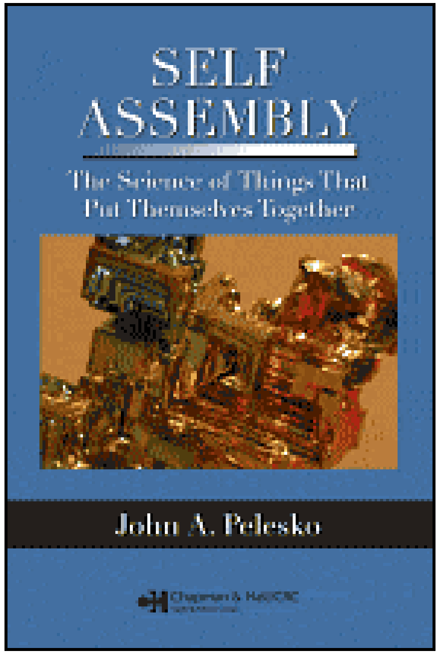
Self-Assembly

Lecture 1

Introduction to Self-Assembly

Course schedule

1. Principles of Self-Assembly.
2. Models of Self-Assembly
3. SAM and LB films: structures and applications
4. Surfactant self-assembly I
5. Surfactant self-assembly II
6. DNA and RNA self-assembled structures
7. DNA-protein interaction
8. Dynamic self-assembly: forming order in out-of-equilibrium systems



Self-Assembly

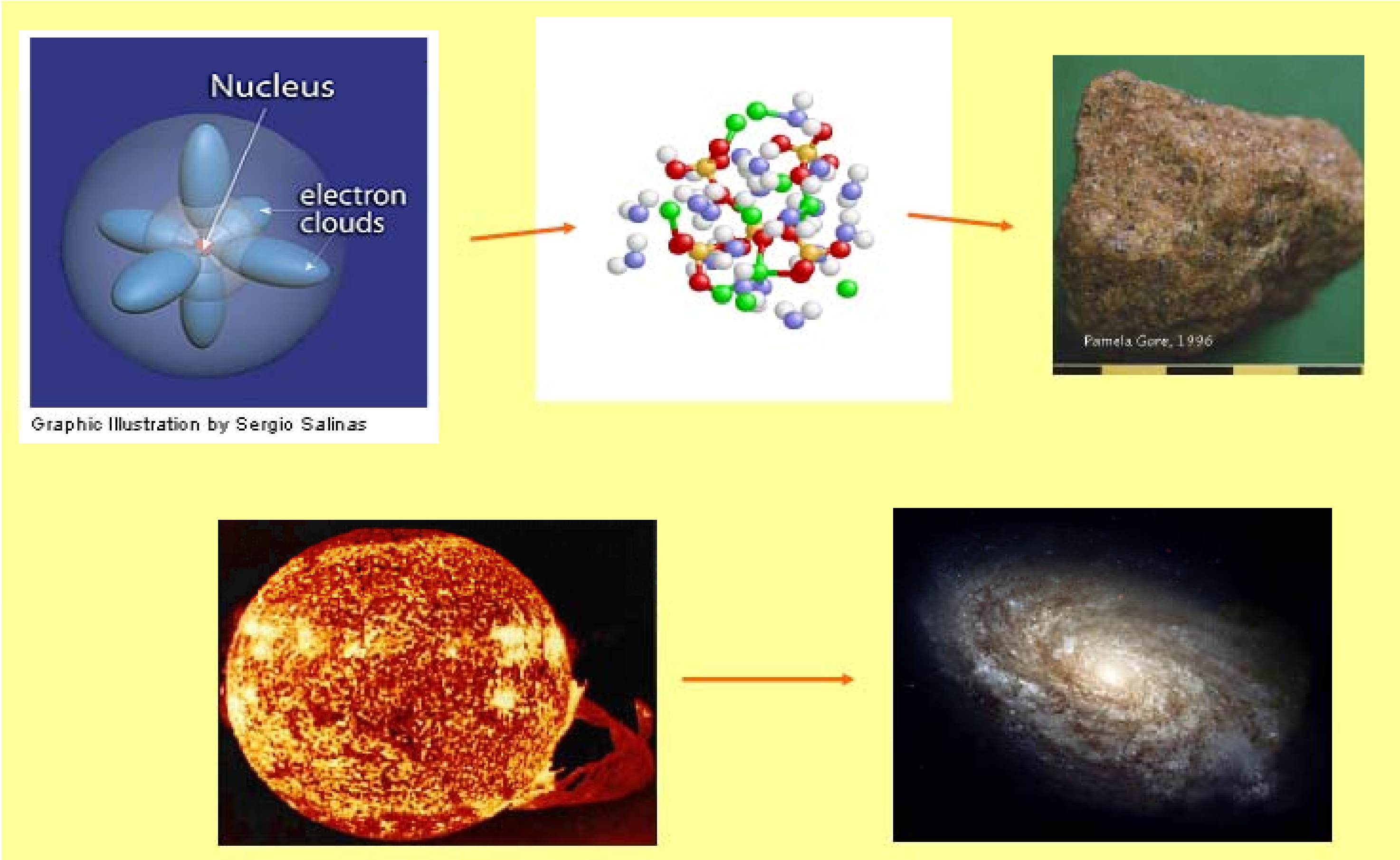
- "Self assembly is the science of system that put together themselves."

  John A. Pelesko
- ".. We limit SA to the spontaneous formation of organized structures from many discrete components that interact with each other directly and/or indirectly through their environment. In addition, the assembling components may also be subject to various global (confining) potentials such as externally imposed electromagnetic fields or chemical gradients“.

  Bartosz A. Grzybowski
- "… we limit the term to processes that involve pre-existing components, are reversible and can be controlled by the proper design of the components."

  George M. Whitesides

Self-Assembly on all scales



Self-Assembly

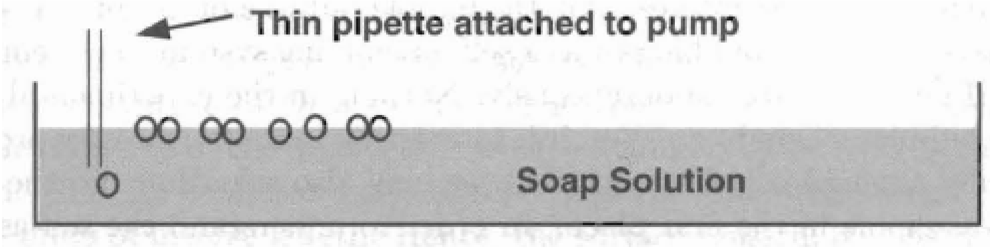
Why Studying Self-Assembly?

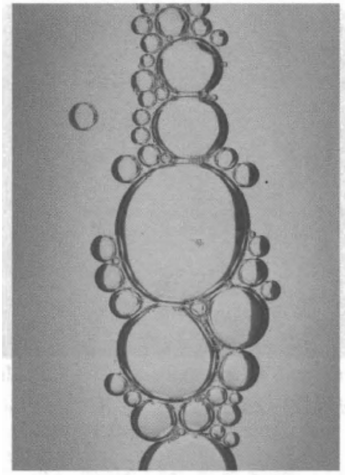
- Self-assembly is central for the **study of life.**
- Self-assembly is a main tool for the construction of **complex materials:** Molecular crystals, liquid crystals, semicrystals and phase separated polymers
- Self-assembly offers one of the most general strategies for **constructing nano-devices.**
- Self-assembly can lead to novel **computational schemes**

Principal Components of Self-Assembly

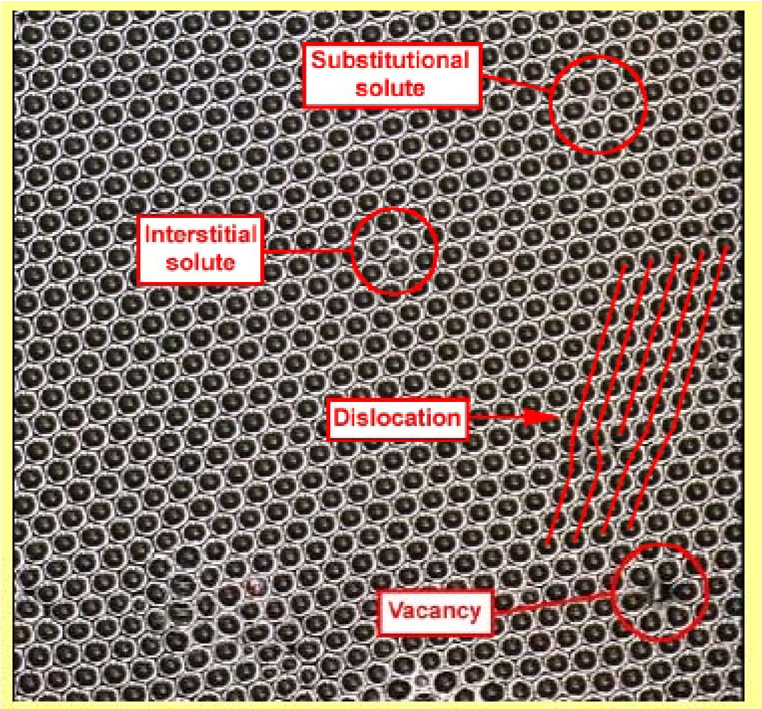
- **structured particles**: shape, size and condition of the components define the resulting object.
- a **binding force**: components interact with each other
- (a certain degree of) **reversibility** or adjustability
- an **environmen**t
- **driving force** (e.g. mass transport and agitation.)

Example: Bubble raft





- Invented by Bragg and Nye in 1940th as a model to study crystallization
- Pump-pipette technology allows to produce bubbles of identical size



Interaction in Self-Assembly

Molecular scale:

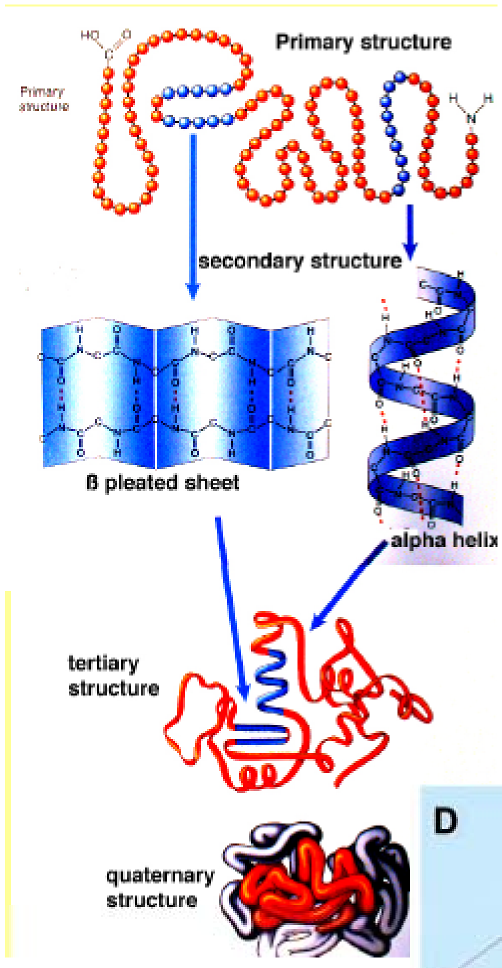
- Covalent bonds
- Hydrogen bonds
- Van der Waals forces
- Electrostatic forces

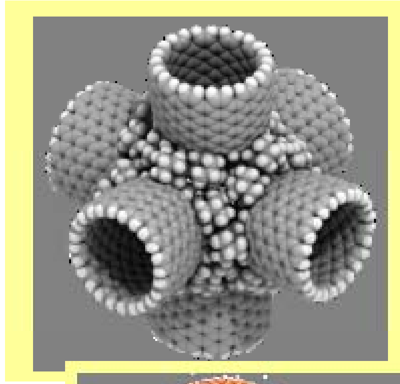
Mesoscopic scale

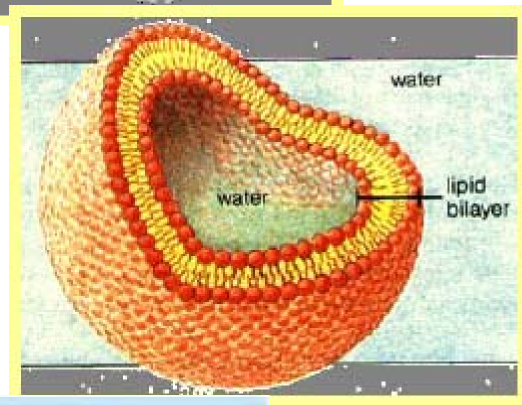
- Hydrophobic effects
- Entropic forces
- Electrostatic forces

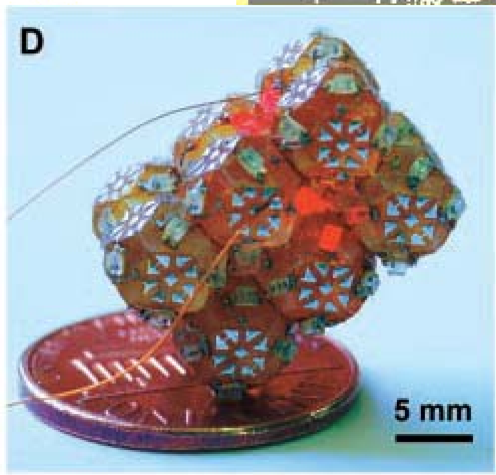
Macroscopic scale

- Magnetic forces
- Capillary forces
- Mechanic forces (grippers, mechanic links, etc).

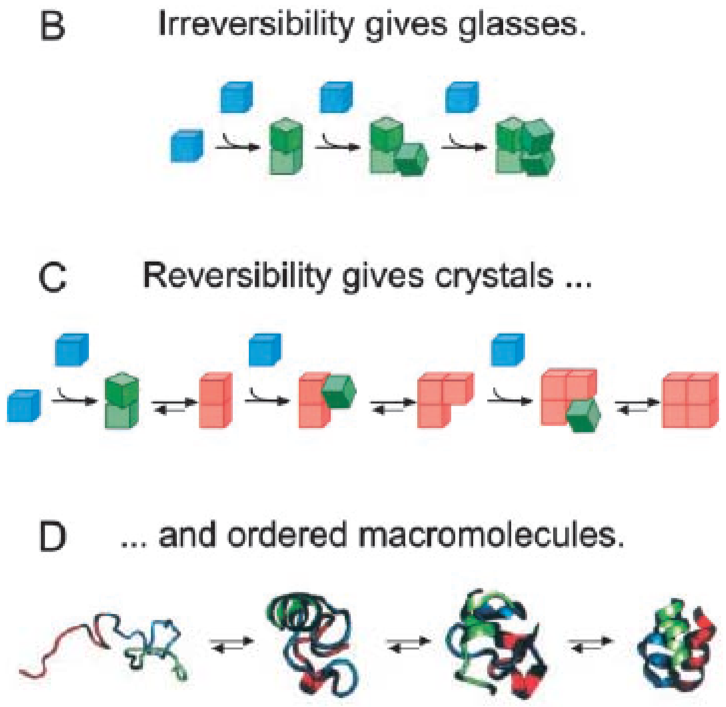








Reversibility/Adjustability



- "For self-assembly to generate ordered structures, the association either must be reversible or must allow the components to adjust their positions within an aggregate once it has formed. The strength of the bonds between the components, therefore, must be comparable to the forces tending to disrupt them. For molecules, the forces are generated by thermal motion. Processes in which collision between molecules leads to irreversible sticking generate glasses, not crystals"

Whitesides & Boncheva, PNAS ***April 16, 2002 vol. 99 no. 8 4769–4774***

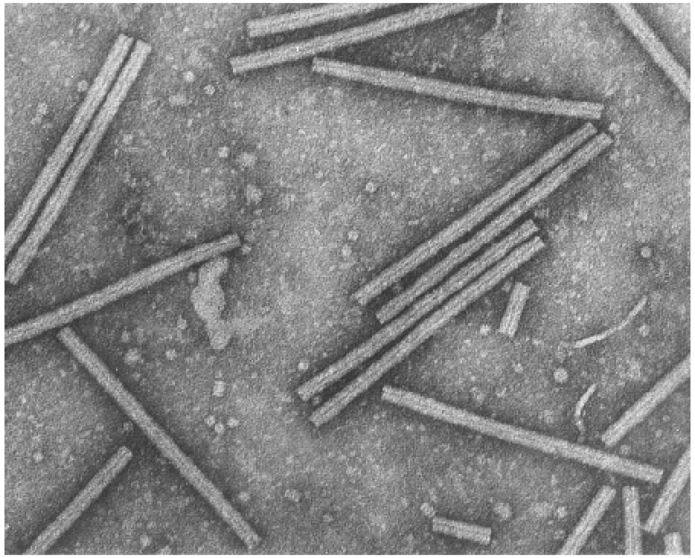
Environment

The environment plays an important role in most self-assembly processes:

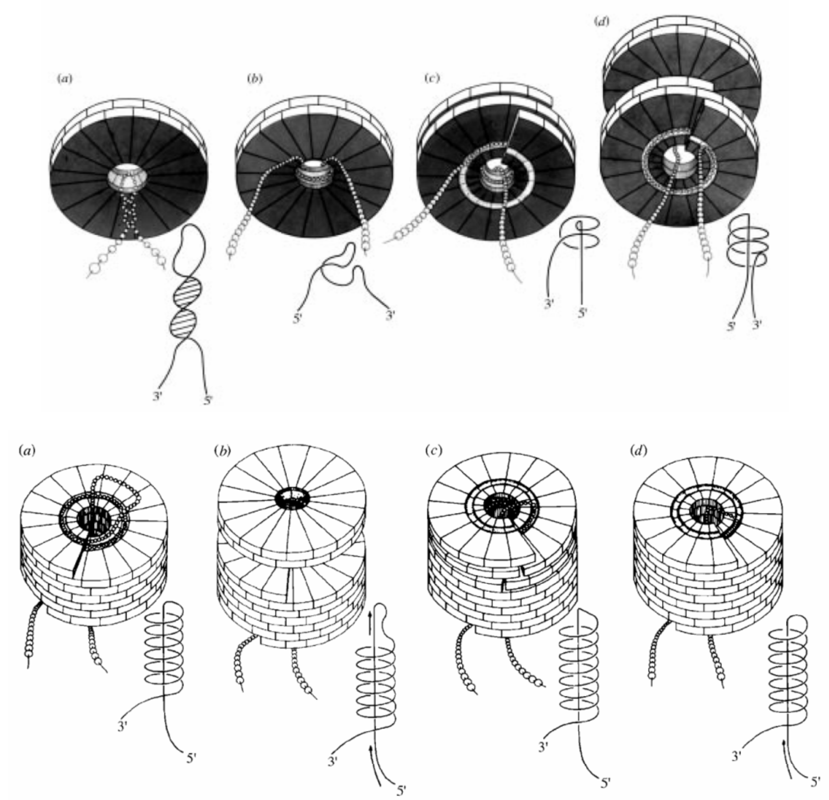
- It provides energy for thermal agitation
- If the environment is an aqueous solution, hydrophobicity takes effect.
- It provides necessary conditions for the particles structure and interaction, e.g. ionic strength, pH, temperature etc.
- It leads to entropic/depletion forces

Tobacco Mosaic Virus (TMV)

- Self-Assembly in vitro demonstrated by H.Fraenkel-Conrat and R.Williams in 1955

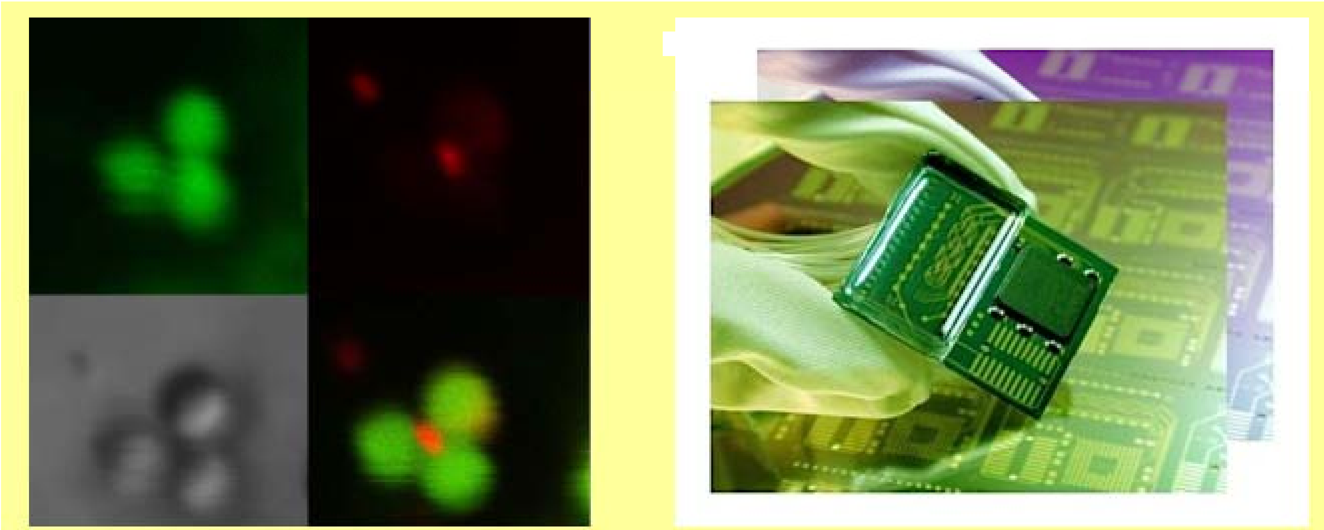


18 X 300 nm Rods



Assisted Self-Assembly

- Brownian motion cannot drive the self-assembly of larger objects. Therefore, we need some external, non-thermal support: **Assisted Self Assembly,** e.g by (micro) flows or by external fields.



Design by Self-Assembly

- What self-assembling systems can we build and how we do it?

- From engineering prospective:
  - **forward problem**: given a set of particles, environment and the driving force, what structures will the form
  - **backward problem**: given the desired structure, how we choose the set of particles, environment and driving force
  - **yield problem**: how to maximize the yield

Types of Self-Assembly (Whitesides)

- **Static self-assembly: The final configuration is an equilibrium state of minimal free energy.**
- **Dynamic self-assembly:** The attained configuration only appears if the system **dissipates energy.**
- **Templated self-assembly:** The self-assembly process is not completely determined by local interactions between the components, but employs **patterns in the environment.**
- **Biological self-assembly: Information processing** and versatile responses and adaptations to the given situation play an important role, also **development**

Static Self-Assembly

- Static self-assembly – the most developed and the best understood area of self-assembly.
- Operates via principle of energy minimization: system slides to global or local minimum, essentially similar to crystallization.
- Various mechanisms can be involved:
  - capillary forces,
  - magnetic forces,
  - template driven self-assembly,
  - surface energy minimization,
  - self-assembly by folding, etc

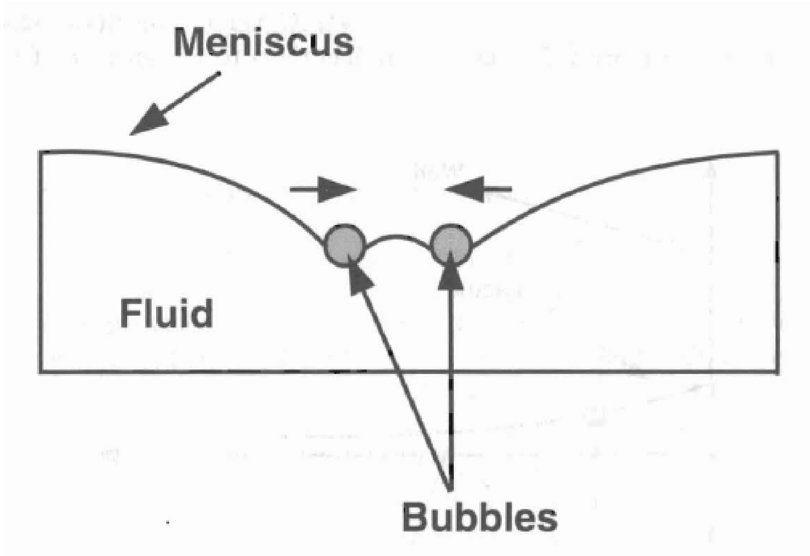
Capillary forces

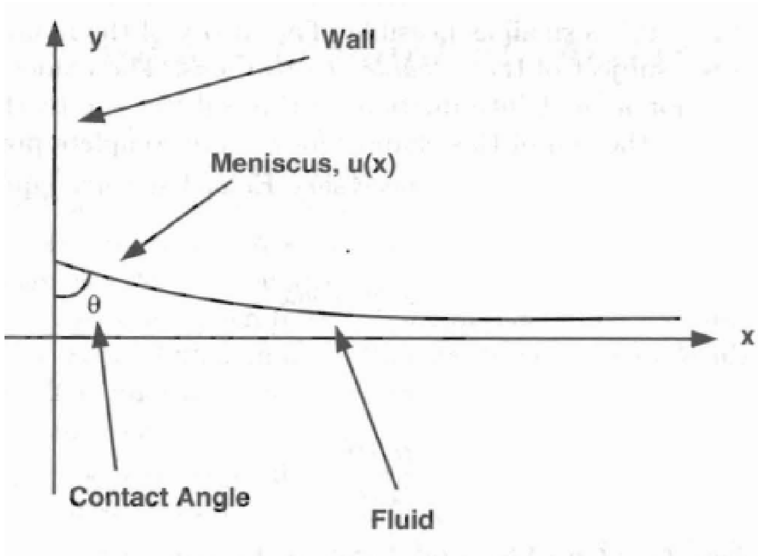
- Total energy of the system consisting of **surface** and **gravitational** energies is minimized

$$E_s = \gamma\left(\int_0^\infty \sqrt{1+u'^2}\,dx - A_0\right) \approx \int_0^\infty \frac{u'^2}{2}\,dx$$

$$E_g = \rho g \int_0^\infty \int_0^{y(x)} y\,dy\,dx = \rho g \int_0^\infty \frac{u^2}{2}\,dx$$

$$E\left(u(x)\right) = \int_0^\infty \left(\gamma \frac{u'^2}{2} + \rho g \frac{u^2}{2}\right) dx$$





Capillary forces

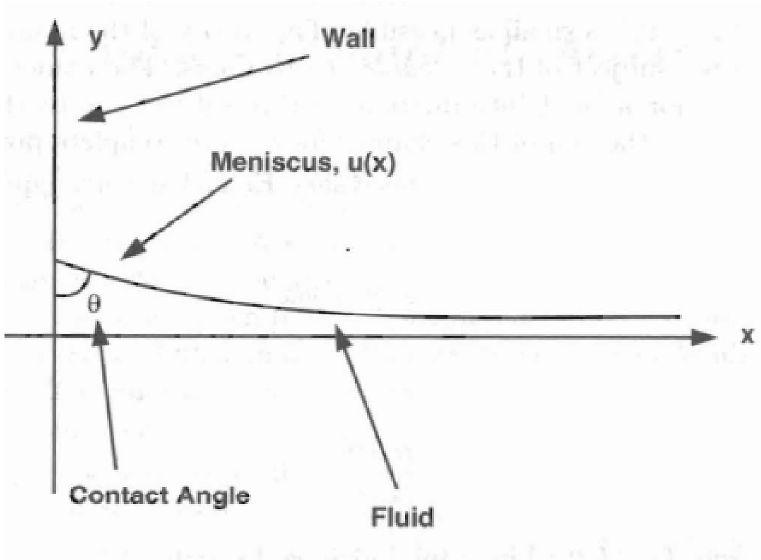
- We minimize the total energy using Euler-Langrange equation:

$$E(u(x)) = \int_0^\infty \left(\gamma \frac{u'^2}{2} + \rho g \frac{u^2}{2} \right) dx$$

$$\frac{\partial E}{\partial u} - \frac{\partial}{\partial x} \frac{\partial E}{\partial u'} = 0$$

$$\frac{d^2 u}{dx^2} - \frac{\rho g}{\gamma} u = 0$$

$$u(x) = c_0 \exp\left(-\sqrt{\frac{\rho g}{\gamma}} x \right) + c_1 \exp\left(\sqrt{\frac{\rho g}{\gamma}} x \right)$$

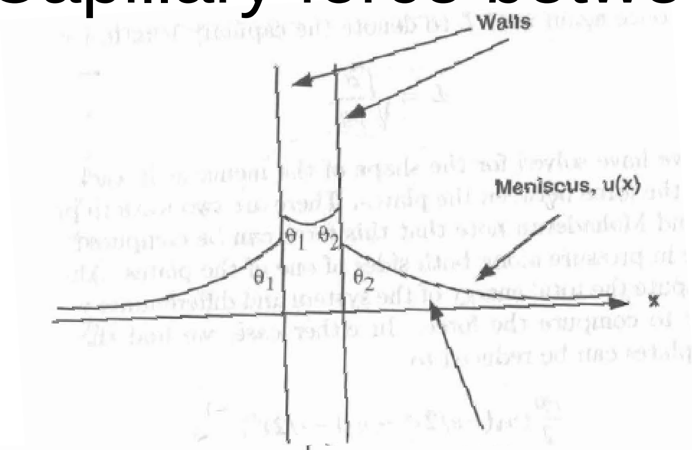


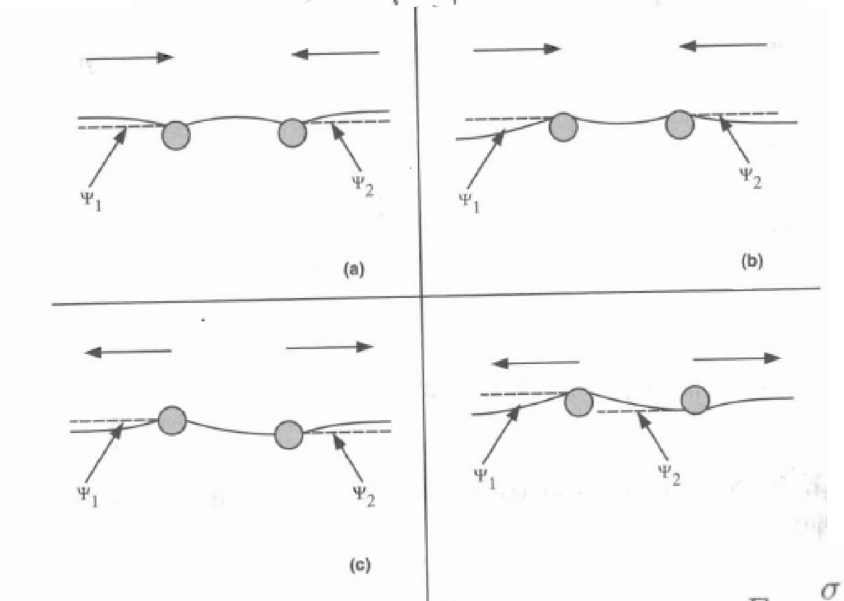
$$u'(0) = -\cot(\theta)$$

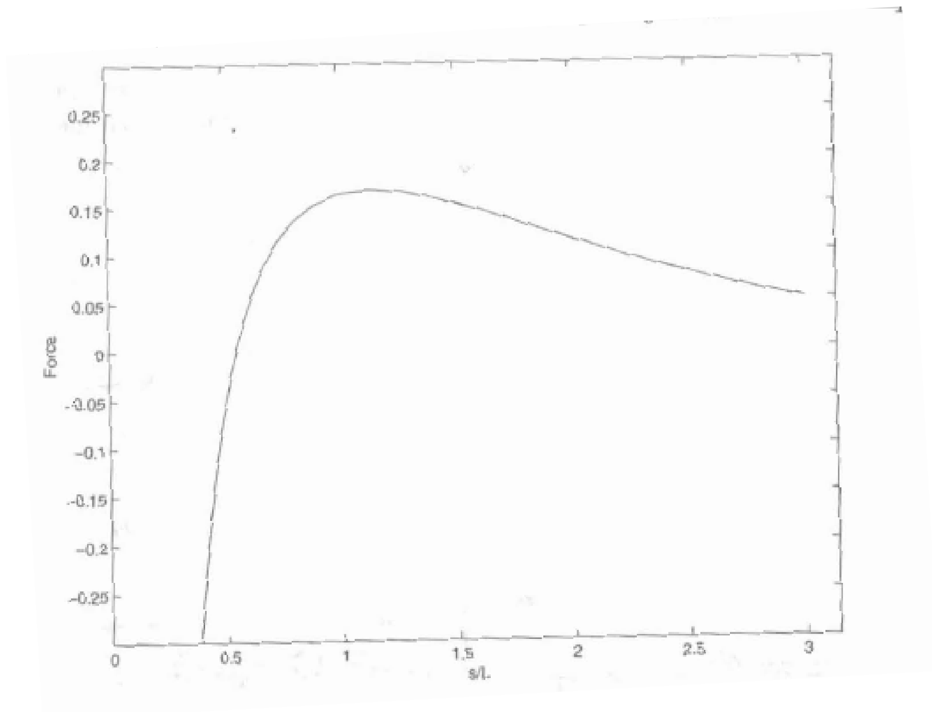
$$u(x) = c_0 \sqrt{\frac{\gamma}{\rho g}} \cot(\theta) \exp\left(-\sqrt{\frac{\rho g}{\gamma}} x \right)$$

Assembly via capillary forces

- Capillary force between two plates





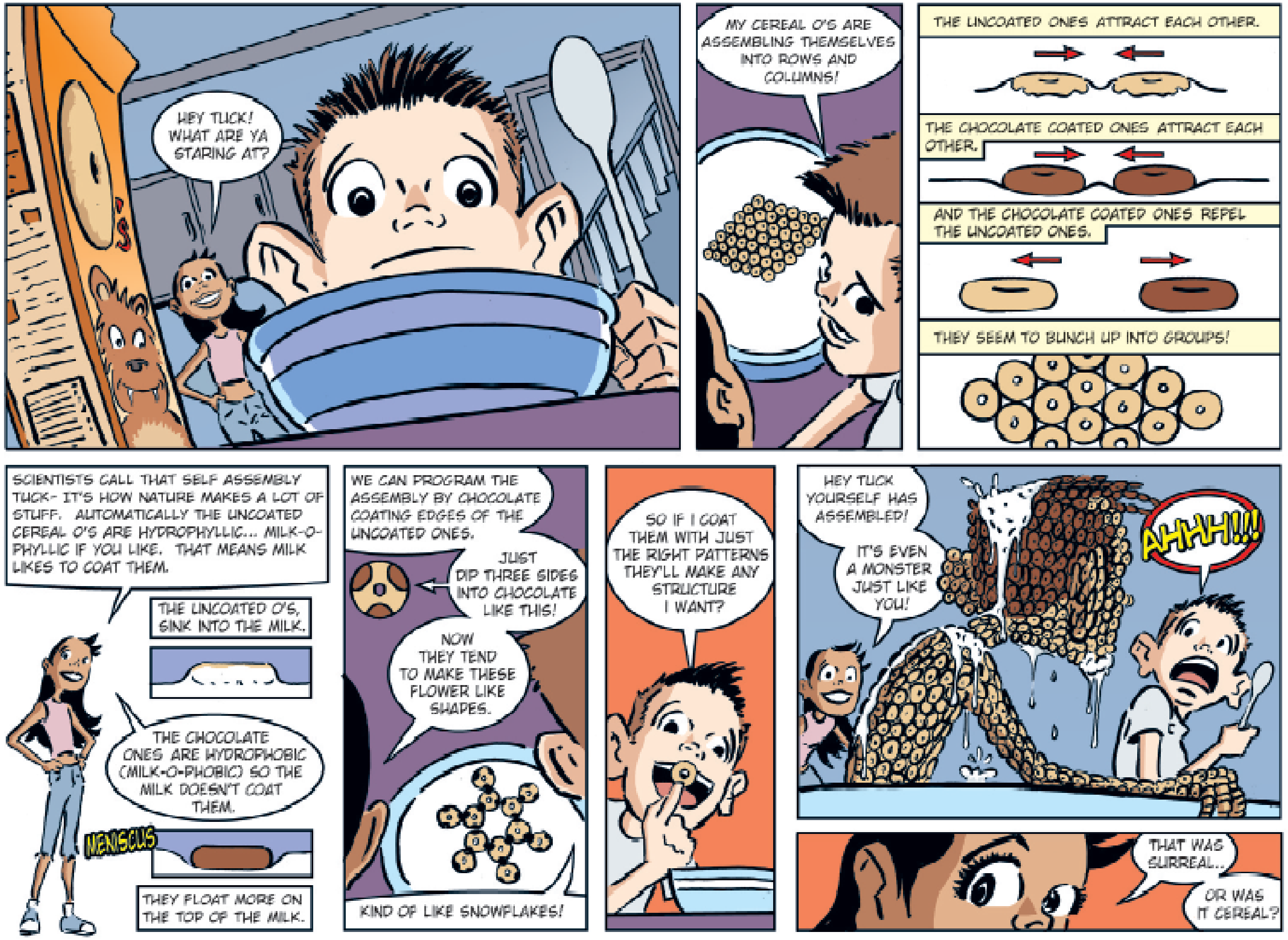


$$F = \frac{\sigma}{2}\left(\cot^2(\theta_1) - \frac{(\cot(\theta_1)\cosh(s/L) + \cot(\theta_2))^2}{\sinh^2(s/L)}\right).$$

$$L = \sqrt{\frac{\sigma}{\rho g}}.$$

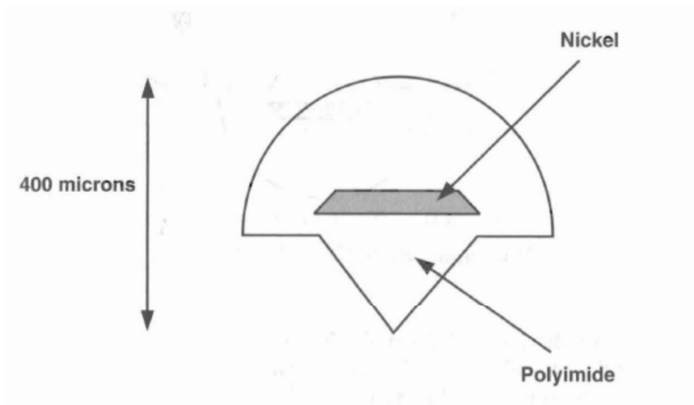
Capillary forces

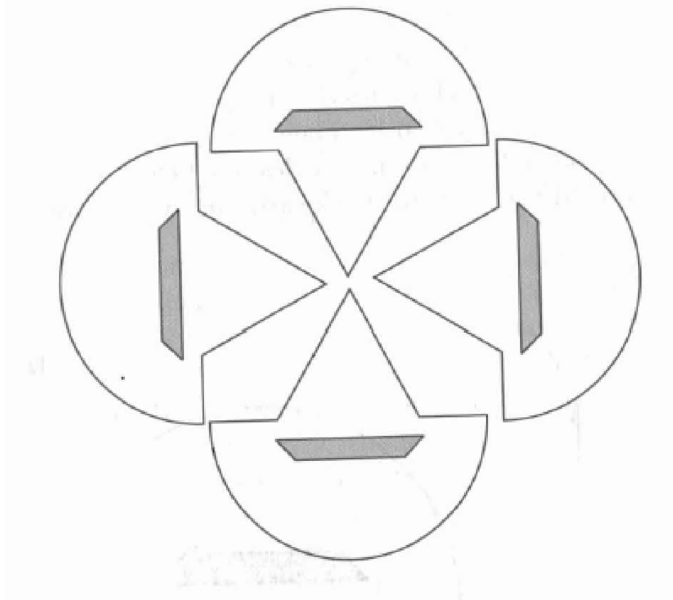
- Cheerios self-assembly (Saul Griffith, MIT)

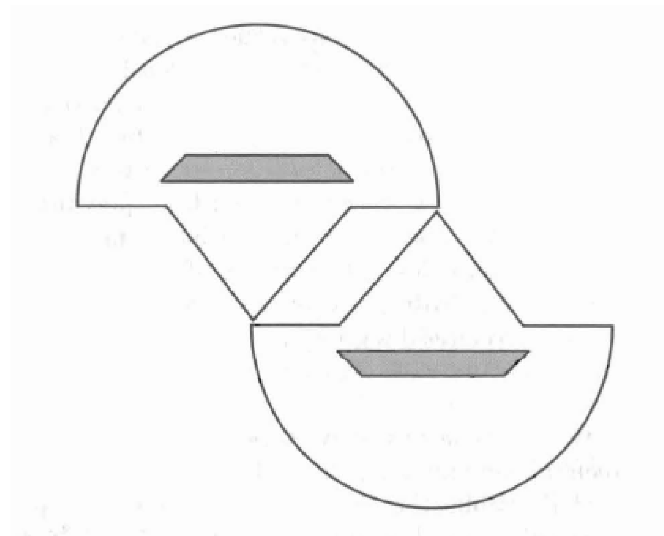


Assembly via capillary forces

- Hosokawa system (1996)

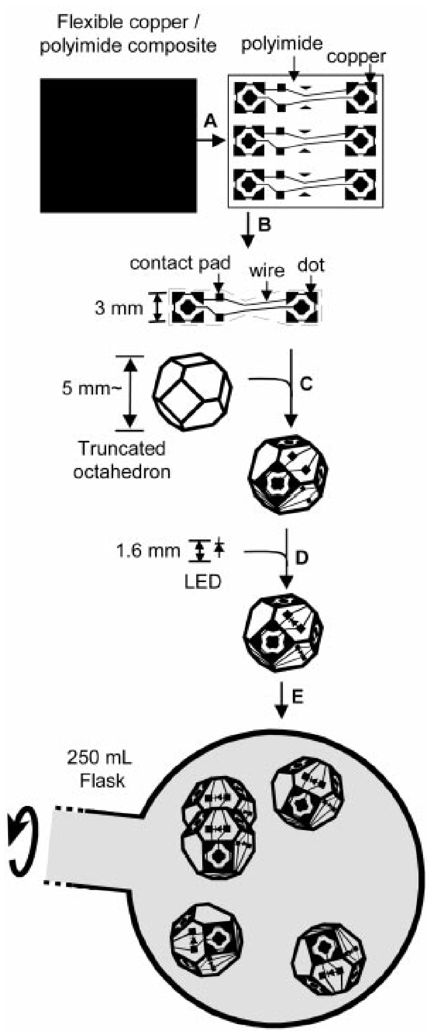


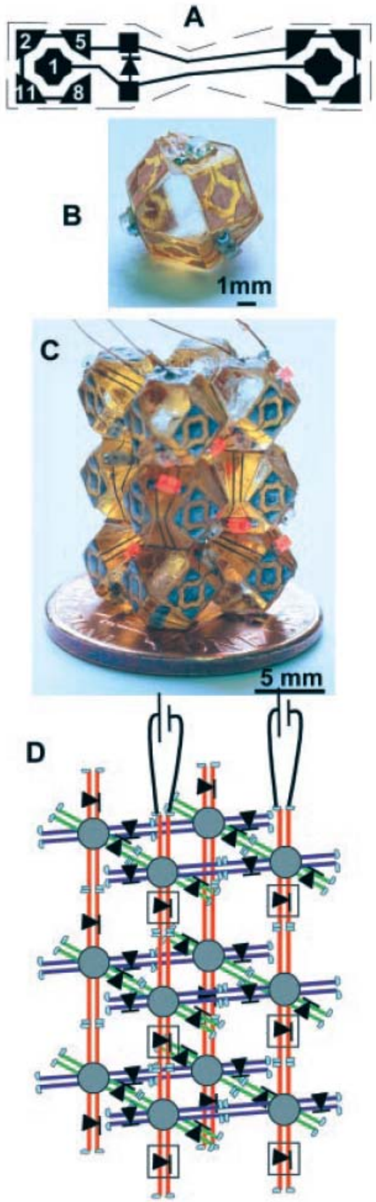


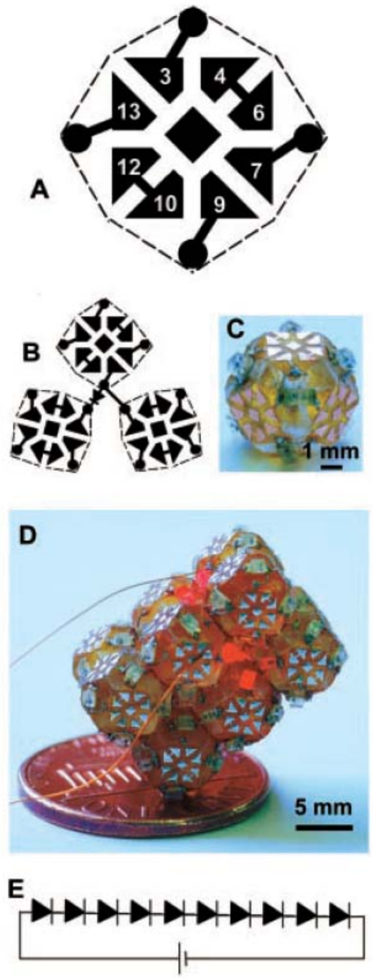


3D assembly

- Self-Assembly of functional electrical circuits

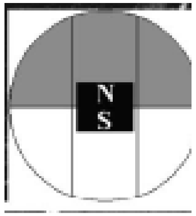






Whitesides et al, Science 289, 1170 (2000)

Magnetic forces



System:

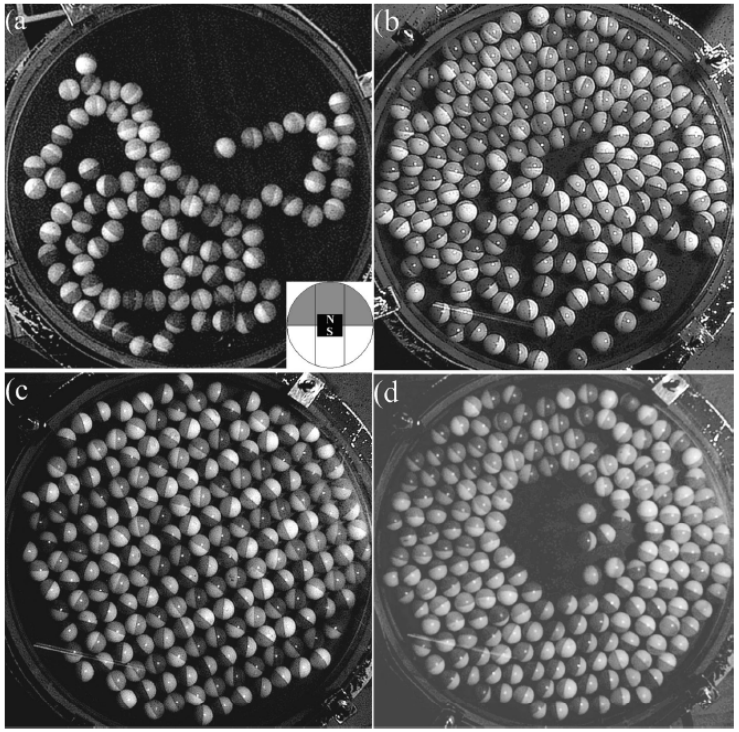
- a magnet encapsulated in a plastic sphere. Two cases considered “short magnet” (s=0.69cm) and a “long magnet”(s=1.42cm), for both sphere size is d=1.69cm
- system is shaken to achieve equilibrium
- The case of short magnets:

a) low density

b) high density

c) square packaging

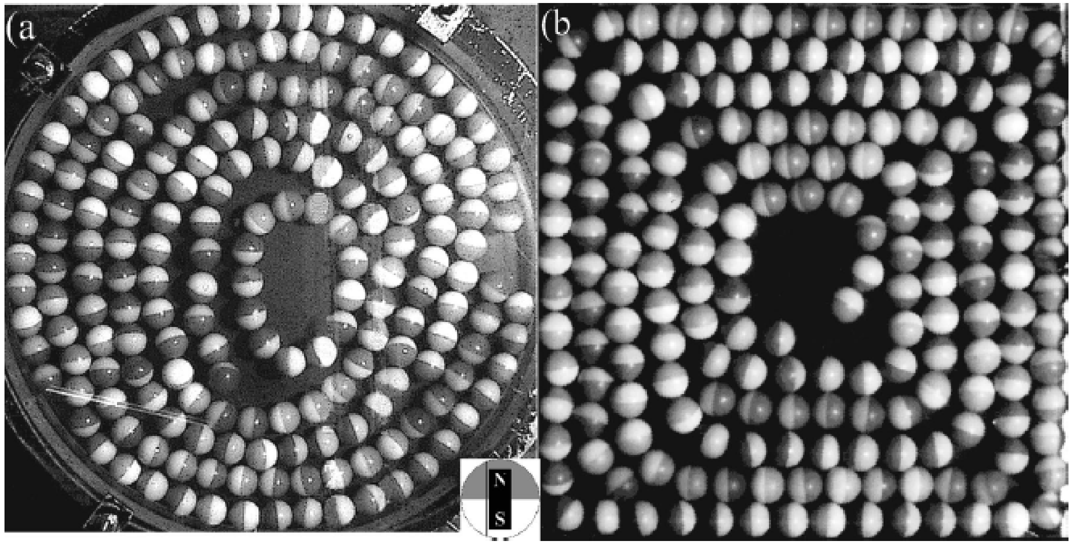
d) macrovortex state



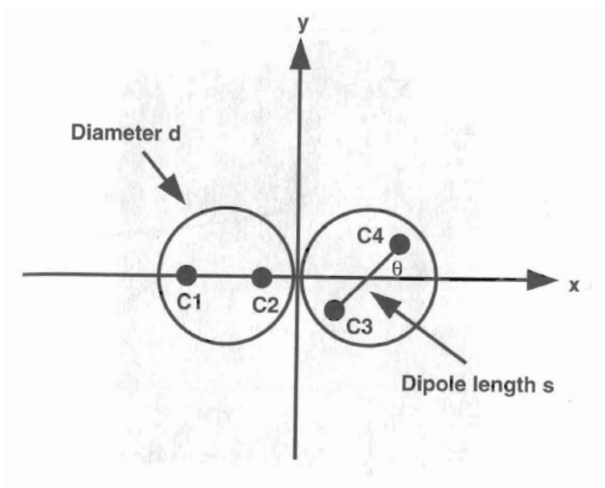
J. Stambaugh et al., Phys.Rev. E ***68****, 026207 (2003)*

Magnetic forces

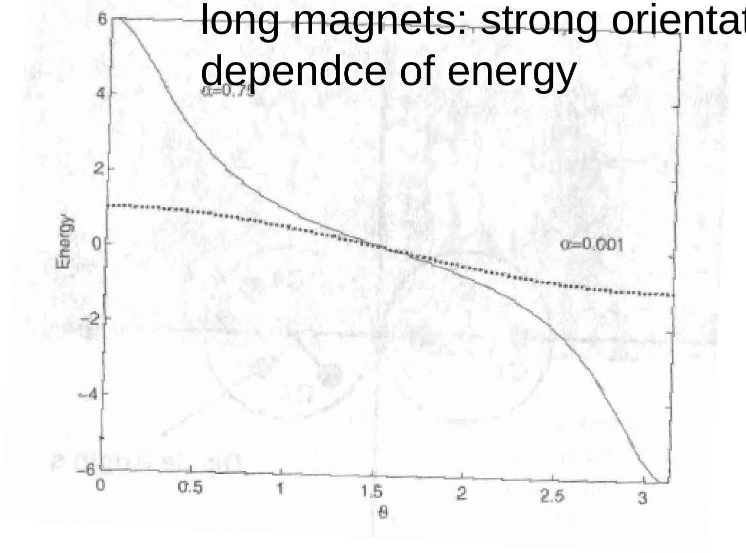
- dense system of long magnets in a round and square containers



$$U_{ij} = \frac{\mu_0}{4\pi}\frac{m_i m_j}{r^3}$$



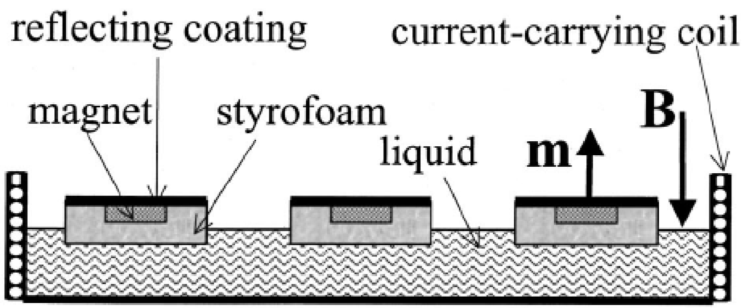
short magnets: no prononced minimum
long magnets: strong orientation dependce of energy

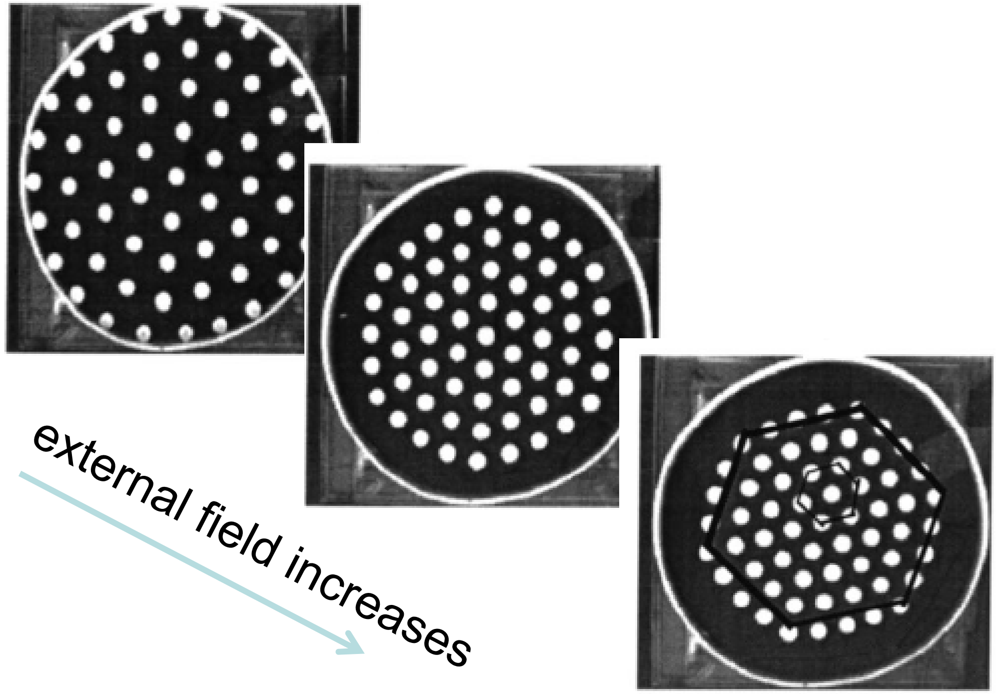


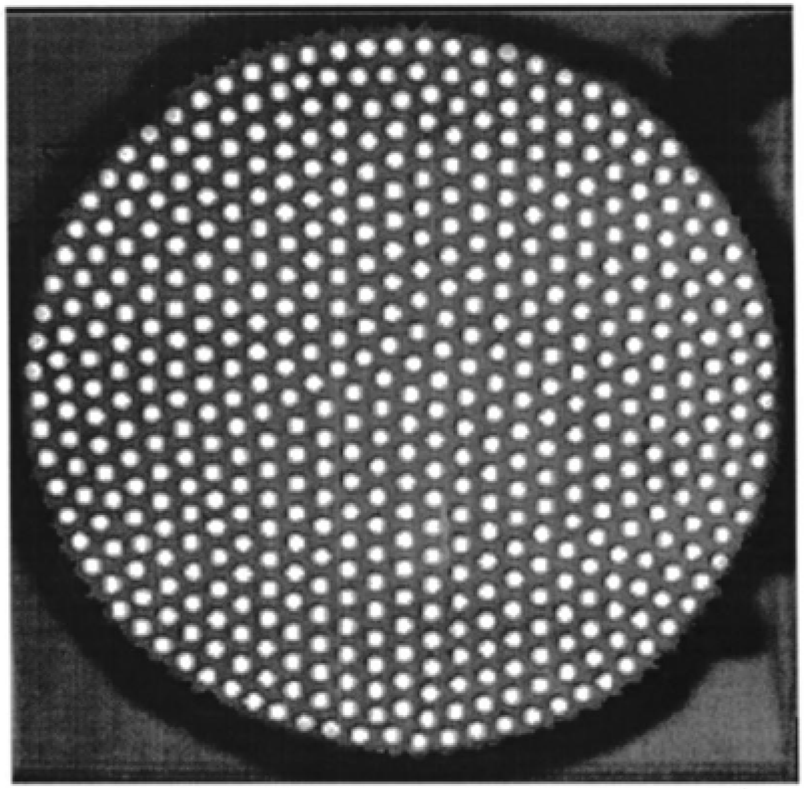
*J. Stambaugh et al., Phys.Rev. E **68**, 026207 (2003)*

Magnetic forces

- Ordered array of magnetic particles can be created with external field.
- Possible application: photonic gap materials



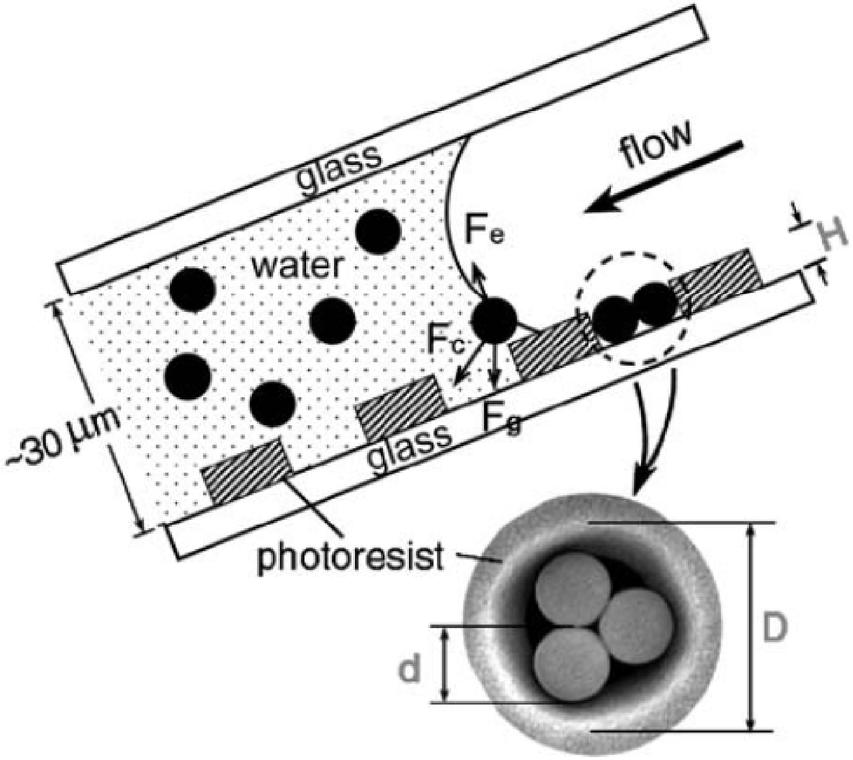


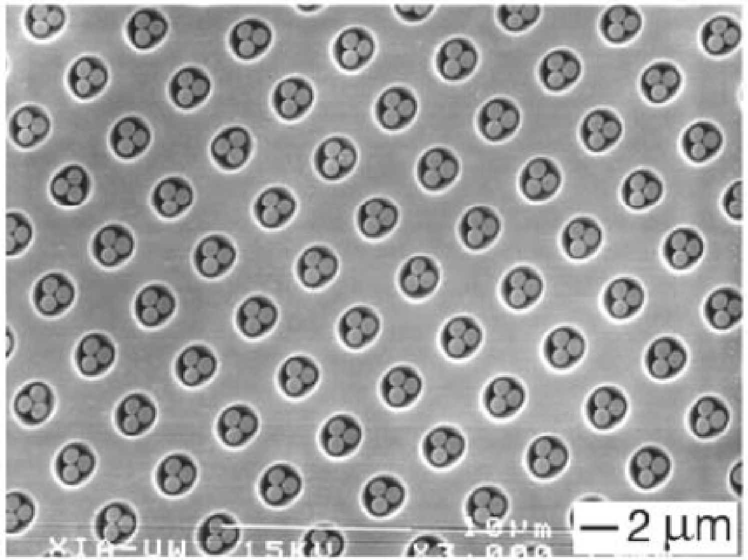


Golosovsky et al, Appl.Phys.Lett. 75, 4168 (1999)

Template assisted self-assembly

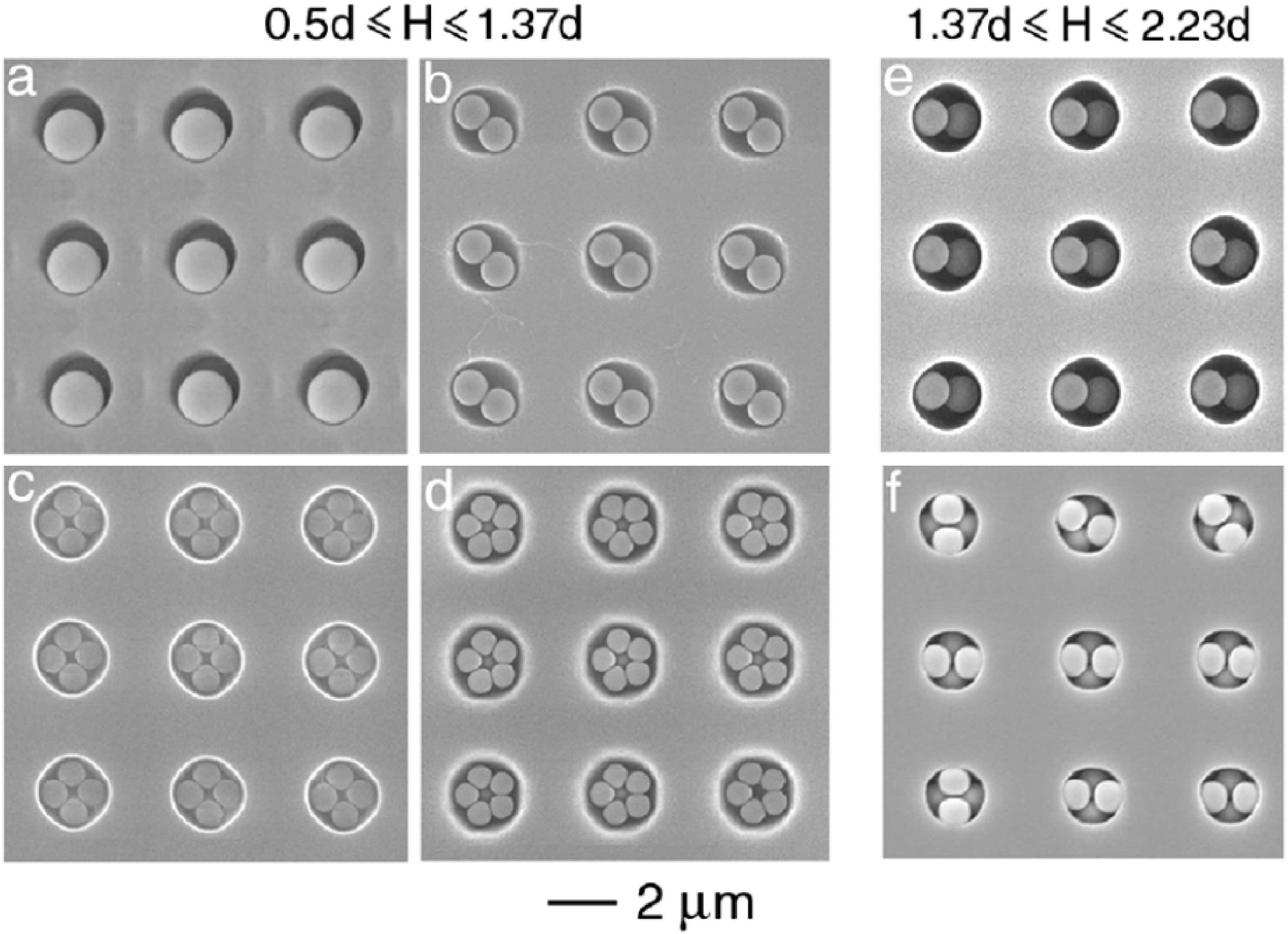
- Self-assembly of polystyrene beads (colloids)



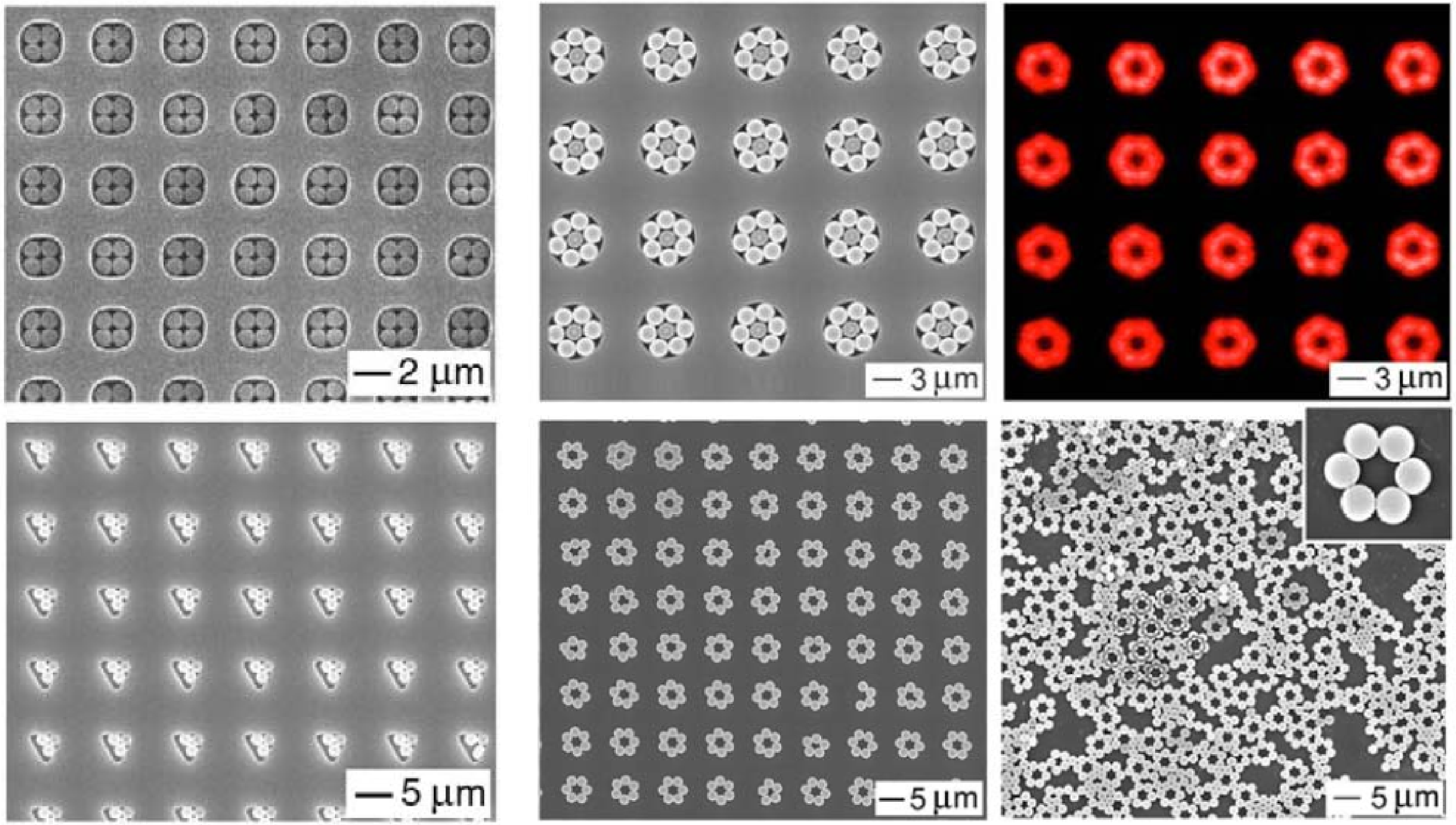


Yin & Xia, Advaced Materials 2001, 13, 267
Yin, Lu, Gates & Xia, J. Am. Chem. Soc. 2001, 123, 8718
Xia, Yin, Lu & McLellan, Advanced Functional Materials 2003, 13, 907

Template assisted self-assembly

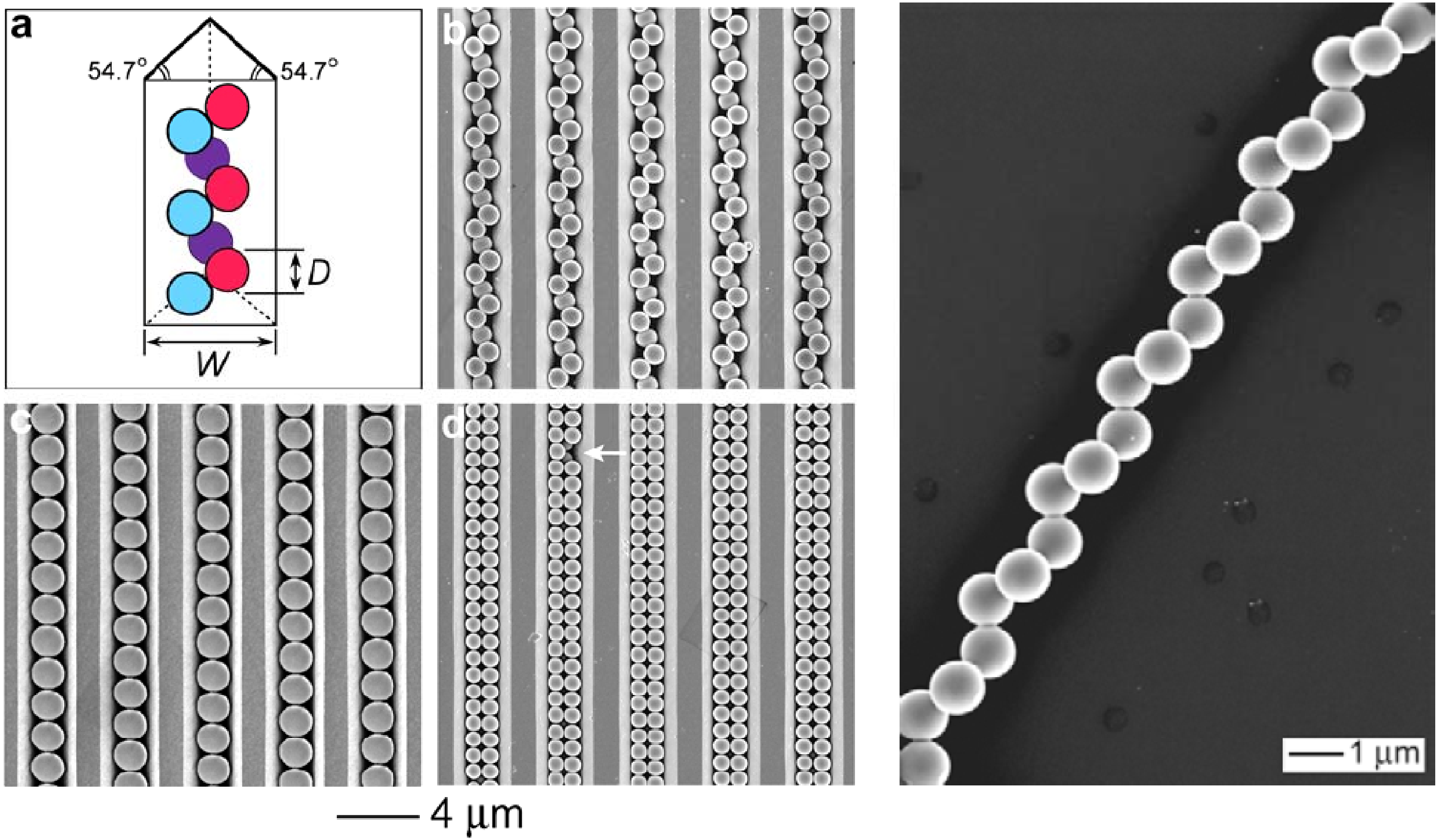


Template assisted self-assembly



Template assisted self-assembly

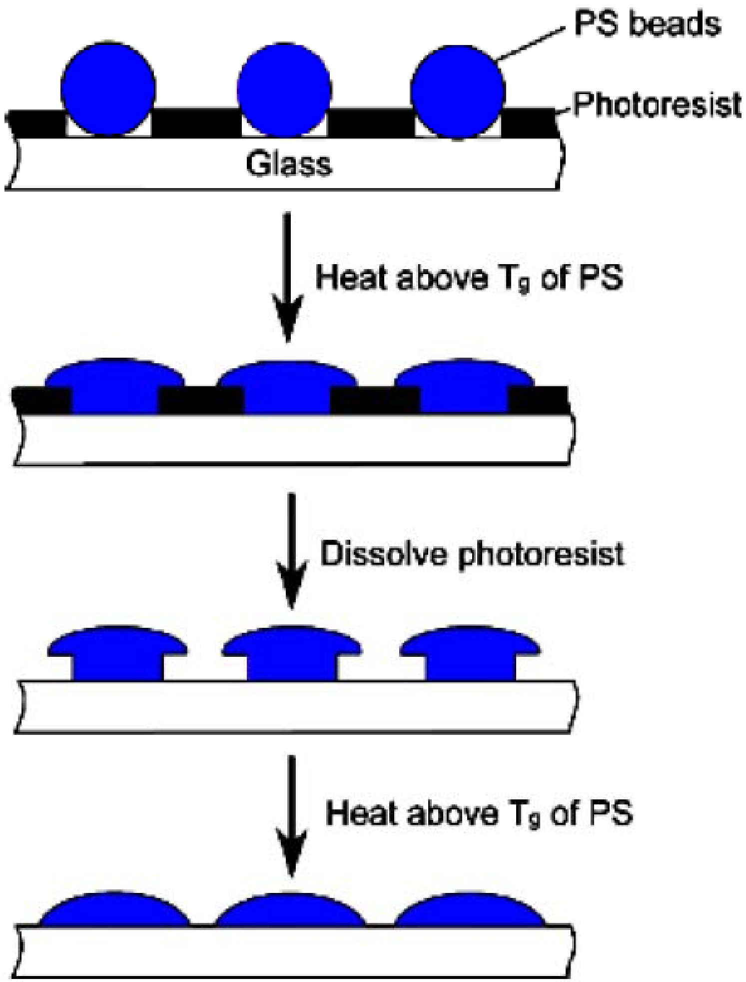
- formation of helical structures out of achiral spherical colloids

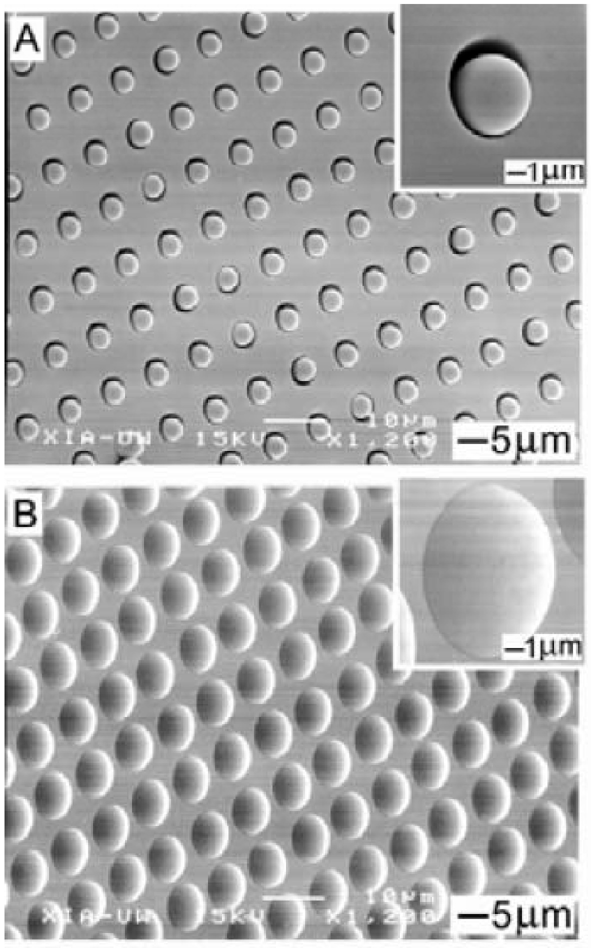


Yin & Xia, J. Am. Chem. Soc. 2003, 125, 2048

Structured Surfaces

- **Fabrication of Arrayed Polymer Microlenses**

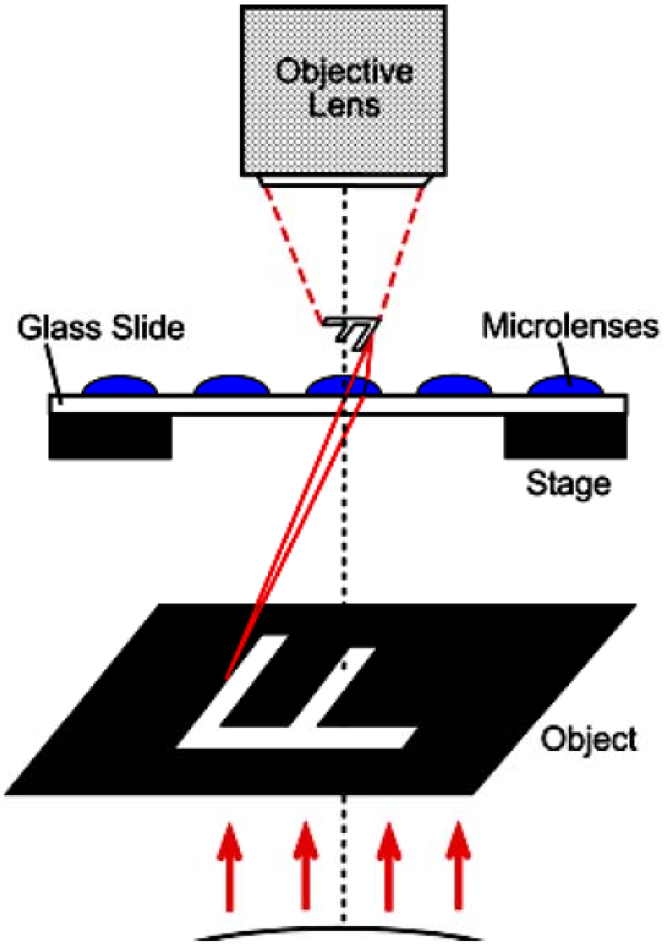


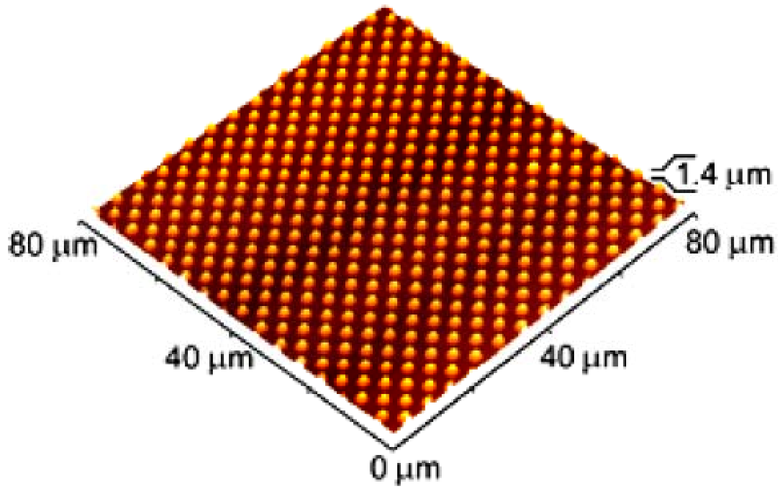


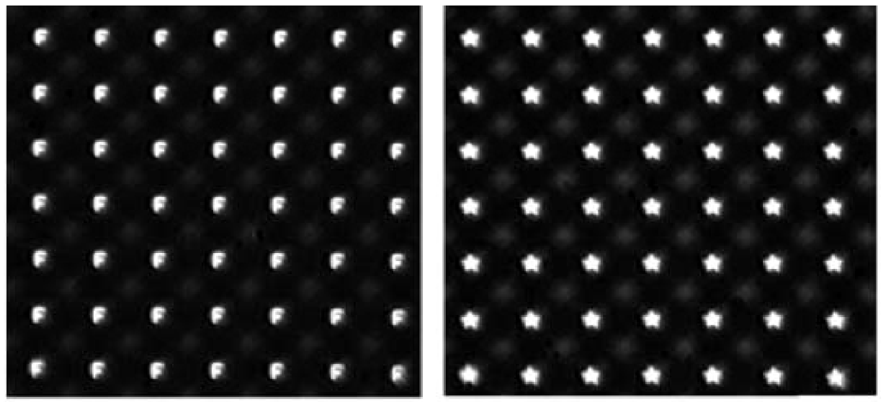
Lu, Yin & Xia, Advanced Materials 2001, 13, 34

Structured Surfaces

- **Imaging through Arrayed Polymer Microlenses**







Lu, Yin & Xia, Advanced Materials 2001, 13, 34

Problems

- Class: P3-15
- Home: P3-7, P3-13