Chaos and complexity in nanotechnology: the challenge of characterizing nanotextured surfaces

Vassilios Constantoudis

Institute of Nanoscience and Nanotechnology, **NCSR Demokritos**, Agia Paraskevi, Greece

Nanometrisis p.c., Agia Paraskevi, 153 41, Greece

Acknowledgements

3DNano Traceable 3D nanometrology

EMPIR

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

HARMoNIC HierARchical Multiscale NanoInterfaces for enhanced Condensation processes
Horizon 2020-2024

SuperClean Clean water technology with membrane distillation
EIC 2024-2027

resin green Developing resist materials and nanometrology methods to reduce the environmental footprint of digital technology
ChipsJU 2024-2027

Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

Efi-Maria Papia

Alex Kondi

Athanasios Arapis

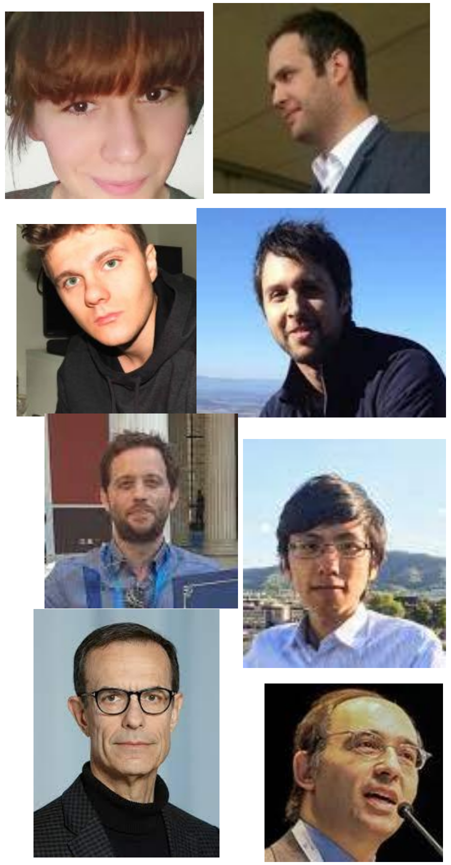
George Papavieros

Athanasios Milionis

Cheuk Wing Edmond Lam

Dimos Poulikakos

Evangelos Gogolides



National and Kapodistrian University of Athens

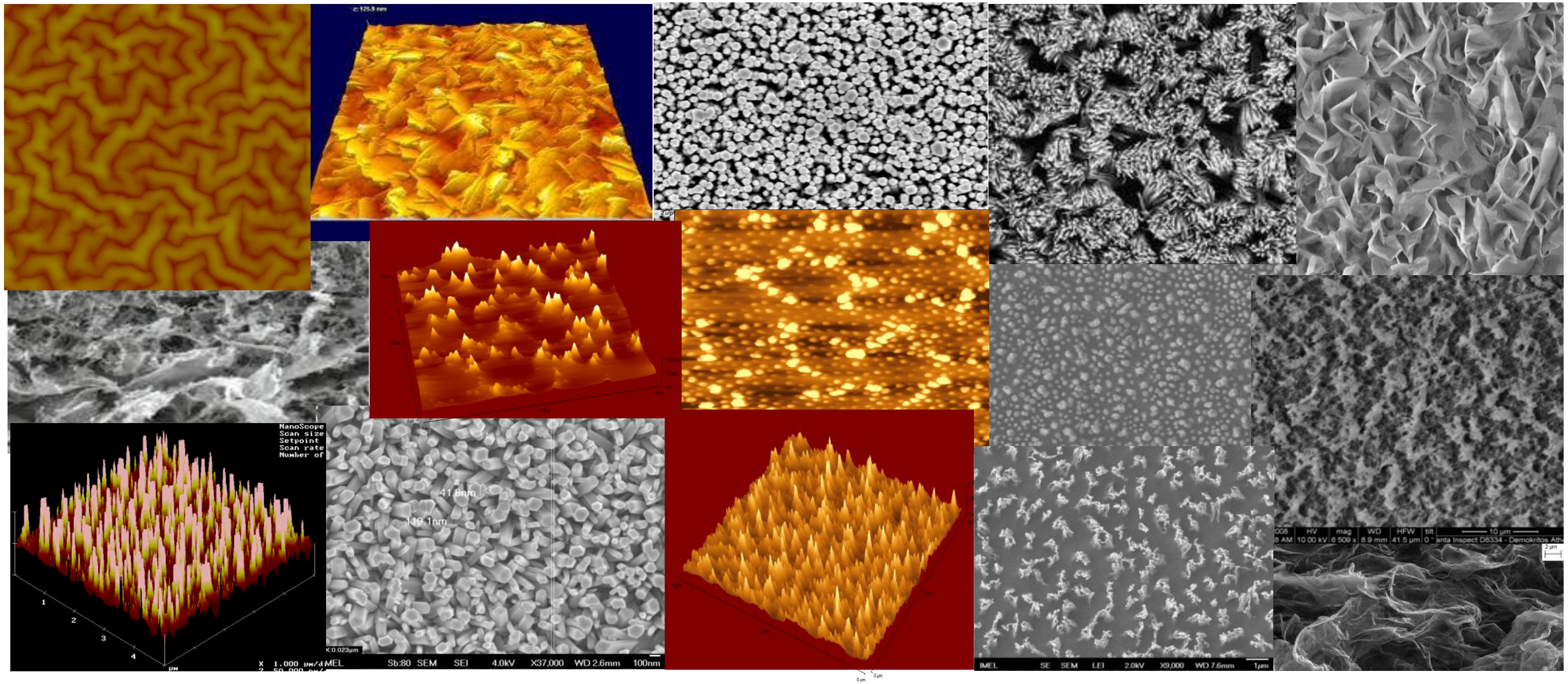
Outline

- Motivation - context
- The challenge of nanostochasticity
- Mutiscale Shannon-entropy
- Chaos-based approach
- Hierarchal micro-nano surfaces
- Conclusions

A few words on nanotechnology

Nanotechnology: the theory, design, manufacturing, characterization and performance of devices and systems enabled by embedded structures with at least **one dimension <100nm (nanostructures)**

Two main pillars : nanofabrication techniques + microscopies



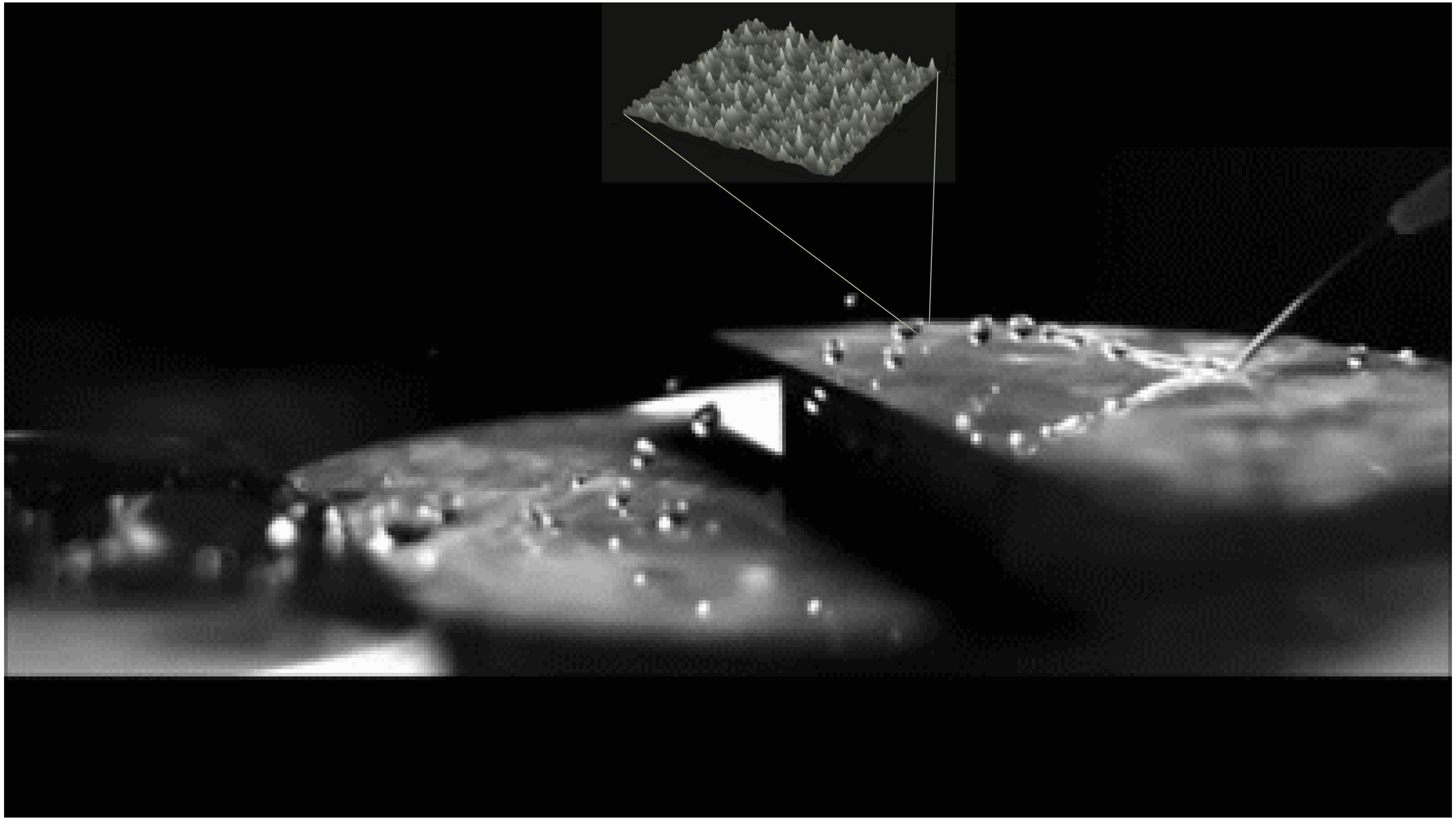
rough/stochastic/random surfaces/morphologies

DEMOKRITOS

Nanotechnology in products

Nano-enabled properties of surfaces and materials

Friction, wetting, catalysis, reflectance, bio-adhesion,…



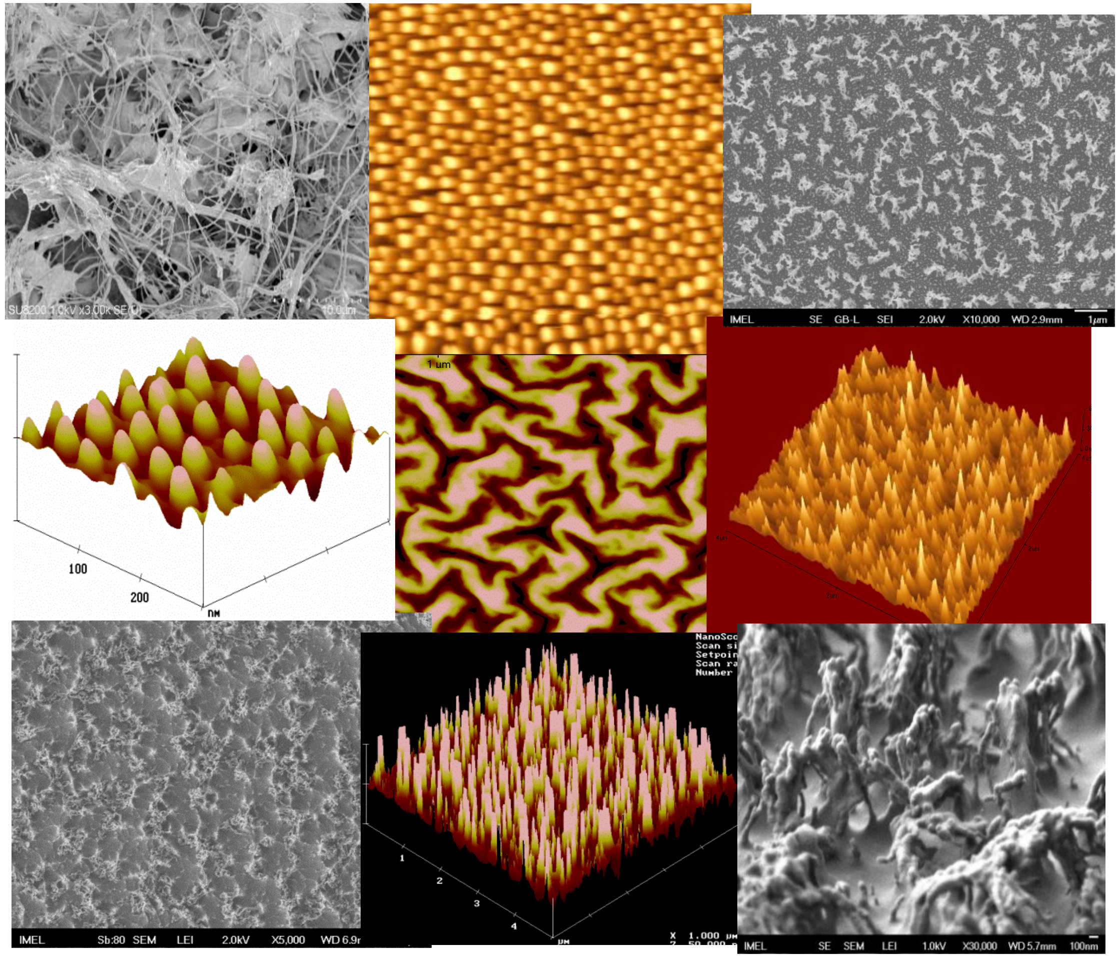
Hydrophobicity + roughness => Superhydrophobic surfaces

The main questions

- What is the mathematical language of the nanoworld?
- How can we characterize, quantify, model and understand better this wide diversity of nanomorphologies?
- Why may we need inspiration from chaos and complexity methods?

The challenge of nanostochasticity

Nanostructured surfaces
(nanotress, nanoforests, nanocorals, nanograss,…)



Quantitative/mathematical characterization & measurement

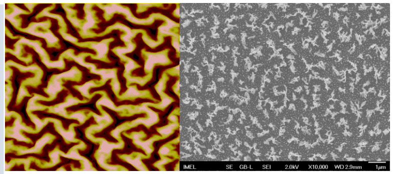
?

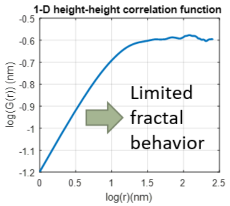
➢The grand challenge :
Quantify nanostocasticity activating novel math/computational tools

8

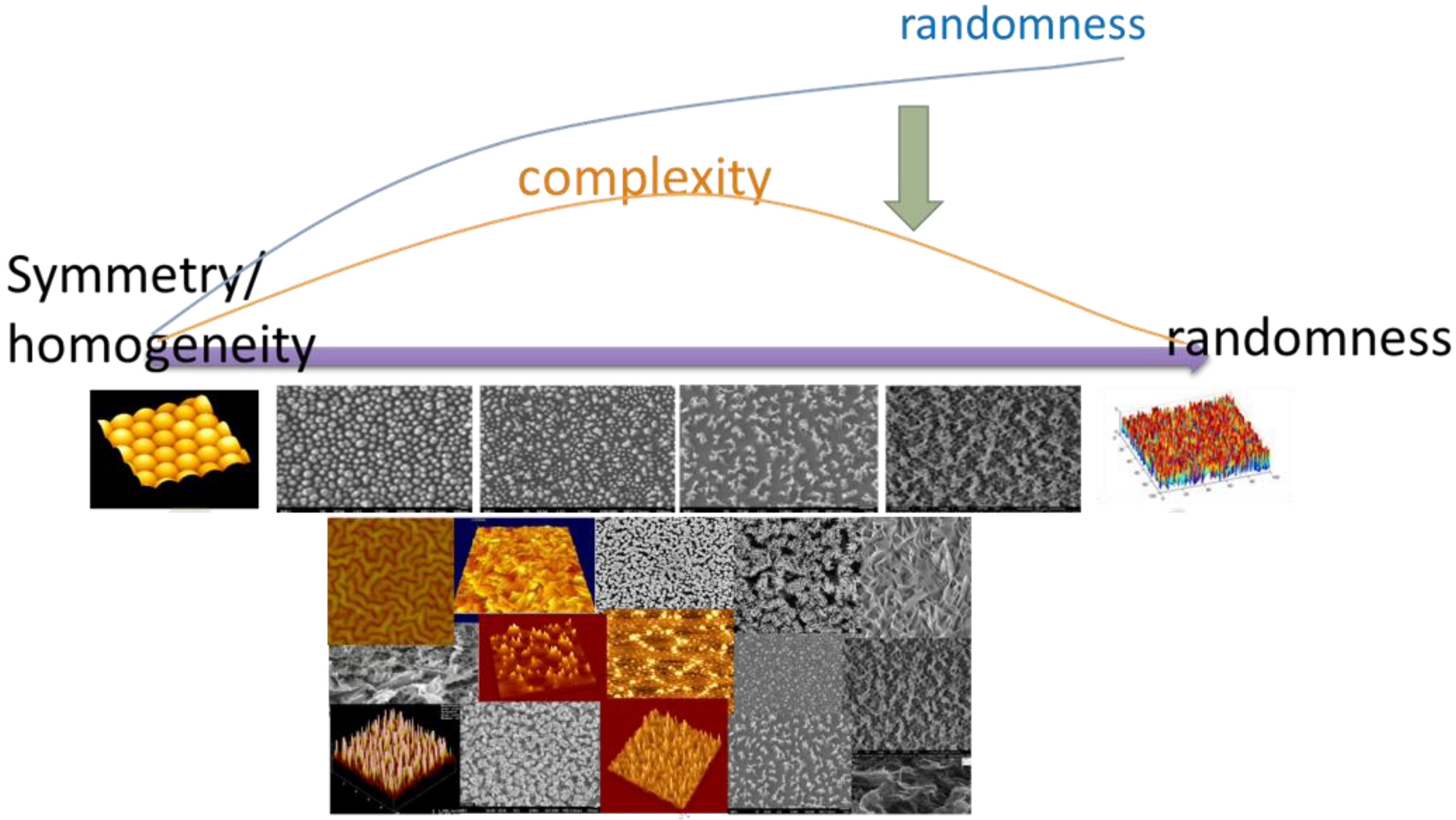
Conventional vs alternatives

	Conceptual Background	Methodologies
conventional	▪ Surface: A collection of surface atoms ▪ Surface Roughness: Deviation from flatness/smoothness	• Random fields for Surface roughness Limitation: Non-typical morphologies • Fractal Approach – Scaling symmetry hypothesis Limitation: Self-affinity is scale-limited due to nanoscale
alternative	➢ Surface: Information channel of material to communicate with environment ➢ Surface roughness: the “language” of this communication channel	?





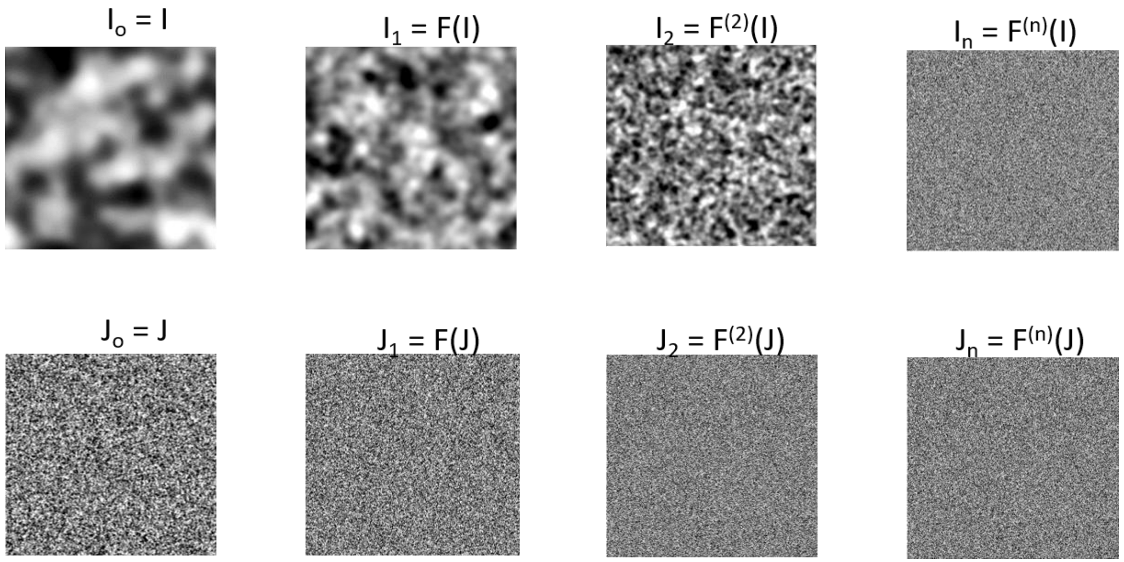
Nanostochasticity or nanocomplexity



- Seeking a quantity maximizing between order and randomness

Our approach

Complexity => "resistance" of surface morphology to homogenization caused by a destructuring (destroying the structure) transformation to surface image (smoothing, mixing)*



- **1st idea - Destructuring: Smoothing through local averaging**
  Surface information => Multiscale Shannon entropy-based complexity

- **2nd idea - Destructuring: Gradual mixing of surface pixels by nonlinear dynamics**
  Surface virtual dynamics=> Chaos-based spatial complexity

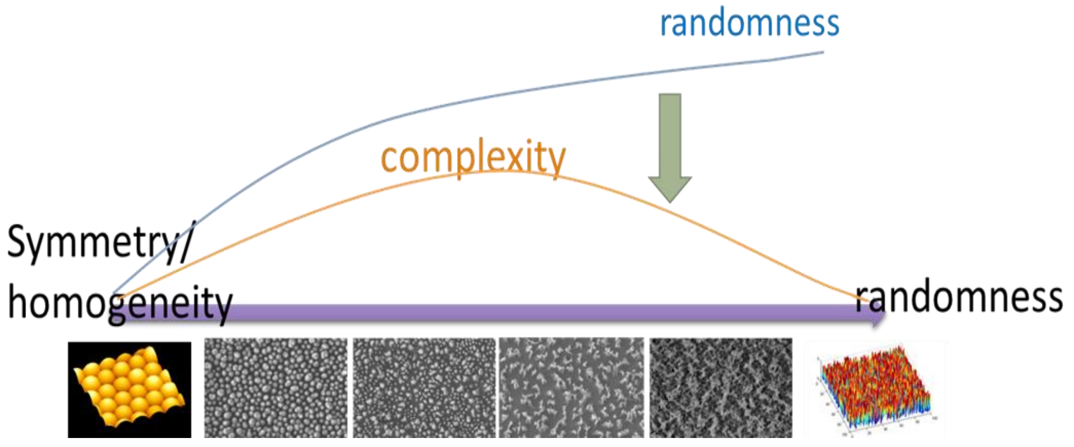
* Reminds the first noising phase of Denoising Diffusion Probabilistic ML models -> more exploration

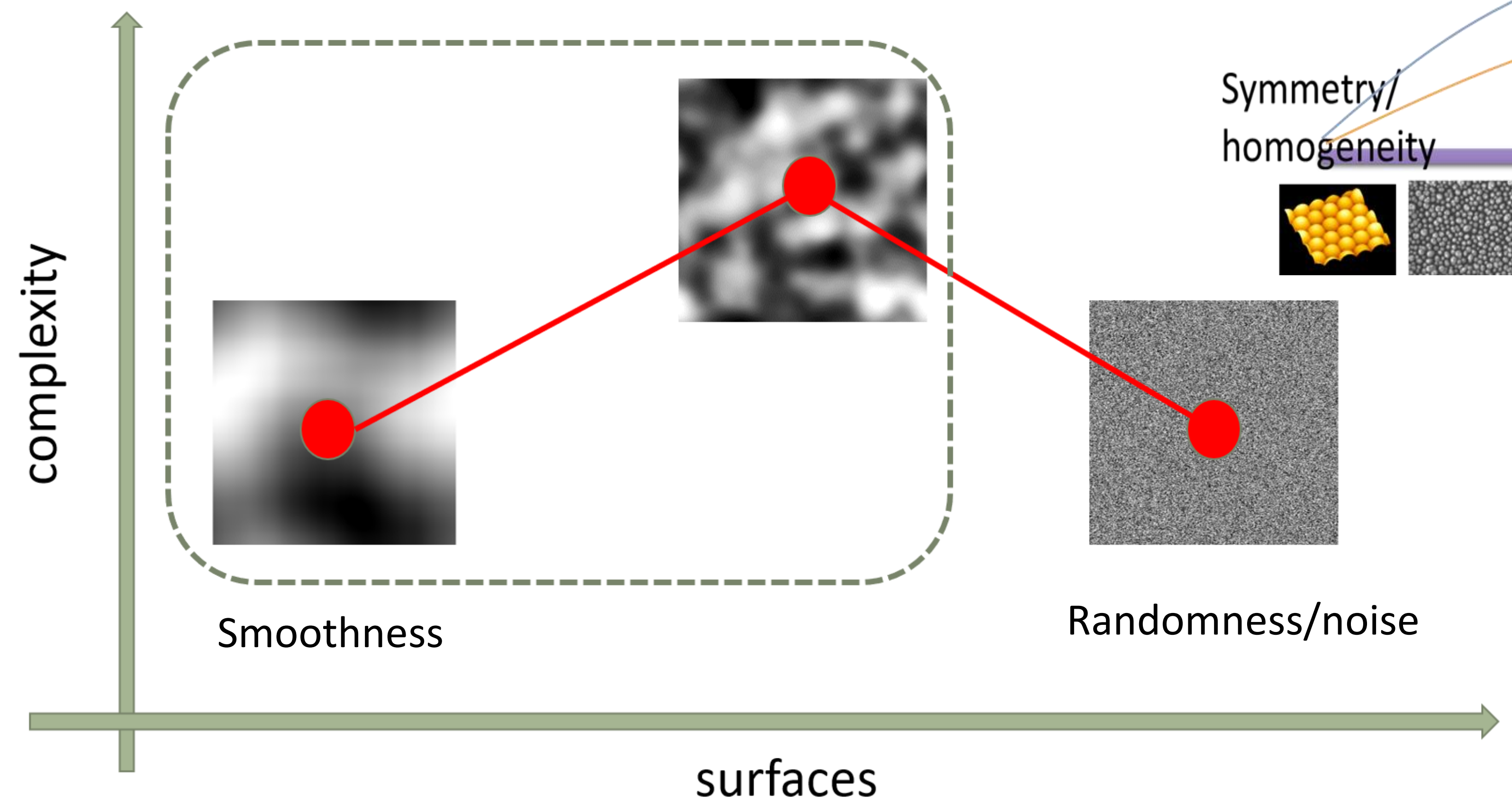
Outline

- Motivation - context
- The challenge of nanostochasticity
- Mutiscale Shannon-entropy
- Chaos-based approach
- Hierarchal micro-nano surfaces
- Conclusions

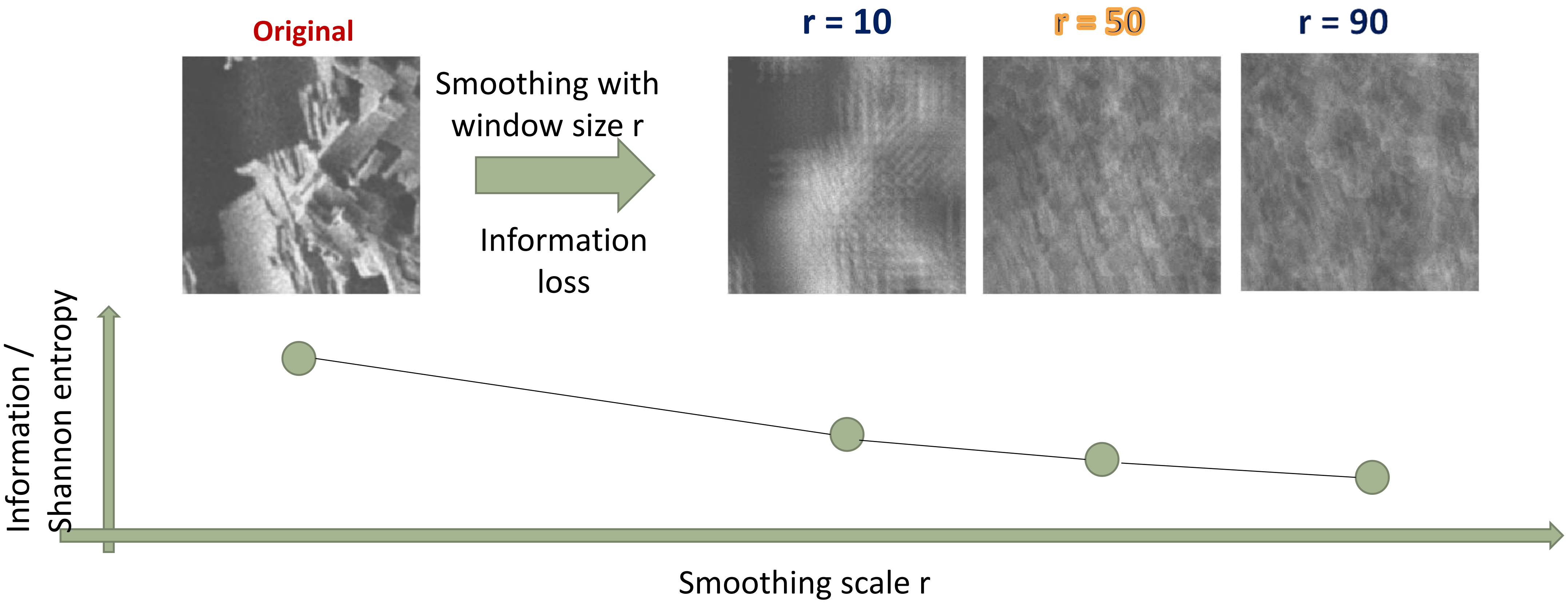
Entropy-based complexity

- Key requirement for a complexity measure: to decrease at the limits of noise and order/flatness (smoothness)





Entropy-based complexity : the key idea



Complexity => “resistance” of surface morphology to homogenization caused by local averaging (smoothing)

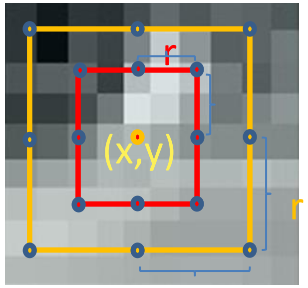
=> a measure of multiscale surface heterogeneity (information content)

R. Alamino J. Phys. A 2015, 2017, A. Arapis and V.C. Mat. Today Proc. 2022, A. Kondi and V.C. Mathematics 2025

Entropy-based complexity: method for its estimation

Implementation in 3 steps :

- 1st step: Smoothing of the image I by local averaging => generate the “mass” fields m(x,y;r) at each averaging scale r



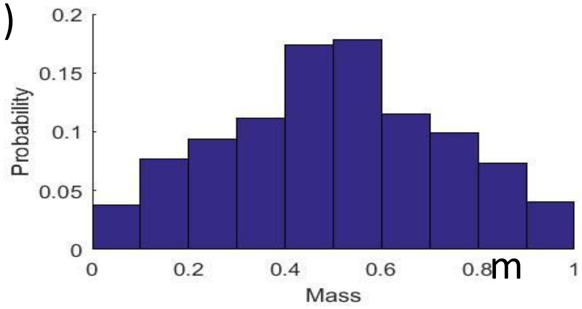
$$I(x,y) \Rightarrow m(x,y;r) = \frac{1}{9}\sum_{i\varepsilon K}\sum_{j\varepsilon M} I(i,j)$$

$K = \{x-r, x, x+r\}$

$$K = \{x-r, x, x+r\}$$

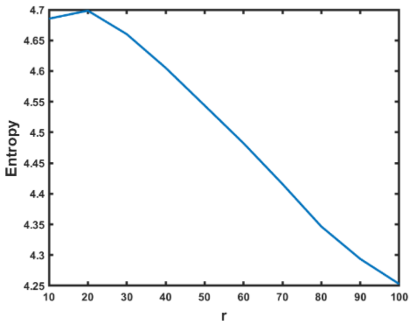
$$M = \{y-r, y, y+r\}$$

- 2nd step: At each scale r, quantify the “mass” field hetetogeneity (information content) through the Shannon entropy E(r) of the normalized mass distributions λ(m|r)



$$E(r) = -\sum_m \lambda(m|r) ln\lambda(m|r))$$

Entropy vs r



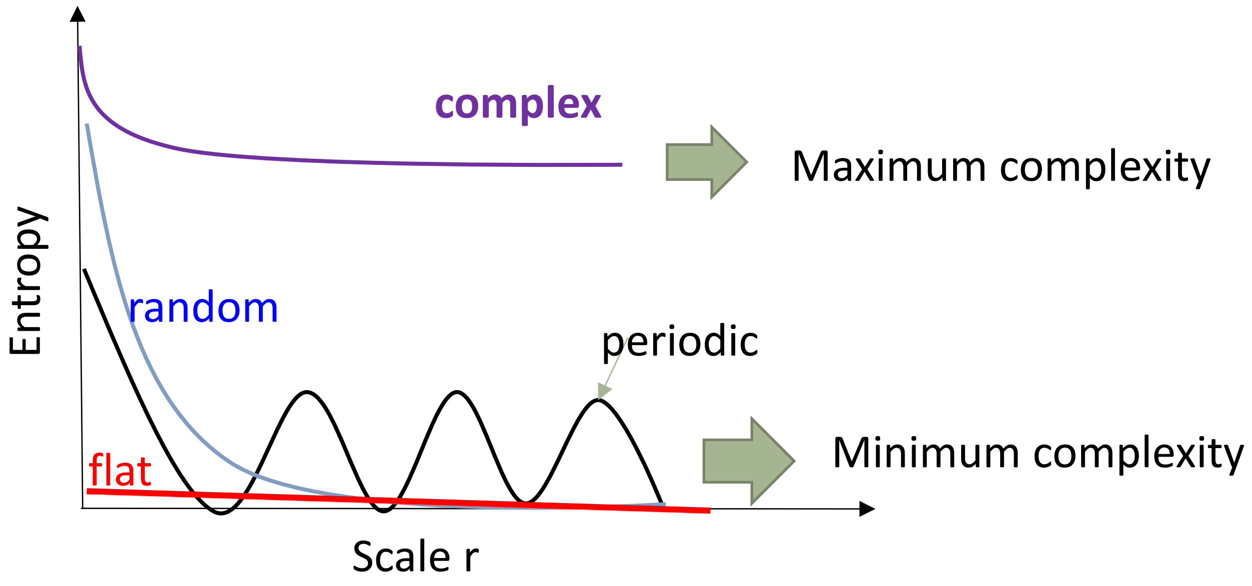
- 3rd step: Average over all scale entropies and get the complexity of the surface

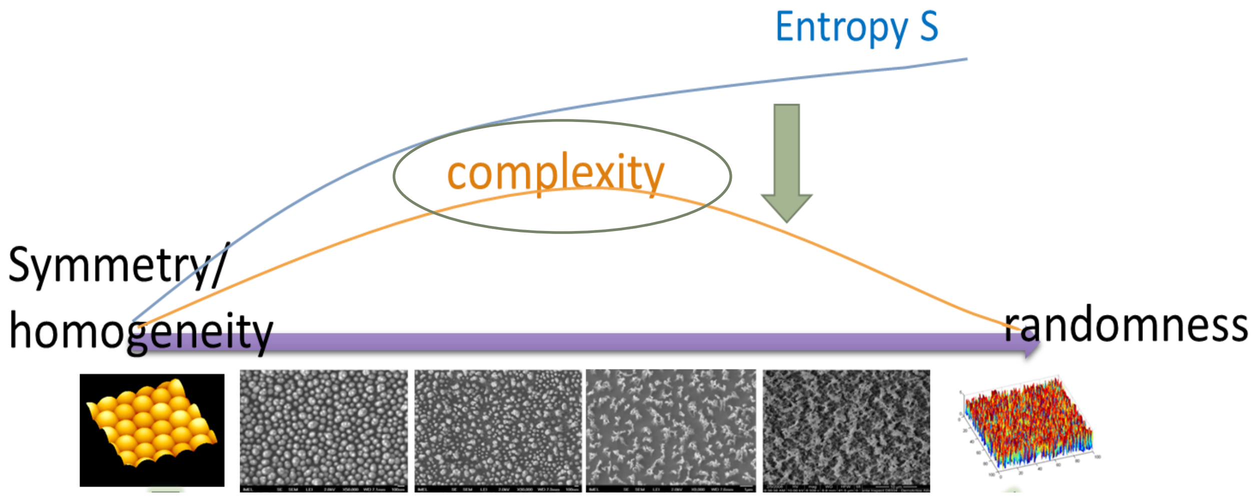
$$Complexity\ (R) = < E(r) >_{r=1:R}$$

Complexity = Average of Shannon Entropies over all scales r

Entropy-based complexity and randomness/order

- **Complexity** as average over multiscale entropy has been designed to exhibit **maximum** between full **symmetry** (homogeneity) and full **randomness**
- **Surface complexity: structural heterogeneity persisting in multiple scales**

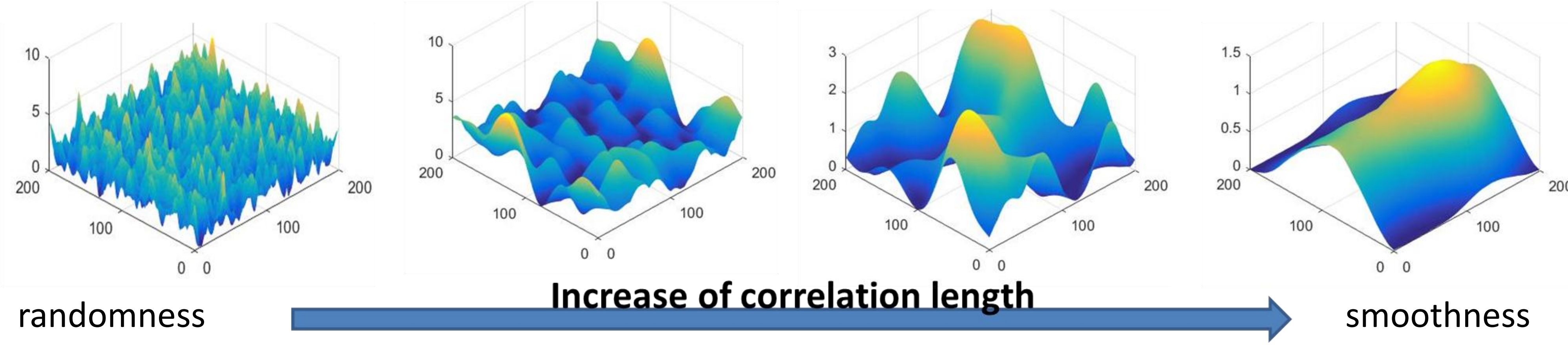


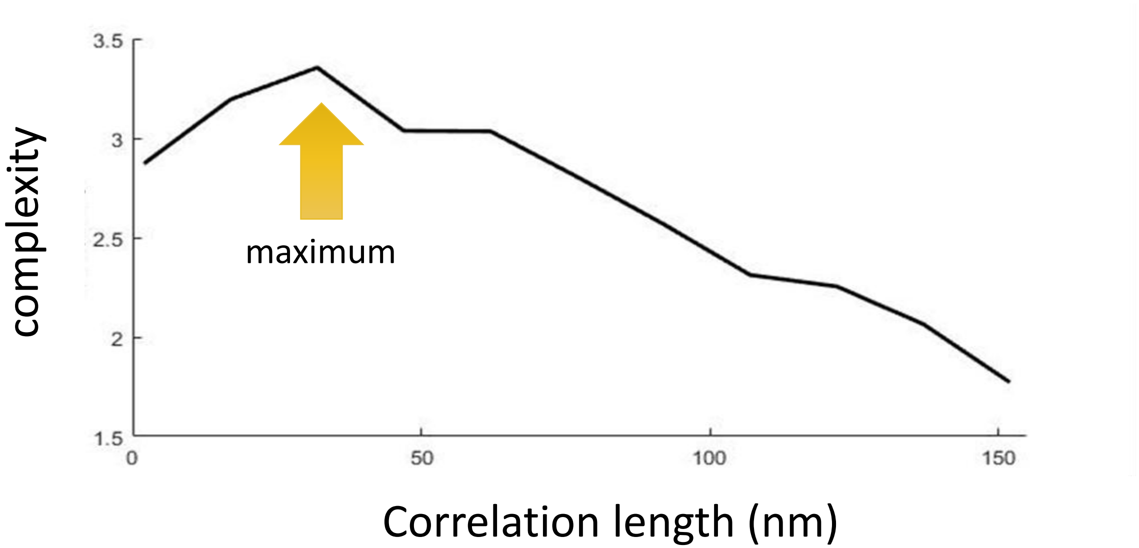


Entropy-based Approach - Applications

A. Simulated surfaces

1. Rough surfaces with increased correlation length



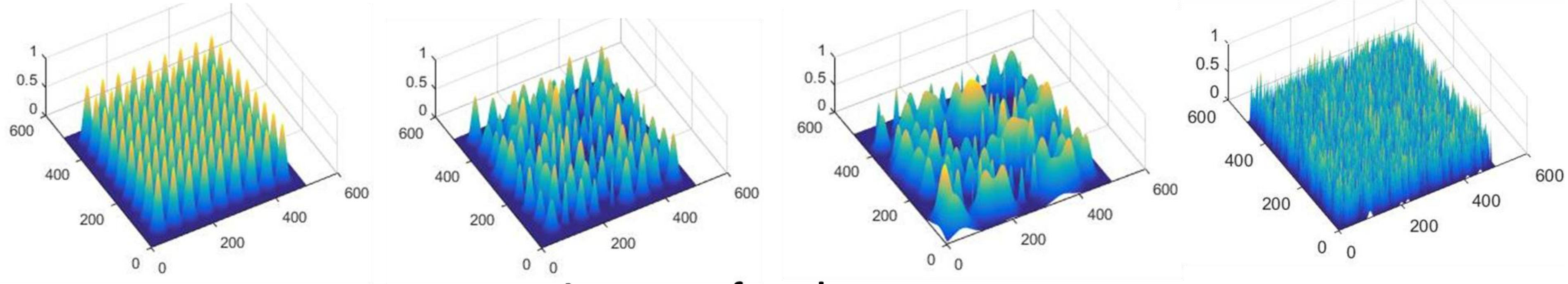


DEMOKRITOS

Entropy-based Approach - Applications

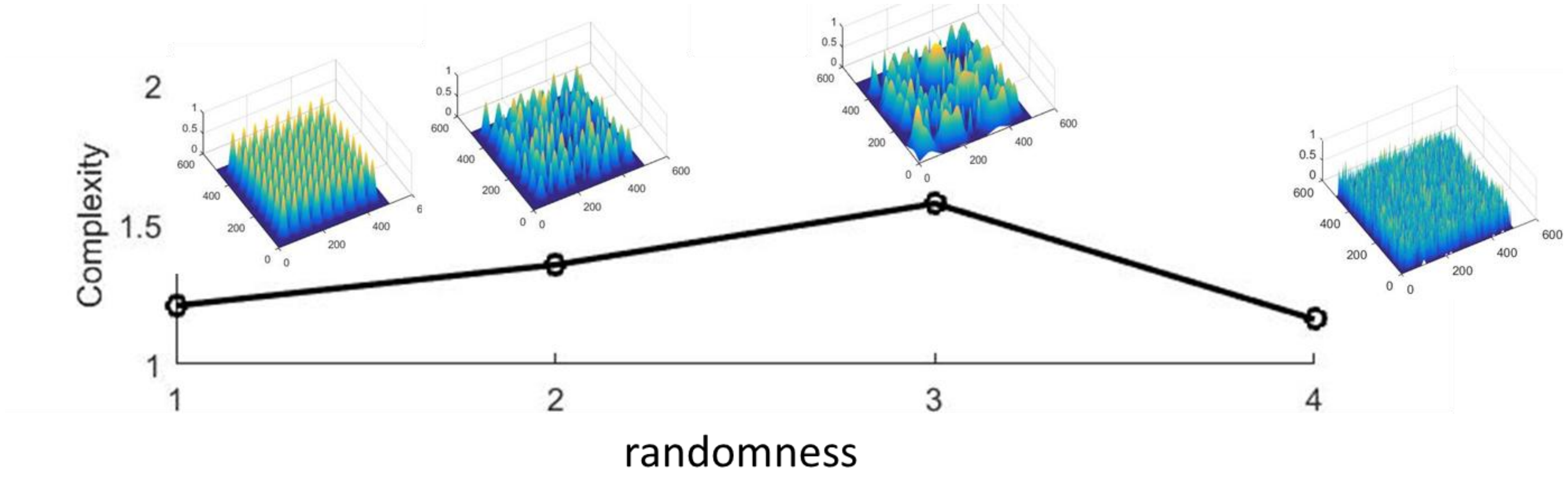
A. Simulated surfaces

2. Mound surfaces with increased randomness of mound position and shape



Increase of randomness

Order/periodicity → Noise

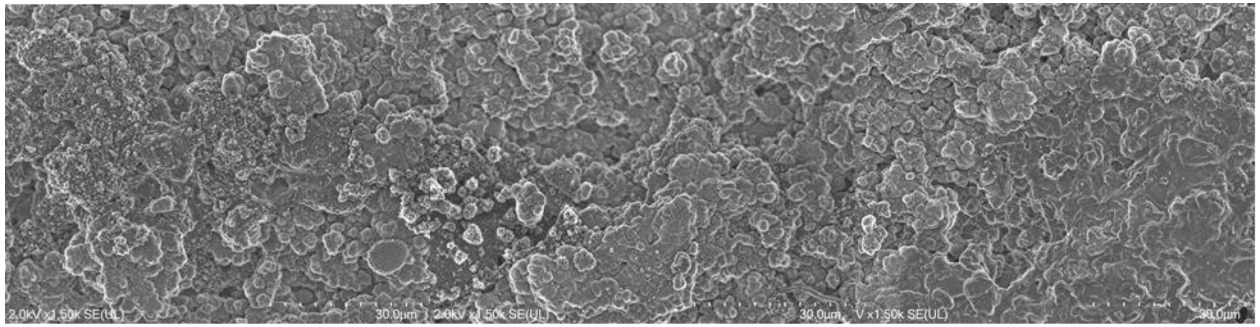


2^{nd} idea : APPLICATIONS

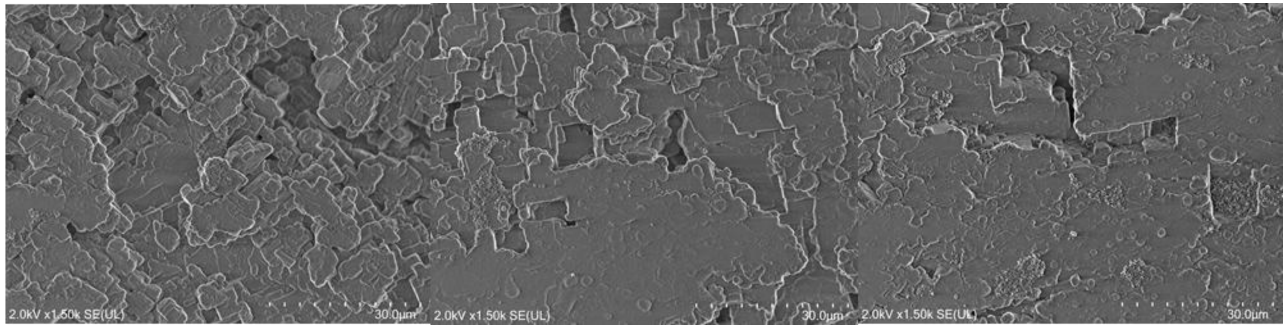
B. Experimental

1. Aluminium surfaces after wet etching in $CuCl_2$ or $FeCl_3$ and boiling

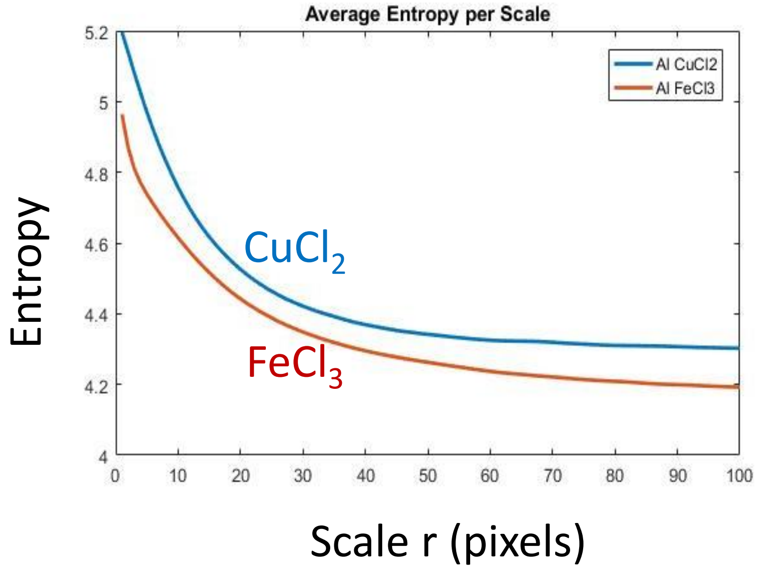
Etching with $CuCl_2$

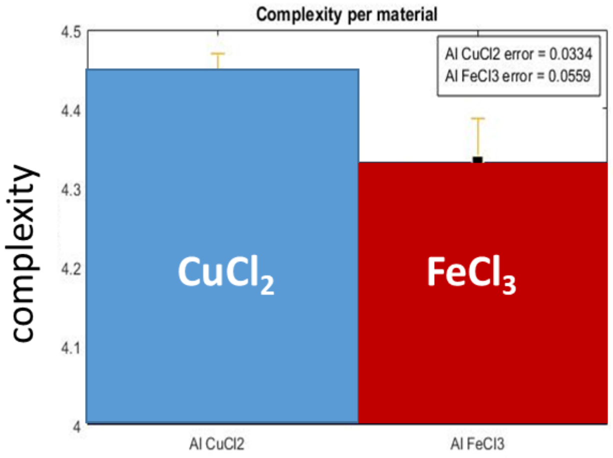


Etching with $FeCl_3$

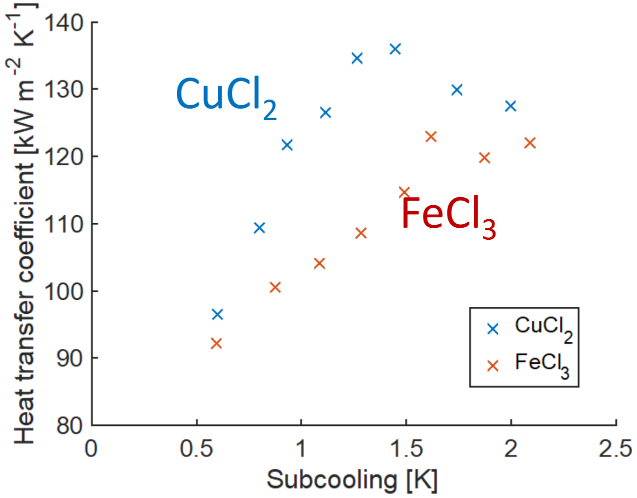


Entropy and complexity analysis





Experimental results: Heat transfer



Higher complexity => larger heat transfer coefficient

A. Arapis and V.C. Mat. Today Proc. 2022

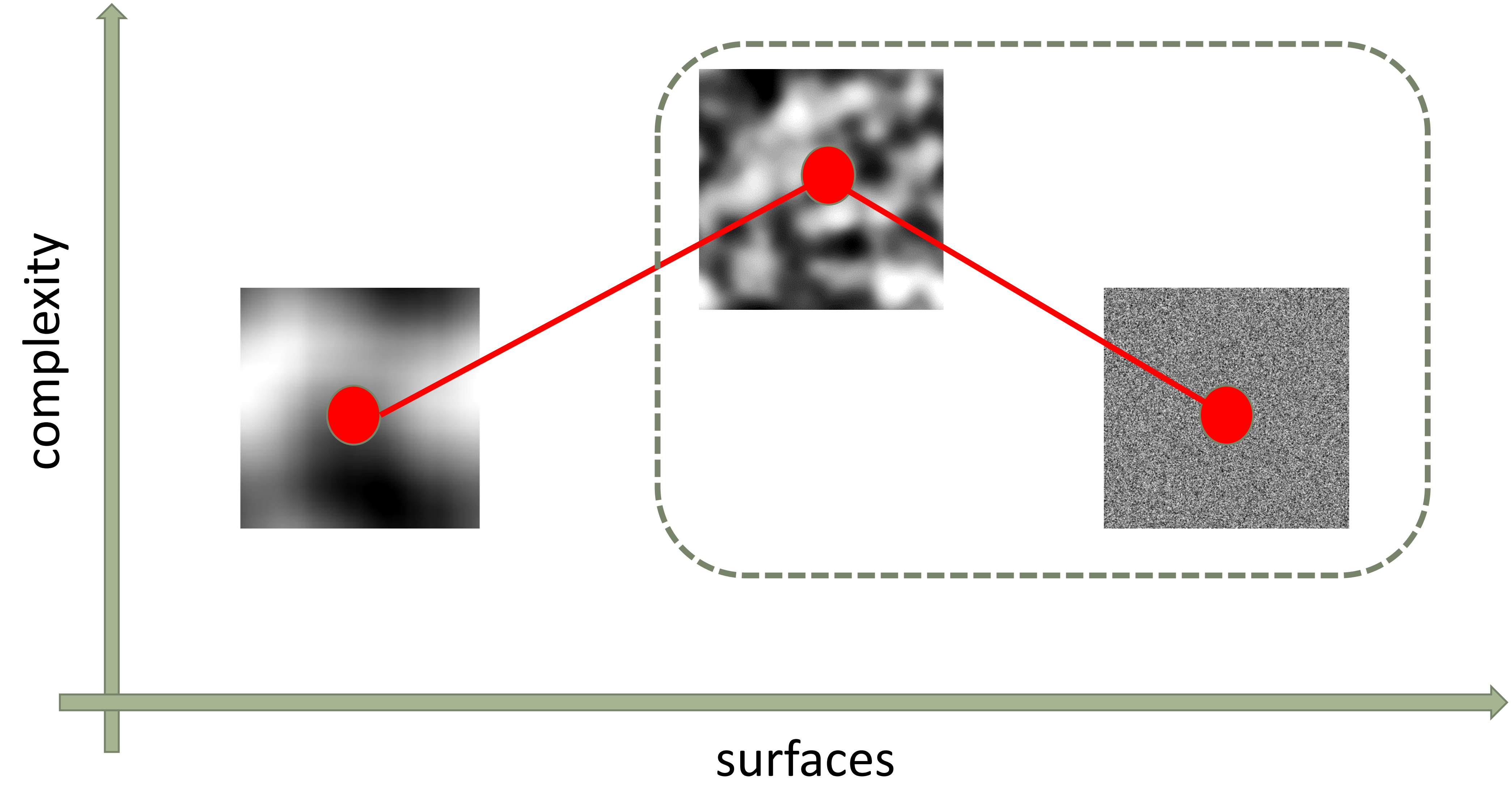
DEMOKRITOS

Outline

- Motivation - context
- The challenge of nanostochasticity
- Mutiscale Shannon-entropy
- Chaos-based approach
- Hierarchal micro-nano surfaces
- Conclusions

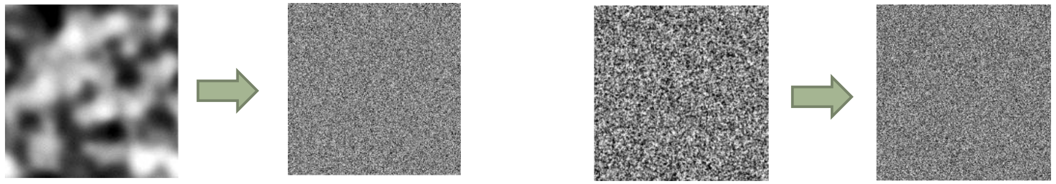
Chaos-based complexity

- Key requirement for complexity measure: to decrease at the limits of noise and order/flatness (smoothness)



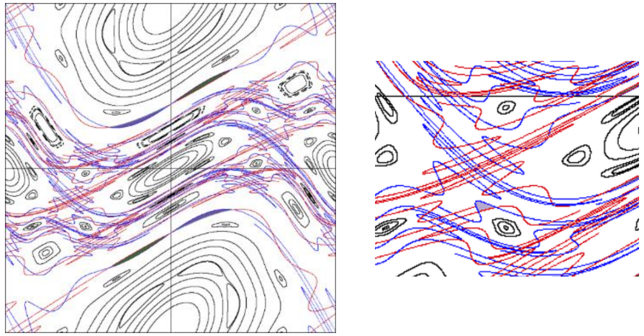
Chaos-based complexity

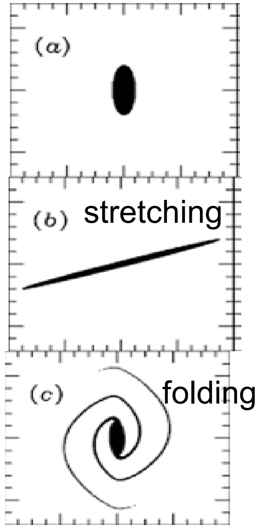
- Simple permutation of the pixel coordinates does not work: transformation to noise in a single step



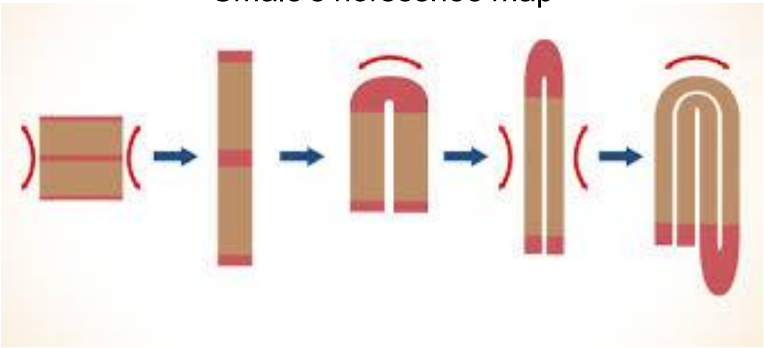
- What we need is a gradual mixing of surface points
- But **mixing** is a property of **chaotic motion in phase space**: *collections of initial points in phase space mix together towards a uniform randomness through chaotic dynamics*
- This is achieved through the **stretching and folding of initial conditions**

Manifolds of unstable periodic orbits





Smale's horseshoe map



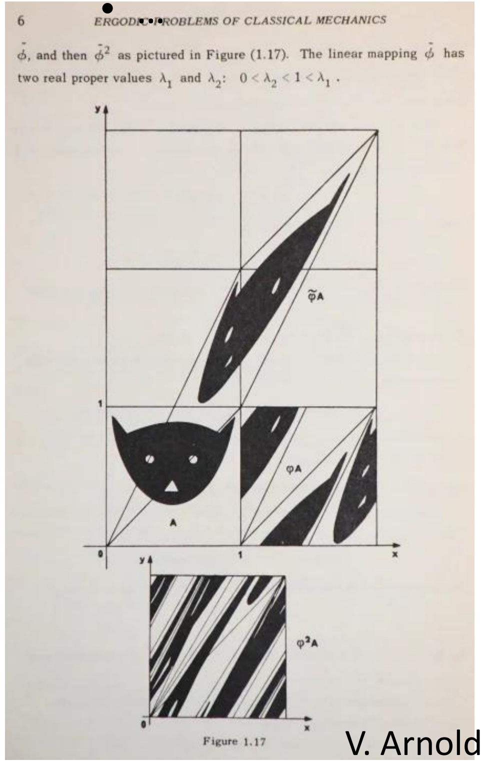
➢ **Chaos** : **Stretching and folding** of trajectories in phase space => **sensitivity to initial conditions** in bound systems => butterfly effect

➢ Stretching and folding for measuring the spatial complexity of a surface or an image???

Chaos-based complexity : Arnold cat map

$$x_{n+1} = x_n + y_n$$
$$y_{n+1} = x_n + 2y_n \qquad \text{mod } 1$$

- Invertible
- Area preserving
- Ergodic
- Mixing
- ...

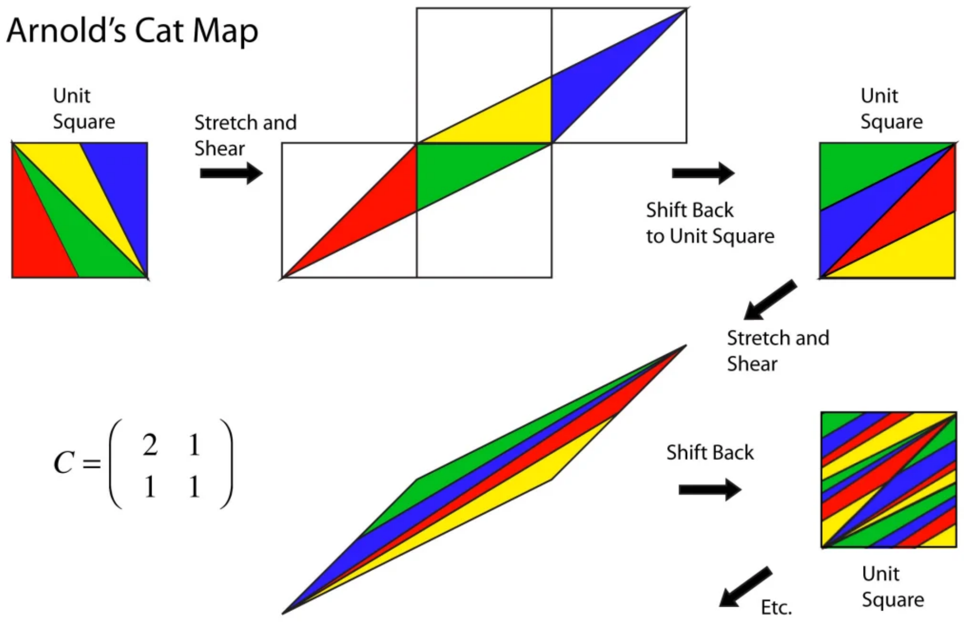


6 ERGODIC PROBLEMS OF CLASSICAL MECHANICS

$\vec{\phi}$, and then $\vec{\phi}^2$ as pictured in Figure (1.17). The linear mapping $\vec{\phi}$ has two real proper values λ_1 and λ_2: $0 < \lambda_2 < 1 < \lambda_1$.

Figure 1.17

V. Arnold "Classical Mechanics" 1968



$$C = \begin{pmatrix} 2 & 1 \\ 1 & 1 \end{pmatrix}$$

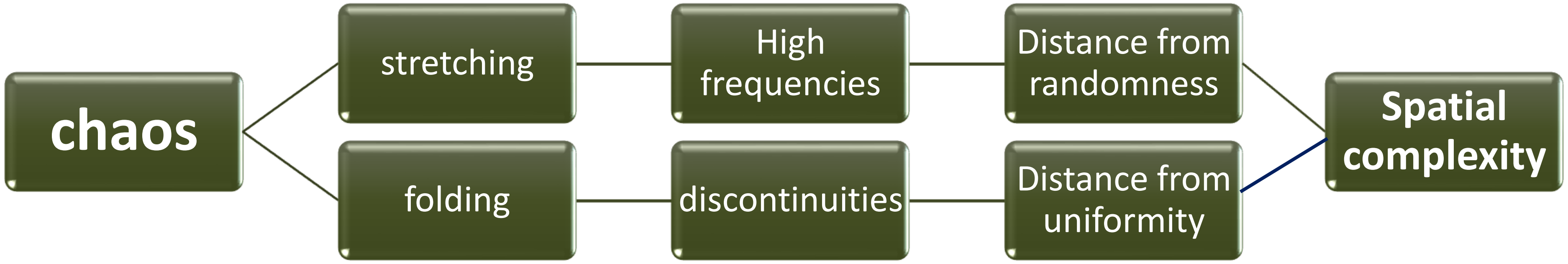
Chaotic mixing = randomization process

- Stretching=> Enhancement of high frequencies
- Folding=> Increase of discontinuities

Chaos-based complexity

- Resistance to destructuring / distance from noise= variance of the iterations of Arnold cat map on the surface under investigation
- GREAT NEWS: The Arnold map can be also used for the quantification of the distance of surface from uniformity through the discontinuities caused by folding process.

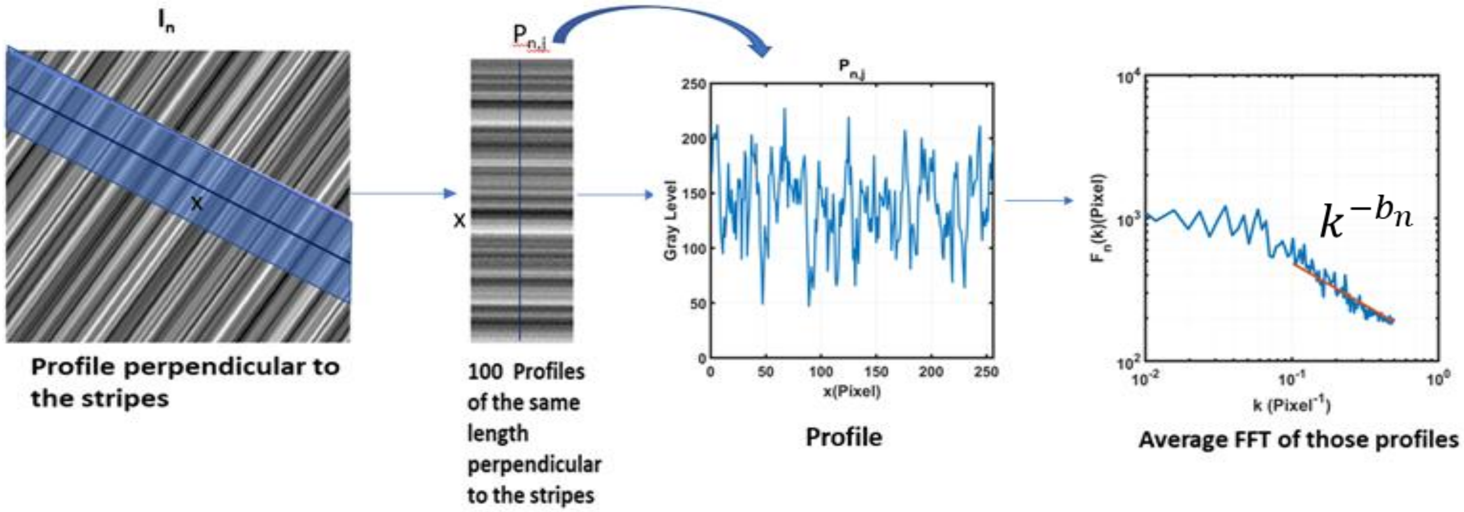
The key idea

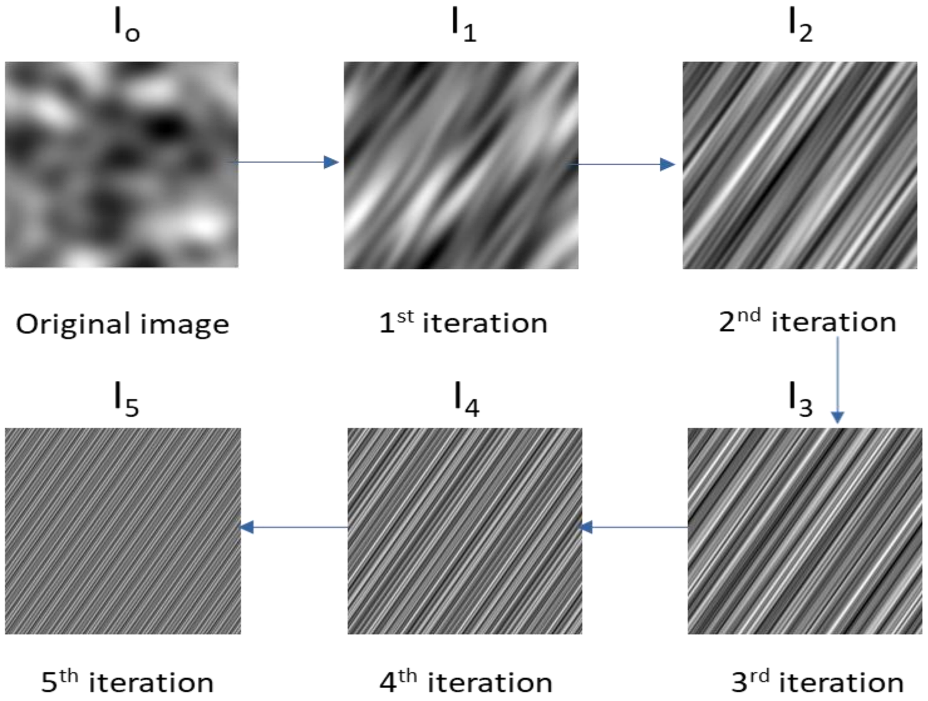


How?

Quantification through Fourier analysis

Chaos-based complexity : Methodology





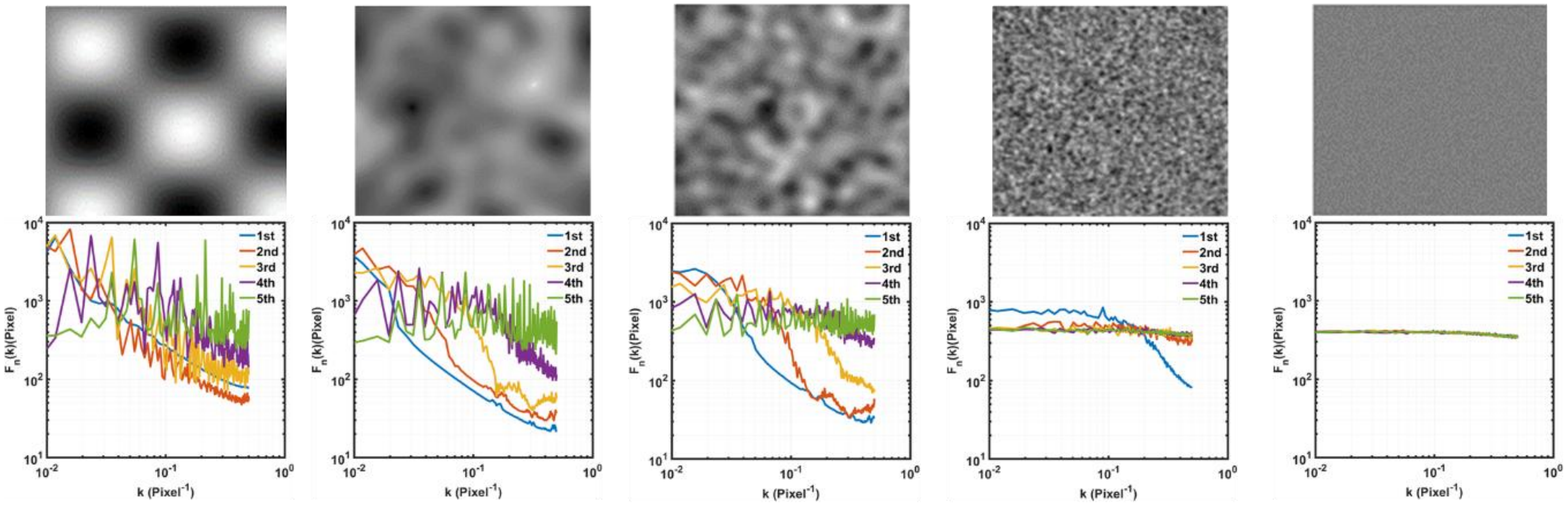
Chaos-based complexity measure

$$SD_b(I_o) = \sqrt{\frac{1}{5}\sum_{n=1}^{5}(b_n - \langle b_j \rangle_j)^2}$$

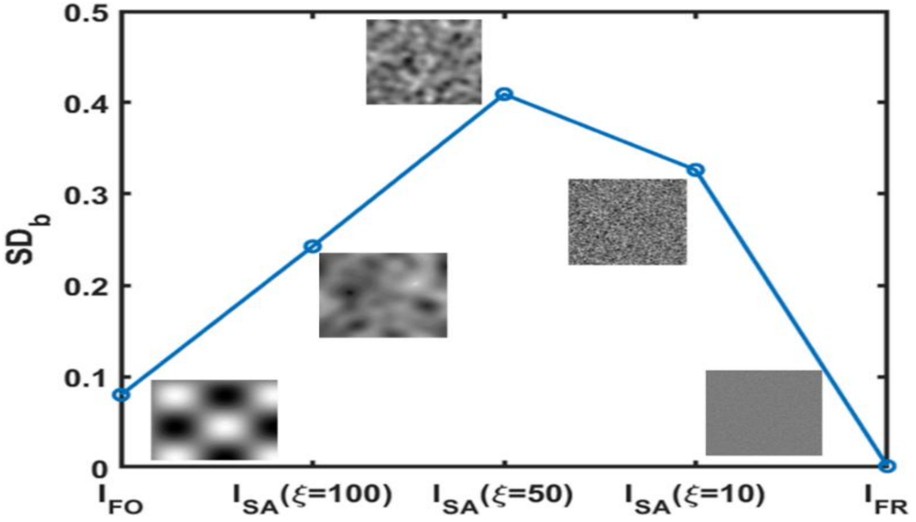
A. Kondi, V.C. et al. Phys. Rev. E 107 (1), 014206 (2023)

Chaos-based complexity : Simulated surfaces

2D Sinusoidal | ξ = 100 (Pixel) | ξ = 50 (Pixel) | ξ = 5 (Pixel) | Noise



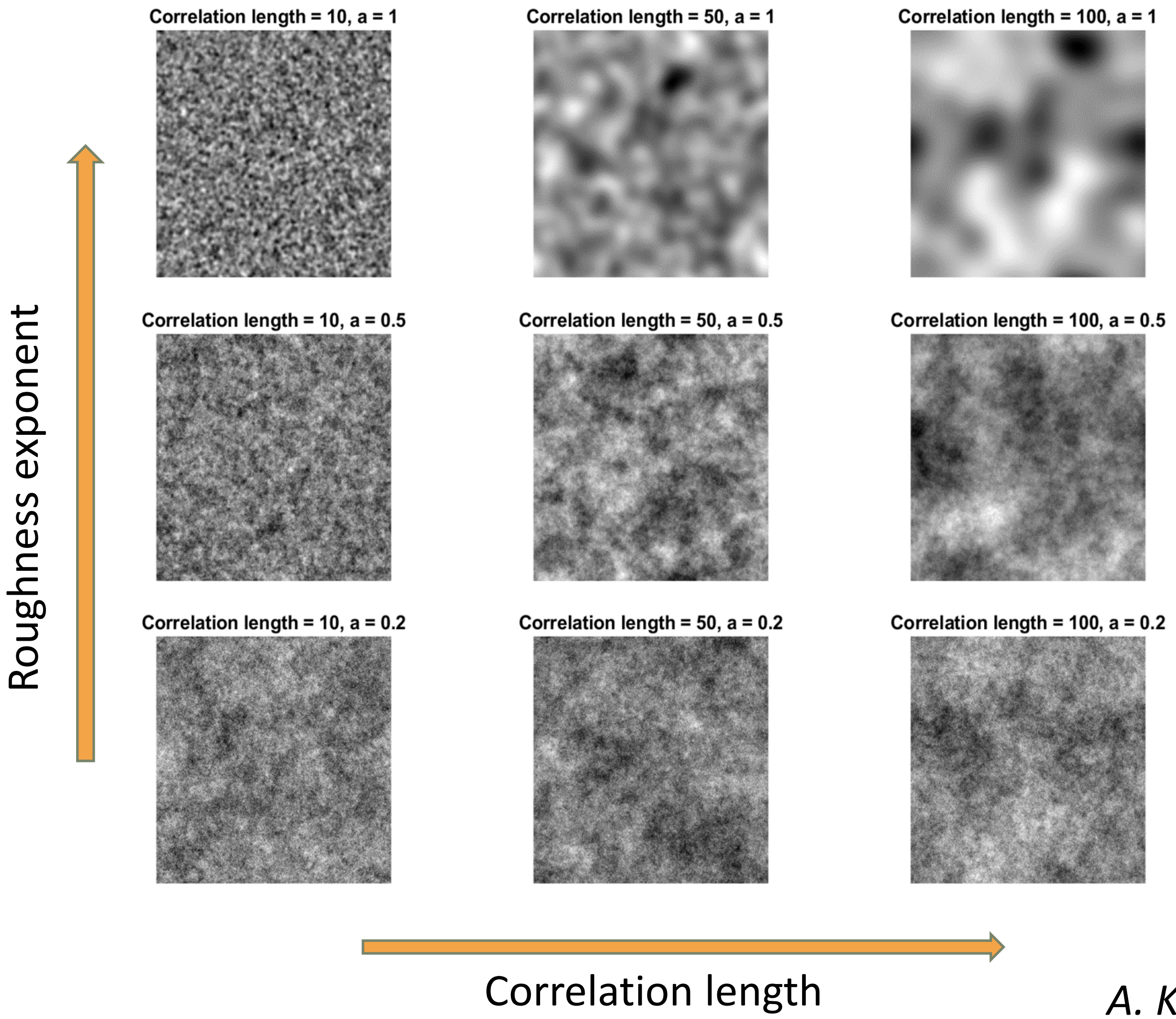
Folding => discontinuities



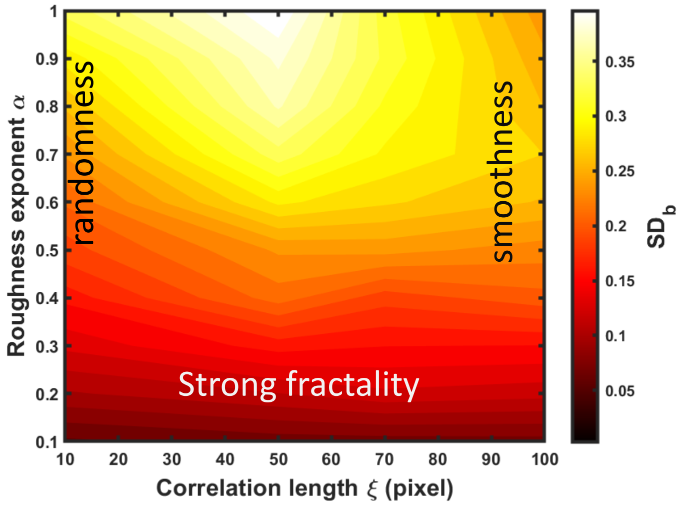
Stretching => randomization

Chaos-based complexity : Simulated surfaces

- Computer generated rough self-affine surfaces with controlled correlation length and roughness exponent a(=2-Fractal Dimension)



SD_b vs. correlation length and roughness exponent



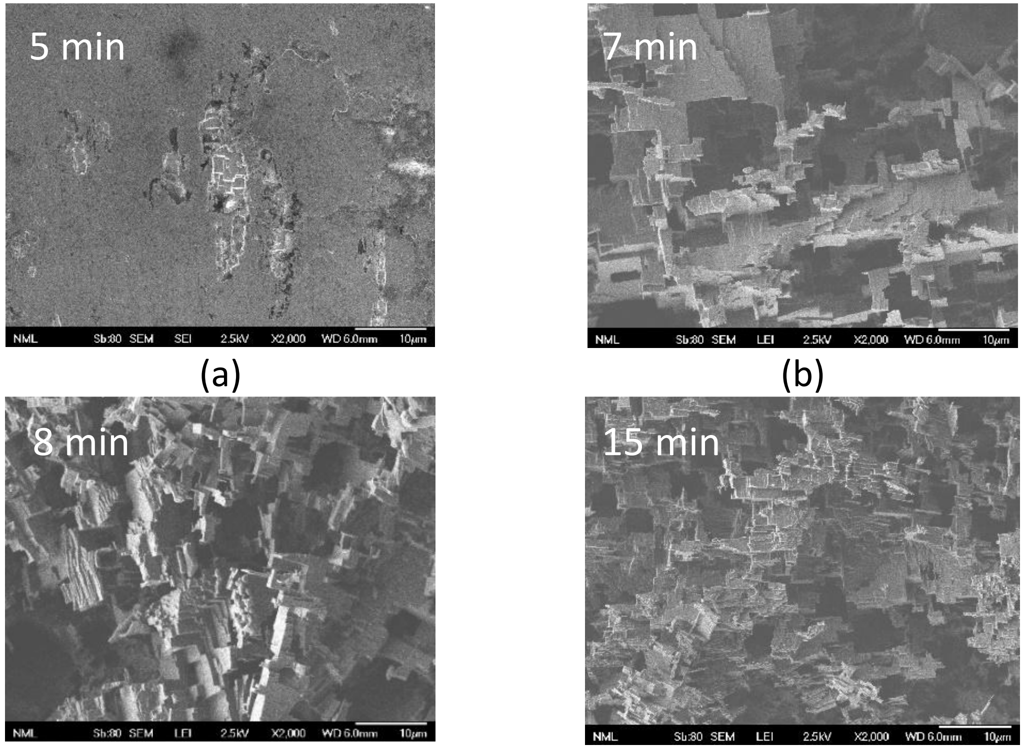
- SD_b is maximized at ξ=50 pix and α tending to 1

A. Kondi, V.C. et al. Phys. Rev. E 107 (1), 014206 (2023)

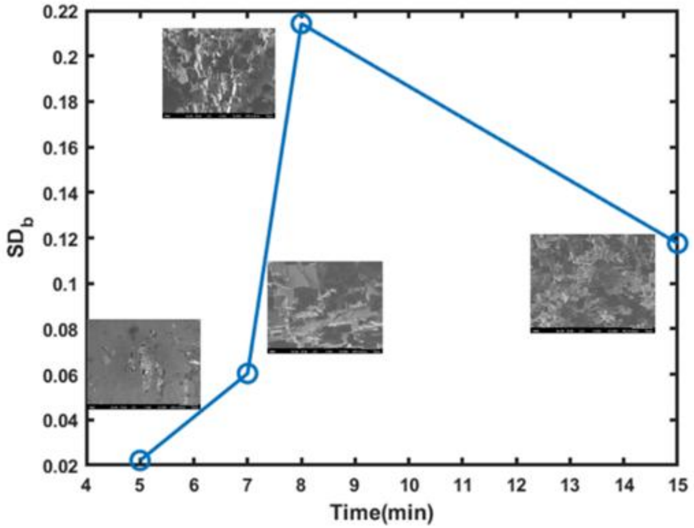
DEMOKRITOS

Chaos-based complexity : Experimental surfaces

Aluminum etched in hydrochloric acid HCl for different times – Top-down SEM images



(a) (b) (c) (d)



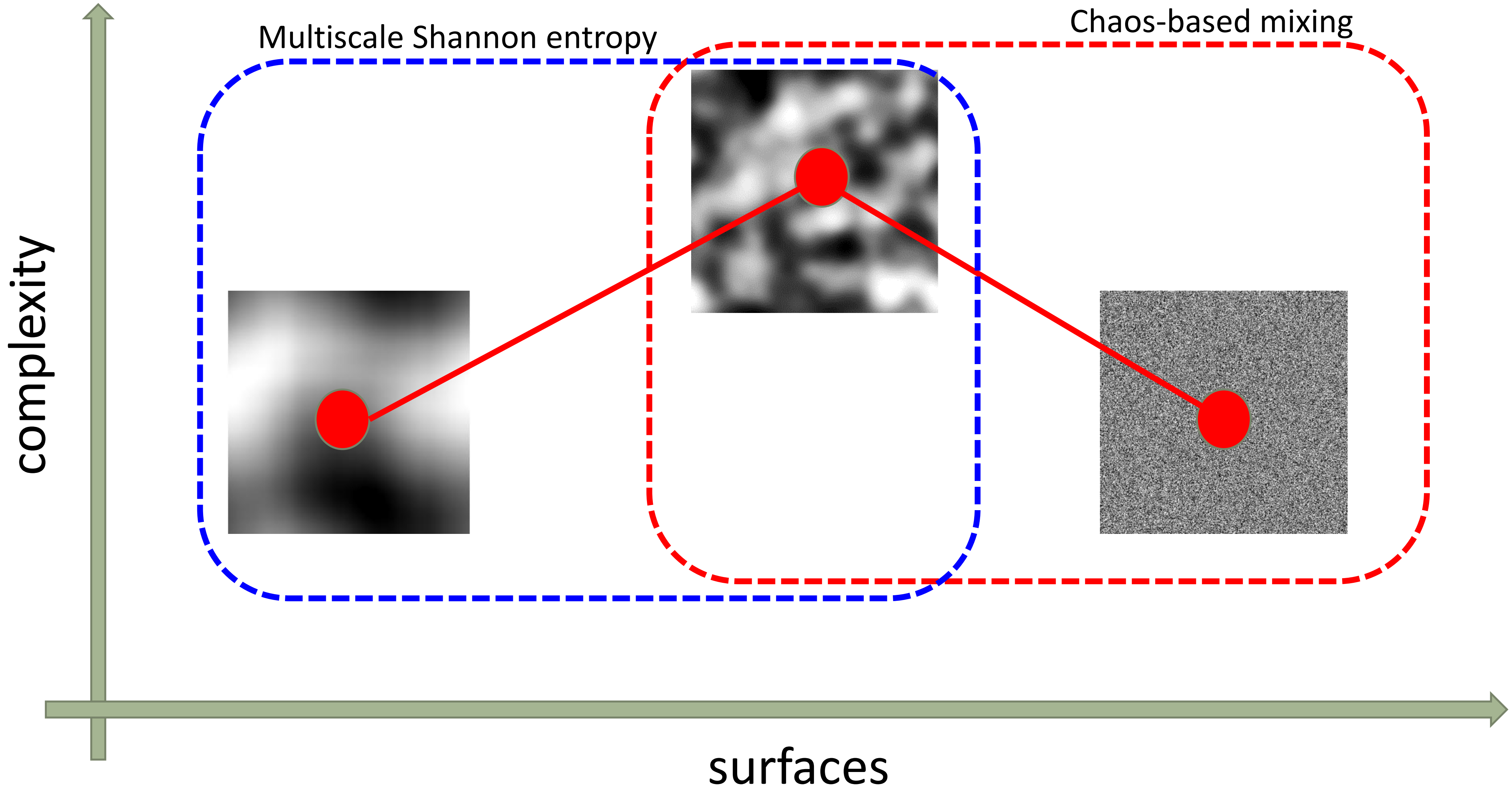
- SD_b is maximized at t=8min

Experimental result : Maximization of water condensation

A. Kondi, V.C. et al. Phys. Rev. E 107 (1), 014206 (2023)

Synopsis of both methods

- Key requirement for complexity measure: to decrease at the limits of noise and order/flatness (smoothness)

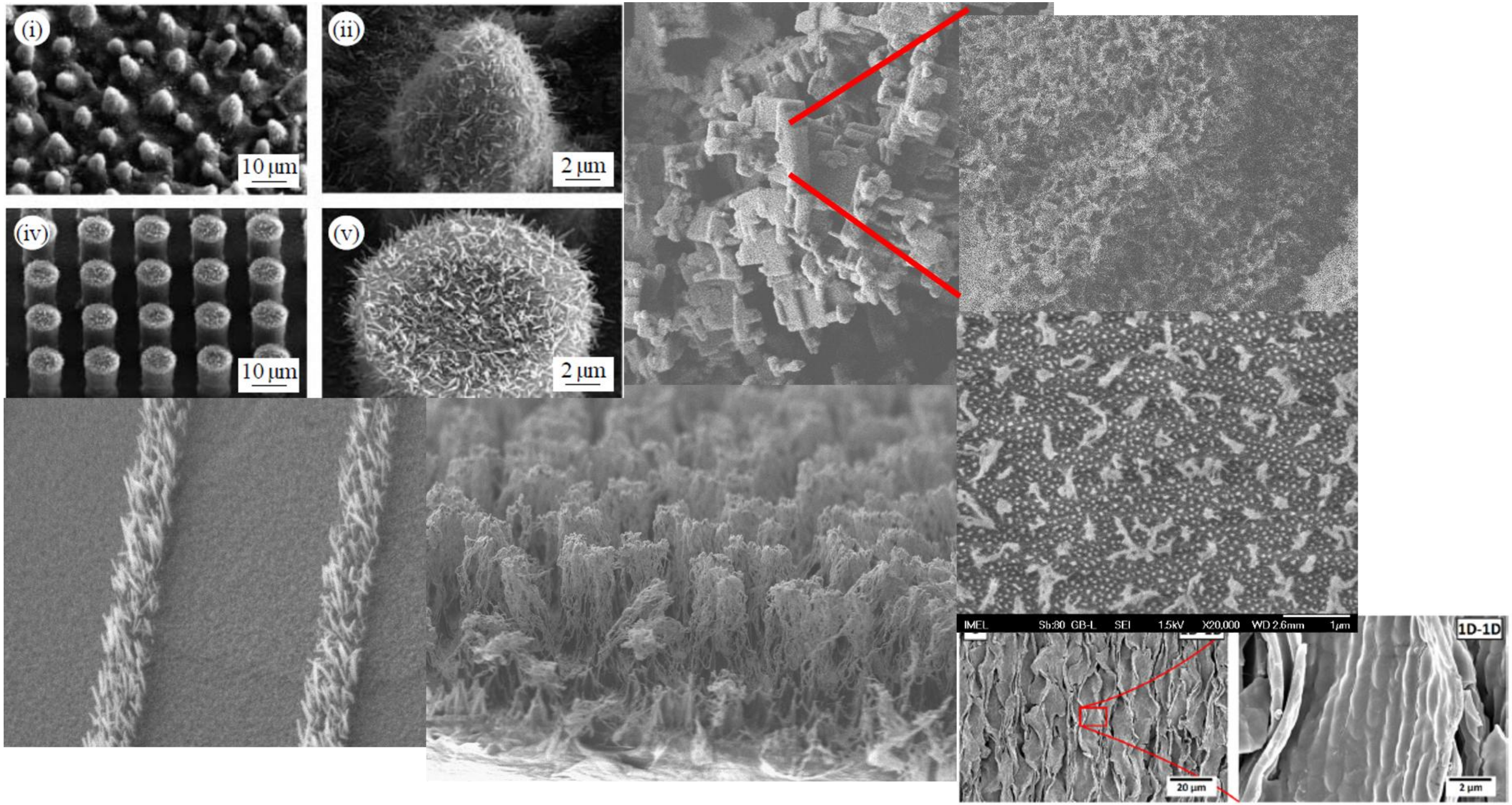


Outline

- Motivation - context
- The challenge of nanostochasticity
- Mutiscale Shannon-entropy
- Chaos-based approach
- Hierarchal micro-nano surfaces
- Conclusions

Hierarchical surfaces in nature and laboratory

- **Hierarchy supports the multifunctionality of surfaces enabling multiple-scale properties**



Hierarchical surfaces

- Hierarchical surfaces/structures is a rather vague concept
- Can we make it more well-defined, quantitative, useful, effective?

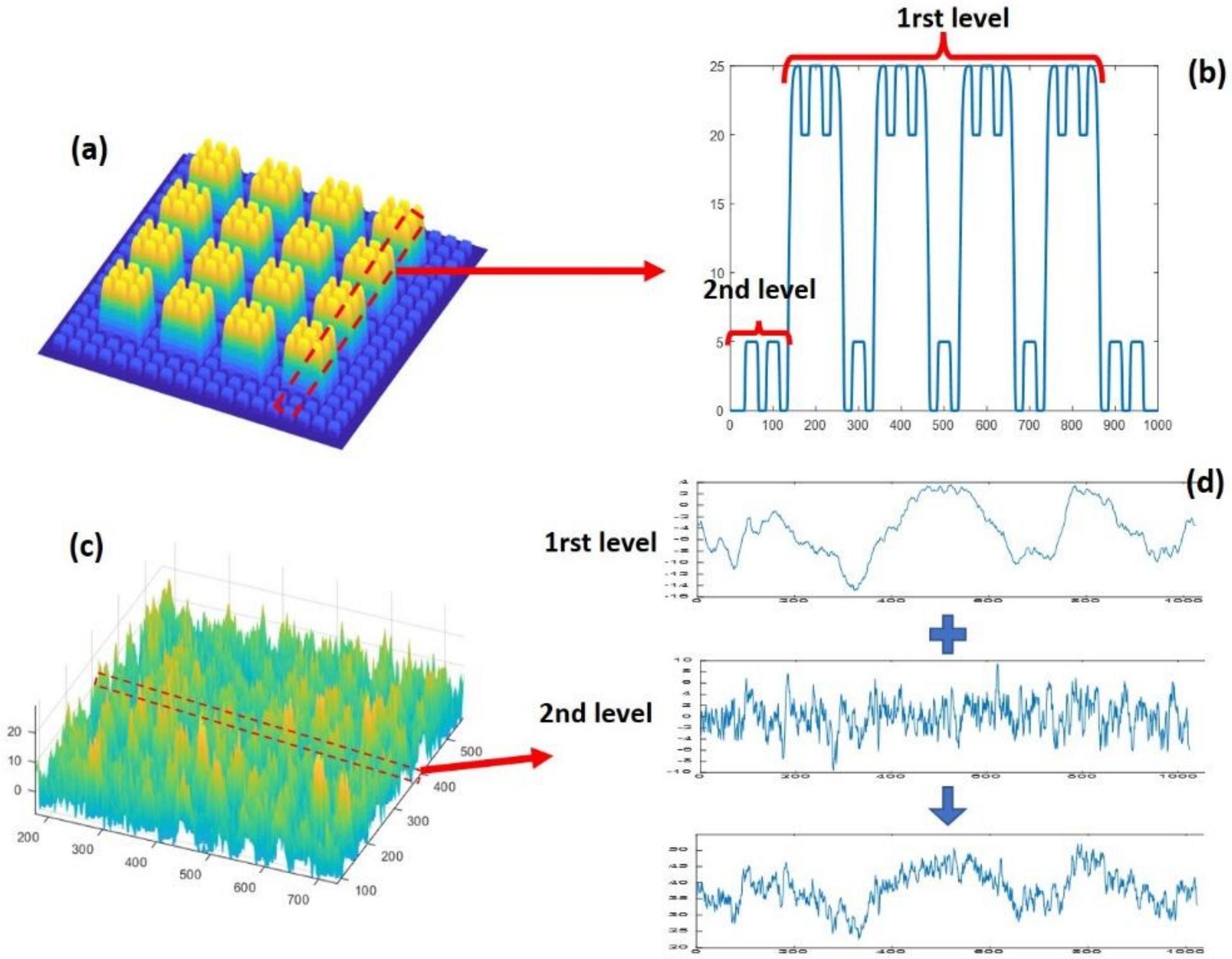
➢ **Towards building a theoretical framework of hierarchical surfaces to enable better characterization and understanding?**

➢ **Key question: Characterization of hierarchy level interactions**

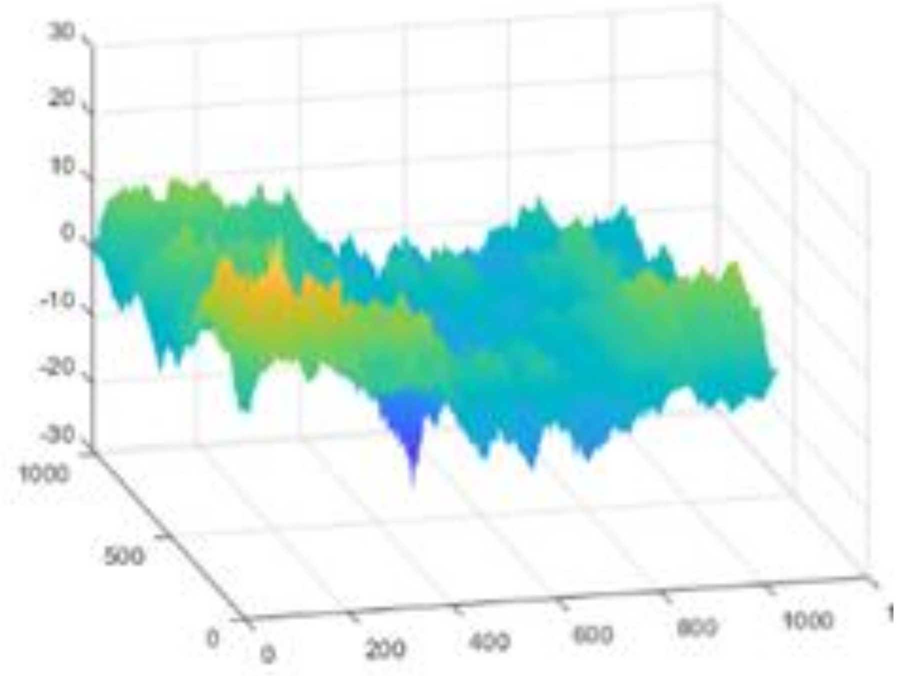
- **Definitions**
- **Classifications**
- **Characterization/Modeling**
- **Applications**

Hierarchical surfaces: Definitions

- <u>A Hierarchical surface</u> is a combination of surfaces (levels) characterized by <u>specific and discrete</u> spatial scales



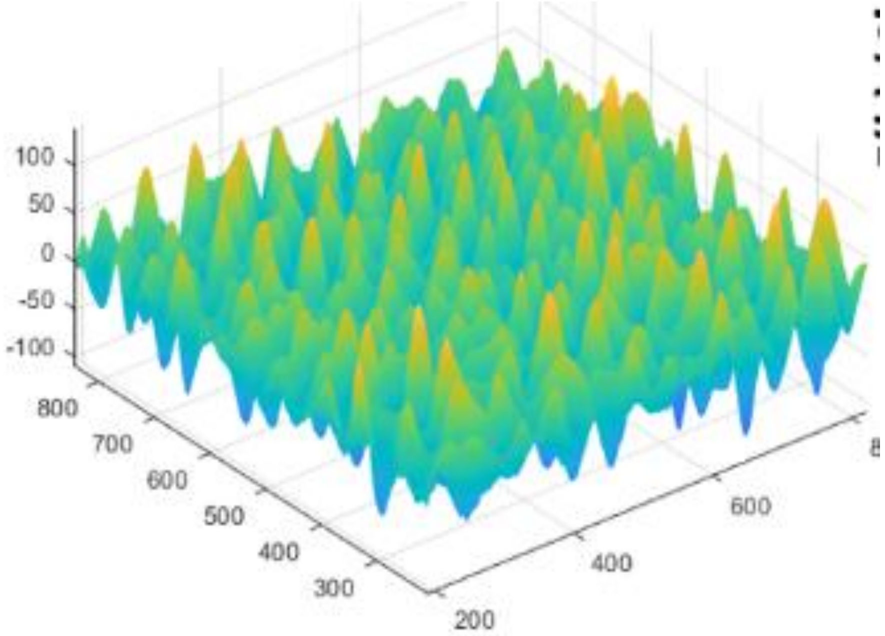
- Fractal vs. hierarchical surfaces (fractal surfaces: similar motif is repeated reduced at all scales continuously => no discrete levels)



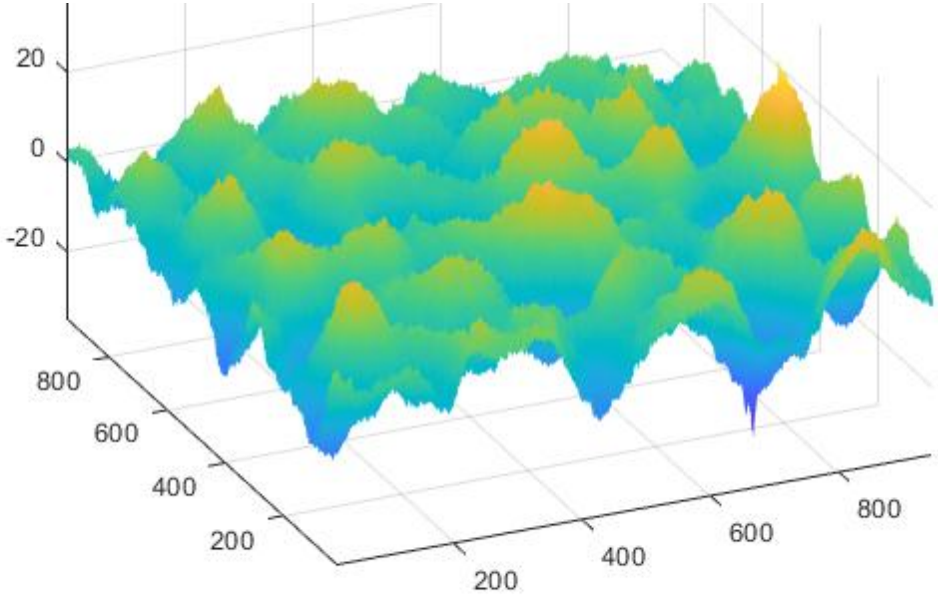
Hierarchical surfaces: Definitions

- **Hierarchy levels :**

Mound surfaces



Stochastic surfaces



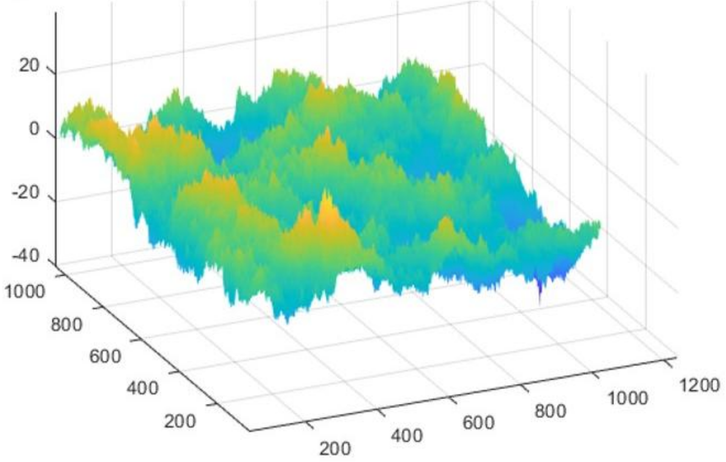
Characteristic lengths : Mound distance and width

Characteristic lengths : Correlation length

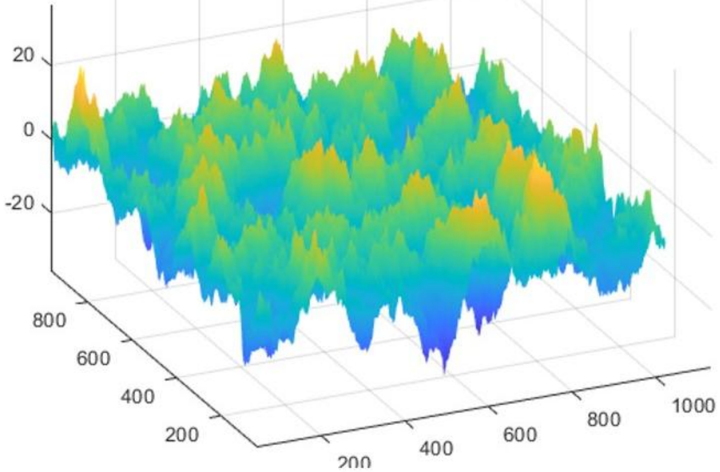
Hierarchical surfaces: classification

- Based on the type of involved hierarchy levels/surfaces

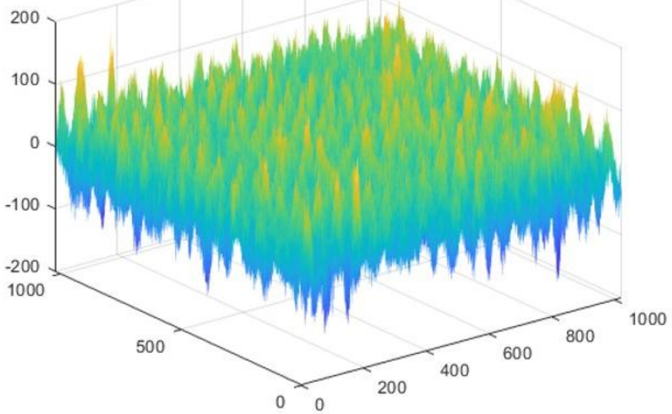
Stochastic - Stochastic



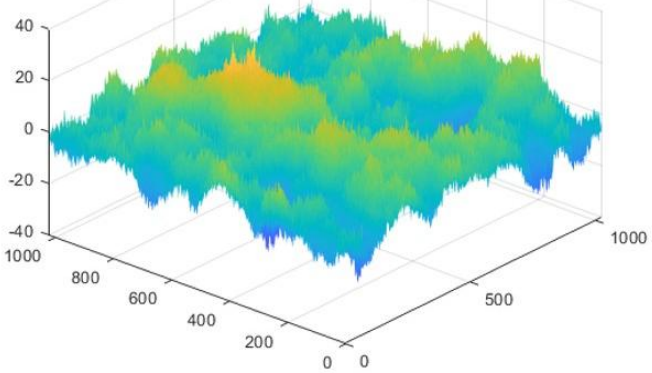
Mound - Stochastic



Mound - Mound



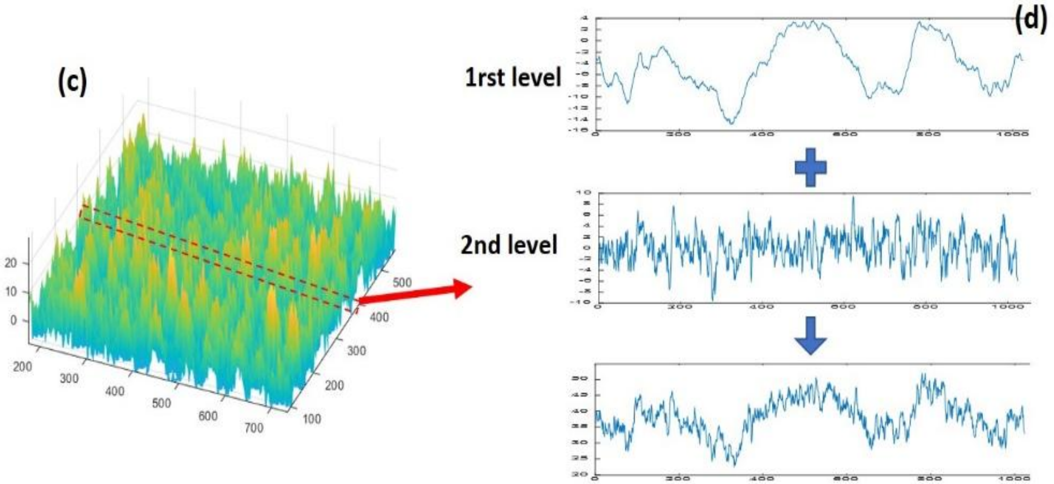
Stochastic - Mound

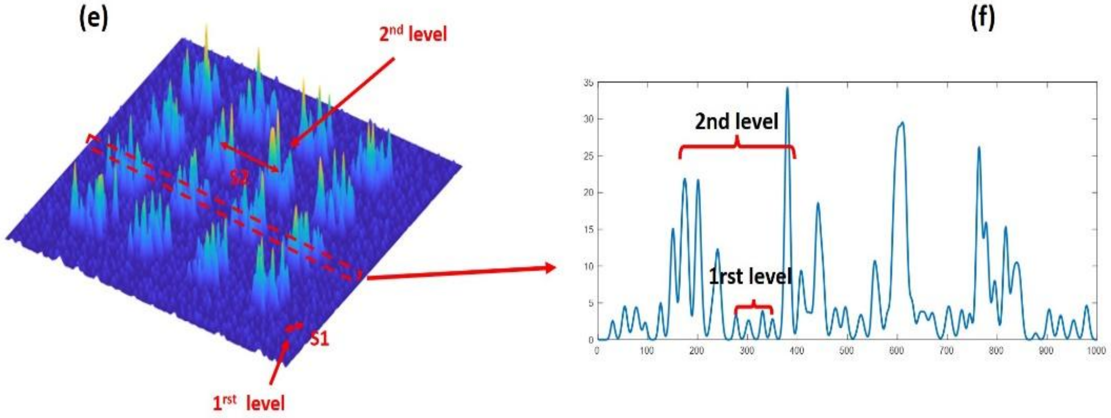


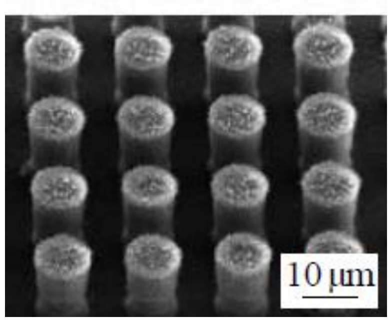
Hierarchical surfaces: classification

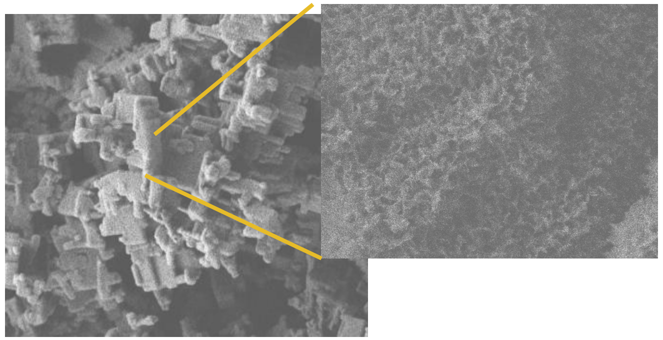
➢ Based on the type of combination of hierarchy levels/surfaces

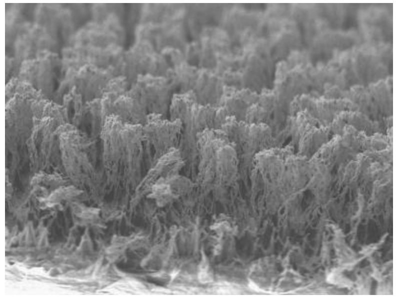
additive | **versus** | **Spatial/multiplicative**

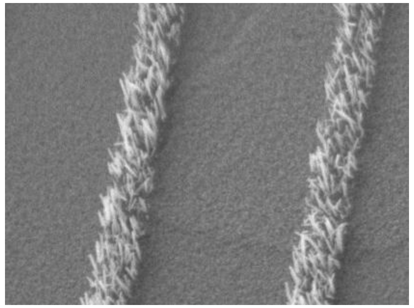








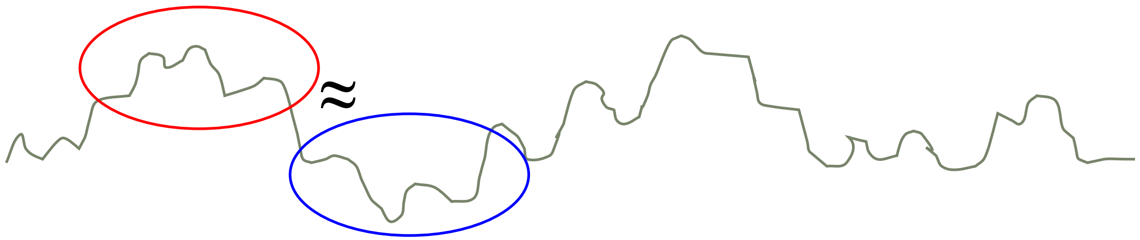


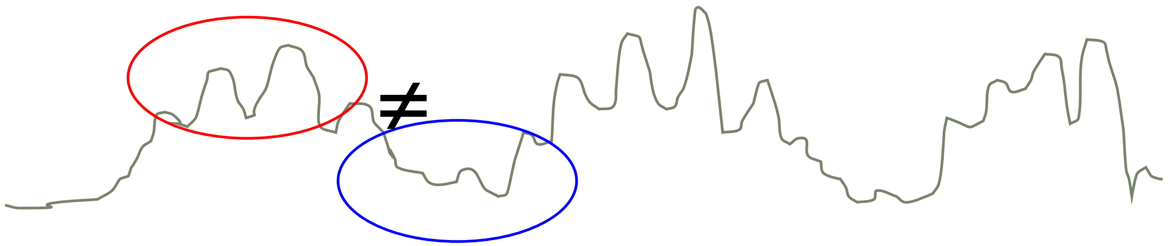


Hierarchical surfaces: classifications

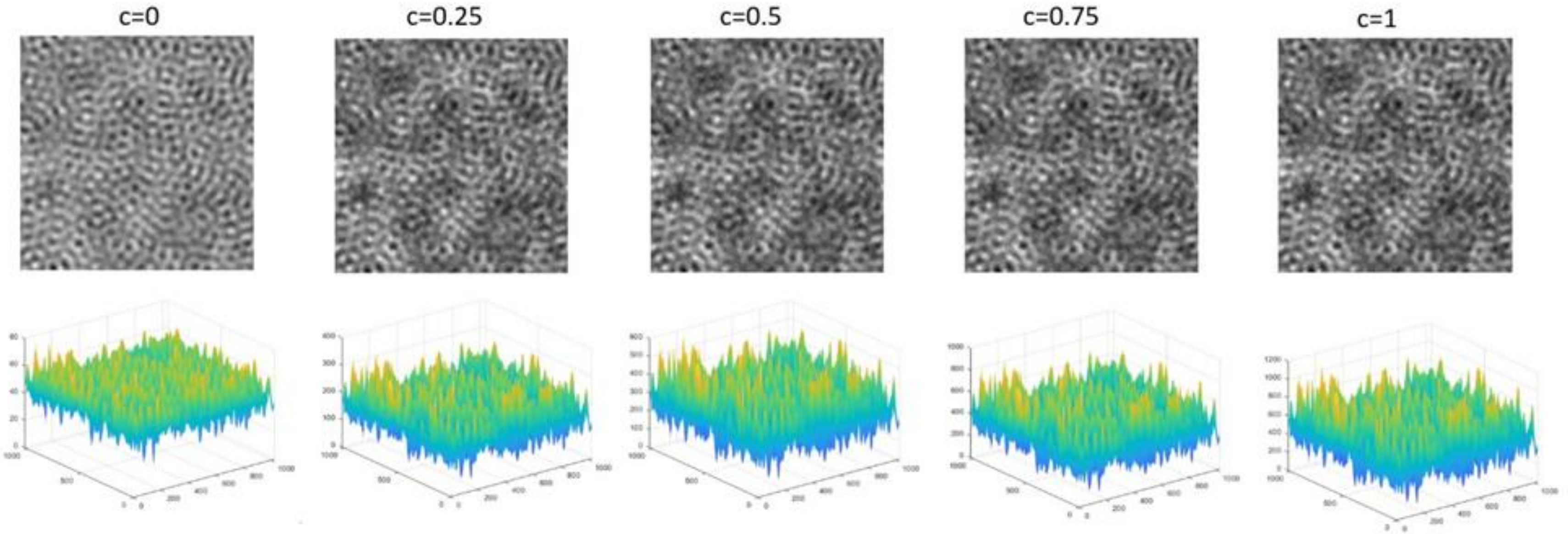
- Based on the form (linear or nonlinear) of combined levels $z_h(x,y) = z_1(x,y) + b * \ z_2(x,y)$

Linear (b=1) **versus** **nonlinear hierarchy ($b=b(z_1)$)**





$b(z_1)=1\text{-}c+c{*}z_1.$



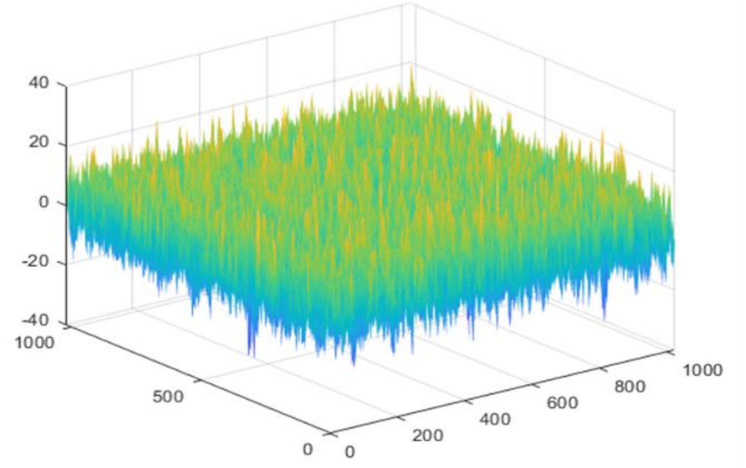
$z_h(x,y) = z_1(x,y) + z_2(x,y)$

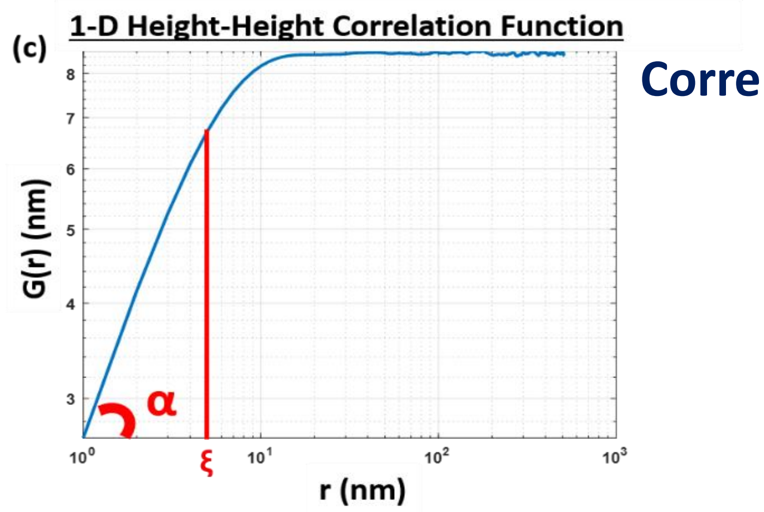
$z_h(x,y) = z_1(x,y) + z_1 \ z_2(x,y)$

G. Papavieros, V.C. et al. Nanotechnology (2023)

Hierarchical surfaces: characterization

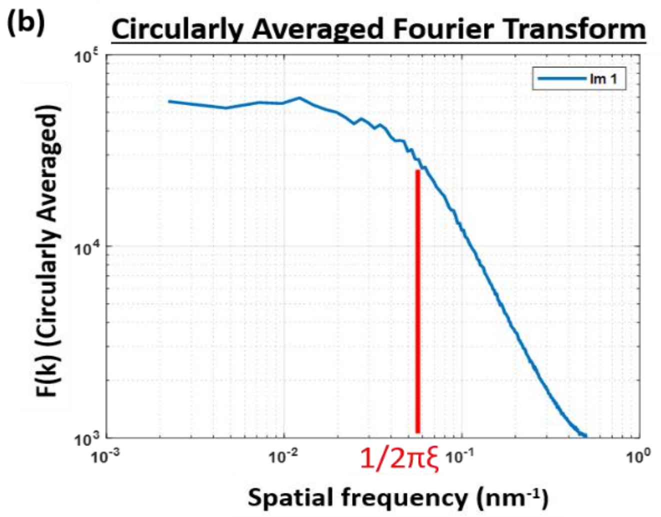
- The basic math tools for “sensing” hierarchy

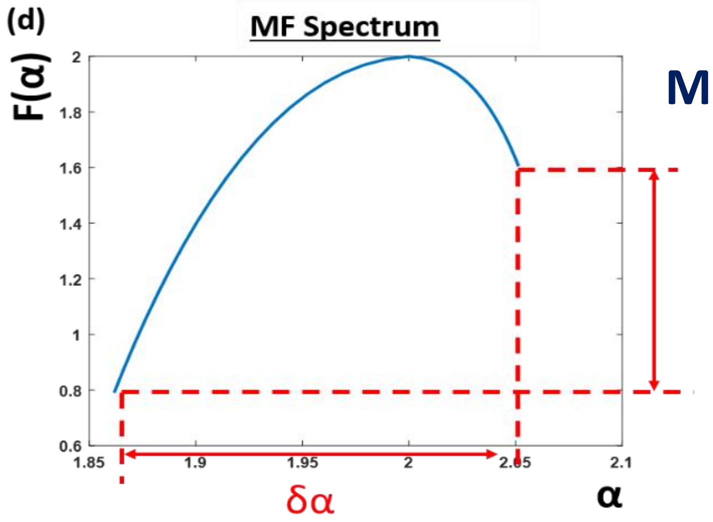




Correlation Function

Fourier analysis

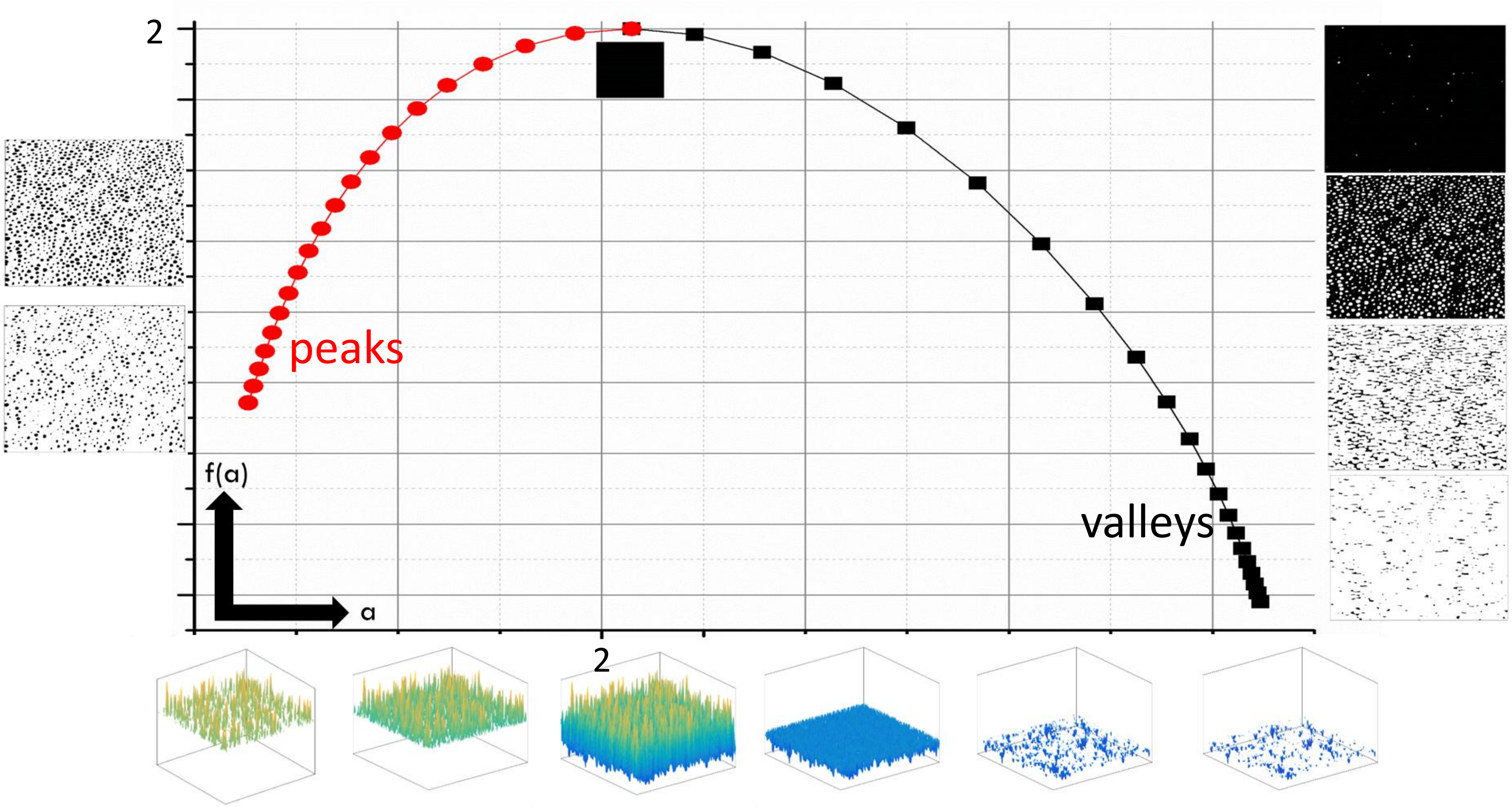




Multifractal spectrum

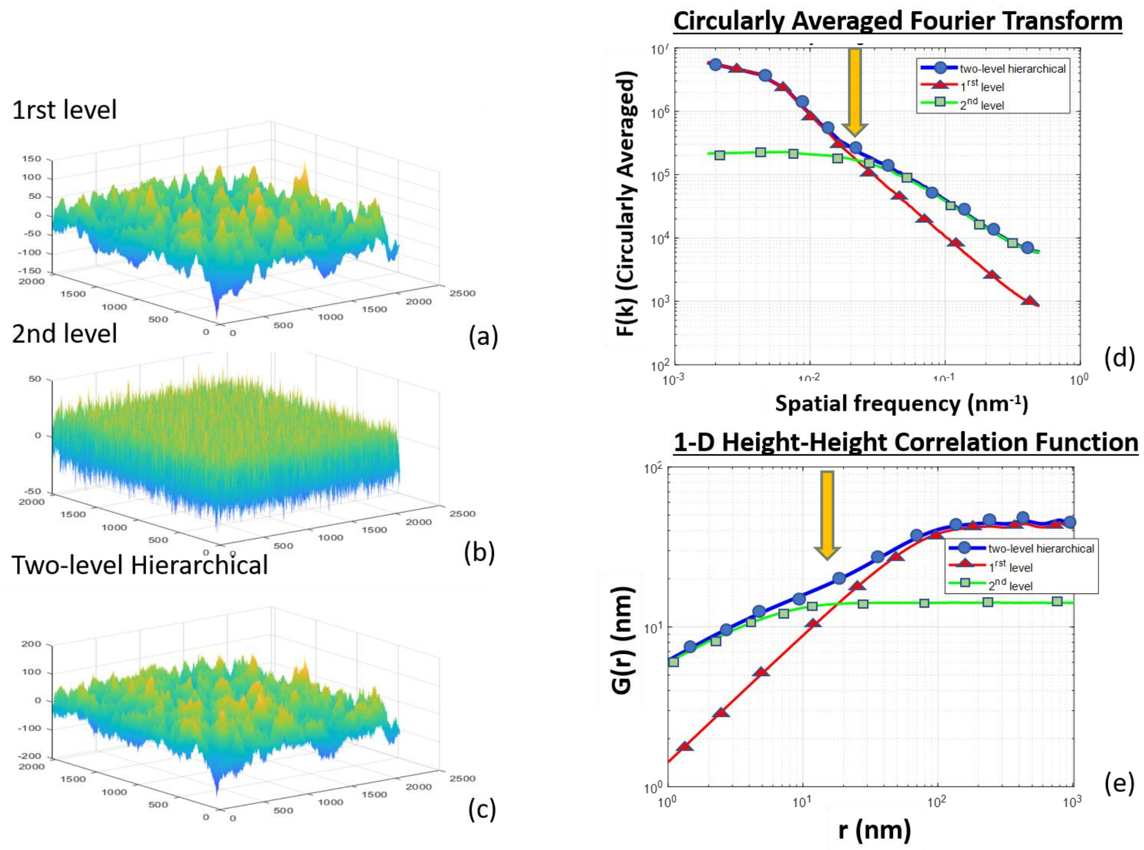
Hierarchical surfaces: characterization

- The physical meaning of **multifractal spectrum** of surfaces: quantify scaling behavior vs surface heights

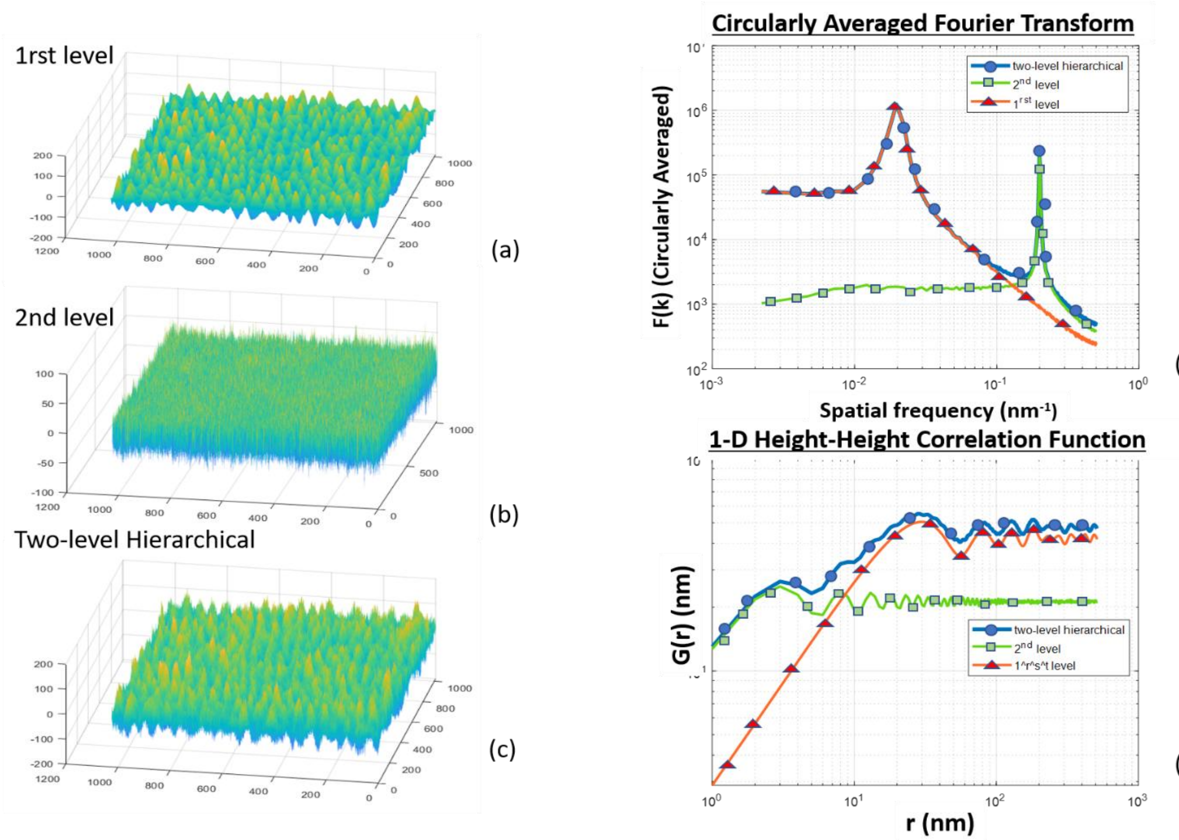


Hierarchical surfaces: characterization

Stochastic – Stochastic Hierarchy



Mound – Mound Hierarchy



- ➢ Change of slope : knee point

- ➢ Fourier : two peaks
- ➢ Correlation : two-period oscillations

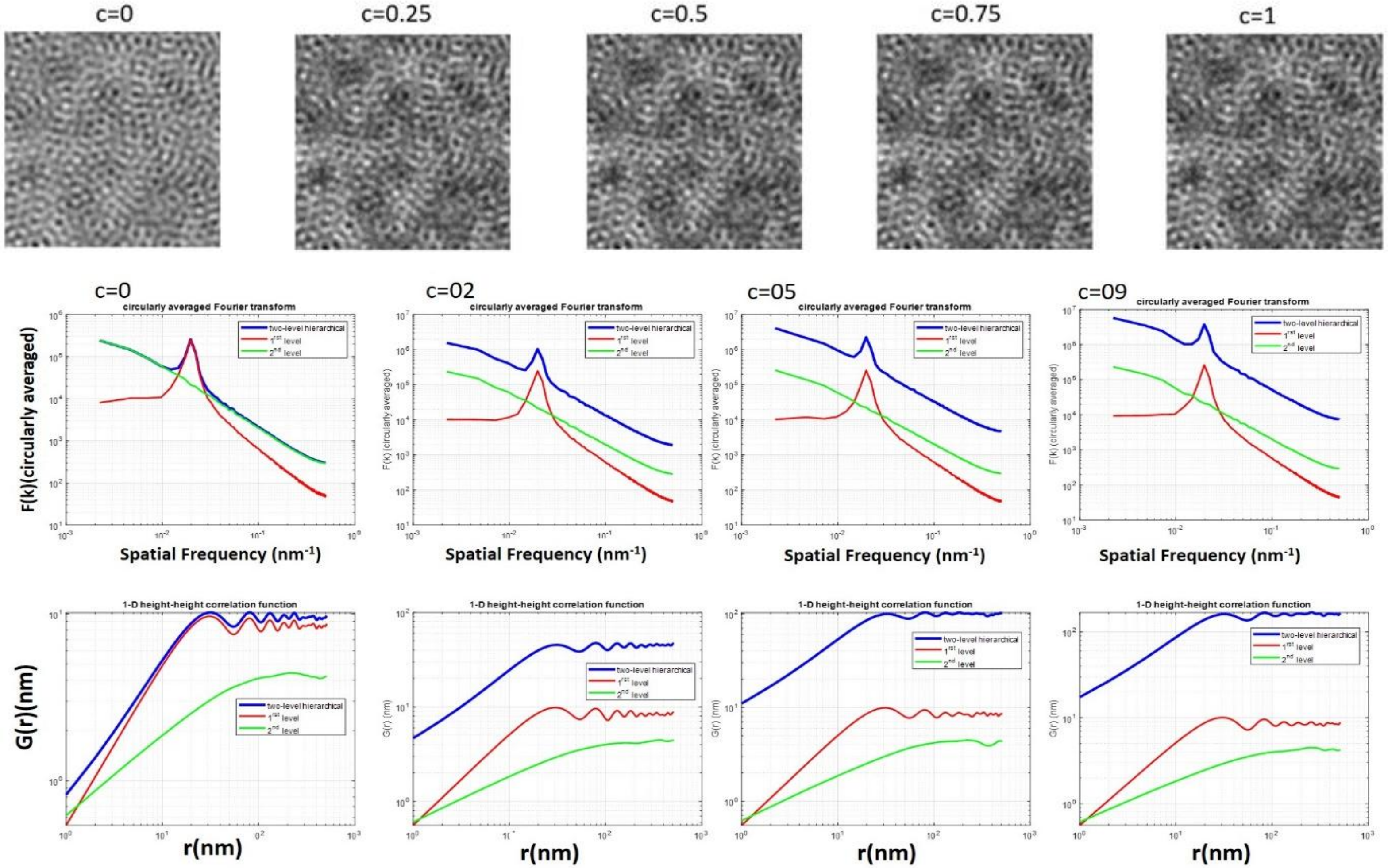
G. Papavieros, V.C. et al. Nanotechnology (2023)

Hierarchical surfaces: characterization of nonlinear hierarchy

Surfaces

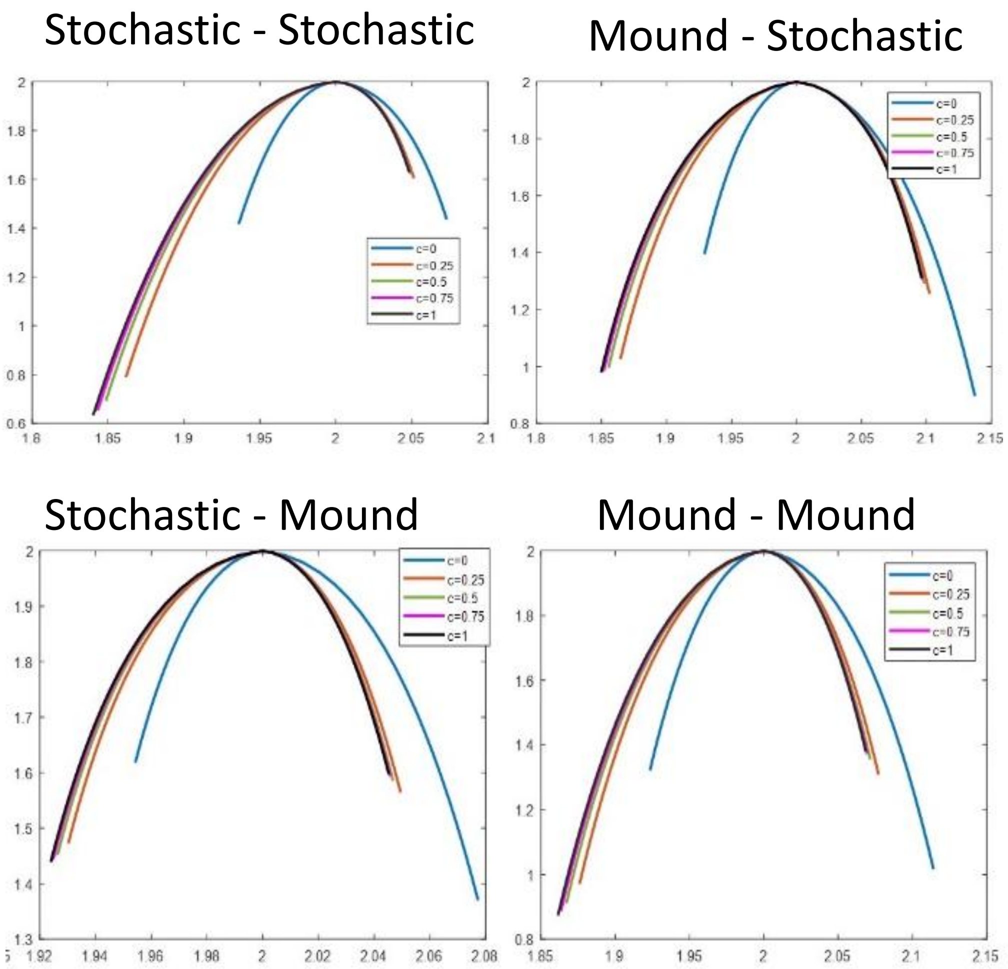
Fourier spectra

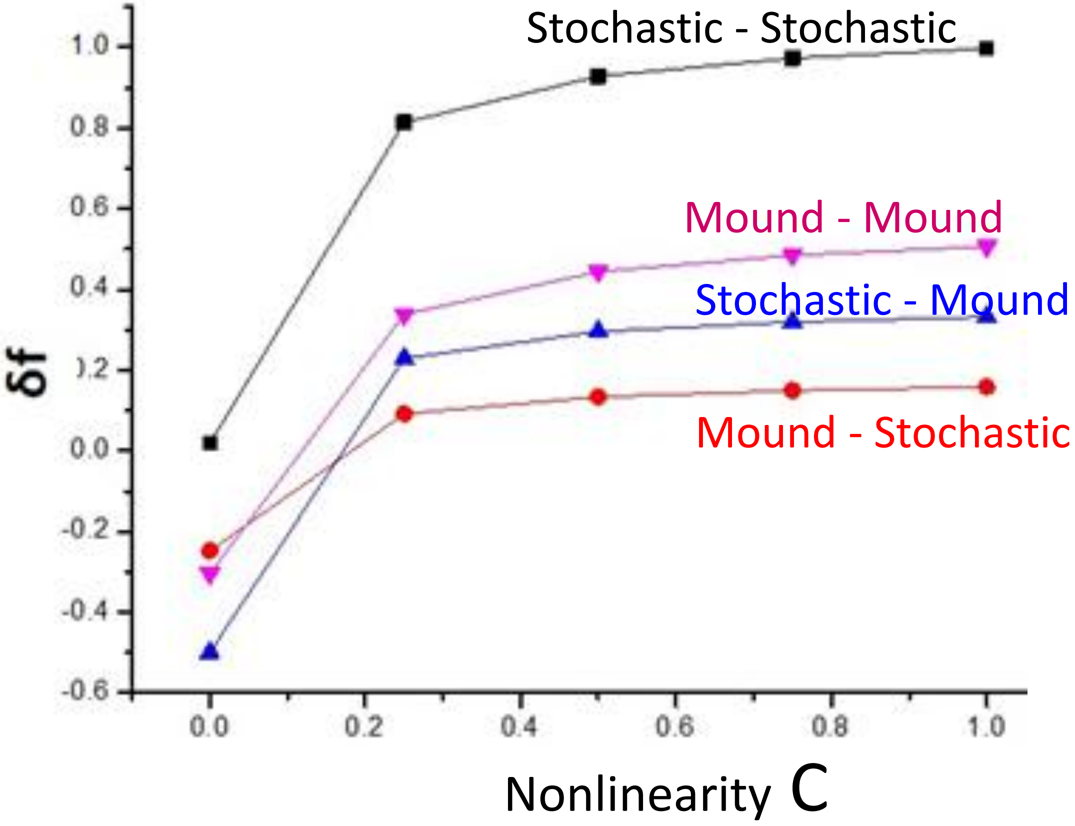
Correlation function



➢ **Nonlinearity** in hierarchical surfaces **cannot** be detected by Fourier and Correlation diagrams

Hierarchical surfaces: characterization of nonlinear hierarchy





- ➢ **Multifractality (δf) is positively sensitive to nonlinear interaction between levels in hierarchical surfaces**

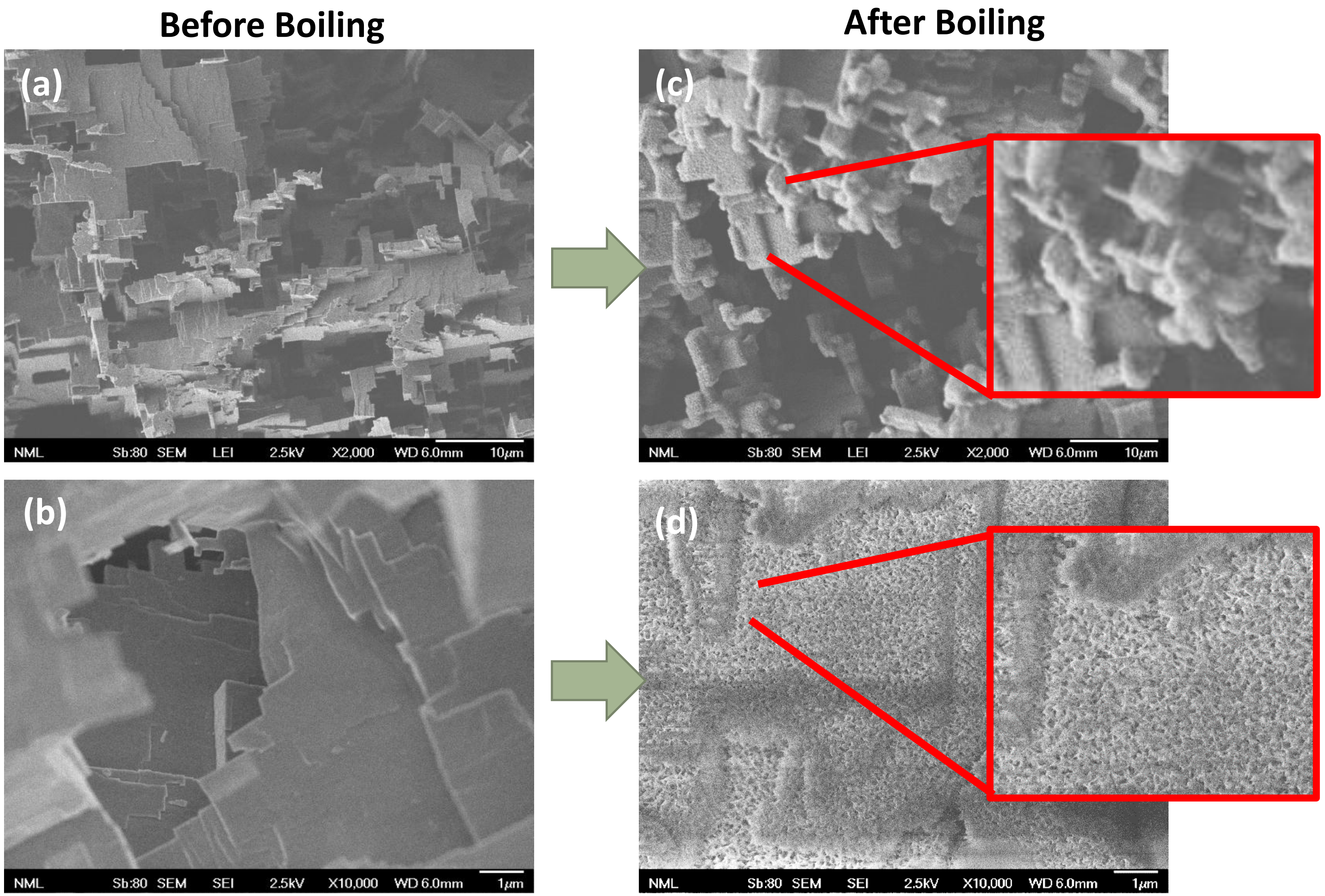
Hierarchical surfaces: characterization
Synopsis

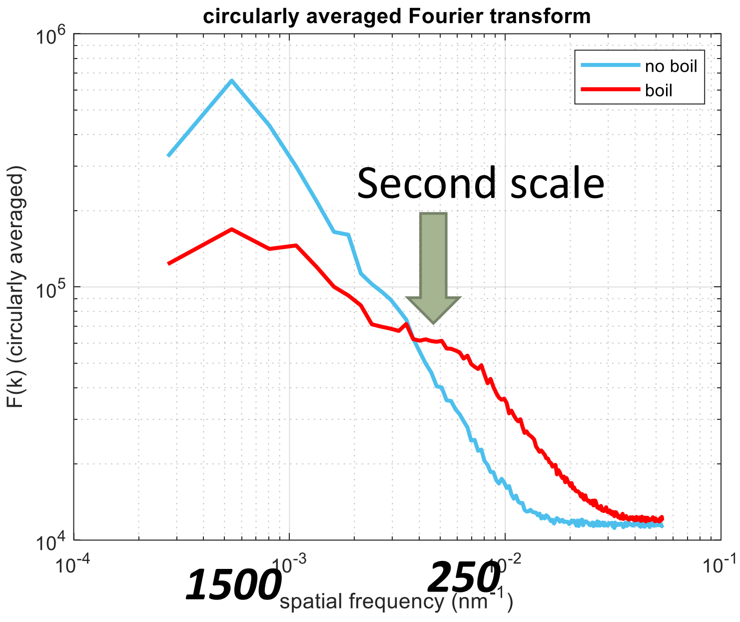
Math sensors of hierarchy features

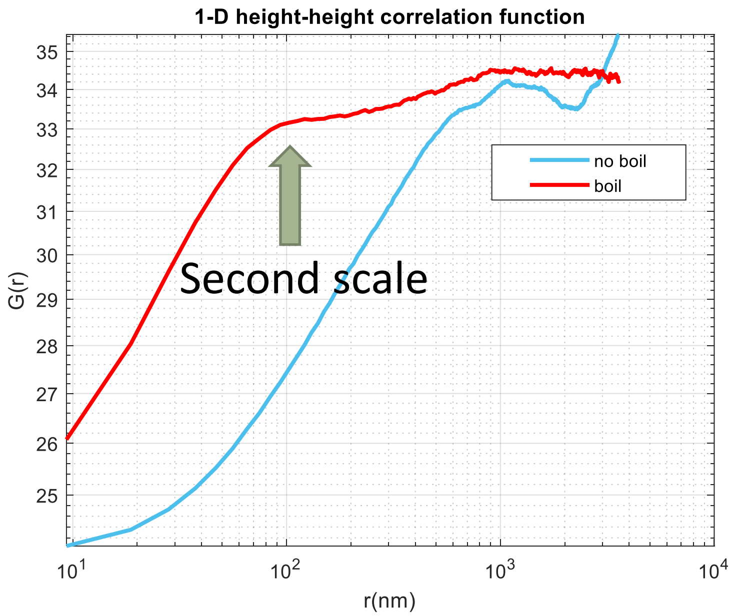
	FT	HHCF	MFA
Detection of Hierarchy	x	x	
Determination of levels	x	x	
Quantification	x	x	
Detection and quantification of nonlinear hierarchy			x

Additive Hierarchy: experimental results

- *Wet etched Al surfaces with HCl before and after boiling in water*
  => detecting the emergence of the second scale after boiling

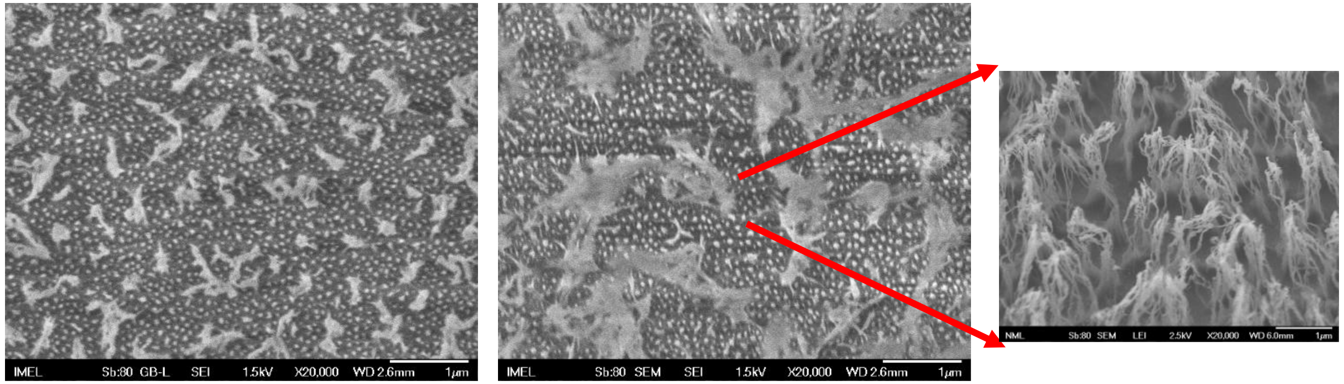




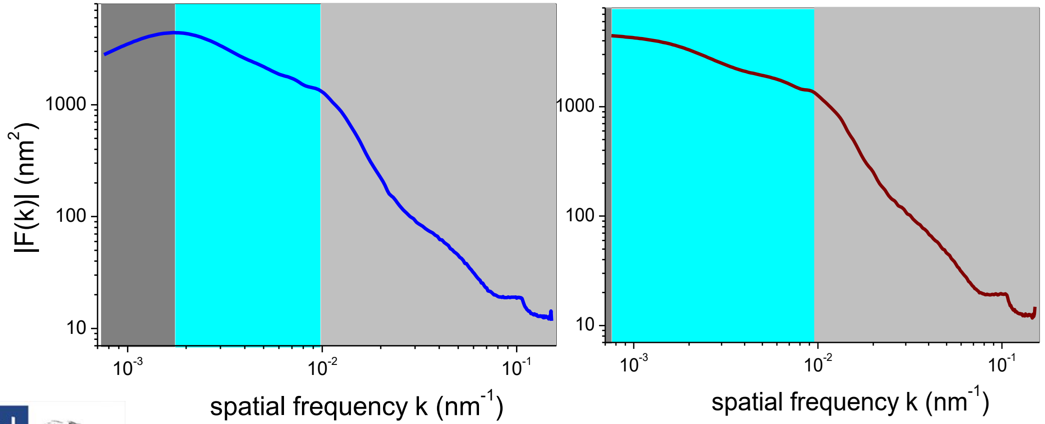


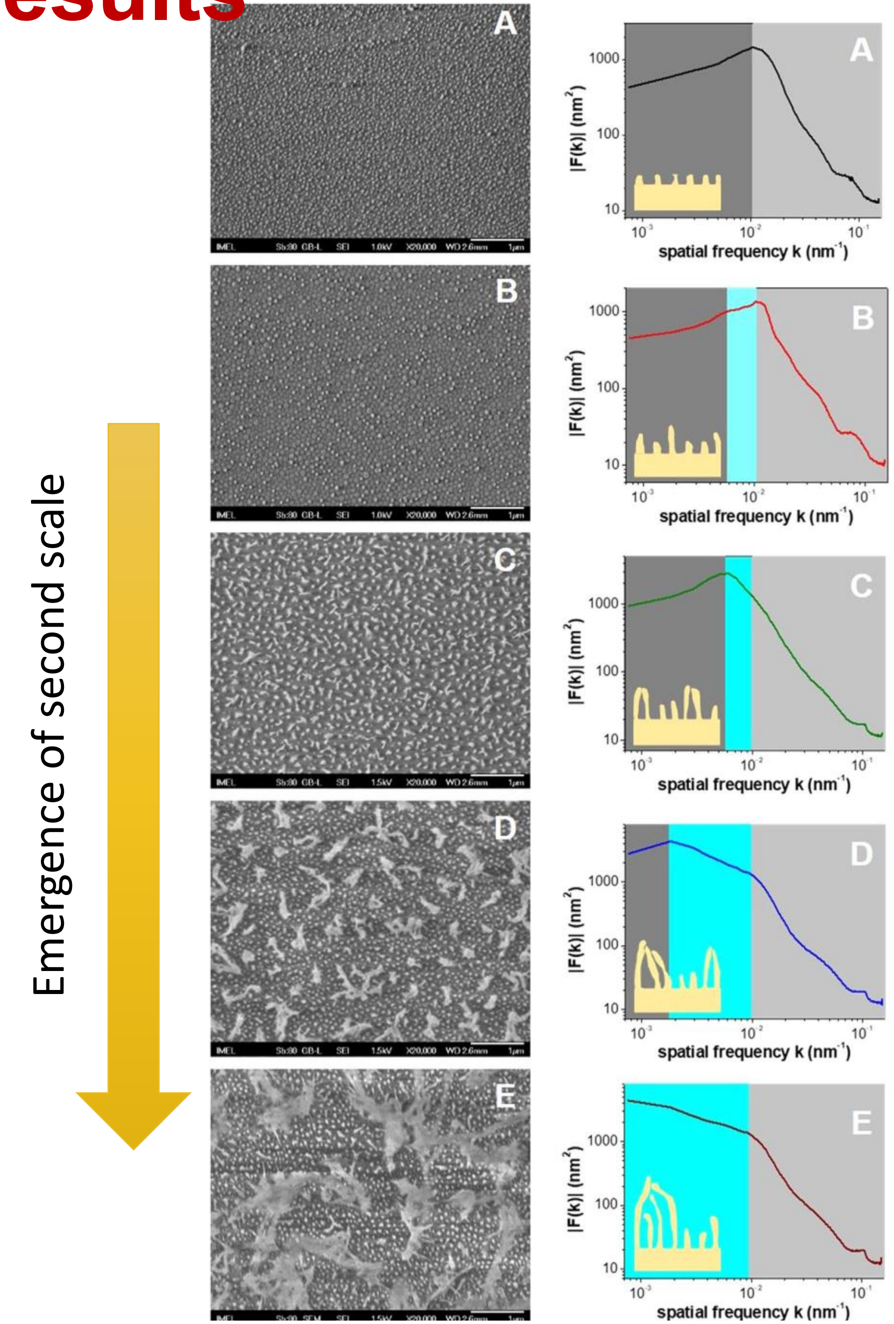
Spatial Hierarchy: experimental results

- *PMMA surfaces etched by O2 plasma in our homemade plasma reactor equipped with inhibitor controllers*
- *Emergence of second scale versus etching time / increase of inhibitors*



Fourier spectra





DEMOKRITOS

Conclusions

- **The challenge of nanostochasticicty: random-like, complicated surfaces and structures with a grand variety of forms, shapes and appearances encountered in almost all nanofabrication techniques**
- **Aim: Develop complexity concepts and methodologies adapted to surfaces inspired by recent advances in complexity science**
- **1st approach: Entropy-based complexity**
- **Consider the information content of surfaces and quantify it using a multiscale option of Shannon entropy to characterize multiscale surface heterogeneity**
- **2nd approach: Chaos-based complexity**
- **A novel use of the basic ingredients of chaos (stretching and folding) for the characterization of surface complexity maximizing between full order and noise**
- **First applications show promising results to reveal links with surface properties**
- **Application of chaos-based complexity to image analysis – an entirely new field of research)**
- **FUTURE WORK: Better foundation and formulation of methods and more applications**

Conclusions

- The challenge of hierarchical morphologies: Building a sound theoretical framework for hierarchical surfaces
- Fourier and correlation functions detect hierarchy and types of involved surface levels
- Multifractality is able to reveal nonlinear interactions between hierarchy levels
- First applications show detection and quantification of hierarchy in metal and polymer surfaces
- FUTURE WORK: From mathematics to the physics of complex hierarchical surfaces

Thank you very much!!

v.constantoudis@inn.demokritos.gr

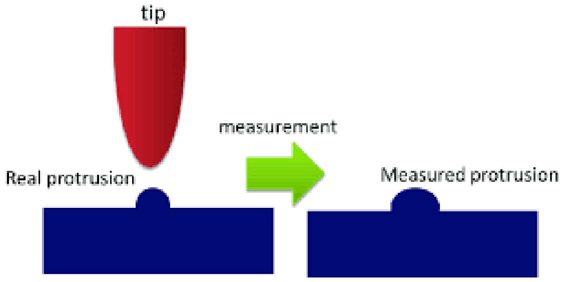
Questions?

Kusama, Infinity mirrored room

- Surfaces versus images/measurements/micrographs

Image = Measurement process $\oplus$ Surface

probe detector



Assumption : P(Image) ≈ P(surface) => C(image) ≈ C(surface)