Capillarity driven self-organization
- a spring-block model approach -

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More precisely:
- pattern formation during drying
- thin layers of wet granular materials or nanoparticles
- Simulation of the pattern formation phenomenon

Collaborators:

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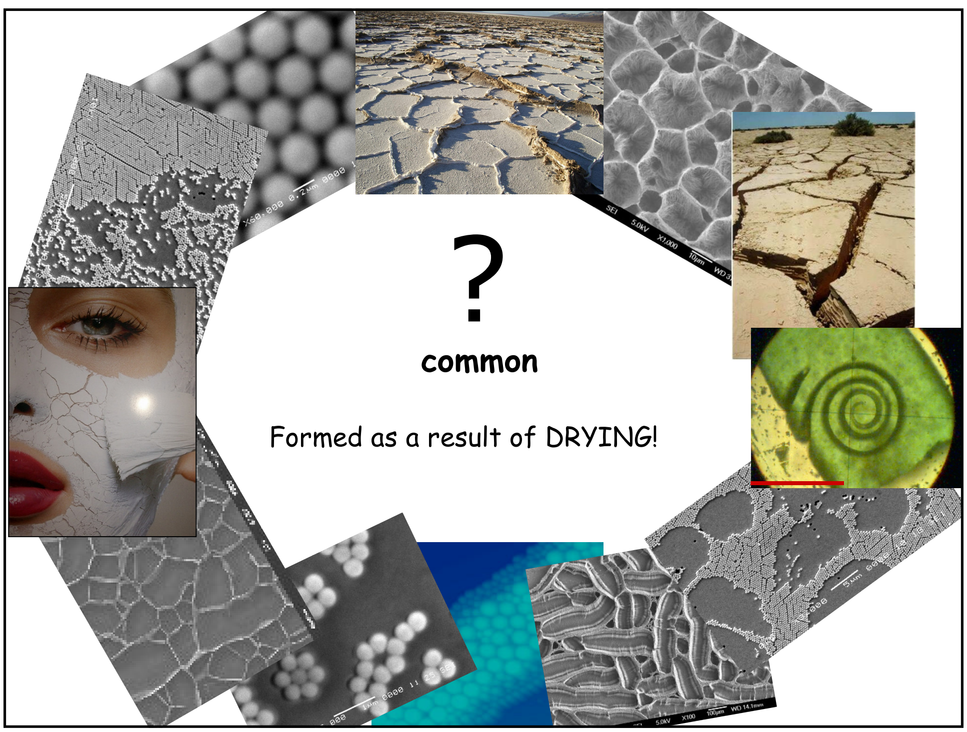
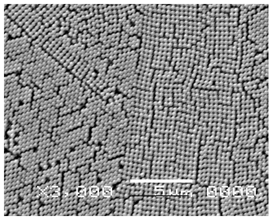
F. Járai-Szabó, S. Aştilean, M. Ravasz, L. Józsa and A. Kuttesch, C. Farcău *(Babeş-Bolyai University, Cluj, Romania)*

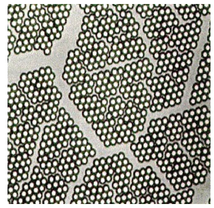


The scales of the patterns



nanospheres

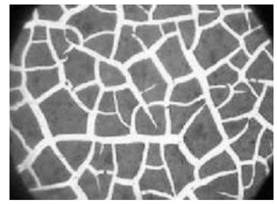
10^{-6} m



50μm

microspheres

10^{-4} m



1 mm

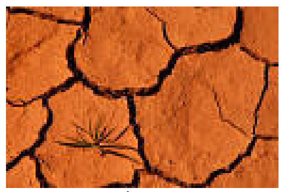
precipitates

10^{-3} m

7 orders of magnitude !

mud

10^{-2} m



clay

10^{-1} m

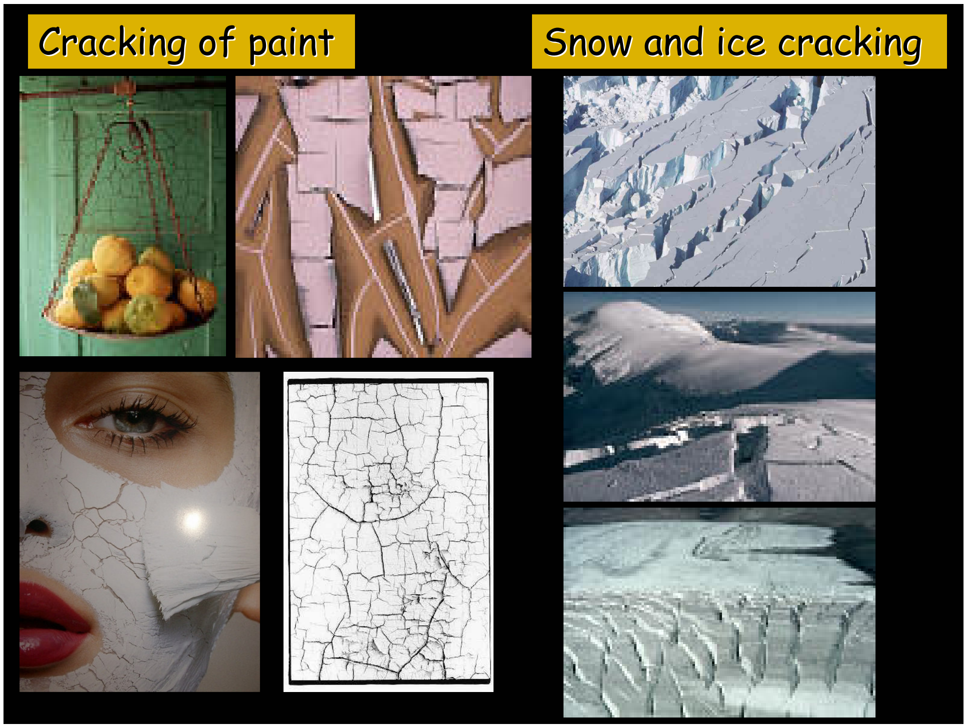
salt

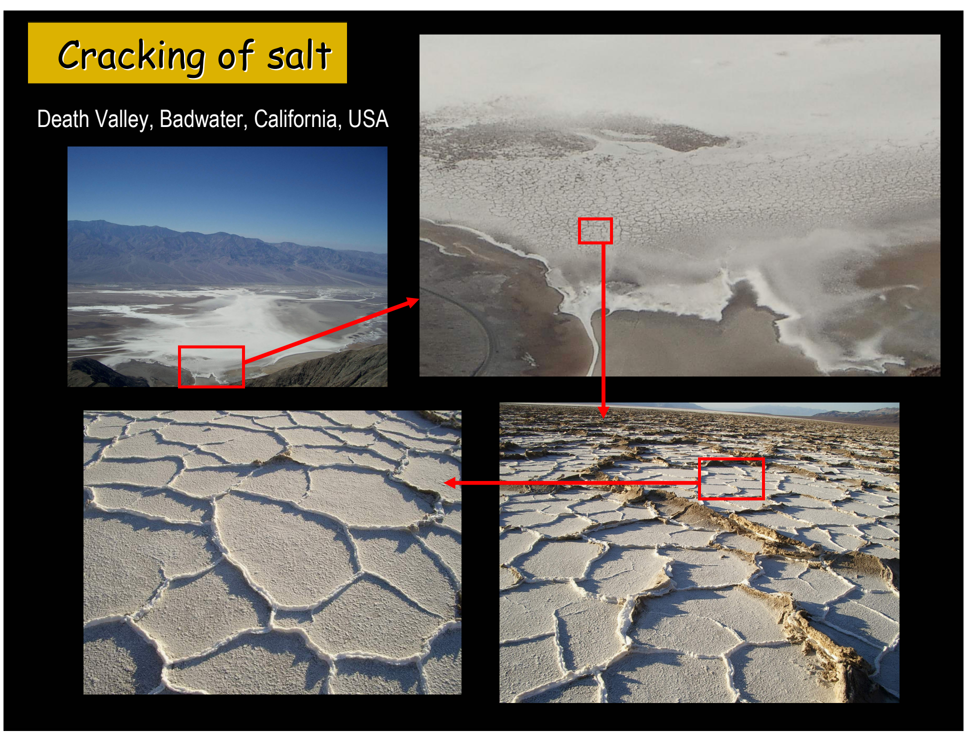
1-10 m

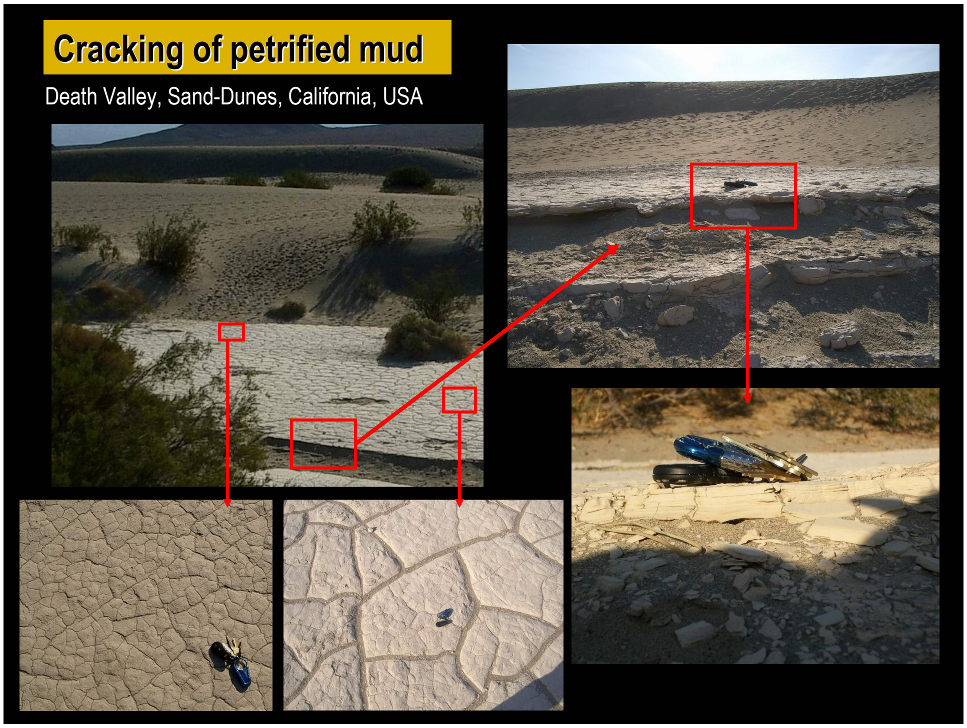
Outline

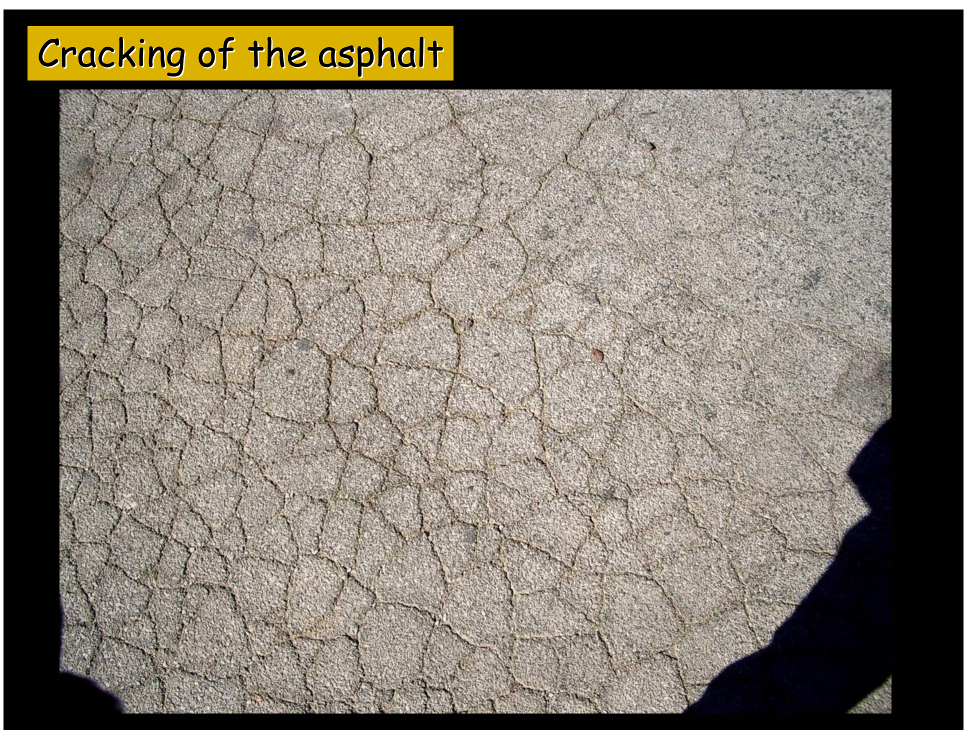
1. **Pattern formation in drying granular materials**
   - experimental results, self-similarity, scaling laws
   - a simple spring-block model approach
   - bonus patterns … smoothly curving fracture lines
2. **Patterns in nanosphere-litography**
   - experimental results, patterns
   - adaptation of the spring-block model to the nanosphere system
   - pattern optimization
3. **Patterns in a drying nanotube system**
   - experimental results, patterns
   - spring-block model for the nanotube system

1. Granular materials


Cracking of paint
Snow and ice cracking

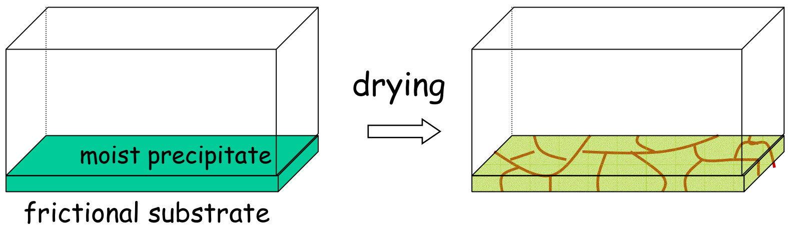

Cracking of salt
Death Valley, Badwater, California, USA


Cracking of petrified mud
Death Valley, Sand-Dunes, California, USA


Cracking of the asphalt

Experiments

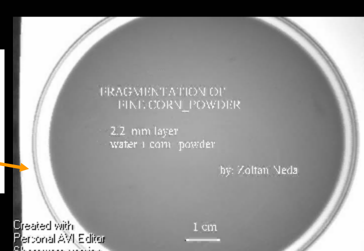
- Drying of wet corn-starch
- Drying of precipitate: $Ni_3(PO_4)_2$ $Fe_4[Fe(CN)_6]_3$
- Drying of a suspension of nanospheres $Fe(OH)_3$
- in situ observation of the dynamics
- fragmentation as a function of the layer thickness
- image analysis
  - fragment size statistics and scaling

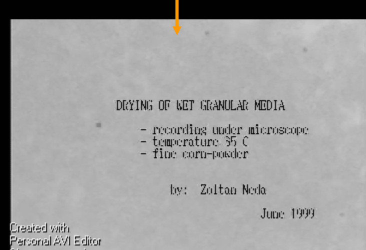


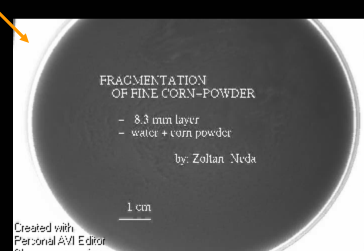
drying causes contraction, but hindered by friction ⇨ stresses ↑ ⇨ relieved by cracking (to lower the energy)

Fragmentation dynamics in corn-starch some movies

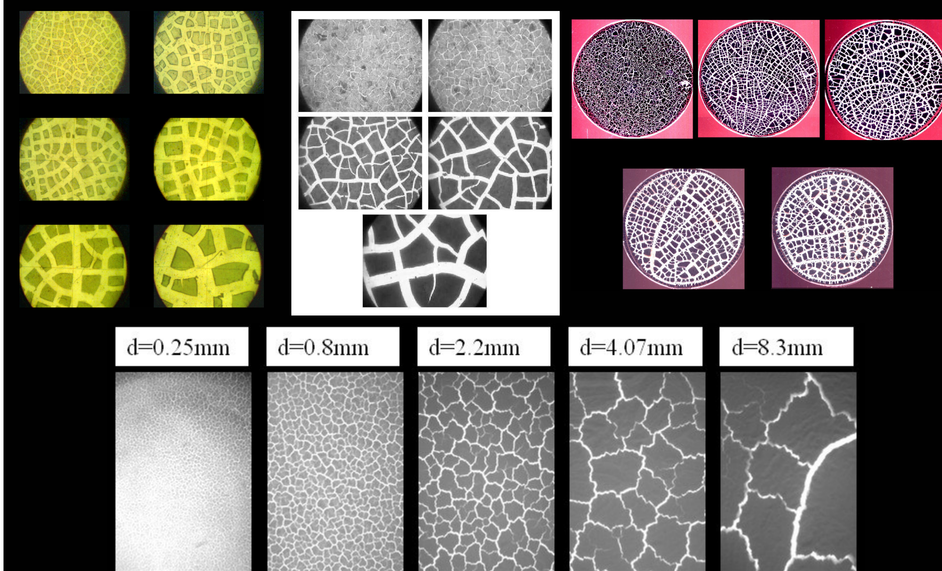
- fragmentation of drying corn-starch
- different layer thickness
- under microscope





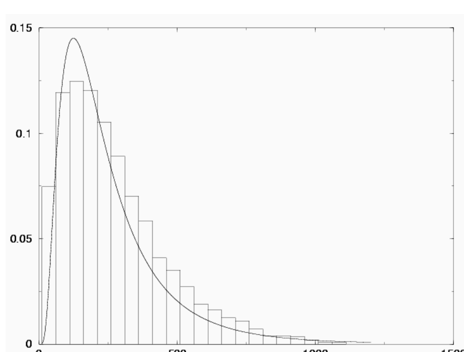


Fragmentation of drying precipitates and corn-starch for different layer thickness



Fragment-size statistics

- mean fragment-area scales as a function of layer thickness
- exponent: 1.3 - 1.4 thick layers
-exponent: 1.6 - 1.7 thin layers
-A cut-off where the self-similarity and scaling breaks down!



- fragment-size distribution :

Log-normal distribution

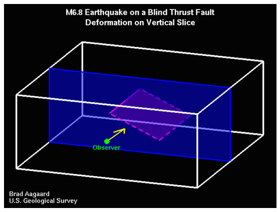
$$P(x, x+dx) = \frac{1}{Bx\sqrt{2\pi}} \exp\left(-\frac{[\ln(x) - A]^2}{2B^2}\right) dx$$

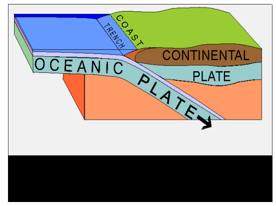
A simple spring-block stick-slip model

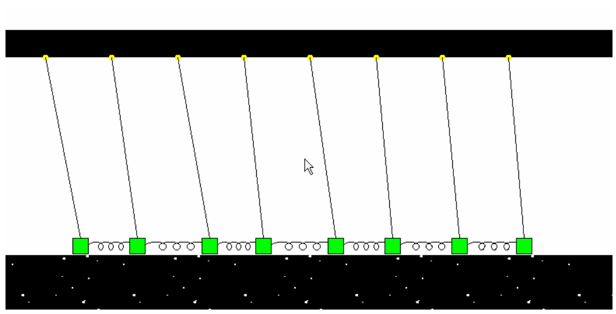
a Burridge-Knopoff type model

For simulating earthquakes

R. Burridge and L. Knopoff,
Bull. Seis. Soc. Amer. Vol. 57, (1967) 341.



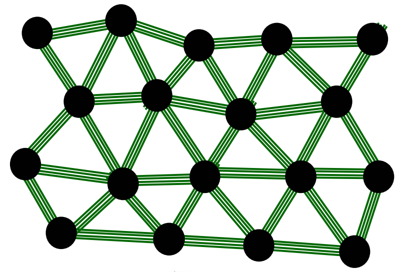


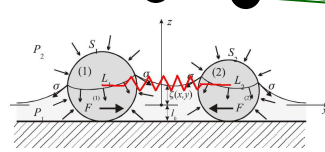


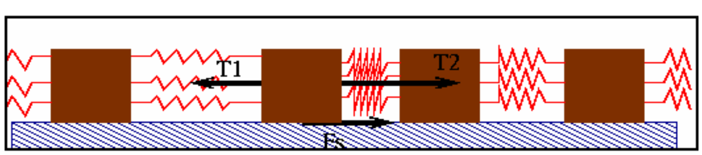
- **quasi 3D model**; grains --> blocks; water bridges --> springs; thickness of the layer --> bundles; blocks on triangular lattice

forces on a block:

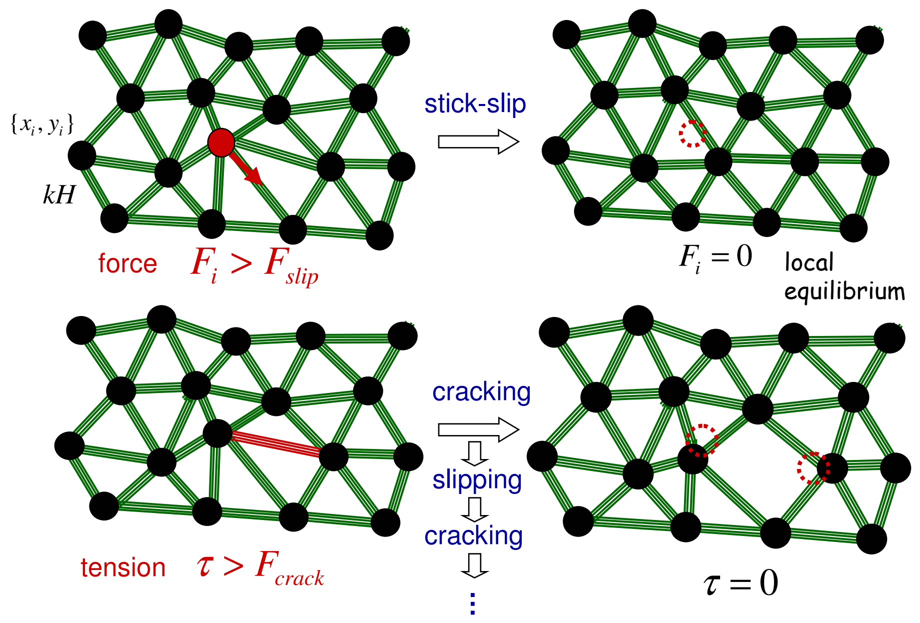
- **tension** in the attached springs (maximal supported tension: F_c) $T>F_c$ --> the spring breaks
- **friction** with the substrate (maximal friction force: F_s) $F>F_s$ --> the block slips to its equilibrium position

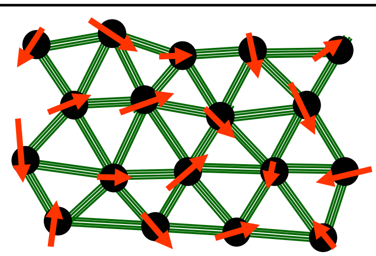






Simulating the cracks



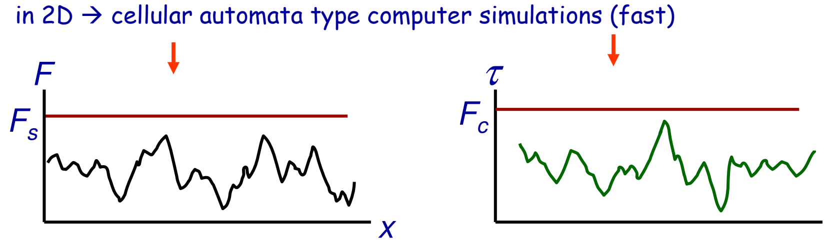


Force threshold: $F_c = \kappa F_s$ Initial strain: $s = (a-l)/l > 0$

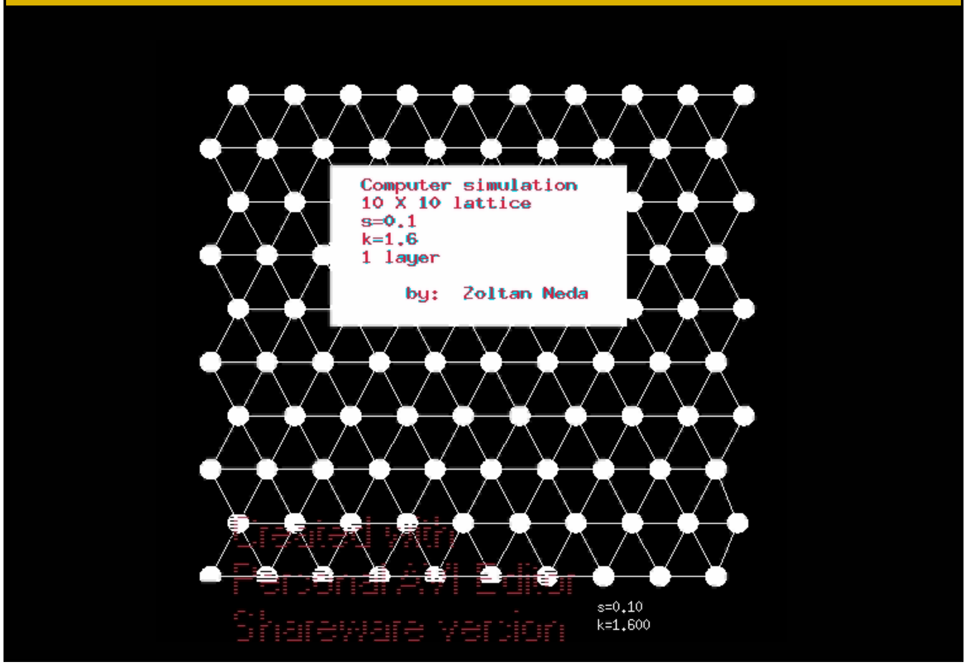
Driving: material stiffens K ↑ ⟺ Weakening F_s ↓ , F_c ↓

the model is analytically solvable in 1D

in 2D → cellular automata type computer simulations (fast)

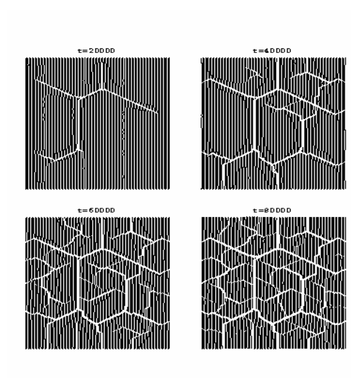


The model on computer - a movie

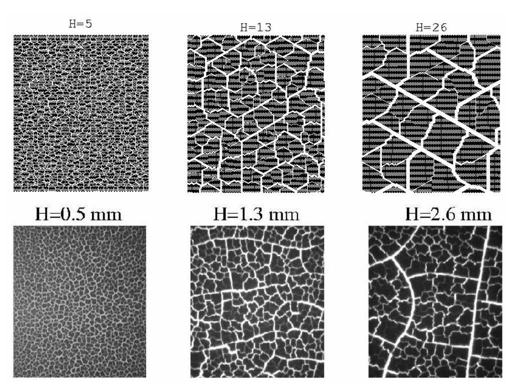


Fragmentation by simulation

characteristic time evolution (L=100, s=0.1, *K*=0.5, H=9)



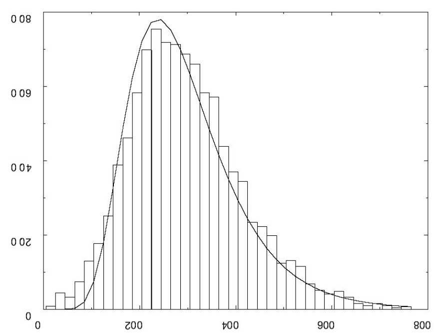
visual comparison with corn-starch fragmentation (L=100, s=0.1, *K*=0.25)



K.-t. Leung and Z. Néda: Phys. Rev. Lett. vol. 85, 662-665 (2000)

Fragment-size statistics (simulation & theory)

Distribution of fragment sizes
Log-normal in good approximation
(L=200, s=0.1, K=0.5, H=7)

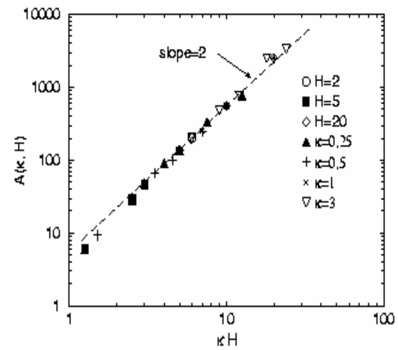


K.-t. Leung and Z. Néda: Phys. Rev. Lett. vol. 85, 662-665 (2000)

Scaling of mean fragment area A in thickness and substrate property

(L=100, s=0.1, either fixed κ or H as indicated)

$$A \sim (\kappa H)^2$$



the scaling breaks down after a given thickness!

Bonus patterns inside one fragment

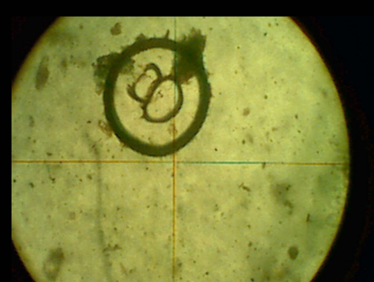
K.-t. Leung, L. Jozsa, E. Ravasz and Z.Néda-NATURE, vol. 410, 166-166 (2001)

isolated spiral

circle

concentric circles

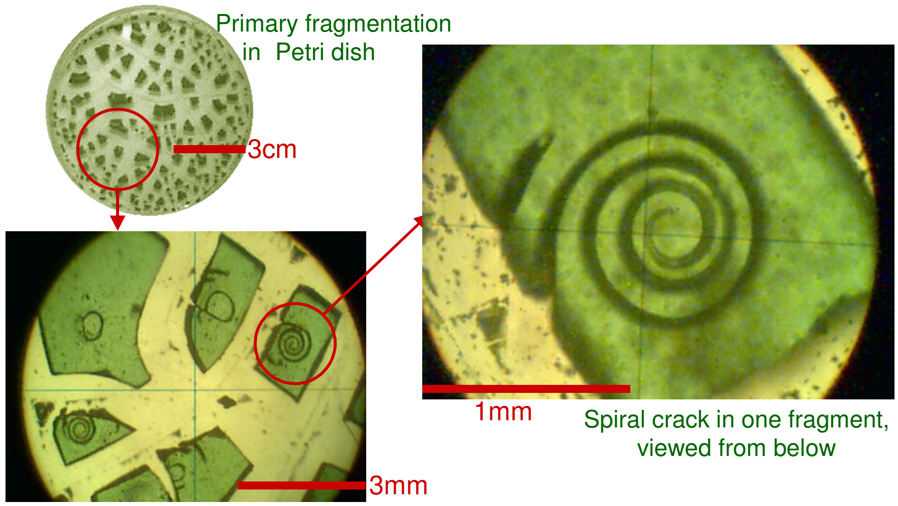
figure '8'



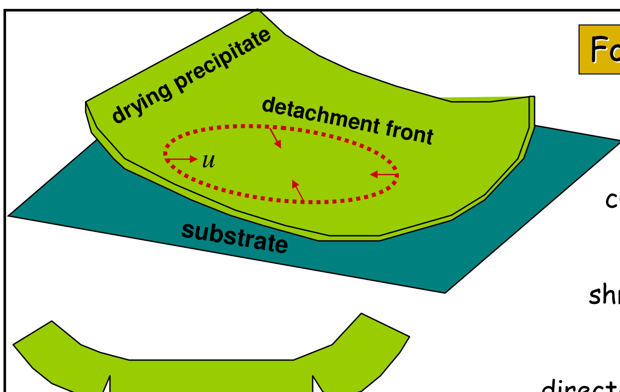
nested figure '8'

Spiral cracks from drying precipitate of $Ni_3(PO_4)_2$

K.-t. Leung, L. Jozsa, E. Ravasz and Z.Néda-NATURE, vol. 410, 166-166 (2001)



Also observed in ferrous compounds $Fe_4[Fe(CN_6)]_3$ & $Fe(OH)_3$. All have fine powder (nm scale) and very large contraction during drying.



Formation mechanism

drying

⇩

curling & detachment

⇩

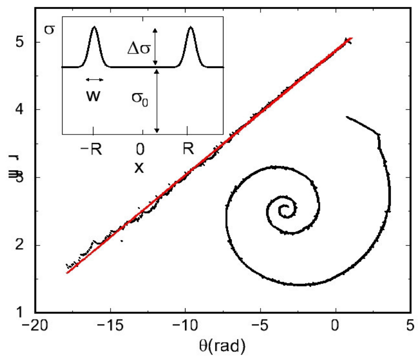
shrinking stress front

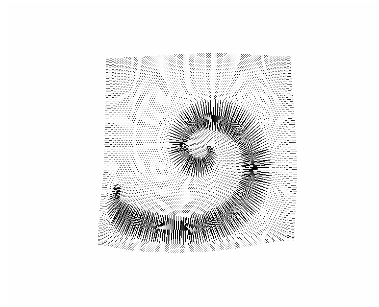
⇩

directional tunneling crack

overview of spiral cracks

Simulating the spiral cracks





Same simulation method

-inside one stable fragment

-imposing an inward propagating extra stress-front

-logarithmic spirals successfully reproduced

Z. Néda, K.-t. Leung, L. Józsa and M. Ravasz: .
Phys. Rev. Lett. vol. 88, Art. No. 095502 (2002)

2. Nanosphere systems

Experimental method and results

The drop-coat method

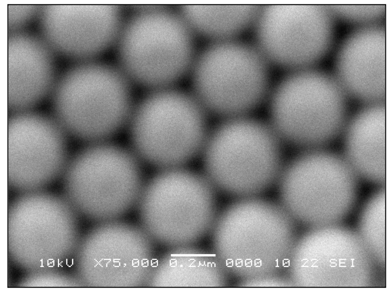
first step: to render the surface (silica glass) hydrophilic and improve its wettability (achieved by etching the substrate in a solution of sulphuric acid/hydrogen peroxide (3:1) for a period of 3 hours. Then washed in deionized water, immersed in a solution of ultra pure water/ammonium hydroxide/hydrogen peroxide (5:1:1) for 2 hours and sonicated in an ultrasonic bath for 1 hour. Finally, the substrates were thoroughly rinsed in ultra pure water and stored under ultra pure water)

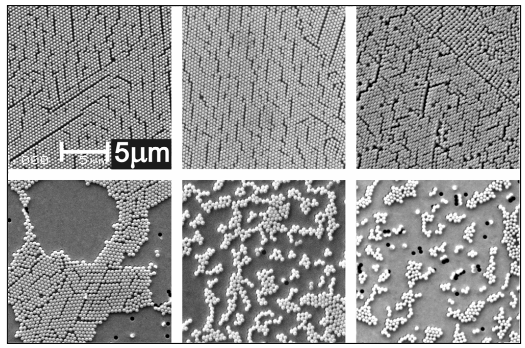
second step: preparing the monodisperse (220 nm diameter) polystyrene nanospheres suspension (nanospheres with a strongly hydrophobic nature) The original suspension of polystyrene nanospheres in deionised water

(wt 4%) was diluted by 10

third step: a volume of 100 µl diluted solution was evenly spread on the pre-treated substrates. The samples were dried in an oven at 65 0C for 45 minutes.

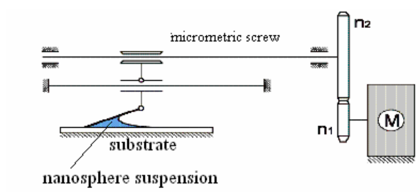
The microstructure of the samples were studied by scanning electron microscopy (SEM) using a JEOL JSM 5600 LV electronic microscope.

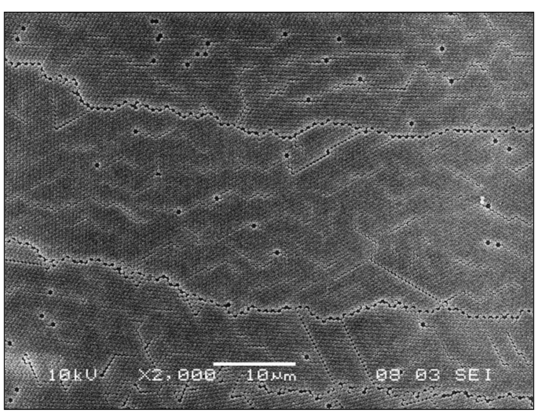


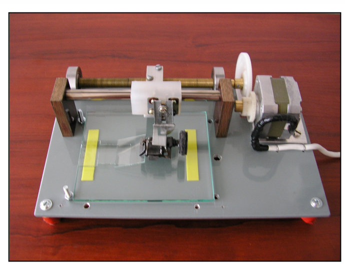


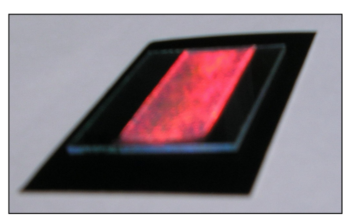
The horizontal drag method

- a drag apparatus with a computer-controlled step by step motor
- appropriate to make controlled monolayers





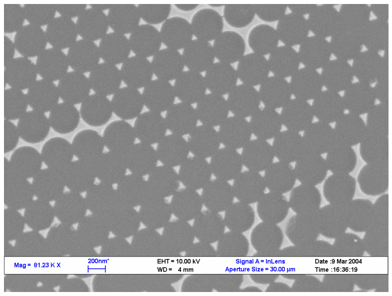


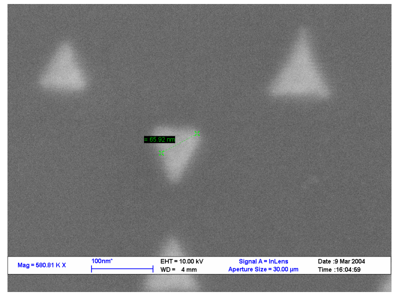


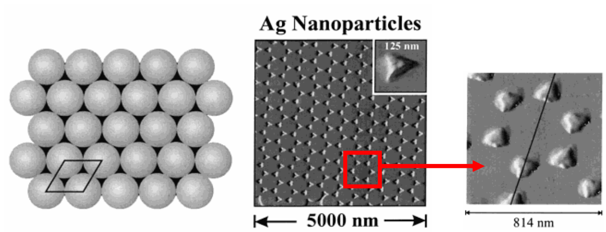
Practical importance of the obtained structures

Patterns for nanosphere litography

potential applications as optical grids, filters or fabrication of nano-wires.

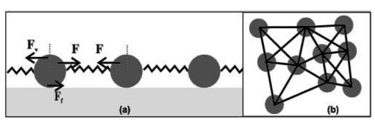


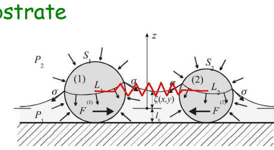




Modelling pattern-formation in nanospheres

nanospheres → blocks that can slide on a frictional substrate



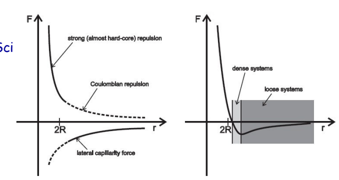


forces →

1. lateral attractive capillarity forces $F_c \sim 1/r$

P.A. Kralchevsky, V.N. Paunov, N.D. Denkov, I.B. Ivanov, K. Nagayama, J. Colloid Interface Sci 155, 420 (1993); V.N. Paunov, P.A. Kralchevsky, N.D. Denkov, K. Nagayama, K. Nagayama, J. Colloid Interface Sci. 157, 100 (1993).

2. electrostatic interaction between $F_e \sim 1/r^2$ the nanospheres and their hard-core repulsion



1+2 → springs interconnecting the blocks
+ hard-core repulsion

3. pinning between the substrate and nanosphere → friction force with a slipping threshold

4. friction between the nanospheres and water → viscosity, Fv which makes the motion an overdamped one!

topology → 2D, but no predifined lattice. geometric condition for putting a spring

simulation → molecular dynamics, the same relaxation dynamics with a fixed F_{break} and F_{slip}

F. Járai-Szabó, S. Astilean and Z. Néda
Chem. Phys. Lett., Vol. 408, 241-246 (2005)

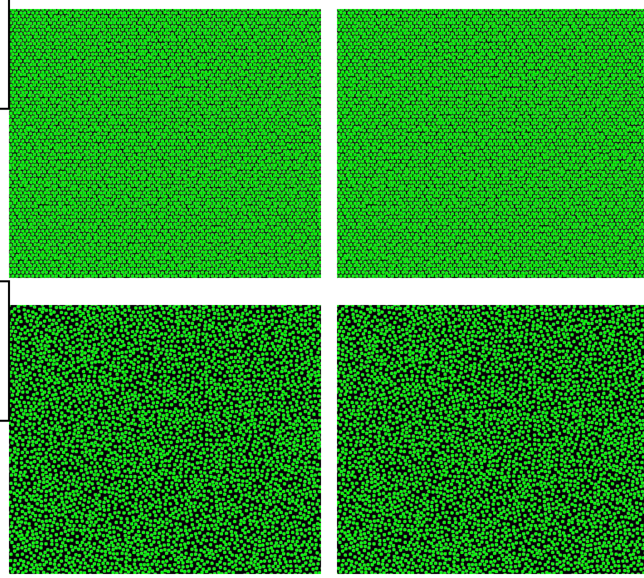
Some evolution movies

Parameters

SpringConst 0.1
FrictionForce 0.01
InterForceCoeff 40.0
DiskRadius 1.0
SprConstIncr 0.005
MaxSpringForce 0.05
SpaceFilling 0.749

Parameters

SpringConst 0.1
FrictionForce 0.003
InterForceCoeff 40.0
DiskRadius 1.0
SprConstIncr 0.005
MaxSpringForce 0.05
SpaceFilling 0.749

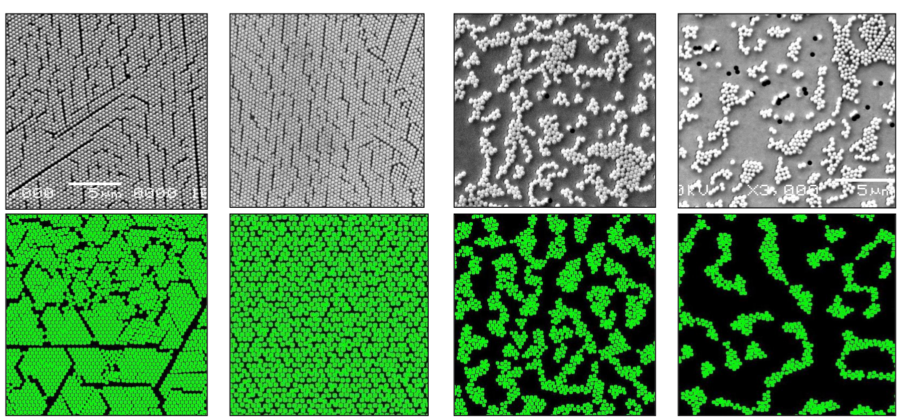


Parameters
SpringConst 0.1
FrictionForce 0.01
InterForceCoeff 40.0
DiskRadius 1.0
SprConstIncr 0.005
MaxSpringForce 0.1
SpaceFilling 0.512

Parameters

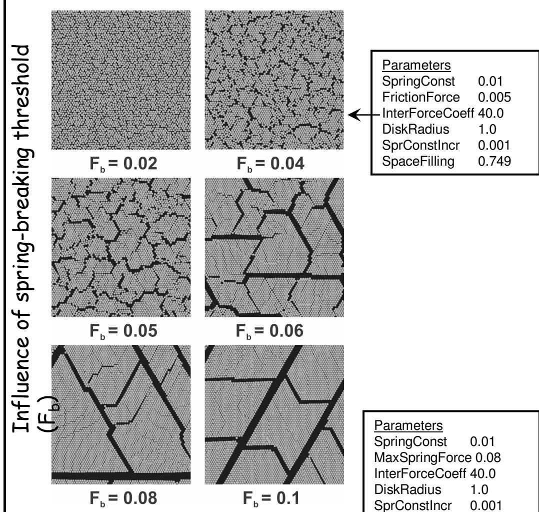
SpringConst 0.1
FrictionForce 0.01
InterForceCoeff 40.0
DiskRadius 1.0
SprConstIncr 0.005
MaxSpringForce 0.3
SpaceFilling 0.512

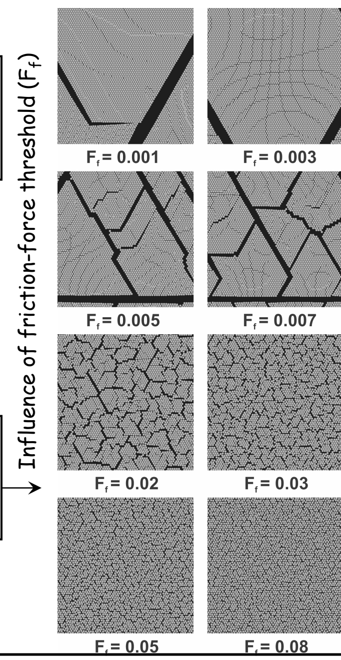
Qualitative comparison between experimental and simulated structures



SimulFieldSize 200.0	SimulFieldSize 200.0	SimulFieldSize 200.0	SimulFieldSize 200.0
SpringConst 0.1	SpringConst 0.1	SpringConst 0.1	SpringConst 0.1
FrictionForce 0.01	FrictionForce 0.005	FrictionForce 0.2	FrictionForce 0.2
InterForceCoeff 40.0	InterForceCoeff 40.0	InterForceCoeff 40.0	InterForceCoeff 40.0
MaxSpringForce 0.05	MaxSpringForce 0.02	MaxSpringForce 0.5	MaxSpringForce 0.5
SprConstIncr 0.02	SprConstIncr 0.02	SprConstIncr 0.002	SprConstIncr 0.002
GenRadMultiply 1.1	GenRadMultiply 1.1	GenRadMultiply 1.5	GenRadMultiply 2.0
Fix boundaries	**Fix boundaries**	**Free boundaries**	**Free boundaries**
Central region	**Central region**	**Central region**	**Central region**

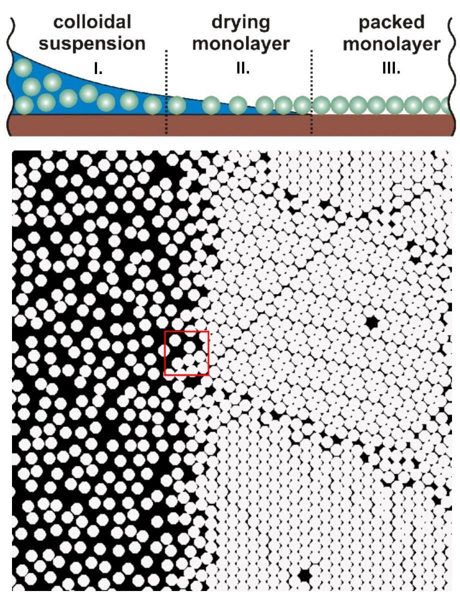
controlling the structures

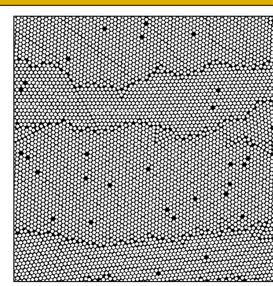




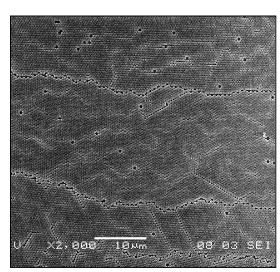
F. Járai-Szabó, S. Astilean and Z. Néda; Chem. Phys. Lett., Vol. 408, 241-246 (2005)

simulating the drying process more realistically- the horizontal drag method





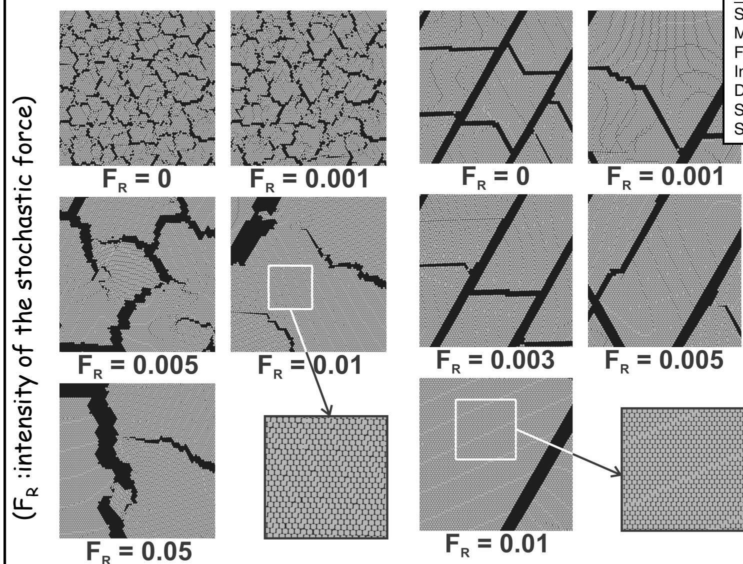
simulated



experimental

making more ordered structures by shaking

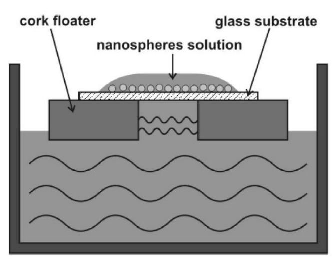
Effect of an uncorrelated stochastic force



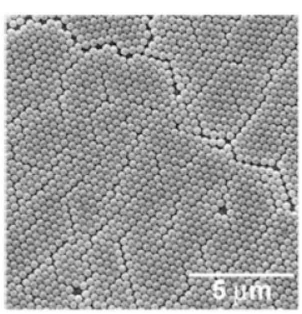
Parameters	
SpringConst	0.01
MaxSpringForce	0.05 / 0.1
FrictionForce	0.005
InterForceCoeff	40.0
DiskRadius	1.0
SprConstIncr	0.001
SpaceFilling	0.749

F. Jarai-Szabo, Z. Neda, S. Astilean, C. Farcau, and A. Kuttesch; Eur. Phys. J. E 23, 153-159 (2007)

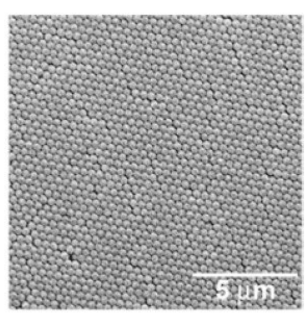
experimental realization



-shaking: induced by ultrasound during evaporation



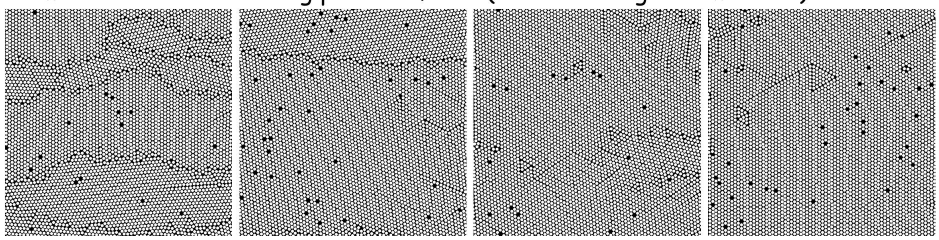
non-sonicated sample



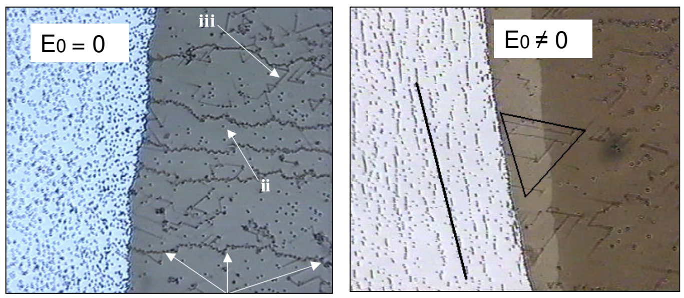
sonicated sample

Shaking induced by an oscillating electric field

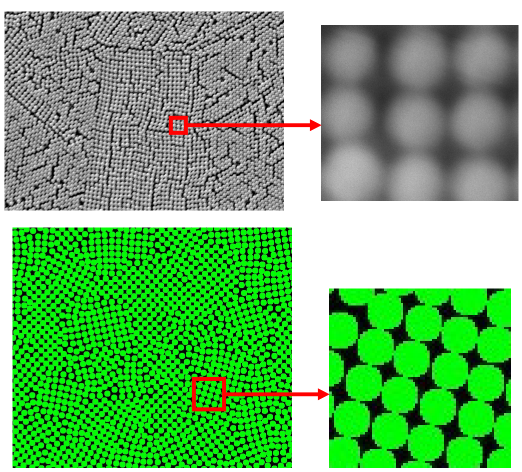
Simulation with increasing periodic force (the three region simulation)

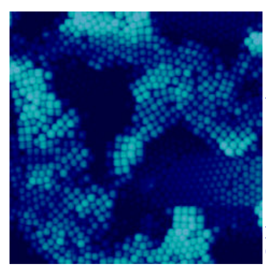


Experimental (Hans Joachim Schöpe, *J. Phys.: Condens Matter*, 15, L533, 2003)



An interesting square-lattice crystallization phase





Eddie W. Ong et al.,
Arizona State University

The simulations reproduce this meta-stable phase as an intermediate state during drying, (not completely relaxed system) when the density of spheres and spring-breaking thershold is high!

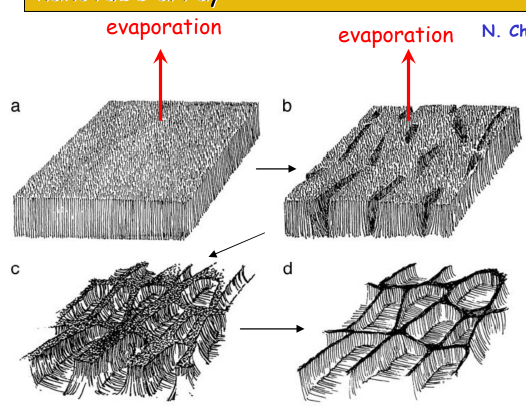
SpringConst	0.1
DiskRadius	1.0
SprConstIncr	**0.001**
MaxSpringForce	**0.5**
FrictionForce	0.005
SpaceFilling	0.749

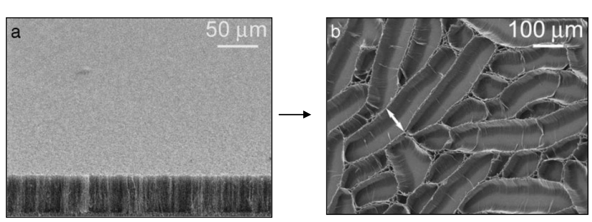
In experiments the square-lattice phase arises when quick evaporation is imposed!

3. Nanotube systems

Capillarity-driven self-organization in a two-dimensional carbon nanotube array

N. Chakrapani et al., PNAS vol. 101, 4009 (2004)





- Vertically aligned multiwalled nanotube arrays (wetted by water) are grown on rigid silica substartes

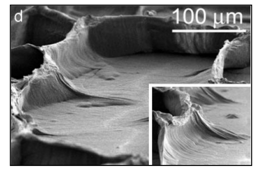
-The arrays are immersed into liquid (water)

-- the cellular patterns are obtained after the evaporation of the liquid

Experimental procedure

-The the multiwall nanotube arrays were grown by chemical vapor deposition based on the decomposition of ferrocene and xylene

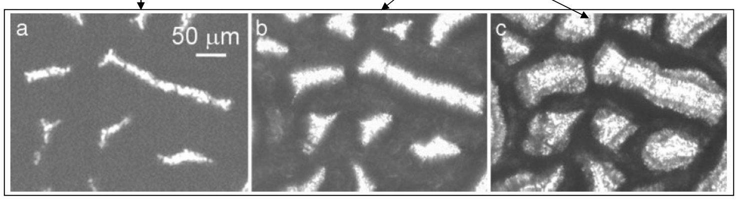
- The vertically aligned nanotube arrays were oxidized in an oxygen plasma at room temperature and 133 Pa pressure for 10 minutes
- as wetting liquid water was used
- patterns studied visually by optical microscopes



Characteristic time evolution

First stage: appearance of cracks

Second stage: cell growth via compactation and bending of nanotubes



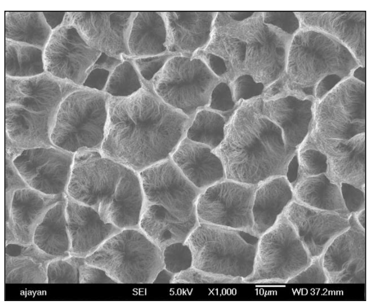
N. Chakrapani et al., PNAS vol. 101, 4009 (2004)

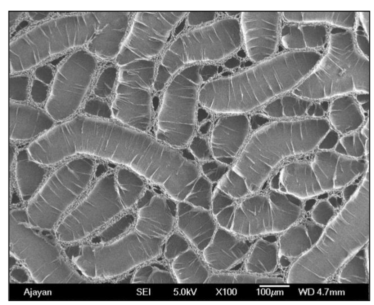
Patterns **are controlled by** varying the nanotube height, rate of evaporation of liquid and patterning the nanotube array

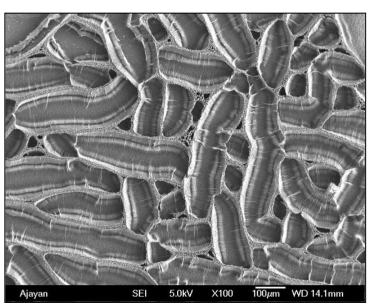
Potential Applications: - shock absorbent reinforcement in nano-filtration devices

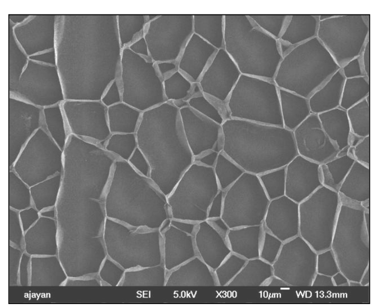
- biological applications (storage or growth of biological cells)

A collection of experimentally observed patterns



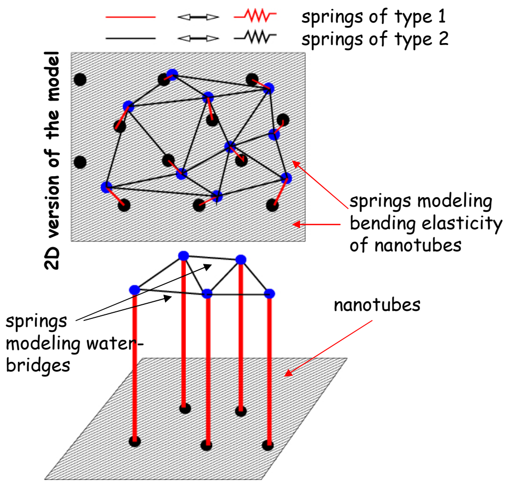






Modeling the cellular patterns

The model ⟶ a modified 2D spring-block model



- The bottom (basis) of nanotubes are arranged on a triangular lattice (black disks)

- The top of nanotubes are modeled by blocks, initially on the defined triangular lattice (blue disks)

- The blocks (top of nanotubes) are connected with their nearest neighbors by springs of type 2 (blue springs, modeling the capillarity of water between the nanotubes)

- Springs of type 2, have a breaking threshold F_b (if the tension is bigger than F_b the springs will break and are irreversibly taken out from the system)

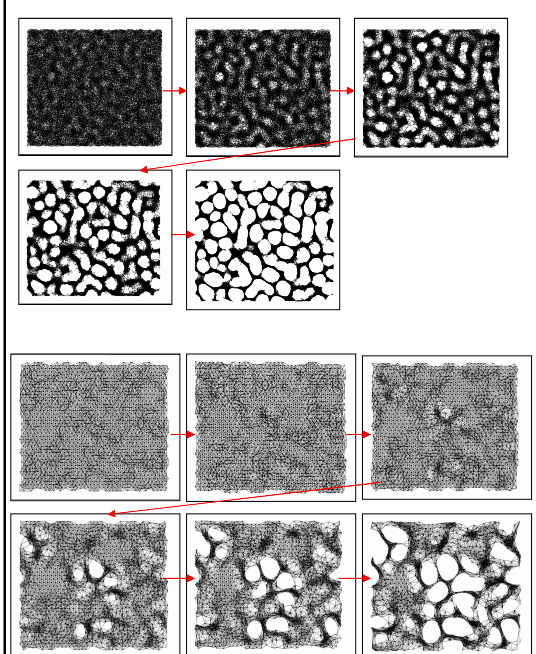
- The blocks are connected with the centers of the triangular lattice (bottom of nanotubes) with springs of type 1. (red springs, modeling the bending elasticity of nanotubes)

- Springs of type 2 have no breaking threshold (never break)

- The blocks have no friction with the surface, there are in equilibrium when there is no resultant force from springs of type 1 and type 2.

- There is a viscosity tempering the free slide of the blocks (stabilizing unrealistic oscillations).

Dynamics of the model



1. The blocks are placed on o triangular lattice and the interconnecting sping-network is constructed. The spring constants for springs of type 1 and 2 are assigned. Spring constant for spring 1 are take small, so that the tension in each spring is smaller than F_b

2. A small number of links (springs of type 1 are removed) → creating an initial randomness in the system

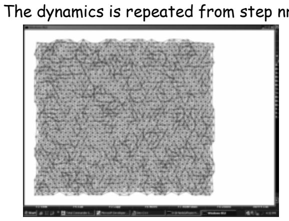
3. The dynamics towards equilibrium of blocks is realized through an over-damped molecular dynamics simulation (parallel update) with time-step:dt

$$\frac{d^2\vec{r}_i}{dt^2} = \sum_j \vec{F}^1_{ij} + \vec{F}^2_i + \eta \frac{d\vec{r}_i}{dt}$$

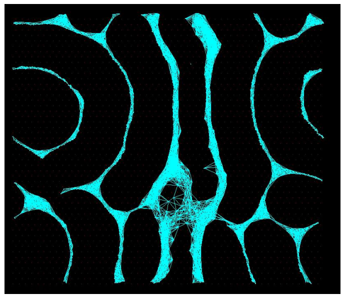
4. Whenever the tension in a spring of type 1 is greater than F_b the spring is removed.

5. After all blocks reach equilibrium (the largest displacement per unit time is smaller than a fixed small value) the spring constants for springs of type 1 is increased by a small dk value.

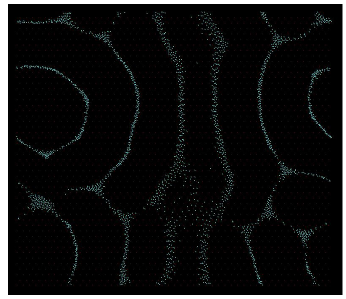
6. The dynamics is repeated from step nr. 3



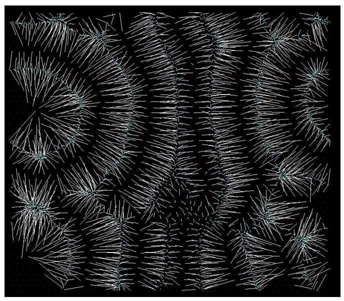
Various view of the simulated patterns



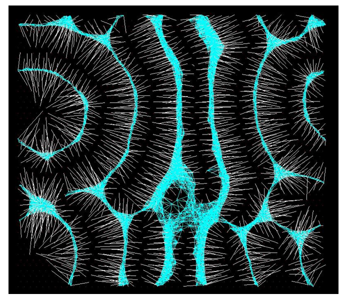
Unbroken springs of type 2



Top of the nanotubes

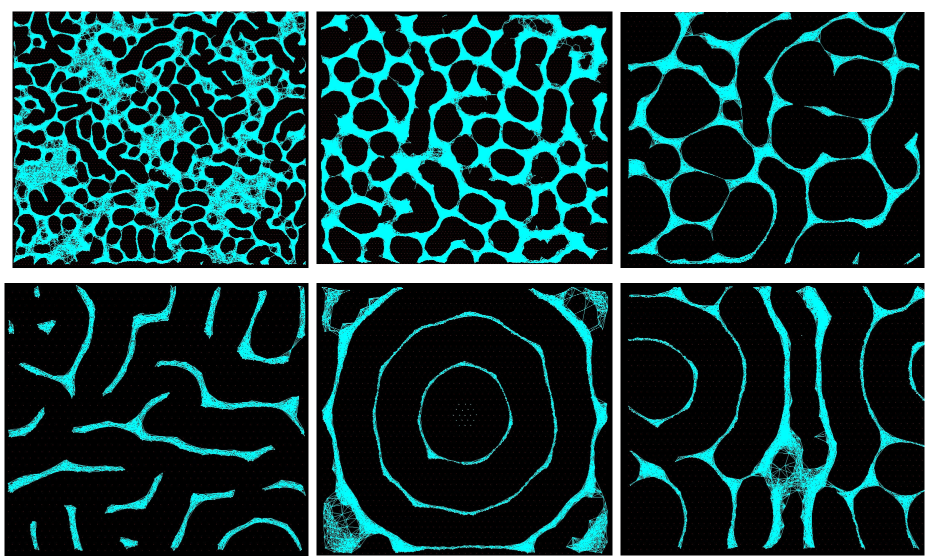


Top of nanotubes + horizontal projection of nanotubes



Unbroken springs of type 2 + horizontal projection of nanotubes

A preliminary collection of simulated patterns



F. Járai-Szabó, A. Kuttesch, S. Astilean, Z. Néda, N. Chakrapami, P.M. Ajayan and R. Vajtai: **JOAM** Vol. 8, 1083-1087 (2006)

Conclusions

1. A large variety of patterns can be obtained by capillarity-driven self-organization of granular materials or nanoparticles.

2. A simple spring-block stick-slip model is appropriate for successfully reproducing all these structures

3. By computer simulations one can investigate the dynamics of the pattern formation mechanism and the influence of the experimentally controllable parameters (this can help optimizing the patterns)

Selected publications:

1. K.-t. Leung and Z. Neda; **Phys. Rev.Lett.**, vol. 85, 662 (2000)
2. K.-t. Leung, L. Jozsa, E. Ravasz and Z. Neda, **Nature**, vol. 410, 166 (2001)
3. Z. Neda, K.-t. Leung, L. Jozsa and M. Ravasz; **Phys. Rev. Lett.** Vol. 88, 095502 (2002)
4. F. Járai-Szabó, S. Astilean and Z. Néda: **Chem. Phys.Lett.**, Vol. 408, 241(2005)
5. F. Jarai-Szabo, Z. Neda, S. Astilean, C. Farcau, and A. Kuttesch; **Eur. Phys. J. E** 23, 153–159 (2007)

Pattern formation on anisotropic surfaces

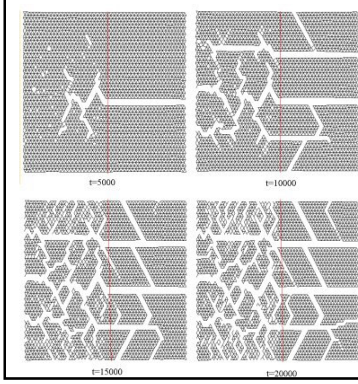
Anisotropy parameter

$$f = \frac{F_{sx}}{F_{sy}}$$

Experimental surface

Experimental results for different thickness

Evolution in time



On the left side of the red line we use anisotropic surface, on the right side there is an isotropic surface

(L=50, H=1,3,5,10, s=0.1; K=1.5; f=10)

Simulation results for different thickness