Method

1. Following the same procedure for derivation of the Gouy-Chapman solution shown in Lecture 11, show that:

$$\frac{d\psi}{dx}(x=0) = -\text{sgn}(\psi_0) \sqrt{\frac{2k_B T}{\epsilon_0 \epsilon_r} \left[c_{+0} \exp\left(\frac{-z_+ e\psi}{k_B T}\right) + c_{-0} \exp\left(\frac{-z_- e\psi}{k_B T}\right) \right]} \Bigg|_{\psi_{h/2}}^{\psi_0} \quad (7)$$

where sgn is the sign function (https://en.wikipedia.org/wiki/Sign_function)

2. Using Equation 7, please write a numerical function using ψ_0 and h as the input variables to determine $\psi_{h/2}$ exactly. (Hint: you may use the shooting method as in Question 1 of Homework Assignment 2, like (i) solve the Poisson-Boltzmann equation of $\psi(x)$ for $0 : h/2$. (ii) guess the initial boundary condition of $\frac{d\psi}{dx}(x=0)$ until your solution fulfills Equation 7.)
3. Consider two semi-infinite, positively-charged walls with $\psi_0 = 40$ mV immersed in 1mM NaCl solution at 300 K. Use your function in Q1.2 to calculate $\psi_{h/2}$ for $h = 10$ nm - 100 nm. Compare your result with that of additive potential assumption discussed in Lecture 13, such that:

$$\psi_{h/2} = 2\psi_{\text{single}}(x = h/2) \quad (8)$$

where ψ_{single} is the potential of single charged wall calculated using the Gouy-Chapman model.

Finite Difference (FD) Method

As you have observed, the shooting method is straightforward to be programmed, but the accuracy depends highly on the initial guess of solutions, and sometimes can be extremely sensitive. A more widely used numerical approach to solve the differential equations, is the finite difference (FD) method. We will use it to solve the 1D Poisson-Boltzmann under Gouy-Chapman assumption from this task.

Consider a function y on domain X , the idea of FD is to discretize the domain into finite number of points, and represent the differential equation as linear combination on discrete points. For instance, we can uniformly discretize $X = [a, b]$ into $n+2$ points $x_0, x_1, x_2, \dots, x_n, x_{n+1}$, with a spacing $d = (b - a)/(n + 1)$, as shown in Figure 4. For any point x_i ($1 \leq i \leq n$), the second derivative can be approximated by:

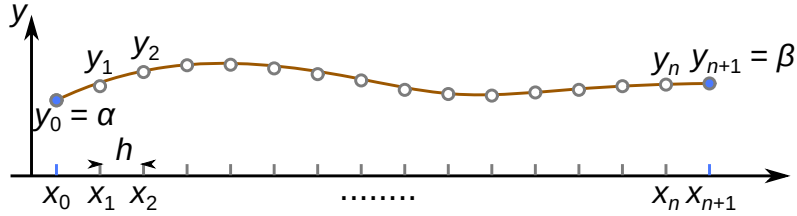


Figure 4: Scheme of FD discretization. The values of y is evaluated as discrete points $x_0, x_1, \dots, x_n, x_{n+1}$, with a point spacing of h .

$$\frac{d^2y}{dx^2}(x_i) \approx \frac{1}{d^2}(y_{i+1} - 2y_i + y_{i-1}) \quad (9)$$

where y_i is the value of function y on point x_i . For a general form Poisson equation $-\frac{d^2y}{dx^2} = f(x)$, with Dirichlet type boundary conditions $y(x_0) = \alpha$ and $y(x_{n+1}) = \beta$, the finite differential equation can be expressed as:

$$\begin{aligned} \frac{1}{d^2}(-\alpha + 2y_1 - y_2) &= f(x_1) \\ \frac{1}{d^2}(-y_1 + 2y_2 - y_3) &= f(x_2) \\ &\vdots \\ \frac{1}{d^2}(-y_{n-2} + 2y_{n-1} - y_n) &= f(x_{n-1}) \\ \frac{1}{d^2}(-y_{n-1} + 2y_n - \beta) &= f(x_n) \end{aligned} \quad (10)$$

4. Equation 10 can be expressed as a matrix form $\mathbf{A}\mathbf{y} = \mathbf{f}$, where $\mathbf{y} = [y_1, y_2, \dots, y_n]^T$. Please show the form of matrix \mathbf{A} and vector \mathbf{f} according to Equation 10.
5. Now let's use Equation 10 to write a solver for the Poisson-Boltzmann equation. Please follow these steps:

- i Write down the boundary conditions of the Poisson-Boltzmann function on the domain $\mathbf{x} = [0 \cdots h]$ (i.e. what are the α and β here?)
- ii Based on Equation 10, write a numerical function for your Poisson-Boltzmann equation using the following form:

$$\mathbf{A}\Psi = F(\Psi) \tag{11}$$

where $\Psi = [\psi(x_0), \psi(x_1), \cdots \psi(x_{n+1})]$, and F is a non-linear function that converts Ψ to \mathbf{f} . Be careful with the boundary conditions and initial guess for Ψ .

- iii Now use a non-linear solver (e.g. `fsolve` in Matlab) to solve the equations series $\mathbf{A}\Psi - F(\Psi) = 0$ with values for the initial guess of Ψ .
6. Let's compare the shooting method and finite difference method. Consider the same assumptions and boundary conditions Q2.3. Use your solver in Q2.5 to calculate $\psi_{h/2}$ again for $h = 10 \text{ nm} - 100 \text{ nm}$. Compare your result with the ones from Q2.3. What do you observe?