Self-Assembly

Lecture 7

Dynamical Self-Assembly

Dynamic Self-Assembly

The biological example of writing information on a small scale has inspired me to think of something that should be possible. Biology is not simply writing information; it is doing something about it. A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvelous things - all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small which does what we want - that we can manufacture an object that maneuvers at that level!

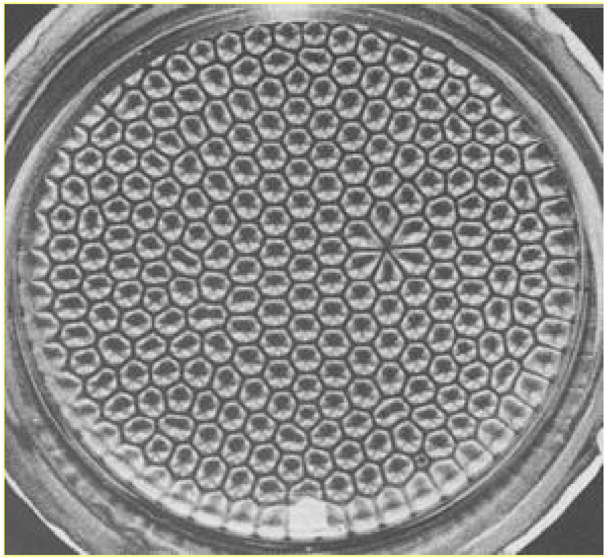
R.Feynman

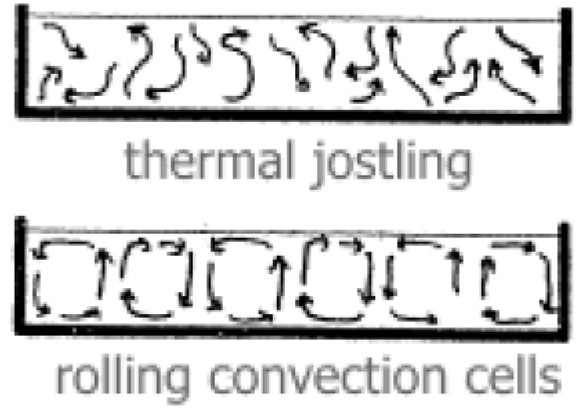
Complexity (Ilya Prigogine)

- “simple” processes (newtonian laws of motion, perfect gas etc.) – deterministic behaviour, future and past play the same role (time reversibility)
- “complex” processes: irreversible and stochastic (biological, climate changes, oscillating chemical reactions).

Bénard instability

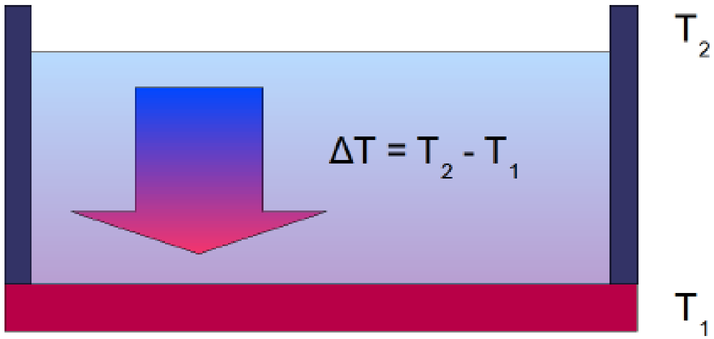
- Spontaneous self-organization in a liquid due to vertical temperature gradient





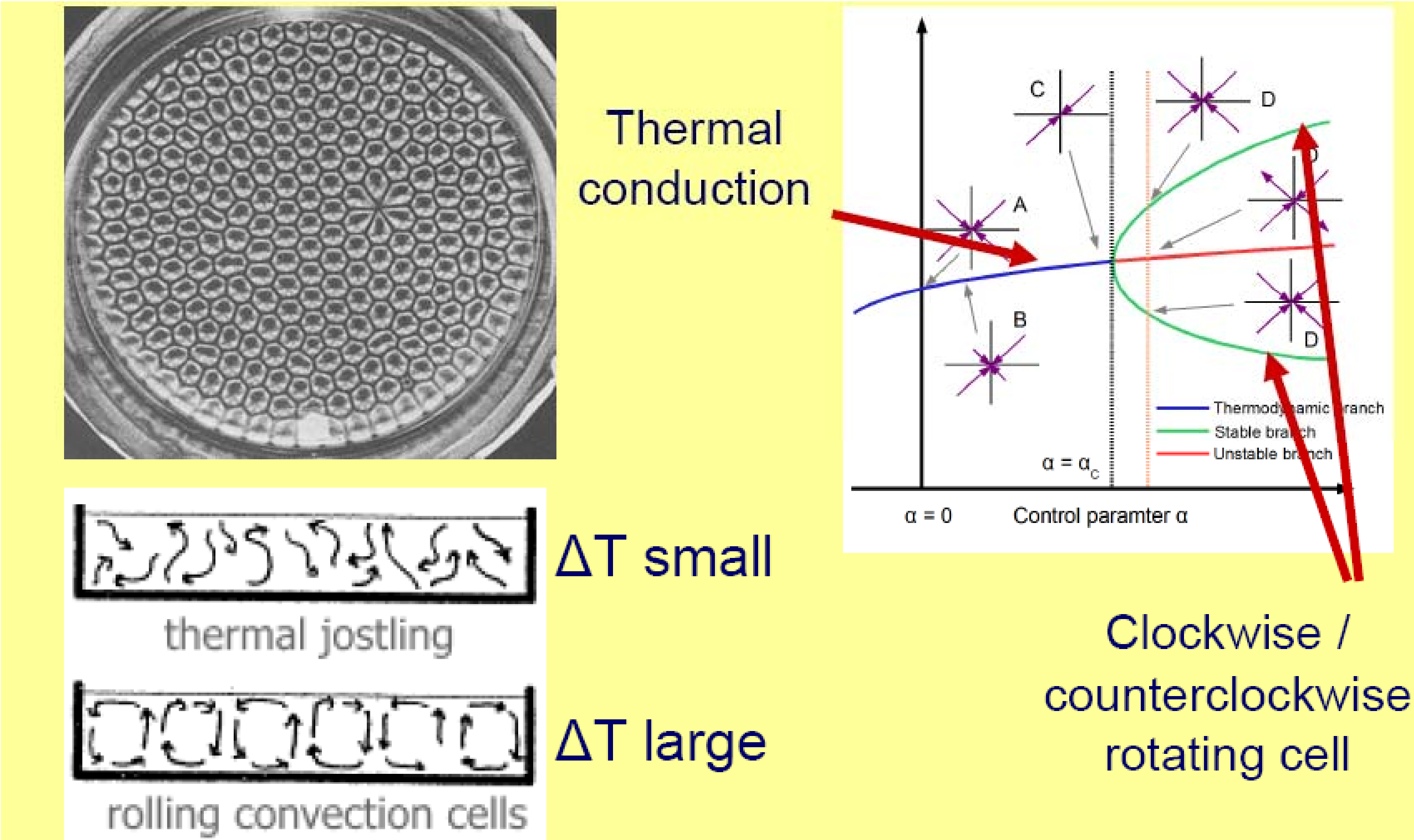
ΔT small

ΔT large



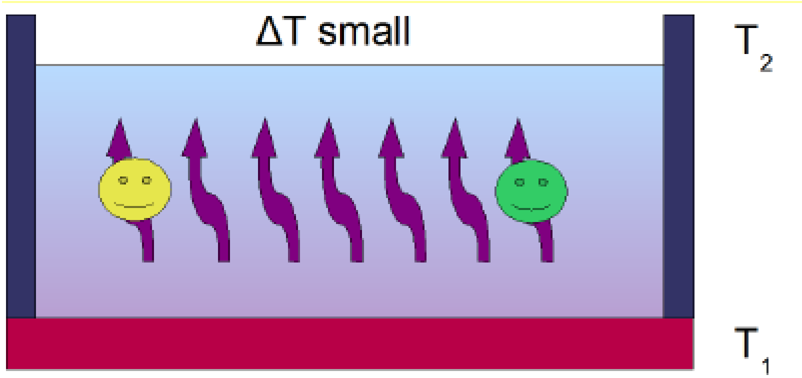
Bénard instability

I.Prigogine: “A characteristic feature of **far-from-equilibrium** conditions is the possibility of **bistability**. For given boundary conditions, there may be more than one stable solution”



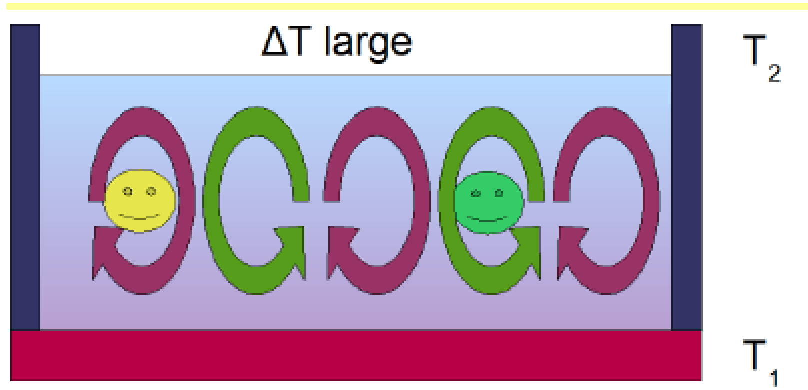
Bénard instability

- Symmetry breaking



Environment( ) = Environment( )

The world is uniform. Space is everywhere the same. A little observer has no notion of space.



Environment( ) ≠ Environment( )

The world is patterned. Space is heterogeneous. A little observer has the possibility to say where she is

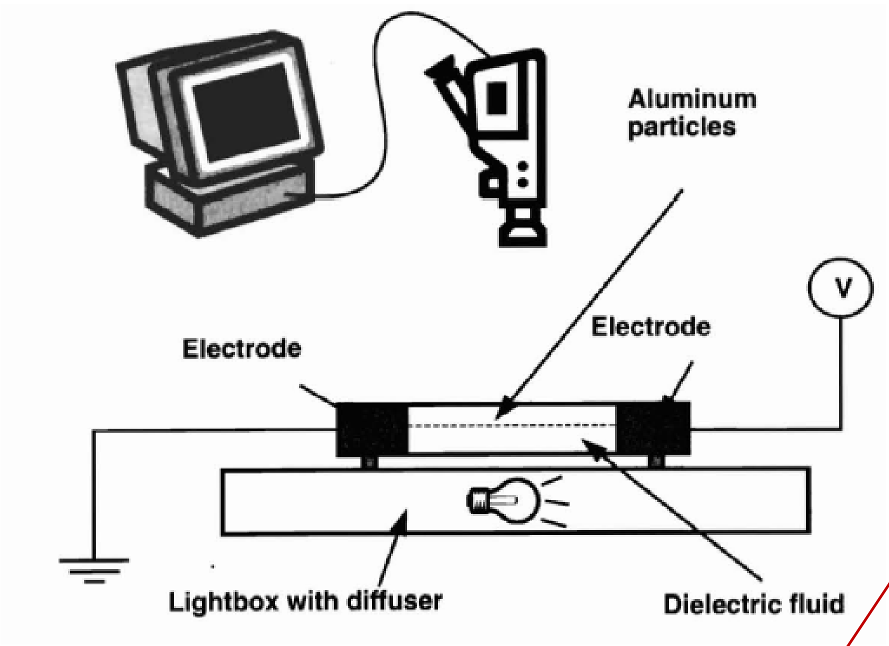
The interactions between the water molecules have a range of about 10^{-10}meter. The structures we observe are of the size of 10^{-3}metres.
10^{21}molecules have to move in a correlated manner!

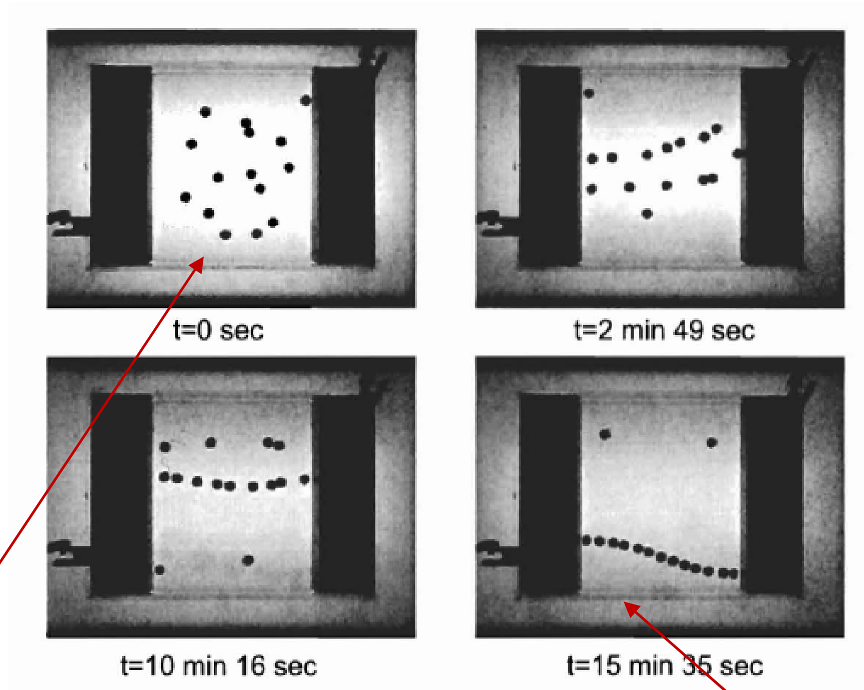
Dynamic self-assembly

- States to achieve are **not in thermodynamic equilibrium.**
- The system **dissipates energy**.
- Interactions between components are not constant, but may change between attraction and repulsion.
- Remain ordered only so long as the system continue to **dissipate energy**

Dynamic self-assembling wires

- Example: self-assembly of aluminium particles “Pelesko chain”





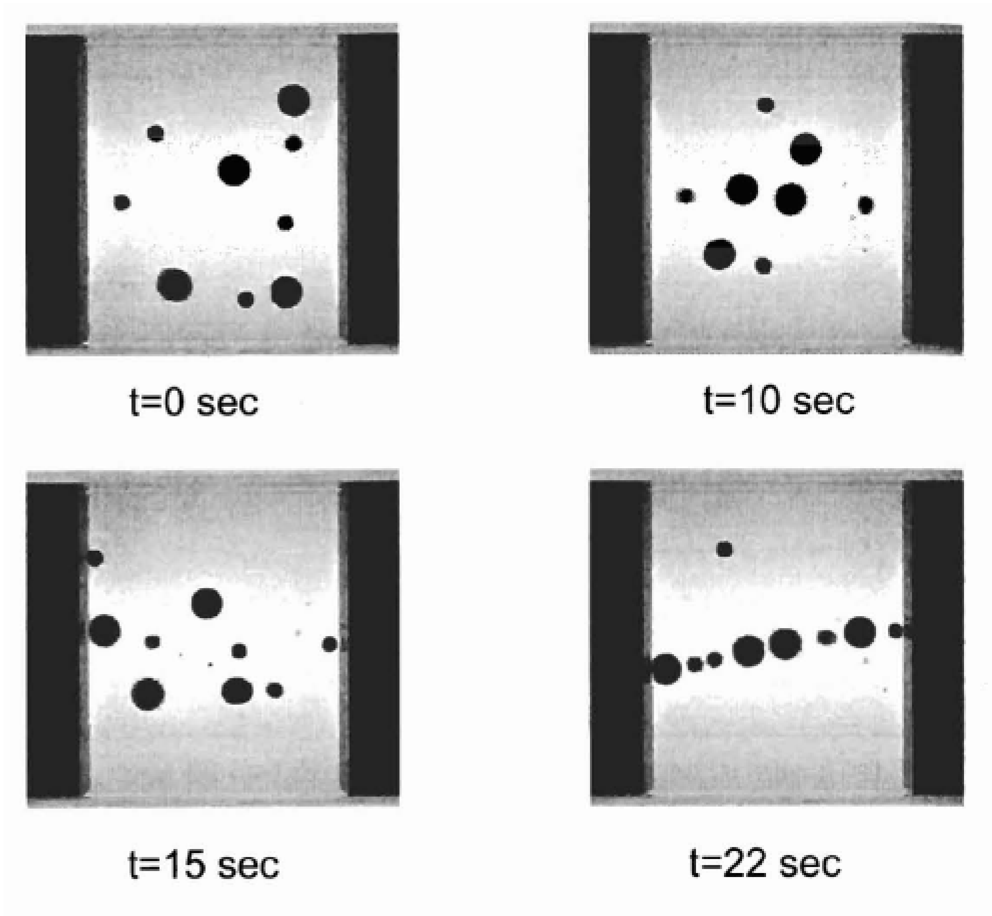
A positively charged disc moves to the negative electrode, switches its charge, and floats to the positive electrode.

chain of oscillating particles

- structured particles: Aluminium disks
- binding force: electrostatic force. Presence of electric field and electrodes causes formation of chain and oscillation
- environment: viscous liquid, gravity and lift forces

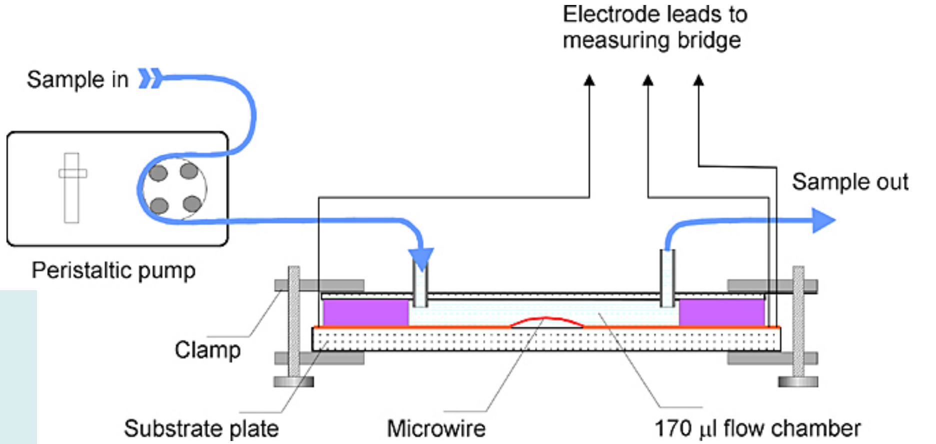
Dynamic self-assembling wires

- Self-assembly of large and small particles. $V_{applied}$~19.8 kV



Self-assembling microwires

- The approach described above can be scaled down
- Dielectrophoretically driven assembly can be used to create contacts on a microscale

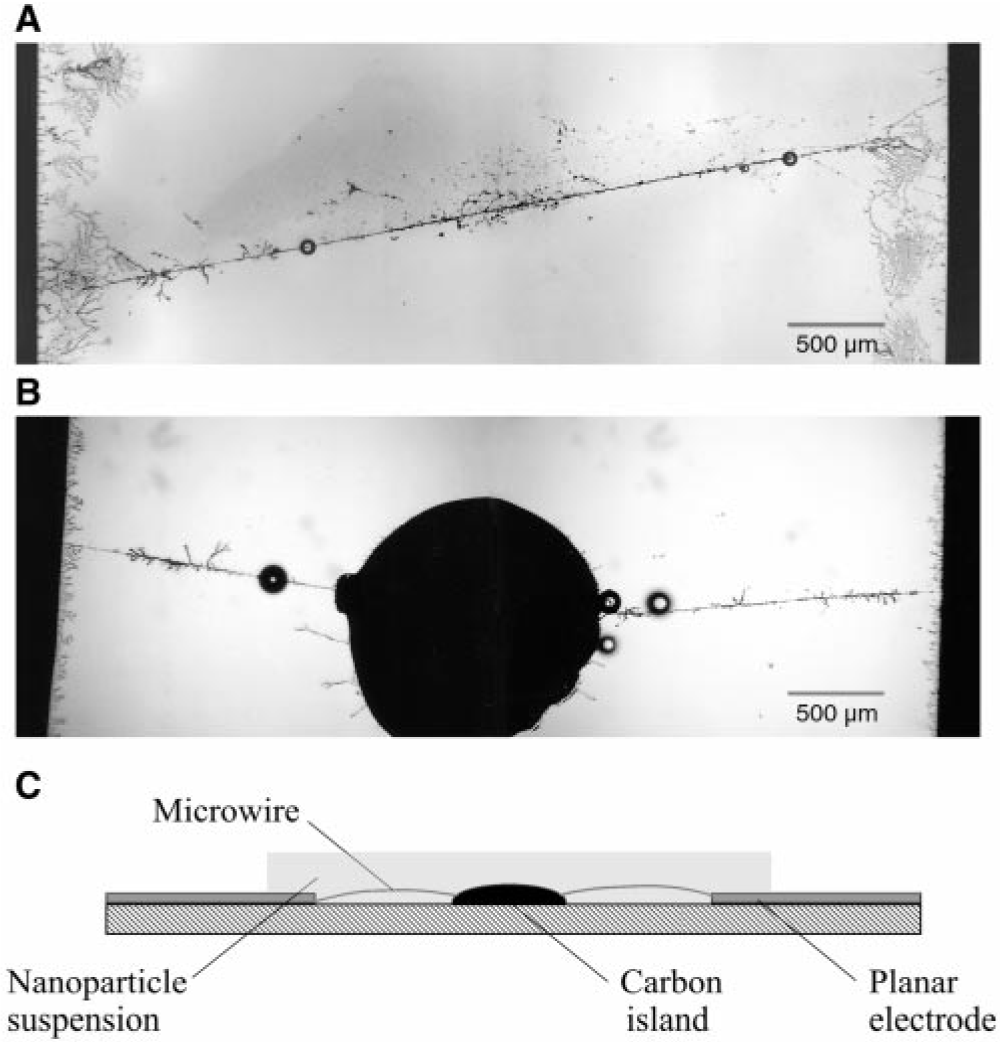


- Experimental conditions:
- Gap between electrodes: 2mm-1cm
- Voltage 50-250Vac; 50-200Hz
- Field ~250V/cm

K.Hermanson et al, Science 294, 1082 (2001)

Self-assembling microwires

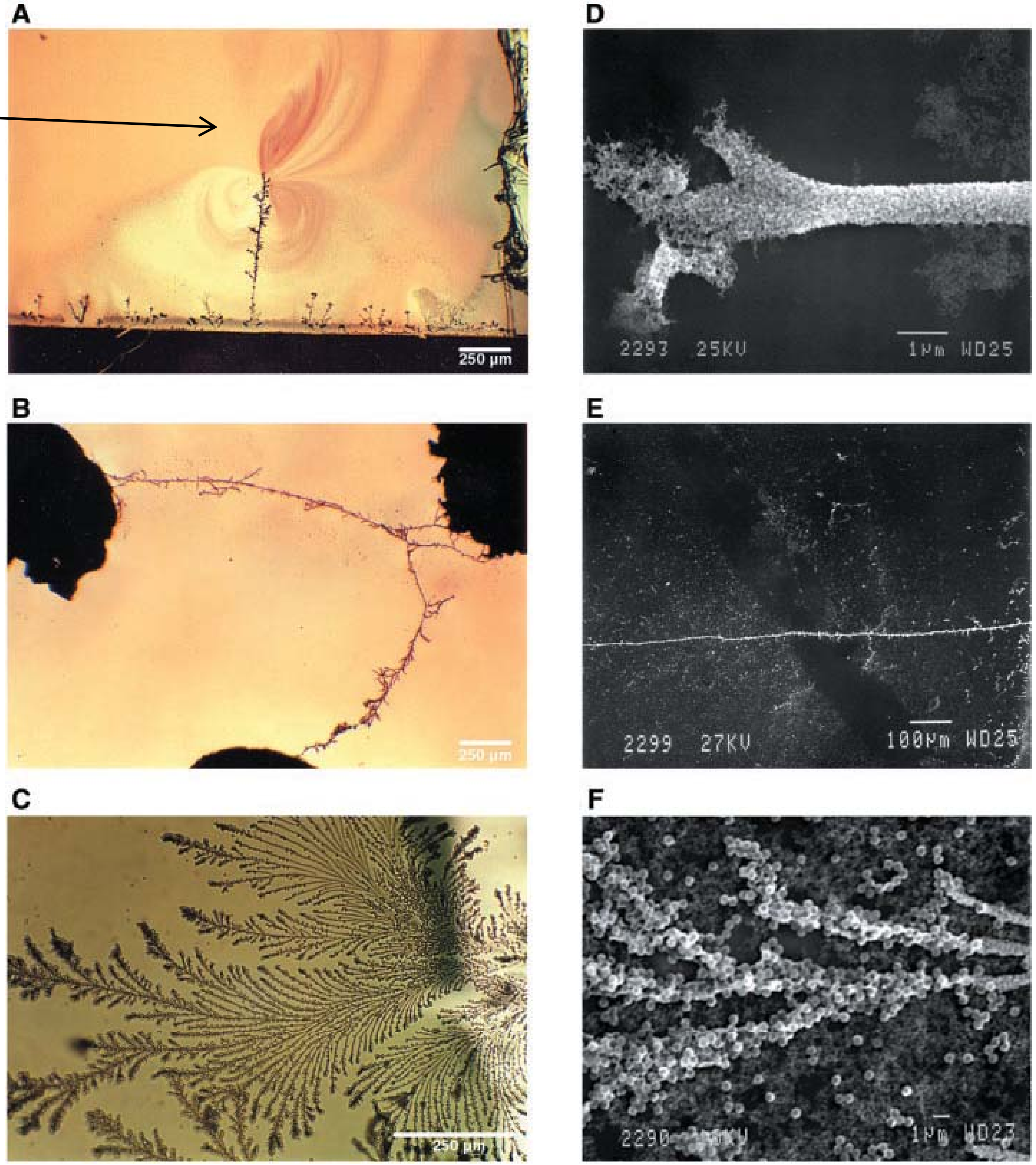
- the wire starts to propagate immediately when nanoparticles are added
- typical propagation speed ~50µm/s



Calculation shows that DEP forces are not sufficient to assemble particles, how then it works?

Self-assembling microwires

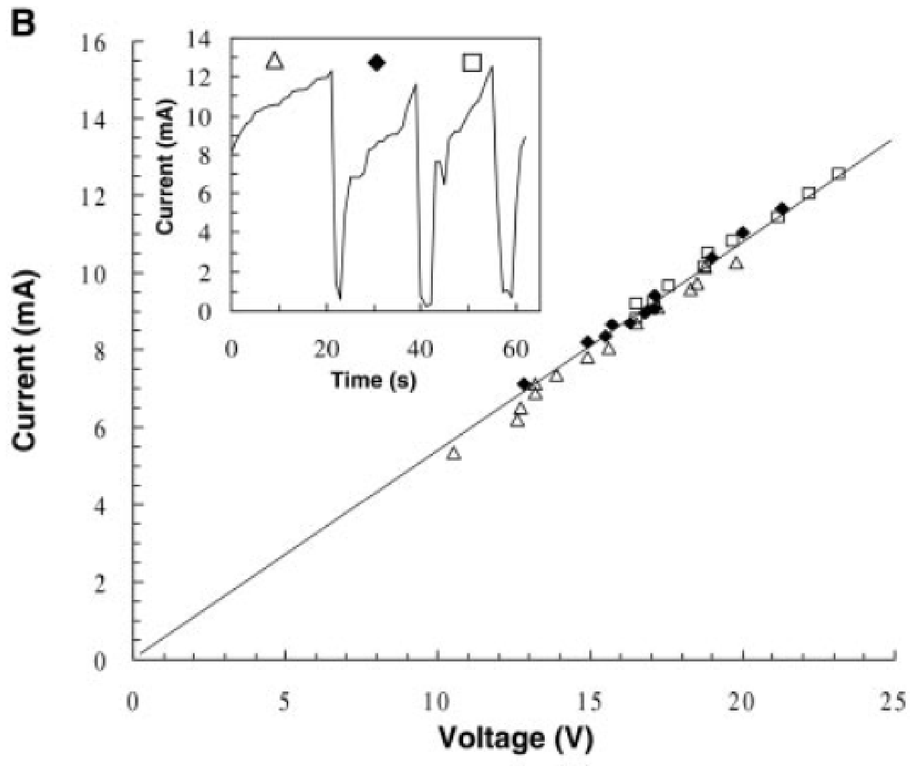
- growth mechanism: collective effect: upconcentration in front of the growing wire
- smaller particles lead to slower growth and more **fractal** wire morphology
- **electrolyte** concentration increase, makes aggregation faster
- composite wires of Au-NP and polystyrene spheres can be created
- wires are **self-repairing**
- wires show linear **ohmic behaviour**
- resistance changes if e.g. thiols are added



Self-assembling microwires

- Conductivity and self-repair of the wires

wires self-repair



Self-assembling microwires

- Summary of parameters affecting micro-wire growth

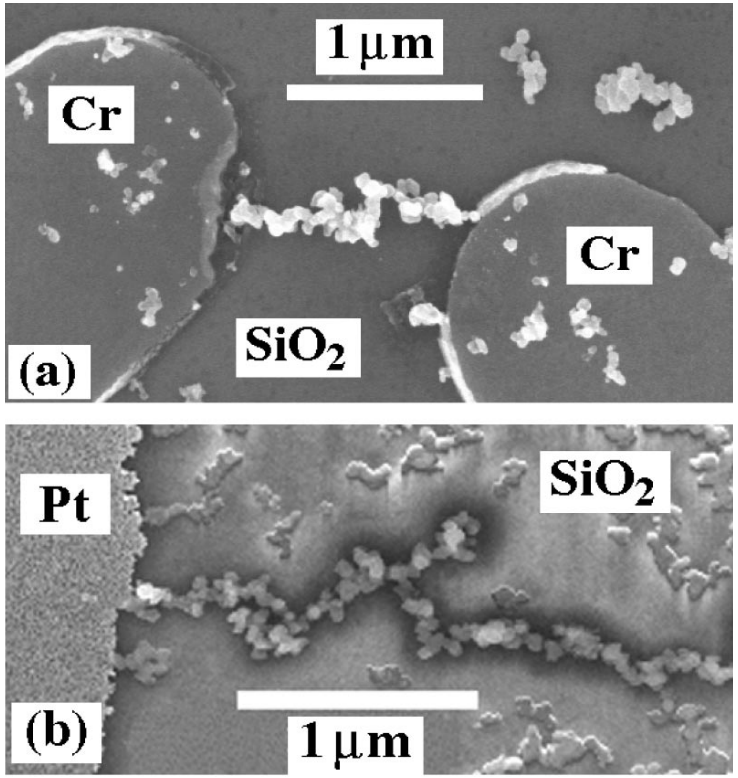
Parameter	Range	Growth rate	Branching	Thickness
Voltage ↑	$23\,\frac{V}{mm} <$ slow $> 40\,\frac{V}{mm}$ fast $> 45\,\frac{V}{mm}$	↑	↓	↓
Frequency ↑	10 Hz < > 150 Hz	↓	↑	↓
Particle concentration ↑	> 0.13%	↑	Constant	↑
Particle size ↑ (constant weight %)	15–30 nm	↓	↓	Constant
Particle size ↑ (constant particle concentration)	15–30 nm	↑	↓	↑
Electrolyte concentration ↑	$(0–3) \times 10^{-4}$ M NaCl	↑	Constant	↑

Self-assembling nanowire

- 1D nanoparticles arrays are expected to exhibit unusual electical behaviour
- Question: how to arrange nanoparticles into a device

Experiment:

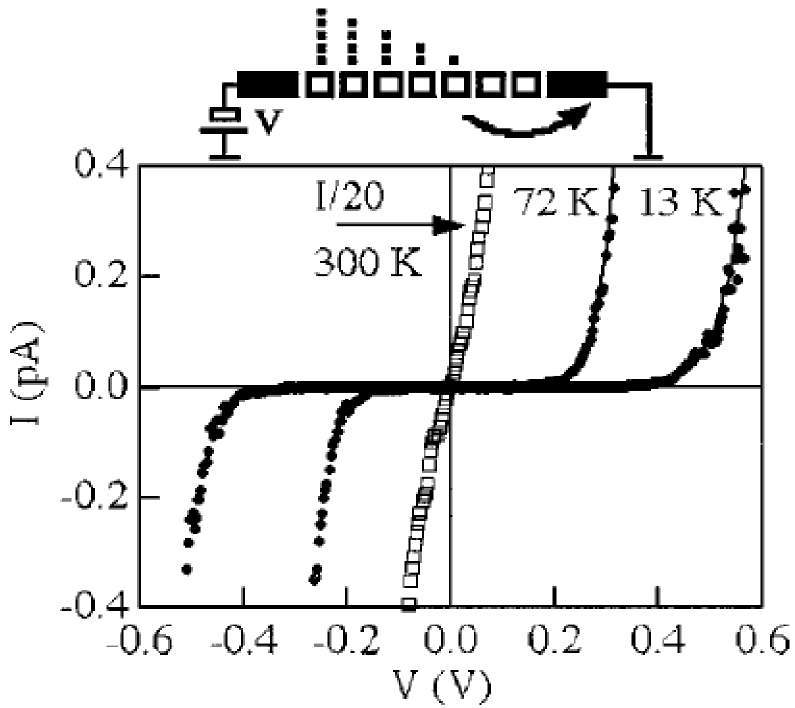
- Cr-microelectrodes on SiO_2/Si
- 40Vdc through 1GOhm resistor
- 30nm graphite nanoparticles suspended in toluene

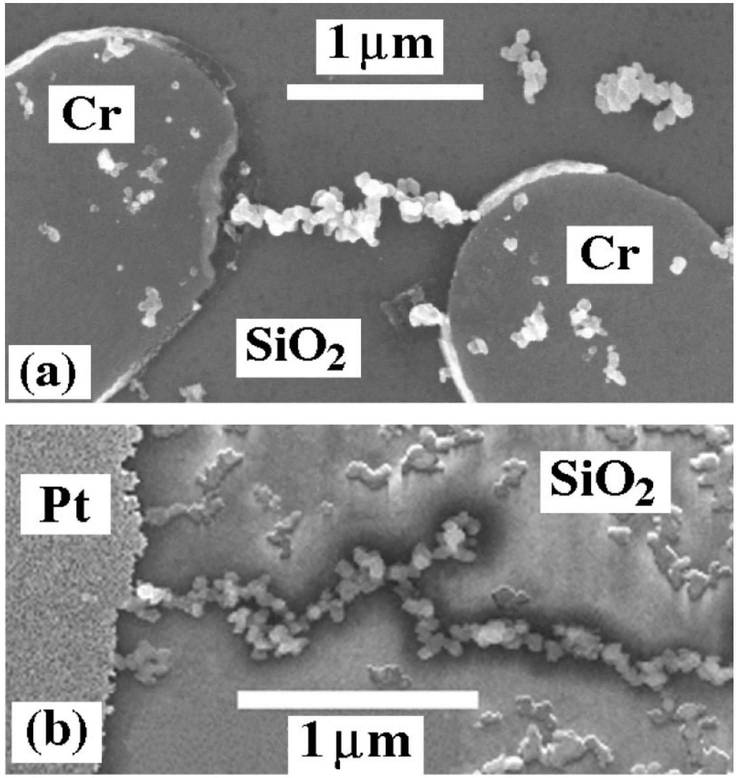


Bezryadin et al, Appl.Phys.Lett 74, 2699 (1999)

Self-assembling nanowire

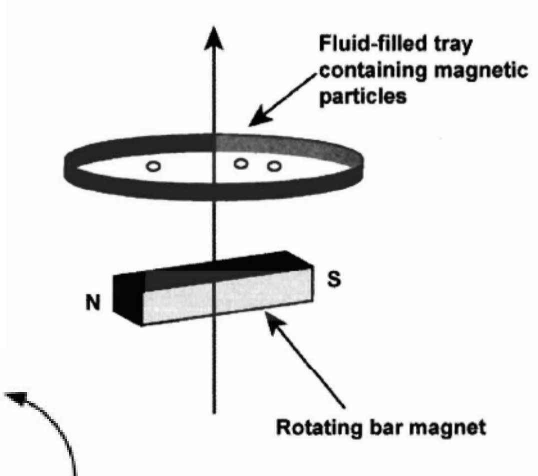
- IV-characteristics of nanowires show threshold voltage at lower temperature (72K and below).

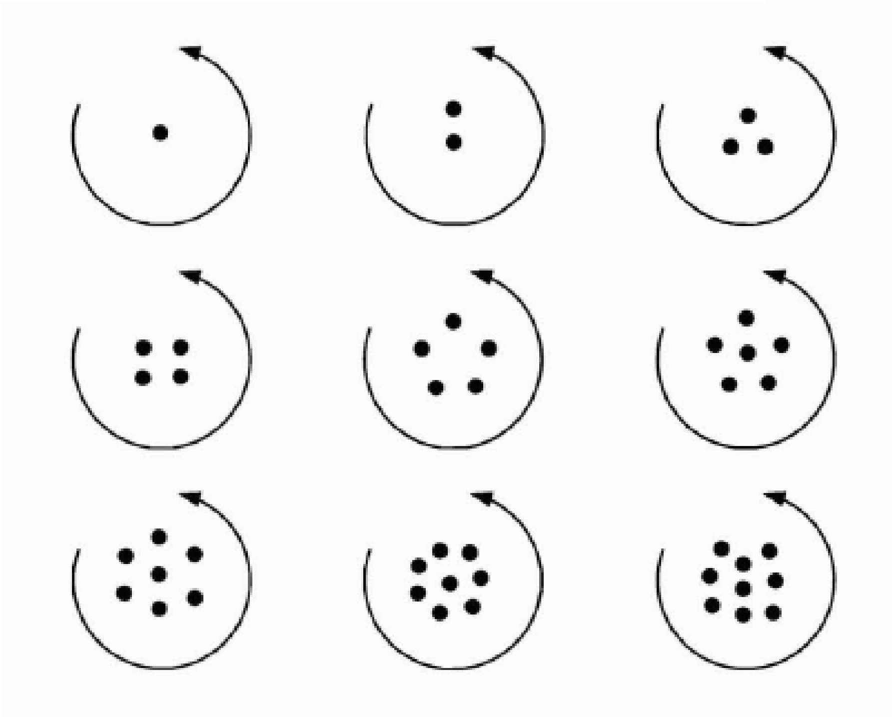




Magnetically driven dynamic systems

- rotating magnetic field draws particles to the center while hydrodynamic forces counteract the movement





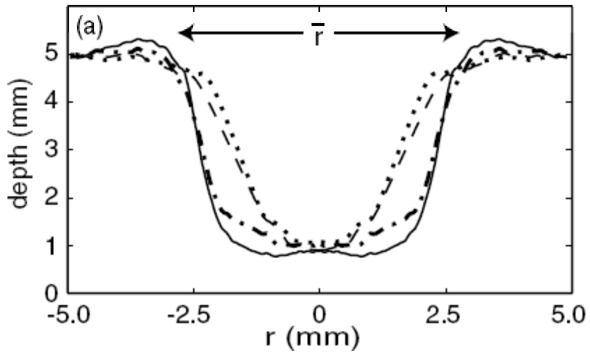
Mechanically driven dynamic systems

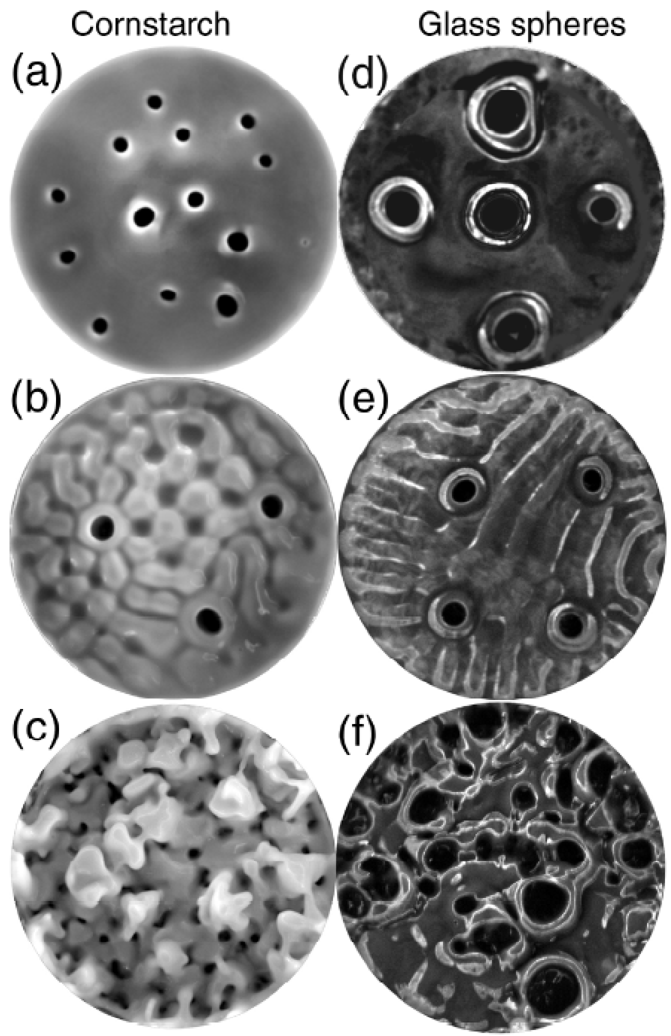
- Mechanical vibration of particle suspension in liquid can lead to dynamic self-assembly due to interplay of mechanical and hydrodynamic forces

Experiment:

- cornstarch or class microspheres in liquid are oscillated vertically with frequency with 50-180 Hz

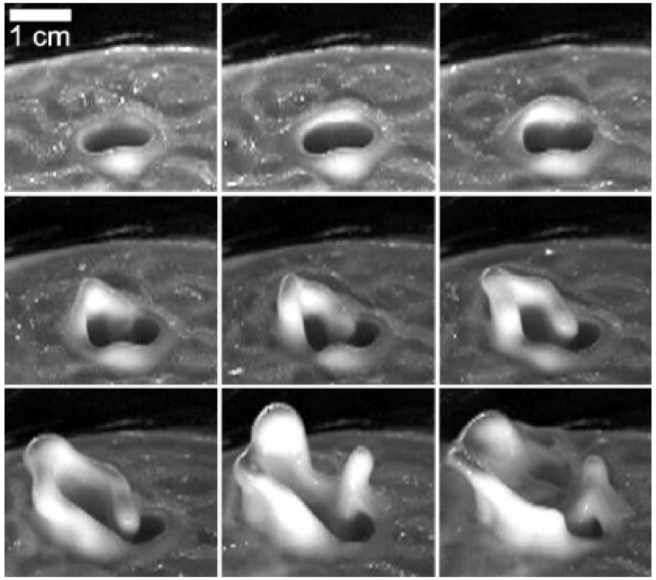
Cross section of a hole:

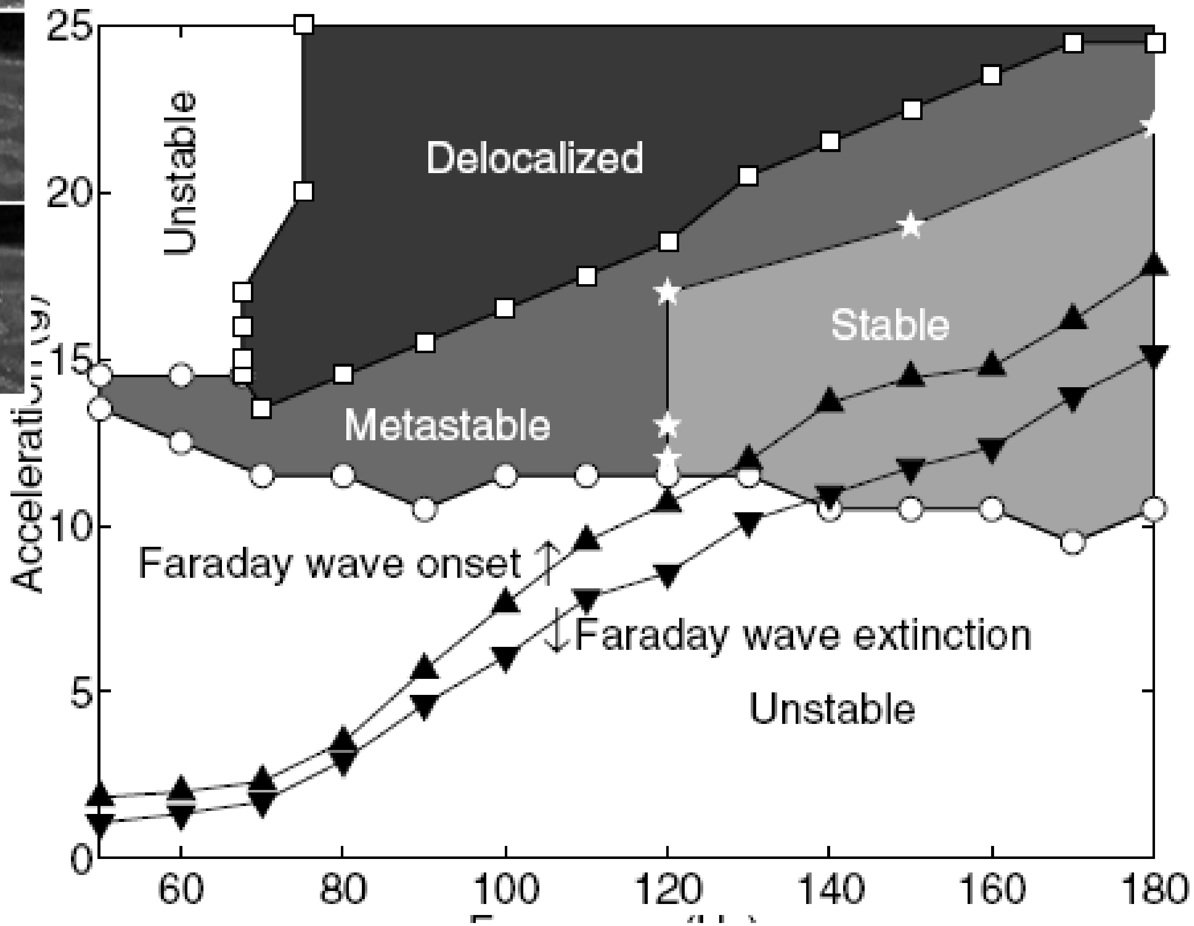




Mechanically driven dynamic systems

- Phase diagram for the hole formation

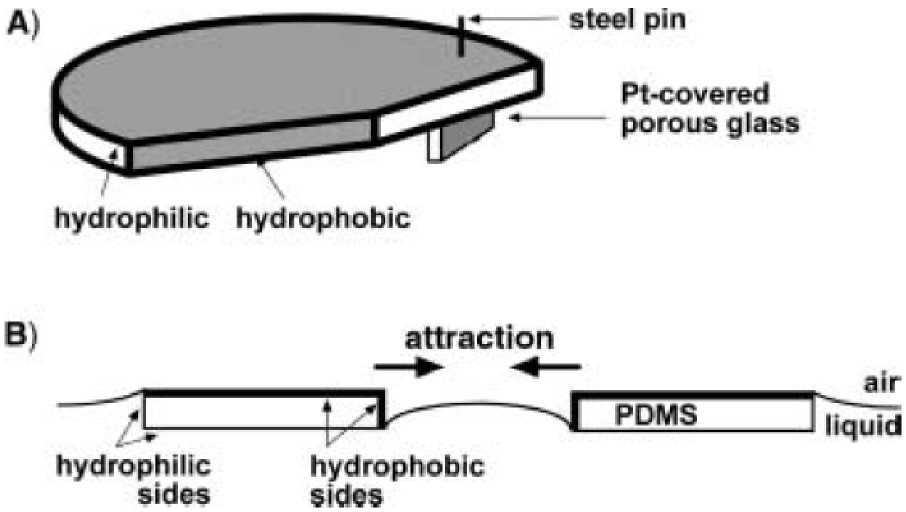




the onset of
delocalized state

Self-propelled systems

- Many complex systems can both **move** and **interact** with each other

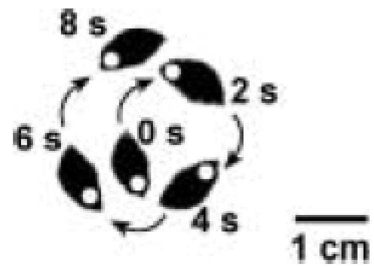


plates can move autonomously for several hours due to catalytic evolution of O_2 from H_2O_2 solution on Pt-covered fin

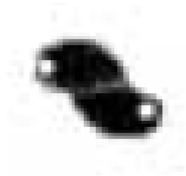
Whitesides et al, Angew.Chem. 41, 652 (2002)

Self-propelled systems

- Particles are **chiral** (left-right symmetry is broken). Single plate rotates in the direction determined by its chirality
- Two pairs configuration are possible: the same or opposite chirality



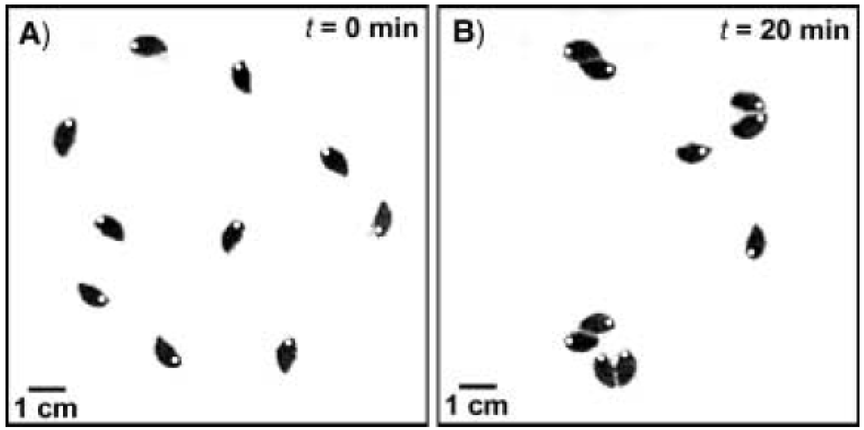
individual particle



opposite chirality, move straight

same chirality, rotate

Observed: Pair formation that slows down in time due to decrease in amount of available partners. No preference for pairs of same or opposite chirality

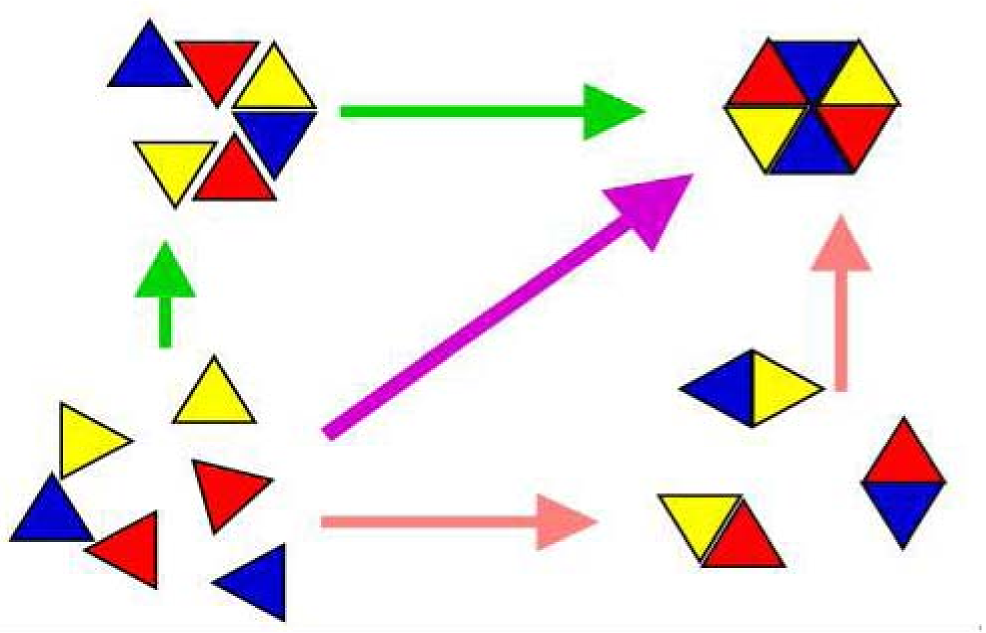


- The question: How many autonomous components required to observe emergence in a system?

Whitesides et al, Angew.Chem. 41, 652 (2002)

Programmable self-assembly

- The “structured particles” discussed before are dumb ☺, biological particles are smart, they can change the interaction depending on the environment



Static self-assembling system:

- the lowest energy state corresponds to hexagons
- due to local minima the other shapes are produced, but their concentration will drop in time

Programmable self-assembly

- From reaction point of view:

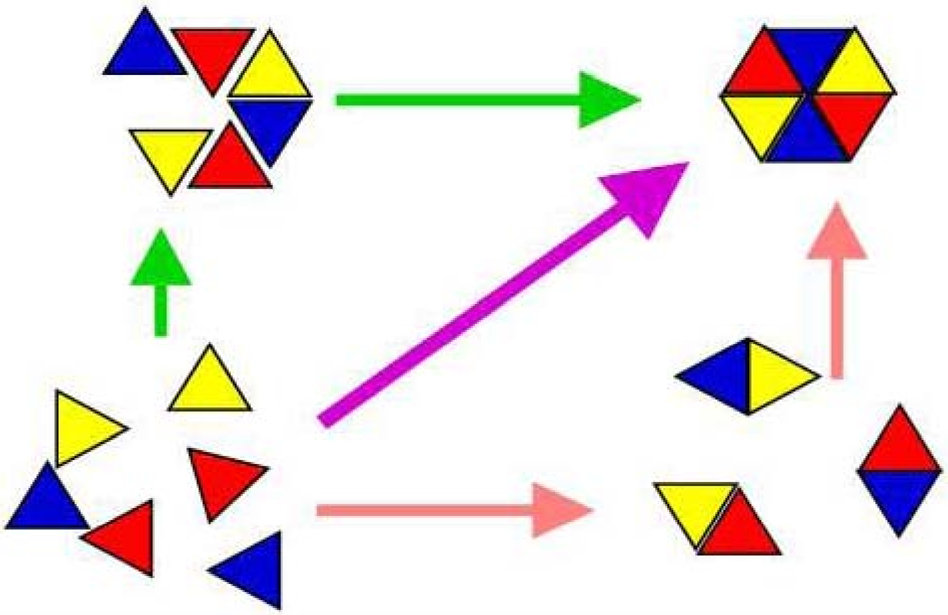
$$P_1 + P_1 \rightarrow P_2$$

$$P_1 + P_2 \rightarrow P_3$$

$$\frac{dp_1}{dt} = -kp_1^{\ 2} - kp_1 p_2$$

$$\frac{dp_2}{dt} = kp_1^{\ 2} - kp_1 p_2$$

$$\frac{dp_3}{dt} = kp_1 p_2$$

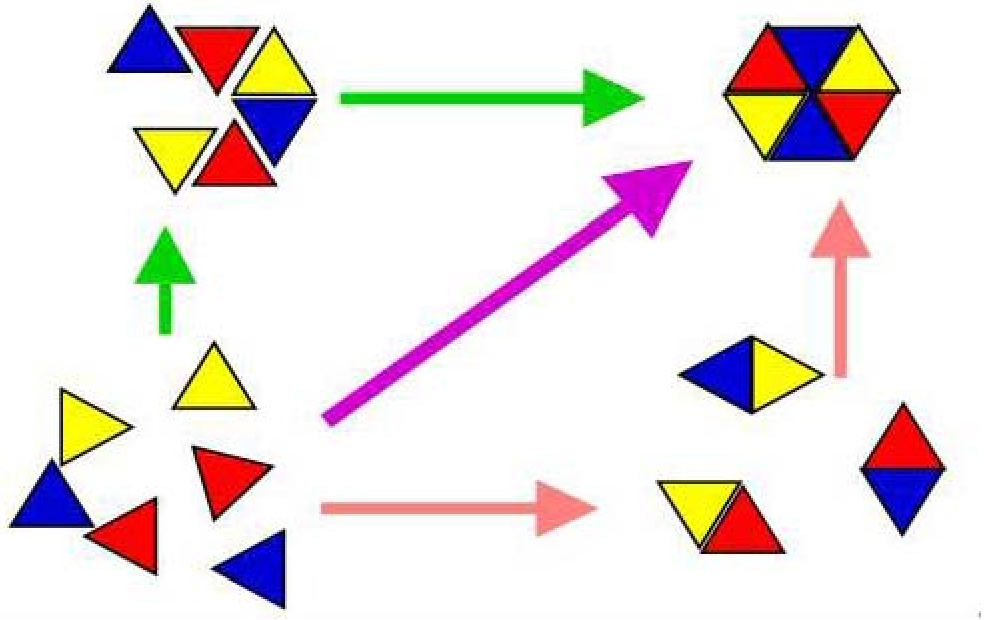


- Generally p_2 will go to zero.

Programmable self-assembly

- If we need to stabilize, say dimers, we can add a programmed reaction pathway:

$$P_3 \rightarrow P_1 + P_2$$



$$\frac{dp_1}{dt} = -kp_1^{\,2} - kp_1 p_2$$

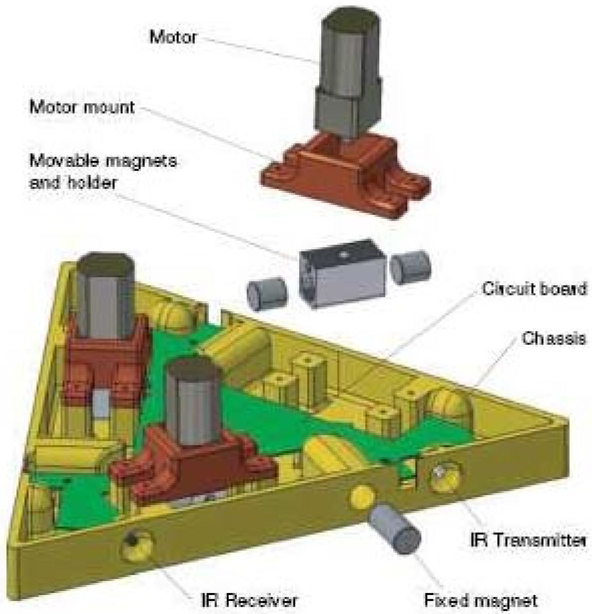
$$\frac{dp_2}{dt} = kp_1^{\,2} - kp_1 p_2 + k_p p_3$$

$$\frac{dp_3}{dt} = kp_1 p_2 - k_p p_3$$

- Breakup of P_3 will lead to desired P_2! But to do this the particles need to know if they are part of P_2 or P_3.

Programmable self-assembly

- Embodied process control: a particle can take decision based on its state and the state of the neighbours
  (Pfeifer: "a part of the computation necessary to fulfill a given mechanical task can be outsourced to the body").



Each particle contains: three controllable magnetic latches, three infrared tranceivers and a logical circuit

Fig. 1. Four programmable parts partially assembled into a triangle. The parts bind upon random collisions and communicate via IR, deciding whether to remain bound or to detach. A graph grammar stored on the microcontroller of each part determines the ultimate global structure that will emerge. The parts are not self-motive but instead are "mixed" on an air table by overhead oscillating fans.

Eric Klavins and Nils Napp, 2005

Dynamic self-assembly: conclusion

- For dynamic self-assembly to occur out-of-equilibrium conditions with energy flow are required
- Competitive and cooperative efforts of various forces lead to formation of spatial and temporal structures
- Use of external driving forces may be avoided by creating self-propelling particles
- Embodied process control may be a relevant source for design principles for dynamic self-assembly.
- Dynamic self-assembly, where systems dissipate energy, is only at its beginning.