The toposcopy: how to deduce the shape of an electrode from a black box measurement?

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Physique de la Matière Condensée

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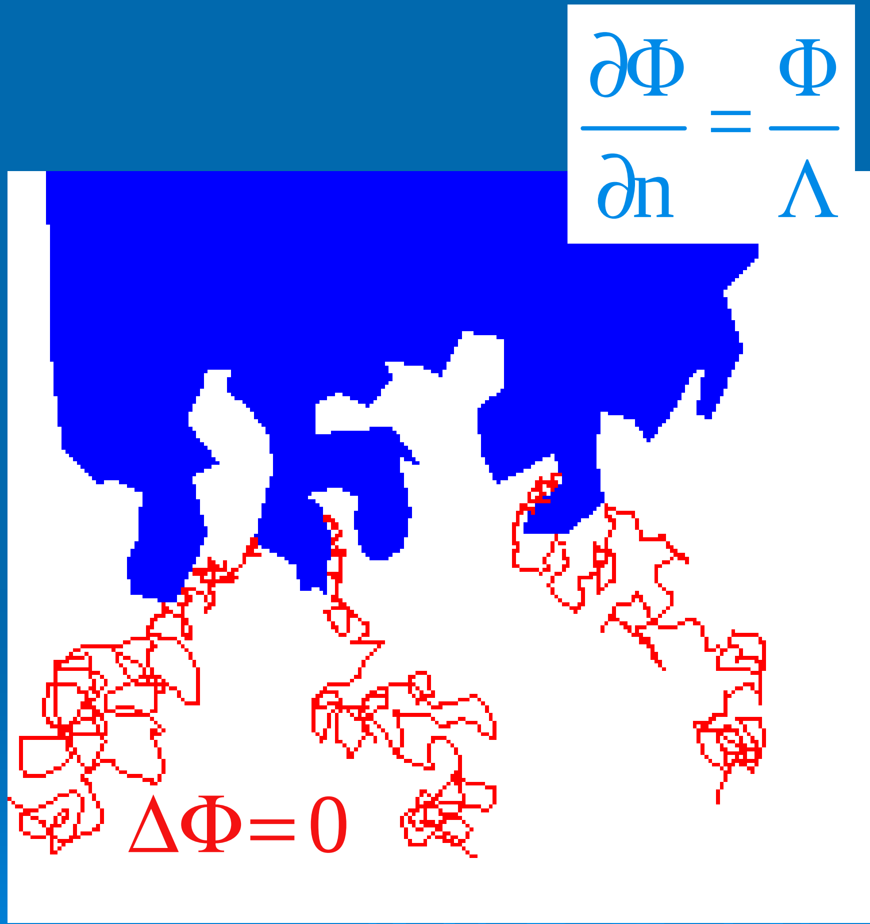
Joint work with B. Sapoval and D.S. Grebenkov

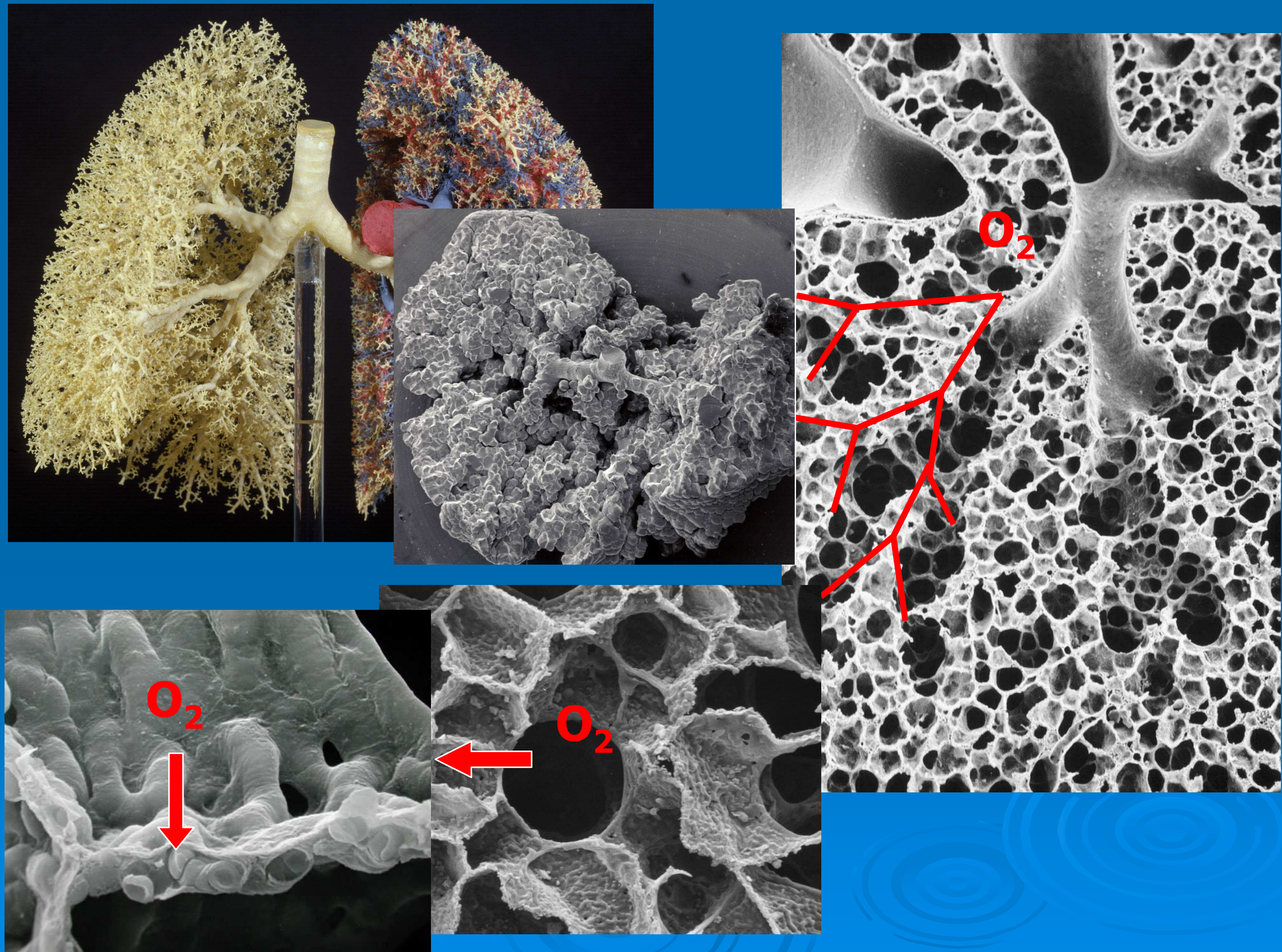
Laplacian Eigenvalues and Eigenfunctions: Theory, Computation, Application
IPAM Program, Feb 9-13 2009

How are related the geometrical and the transfer properties of an irregular interface?

- **Electrochemistry**
- **Heterogeneous catalysis**
- **NMR**
- **Biological membranes**



Gas exchange driven by diffusion

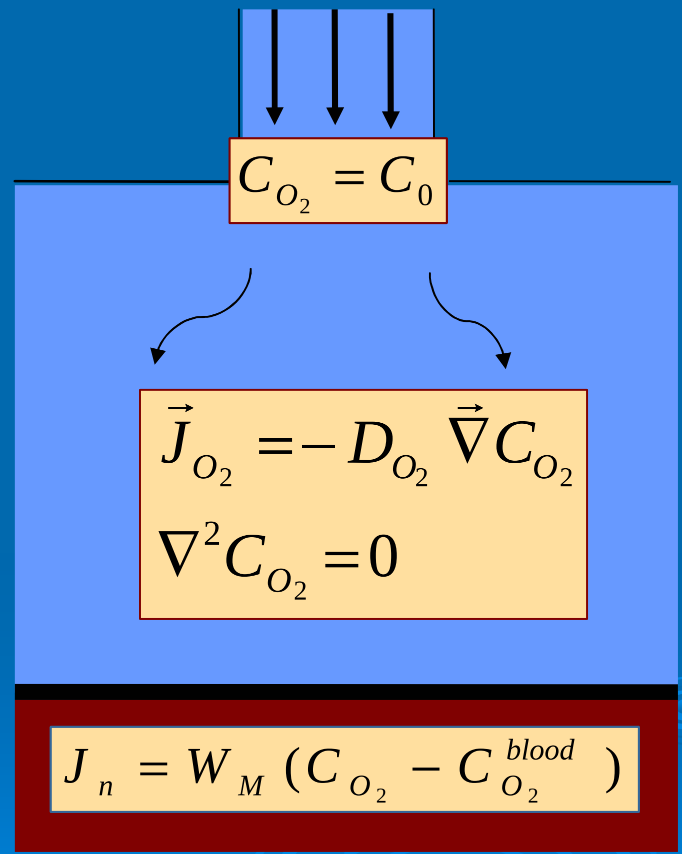


The oxygen transfer in the lung

- subacinus entrance
  = diffusion source

- into the alveolar air:
  Steady-state diffusion → Fick's law

- at the air-blood interface:
  Membrane of permeability W_M



The oxygen transfer in the lung

$$P \equiv P_{O_2} - P_{O_2}^{blood}$$

↓

Linear PDE Problem

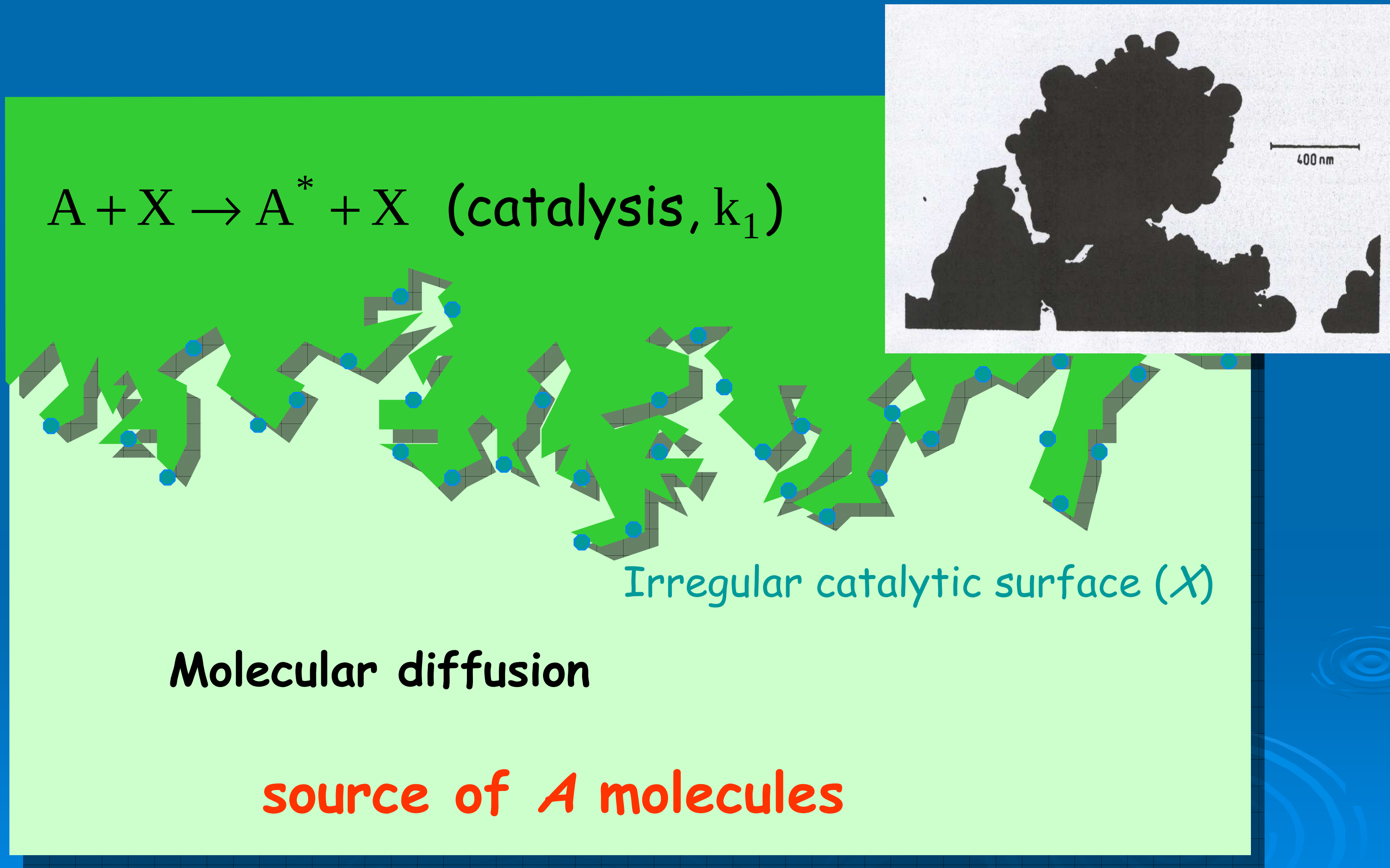
$$\nabla^2 \mathbf{P} = 0 \quad \text{in the bulk}$$

$$\frac{\partial \mathbf{P}}{\partial \mathbf{n}} = -\frac{1}{\Lambda}\mathbf{P} \quad \text{on the alveolar membrane}$$

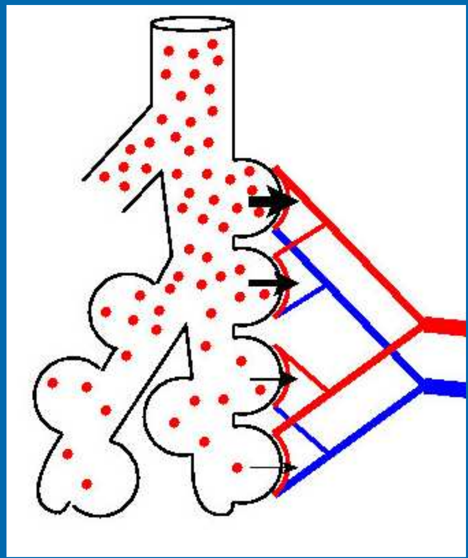
$$\mathbf{P} = \mathbf{P}_0 \quad \text{at the acinus entrance}$$

$\Lambda \equiv D/W$ **unscreened perimeter length**

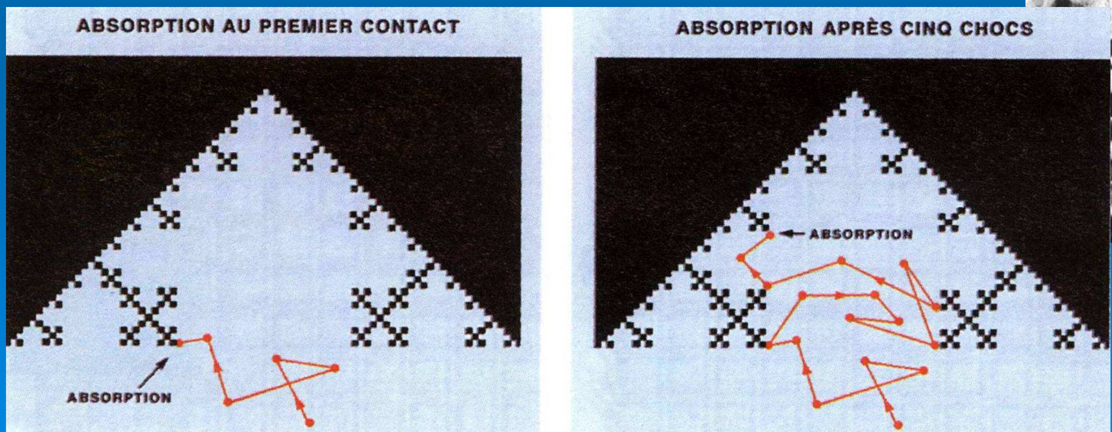
Heterogeneous catalysis

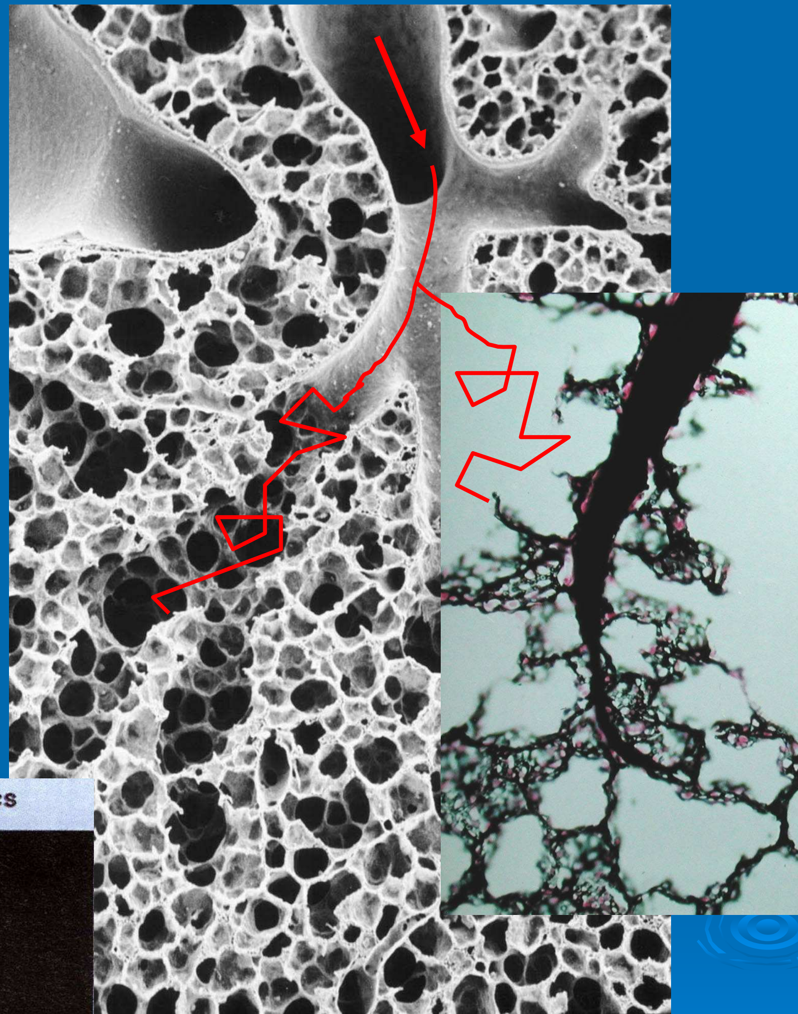


Diffusion screening



Fractal electrode





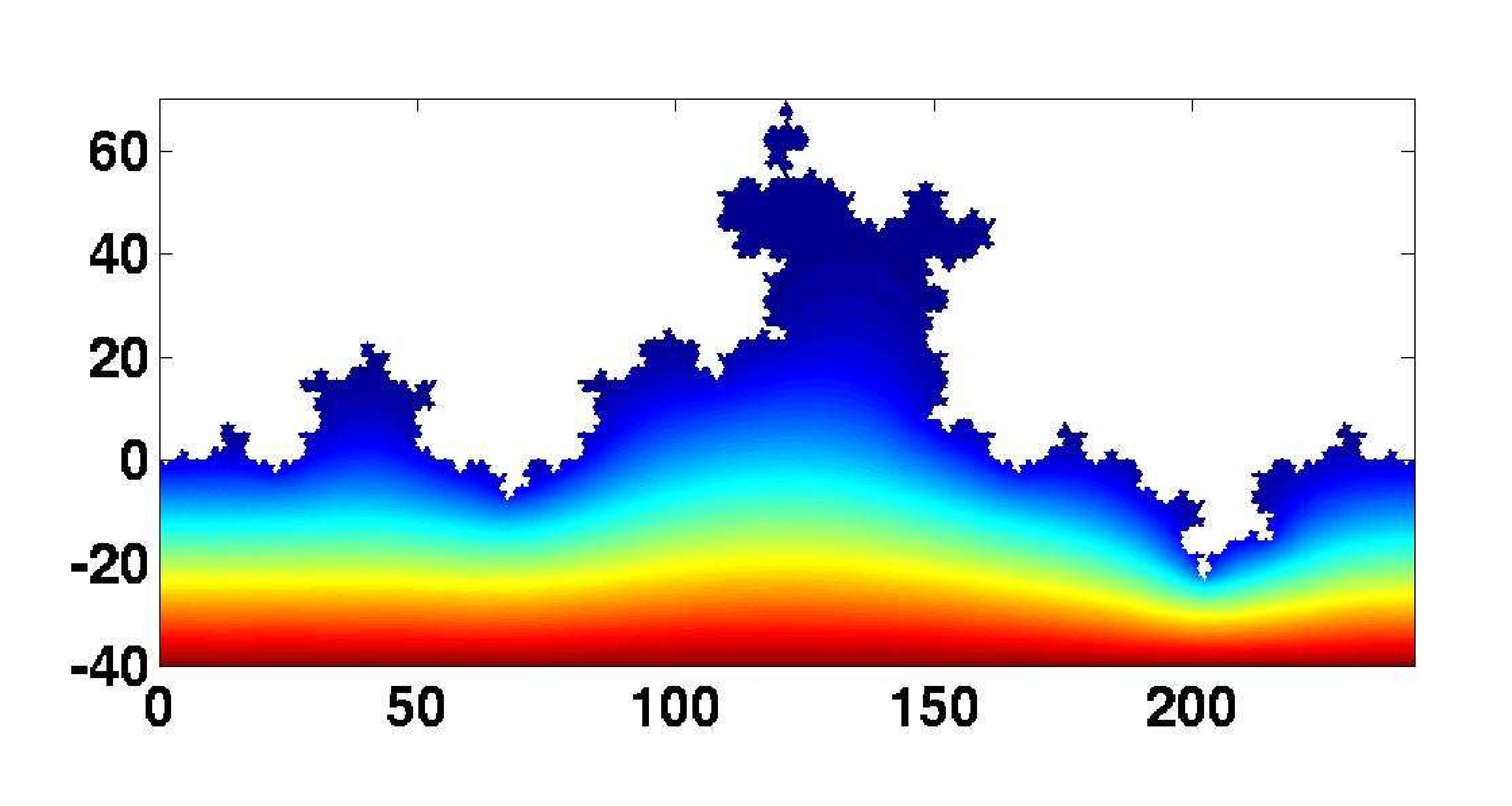
B. Sapoval

Diffusion screening

Makarov, 1985

Concentration

Current density



The physical meaning of Λ

- Conductance to reach a part of the boundary:

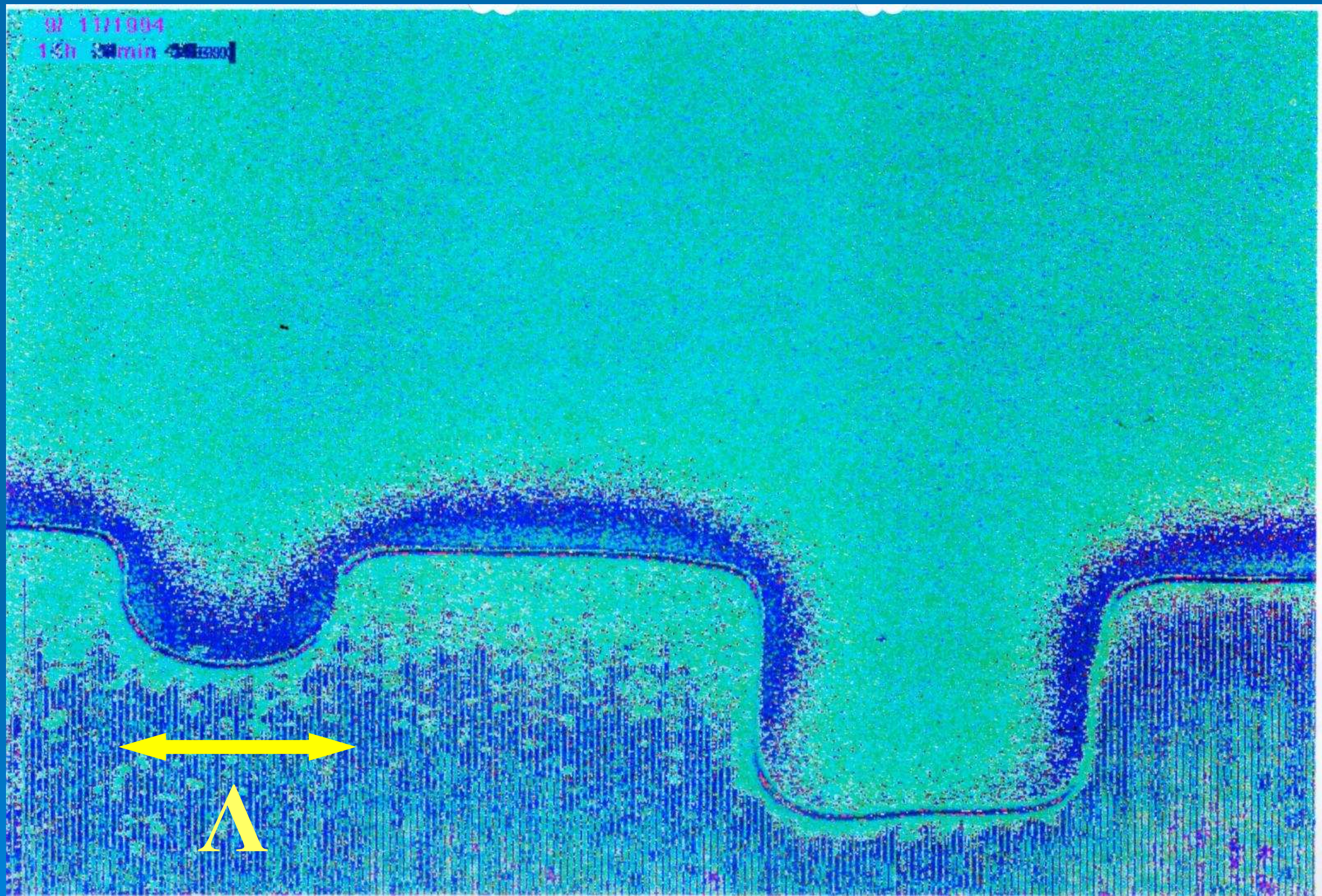
$$Y_{reach} \sim D$$

- Conductance to cross a part of the boundary:

$$Y_{tra} \sim W\,L_p$$ (L_p : perimeter of the part)

$$Y_{reach} \approx Y_{cross} \quad \Rightarrow \quad L_p \approx \Lambda$$

Electrochemistry
Copper ion deposit onto an irregular surface



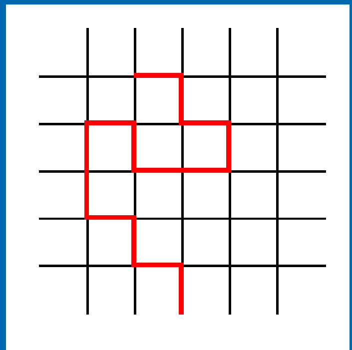
M. Rosso et al., 1997

Question:

If one knows the current crossing the system for any Λ, what do we know about the geometry of the domain?

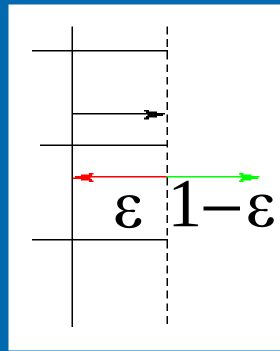
The lattice model

Bulk: random walk on a lattice:

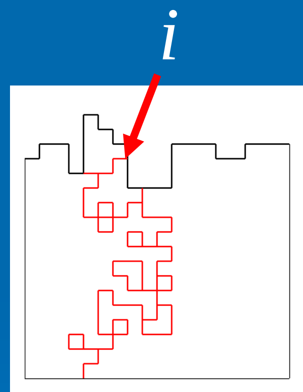


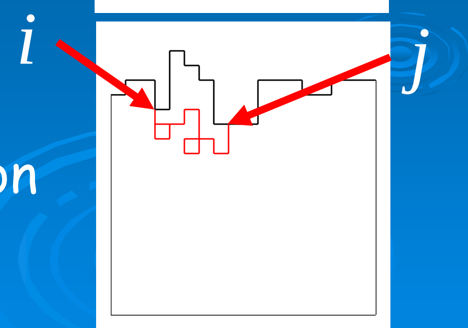
parameters a , τ

Membrane: reflecting boundary



parameter ε





Definitions

P_i^{ε} = probability to reach the site *i* on the membrane when starting from the source

q_{ij} = probability to reach the site *j* on the membrane when starting from the site *i* on the membrane

Continuous limit of the lattice model

Discrete random walk $\xrightarrow{a \to 0, \tau \to 0, \varepsilon \to 1}$ **Brownian Motion** $\xrightarrow{N_{walk} \to \infty}$ **Laplace equation**

Lattice	Continuous
$D = \frac{a^2}{2d\tau}$	$\vec{J} = -D\vec{\nabla}C$
$W = \frac{a}{2d\tau}\frac{1-\varepsilon}{\varepsilon}$	$\vec{J}\cdot\vec{n} = -W\Phi$
$\Lambda = a\frac{\varepsilon}{1-\varepsilon}$	$\frac{\partial\Phi}{\partial n} = \frac{\Phi}{\left(\frac{D}{W}\right)} = \frac{\Phi}{\Lambda}$
$I = C_S\left(\frac{a^d}{2d\tau}\right)\sum_i P_i^{\varepsilon}$	$I = -D\int_{\partial\Omega}\left(\frac{\partial\Phi}{\partial n}\right)ds$

"Black box" measurement

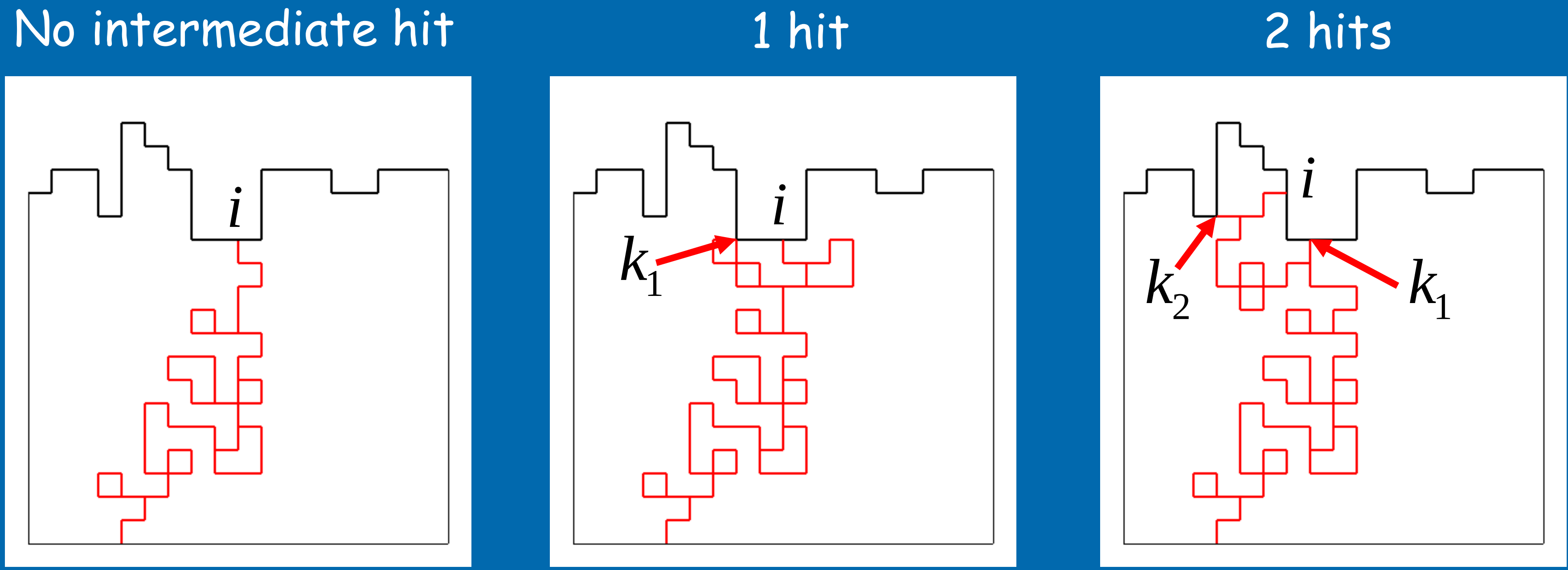
System impedance : $Z_{system} = \frac{C_0}{I}$

$$Z_{memb}(W) = Z_{system}(W) - Z_{system}(W = \infty) = C_0 \left[\frac{1}{I(W)} - \frac{1}{I(\infty)} \right]$$

Flux across the system : $I(\varepsilon) = C_S \left(\frac{a^d}{2d\tau} \right) \sum_{i \in M} P_i^{\varepsilon}$

Problem : Compute the probabilities P_i^{ε}

Transfer through a permeable membrane: a Markov process



$P_i^0(1-\varepsilon)$ $\quad$ $\sum_{k_1} P_{k_1}^0 \varepsilon q_{k_1,i}(1-\varepsilon)$ $\quad$ $\sum_{k_1,k_2} P_{k_1}^0 \varepsilon q_{k_1,k_2} \varepsilon q_{k_2,i}(1-\varepsilon)$

$$P_i^{\varepsilon} = P_i^0(1-\varepsilon) + \sum_{k_1} P_{k_1}^0 \varepsilon\, q_{k_1,i}(1-\varepsilon) + \sum_{k_1,k_2} P_{k_1}^0 \varepsilon\, q_{k_1,k_2} \varepsilon\, q_{k_2,i}(1-\varepsilon) + \ldots$$

M.F. and B. Sapoval, 1999

The "spreading operator"

$$Q = \left(q_{ij}\right)$$

"transport" probability matrix

Properties:

- Probabilities → real
- Random walk → symmetric
- $\sum_j q_{ij} < 1$ → contraction

$$\vec{P}^{\varepsilon} = \left(P_i^{\varepsilon}\right)$$

current distribution crossing the membrane

Markov process: $\vec{P}^{\varepsilon} = (1-\varepsilon)\,\vec{P}^{0} + \varepsilon(1-\varepsilon)Q\vec{P}^{0} + \varepsilon^{2}(1-\varepsilon)Q^{2}\vec{P}^{0} + \ldots$

$$\vec{P}^{\varepsilon} = (1-\varepsilon)\left[I-\varepsilon Q\right]^{-1}\vec{P}^{0}$$

The electrode impedance

<u>Discrete impedance</u>:

$$Z_{spec.} = \frac{2d\tau}{a^d}\left(\frac{\varepsilon}{1-\varepsilon}\right)\frac{\vec{P}^{\varepsilon}\cdot\vec{P}^{0}}{\left(\vec{P}^{\varepsilon}\cdot\vec{1}\right)\left(\vec{P}^{0}\cdot\vec{1}\right)}$$

continuous limit $Z_{memb.} = \frac{2d\tau}{a}\frac{\varepsilon}{1-\varepsilon}\left[\frac{\vec{P}^{\varepsilon}}{a^{d-1}\left(\vec{P}^{\varepsilon}\cdot\vec{1}\right)}\cdot\frac{\vec{P}^{0}}{a^{d-1}\left(\vec{P}^{0}\cdot\vec{1}\right)}\right]a^{d-1} \rightarrow \frac{1}{W}\int_{\partial\Omega} h_{\Lambda}(x)\,h_0(x)\,ds$

M.F and B. Sapoval, 1999

<u>Diagonalization</u>: $Qv = \sum_{\alpha}\lambda_{\alpha}(v\cdot\vec{u}_{\alpha})\vec{u}_{\alpha}$ $(\lambda_{\alpha},\vec{u}_{\alpha})$ eigenvalues,–vectors of Q

$$\Rightarrow \quad \vec{P}^{\varepsilon}\cdot\vec{P}^{0} = \sum_{\alpha}\frac{1-\varepsilon}{1-\lambda_{\alpha}\varepsilon}\left(\vec{P}^{0}\cdot\vec{u}_{\alpha}\right)^2$$

continuous limit $\mu_{\alpha} = \frac{1-\lambda_{\alpha}}{a}$

$$\frac{1-\varepsilon}{1-\lambda_{\alpha}\varepsilon} = \frac{1}{1+\left(\frac{a\varepsilon}{1-\varepsilon}\right)\mu_{\alpha}}$$

The "geometrical spectrum"

$$Z_{memb.} = \frac{2d\tau}{a}\frac{\varepsilon}{1-\varepsilon}\left(\frac{\vec{P}^{0}\cdot\vec{1}}{\vec{P}^{\varepsilon}\cdot\vec{1}}\right)\sum_{\alpha}\frac{1}{1+\frac{\varepsilon a}{1-\varepsilon}\mu_{\alpha}}\left(\frac{\vec{P}^{0}}{a^{d-1}\vec{P}^{0}\cdot\vec{1}}\cdot\vec{u}_{\alpha}a^{\frac{d-1}{2}}\right)^{2}$$

$$\frac{1}{W}=\frac{\Lambda}{D} \qquad \frac{Z_0+Z_{memb.}}{Z_0} \qquad \frac{1}{1+\Lambda\mu_\alpha} \qquad \left|u_\alpha . h_N^0\right|^2$$

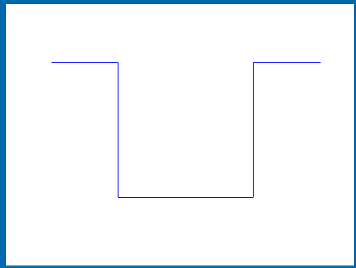
only depends on the geometry of the boundary → ***"geometrical spectrum"***

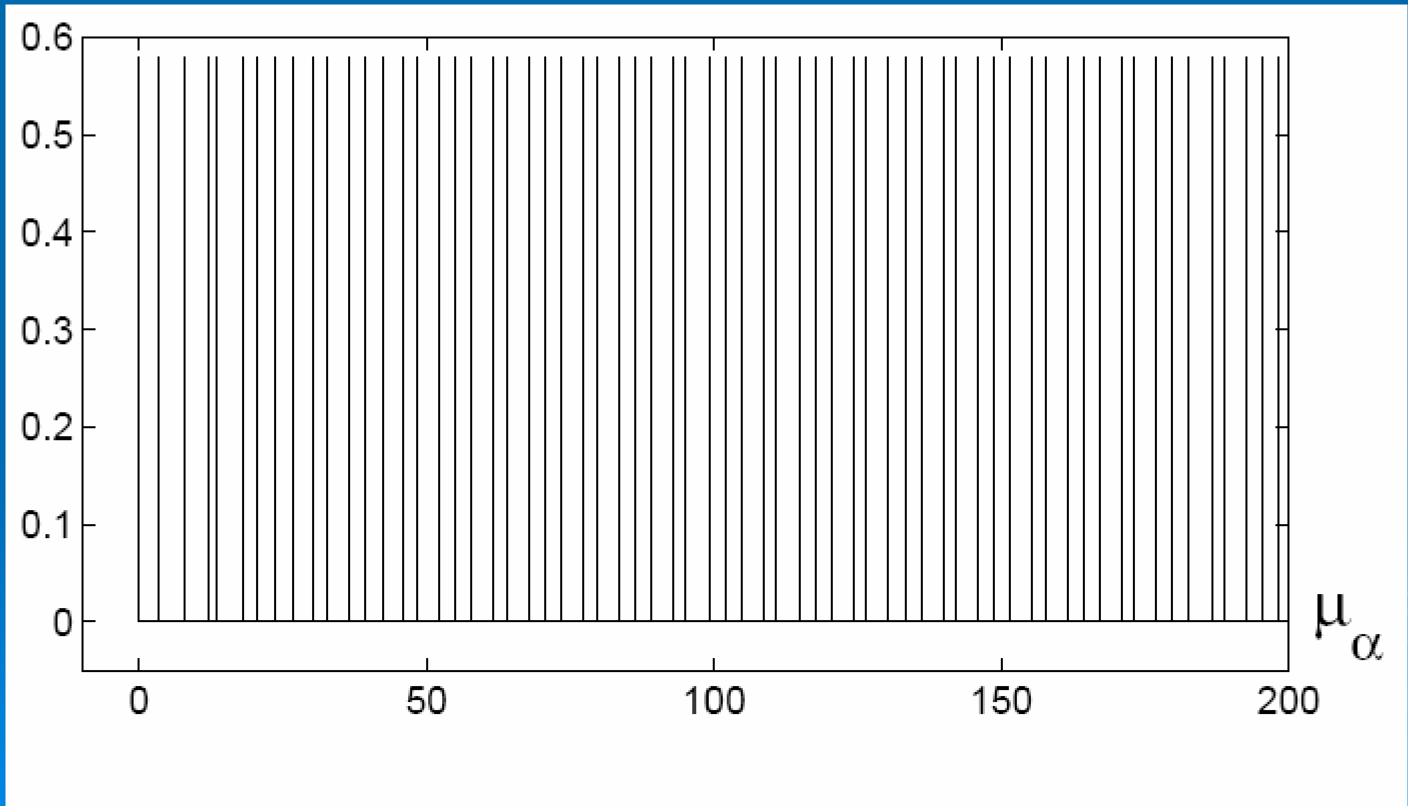
continuous limit:

$$Z_{memb.}=\frac{\Lambda}{D}\sum_{\alpha}\frac{F_\alpha}{1+\Lambda\mu_\alpha}$$

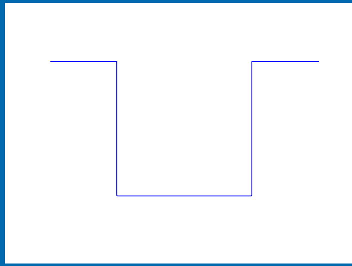
D.S. Grebenkov, M.F., B. Sapoval, 2004

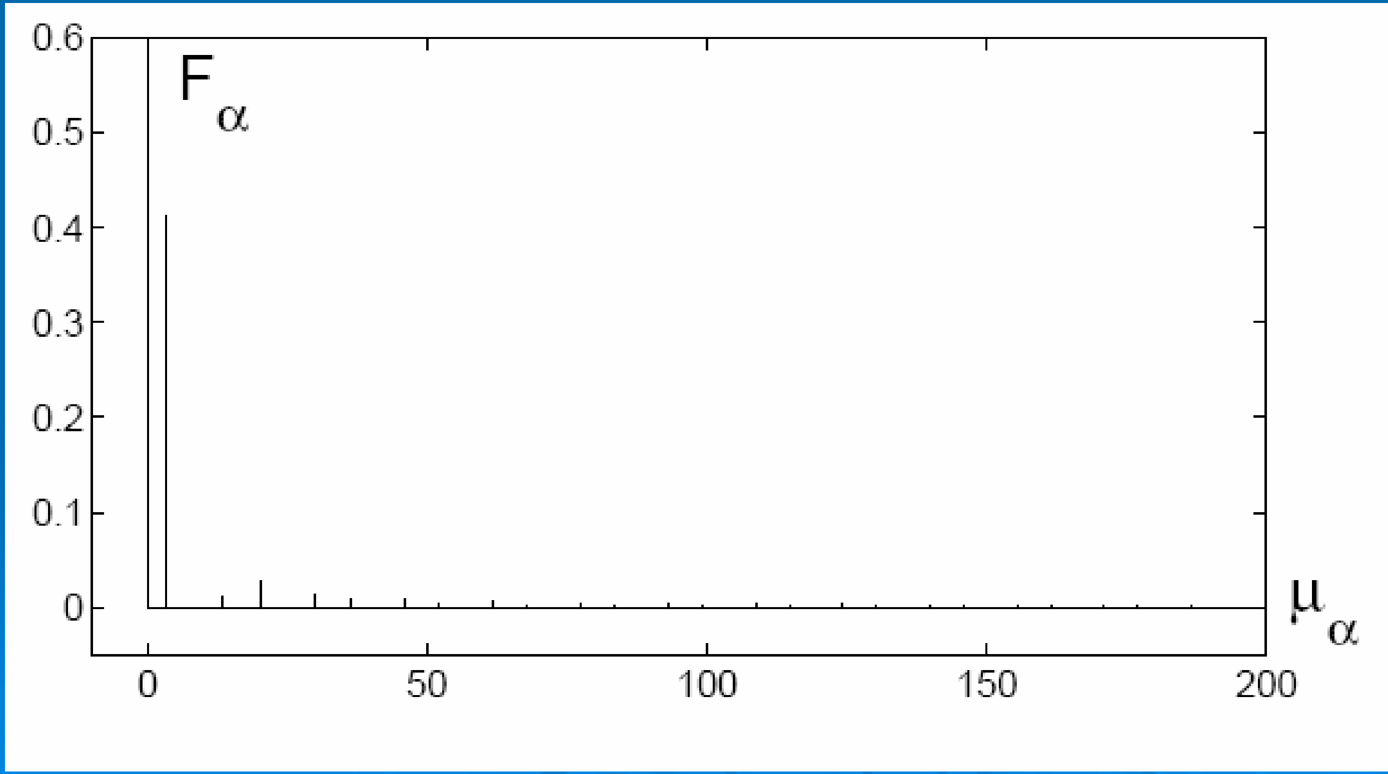
Dirichlet-to-Neumann operator spectrum



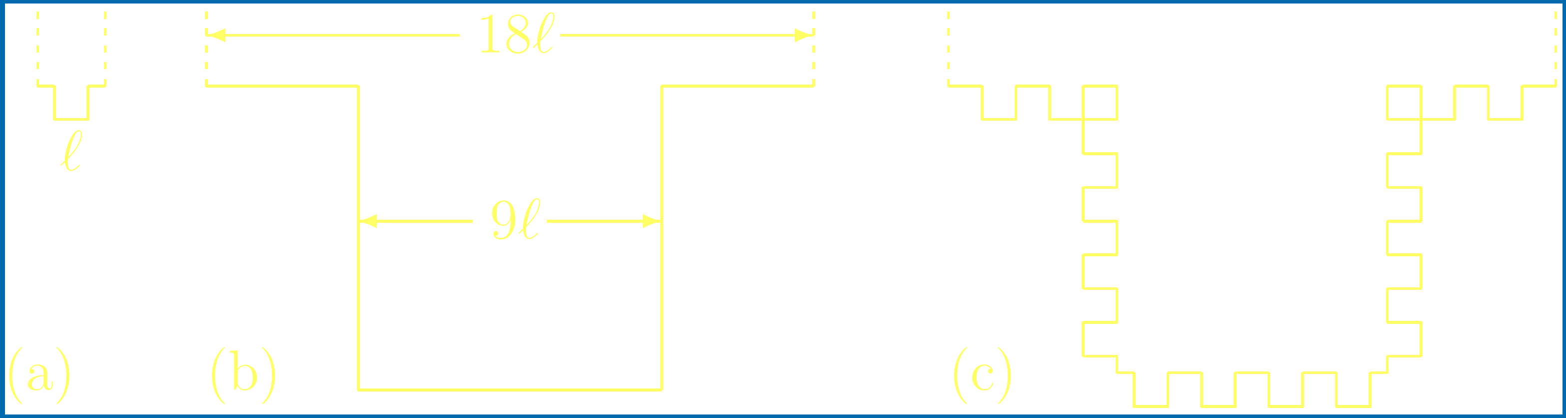


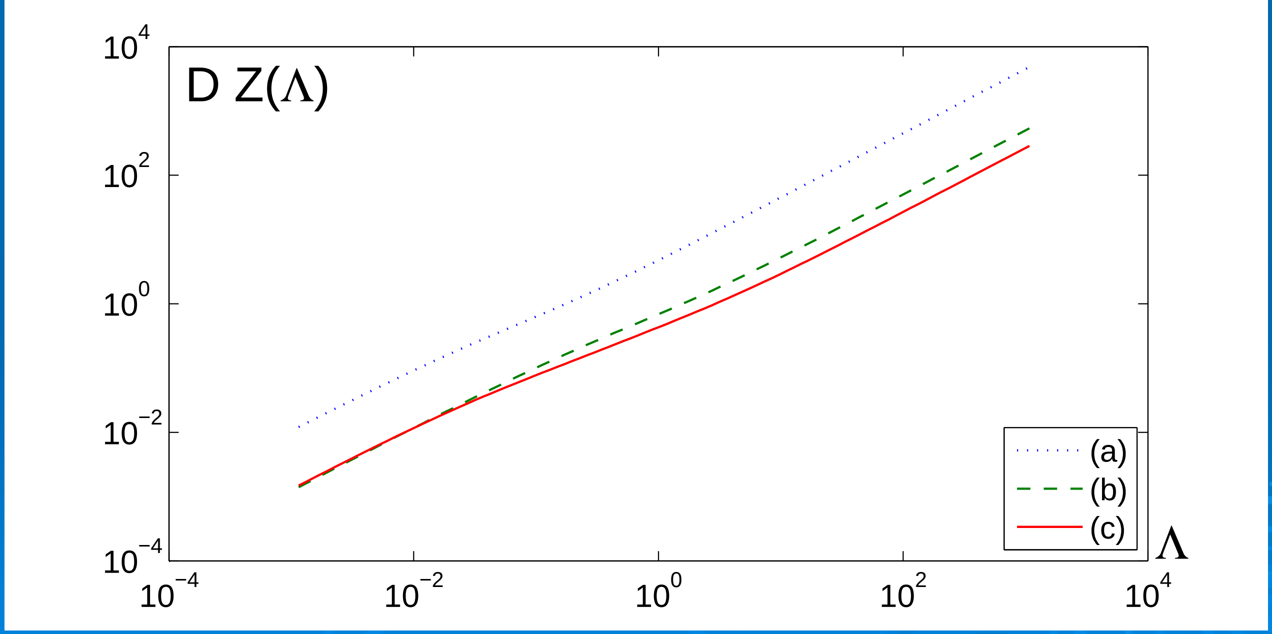
Decomposition of the harmonic measure





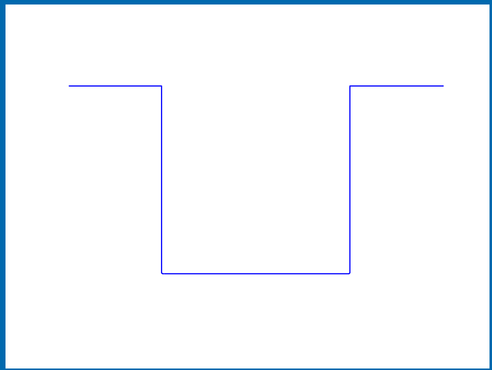
Numerical test: 2D electrodes

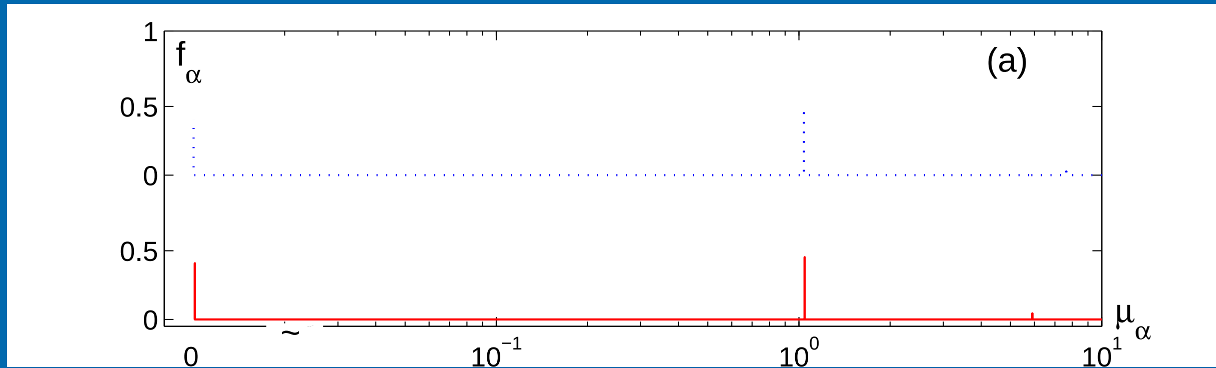


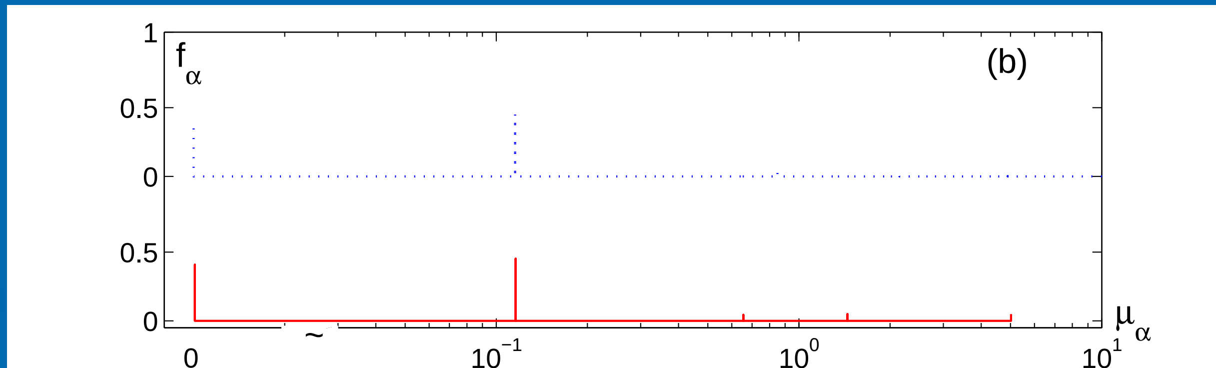


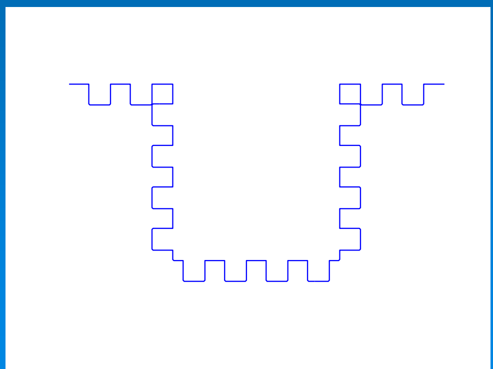
M.F. and D.S. Grebenkov, 2008

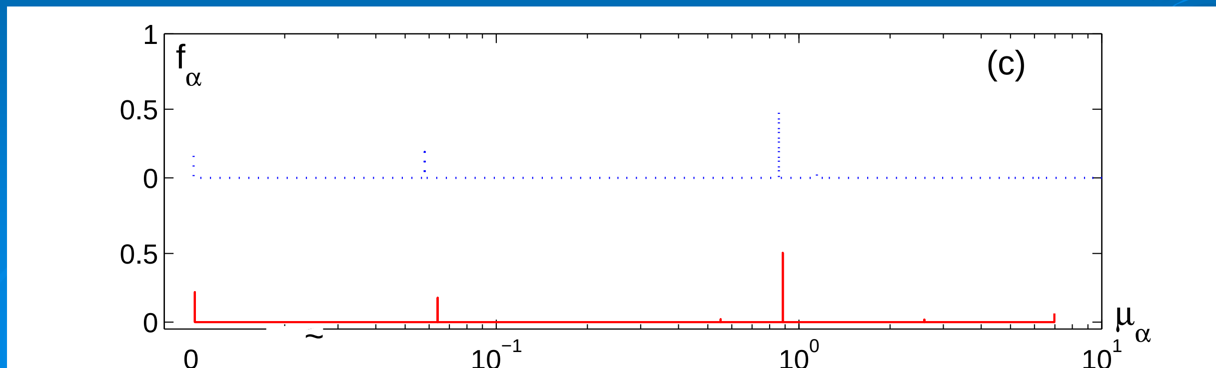
Extracting the “harmonic geometrical spectrum”





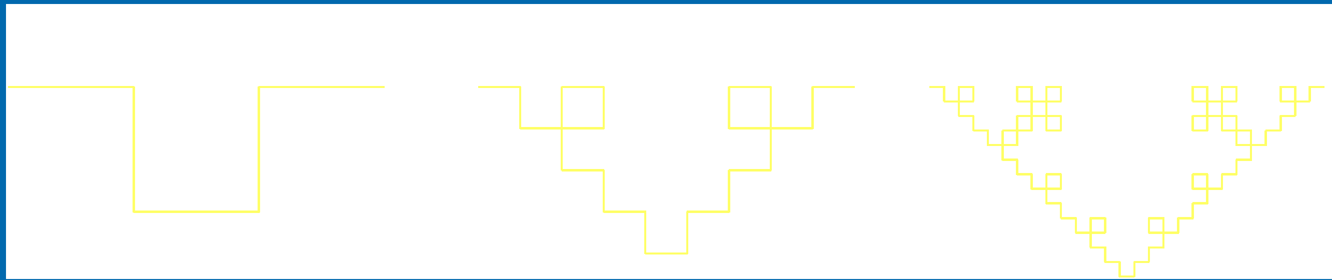


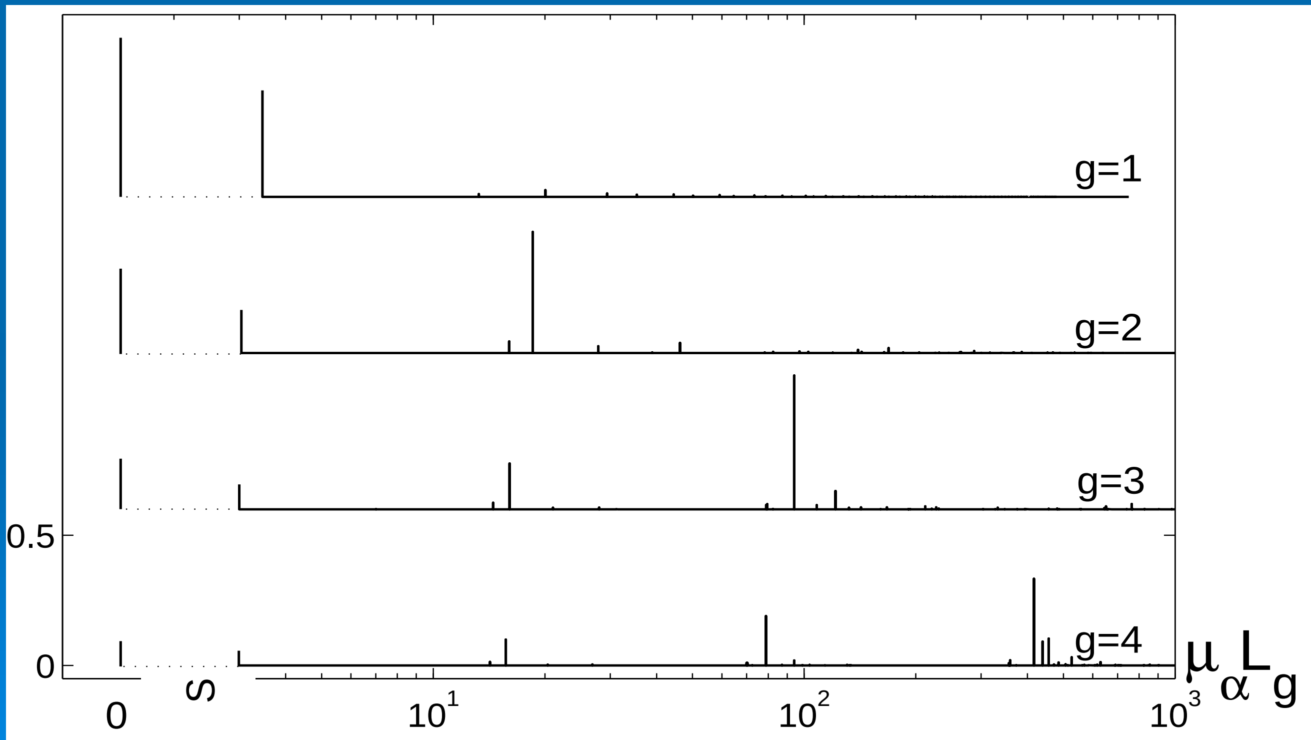




Self-similar electrodes

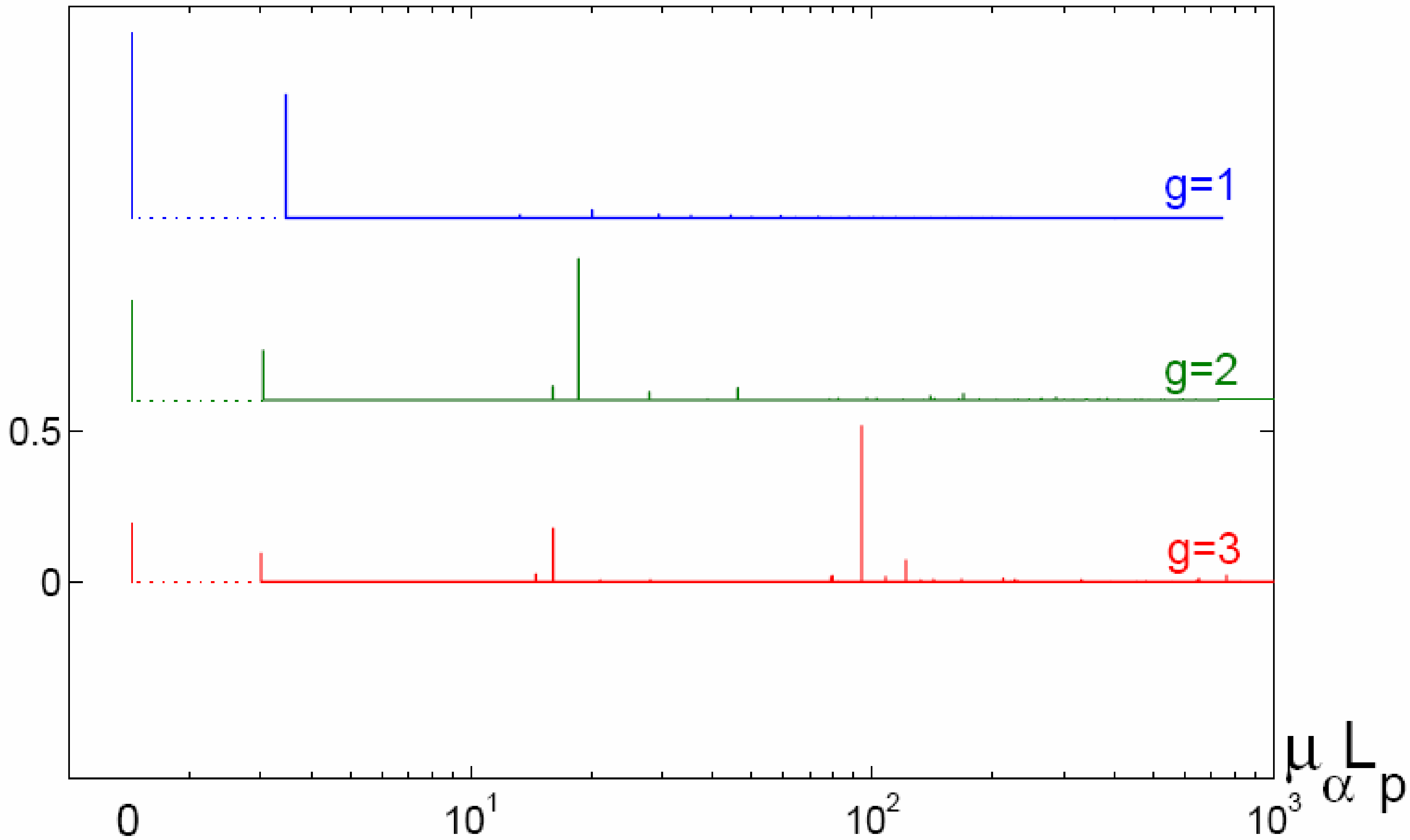
Quadratic Von Koch curves



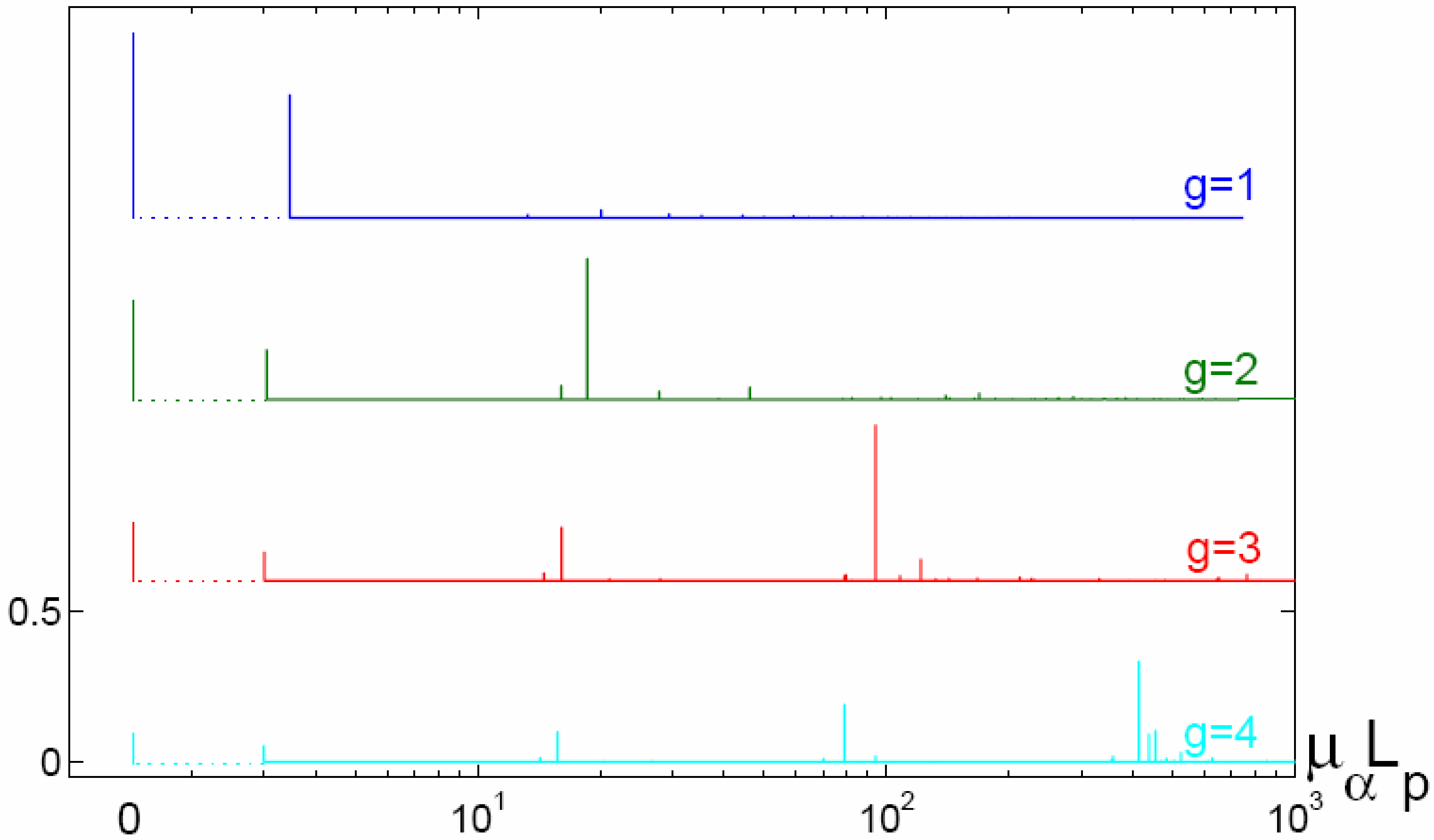


D.S. Grebenkov, M.F., B. Sapoval, 2007

Mode reduction

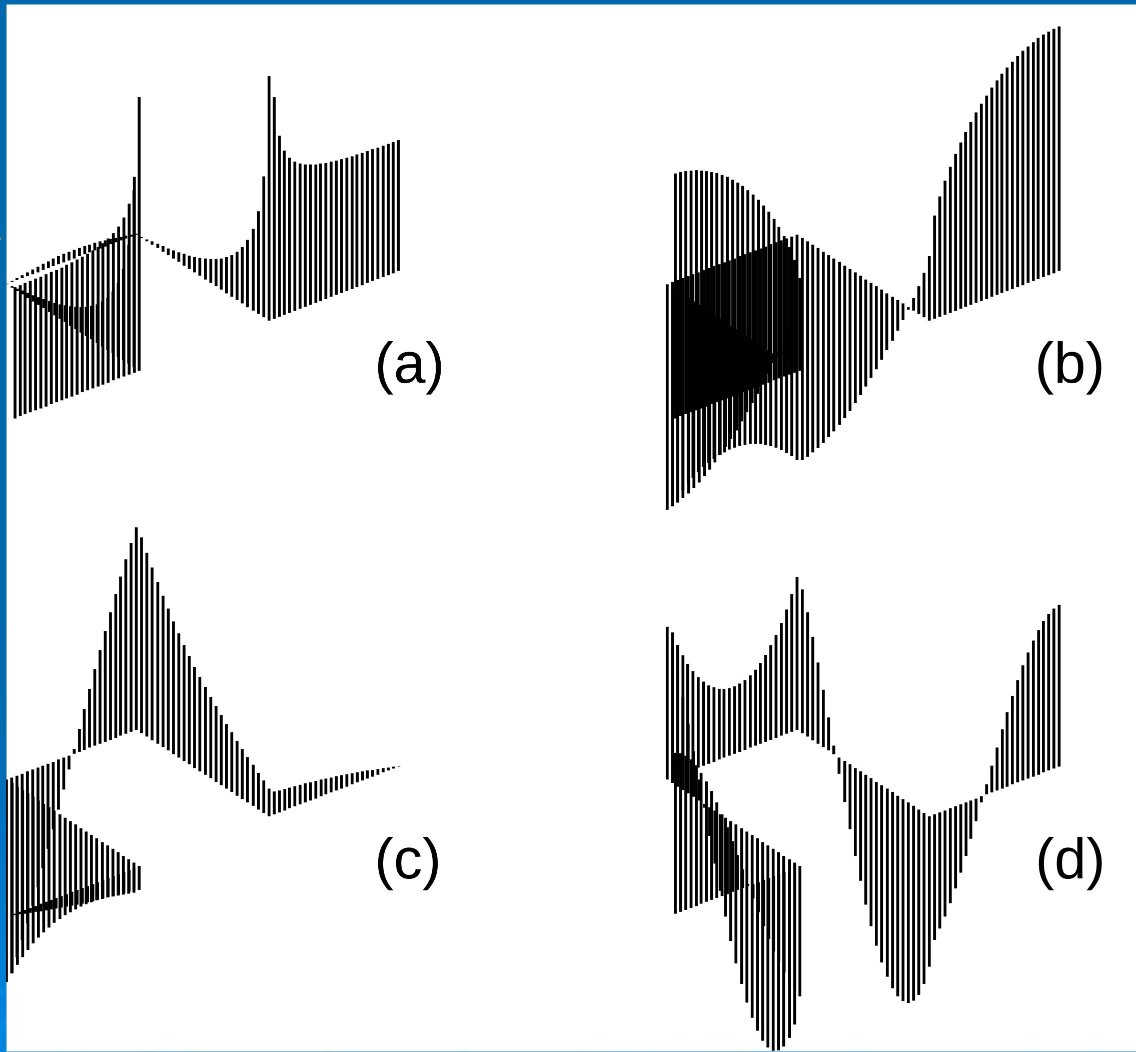


Mode reduction

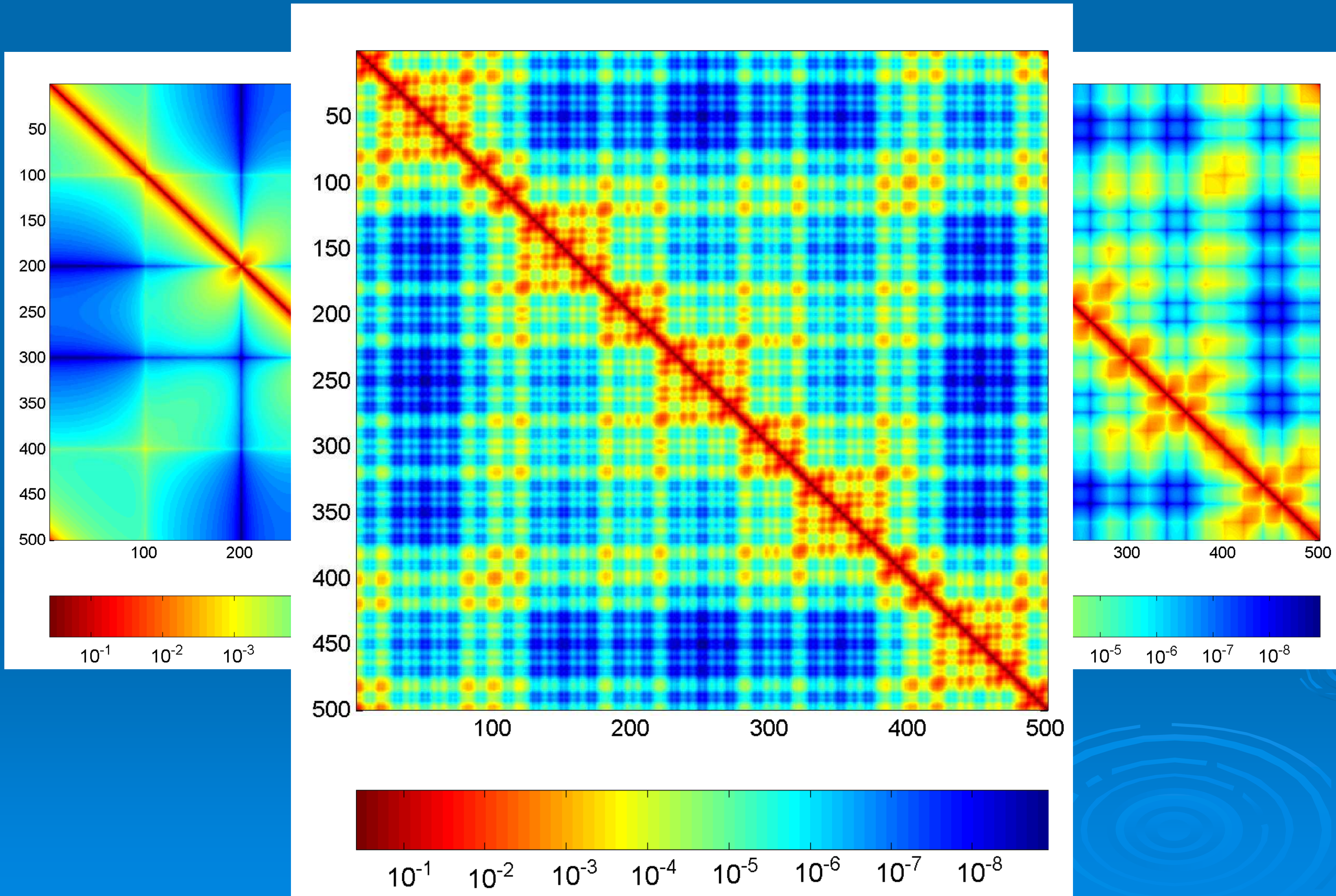


Eigenvectors of the Dirichlet-to-Neumann operator

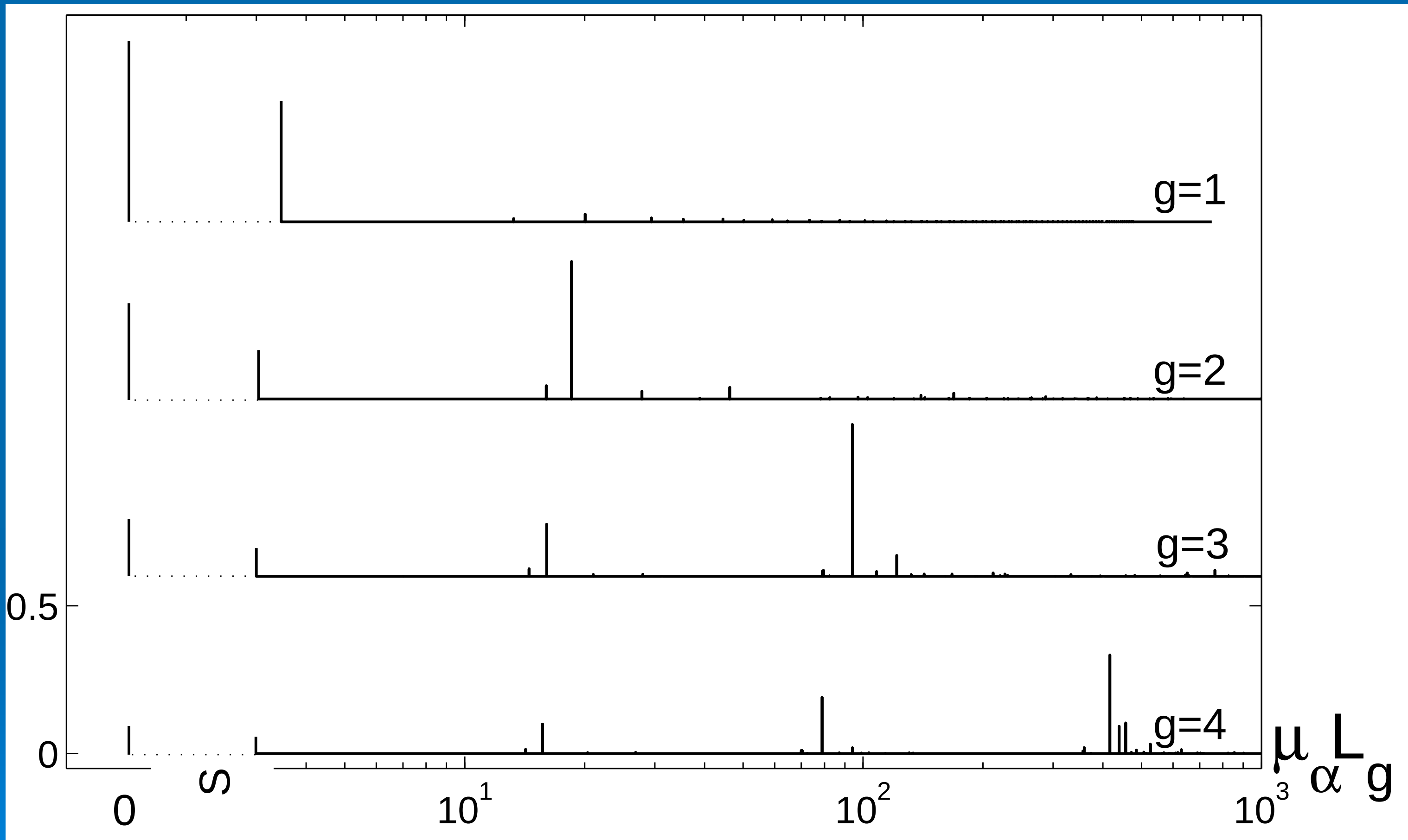
Harmonic measure density →



Structure of the probability matrix



Hierarchical spectra



"Analytical" model of the electrode

	g	$k=0$ ($\alpha=0$)	$k=1$ ($\alpha=1$)	$k=2$ ($\alpha=7$)	$k=3$ ($\alpha=37$)	$k=4$ ($\alpha=187$)
$\mu_\alpha L_g$	1	0	3.480			
	2	0	3.050	18.857		
	3	0	3.008	16.184	97.028	
	4	0	2.992	15.687	78.929	416.336
$\mu_k^{(g)} L_g$		0	3	15	75	375
$F_\alpha L_g$	1	1.000	0.686			
	2	1.000	0.463	1.335		
	3	1.000	0.441	0.822	2.545	
	4	1.000	0.437	0.772	1.465	2.573
$F_k^{(g)} L_g$		1.000	0.667	1.111	1.852	3.086

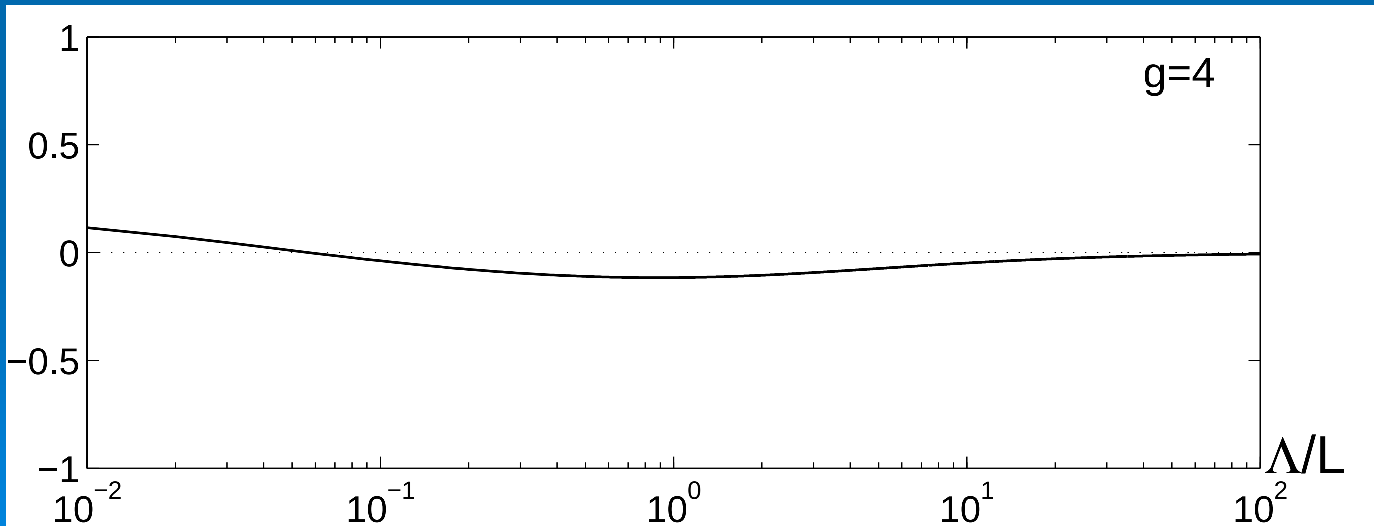
Table 1: Comparison between the main contributing peaks of the harmonic geometrical spectra for the first four generations of the quadratic Koch curve of fractal dimension $\ln 5/\ln 3$ and the model scaling relations for $\mu_k^{(g)}$ and $F_k^{(g)}$.

Analytical model

$$\mu_k^{(g)} L_g \approx \begin{cases} 0.6 \times 5^k & ,k > 0 \\ 0 & ,k = 0 \end{cases}$$

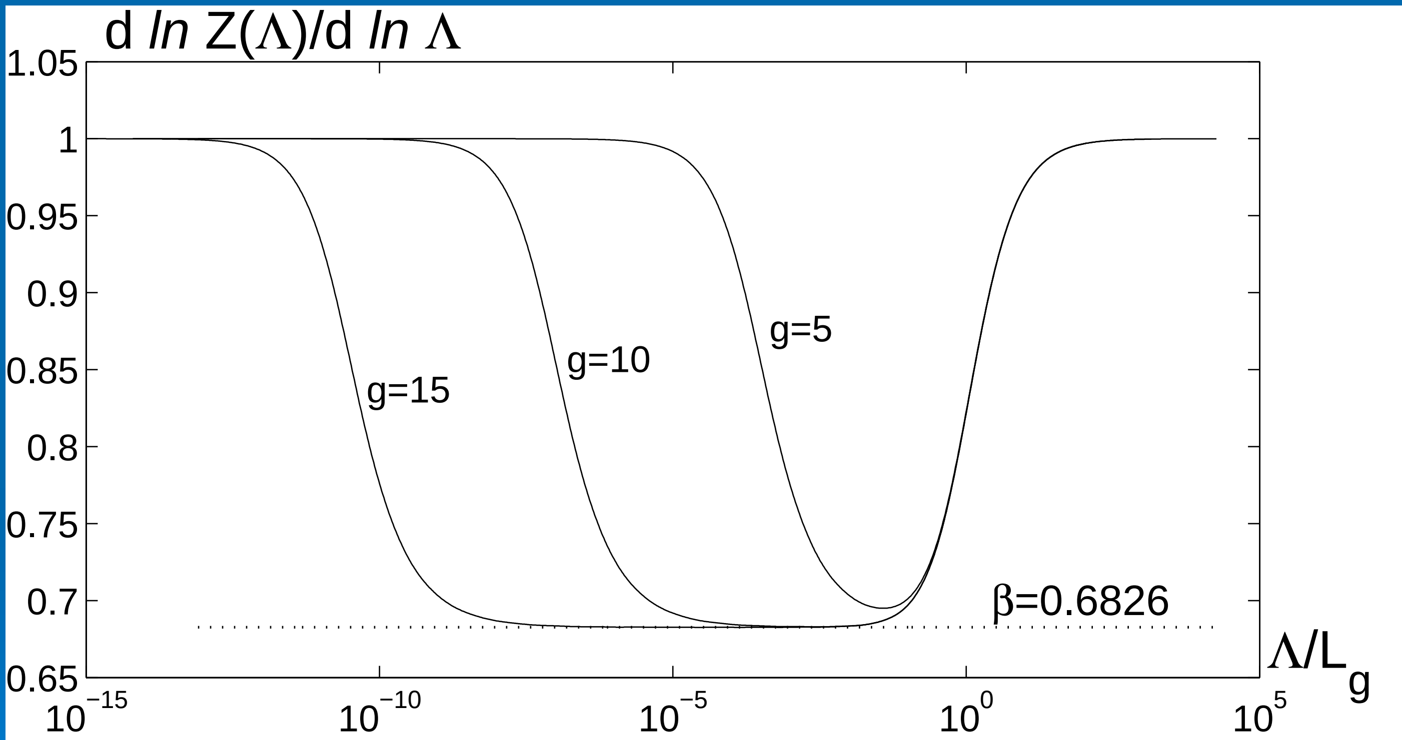
$$F_k^{(g)} L_g \approx \begin{cases} 0.4 \times (5/3)^k & ,k > 0 \\ 1 & ,k = 0 \end{cases}$$

Relative error of the model impedance

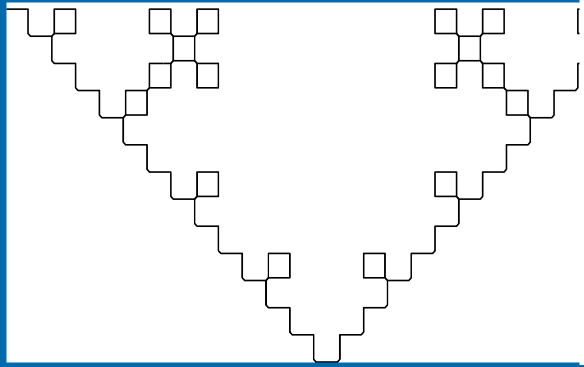


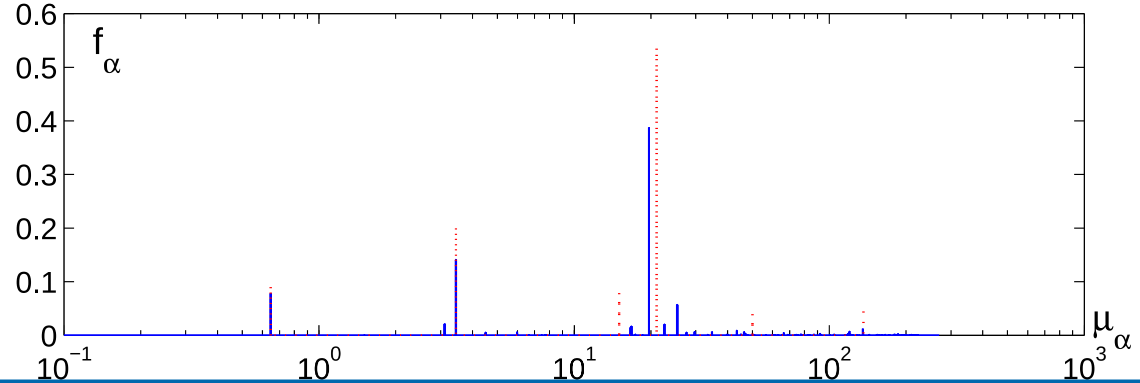
D.S. Grebenkov, M.F., B. Sapoval, 2007

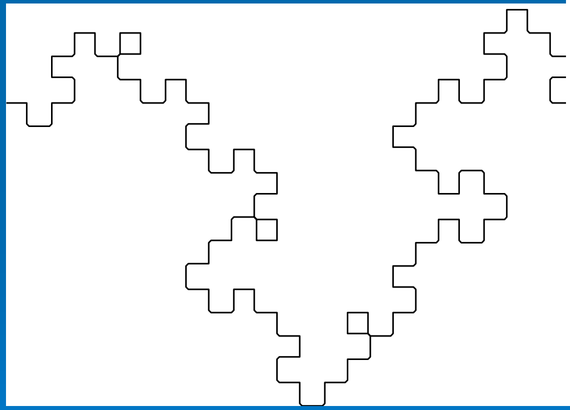
Reconstructed impedance for large generations

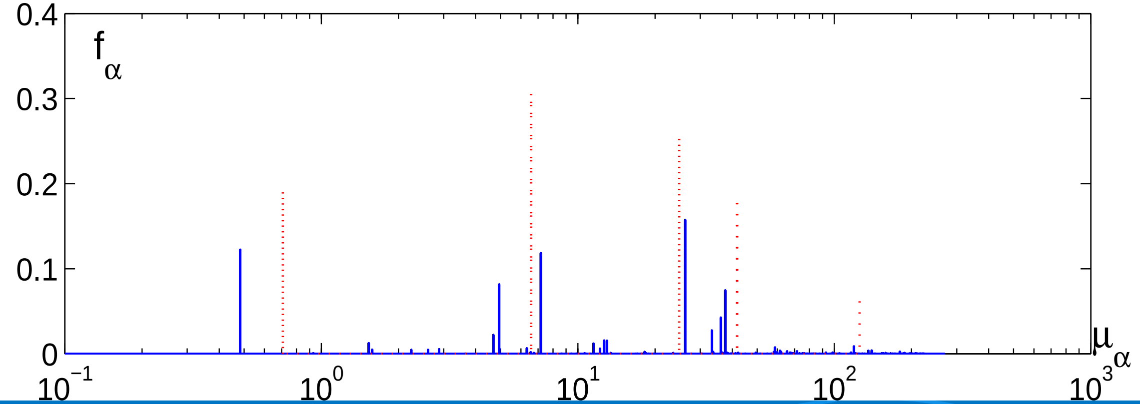


Deterministic vs random

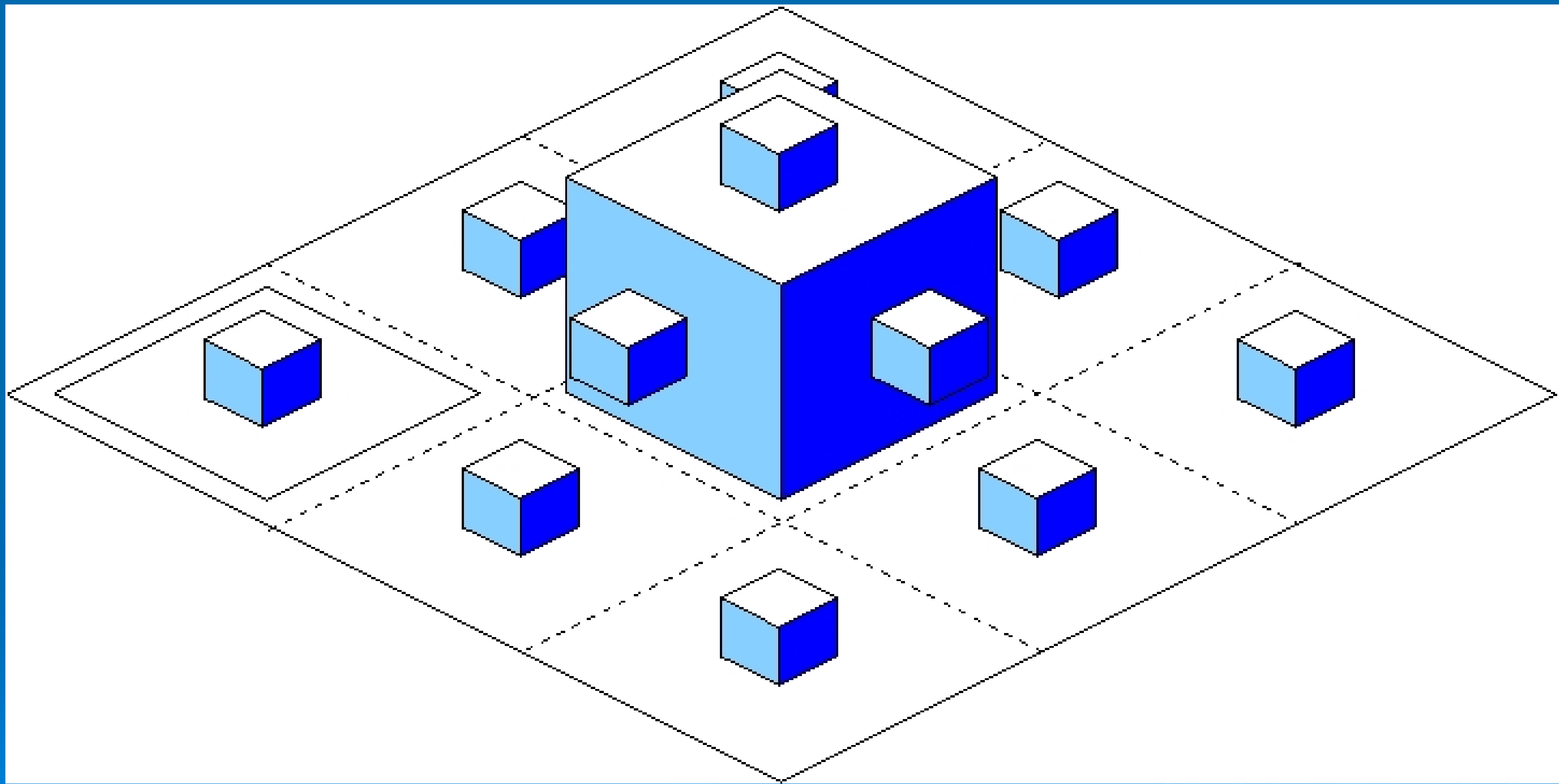




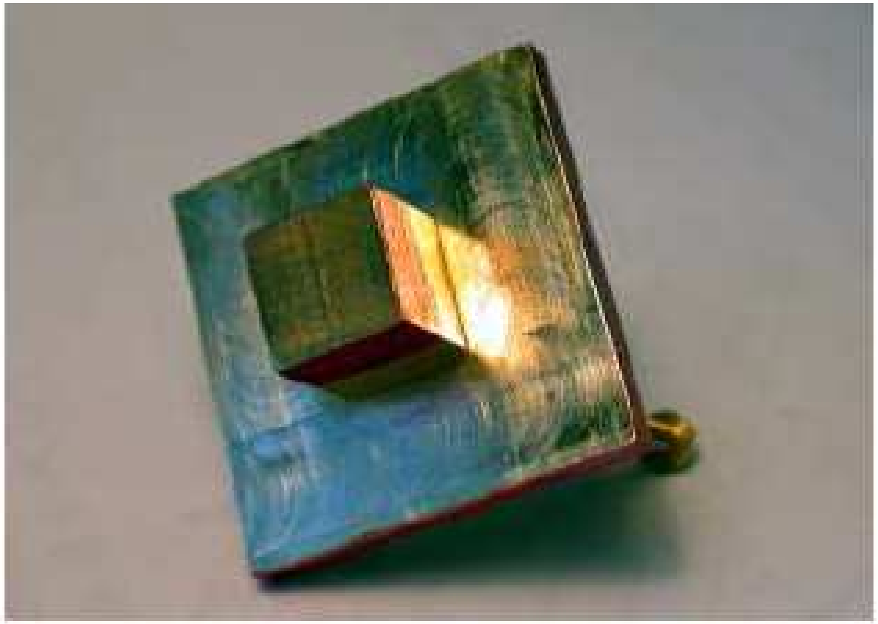




Model electrode : Von Koch surface



Experimental study on prefractal electrodes



Concave vs Convex

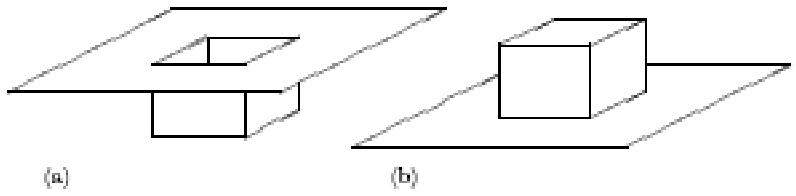


Figure 11: Generators for two cubic Koch surfaces of fractal dimension $\ln 13/\ln 3$: concave (a) and convex (b).

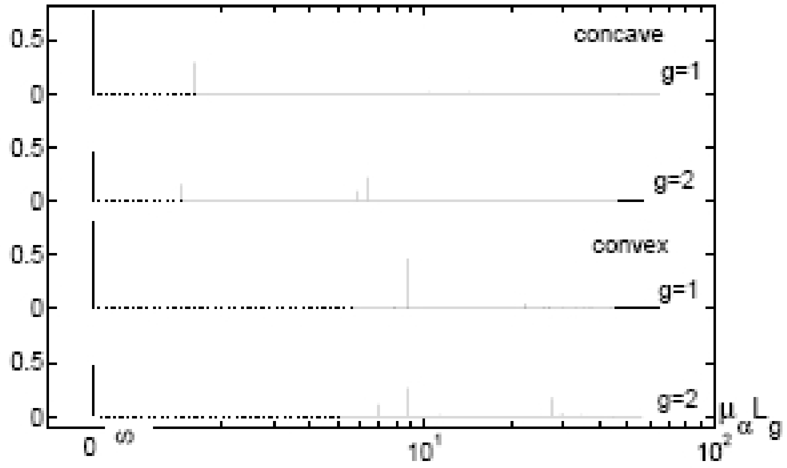


Figure 12: Harmonic geometrical spectra $F_\alpha(\mu_\alpha)$ for the first two generations of two cubic Koch surfaces of fractal dimension $\ln 13/\ln 3$.

Fast random walk in deterministic self-similar Von Koch domains

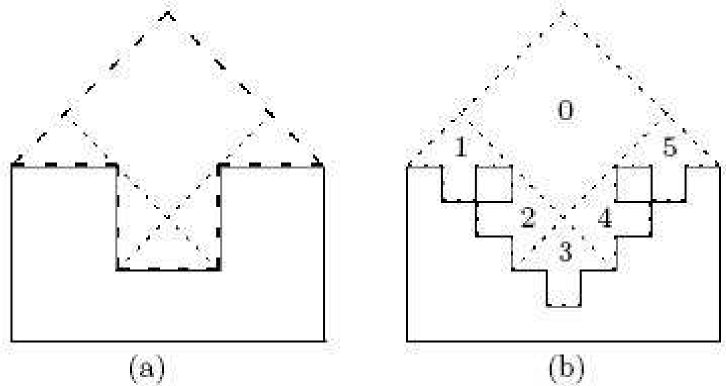


FIG. 2: (a) Initial arrow-like cell $\mathcal{A}$ is divided into the rotated square and five small triangles; (b) when random particle arrives into a small triangle, it can "see" the following generation.

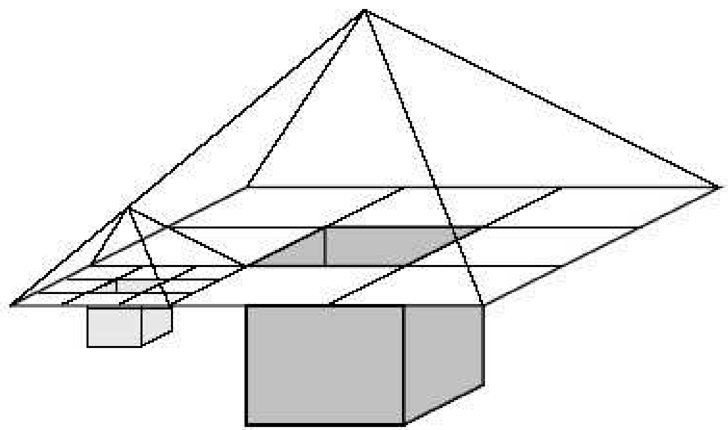
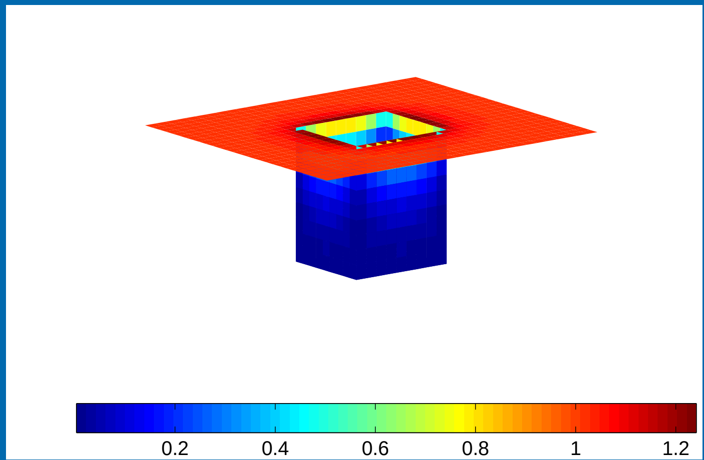
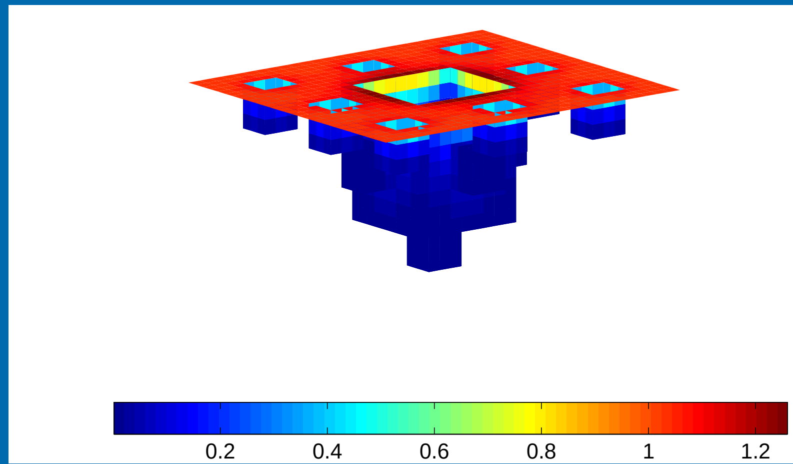


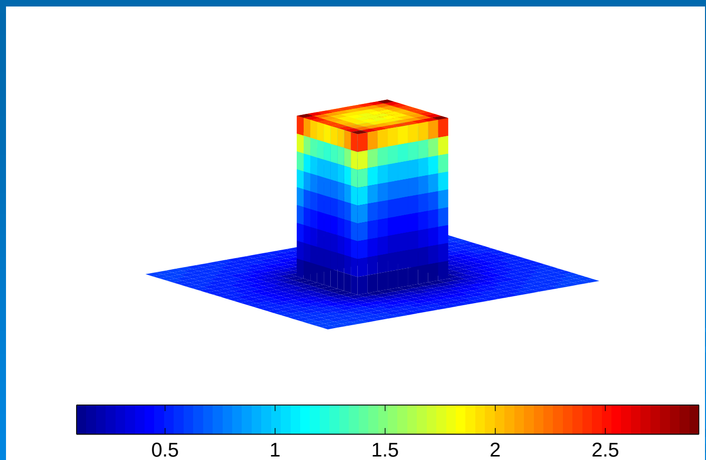
FIG. 3: First generation of the cubic Koch surface. Three-dimenional cell $\mathcal{A}$ is composed of the pyramid (of square base $L \times L$ and of height $L/2$) and small cube (with edge $L/3$). This cell is divided onto 13 smaller cells $\mathcal{A}_k$ and the volume $\mathcal{A}_0$ of the rest.

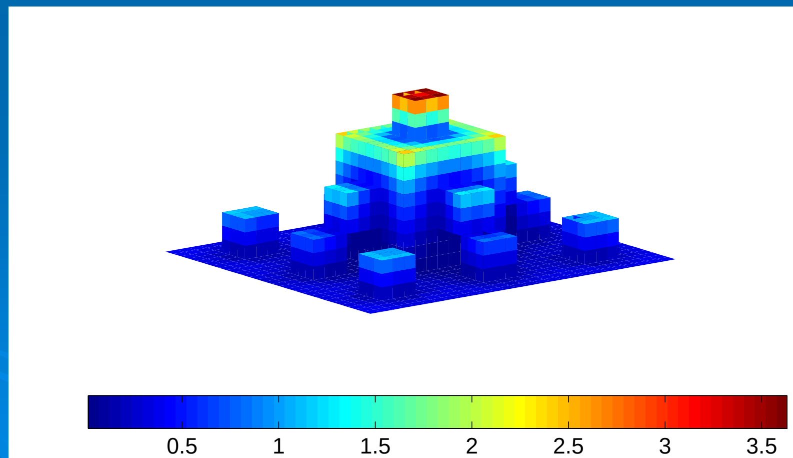
D.S. Grebenkov, A.A. Lebedev, M.F., B. Sapoval, 2005

Numerical simulations of the harmonic measure

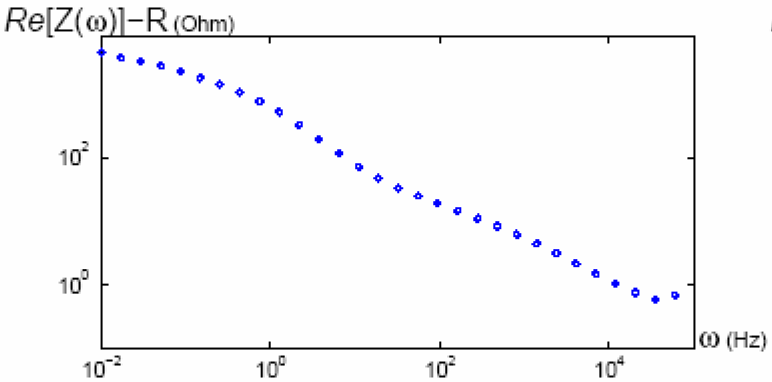


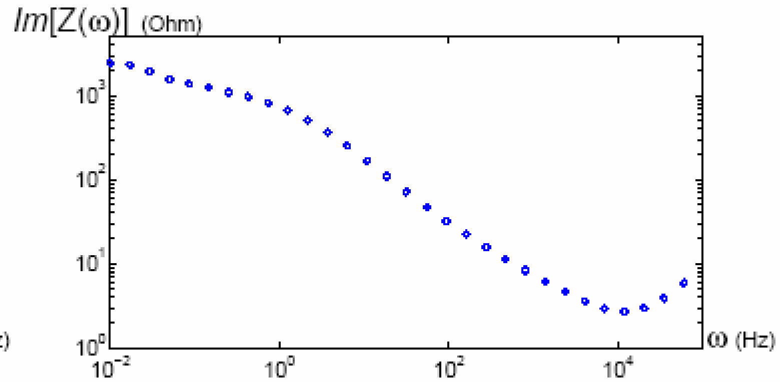






Deuxième génération : expérience et théorie





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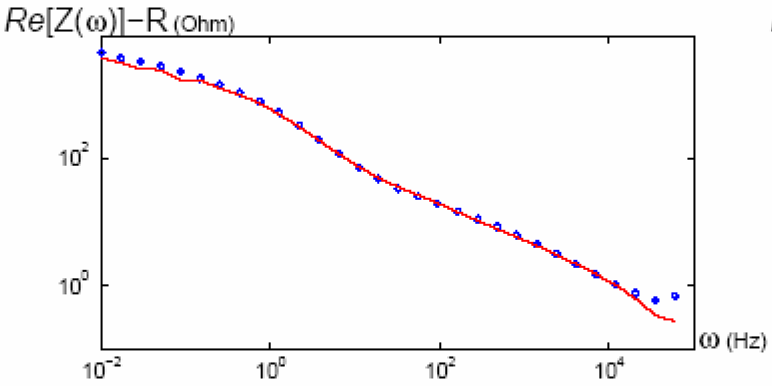
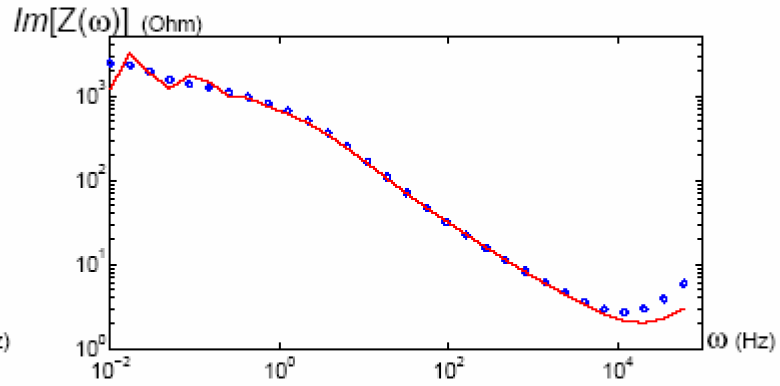
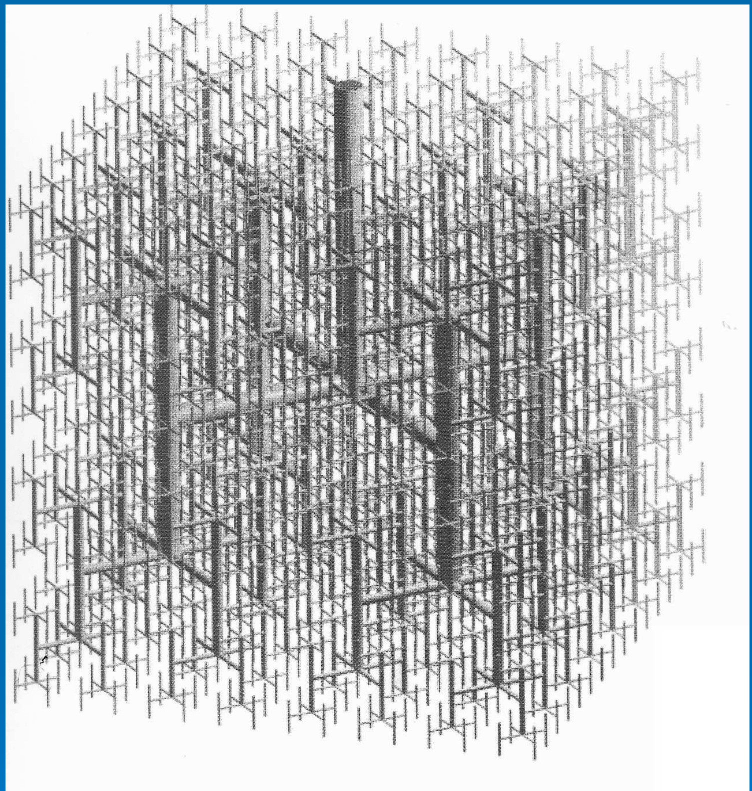
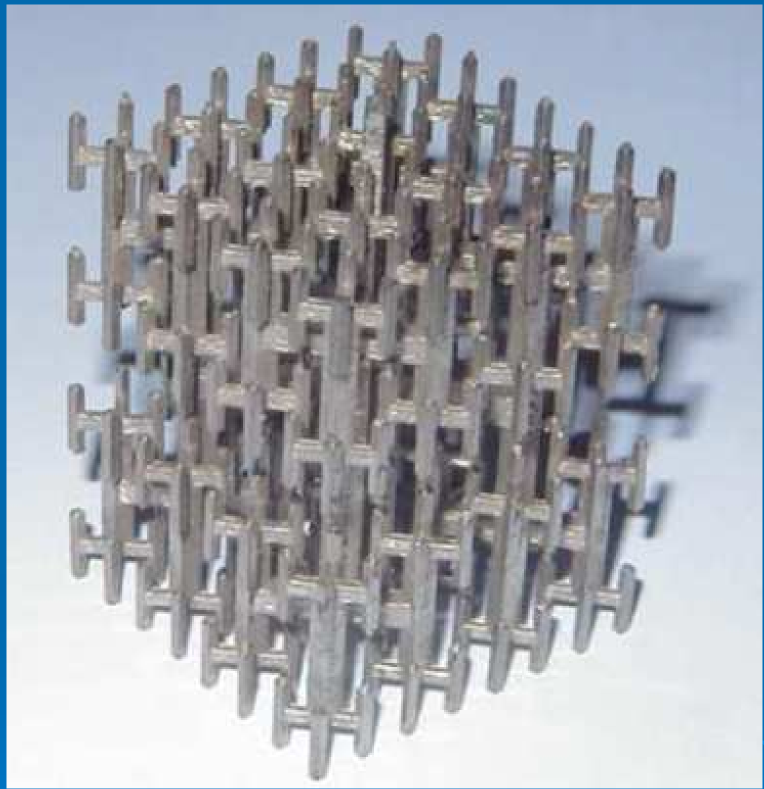




Prefractal electrode of dimension 3





E. Chassaing, M.F., B. Sapoval, 2004

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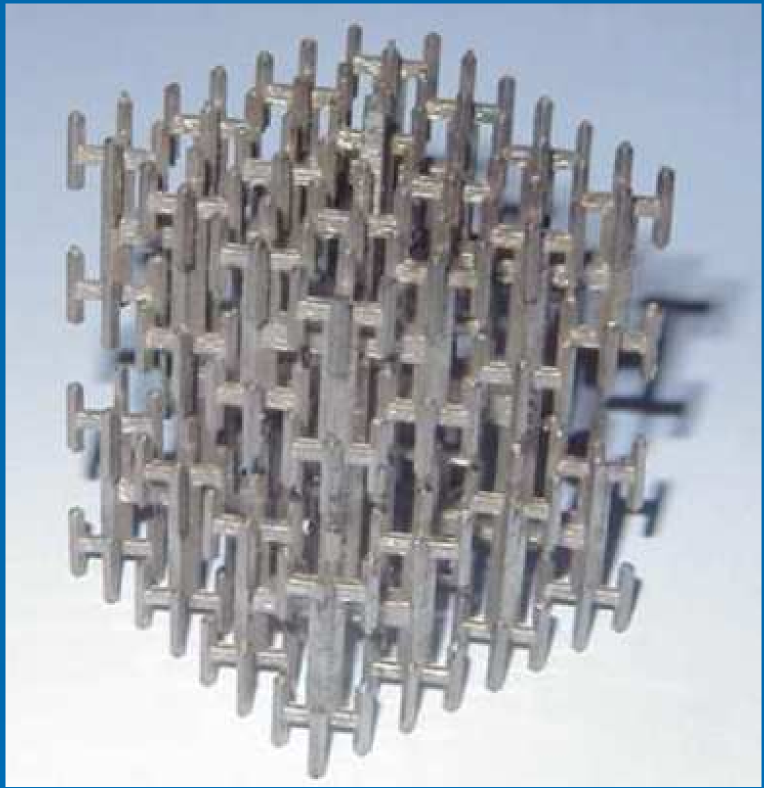

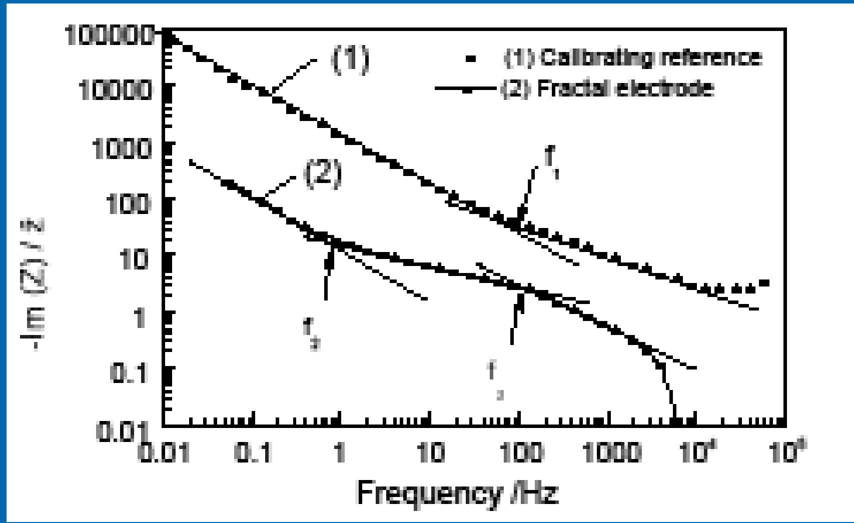

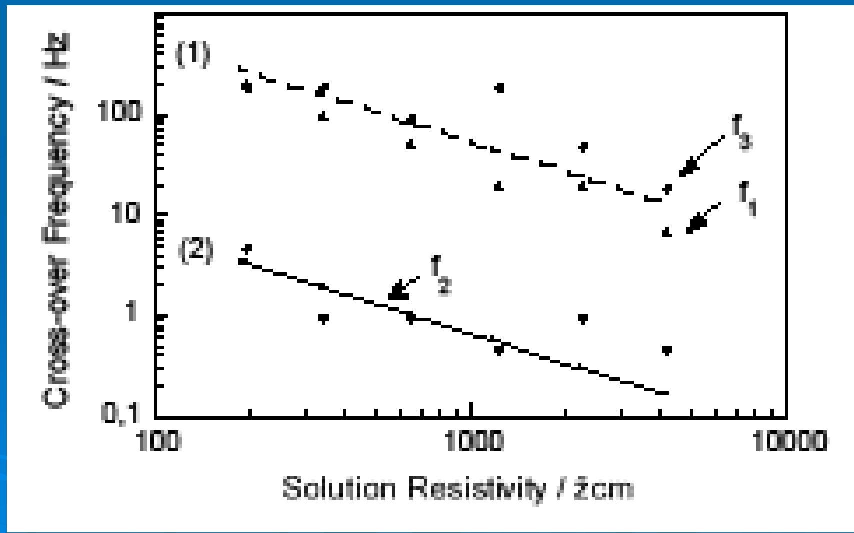

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Open questions

- Spectral properties of the Dirichlet-to-Neumann operator (fractal boundaries).
- Knowing (F,μ) of a boundary, what can we say about its geometry?
- Properties of the "spread harmonic measure"
- Link between RBM and Dirichlet-to-Neumann
- Transient operators?