Modeling Bipolar Electrochemistry in Order to create a Basis for Computational Tribology Experiments

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引言： In the field of boundary lubrication, surfactant adsorption plays an important role. Recently, several experiments [1][2] focused on controlling adsorption behavior electrodynamically. In this context, Zhang [2] investigated the adsorption behavior of SDS (sodium dodecyl sulfate) on steel BPE (bipolar electrode). Here we aim on establishing a virtual model in order to reproduce Zhang's experimental findings and furthermore to predict or validate related experiments. The first step is a complete model of BPE, explicitly including the full diffuse double layer (DDL) structure.

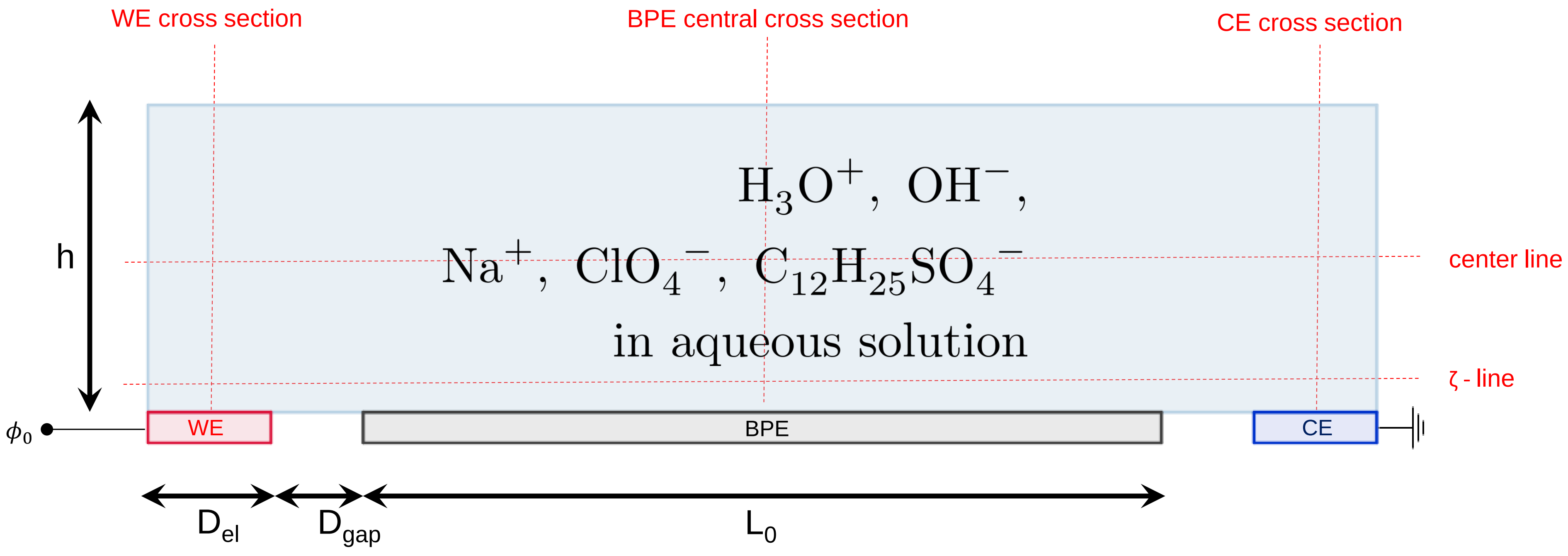

图 1. Model of BPE cell

计算方法： Our 2d model electrochemical cell consists of working electrode WE, counter electrode CE, BPE and electrolyte. Inspired by Bazant [3], the full Poisson-Nernst-Planck (PNP) equation system is solved within the electrolyte domain

$$\mathbf{N_i} = -D_i \nabla c_i - u_i z_i F c_i \nabla \phi \quad \text{(Nernst-Planck)}$$

$$\nabla \cdot (-\epsilon \nabla \phi) = \rho \quad \text{(Poisson)}$$

with conservation law $\nabla \cdot \mathbf{N_i} = 0$ and physics-coupling through charge density $\rho = F \sum_i z_i c_i$.

Ion species H_3O^+, OH^-, Na^+, ClO_4^- and $C_{12}H_{15}SO_4^-$ in aqueous solution correspond to Zhang's setup.

Three governing surface reactions at the electrodes， namely the dissolution of iron and electrolysis of water, state the boundary conditions:

$$\mathrm{Fe} \longrightarrow \mathrm{Fe^{2+}} + 2\,\mathrm{e^-} \qquad \text{anodic}$$

$$6\,\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\,\mathrm{H_3O^+} + 4\,\mathrm{e^-} \qquad \text{anodic}$$

$$\mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2} + 2\,\mathrm{OH^-} \qquad \text{cathodic}$$

Those half-reactions lead to species flux at WE, BPE and CE governed by electrochemical kinetics. Each reaction thus imposes boundary conditions given by the following flux expression related Butler-Volmer equation,

$$N = K_a \cdot c_{\mathrm{R}} \cdot e^{\frac{F\alpha_a z\eta}{RT}} - K_c \cdot c_{\mathrm{Ox}} \cdot e^{-\frac{F\alpha_c z\eta}{RT}}$$

where c_R and c_{Ox} are the local surface concentrations of reductant and oxidant. The potential difference between solid electrode phase and liquid electrolyte phase is expressed as the overpotential $\eta = \phi_s - \phi_l$, here the potential drop across the DDL stretching out to the ζ-plane at Debye length λ_D. Methods to determine the potential at isolated BPE stem from [4].

结果： At the current stage, a qualitative steady state model with pseudo parameters including only one half-reaction has been solved.

name	value	unit
L_0	10	nm
D_{el}, D_{gap}	1	nm
λ_D	0.34	nm
h	10 * λ_D	nm
φ_0	0.1	V
c_{H30+}^{∞}	1E-4	mol/m³

表 1. parameters

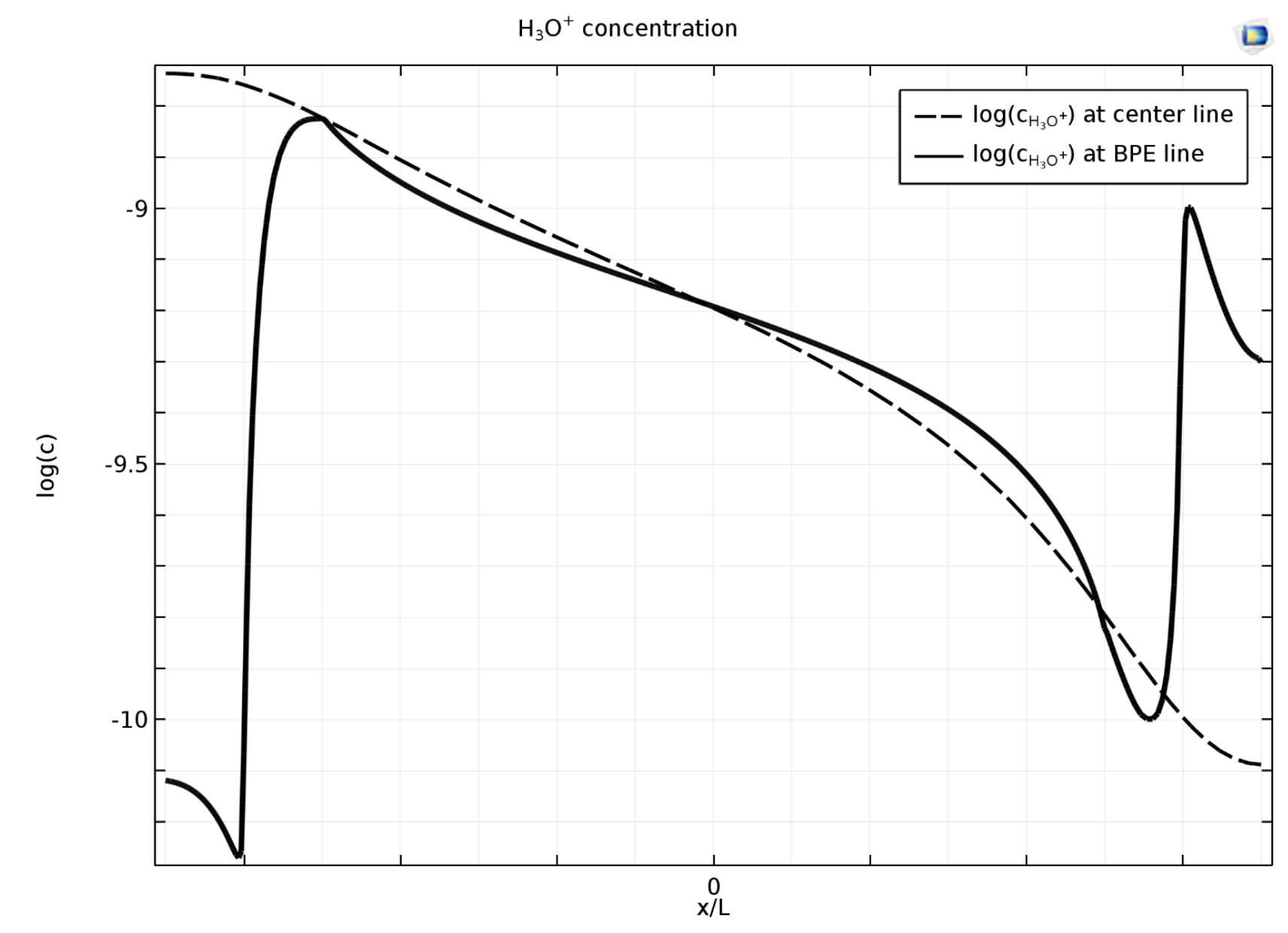

图 2. log H_3O^+ concentration

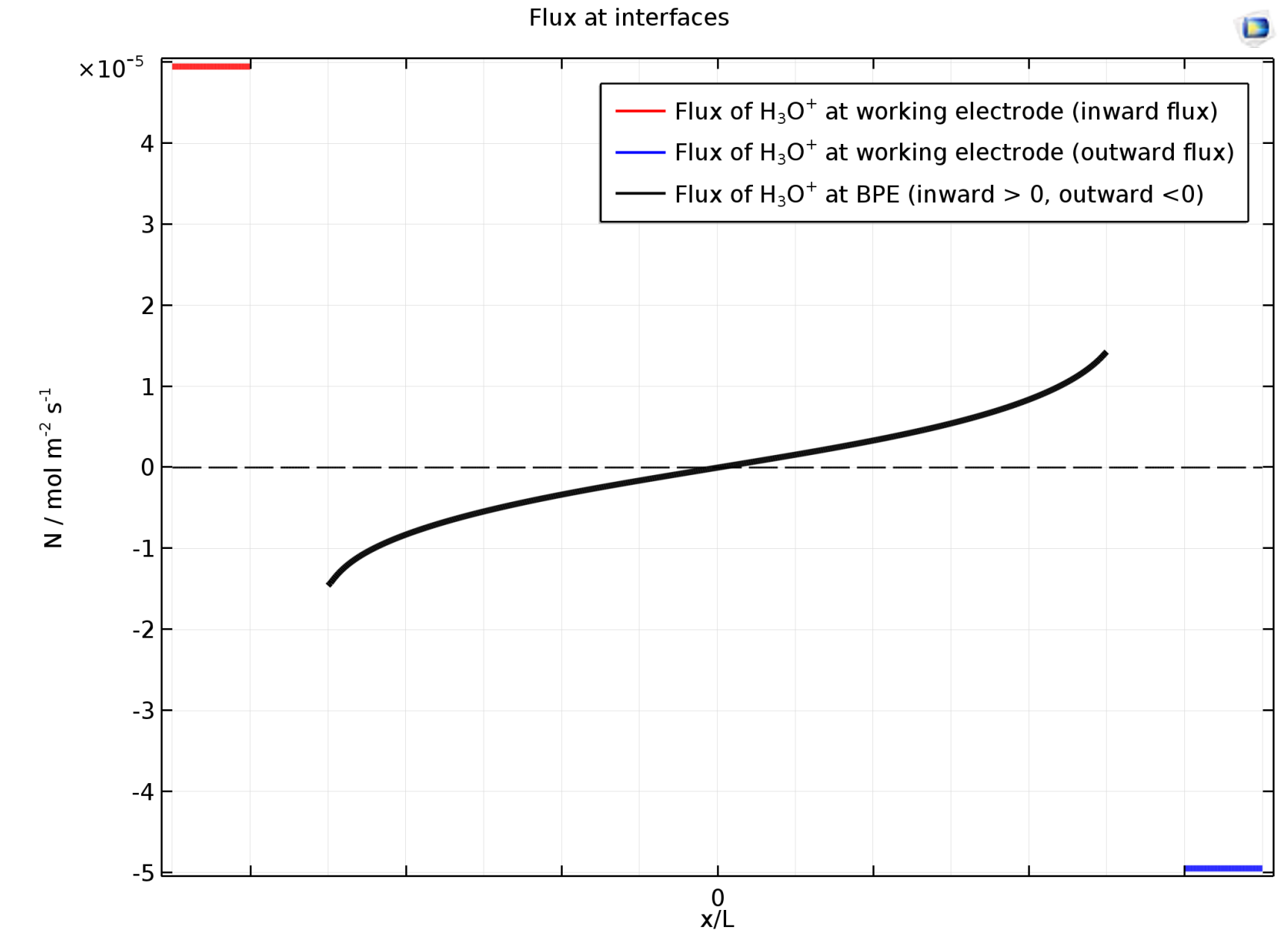

图 3. Flux at electrodes

结论： Convergence is difficult to be guaranteed for this highly non-linear PNP system. Mesh-related deviations are likely to occur. In case those issues can be solved, present results promise the realization of [2] and extension to other problems.

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