# Introduction to scanning electrochemical microscopy (SECM)

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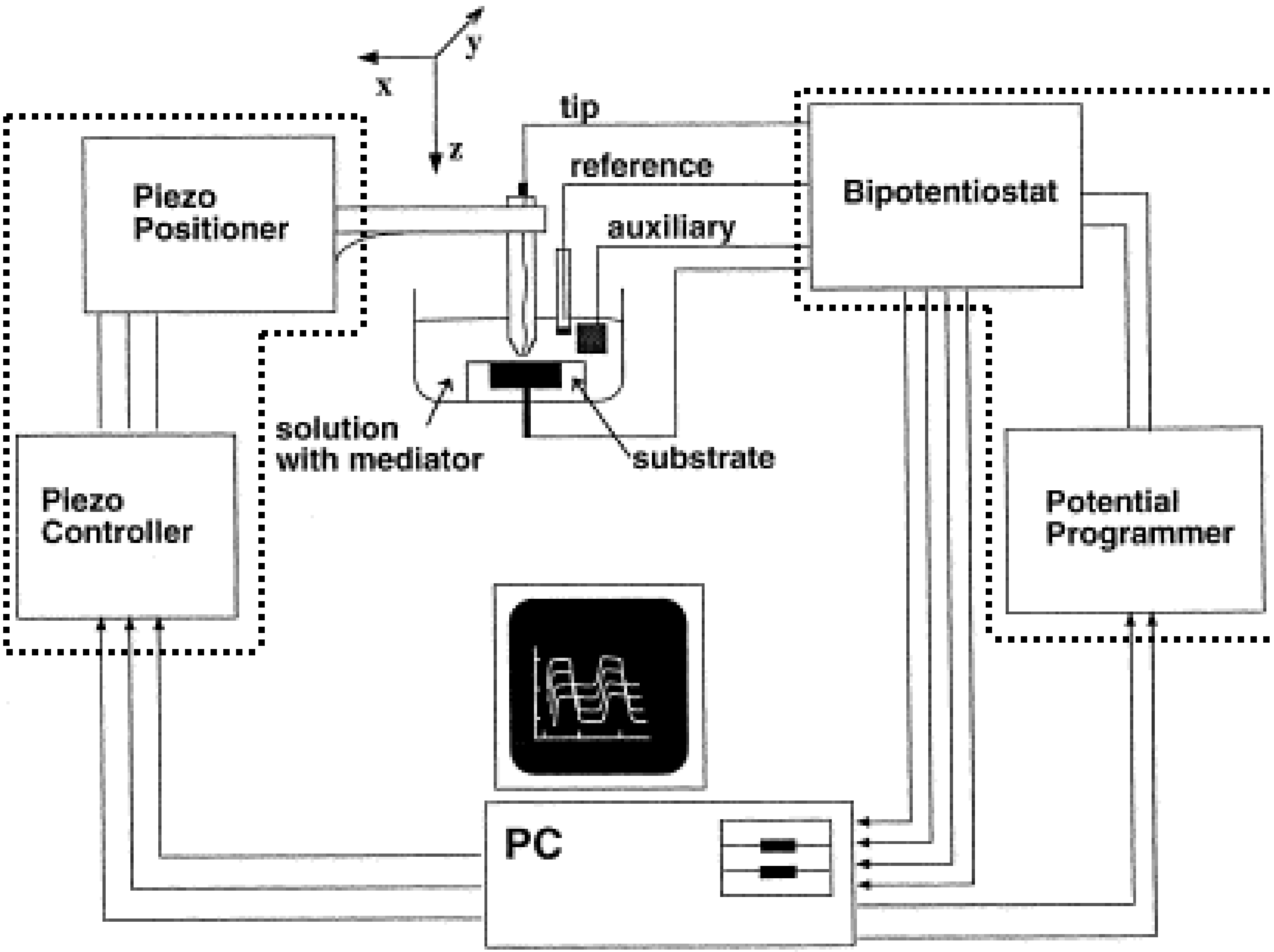
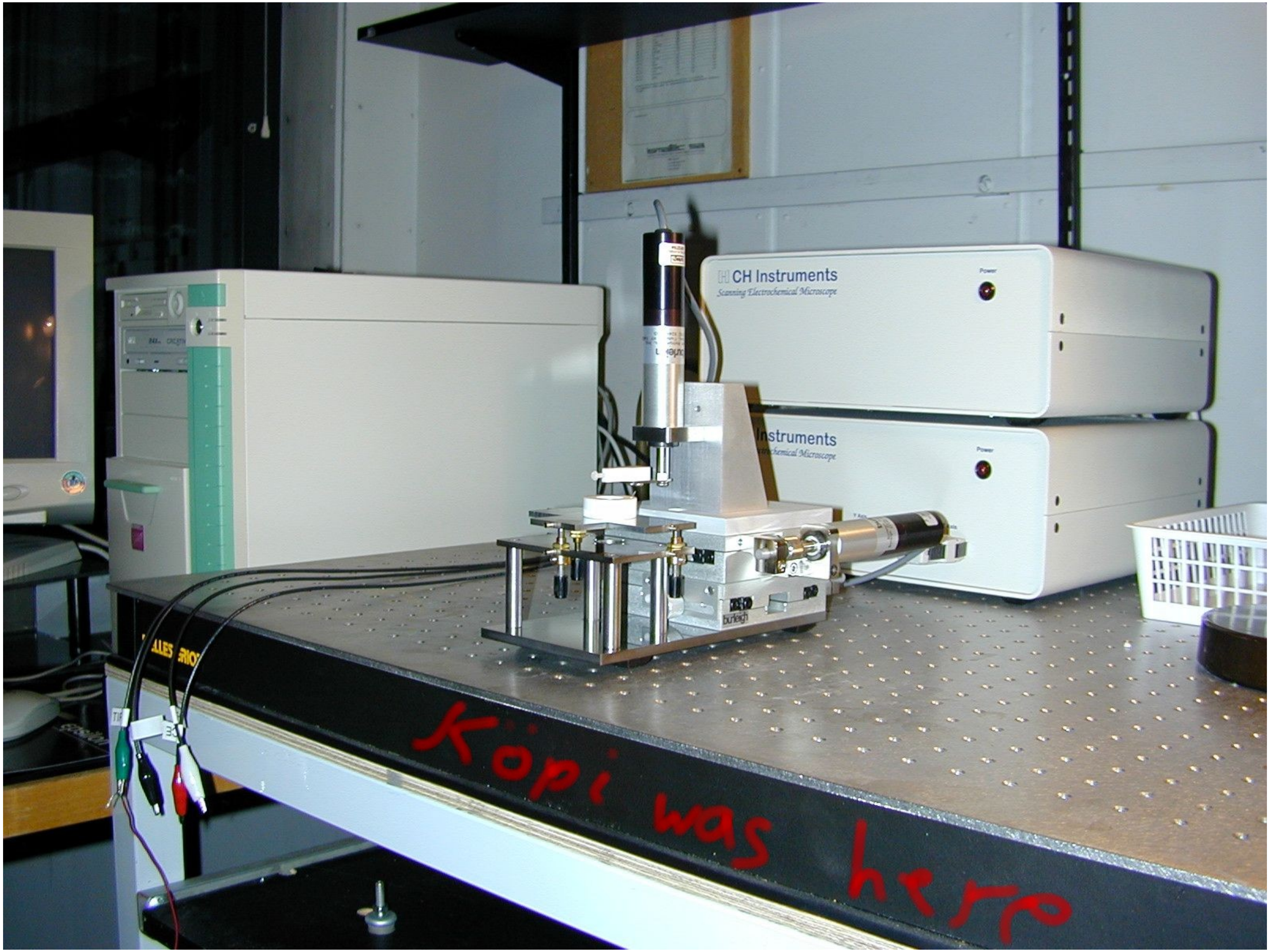
# Scanning electrochemical microscopy:

- Current flow at a probe electrode, “SECM tip”, is measured
- Can be used to probe the reactivity of insulating, conducting and semi-conducting substrates
- Member of the scanning probe microscopy (SPM) - family
- First introduced in the late 1980s by Engstrom et al. and by Bard et al.
- Subsequently developed into an established electrochemical technique


x
y
z
tip
reference
auxiliary
Bipotentiostat
Piezo Positioner
solution with mediator
substrate
Piezo Controller
Potential Programmer
PC


CH Instruments
Scanning Electrochemical Microscope
Power
Instruments
Power
burleigh
Köpi was here


CH Instruments
CH Instruments

CH Instruments
Burleigh

# Different SECM operating modes:

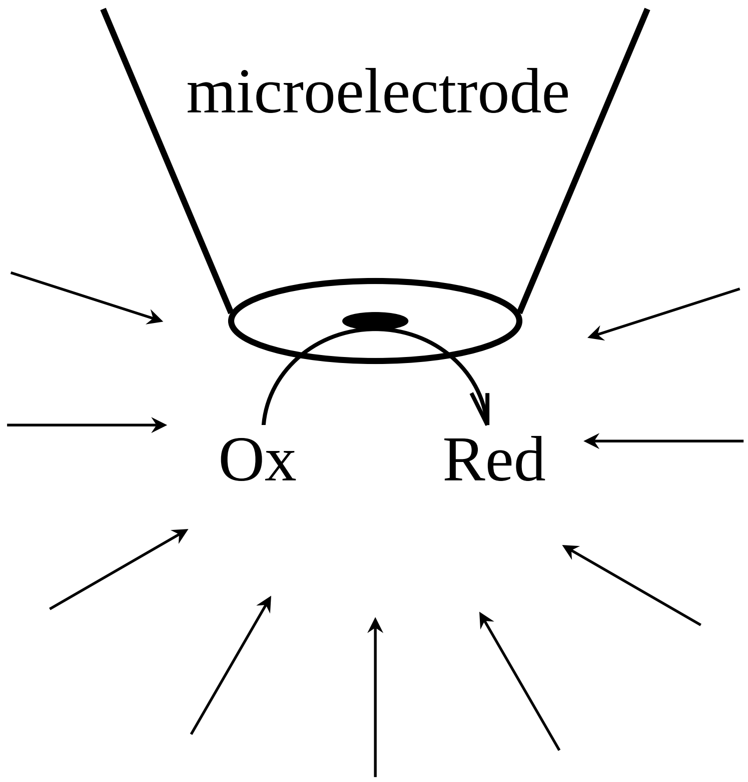
- Amperometric feedback mode
- Generation / collection mode
- Potentiometric detection
- Transient methods

    Equilibrium perturbation

    Double potential step chronoamperometry

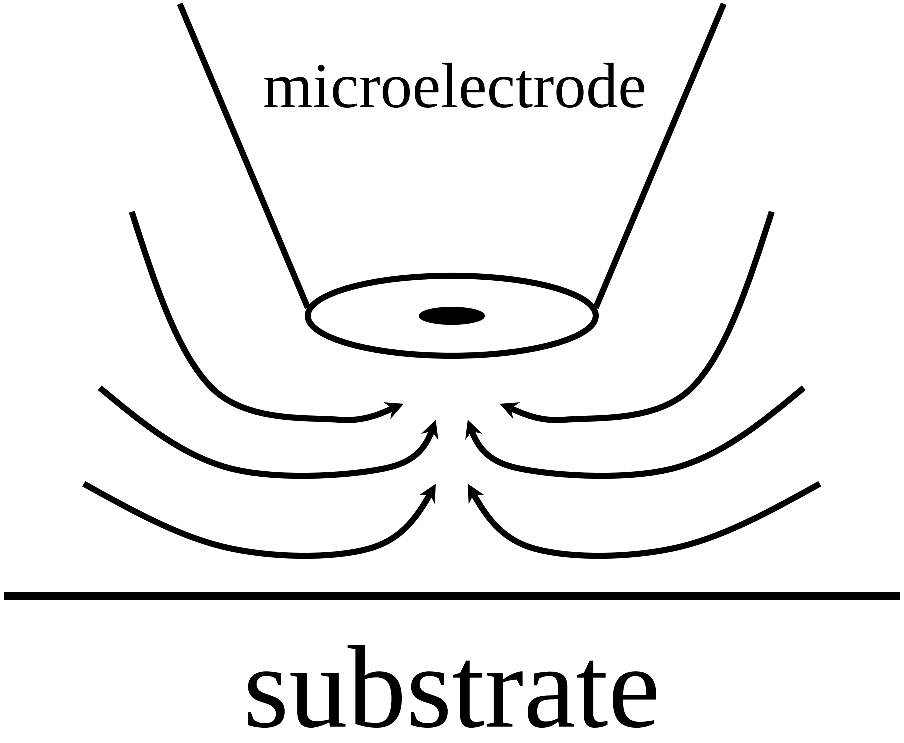
- Scanning mode

# Amperometric feedback mode



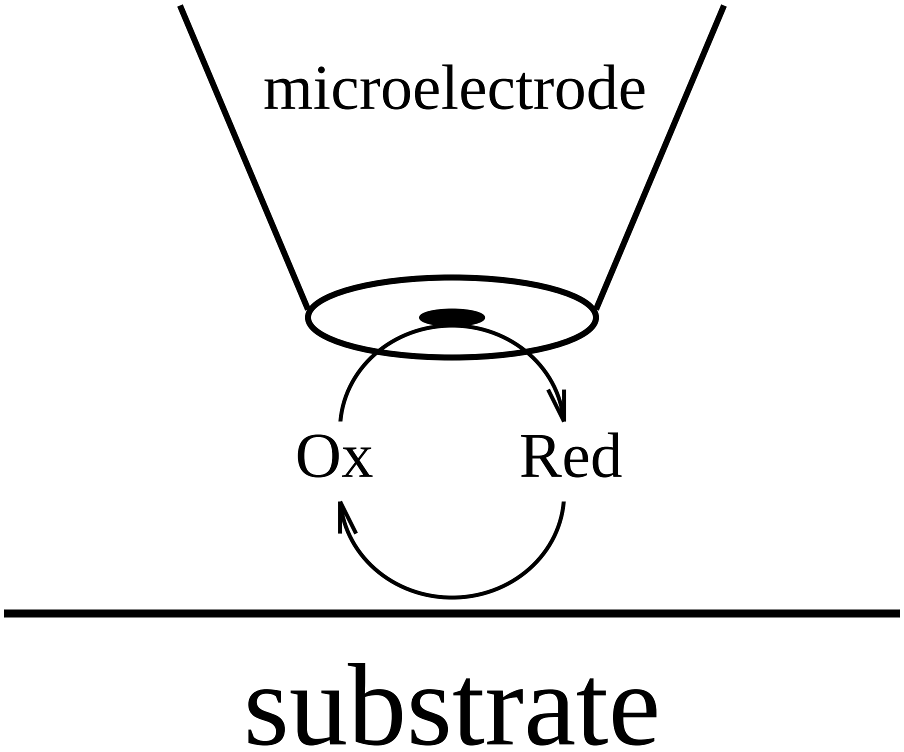

- Diffusion to a microelectrode
- Measure the change due to the proximity of a surface
- Relate this change to the reactivity and topography of the surface

# Negative feedback:

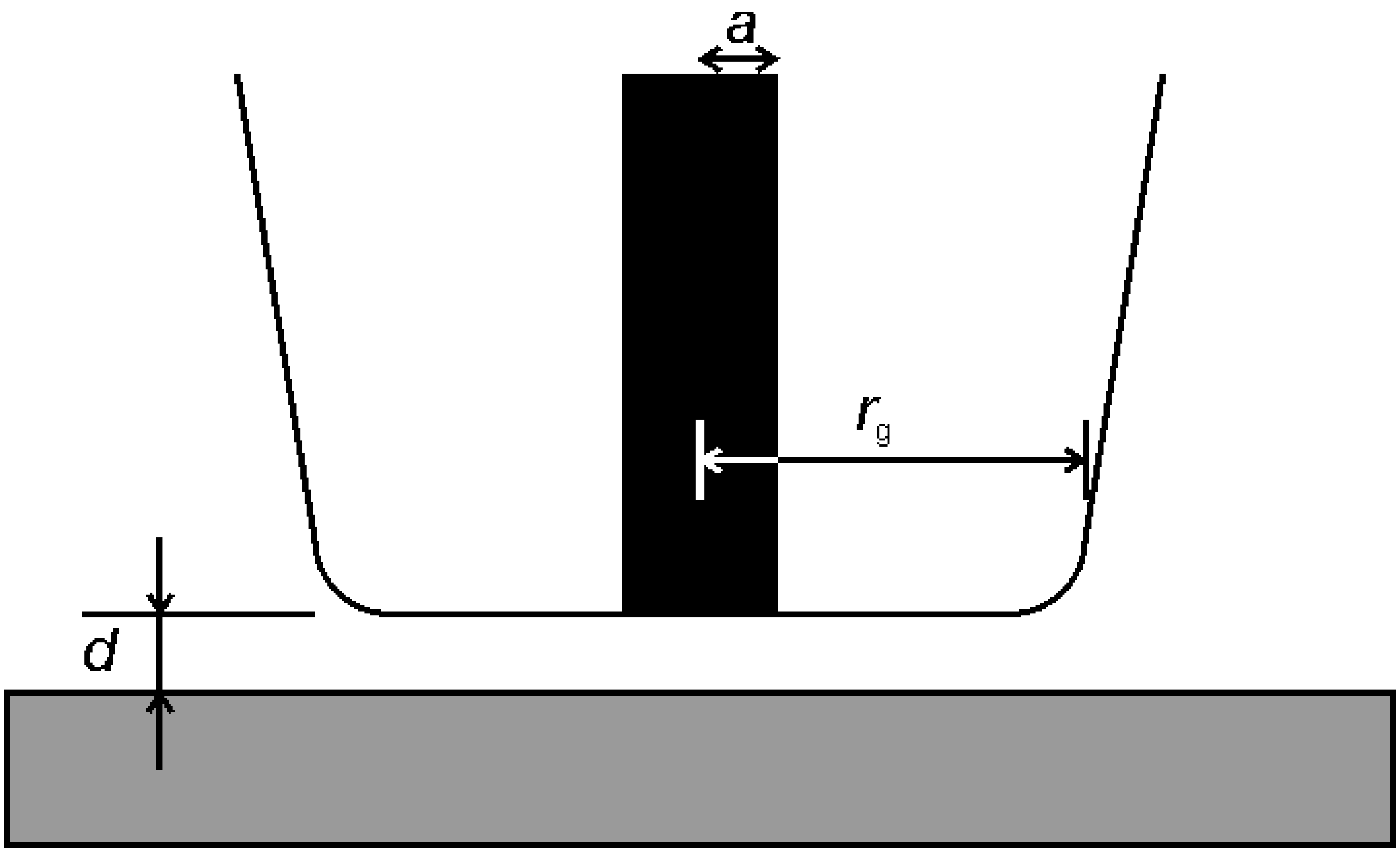



- Hindered diffusion due to the presence of the substrate
- The measured current lower than in the bulk

## Positive feedback:




- Redox mediator regeneration occurs at the substrate
- The measured current higher than in the bulk




dimensionless coordinates:

$$L = d / a$$

$$R_g = r_g / a$$

Fick's second law:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right)$$

dimensionless quantities

$C = c / c^{b}$; $R = r / a$;

$Z = z / a$; $T = t D / a^2$

$$\boxed{\rightarrow \quad \frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial Z^2}}$$

At steady-state:

$$\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} + \frac{\partial^2 C}{\partial Z^2} = 0$$

Initial condition

$$c_{Ox}(r,z,t{=}0) = c^b$$

Reaction at the tip,

$$\text{Ox} + ne^- \rightarrow \text{Red}$$

at a diffusion controlled rate, hence

$$c_{Ox}(r < a, \text{z}{=}0, t) = 0$$

If $D_{Ox} = D_{Red}$, the principle of mass-conservation gives

$$c_{Red}(r,z,t) = c^b - c_{Ox}(r,z,t)$$

and only a single species needs to be considered.

<u>This always applies at steady-state.</u>

Initial condition

$$C(R,Z,T{=}0) = 1$$

At an insulating substrate

$$\partial C \,/\, \partial Z = 0$$

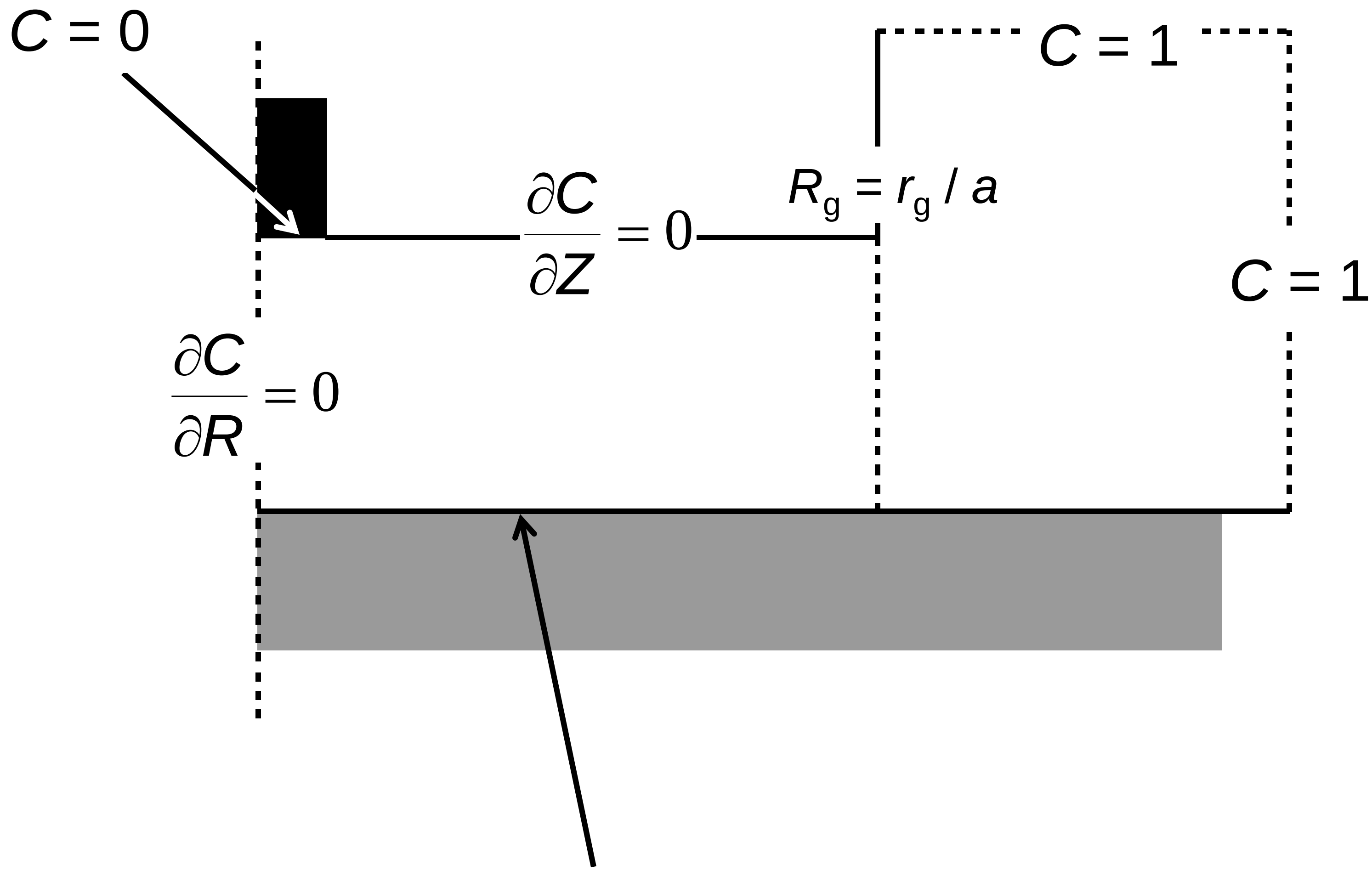
At a conducting substrate

$$\mathrm{Red} \rightarrow \mathrm{Ox} + ne^-$$

at a diffusion controlled rate

$$c_{\mathrm{Red}}(r,z{=}\mathrm{d},t) = 0$$

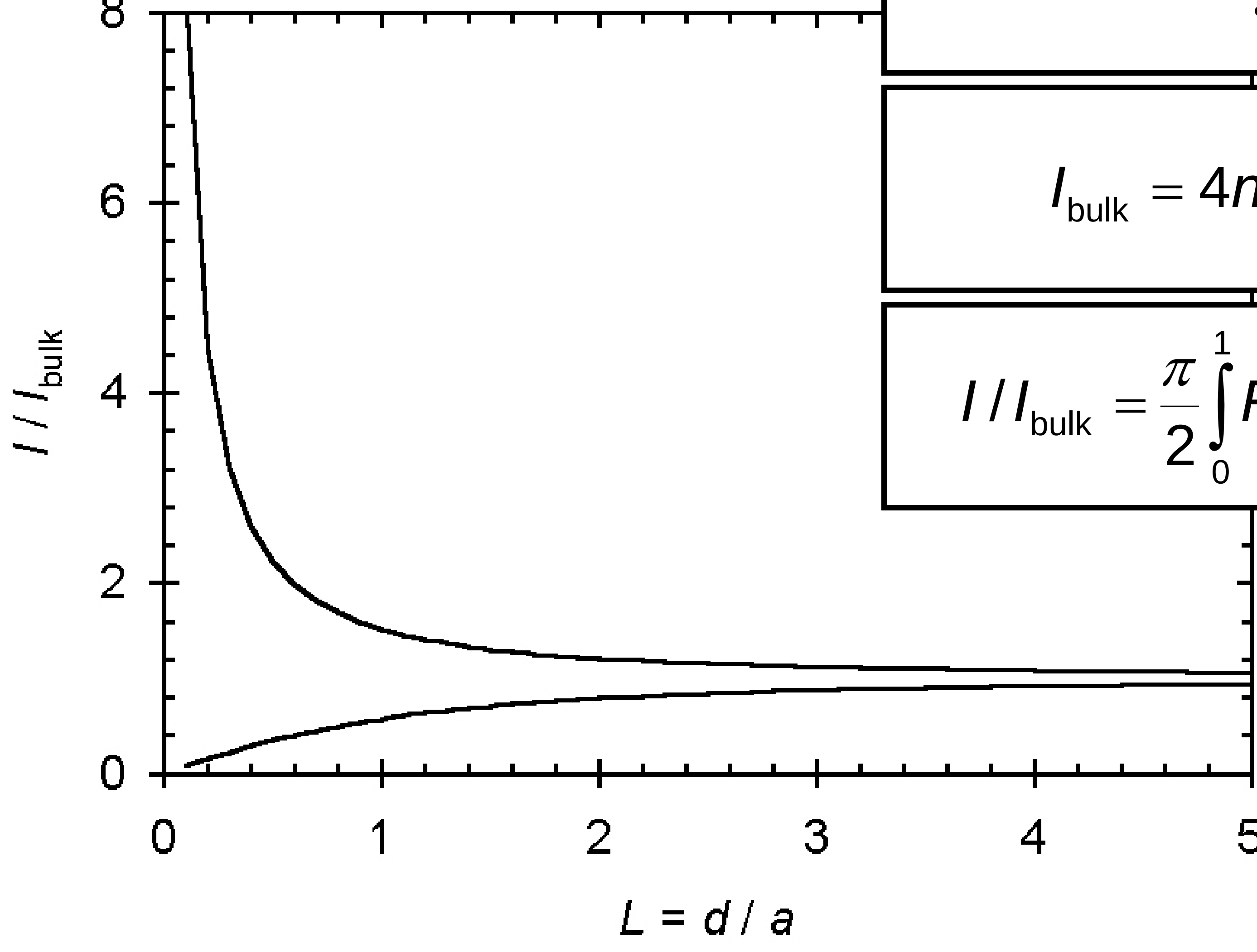
$$\Rightarrow C(R,Z{=}L,T) = 1$$




boundary condition at the substrate:

$C = 1$ (conducting)

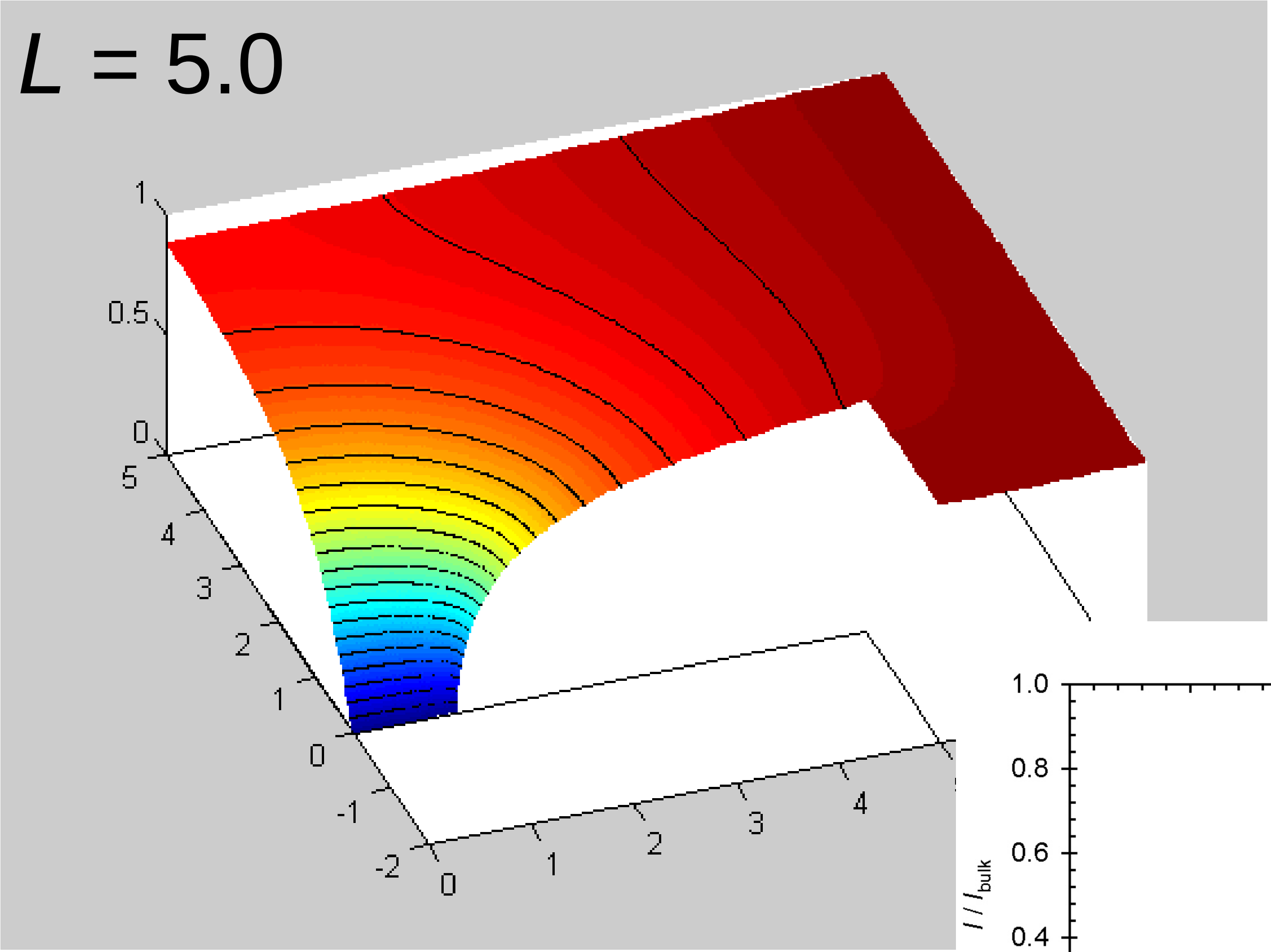
$\partial C / \partial Z = 0$ (insulating)

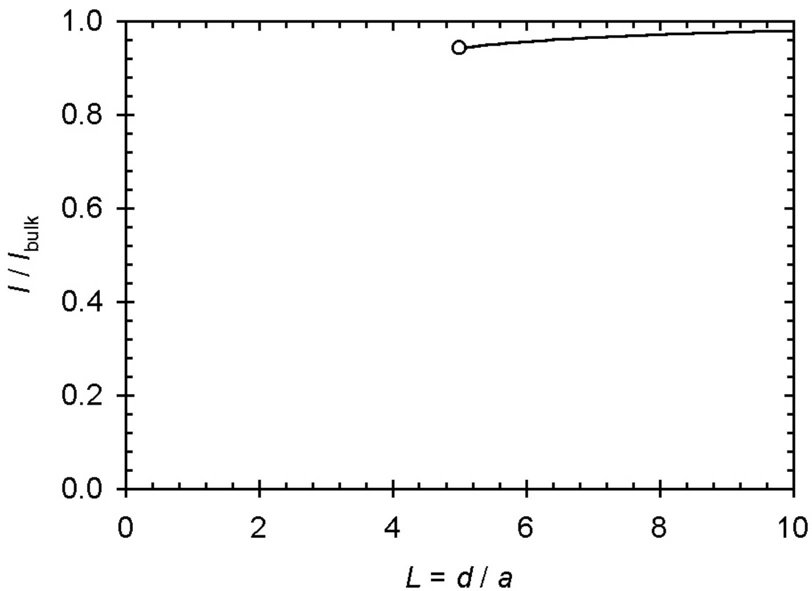


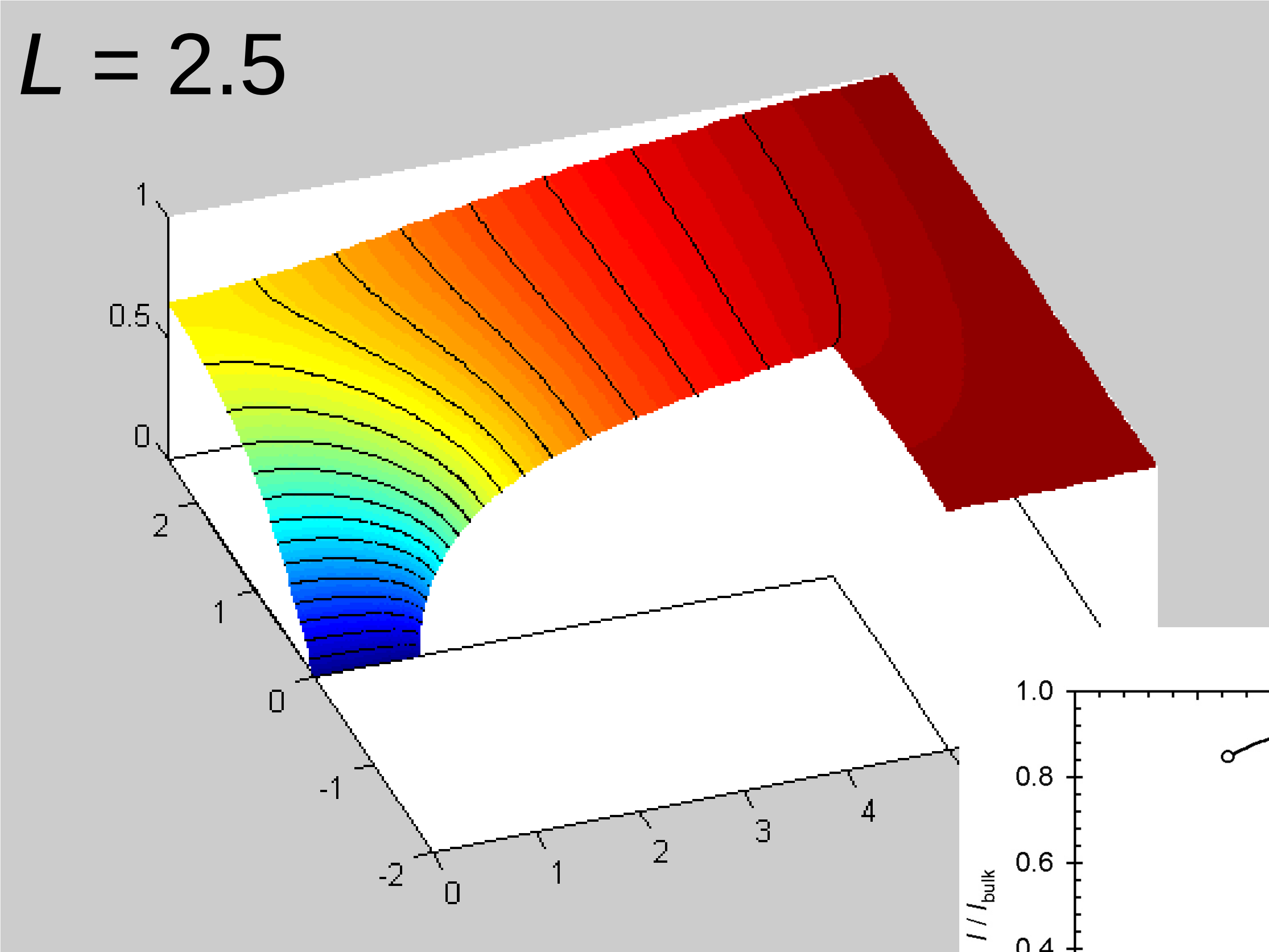

$$I = 2\pi nFDc^{\mathrm{b}}a\int_0^1 R\left.\frac{\partial C}{\partial Z}\right|_{Z=0}\mathrm{d}R$$

$$I_{\mathrm{bulk}} = 4nFDc^{\mathrm{b}}a$$

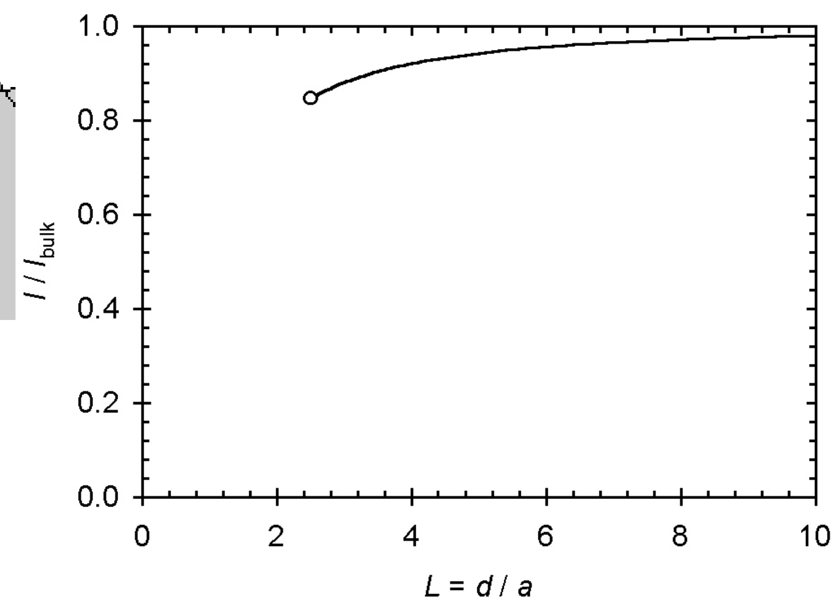
$$I / I_{\mathrm{bulk}} = \frac{\pi}{2}\int_0^1 R\left.\frac{\partial C}{\partial Z}\right|_{Z=0}\mathrm{d}R$$


L = 5.0
1
0.5
0
5
4
3
2
1
0
-1
-2
0
1
2
3
4

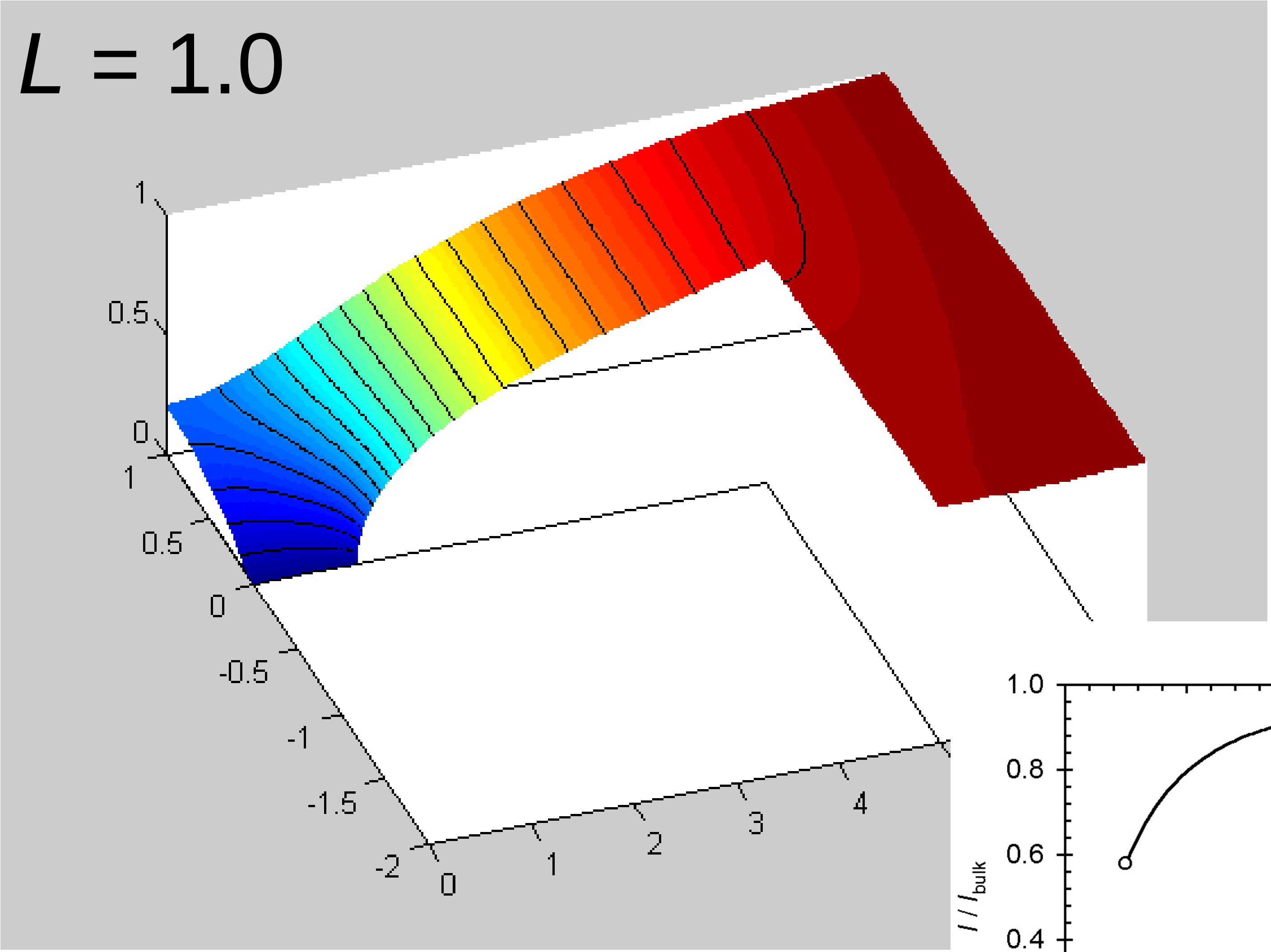

1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
I / I_bulk
L = d / a



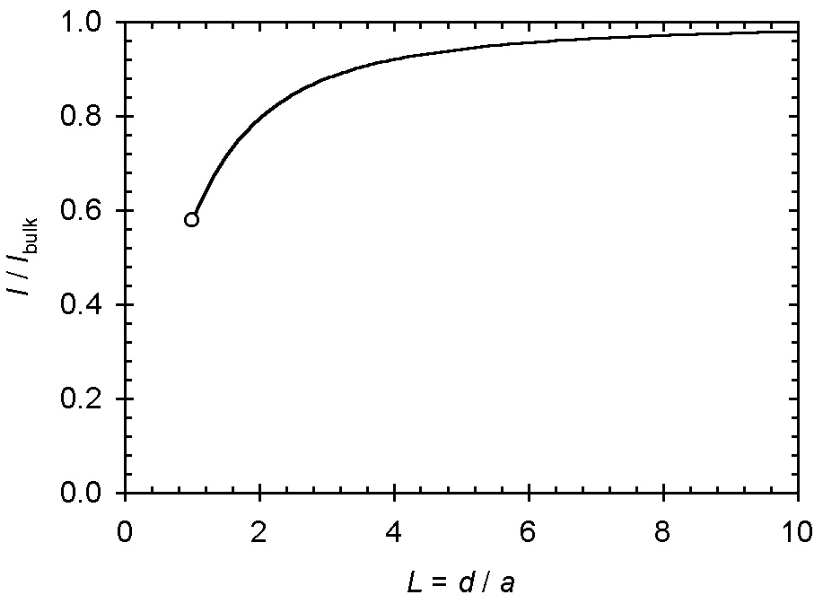
$L$ = 2.5
1
0.5
0
2
1
0
-1
-2
0
1
2
3
4

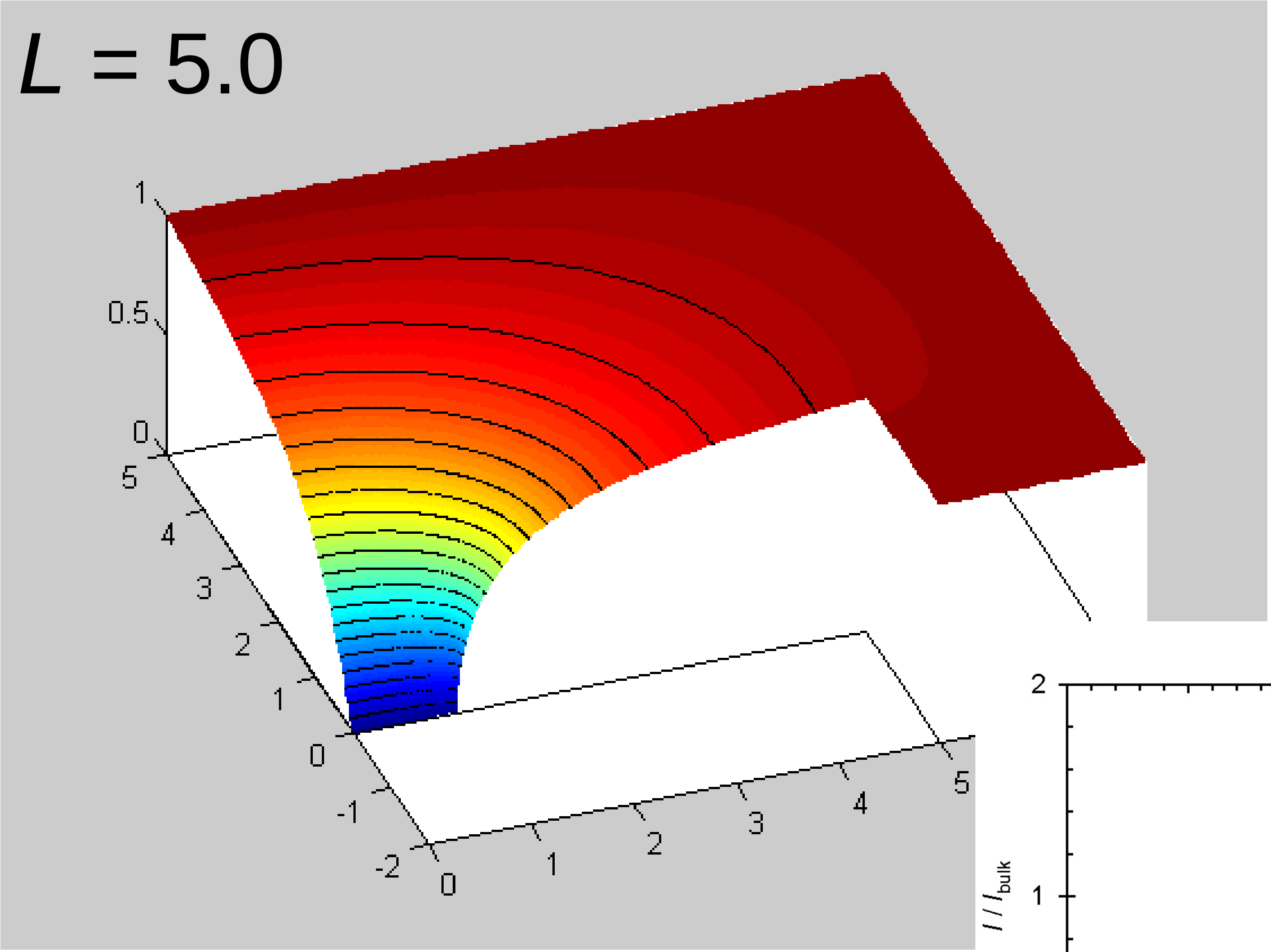
1.0
0.8
0.6
0.4
0.2
0.0
$I$ / $I_{bulk}$
0
2
4
6
8
10
$L$ = $d$ / $a$



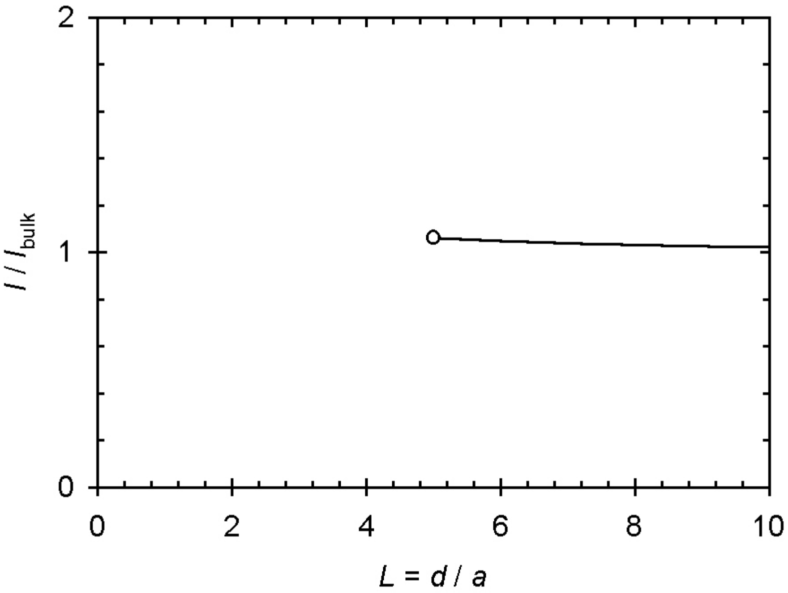
L = 1.0
1
0.5
0
1
0.5
0
-0.5
-1
-1.5
-2
0
1
2
3
4

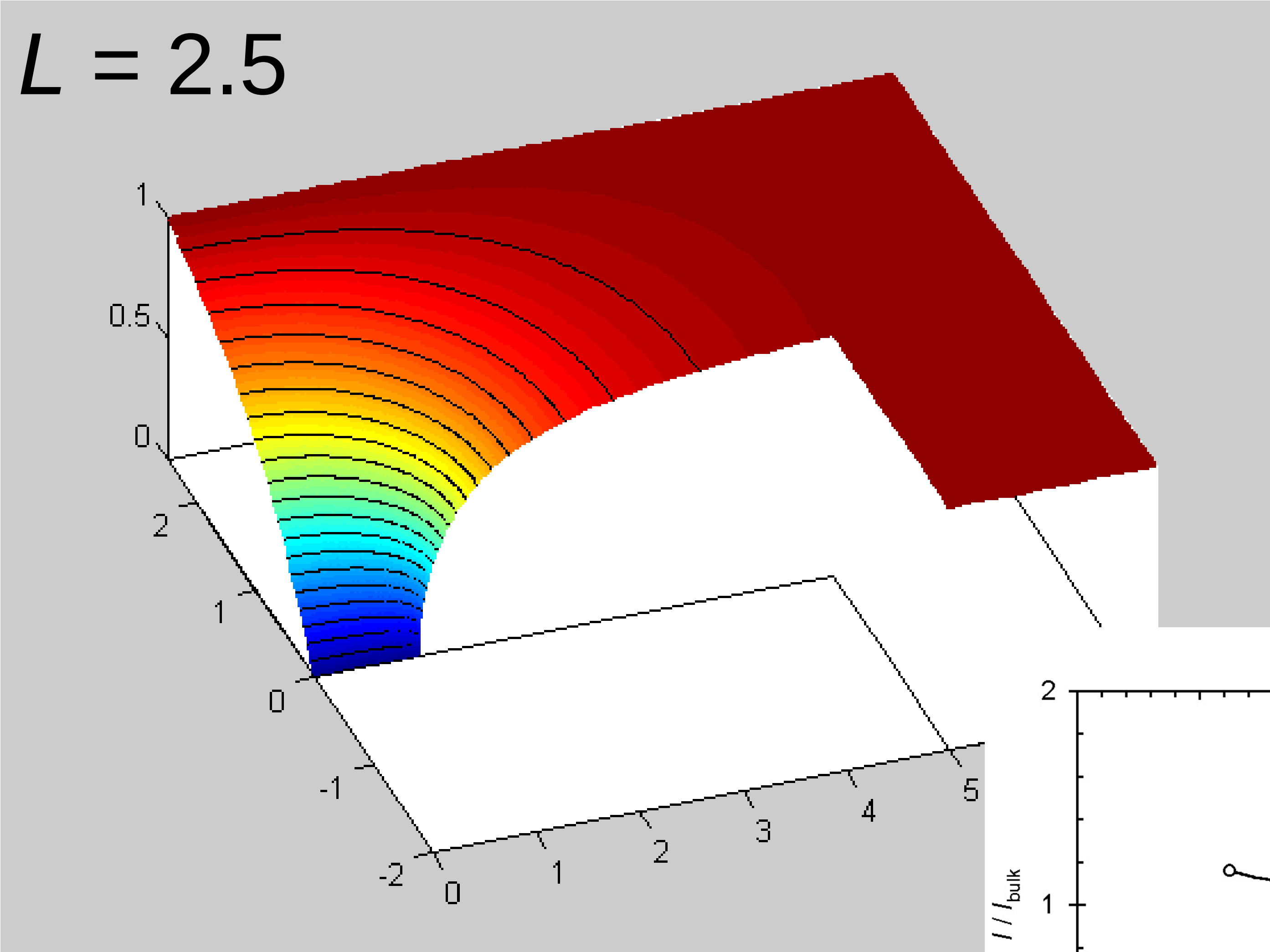
1.0
0.8
0.6
0.4
0.2
0.0
I / I_bulk
0
2
4
6
8
10
L = d / a

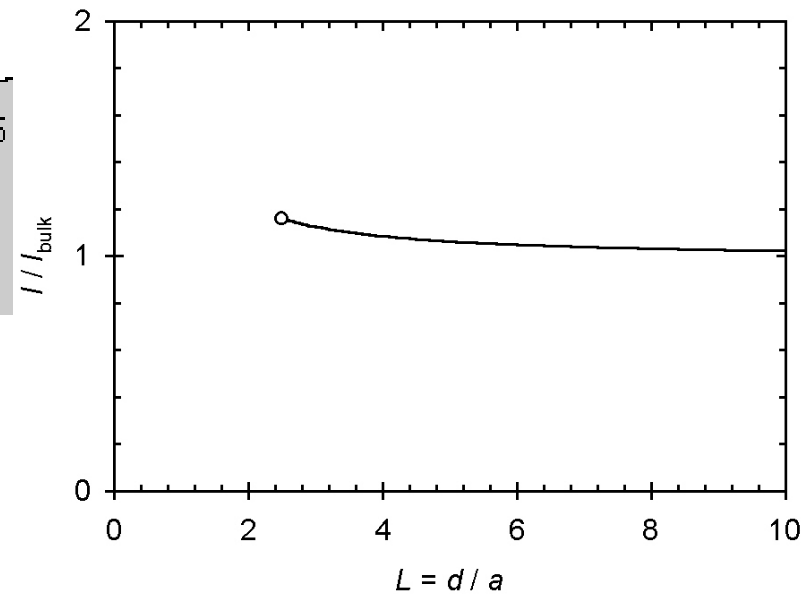


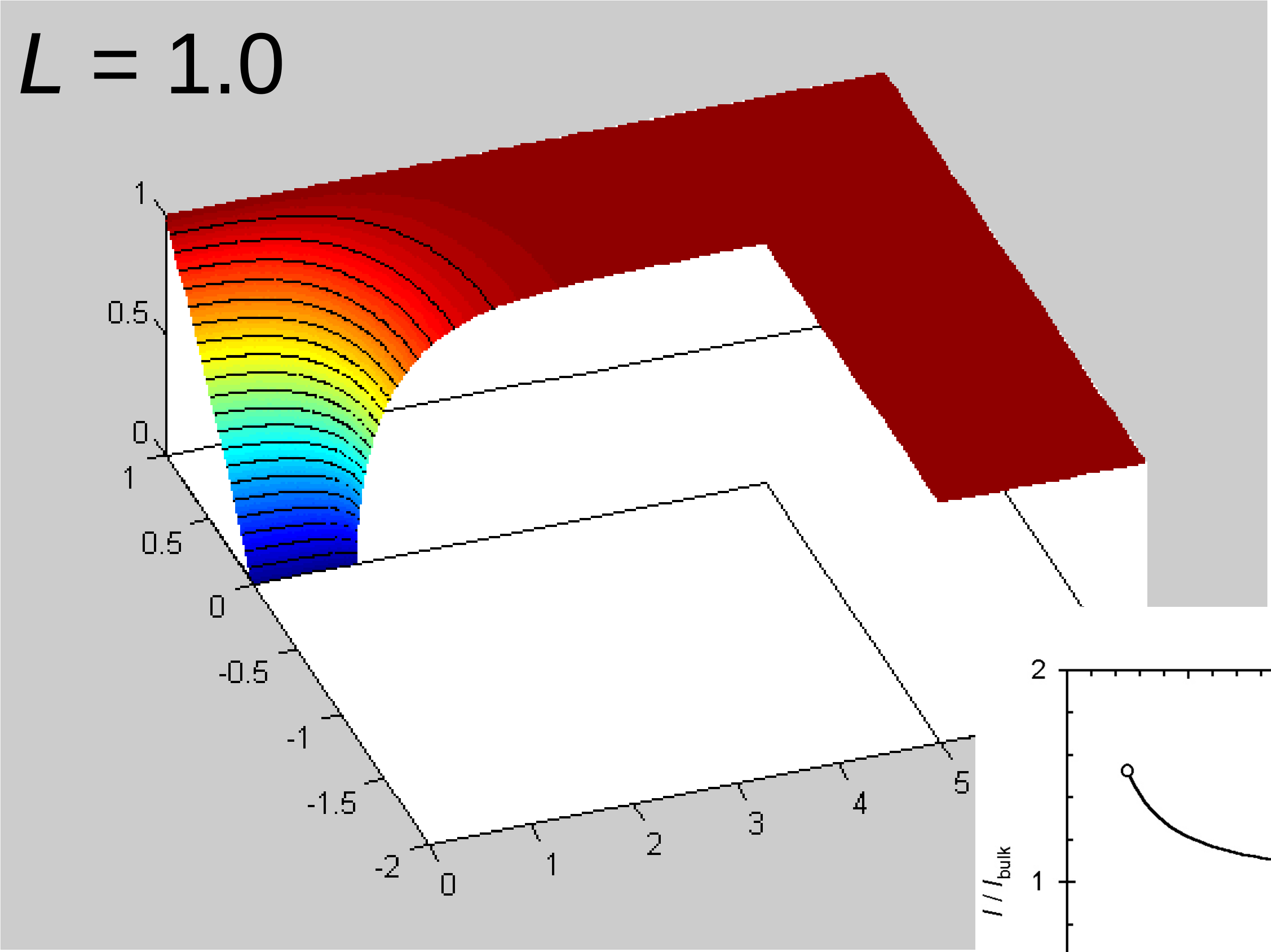
L = 5.0
1
0.5
0
5
4
3
2
1
0
-1
-2
0
1
2
3
4
5

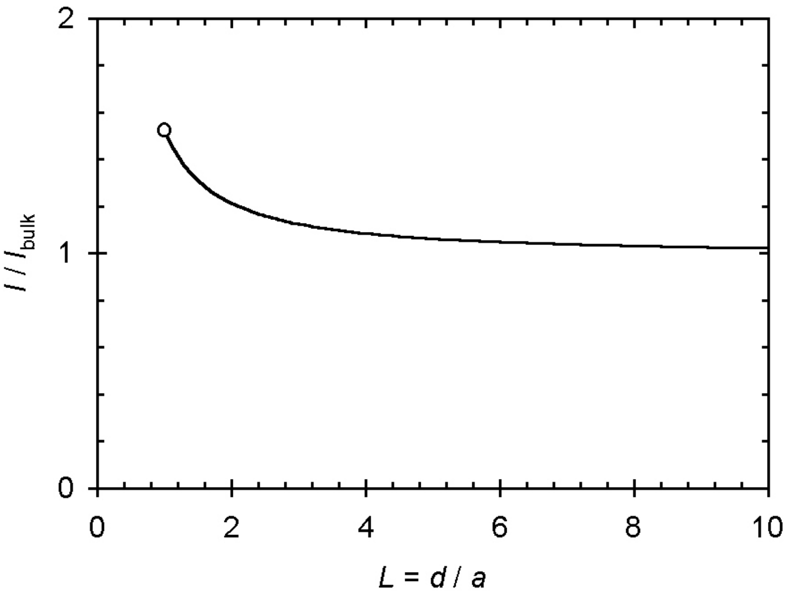
2
1
0
I / I_bulk
0
2
4
6
8
10
L = d / a


L = 2.5
1
0.5
0
2
1
0
-1
-2
0
1
2
3
4
5

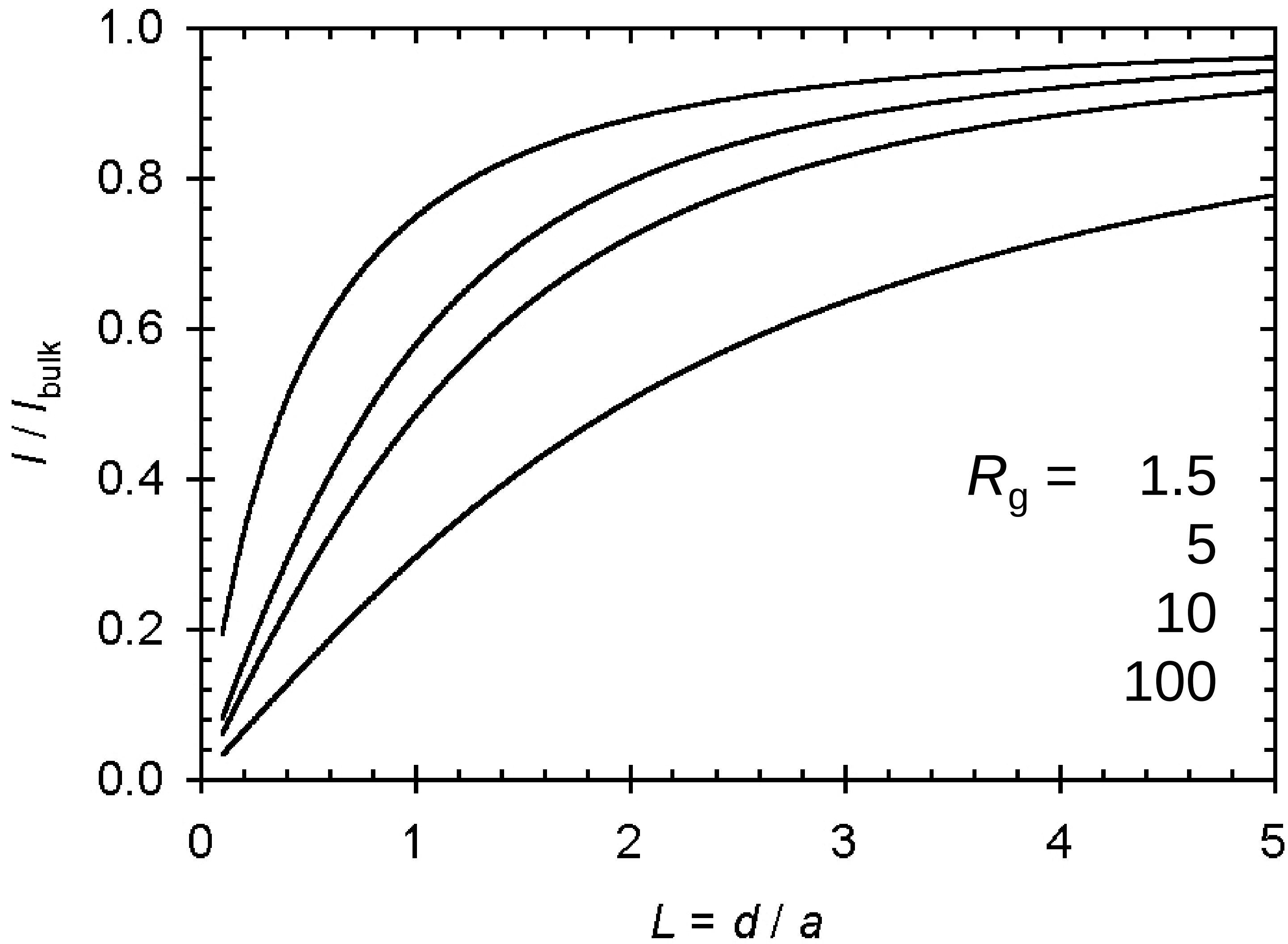

I / I_bulk
2
1
0
0
2
4
6
8
10
L = d / a

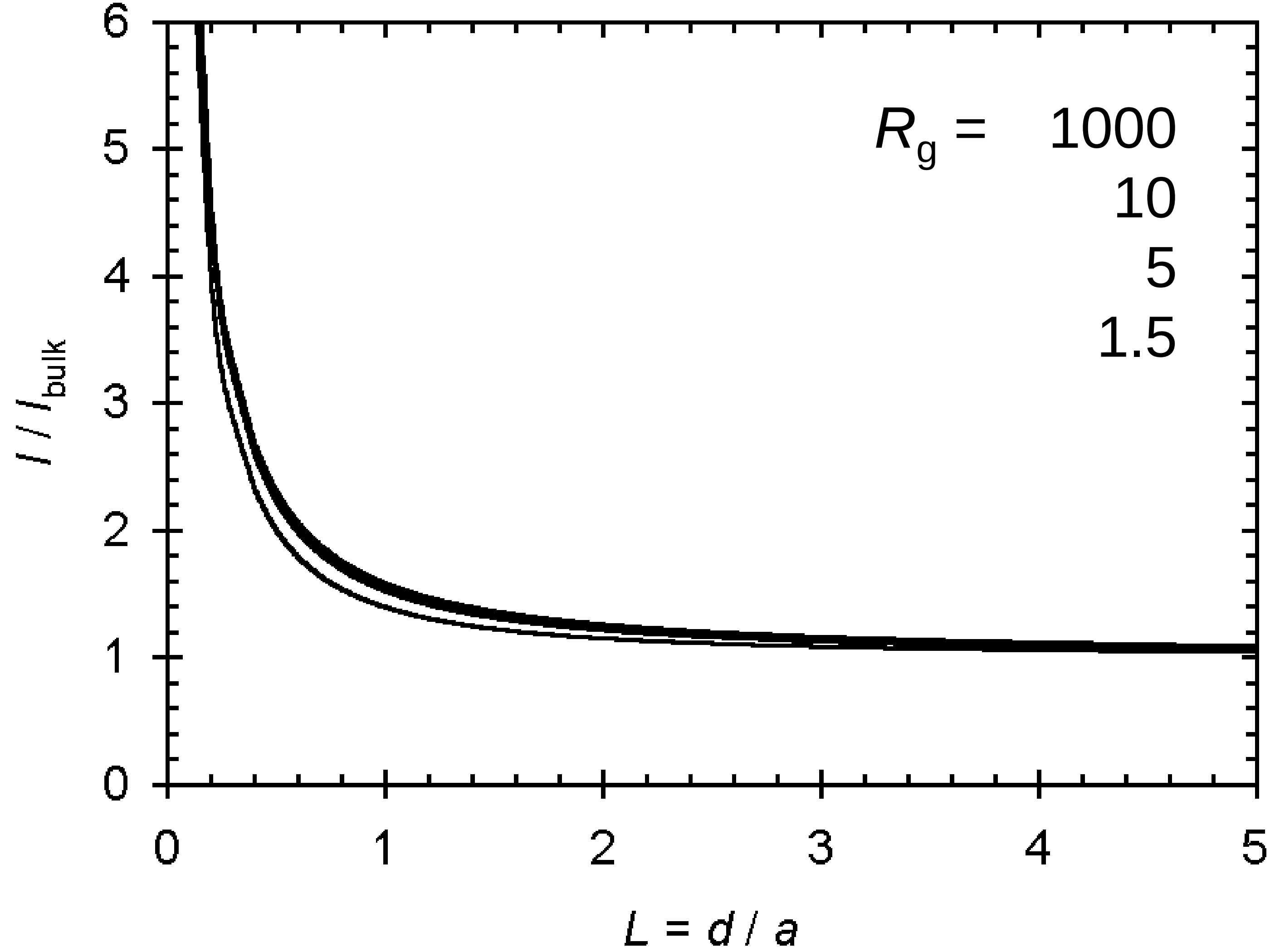


L = 1.0
1
0.5
0
1
0.5
0
-0.5
-1
-1.5
-2
0
1
2
3
4
5

2
1
0
0
2
4
6
8
10
I / I_bulk
L = d / a


1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
I / I_bulk
L = d / a
R_g = 1.5
5
10
100



6
5
4
3
2
1
0
0
1
2
3
4
5
I / I_bulk
L = d / a
R_g = 1000
10
5
1.5

Kinetics at the substrate:

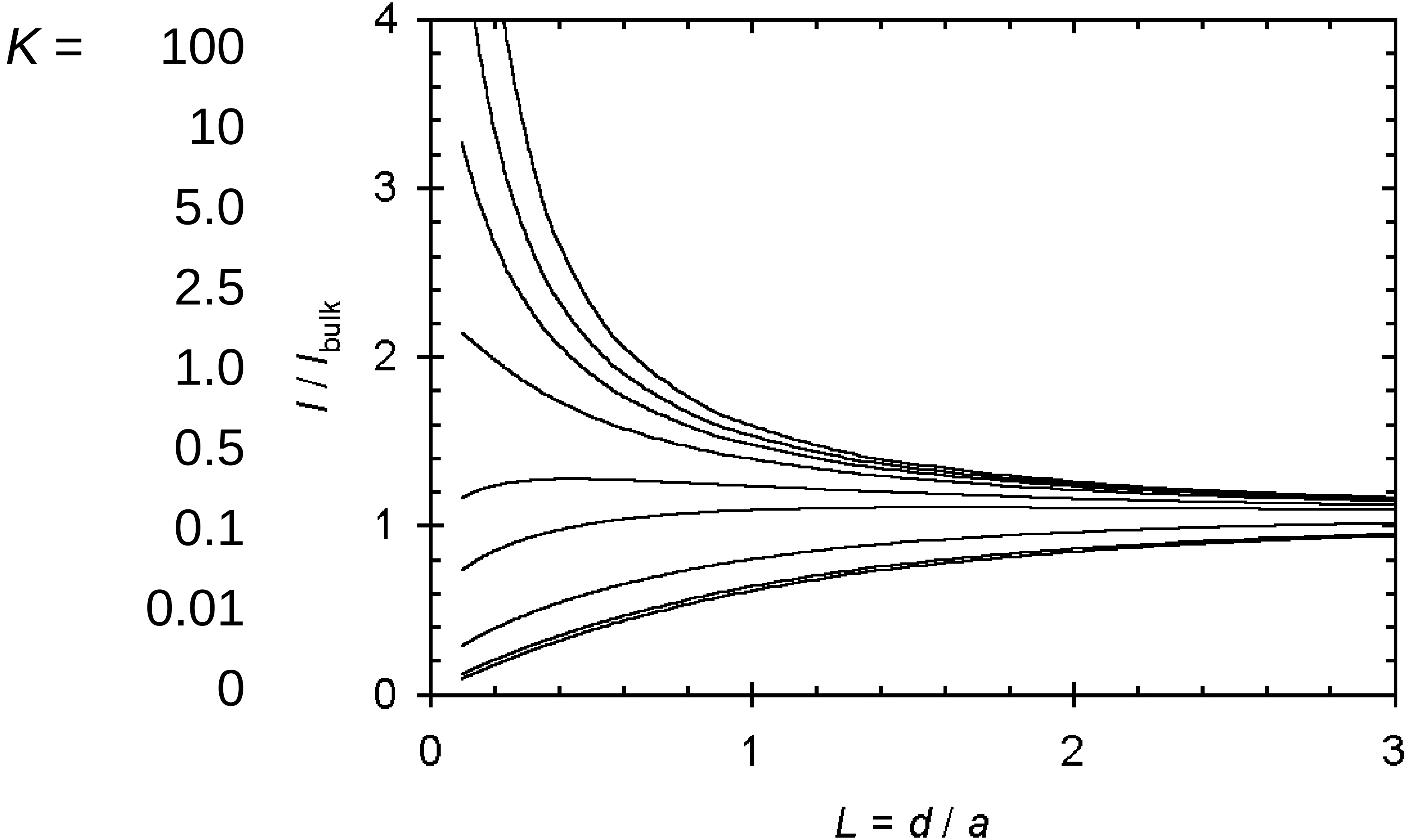
$$\mathrm{Red} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{Ox} + n\mathrm{e}^-$$

$$D_\mathrm{Ox} \left.\frac{\partial c_\mathrm{Ox}}{\partial z}\right|_{z=d} = -D_\mathrm{Red} \left.\frac{\partial c_\mathrm{Red}}{\partial z}\right|_{z=d}$$

$$D_\mathrm{Ox} \left.\frac{\partial c_\mathrm{Ox}}{\partial z}\right|_{z=d} = k_\mathrm{f} c_\mathrm{Red}(r, z=d, t) - k_\mathrm{b} c_\mathrm{Ox}(r, z=d, t)$$

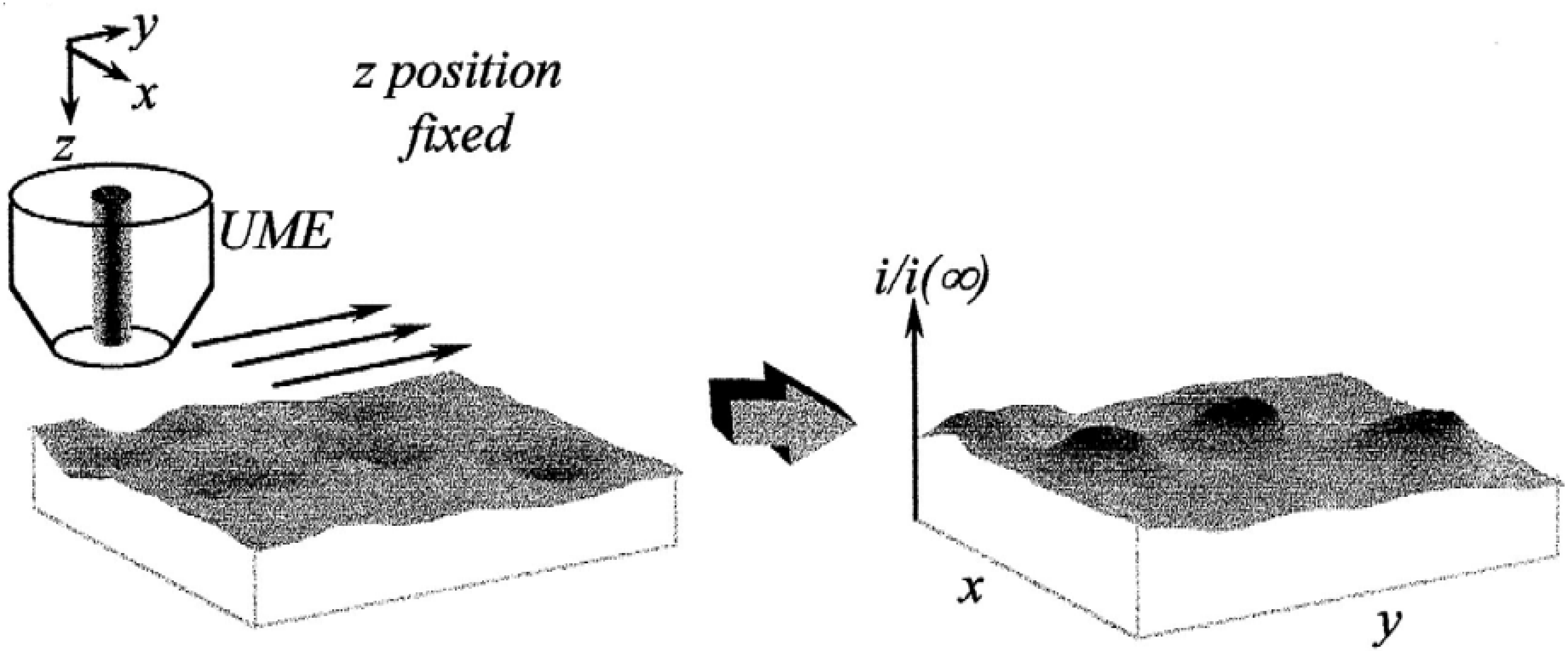
In dimensionless form, with mass-conservation, for an irreversible reaction, $k_\mathrm{b} = 0$

$$\left.\frac{\partial C}{\partial Z}\right|_{Z=L} = K(1-C) \qquad \text{where } K = k_\mathrm{f}\, a / D$$

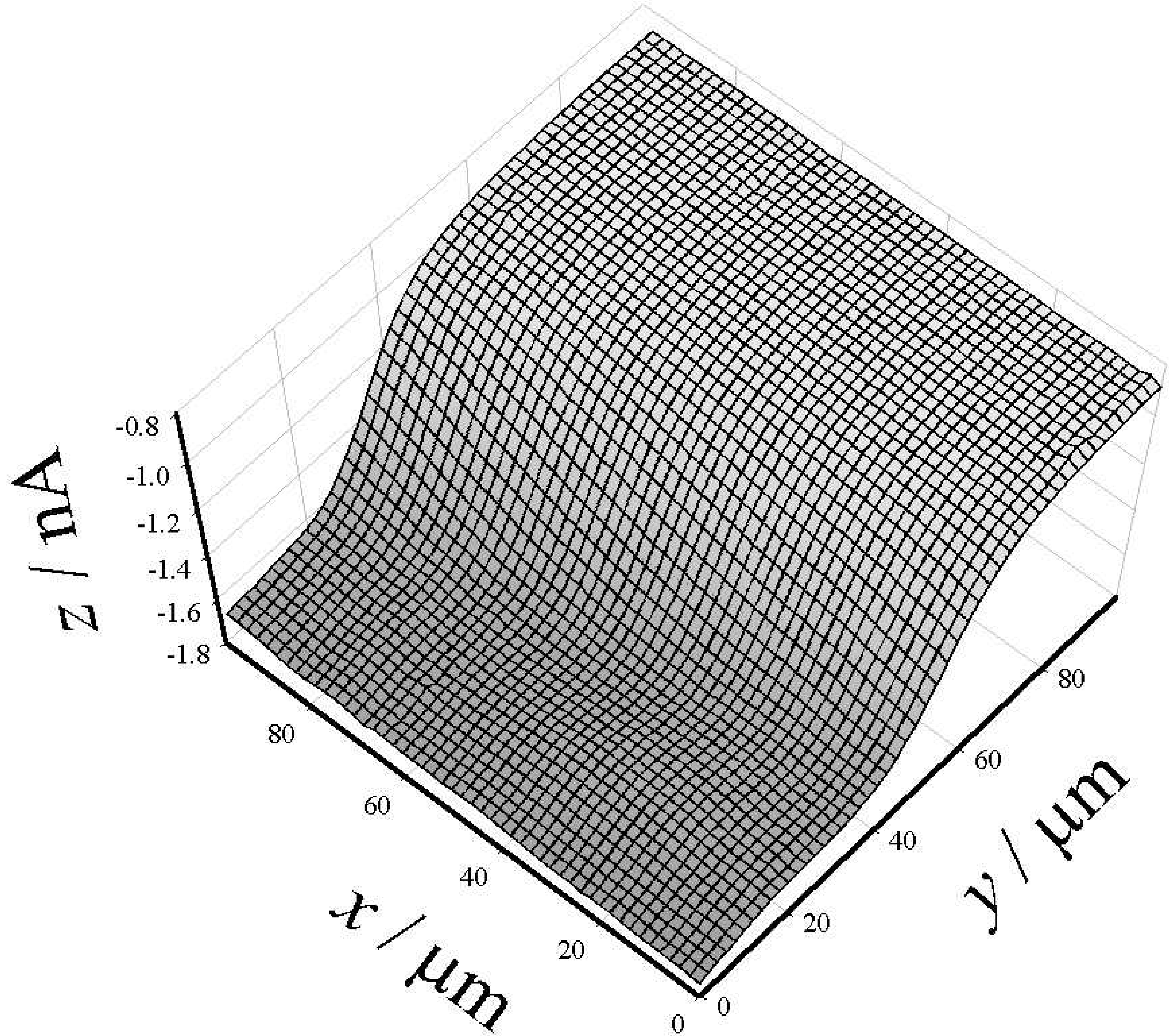

K =
100
10
5.0
2.5
1.0
0.5
0.1
0.01
0
I / I_bulk
0
1
2
3
4
L = d / a

Scanning

mode



y
x
z
z position
fixed
UME
i/i(∞)
x
y



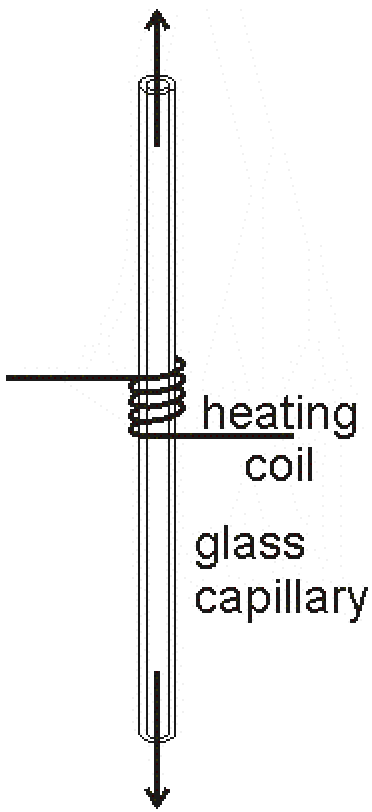
z / nA
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
x / µm
80
60
40
20
0
y / µm
0
20
40
60
80

# The scanning mode:

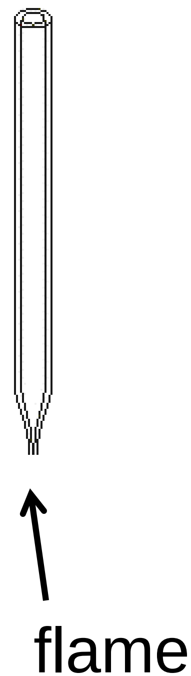
- Gives information on both the topography and the local reactivity of the substrate
- The resolution is of the order of the tip radius and dependent on the tip-sample distance
- atomic resolution not possible (SECM vs. STM)
- Two principal types: constant height and constant current
- Two principal modes: feedback and collection
- Variations exist: use of a chemical lens, modulation techniques, shear force detection etc.

# Tip preparation

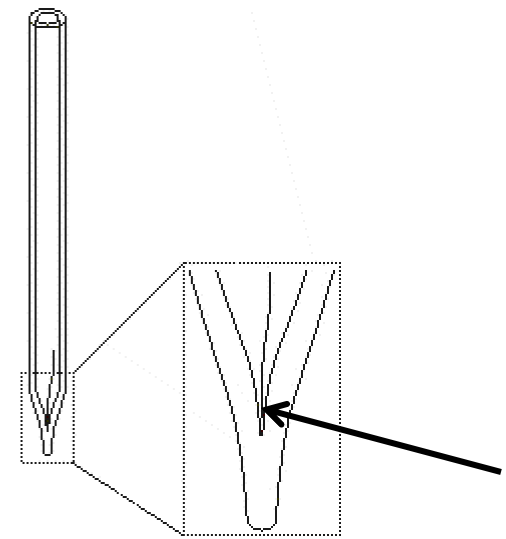
1. pull a glass capillary




2. seal the end with a Bunsen burner



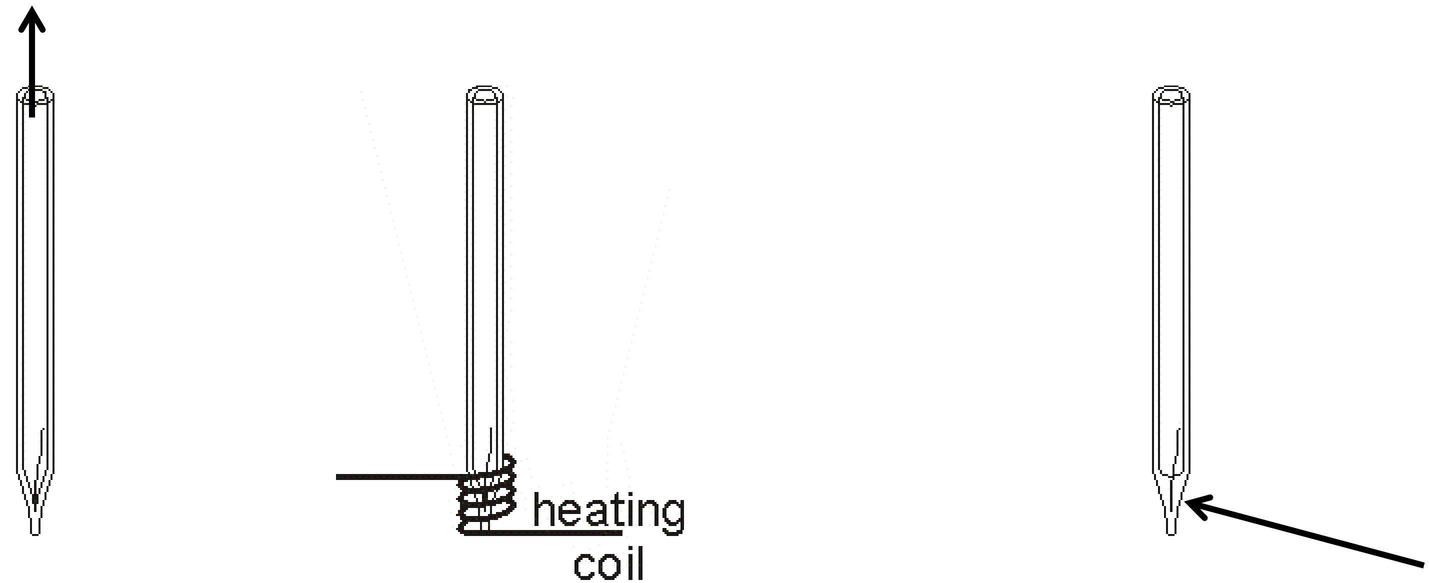

3. insert a metal wire of desired thickness into the end of the capillary



4. draw a vacuum in the capillary

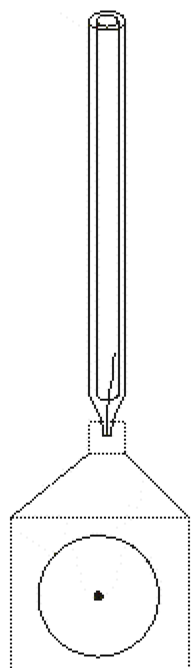
5. melt the glass around the metal wire

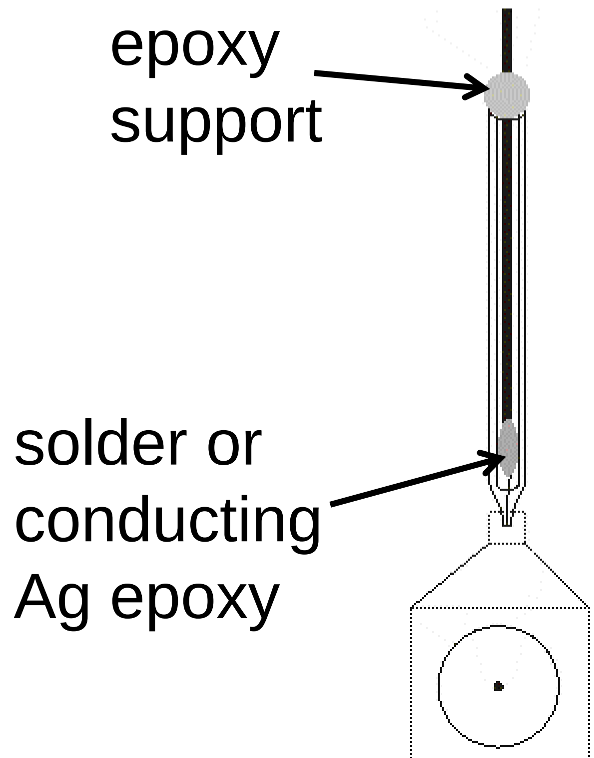
6. metal wire sealed inside the glass



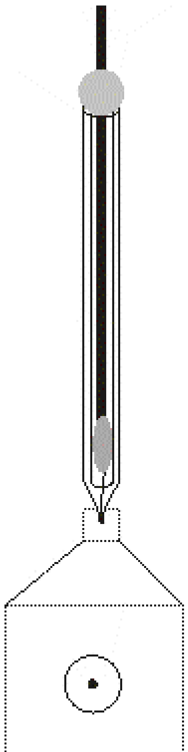
7. grind back to expose the electrode and polish with subsequently finer grinding paper or alumina slurry

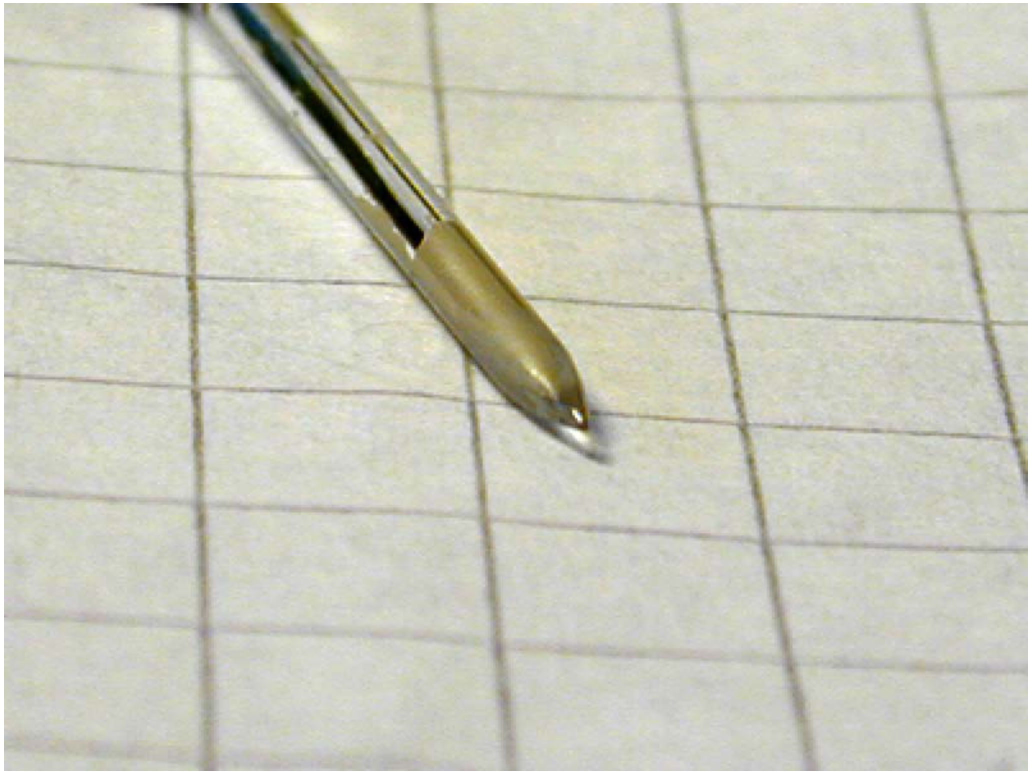
8. make electrical connection to the tip and run a test CV

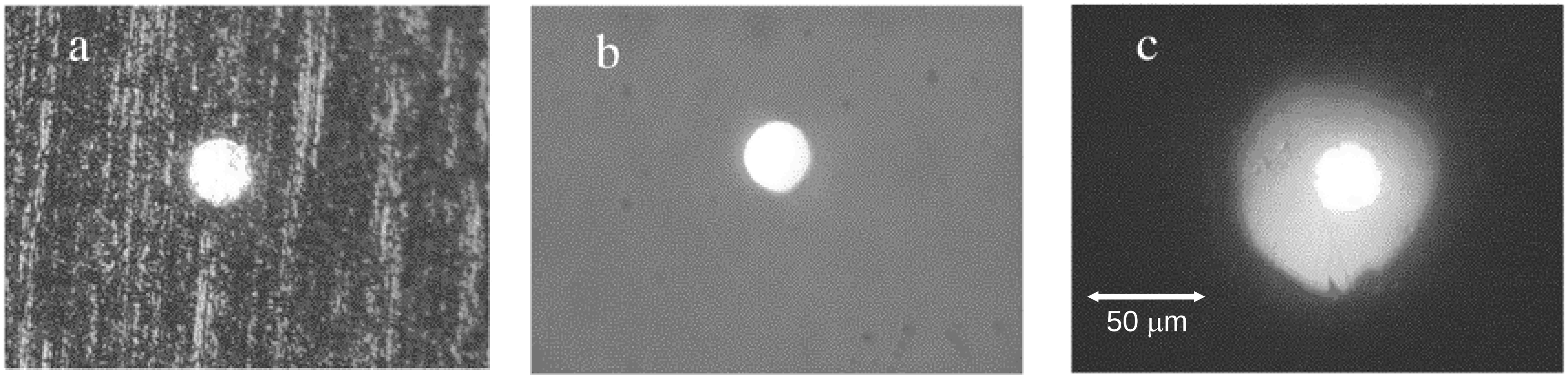




9. sharpen until the radius of the glass sheath is < 10*a*







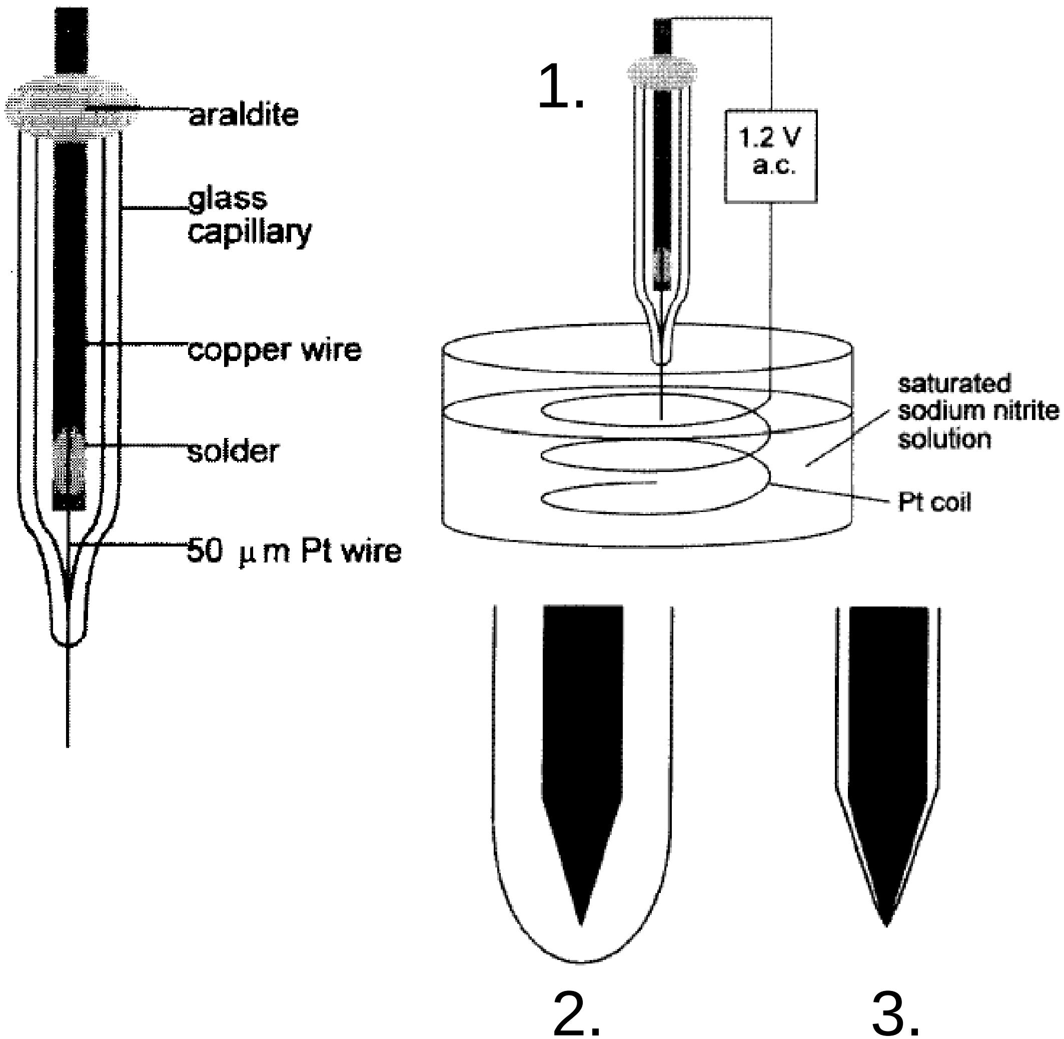

unpolished microelectrode

polished microelectrode

finished SECM tip

Z. Ding, B.M. Quinn, A.J. Bard, *J. Phys. Chem. B* **105** (2001) 6367-6374

# Nanometre electrodes:



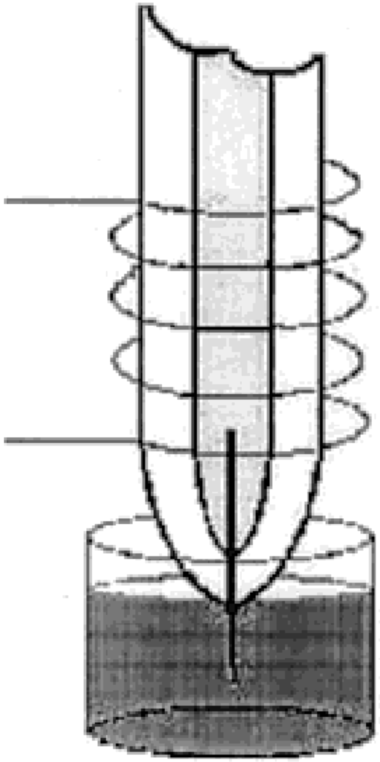

1. Electrochemical etching

2. Electrodeposition of cathodic or anodic electrophoretic paint

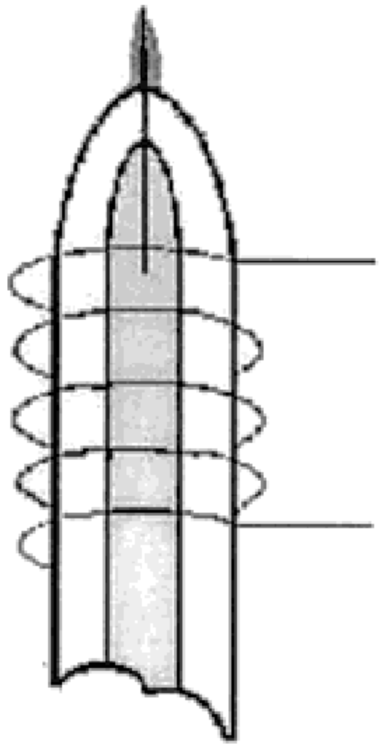
3. Thermal curing causes the paint to shrink, exposing a tiny conical electrode

C.J. Slevin, N.J. Gray, J.V. Macpherson, M.A. Webb, P.R. Unwin, *Electrochem. Commun.* **1** (1999) 282-288

# Nanometre electrodes, part deux:



2.



3.

1. Start as previously, electrochemically etch a Pt wire

2. Heat induced polymerisation of an imide

3. Thermal curing at ca. 200°C

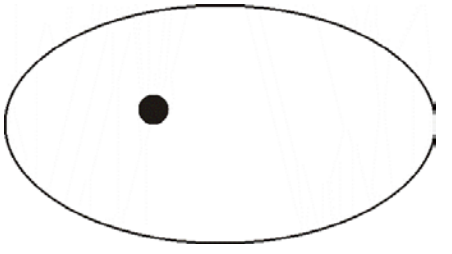
P. Sun, Z. Zhang, J. Guo, Y. Shao, *Anal. Chem.* **73** (2001) 5346-5351

# Experimental aspects

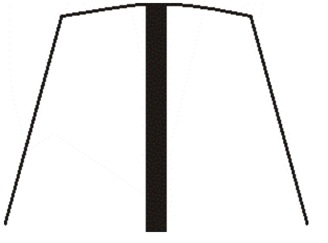
# Tip shape

- concentricity of the disk and the insulating glass sheath

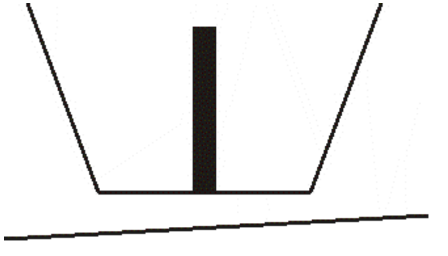
  $\rightarrow$ effective $R_g$



- highest point on the tip

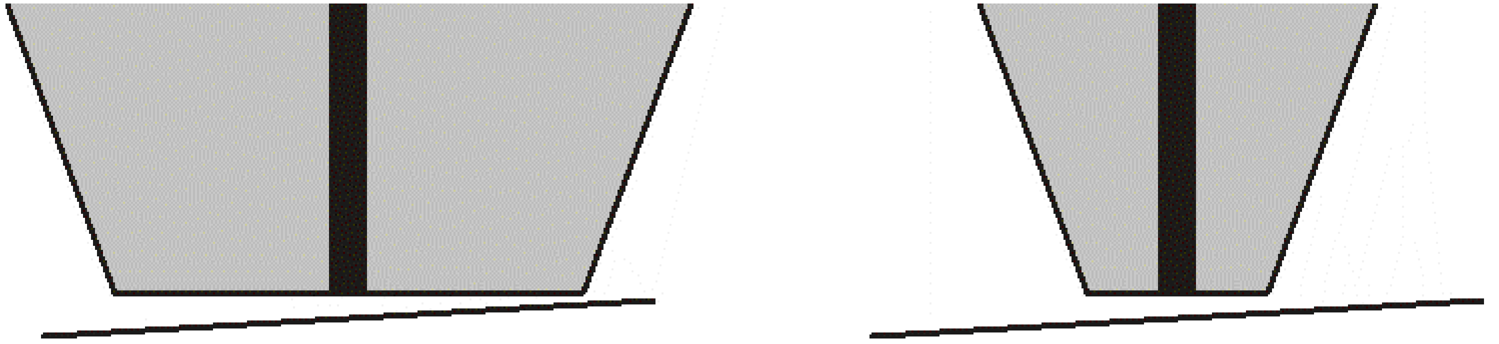


- alignment of the tip



# Effect of $R_g$

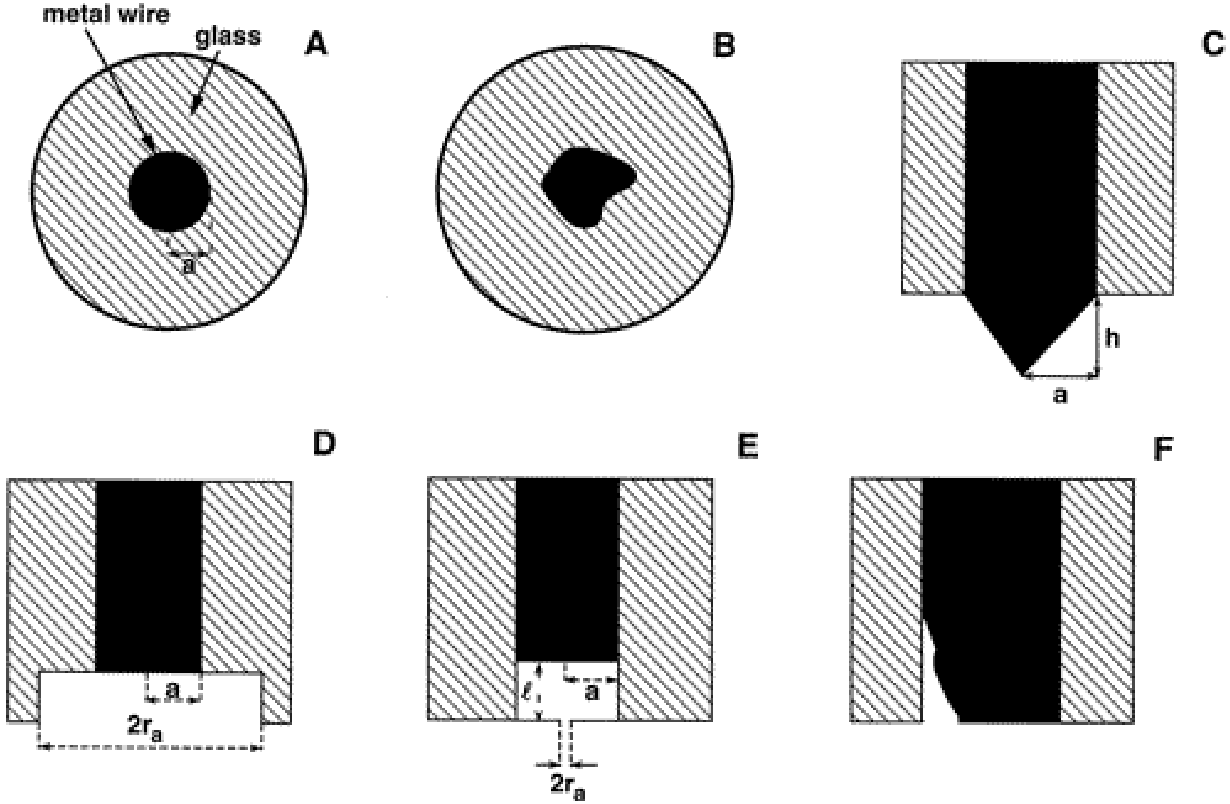
- Small $R_g$ makes it easier to get close to the substrate



O. Sklyar, G. Wittstock, *J. Phys. Chem. B* **106** (2002) 7499-7508

# Various imperfections

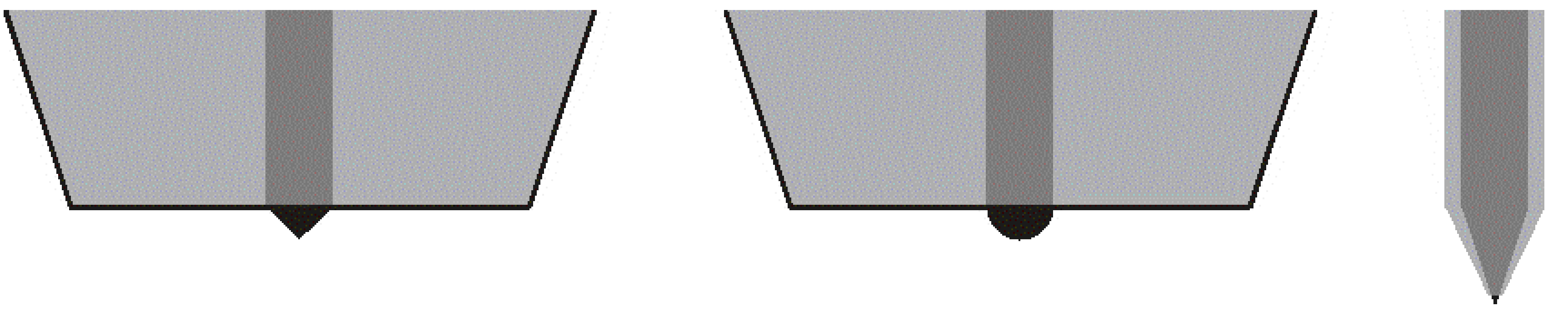
- Perfect electrode (A), irregularly shaped electrode (B), a recessed electrode (D), a “lagooned” electrode (E) and a leaky UME (F)




Y. Shao, M.V. Mirkin, G. Fish, S. Kokotov, D. Palanker, A. Lewis, *Anal. Chem.* **69** (1997) 1627-1634

# Effect of tip geometry

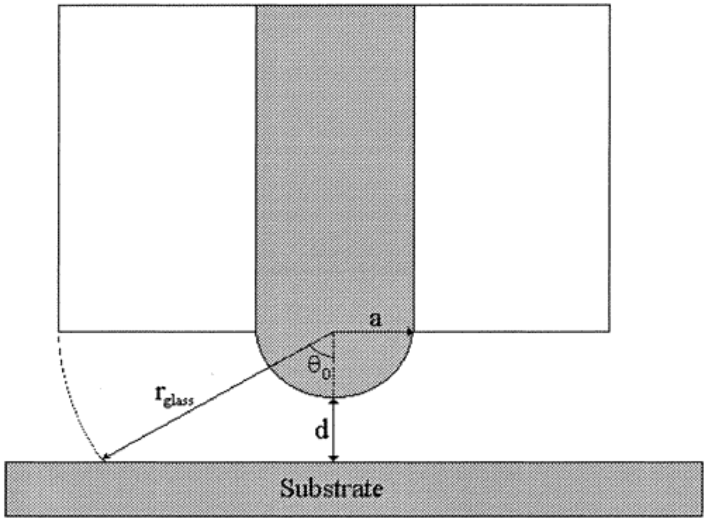
- Disk preferred, however, especially small electrodes usually have conical or hemi-spherical shape

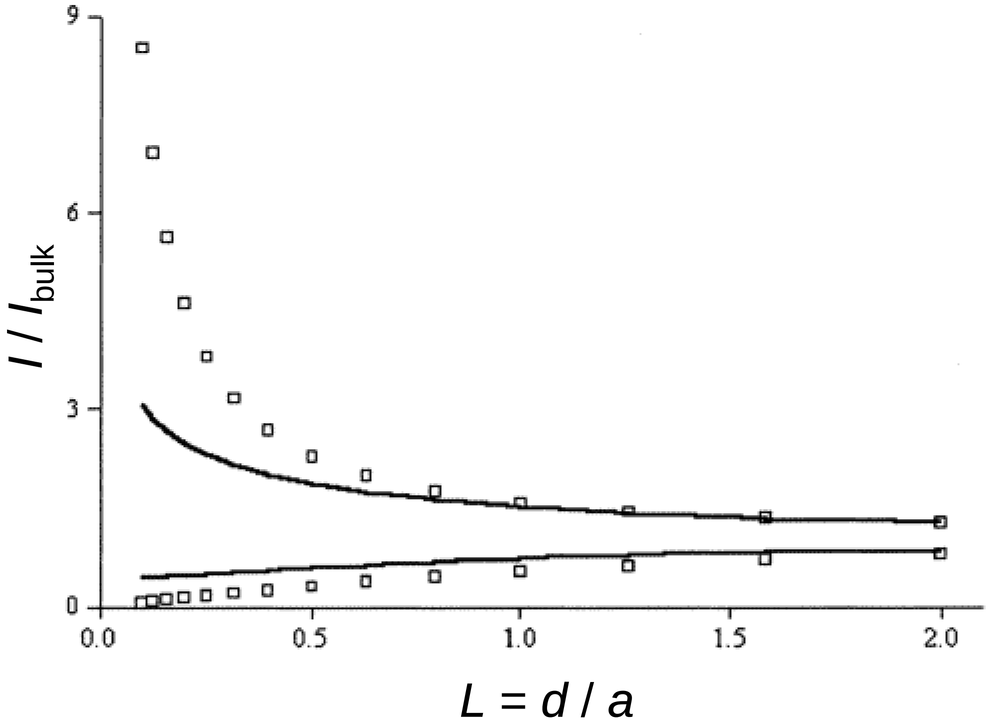


conical hemi-spherical

# Effect of tip geometry on the approach curves

- Generally makes the response less sharp




Y. Selzer, D. Mandler, *Anal. Chem.* **72** (2000) 2383-2390