Multi-scale patterns formed by Sodium Sulphate in a drying droplet of Gelatin: Experiment and simulation

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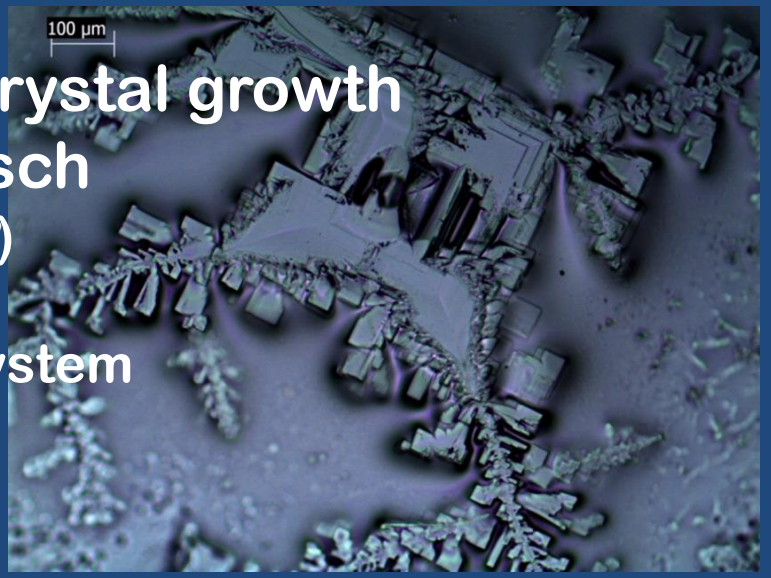
The interest and importance of Study of DROPLETS is Quite evident from the number of recent conferences exclusively Dedicated to this topic!!

Review: K. Sefiane, Adv. Colloid, Int. Science, 206, 372, 2014

Book: Droplet wetting and evaporation, D. Brutin, Academic Press, 2015

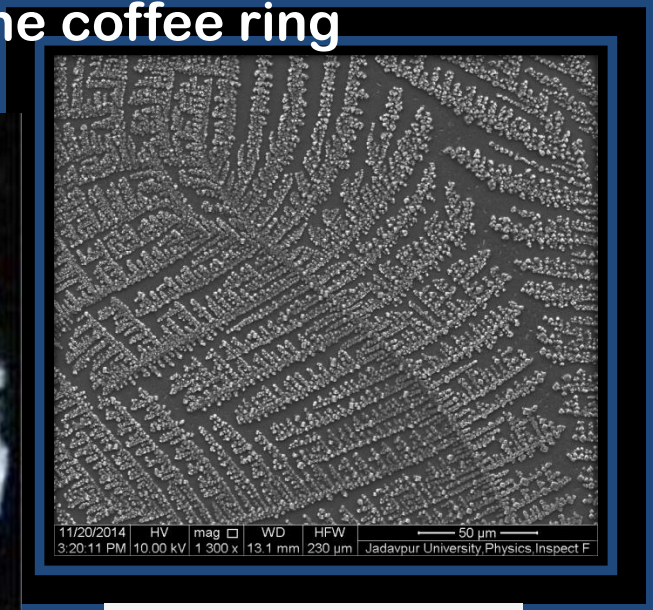
The role of gels in formation of crystal growth has been long known (H.K. Henisch *Crystals in Gels and Leisegang Rings, 1988*)



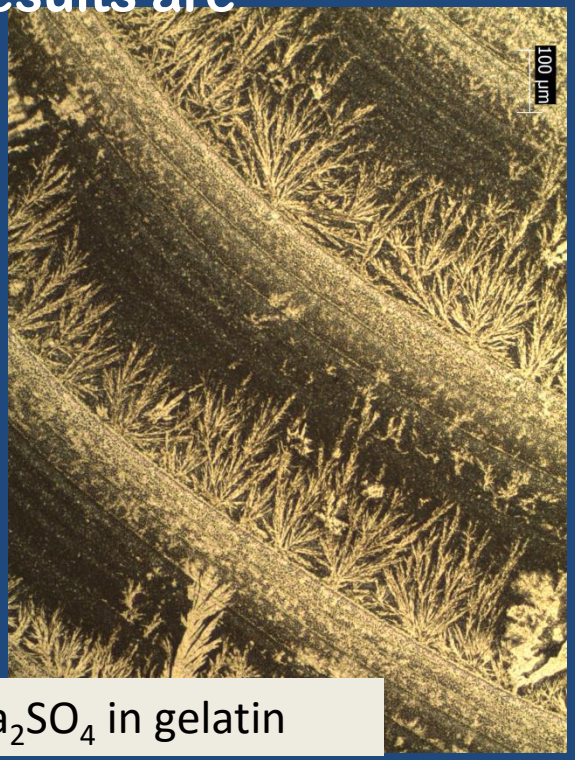
A drying droplet containing a gel is a system
Showing very interesting behavior.

The gel inhibits convection during drying, so results are
More complex than the coffee ring

NaCl in potato starch gel



SEM image NaCl in gelatin



Na_2SO_4 in gelatin

Plan of talk

- Description of experiments and observations
- Simulation and results

Materials and Methods

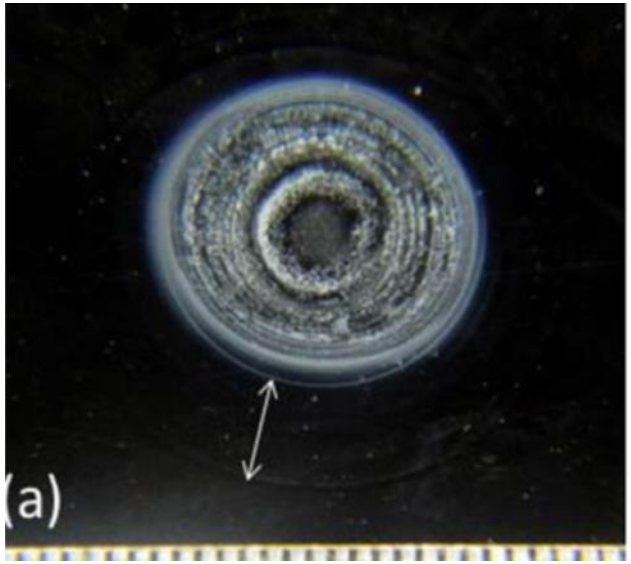
Method

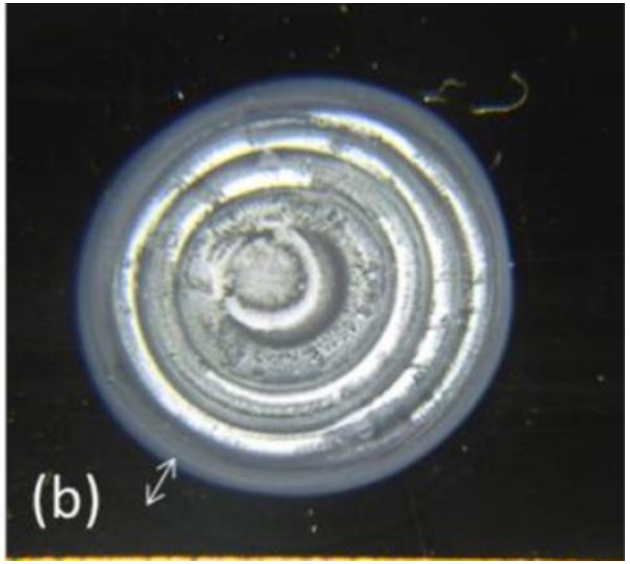
(0.142g of Na_2SO_4 +(50 ml)H_2O = solution of 0.02 M conc.

+

0.5g **dry** gelatin powder)

Mixture stirred at 60^oC until dissolved completely





Rings disappear for conc. > 0.02 M

Physical properties of the different complex solutions:

Angle of contact (Na_2SO_4 , gelatin): 18 ± 2^o

Sample	Surface tension	Viscosity (cP)
Gelatin solution	39.0	2.06
Na_2SO_4 solution	70.0	1.65
Gelatin + Na_2SO_4	40.6	2.15

Ambient conditions during measurement:

Temperature: 30^oC

Relative humidity: 52%

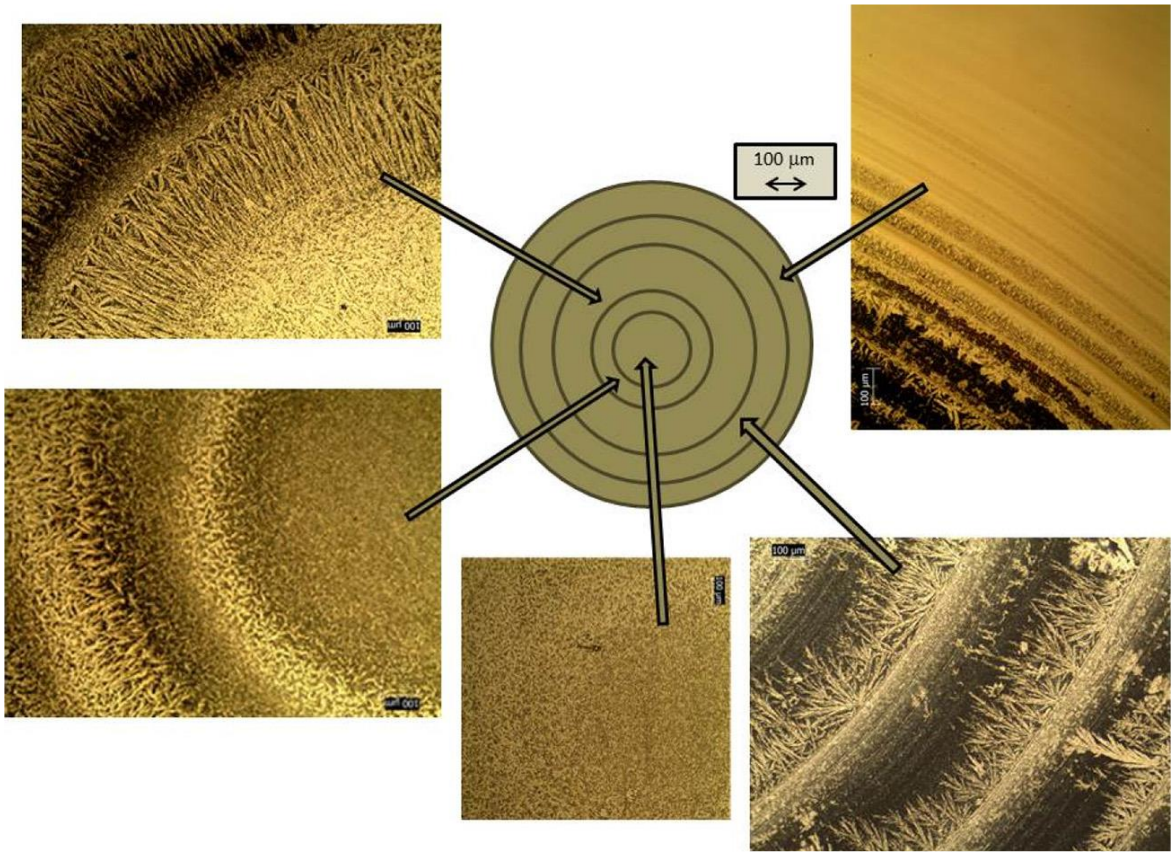
Concentration:

gelatin solution: 1% by weight

Na_2SO_4 solution: 0.02 M

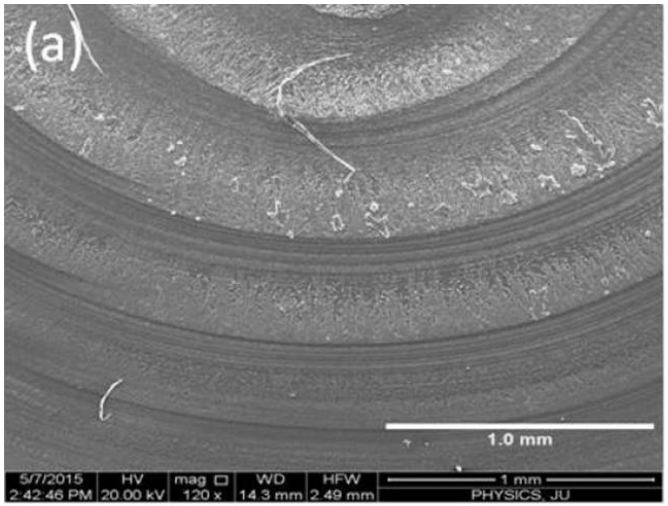
View under microscope: Rings are actually BANDS !!

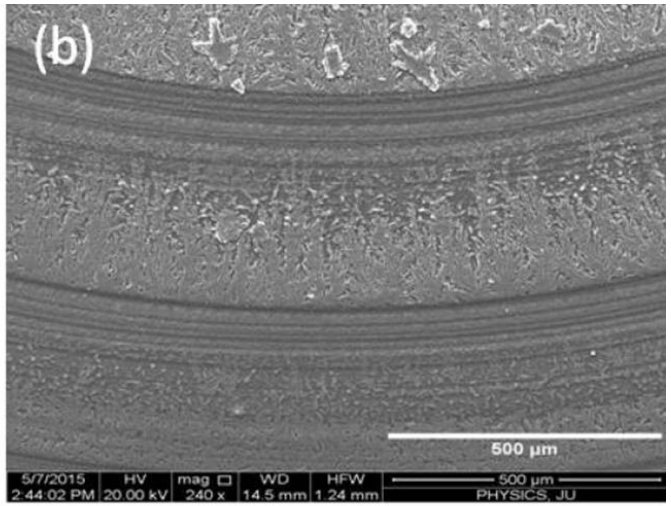
- Rings are not equi-spaced
- There is an order in the spacing

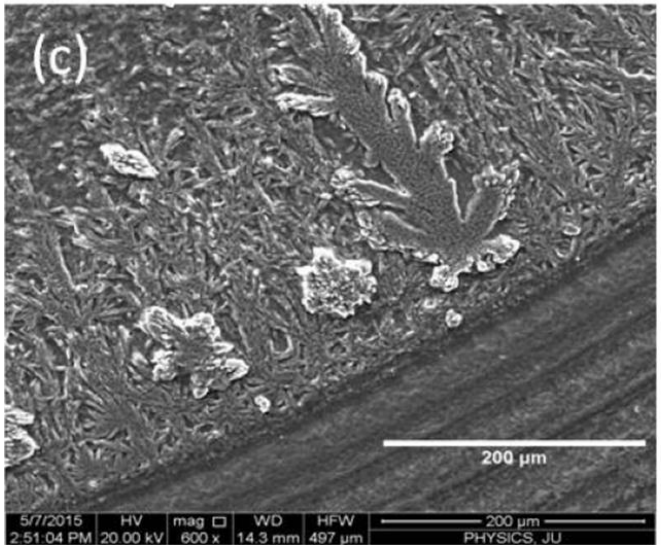


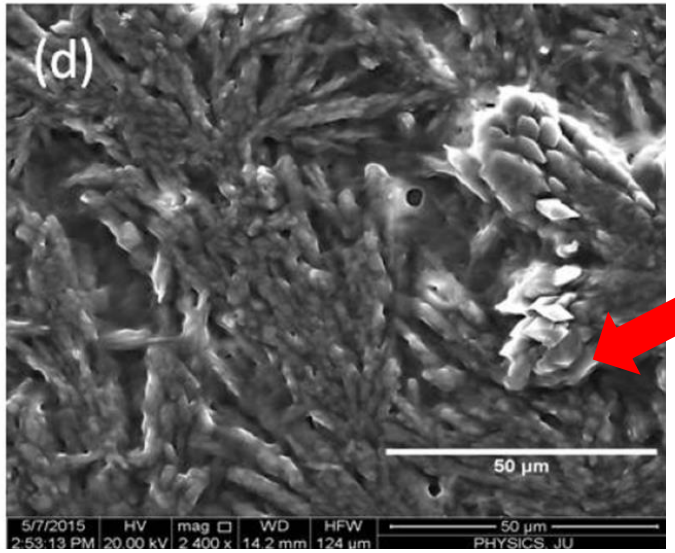
Set of rings with dendritic crystals growing in between them

FESEM Image







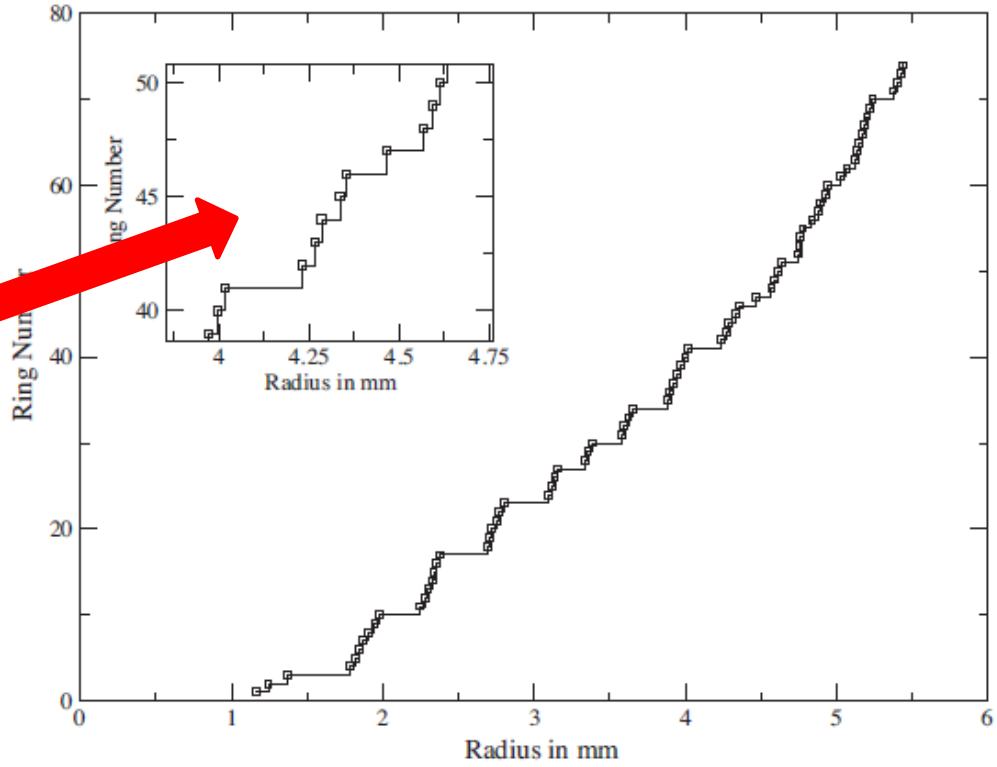


Diamond shaped crystallites of Na_2SO_4

Pattern Analysis

Ring number plotted against radius measured with respect to centre

a zoomed up portion demonstrating the self-similarity.

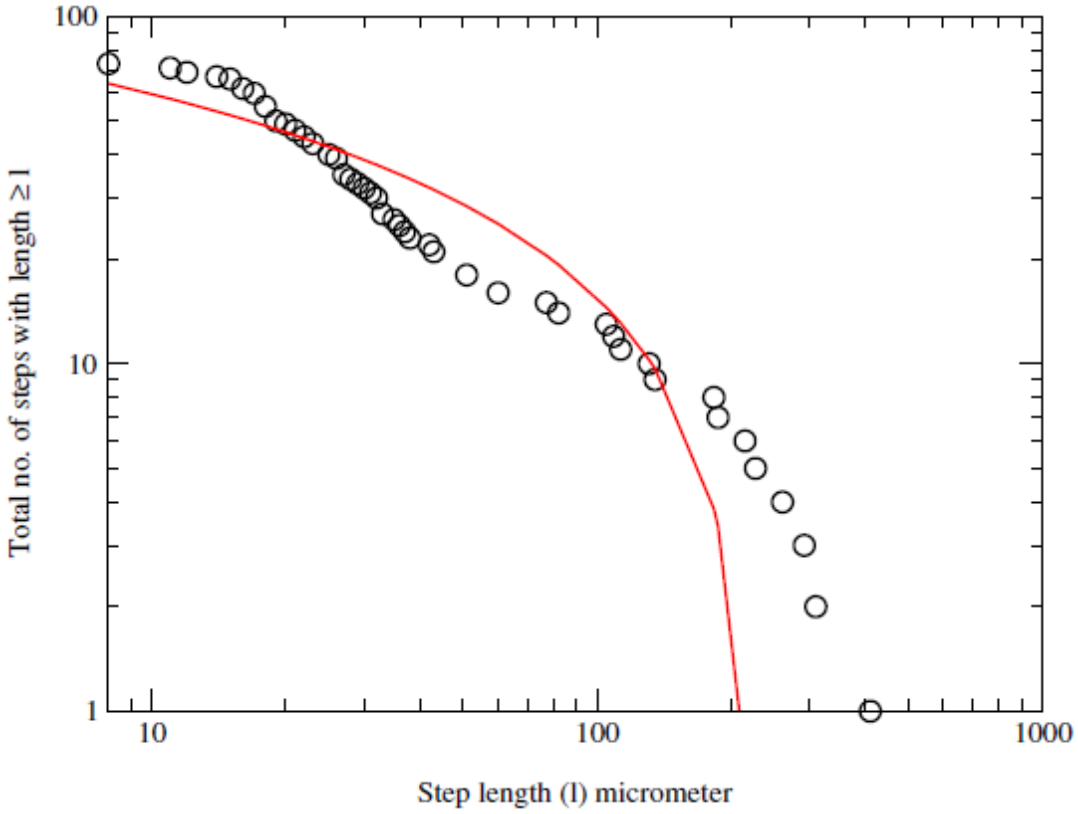


Pattern resembles a Devil's Staircase!

- At higher resolutions new rings appear, i.e. new steps appear between the existing ones.
- Ideally infinite number of steps exist between any two steps.
- For real systems finite cut-off.

Cumulative distribution of step lengths

Number N_l of steps with length ≥l and plotting N_l against l.



Curve can be approximately fit by a logarithmic function of the form

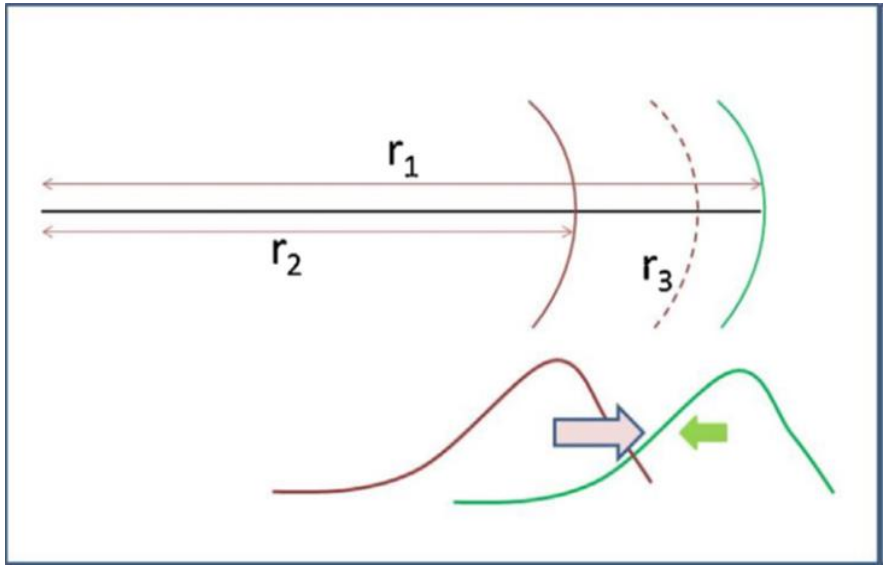
$Y = -A - B \ln X$

Roy et al. Applied Surface Science, 2015;357:10001006.

A Simple Deterministic Model

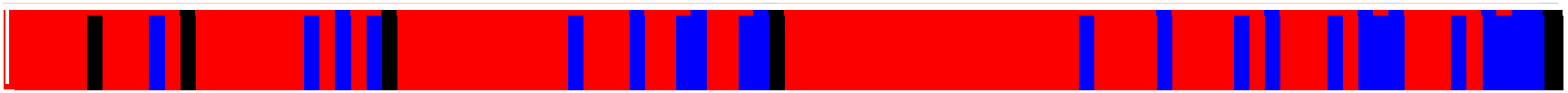
Advection-Diffusion:

Produces rings whose radii are related by a constant ratio b = r2/r1.



Only Diffusion :

Produces rings whose radii are related by a constant ratio c = r2'/r1'.



$$r_{n+1} = r_n(1-b)+br_1$$

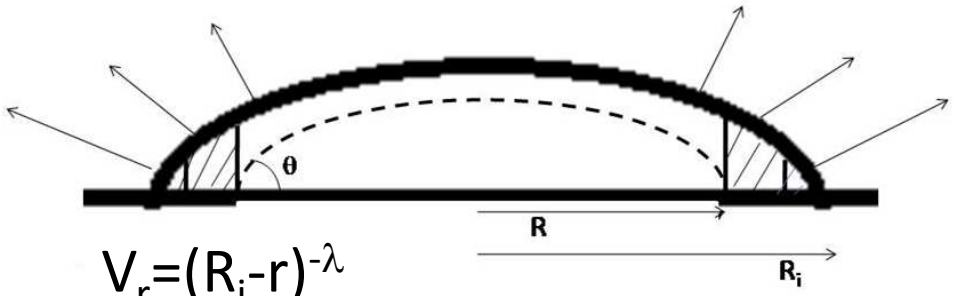
$$r'_{m+1} = r'_m(1-c)+br'_2$$

Kaya et al., J. Chem. Phys., 2010;133:114905.

Simulation

- Solution distributed on a square grid with initial uniform concentration

- Periodic boundary conditions in concentration and velocity



$V_r=(R_i-r)^{-\lambda}$

Where $\lambda = (\pi-2\theta)/(2\pi-2\theta)$

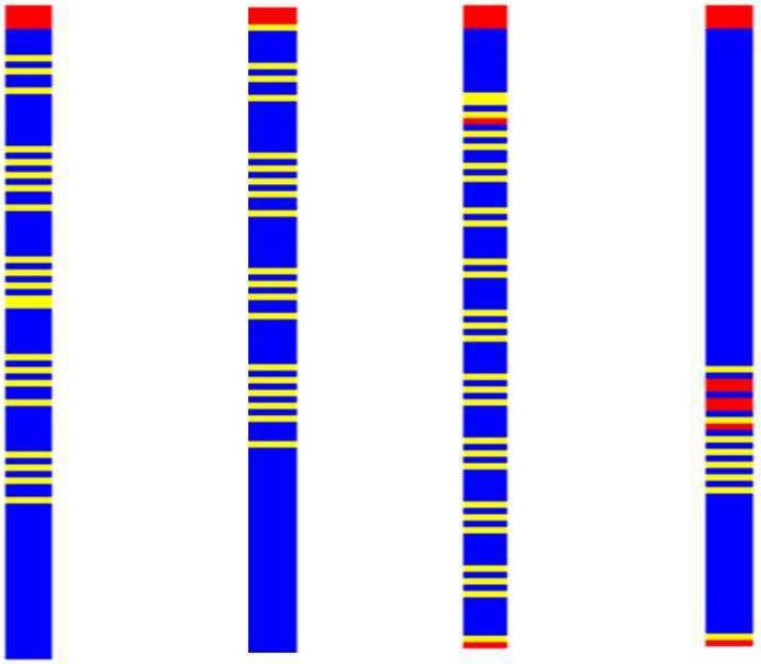
- Discretized advection equation (1) and diffusion equation (2) solved on grid alternately, using finite difference method to update concentration.

$$c_{i,j}^{t+1} = c_{i,j}^{t} + (\triangle t/(2 \triangle x)(v_{i,j+1}^{t} c_{i,j+1}^{t} - v_{i,j-1}^{t} c_{i,j-1}^{t}) \quad \text{....(1)}$$

$$c^{t+1}_{i,j} = \alpha(c^{t}_{i,j} + c^{t}_{i-1,j} + c^{t}_{i,j-1} + c^{t}_{i,j+1} + (1-4\alpha)c^{t}_{i,j} \quad \text{....(2)}$$

$$\alpha = D \triangle t/(\triangle x)^2 \quad \text{....(3)}$$

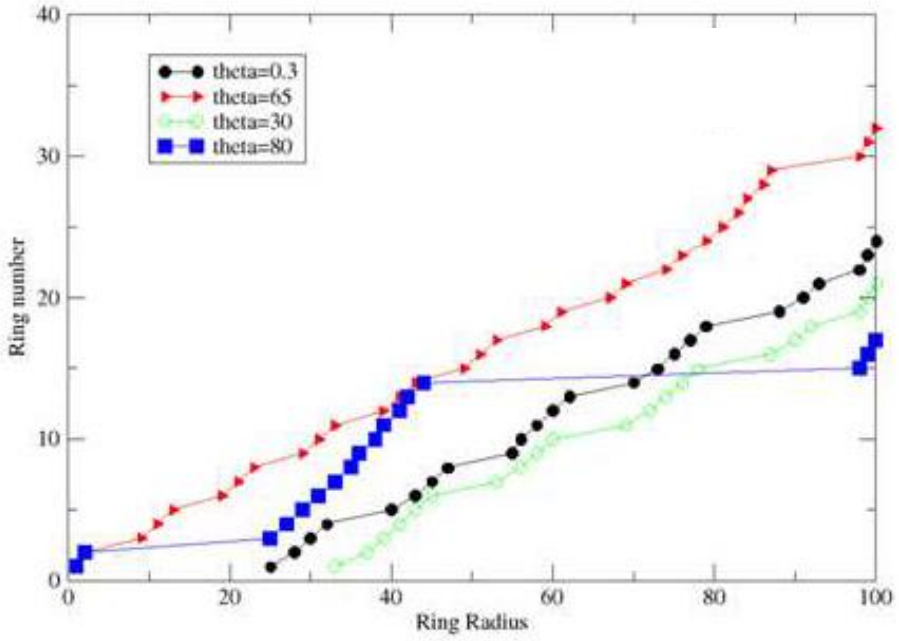
- If concentration exceeds C_{crit} , precipitation of solute occurs



θ=0.3 3.0 65.0 80

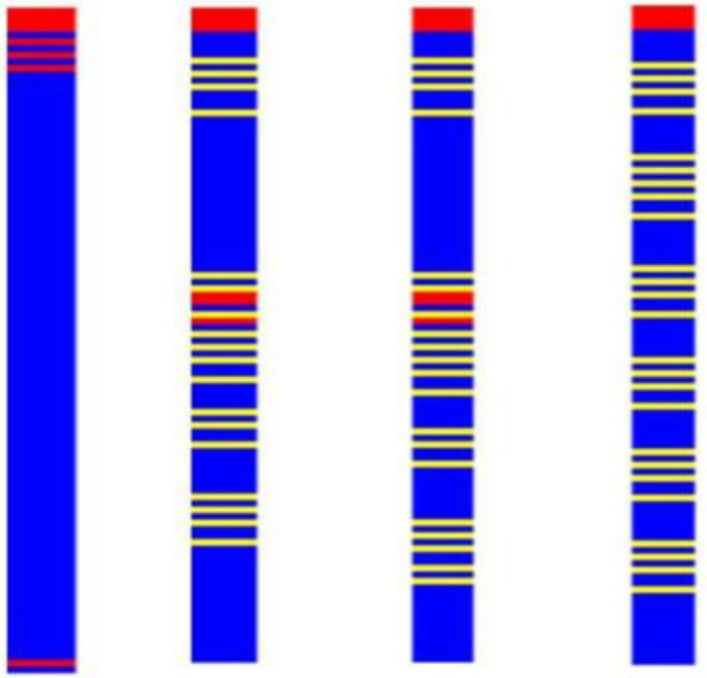
Effect of variation of contact angle

Diffusion coefficient constant: D= 1.5

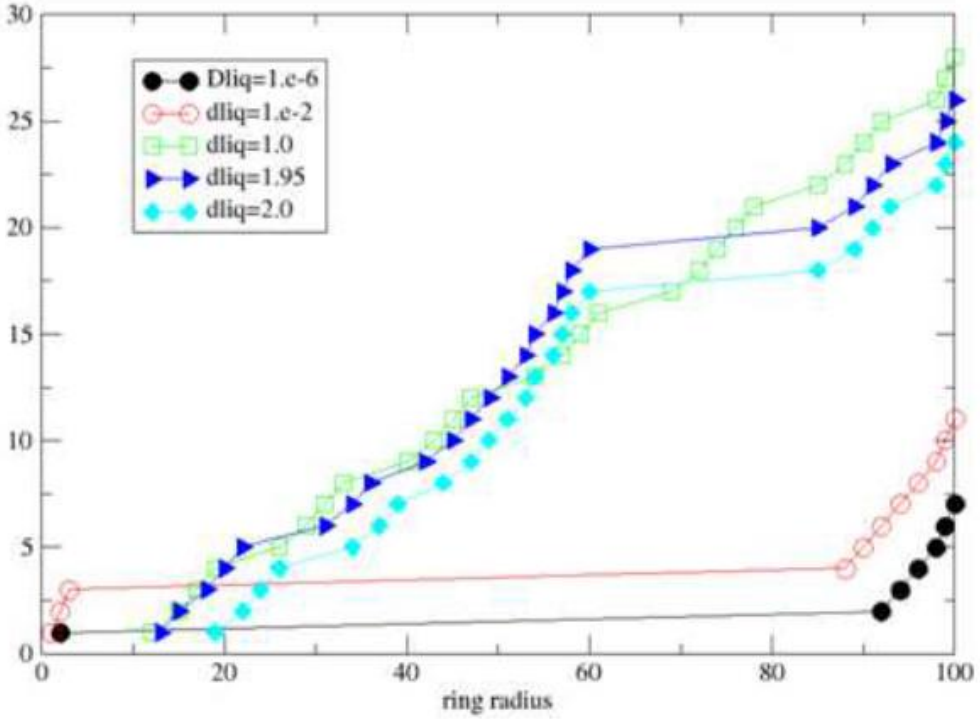


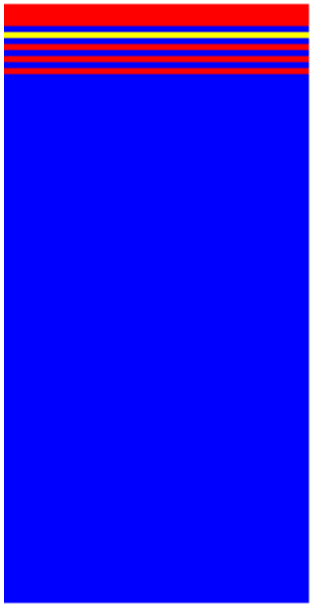
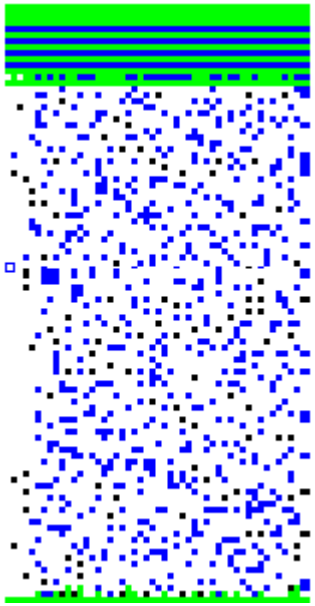
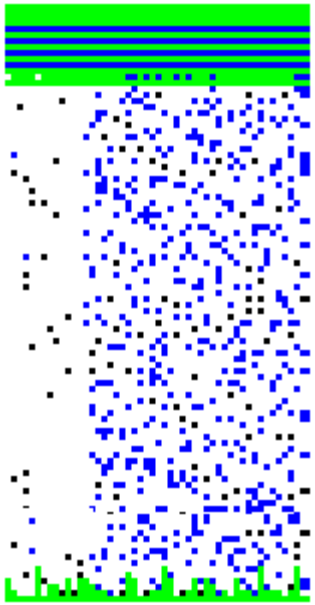
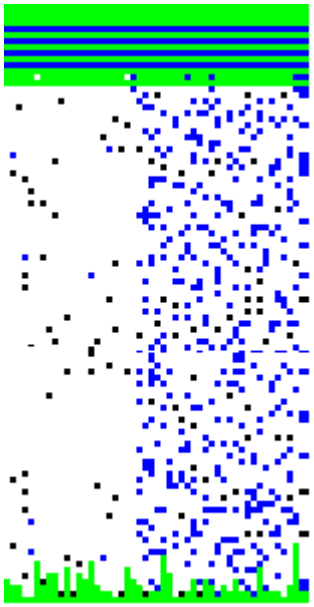
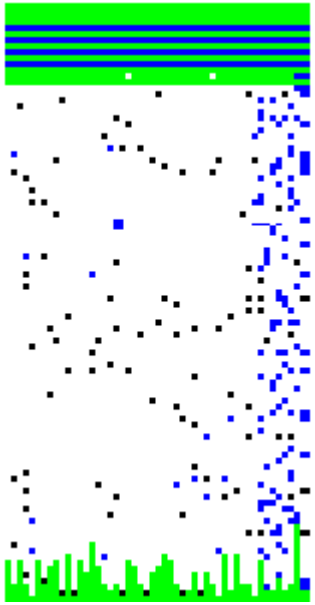
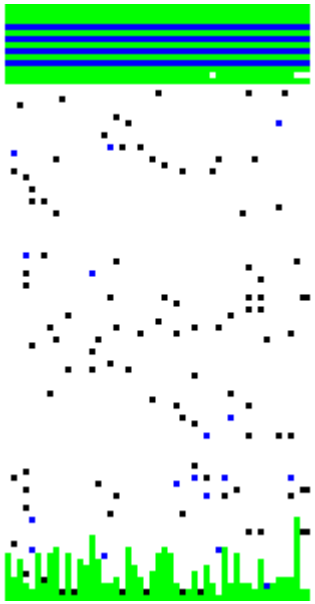
Variation of Diffusion Coefficient D

Contact angle constant= 30°



D= 1.10^{-2} 1.0 1.95 2.0



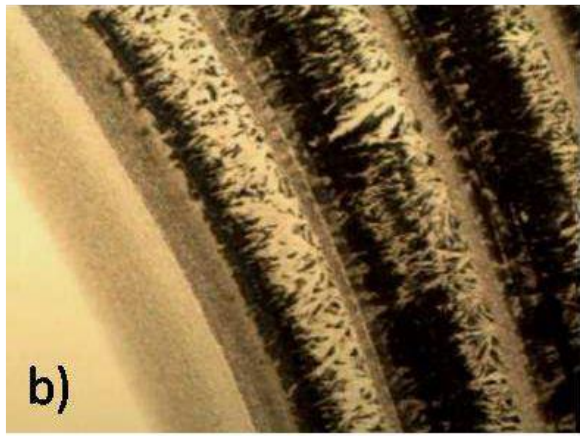
Dendritic growth

- Develops at precipitated rings
- The solute(ions) deposit on random ring site with a prob.

$$P=\nabla C.\ 1/k^{b}$$

k ≡ no. of neighbours

b ≡ parameter



D. Chowdhury et al., Soft Matter,2015.

Discussions

- The presence of high viscous gelatin solvent suppresses the growth of a prominent ‘coffee-ring’ and produces self-similar ring pattern that resembles the ‘Devil’s staircase’ through advection in conjunction to diffusion.

- Highly branched dendritic aggregates grow from the rings.

- salt crystallites form in the initial stages of evaporation, on further drying these crystallites act as seeds for dendritic growth.

The whole pattern encompasses multiple scales!

from nano-sized single crystals to
micron-sized dendrites and finally
rings with diameter of the order of centimeters

Things yet to be done

- Check for all the features on a circular geometry

- Incorporate the 3-dimensional aspect of droplet drying

Thank **You!**