Max-Planck Institut für Eisenforschung GmbH
Interface Chemistry and Surface Engineering Department
Atomistic Modeling Group (AMG) IMPRS-SurMat

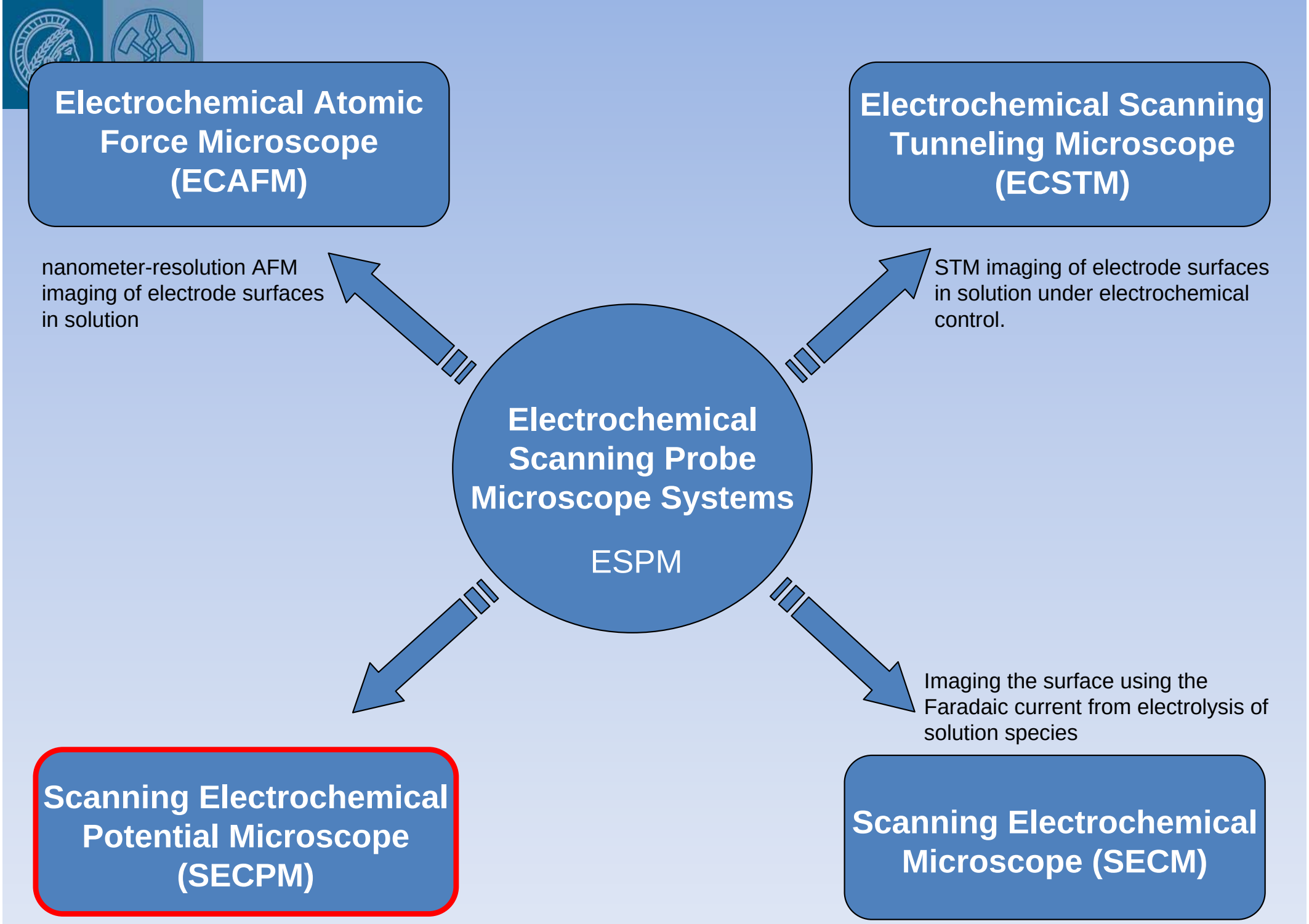
Presented at the COMSOL Conference 2008 Hannover

COMSOL CONFERENCE HANNOVER 2008

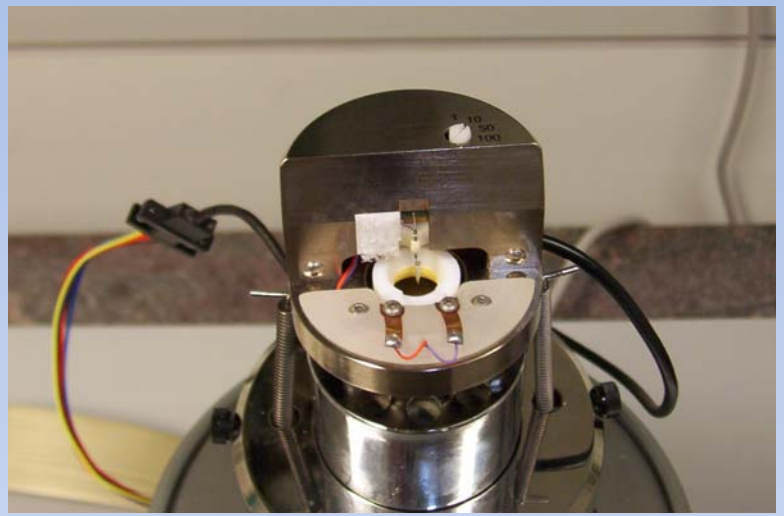
FEM simulation of the scanning electrochemical potential microscopy (SECPM)

Fayçal. R. Hamou

P.U. Biedermann, M. Rohwerder, A.T. Blumeneau


Electrochemical Atomic Force Microscope (ECAFM)
Electrochemical Scanning Tunneling Microscope (ECSTM)
nanometer-resolution AFM imaging of electrode surfaces in solution
STM imaging of electrode surfaces in solution under electrochemical control.
Electrochemical Scanning Probe Microscope Systems
ESPM
Imaging the surface using the Faradaic current from electrolysis of solution species
Scanning Electrochemical Potential Microscope (SECPM)
Scanning Electrochemical Microscope (SECM)

Scanning Electrochemical Potential Microscopy (SECPM)

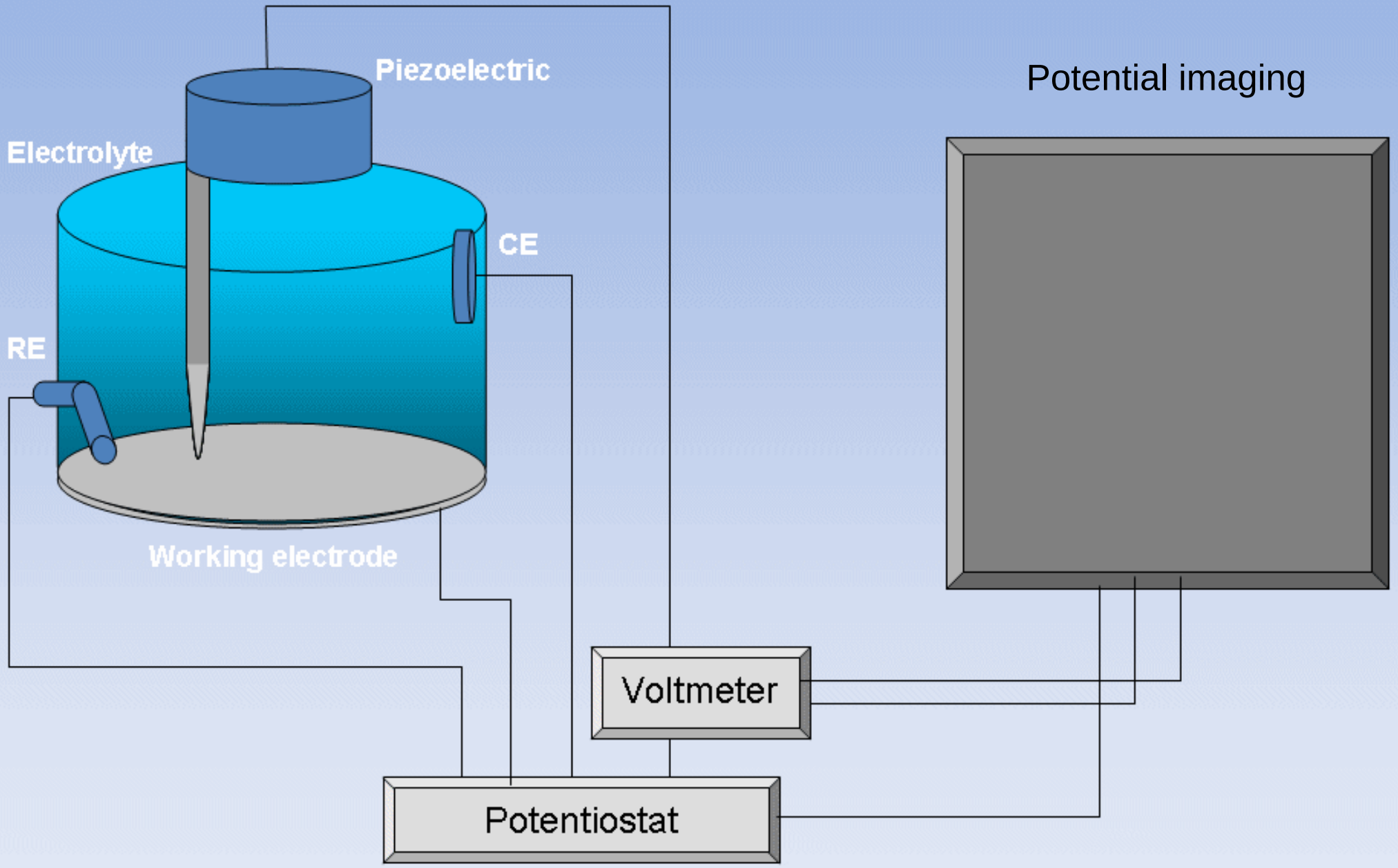


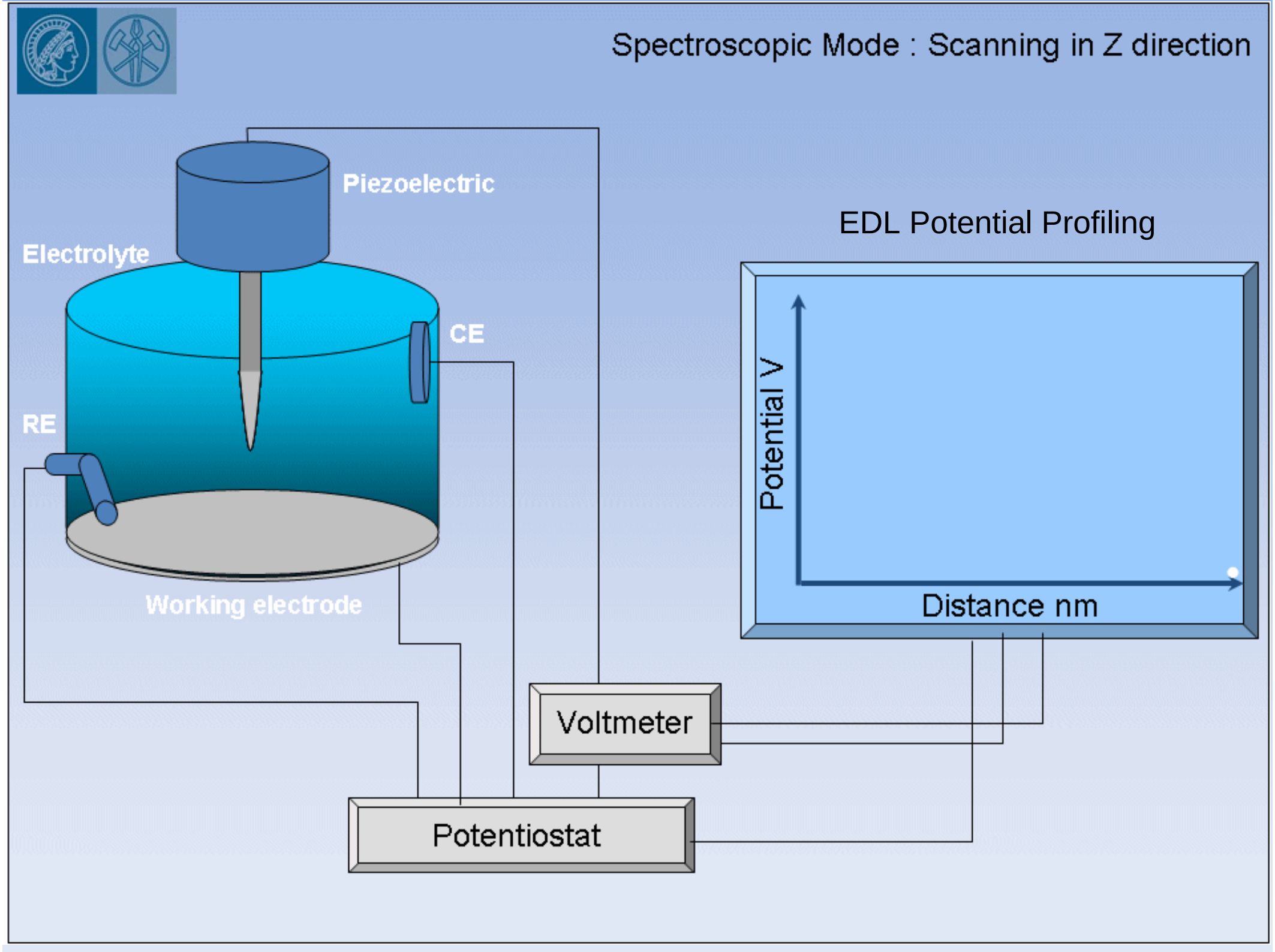
•*in-situ* imaging or potential mapping of the electrode surface with nanometer-scale resolution

•Measure the profile of Electrochemical Potential at the metal/electrolyte interface

Applications: electroplating, corrosion, and battery research and development.

1. Constant Potential Mode
2. Constant Height Mode




Spectroscopic Mode : Scanning in Z direction
Piezoelectric
Electrolyte
CE
RE
Working electrode
EDL Potential Profiling
Potential V
Distance nm
Voltmeter
Potentiostat

Potential Profiling:

SECPM measurement

- Low concentration
- Polar liquids
- Totally Inert metallic probe

Interpretation of the SECPM measurement

Theoretical model : Gouy-Chapmann-Stern

Fitting the results

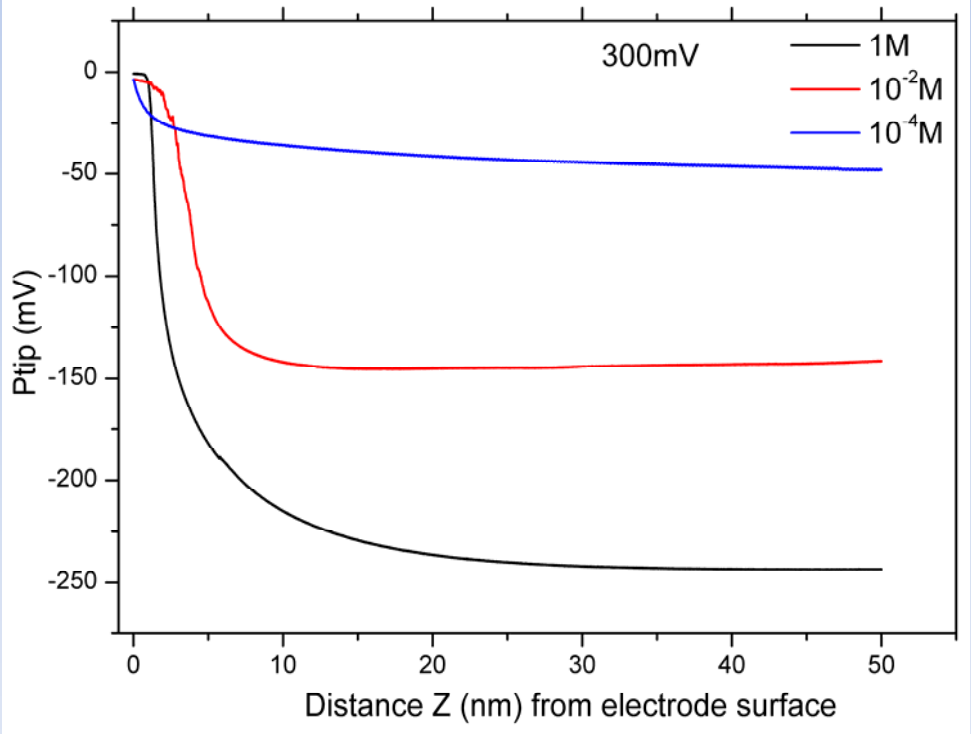
Estimation of the parameters:

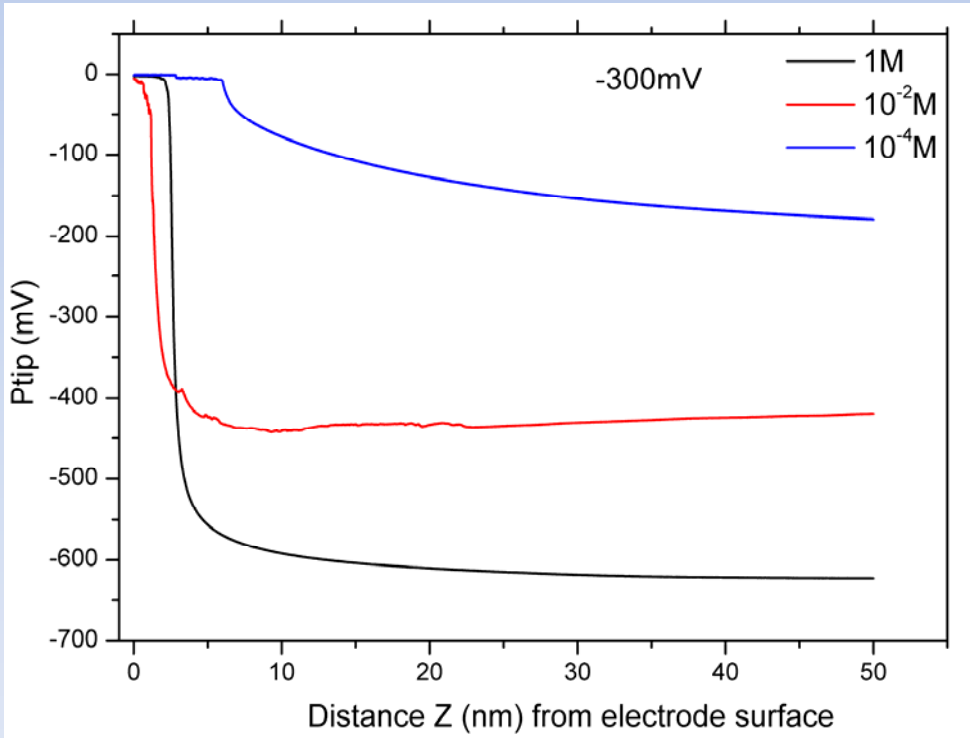
- Debye length
- Concentration profile at the interface.

Recent experimental results

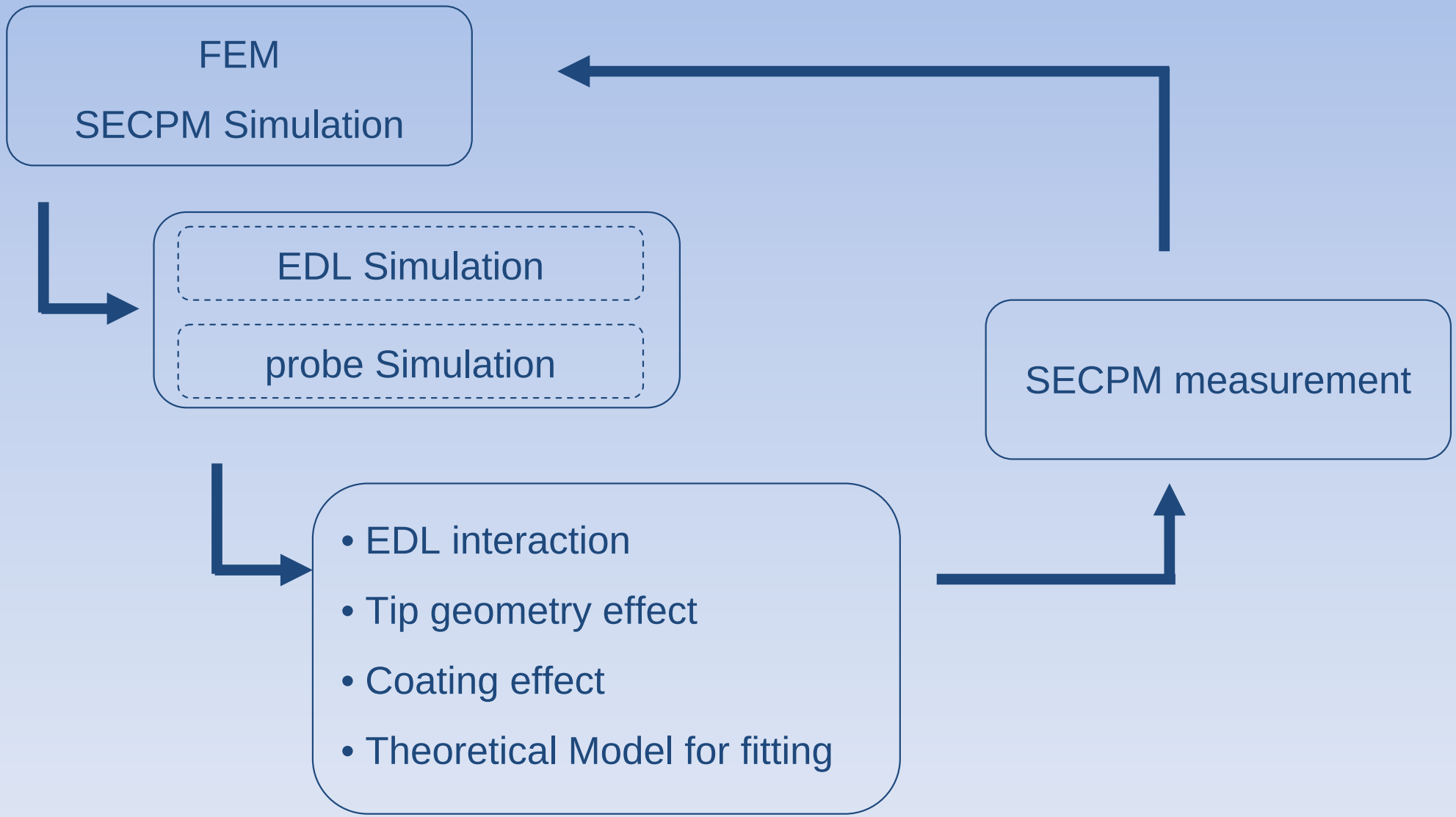
C. Hurth, C. Li, and Allen J. Bard, *J. Phys. Chem. C* **2007,** *111,* 4620-4627

- The Gouy-Chpmann-Stern failed to describe the experiment results
- Non-Boltzmannian distribution of the ions
- The tip perturbs the electric double layer (EDL interaction)
- Theoretical approach is needed to interpret the SECPM measurement

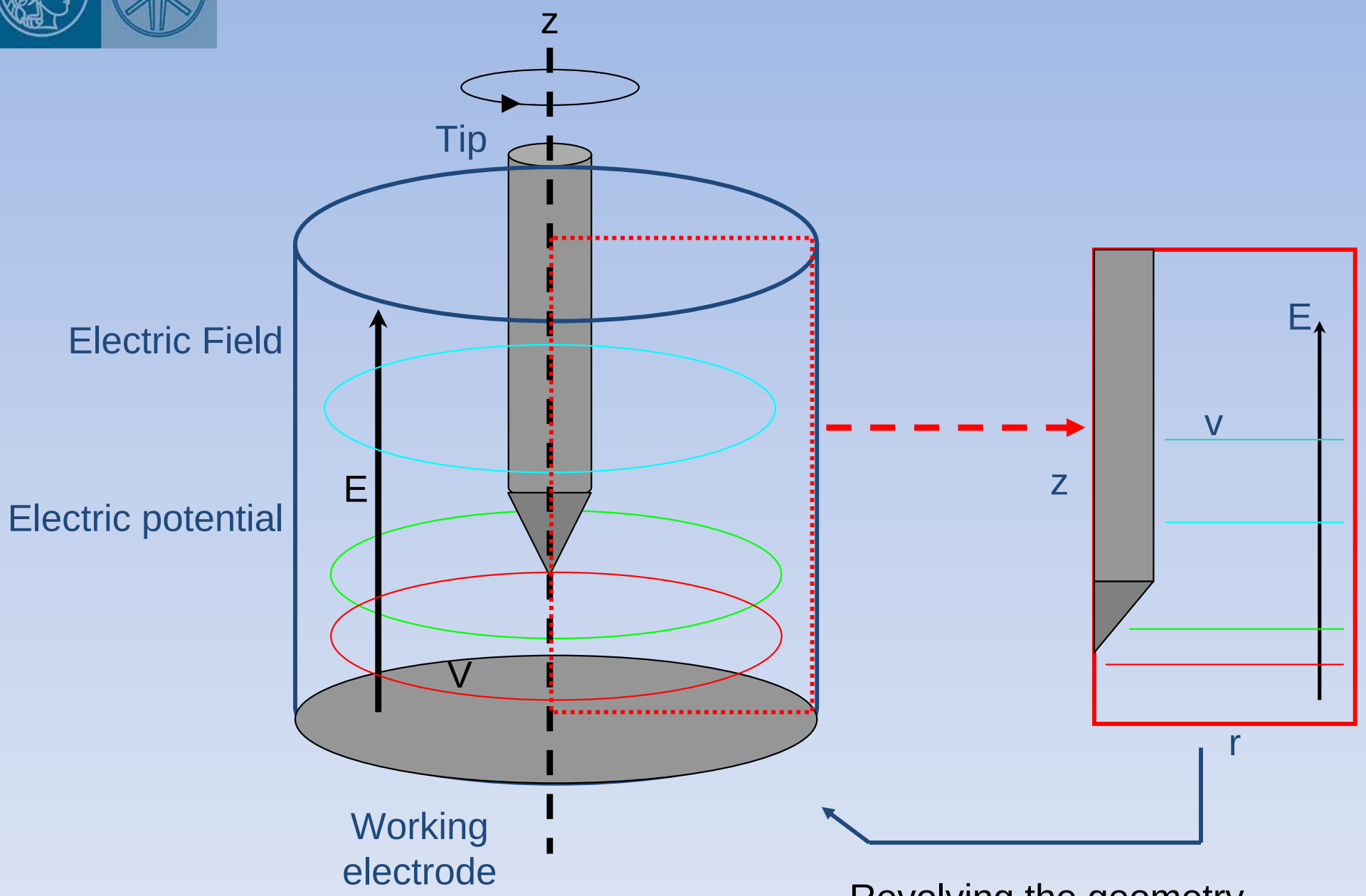




Motivation


FEM
SECPM Simulation
EDL Simulation
probe Simulation
SECPM measurement
• EDL interaction
• Tip geometry effect
• Coating effect
• Theoretical Model for fitting

Axial symmetric Model



Nernst-Planck Equation in the steady state

Symmetric electrolyte 1:1

$$-D_1\nabla^2 C_1 - D_1\frac{zF}{RT}\nabla\left(C_1\nabla V\right)=0$$

$$-D_2\nabla^2 C_2 - D_2\frac{zF}{RT}\nabla\left(C_2\nabla V\right)=0$$

$$-\nabla\left(\varepsilon_o\varepsilon\ \nabla V\right)=\rho=\sum NC_i zq$$

EDL

$$\varepsilon_0\varepsilon\ \nabla V_t=\rho_t \quad Gauss'\ equation$$

$$Q=\int N\ z_1 q\,C_1(x,y)+N\ z_2 q\,C_2(x,y)$$

Surrounding the metallic tip

Probe

SECPM

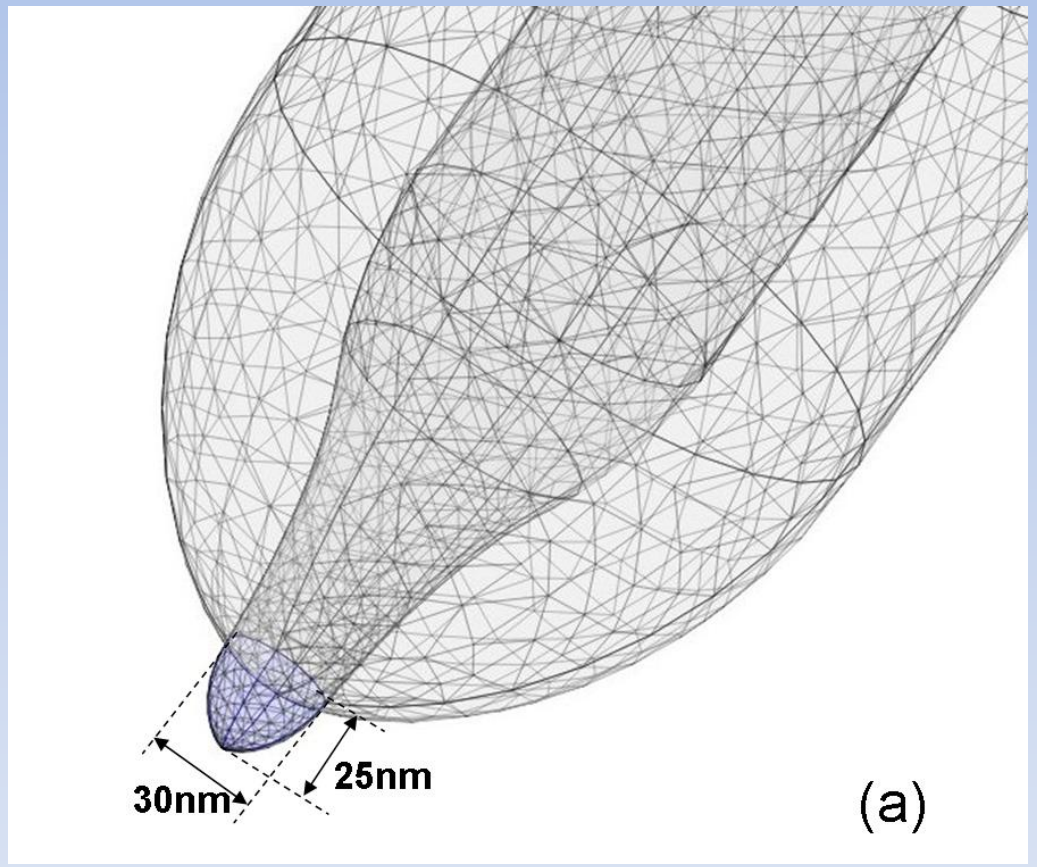
Solving the PD equations for C_1 C_2 V and V_t

Finite element method

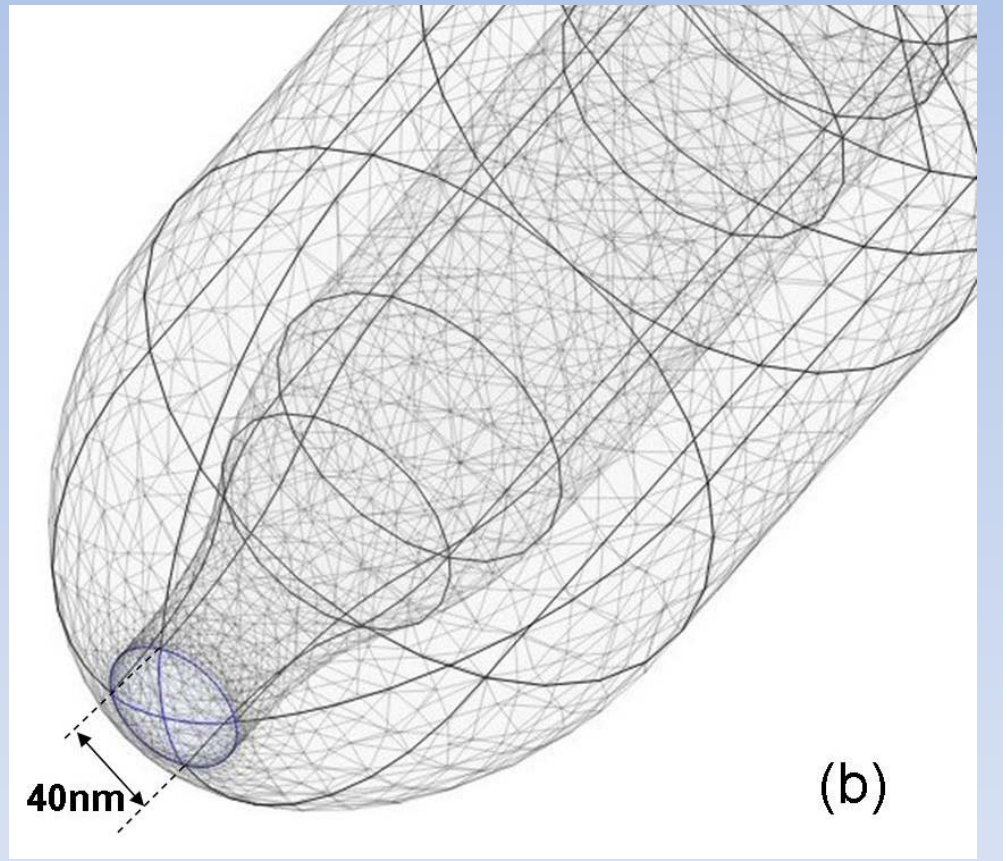
Multiphysics Modelling

Tip geometry effect

Protruding tip

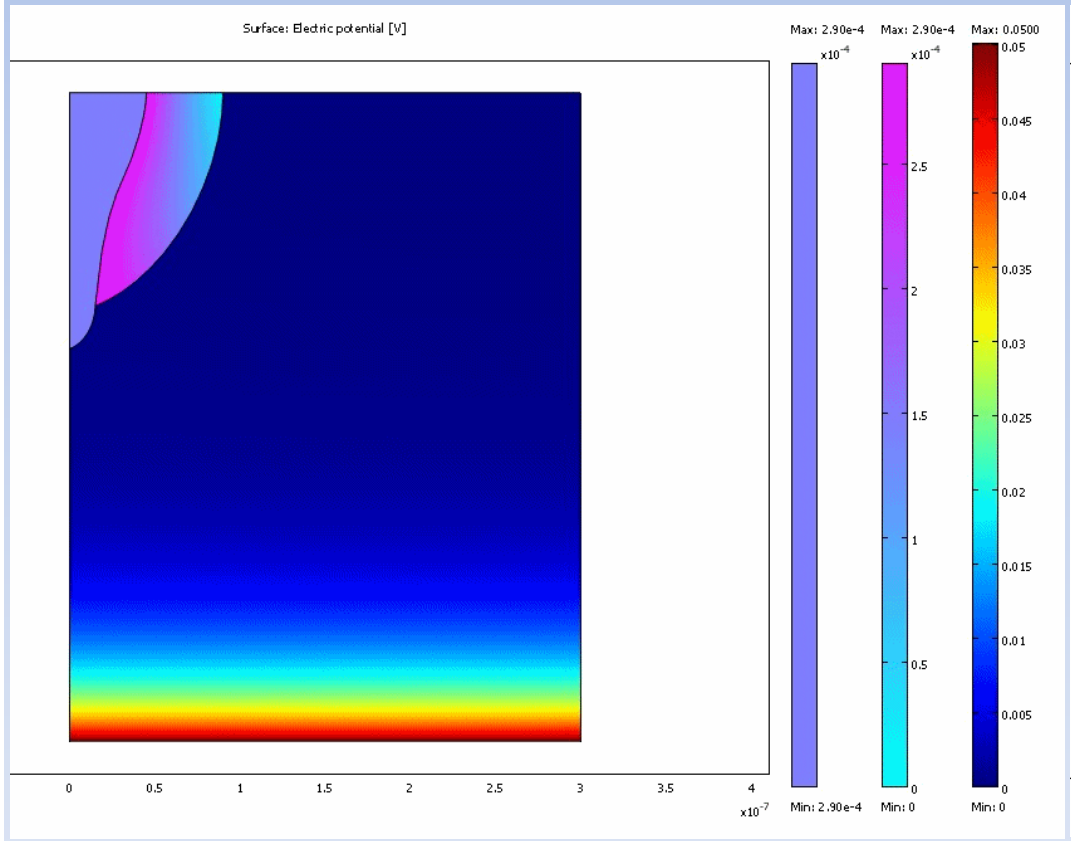


Non-Protruding tip

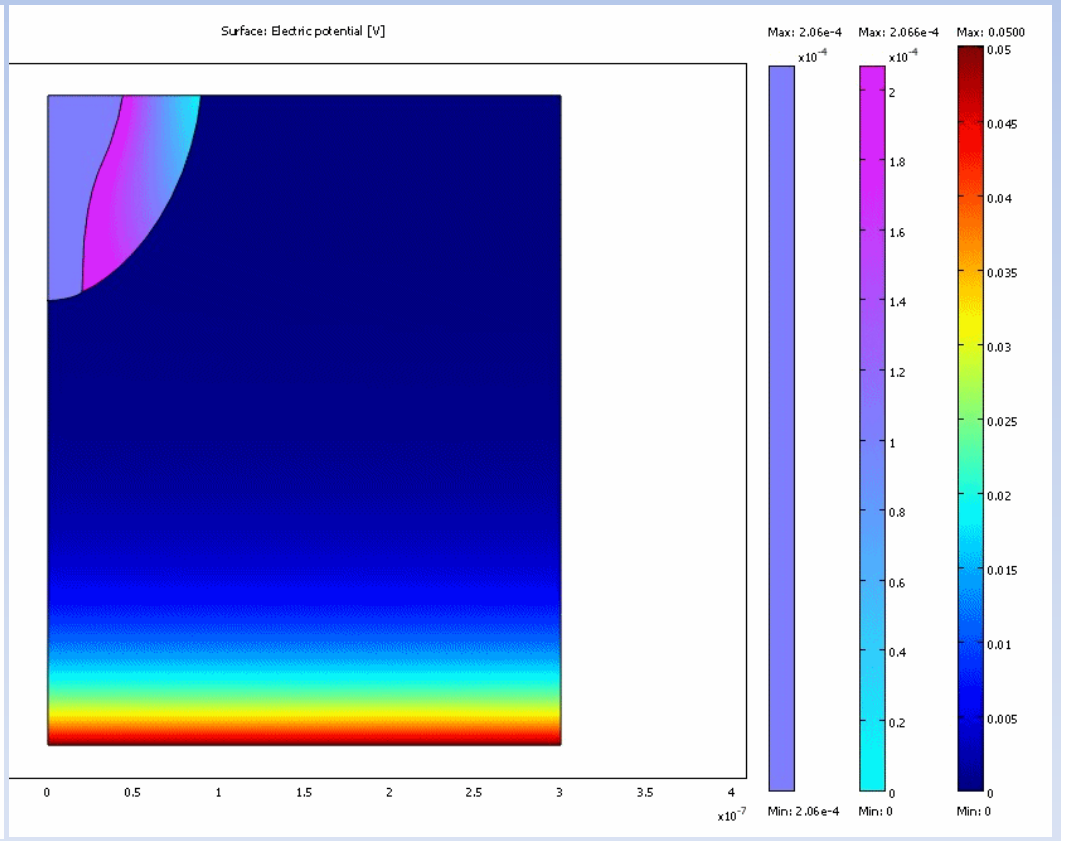


Tip geometry effect: Electric potential distribution

Protruding tip

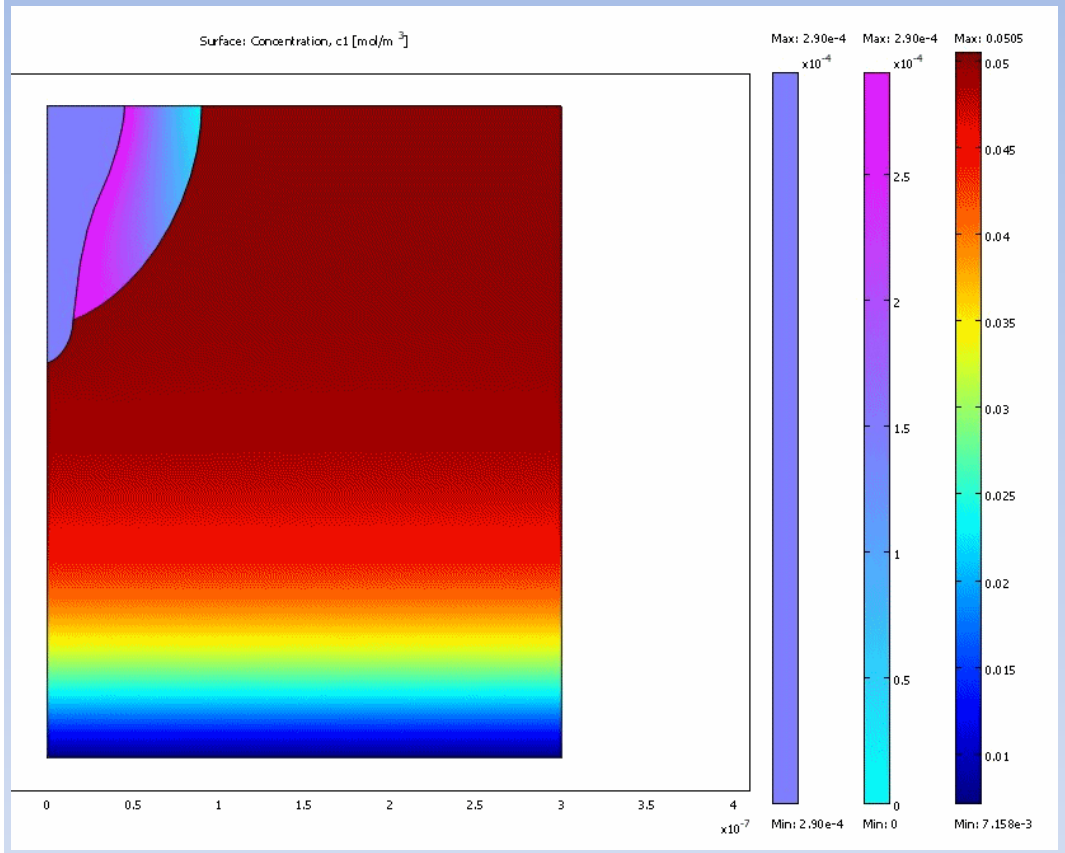


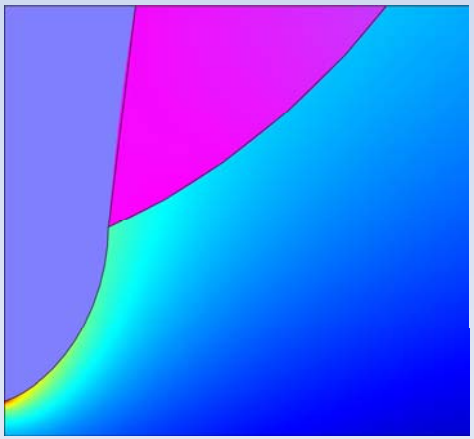
Non-Protruding tip



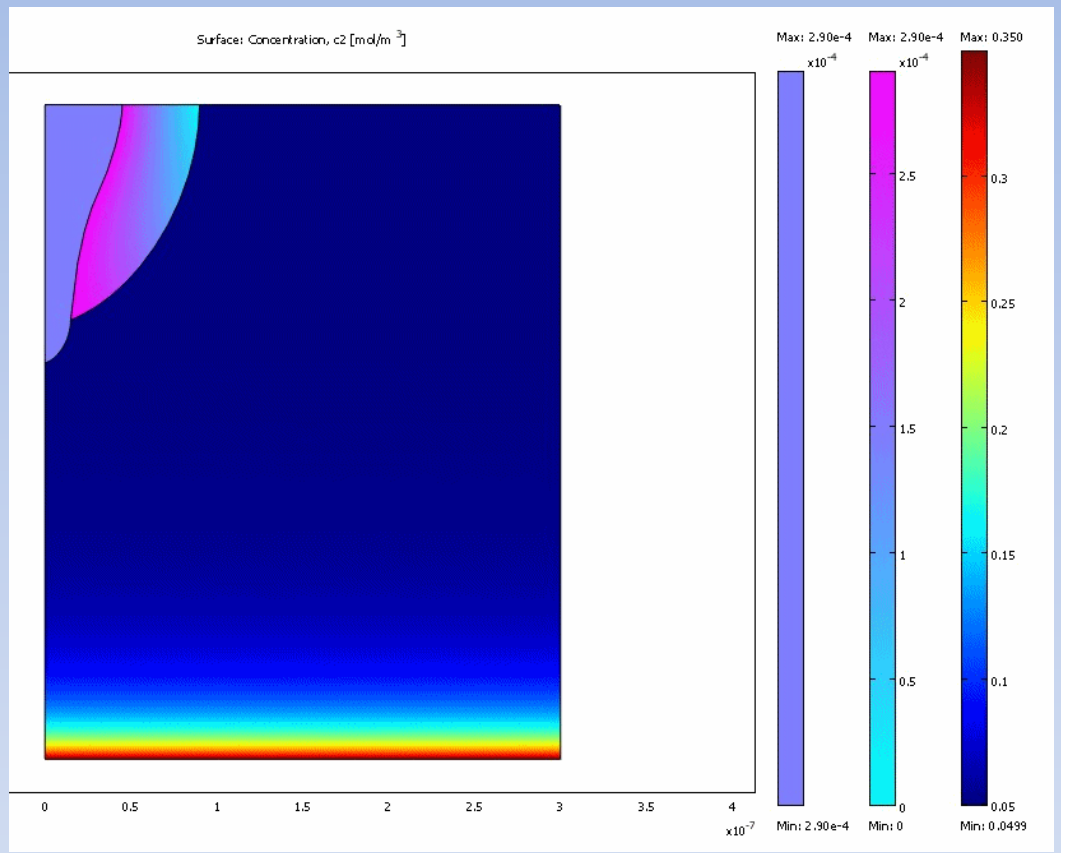
Tip geometry effect: Ions distribution

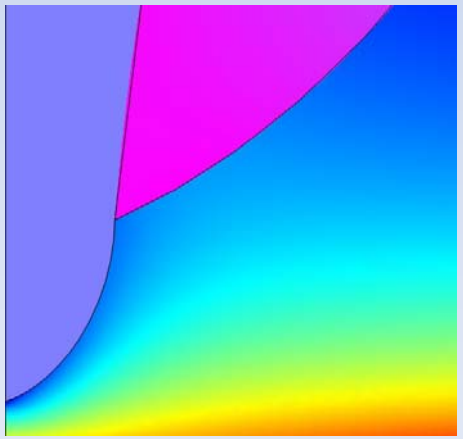
Cation





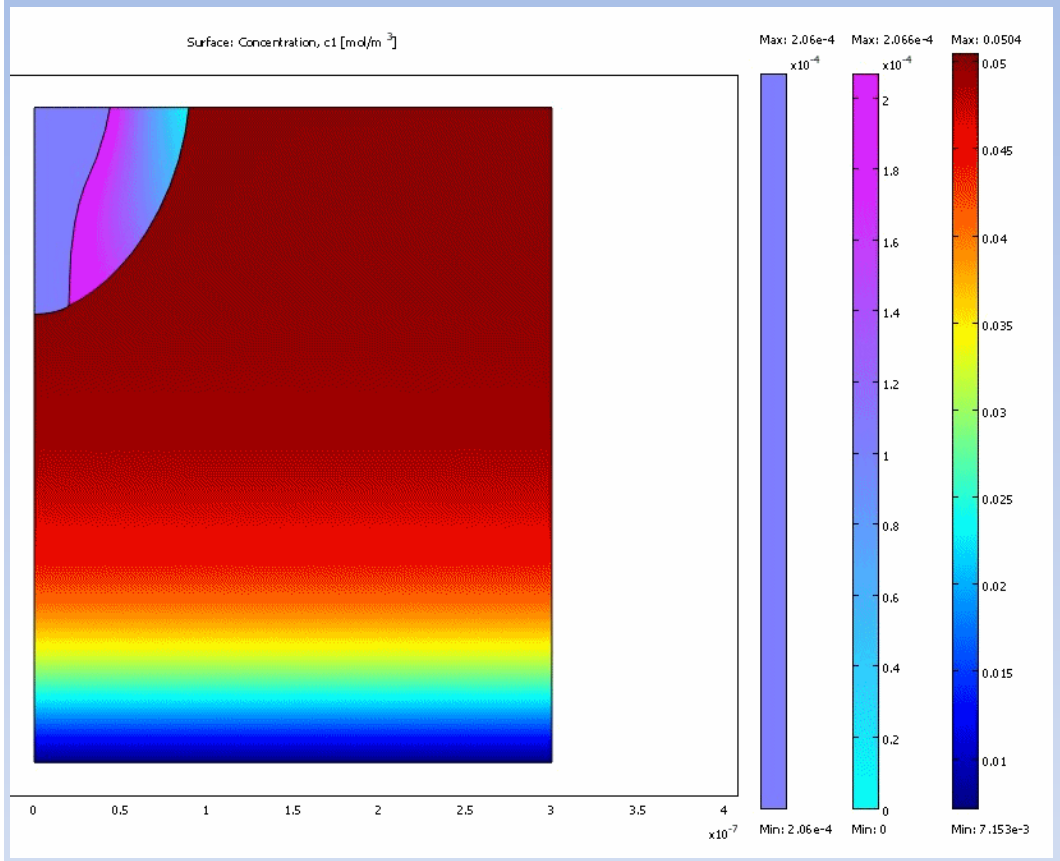
Anion

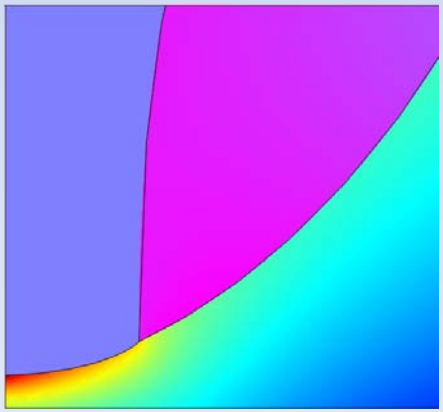




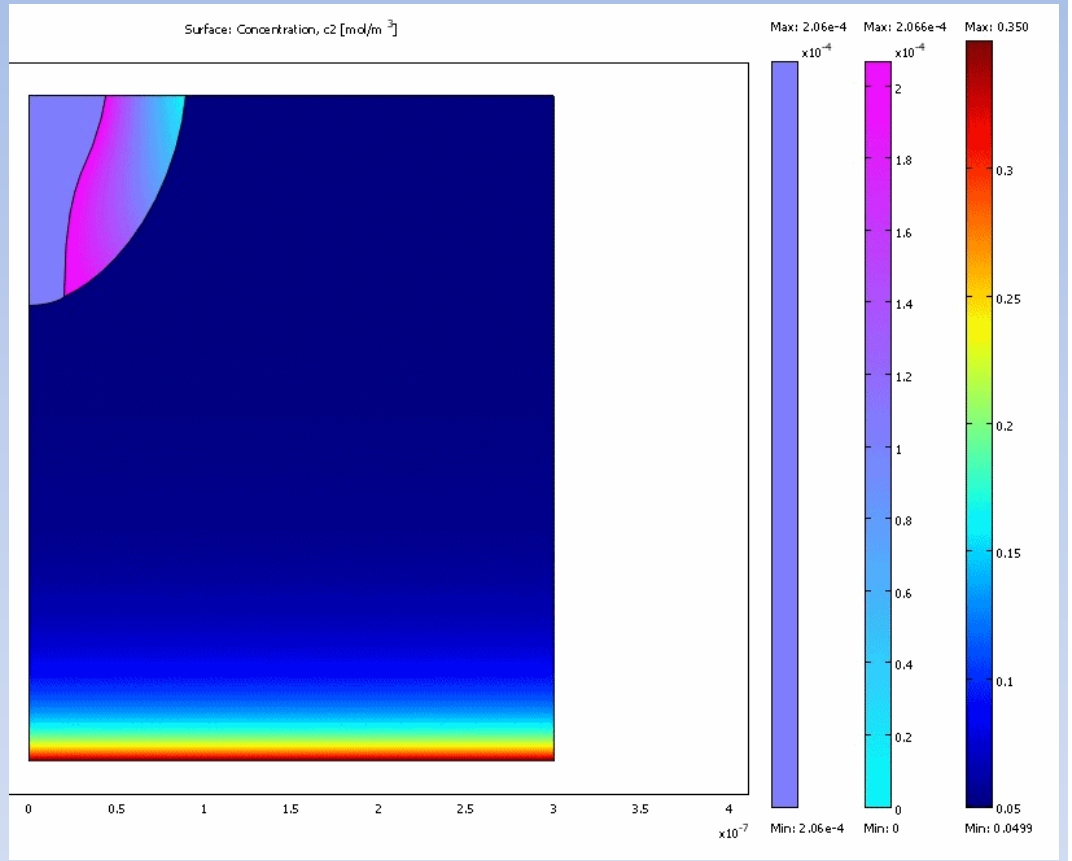
Tip geometry effect: Ions distribution

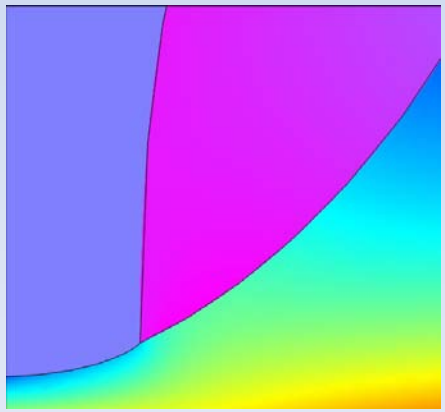
Cation



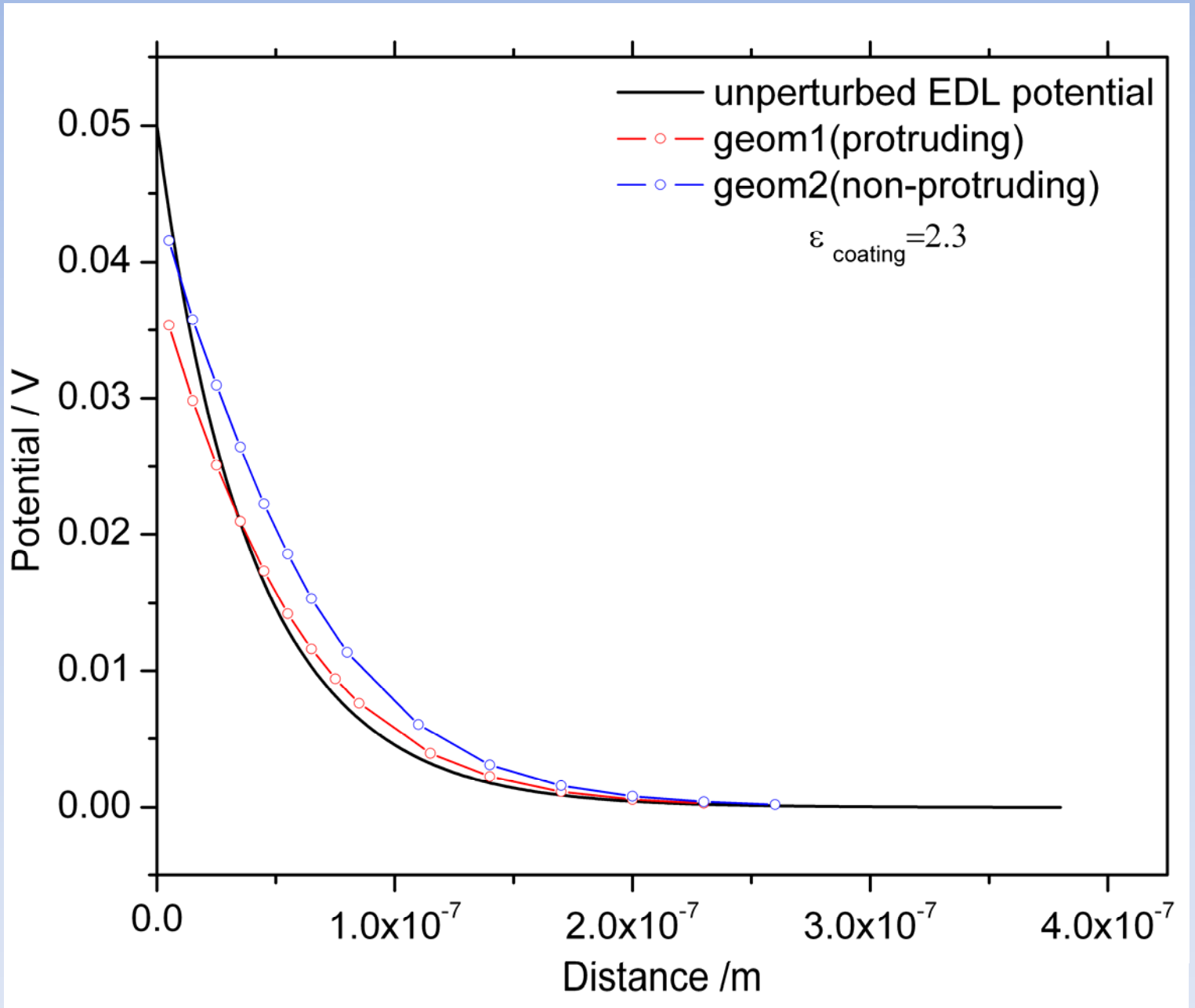


Anion

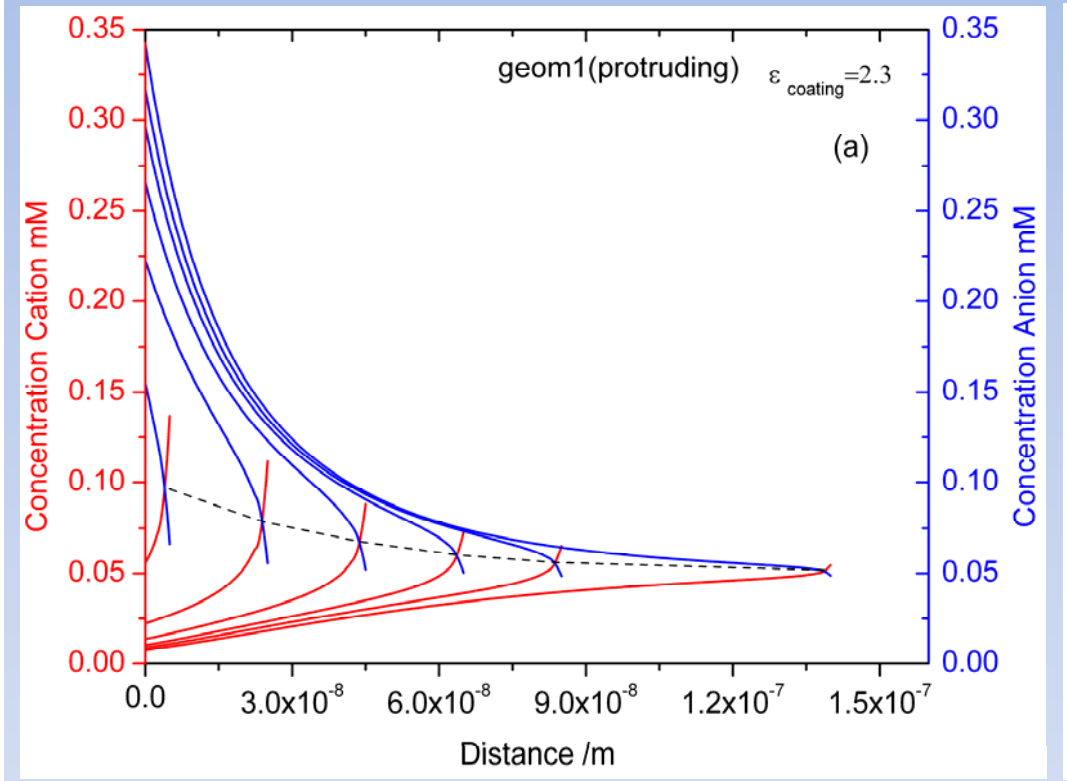


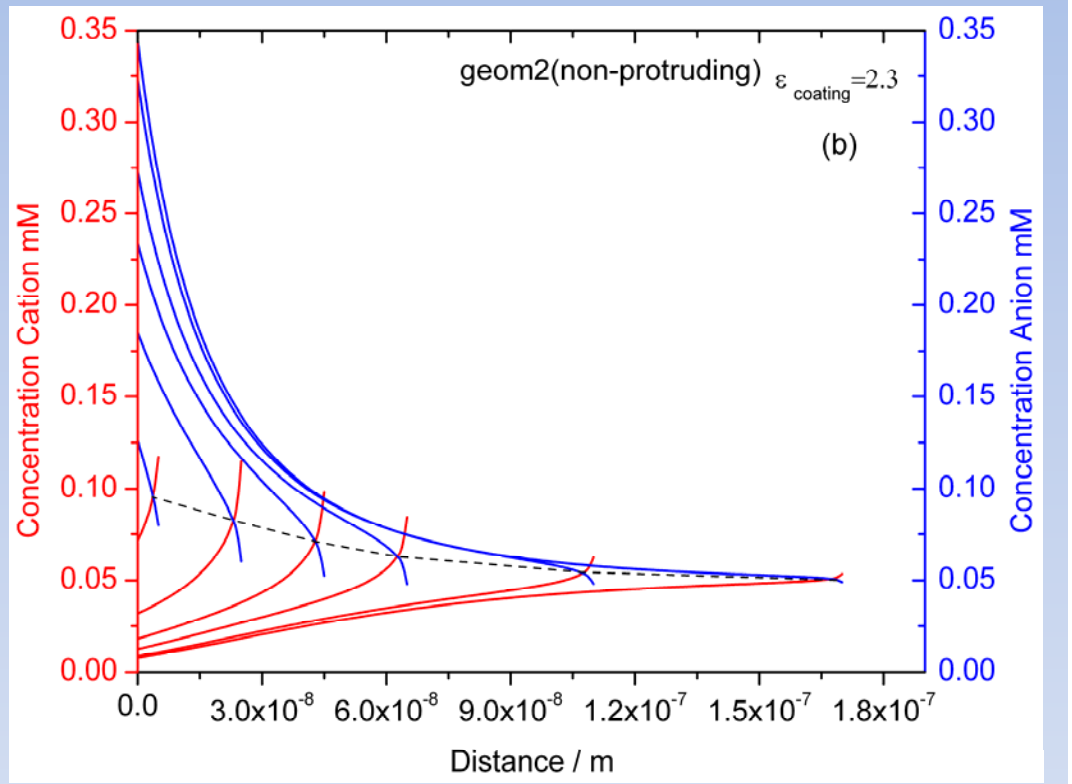


Tip geometry effect: electric potential



Tip geometry effect: ions distribution

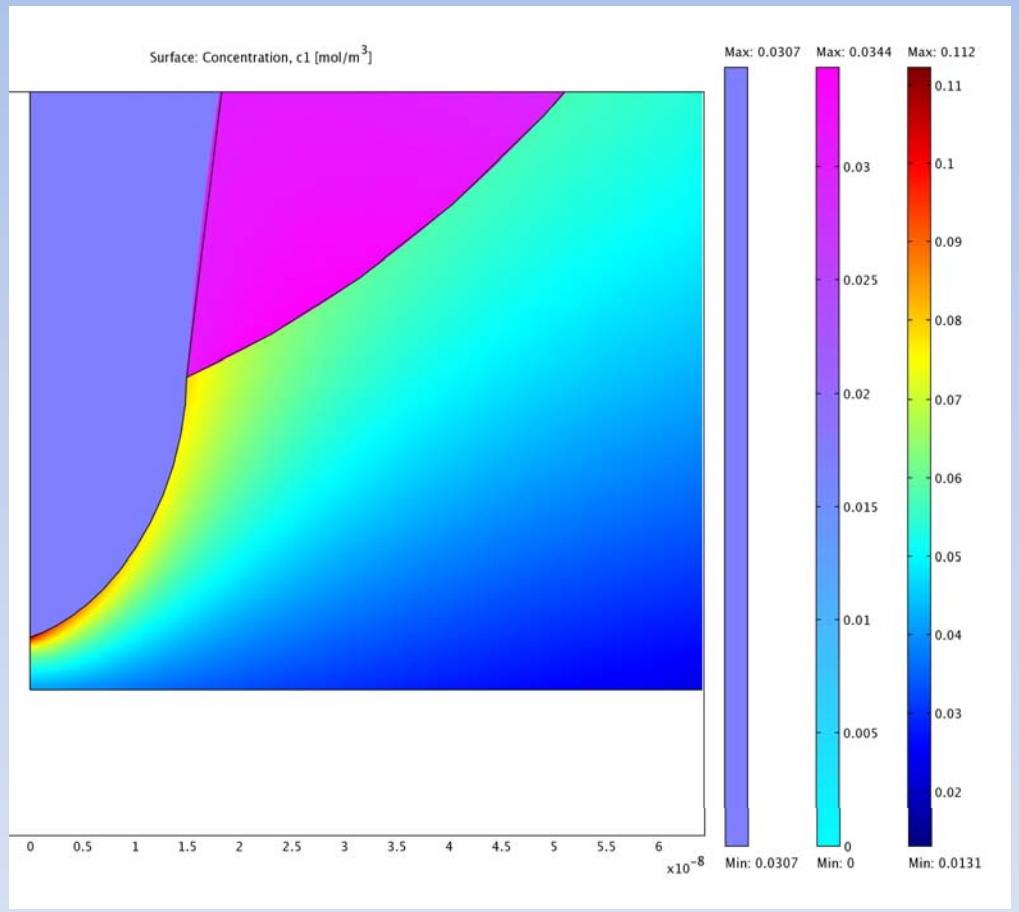




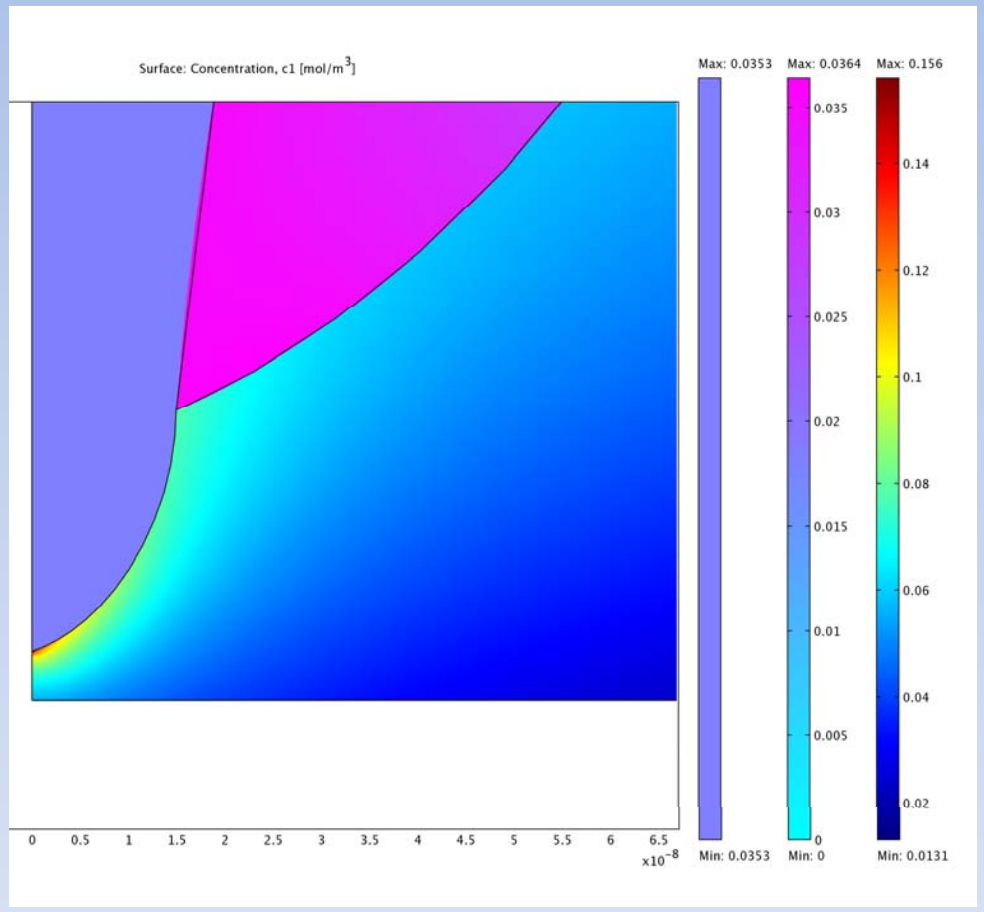
Coating effect

Cation distribution

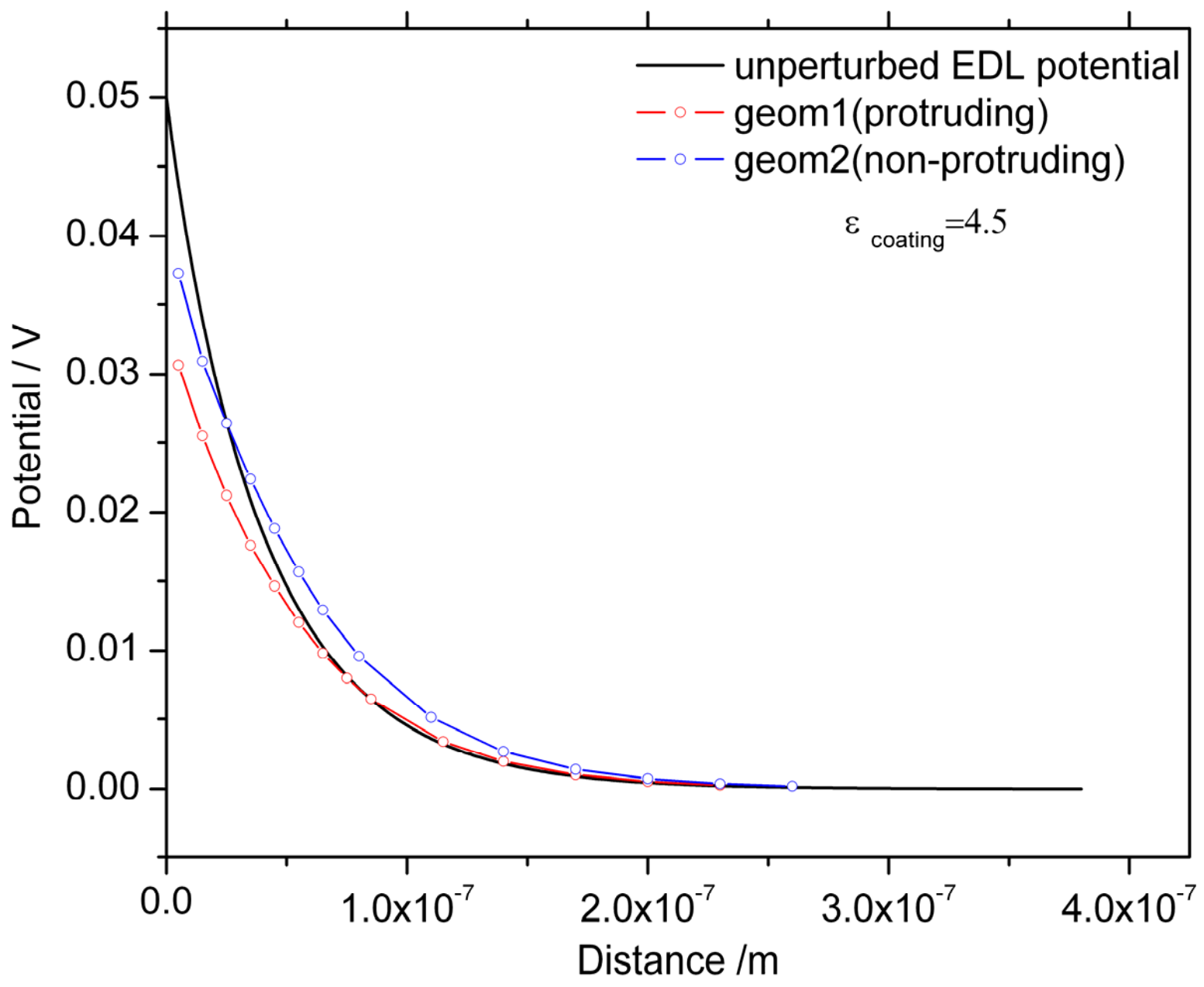
ε =4.5



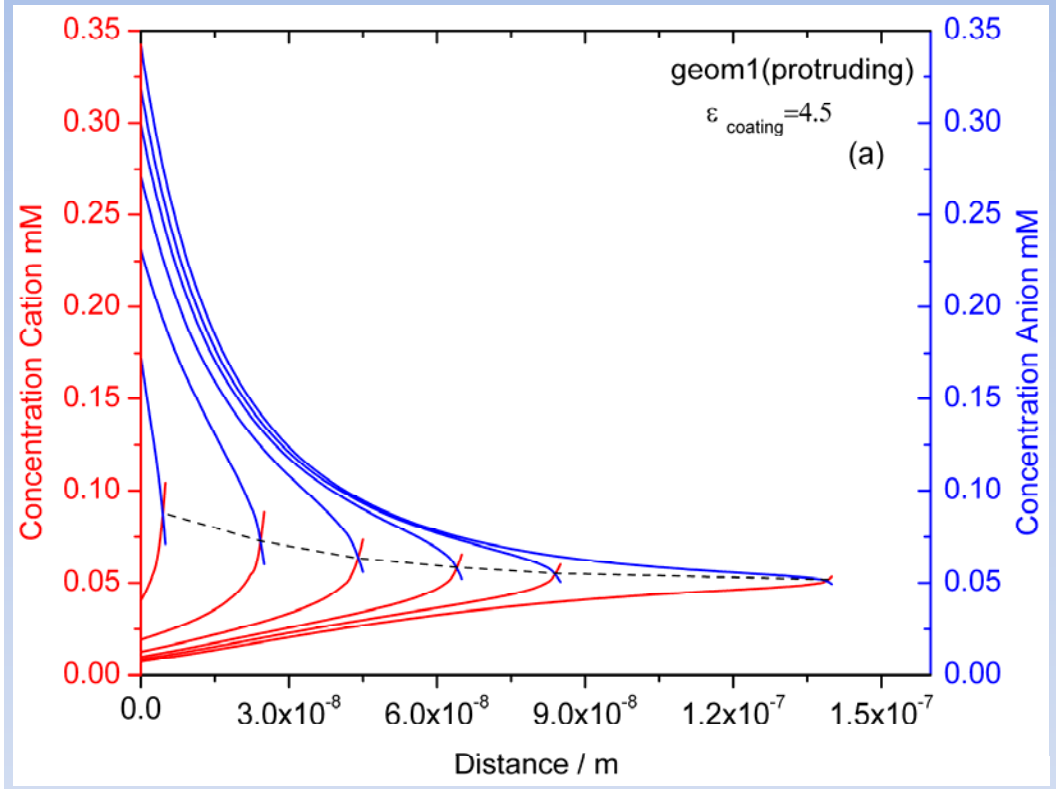
ε =2.3

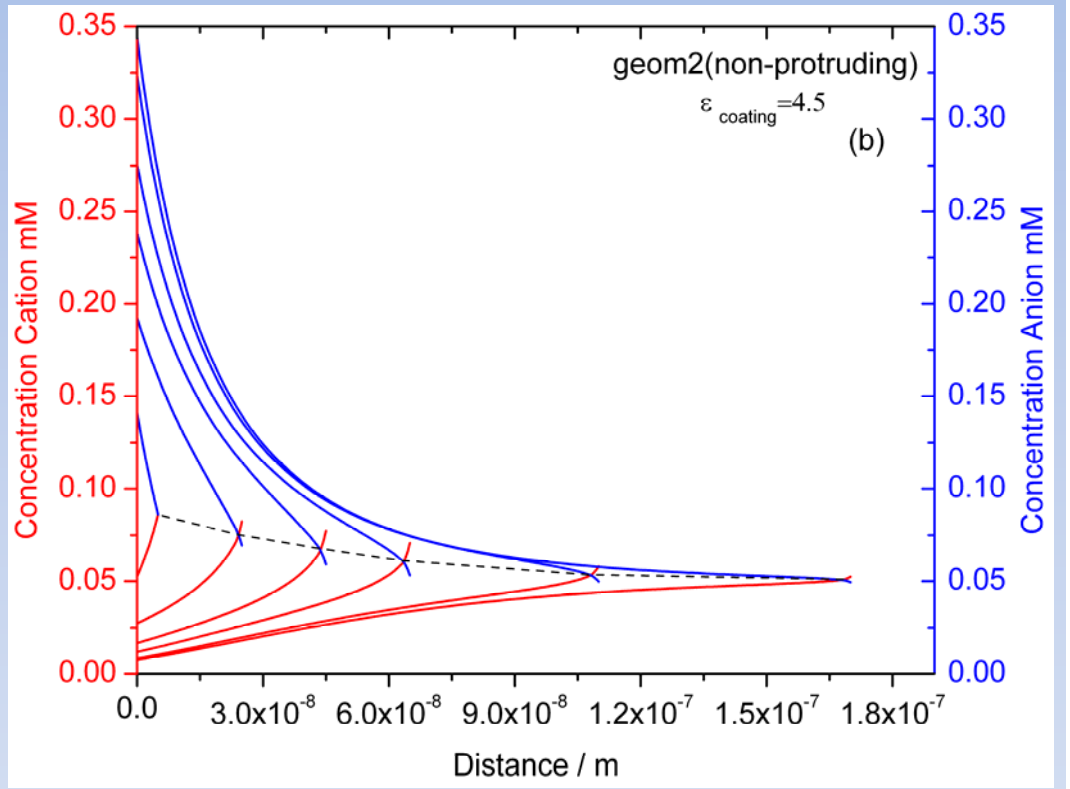


Coating effect: electric potential



Coating effect: ions distribution





Outlook: Ion size effect, steric effect

SECPM experiment: applied electric potential >200 mV

↓

Steric effect

↓

The Gouy-Chapmann-Stern Model not valid for SECPM fitting or simulation

↓

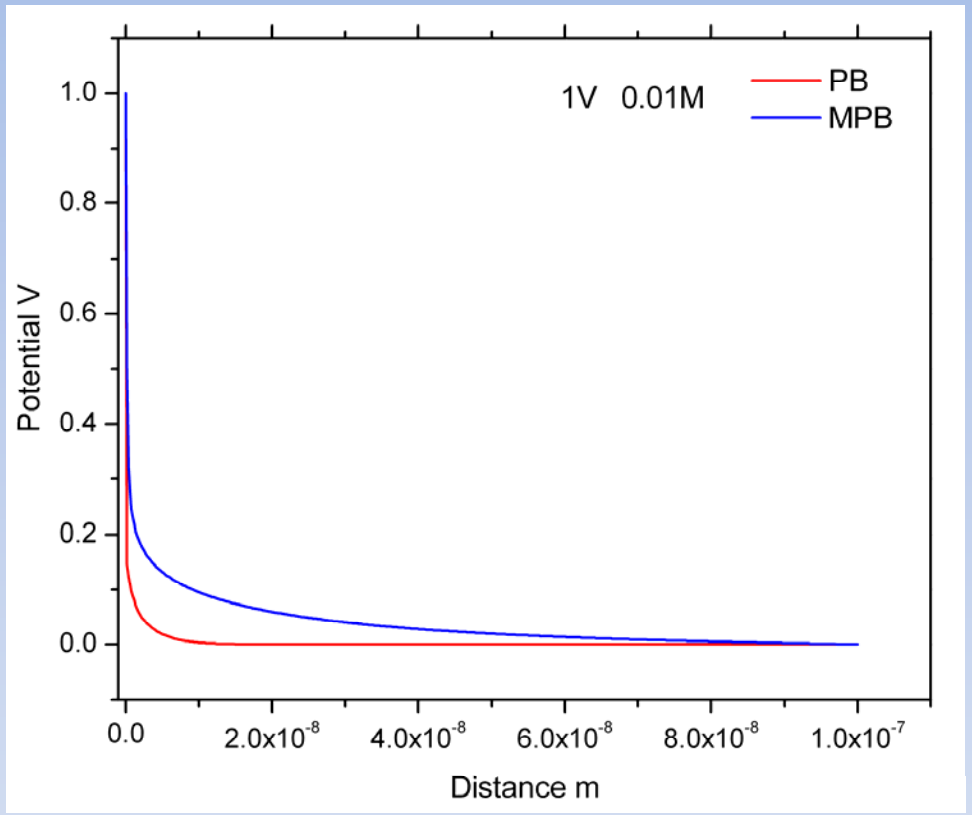
Modified Poisson Boltzmann

$$\nabla^2 V = \frac{NzqC_b}{\varepsilon\varepsilon_0} \frac{2\sinh\left(\frac{zqV}{kT}\right)}{1+2\upsilon\sinh^2\left(\frac{zqV}{kT}\right)}$$

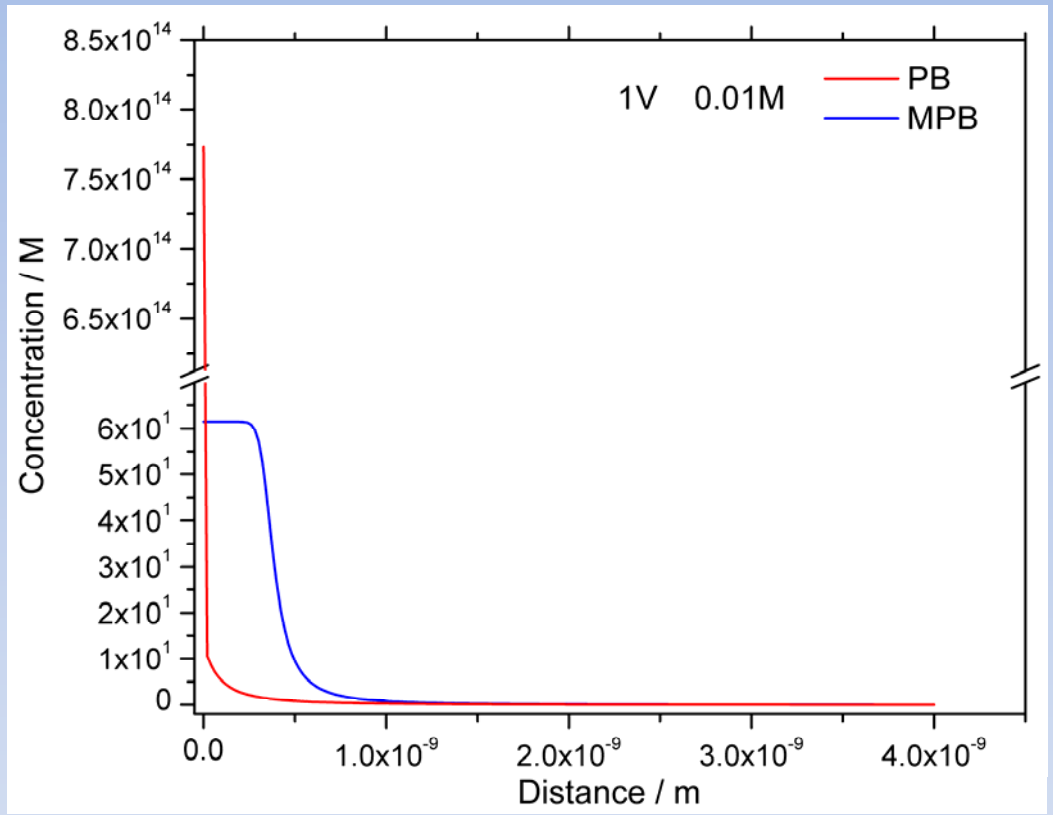
M. S. Kilic, M.Z Bazant and A. Ajdari: *Phys. Rev. E,* 75, 021502 (2007)

Steric effect

Potential



Cation concentration



Near future: SECPM Simulation with the modified Poisson-Boltzmann Model

Thanks to:

- IMPRS-SurMat program for financial support
- Dr. Andreas Erbe form MPIE
- YOU for listening