PARAMETRIC STUDY

Gouy–Chapman, Gouy–Chapman–Stern, Symmetric Bikerman & Asymmetric Bikerman

May 8, 2025 | O. Schmidt | Theory and Computation of Energy Materials (IET-3)

JÜLICH Forschungszentrum

AIM OF TODAY'S EXERCISES

Today, we will investigate how changing the parameters - and therefore the environment of the system - will change the following models:

- Gouy–Chapman
- Gouy–Chapman–Stern
- Symmetric Bikerman
- Asymmetric Bikerman

This method of studying a model using different parameters is called a parametric study.

$\longrightarrow$ Exercises_Python $\longleftarrow$

The student is expected to use the following source: *A beginners' Guide to Modelling of Electric Double Layer under Equilibrium, Nonequilibrium, and AC Conditions*

QUESTION SETUP

The question setup is for the next slides are as follows:

Ordinary Differential equation
Boundary Condition 1
Boundary Condition 2

Anion concentration
Cation concentration

Question: $\cdots$

QUESTION 1 – GOUY–CHAPMAN–STERN

The differential equations system describing the Gouy–Chapman–Stern case is provided by:

$$\text{GCS (1D)}: \begin{cases} \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{Fc_b}{\epsilon_s}\sinh\left(\frac{F\phi}{RT}\right), & x \in]0, \infty[\\ \phi(x=0) = \phi_M - \phi_{\text{pzc}} + \left.\frac{\partial \phi}{\partial x}\right|_{x=x_{\text{HP}+}} \frac{\epsilon_S}{\epsilon_{\text{HP}}}\delta_{\text{HP}}, & x = 0 \\ \lim_{x\to\infty}\phi(x) = 0, & x \to \infty \end{cases} \tag{2.1}$$

with:

$$c_- = c_b \exp\left(-\frac{F\phi}{RT}\right) \tag{2.2}$$

$$c_+ = c_b \exp\left(+\frac{F\phi}{RT}\right) \tag{2.3}$$

Question: How does the differential double-layer capacitance change with varying c_b?

QUESTION 2 – SYMMETRIC BIKERMAN

The differential equations system describing the Symmetric Bikerman case is provided by:

$$\text{SB (1D)}: \begin{cases} \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{Fc_b}{\epsilon_S} \frac{2\sinh\left[\frac{F\phi}{RT}\right]}{1+2v\sinh^2\left[\frac{F\phi}{2RT}\right]}, & x \in]0,\infty[\\ \phi(x=0) = \phi_M - \phi_{\text{pzc}} + \left.\frac{\partial\phi}{\partial x}\right|_{x=x_{\text{HP}^+}} \frac{\epsilon_S}{\epsilon_{\text{HP}}}\delta_{\text{HP}}, & x = 0 \\ \lim_{x\to\infty}\phi(x) = 0, & x \to \infty \end{cases} \tag{3.1}$$

with:

$$c_+ = \frac{c_b \exp\left(\frac{F\phi}{RT}\right)}{1 + 2v\sinh^2\left[\frac{F\phi}{2RT}\right]} \tag{3.2}$$

$$c_- = \frac{c_b \exp\left(-\frac{F\phi}{RT}\right)}{1 + 2v\sinh^2\left[\frac{F\phi}{2RT}\right]} \tag{3.3}$$

Question: How does the differential double-layer capacitance change with varying v?

JÜLICH Forschungszentrum

QUESTION 3 – ASYMMETRIC BIKERMAN

The differential equations system describing the Asymmetric Bikerman case is provided by:

$$\text{AB (1D)}: \begin{cases} \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{Fc_b}{\epsilon_s}\frac{\sinh\left(\frac{F\phi}{RT}\right)}{1+\frac{v}{2}\left(\gamma_+\left[\exp\left\{-\frac{F\phi}{RT}\right\}-1\right]+\gamma_-\left[\exp\left\{\frac{F\phi}{RT}\right\}-1\right]\right)}, & x\in]0,\infty[\\ \phi(x=0) = \phi_M - \phi_{\mathrm{pzc}} + \left.\frac{\partial\phi}{\partial x}\right|_{x=x_{\mathrm{HP}+}}\frac{\epsilon_S}{\epsilon_{\mathrm{HP}}}\delta_{\mathrm{HP}}, & x=0 \\ \lim_{x\to\infty}\phi(x) = 0, & x\to\infty \end{cases} \tag{4.1}$$

with:

$$c_- = \frac{c_b\exp\left(\frac{F\phi}{RT}\right)}{1+\frac{v}{2}\left(\gamma_+\left[\exp\left\{-\frac{F\phi}{RT}\right\}-1\right]+\gamma_-\left[\exp\left\{\frac{F\phi}{RT}\right\}-1\right]\right)} \tag{4.2}$$

$$c_+ = \frac{c_b\exp\left(-\frac{F\phi}{RT}\right)}{1+\frac{v}{2}\left(\gamma_+\left[\exp\left\{-\frac{F\phi}{RT}\right\}-1\right]+\gamma_-\left[\exp\left\{\frac{F\phi}{RT}\right\}-1\right]\right)} \tag{4.3}$$

Question: How does the differential double-layer capacitance change with varying γ_+ and γ_-?

JÜLICH Forschungszentrum