Summer School on Soft Matter Self-Assembly, 2015, June 28-July 7

Lecture 1: Colloids

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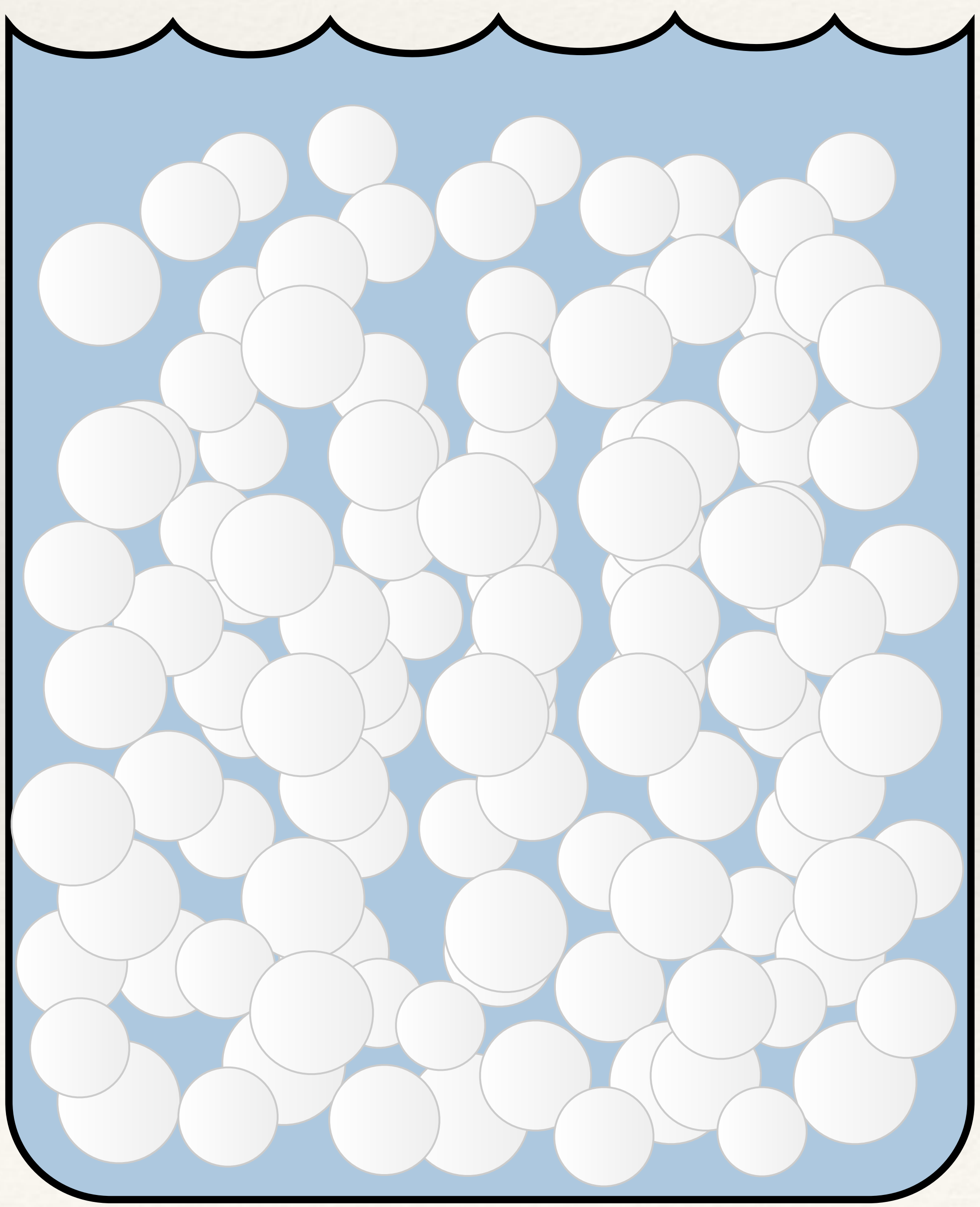
What are colloids?

Small particles suspended in a liquid



Particles:

★ Diameters: ~ 2 nm to ~ 2 μm

★ Concentration ~0.1% to ~70% by volume

★ Materials

- Plastic: polystyrene, PMMA, …
- Inorganic: silica (SiO_2), titania (TiO_2), …
- Semiconductor: CdSe, …
- Metal: Au, Ag, …
- Fat, protein: milk, …
- Emulsions: oil droplets in water or vice versa (will not discuss emulsions)

Liquid (continuous) part:

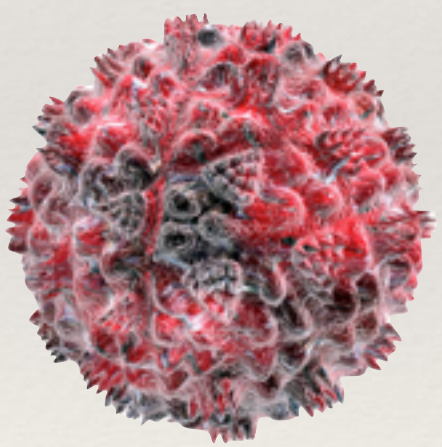
★ Water

★ Oil

Gels: when particles are linked (by direct contact or by polymers)

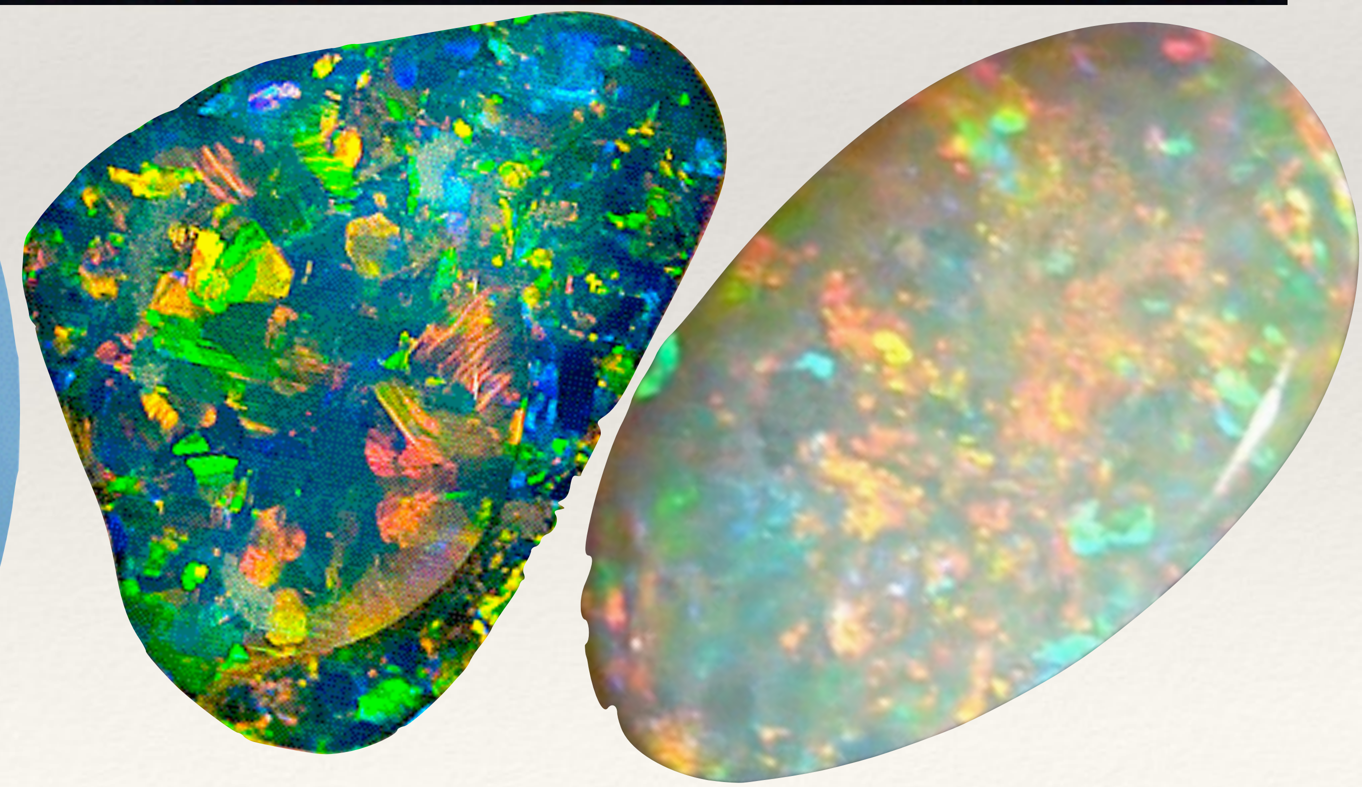
Some examples of colloids

virus



gold

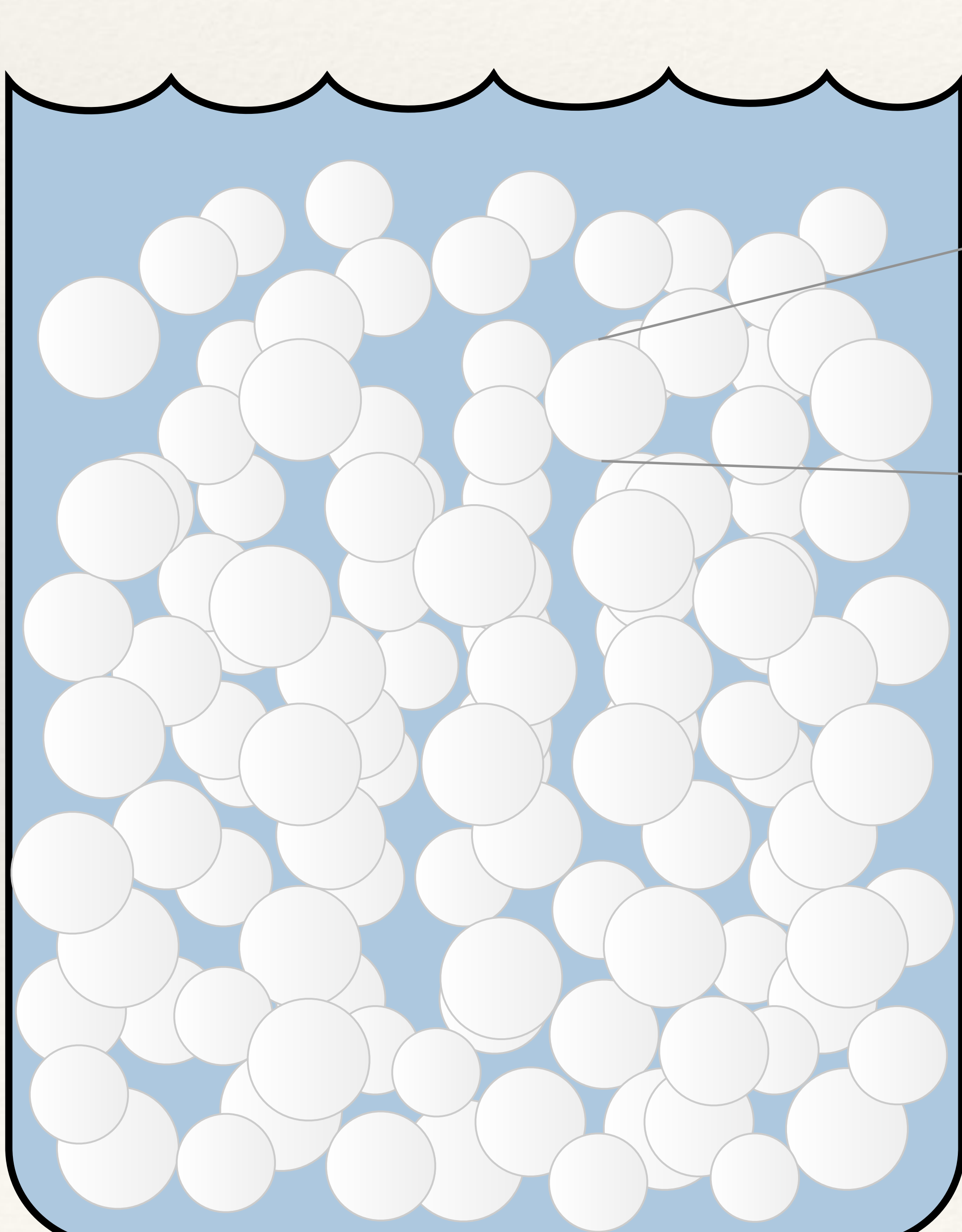
milk

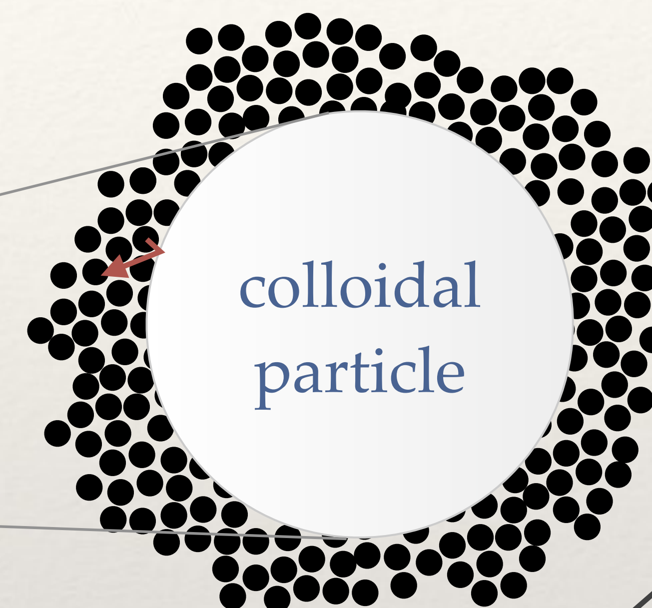


opals (petrified colloids)

Brownian motion

Particles are agitated by collisions with molecules





random fluctuating force from collisions with solvent (10^{-12} s)

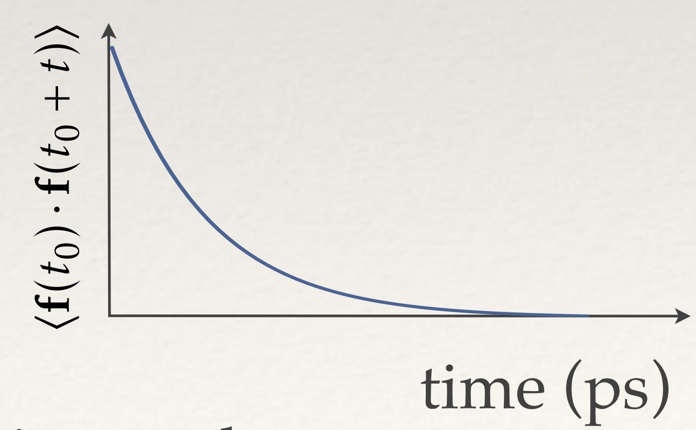
$$m\frac{d\mathbf{v}}{dt} = -\zeta\mathbf{v} + \mathbf{f}(t)$$

mass of particle

viscous friction

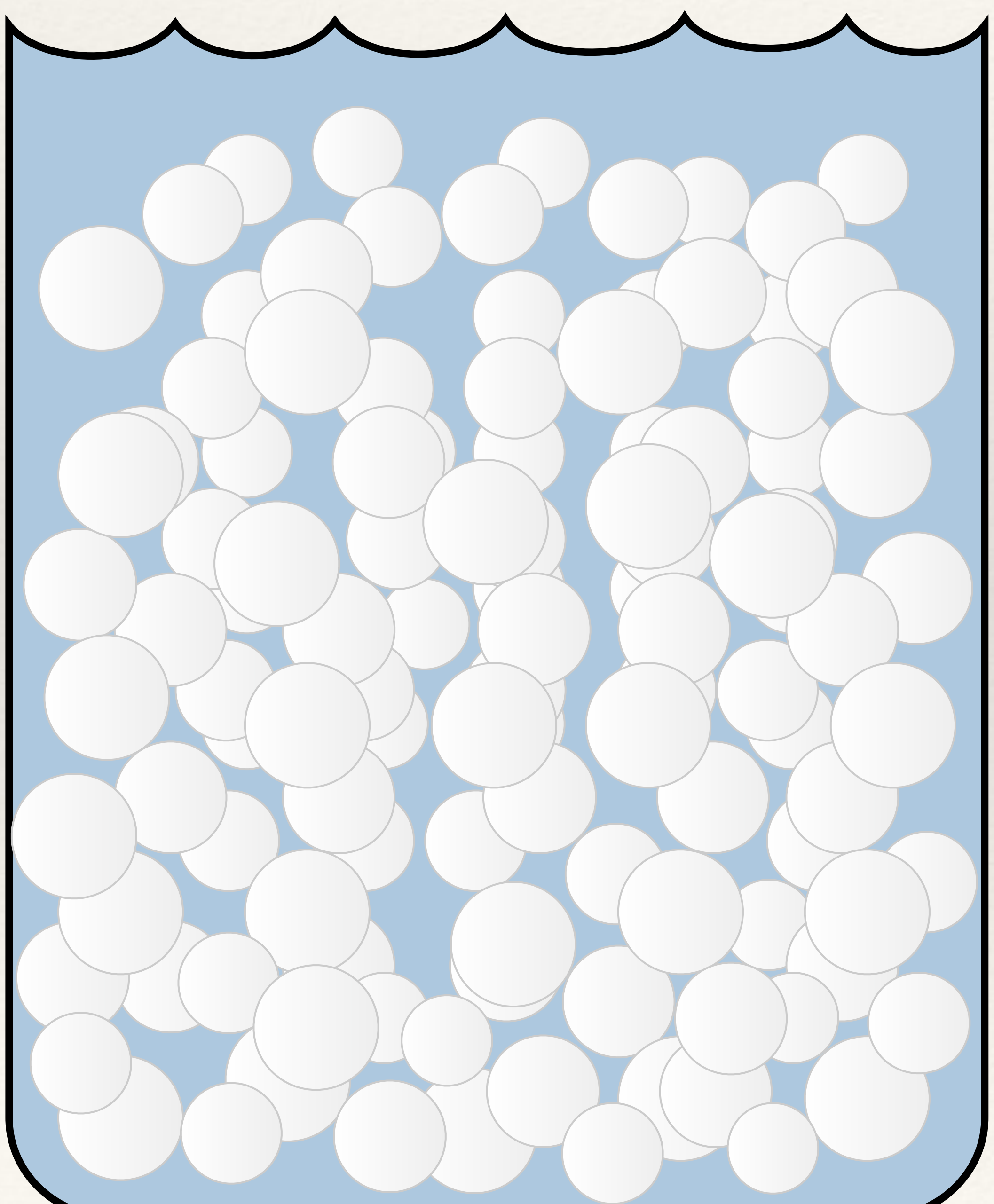
$\zeta = 6\pi\eta R$ for sphere

$$\tau = \frac{m}{\zeta} \sim 10^{-7}\ \text{s}$$ inertial time scale

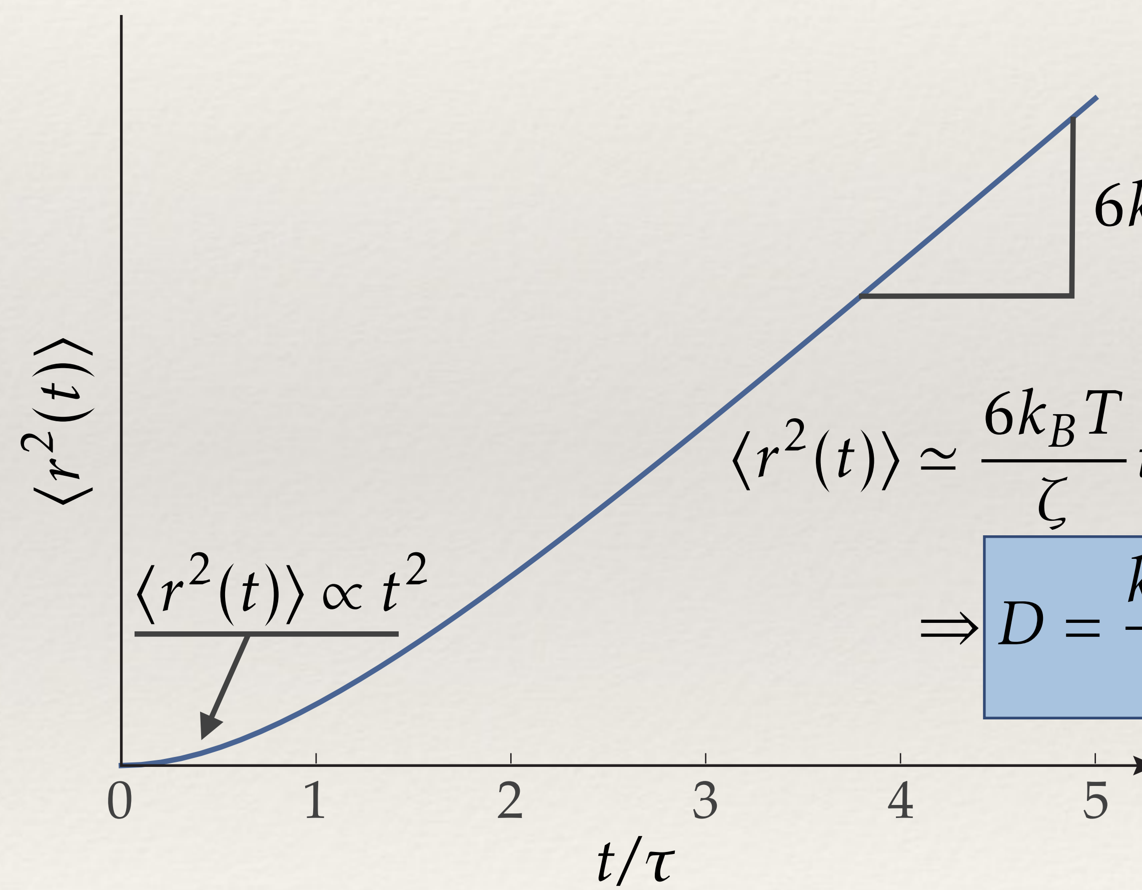


Brownian motion

Particles are agitated by collisions with molecules



$$\langle r^2(t)\rangle = \frac{6k_BT}{\zeta}\left[t - \tau\left(1 - e^{-t/\tau}\right)\right]$$



$$\langle r^2(t)\rangle \simeq \frac{6k_BT}{\zeta}t = 6Dt$$

$$\Rightarrow D = \frac{k_BT}{\zeta} = \frac{k_BT}{6\pi\eta R}$$

Stokes-Einstein relation

$D \sim 1\ \mu\text{m}^2/\text{s}$

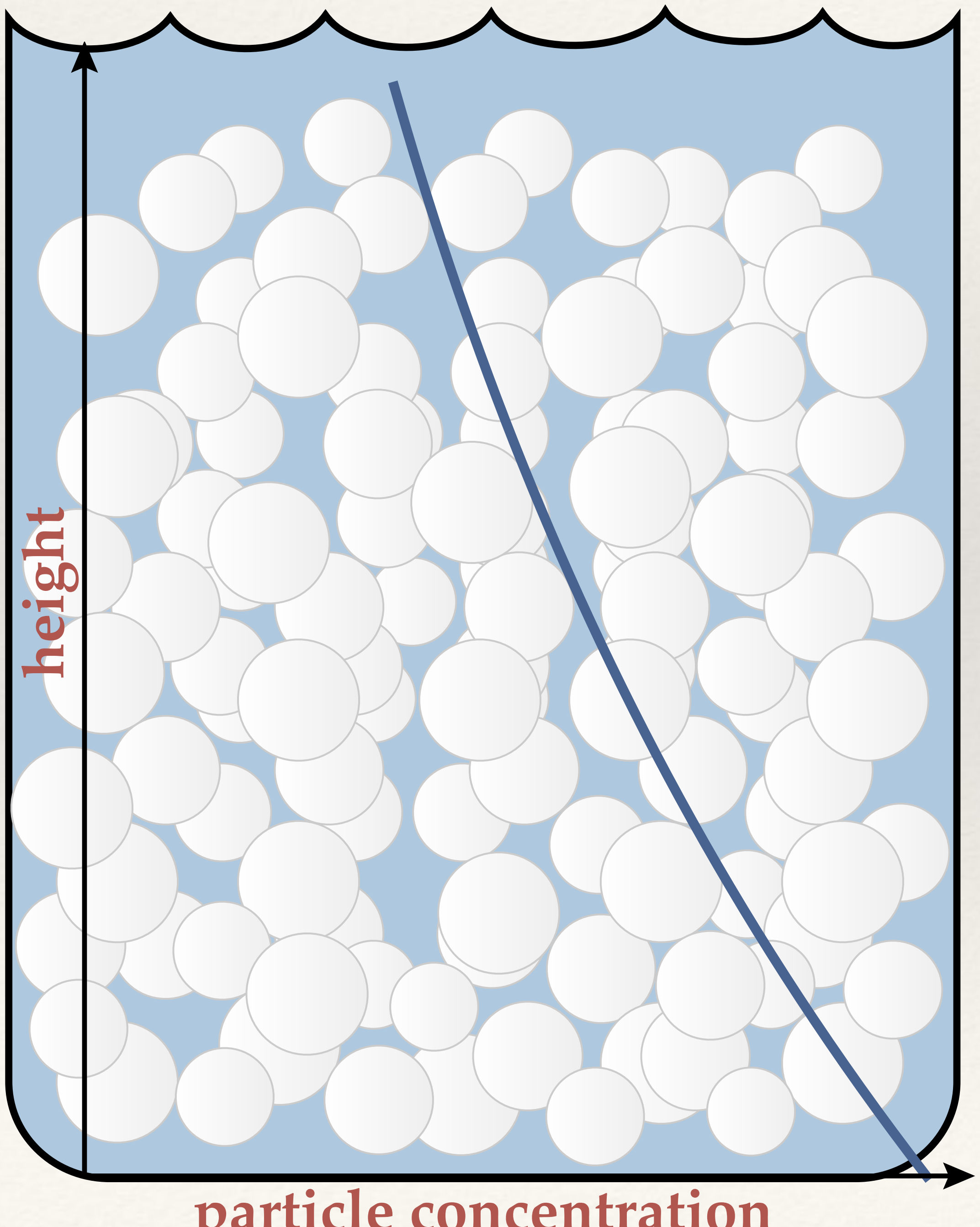
for 1 µm particle

$$\tau = \frac{m}{\zeta} \sim 10^{-7}\ \text{s}$$

inertial time scale

Gravity ⇒ Sedimentation

Probability of finding a particle at height z is given by Boltzmann factor



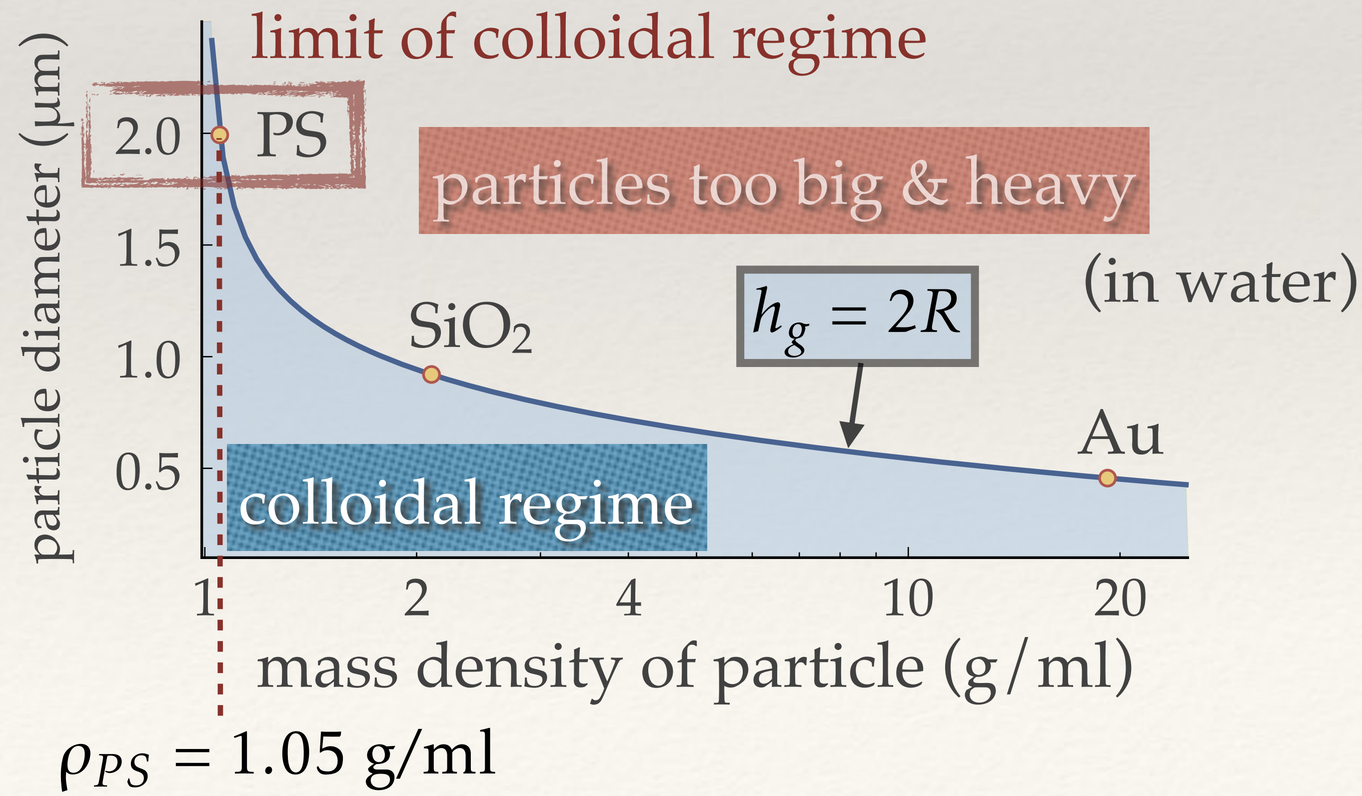
$$P(z) = P_0 e^{-U(z)/k_B T} = P_0 e^{-\Delta m g z/k_B T} = P_0 e^{-z/h_g}$$

Archimedes

$$U(z) = \Delta m g z$$

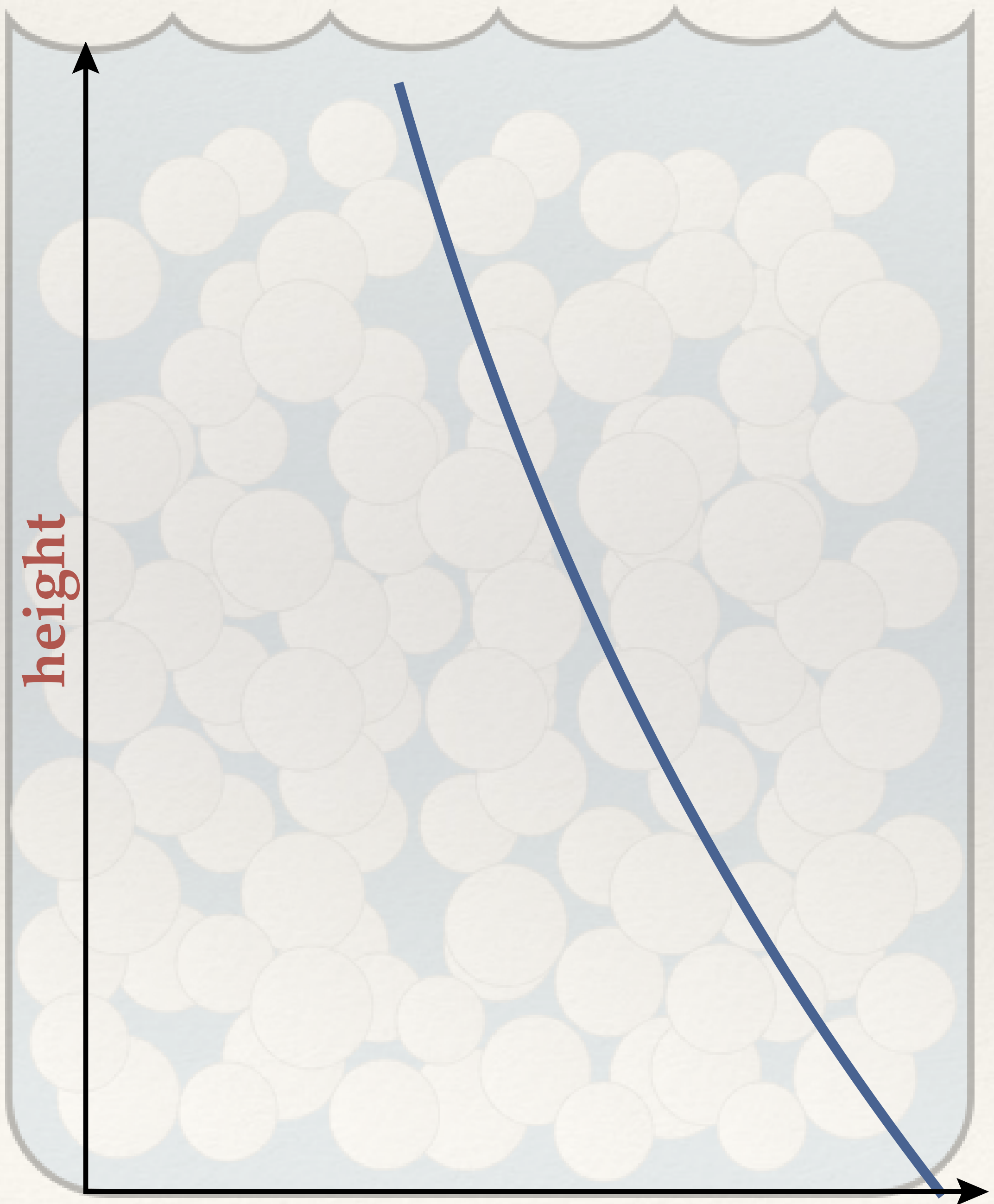
gravitational height

$$h_g = \frac{k_B T}{\Delta m g} = \frac{3 k_B T}{4\pi R^3 \Delta\rho g}$$



Diffusion

Einstein's argument



At equilibrium, the sedimentation of particles downward is balanced by the diffusive flux of particles upward.

Sedimentation

$$F = -\Delta mg - \zeta v_s = 0 \quad \Rightarrow \quad v_s = -\frac{\Delta mg}{\zeta}$$

Diffusion + sedimentation

$$\text{Flux} = J = -D\frac{dc}{dz} + cv_s = 0\,, \qquad c(z) = c_0 e^{-z/h_g}$$

$$-D\left(\frac{-1}{h_g}\right)c(z) + c(z)v_s = 0\,, \qquad \Rightarrow D = -v_s h_g$$

$$D = -v_s h_g = \left(\frac{\Delta mg}{\zeta}\right)\left(\frac{k_B T}{\Delta mg}\right) = \frac{k_B T}{\zeta}$$

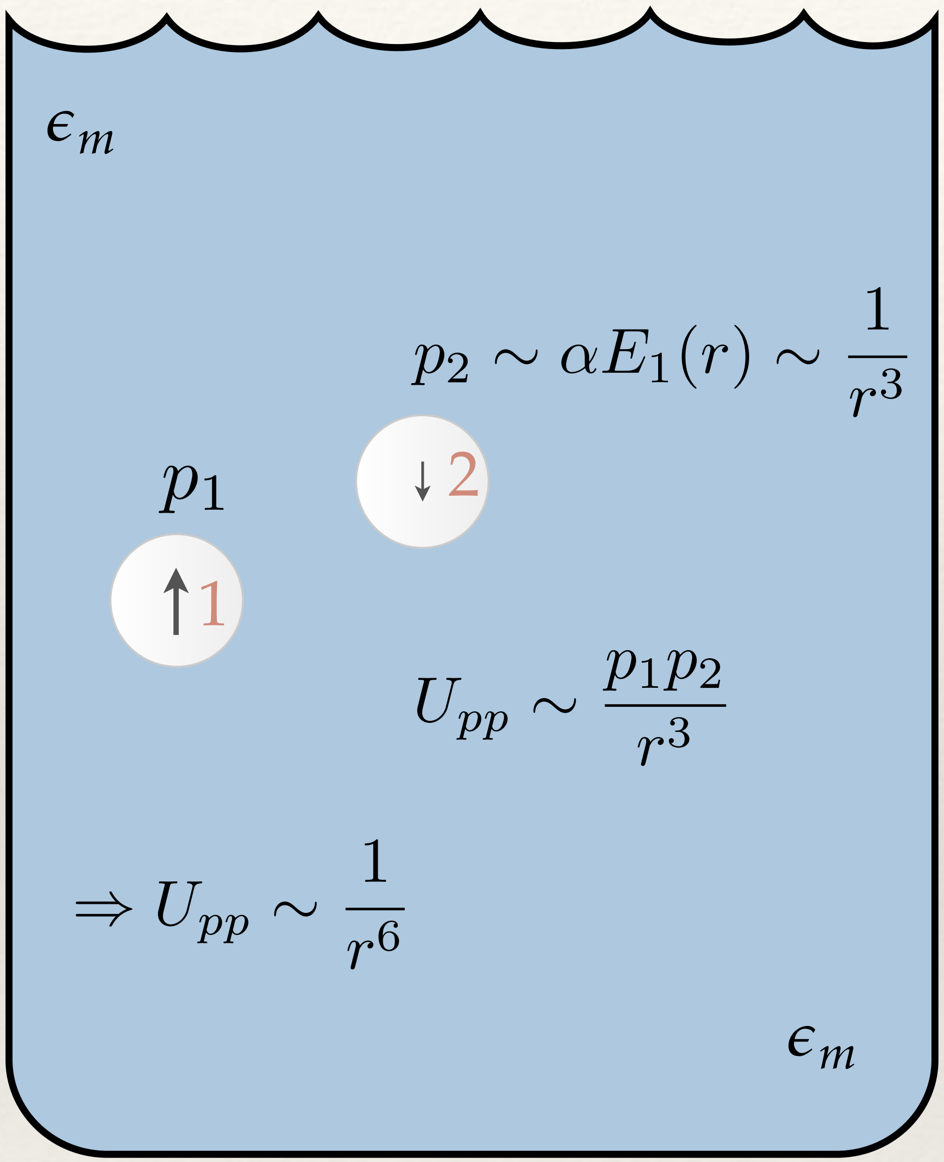
$$D = \frac{k_B T}{6\pi\eta R}$$

Stokes-Einstein relation

Colloidal forces

- van der Waals (usually attractive, range ~ few nm)
- screened Coulomb (range ~ from nm to μm)
- polymer brush (range ~ length of polymer ~ 5-20 nm)
- depletion (range ~ size of "depletant particle" ~ 5-100 nm)
- ssDNA hybridization (range ~ length of polymer ~ 5-20 nm)
    - Friday

van der Waals



(fluctuating induced dipole)

$$U(r) \simeq -\frac{A_{\text{Ham}}}{\pi^2} \int_{V_1} \int_{V_2} \frac{1}{r^6} dV_1 dV_2$$

proportional to volumes

$\Rightarrow$ much bigger for micron than for nanometer particles

$$A_{\text{Ham}} \sim \frac{3k_B T}{2} \sum_{\omega} \left(\frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + \epsilon_m} \right) \left(\frac{\epsilon_2 - \epsilon_m}{\epsilon_2 + \epsilon_m} \right)$$

depends on dielectric contrast (polarizability)

fluctuations at optical frequencies most important

$\Rightarrow$ index matching greatly reduces vdW interactions

$$U(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\mathbf{p}_2 \cdot \hat{\mathbf{r}})}{r^3}$$

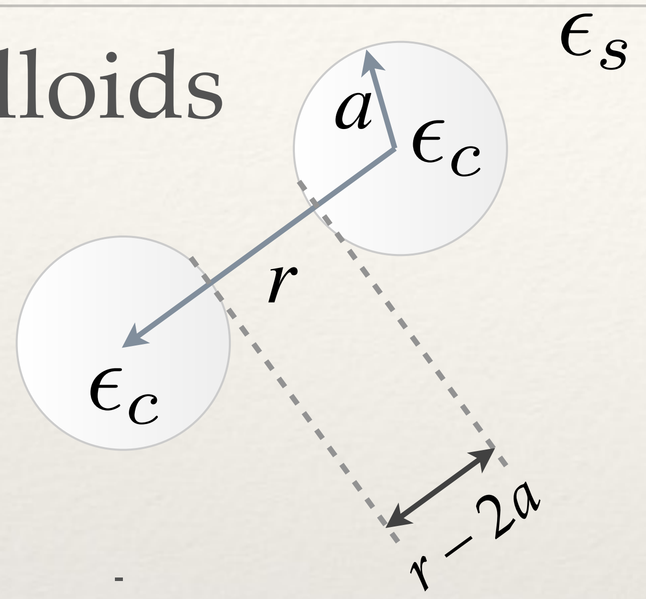
$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{3(\mathbf{p} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}}{r^3}$$

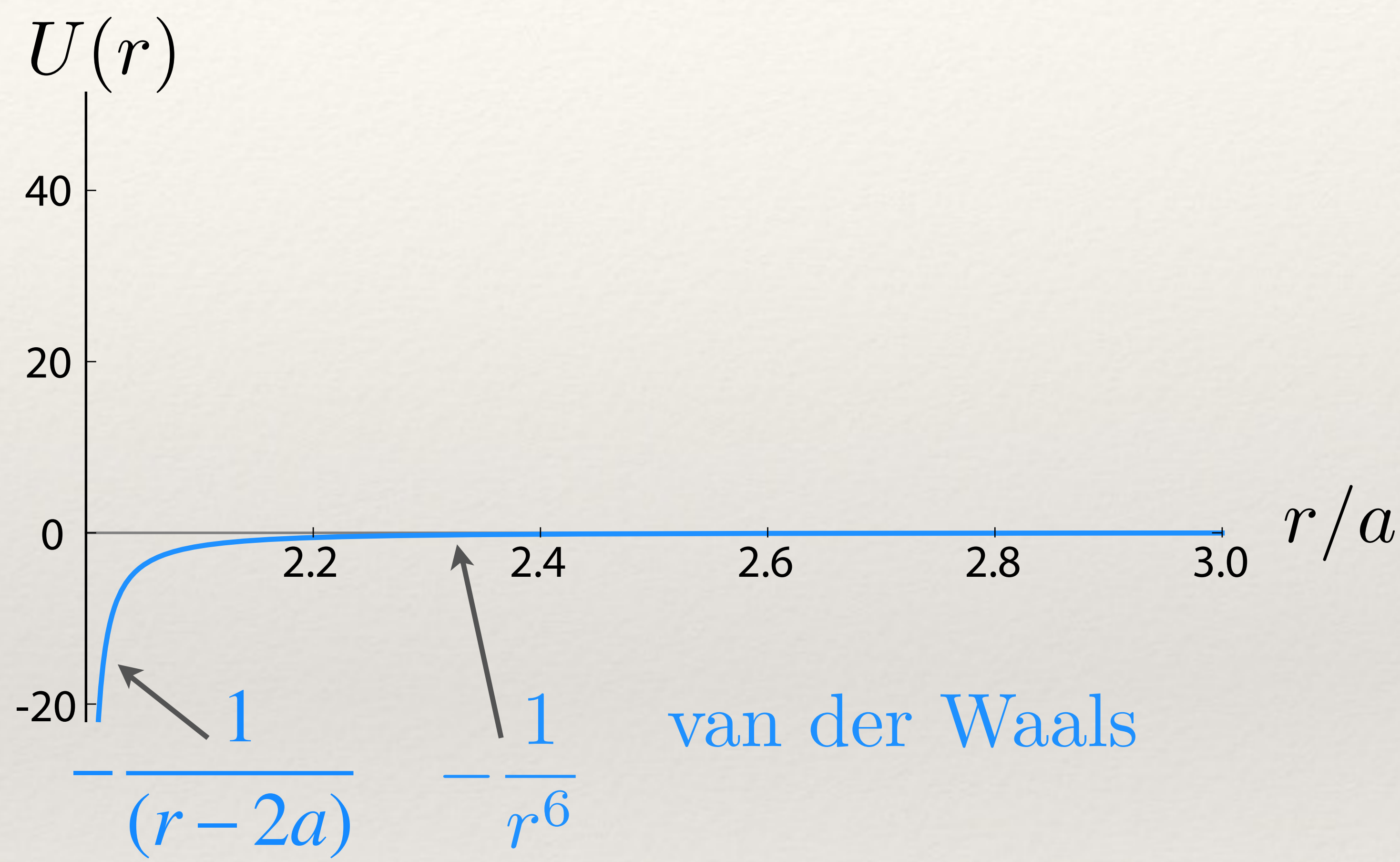
$$\mathbf{p}_2 = \alpha_2 \mathbf{E}_1(\mathbf{r})$$

$$U(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left\langle \frac{\mathbf{p}_1 \cdot \alpha_2 \mathbf{E}_1(\mathbf{r}) - 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\alpha_2 \mathbf{E}_1(\mathbf{r}) \cdot \hat{\mathbf{r}})}{r^3} \right\rangle \sim -\frac{\alpha_1 \alpha_2}{r^6}$$

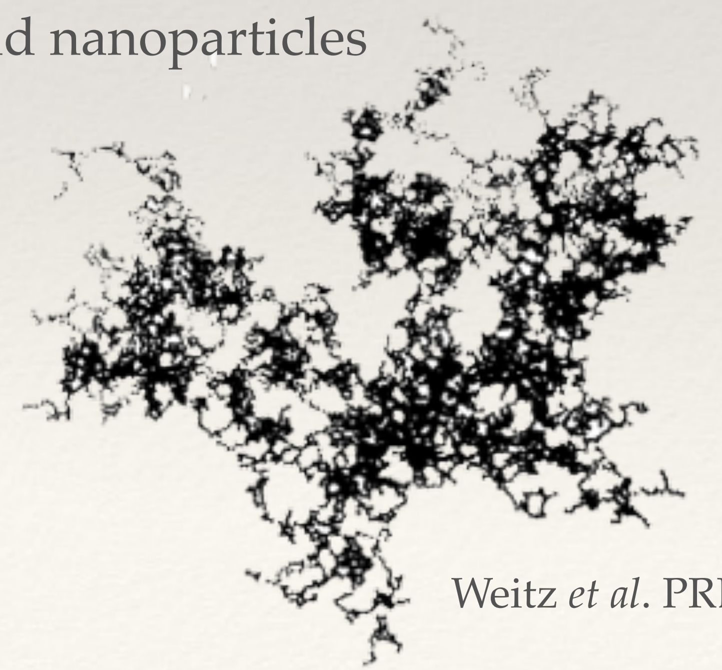
van der Waals

colloids





gold nanoparticles

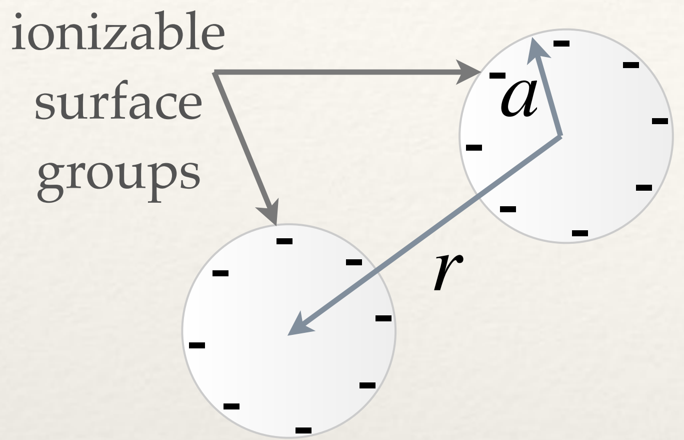


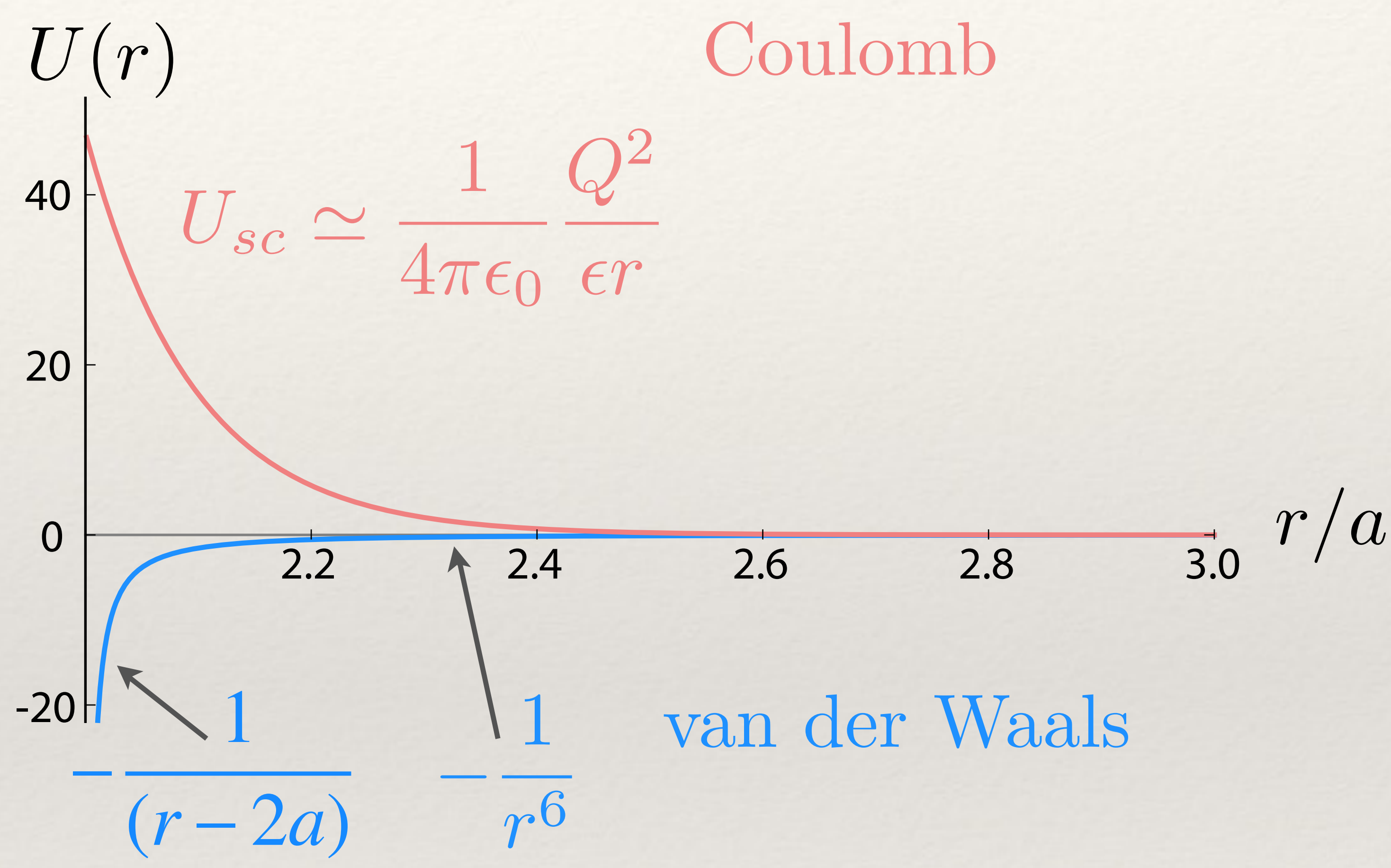
Weitz *et al*. PRL **54**, 1416 (1985)

van der Waals attraction makes colloids aggregate

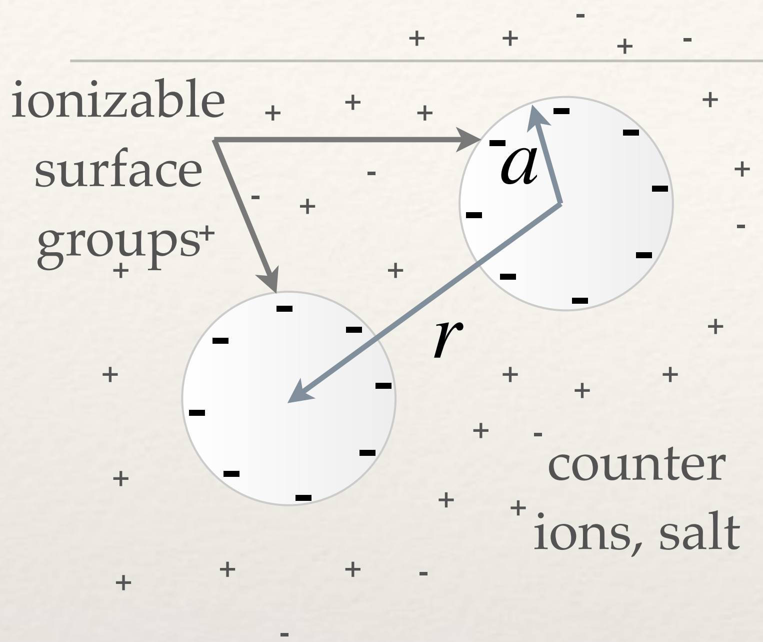
$\Rightarrow$ colloids unstable

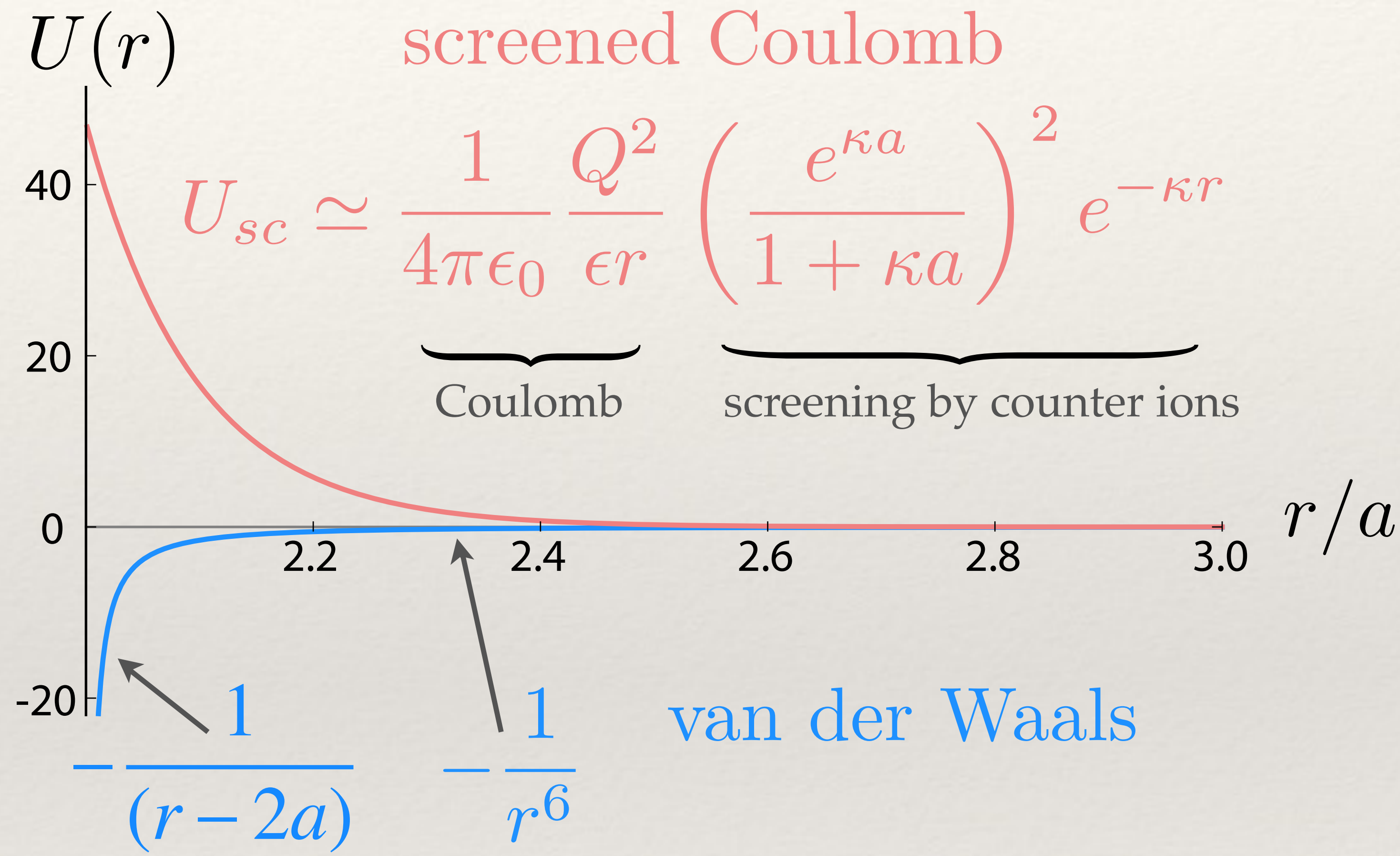
Screened-Coulomb (repulsion)





Screened-Coulomb (repulsion)





$$U_{sc} \simeq \underbrace{\frac{1}{4\pi\epsilon_0}\frac{Q^2}{\epsilon r}}_{\text{Coulomb}} \underbrace{\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^2 e^{-\kappa r}}_{\text{screening by counter ions}}$$

$$-\frac{1}{(r-2a)} \qquad -\frac{1}{r^6}$$

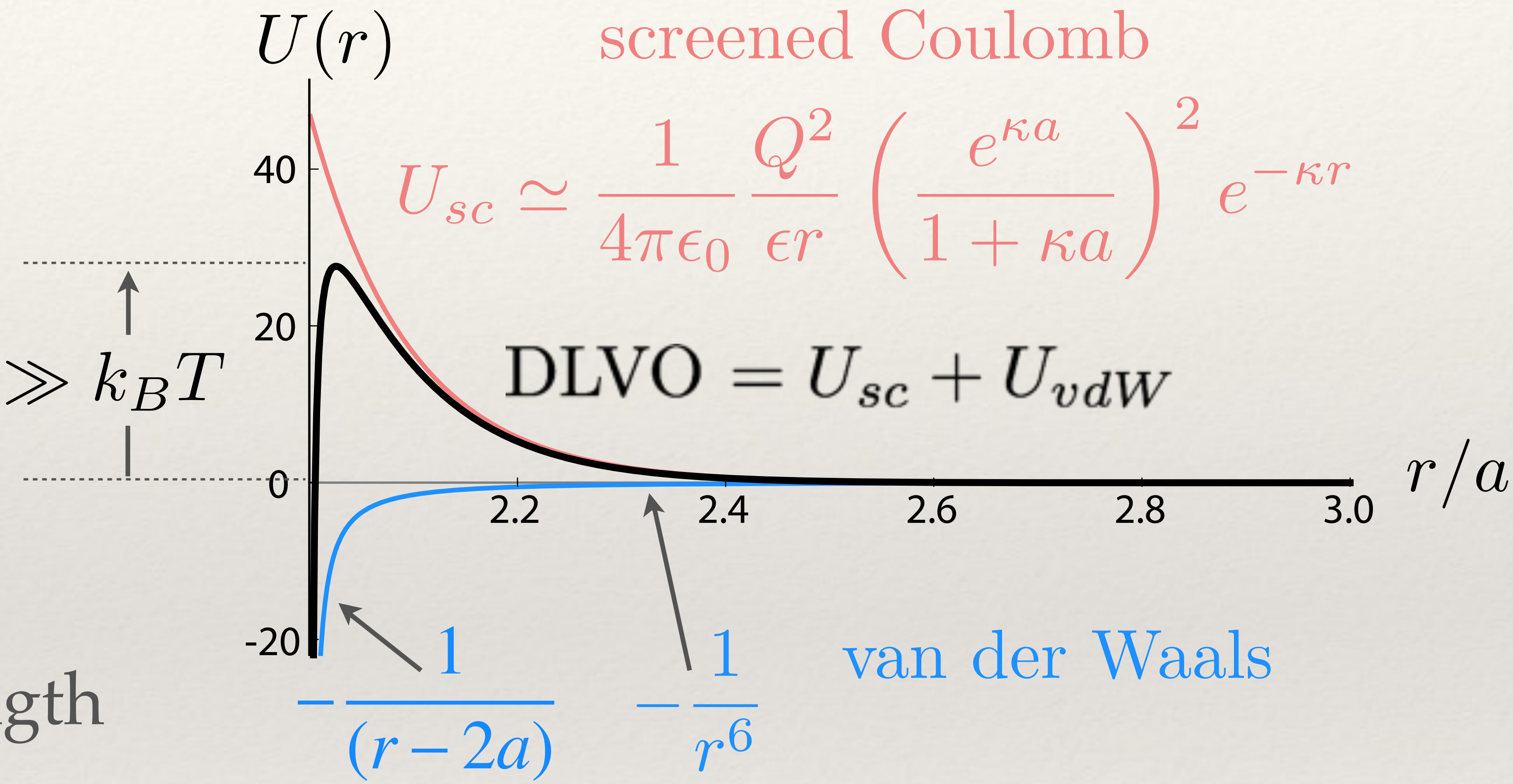
Debye screening length

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i z_i^2 e^2 c_i^0}}$$

~ 4 nm - 400 nm

DLVO*

(vdW +screened Coulomb)



Debye screening length

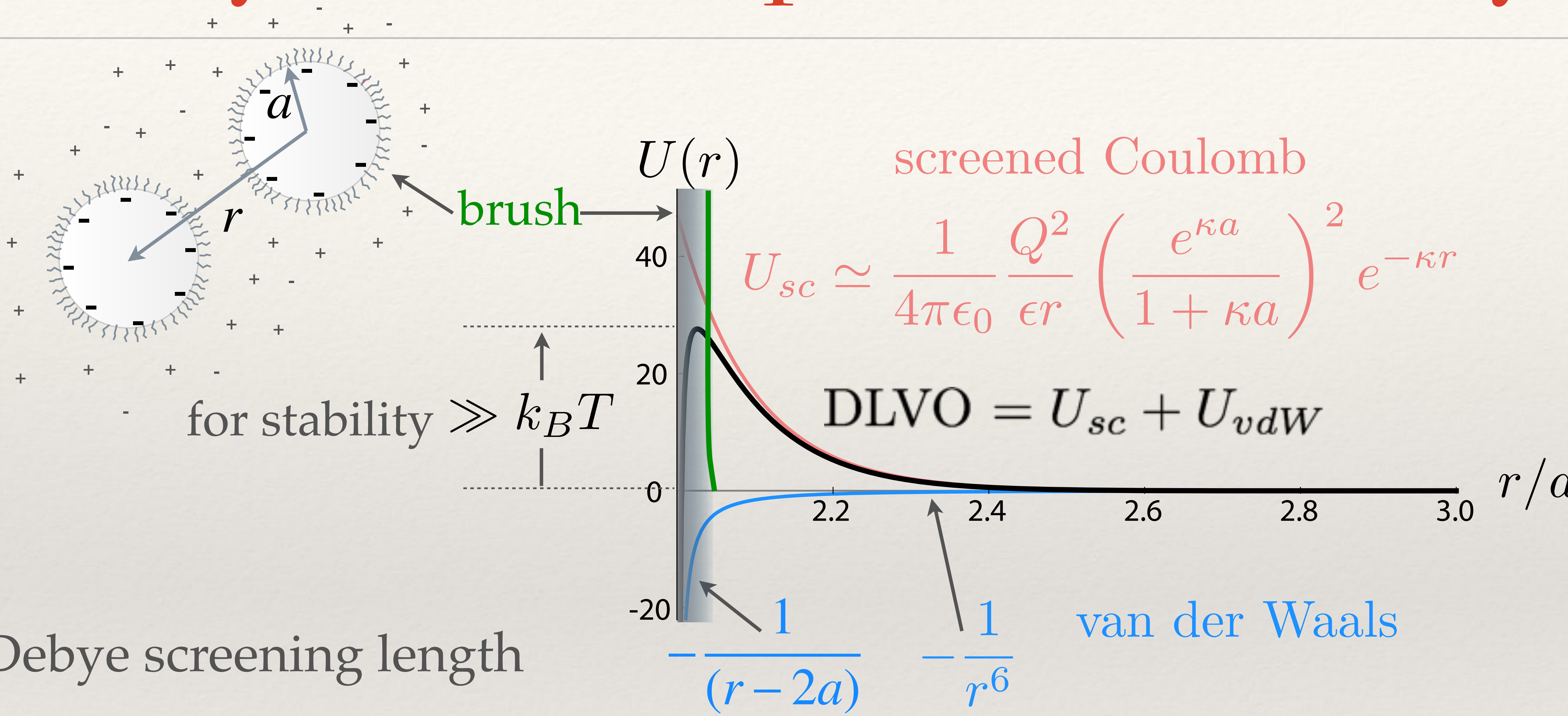
$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i z_i^2 e^2 c_i^0}}$$

salt reduces screening length and barrier height

$\Rightarrow$ salt can destabilize colloids

*Derjaguin, Landau, Verwey, Overbeek

Polymer brush provides stability



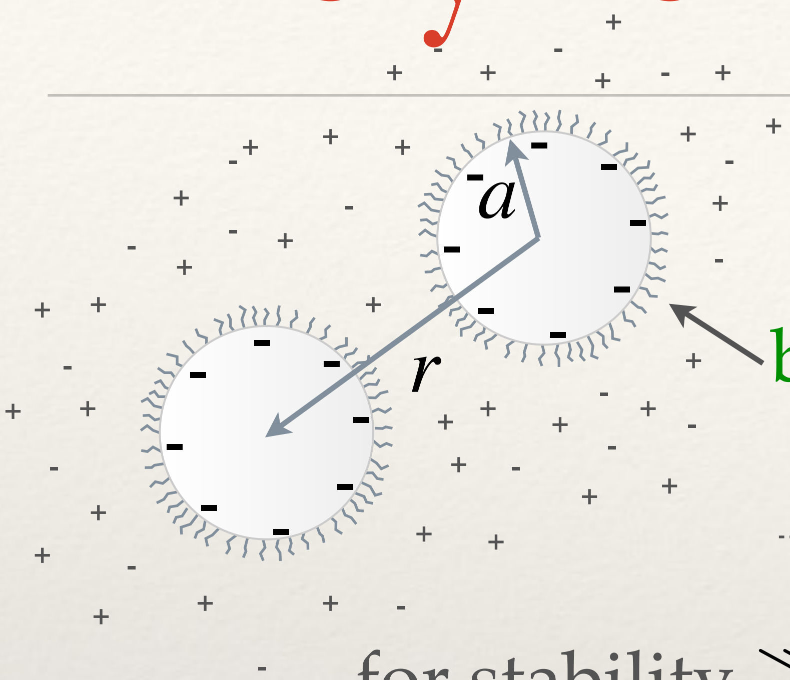
Debye screening length

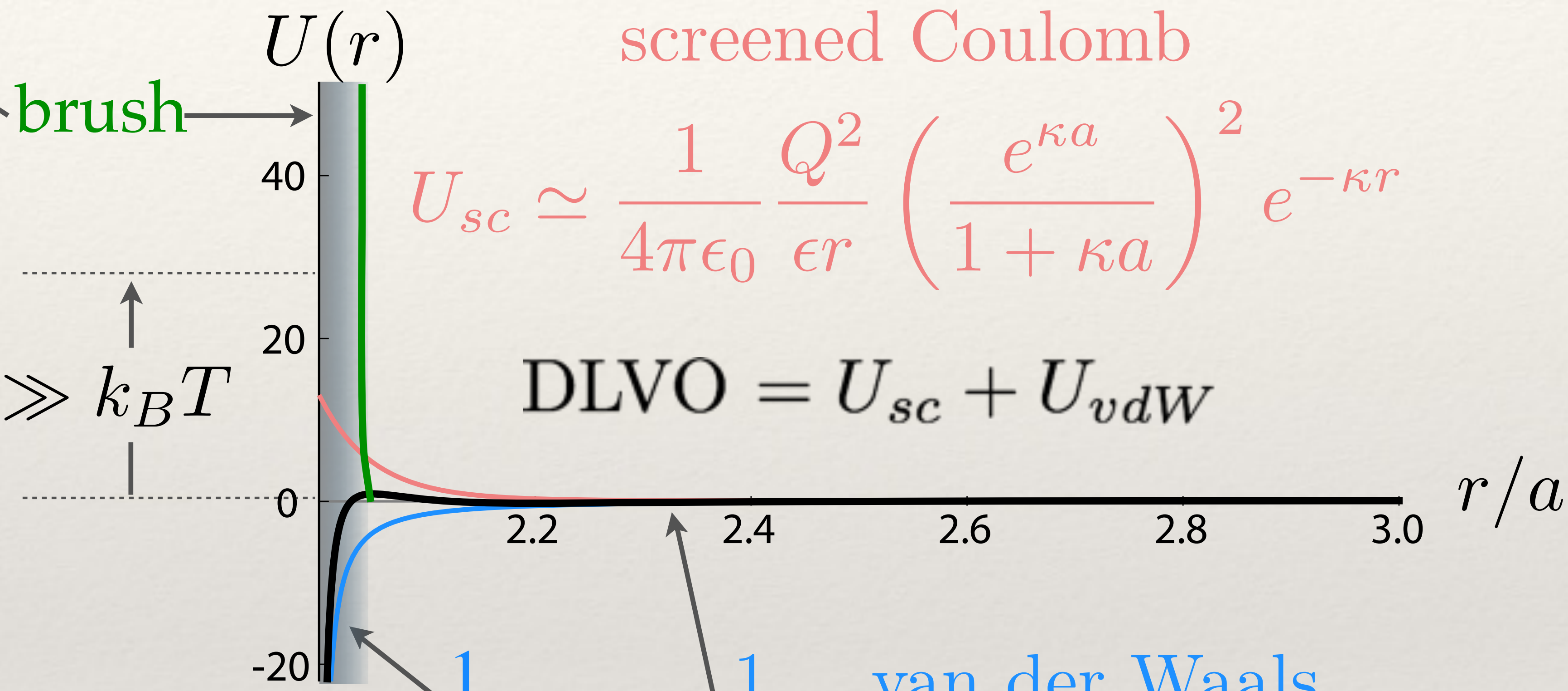
$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i z_i^2 e^2 c_i^0}}$$

Polymers in brushes are compressed, reducing their entropy, when particle surfaces are less than polymer radius of gyration apart.

Polymer brush provides stability

when salt screens Coulomb repulsion





for stability $\gg k_B T$

screened Coulomb

$$U_{sc} \simeq \frac{1}{4\pi\epsilon_0}\frac{Q^2}{\epsilon r}\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^2 e^{-\kappa r}$$

$$\mathrm{DLVO} = U_{sc} + U_{vdW}$$

$$-\frac{1}{(r-2a)} \qquad -\frac{1}{r^6}$$

van der Waals

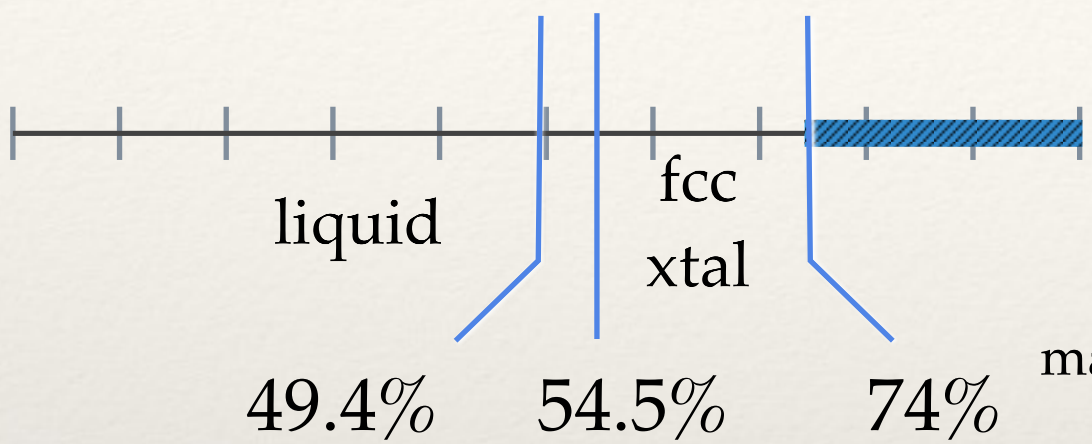
Debye screening length

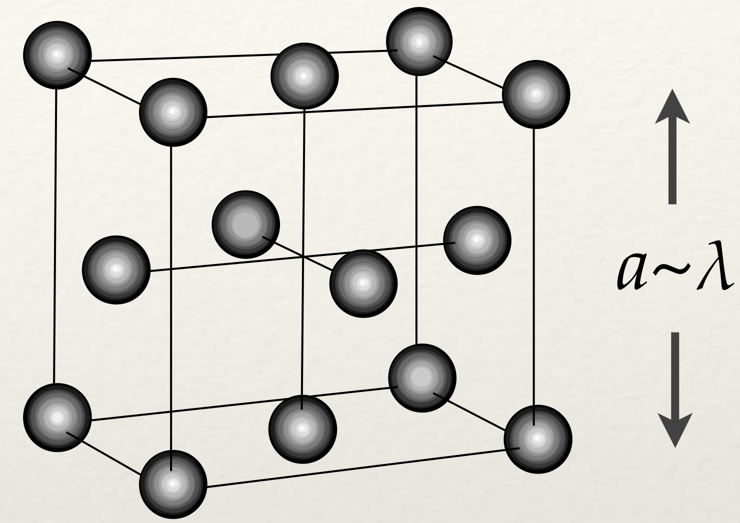
$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i z_i^2 e^2 c_i^0}}$$

nearly hard-sphere potential

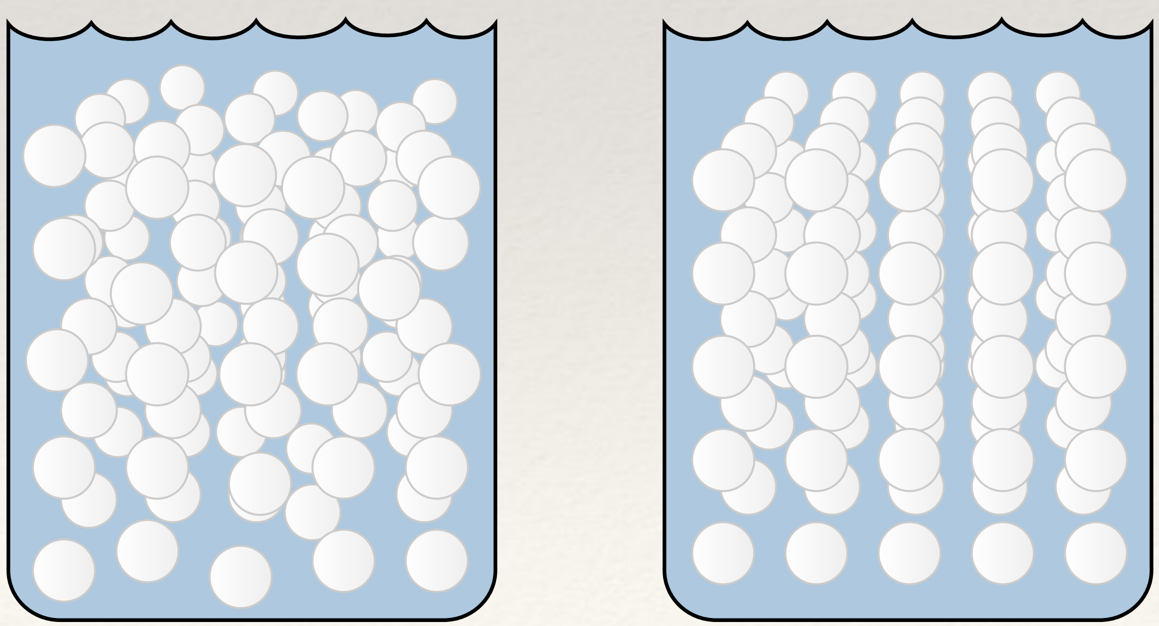
Phase diagram of hard-sphere colloids

Hard-sphere phase diagram (athermal)

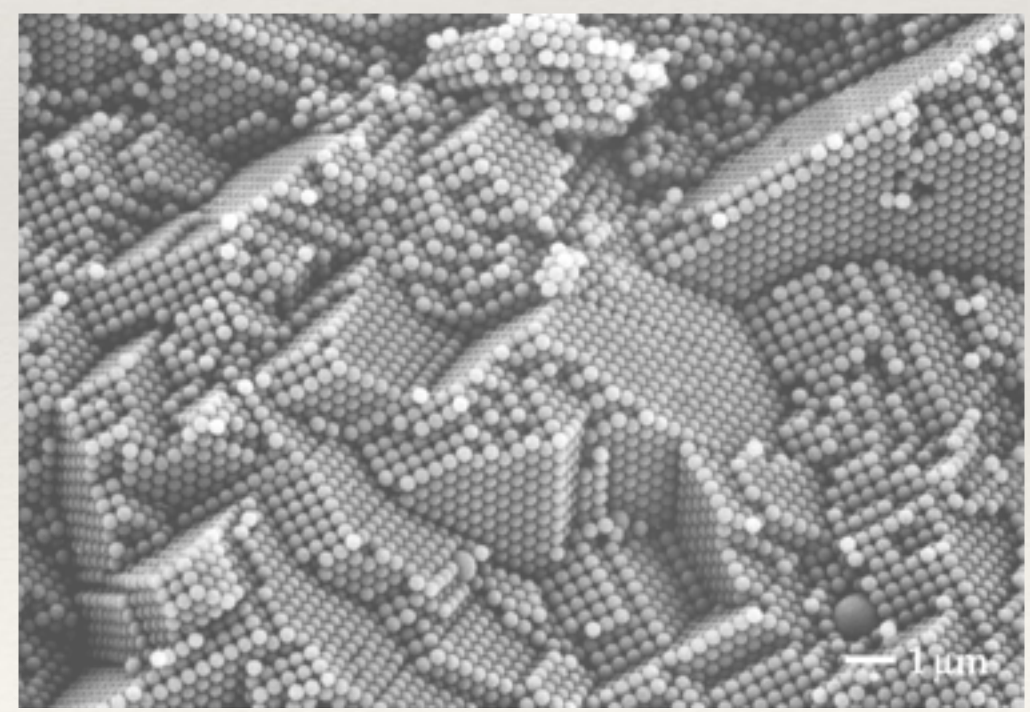




Crystallization driven by entropy



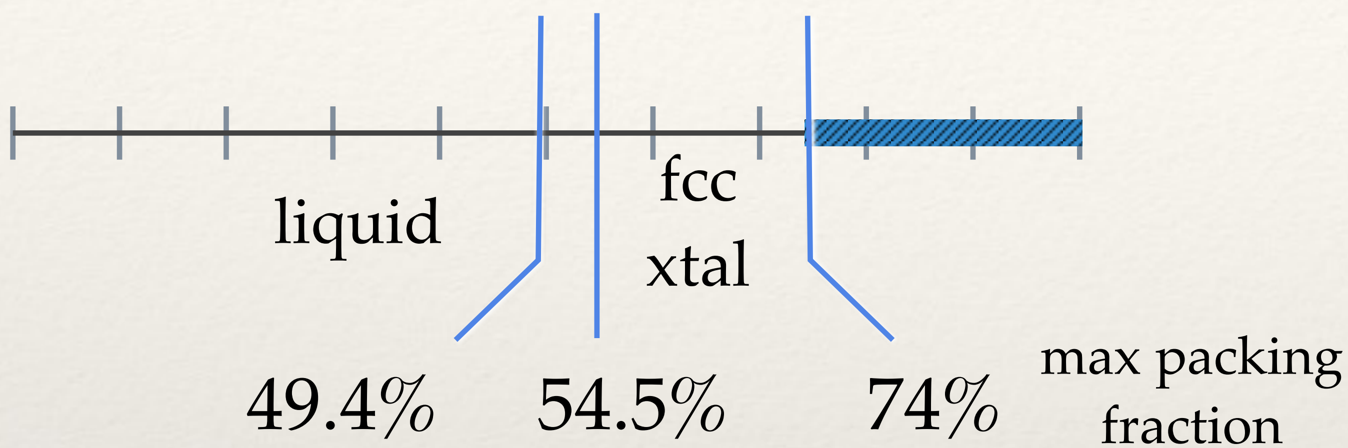
Hard spheres: Colloids used as model systems

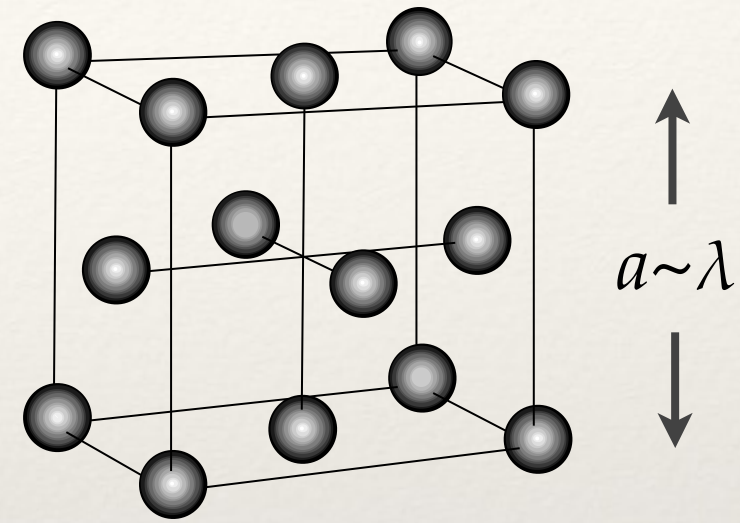


colloidal crystal with
lattice constant ~ 0.5 μm

Phase diagram of hard-sphere colloids

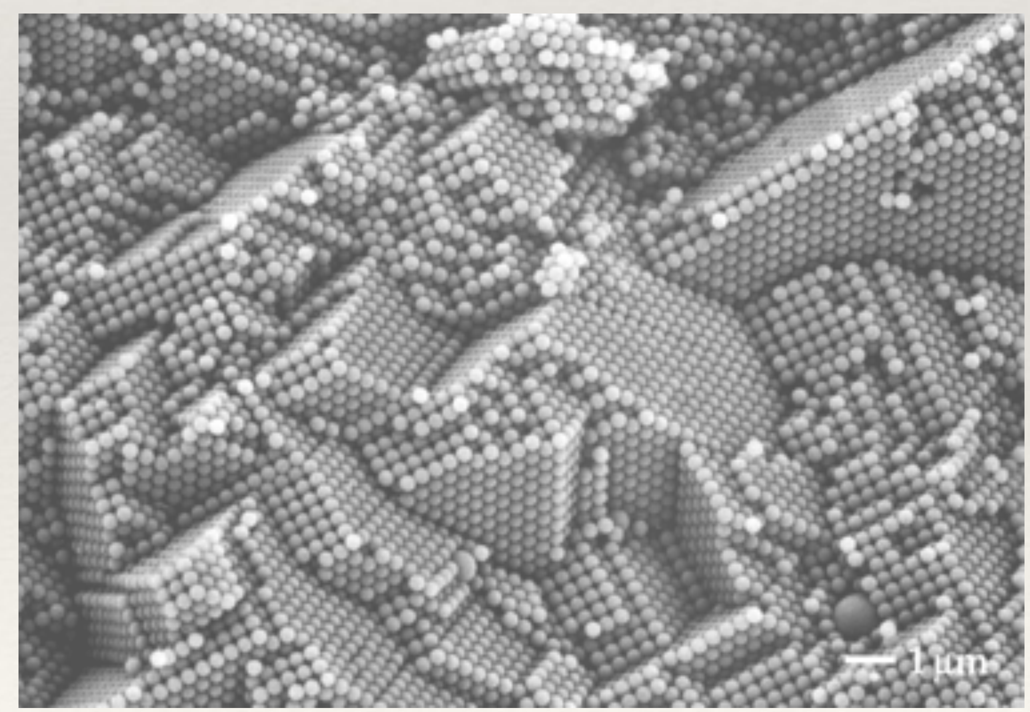
Hard-sphere phase diagram (athermal)





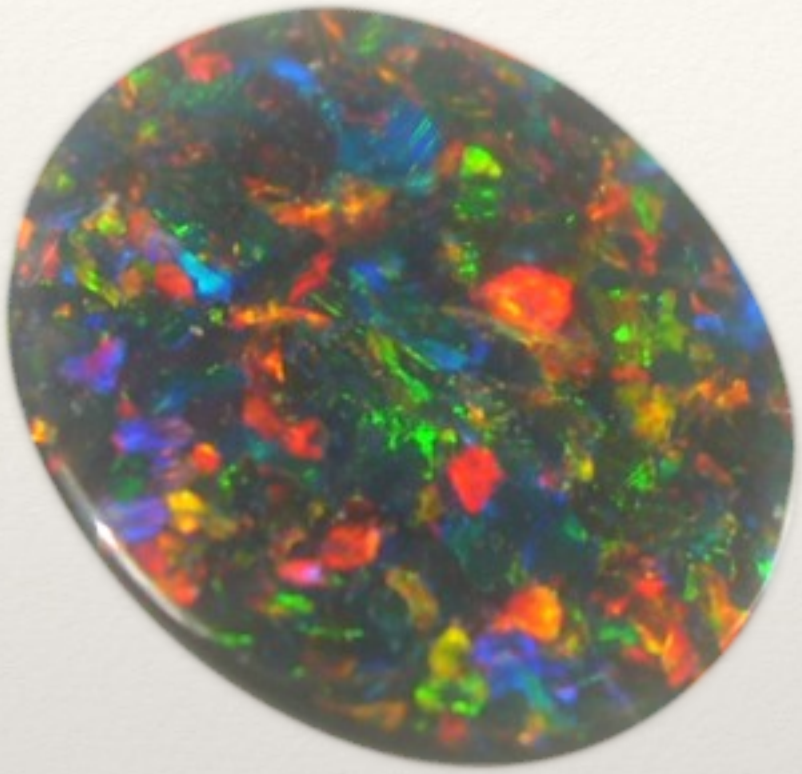
Crystallization driven by entropy

Hard spheres: Colloids used as model systems

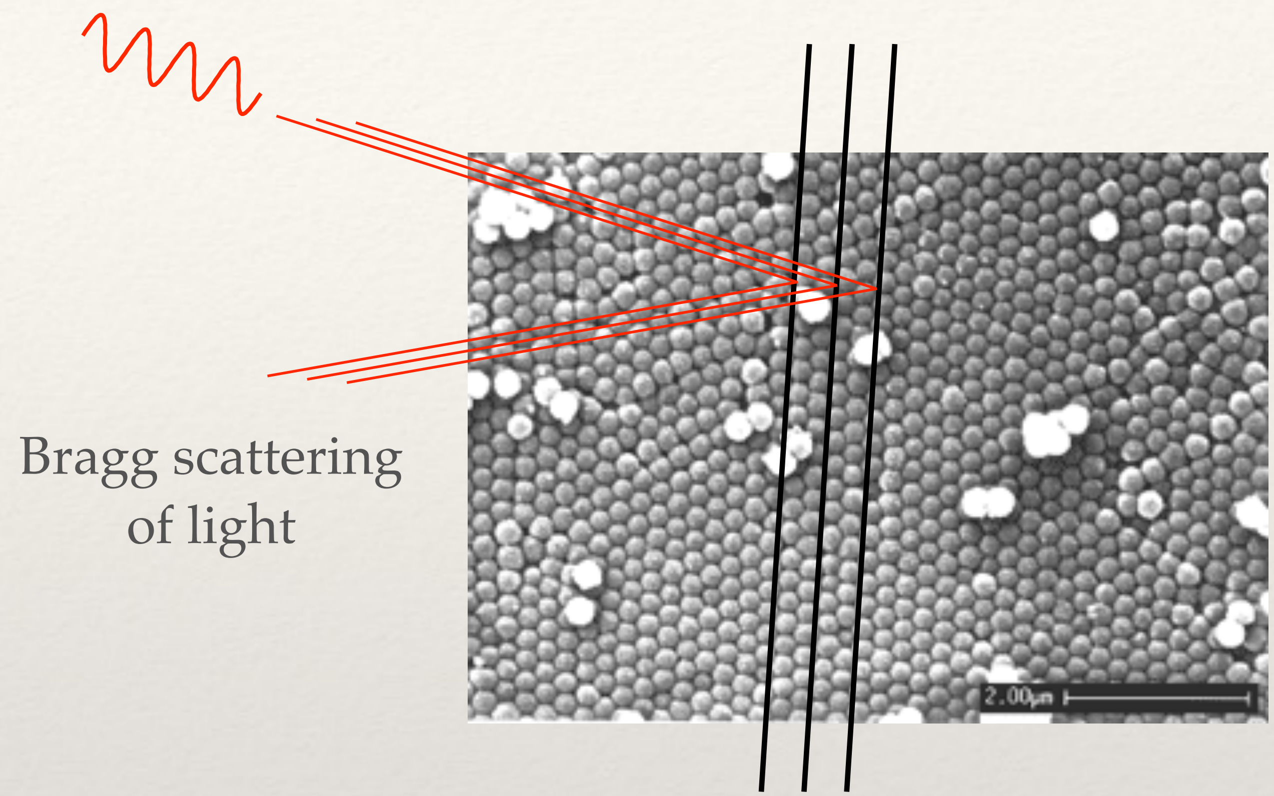


colloidal crystal with
lattice constant ~ 0.5 μm

Naturally occurring colloidal crystals



Gem quality opal from Australia

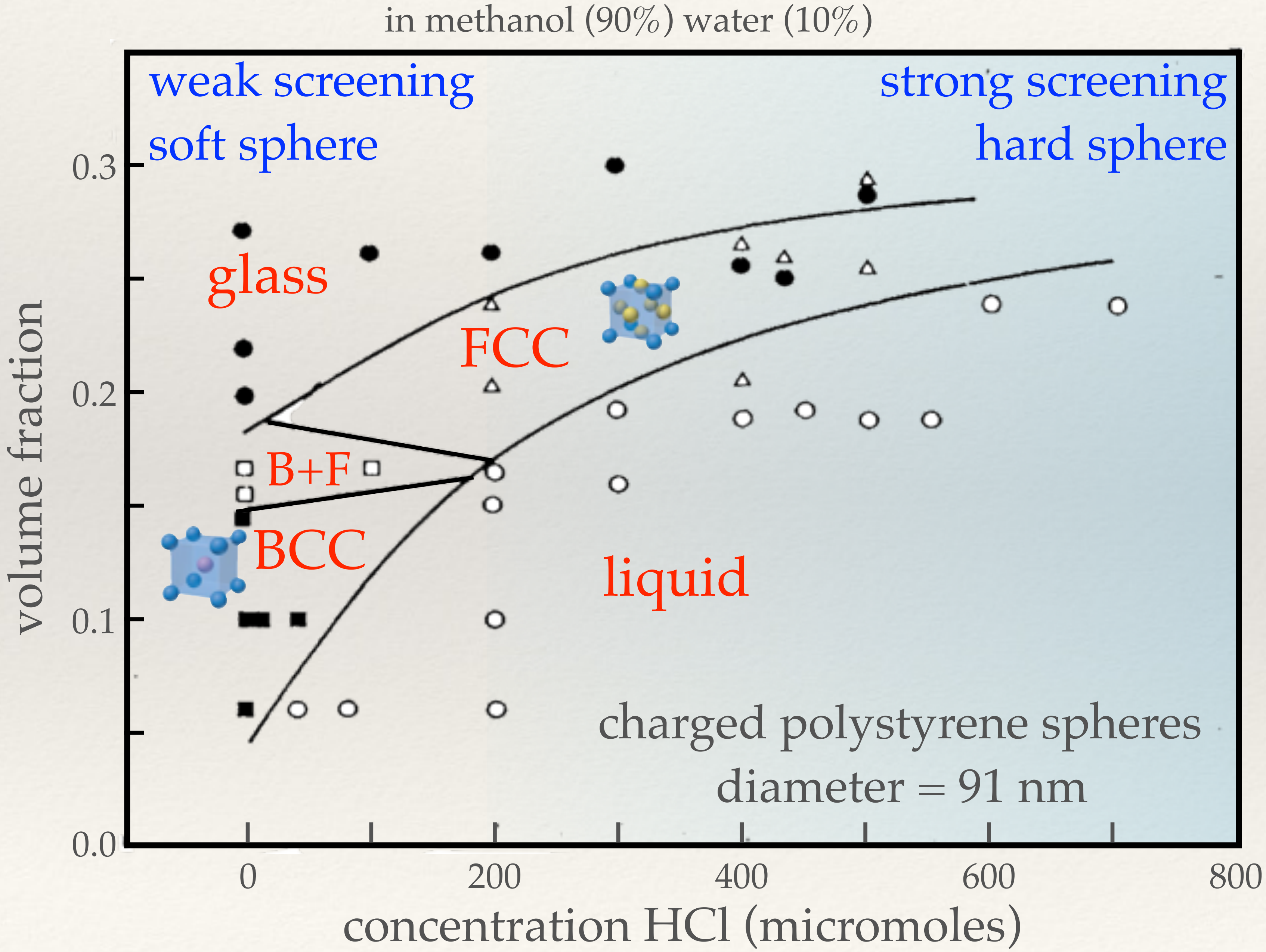


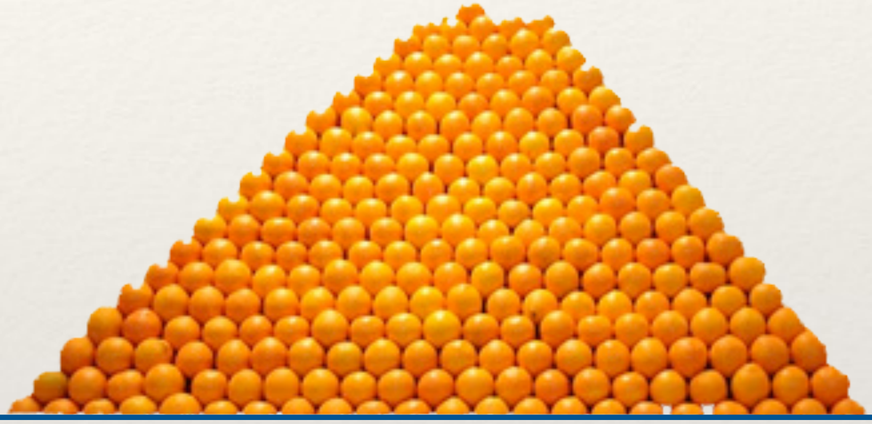
Natural opals consist of tiny FCC ordered glass spheres (~200 nm)

Bragg scattering from different crystalline planes produce different colors

Phase diagram of charged colloids

Electrically charged colloids spontaneously form ordered structures



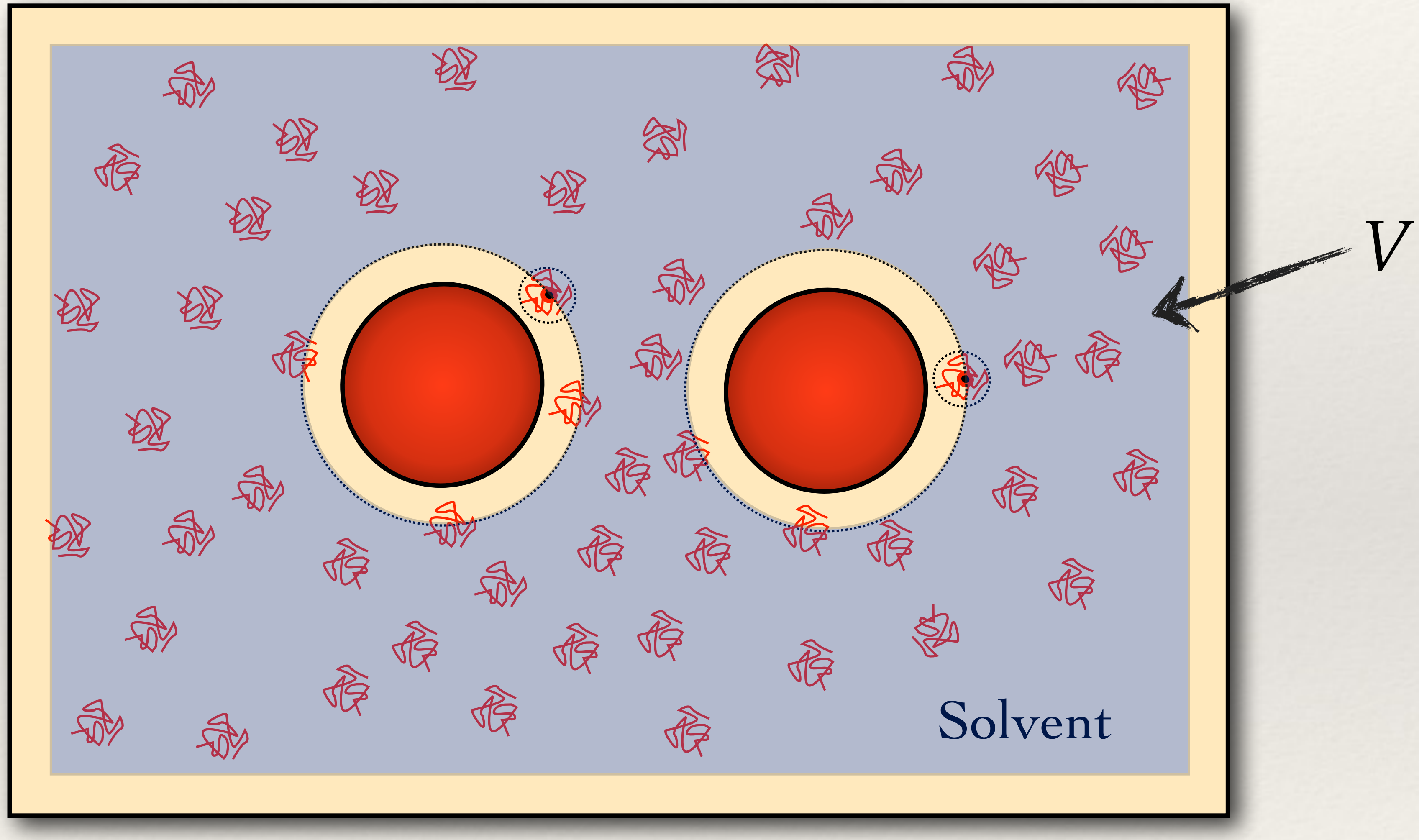


Crystallization driven by repulsive interactions and entropy

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

Depletion interaction

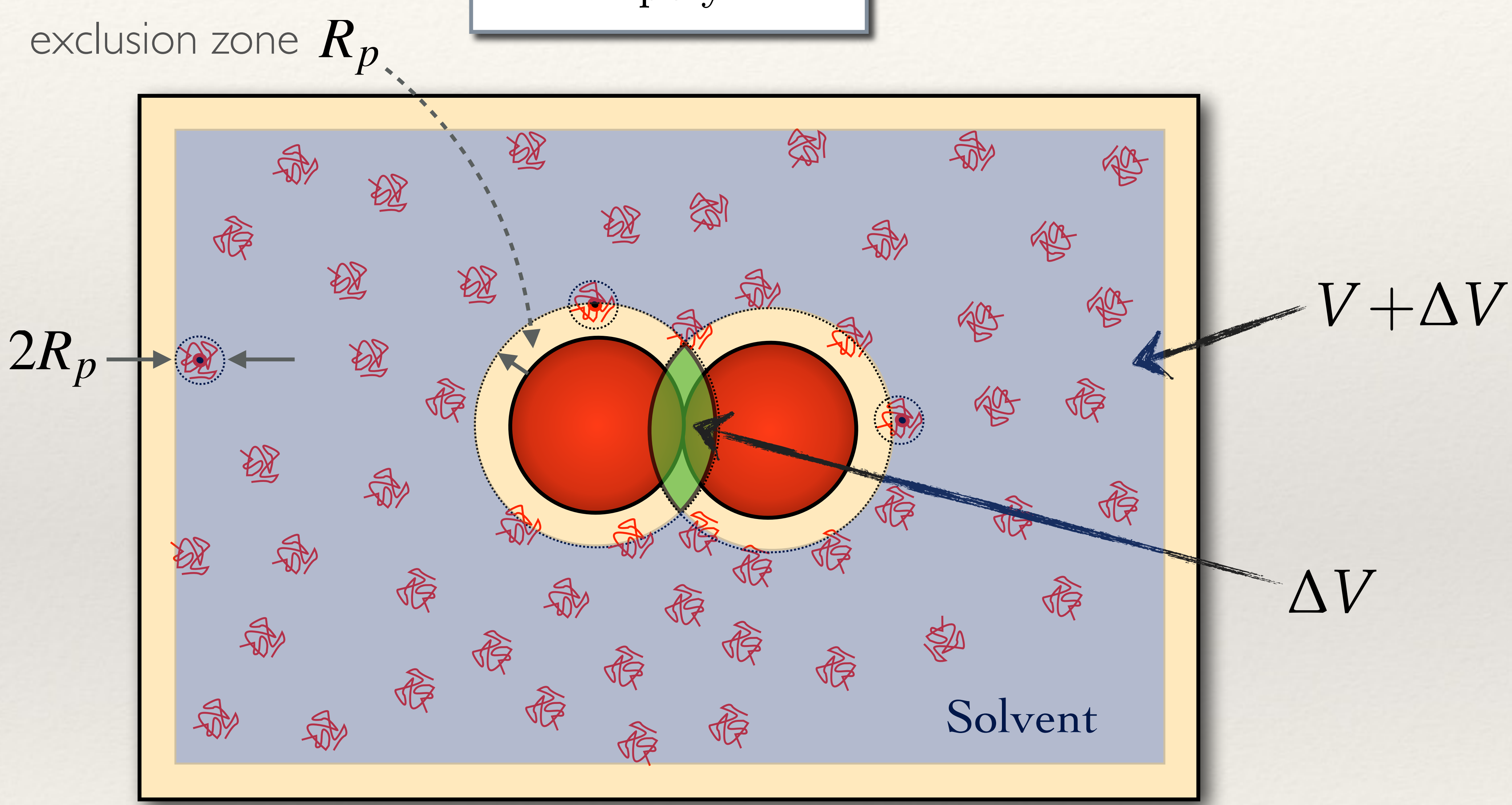
$$S \sim n_{\text{poly}} \ln V$$



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

Depletion interaction

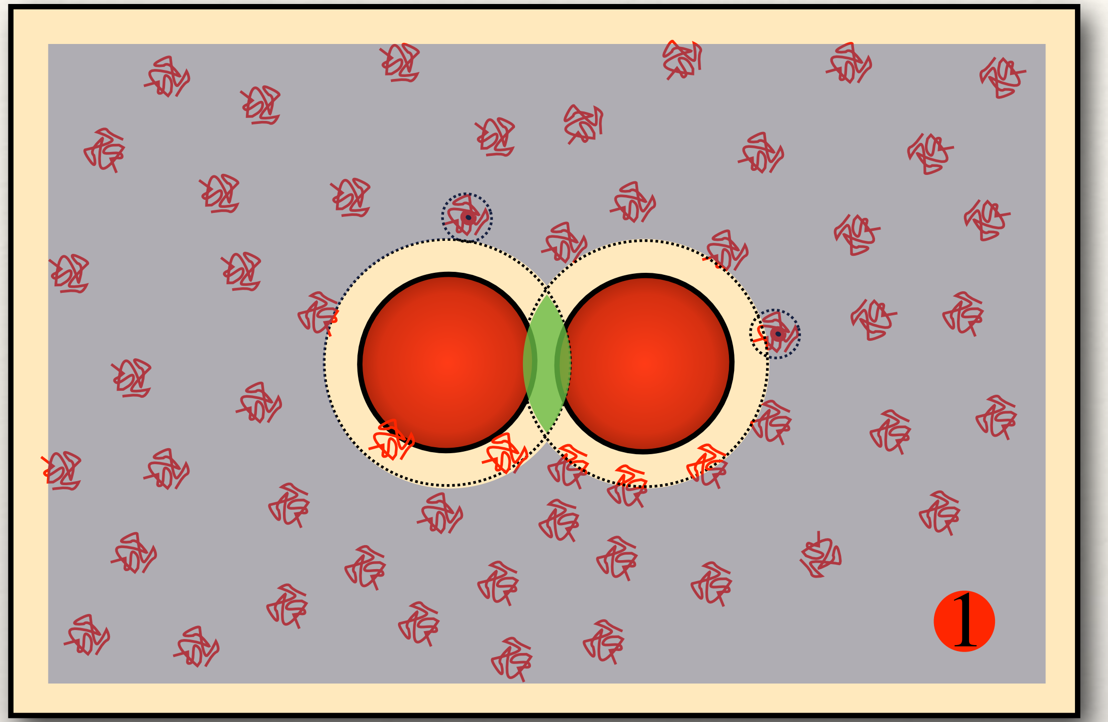
$$S \sim n_{\text{poly}} \ln V$$

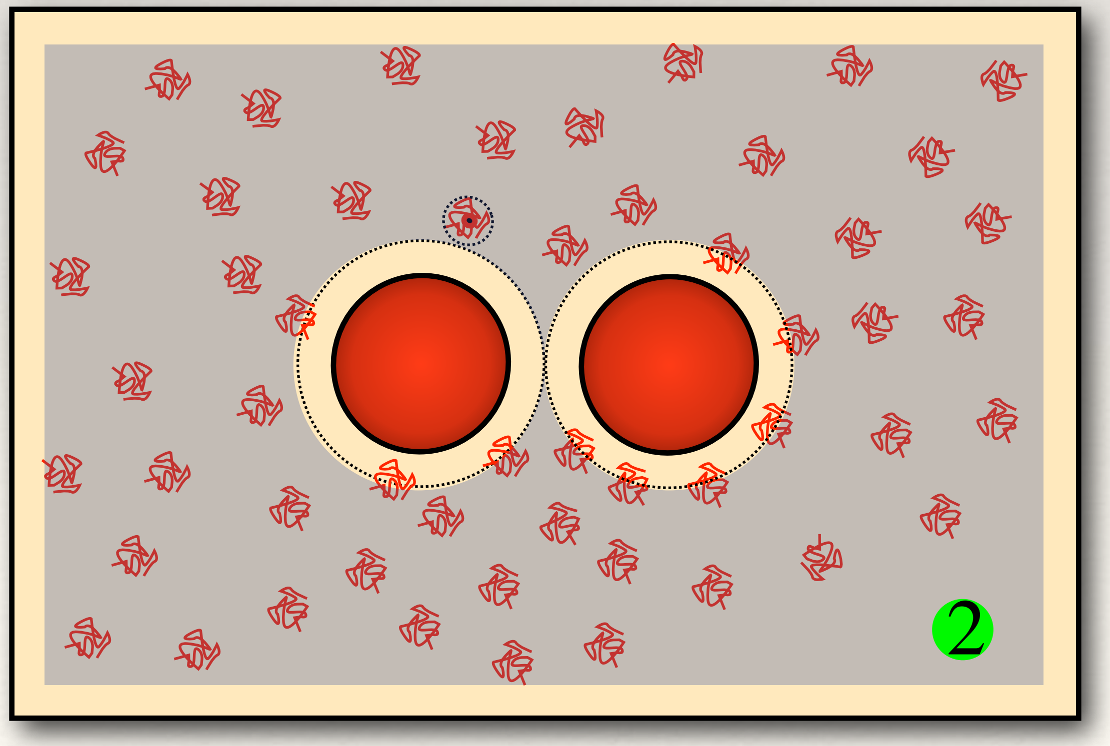


$$\Delta S \sim n_{\text{poly}} \frac{\Delta V}{V}$$

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

Depletion interaction





$$F(V,T) = -k_B T \ln Z(V,T)$$

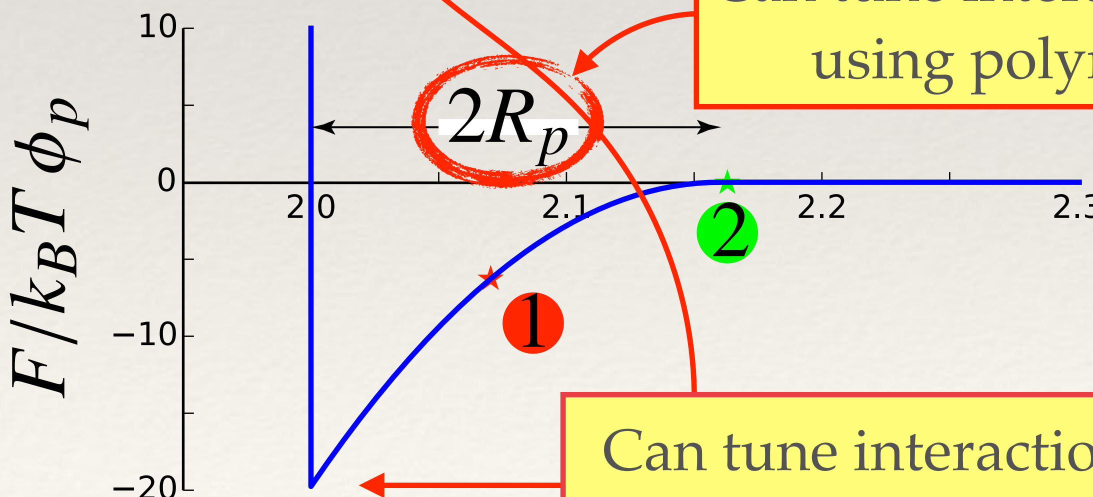
ideal gas of N_p
polymers of radius R_p

$$Z(V,T) = \frac{1}{N_p!}\left(\frac{V}{\lambda}\right)^{N_p}$$

$$\Rightarrow dF = -N_p k_B T \frac{dV}{V}$$

$$\Delta F = -k_B T \phi_p \left(1 + \frac{a}{R_p} - \frac{r}{2R_p}\right)^2 \left(1 + \frac{a}{R_p} + \frac{r}{4R_p}\right)$$

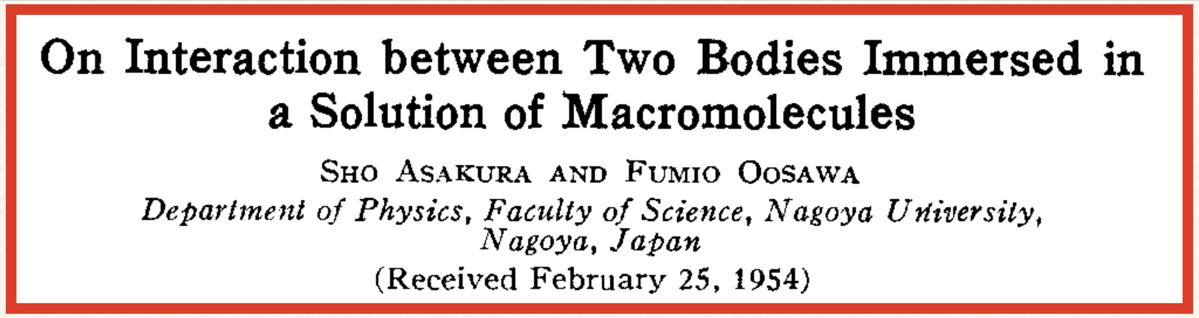
Can tune interaction range using polymer size



Can tune interaction strength using polymer concentration

spheres touching

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


On Interaction between Two Bodies Immersed in a Solution of Macromolecules

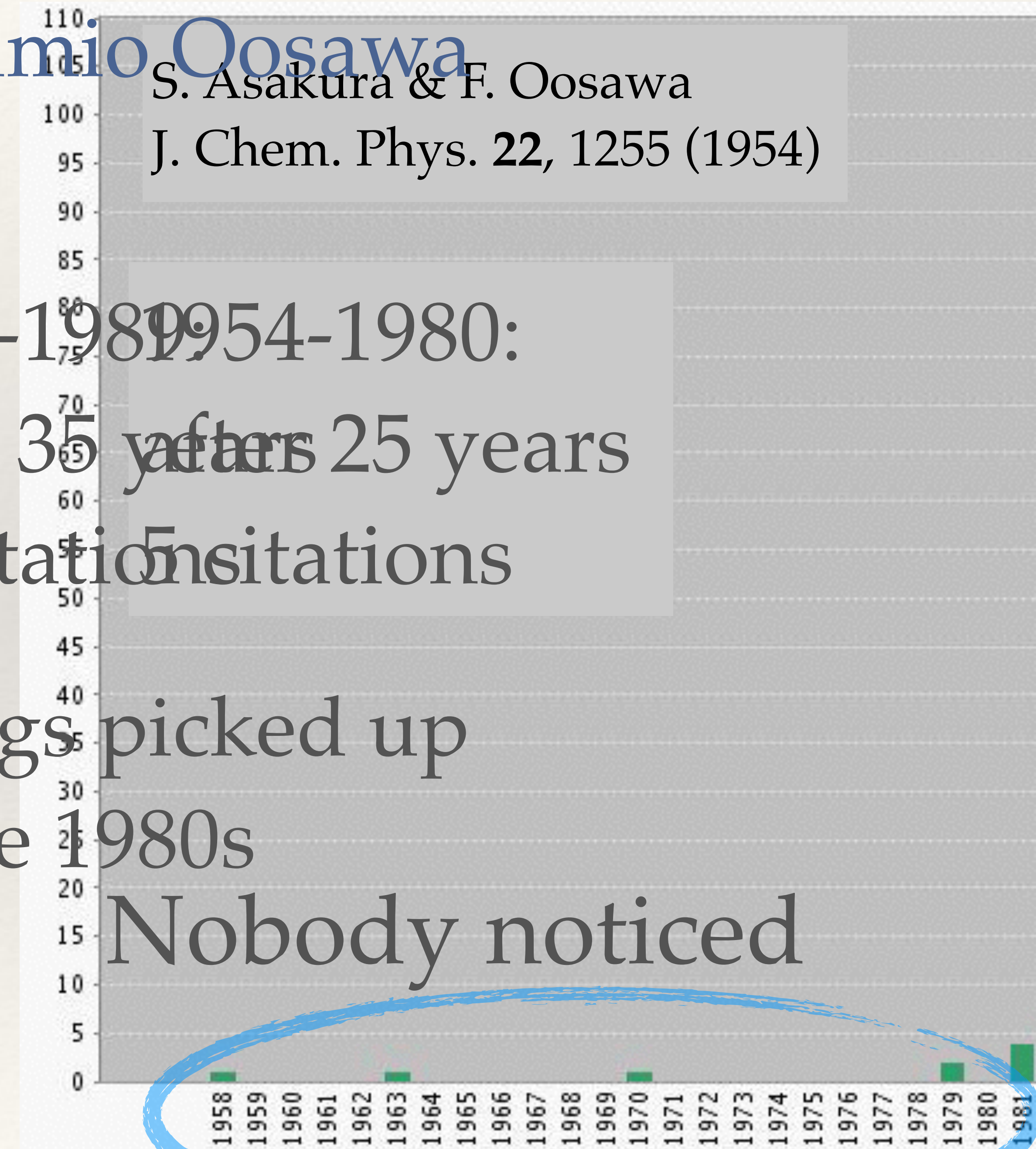
SHO ASAKURA AND FUMIO OOSAWA

Department of Physics, Faculty of Science, Nagoya University, Nagoya, Japan

(Received February 25, 1954)

Citations for original paper on the depletion interaction

by Sho Asakura & Fumio Oosawa



S. Asakura & F. Oosawa

J. Chem. Phys. **22**, 1255 (1954)

1954-2015:
after 60 years
1676 citations

A classic

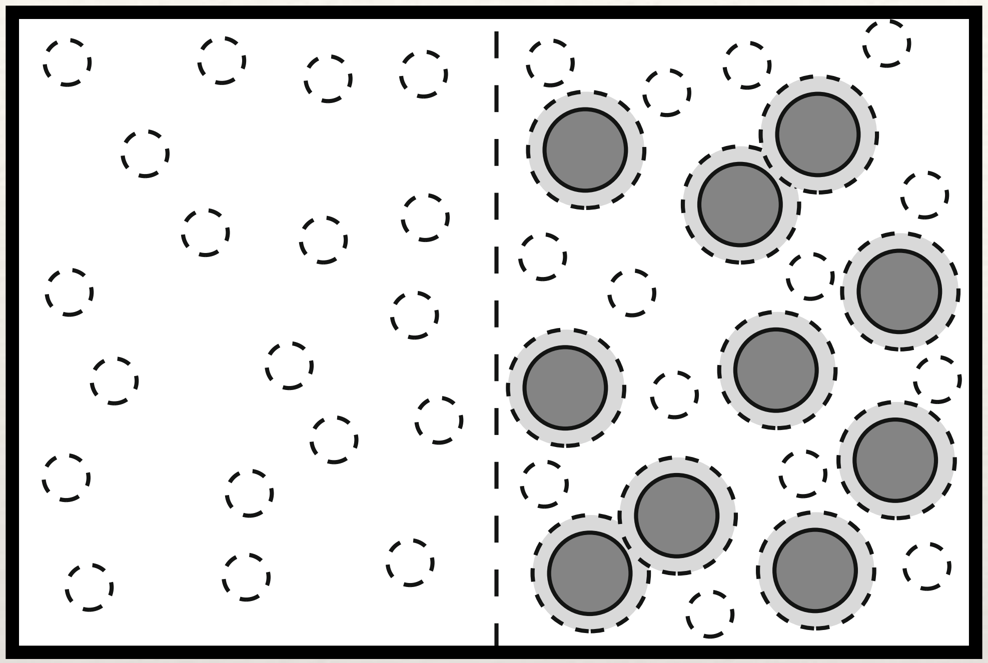
1954-1989:
after 35 years
63 citations

Things picked up
in the 1980s

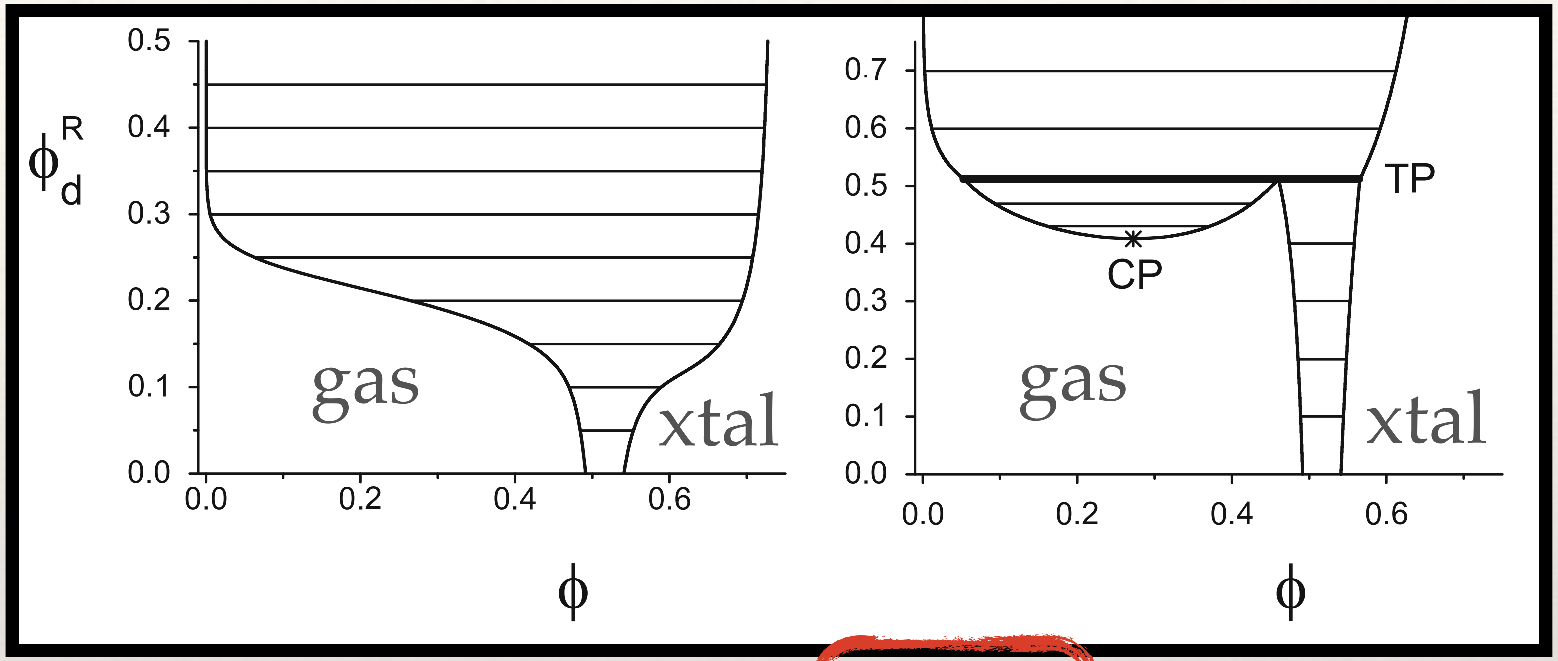
1954-1980:
after 25 years
5 citations

Nobody noticed

Phase diagrams for colloids with depletion interaction



semi-permeable membrane



from *Colloids and the Depletion Interaction*, by Lekkerkerker & Tuinier, Springer 2011.

ϕ_d^R = volume fraction of depletant in reservoir

Lek(ker)³

ϕ = volume fraction of colloid

- Depletants create short-range attractive interaction similar to attractive interactions between atoms & molecules
- Phase diagrams are similar to common gas-liquid-solid phase diagrams

Summer School on Soft Matter Self-Assembly, 2015, June 28-July 7

Lecture 2: Lock & key particles

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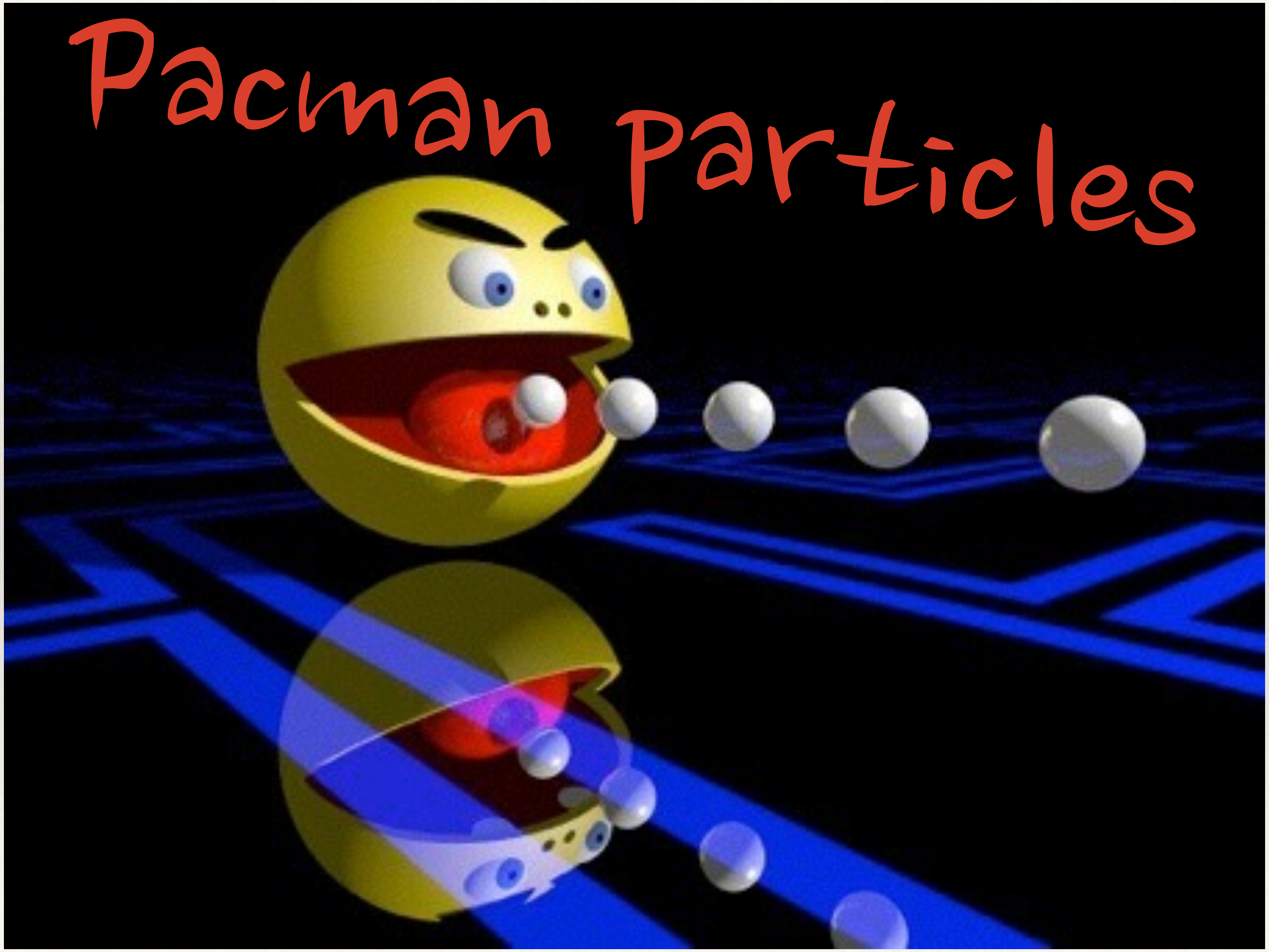
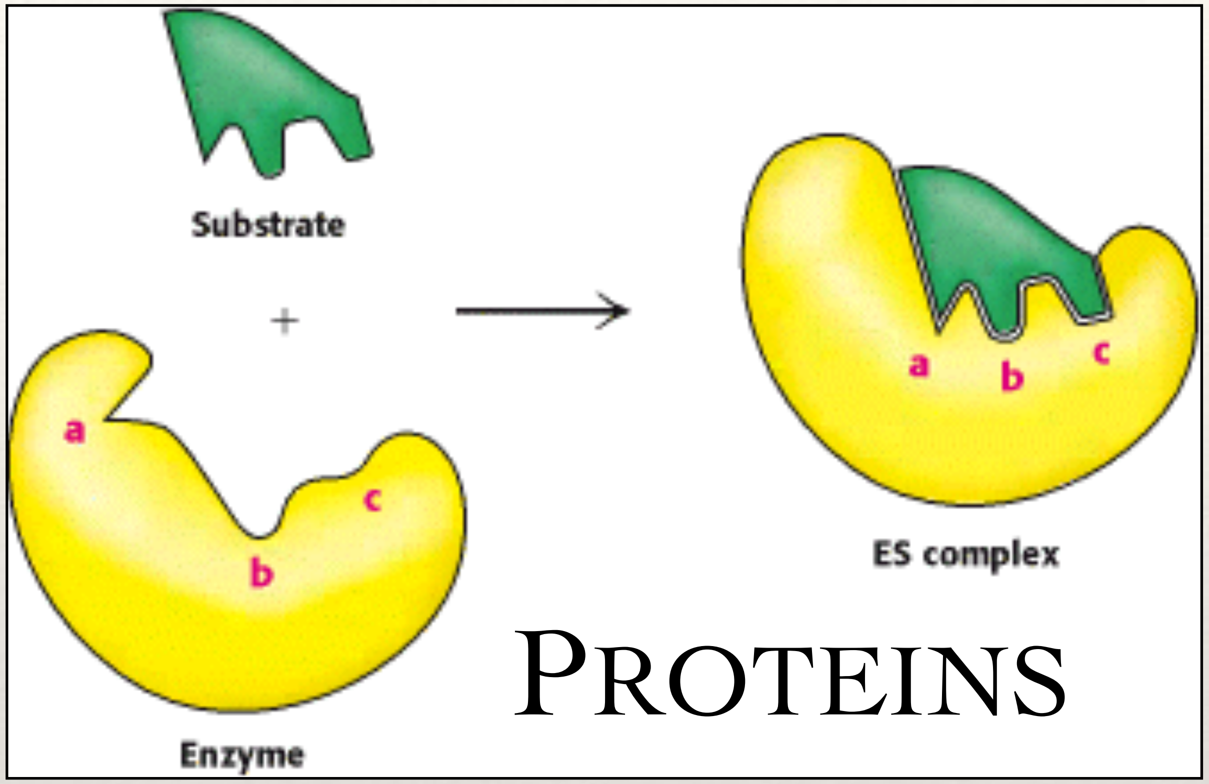
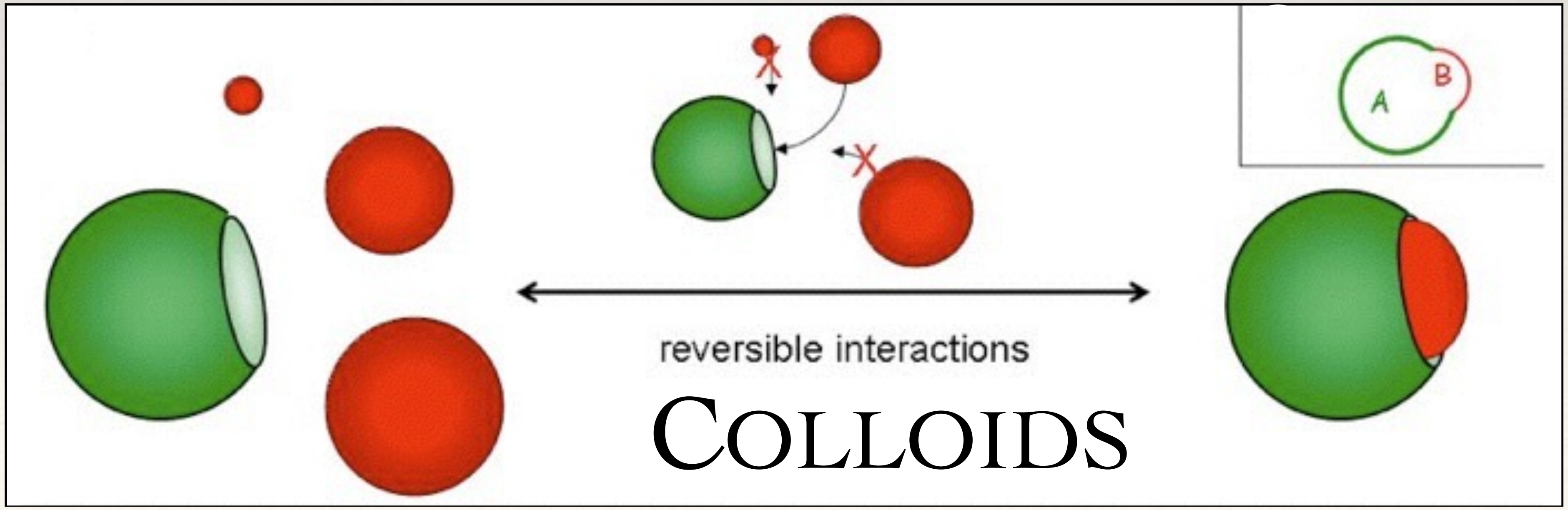
NYU

Lock & key colloids

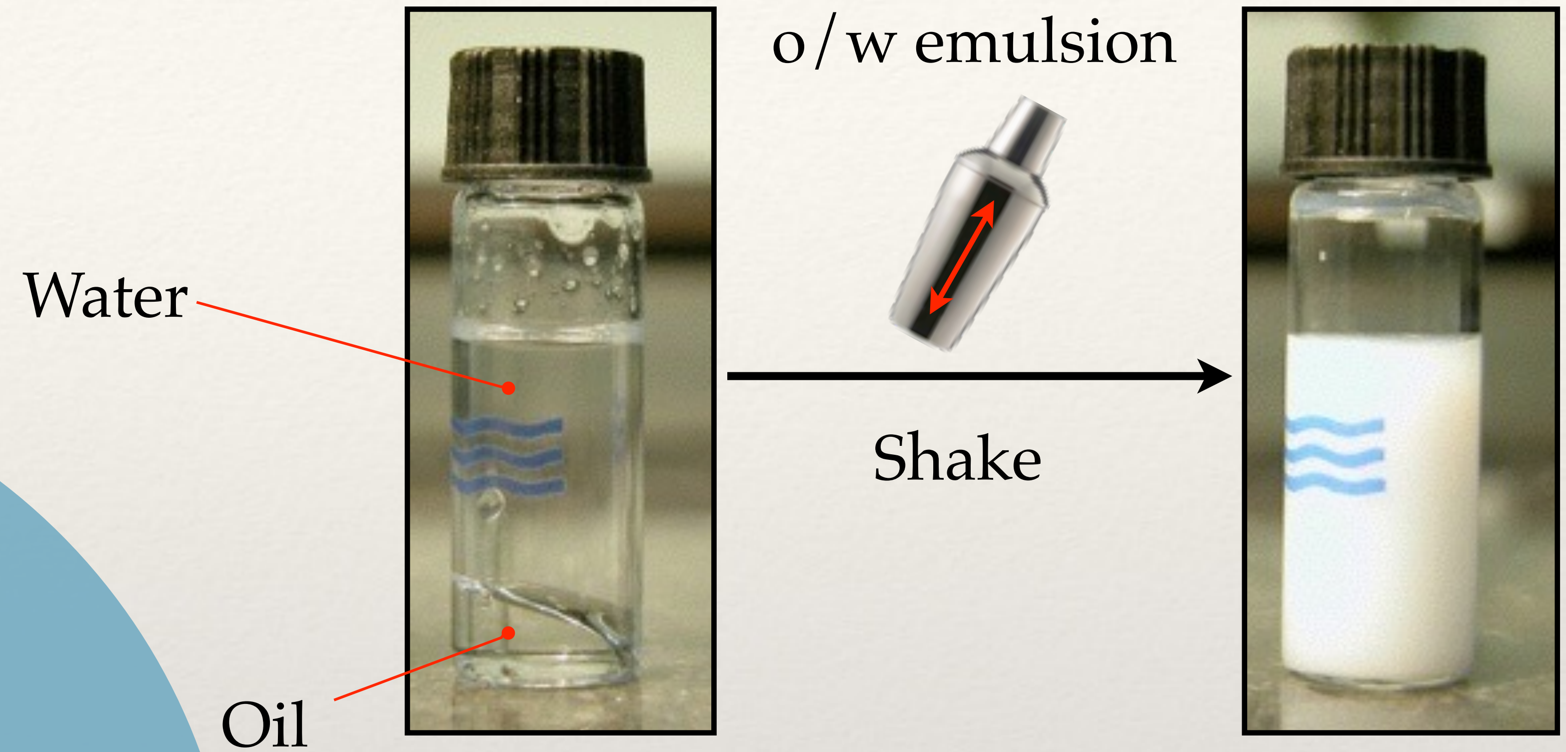


Inspiration: Lock & key proteins





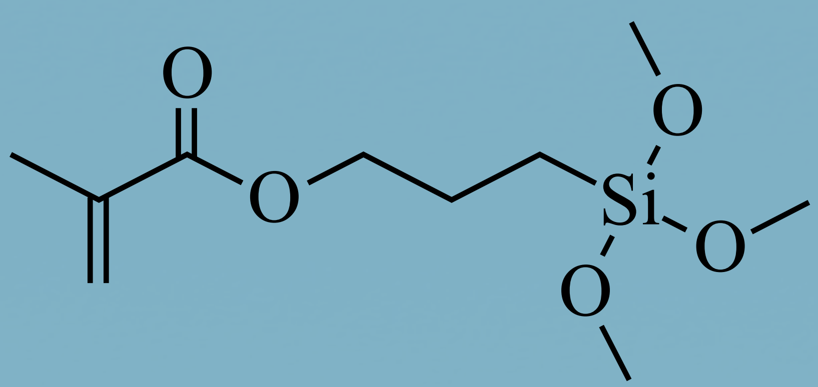
Pacman particle synthesis



Oil = "TPM"

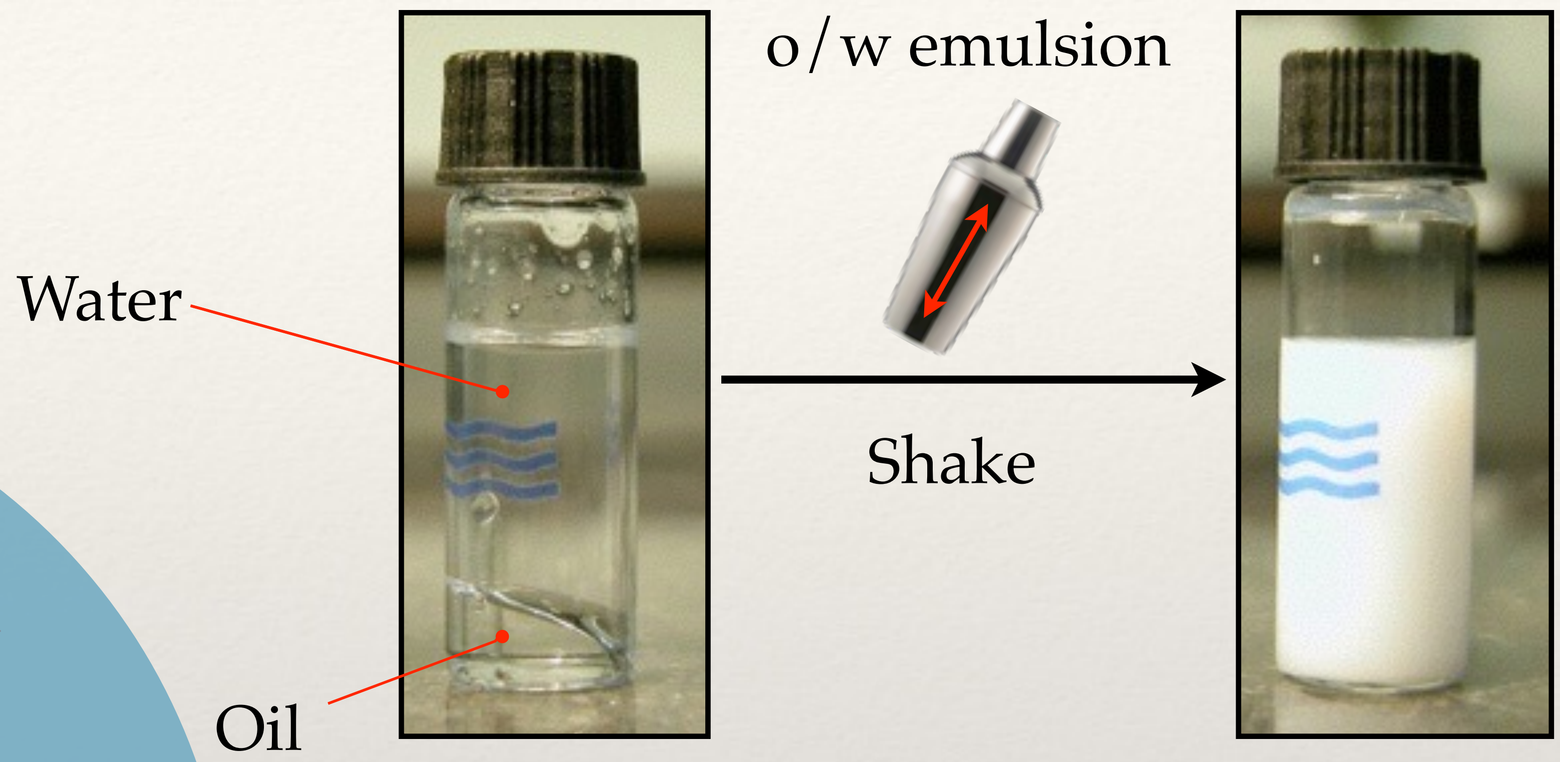
= 3-methacryloxypropyl trimethoxysilane

TPM =



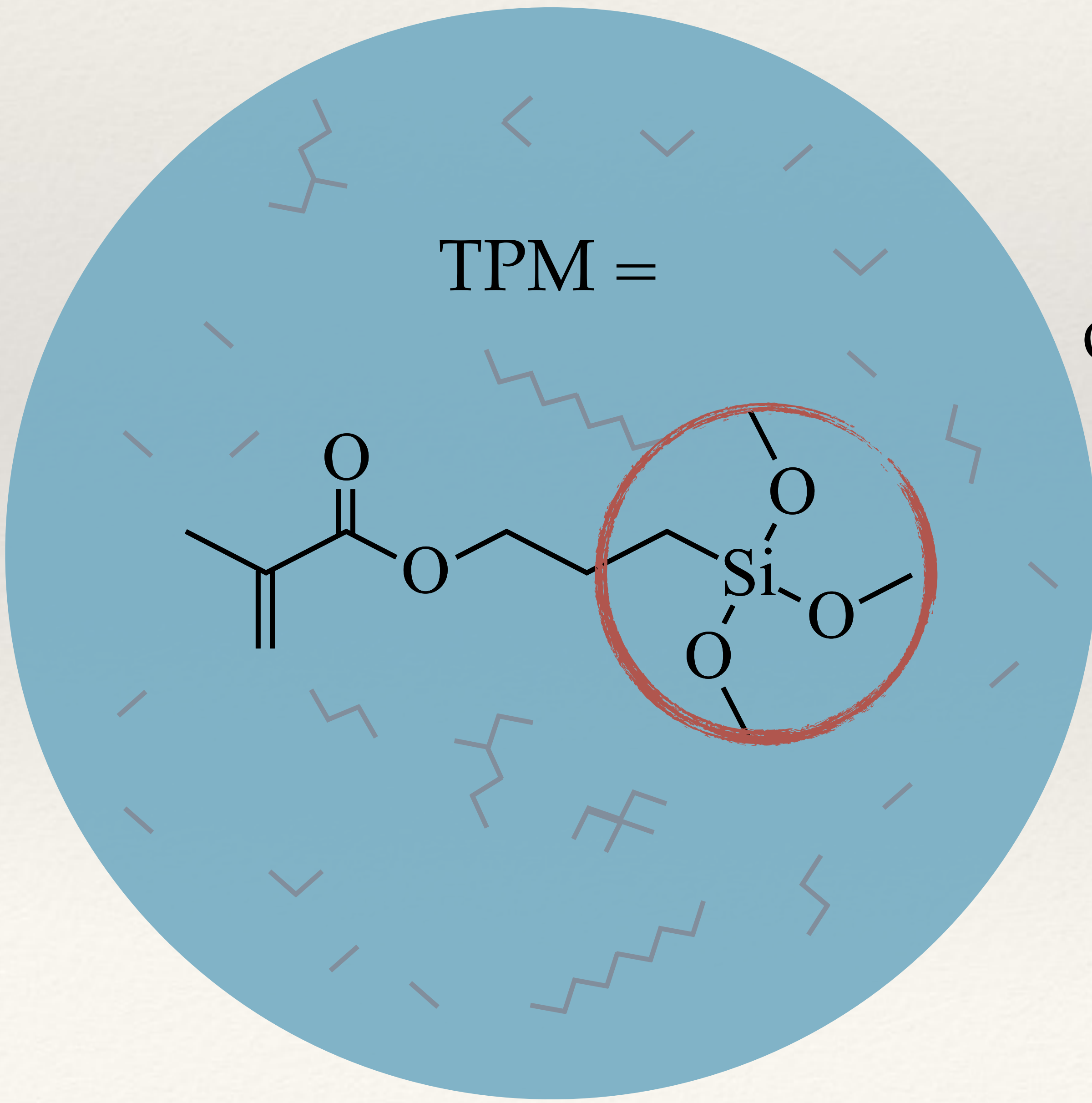
Make emulsion
(oil droplets in water)

Pacman particle synthesis

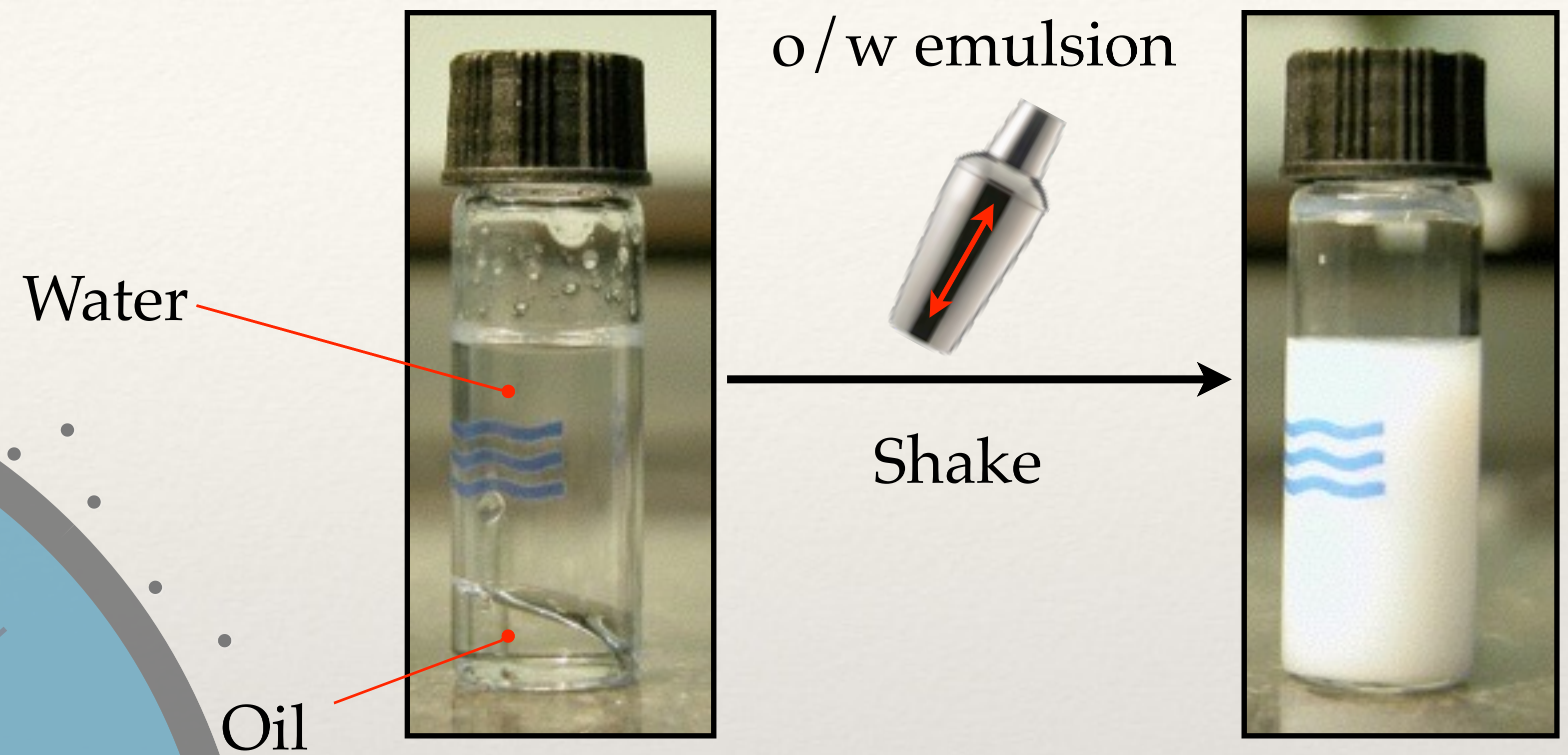


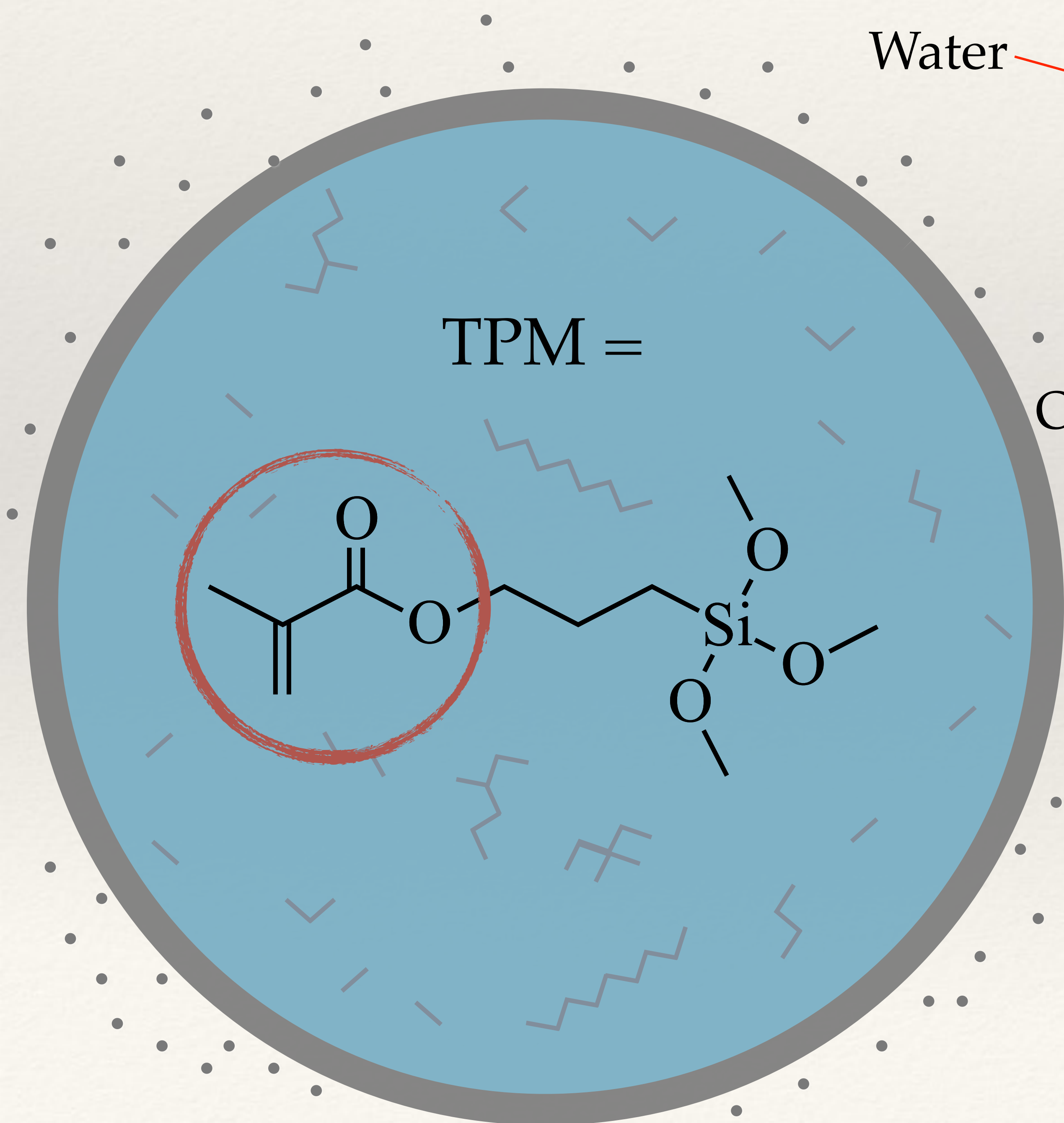
Oligmerize oil

✦Oligomerize Si-O groups (pH⬆) N~1-10



Pacman particle synthesis





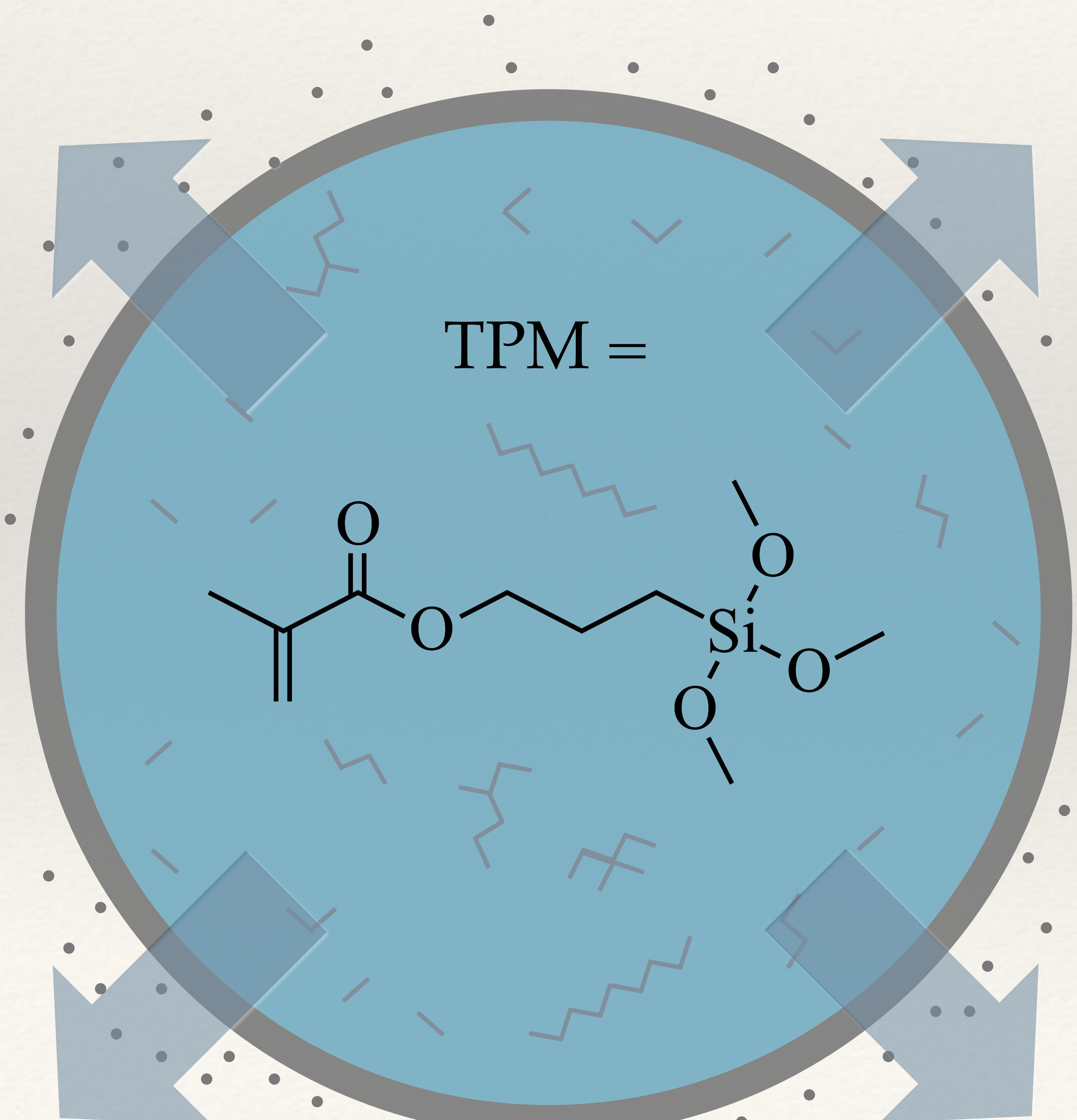
Polymerize oil

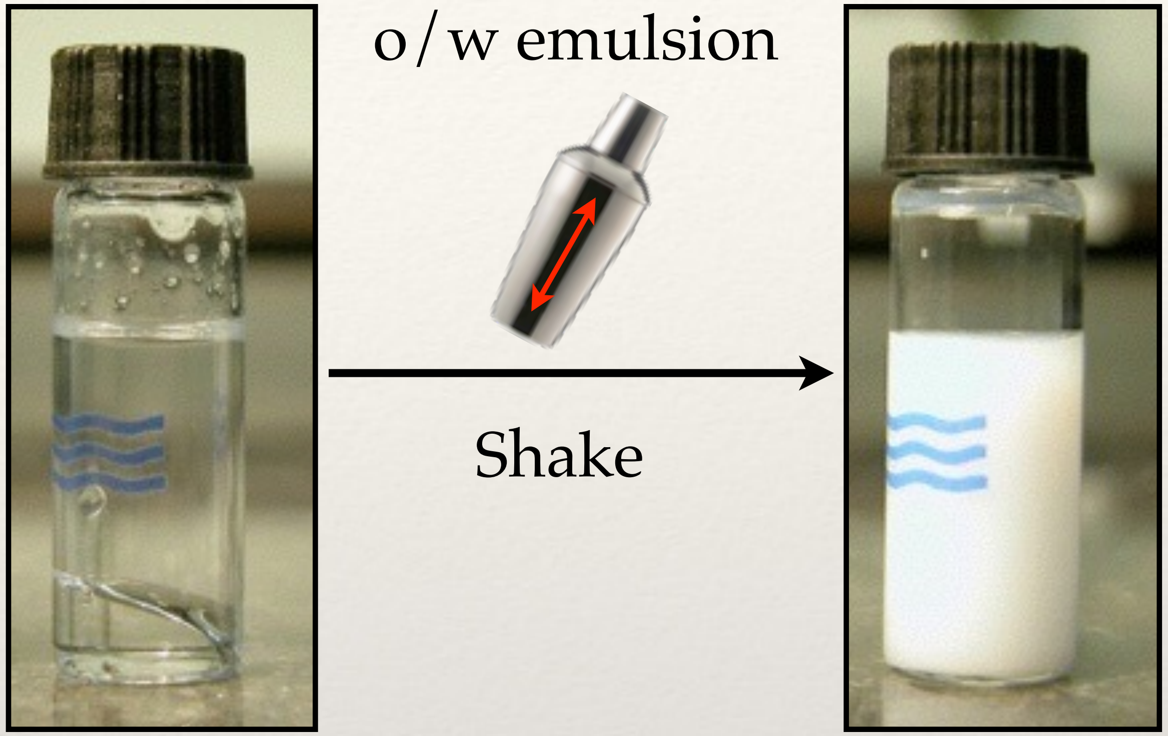
✦Oligomerize Si-O groups (pH⬆) *N*~1-10

✦Polymerize methacrylate groups (free radical)

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

Pacman particle synthesis





Polymerize oil

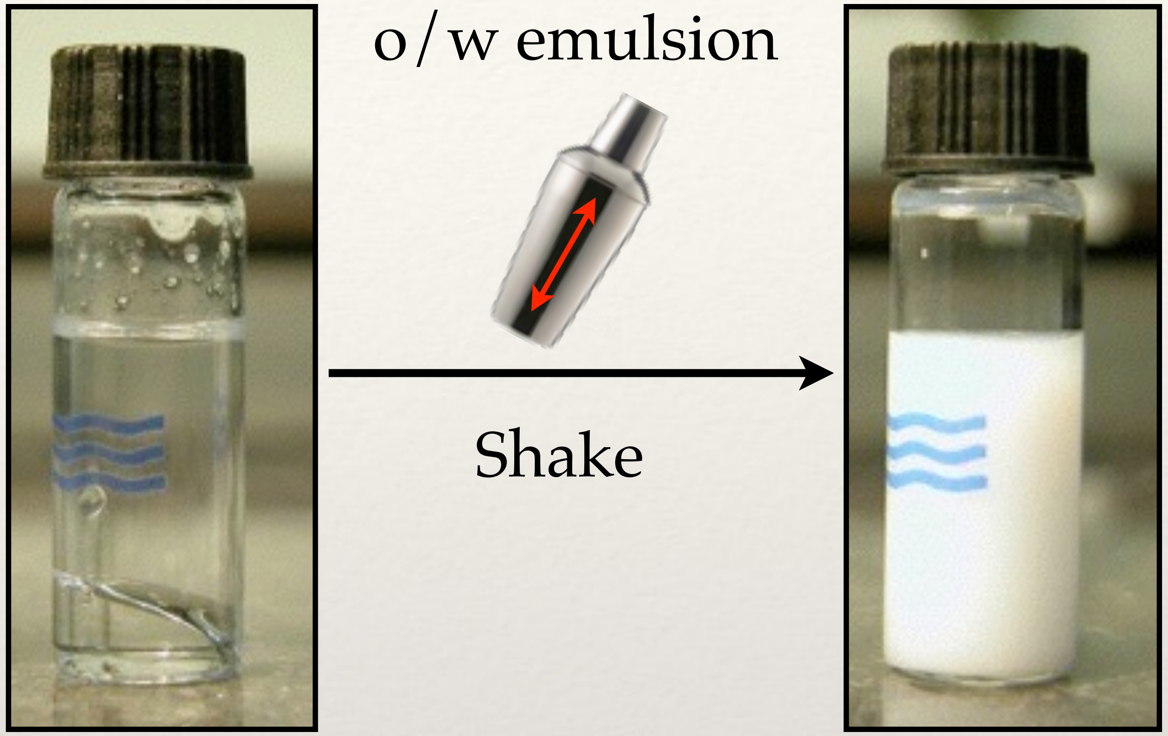
✦Oligomerize Si-O groups (pH⬆) *N*~1-10

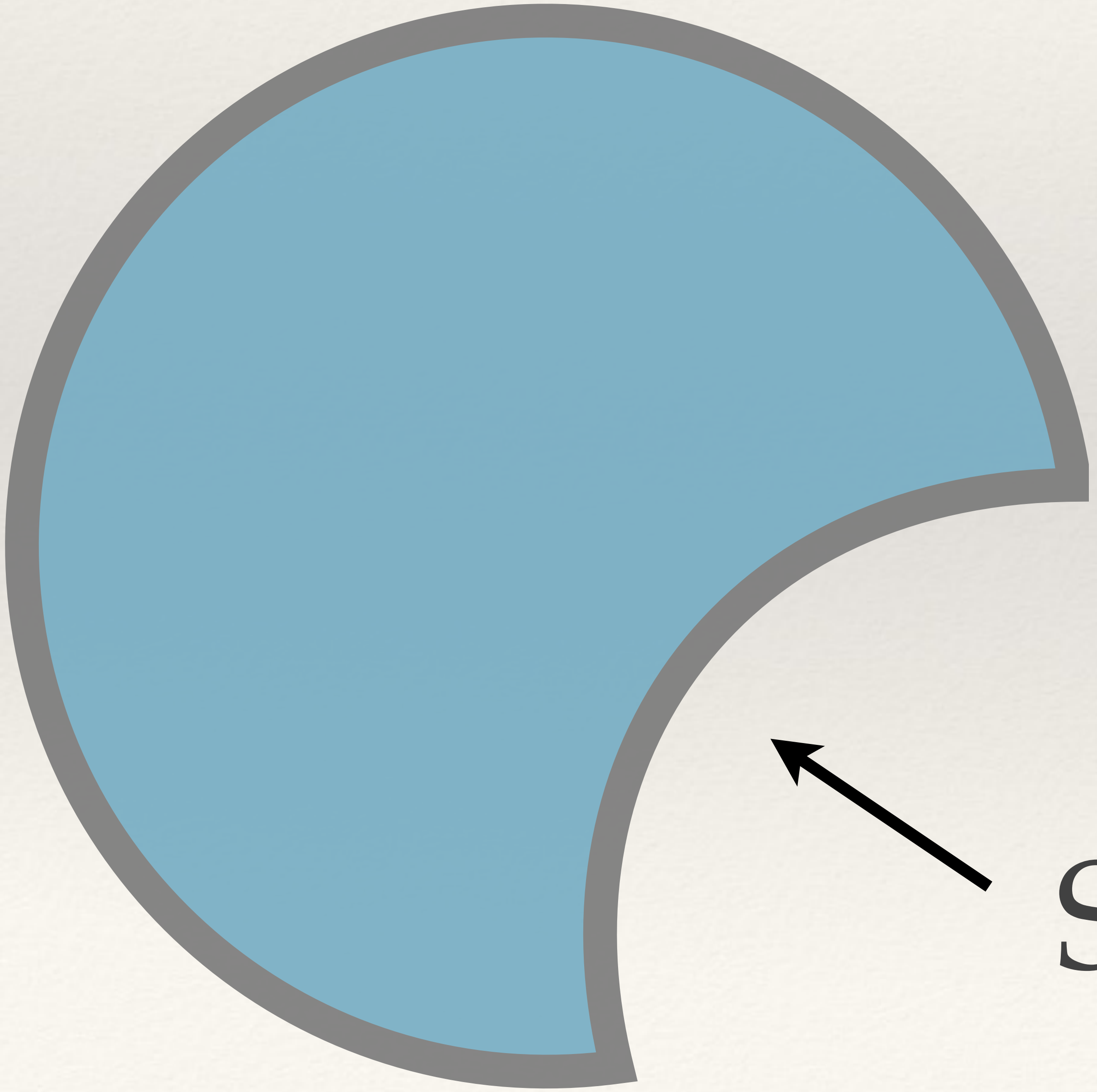
✦Polymerize methacrylate groups (free radical)

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

And …

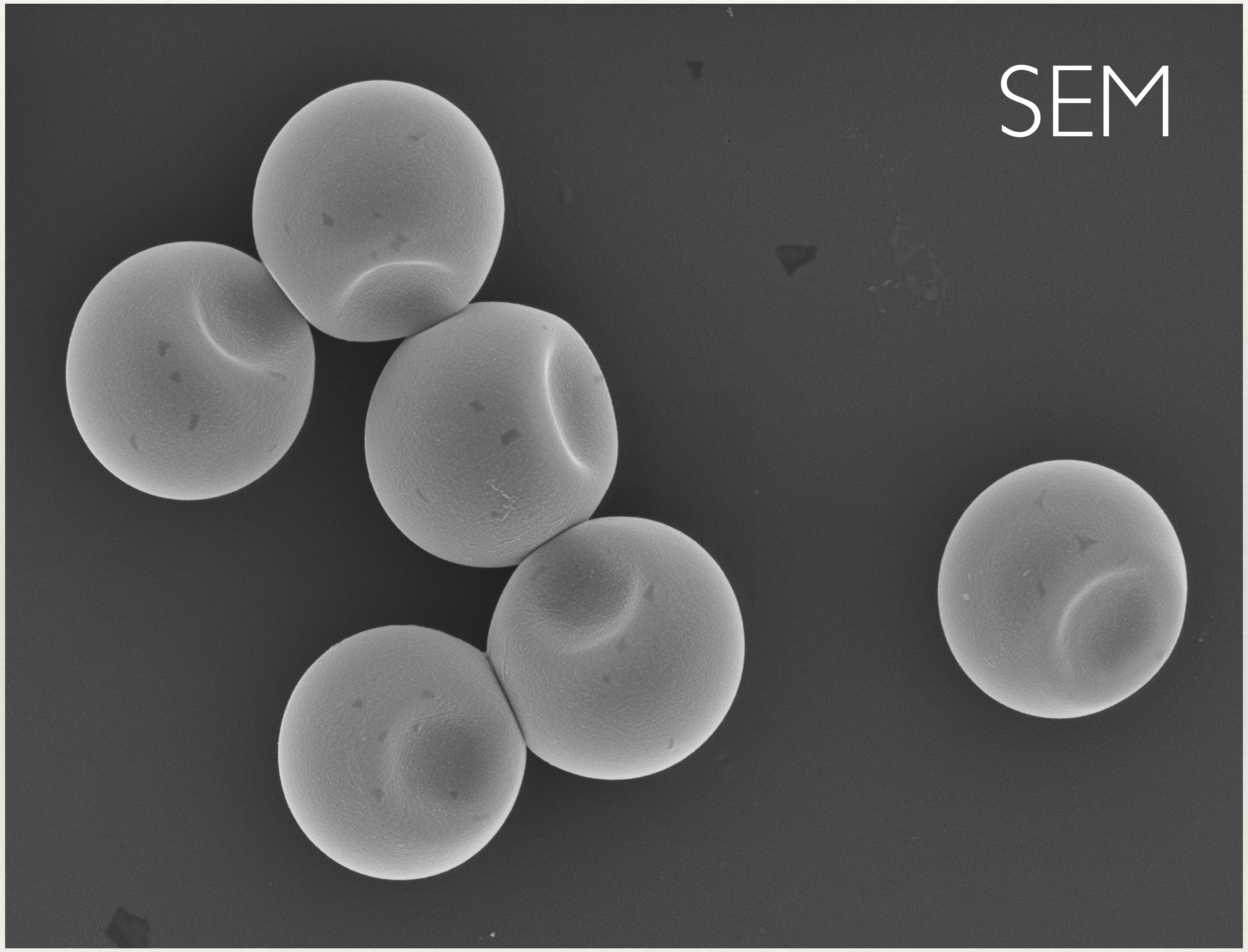
Pacman particle synthesis





Shell buckles

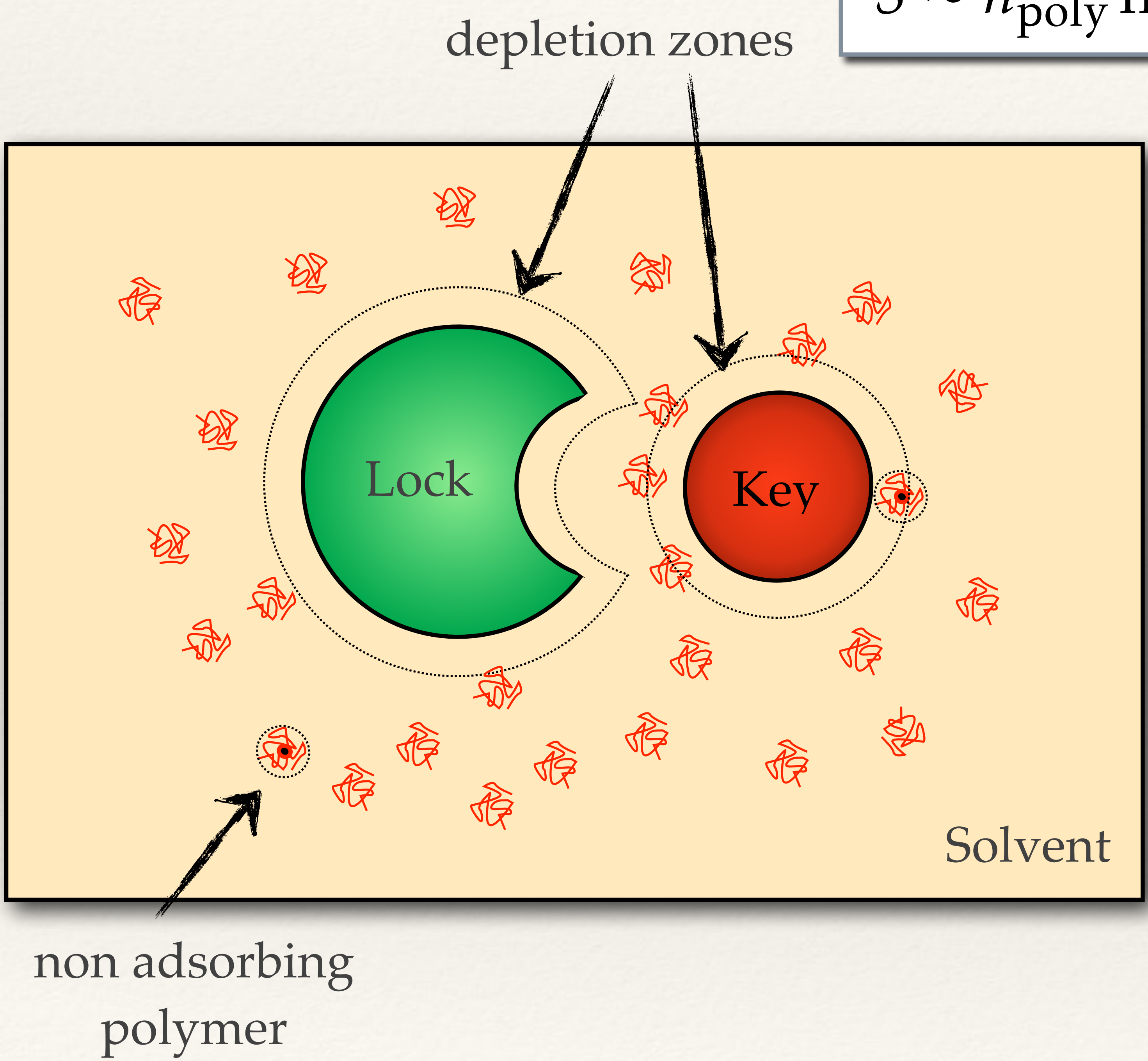
Pacman particles



micrometer-size particles with mouths

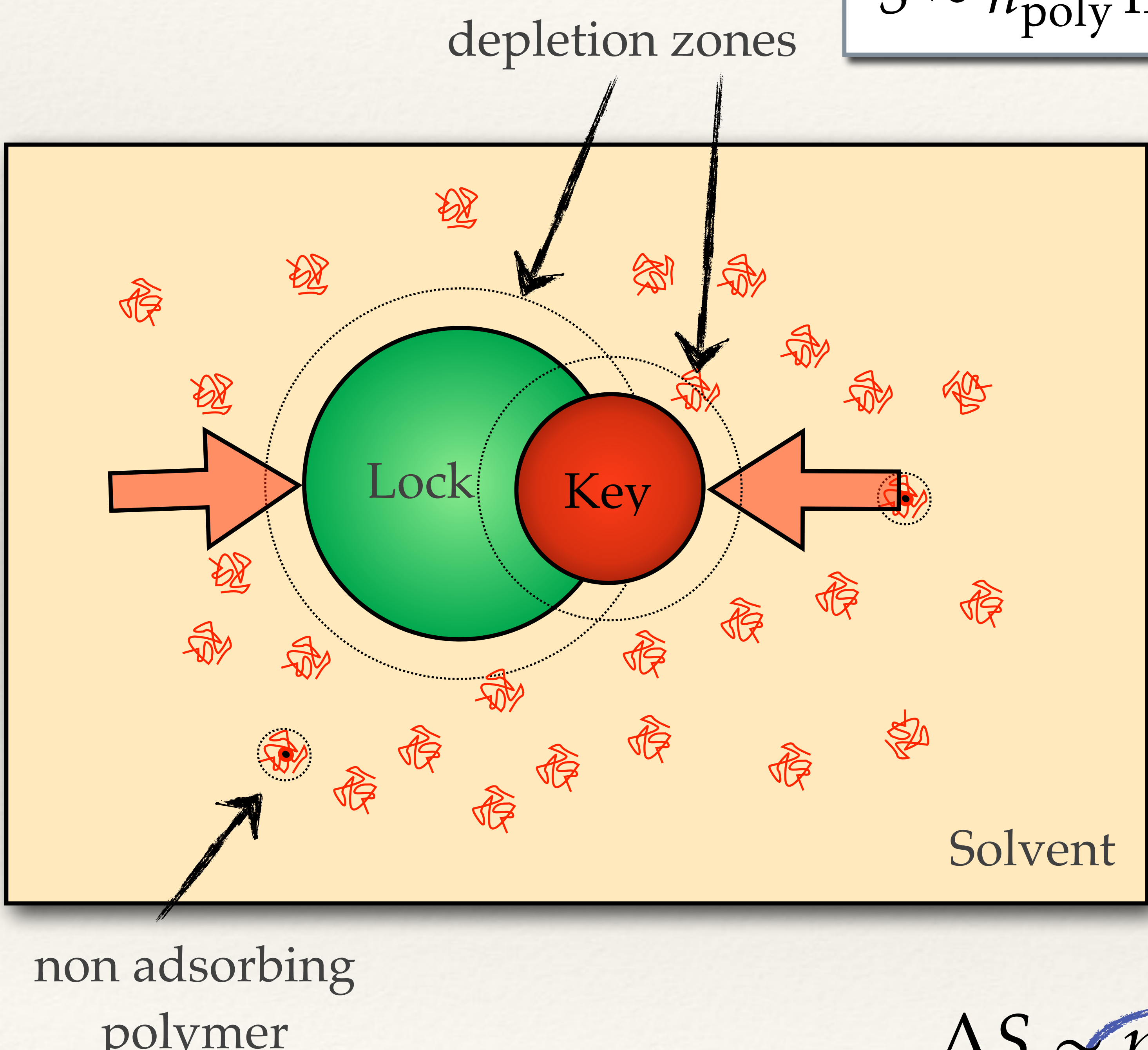
Packman lock & key

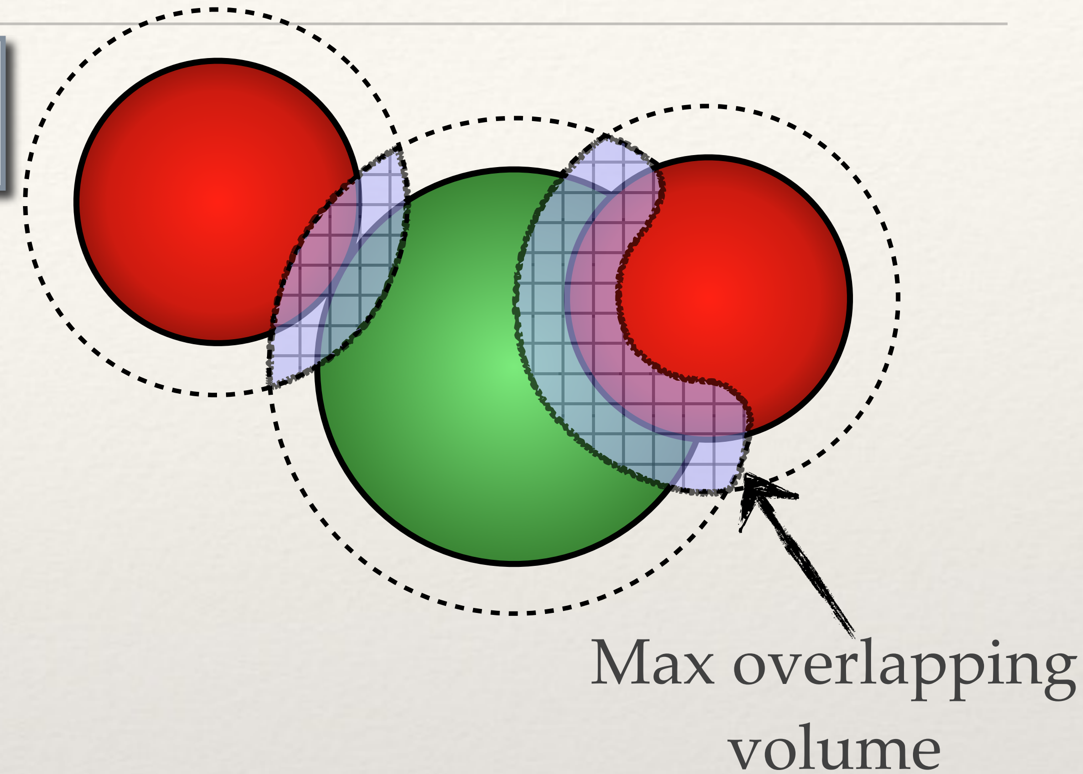
$$S \sim n_{\text{poly}} \ln V$$

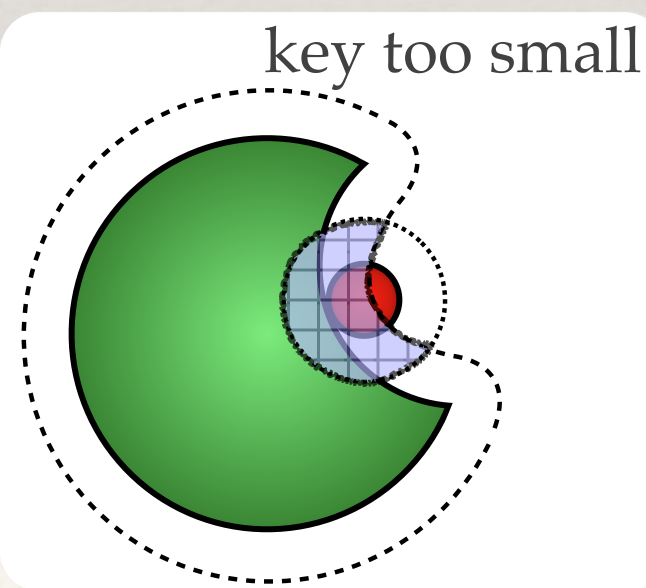


Packman lock & key

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



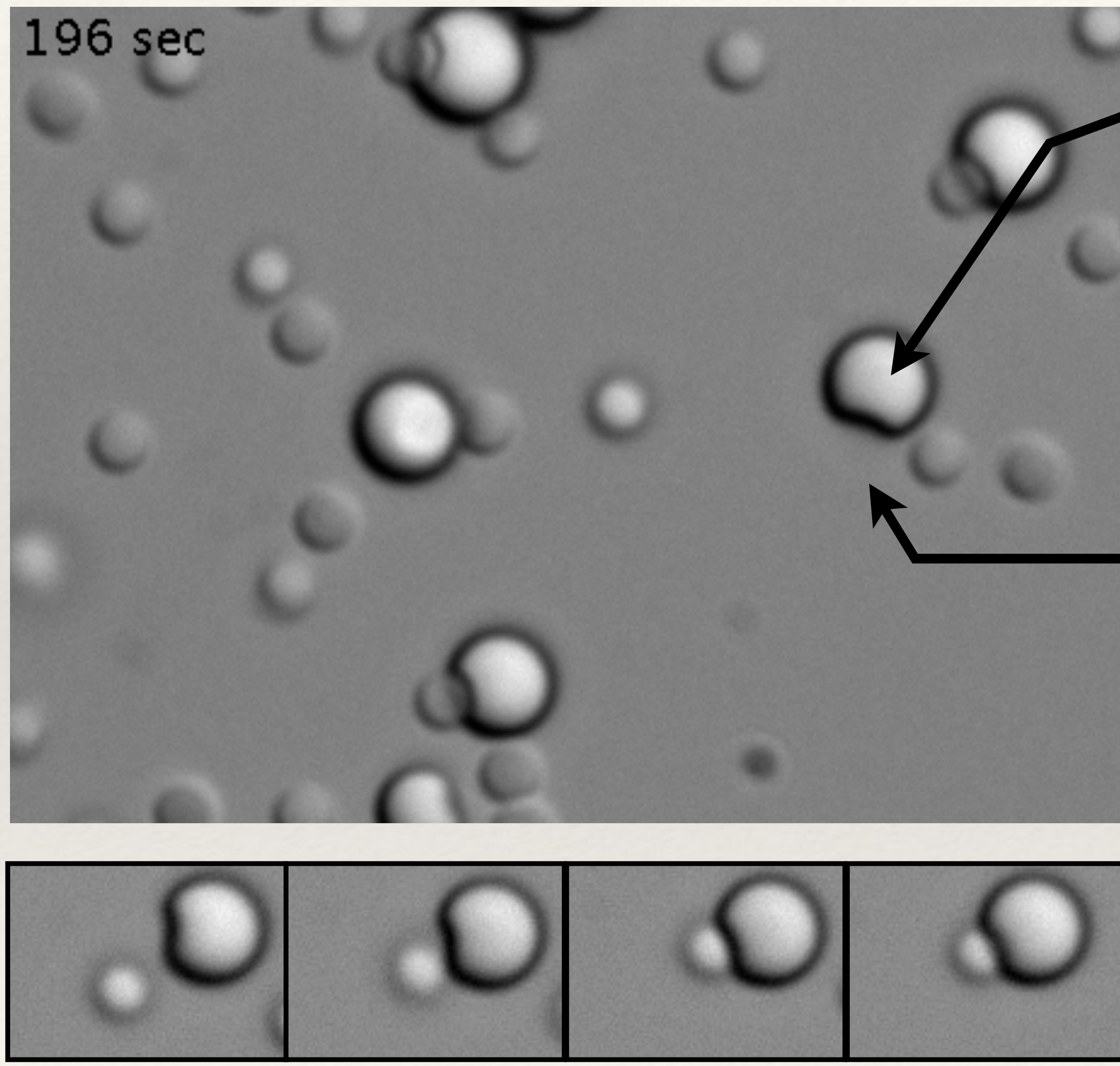




can tune interaction strength

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

Pacman depletion movie

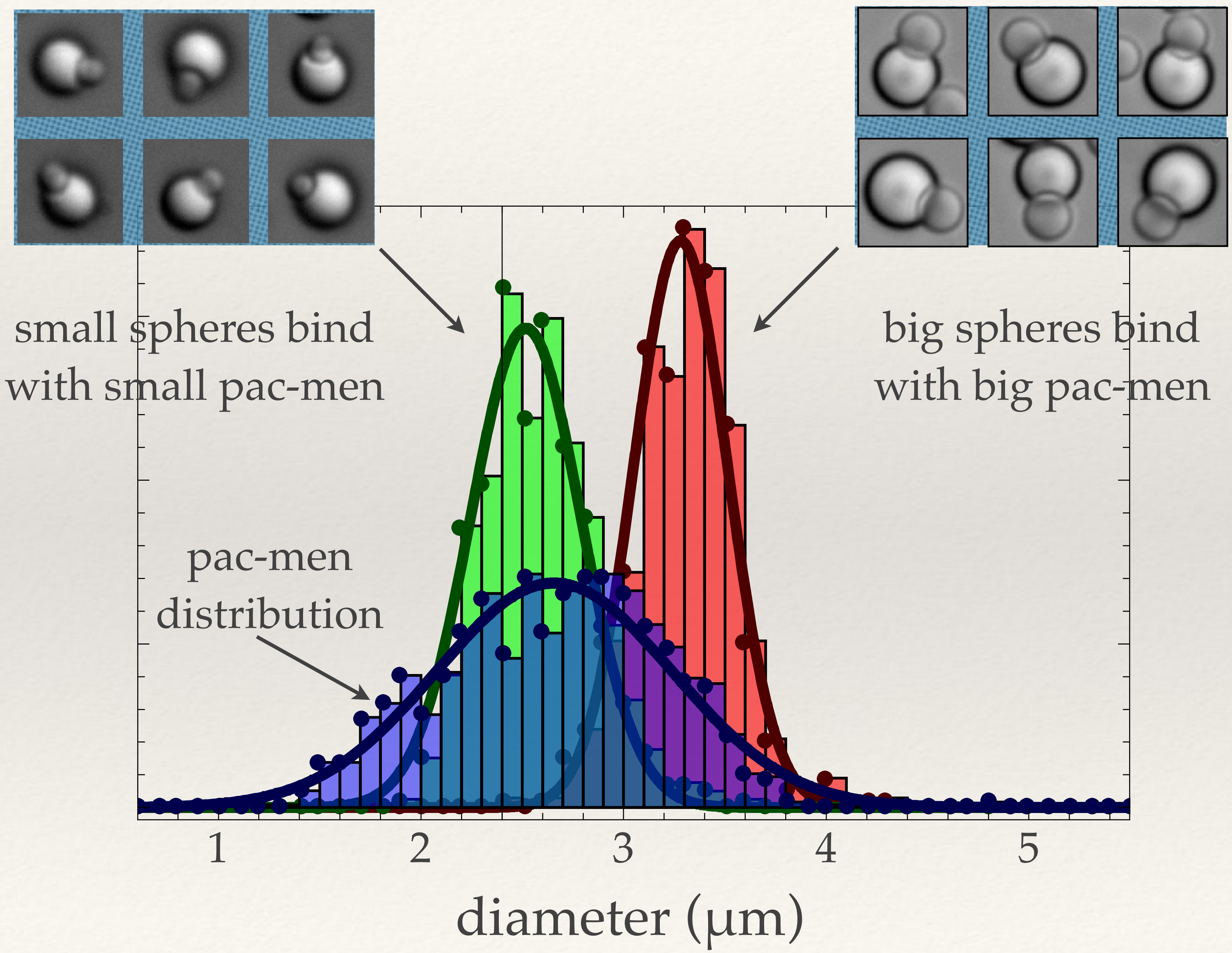


Watch this pac-man

Particle (key) binds to PacMan (lock)

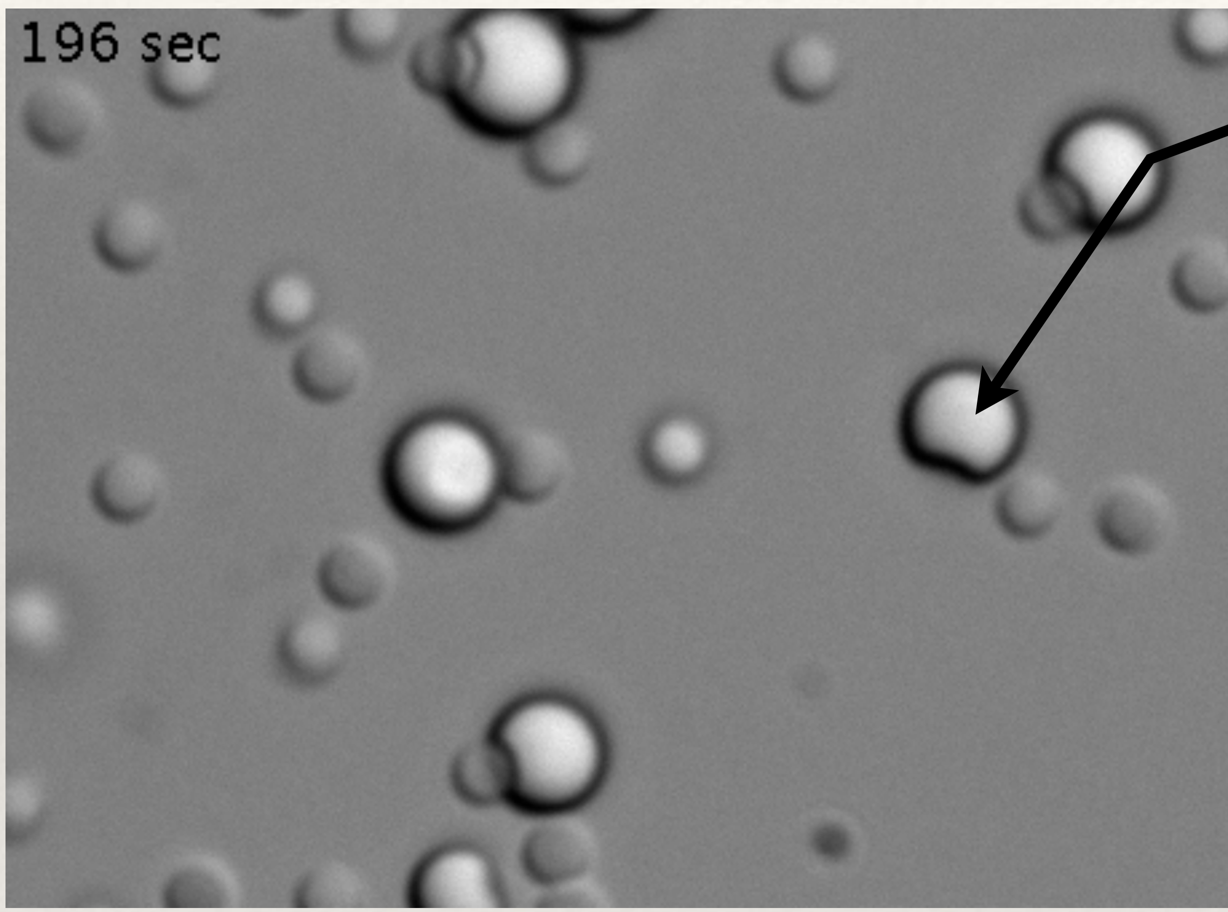
Sacanna *et al.*, Nature **464**, 575–578 (2010)

Size selectivity

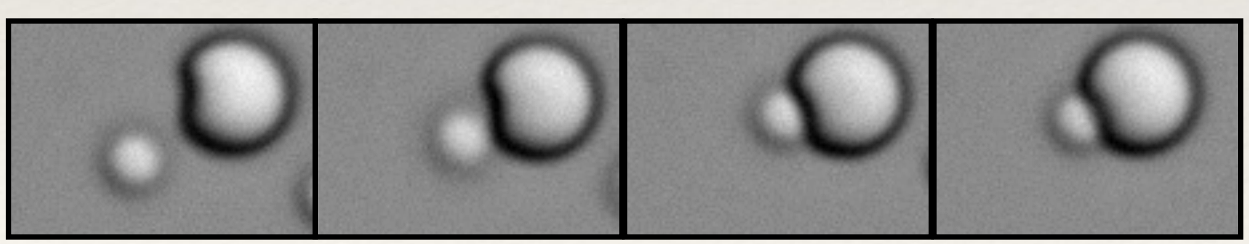


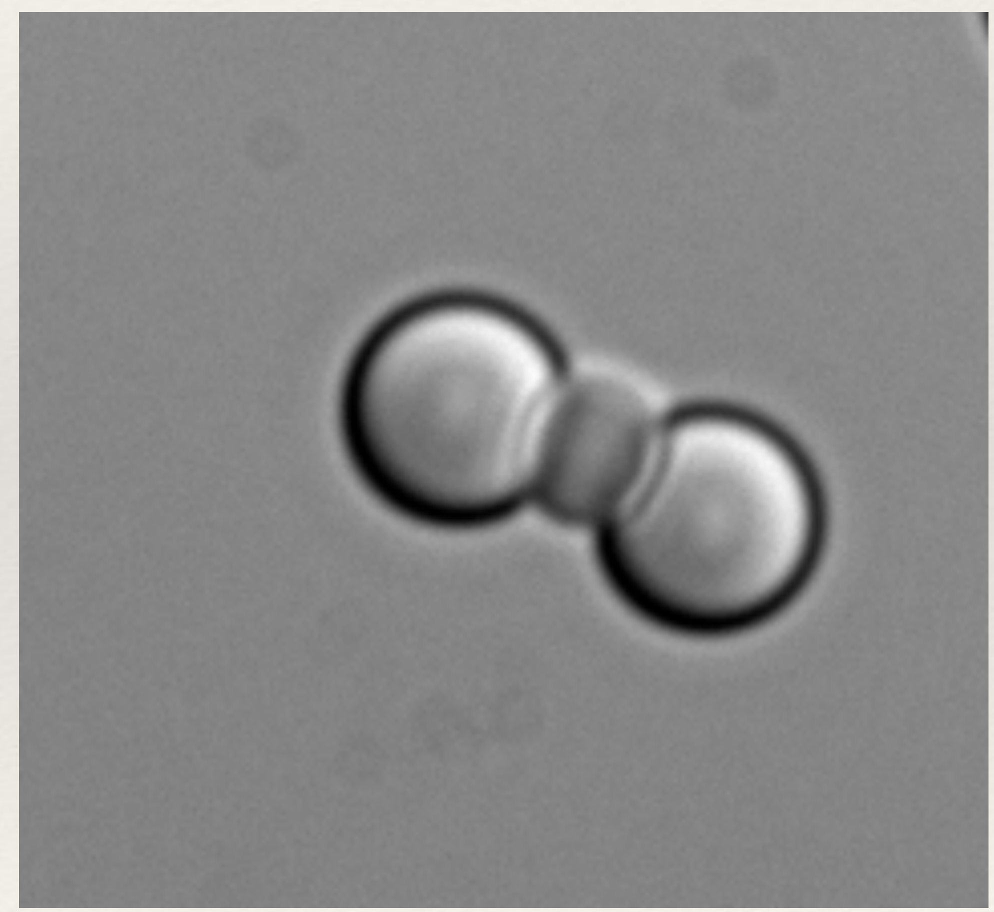
Sacanna *et al.*, Nature **464**, 575–578 (2010)

Pacman depletion movie



Watch this pac-man





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

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)

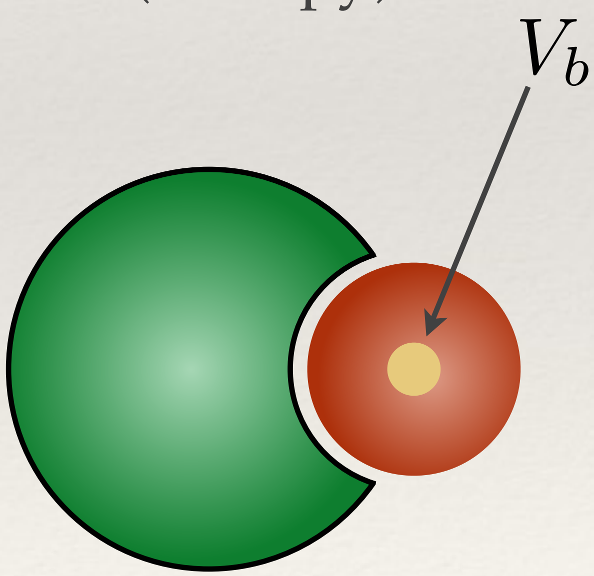
overlap area

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

polymer (depletant) radius

equilibrium separation

Debye screening length (repulsion)

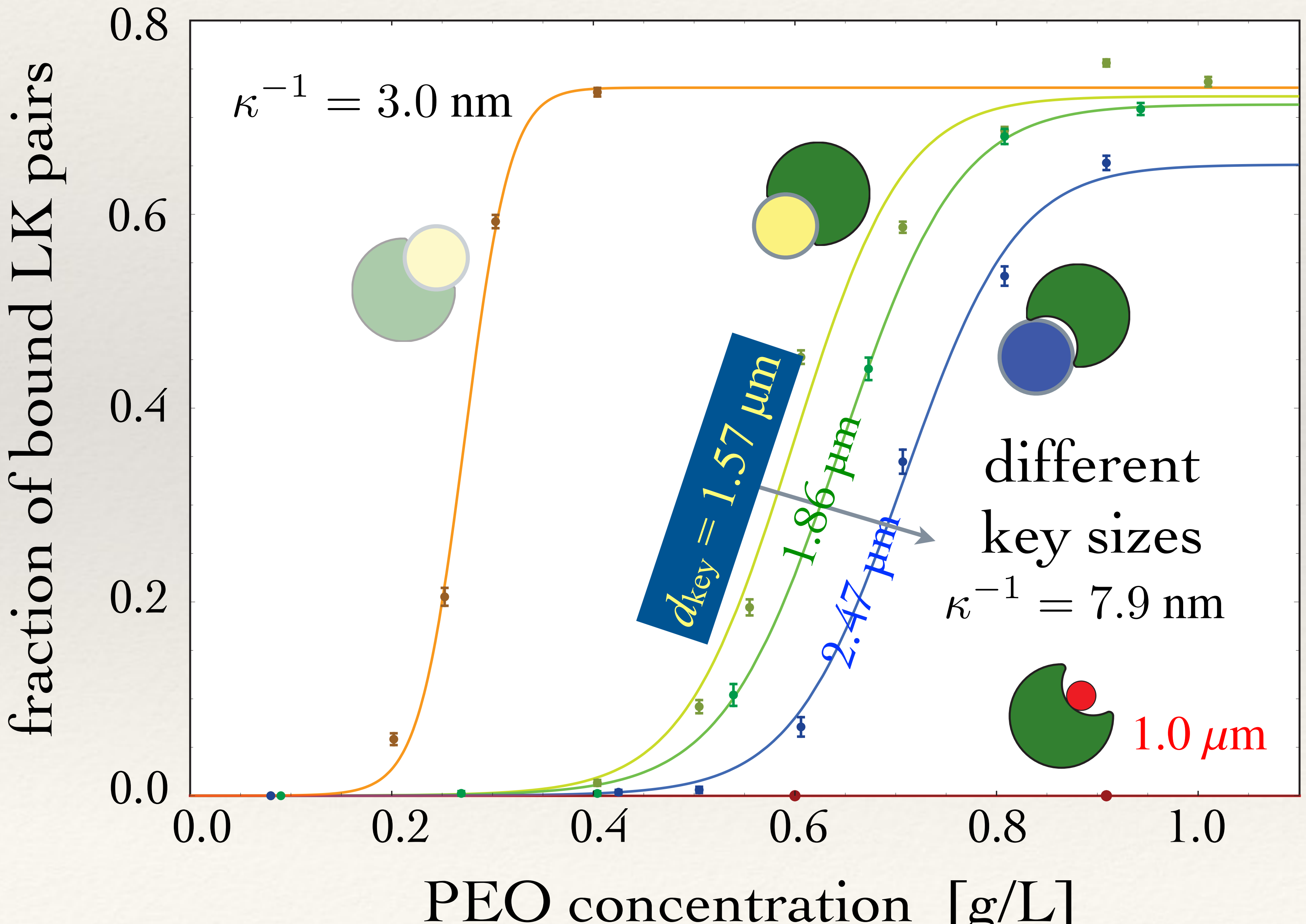


Lock & key binding energy: balance between electrostatic repulsion and depletion attraction

Entropy: binding volume vs unbound volume per key

Lock-and-key binding data

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



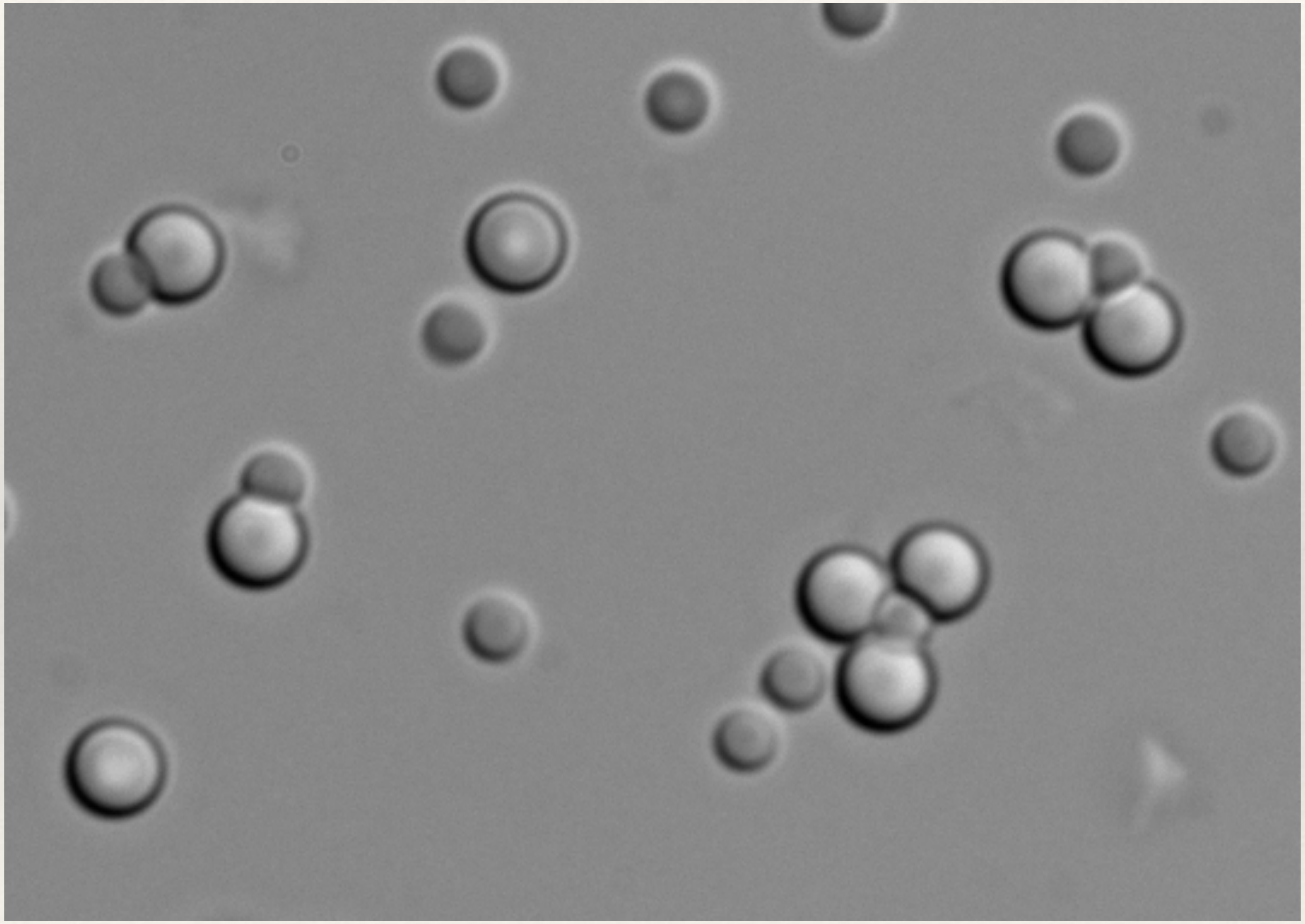
<u>fitting parameters</u>

$A \approx 0.5\ \mu\mathrm{m}^2$

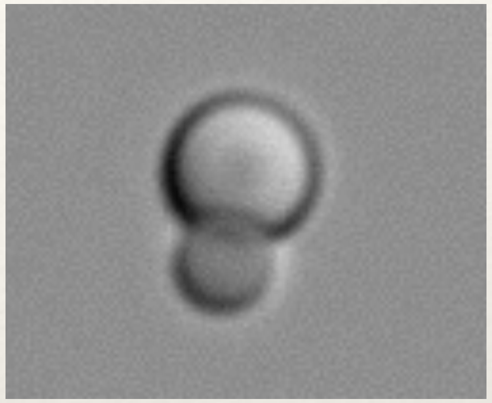
$\approx 1/15^{\mathrm{th}} A_{\mathrm{sphere}}$

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

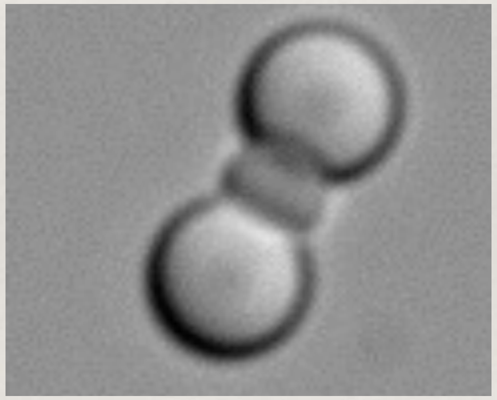
Colloidal couplings



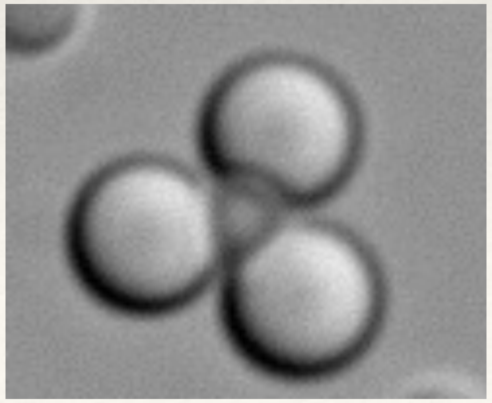
monomer



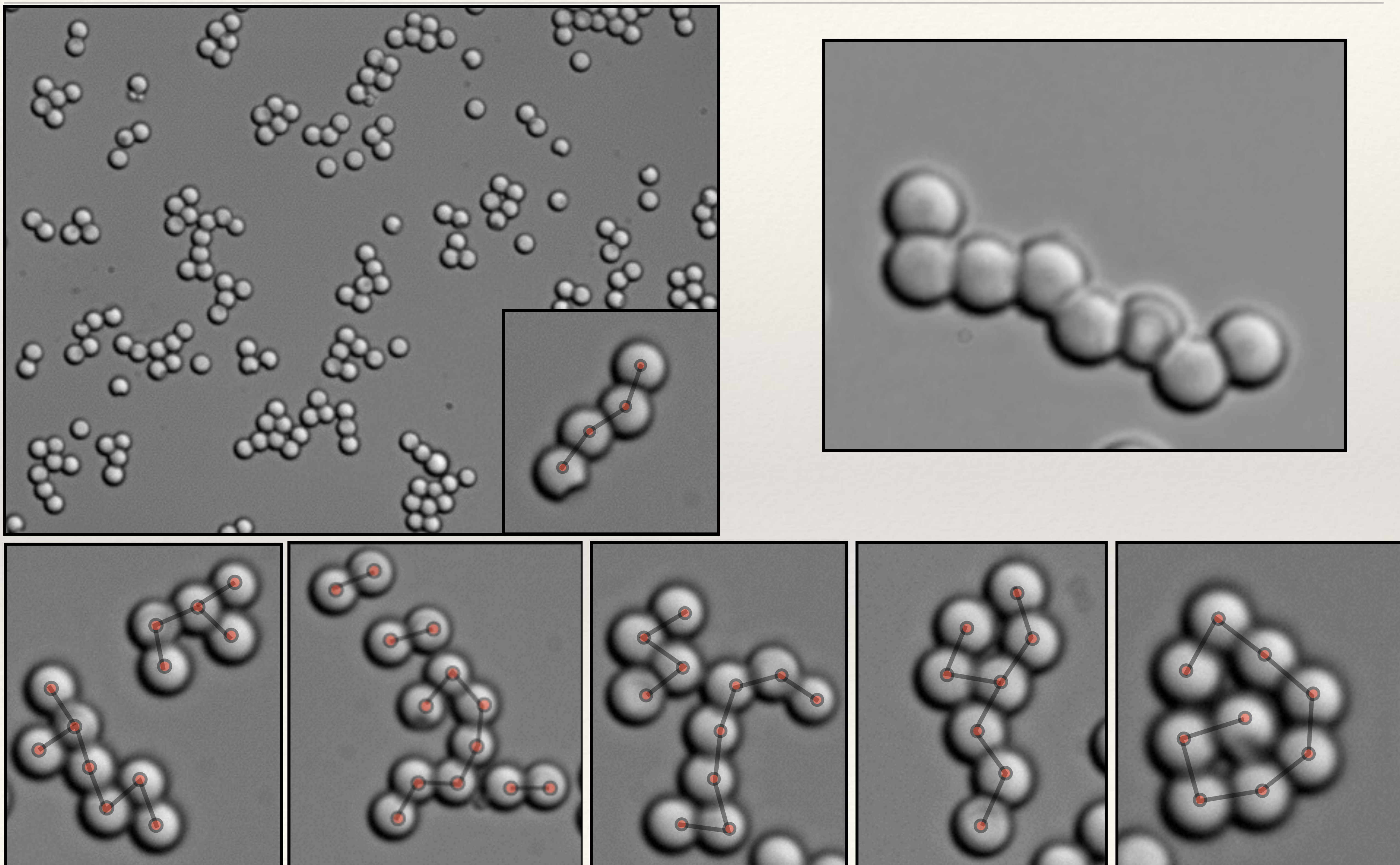
dimer



trimer



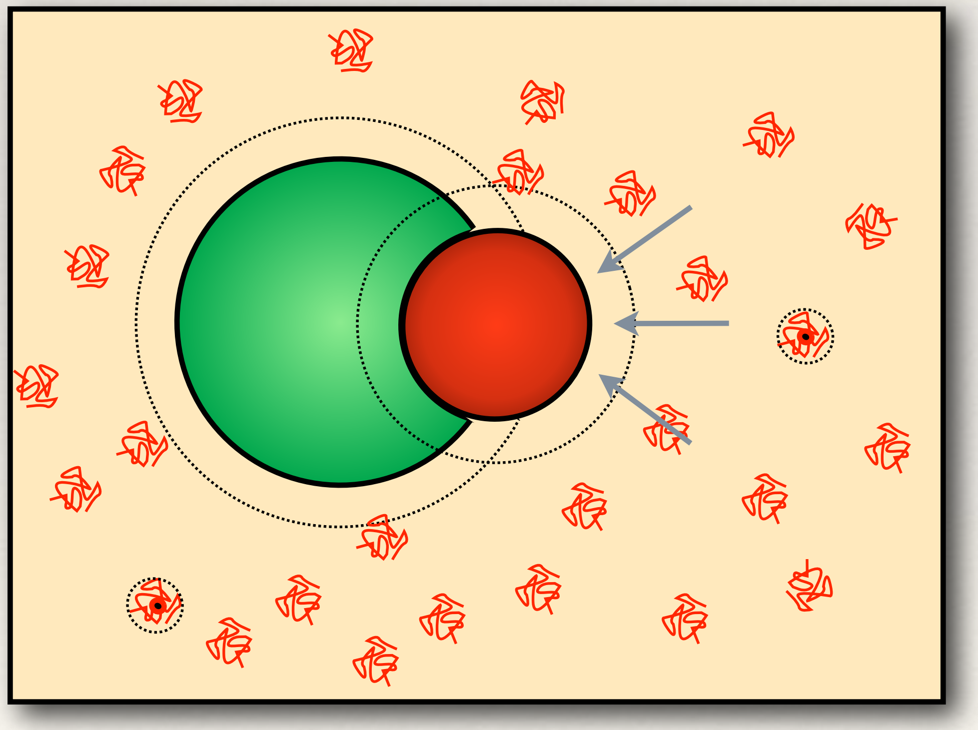
Pacman polymers



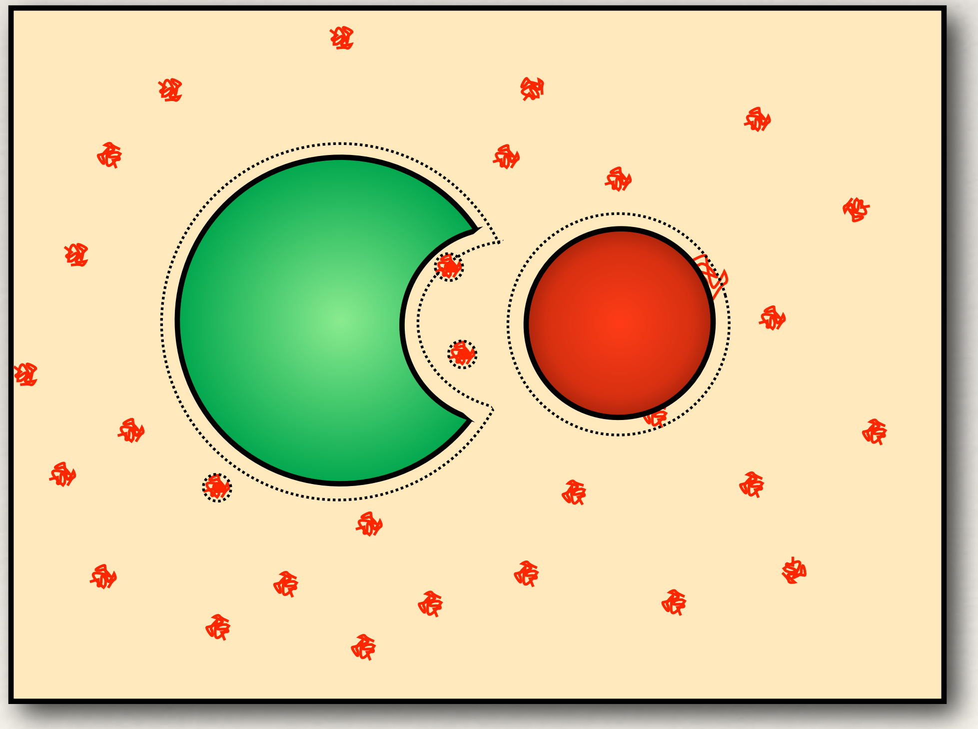
Tunable depletion attraction

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

NIPAM gel particles shrink when heated above 39°



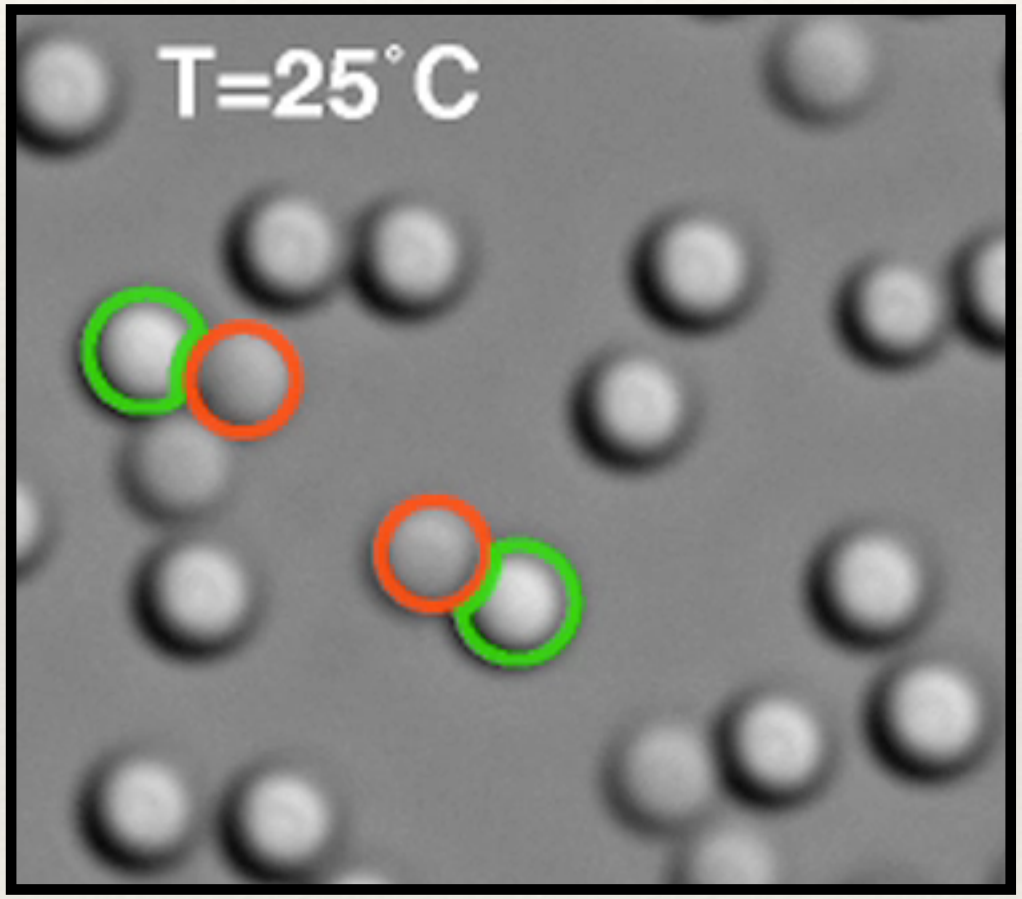
$T \approx 25^{\circ}$



$T \approx 40^{\circ}$

Tunable melting

Start at 25°C, then heat to 40°C

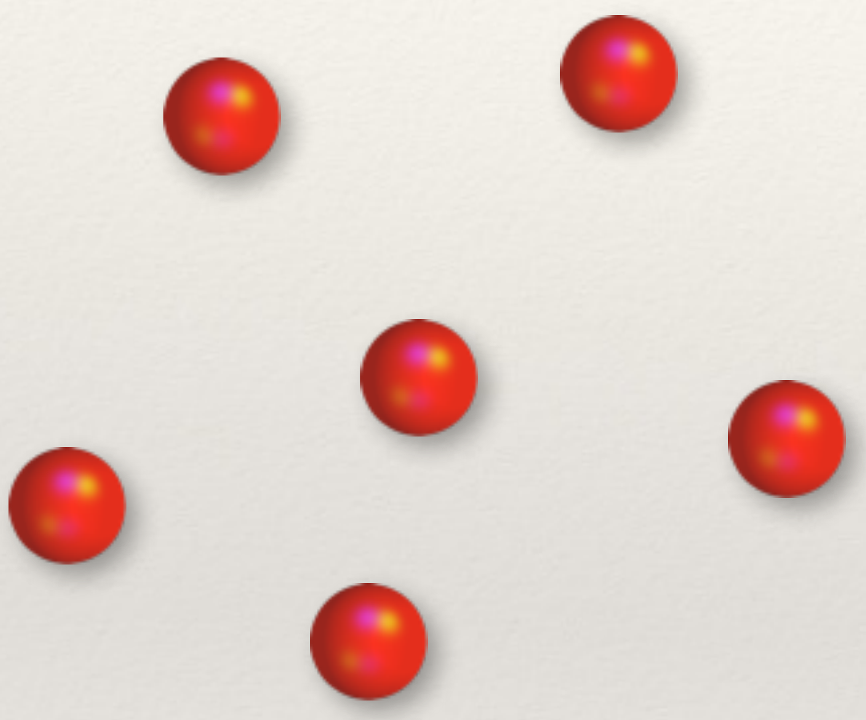


3x speed

Particle pairs dissociate at 40°C

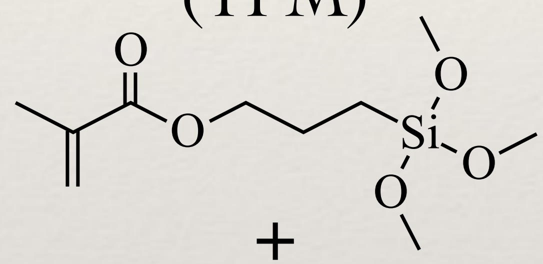
More perfect pacmen

Heterogeneous nucleation



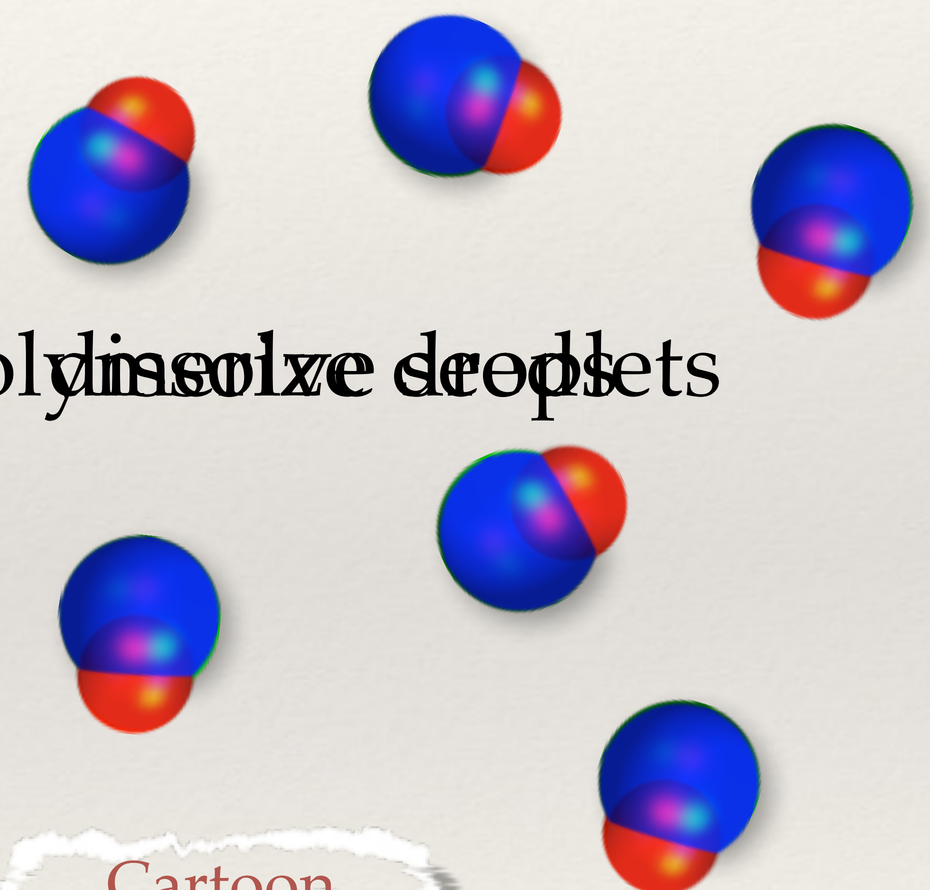
Monodisperse seeds
(PS, PMMA, silica, etc.)

grow droplets



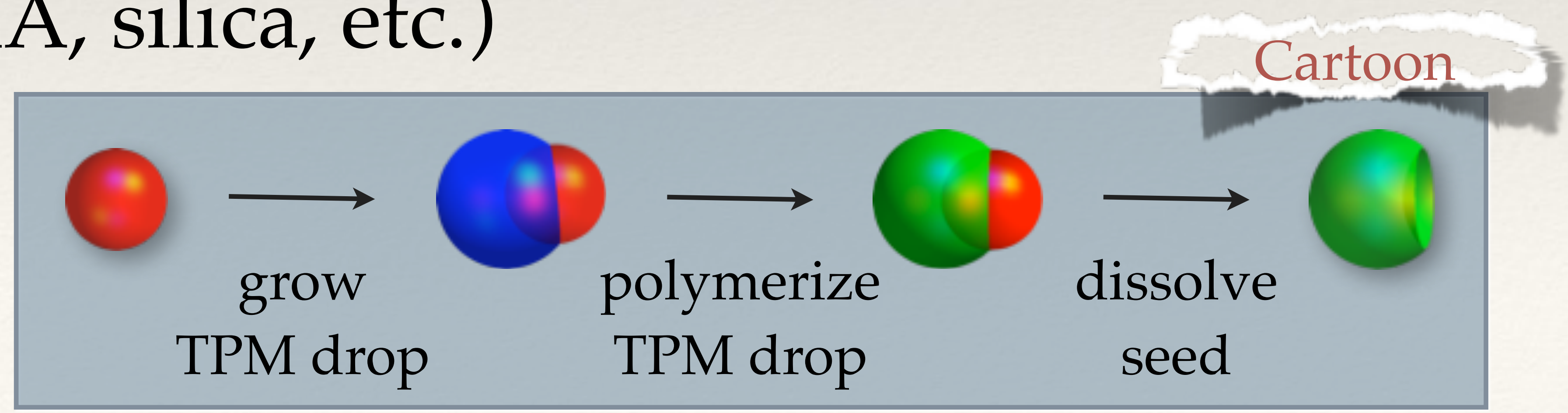
+

NH_3



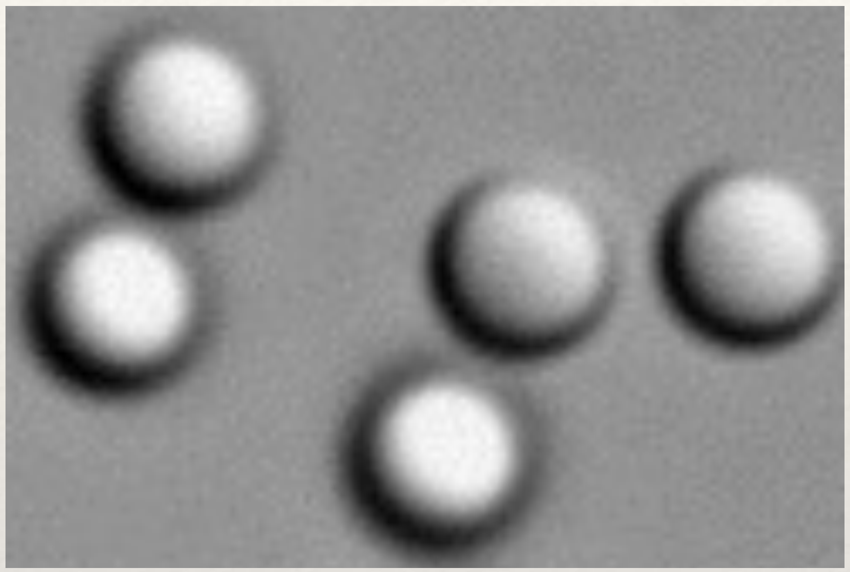
polymerize droplets

dissolve seeds

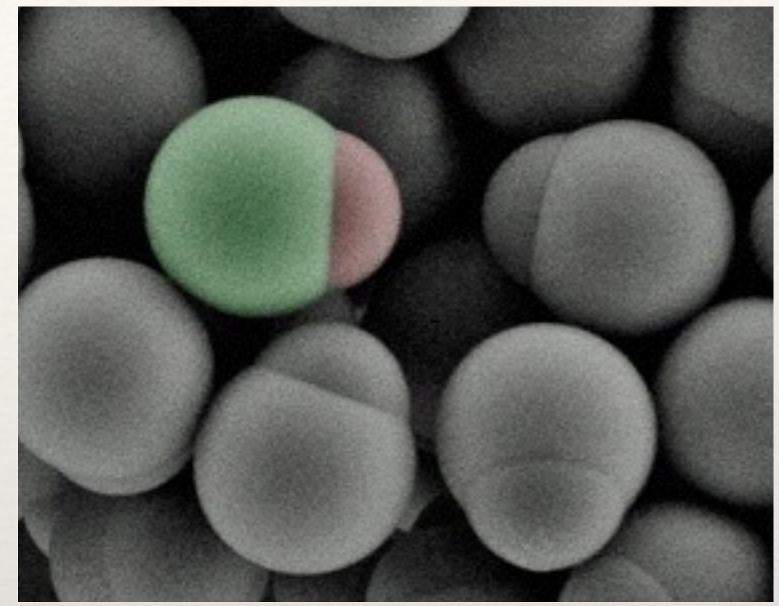


The real colloids

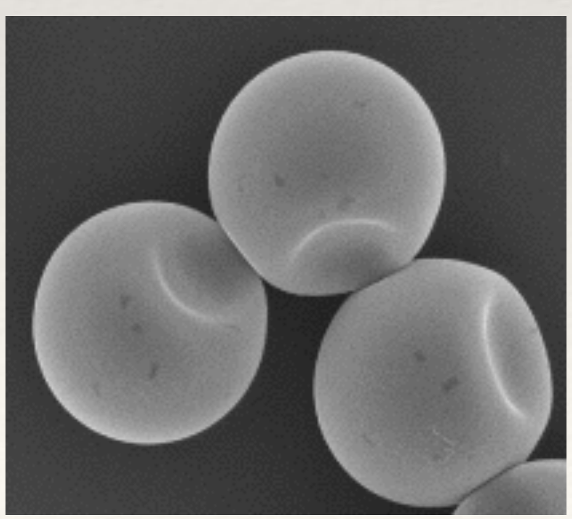
seeds



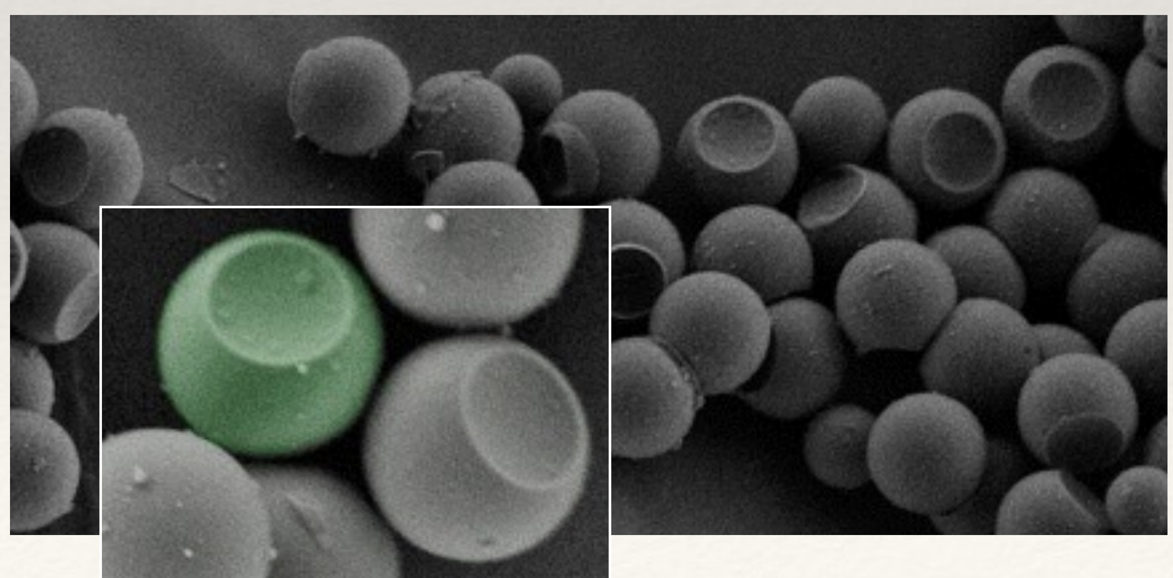
TPM on seeds



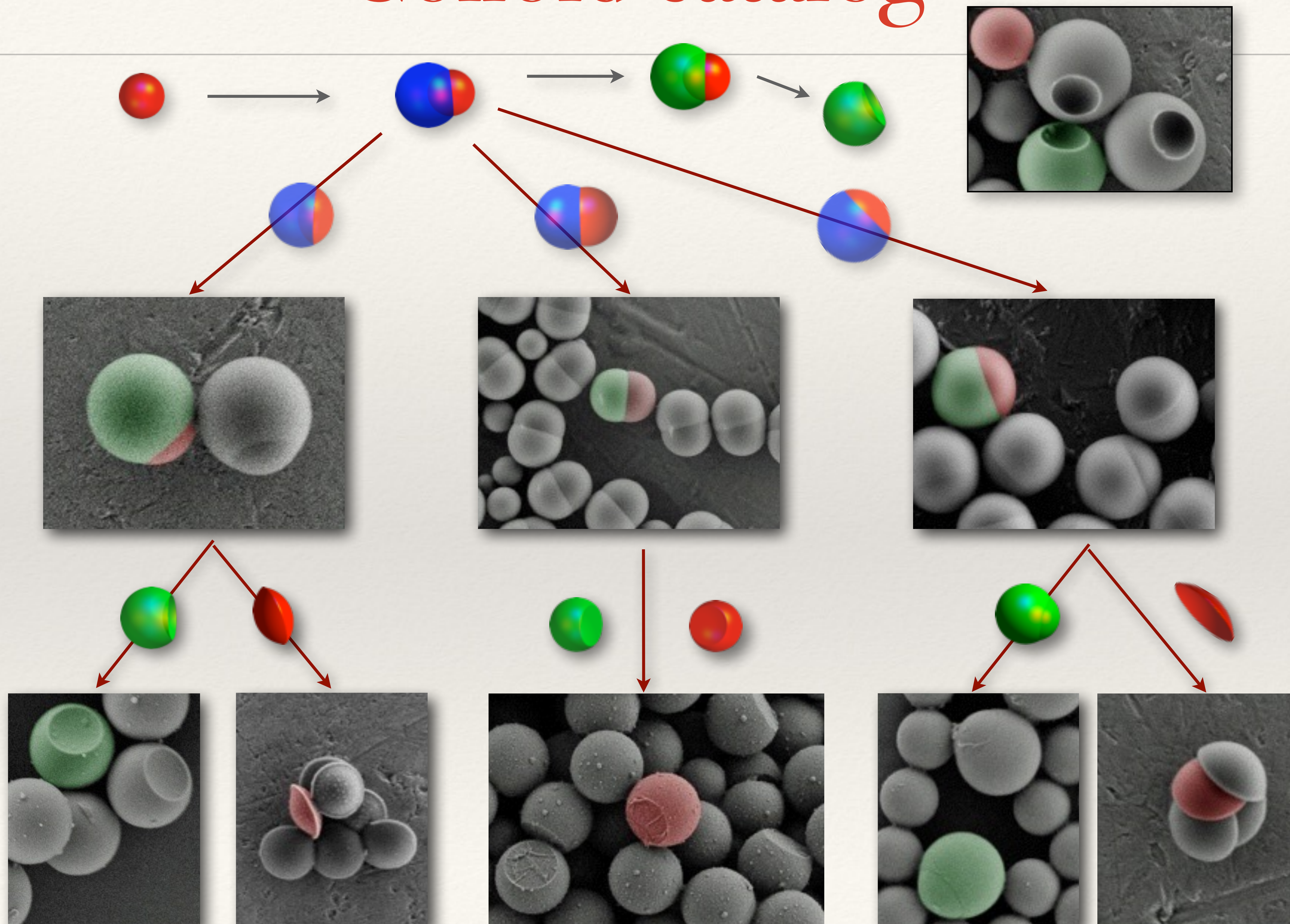
old pacmen



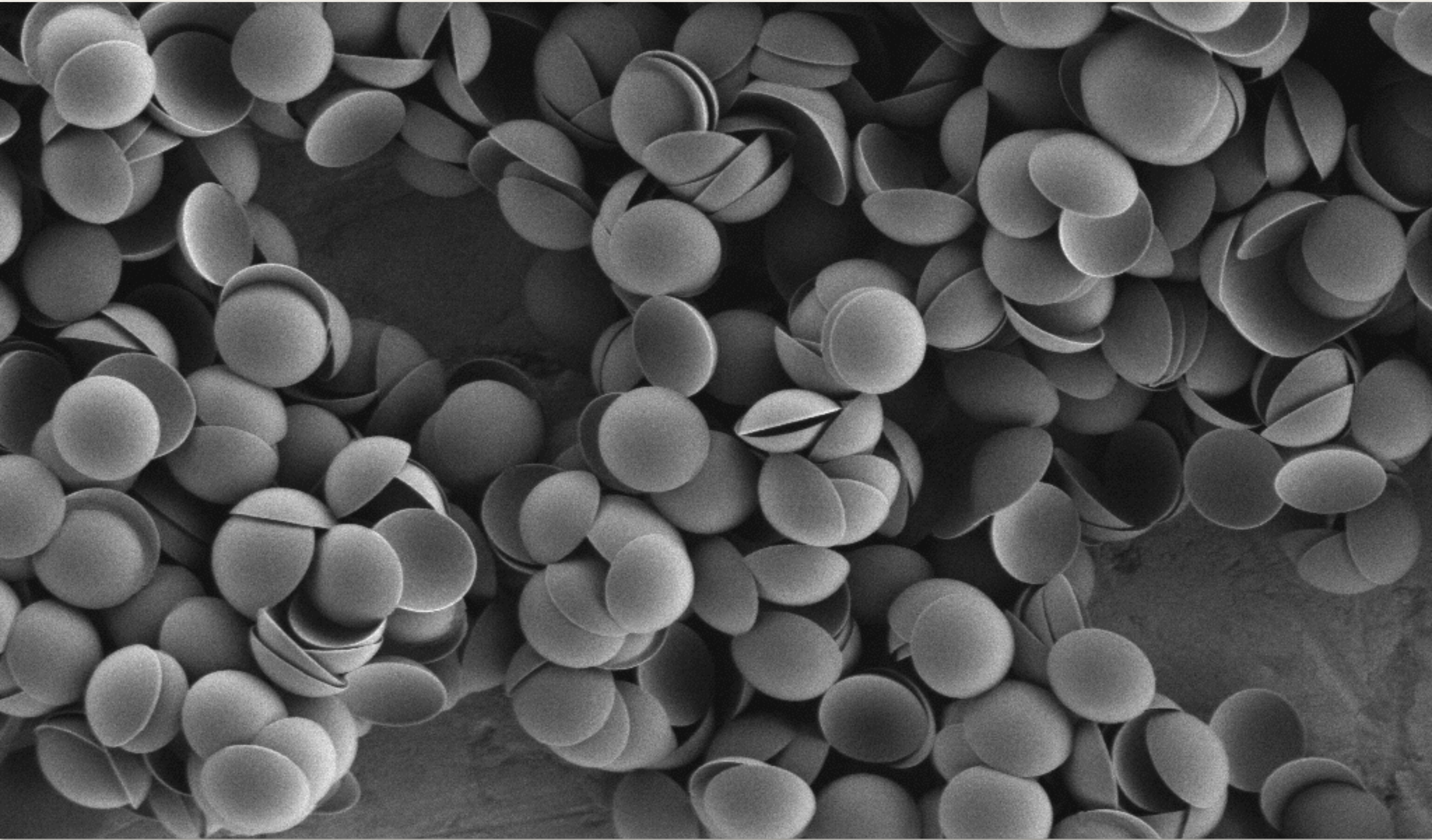
pacmen



Colloid catalog



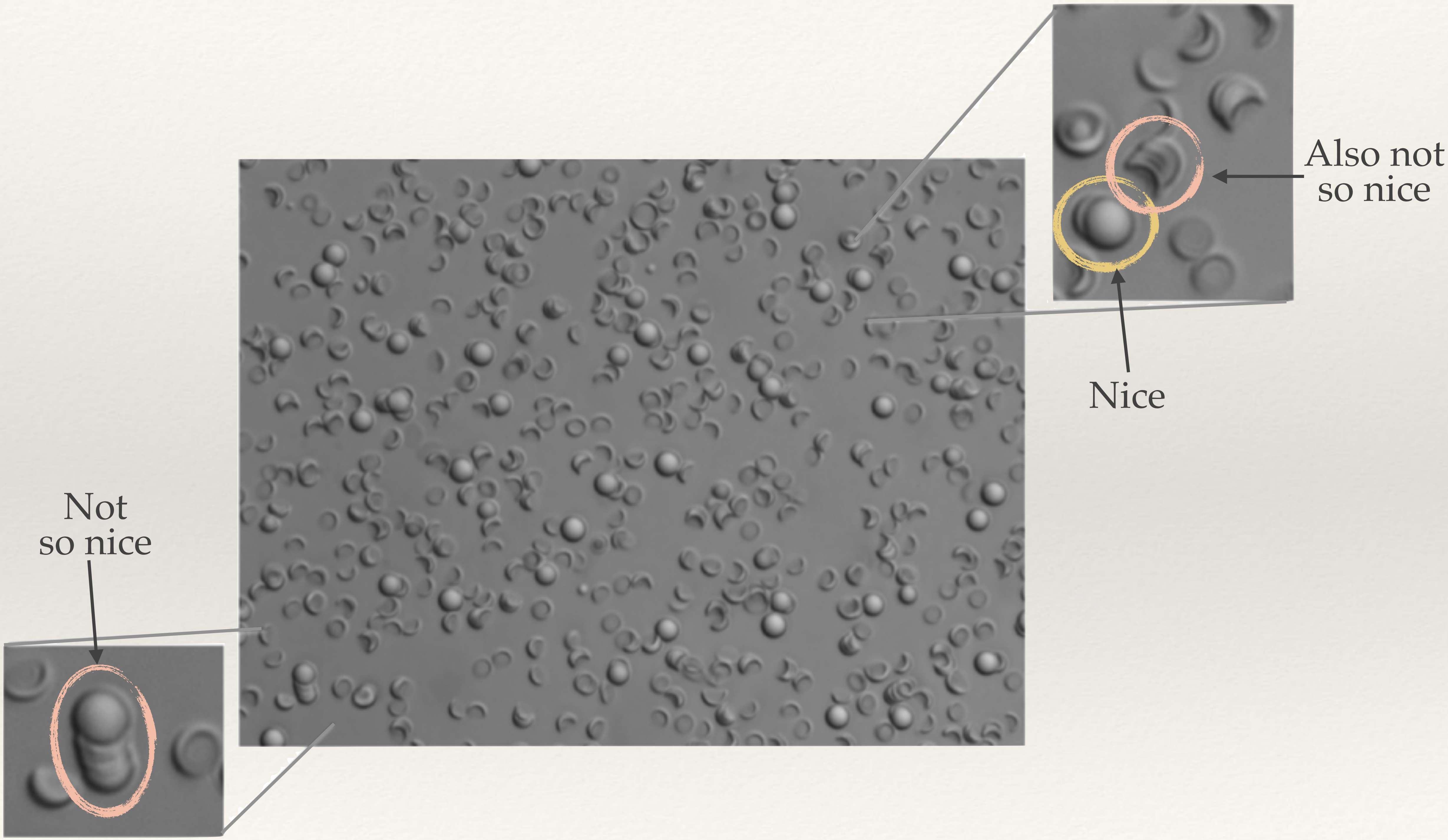
Micrometer size lenses



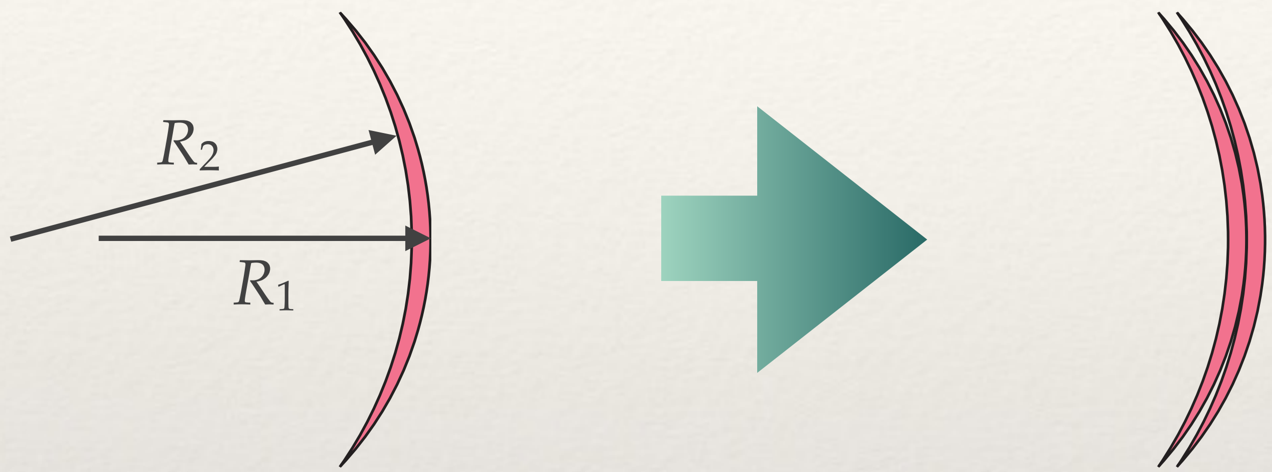
900 nm plastic lens particles dancing in water


Chains form when PEO depletant is added

Placing lenses on spheres

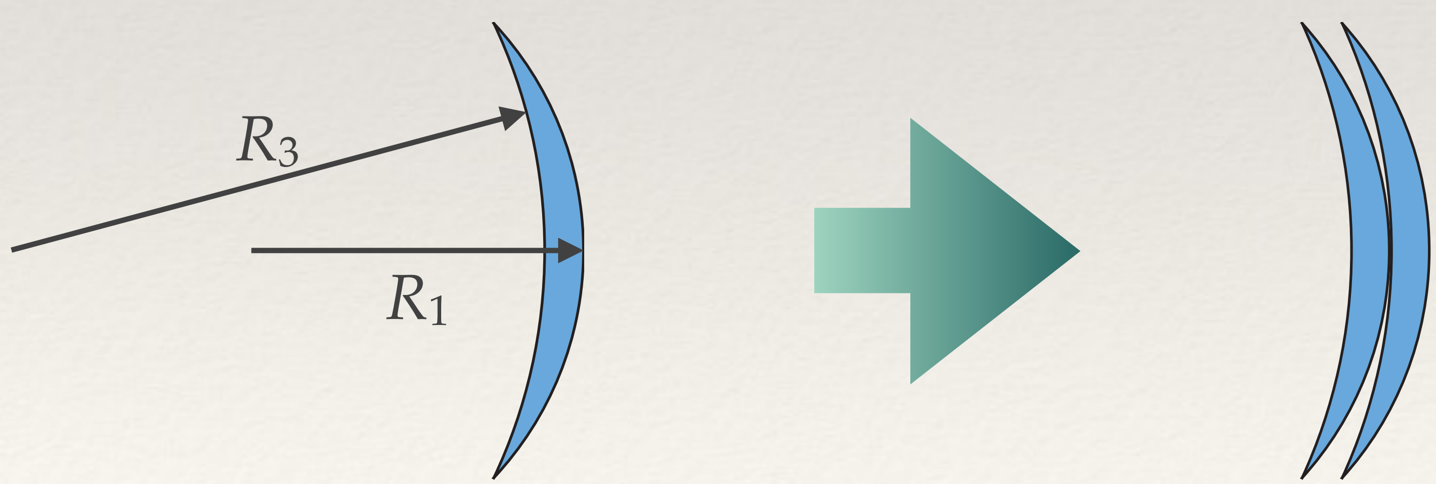


Get off my back!



more overlap
binding

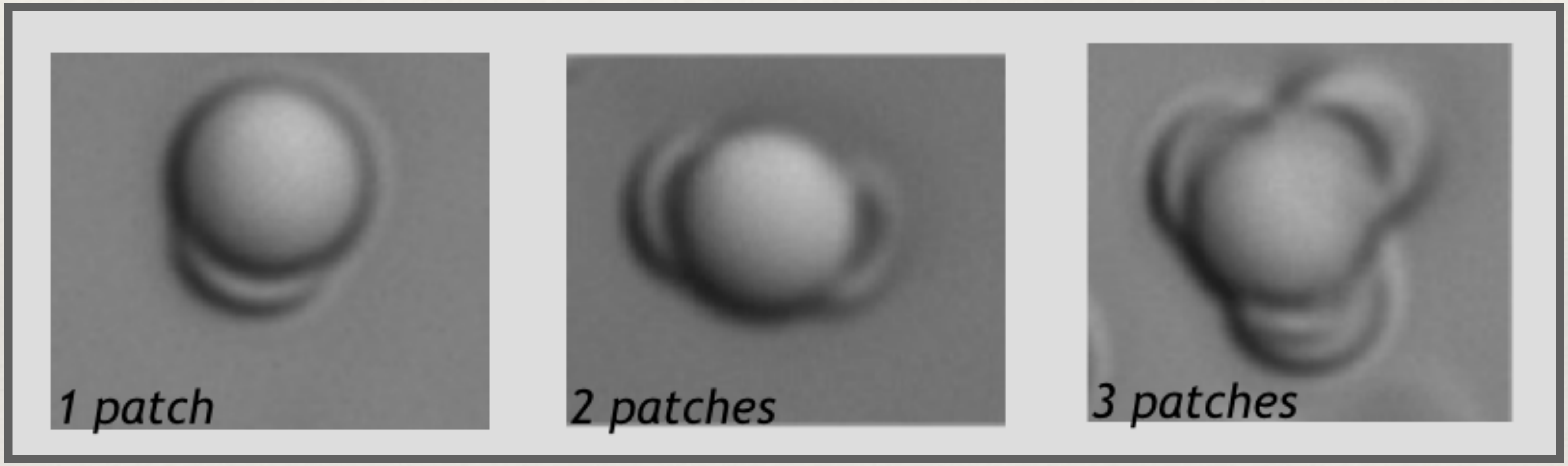
$R_1 < R_2 < R_3$



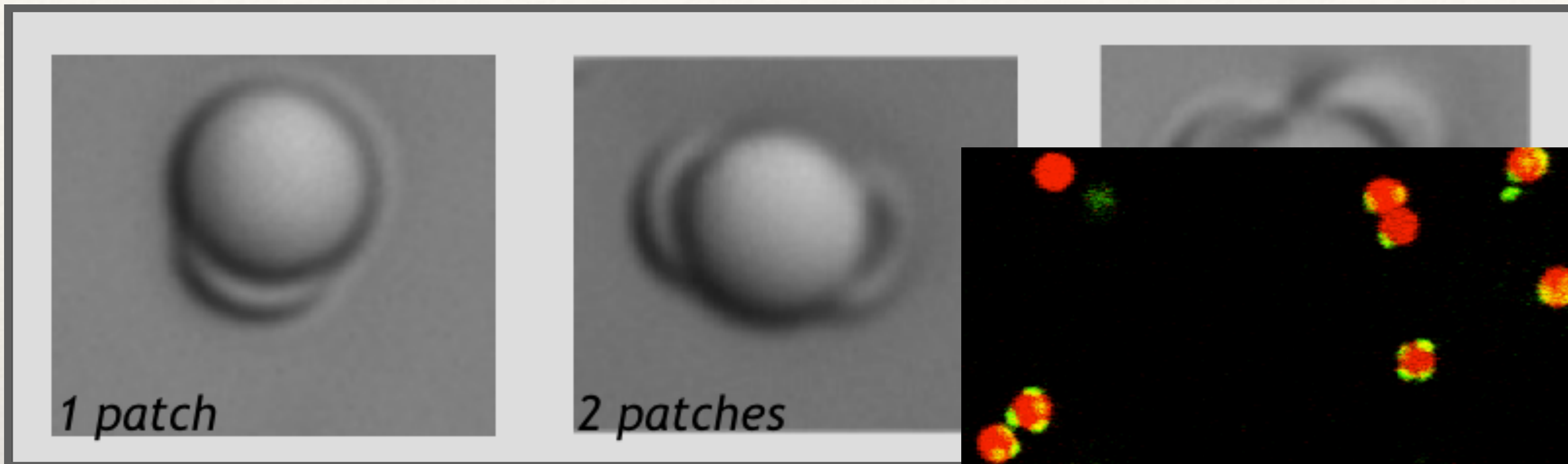
less overlap
no binding

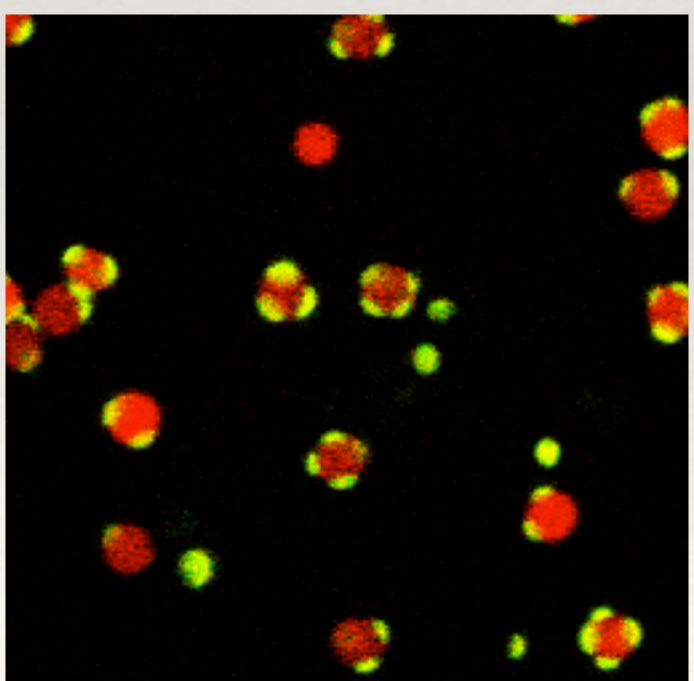
Single lenses make nice patchy particles

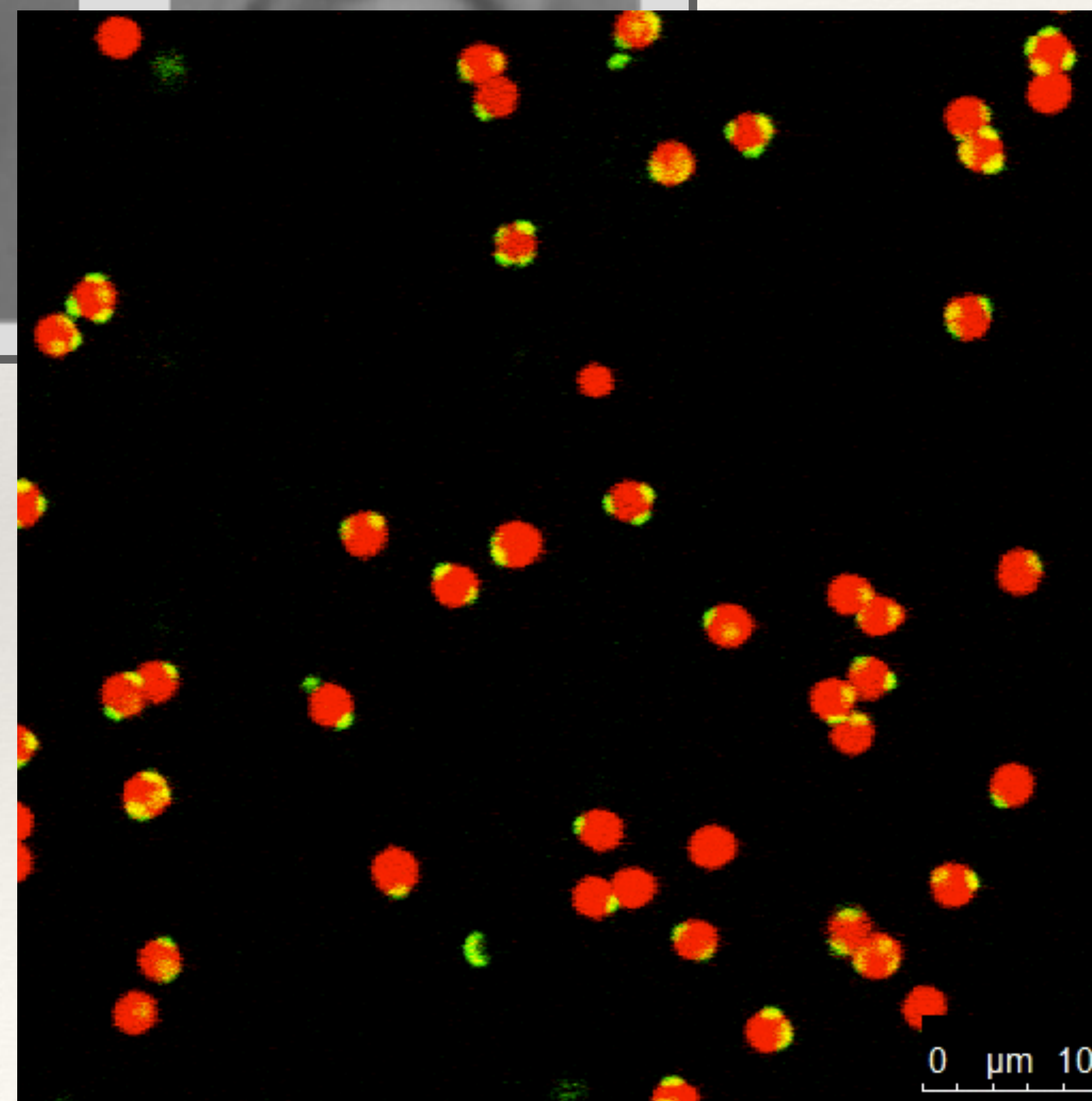
Lens particles attached to spheres using depletion interaction



Fluorescent mobile patches







Next lectures …

Patchy colloids with DNA

(or diamonds are a boy's best friend)