Homework assignment 1

Charge transport

<u>Note:</u> The submission of homework assignments 1 to 4 is mandatory to pass the course. The assignments lead from the mathematical formulation of a model problem to the numerical solution of this problem. They build on each other. You must achieve at least 50 of the achievable points on each assignment.

For all tasks, include the solution steps and intermediate results. The final result alone is not sufficient! We recommend that you use Python for the solution of numerical tasks. If you use a Jupyter notebook, you can simply submit the notebook directly as a solution. In all other cases, please create a PDF and attach the numerical codes as a separate file.

Problem 1 Steady-state solution of the diffusion equation

8 achievable points

Consider the one-dimensional steady-state diffusion equation

$$\frac{\partial^2 c(x)}{\partial x^2} = \frac{f(x)}{D} \tag{1.1}$$

with the source term

$$f(x) = \left[-\delta(x - L/3) + \delta(x - 2L/3)\right]\ \mathrm{m}^{-2}\ \mathrm{s}^{-1} \tag{1.2}$$

where $\delta(x)$ is a Dirac impulse. The quantity $c(x)$ is the concentration and D the diffusion constant.

Task 1. Explain why the unit of the source term, Eq. (1.2), is $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$.

Task 2. Use the Fourier series to determine a solution of the differential equation in a periodic domain of length L. Also discuss what the coefficient c_0 of the Fourier solution means.

Task 3. Determine the exact analytic solution by integrating Eq. (1.1).

Task 4. Plot both solutions (Fourier and exact). You need to truncate the Fourier series to be able to compute it. Truncate the Fourier series at $N = 1$, 5, 10 and 20 and show these truncated solutions in the plot. Use the following additional parameters for plotting:

- $L = 3$ m
- $D = 0.8\ \mathrm{m}^2\,\mathrm{s}^{-1}$
- $1/L \int_0^L \mathrm{d}x\, c(x) = 0.3\ \mathrm{m}^{-3}$

Note:

- For an L-periodic function $s(x)$, the Fourier series is given by $s(x) = \sum_{n=-\infty}^{\infty} s_n \exp\left(i2\pi nx/L\right)$. This sum is often truncated so that it runs from $-N$ to N . The coefficients are given by $s_n = \frac{1}{L}\int_{-L/2}^{L/2} \mathrm{d}x\, s(x) \exp\left(-i2\pi nx/L\right)$.
- For the periodic domain, the Dirac impulse becomes a Dirac comb. The integration of a Dirac impulse is the Heaviside step function.

Problem 2 Poisson-Nernst-Planck equation

5 achievable points

An ion of charge q experiences in an electric field $\vec{E} = -\nabla\Phi$ the Coulomb force $\vec{F}_\mathrm{c} = q\vec{E} = -q\nabla\Phi$, where $\Phi(\vec{r})$ is the electrostatic potential. The ion will start moving, but it will encounter a drag force resisting its motion because it needs to displace surrounding fluid molecules. In a dilute solution, this drag force is approximately given by *Stokes drag*, $\vec{F}_\mathrm{d} = -6\pi\eta a\vec{v}$, where η is the viscosity of the solution and a is the effective ion radius. $\vec{v}$ is the velocity of the particle relative to the fluid. The fluid is at rest.

Task 1. Derive the Nernst-Planck equation that describes the motion of the ion under a combination of this drift-force and additional diffusive forces. Assume a stationary force equilibrium ($\vec{F}_\mathrm{c} = -\vec{F}_\mathrm{d}$) and first derive the relationship between the drift current $\vec{j}_\mathrm{c,drift}$ and electric field $\vec{E}$. The Nernst-Planck equation describes the motion of ions in an electric field, where $\vec{j}_c = \vec{j}_{c,\mathrm{diffusion}} + \vec{j}_{c,\mathrm{drift}}$. Insert the expression for the particle current $\vec{j}_c$ into the continuity equation and write down the resulting transient (time-dependent equation), also known as the Nernst-Planck equation.

Task 2. In a system with N ionic species, the electrostatic potential is determined by the Poisson equation $\nabla^2\Phi = -\rho/\varepsilon$. The Poisson equation and the Nernst-Planck equation are coupled by the charge density

$$\rho = \sum_{i=1}^{N} q_i c_i \tag{1.3}$$

State the Poisson equation using the above expression for the charge density.

<u>**Note:**</u>

- Work in three dimensions.
- $\vec{j}_\mathrm{c,drift} = c\vec{v}_\mathrm{drift}$ where c is the concentration
- The charge carrier mobility is the quantity $\mu = q/(6\pi\eta a)$ that should show up in your equations. The Einstein-Smoluchowski relation links the mobility μ to the diffusion coefficient via $\mu = qD/(k_\mathrm{B}T)$, where k_B is Boltzmann's constant and T the temperature.
- The combination of Poisson and Nernst-Planck equation is often called the Poisson-Nernst-Planck equation(s).

Problem 3 Linearized Poisson-Boltzmann equation

6 achievable points

In this problem you will solve the Poisson-Boltzmann equation for a symmetric electrolyte, i.e. $N = 2$ species with identical charges $q_1 = -q_2 = q$ and $c_1^\infty = c_2^\infty = c^\infty$. This could be a model for NaCl in solution.

Task 1. Derive the Poisson-Boltzmann equation from the Nernst-Planck and the Poisson equation. Use the expression for the charge density (see problem 2) to couple the Poisson equation with the Nernst-Planck equation. Assume the concentration distribution of species i to be a Boltzmann distribution $c_i = c_i^\infty \exp\left(-q_i\,\Phi/k_\mathrm{B}T\right)$. Under which conditions is this justified?

Task 2. Linearize the equation in Φ. Write the linearized Poisson-Boltzmann equation in terms of the Debye length λ. What does this quantity mean physically?

Task 3. Find the analytic solution to the linearized, one-dimensional Poisson-Boltzmann equation subject to Diriclet boundary conditions on both ends of the domain.

Task 4. Plot the solution of the linearized equation for $\Phi_0 = -k_\mathrm{B}T/q$, $\Phi_1 = k_\mathrm{B}T/q$, $L = \lambda$ and $1/\lambda^2 = 20\ \mathrm{m}^{-2}$ on a one-dimensional interval. Here, L is the distance between the plates.

Note:

- For task 1 and 2 work in three dimensions. For task 3 and 4 it is sufficient to consider the one-dimensional Poisson-Boltzmann equation.
- Use a Taylor series around $\Phi = 0$ (up to the 1st order) to linearize the equation.
- The Debye length is $\lambda = \sqrt{\varepsilon k_\mathrm{B}T/(2q^2c^\infty)}$.
- Determine the integration constants with the following boundary conditions: The potential on the left side is $\Phi(x = 0) = \Phi_0$ and the potential on the right side is $\Phi(x = L) = \Phi_1$.