Sample Solutions HW4

22.May.2024

Q1 Controlling Electroosmotic Flow by Gating

Q1.1

In the D-H assumption the capacitance of the double layer is expressed as $C_{el} = \epsilon_r\epsilon_0/\kappa^{-1}$, while the capacitance of the oxide layer is $C_{ox} = \epsilon_d\epsilon_0/d$. The charge neutrality yields:

$$\sigma_M + \sigma_{el} = 0 \tag{1}$$

$$(V_G - \zeta)\frac{\epsilon_d\epsilon_0}{d} - \zeta\frac{\epsilon_r\epsilon_0}{\kappa^{-1}} = 0 \tag{2}$$

$$\zeta(V_G) = V_G\frac{1}{1+\frac{\epsilon_r}{\epsilon_d}\frac{d}{\kappa^{-1}}} \tag{3}$$

The velocity (absolute value) at equilibrium would therefore be:

$$\begin{aligned} u_S &= \frac{\epsilon_r\epsilon_0\zeta}{\mu}E_x \\ &= \frac{\epsilon_r\epsilon_0 V_G}{\mu}\frac{1}{1+\frac{\epsilon_r}{\epsilon_d}\frac{d}{\kappa^{-1}}}E_x \end{aligned} \tag{4}$$

Q1.2

We can use the Gouy-Chapmann conditions to solve ζ as a function of the applied voltage. The charge density in the electrolyte solution would thus be:

$$\begin{aligned} \sigma_{el} &= \epsilon_r\epsilon_0\left.\frac{d\psi}{dx}\right|_{x=0} \\ &= -\epsilon_r\epsilon_0\text{sign}()\sqrt{\left.\{\frac{2kT}{\epsilon_r\epsilon_0}[c_{+0}\exp(\frac{-z_+e\psi}{kT}) + c_{-0}\exp(\frac{-z_-e\psi}{kT})]\}\right|_{x=\infty}^{x=0}} \\ &= -\epsilon_r\epsilon_0\text{sign}()\sqrt{\frac{2kT}{\epsilon_r\epsilon_0}[c_{+0}\exp(\frac{-z_+e\psi}{kT}) + c_{-0}\exp(\frac{-z_-e\psi}{kT})] - (c_{+0}+c_{-0})} \end{aligned} \tag{5}$$

On the other hand, the charge neutrality is valid for the whole metal-insulator-electrolyte capacitor:

$$\sigma_{el}+\sigma_M = -\epsilon_r\epsilon_0\text{sign}()\sqrt{\frac{2kT}{\epsilon_r\epsilon_0}[c_{+0}\exp(\frac{-z_+e\zeta}{kT}) + c_{-0}\exp(\frac{-z_-e\zeta}{kT})] - (c_{+0}+c_{-0})} + \frac{\epsilon_d\epsilon_0}{d}(V_G-\zeta) = 0 \tag{6}$$

Q1.3

Q1.4

The ζ and u_S as functions of V_G using both DH and GC models are shown in Figure 1. It can be observed, that the DH solution is close to the GC solution at lower V_G regimes, which correspond to a low surface potential ζ. In the GC model, the differential capacitance in the double layer significantly increases with ζ, while in the DH model such capacitance is constant.

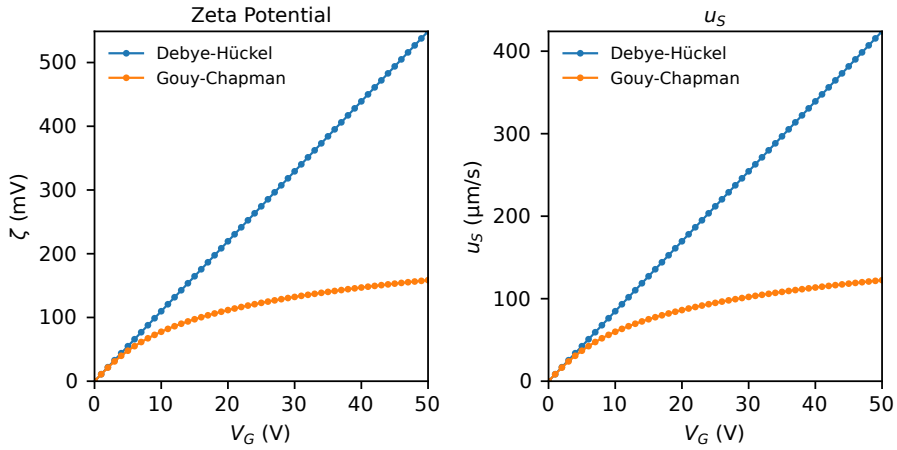

Figure 1: ζ and u_S as functions of V_G in DH and GC models.

Q2 Electroosmotic Flow in a Nanotube

1. Neglecting contributions from anions

   The contributions of anions to the RHS is $\frac{ec_-(0)}{\varepsilon_0\varepsilon_r}\exp(\frac{e\Psi}{k_BT})$. Here $c_-(0)$ is the concentration of anions at $r = 0$. Due to $R \approx \kappa^{-1}$, we have $c_-(0) \ll c_+(0) = c_0$. Also because $\Psi < 0$ (negative surface charge), we can safely assume that the contributions from anions can be ignored.

2. PBE Boundary condition at $r = R$

   We can use the Gauss's law on the surface of the tube as the BC. Consider a segment of tube with length L, the Gauss's law reads:

   $$2\pi RL\left(-\frac{\mathrm{d}\Psi}{\mathrm{d}r}\right)\Bigg|_{r=R} = 2\pi L\int_0^R \rho r\mathrm{d}r \tag{7}$$
   $$\left(\frac{\mathrm{d}\Psi}{\mathrm{d}r}\right)\Bigg|_{r=R} = \frac{\sigma_S}{\varepsilon_0\varepsilon_r}$$

   which is the same as in the case of a charged plane.

3. Expression of surface charge density

Since $R \approx \kappa^{-1}$, $1 - \frac{1}{8}\left(\frac{R}{\kappa^{-1}}\right)^2 > 0$, therefore $\Psi(r) < 0$ and $\frac{\mathrm{d}\Psi}{\mathrm{d}r} < 0$ always hold within $0 \le r \le R$. Using the 1D analytical solution of Φ, the BC (Eq. (7)) is:

$$\frac{k_\mathrm{B}T}{2e}\frac{4R}{R^2 - 8\kappa^{-2}} = \frac{\sigma_\mathrm{S}}{\varepsilon_0\varepsilon_\mathrm{r}} \tag{8}$$

Replace $k_\mathrm{B}T\varepsilon_0\varepsilon_\mathrm{r}/e$ with $\kappa^{-2}c_0 e$, we get:

$$\sigma_\mathrm{S} = \frac{4Rc_0 e}{R^2\kappa^2 - 8} \tag{9}$$

Since $R \approx \kappa^{-1}$, σ_S becomes negative.

4. Maximum solute concentration

   To enure σ_S is *always negative*, we need to have $R^2\kappa^2 - 8 < 0$, which in turn becomes:

$$c_0 < c_\mathrm{max} = \frac{8k_\mathrm{B}T\varepsilon_0\varepsilon_\mathrm{r}}{e^2R^2} \tag{10}$$

5. Osmotic pressure and electrostatic force inside charged tube

   Osmotic pressure In our case, we can still assume that osmotic pressure is controlled by the cations alone, and thus:

$$\Pi \approx k_\mathrm{B}Tc_0 \exp(-\frac{e\Psi}{k_\mathrm{B}T}) \tag{11}$$

   Force On the other hand, F_elec is given by:

$$F_\mathrm{elec} \approx -\frac{\mathrm{d}\Psi}{\mathrm{d}r}c_0 \exp(-\frac{e\Psi}{k_\mathrm{B}T}) \tag{12}$$

   It is easy to observe that $\mathrm{d}\Pi/\mathrm{d}r = -\frac{e}{k_\mathrm{B}T}\Pi\frac{\mathrm{d}\Psi}{\mathrm{d}r}$, and thus $\frac{\mathrm{d}\Pi}{\mathrm{d}r} = F_\mathrm{elec}$. In other words, the total pressure (osmotic + electrostatic) along the radius direction is independent of the size R, which is the same conclusion in parallel charged walls under the Poisson-Boltzmann conditions.

6. Pressure against the wall

   The total pressure P_wall can be regarded as the osmotic pressure $\Pi(r = 0)$ according to the conclusions in Q1.5, such that:

$$\begin{aligned} P_\mathrm{wall} = \Pi(r = 0) &\approx k_\mathrm{B}Tc_0 \\ &\le k_\mathrm{B}Tc_\mathrm{max} \\ &\le \frac{8k_\mathrm{B}^2T^2\varepsilon_0\varepsilon_\mathrm{r}}{e^2R^2} \end{aligned} \tag{13}$$

   Plug in the numbers of R, and ε_r, we get:

   - $c_\mathrm{max} \approx 60$ mM
   - $\Pi_\mathrm{max} \approx 1.50 \times 10^5$ Pa $= 1.48$ atm

7. Governing equation of fluid flow

   Now let's use the steady-state Navier-Stokes equation (Eq. 14.8 in lecture notes) while neglecting the gravity and external pressure terms:

$$\mu\nabla^2 u(r) + \rho e E_z = 0 \tag{14}$$
$$\mu\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}}{\mathrm{d}r}u(r)\right) + c_0\exp(-\frac{e\Psi}{k_\mathrm{B}T})E_z = 0$$

   with BCs:

$$u(r=R) = 0 \qquad \text{Non-slip boundary} \tag{15}$$
$$\frac{\mathrm{d}u}{\mathrm{d}r}(r=0) = 0 \qquad \text{Symmetry}$$

8. Analytical solution of $u(r)$

   Plug the expression of $\Psi(r)$ into Eq. (14), we get:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}}{\mathrm{d}r}u(r)\right) = -\frac{E_z e c_0}{\mu}\frac{r}{\left[1-\frac{1}{8}r^2\kappa^2\right]^2} \tag{16}$$
$$\frac{\mathrm{d}}{\mathrm{d}r}u(r) = -\frac{4E_z e c_0}{\mu\kappa^2}\frac{1}{r[1-\frac{1}{8}r^2\kappa^2]} + \frac{C_1}{r}$$
$$u(r) = -\frac{4E_z e c_0}{\mu\kappa^2}\left\{\ln(r) - \frac{1}{2}\ln\left(1-\frac{1}{8}r^2\kappa^2\right) + C_2\right\} + C_1\ln(r)$$

   Due to the symmetry at $r = 0$, we know that $ln(r)$ term must perish in the final equation. On the other hand, $C_2 = \frac{1}{2}\ln\left(1-\frac{1}{8}R^2\kappa^2\right)$, therefore the final result of $u(r)$ is:

$$u(r) = \frac{2E_z e c_0}{\mu\kappa^2}\ln\left[\frac{1-\frac{1}{8}r^2\kappa^2}{1-\frac{1}{8}R^2\kappa^2}\right] \tag{17}$$

   At the center of the tube, $u(r)$ is maximum and positive (towards the direction of E_z).

9. Flow profile inside tube

   The profiles of $u(r)/u_{\max}$ can be seen in Fig. 2. The profile approaches the Hagen-Poiseuille equation when $\kappa^{-1} \approx R$. However please note this behavior cannot be extrapolated to the regime $\kappa^{-1} < R/\sqrt{8}$, since we need to ensure $\sigma_\mathrm{S} < 0$ (when $c_{\max}$ is achieved.)

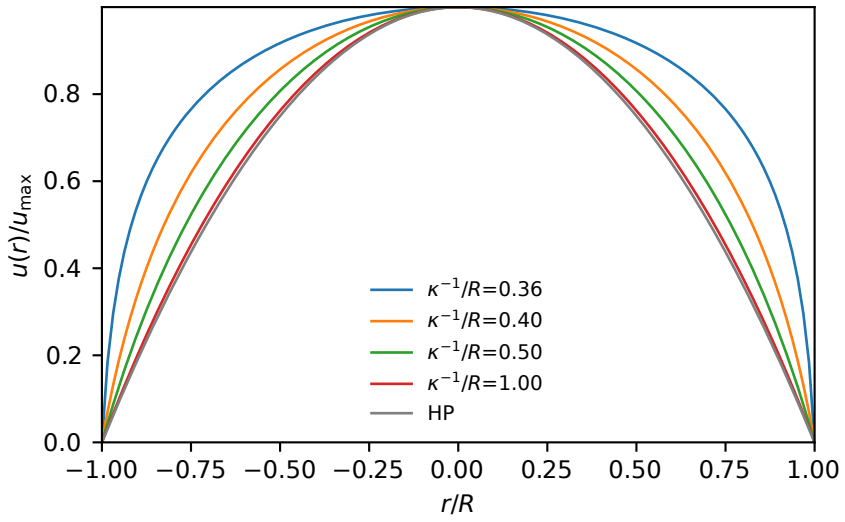

Figure 2: Profiles of $u(r)/u_{\max}$ with different k^{-1}/R values. When k^{-1}/R becomes larger, the profiles approaches the Hagen–Poiseuille (HP, quadratic) equation.

Q3 Solving Poisson Equation Using Simple Finite Difference Method

1. The Poisson-Boltzmann equation under the Gouy-Chapman condition for a $z_+ : z_-$ electrolyte solution is written as:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{e}{\epsilon_r\epsilon_0}[z_+c_{+0}\exp(\frac{-z_+e\psi}{kT}) + z_-c_{-0}\exp(\frac{-z_-e\psi}{kT})] \tag{18}$$

Let $Y = \frac{e\psi}{kT}$, we further get:

$$\begin{aligned}\frac{d}{dx}[(\frac{d\psi}{dx})^2] &= -2\frac{e}{\epsilon_r\epsilon_0}[z_+c_{+0}\exp(\frac{-z_+e\psi}{kT}) + z_-c_{-0}\exp(-\frac{z_-e\psi}{kT})]\frac{d\psi}{dx} \\ &= -\frac{2kT}{\epsilon_r\epsilon_0}[z_+c_{+0}\exp(-z_+Y) + z_-c_{-0}\exp(-z_-Y)]\frac{dY}{dx}\end{aligned} \tag{19}$$

Let's perform an integral of eq 19 from 0 to $h/2$:

$$\int_0^{h/2}\frac{d}{dx}[(\frac{d\psi}{dx})^2]dx = \int_0^{h/2} -\frac{2kT}{\epsilon_r\epsilon_0}[z_+c_{+0}\exp(-z_+Y) + z_-c_{-0}\exp(-z_-Y)]\frac{dY}{dx}dx$$

$$(\frac{d\psi(x)}{dx}\Big|_{x=h/2})^2 - (\frac{d\psi(x)}{dx}\Big|_{x=0})^2 = \int_{Y(0)}^{Y(h/2)} -\frac{2kT}{\epsilon_r\epsilon_0}[z_+c_{+0}\exp(-z_+Y) + z_-c_{-0}\exp(-z_-Y)]dY$$

$$\frac{d\psi}{dx}\Big|_{x=0} = -\mathrm{sgn}(\psi_0)\sqrt{\{\frac{2kT}{\epsilon_r\epsilon_0}[c_{+0}\exp(\frac{-z_+e\psi}{kT}) + c_{-0}\exp(\frac{-z_-e\psi}{kT})]\}\Big|_{x=h/2}^{x=0}} \tag{20}$$

The negative sign is given since $d\psi/dx\Big|_{x=0}$ will be negative for positive $\psi(0)$ values.

It is easy to observe that we can use arbitrary position x' $(0 < x' < h/2)$ as the upper limit of the integral in Equation 20, which gives us a first-order ODE between $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ and

ψ:

$$\left.\frac{d\psi}{dx}\right|_{x=x'} = -\mathrm{sgn}(\psi_0)\sqrt{\left.\{\frac{2kT}{\epsilon_r\epsilon_0}[c_{+0}\exp(\frac{-z_+e\psi}{kT}) + c_{-0}\exp(\frac{-z_-e\psi}{kT})]\}\right|_{x=h/2}^{x=x'}} \tag{21}$$

2. There are several ways to implement such function, either to treat the Poisson-Boltzmann equation as second- or first-order ODE.

   If you treat the PB equation as second order equation, here are the typical procedures that can be adapted (assume your ode function if called `pb`)

   (a) Guess value of $\psi_{h/2}$, and calculate the corresponding value of $\frac{\mathrm{d}\psi}{\mathrm{d}x}(x=0)$

   (b) Use $\frac{\mathrm{d}\psi}{\mathrm{d}x}(x=0)$ from step 1 and ψ_0 as initial conditions of `pb`

   (c) Calculate the values of ψ and $\frac{\mathrm{d}\psi}{\mathrm{d}x}$ at $x = h/2$, they should be $\psi_{h/2}$ (the value guessed in step 1) and 0, respectively. If not, return to step 1 and update your guess of $\psi_{h/2}$.

   Another approach is to use the first-order ODE as in Equation 21. This is approach is more robust than the second-order ODE approach, however you should be careful with the choice of boundary condition (assume your ode function if called `pb`, which requires $\psi_{h/2}$ as an input variable):

   (a) Guess the value of $\psi_{h/2}$, use ψ_0 as initial condition, calculate the values of $\psi(x)$ near $x = h/2$.

   (b) Calculate the second order derivative $\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}$ at $x = h/2$ using finite difference. Check if it is the same as the value calculated with Poisson equation (Equation 18). If not, return to step 1 and update the guess of $\psi_{h/2}$.

   The choice of the boundary condition for the first-order ODE approach, is that the solutions of Equation 21 $\psi(x = h/2)$ is always $\psi_{h/2}$ and $\mathrm{d}\psi/\mathrm{d}x(x = h/2)$ is always 0. The two approaches should yield the same result.

3. The solution of $\psi_{h/2}$ as a function of h can be seen in Figure 3. In addition to the exact solution of the GC equation, we also compare the solution by the overlap-double-layer assumption, that the overall potential between two charged plates are the sum of individual double layer potential.

   It can be found that when $h > 6\kappa^{-1}$, or $h/2 > 3\kappa^{-1}$, the two methods produce almost identical results. This is true since at such separation distance the overlay of double layers does not significantly affect the ion distribution. On the other hand, such simple assumption fails when h is comparable with κ^{-1}, which overestimates the value of $\psi_{h/2}$.

4. The finite difference matrix is written as:

$$\mathbf{A} = \frac{1}{d^2}\begin{bmatrix} 2 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & -1 & & \\ & & \ddots & \ddots & \ddots & \\ & & & -1 & 2 & -1 \\ & & & & -1 & 2 \end{bmatrix} \tag{22}$$

   which is a positive definite matrix. The vector $\mathbf{f}$ is then:

$$\mathbf{f} = [f(x_1) + \frac{\alpha}{d^2}, f(x_2), \ldots, f(x_{n-1}), f(x_n) + \frac{\beta}{d^2}]^{\mathrm{T}} \tag{23}$$

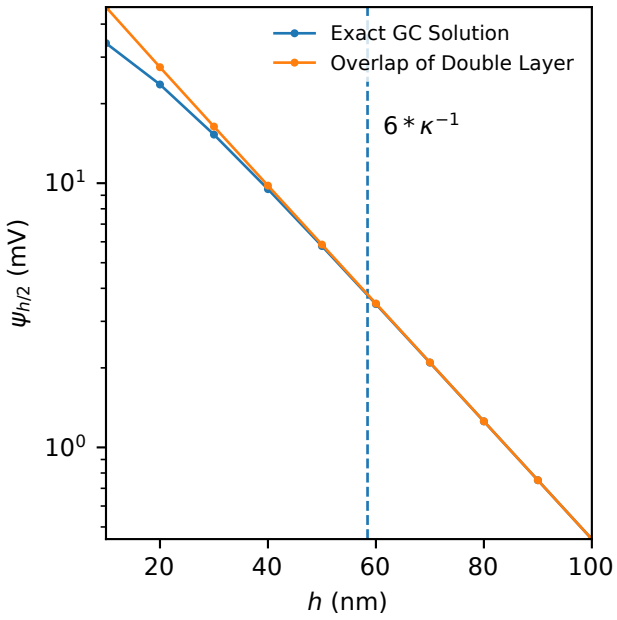

Figure 3: $\psi_{h/2}$ as a function of h for exact solution of the GC equation shown in eq 19, and the assumption that potential overlaps between two adjacent double layers. The two methods produce almost negligible difference when $h > 6\kappa^{-1}$.

5. By following the steps in the exercise one should reach a nonlinear differential equation for $\boldsymbol{\psi} = (\psi_1, \ldots, \psi_n)^T$ of shape:

$$\mathbf{A}\boldsymbol{\psi} - F(\boldsymbol{\psi}) = 0 \tag{24}$$

whereas $\mathbf{A}$ is given from exercise Q2.4 and $F(\boldsymbol{\psi})$ has following shape,

$$F(\boldsymbol{\psi}) = \begin{pmatrix} \frac{d^2\psi_1}{dx^2} + \frac{\alpha}{d^2} \\ \frac{d^2\psi_2}{dx^2} \\ \vdots \\ \frac{d^2\psi_n}{dx^2} \\ \frac{d^2\psi_{n+1}}{dx^2} + \frac{\beta}{d^2} \end{pmatrix}, \tag{25}$$

with $\psi_i = \psi(x_i)$, $\frac{d^2\psi_i}{dx^2}$ being given by the Poisson-Boltzmann equation (18) under Gouy-Chapmann condition evaluated for ψ_i and the boundary conditions $\psi_0 = \alpha = \psi_{n+1} = \beta$. With this one should be able to a solver routine to get the values of $\boldsymbol{\psi}$.

6. The comparison of both methods is visualized in Figure 4. We observe that the finite difference method achieves similar results to the shooting method for a sufficiently large value of n. However the finite difference method excels the shooting method in stability as it doesn't require initial values close to the solutions and in speed as it is significantly faster than the shooting method using the same number of nodes.

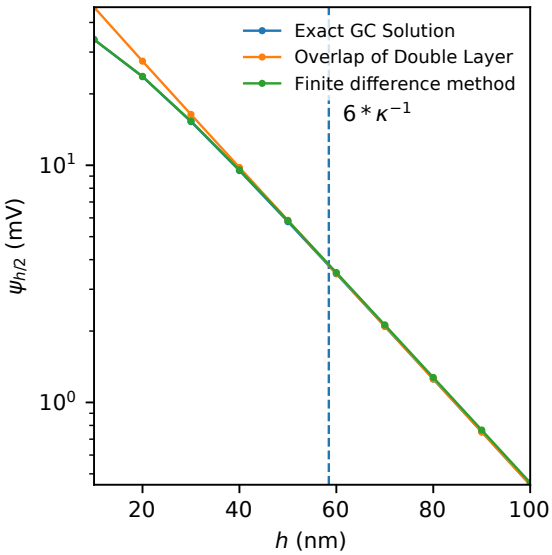

Figure 4: Comparison between the exact solution, the shooting method and the finite difference approach.