Colloidal Self Assembly II: Pacmen & Multivalent Colloids

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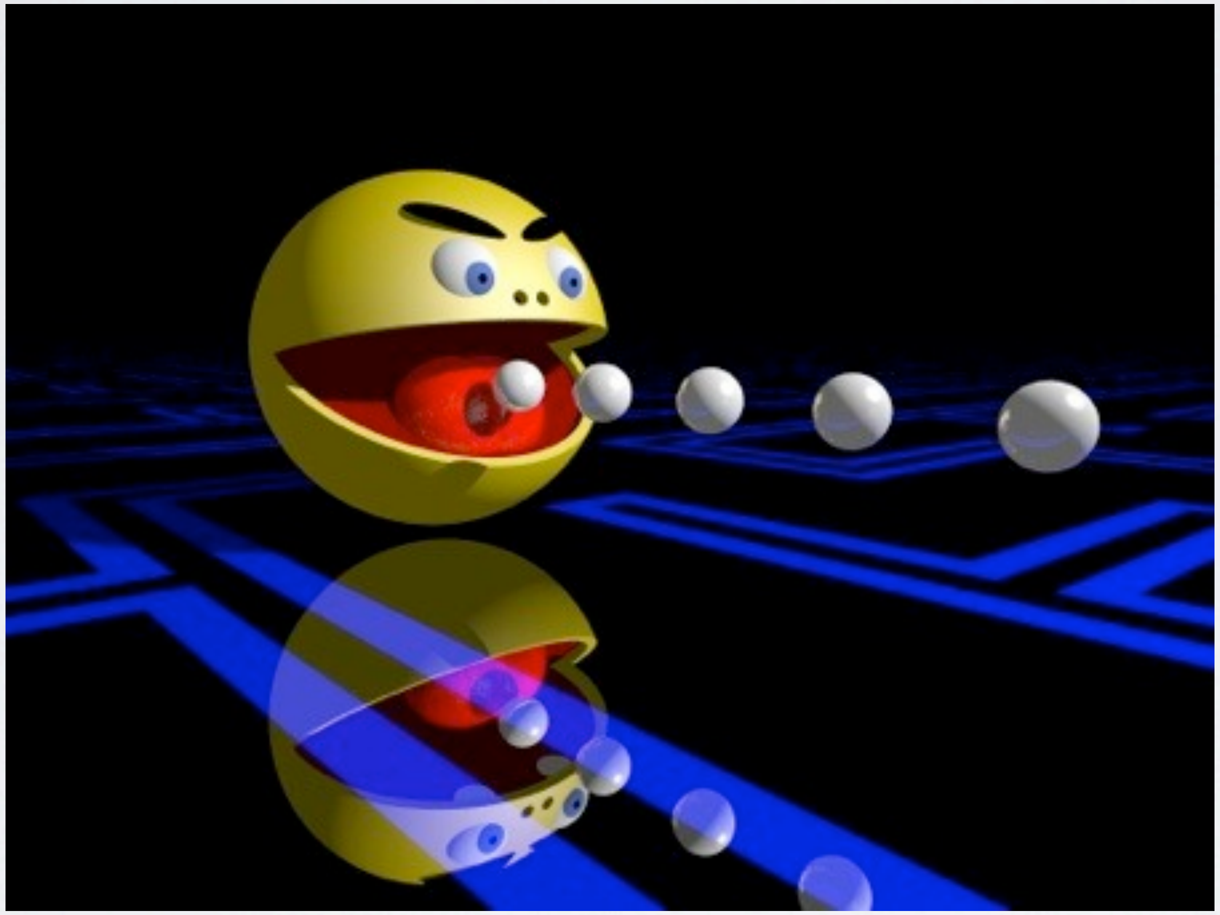
Outline of lectures on colloids

- Lecture I: Yesterday
  - Overview of colloids (sizes, materials)
  - Self-assembly of colloids: (colloidal liquids, crystals, & glasses)
    - photonic crystals (& the diamond lattice)
    - need for directional interactions
  - van der Waals interactions (fluctuating electric dipoles)
  - Electrostatic interaction: Poisson-Boltzmann & Debye-Hückel, DLVO
  - Depletion interaction
  - DNA hybridization
- Lecture II: Today
  - Lock & key colloids
  - Colloids with valence
  - Colloidal molecules: to infinity and beyond

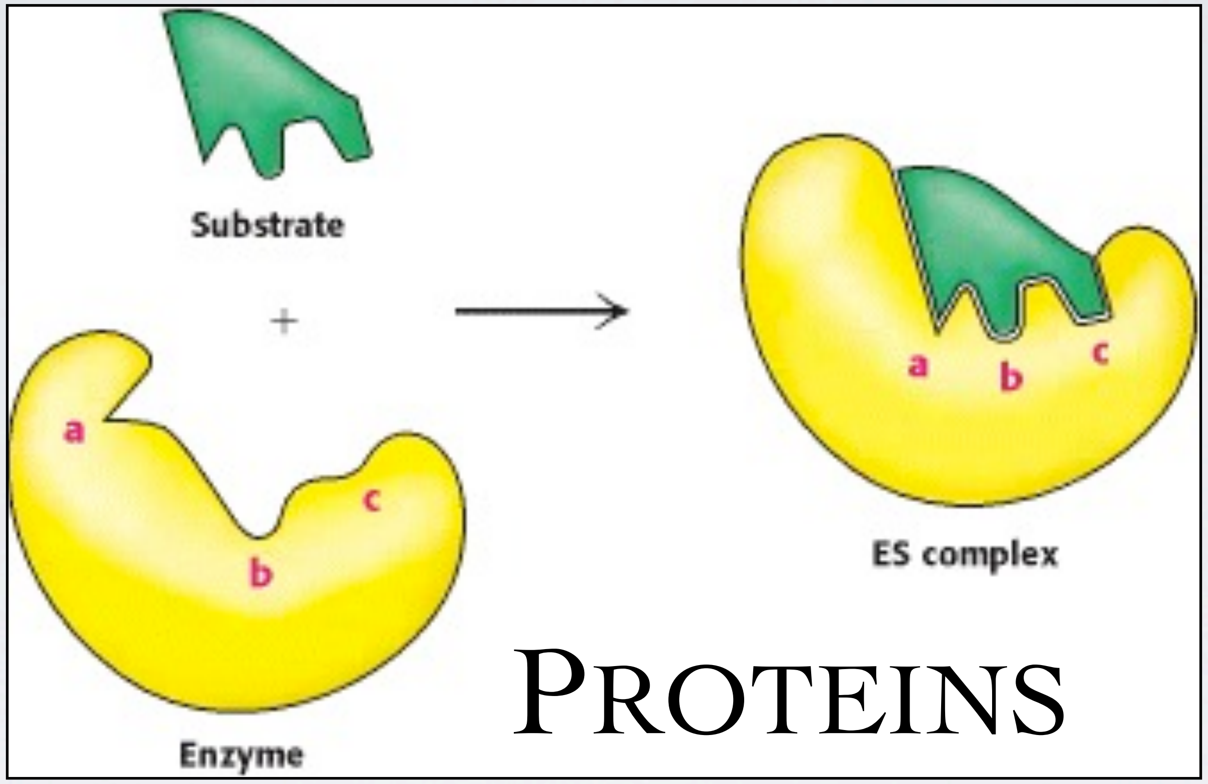
Lock & Key Colloids

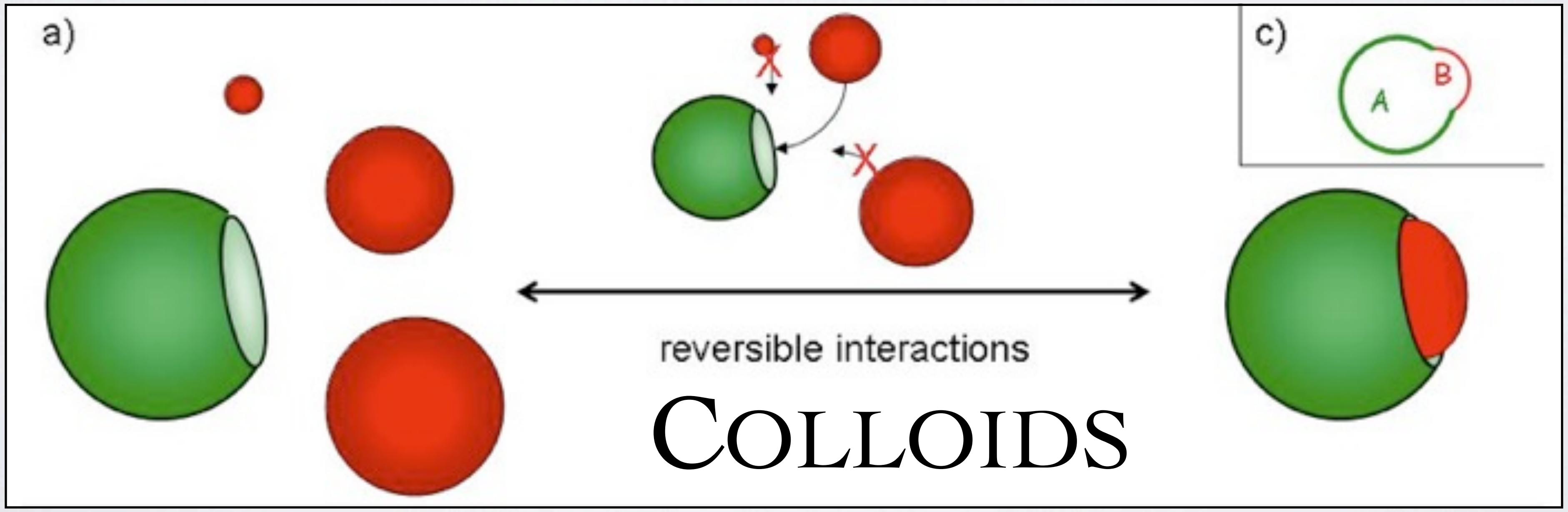
Drawing inspiration from proteins ...



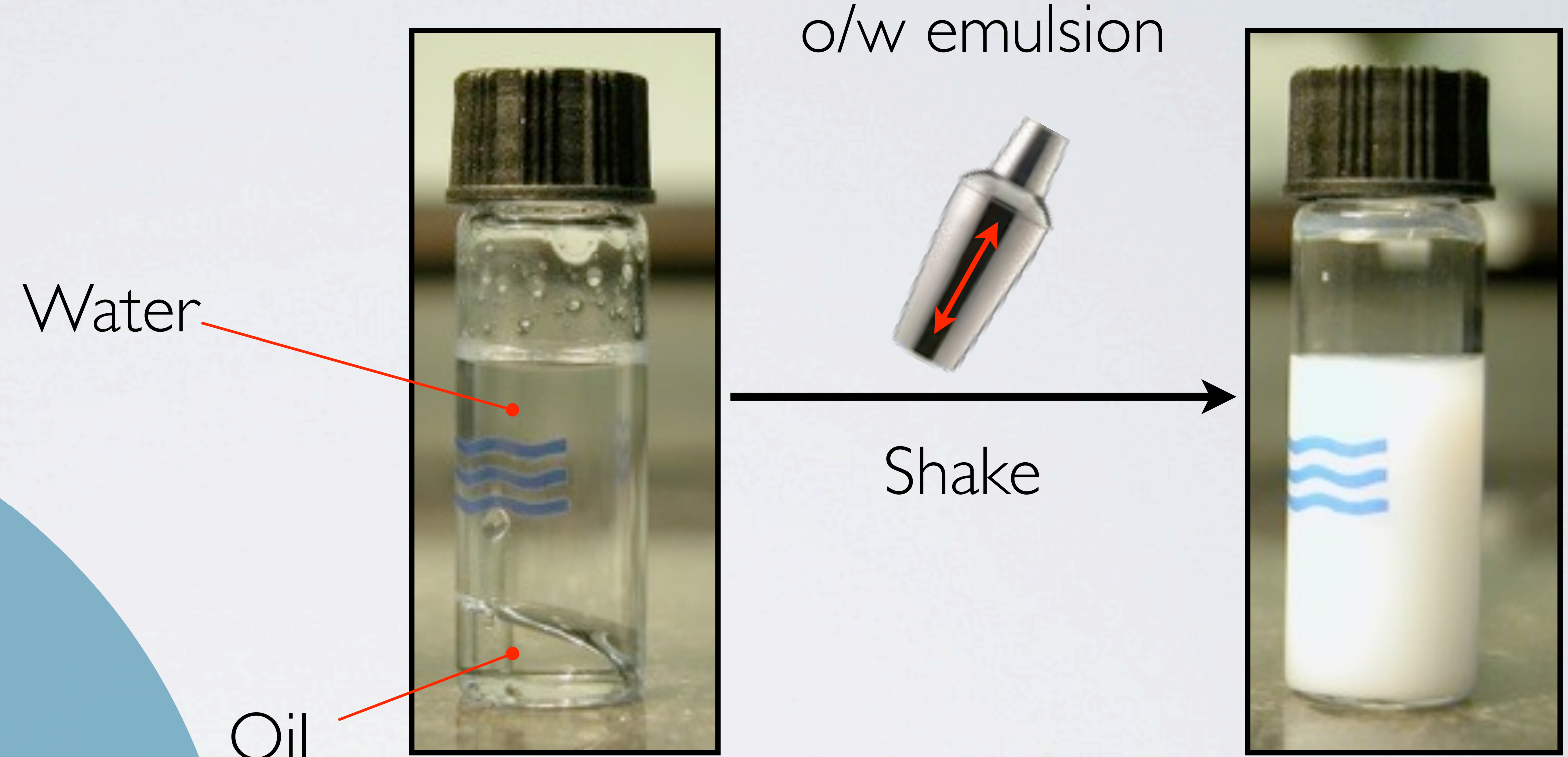
Pac-Man Particles

Lock & Key Colloids



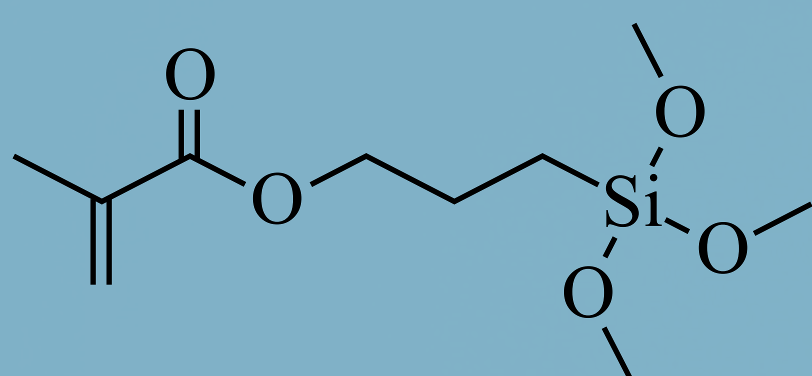


Pacman particle synthesis



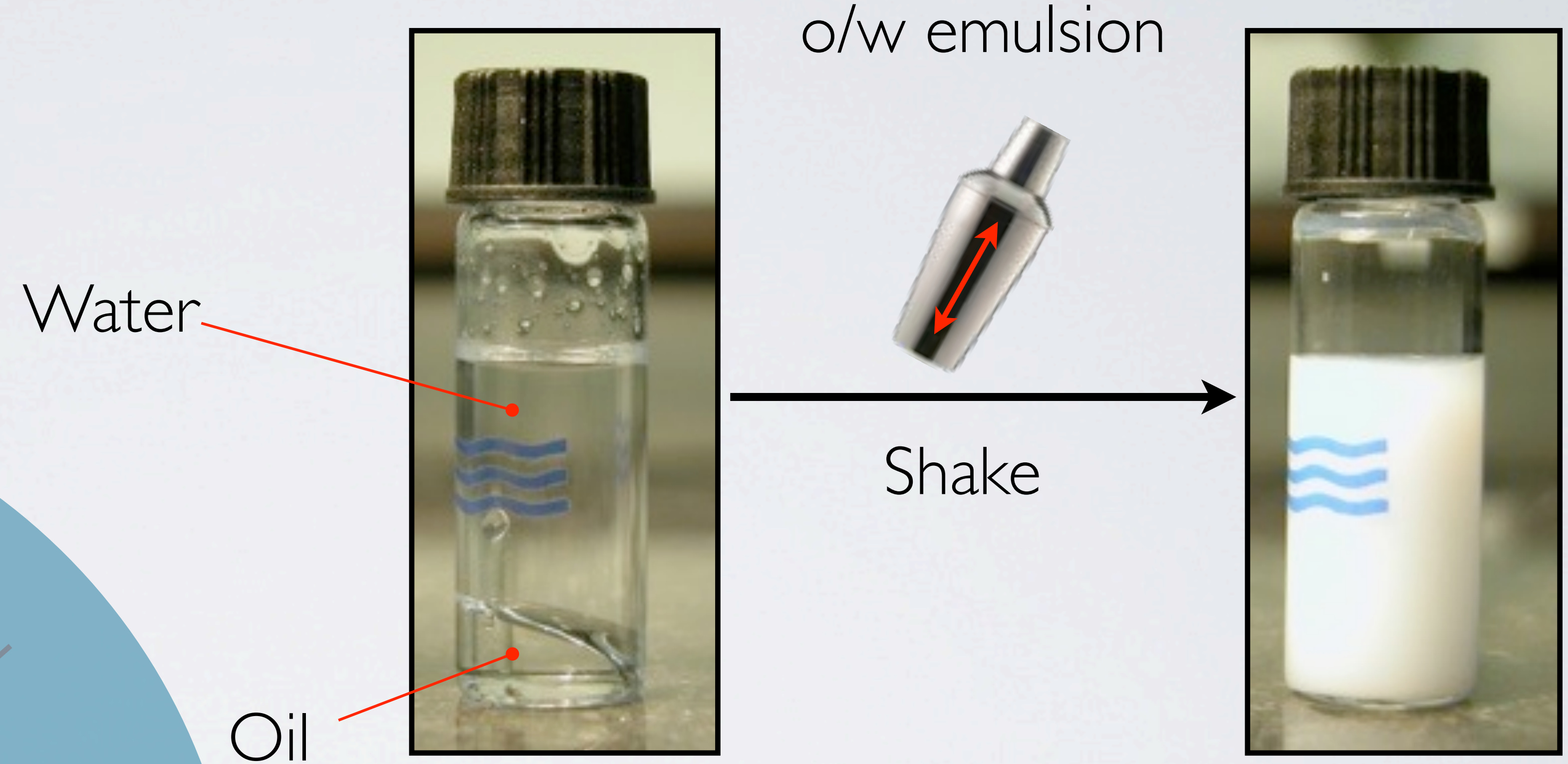
Oil = "TPM" = 3-methacryloxypropyl trimethoxysilane

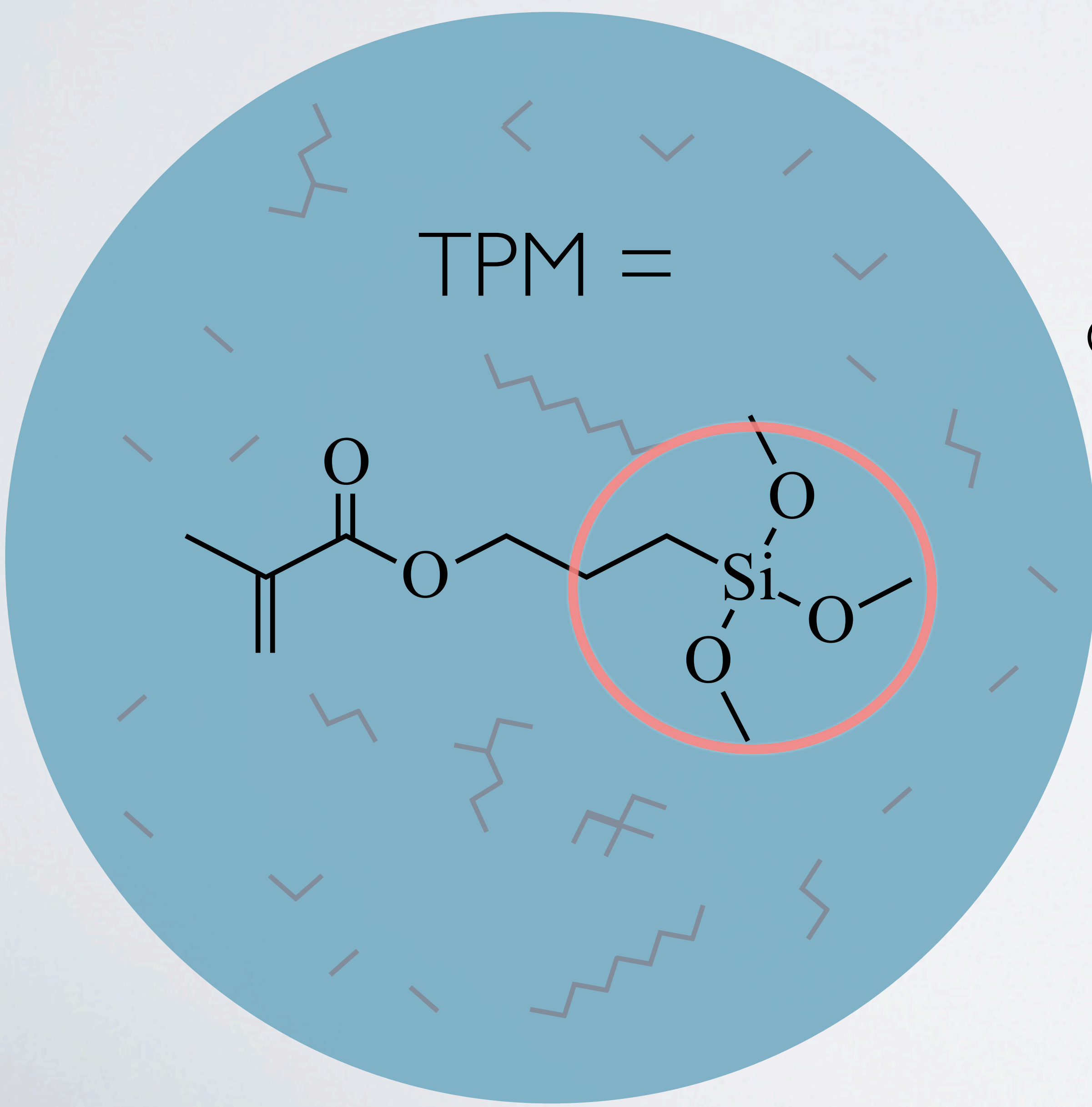
TPM =



Make emulsion
(oil droplets in water)

Pacman particle synthesis

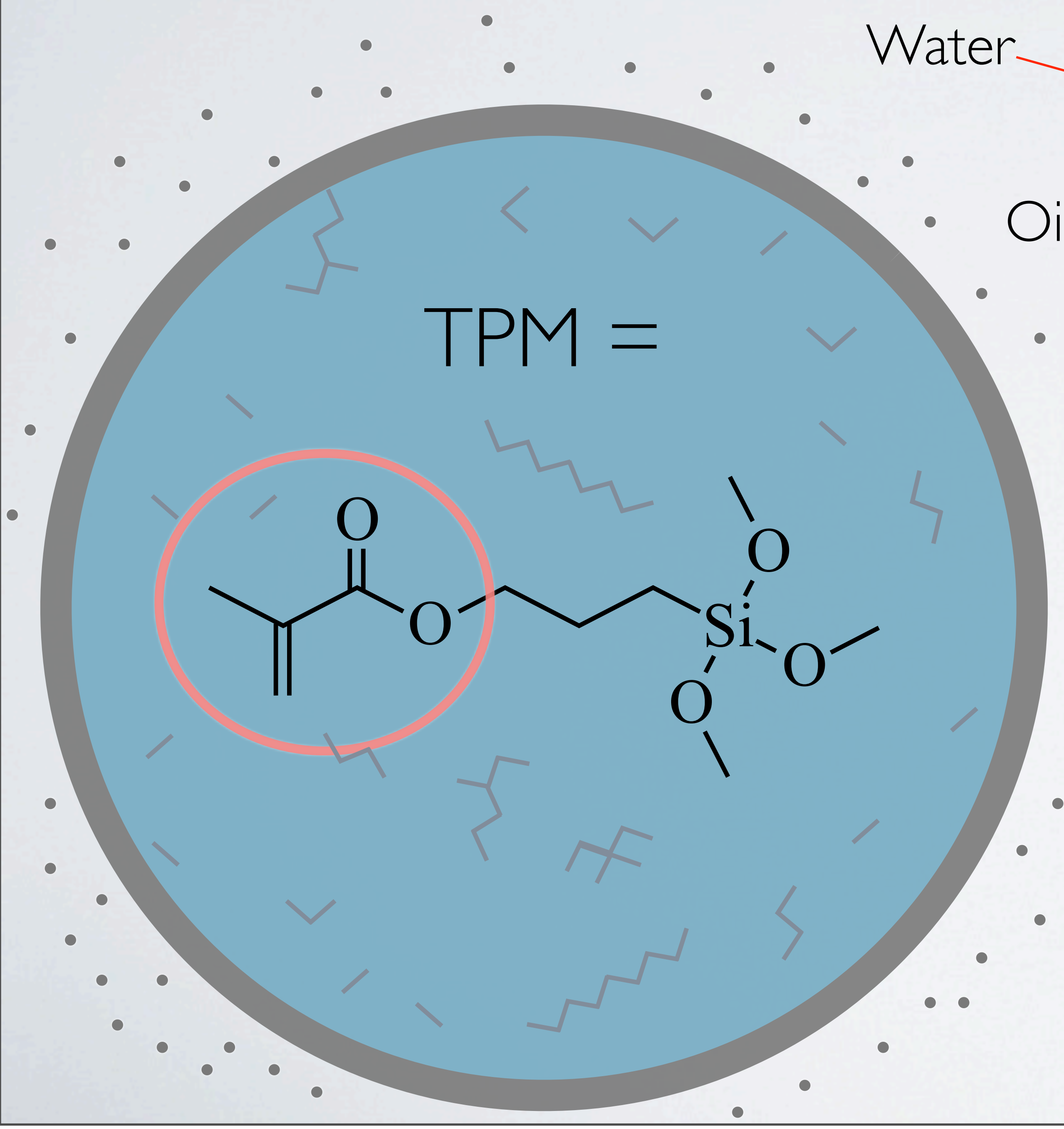


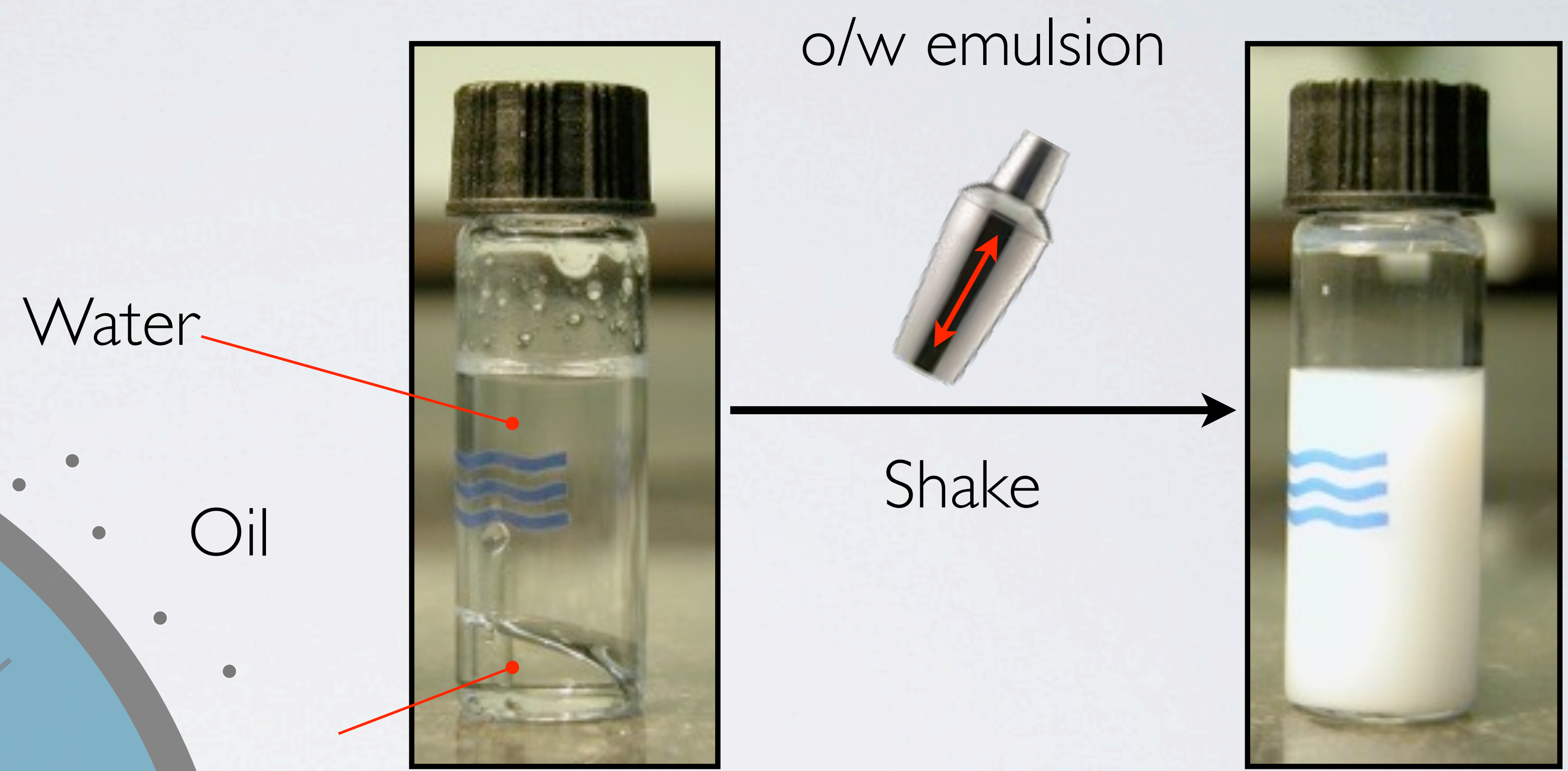


Oligomerize oil

✦Oligomerize Si-O groups (pH⬆) N~1-10

Pacman particle synthesis





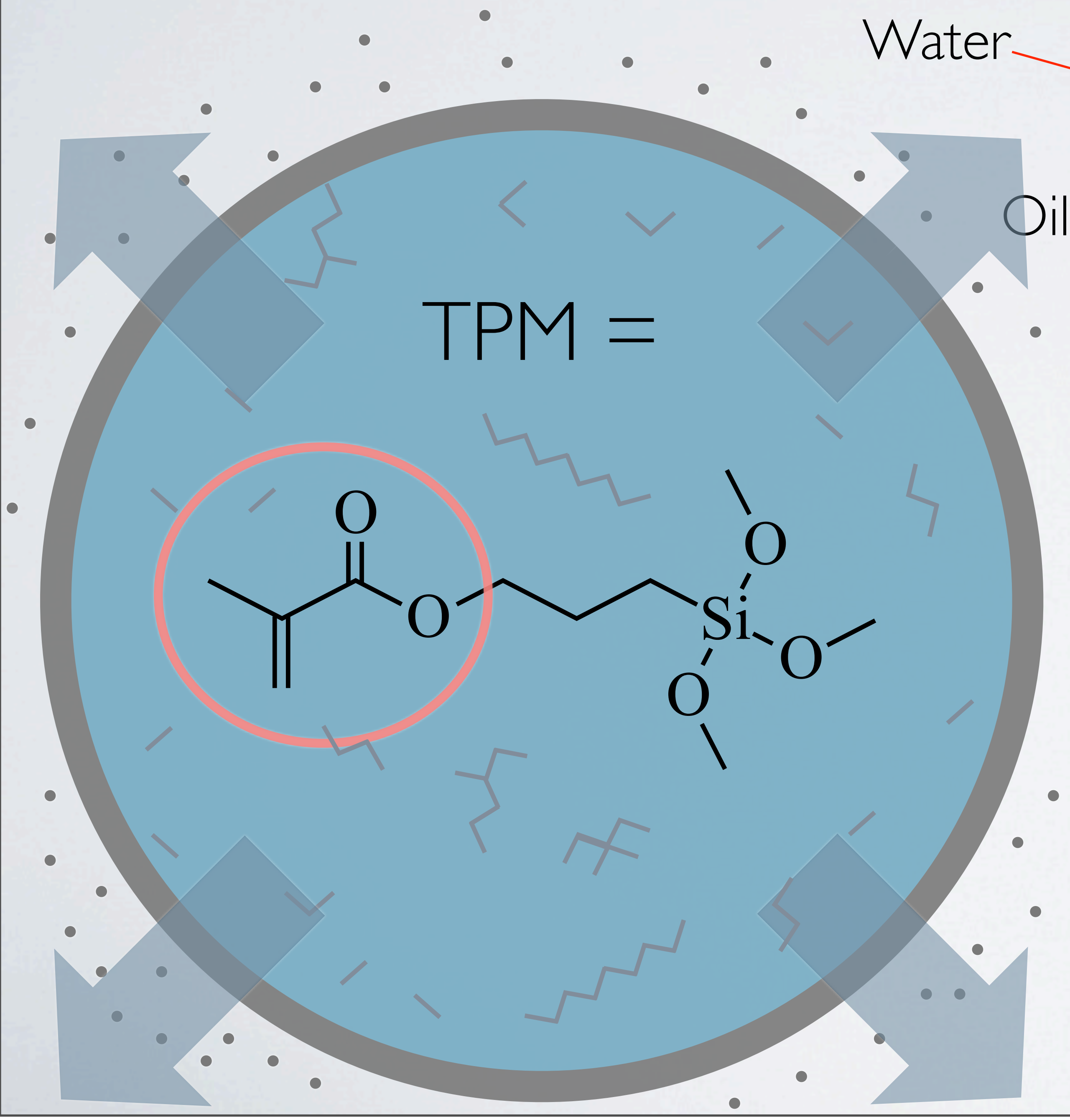
Polymerize shell

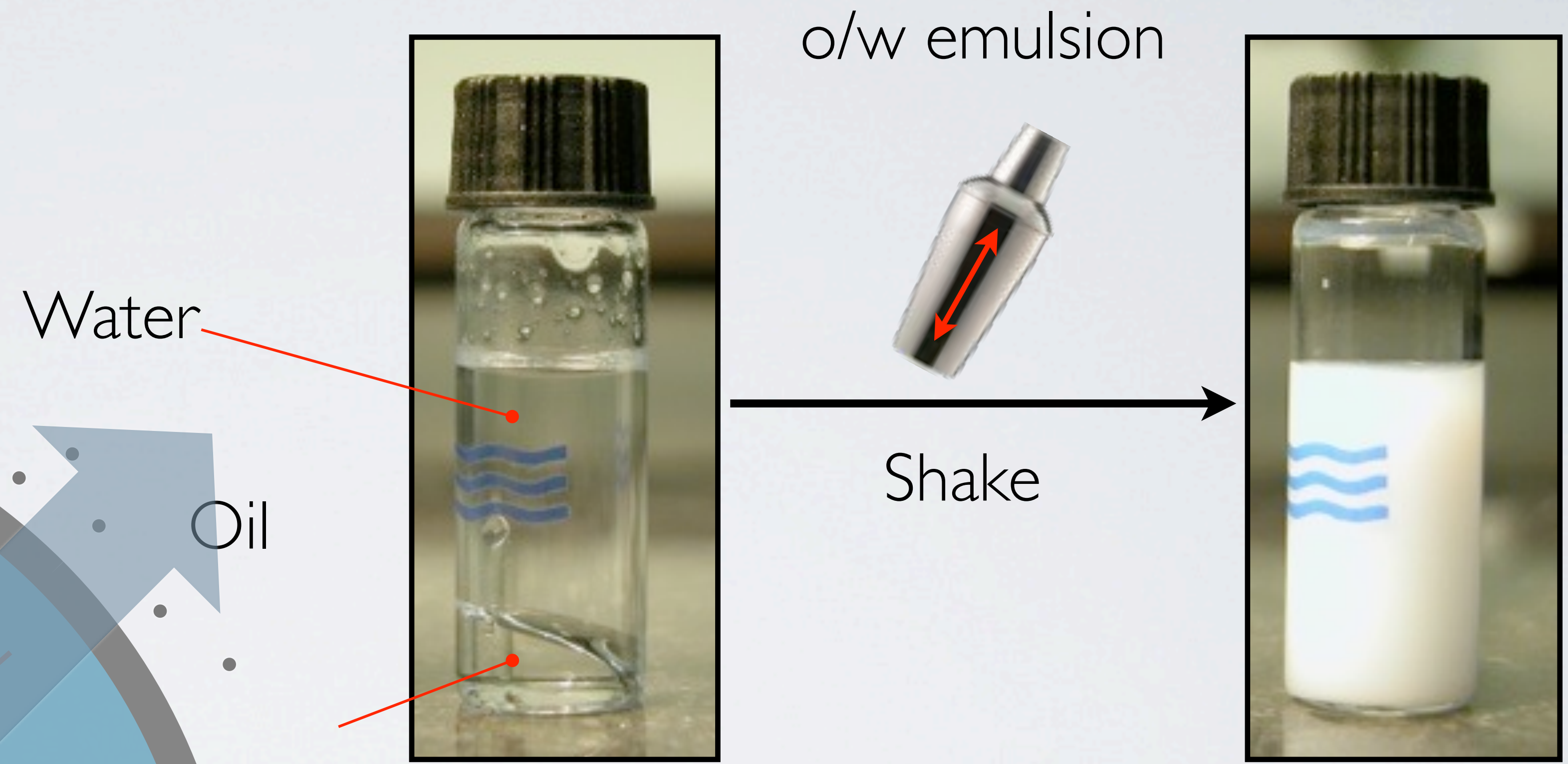
✦Oligomerize Si-O groups (pH⬆) N~1-10

✦Polymerize methacrylate groups (free radical)

- Creates porous shell
- Nucleates TPM nanoparticles in solution outside of TPM droplets

Pacman particle synthesis





Polymerize shell

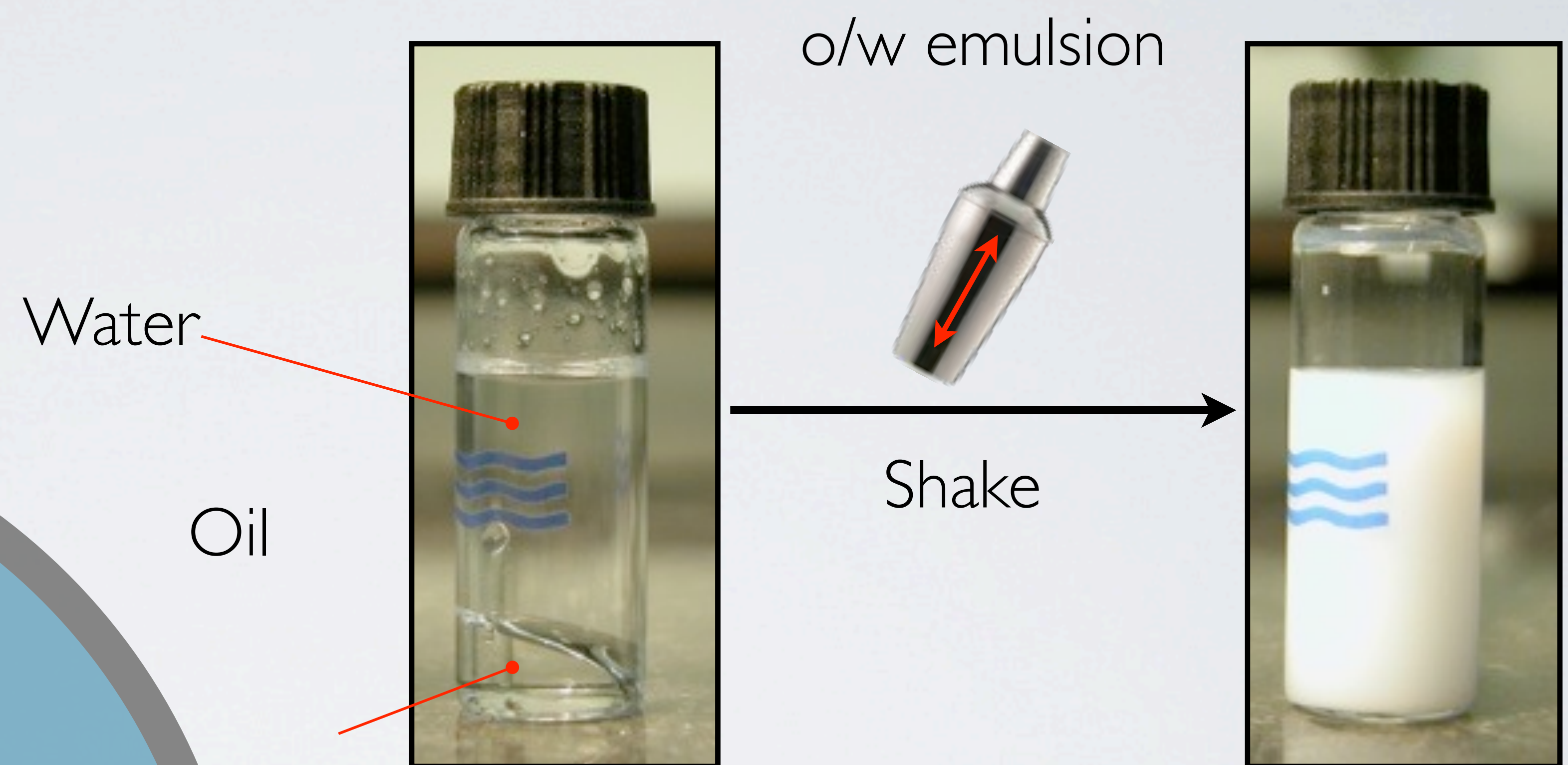
✦Oligomerize Si-O groups (pH⬆) N~1-10

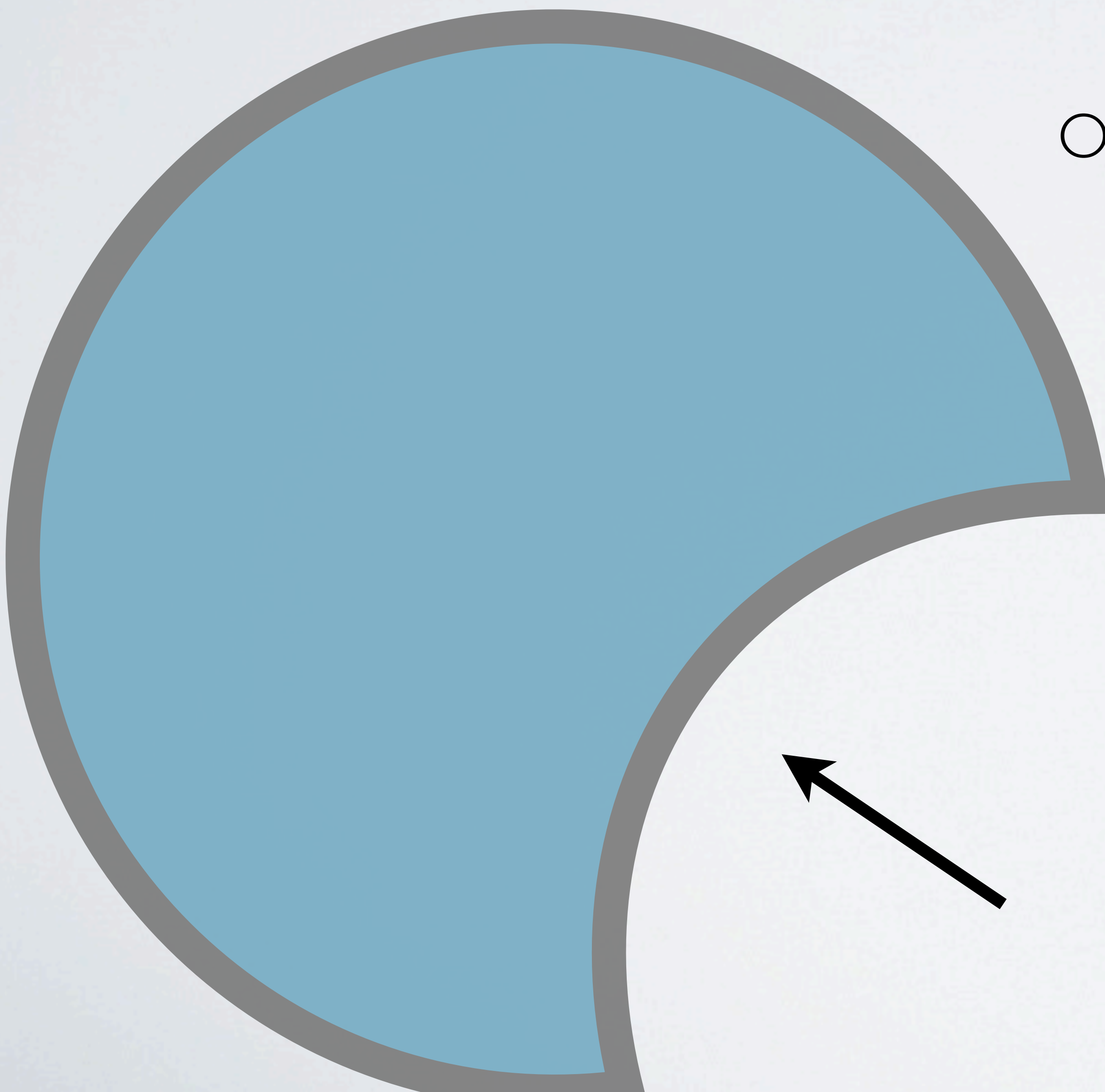
✦Polymerize methacrylate groups (free radical)

- Creates porous shell
- Nucleates TPM nanoparticles in solution outside of TPM droplets
- Osmotic imbalance sucks small oligomers out of TMP droplets (through shell)

And ...

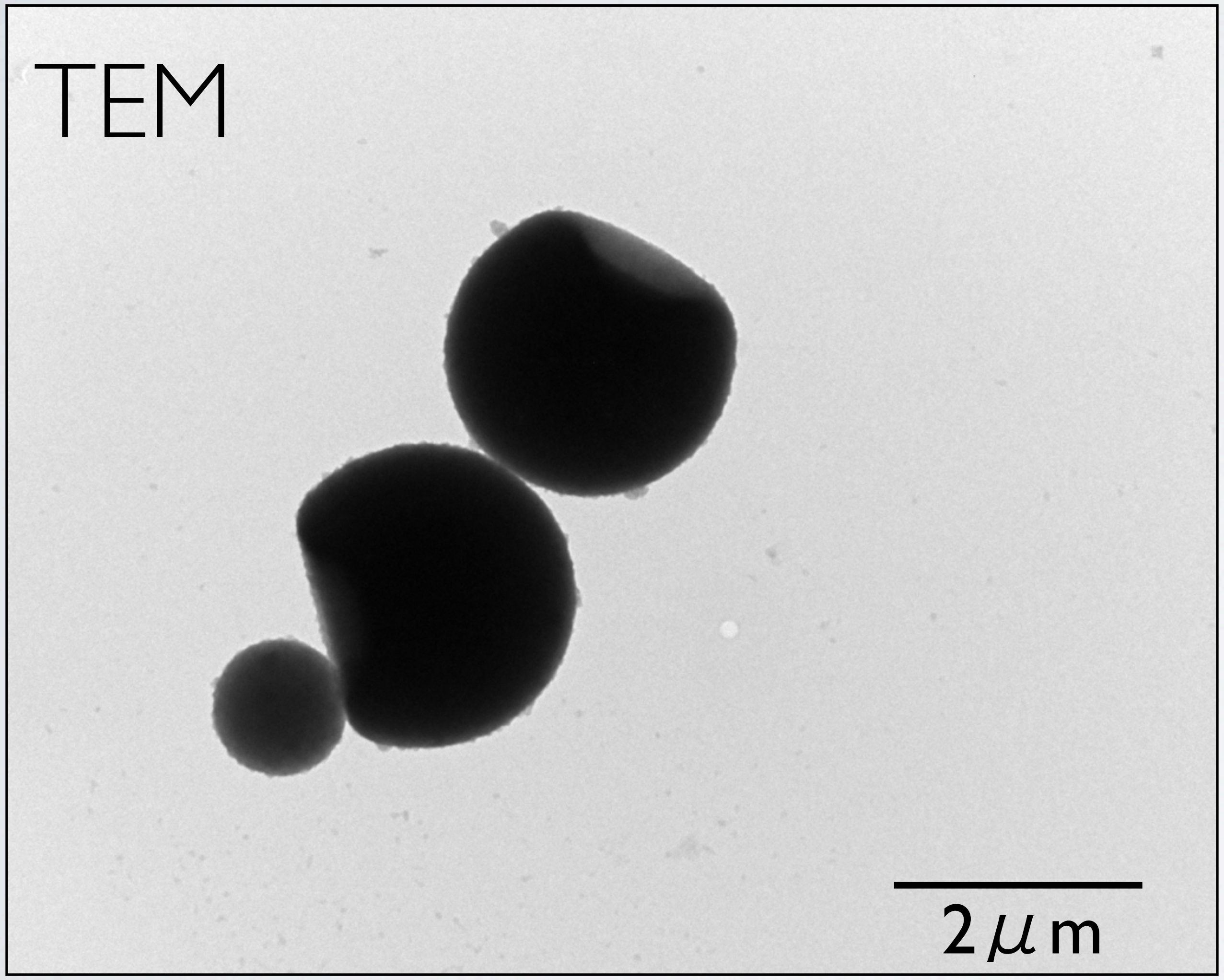
Pacman particle synthesis

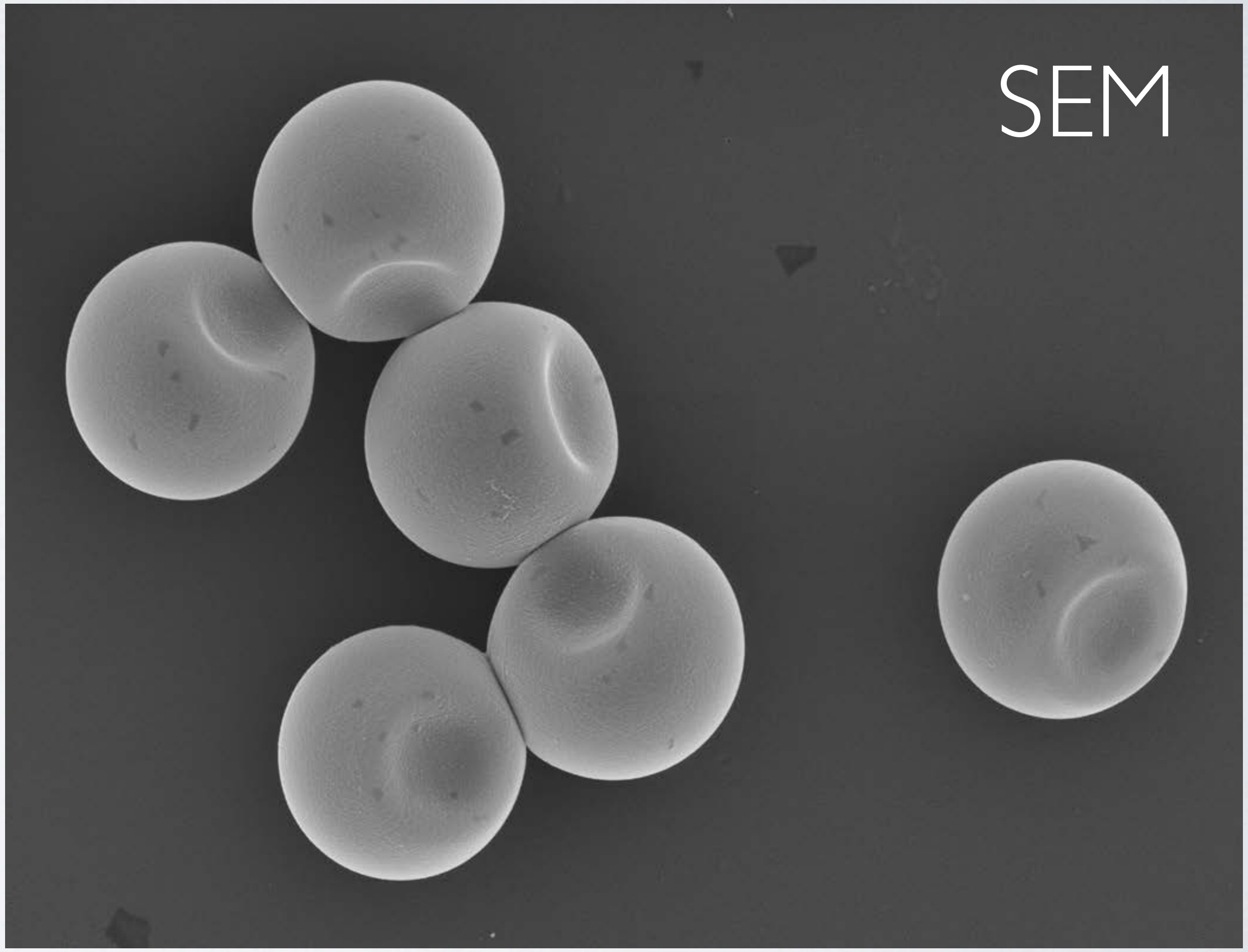




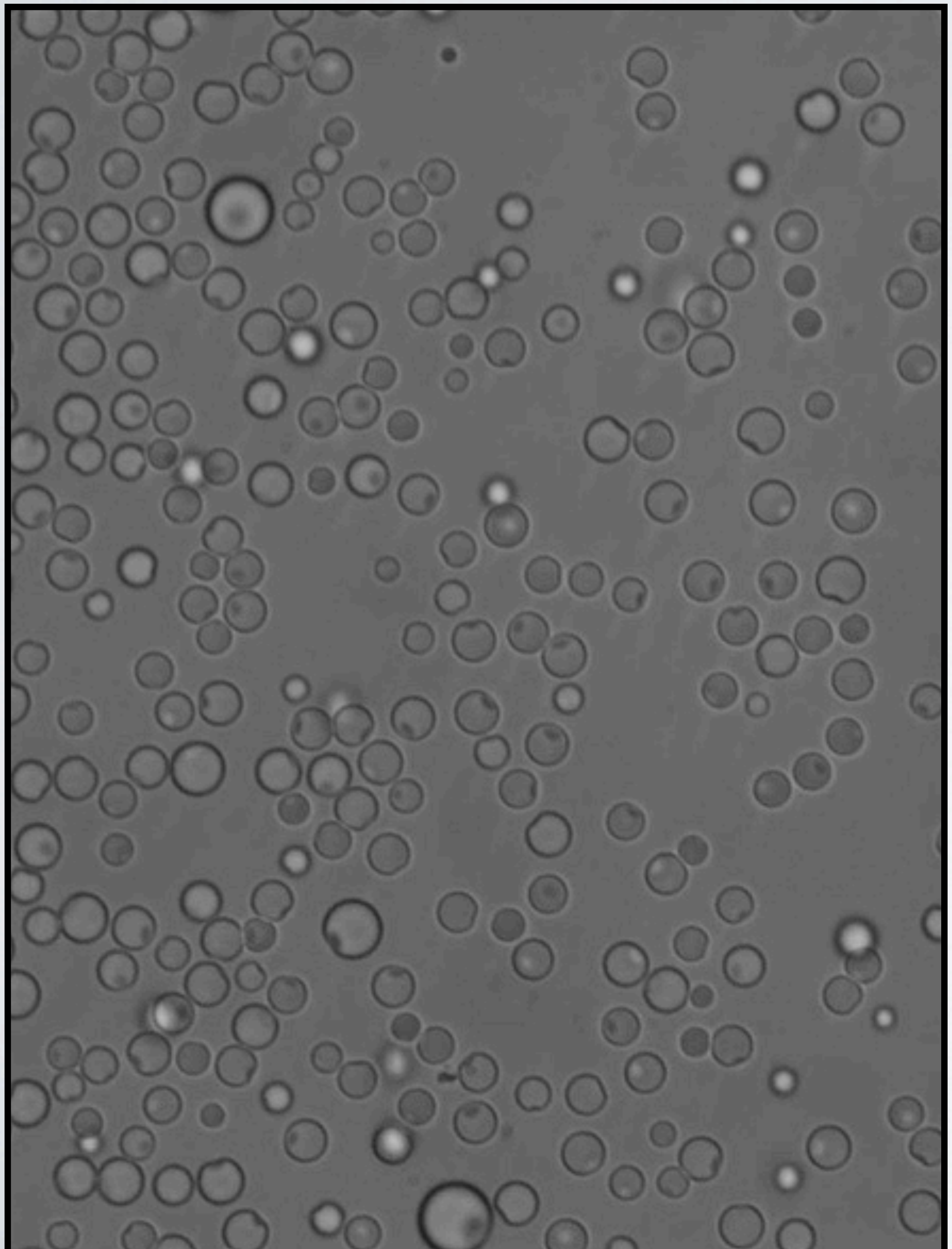
Shell buckles

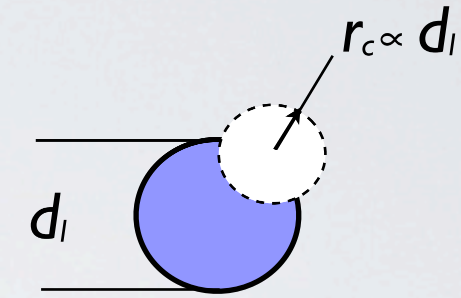
Pacman particles



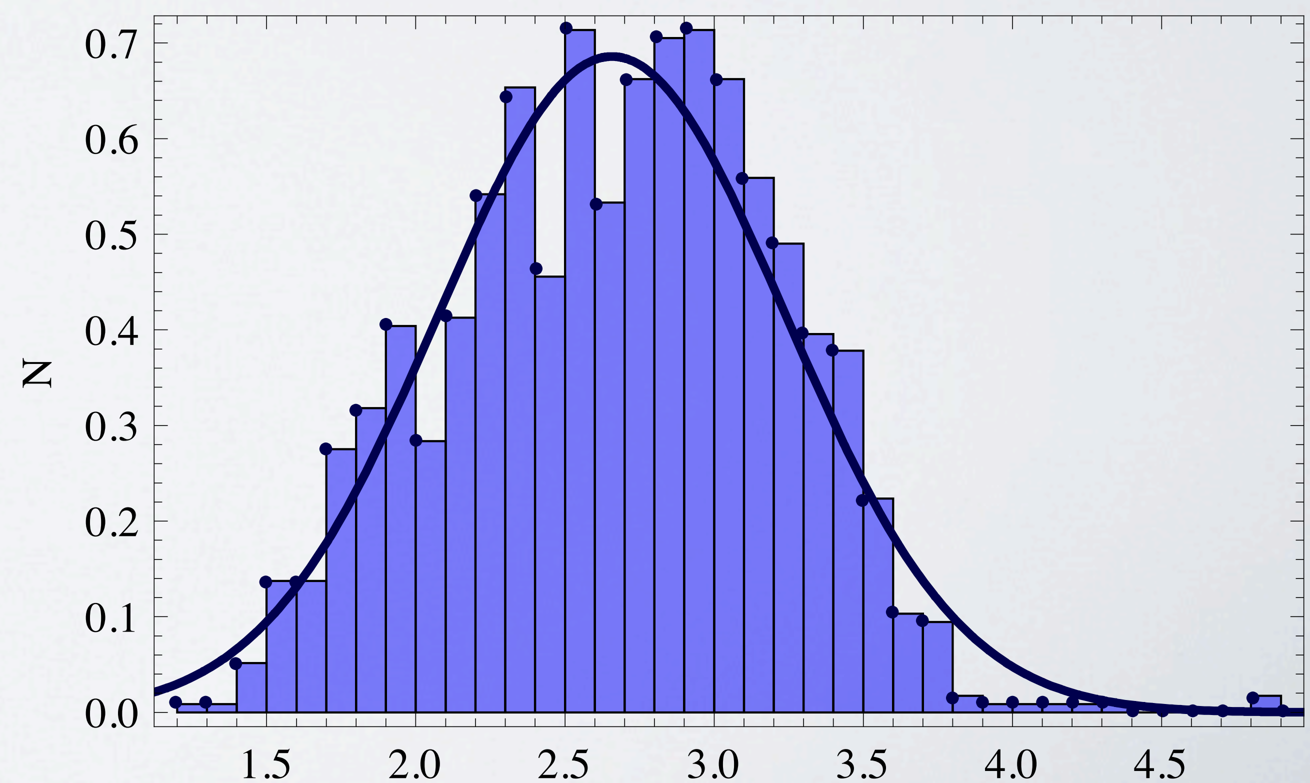


Pacman particles

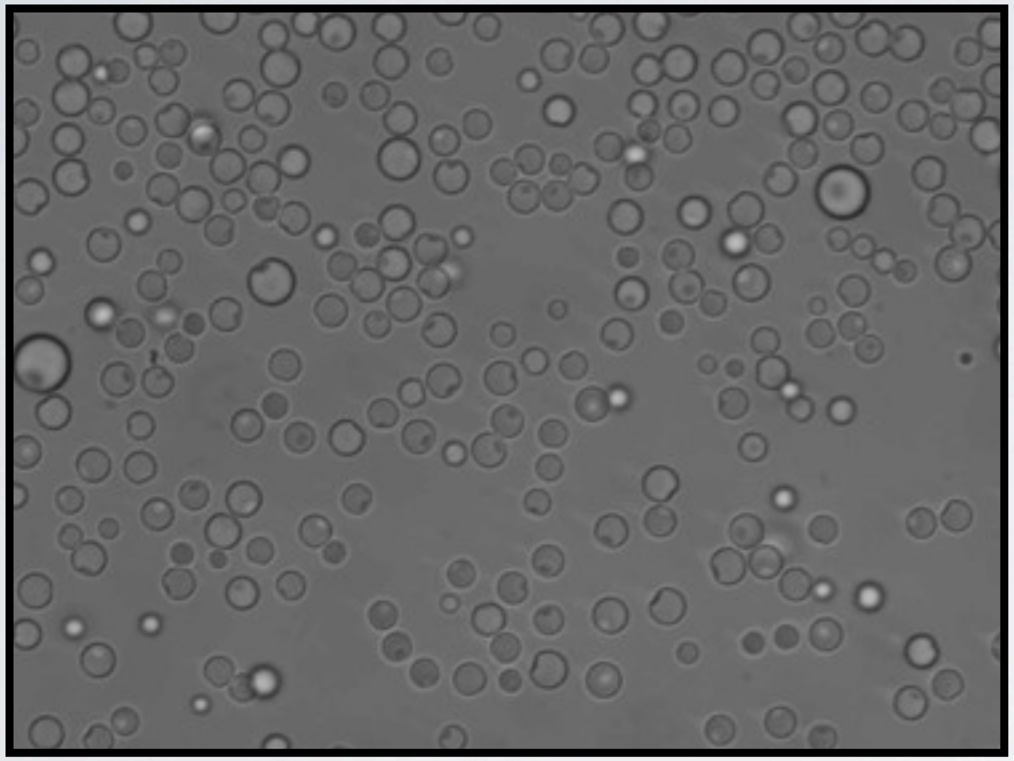


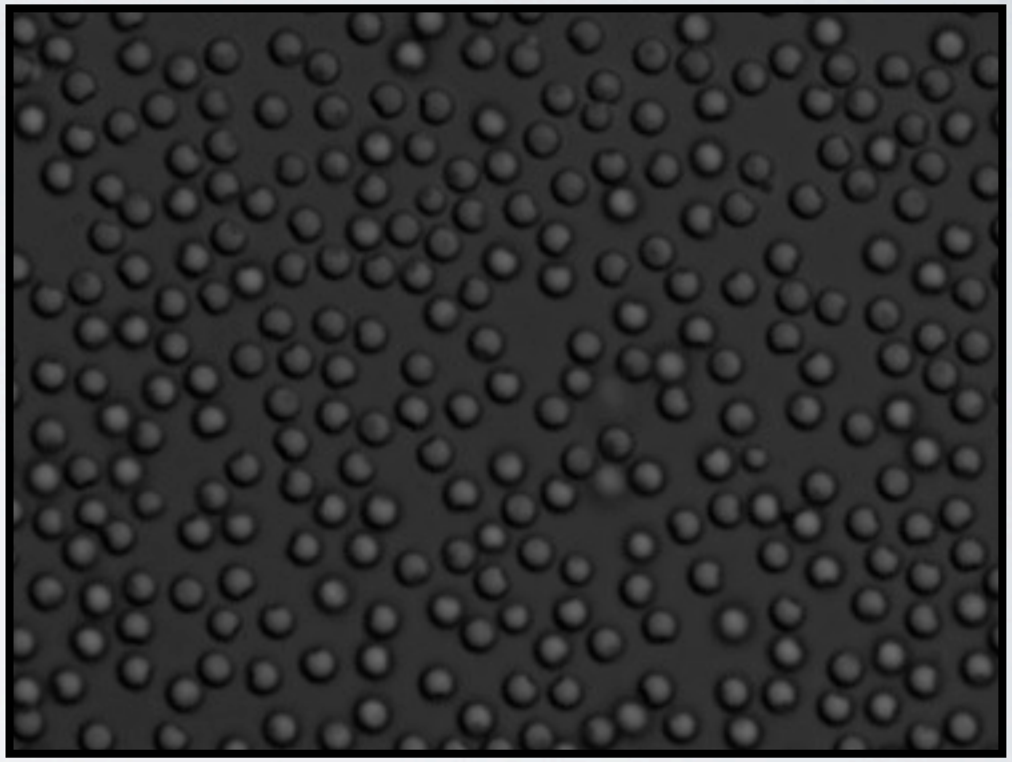


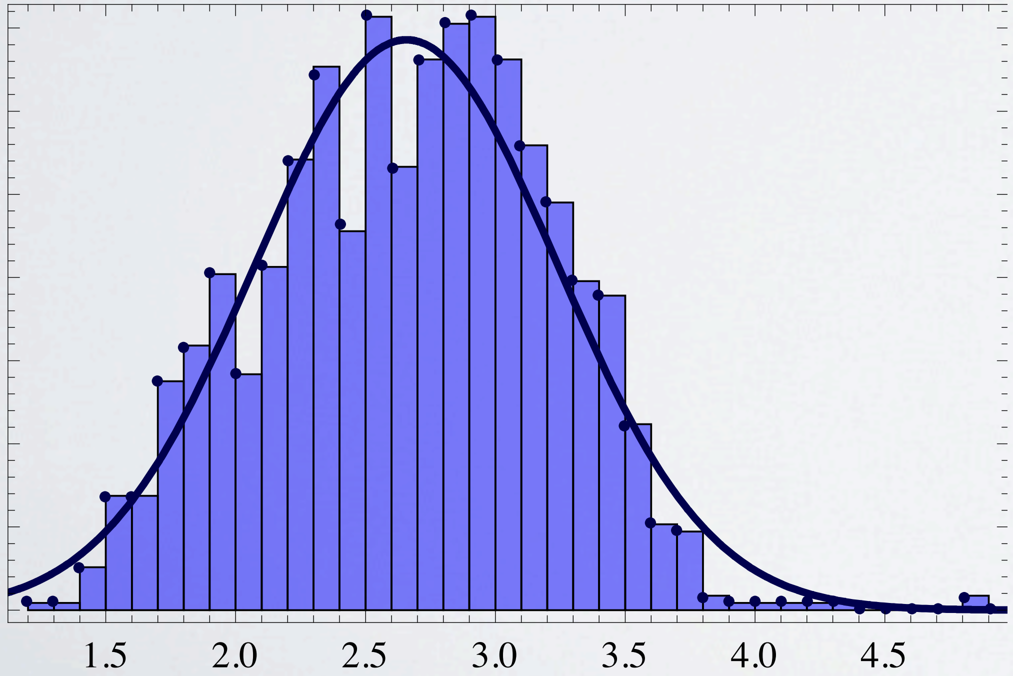
d_l = 1.5 – 3.5 µm



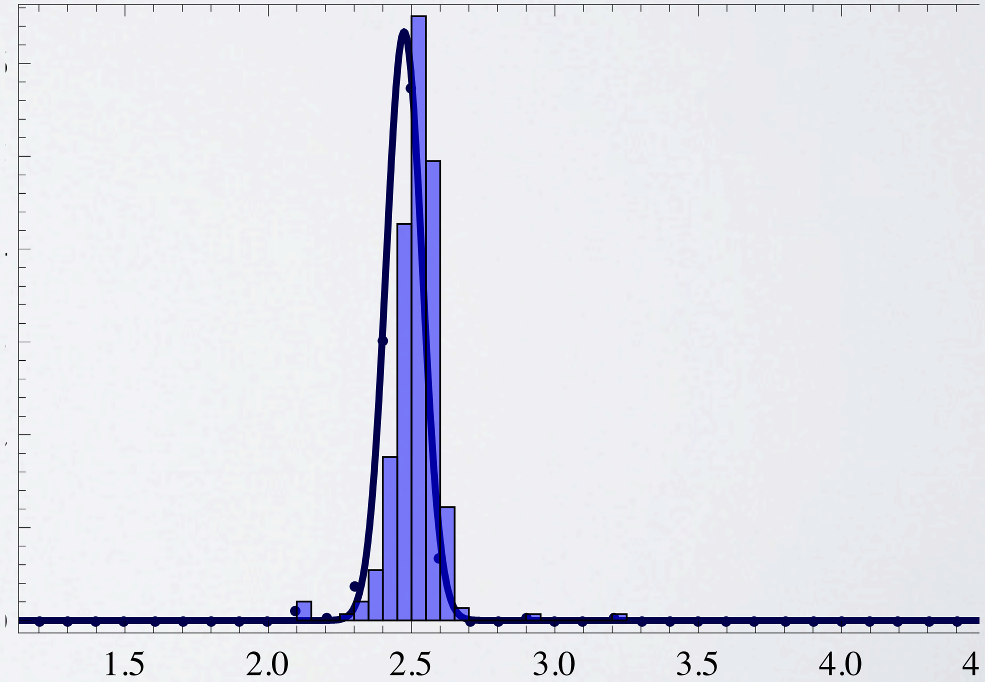
Monodisperse pacman particles







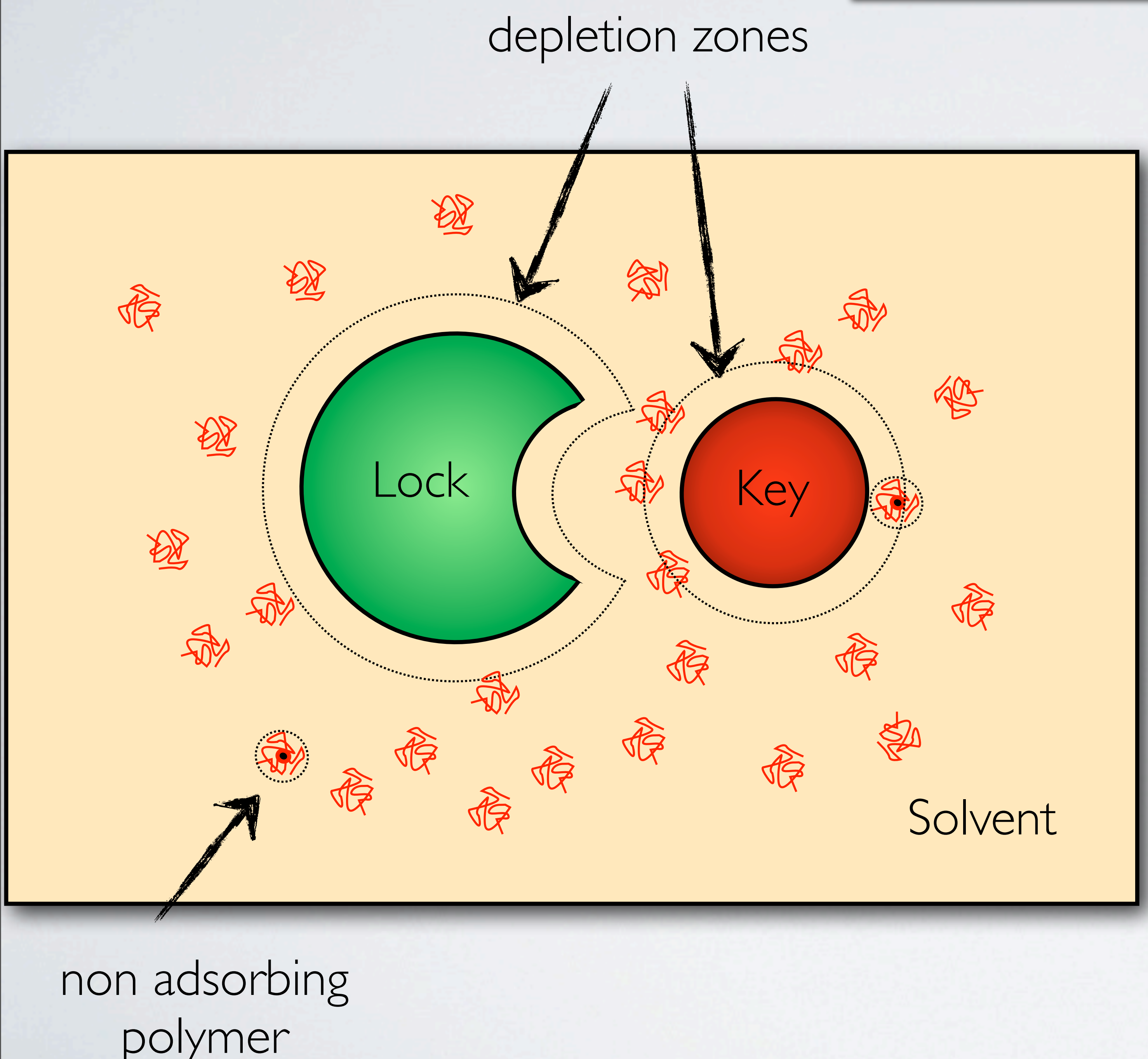
diameter $(\mu\mathrm{m})$



diameter $(\mu\mathrm{m})$

Pacman lock & key

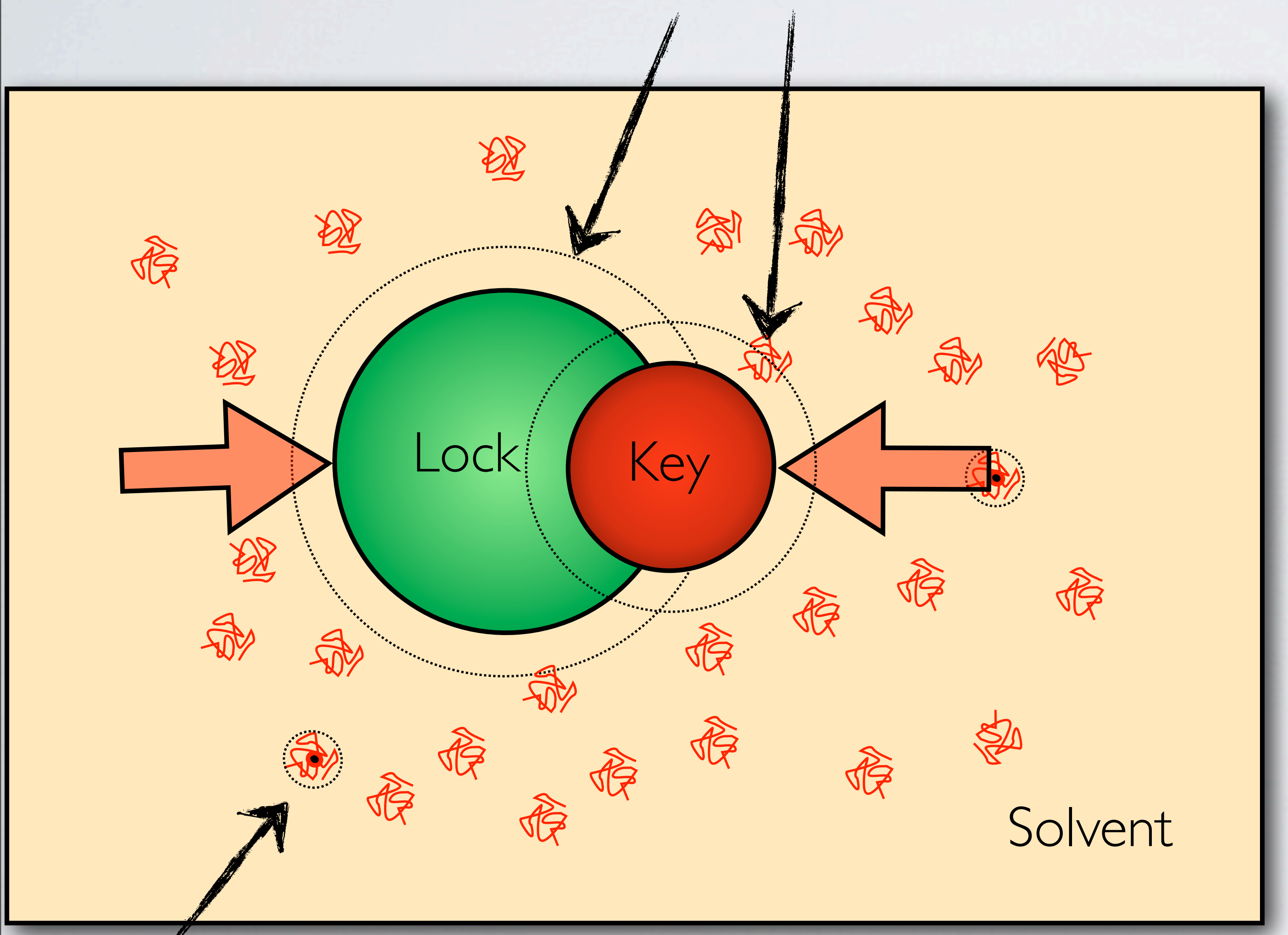
$$\boxed{S \sim n_{\mathrm{poly}} \ln V}$$



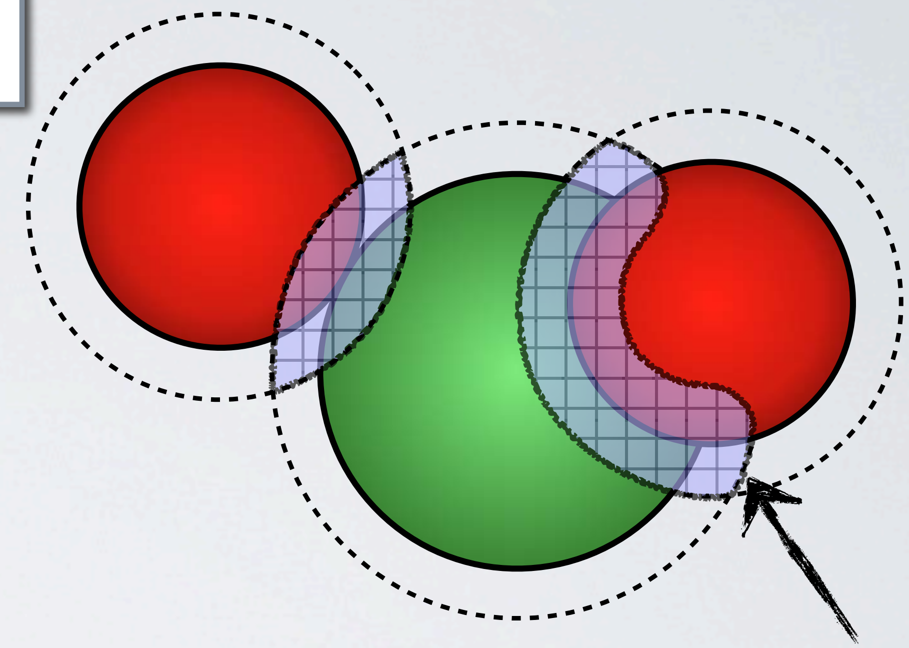
Pacman lock & key

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

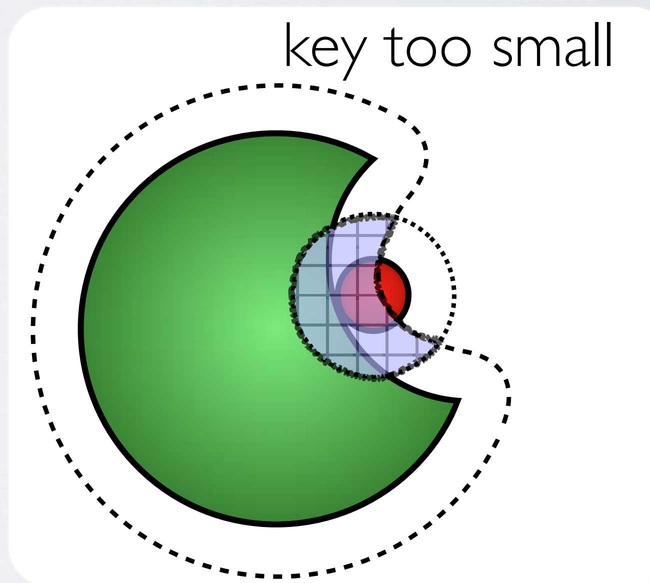
depletion zones



non adsorbing polymer



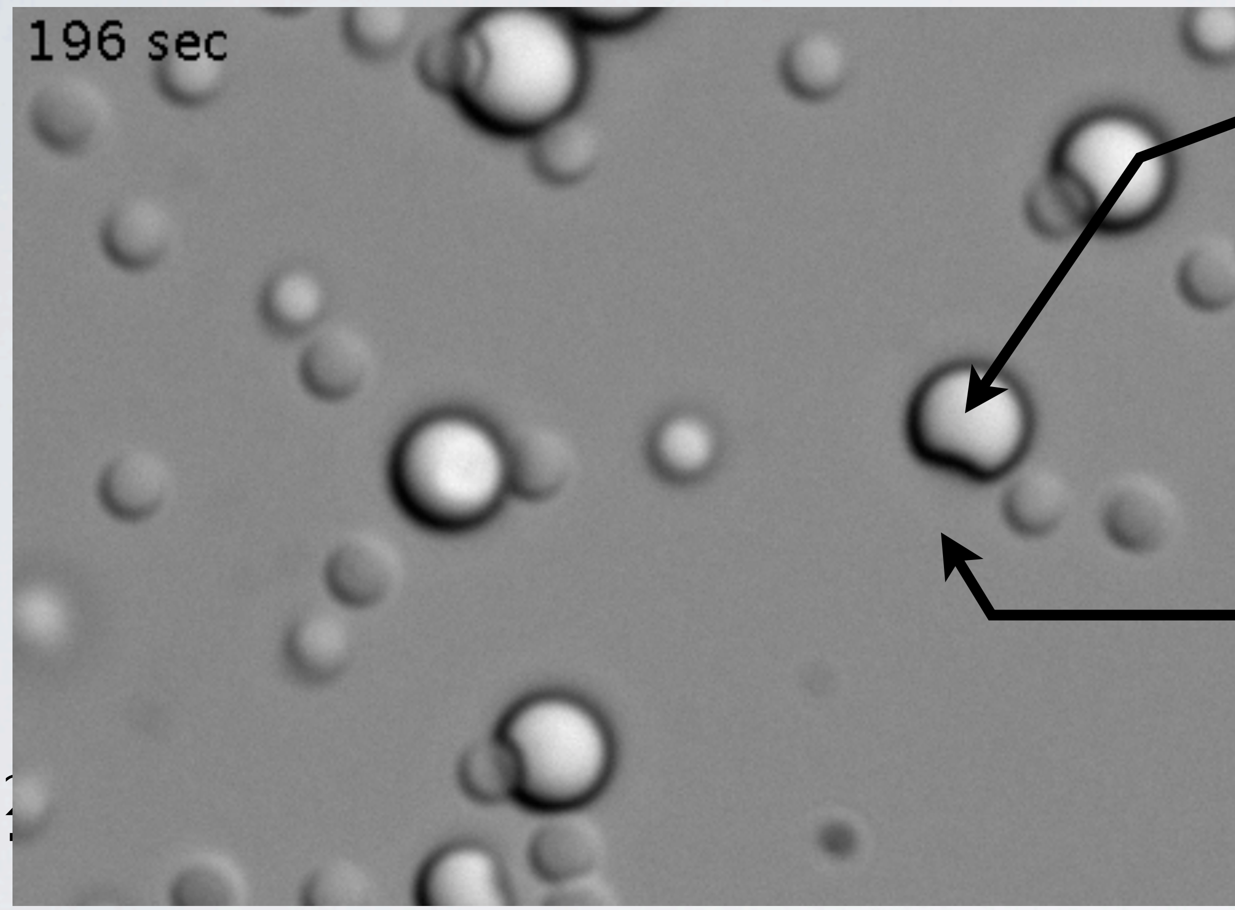
Max overlapping volume

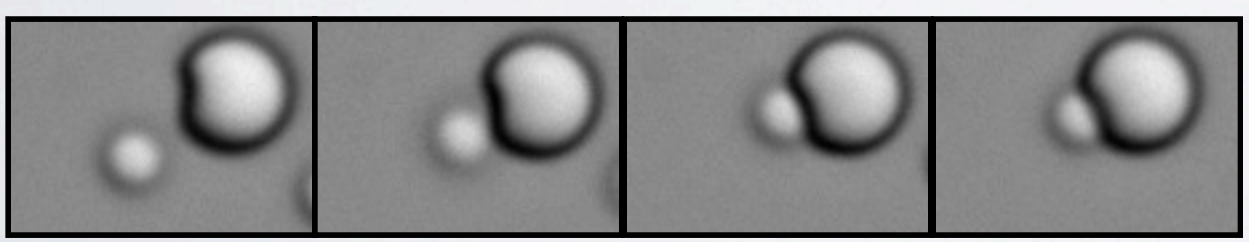


can tune interaction strength

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

Pacman depletion movie

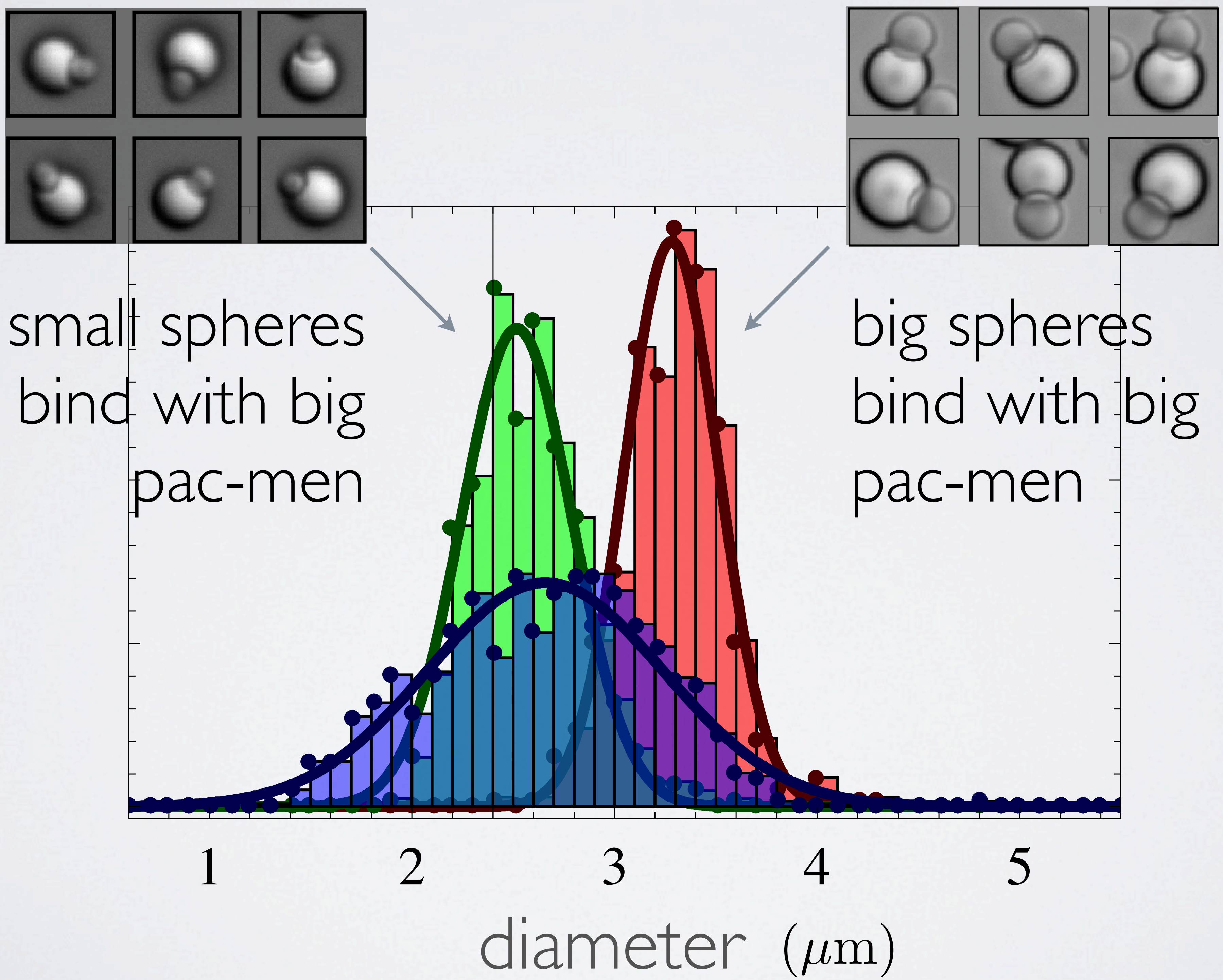




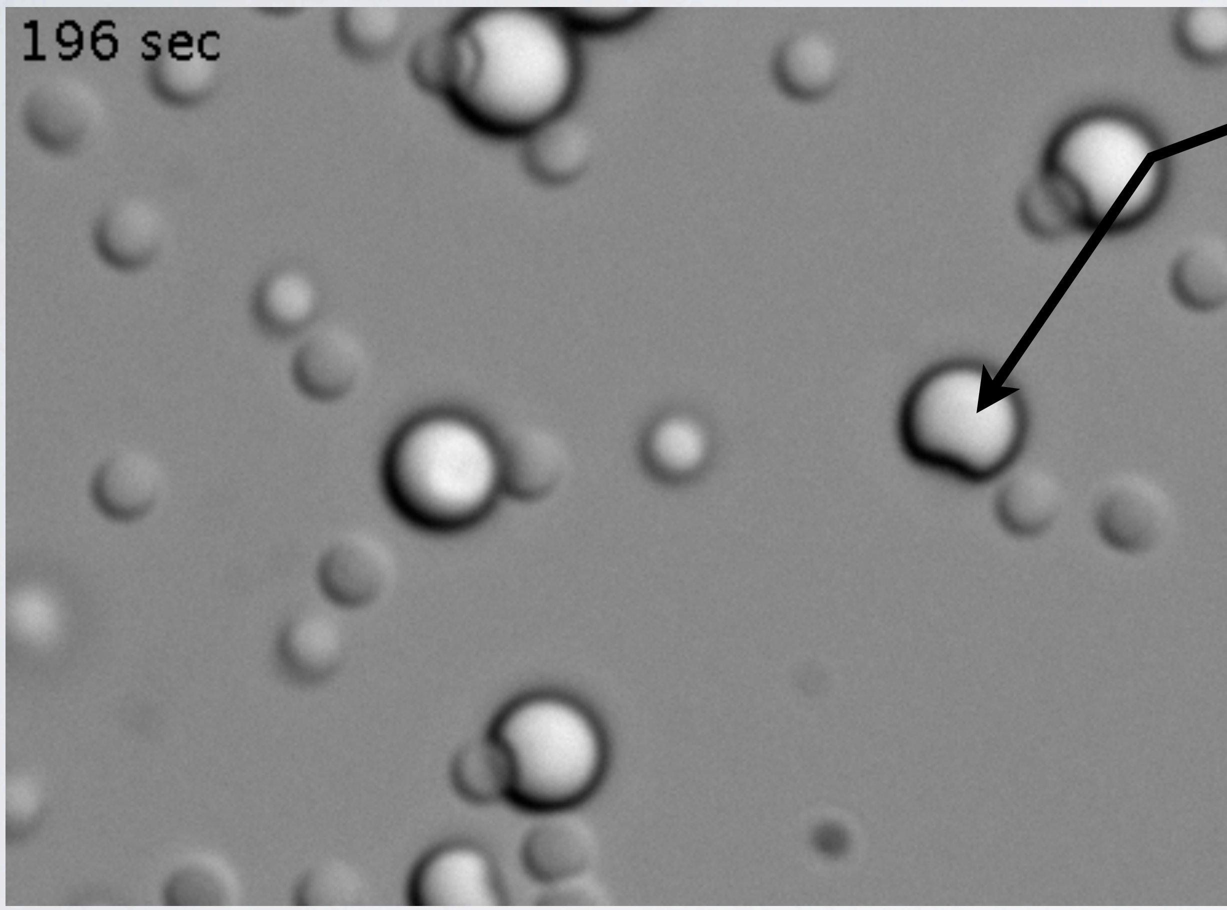
Watch this pac-man

Particle (key) binds to PacMan (lock)

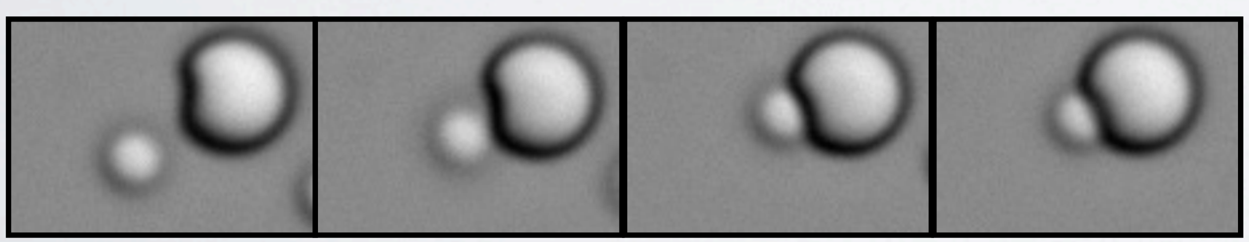
Size selectivity

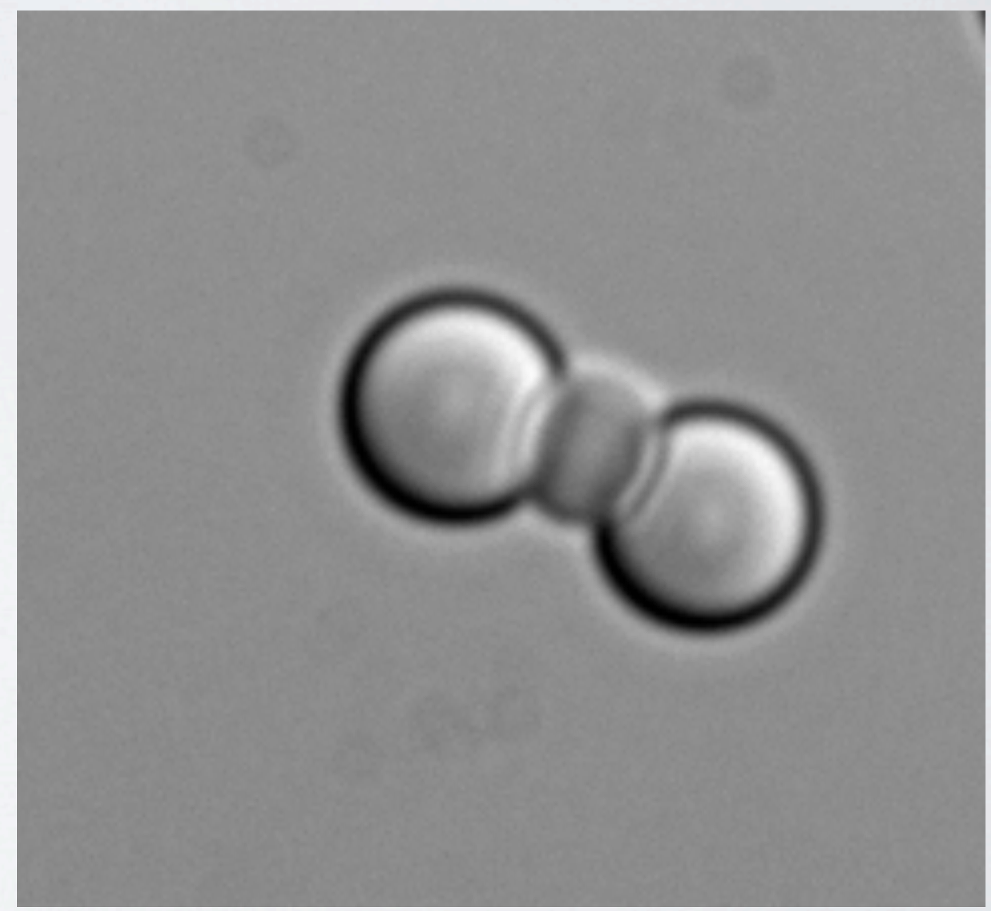


Pacman depletion movie



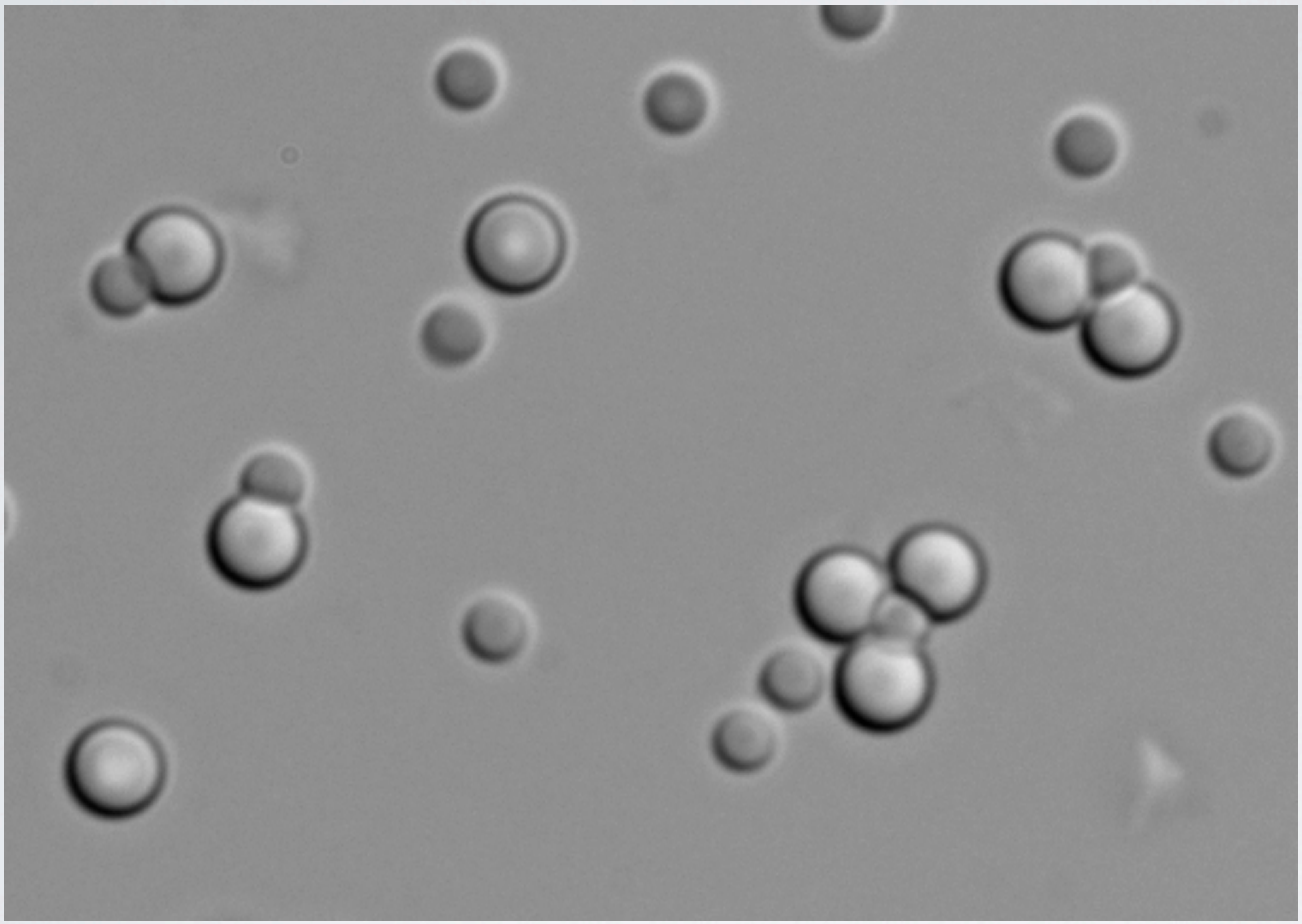
Watch this pac-man



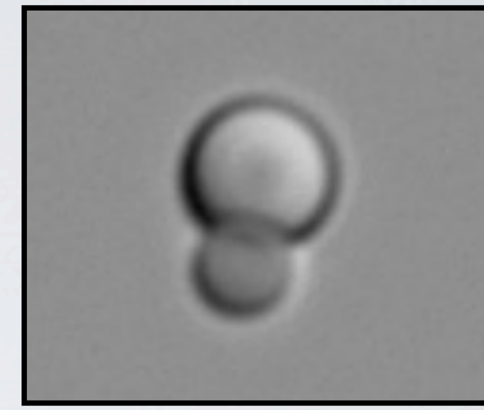


Sacanna et al., Nature **464**, 575–578 (2010)

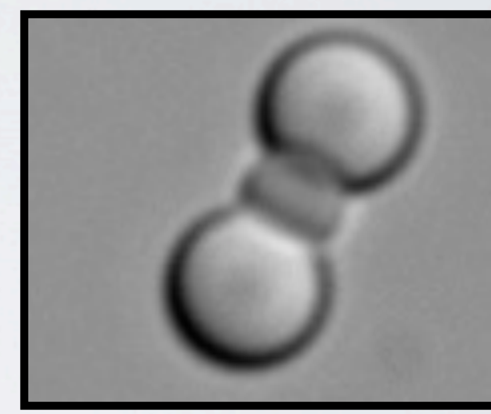
Colloidal couplings



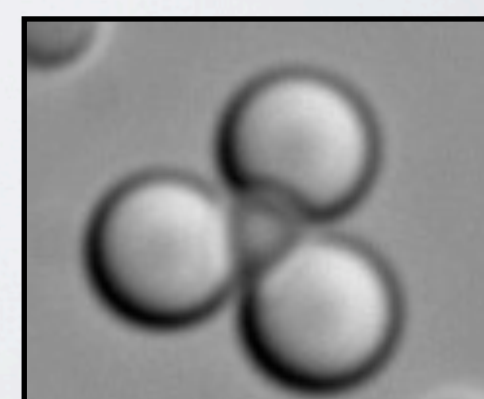
Monomer



Dimer



Trimer



Lock-and-key binding model

$\mathcal{L} + \mathcal{K} \rightleftharpoons \mathcal{LK}$ chemical equilibrium between locks & keys

$$\mu_L + \mu_K = \mu_{LK} \quad \Rightarrow \quad \frac{n_{LK}\, n_0}{n_L\, n_K} = e^{-[E_b + k_B T \ln(V_b n_0)]/k_B T}$$

$$k_B T \ln \frac{V_b}{v_u}$$

binding energy

binding volume (entropy)

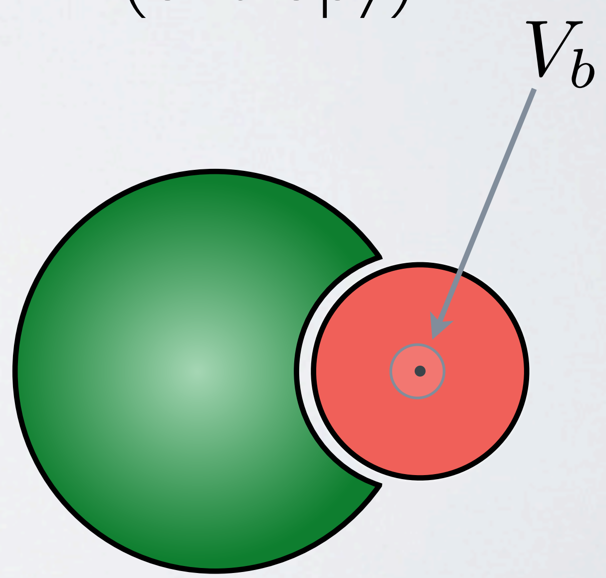
overlap area

$$E_b = -k_B T\, n\, A \left(2r_p - r_0 - \kappa^{-1}\right)$$

polymer (depletant) radius

equilibrium separation

Debye screening length (repulsion)

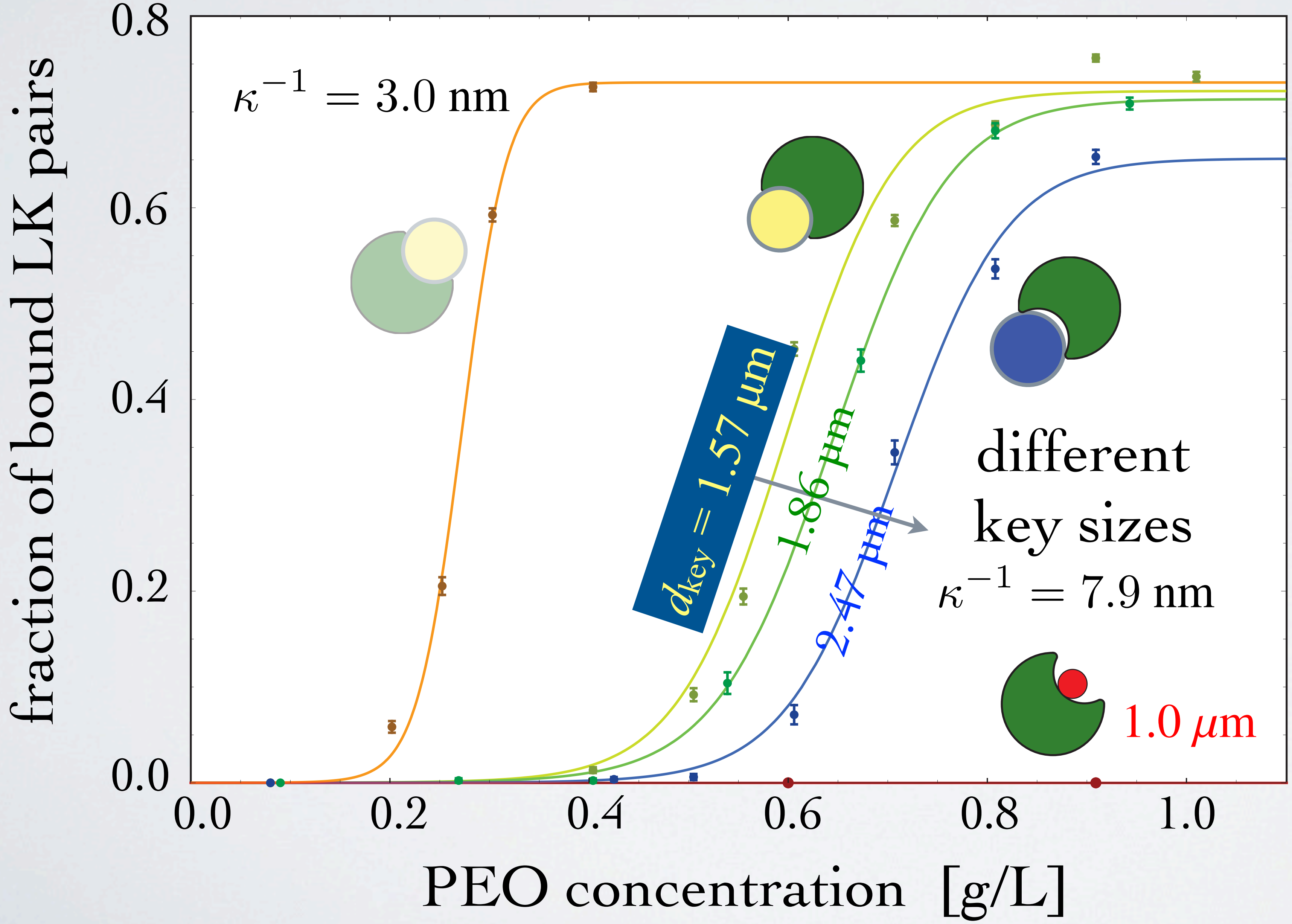


Lock & key binding energy: balance between electrostatic repulsion and depletion attraction

Entropy: binding volume vs unbound volume per key

Lock-and-key binding data

$$\mu_L + \mu_K = \mu_{LK} \quad \Rightarrow \quad \frac{n_{LK}\, n_0}{n_L\, n_K} = e^{-[E_b + k_b T \ln(V_b n_0)]/k_B T}$$

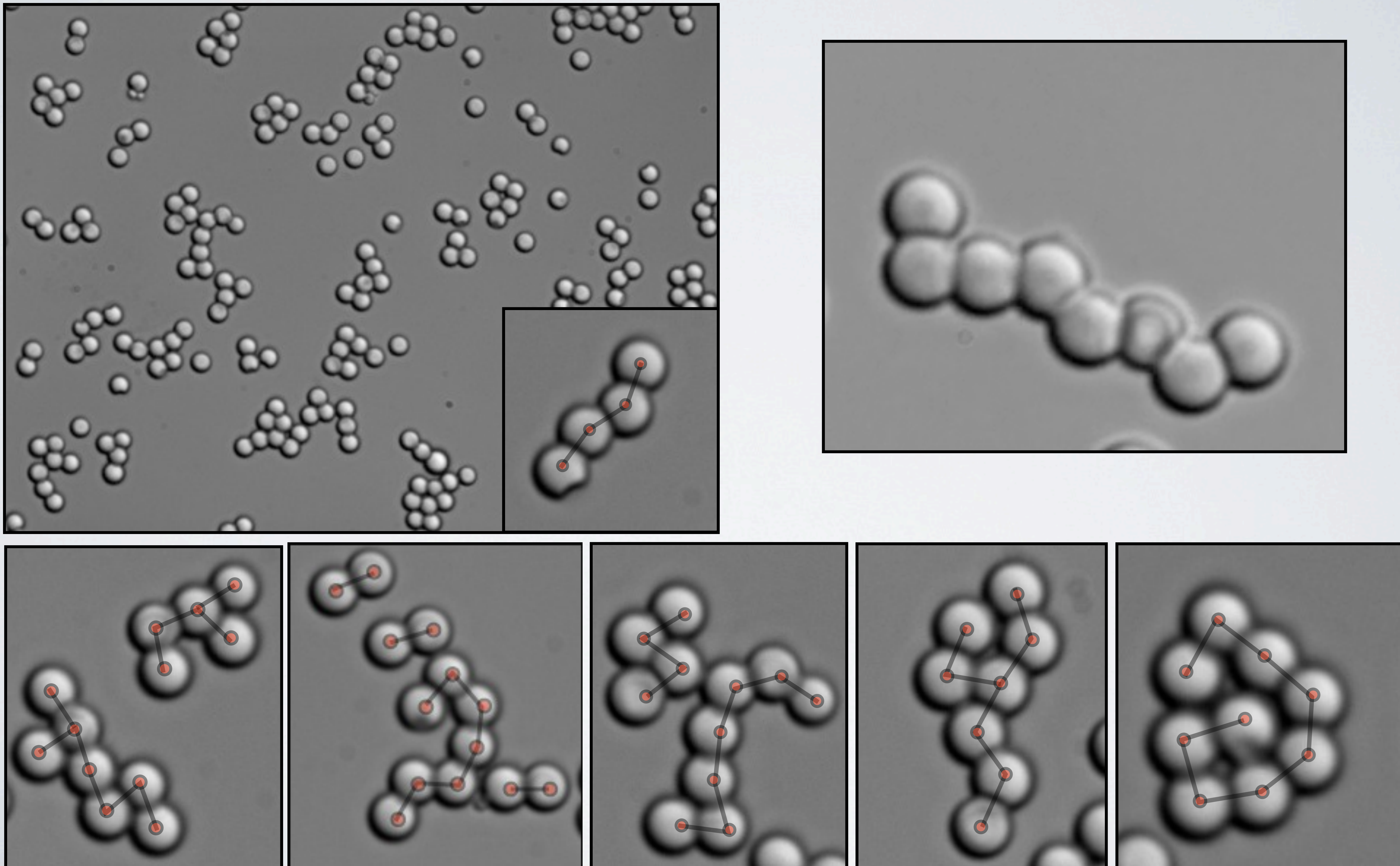


fitting parameters

$$A \approx 0.5\ \mu\mathrm{m}^2$$
$$\approx 1/15^{\rm th} A_{\rm sphere}$$

$$V_b \approx 0.005\ \mu\mathrm{m}^3$$

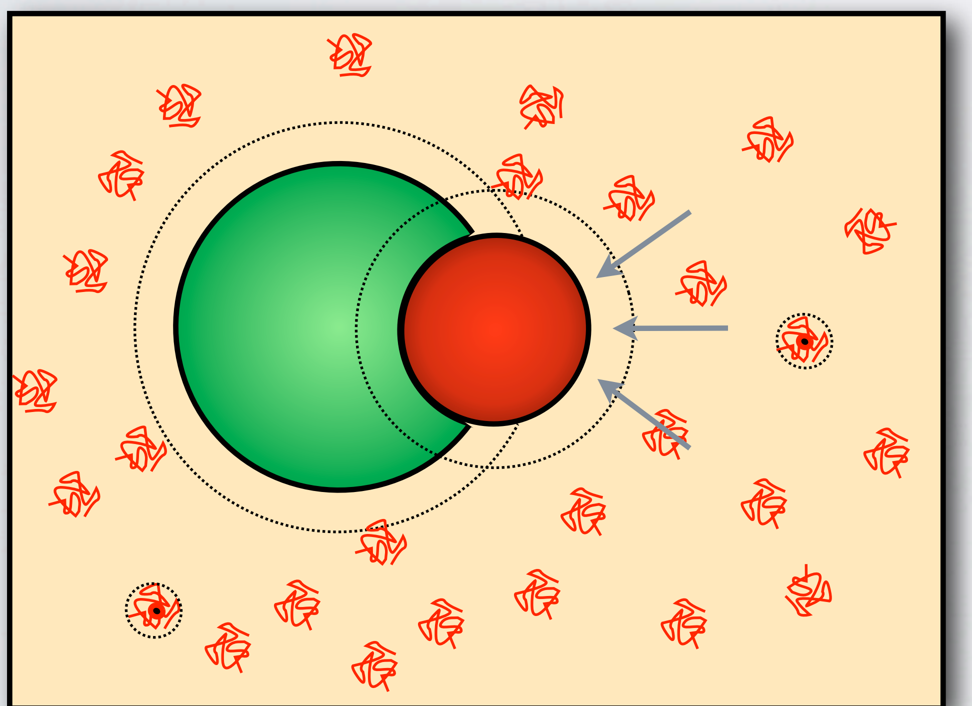
Pacman polymers



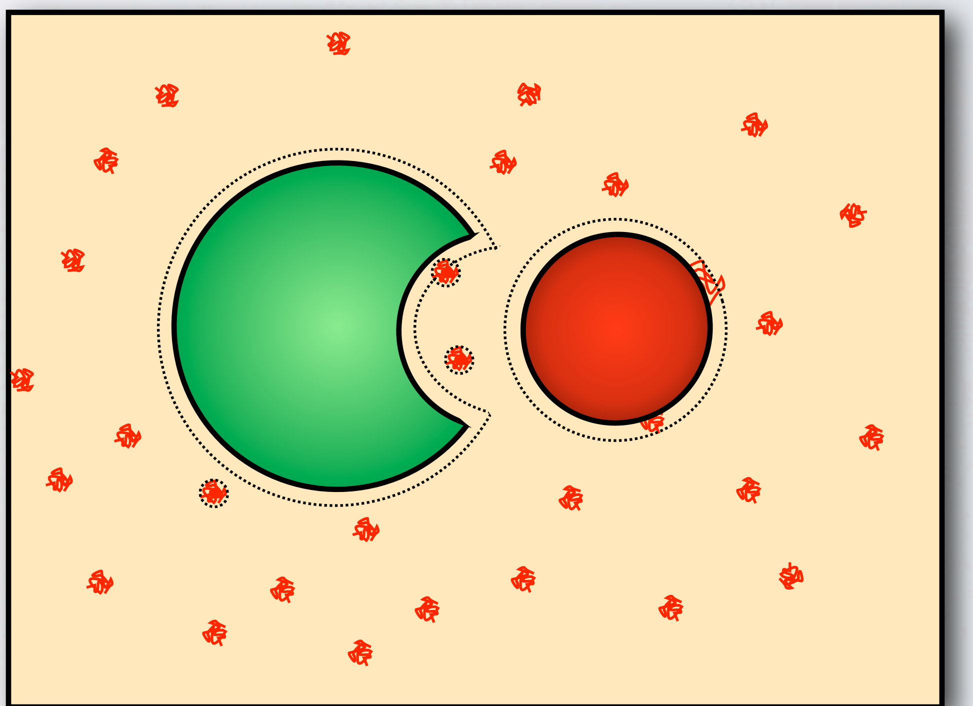
Tunable depletion attraction

$$\Delta S \sim n_p \frac{\Delta V}{V}$$

NIPAM gel particles shrink when heated above 39°



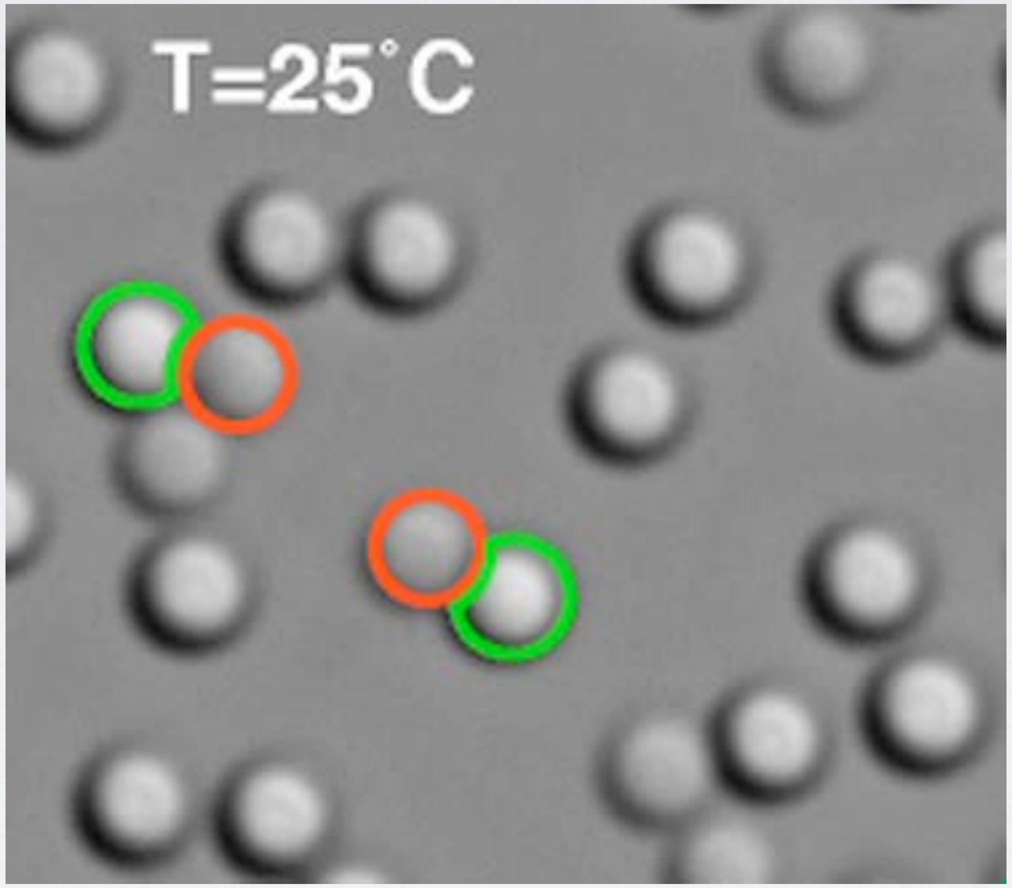
$T \approx 25^\circ$



$T \approx 40^\circ$

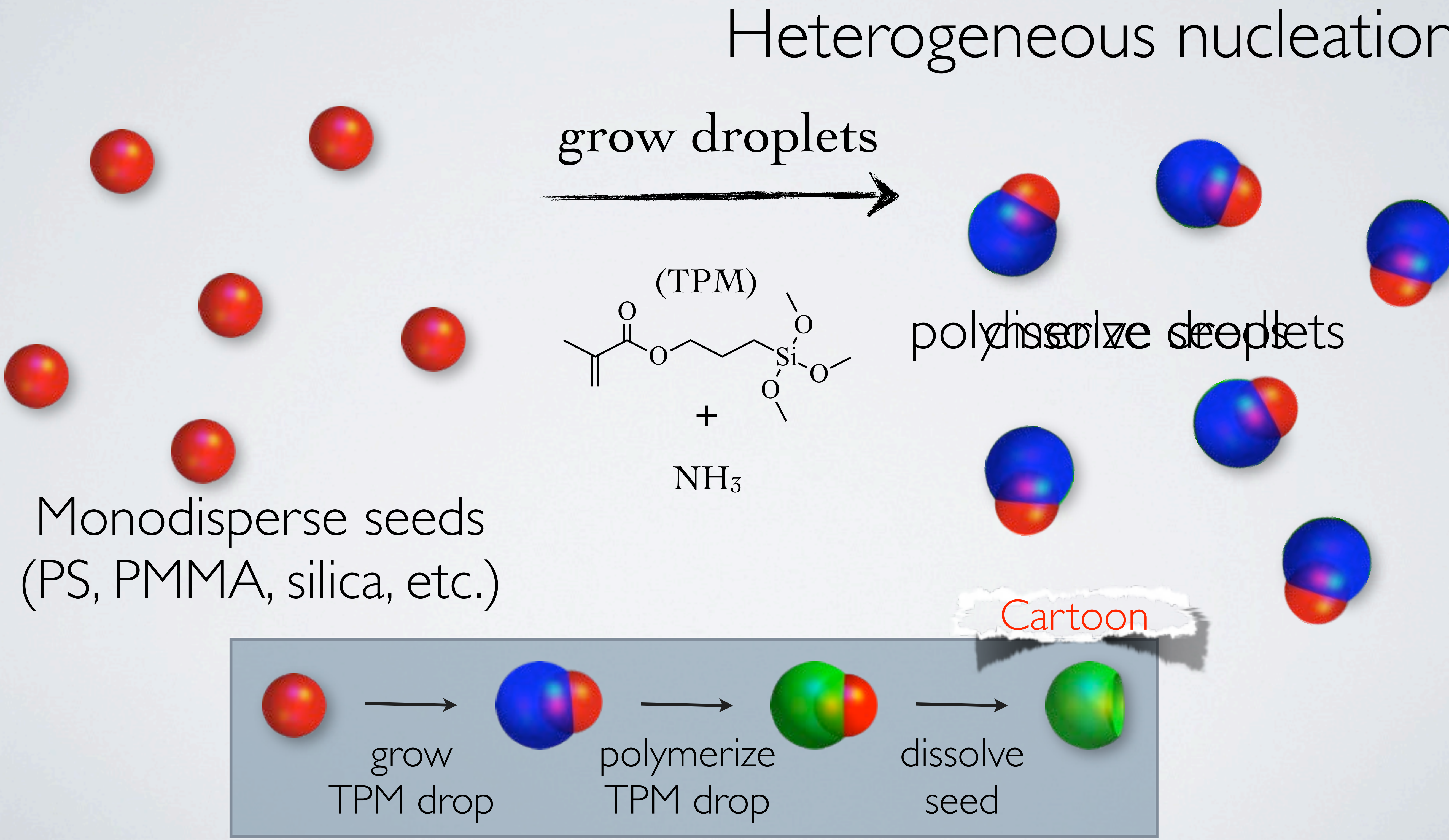
Melting

Start at 25°C, then heat to 40°C



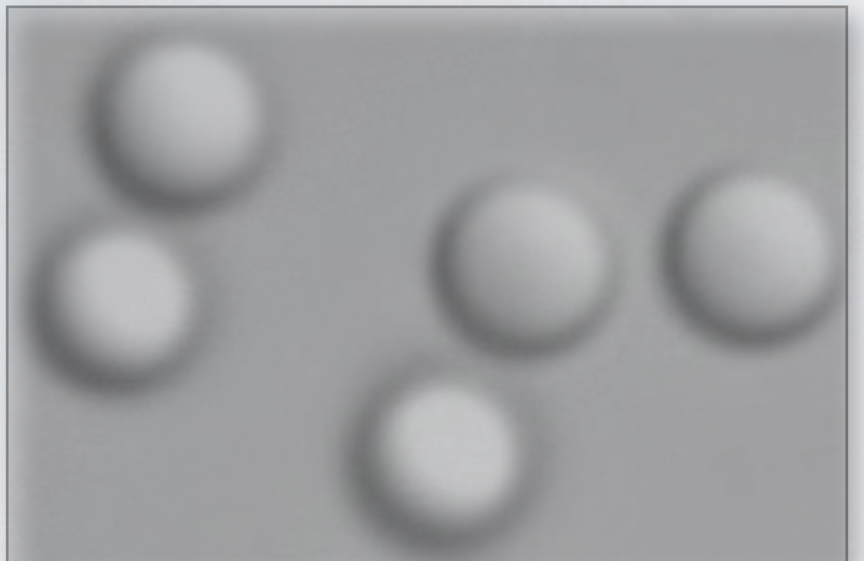
Particle pairs dissociate at 40°C

Towards a more perfect pacman

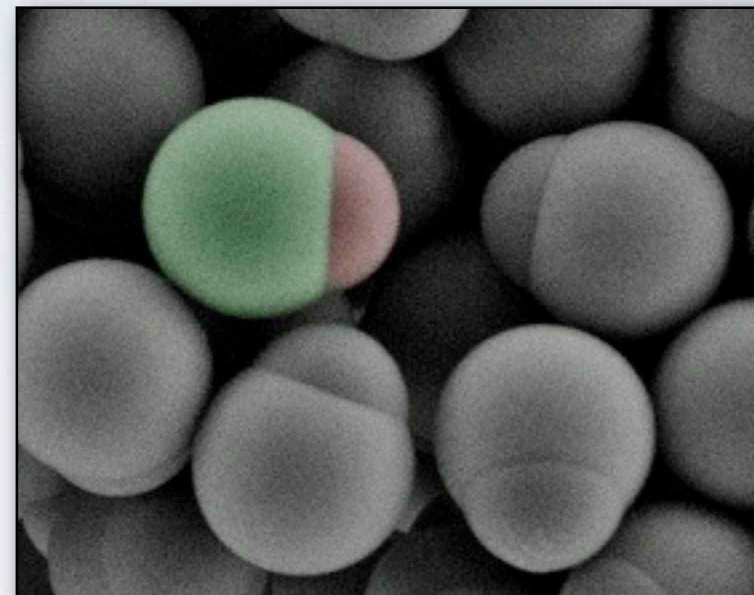


The real colloids

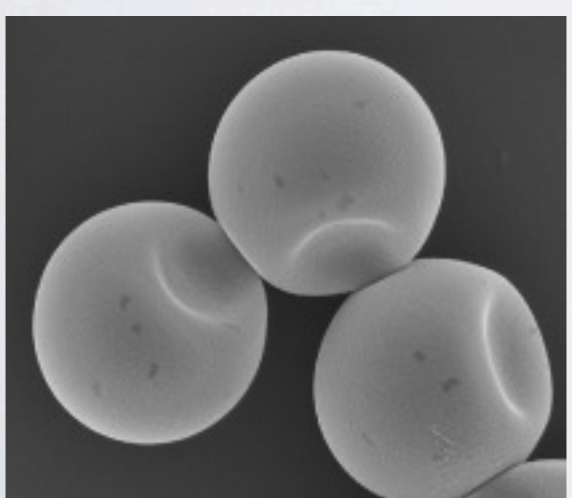
seeds



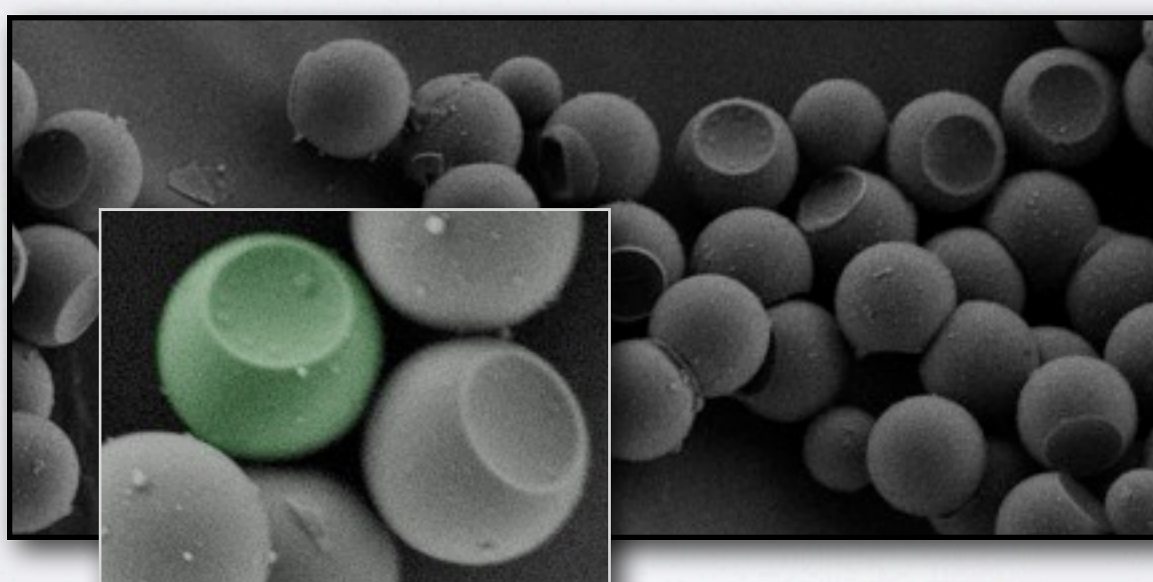
TPM on seeds



old pacmen



pacmen



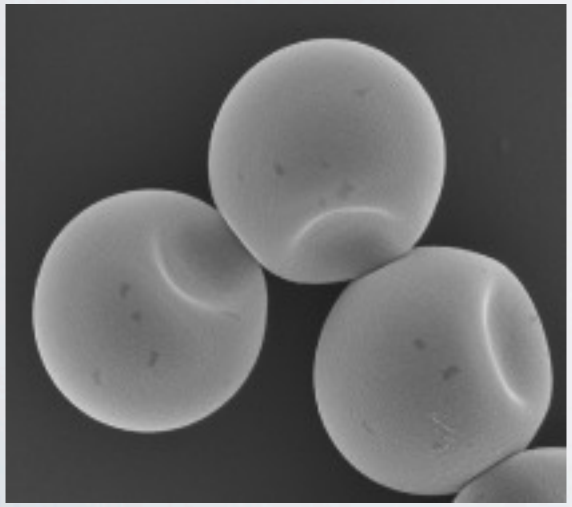
Lock & key interaction

$$\mu_L + \mu_K = \mu_{LK} \quad \Rightarrow \quad \frac{n_{LK}\, n_0}{n_L\, n_K} = e^{-[E_b + k_B T \ln(V_b n_0)]/k_B T}$$

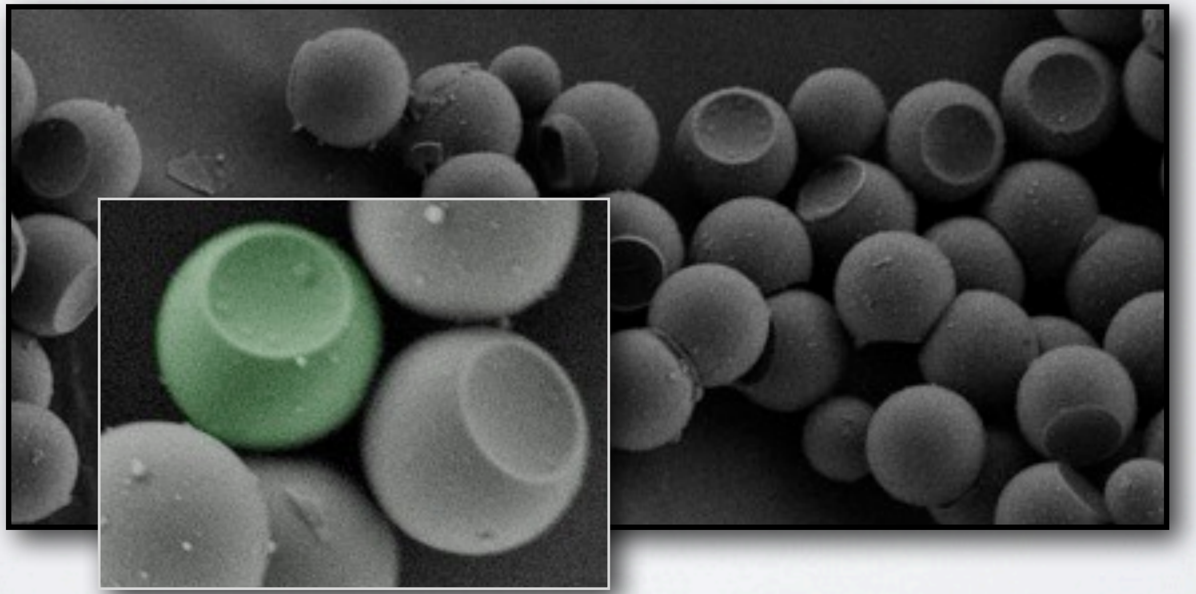
binding energy

binding volume (entropy)

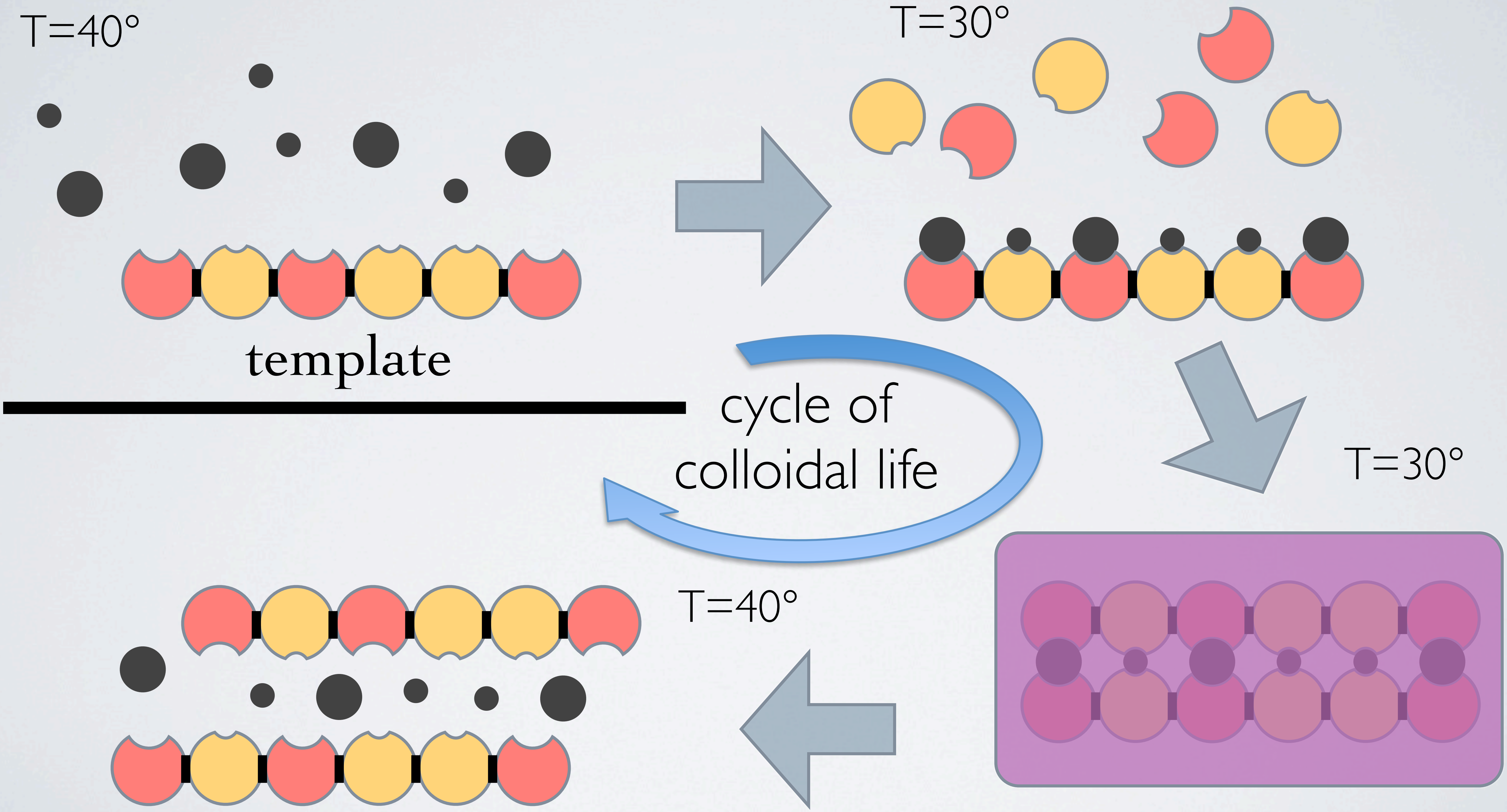
old pacmen



pacmen



Self-replicating pacmen



Colloids with directional bonds

How can we make colloids with multiple direction bonds?

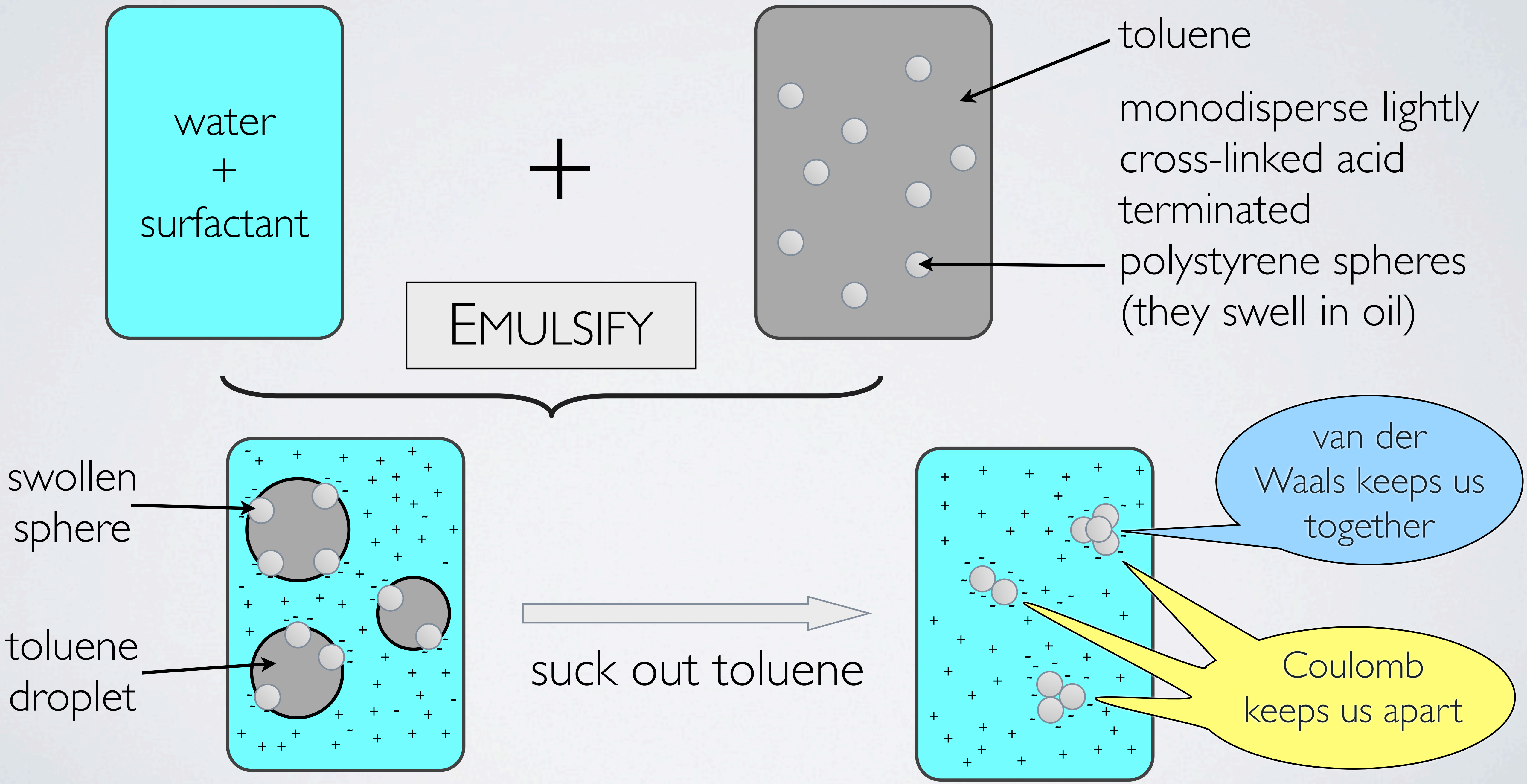
CO_2

CH_4

SO_2

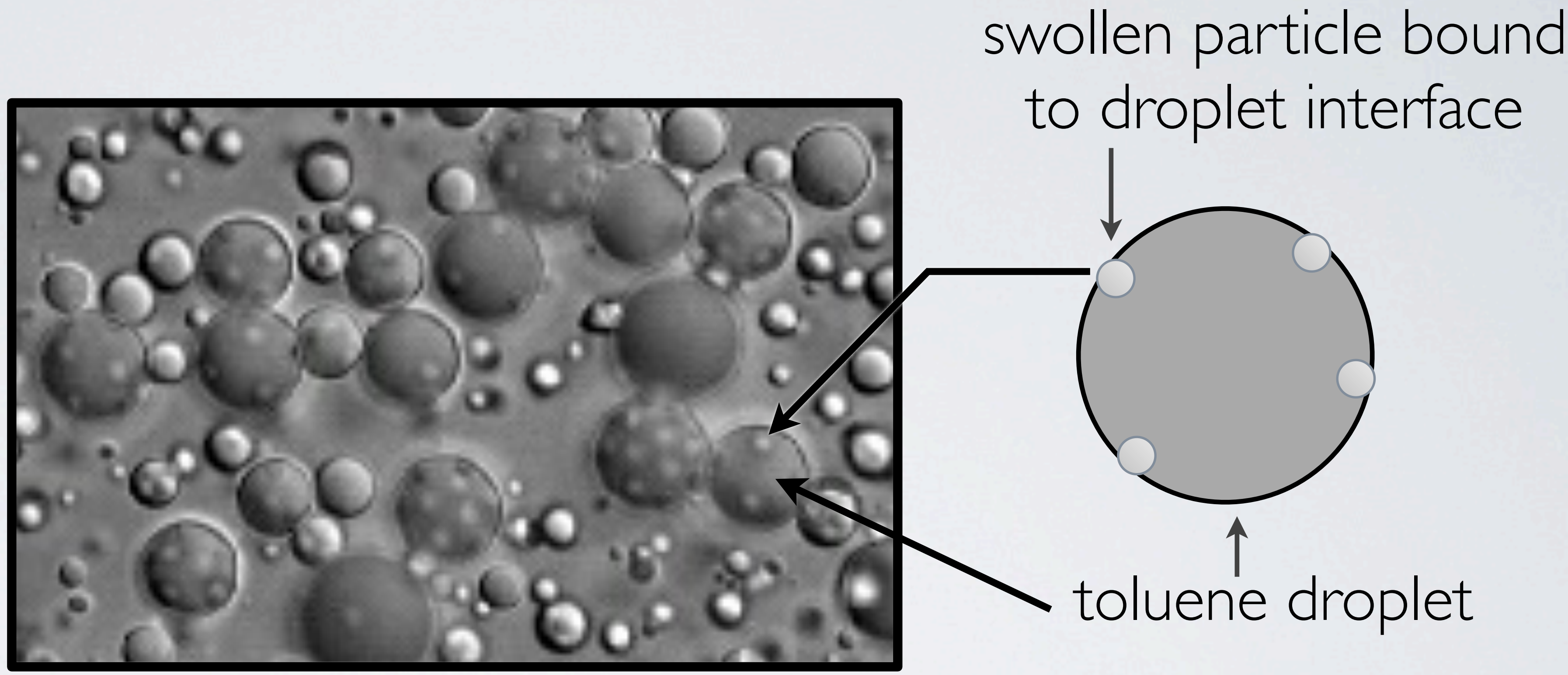
Start by assembling colloids in a controlled way ...

How to make colloidal clusters



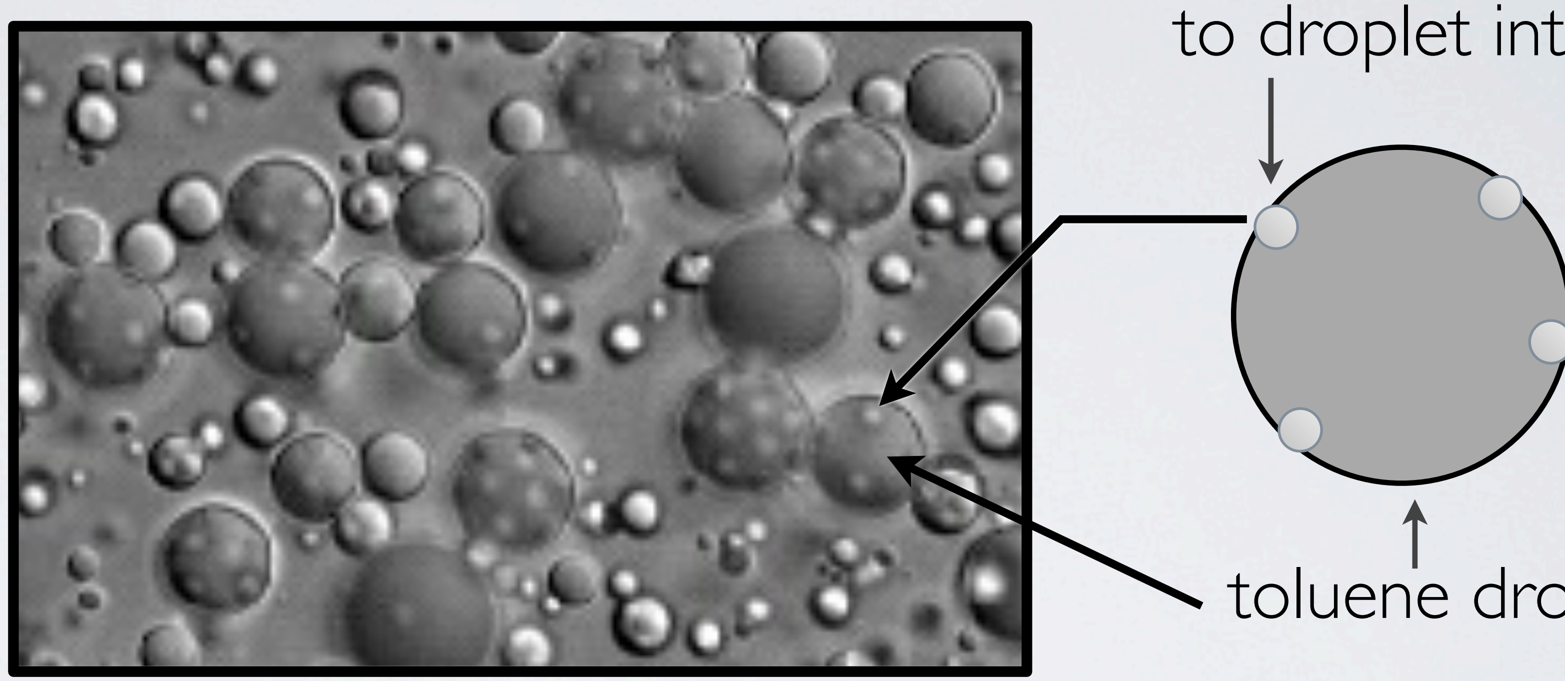
Emulsion pictures

particle-in-oil in
water emulsion

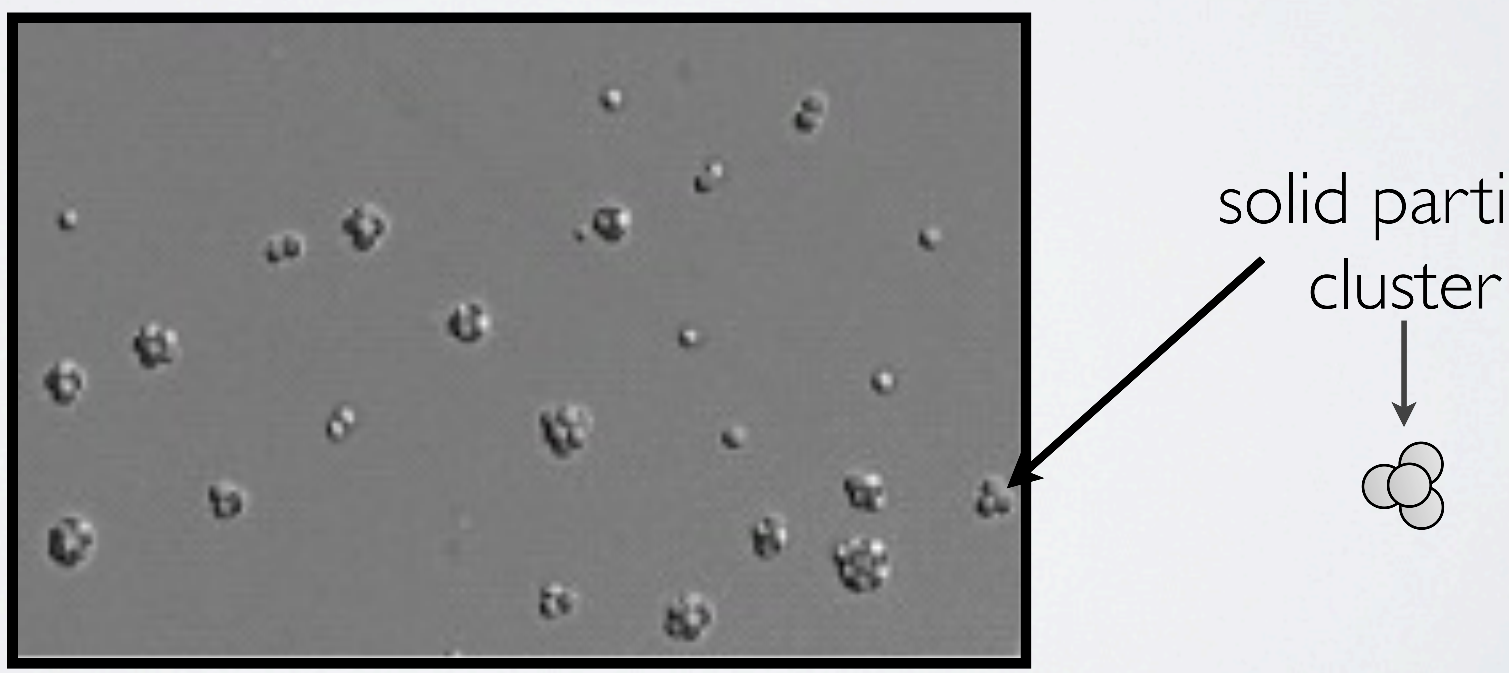


Emulsion & cluster pictures

particle-in-oil in water emulsion

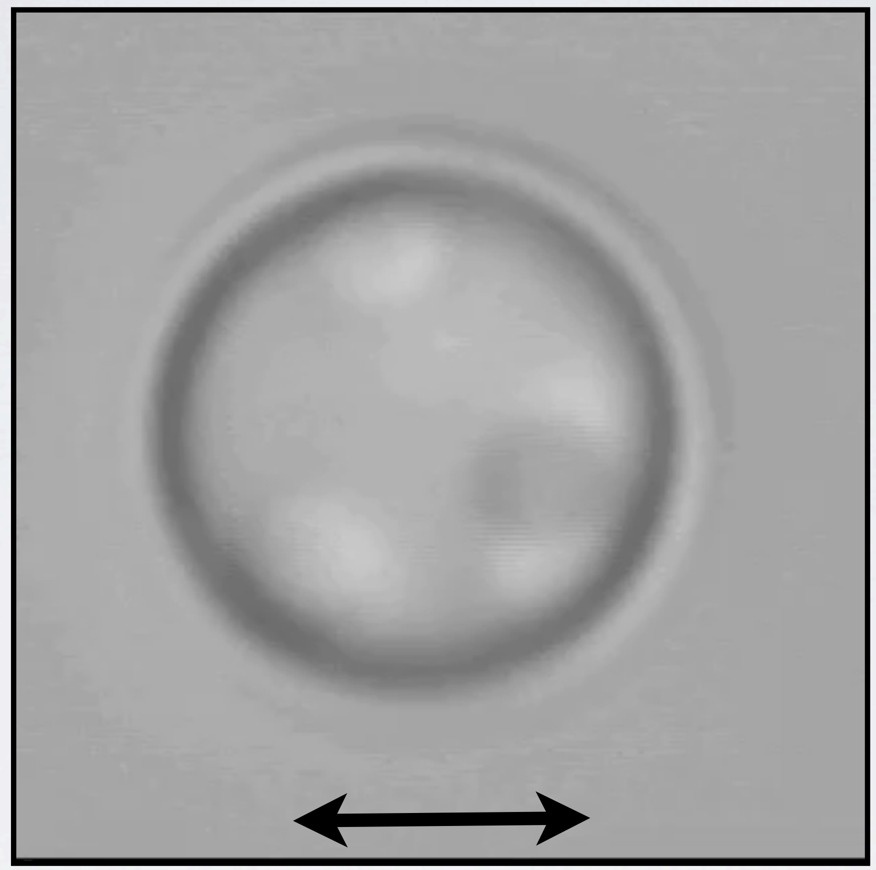


clusters after removal of oil



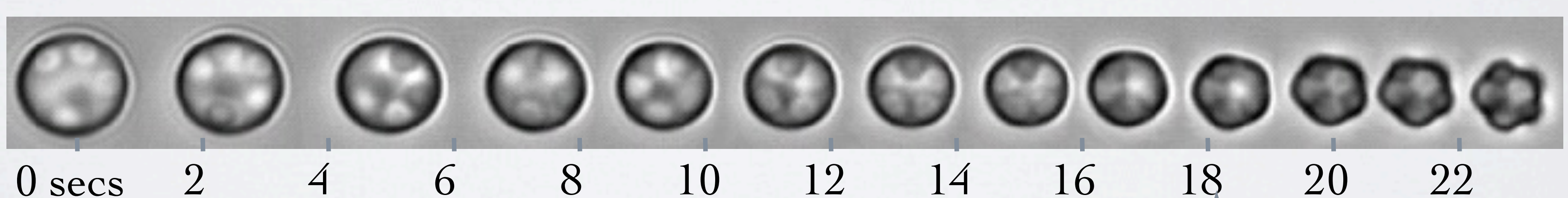
Cluster formation

particles are confined to droplet surface, not the interior



$2\ \mu m$

capillary force pulls spheres towards center



particles move at surface

particles touch and jam

droplet deforms

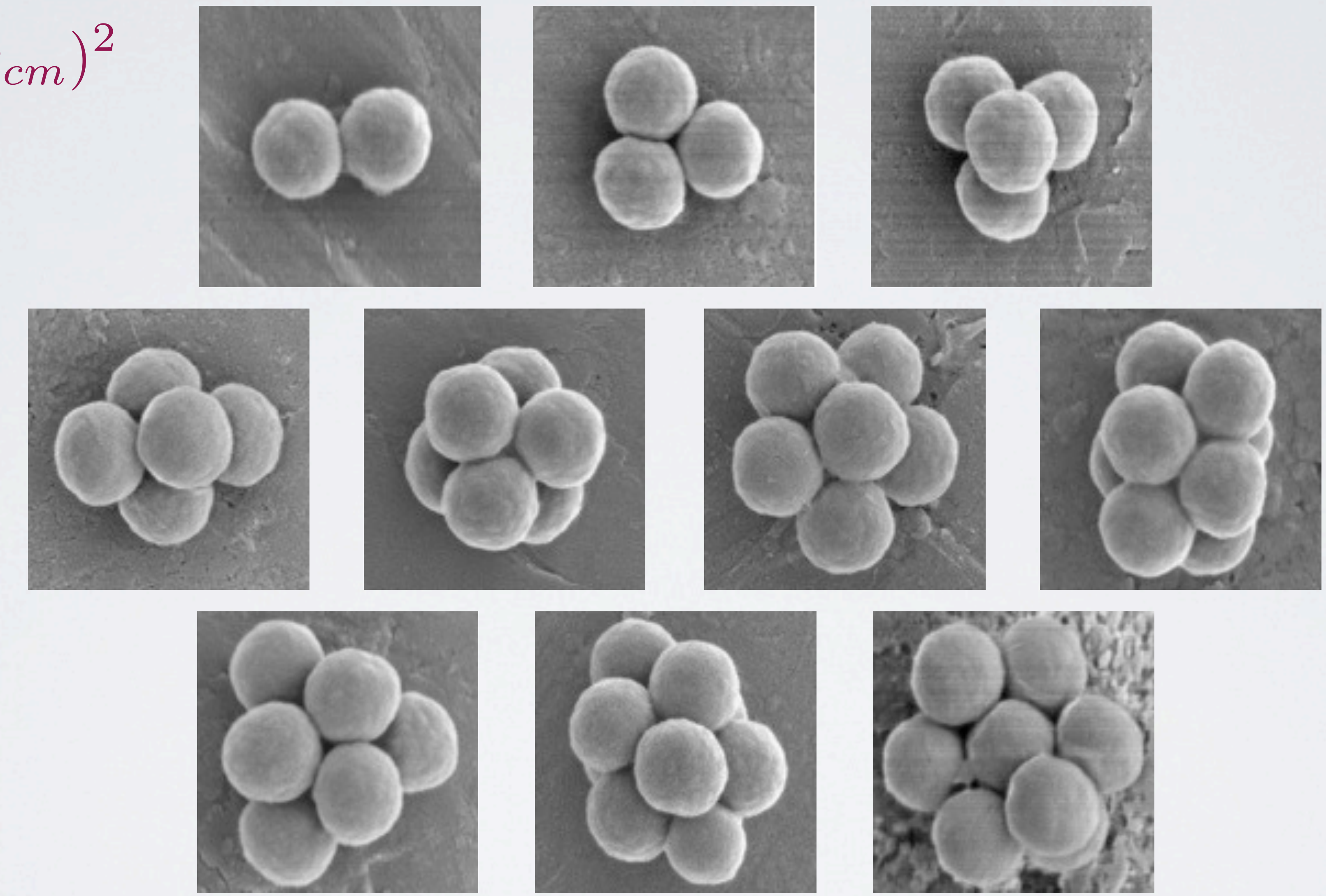
Rearrangement

drying

11 first minimal moment clusters

$$M_2 = \sum_{0}^{n} (\mathbf{r} - \mathbf{r}_{cm})^2$$

John Conway*
(Princeton)



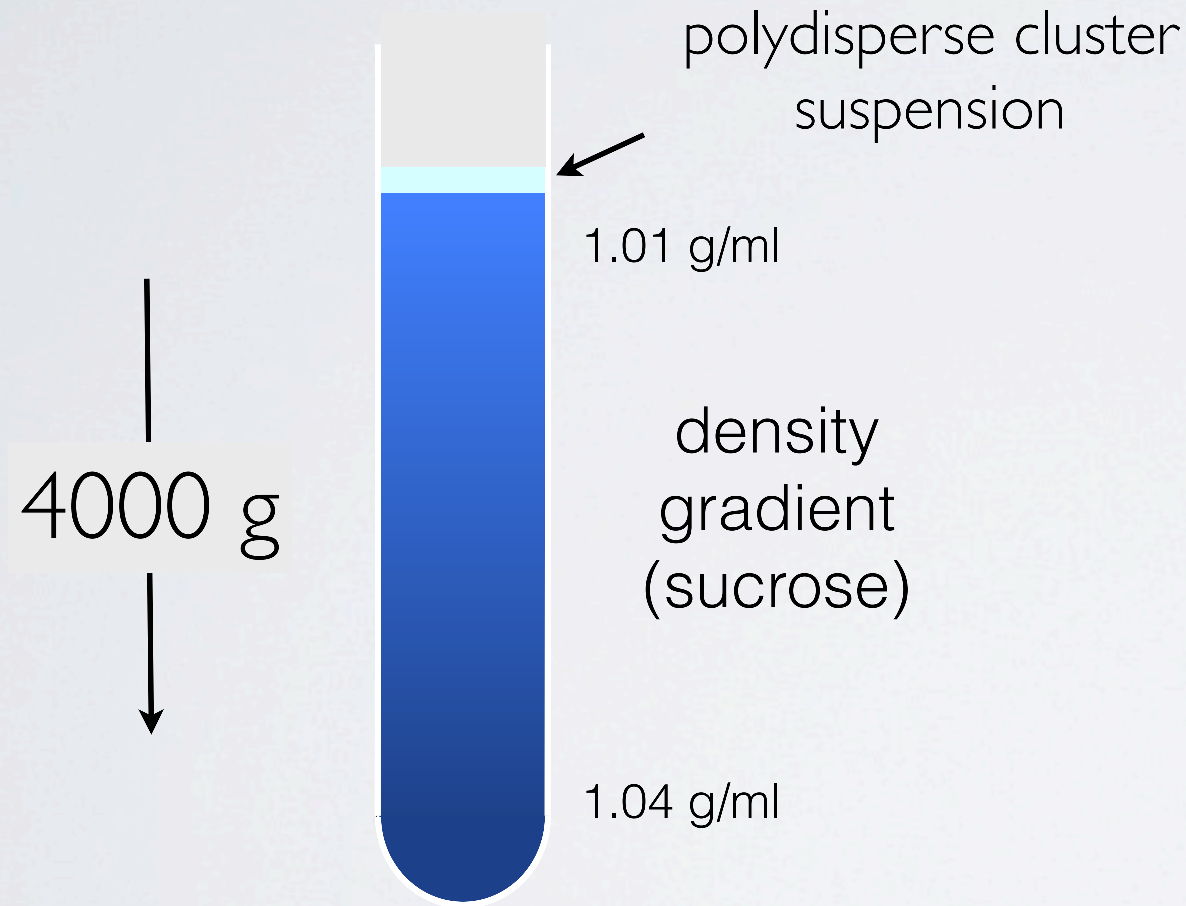
Calculated by John Conway, Neil Sloane et al.

Assembled & measured by Vinny Manoharan et al.

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

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

Separating clusters

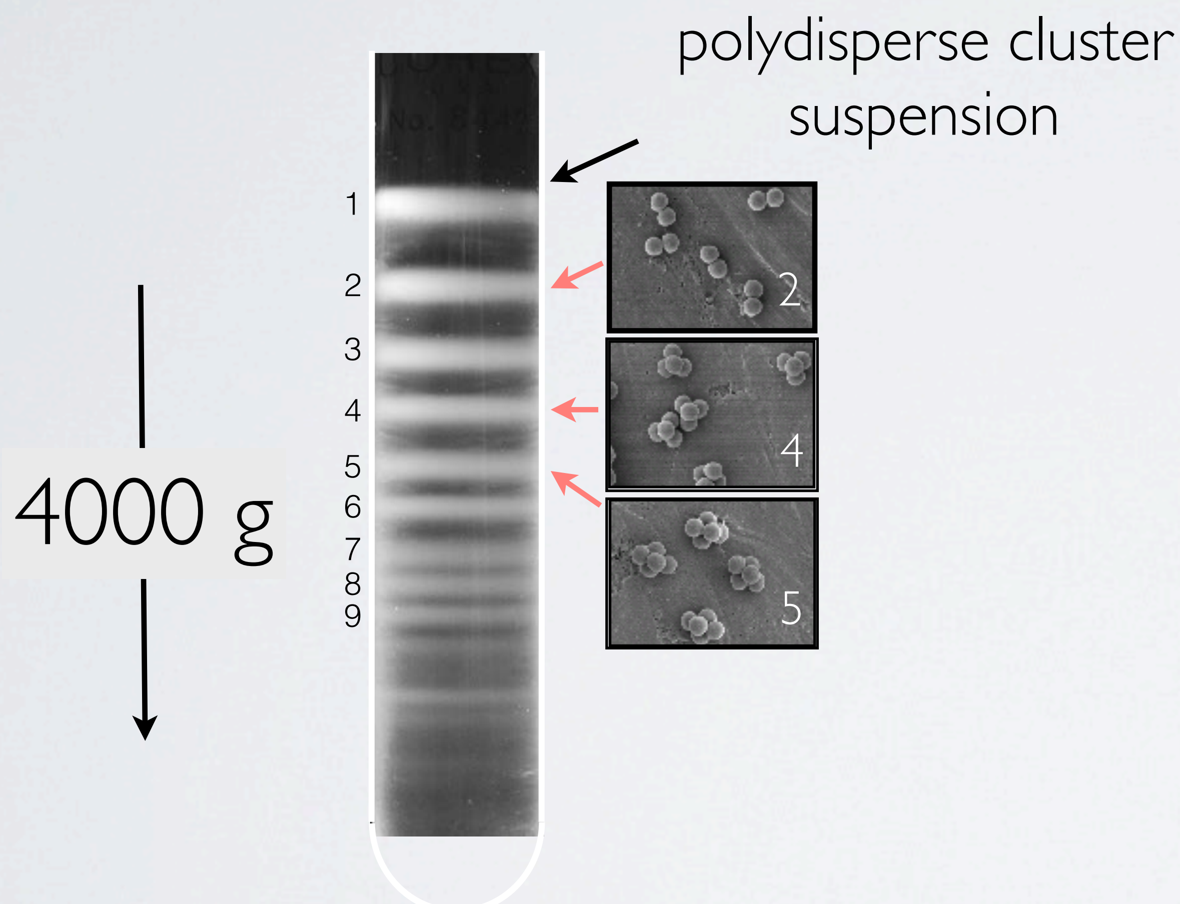


$$\Delta mg = 6\pi\eta R_{hyd} v_{sed}$$

$$\Rightarrow \; v_{sed} = \frac{\Delta\rho}{\eta} R_{hyd}^2 g$$

<u>It's a race</u>

Clusters with large hydrodynamic radius sediment faster



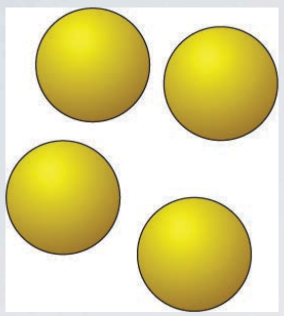
$$\Delta m g = 6\pi\eta R_{hyd} v_{sed}$$

$$\Rightarrow \; v_{sed} = \frac{\Delta\rho}{\eta} R_{hyd}^2 g$$

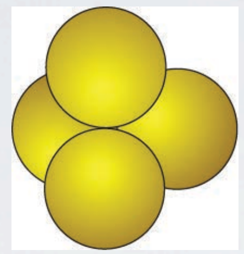
It's a race

Clusters with large hydrodynamic radius sediment faster

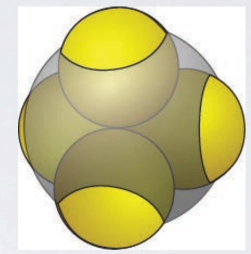
Making patchy particles



amidinated
PS spheres

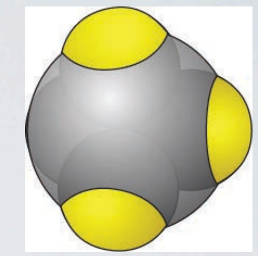


cluster

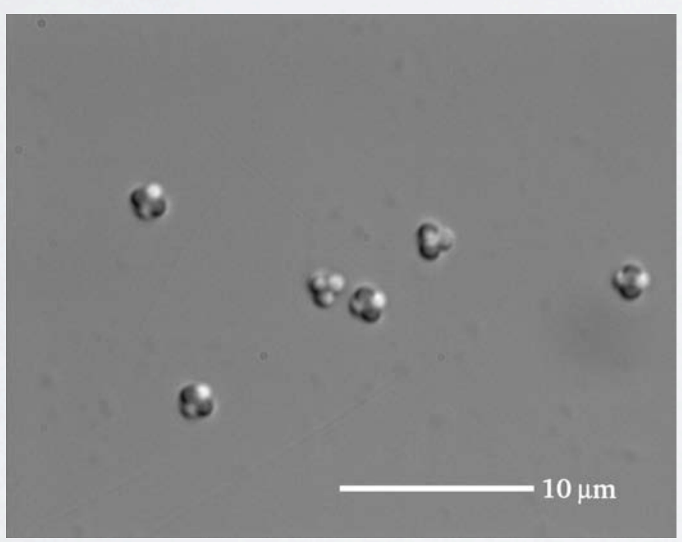


swell cluster with
styrene (emulsion)

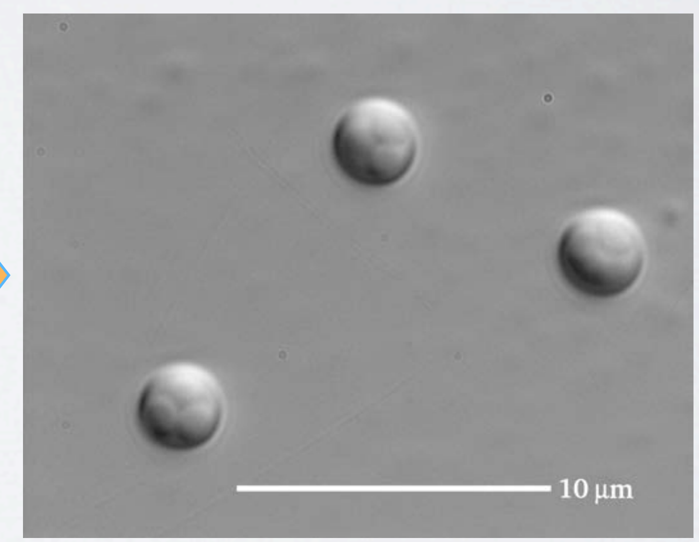
polymerize
styrene



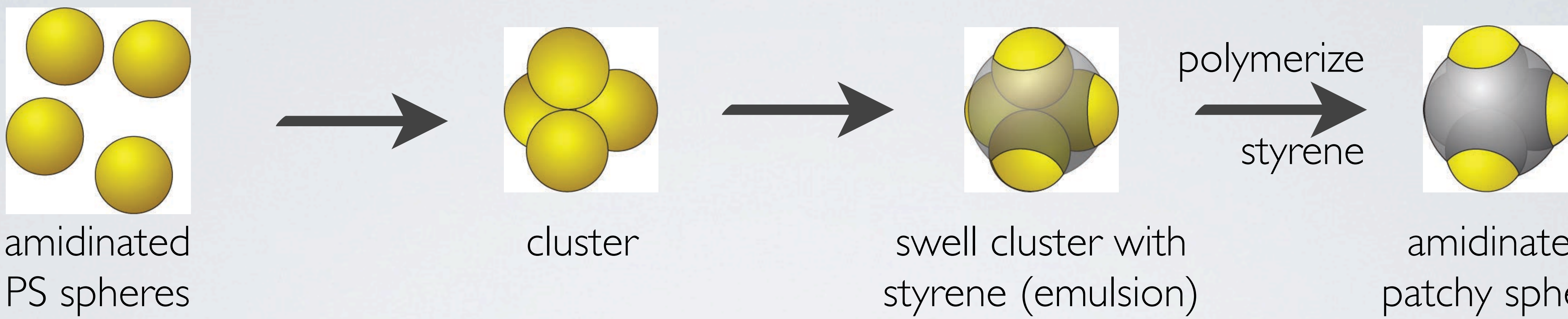
amidinated
patchy sphere

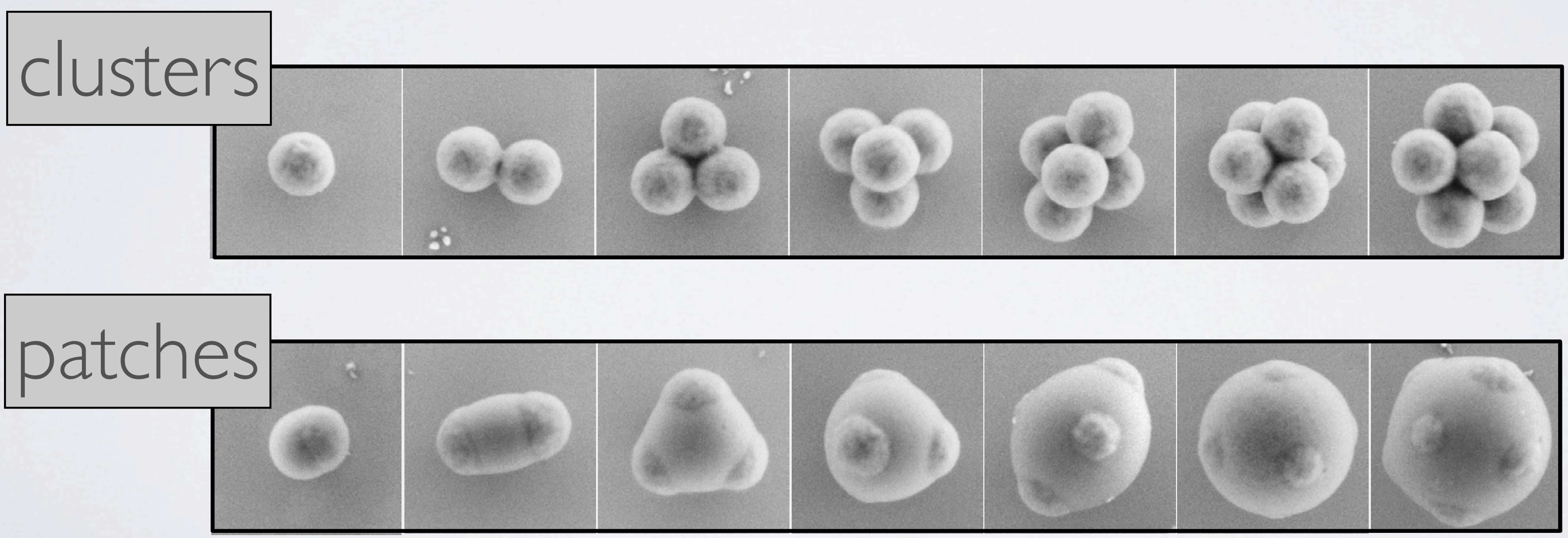


swell with
styrene

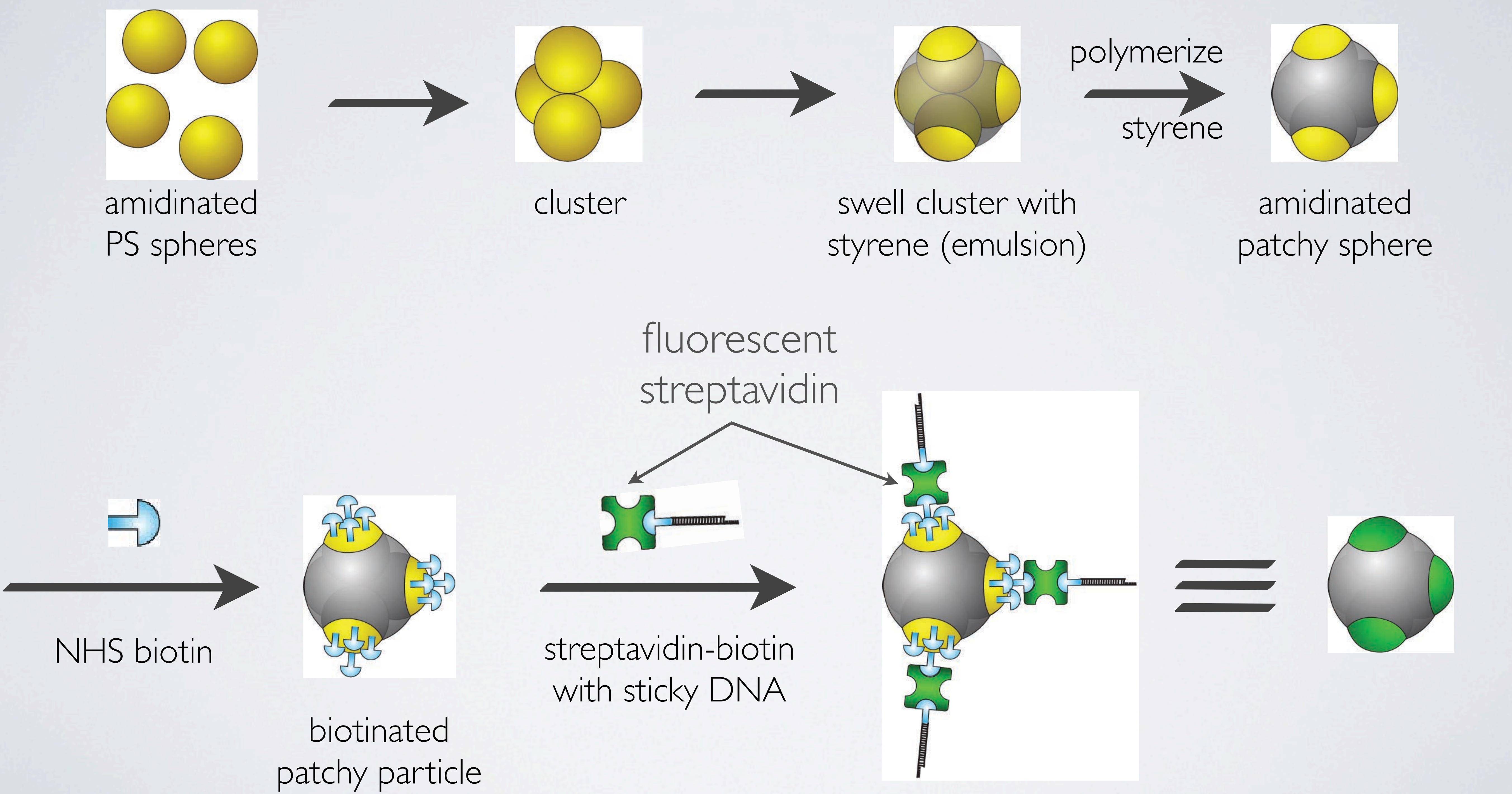


Patchy particles

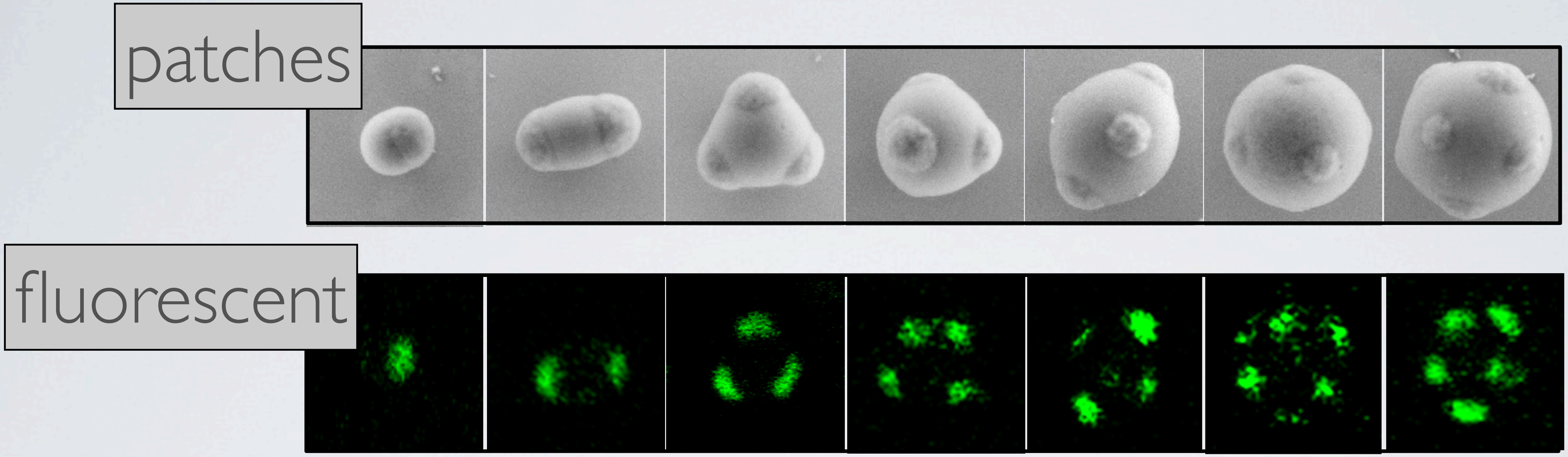


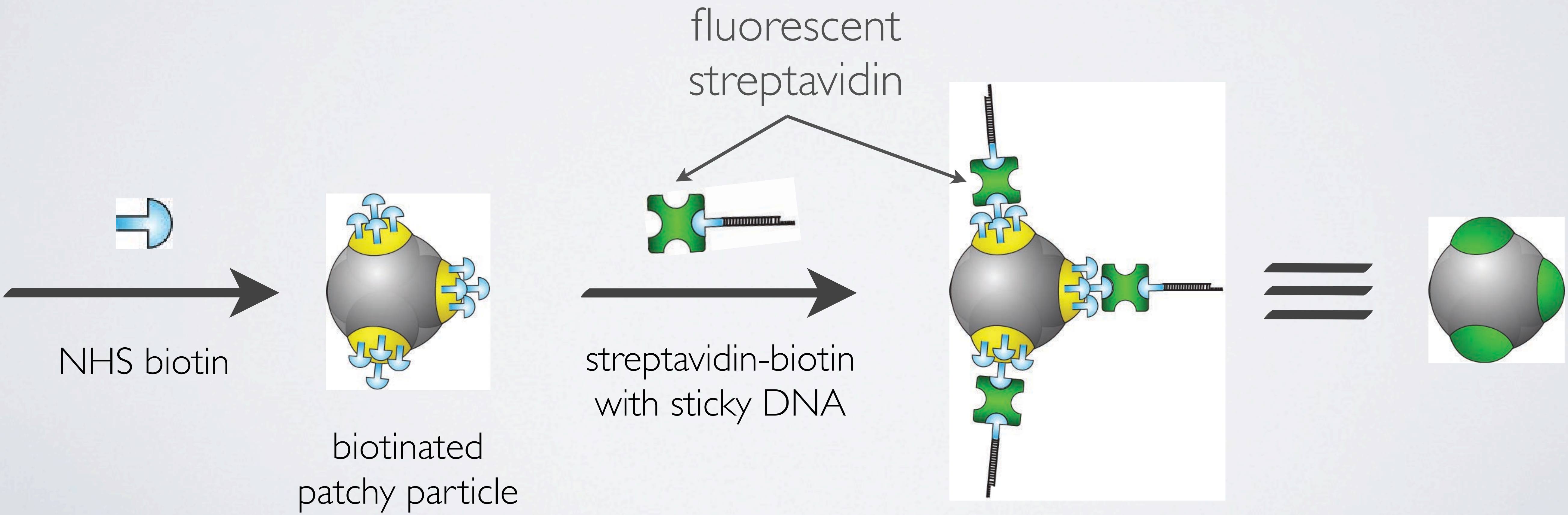


Functionalizing patchy particles



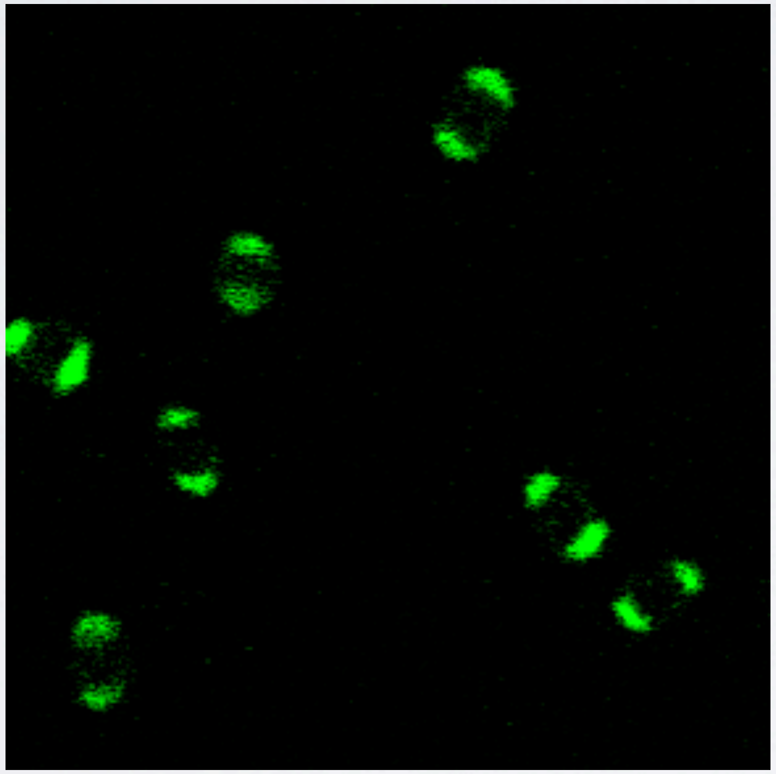
Functionalizing patchy particles



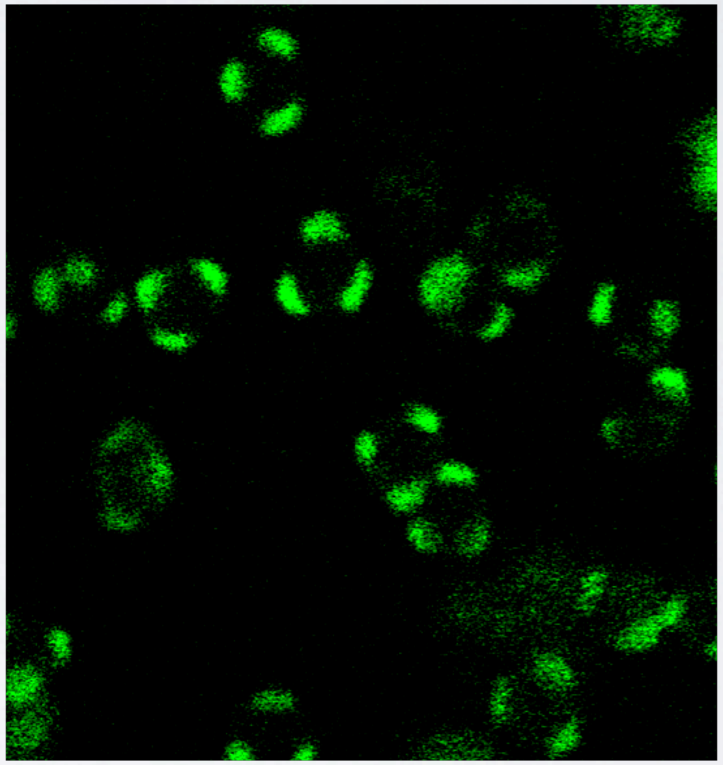


Purified patchy particles

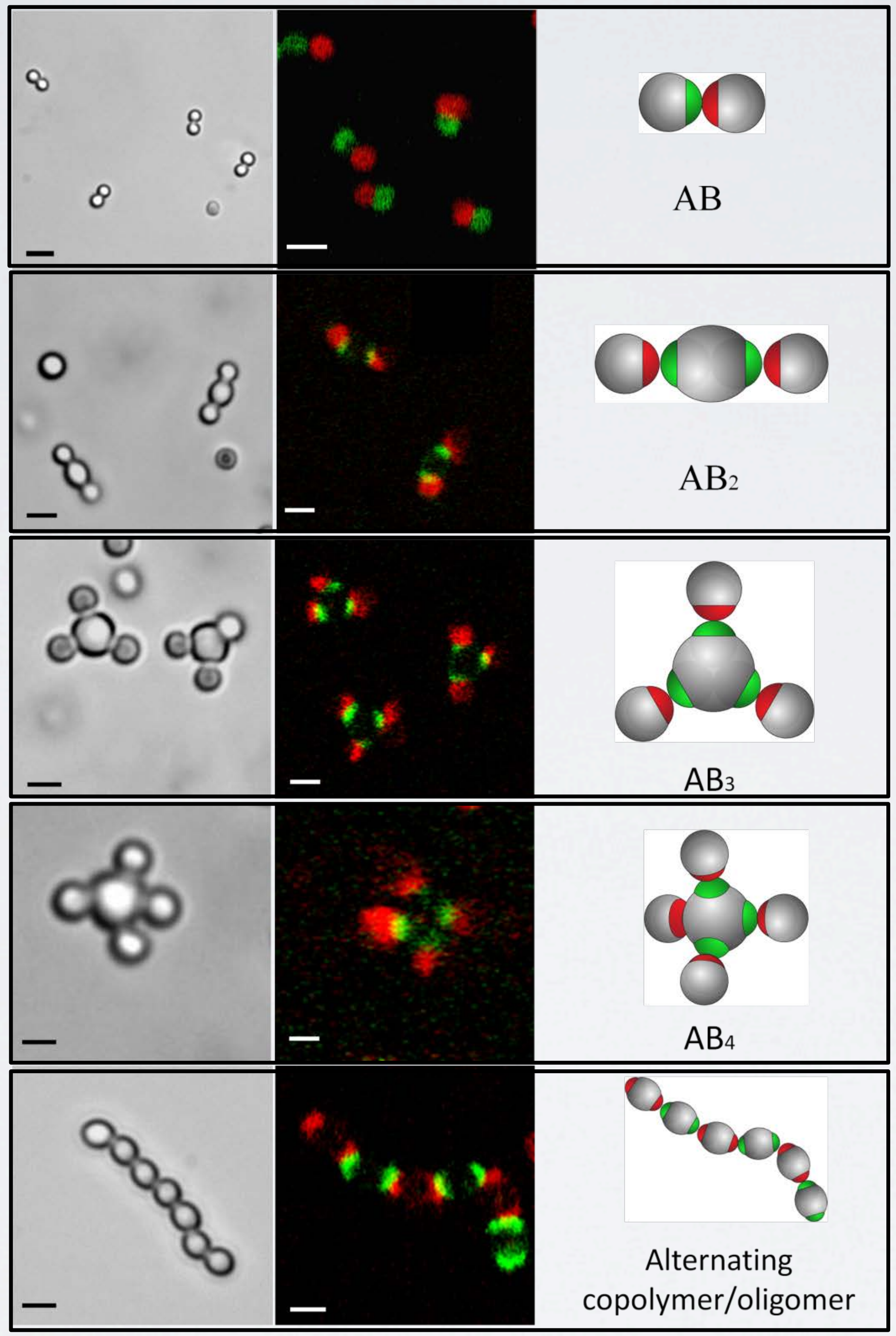
2 patches



3 patches



Linking up: it's specific!



AB

AB_2

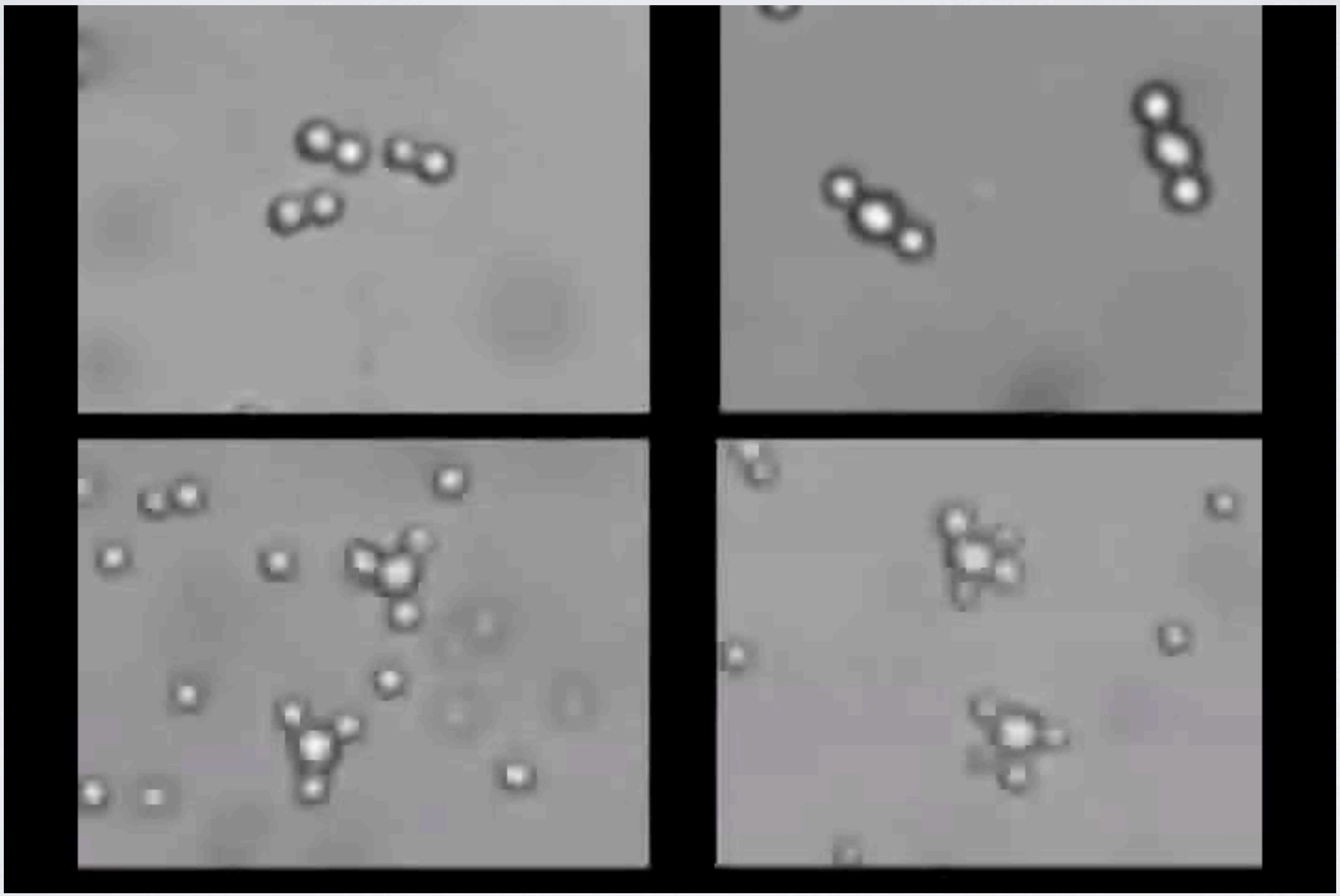
AB_3

AB_4

scale bar = 800 nm

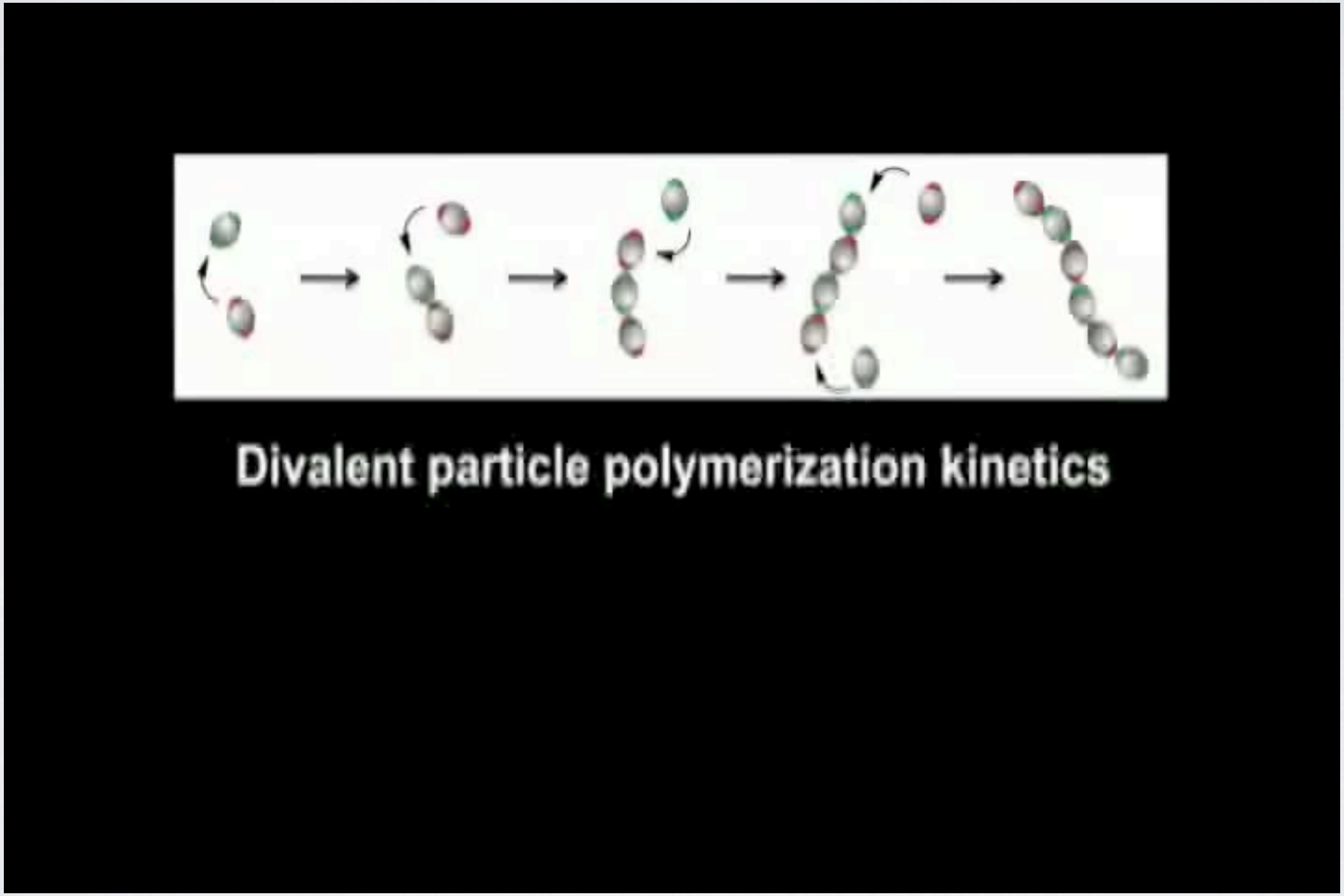
Colloidal molecules

small patches



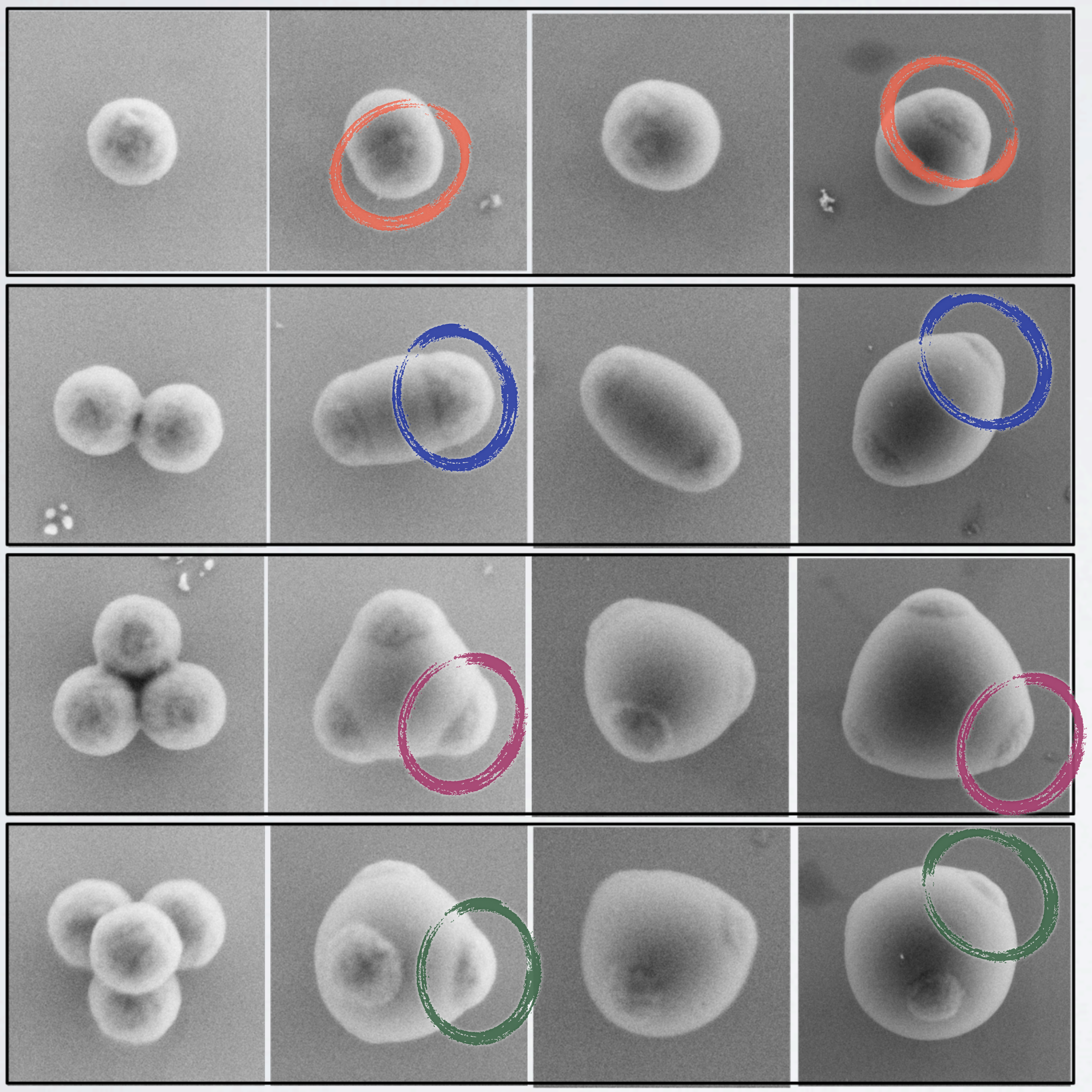
AB_4 formation kinetics

Colloidal polymerization kinetics



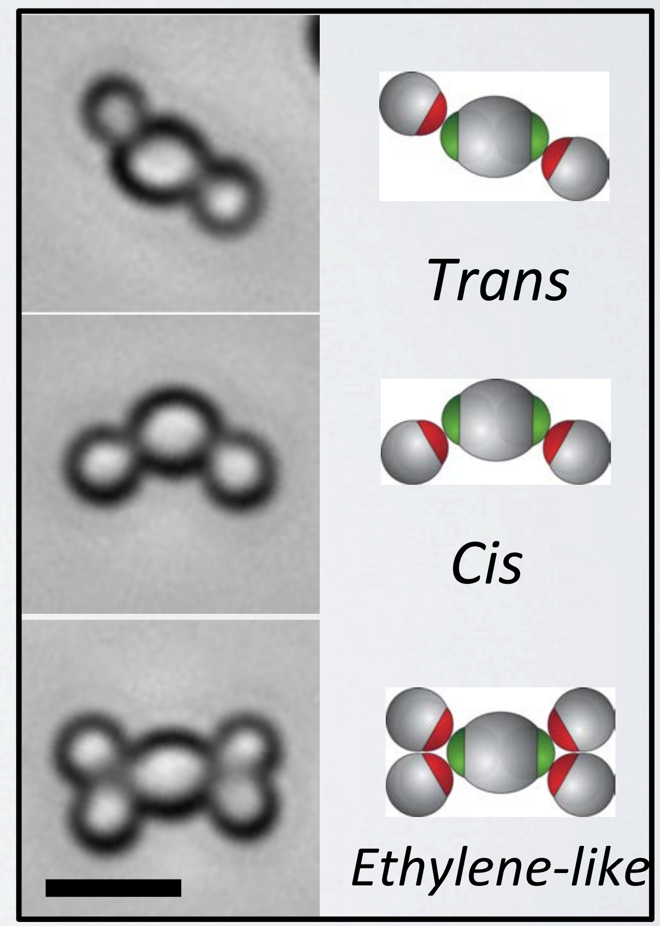
Controlling patch size

decreasing patch size



decreasing patch size

Linking with complementary particles



big patches

Collaborators

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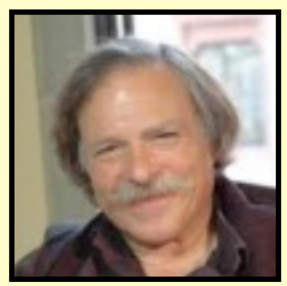

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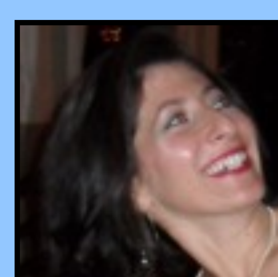

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Pacmen

Colloidal molecules

W. M. Keck Foundation