GOUY–CHAPMAN

Interface theory and Python

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AIM OF TODAY'S EXERCISES

Today we will build a simple solver for the Gouy-Chapman problem, making sure that every step of our implementations is correct. Every question follows the method from the following link:

$\longrightarrow$ Exercises_Python $\longleftarrow$

The student is expected to answer the questions in parallel with the Jupyter Notebook file. Exercise questions are divided into 2 parts:

- Slide questions: These questions arise naturally when we investigate the underlying physics of the system.
- Jupyter Notebook questions: These questions directly influence the numerical calculations.

QUESTION 1 – ANALYTICAL GC

It is well-known that solution to Gouy-Chapman:

$$\text{GC (1D)}: \begin{cases} \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{Fc_b}{\epsilon_s}\sinh(\frac{F\phi}{RT}), & x \in]0, \infty[\\ \phi(x=0) = \phi_0, & x = 0 \\ \lim_{x\to\infty}\phi(x) = 0, & x \to \infty \end{cases} \tag{1}$$

is given by:

$$\phi = 2\ln\left(\frac{\sqrt{\exp(\phi_0)} - \tanh\left(-x\sqrt{\frac{2F^2c_b}{RT\epsilon_s}}\right)}{1 - \sqrt{\exp(\phi_0)}\tanh\left(-x\sqrt{\frac{2F^2c_b}{RT\epsilon_s}}\right)}\right) \tag{2}$$

Show that eq. (2) satisfies the **boundary conditions** of eq. (1) using the following hyperbolic identities:

$$\tanh(x) = \frac{\sinh(x)}{\cosh(x)}, \quad \sinh(x) = \frac{\exp(x) - \exp(-x)}{2}, \quad \cosh(x) = \frac{\exp(x) + \exp(-x)}{2}$$

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QUESTION 2 – PARAMETERS

If we use unphysical parameters, then we get unphysical results. Therefore, we have to make sure that every parameter of choice in our system represents something physical. Hence, we need to make sure that the parameters do not break any physical limitations of the system. We call these limitations *constraints*.

Please fill out the following table (Hint: Use the Jupyter Notebook file).

Name	**Label**	**Constraint**
Temperature	T	$\mathbb{R}^+$
Bulk concentration	c_b	?
Relative permittivity	?	$? <$
Electrode potential	?	?
?	ϕ_{pzc}	?
?	?	$\mathbb{N}$
Minimum **and** Maximum distance	$L_{\text{min}}, L_{\text{max}}$	$? < ?$

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QUESTION 3 – NUMERICAL SOLVER

A numerical solver is numerical scheme which seeks to solve a mathematical system by use of iteration. And the very first iteration is where our knowledge comes to play: we have to choose our initial guess. The closer our initial guess is to the real solution, the quicker our solver will converge. The farther the initial guess is from the real solution, the more likely the system will diverge. Within this exercise, we are working with a differential system and solving for ϕ. You will assess which of the following guesses are best:

- Constant: $\phi^{(0)} = \phi_0$
- Exponential: $\phi^{(0)} = \phi_0 \exp(-x)$
- Cosine: $\phi^{(0)} = \frac{\phi_0}{2}(\cos(-x) + 1)$

Bonus: What is the best initial guess to *our* system? (Hint: it's not on the list, look at slide 2)

QUESTION 4 – TRANSFORMATIONS

In order to rewrite expressions to dimensionless form, we first need to define some dimensionless properties. This is done using transformations. In order to figure out how do transform from non-dimensionless form to dimensionless, one usually uses **dimensional analysis**, which is to say that you *only* look at the units of the terms you are investigating. Let's look at an example: the thermodynamic factor, $\beta = k_B^{-1} T^{-1}$, where k_B is Boltzmann's constant and T is the temperature. $[T] = K$ and $[k_B] = \mathrm{J} \cdot \mathrm{K}^{-1}$, hence:

$$[\beta] = \left[k_B^{-1} T^{-1}\right] = [k_B]^{-1} \cdot [T]^{-1} = \left(\mathrm{J} \cdot \mathrm{K}^{-1}\right)^{-1} \cdot (\mathrm{K})^{-1} = \mathrm{J}^{-1} \cdot \mathrm{K} \cdot \mathrm{K}^{-1} = \mathrm{J}^{-1}$$

Find $\left[\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\right]$ and $\left[\frac{F c_b}{\epsilon_s} \sinh\left(\frac{F\phi}{RT}\right)\right]$. Especially, what is $\left[\frac{F\phi}{RT}\right]$ and could this inspire us to define the dimensionless form corresponding to ϕ?
Use the next slide for hints.

QUESTION 4 – APPENDIX

Here, you will find a list of units for all symbols used for question 4:

Symbol	**Unit**
x	m
ϕ	V
F	$\mathrm{C \cdot mol^{-1}}$
R	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
c_b	$\mathrm{mol \cdot cm^{-3}}$
ϵ_S	None

QUESTION 5 – BENCHMARKING WITH EXPERIMENTS

In order to showcase that the model is actually true, One can compare with experiments. In our model, we can calculate the double-layer capacitance, C_{dl}.

- What kind of experiments could have been done to retrieve the capacitance-voltage plot (hint: choose one of the sources from the slides)?

Assume that you do not have any experimentally found concentration profiles and surface charge densities readily available. How could you rationalize the results?