Colloidal atoms and molecules

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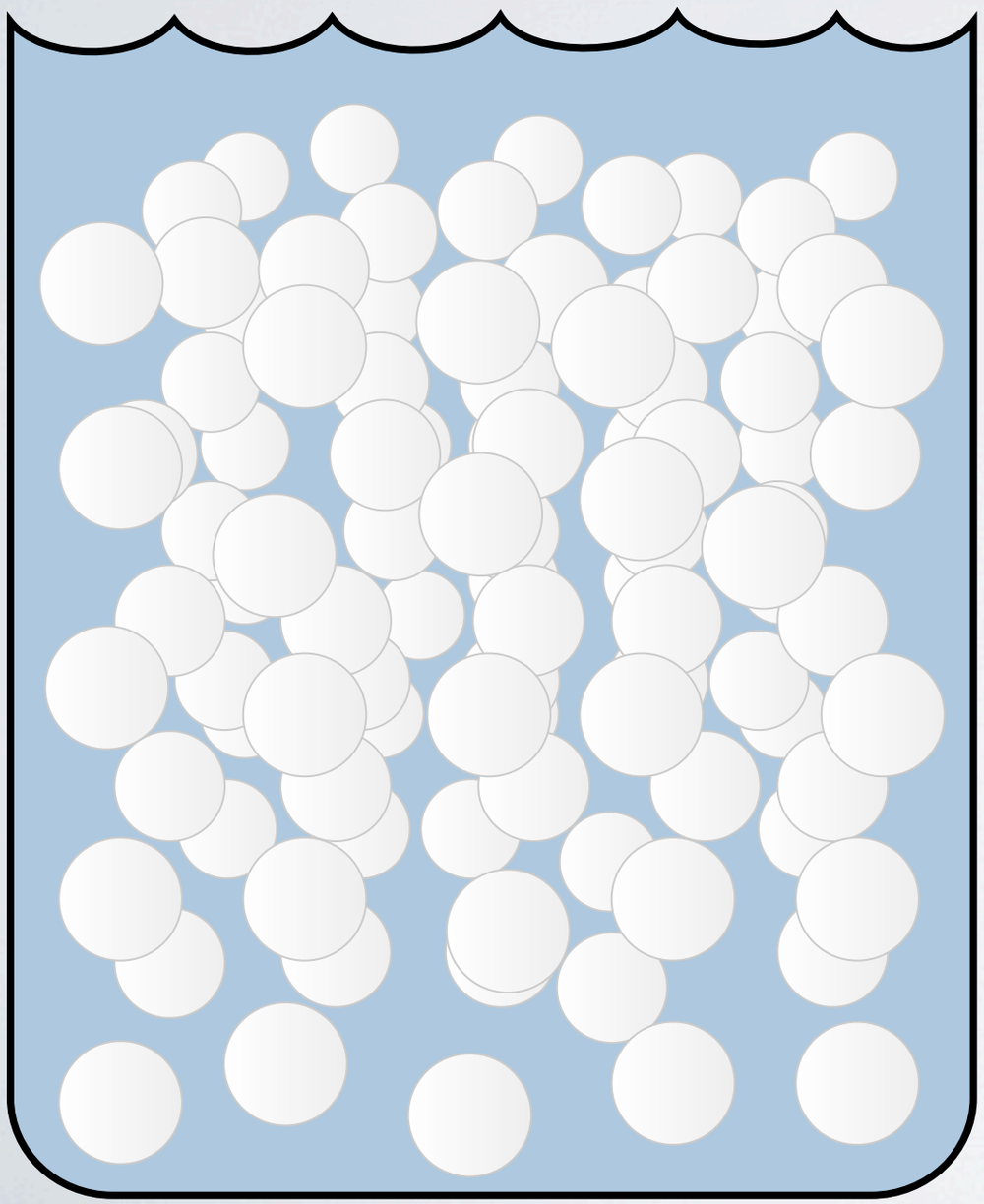
What are colloids?

Small particles suspended in a liquid

Brownian motion is important

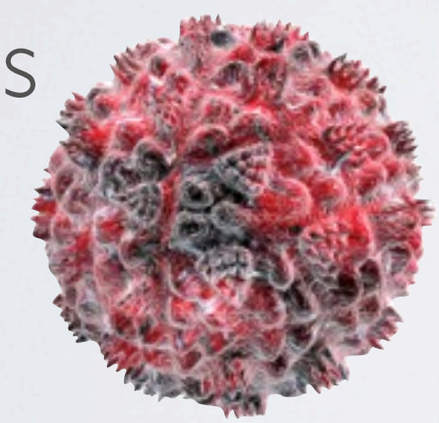


COLLOIDS:

- Diameters ~ 5 nm to 5 μm
  suspended thermally $P(z) \propto e^{-\Delta mgz/k_B T}$
- Materials
  plastic (PS, PMMA, ...)
  inorganic (SiO_2, TiO_2, ...)
  semiconductor (CdSe, ...)
  metal (Au, Ag, ...)

Examples of colloids

virus



gold

milk

quantum dots

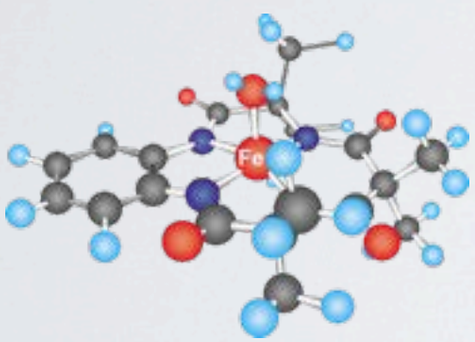
opals

Building materials at different length scales

Complex structures we can make

characteristic size (meters)

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2}

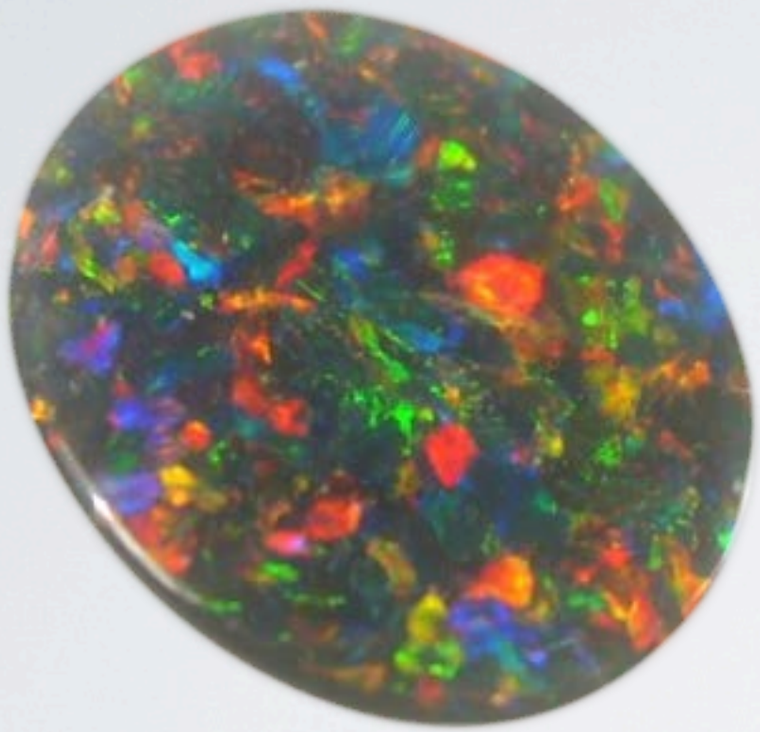


colloidal regime

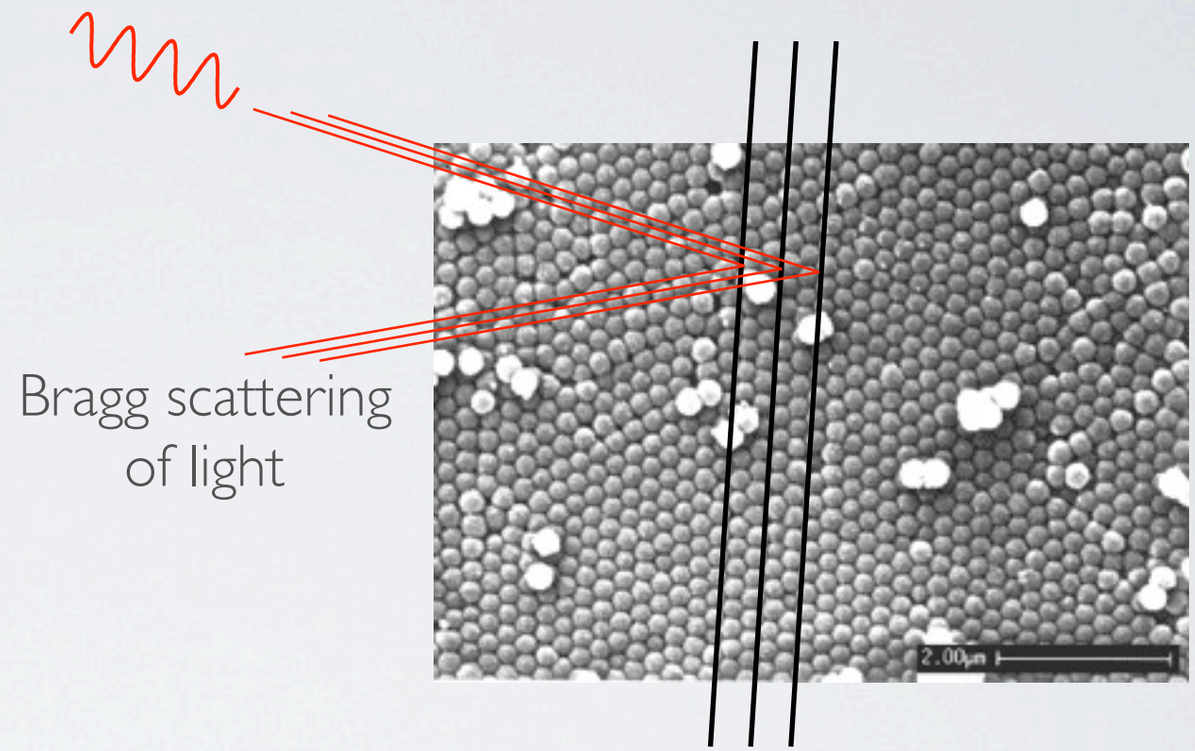
How can we build 3-d structures on the colloidal scale?

"Self assembly"

Structures nature makes with colloids



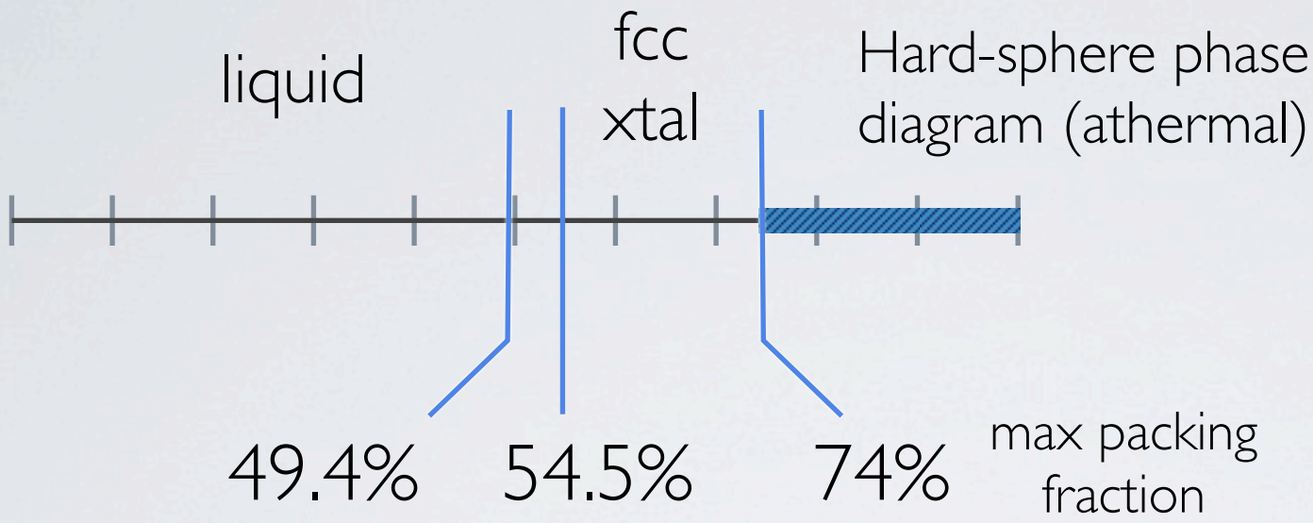
Gem quality opal from Australia

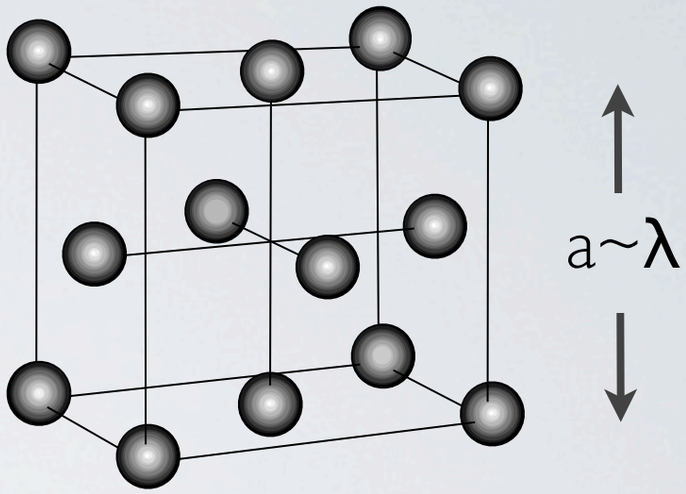


Natural opals consist of tiny FCC ordered glass spheres (~200 nm)

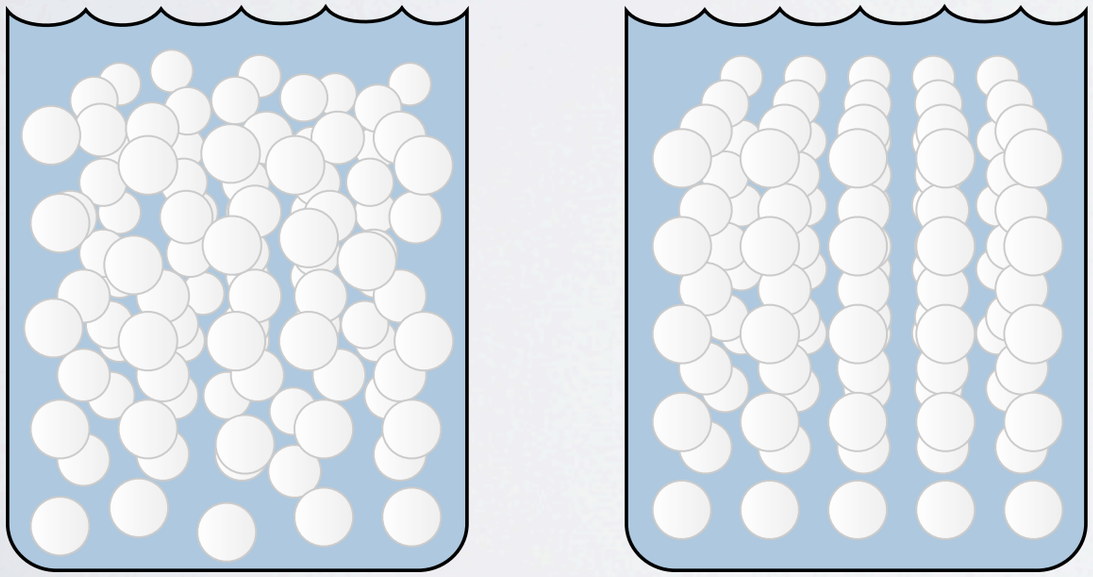
Bragg scattering from different crystalline planes produce different colors

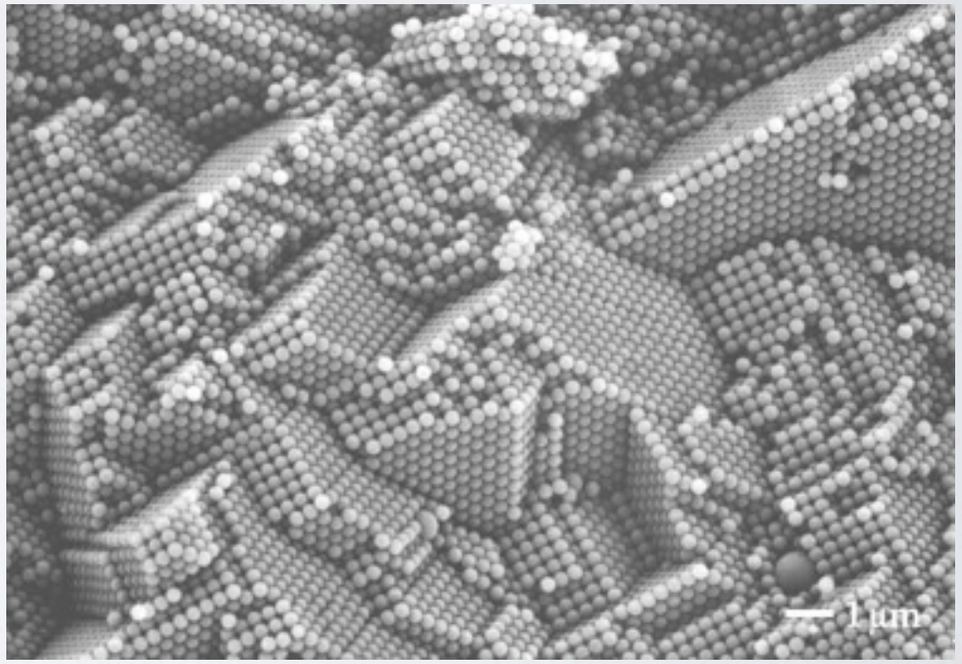
Structures nature makes with colloids





Crystallization driven by entropy





colloidal crystal with
lattice constant ~ 0.5 μm

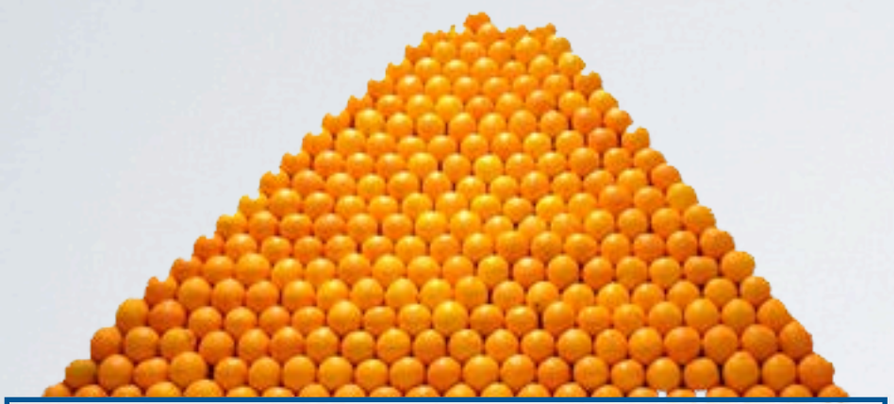
Repulsive systems: Packing is key

Structures people make with colloids

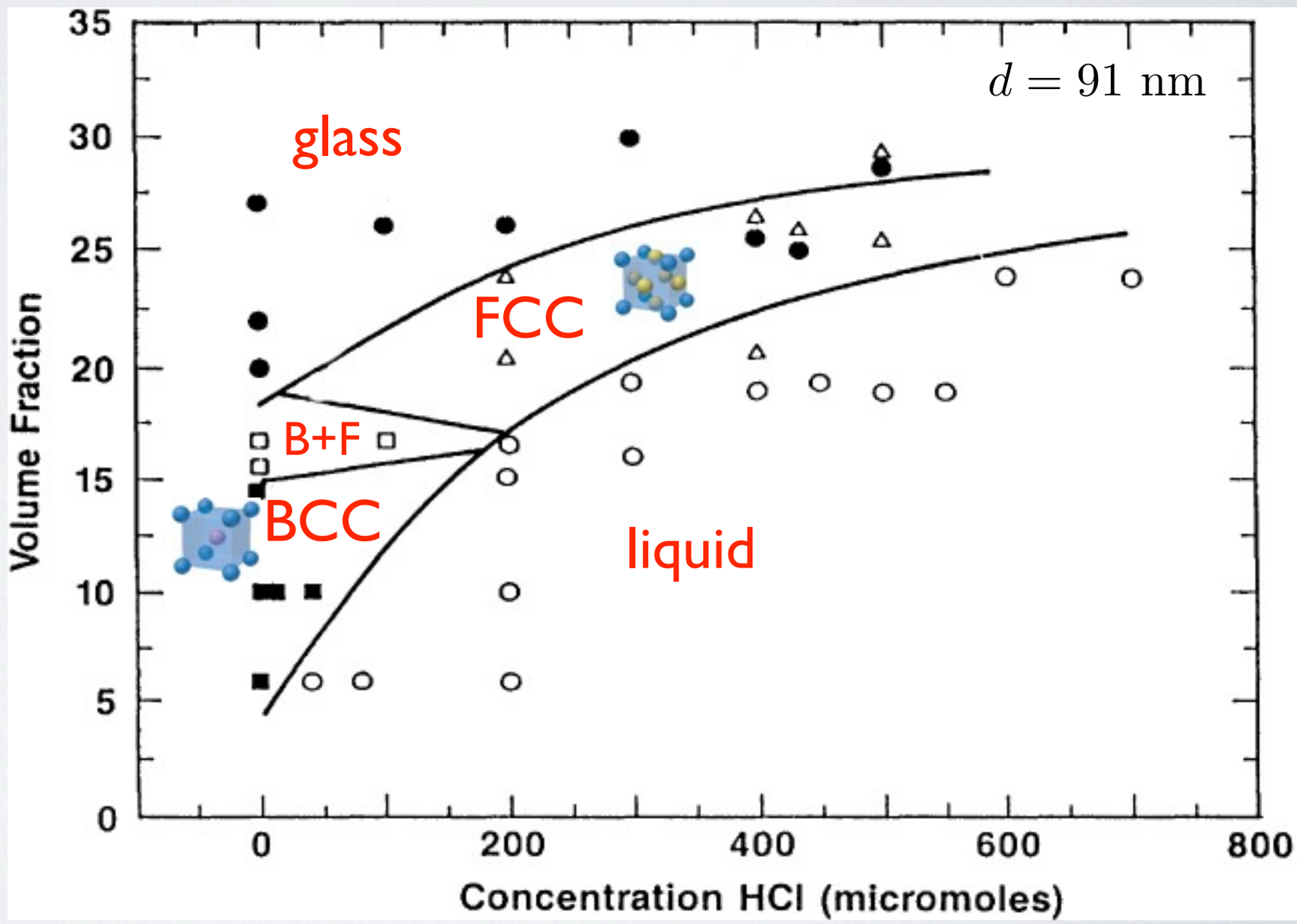
Electrically charged colloids
spontaneously form ordered structures

Coulomb !!

charged polystyrene spheres
in methanol (90%) water (10%)



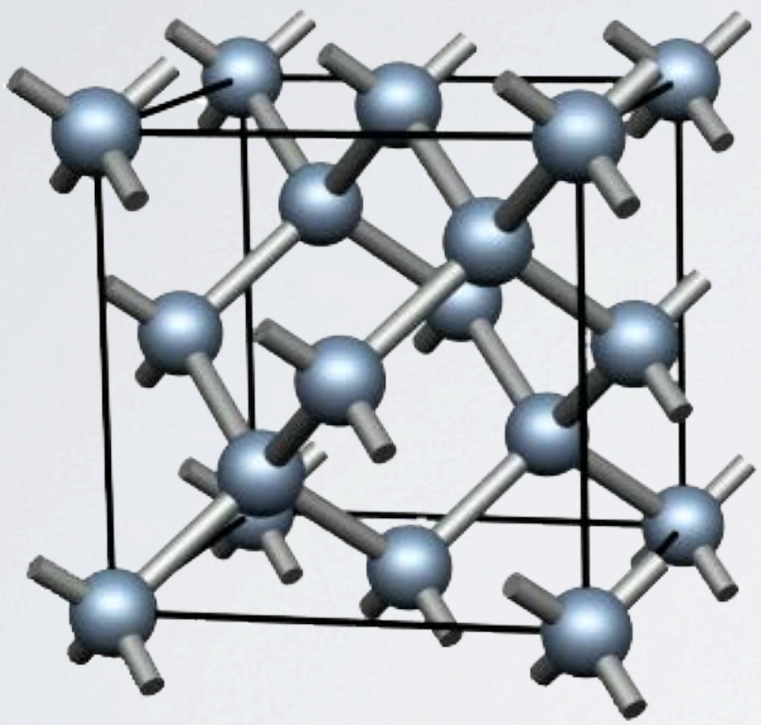
Packing constraints: crystallization driven by repulsive interactions and entropy



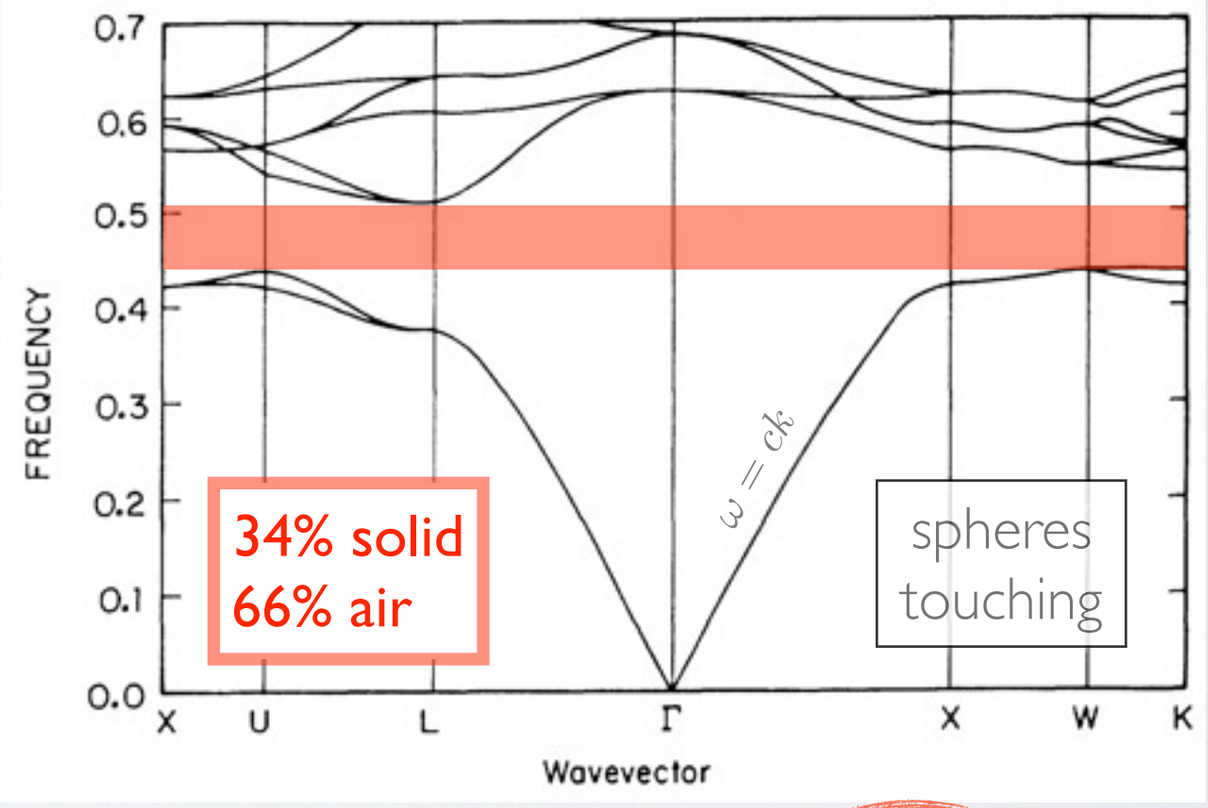
Sirota *et al.* PRL **62**, 1524 (1989)

A Challenge: Make this

diamond lattice



photonic band gap



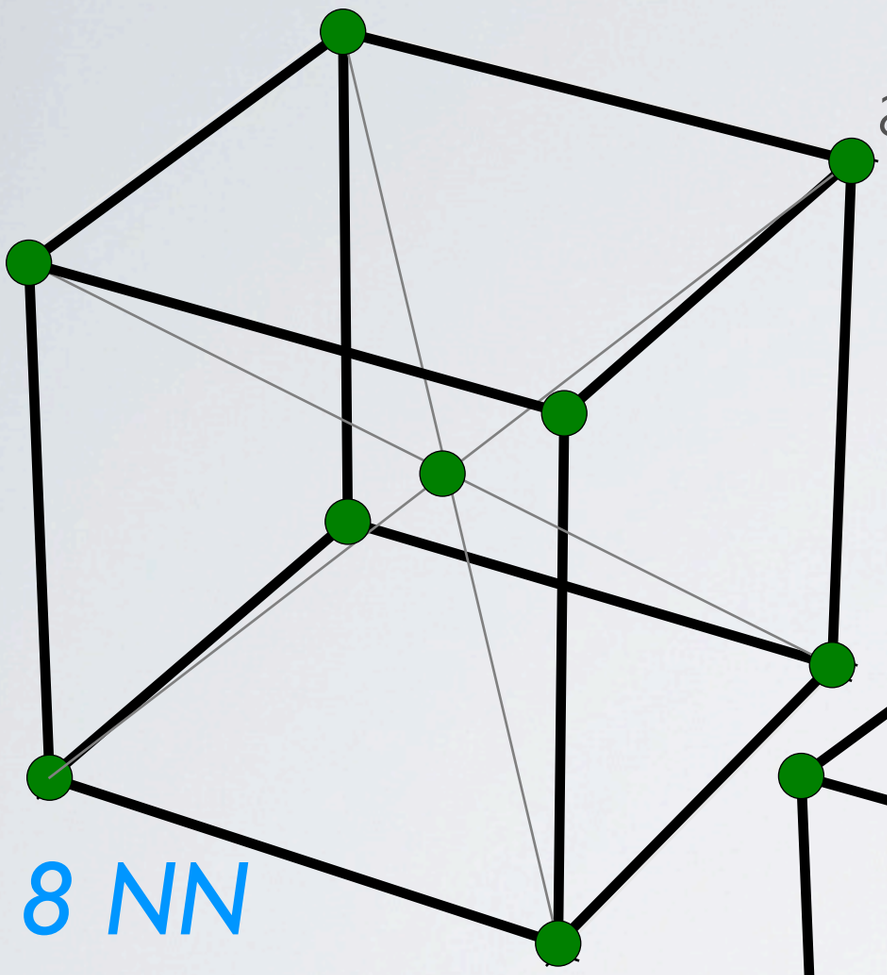
Ho, Chan, Soukoulis, PRL **65**, 3152 (1990)

23 years

Why is assembling the diamond structure so hard?

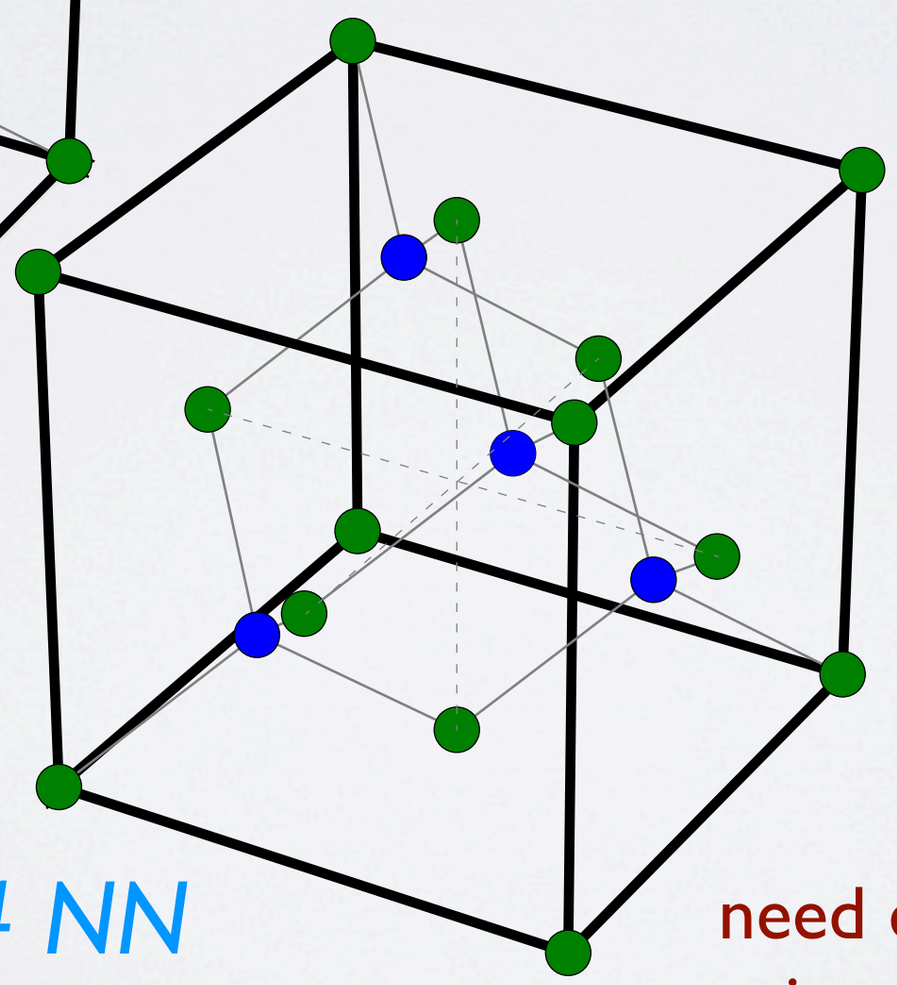
Packing particles: On average, each particle needs $2d$ constraints for stability.

In 3-d: $2d = 6$



8 NN

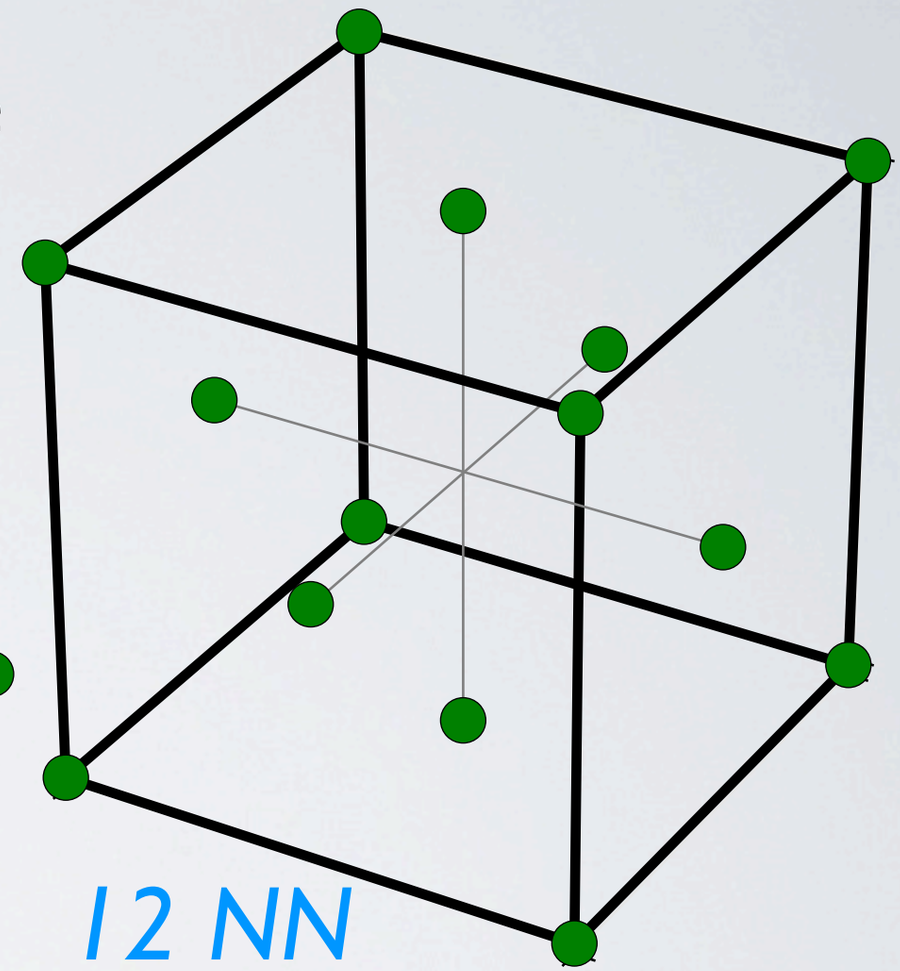
BCC 68%



4 NN

diamond 34%

need directional interactions



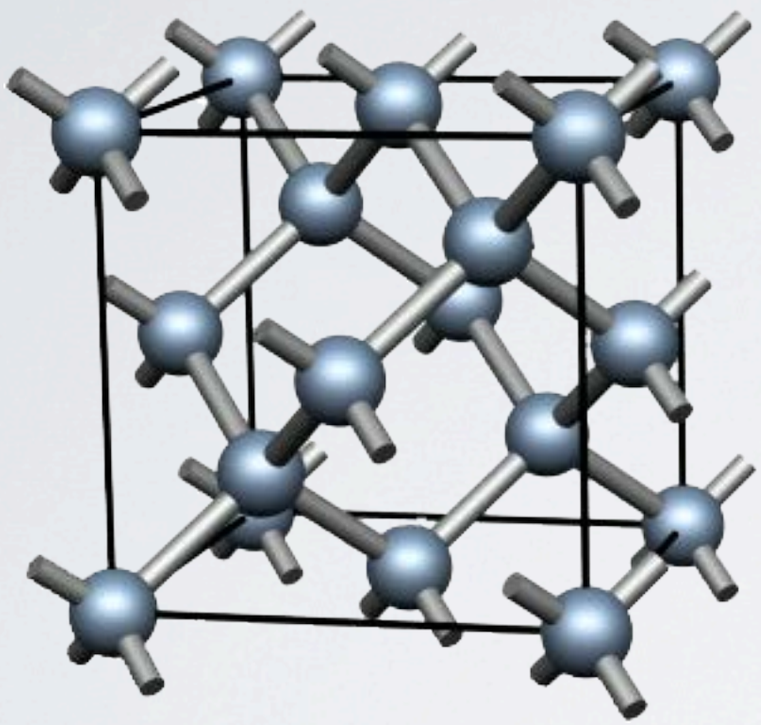
12 NN

FCC 74%

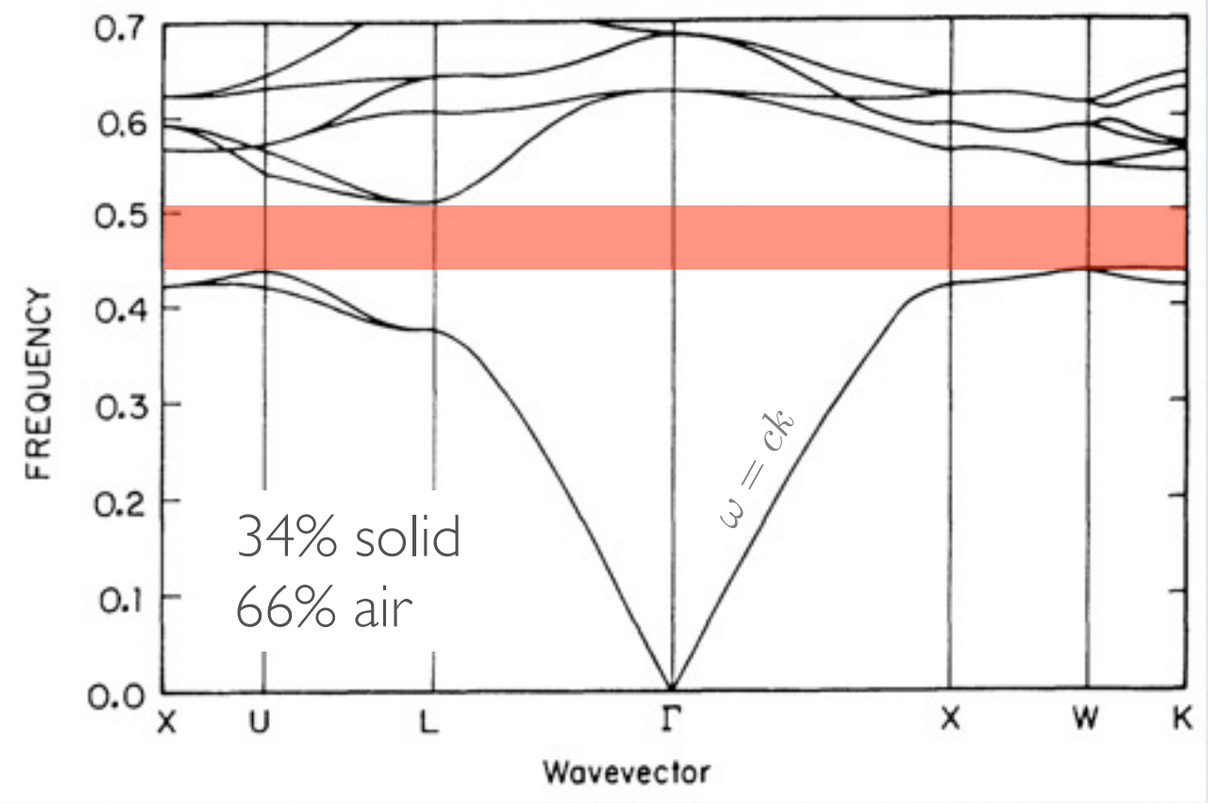
(densest sphere packing)

Colloids with directional interactions

diamond lattice



photonic band gap



Ho, Chan, Soukoulis, PRL **65**, 3152 (1990)

We need colloids with valence

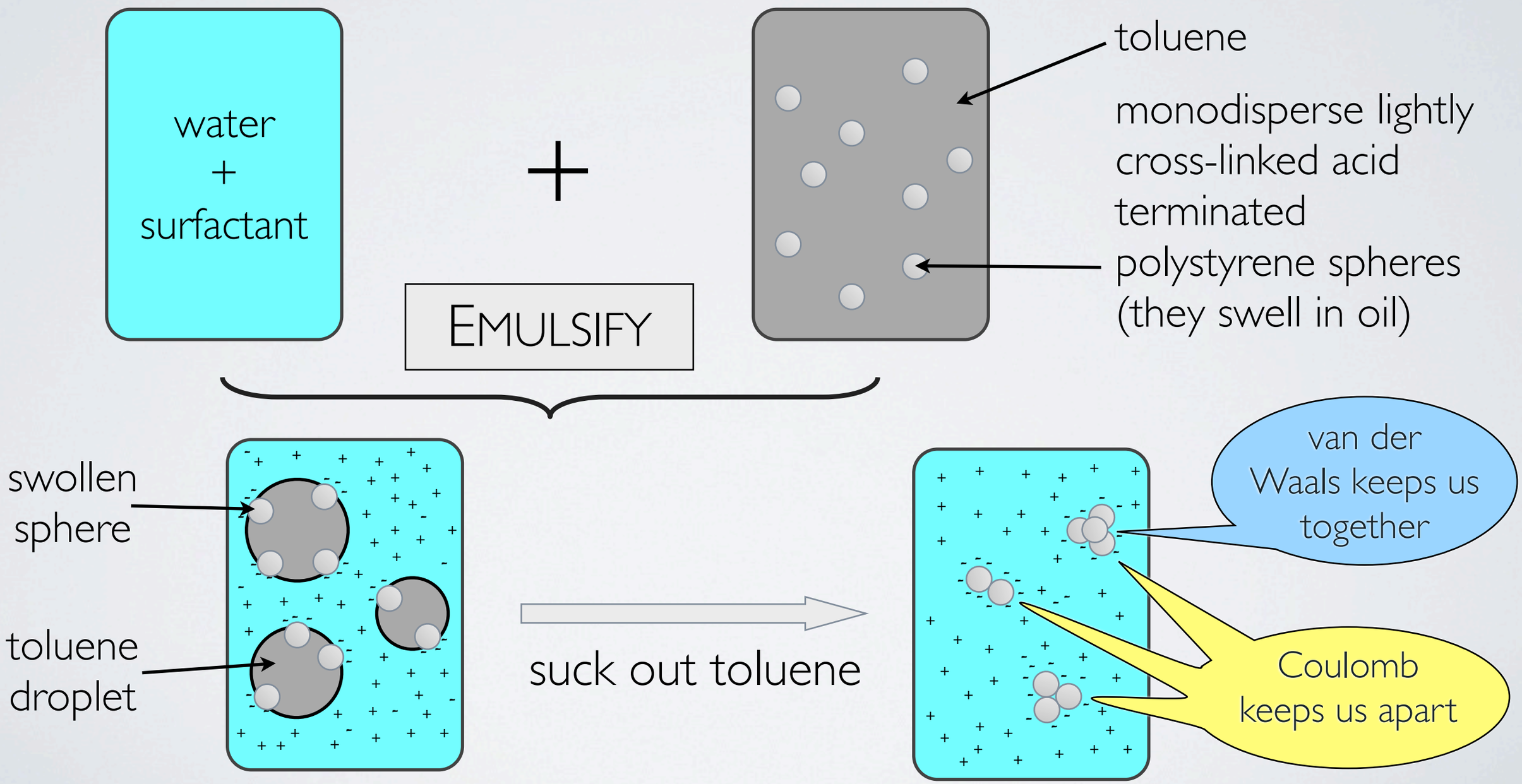
CO_2

CH_4

H_2O

Making colloids with valence:

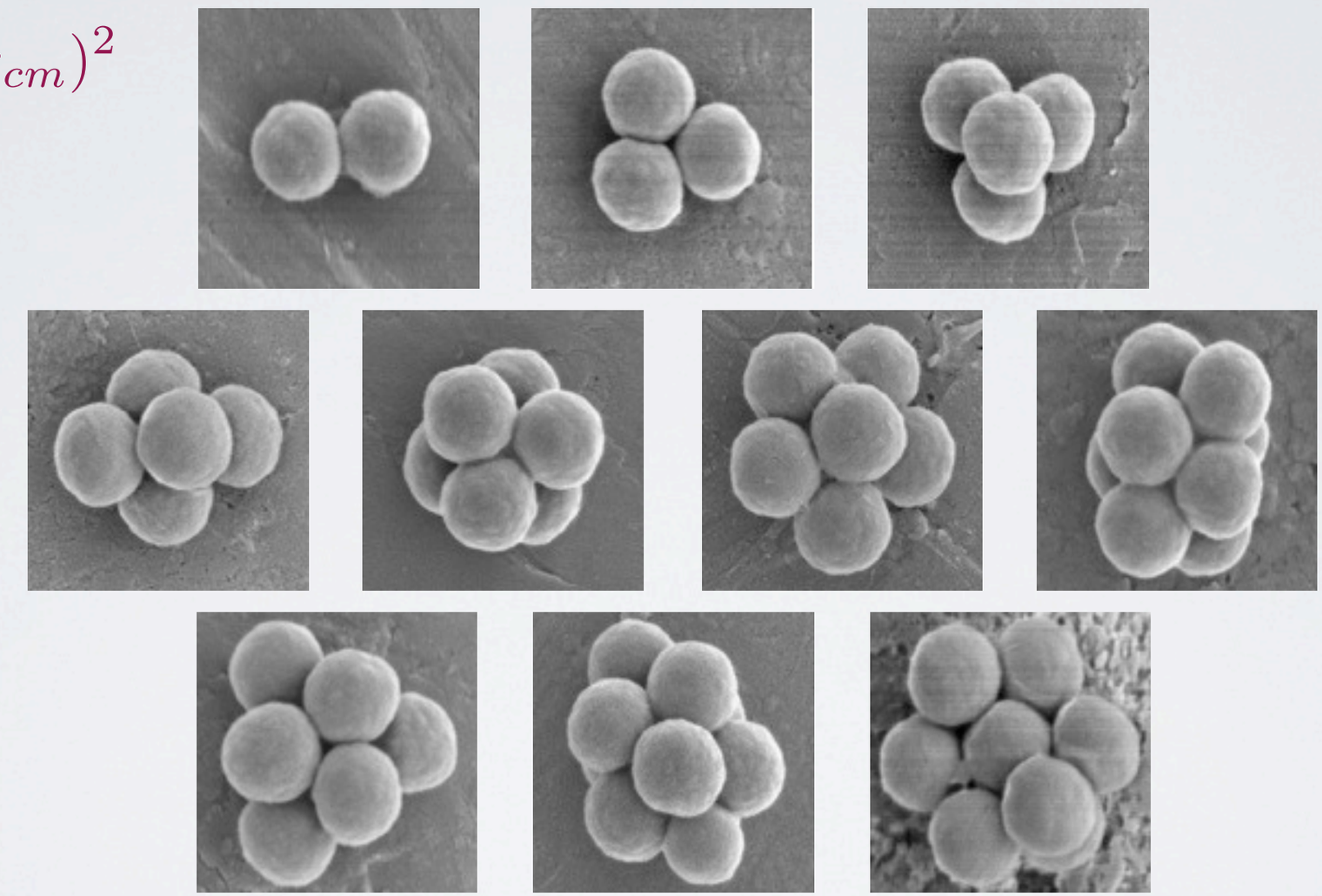
Step #1: Making colloidal clusters



11 first minimal moment clusters

$$M_2 = \sum_0^n (\mathbf{r} - \mathbf{r}_{cm})^2$$

John Conway*
(Princeton)



Calculated by John Conway, Neil Sloane et al.

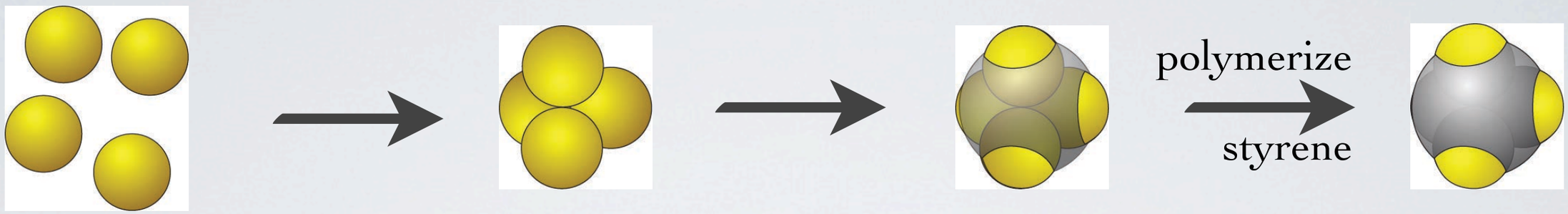
Assembled & measured by Vinny Manoharan

* Conway, Sloane, et al. Discrete Comp. Geom. 14, 237 (1995)

Manoharan et al. Science **301**, 483 (2003)

Making patchy particles

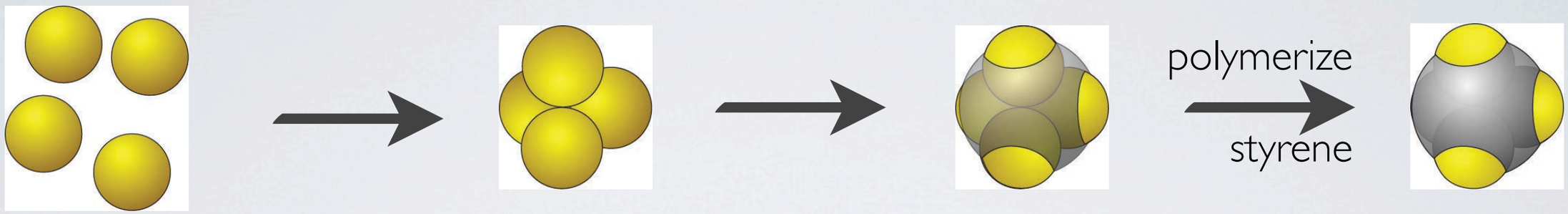
Step #2



amidinated PS spheres → cluster → swell cluster with styrene (emulsion) → (polymerize styrene) → amidinated patchy sphere

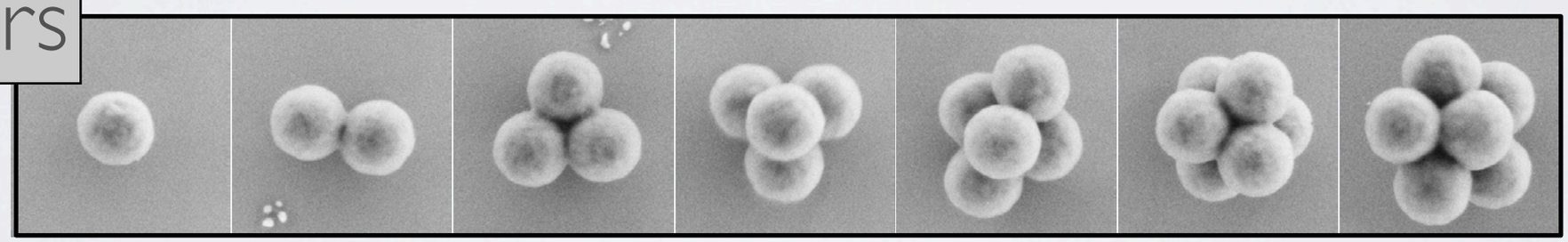
Patchy particles

Step #2



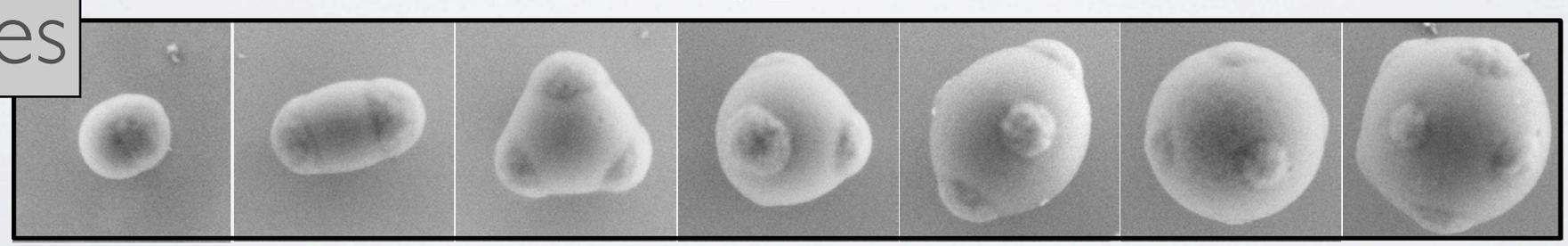
amidinated PS spheres → cluster → swell cluster with styrene (emulsion) → amidinated patchy sphere

clusters



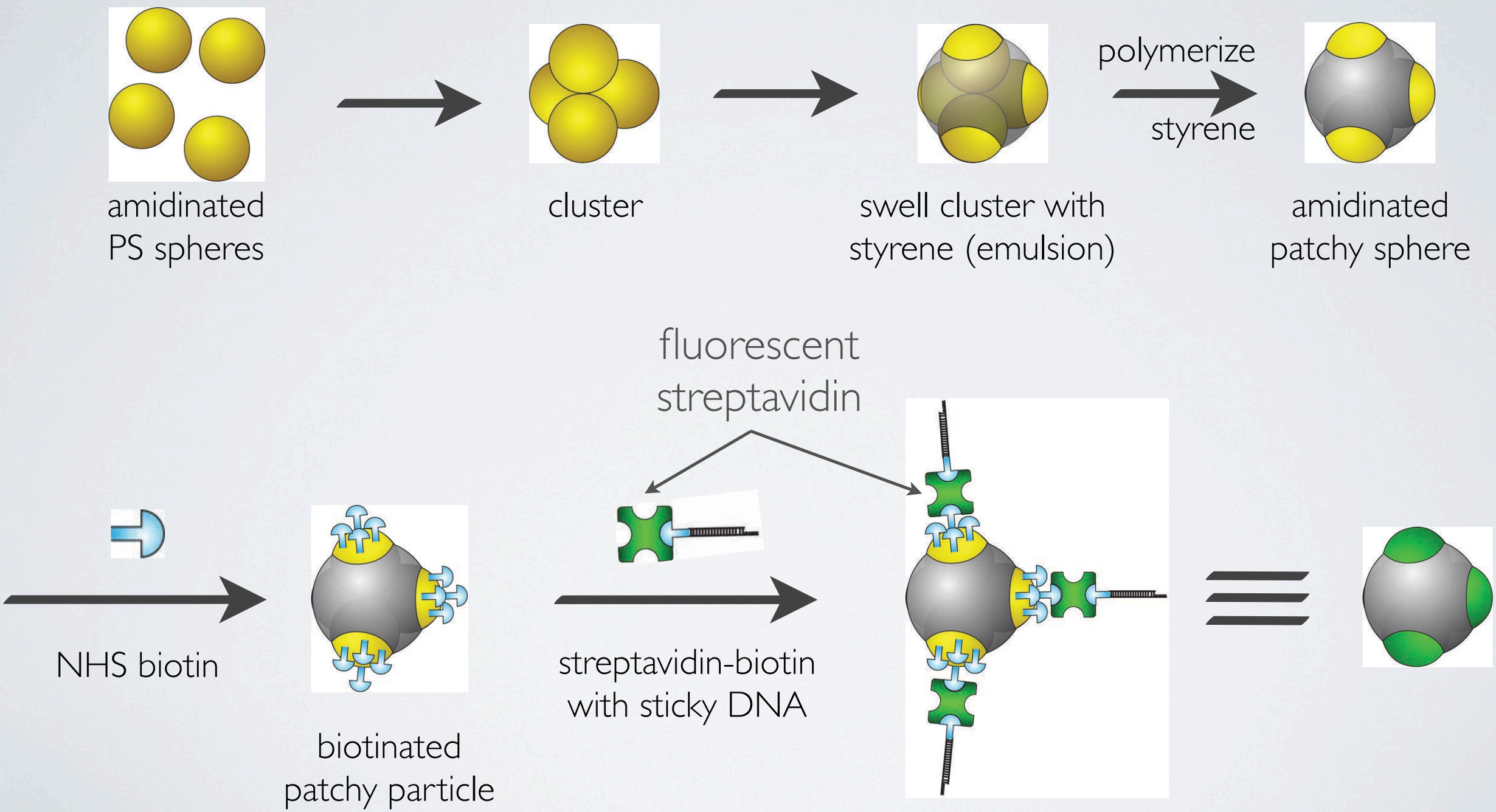
SEM

patches

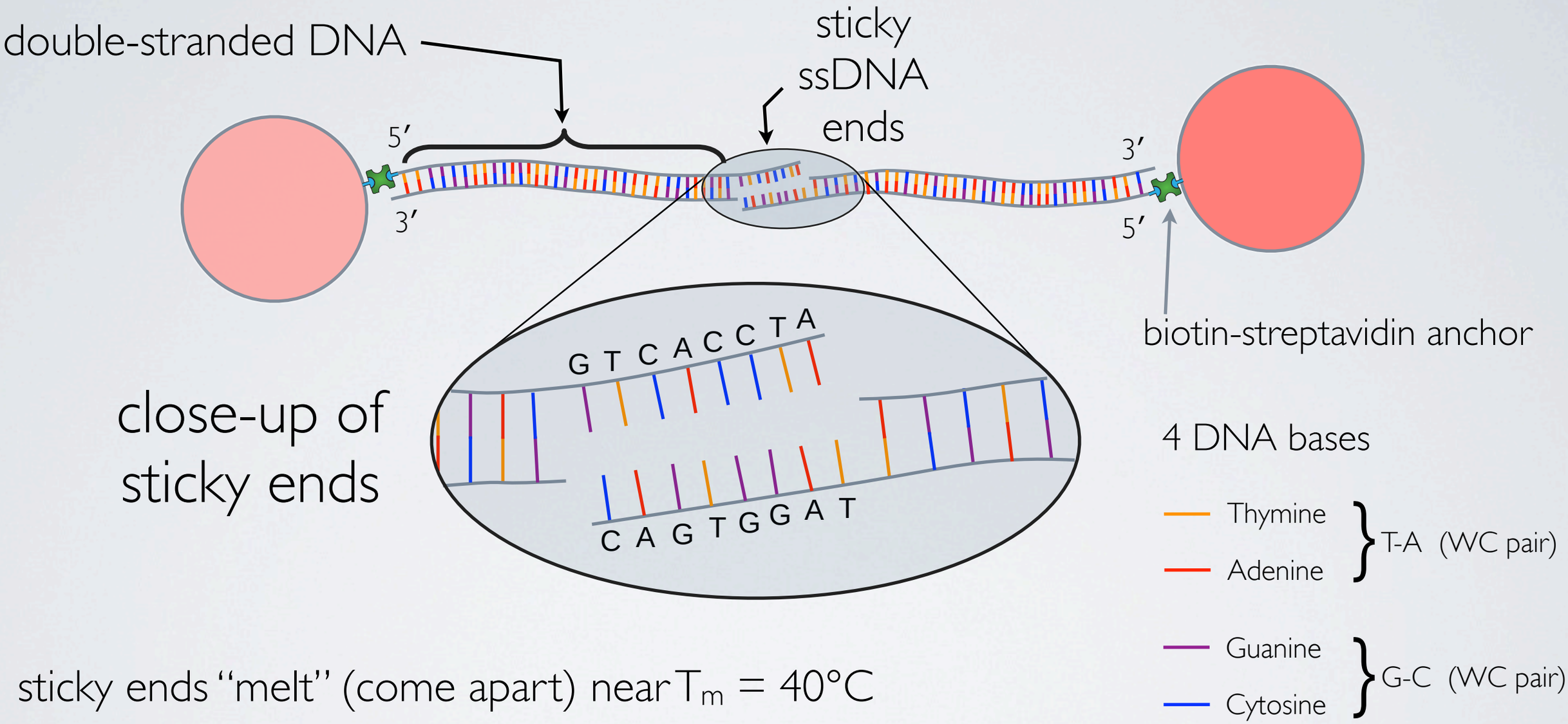


Functionalizing patchy particles

Step #3



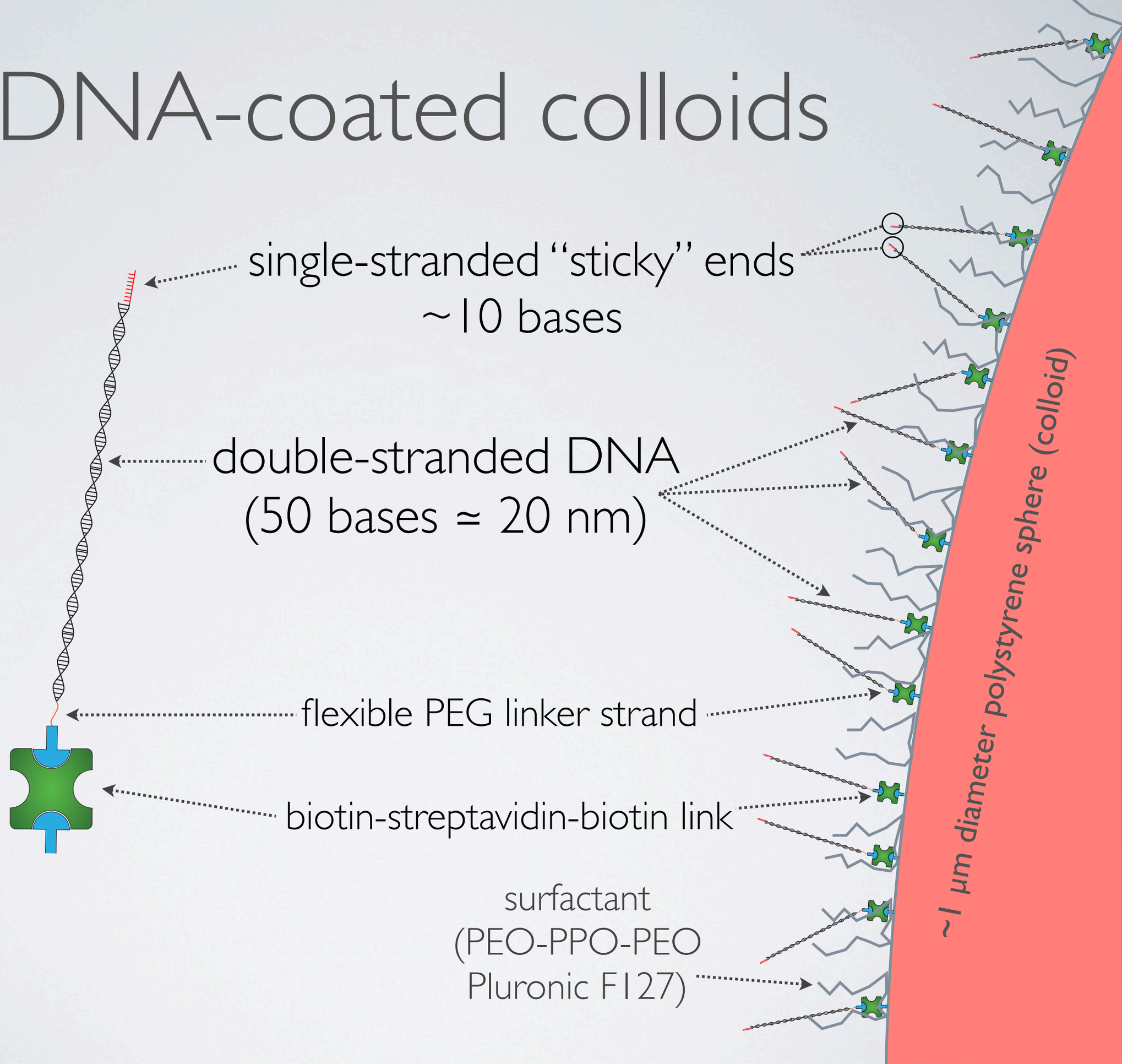
single-stranded DNA (ssDNA)



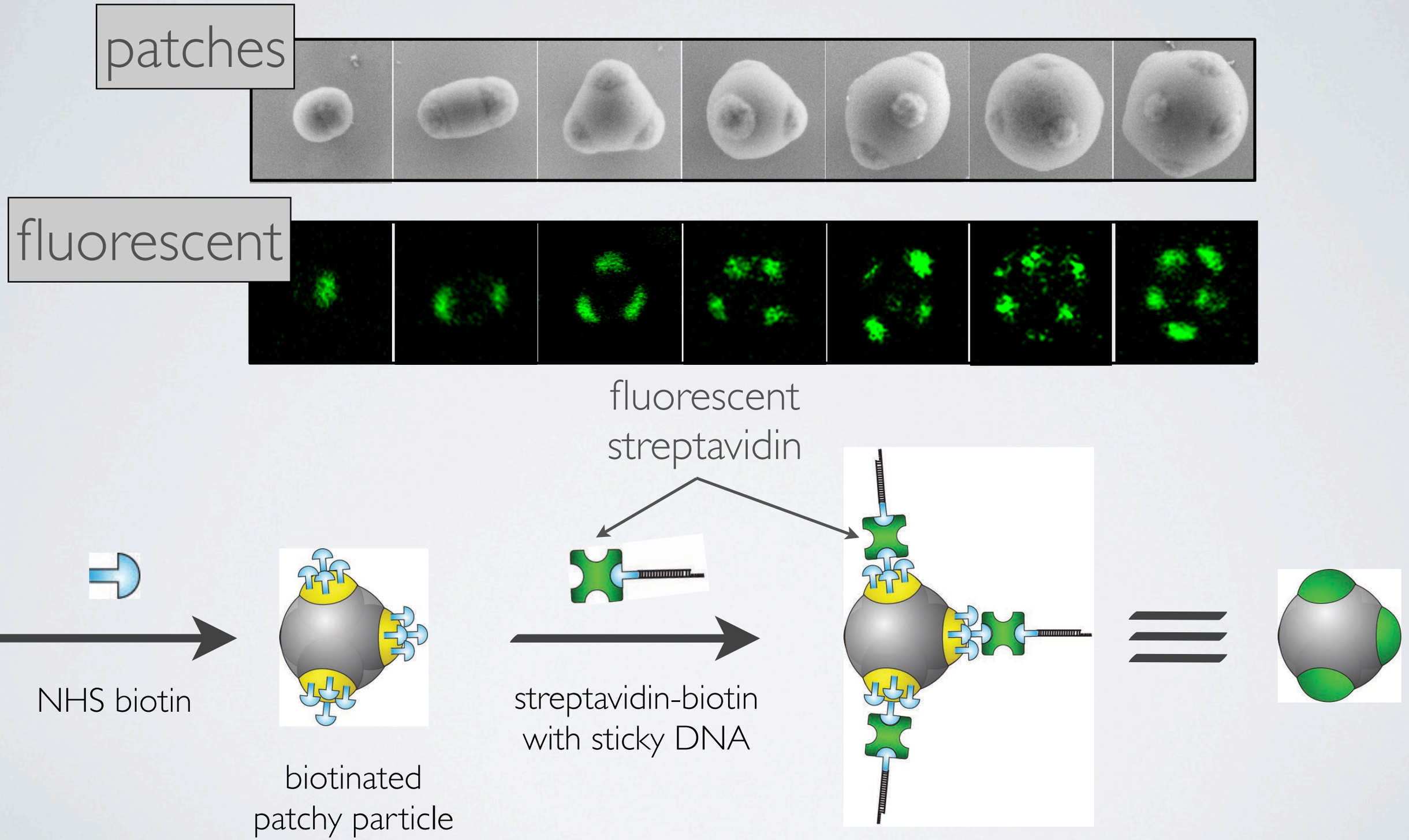
- sticky ends "melt" (come apart) near T_m = 40°C
- T_m depends on number (and kind) of base pairs
- specificity – only complementary strands link:

→ can "program" sticky ends by sequence of bases ⇒ recognition

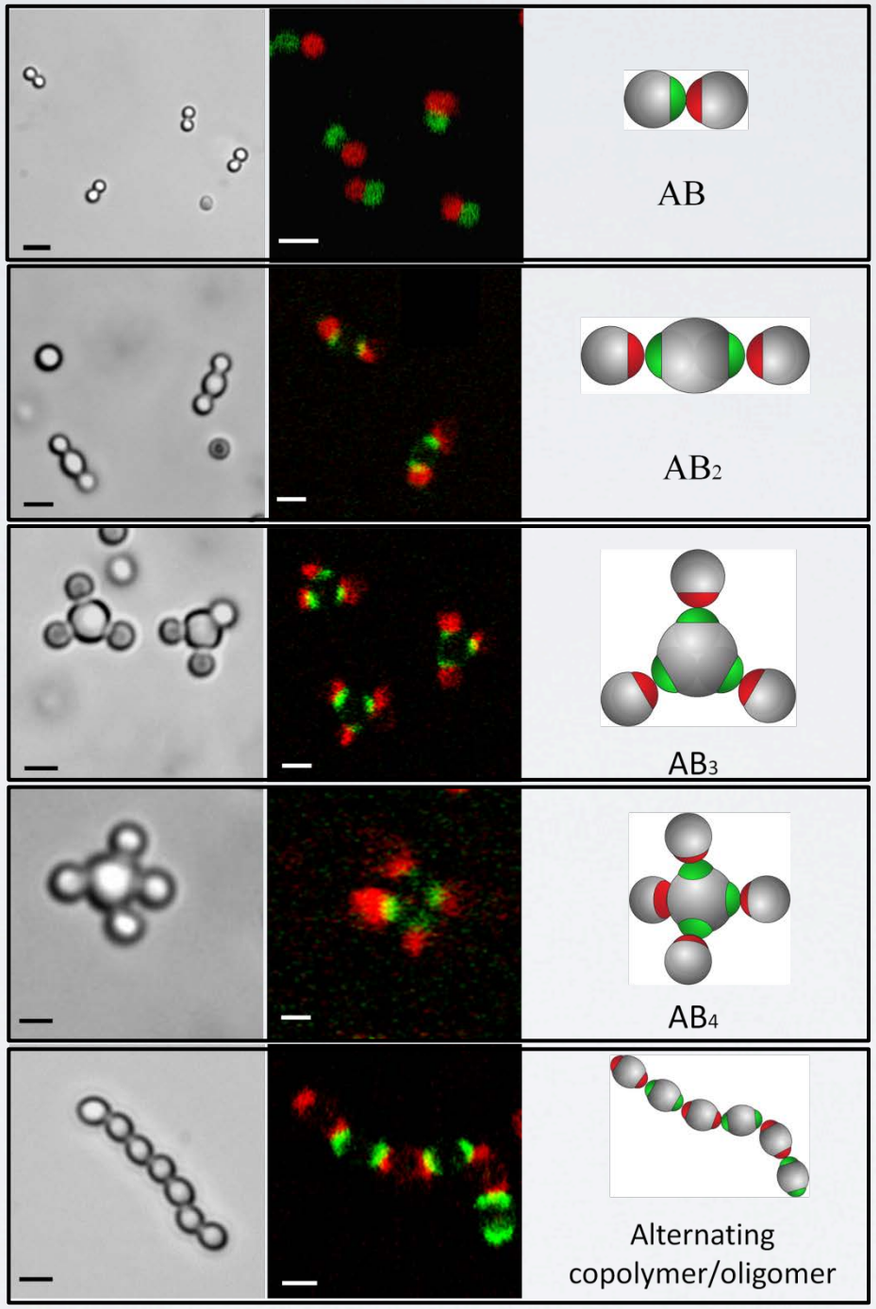
DNA-coated colloids



Functionalizing patchy particles



Linking up: it's specific!



AB

AB_2

AB_3

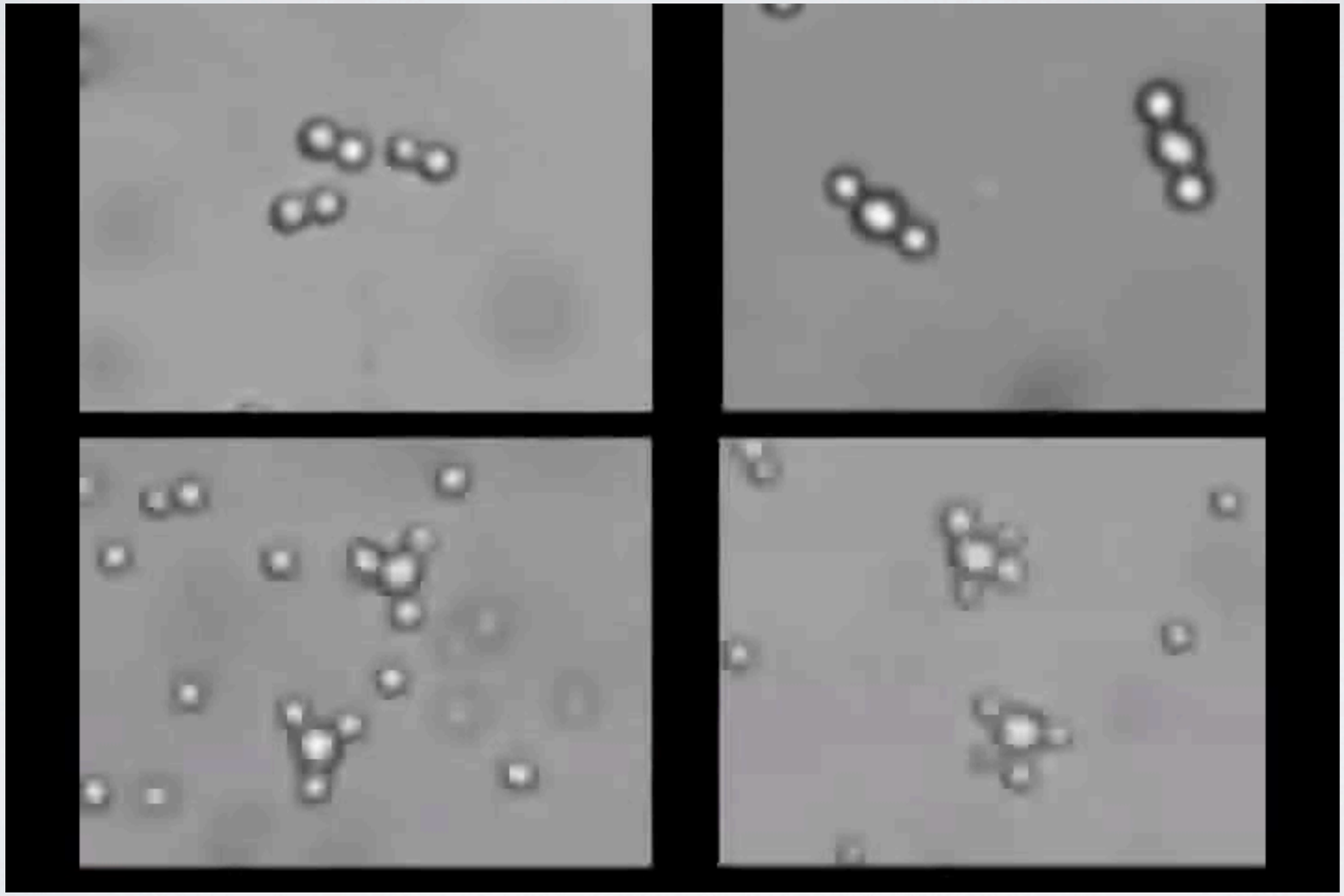
AB_4

scale bar = 800 nm

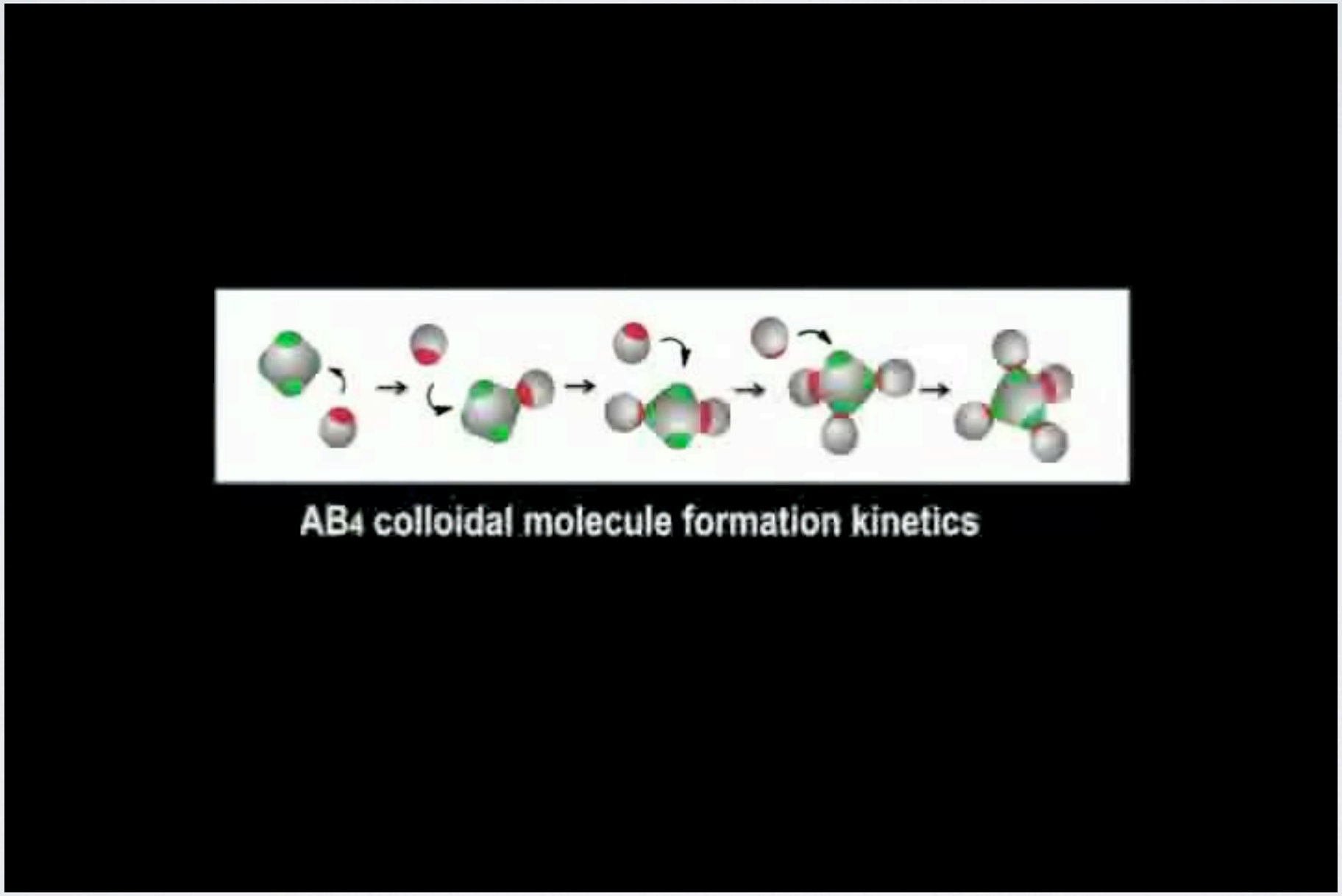
Wang *et al.* Nature **491**, 51-55 (2012)

Colloidal molecules

small patches



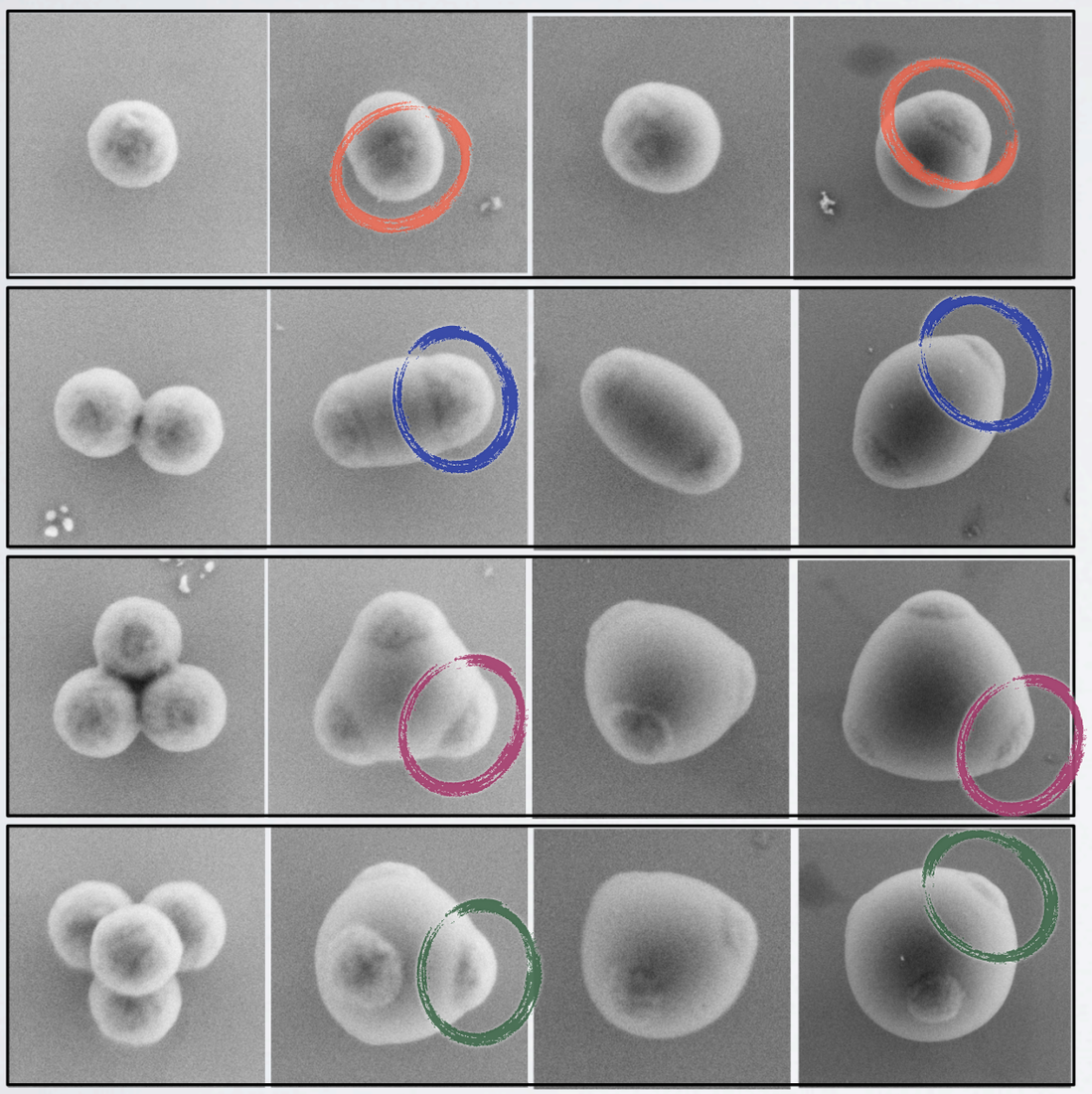
AB_4 formation kinetics



4x play rate

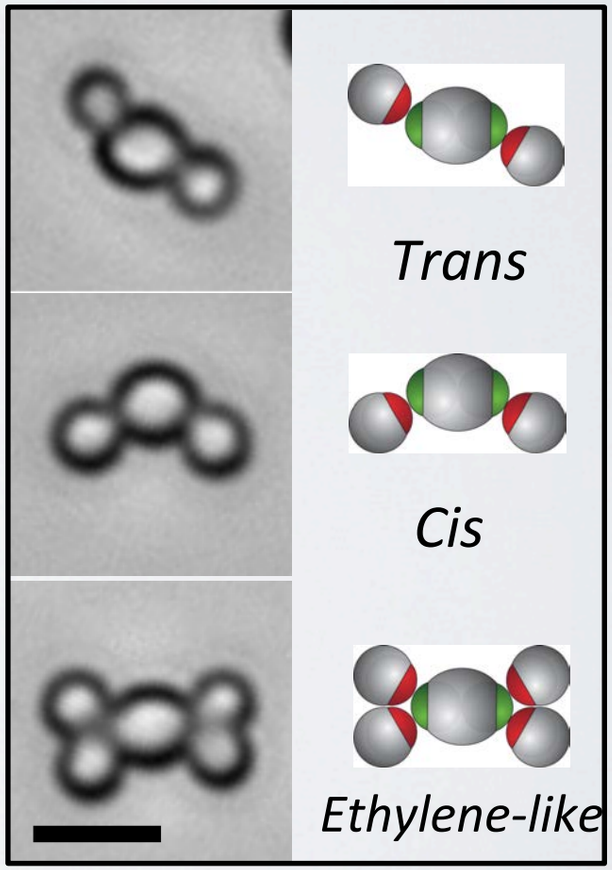
Controlling patch size

decreasing patch size



decreasing patch size

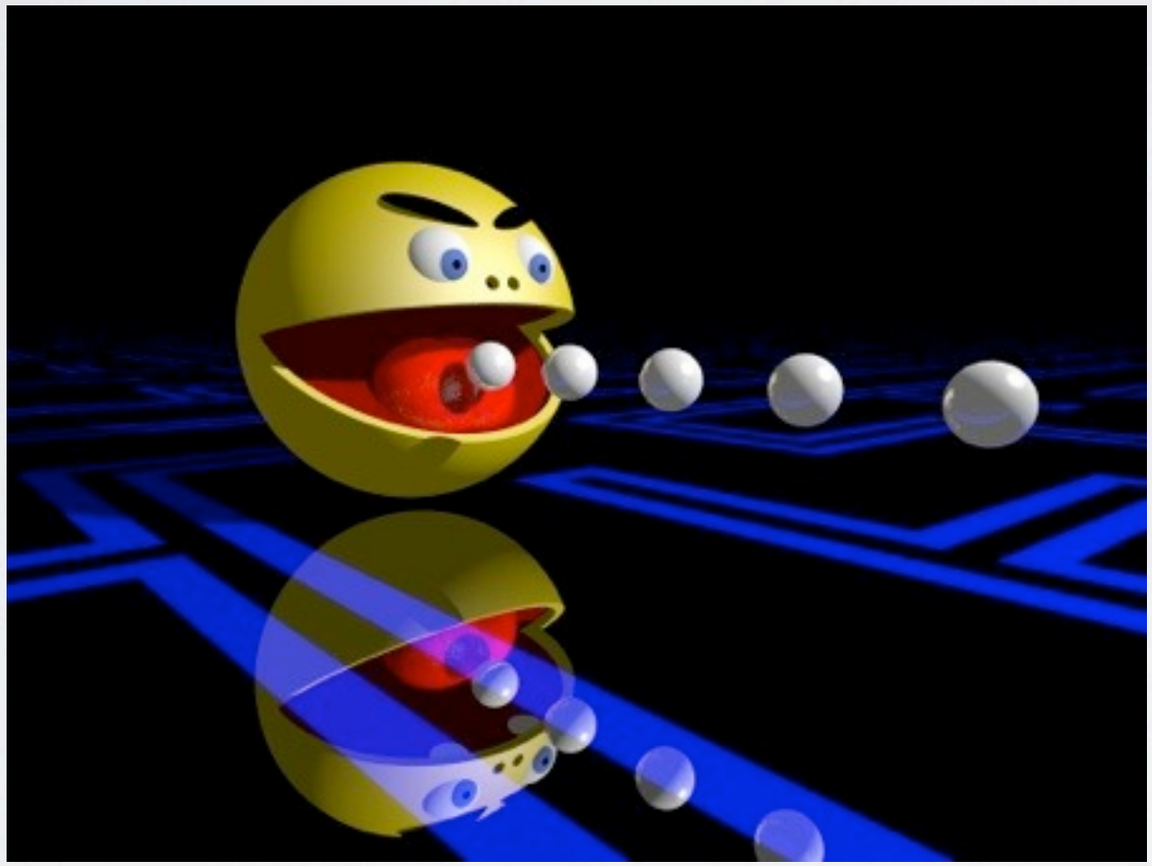
Linking with complementary particles



big patches

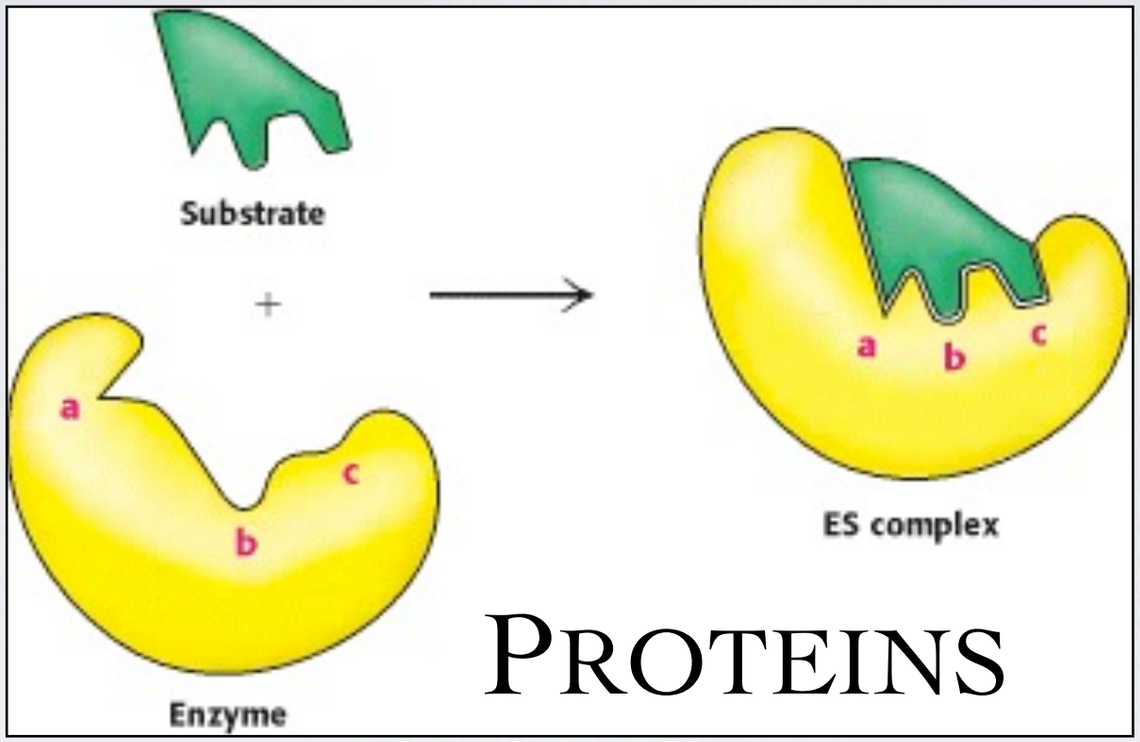
Lock & Key Colloids

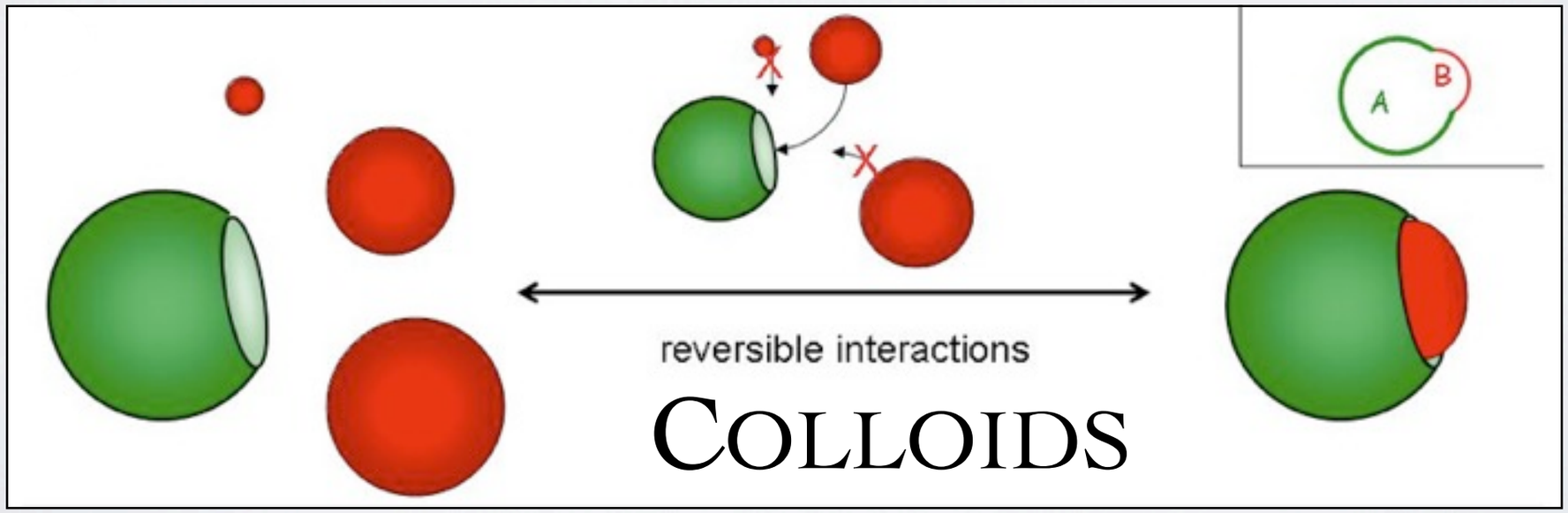
Drawing inspiration from proteins ...



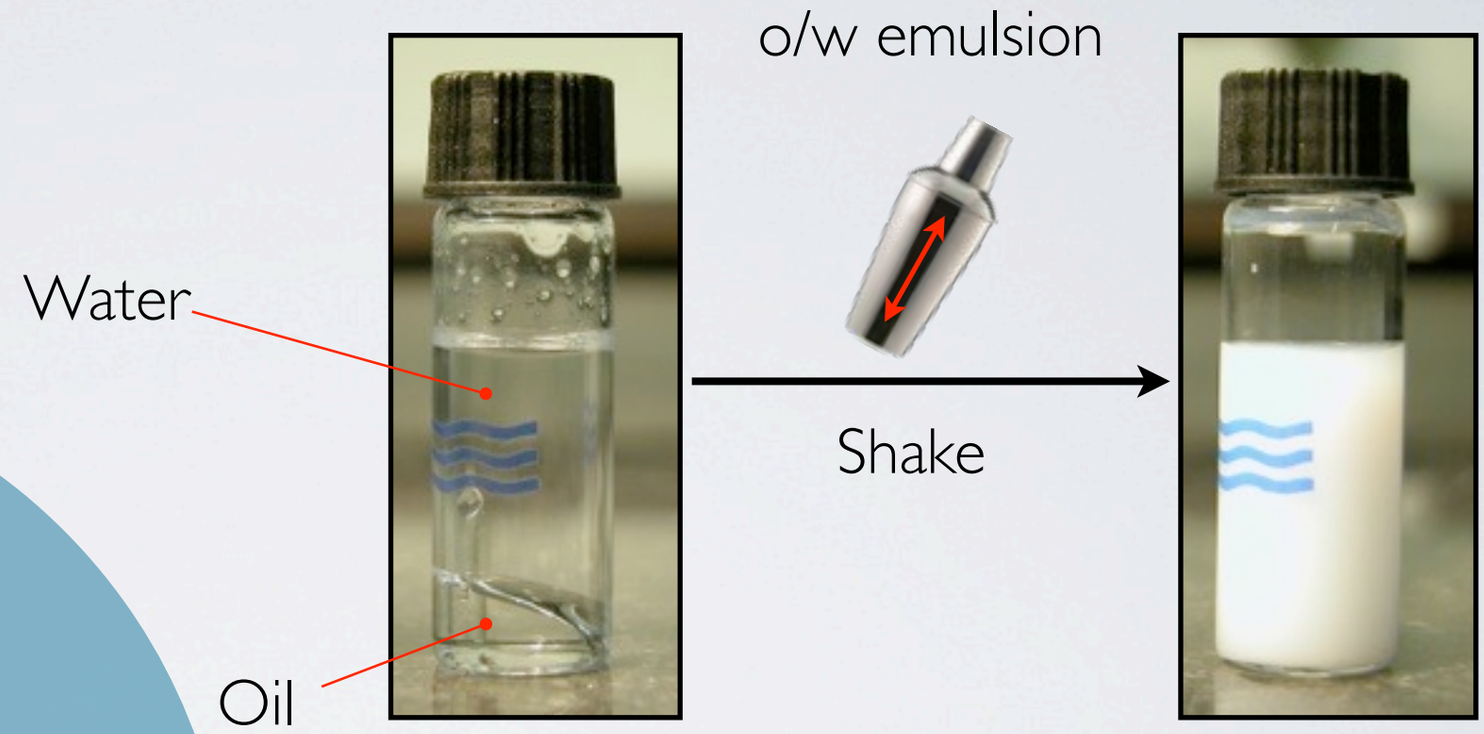
Pac-Man Particles

Lock & Key Colloids



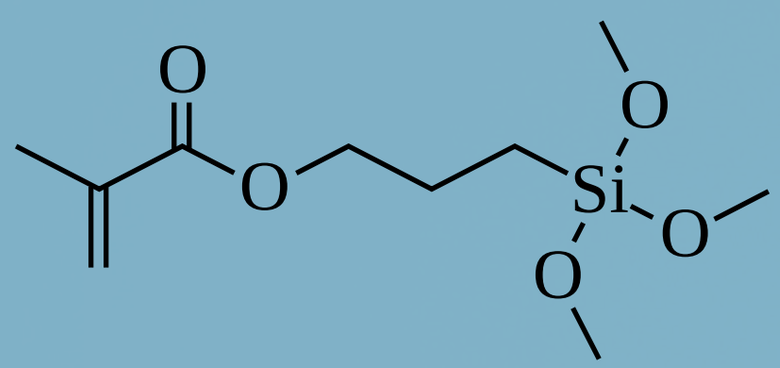


Pacman particle synthesis



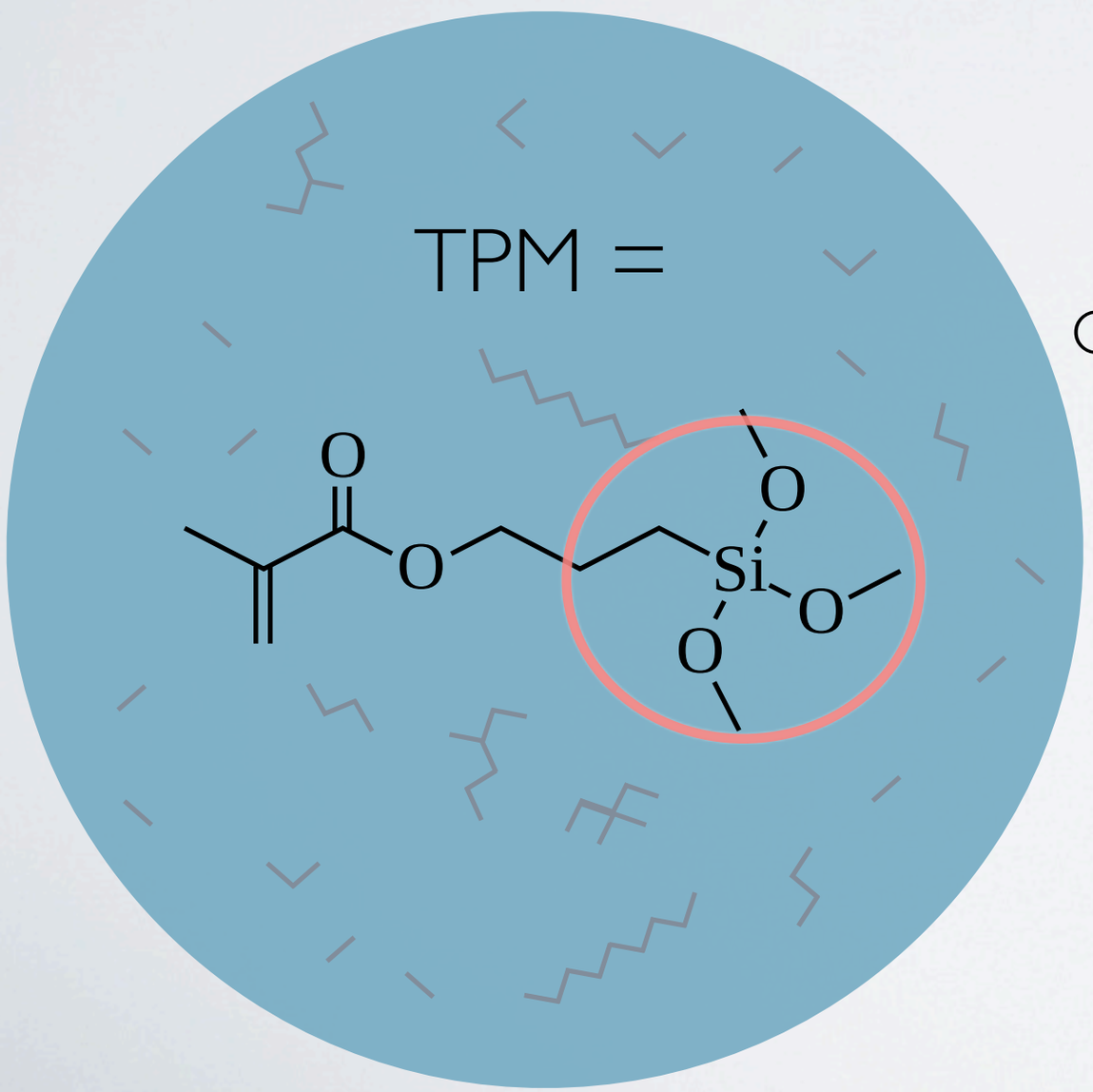
Oil = "TPM" = 3-methacryloxypropyl trimethoxysilane

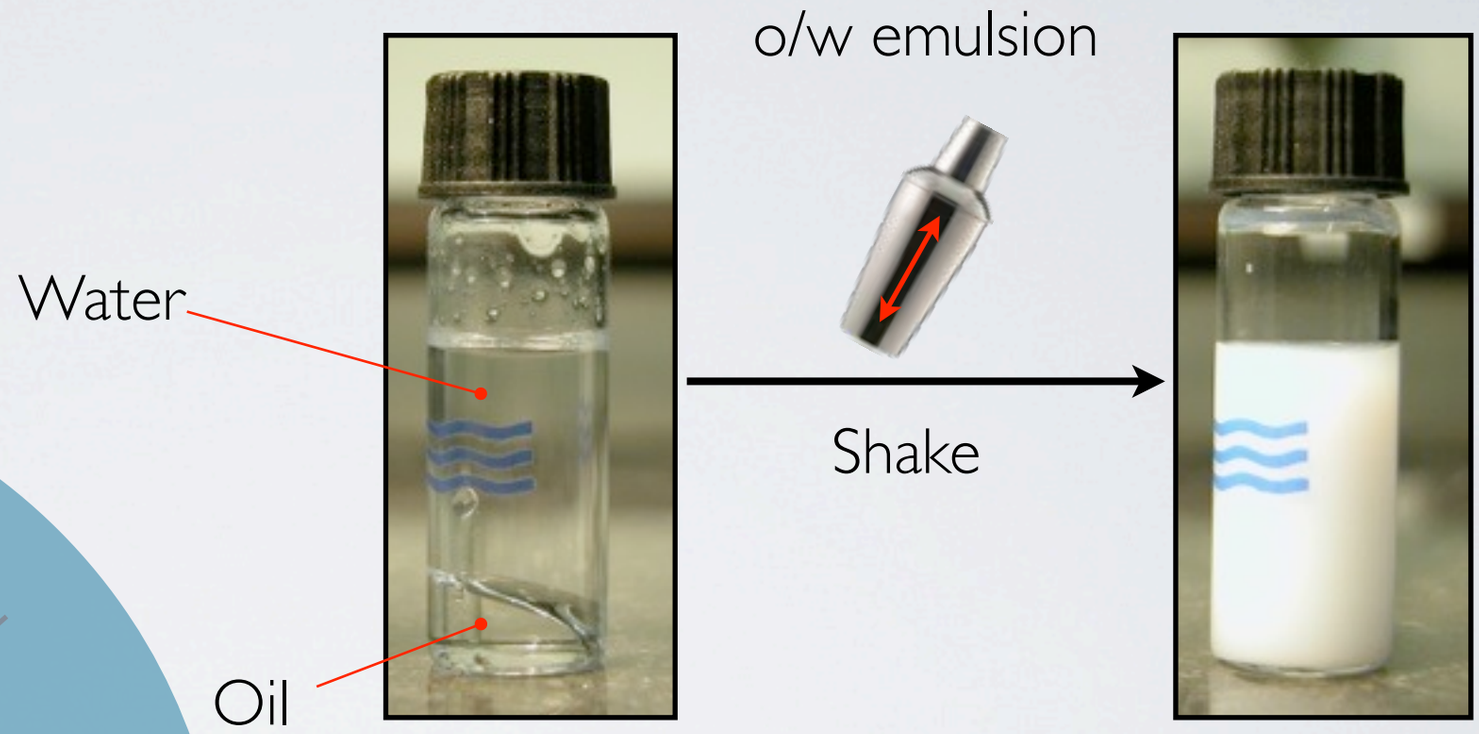
TPM =



Make emulsion
(oil droplets in water)

Pacman particle synthesis

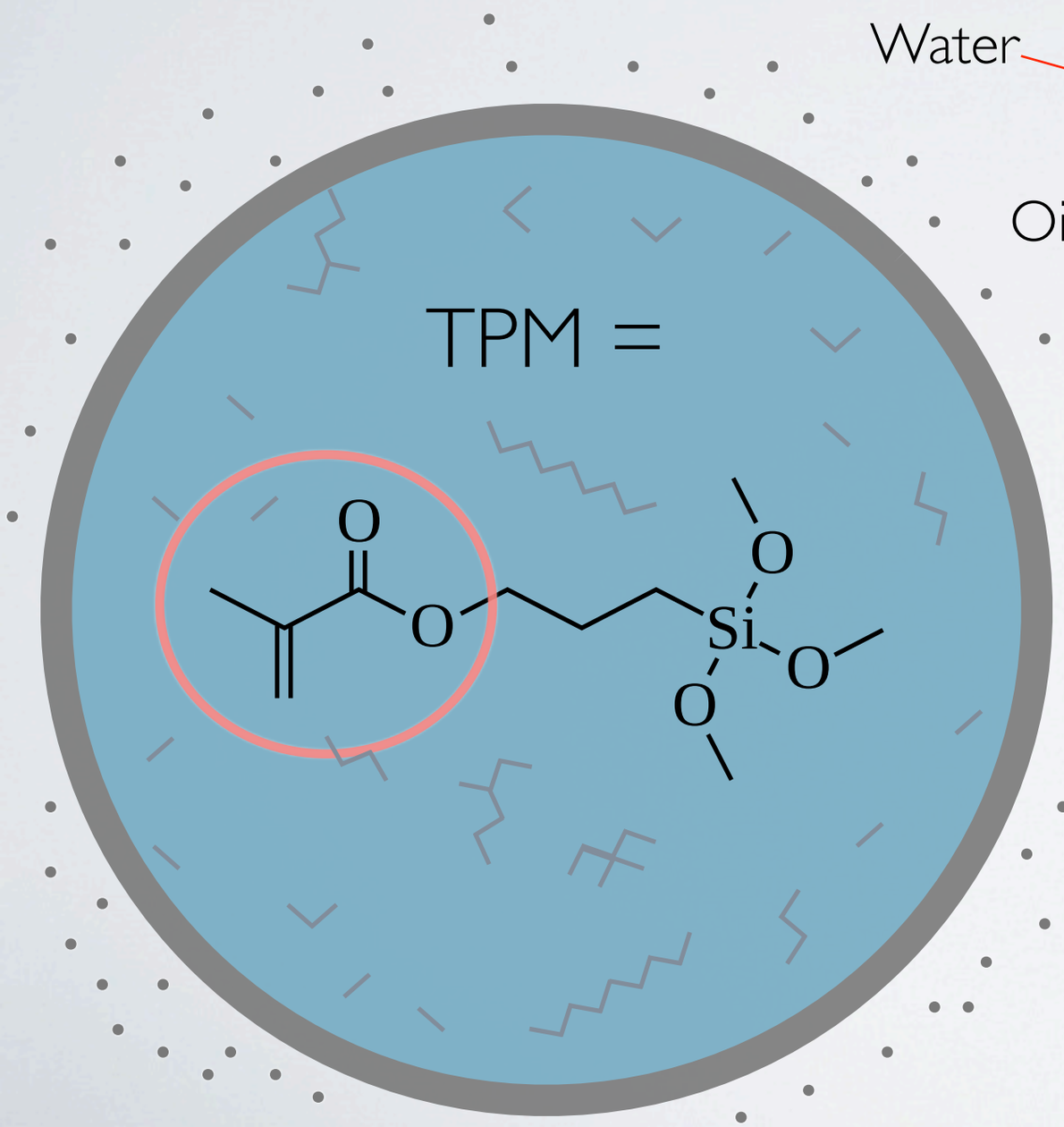


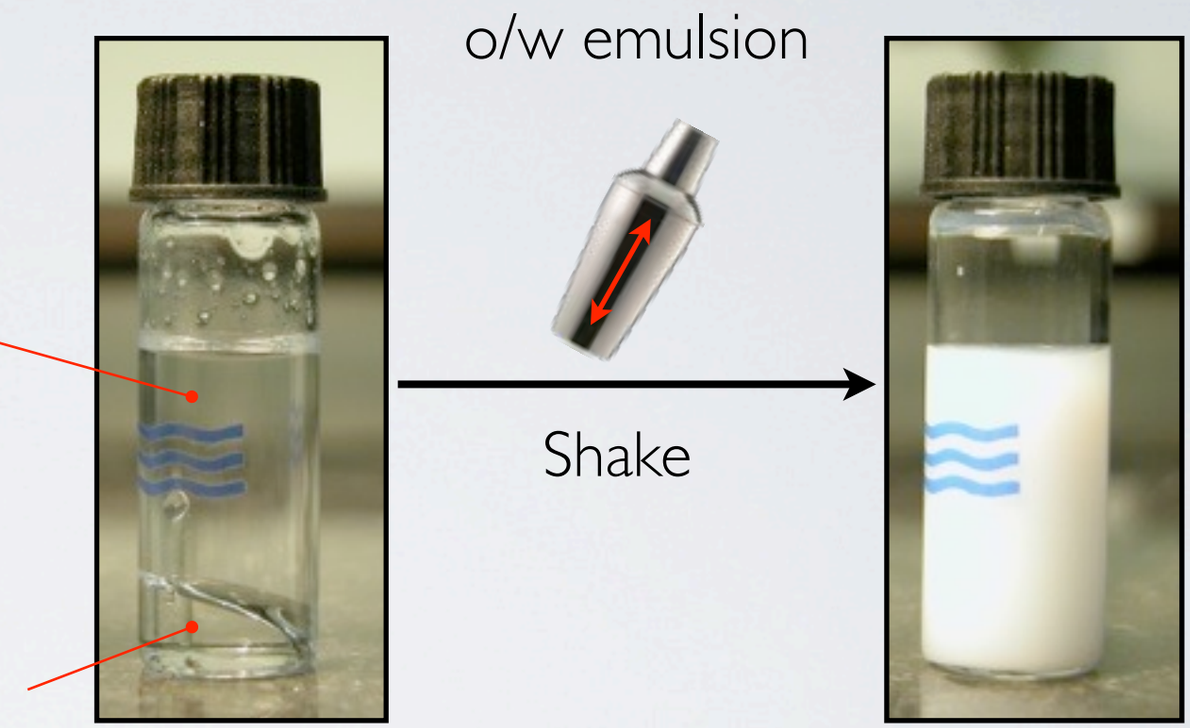


Oligomerize oil

✦Oligomerize Si-O groups (pH⬆) N~1-10

Pacman particle synthesis

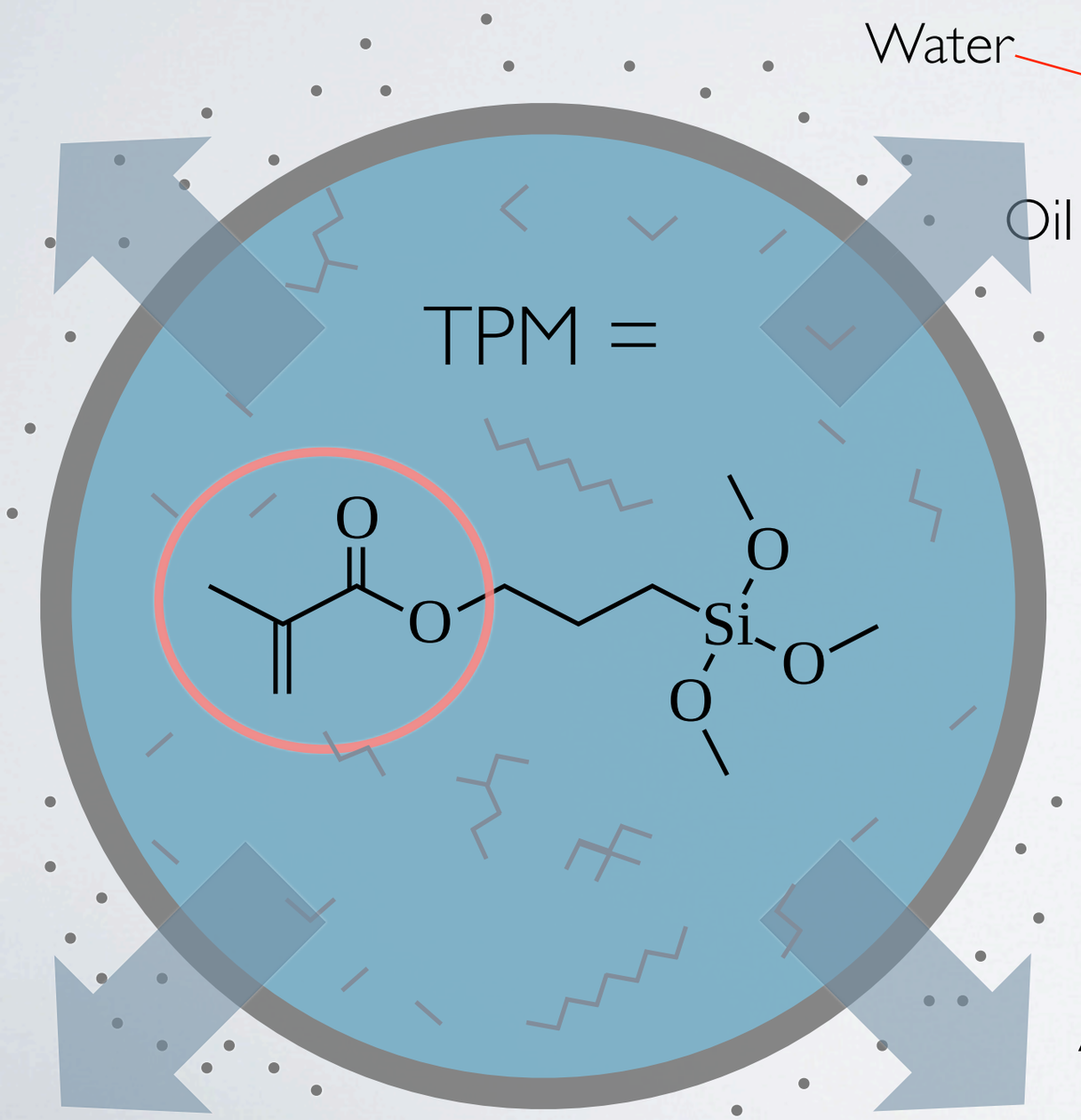


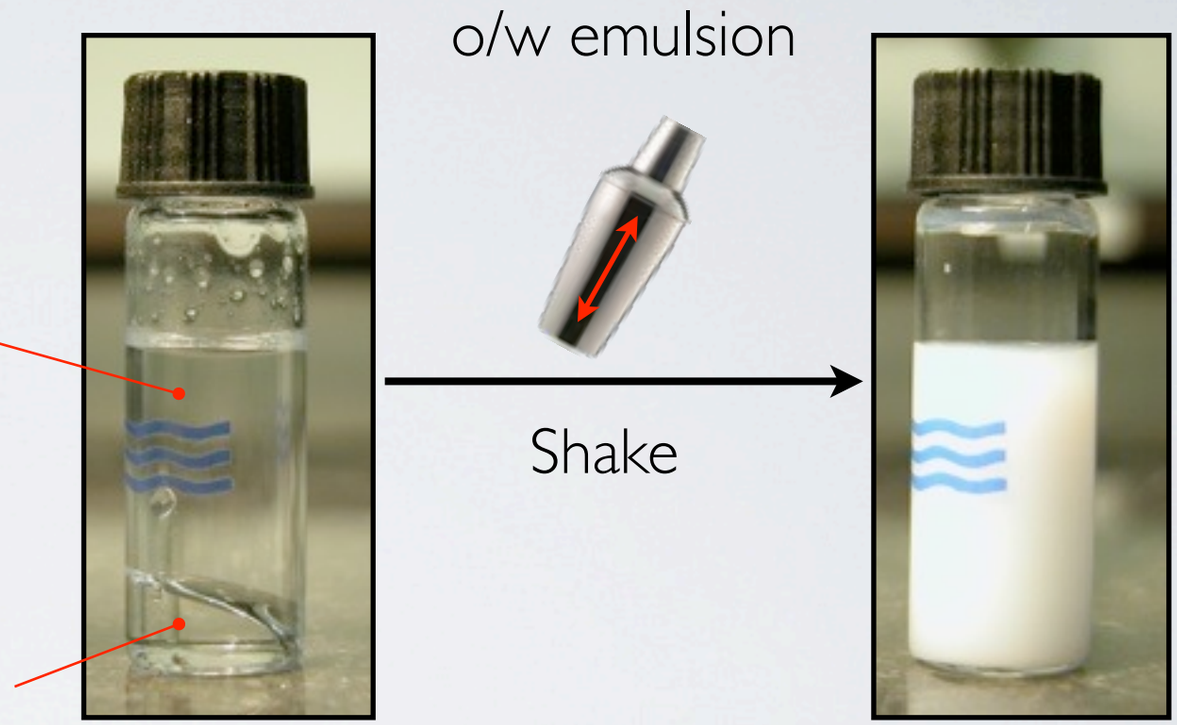


Polymerize shell

- ✦Oligomerize Si-O groups (pH⬆) N~1-10
- ✦Polymerize methacrylate groups (free radical)
  - Creates porous shell
  - Nucleates TPM nanoparticles in solution outside of TPM droplets

Pacman particle synthesis



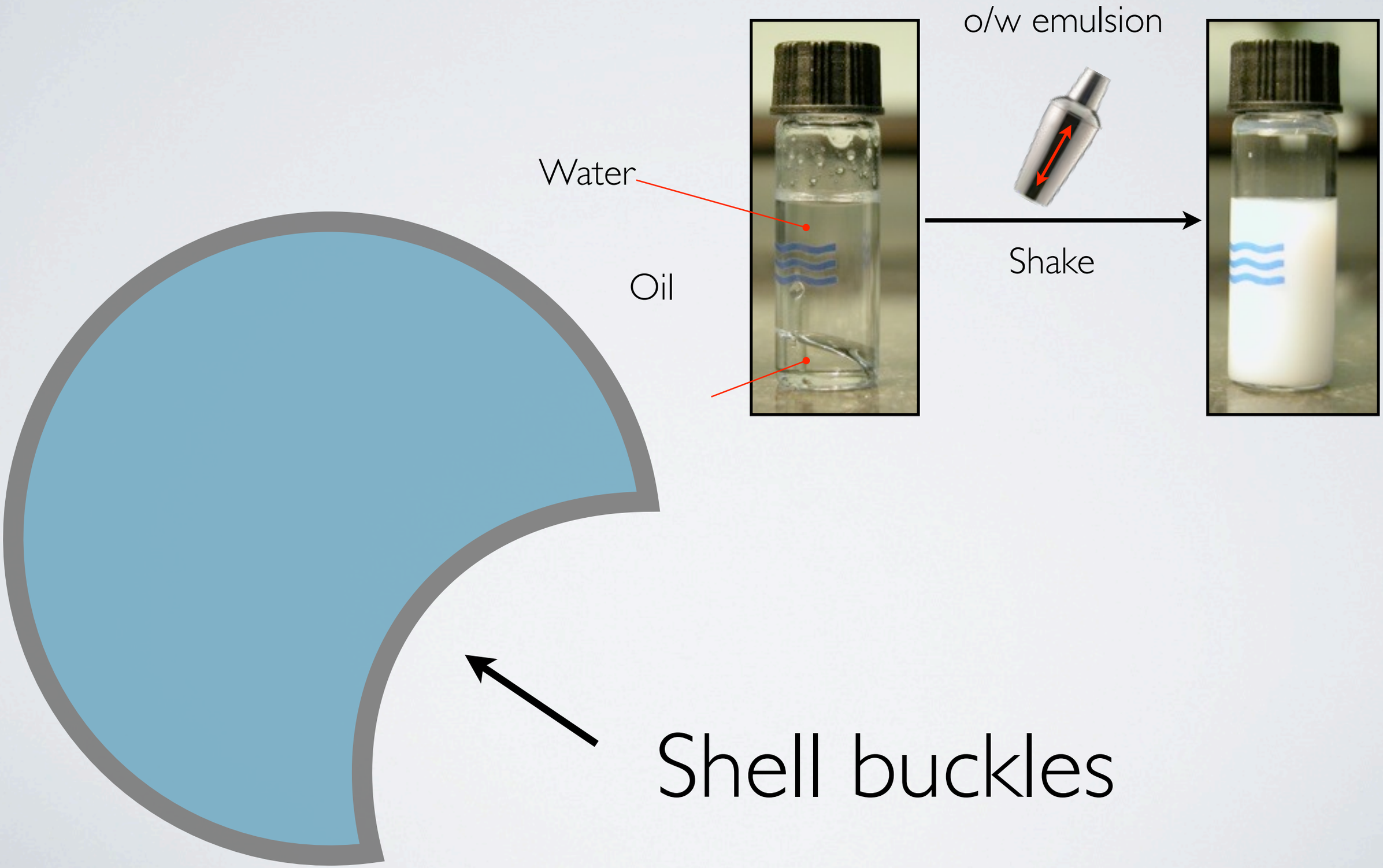


Polymerize shell

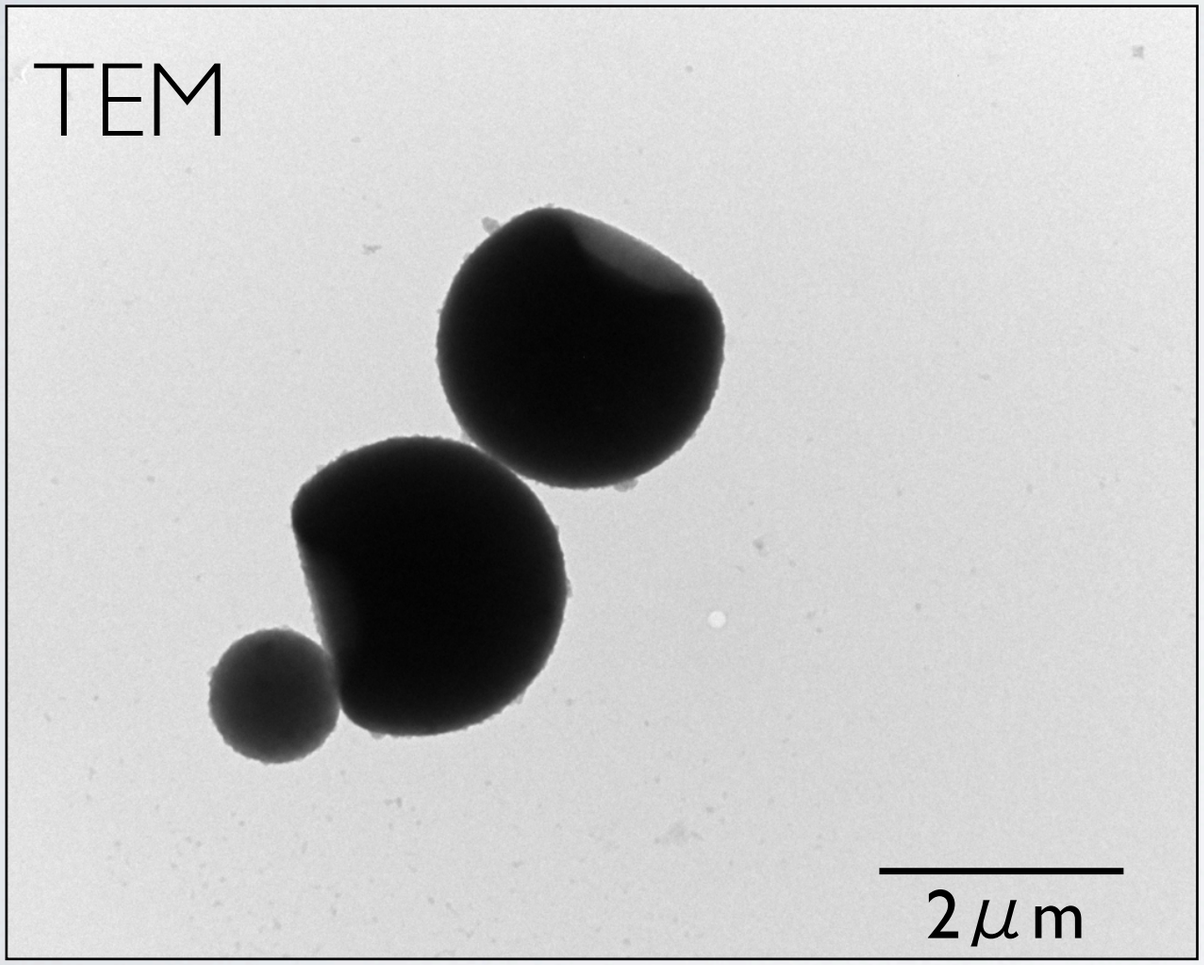
- ✦Oligomerize Si-O groups (pH⬆) N~1-10
- ✦Polymerize methacrylate groups (free radical)
  - Creates porous shell
  - Nucleates TPM nanoparticles in solution outside of TPM droplets
  - Osmotic imbalance sucks small oligomers out of TMP droplets (through shell)

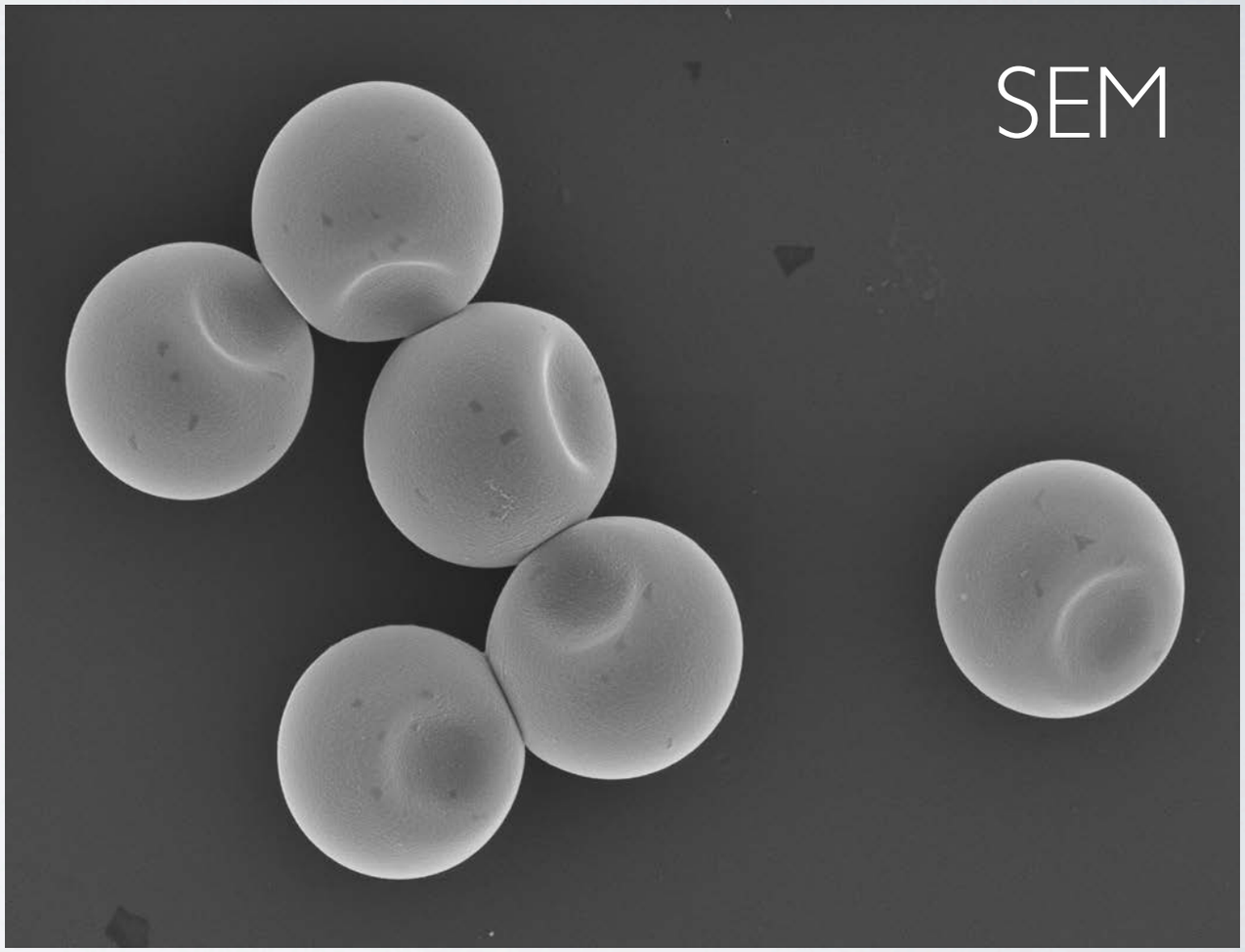
And ...

Pacman particle synthesis



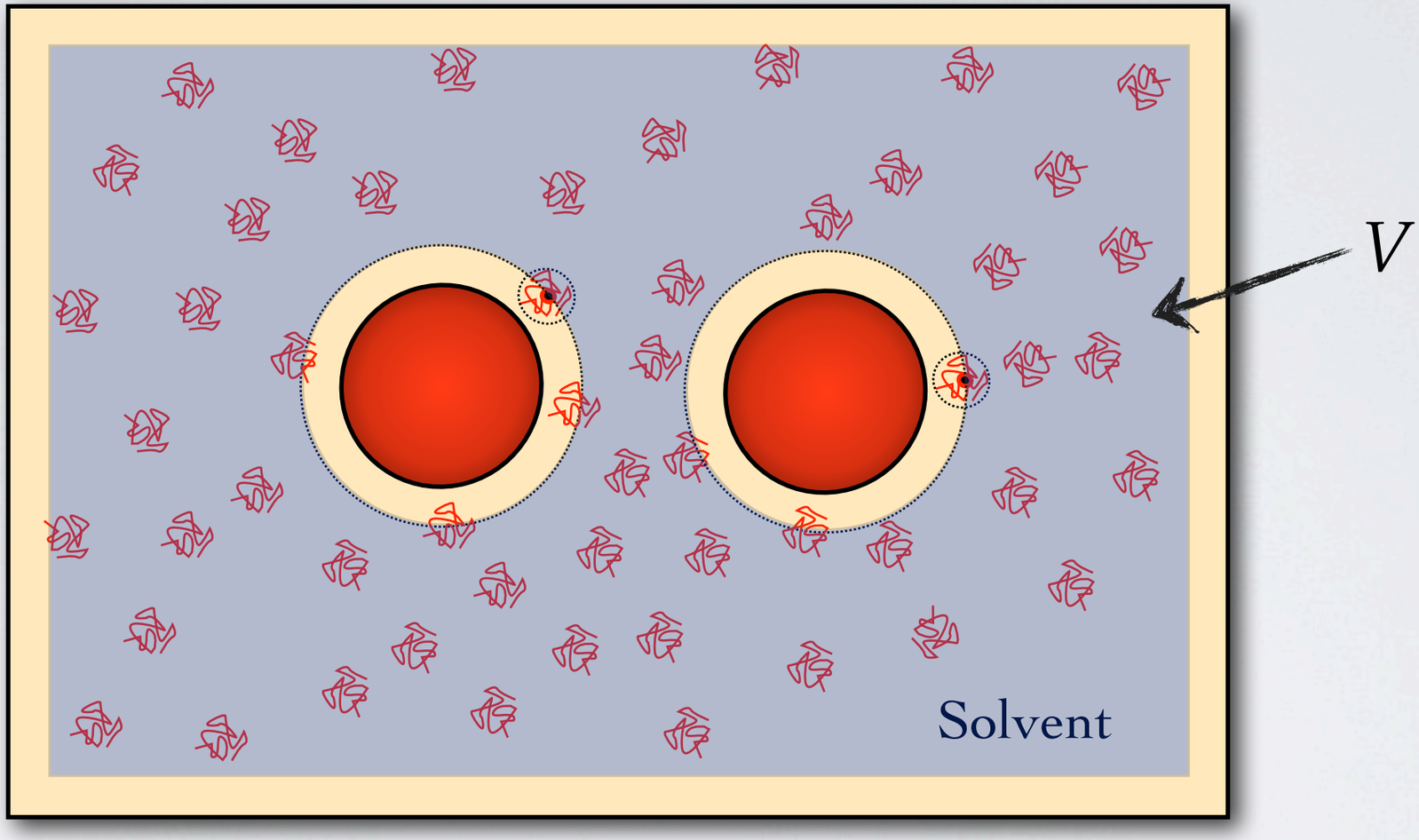
Pacman particles





Depletion interaction

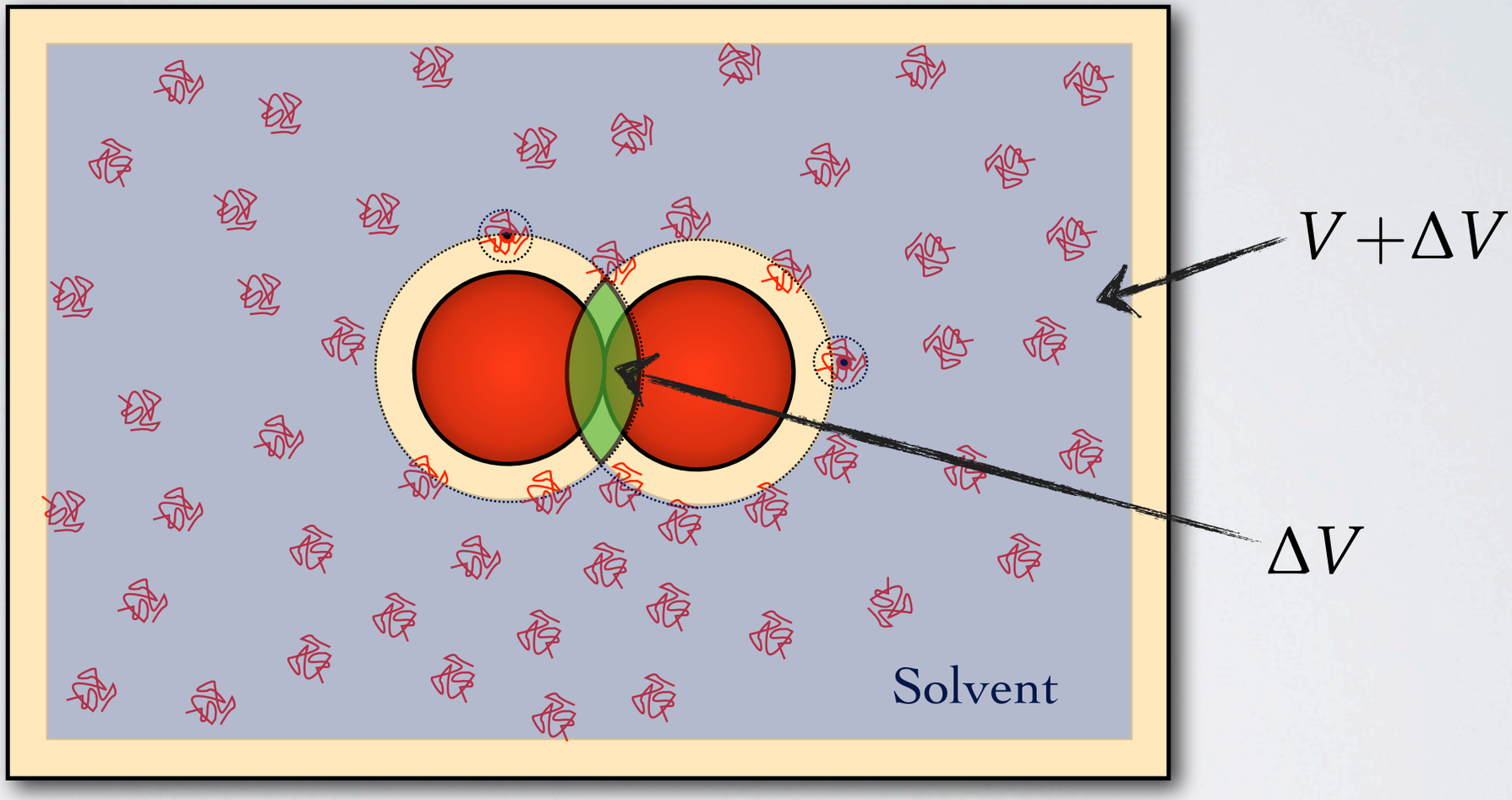
$$S \sim n_{\mathrm{poly}} \ln V$$



Asakura & Oosawa, J. Chem. Phys. **22**, 1255 (1954).

Depletion interaction

$$S \sim n_{\mathrm{poly}} \ln V$$

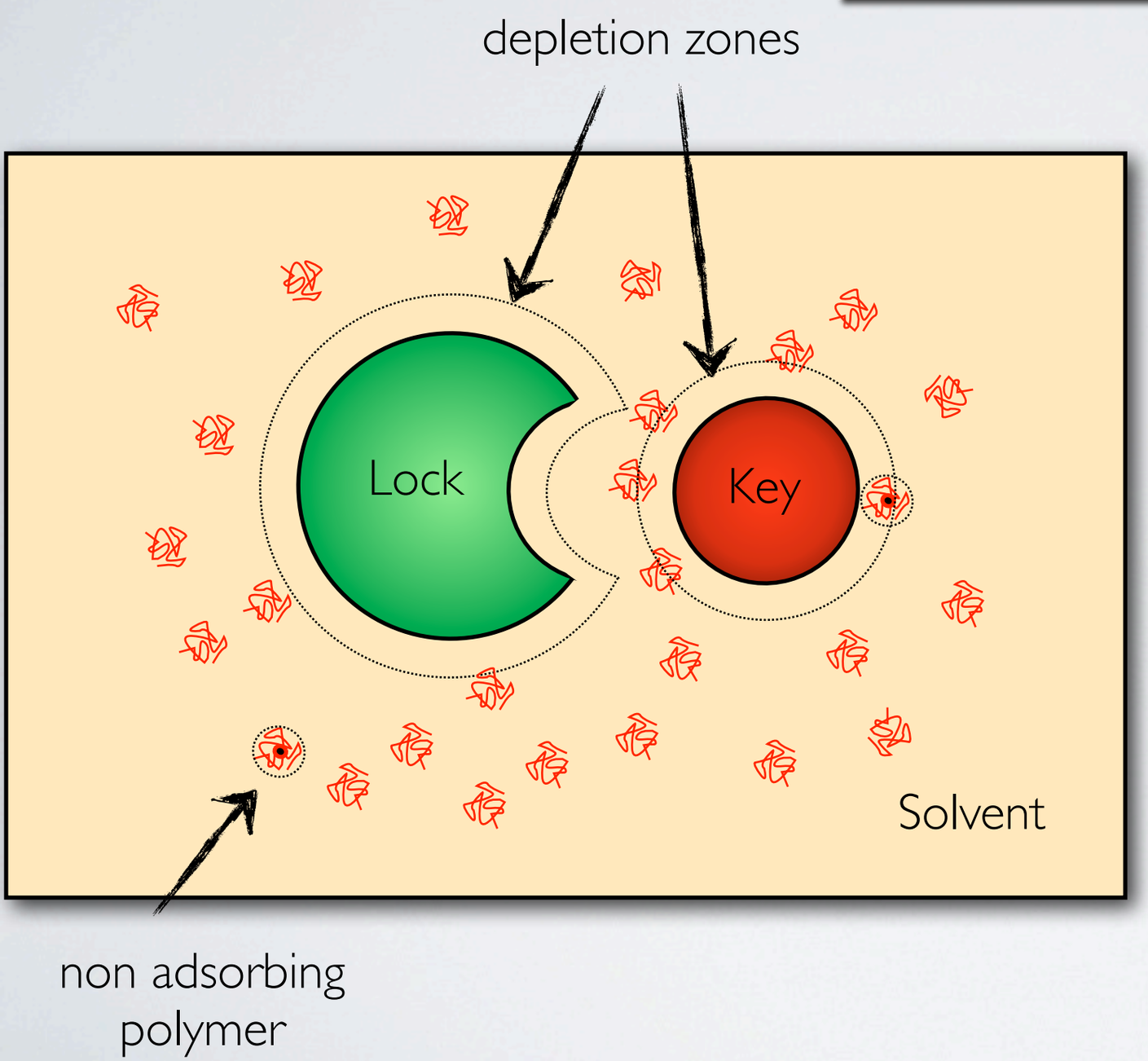


$$\Delta S \sim n_{\mathrm{poly}} \frac{\Delta V}{V}$$

Asakura & Oosawa, J. Chem. Phys. **22**, 1255 (1954).

Pacman lock & key

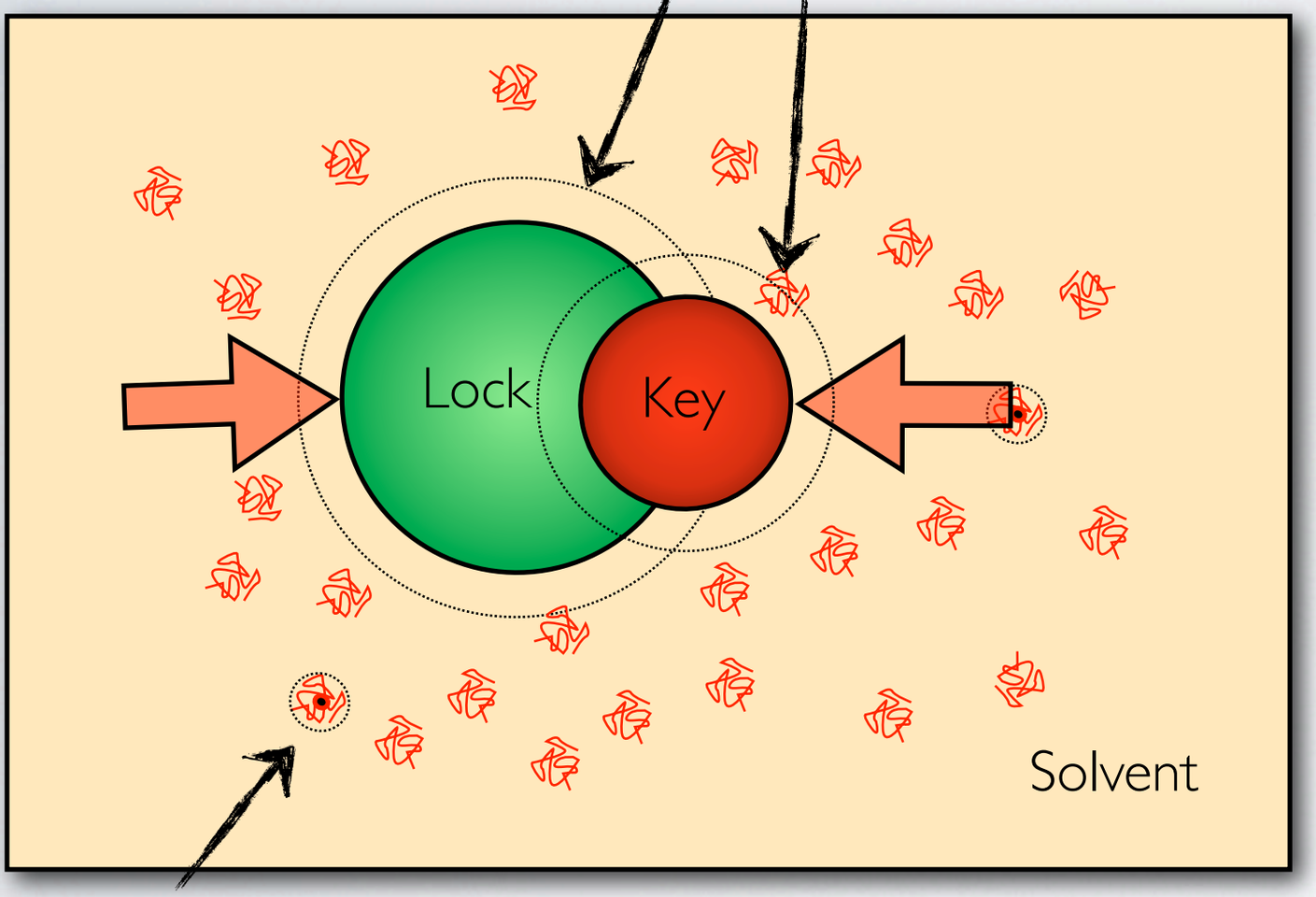
$$S \sim n_{\text{poly}} \ln V$$



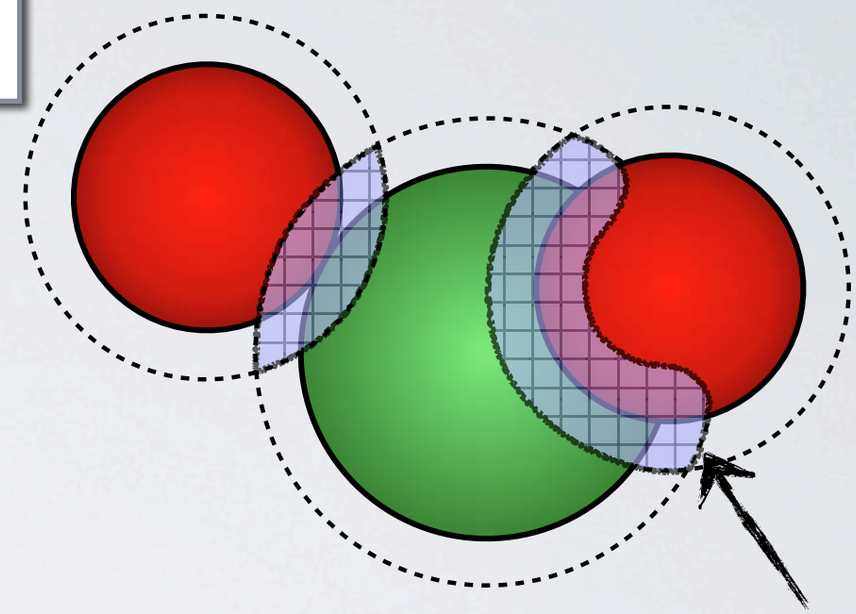
Pacman lock & key

$$S \sim n_{\text{poly}} \ln V$$

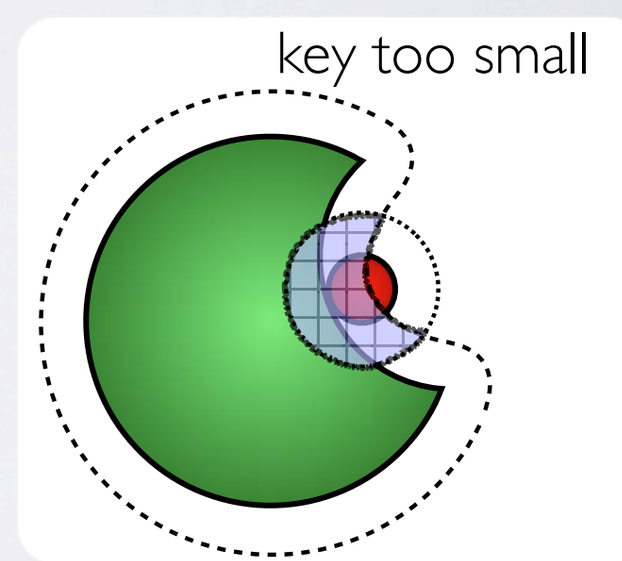
depletion zones



non adsorbing polymer



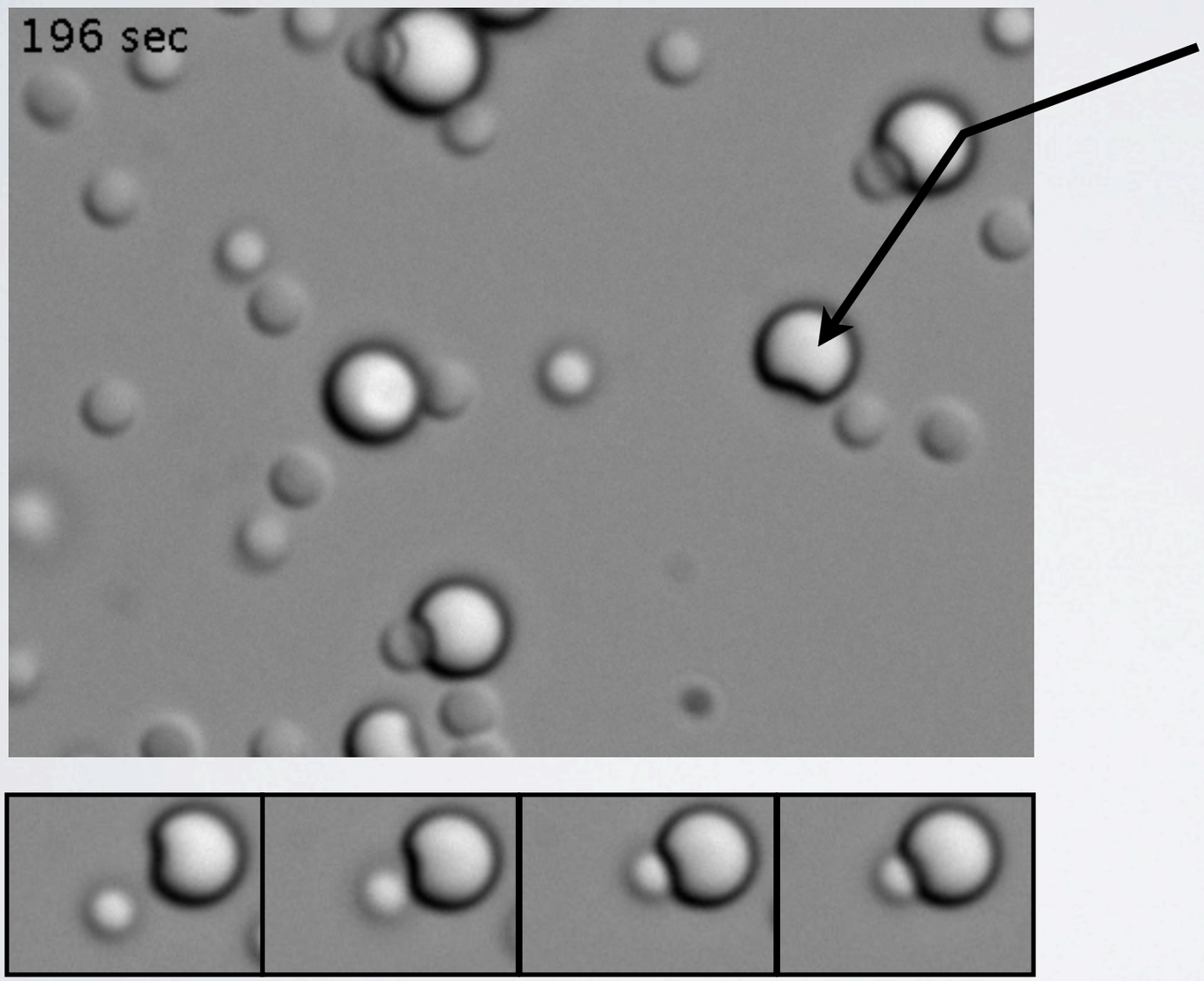
Max overlapping volume

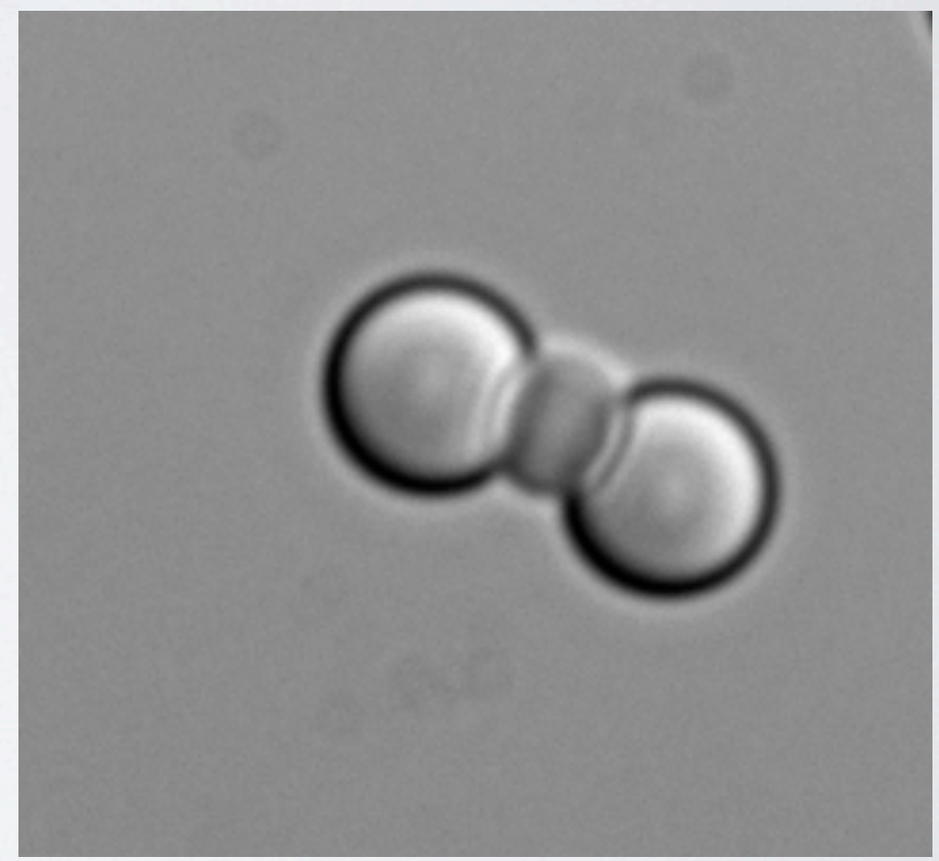


can tune interaction strength

$$\Delta S \sim n_{\text{poly}} \frac{\Delta V}{V}$$

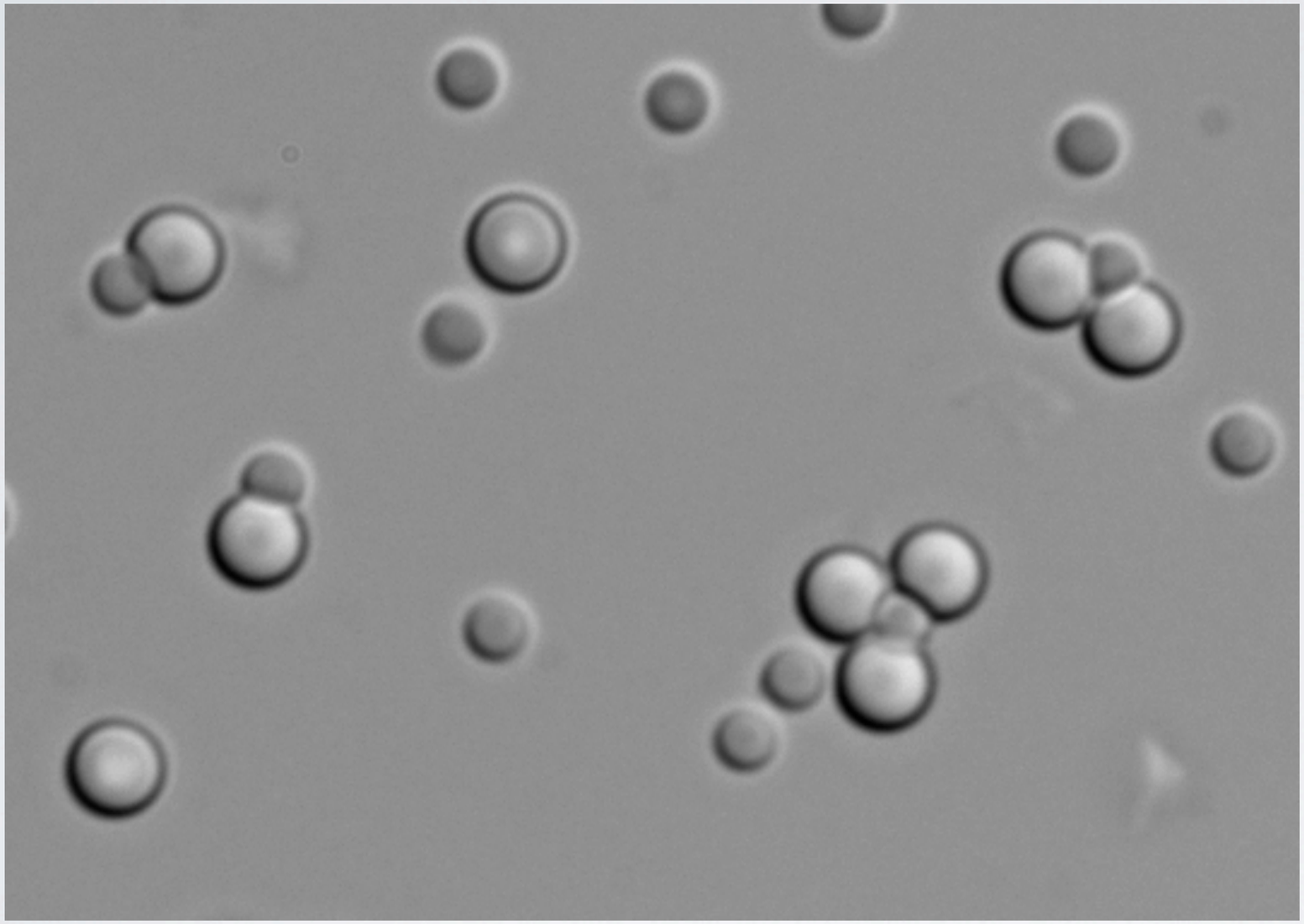
Pacman depletion movie



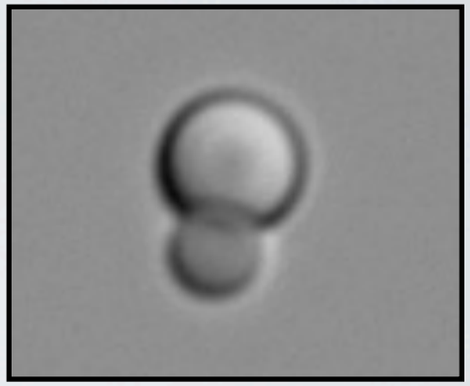


Sacanna et al., Nature **464**, 575–578 (2010)

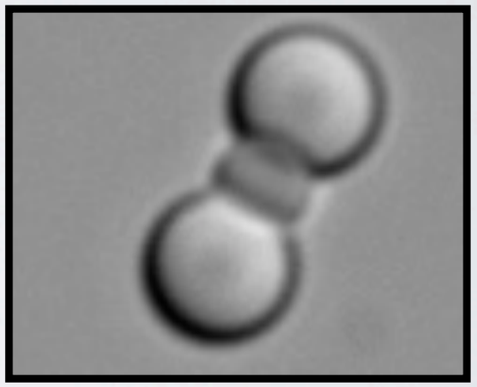
Colloidal couplings



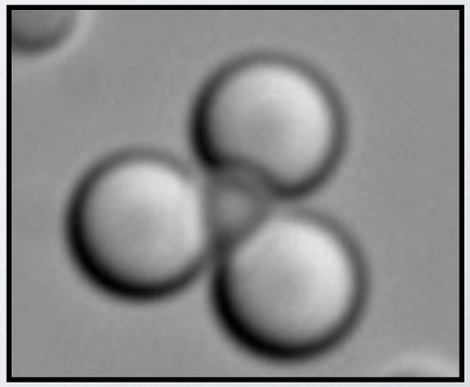
Monomer



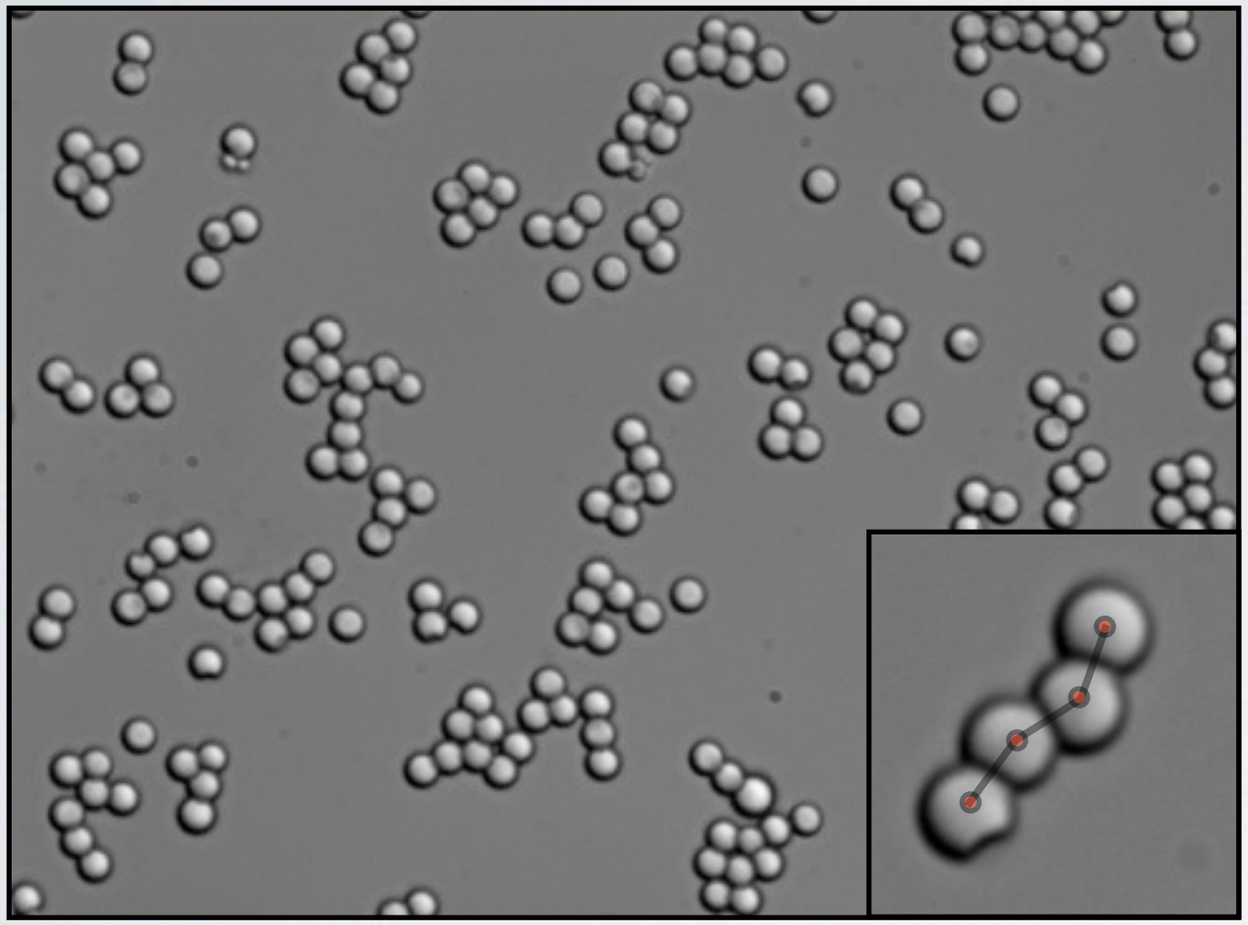
Dimer

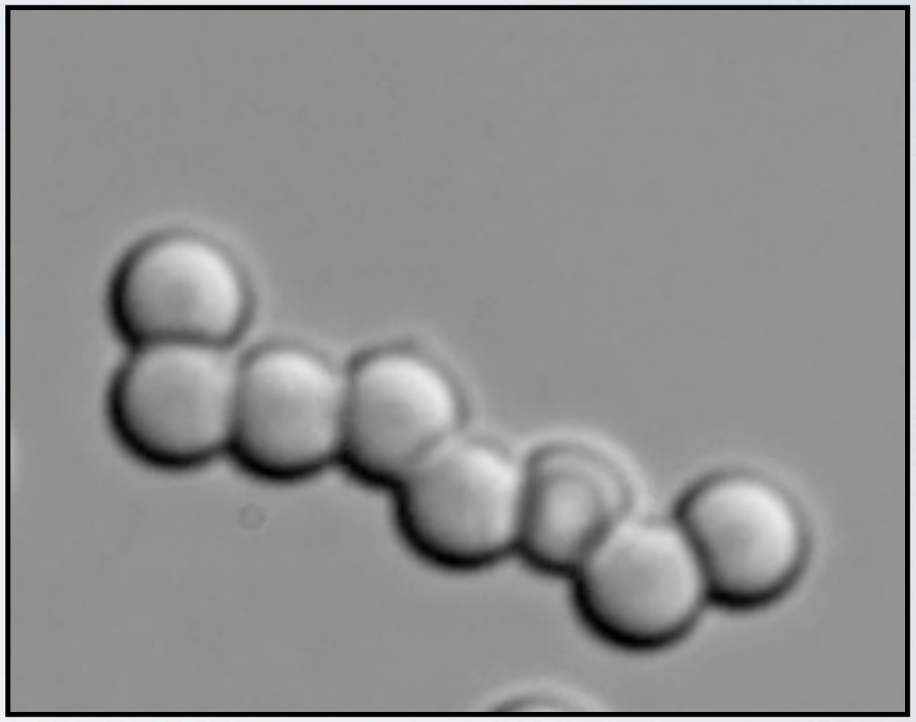


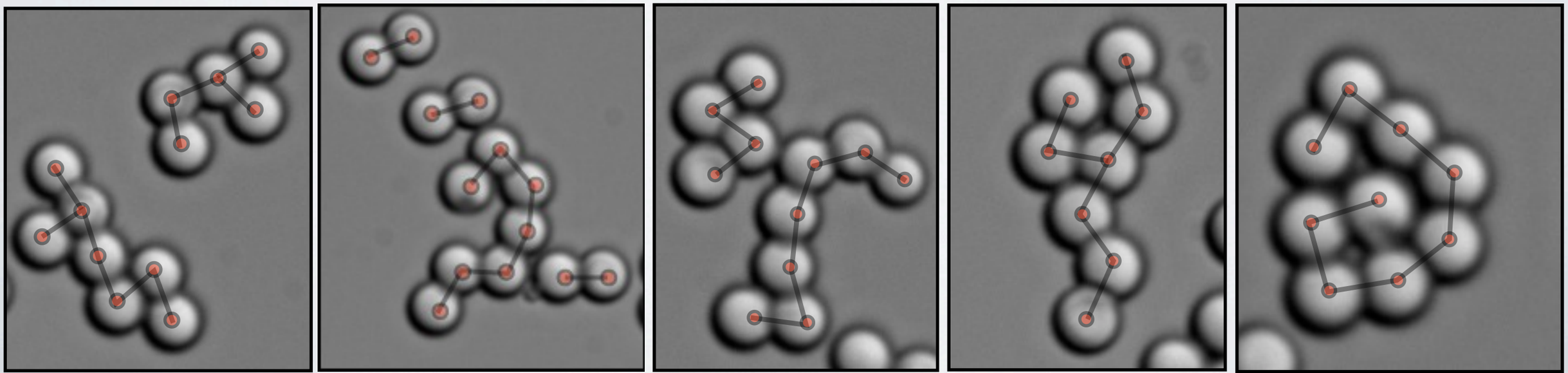
Trimer



Pacman polymers



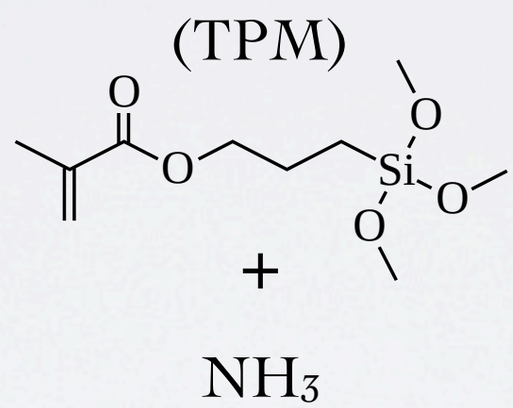




Towards a more perfect pacman

Heterogeneous nucleation

grow droplets

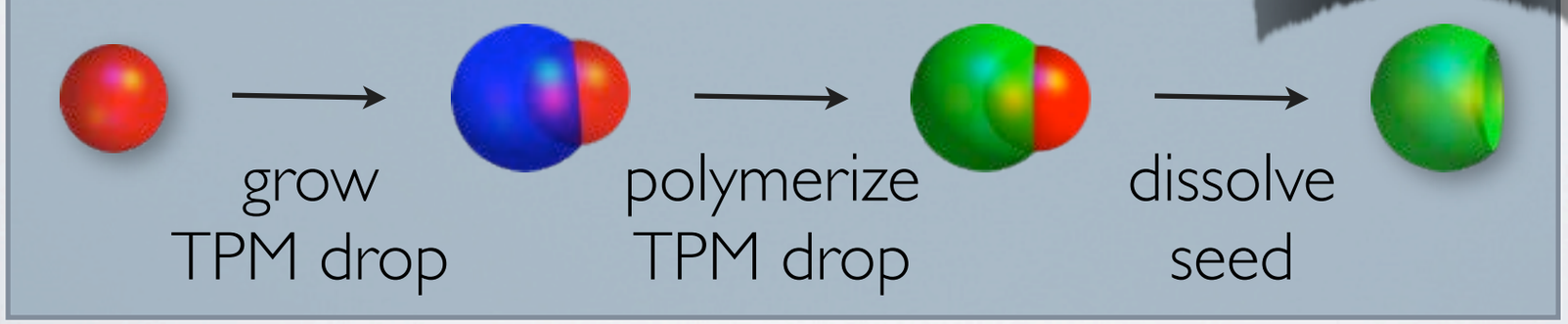


polymerize droplets

dissolve seeds

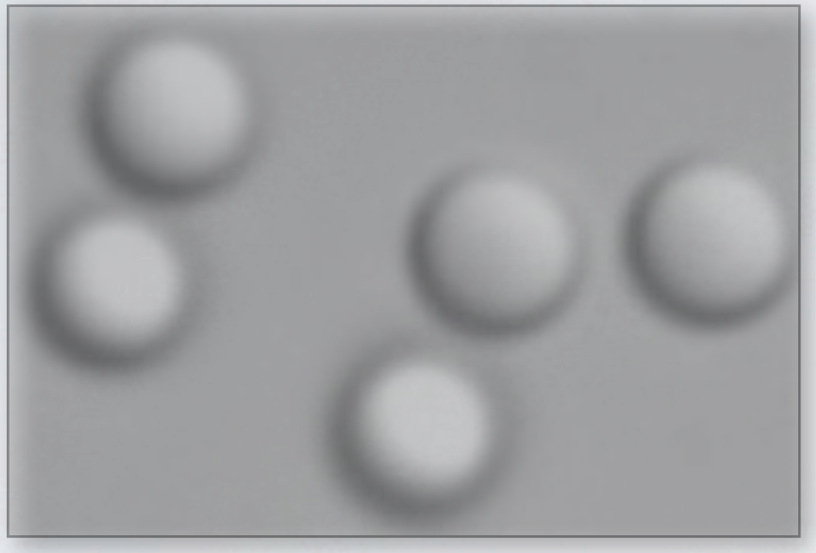
Monodisperse seeds
(PS, PMMA, silica, etc.)

Cartoon

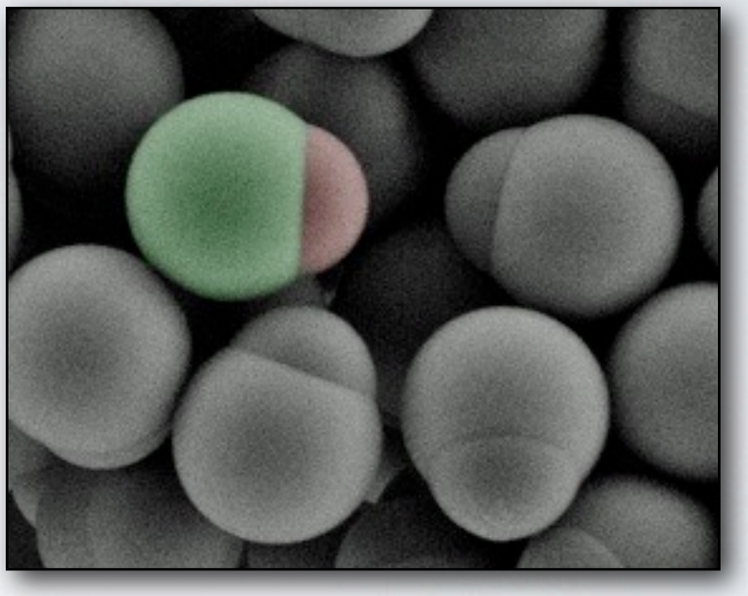


The real colloids

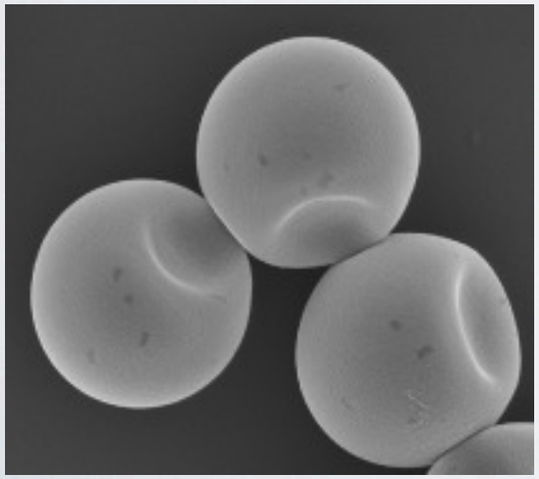
seeds



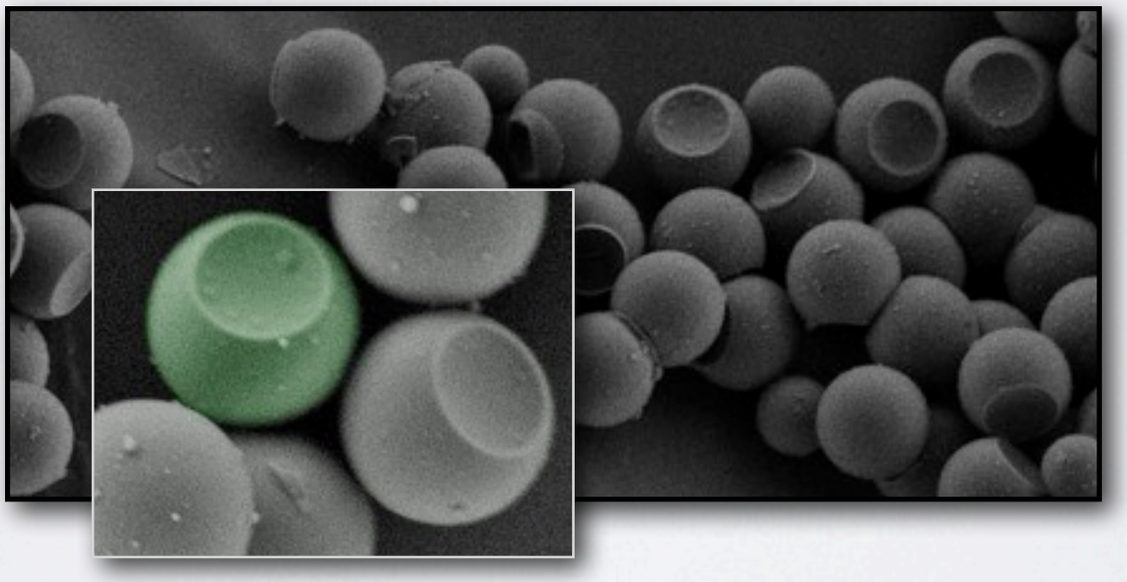
TPM on seeds



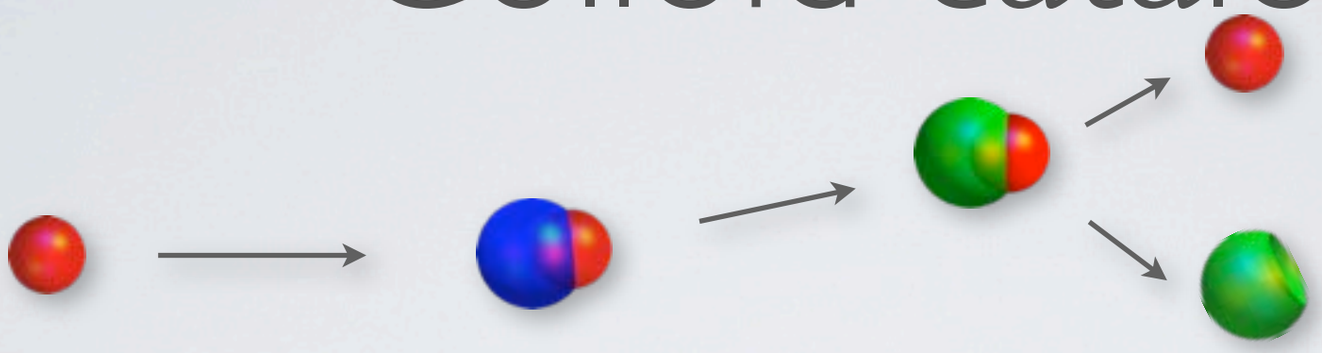
old pacmen

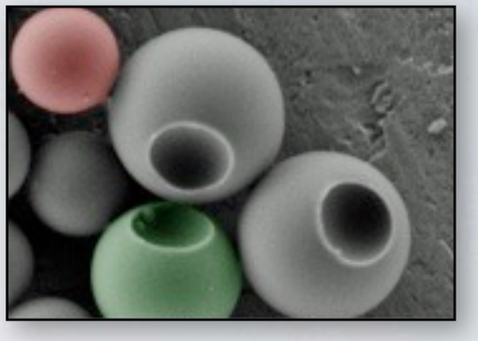


pacmen

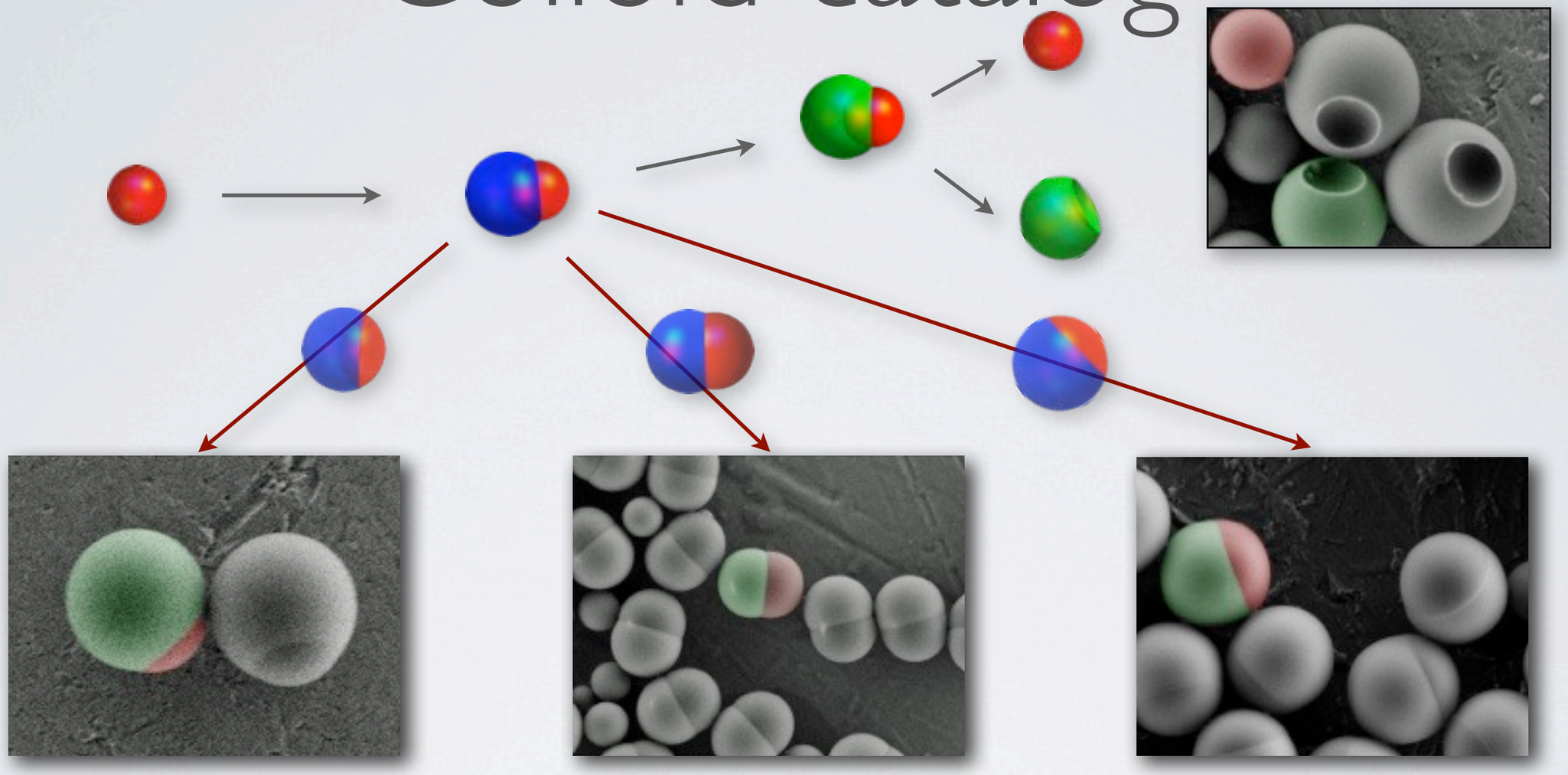


Colloid catalog

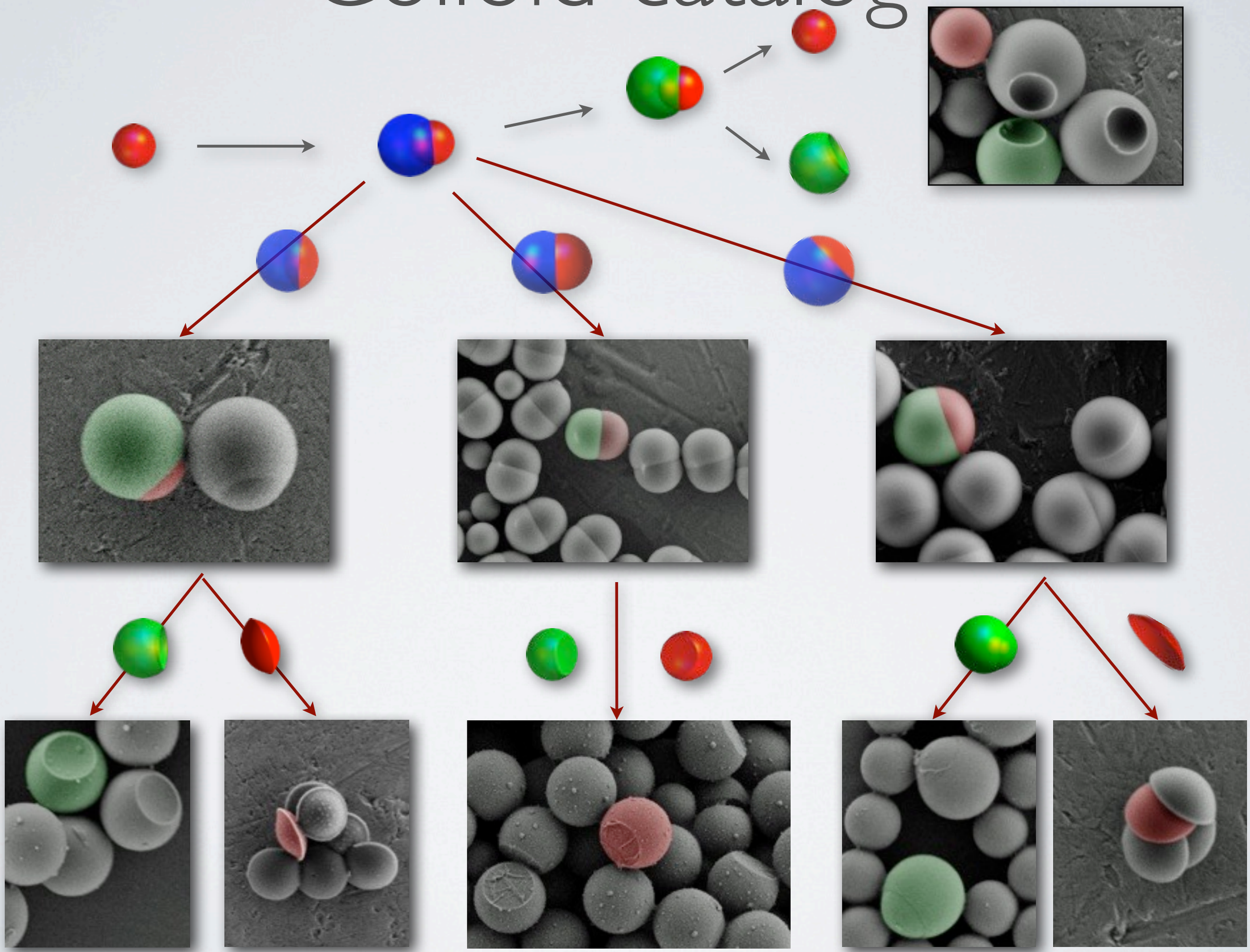




Colloid catalog

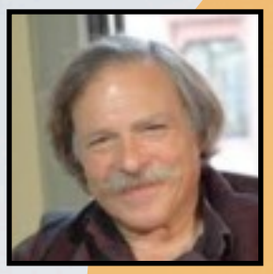


Colloid catalog



Collaborators

PACMEN



Paul Chaikin

William Irvine

Laura Rossi

Stefano Sacanna

LENSES

Kazem Edmond

Tess Jacobson

Gi-Ra Yi

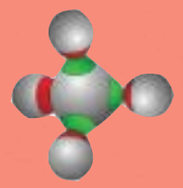
Andy Hollingsworth

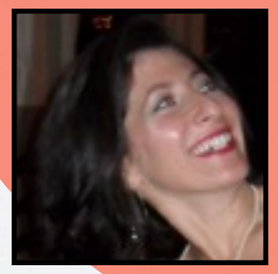
PATCHY PARTICLES

Yufeng Wang

Yu Wang

Marcus Weck





Dana Breed

Vinny Manoharan