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Screening Effects in Probing the Electric Double Layer by Scanning Electrochemical Potential Microscopy (SECPM)

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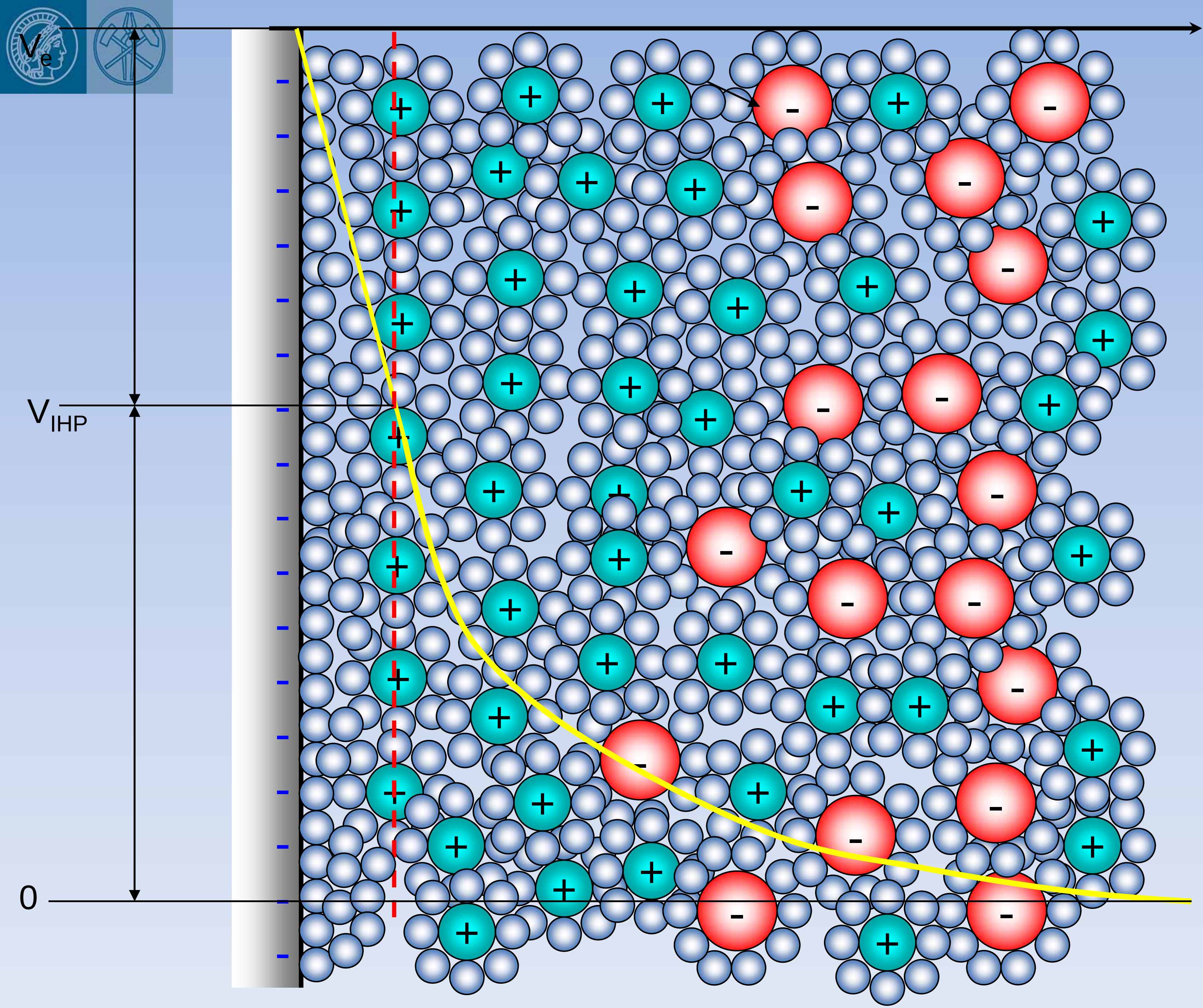


V_e
V_{IHP}
0

Experimental techniques

- Atomic force microscopy
- Scanning tunneling microscopy
- Scanning electrochemical microscopy : EC-STM, SECPM…

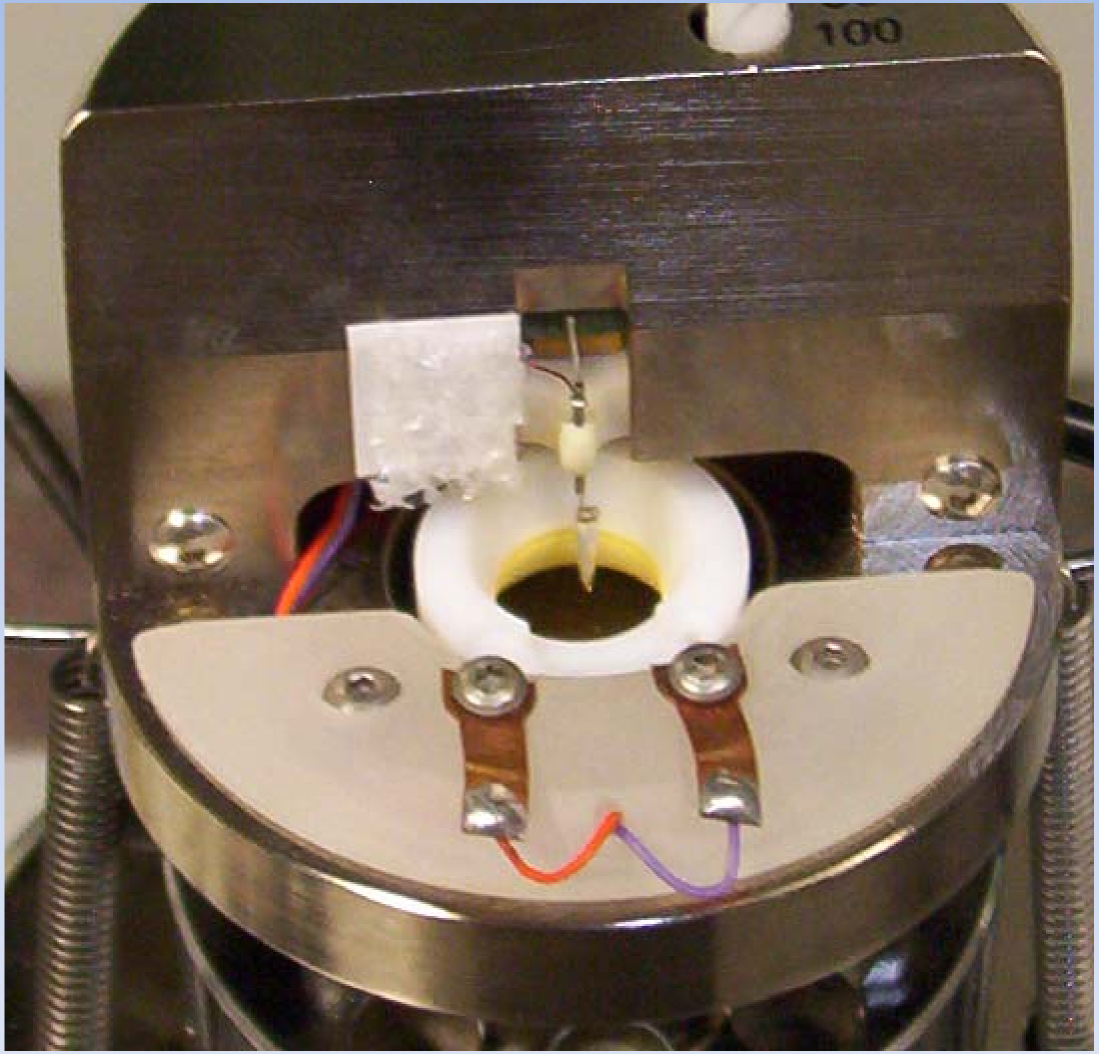
Allow electrochemists to learn more about the structure of the double layer at the atomic level.

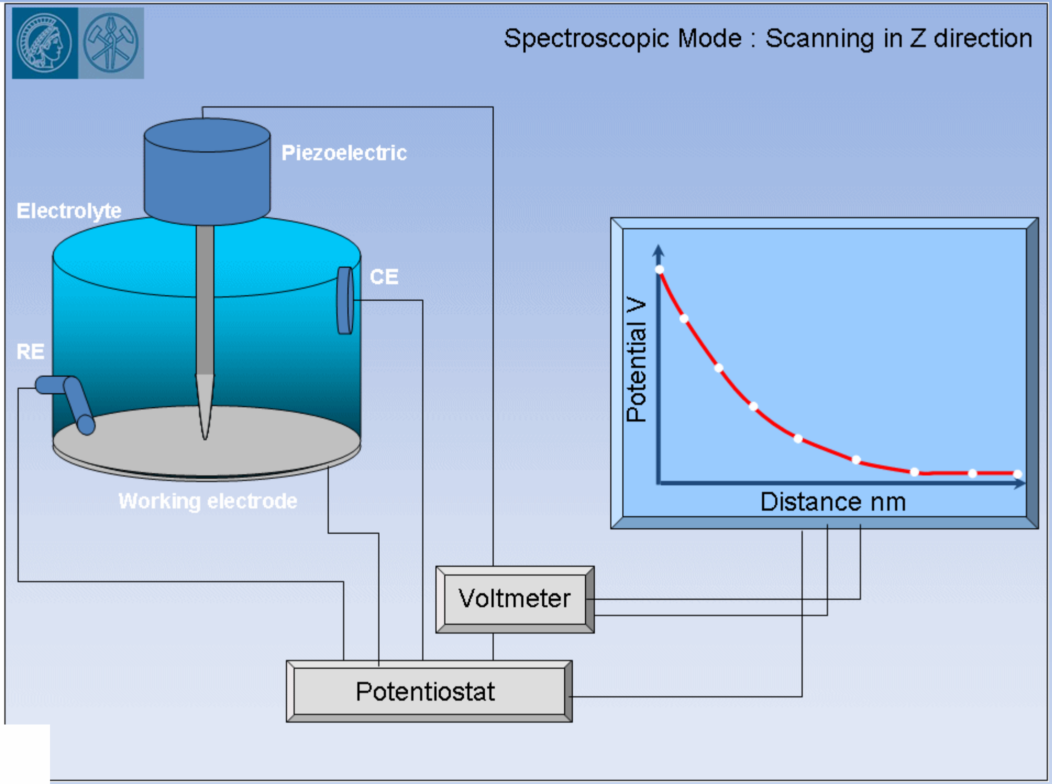
On the theoretical side, the new numerical methods of calculations provide a possibility to simulate, all the changes within the double layer.

Scanning Electrochemical Potential Microscopy (SECPM)

Probing the potential profile of the EDL

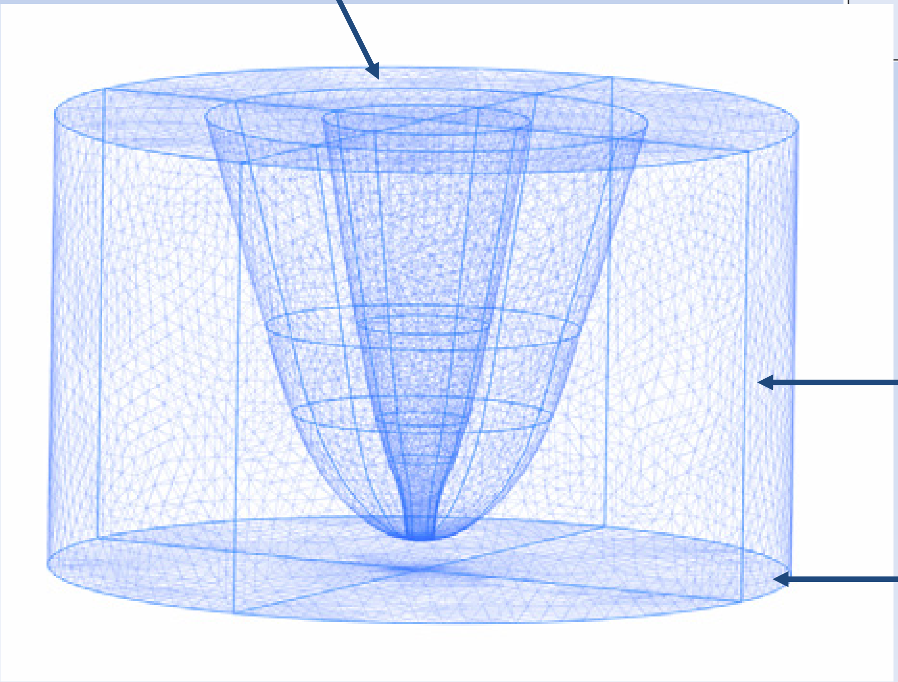
SECPM :Patented in 2007





EDL Potential Profiling

SECPM probe

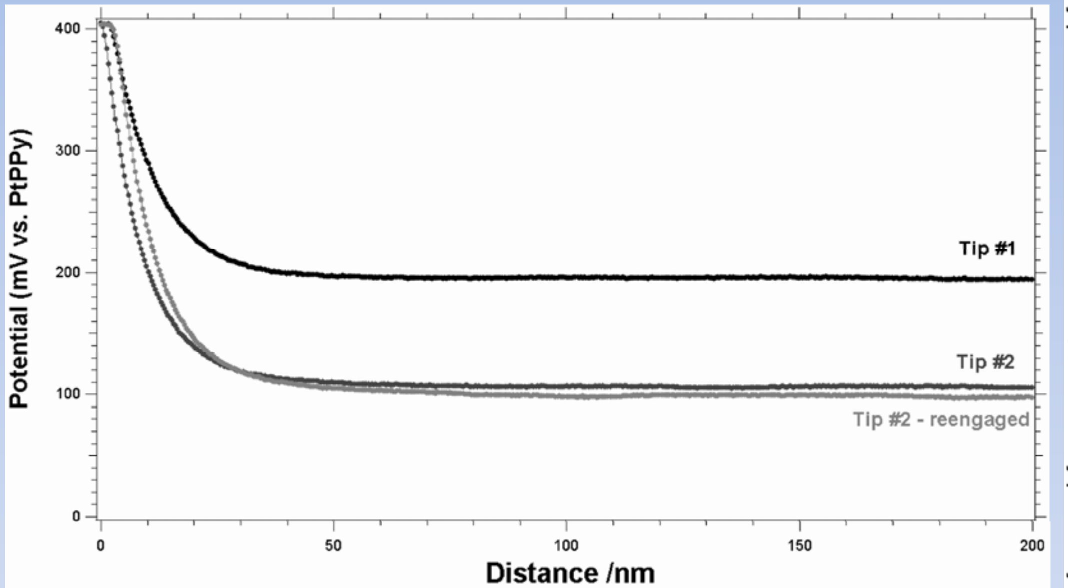


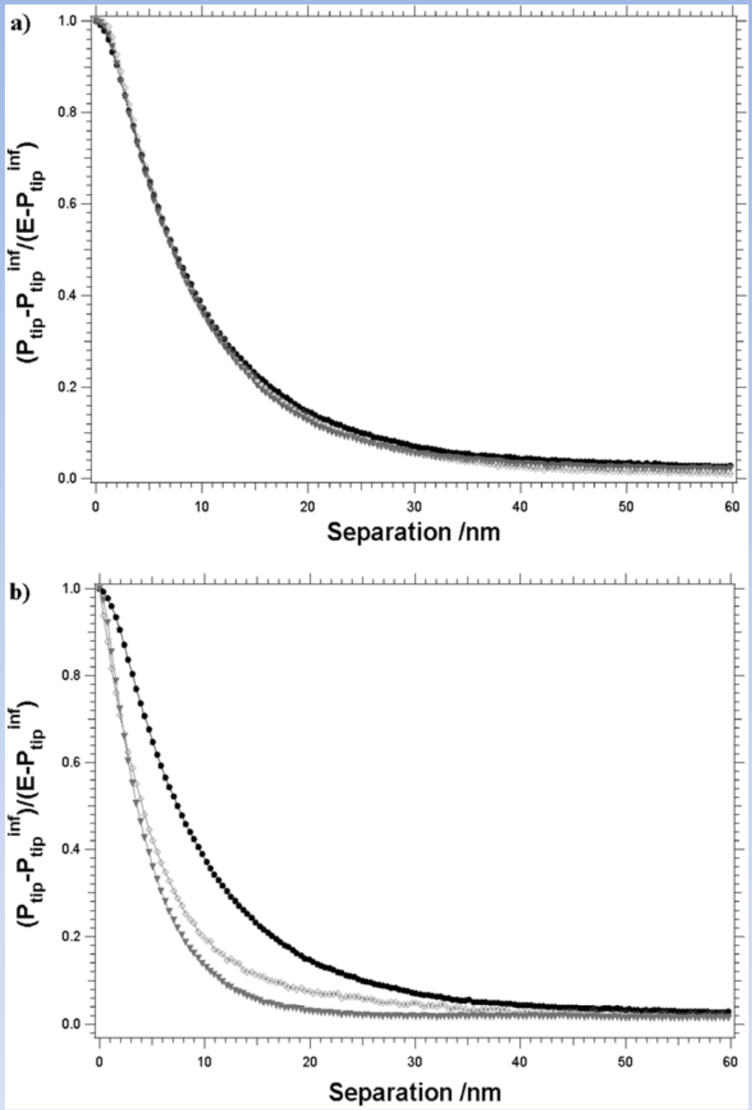
Electrolyte

Electrode

Previous experimental results

Potential profile

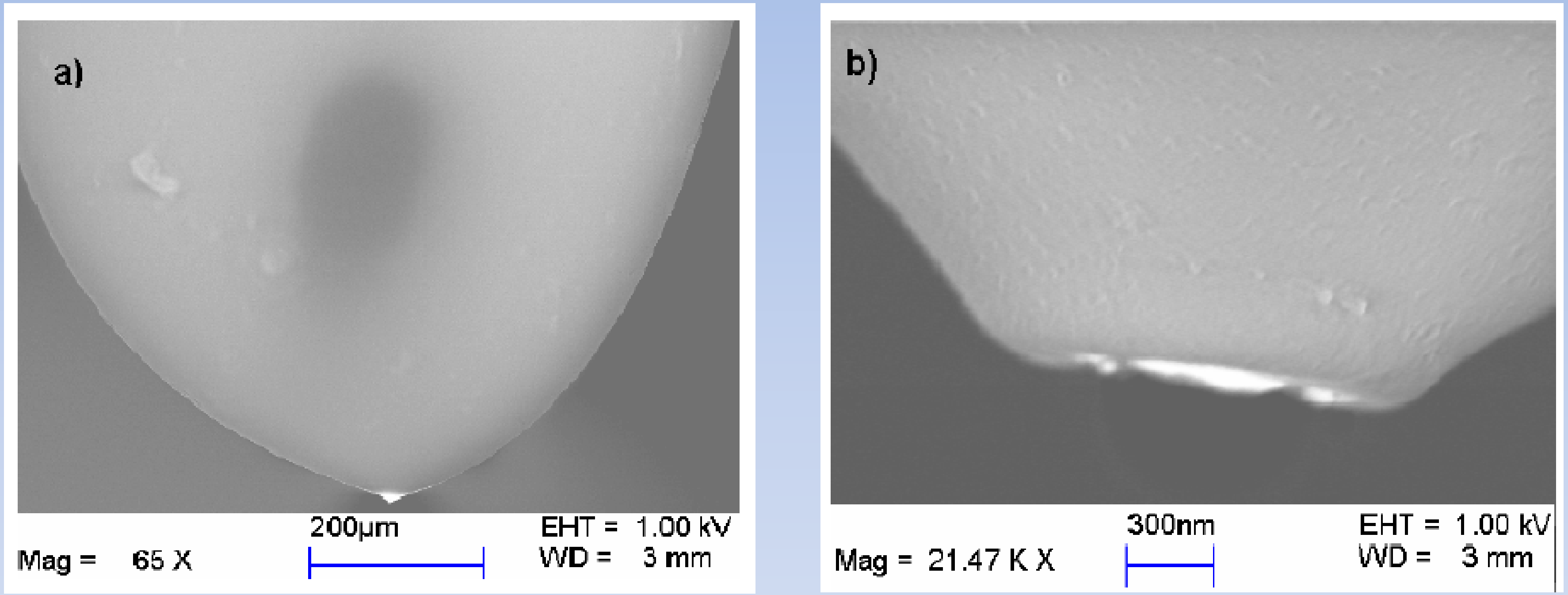




- In the SECPM experiments presented here, the decay length of the potential profile was always smaller than the Debye length from the Gouy−Chapman−Stern theory
- Debye length depends on the applied potential.

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

SECPM probe

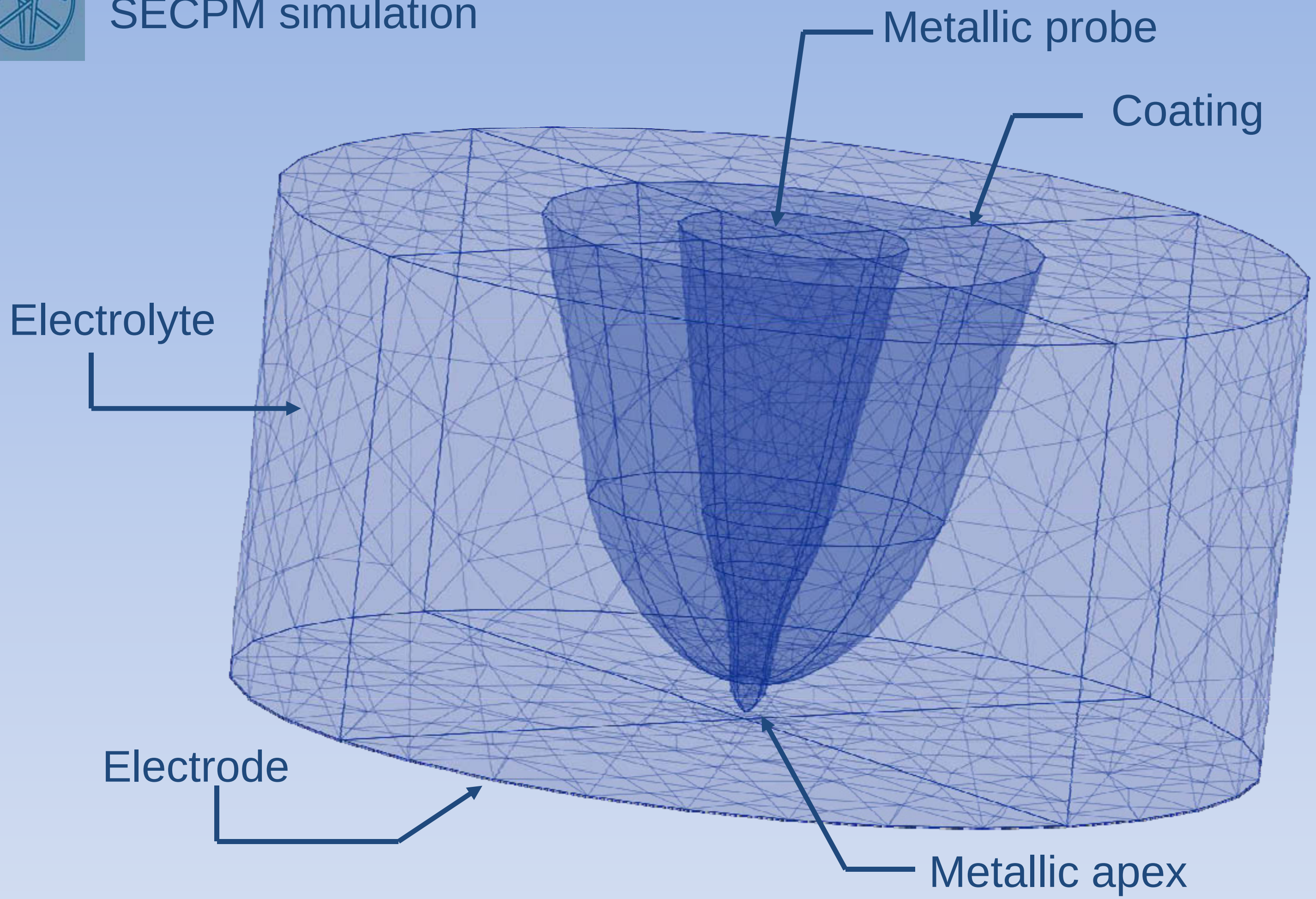


Scanning electron micrographs of a PtIr tip prepared by the procedure described earlier in the text. at low (a) and high (b) magnification.

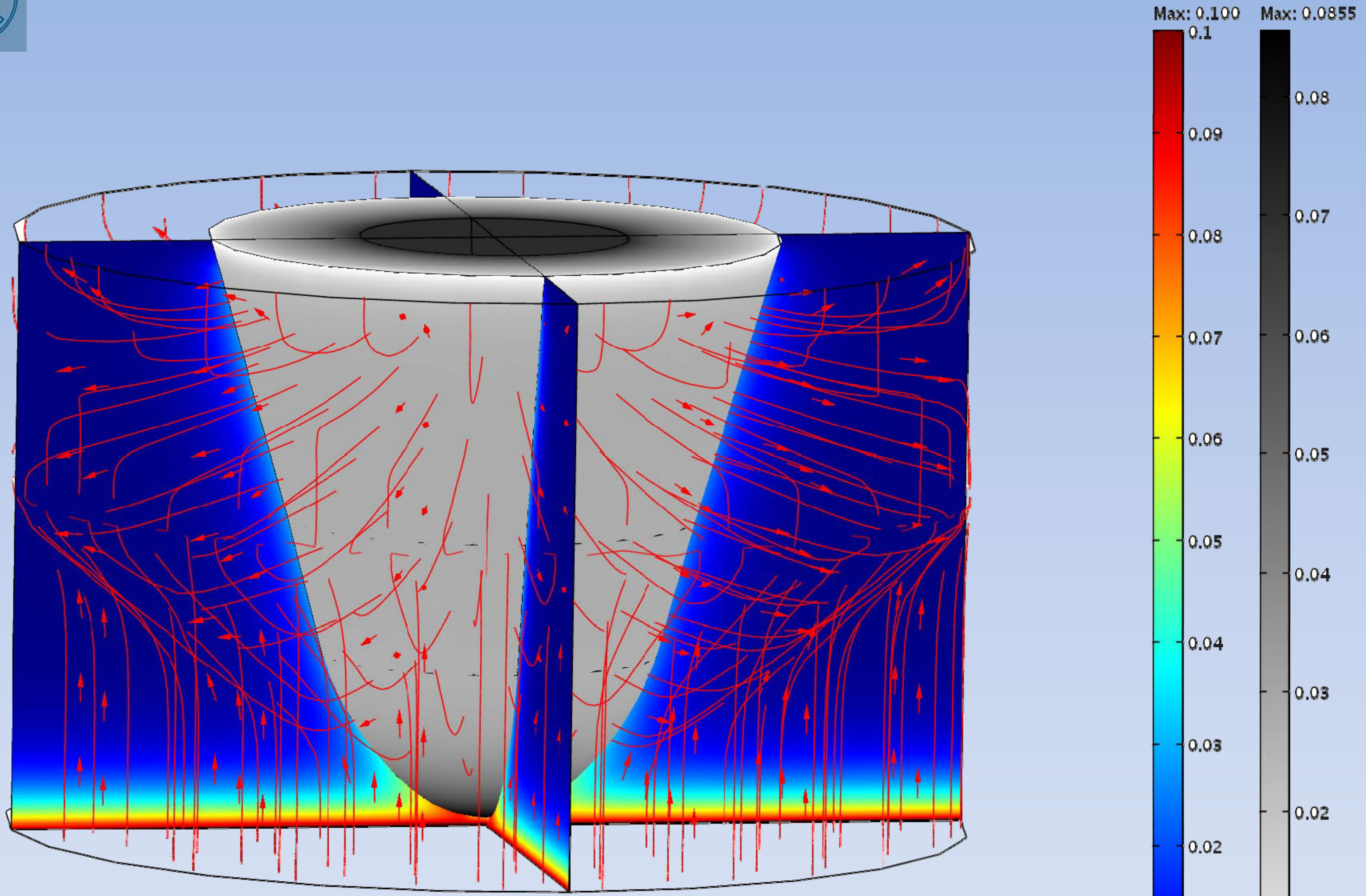
PhD Thesis C. M. Hurth 2005 under the supervision of Prof. Allen J. Bard,

The University of Texas at Austin

SECPM simulation



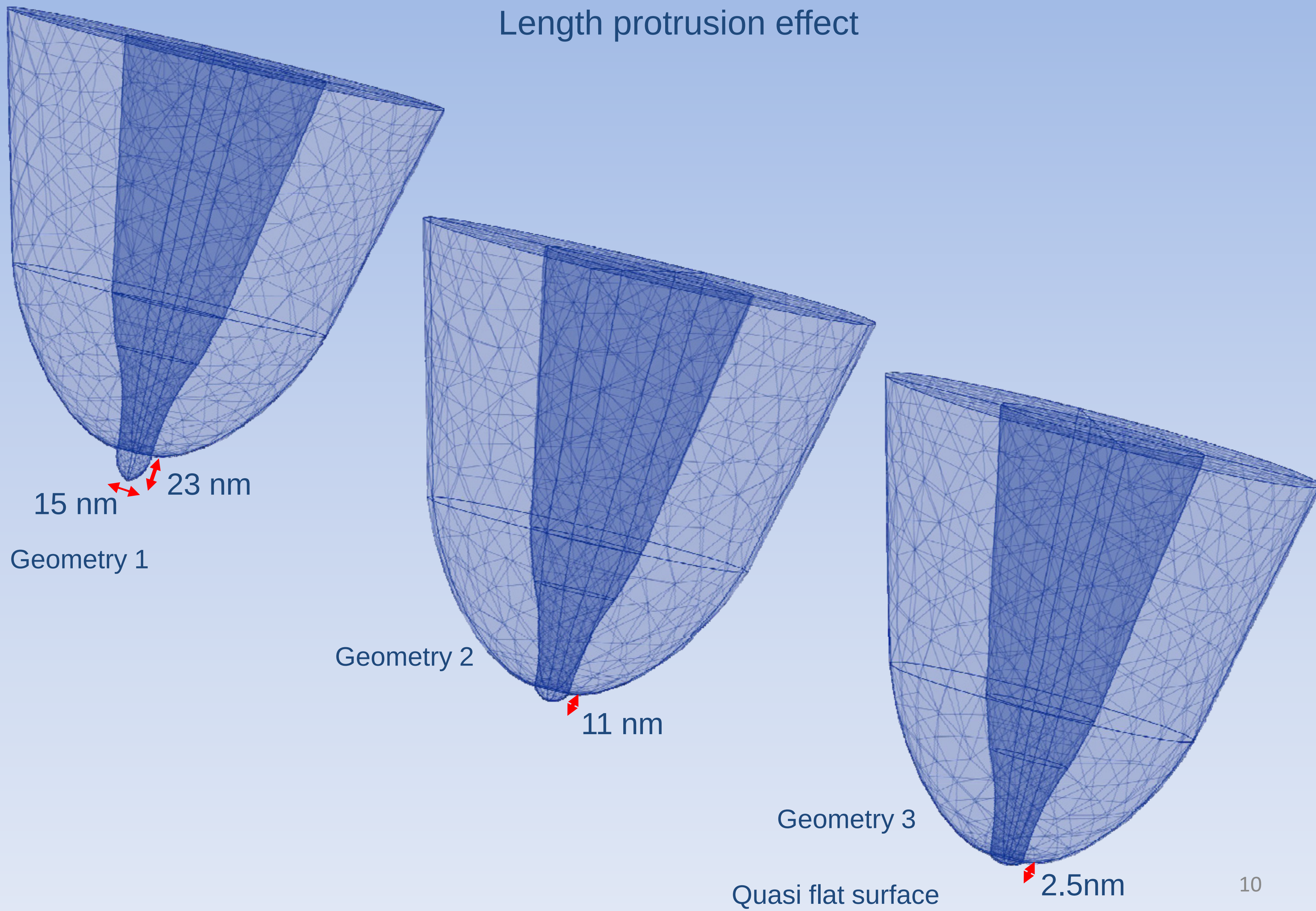
- Using the Poisson-Boltzmann for simulating the EDL (by including a Stern layer)
- Poisson equation to model the dielectric coating
- Suitable boundaries, Moving mesh, time dependent simulation: Probe moving at 10 nm/s
- Using Comsol Multiphysics software

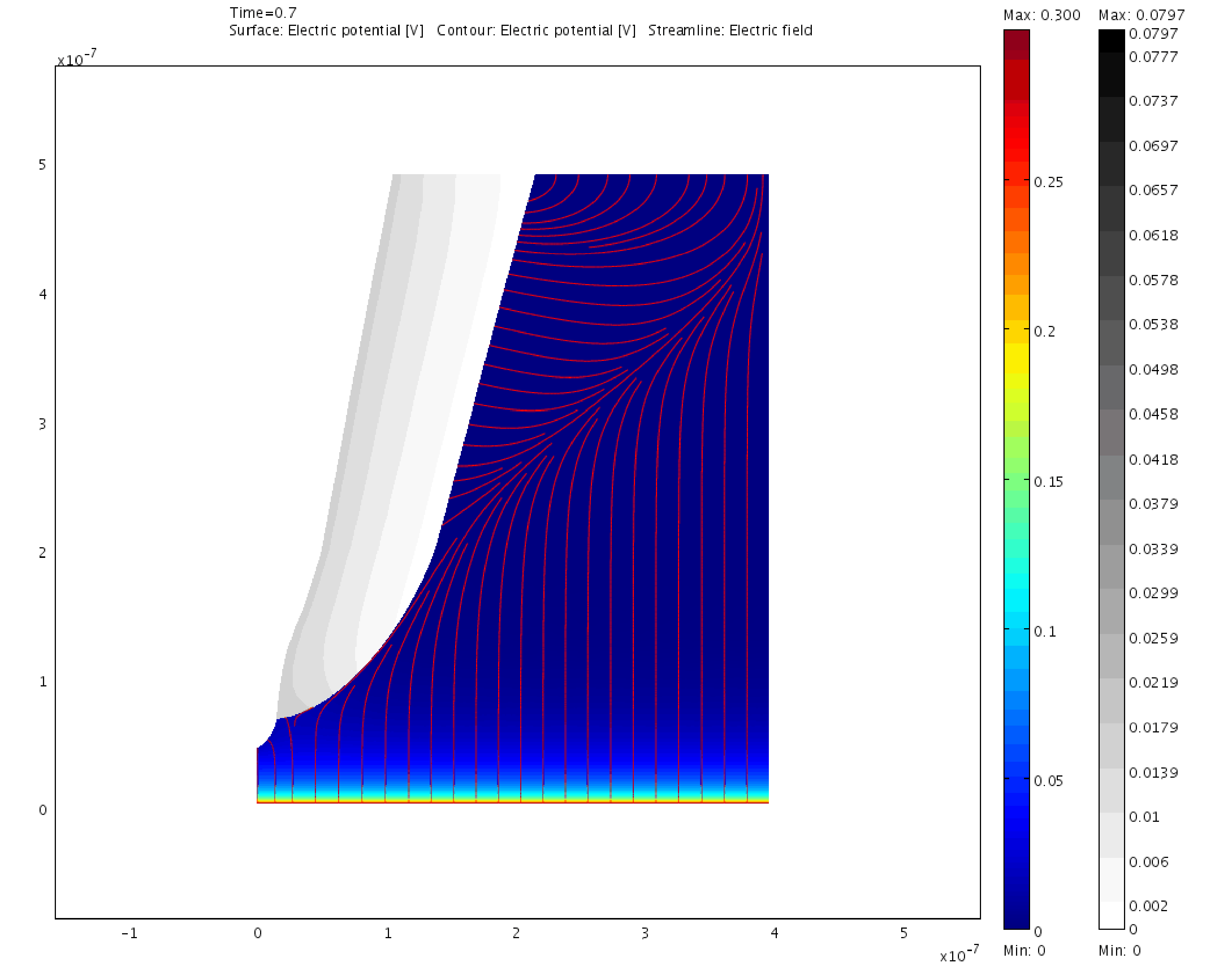


3D distribution of the electric field and potential

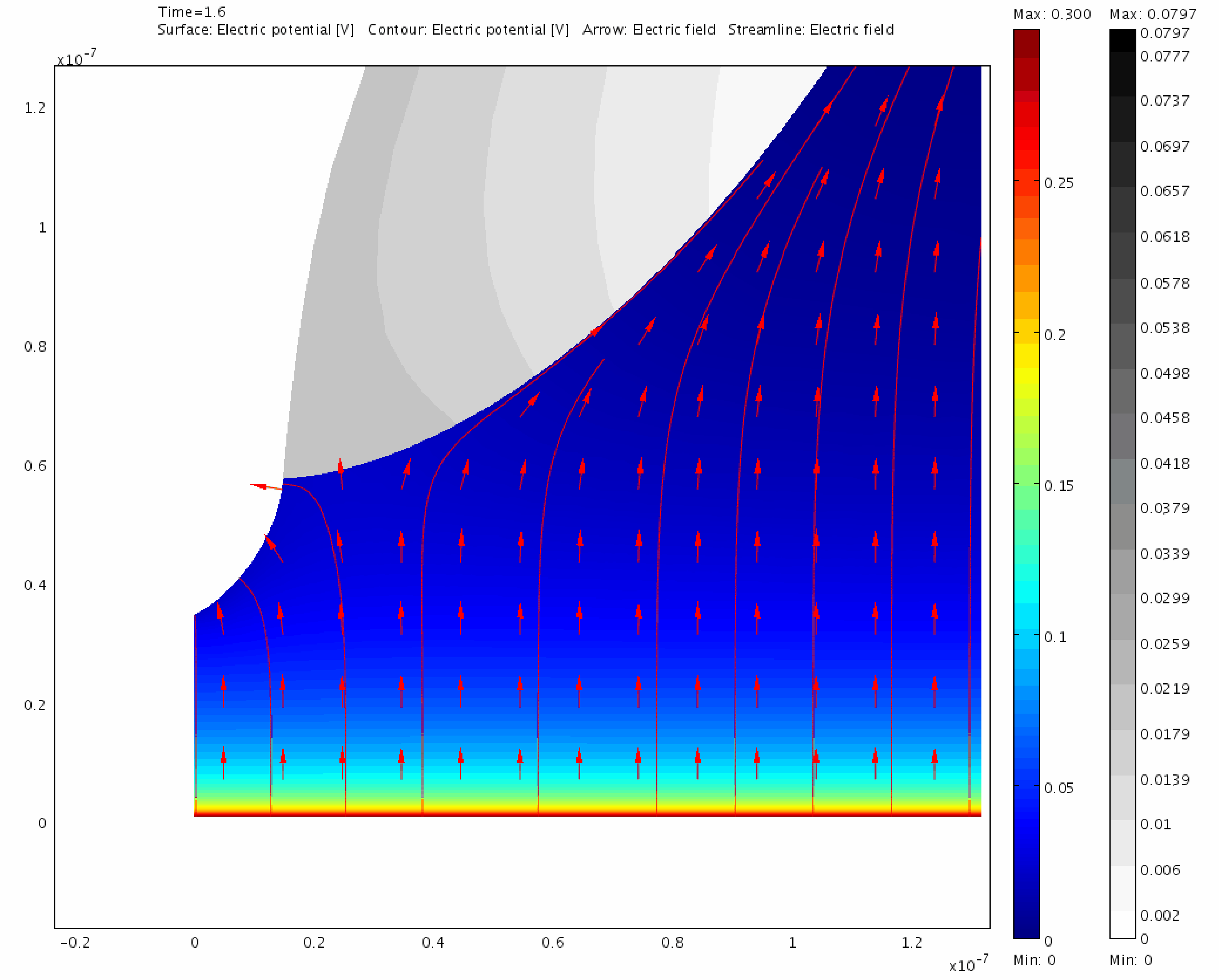
Effect of the metallic apex geometry : protruding probe

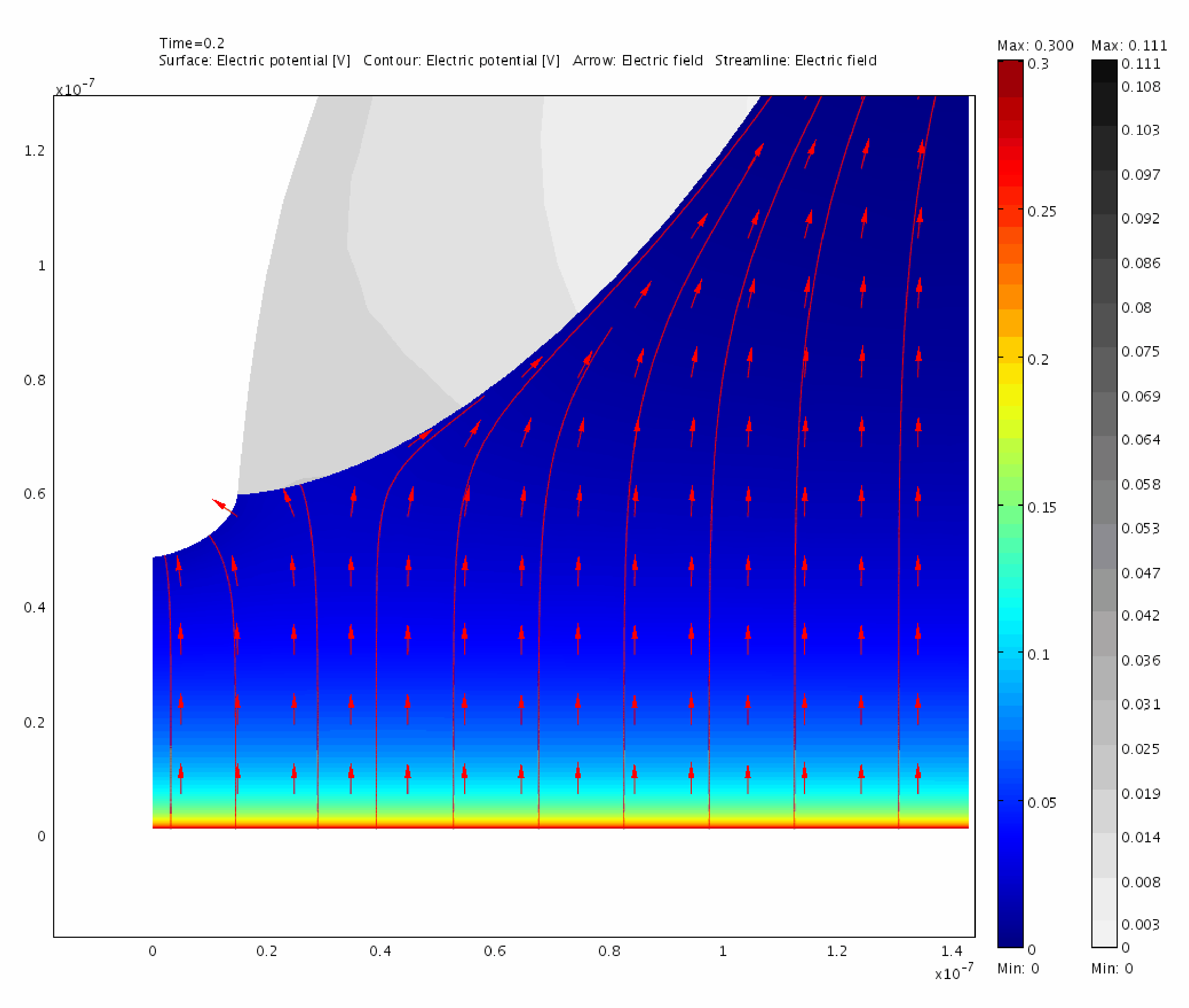
Length protrusion effect





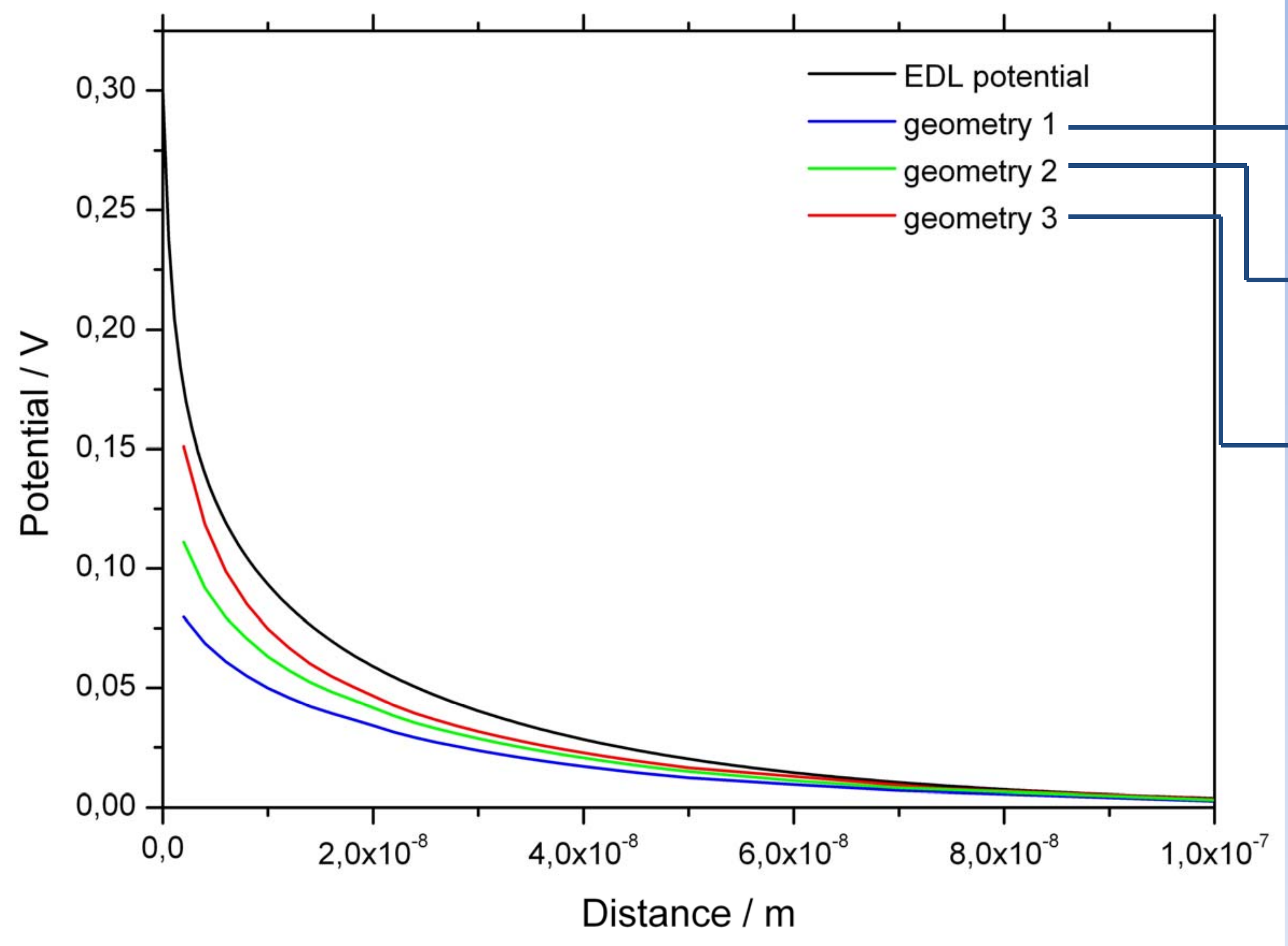
Time=0.7
Surface: Electric potential [V]   Contour: Electric potential [V]   Streamline: Electric field
x10^-7
5
4
3
2
1
0
-1
0
1
2
3
4
5
x10^-7
Max: 0.300
0.25
0.2
0.15
0.1
0.05
0
Min: 0
Max: 0.0797
0.0797
0.0777
0.0737
0.0697
0.0657
0.0618
0.0578
0.0538
0.0498
0.0458
0.0418
0.0379
0.0339
0.0299
0.0259
0.0219
0.0179
0.0139
0.01
0.006
0.002
0
Min: 0

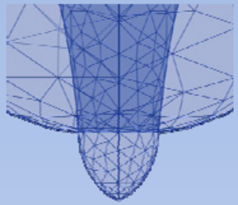

Time=1.6
Surface: Electric potential [V]   Contour: Electric potential [V]   Arrow: Electric field   Streamline: Electric field
x10^-7
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
0.2
0.4
0.6
0.8
1
1.2
x10^-7
Max: 0.300
0.25
0.2
0.15
0.1
0.05
0
Min: 0
Max: 0.0797
0.0797
0.0777
0.0737
0.0697
0.0657
0.0618
0.0578
0.0538
0.0498
0.0458
0.0418
0.0379
0.0339
0.0299
0.0259
0.0219
0.0179
0.0139
0.01
0.006
0.002
0
Min: 0

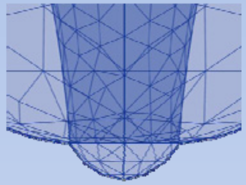


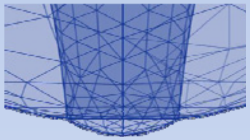
Time=0.2
Surface: Electric potential [V] Contour: Electric potential [V] Arrow: Electric field Streamline: Electric field
x10^-7
1.2
1
0.8
0.6
0.4
0.2
0
0 0.2 0.4 0.6 0.8 1 1.2 1.4
x10^-7
Max: 0.300
0.3 0.25 0.2 0.15 0.1 0.05 0
Min: 0
Max: 0.111
0.111 0.108 0.103 0.097 0.092 0.086 0.08 0.075 0.069 0.064 0.058 0.053 0.047 0.042 0.036 0.031 0.025 0.019 0.014 0.008 0.003 0
Min: 0

Effect of the metallic apex geometry : protruding probe









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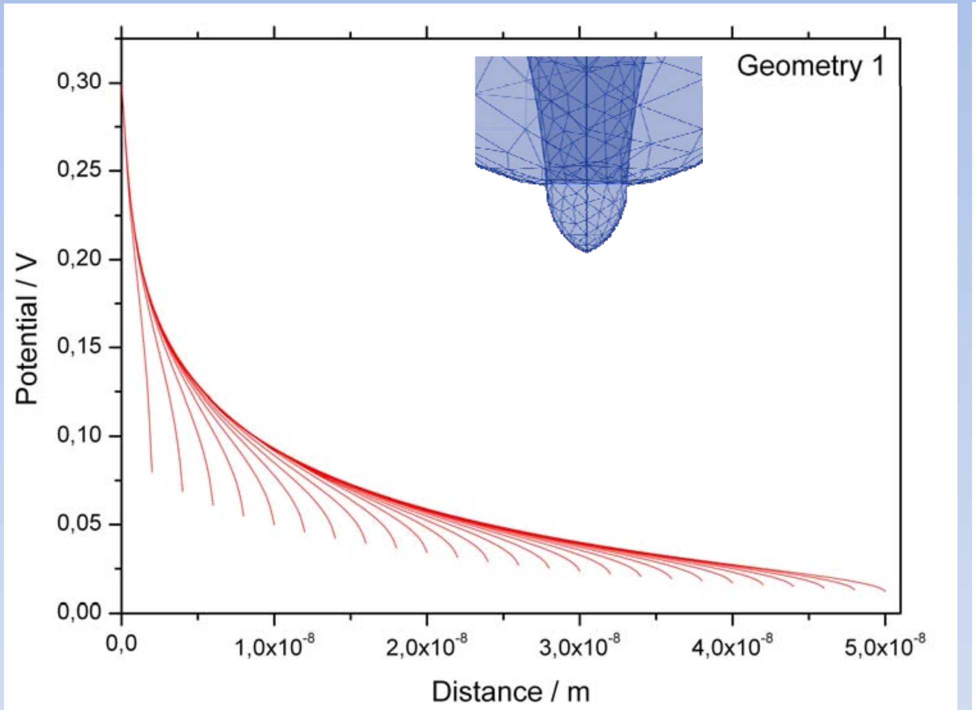
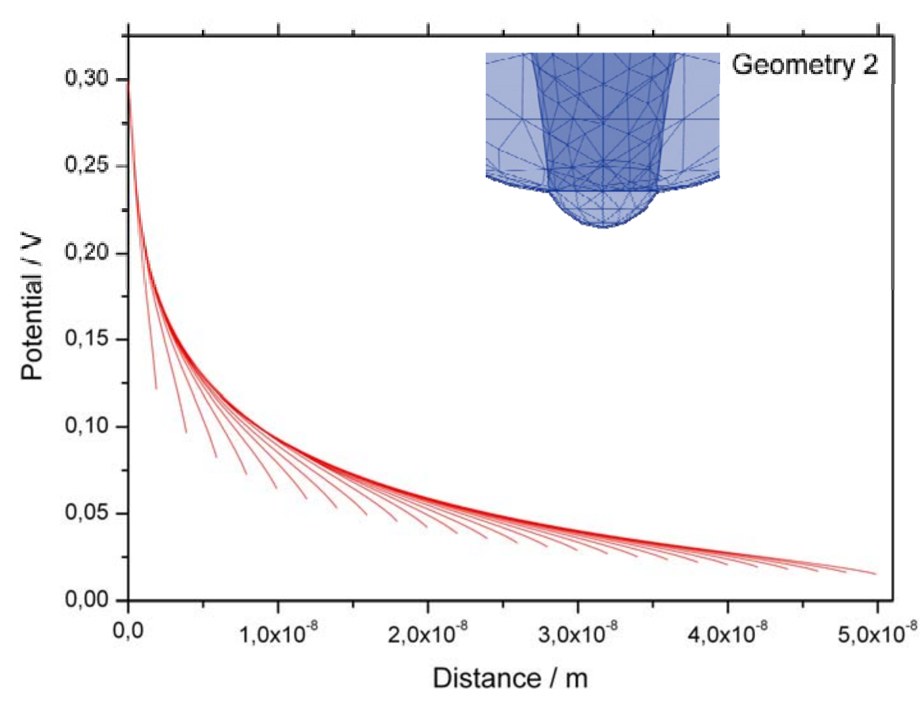
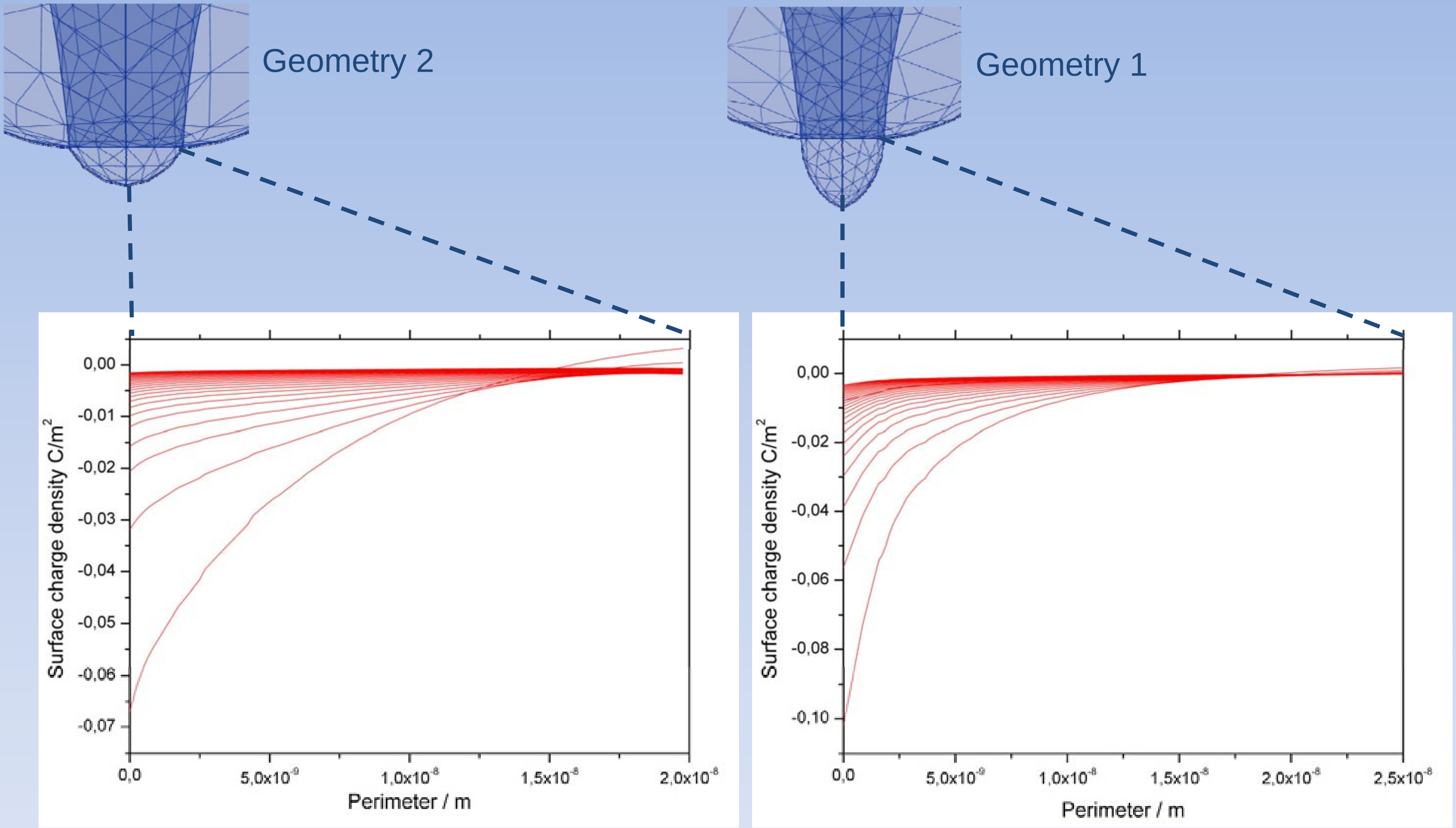




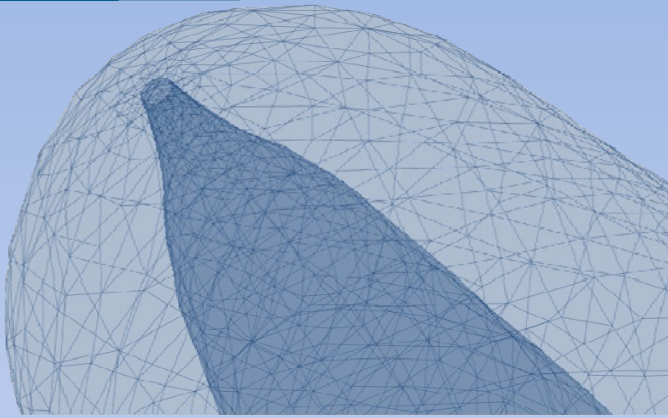
Potential profile between the Probe and the electrode for different separation distances.

Effect of the metallic apex geometry : protruding probe

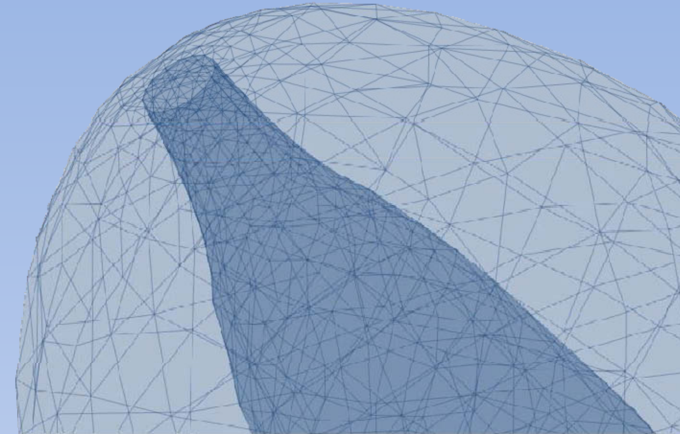


Surface charge density on the metallic protrusion

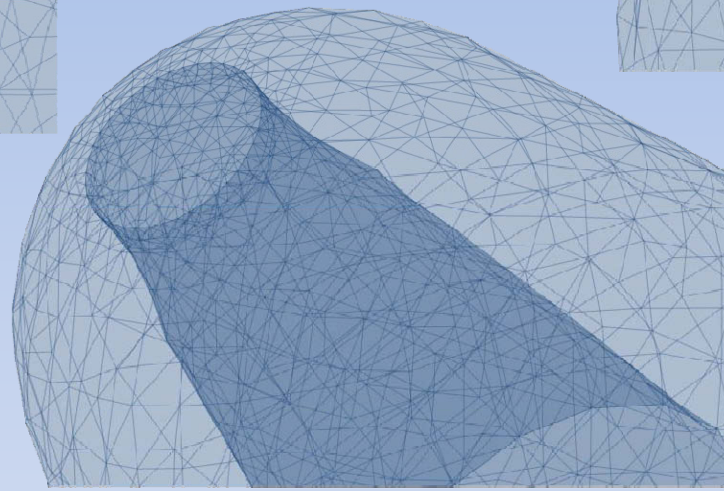
Effect of the exposed metallic surface



r=8nm

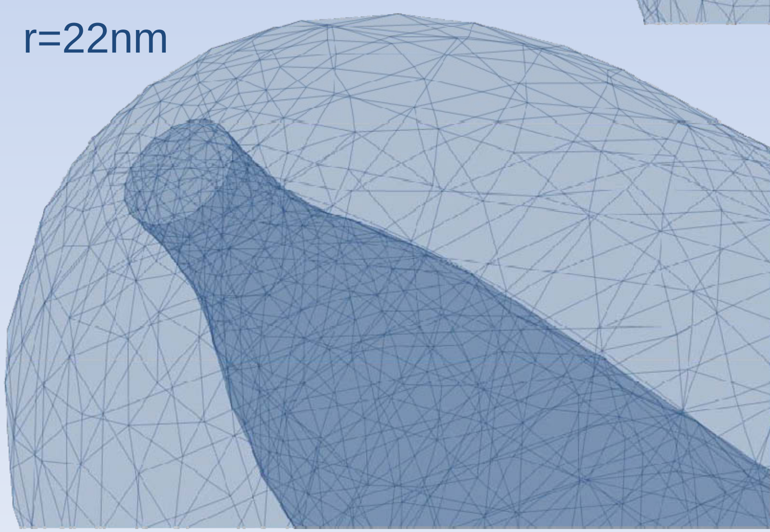


r=15nm

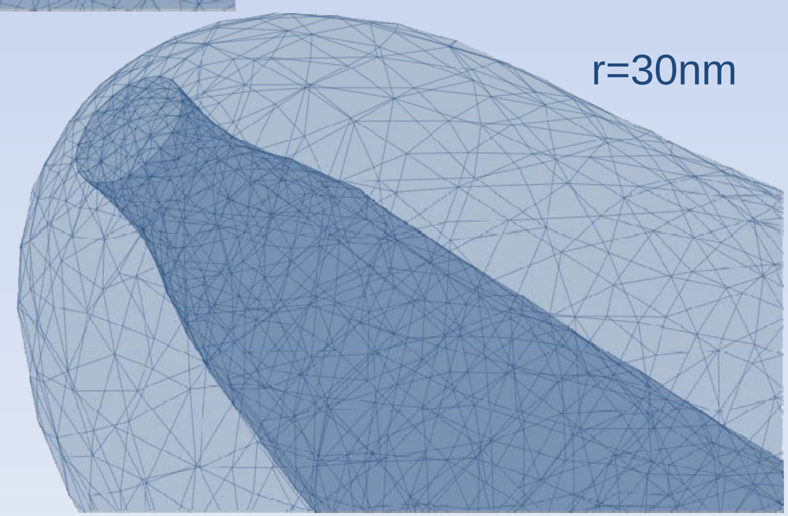


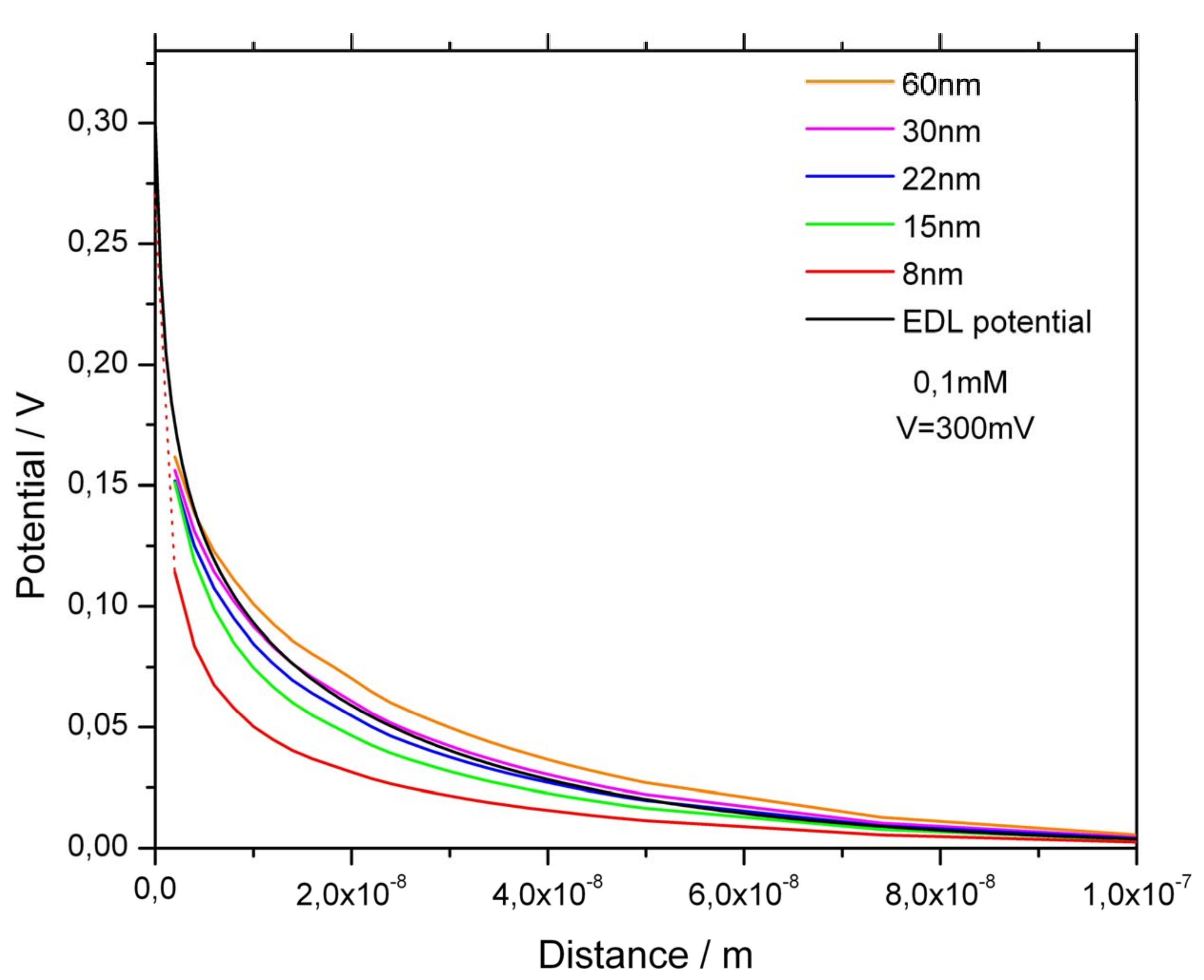
r=60nm

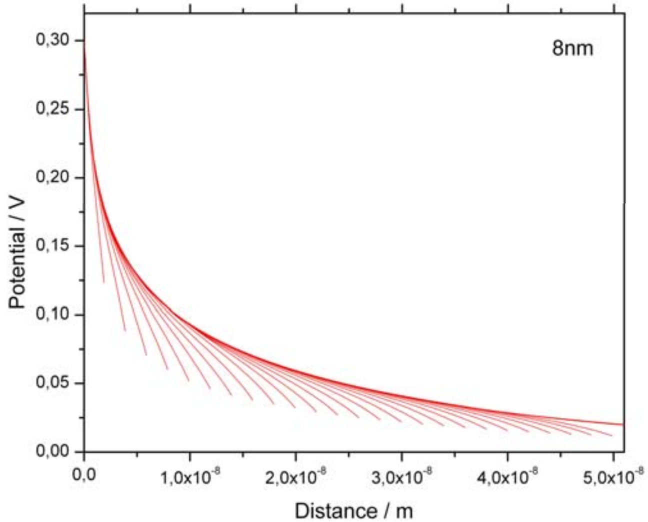
r=22nm

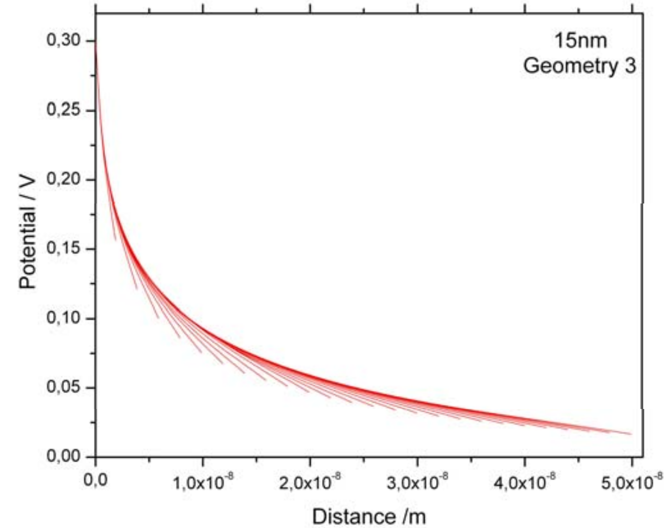


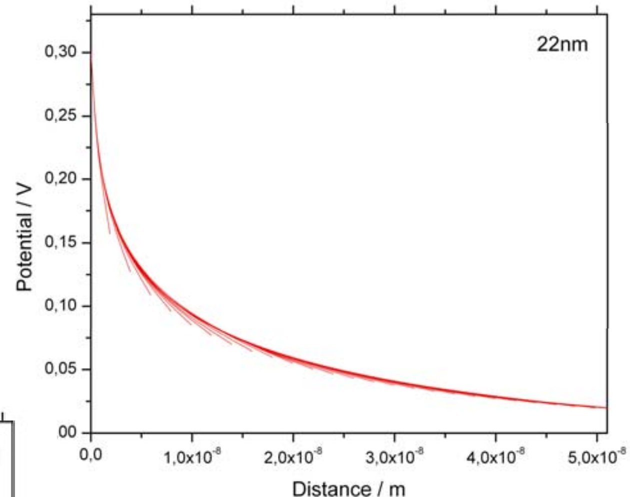
r=30nm

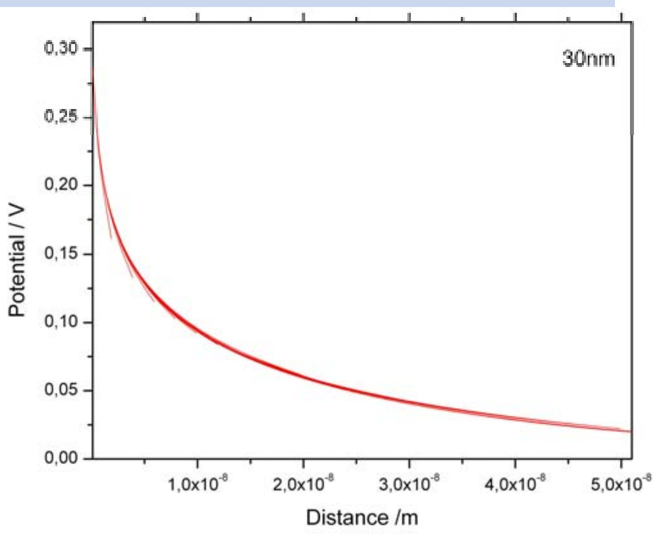


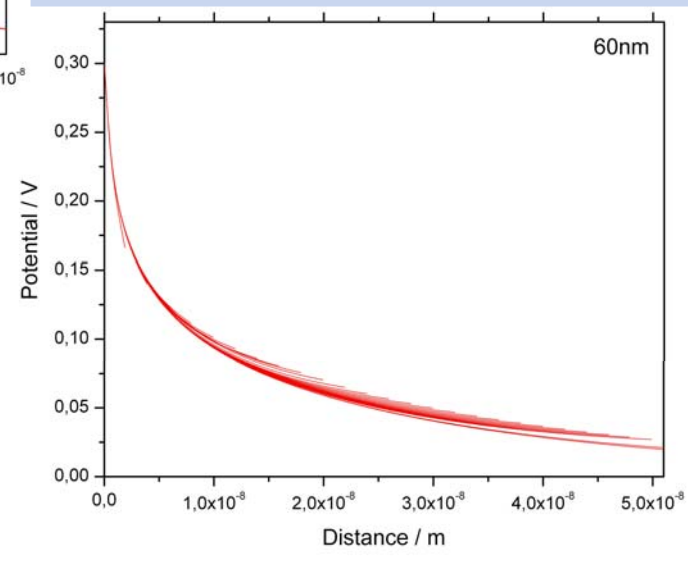

60nm
30nm
22nm
15nm
8nm
EDL potential
0,1mM
V=300mV
Potential / V
0,00
0,05
0,10
0,15
0,20
0,25
0,30
Distance / m
0,0
2,0x10^-8
4,0x10^-8
6,0x10^-8
8,0x10^-8
1,0x10^-7


8nm
Potential / V
Distance / m
0,00 0,05 0,10 0,15 0,20 0,25 0,30
0,0 1,0x10^{-8} 2,0x10^{-8} 3,0x10^{-8} 4,0x10^{-8} 5,0x10^{-8}

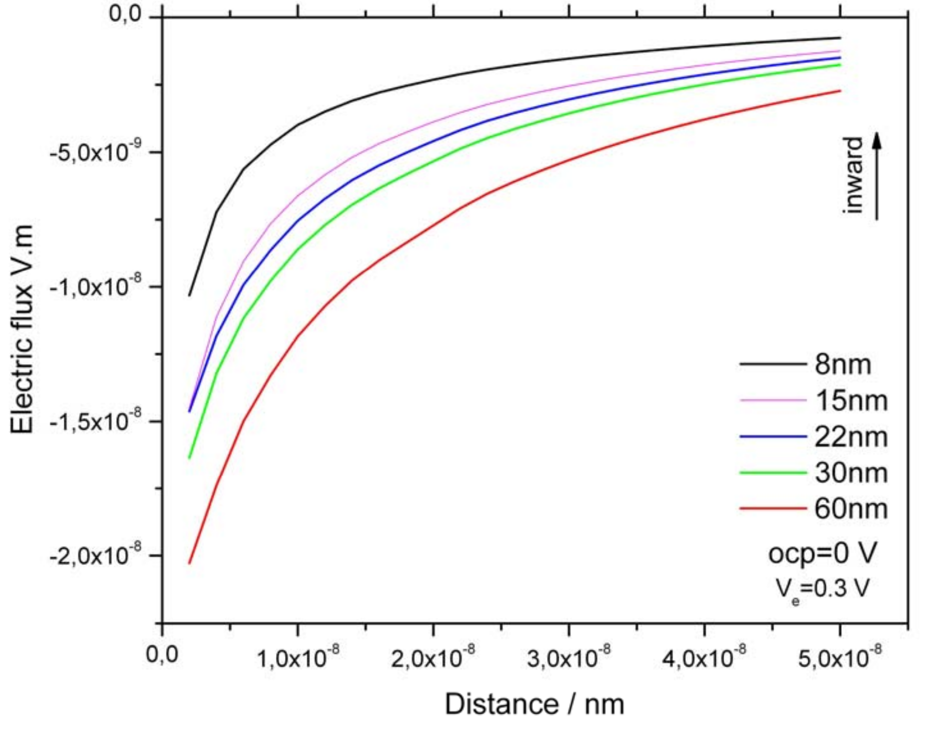

15nm
Geometry 3
Potential / V
Distance /m
0,00 0,05 0,10 0,15 0,20 0,25 0,30
0,0 1,0x10^{-8} 2,0x10^{-8} 3,0x10^{-8} 4,0x10^{-8} 5,0x10^{-8}

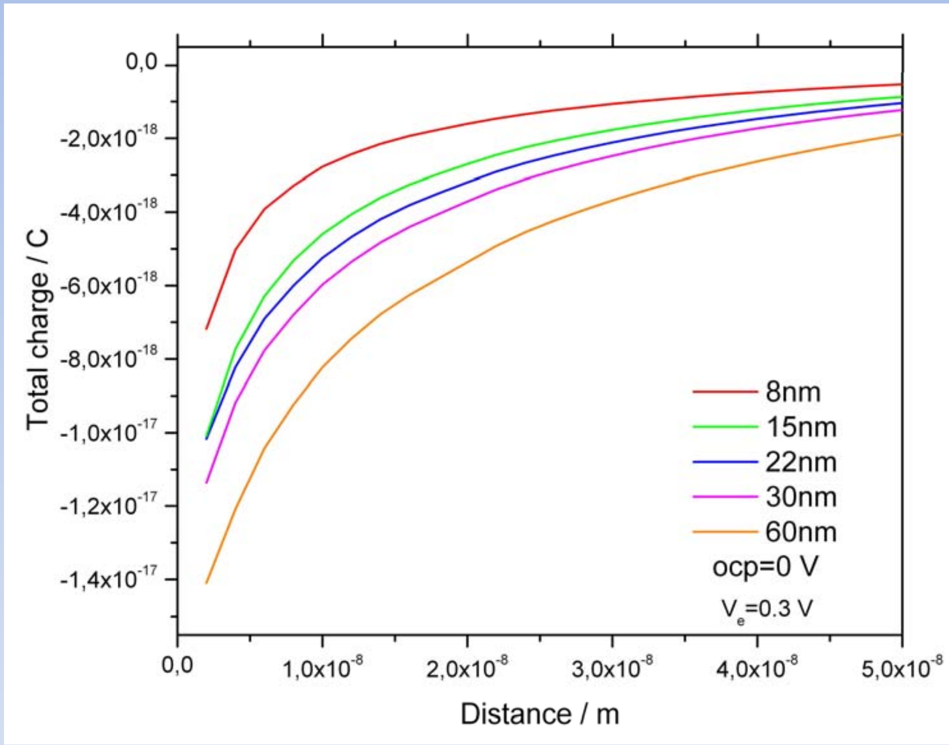

22nm
Potential / V
Distance / m
00 0,05 0,10 0,15 0,20 0,25 0,30
0,0 1,0x10^{-8} 2,0x10^{-8} 3,0x10^{-8} 4,0x10^{-8} 5,0x10^{-8}


30nm
Potential / V
Distance /m
0,00 0,05 0,10 0,15 0,20 0,25 0,30
1,0x10^{-8} 2,0x10^{-8} 3,0x10^{-8} 4,0x10^{-8} 5,0x10^{-8}


60nm
Potential / V
Distance / m
0,00 0,05 0,10 0,15 0,20 0,25 0,30
0,0 1,0x10^{-8} 2,0x10^{-8} 3,0x10^{-8} 4,0x10^{-8} 5,0x10^{-8}

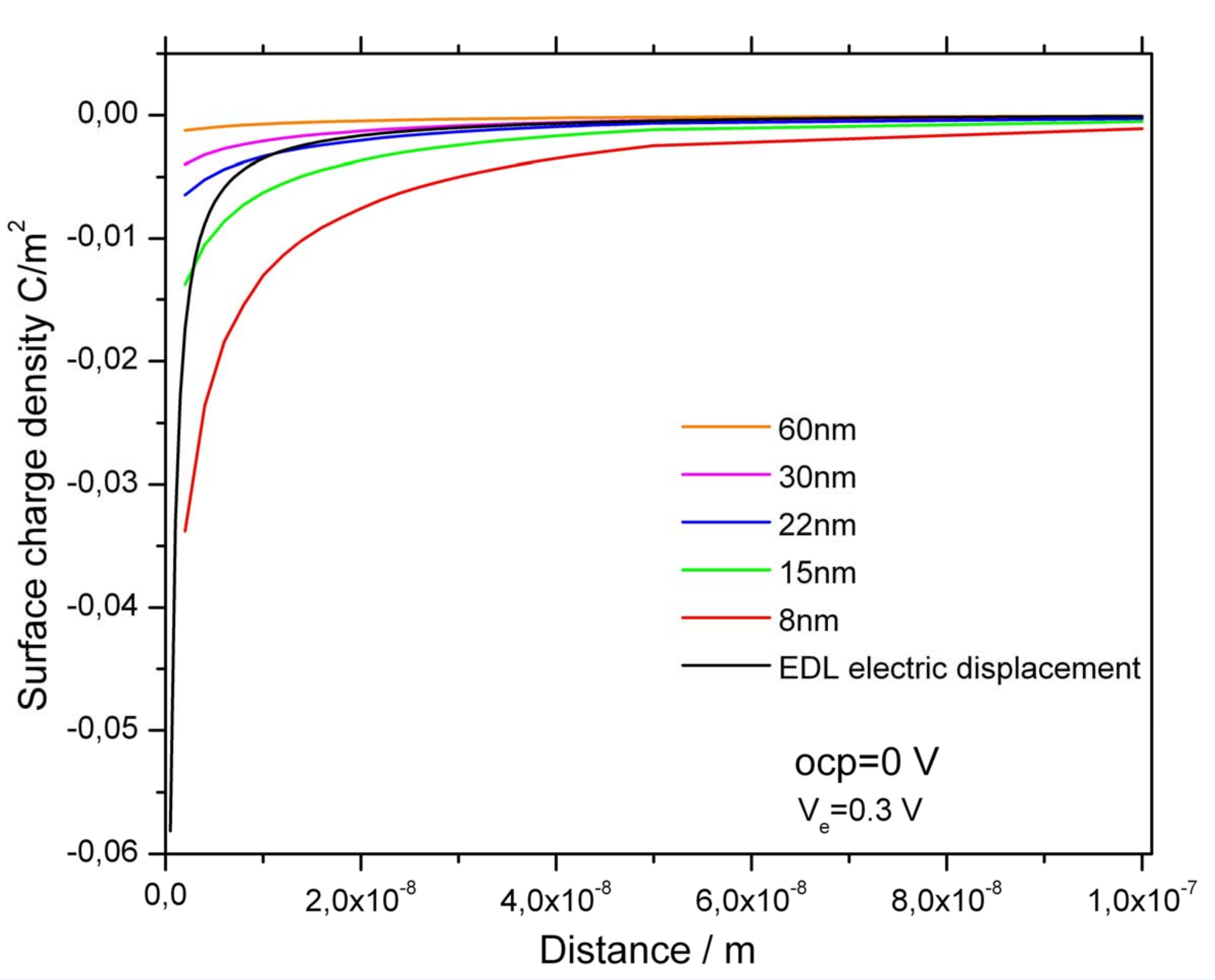
Effect of the exposed metallic surface





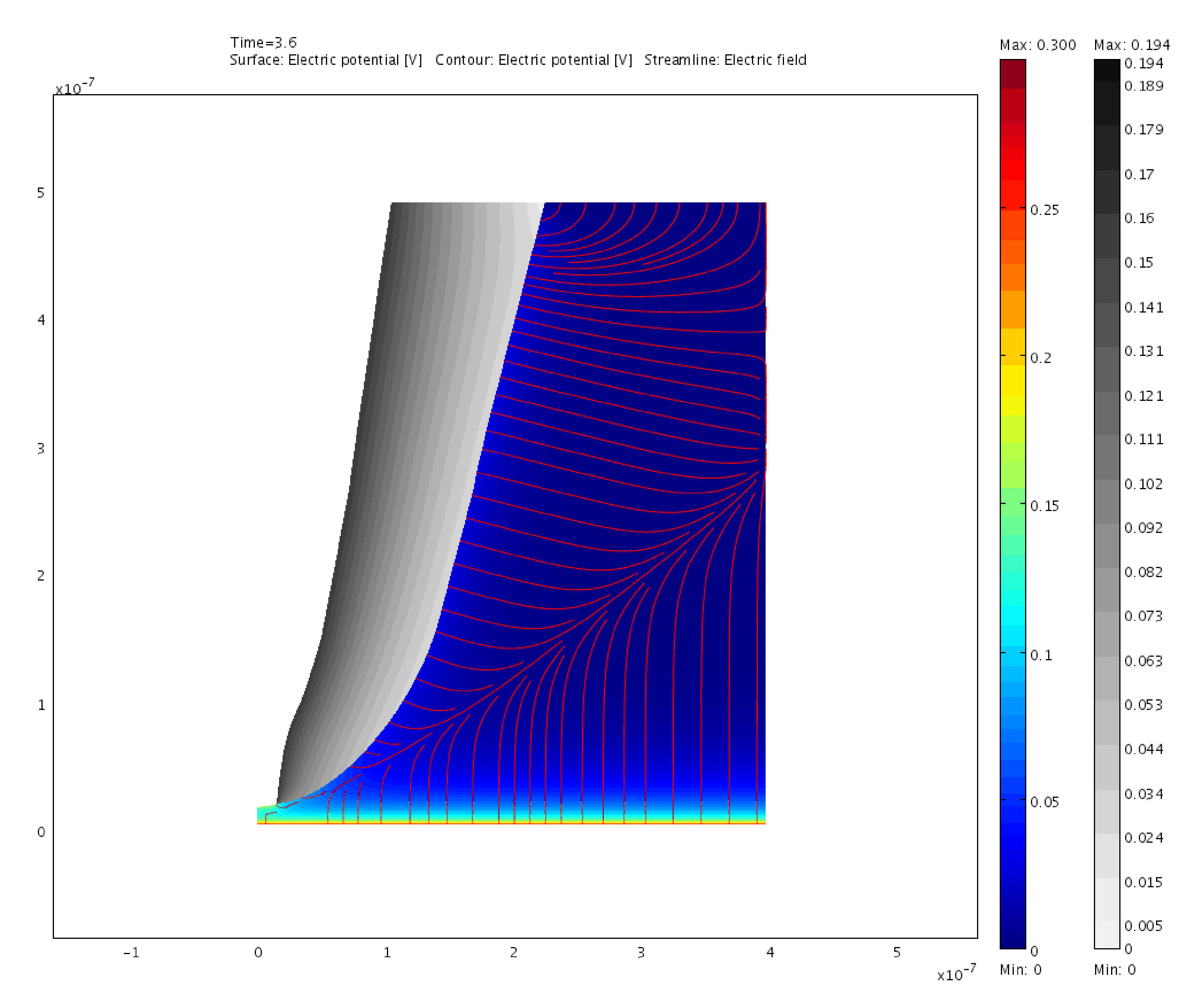
Variation of the electric flux passing through the exposed metallic tip during the approach

Effect of the exposed metallic surface



Variation of the tip surface charge density during the approach

The effect of the Open Circuit Potential: Positively charged



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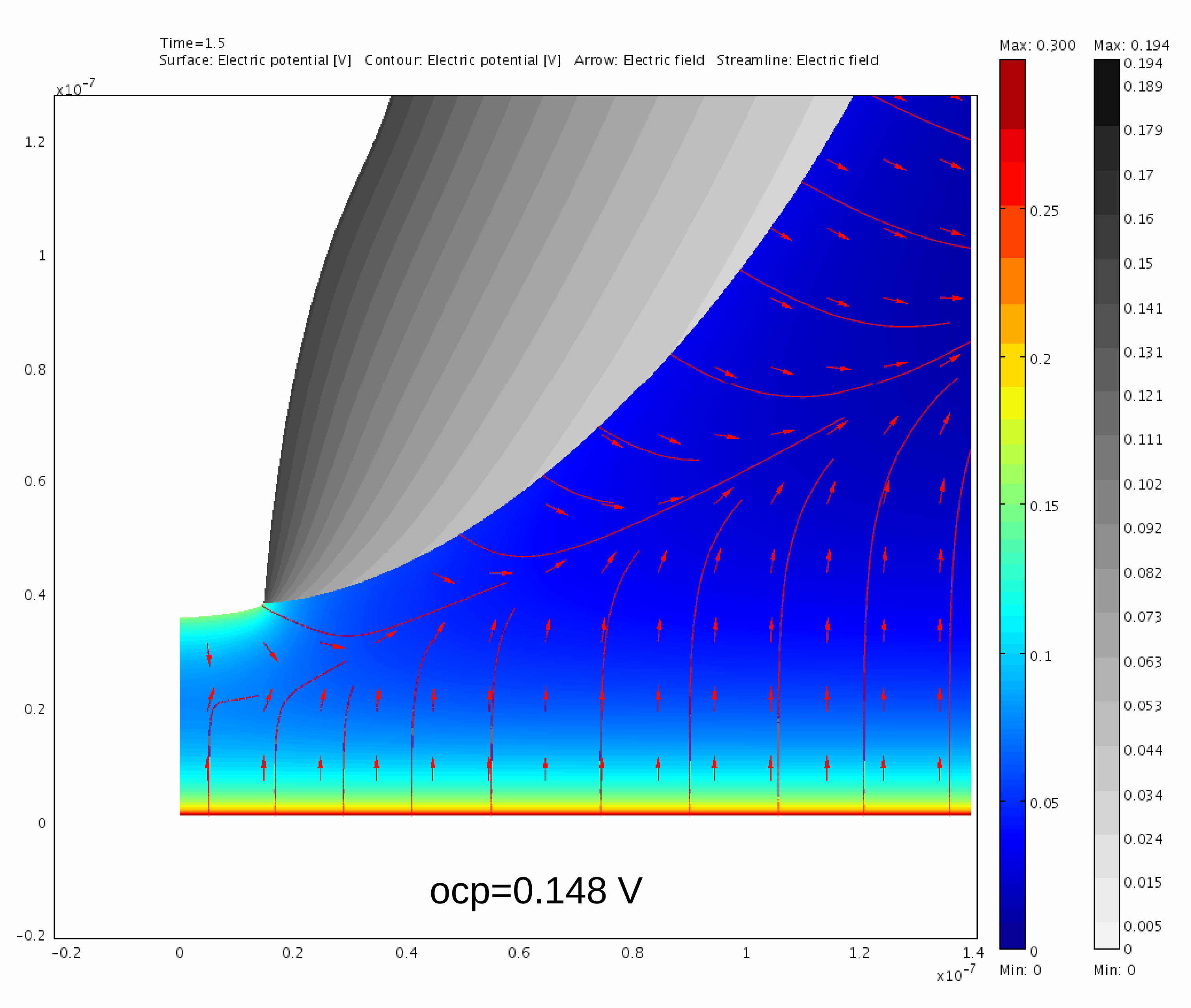

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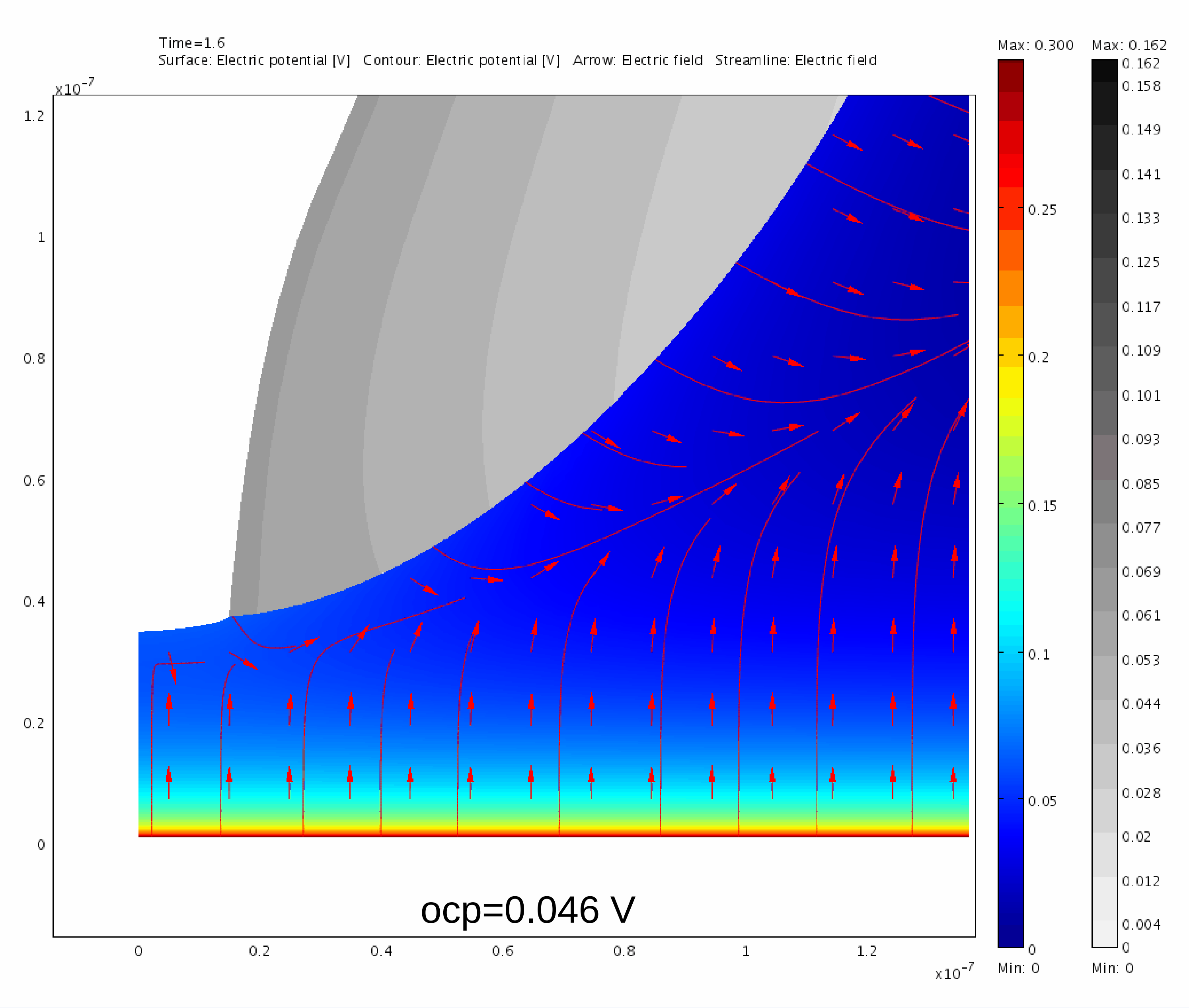

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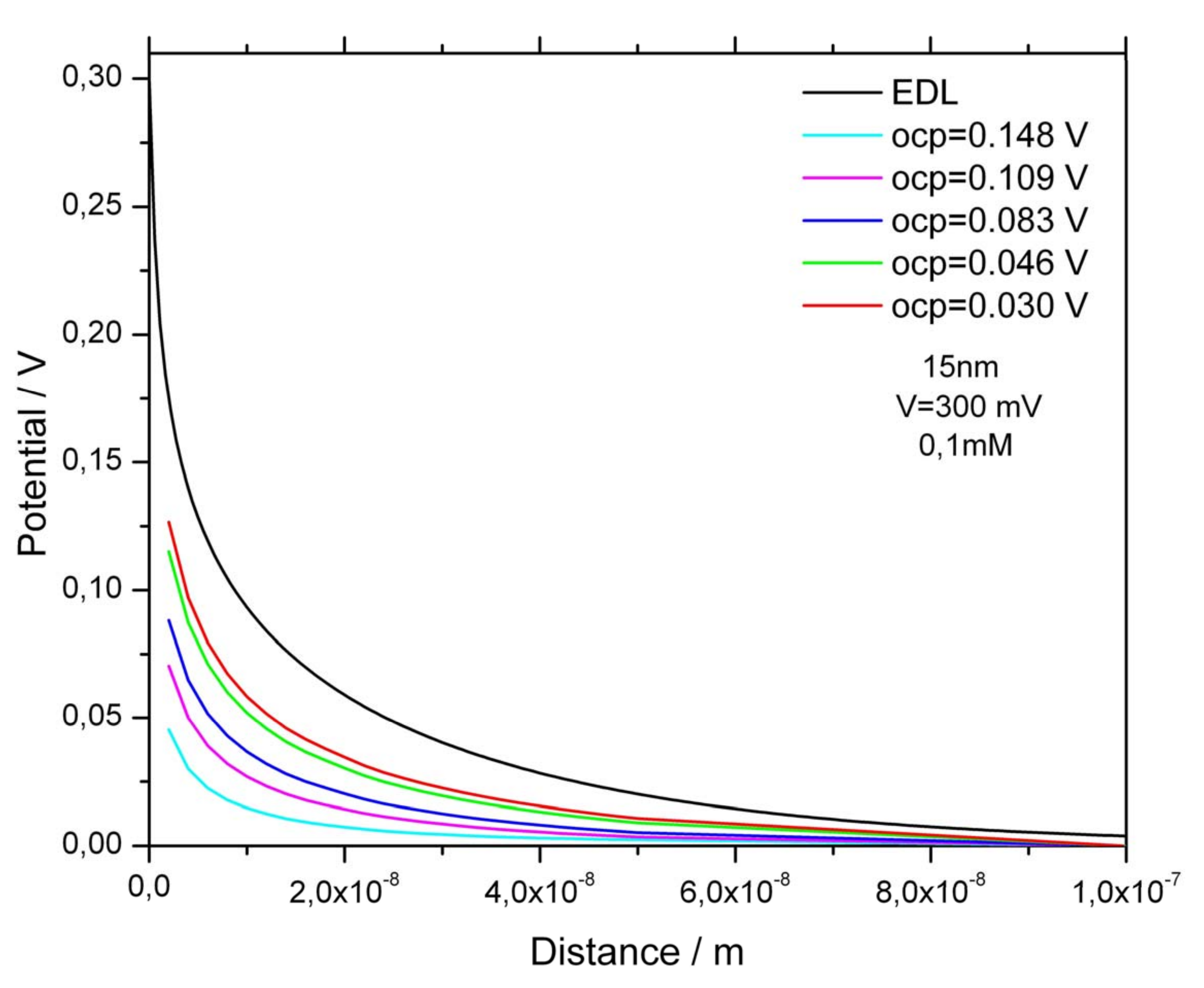

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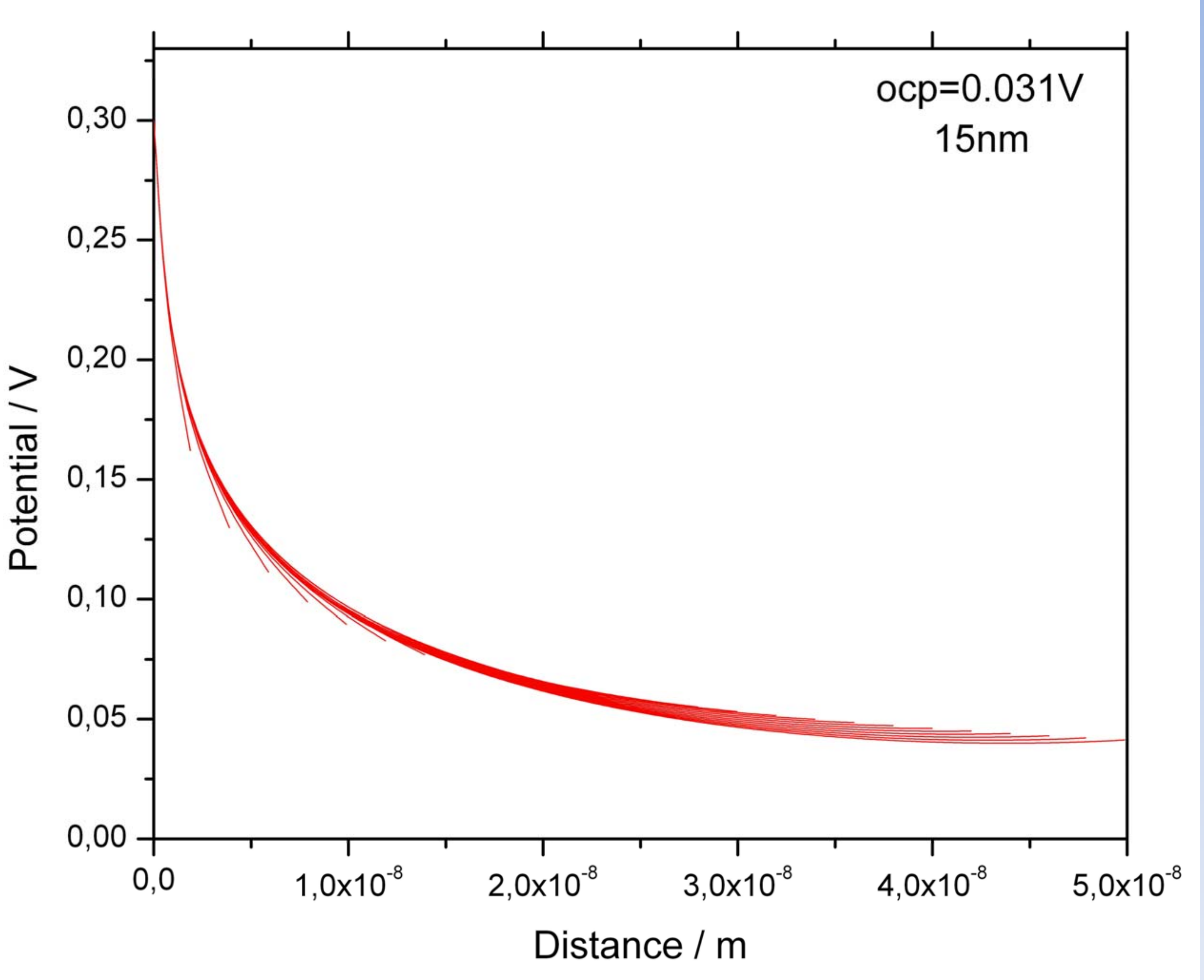

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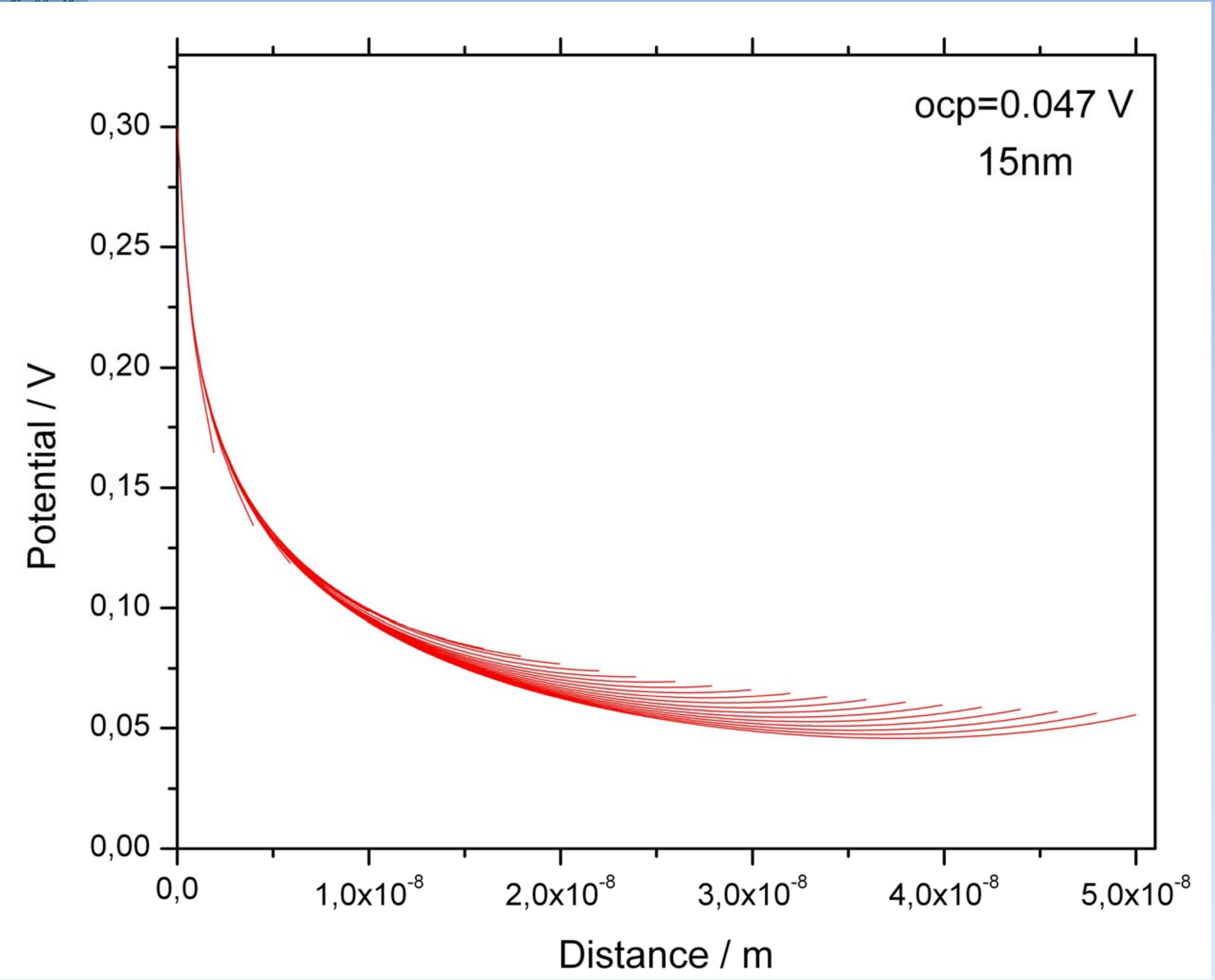

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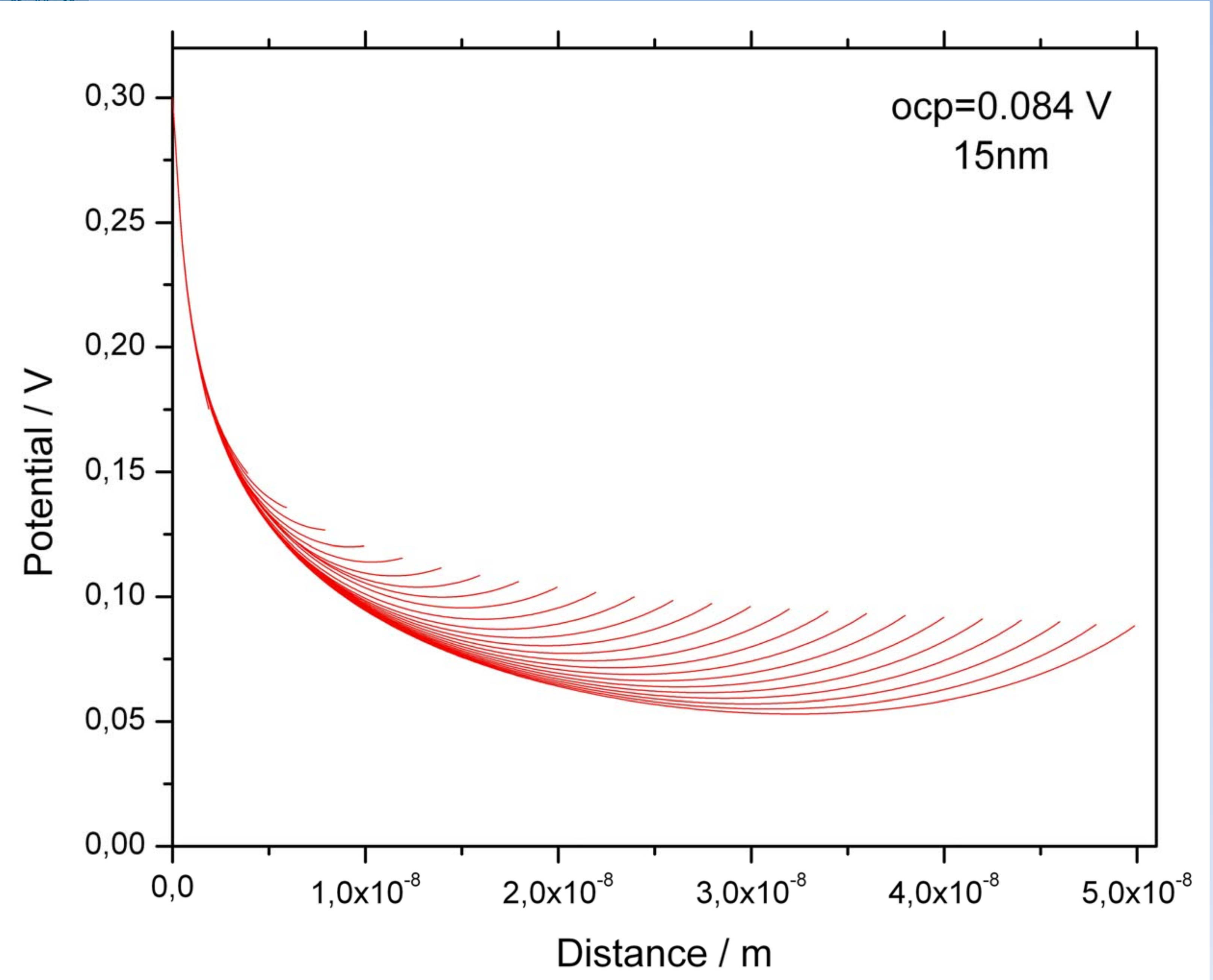

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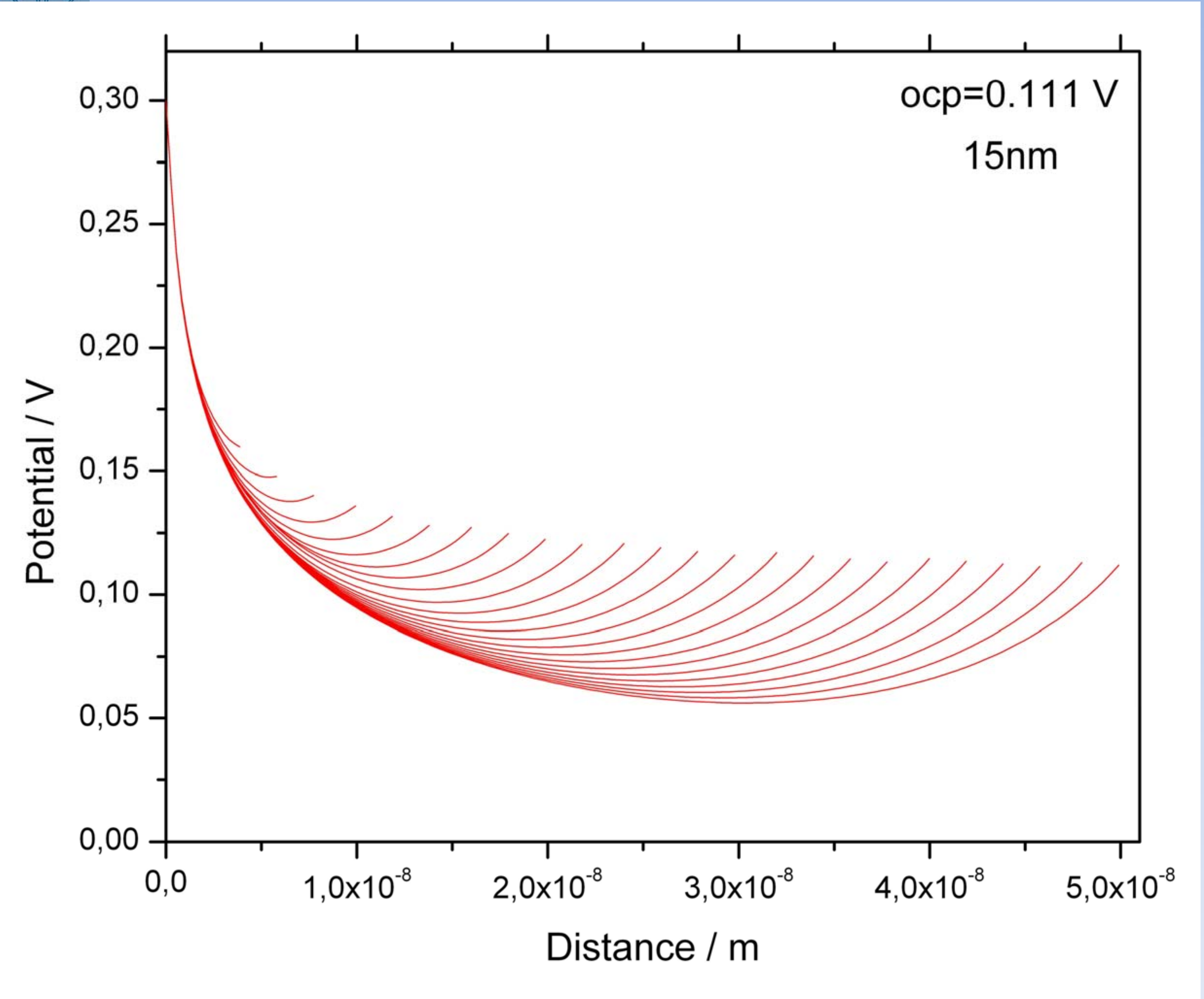

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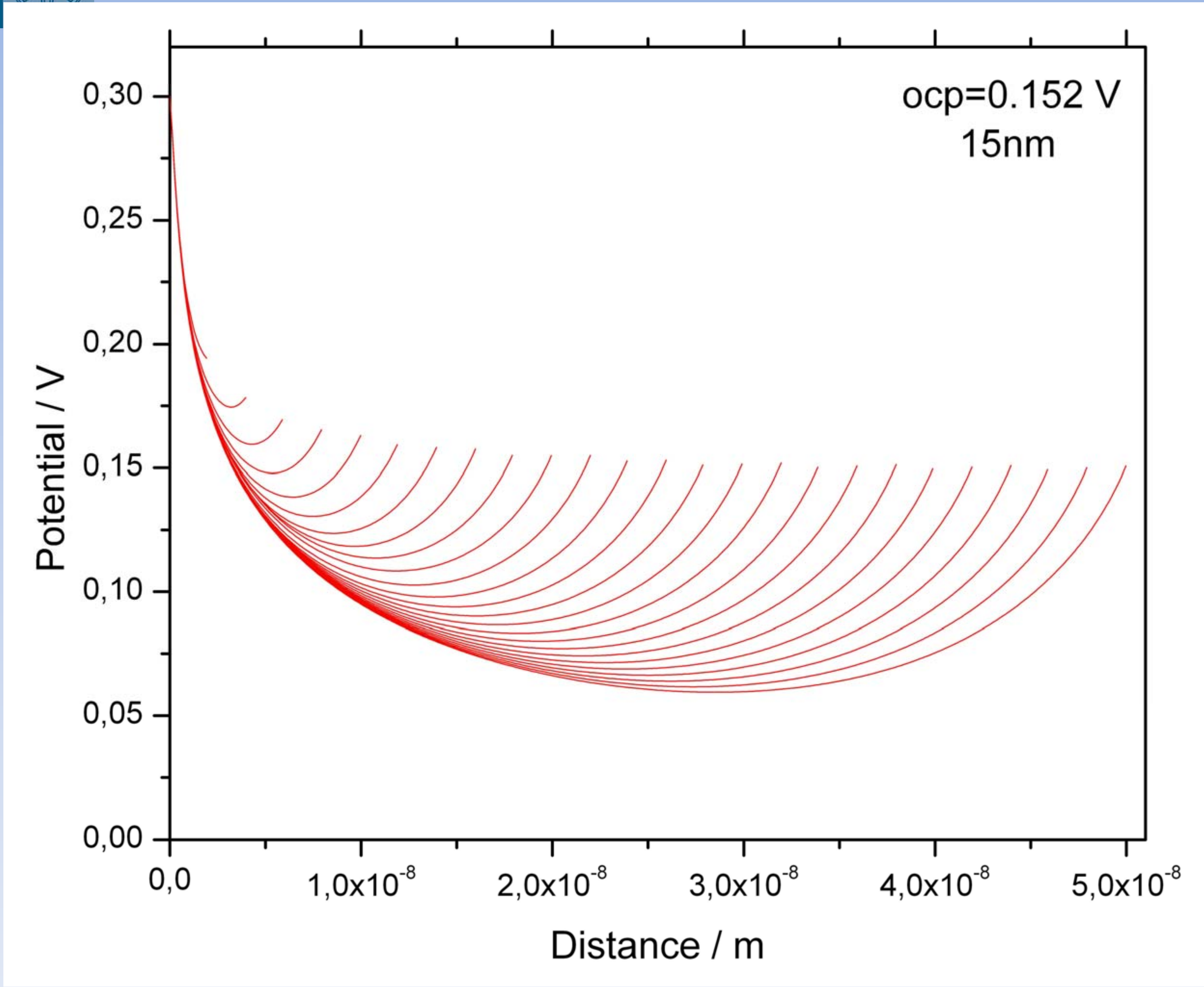

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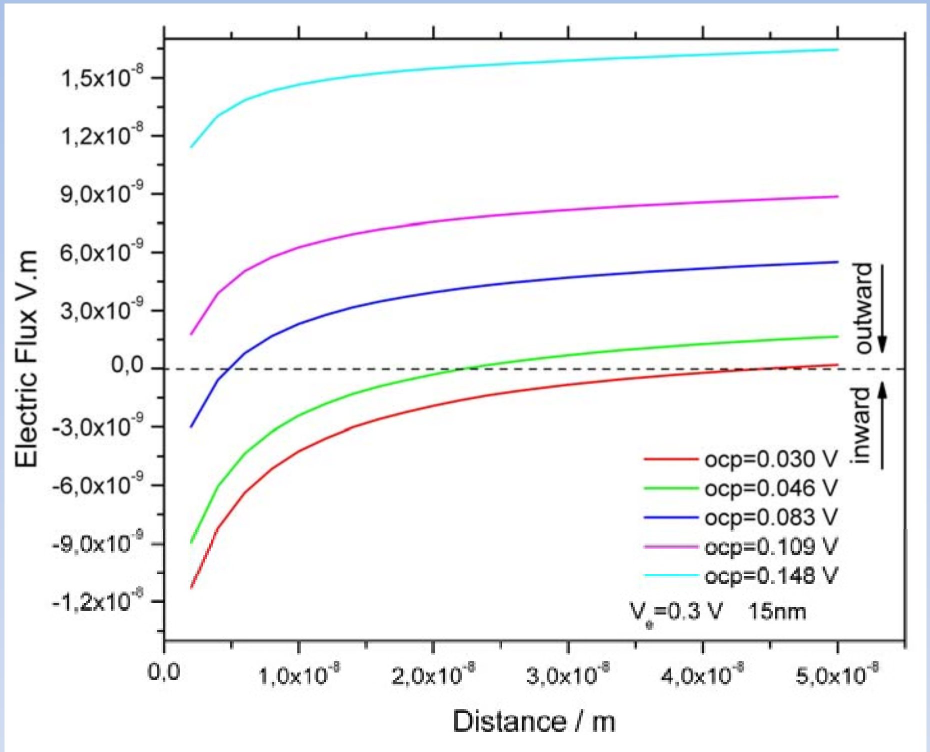
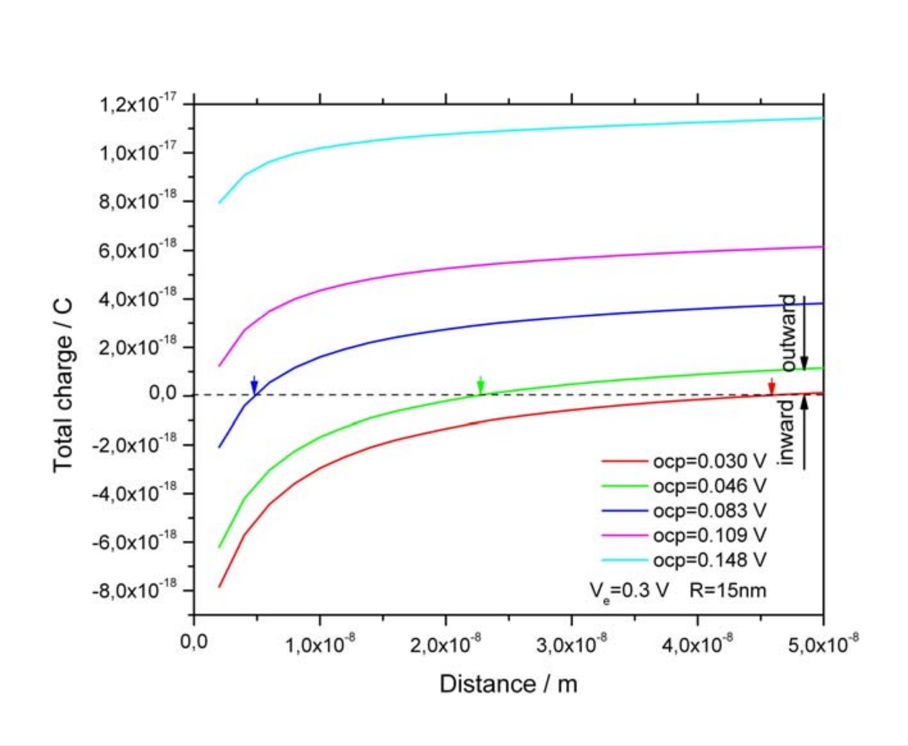
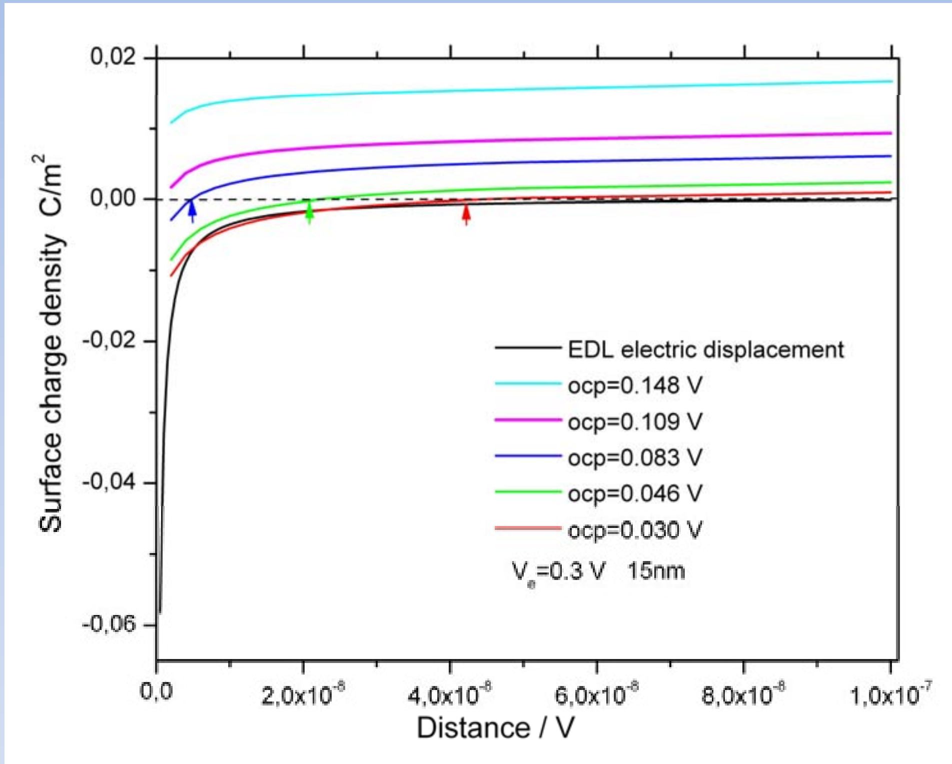
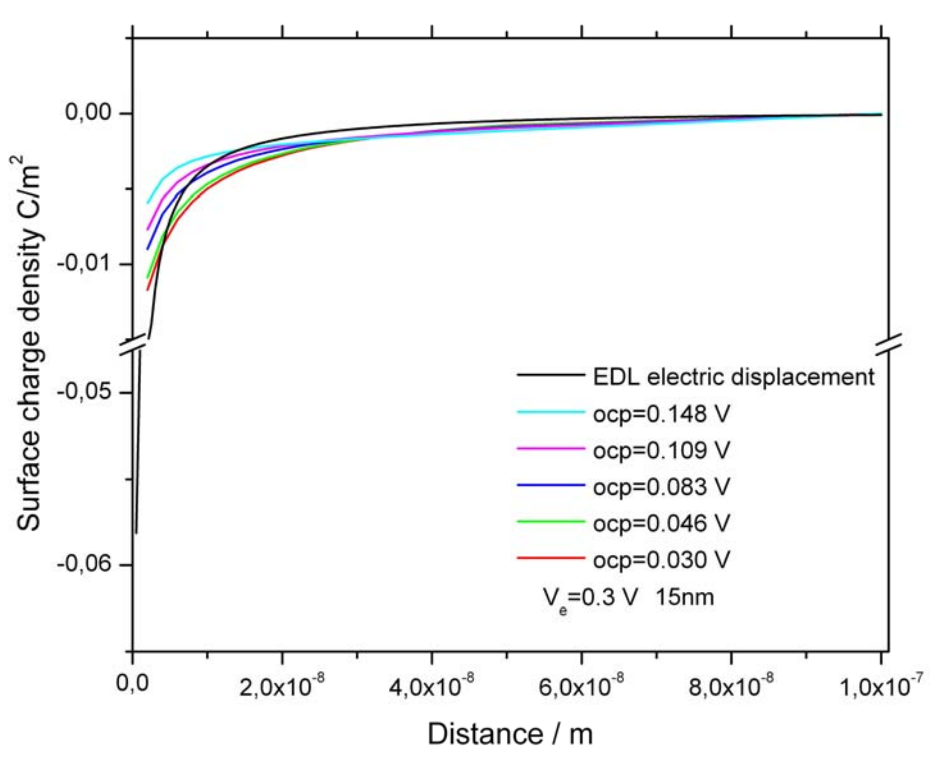




Variation of the electric flux passing through the exposed metallic tip during the approach

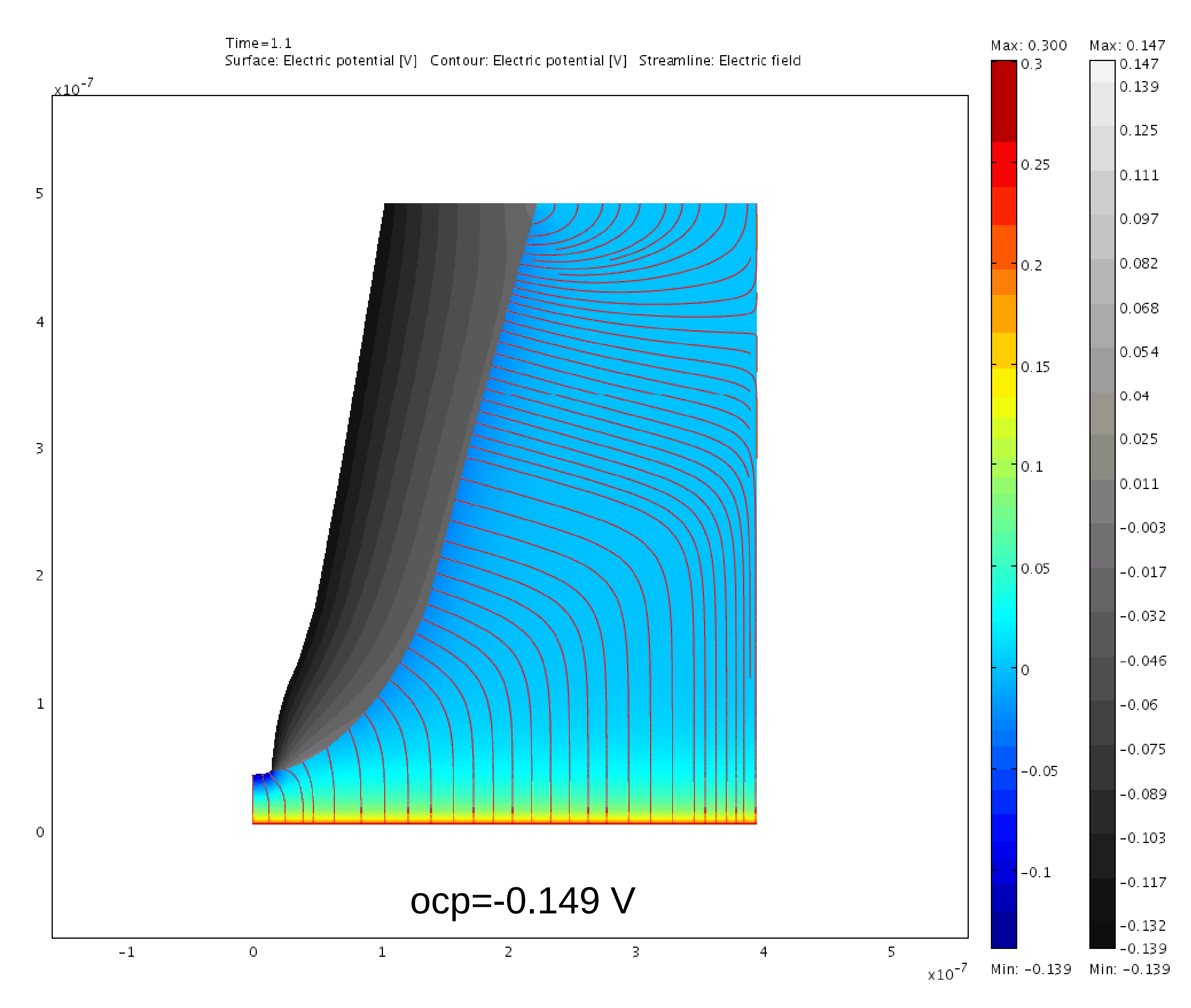
The effect of the Open Circuit Potential: Positive charge



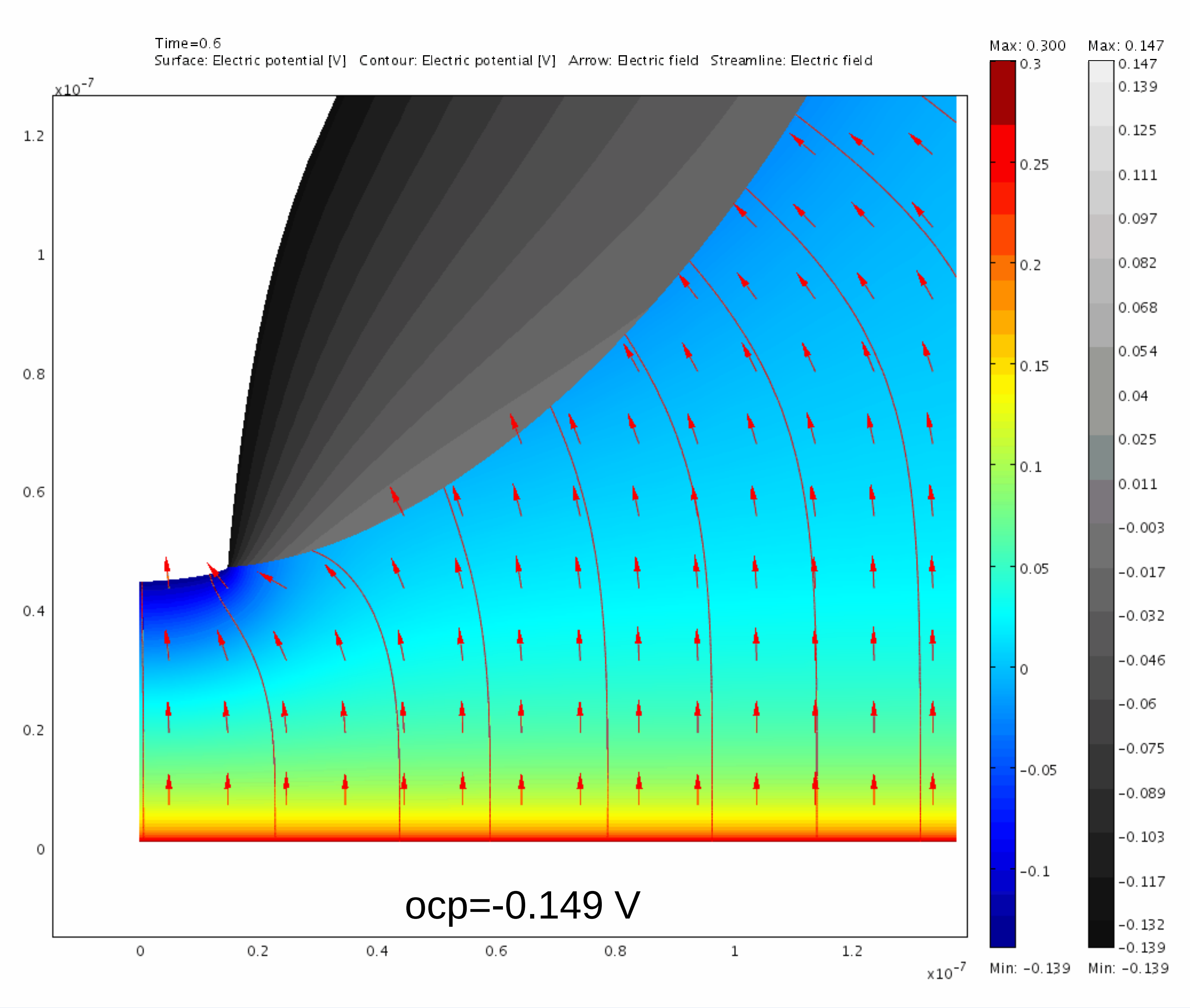


Variation of the tip surface charge density during the approach

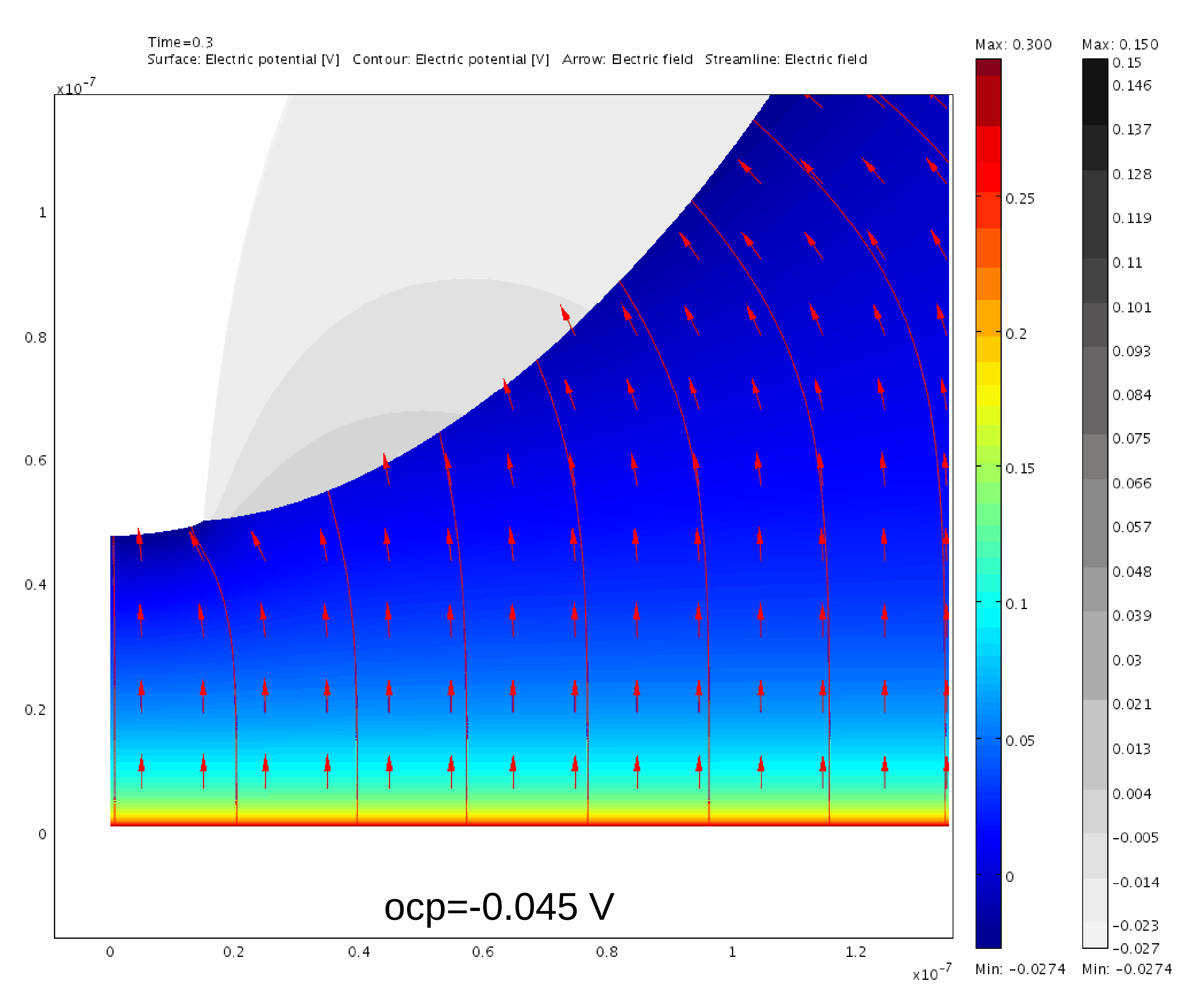
The effect of the Open Circuit Potential: Negatively charged



The effect of the Open Circuit Potential: Negatively charged



The effect of the Open Circuit Potential: Negatively charged



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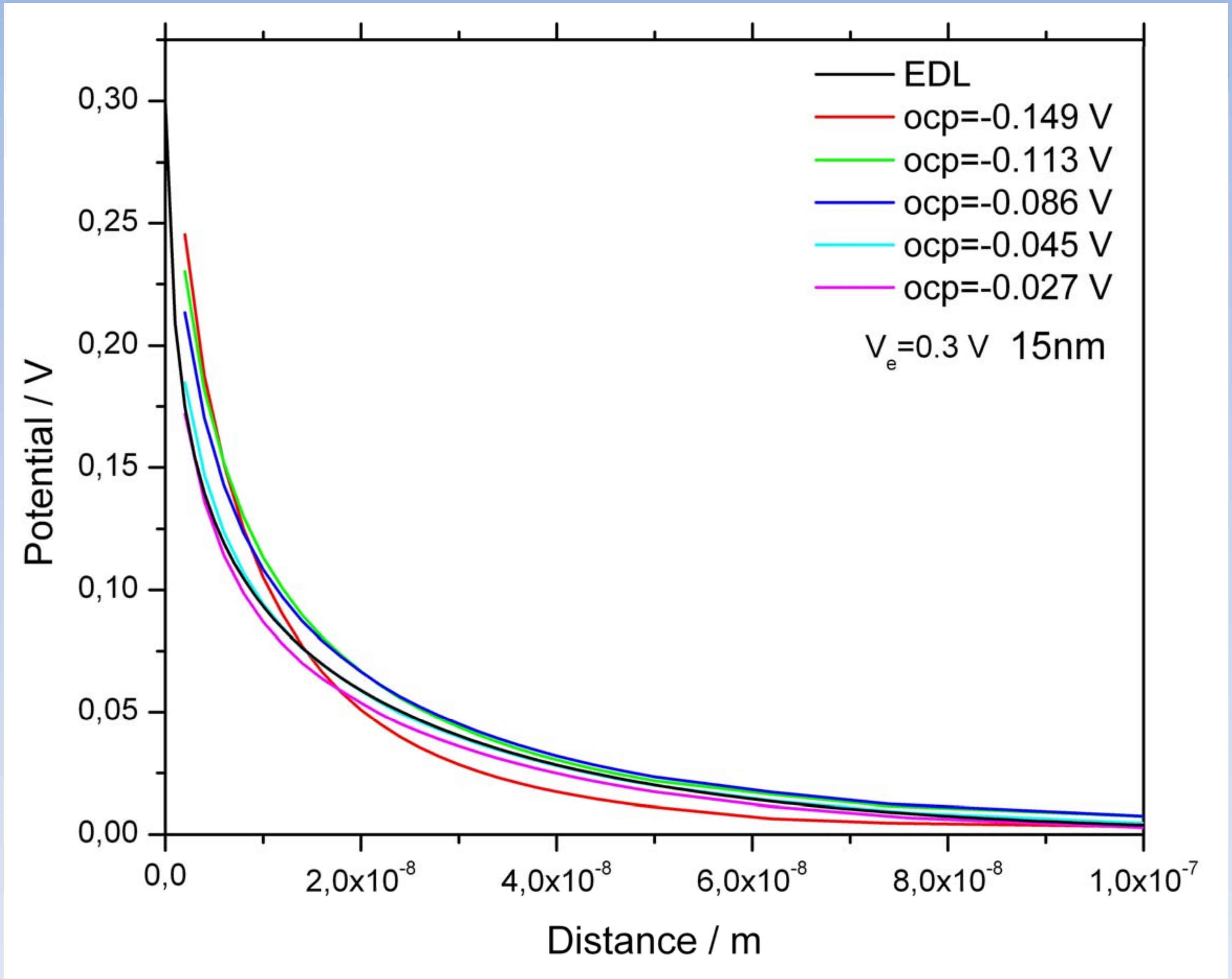

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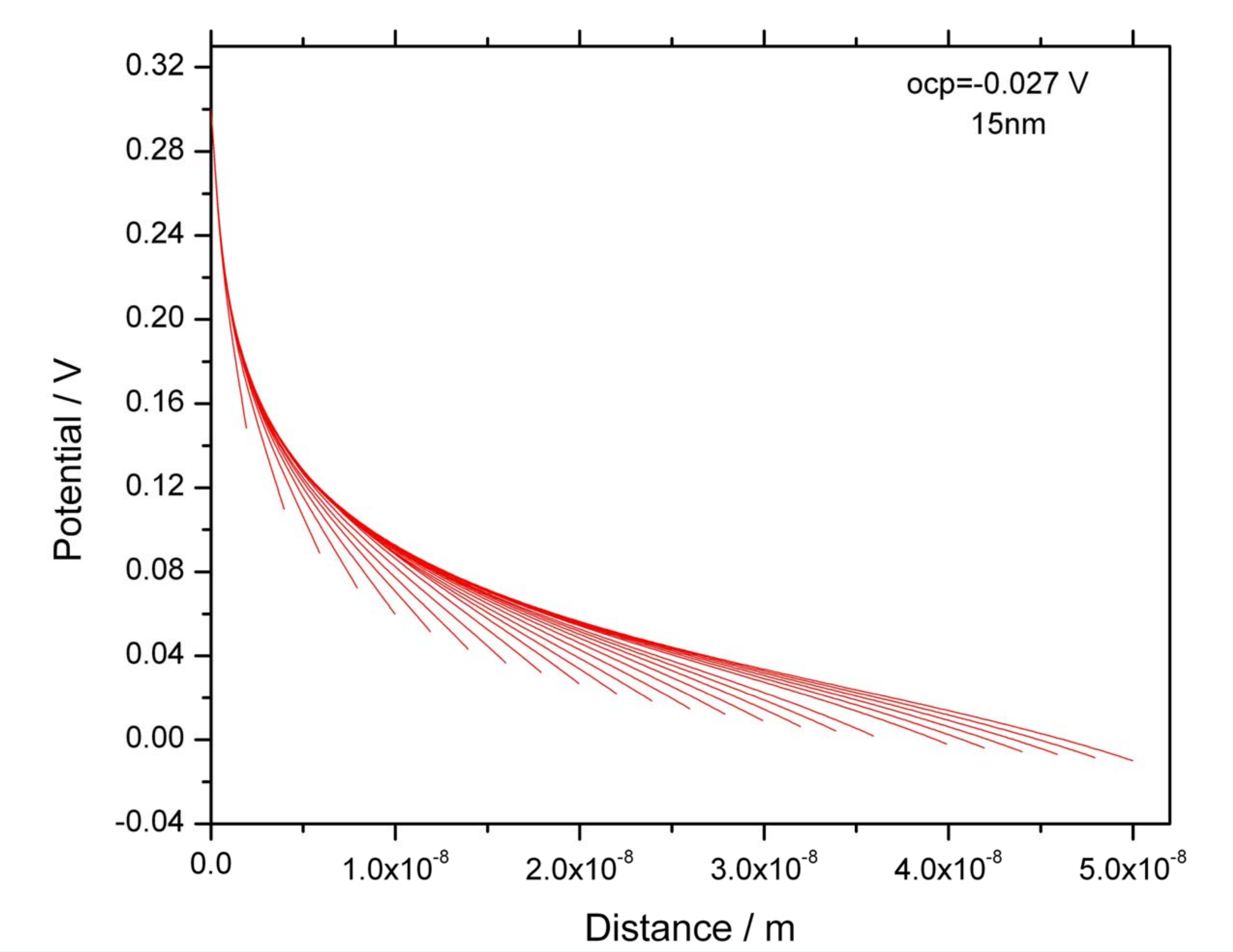

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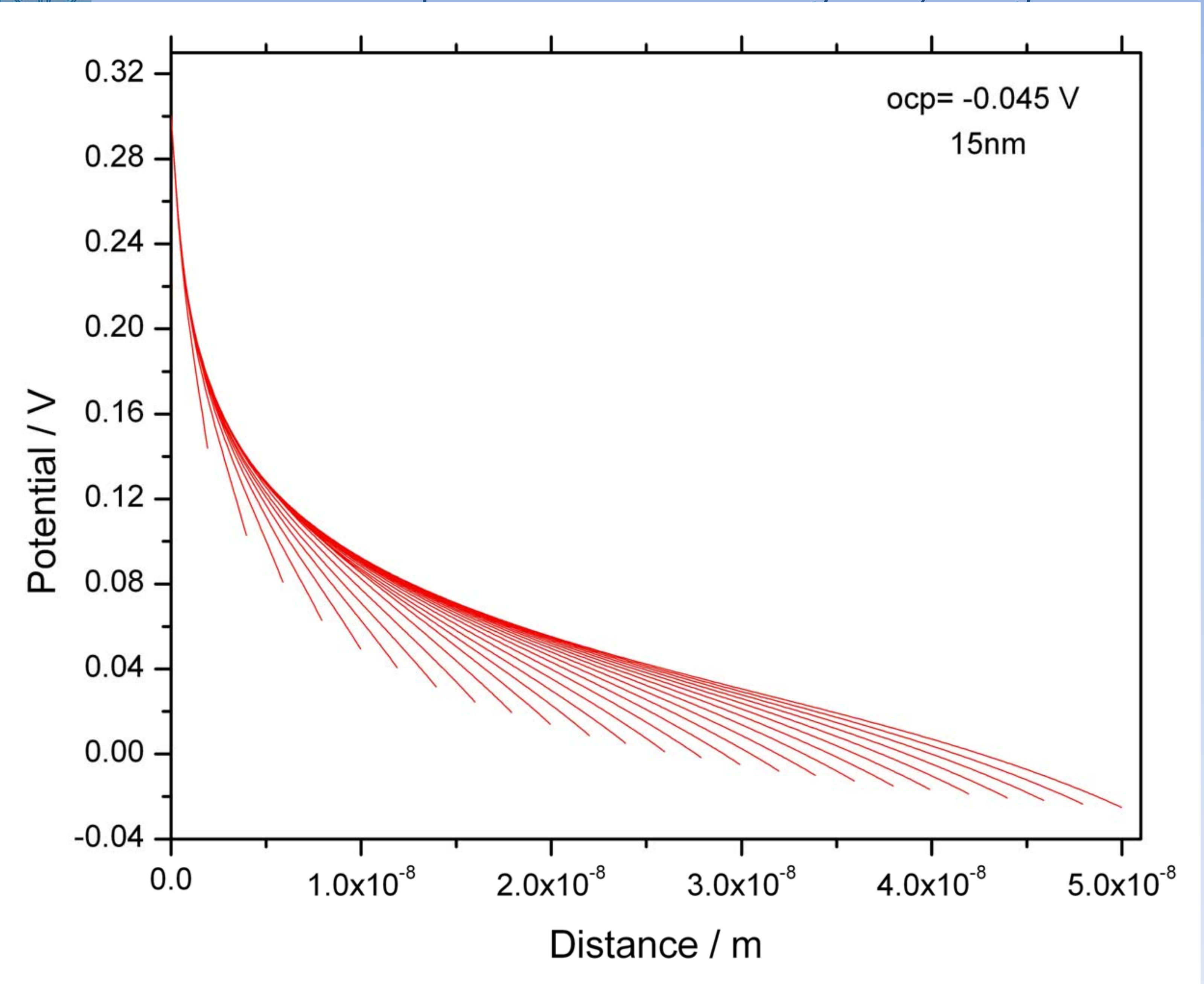

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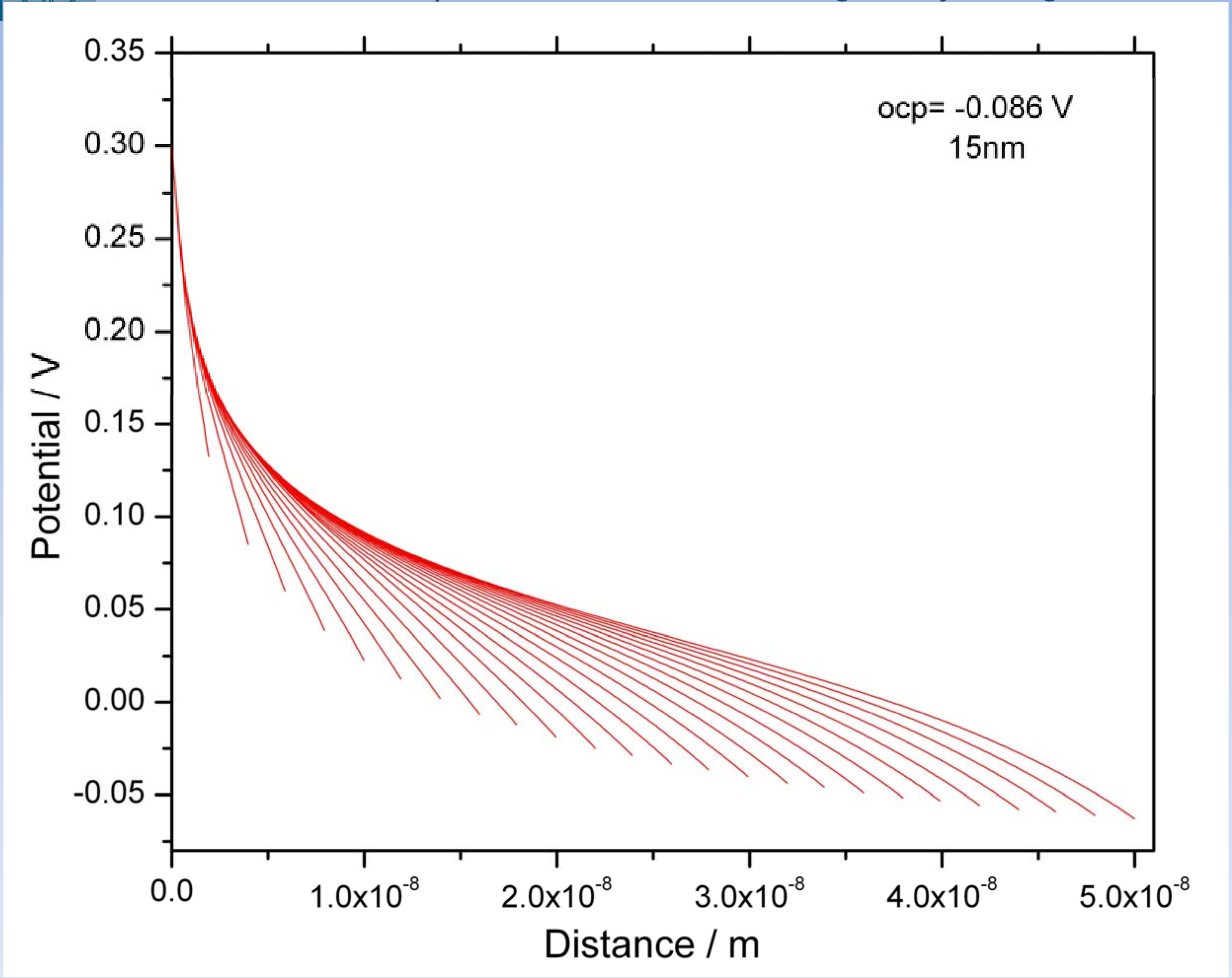

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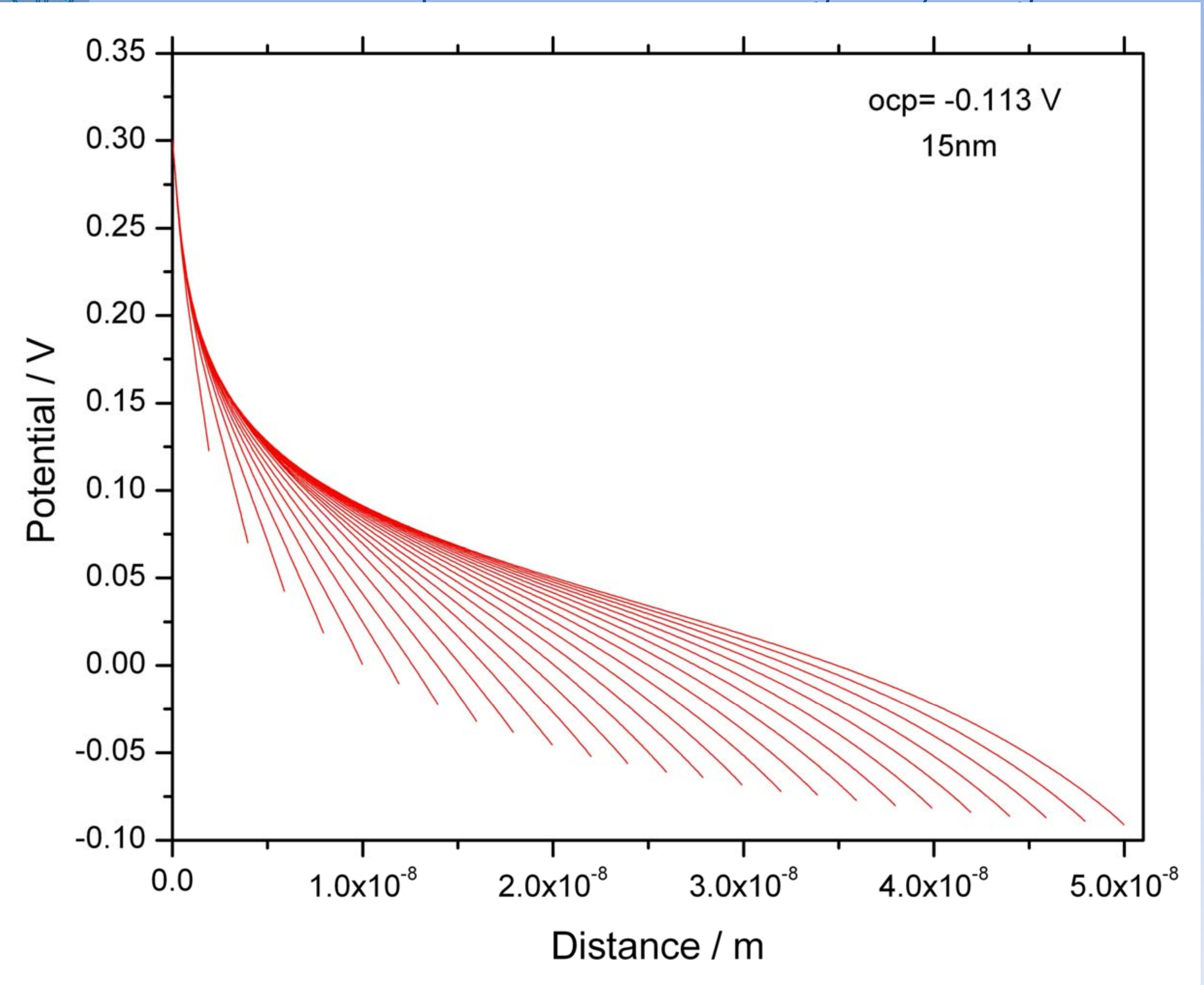

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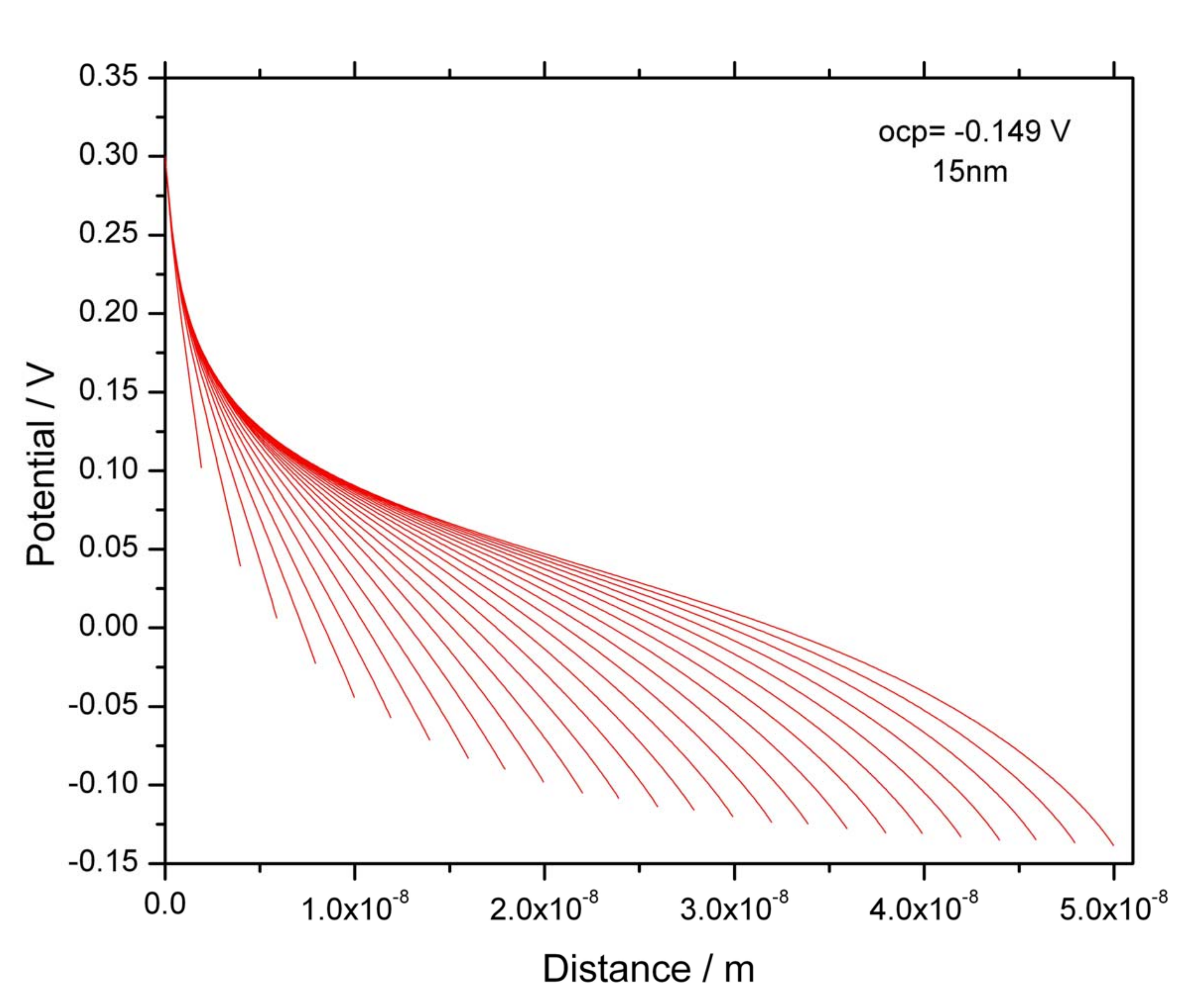
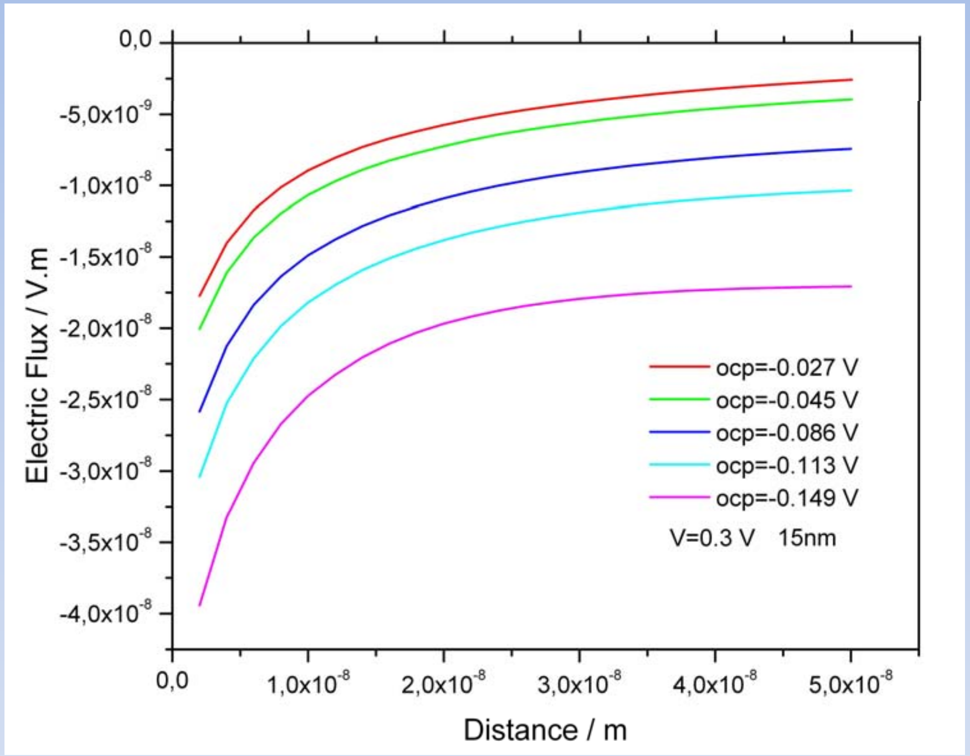
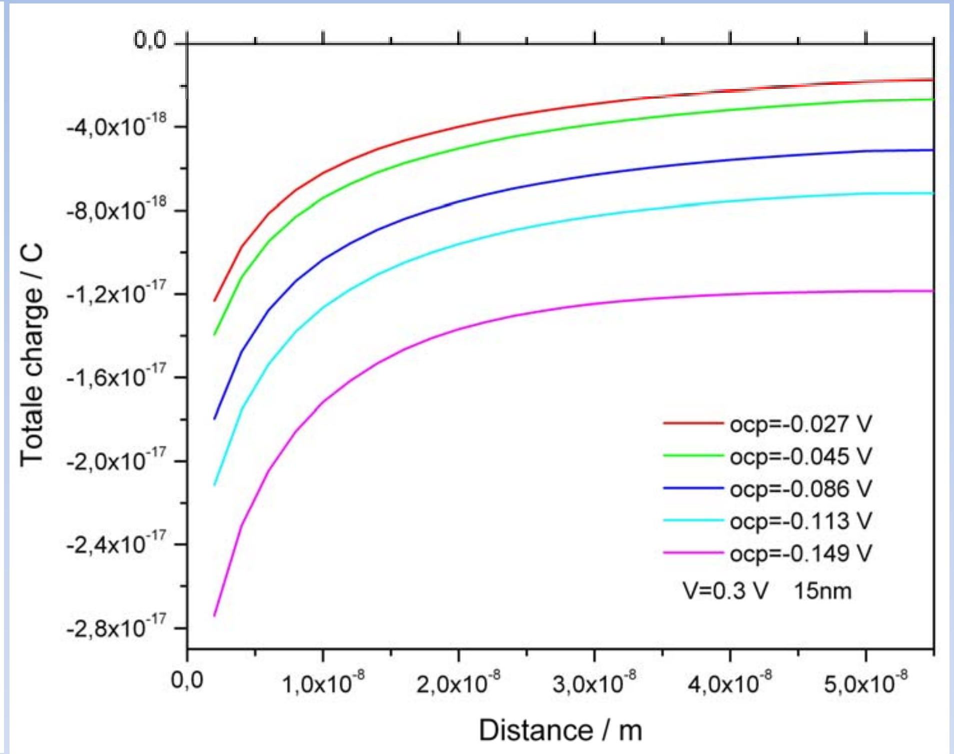


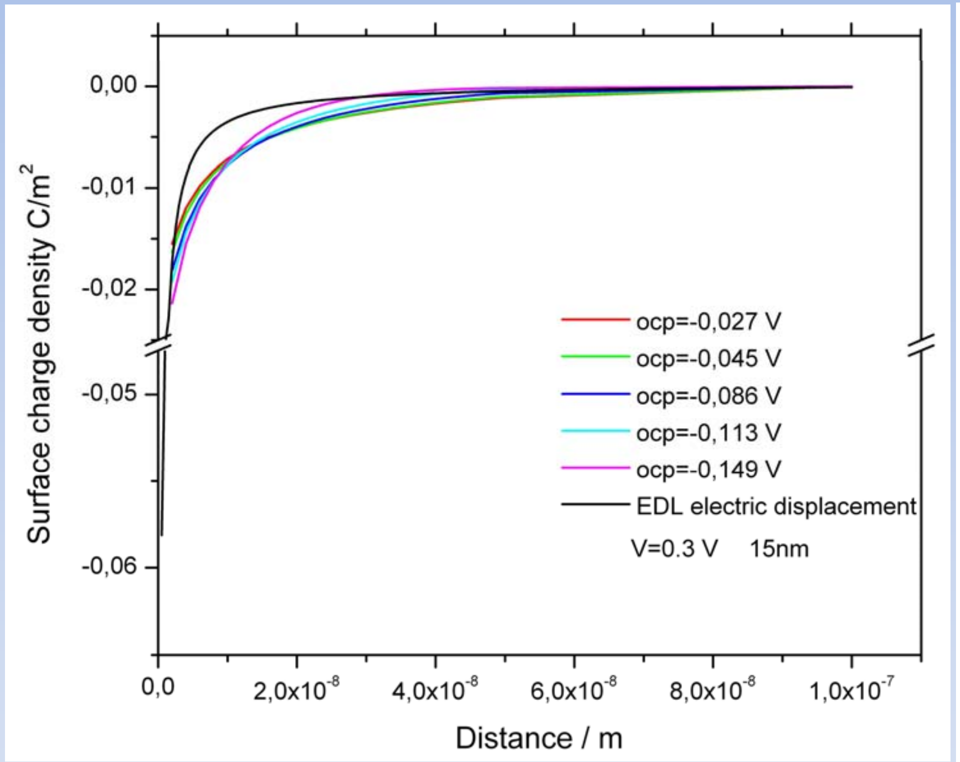
The effect of the Open Circuit Potential: Negatively charged

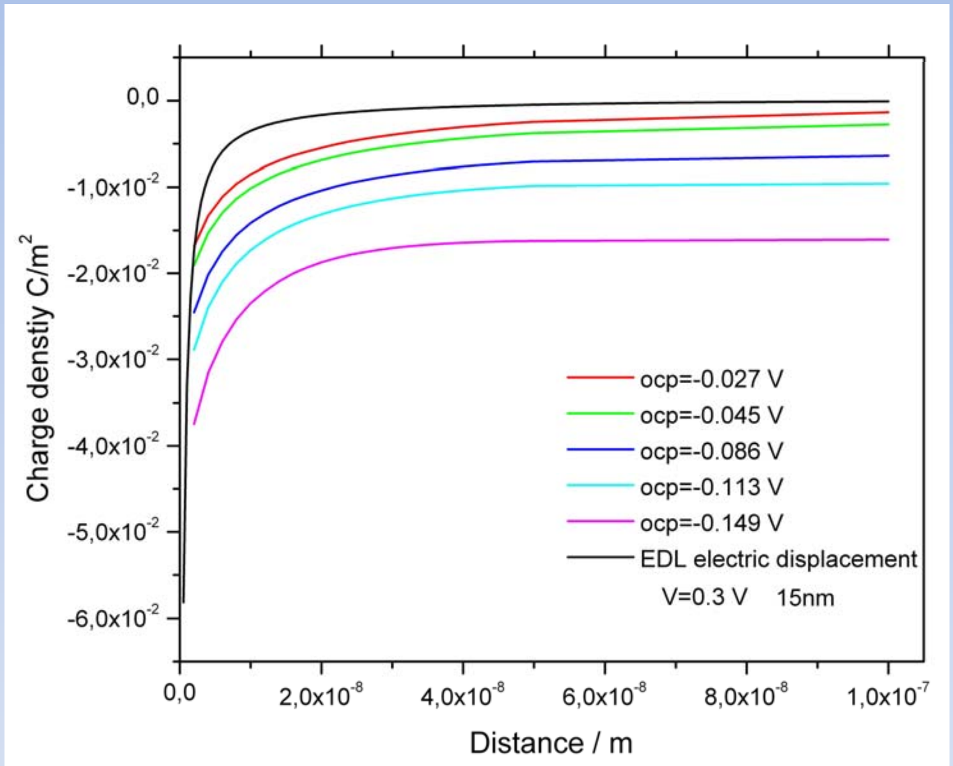




Variation of the electric flux passing through the exposed metallic tip during the approach

The effect of the Open Circuit Potential: Negatively charged





Variation of the tip surface charge density during the approach

Conclusion

•In this investigation it was shown that the tip geometry has an influence on the probed potential. A sharp protrusion distorts the charge distribution, which can effect the probed potential considerably.

•A clear electrostatic screening effects was observed in probing the double layer. This effect depends on the strength of the double layer at the probe.

•This simulation will be extended for the surface potential mapping in order to comprehend better the importance of the effects mentioned above.