

COLLOIDAL SELF ASSEMBLY I: INTERACTIONS & PACMEN

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2012 Boulder Summer School

24 July 2012
Boulder, Colorado

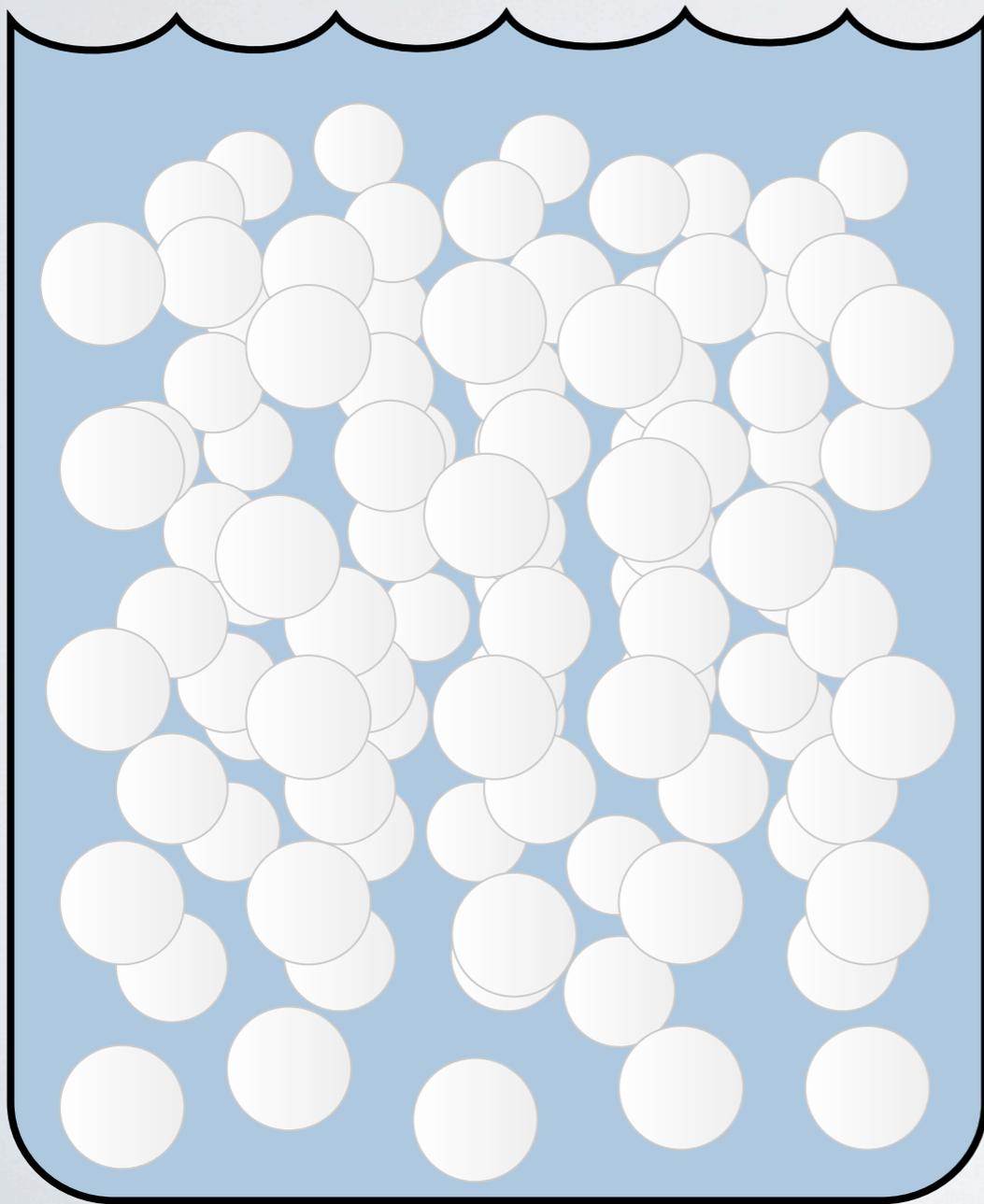
Outline of lectures on colloids

- Lecture I: Today
 - ▶ 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: Tomorrow
 - ▶ Lock & key colloids
 - ▶ Colloids with valence
 - ▶ Colloidal molecules: to infinity and beyond

What are colloids?

Small particles suspended in a liquid

Brownian motion is important



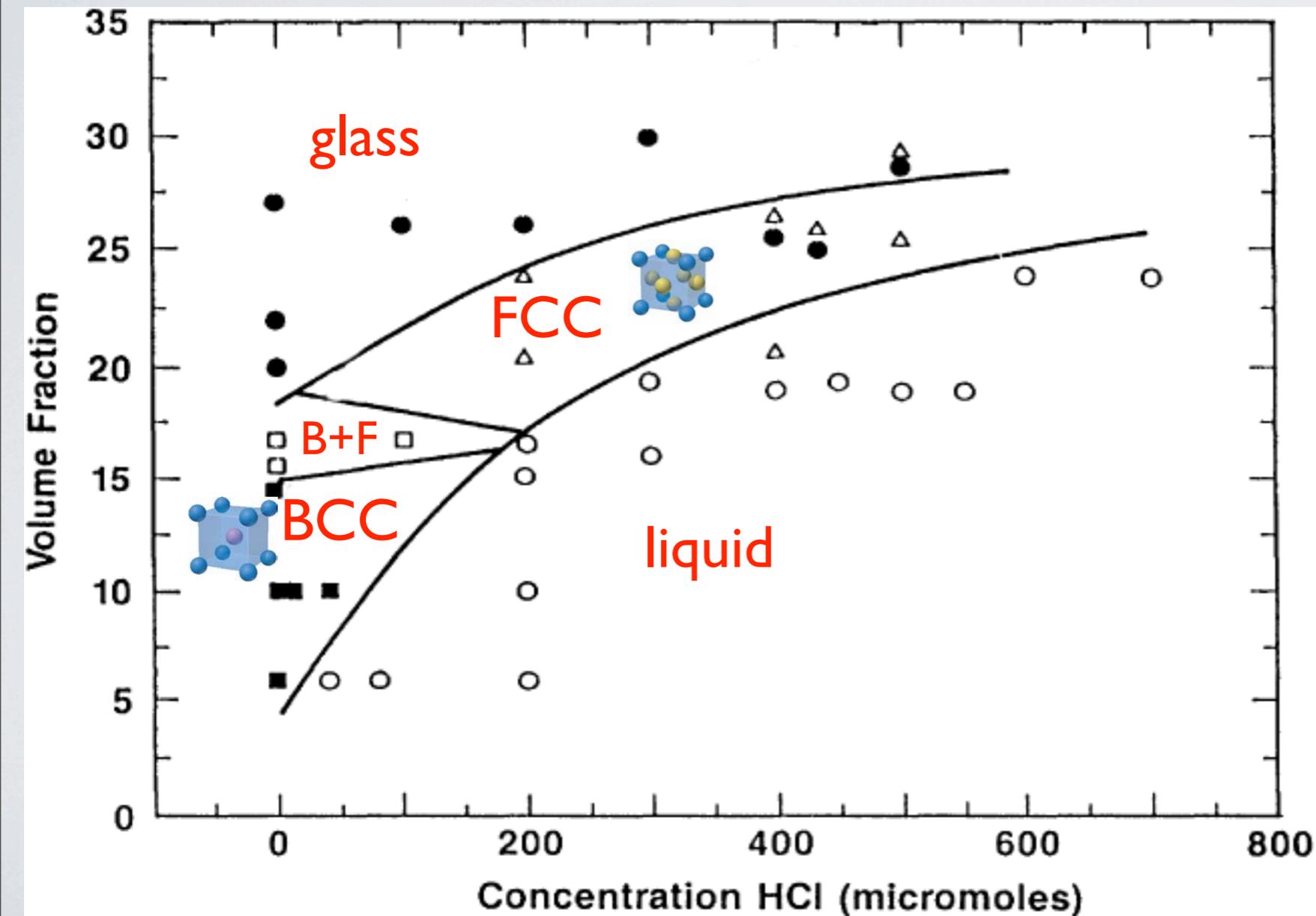
COLLOIDS:

- ✱ Diameters \sim 5 nm to 5 μm
suspended thermally
- ✱ Materials
 - plastic (PS, PMMA, ...)
 - inorganic (SiO_2 , TiO_2 , ...)
 - semiconductor (CdSe, ...)
 - metal (Au, Ag, ...)
- ✱ Stabilized against aggregation by
 - charge
 - surfactants
 - polymer brushes

Self assembly of charged colloids

Electrically charged colloids spontaneously form ordered structures

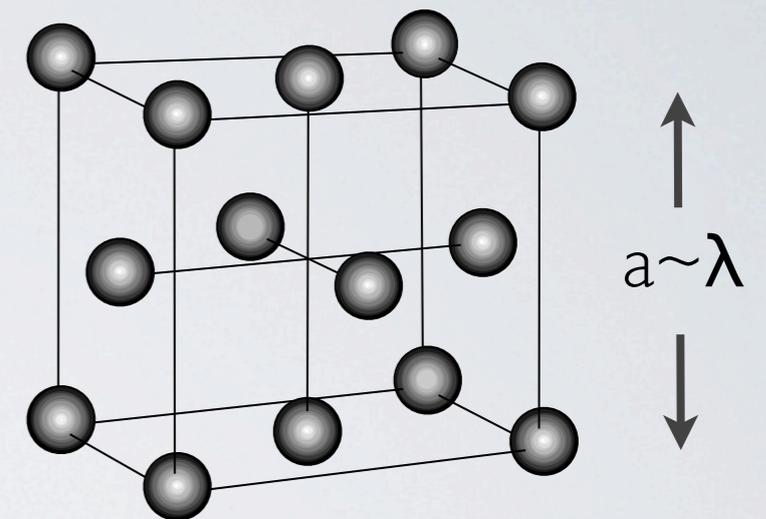
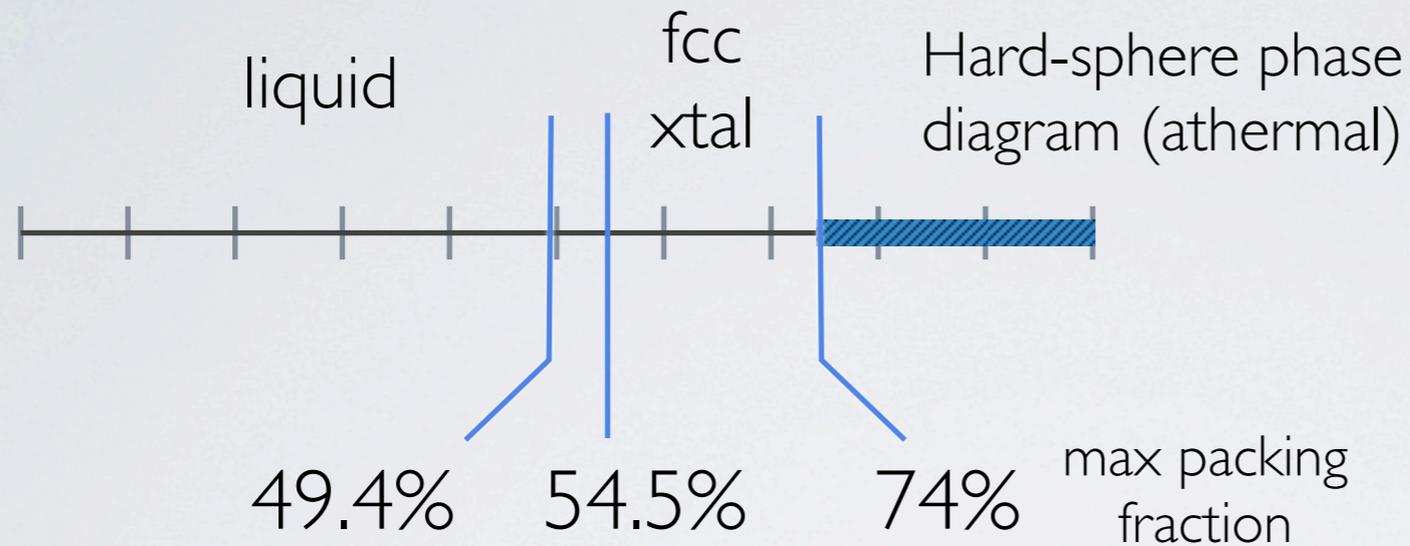
charged polystyrene spheres ($d = 91$ nm)
in methanol (90%) water (10%)



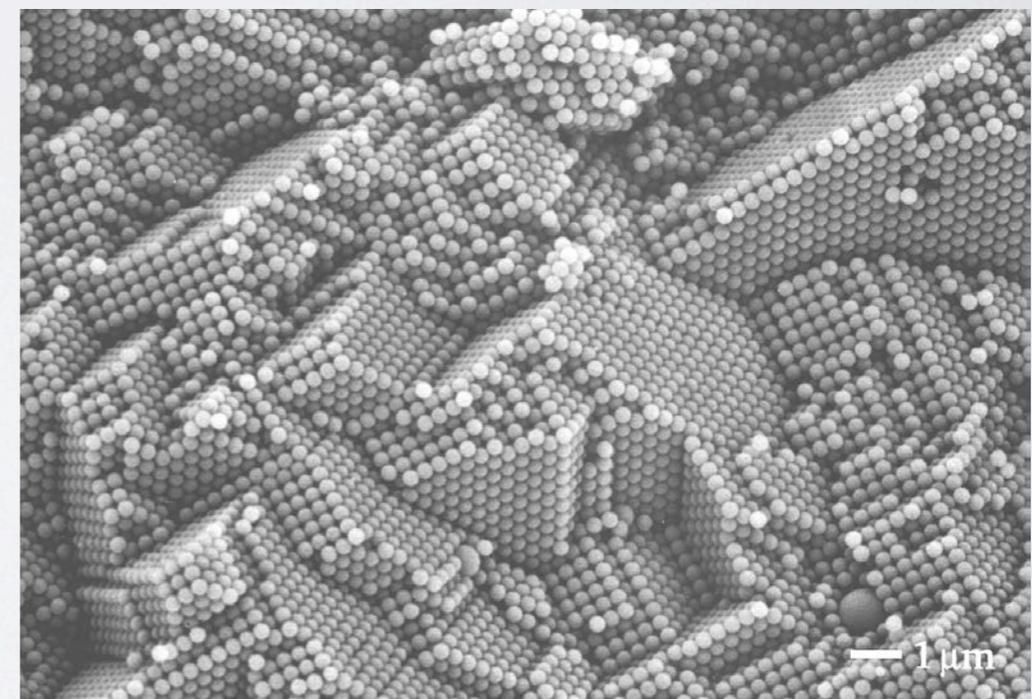
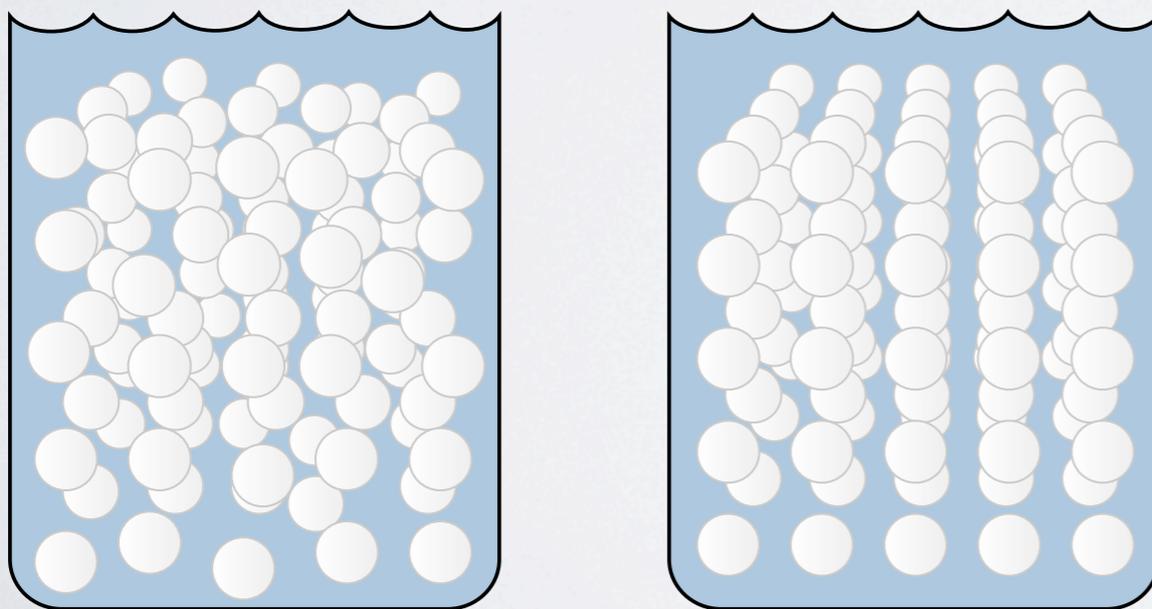
Crystallization driven by repulsive interactions

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

Self-assembly of hard spheres



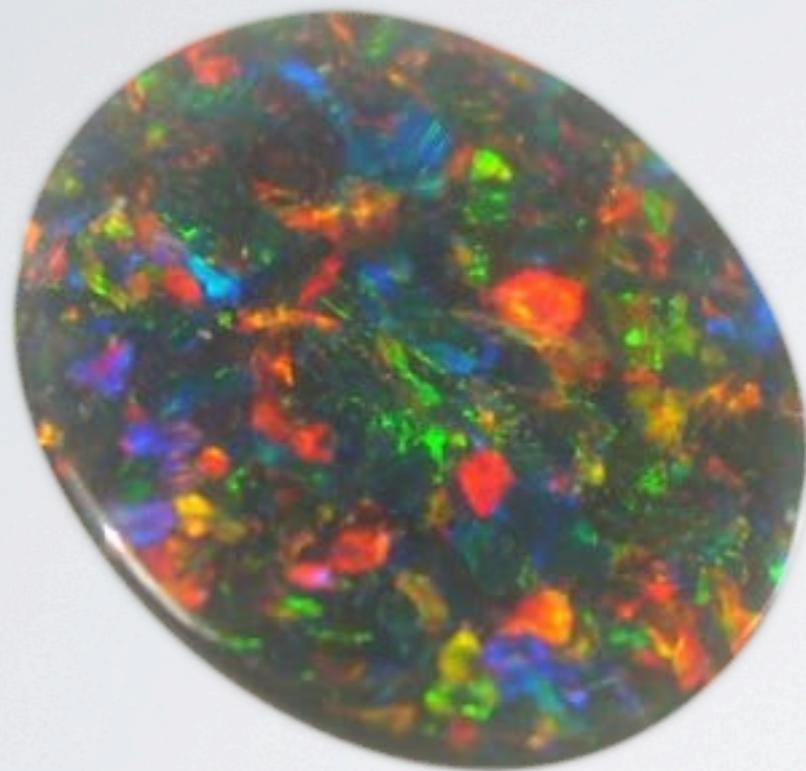
Crystallization driven by entropy



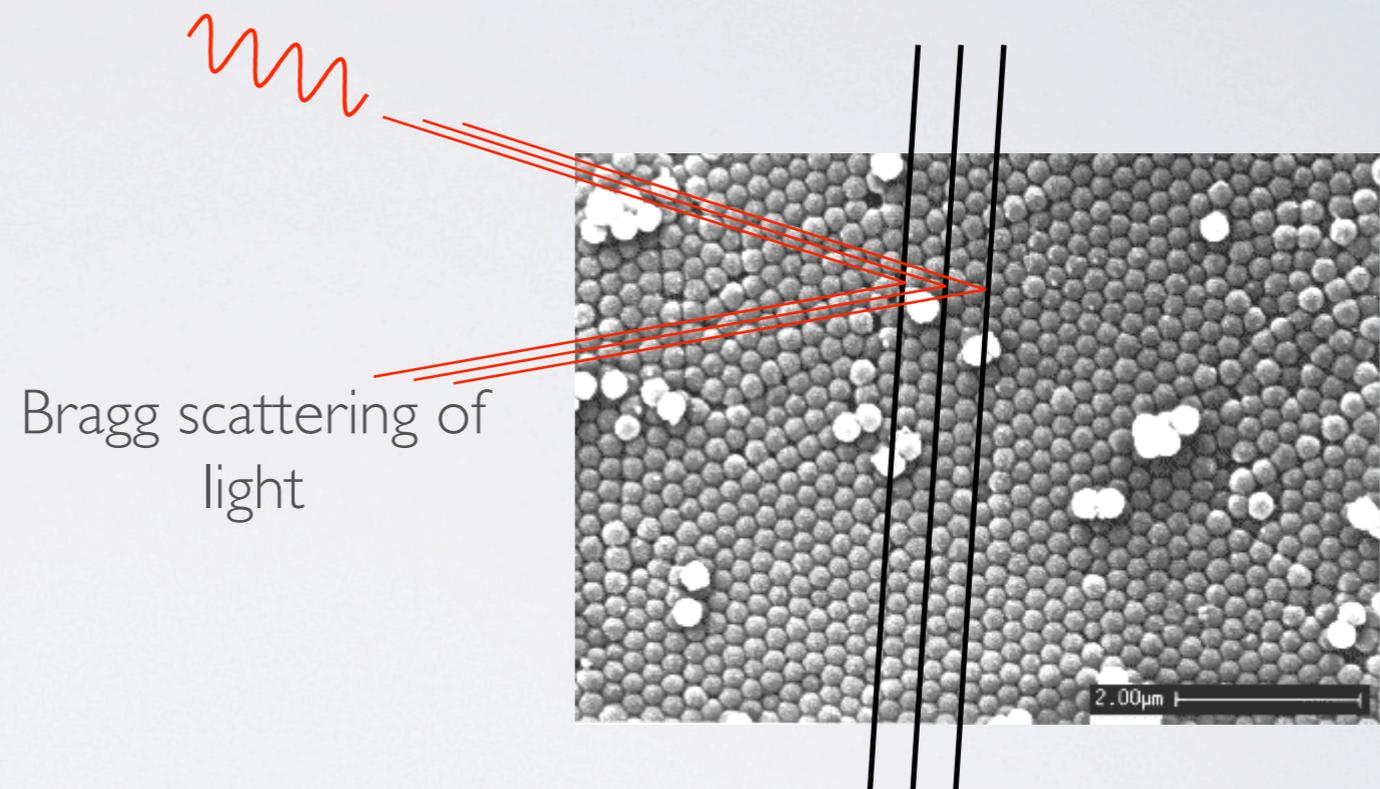
colloidal crystal with lattice constant $\sim 0.5 \mu\text{m}$

Interesting optical properties

Bragg scattering from different crystalline planes produce different colors



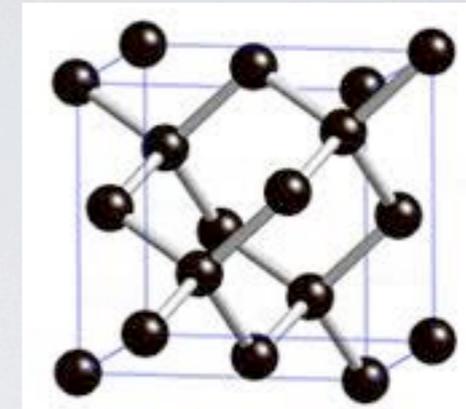
Gem quality opal from Australia



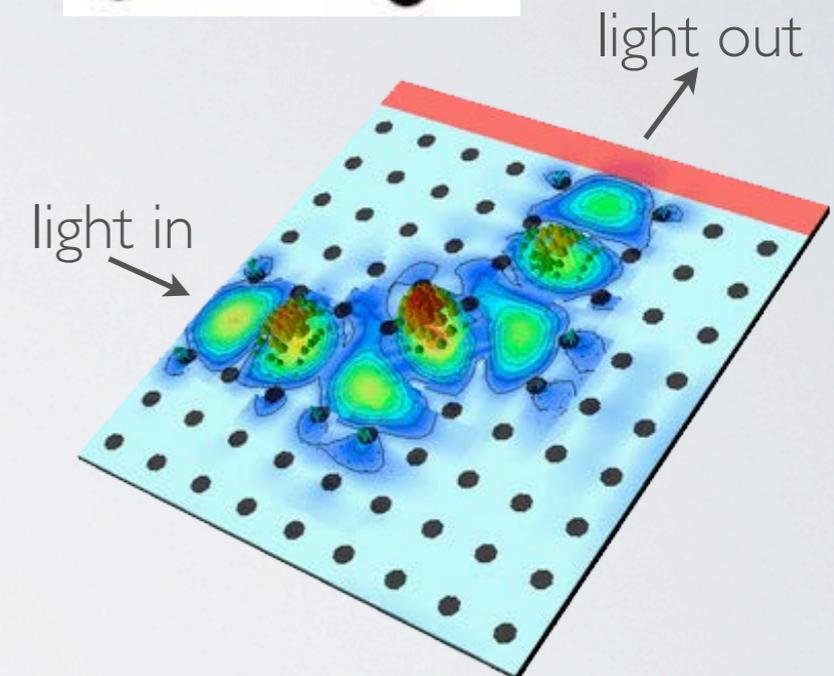
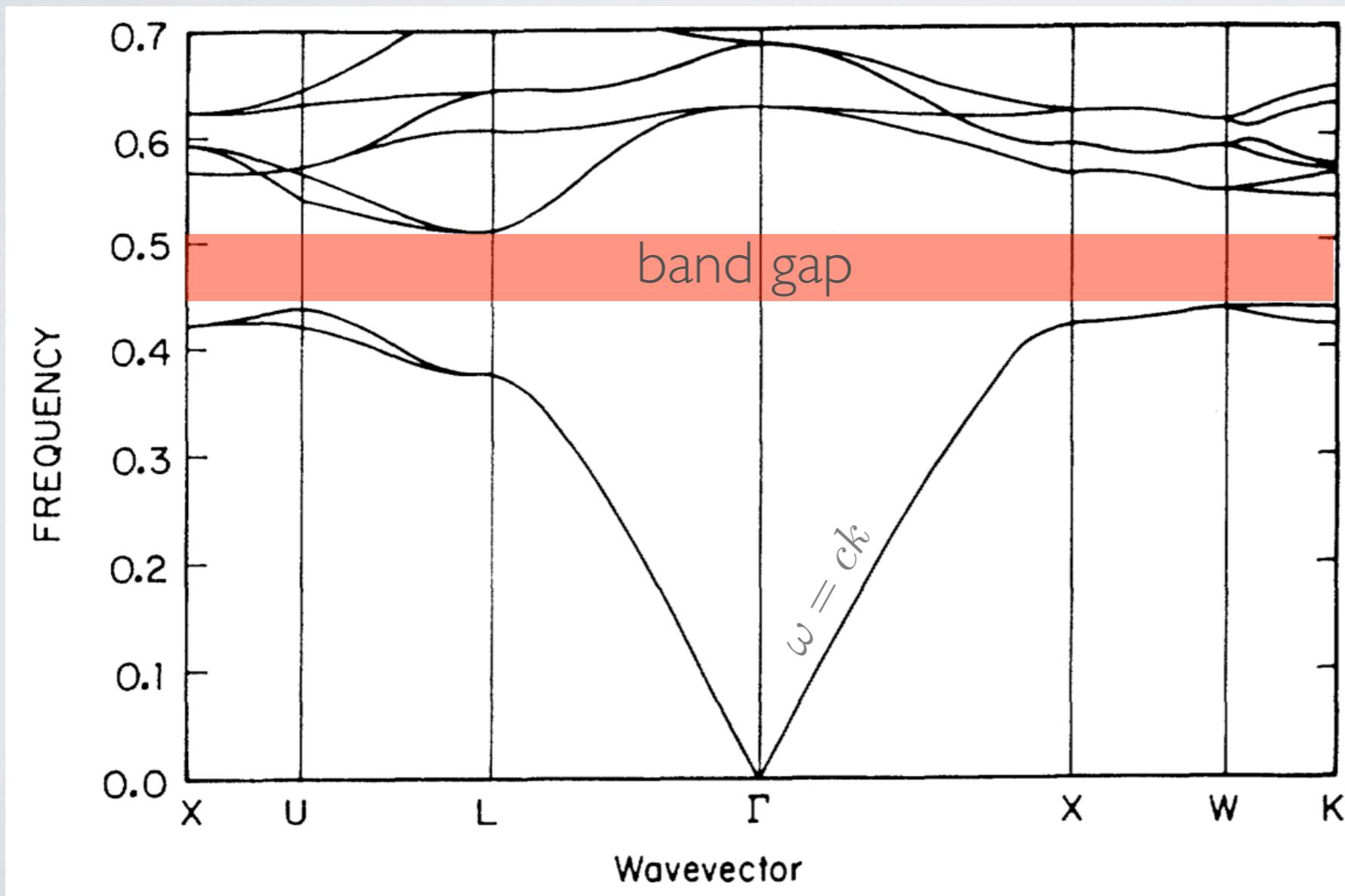
Natural opals consist of tiny FCC ordered glass spheres (~200 nm)

These structures (FCC, BCC) are nice but we would like to make others, such as ...

Diamond crystal structure



Photonic band structure for diamond

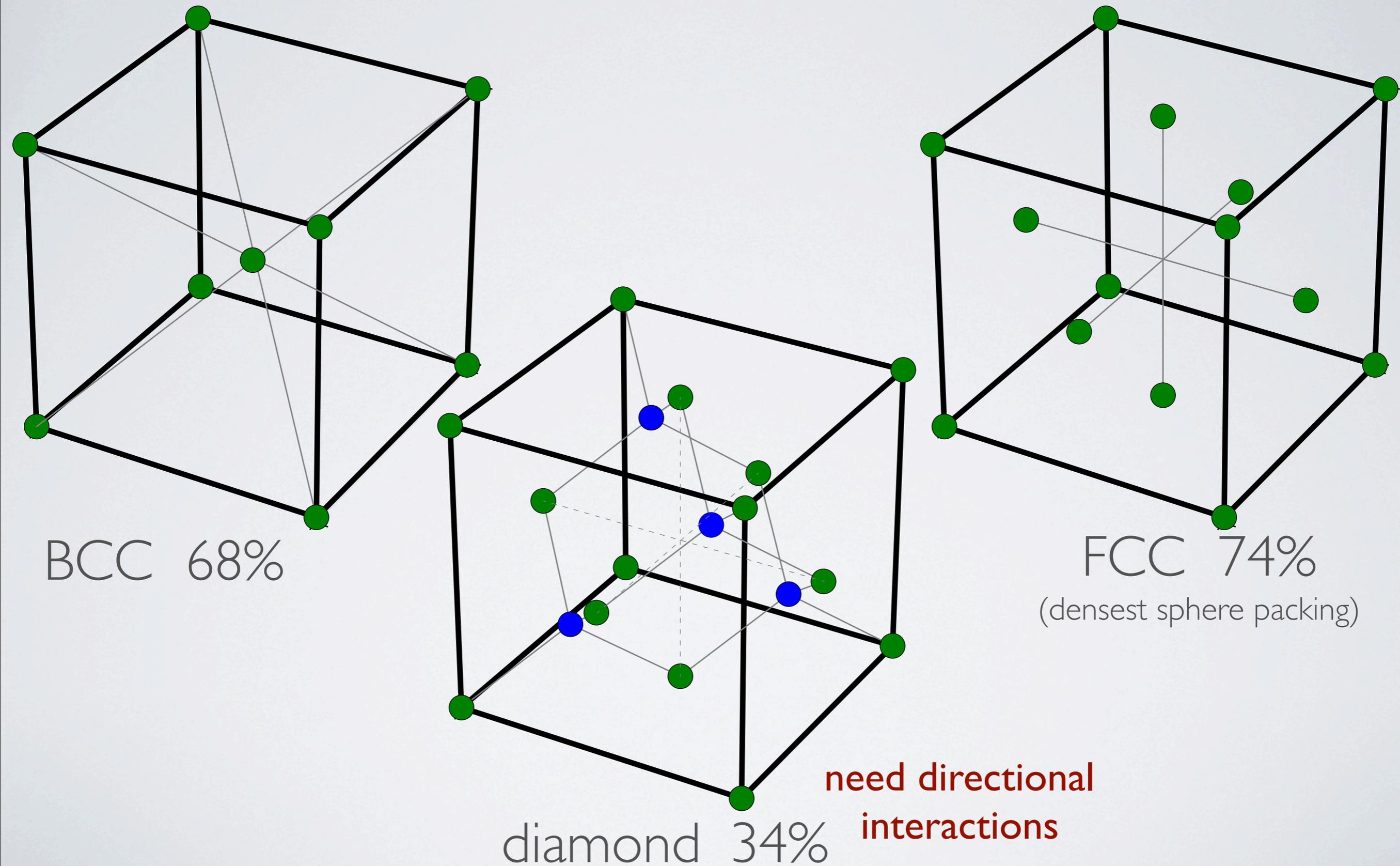


waveguide with sharp turns

Twenty years and counting:
No one can make this 3d
structure on the 100-1000
nm length scale.

Ho et al. PRL **65**, 3152 (1990)

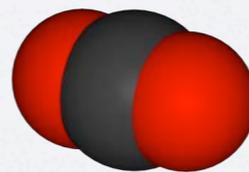
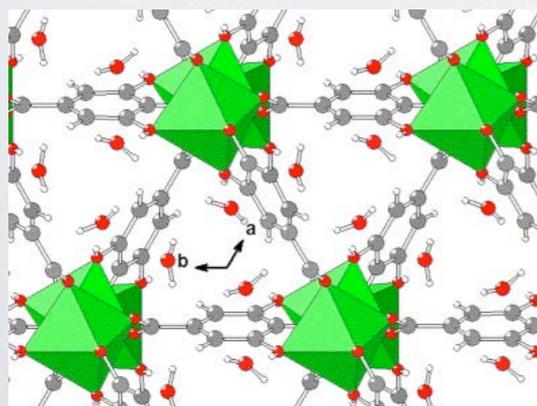
Why is assembling the diamond structure so hard?



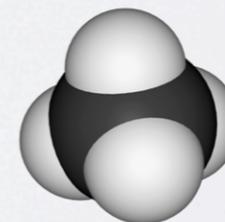
I believe ...

... that if we can learn to make structures from colloids with the control available to make molecules, that is, if we can design and control the structure of materials on the 10-1000 nm scale, it will have enormous practical applications ... in photonics, optics, electronics, solar cells, and many other technologies.

One key will be to develop colloids with directional interactions that can mimic atoms with valence ...



CO₂



CH₄



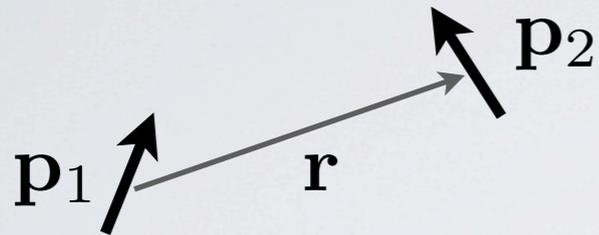
SO₂

Intro to colloidal interactions

- Van der Waals (fluctuation electric dipoles)
 - Screened Coulomb (Debye-Hückel)
 - Polymer brush (“steric” repulsion)
 - Depletion attraction
 - ssDNA hybridization
- } DLVO*

* Derjaguin
Landau
Verway
Overbeek

van der Waals: fluctuating electric dipoles



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

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

$$\mathbf{p}_2 = \alpha_2 \mathbf{E}_1(\mathbf{r}) \quad \text{induced dipole}$$

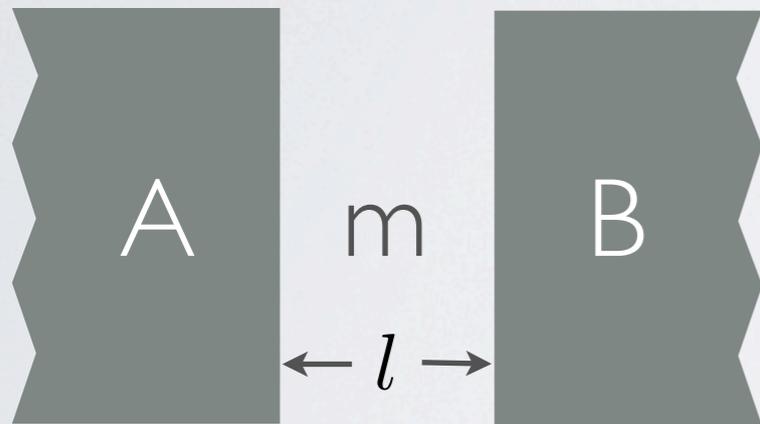
$$U(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \left\langle \frac{\mathbf{p}_1 \cdot \alpha_2 \mathbf{E}_1(\mathbf{r}) - 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\alpha_2 \mathbf{E}_1(\mathbf{r}) \cdot \hat{\mathbf{r}})}{r^3} \right\rangle \sim -\frac{\alpha_1 \alpha_2}{r^6}$$

van der Waals interaction

$$U(r) \simeq -\frac{A_{\text{Ham}}}{\pi^2} \int_{V_A} \int_{V_B} \frac{1}{r^6} dV_A dV_B \quad (\text{fluctuating induced dipole})$$

visible light travels
0.5 μm in one period

$$A_{\text{Ham}} \simeq \frac{3k_B T}{2} \sum_{\omega} \left(\frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left(\frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times \text{Ret}(l)$$



(index-matching reduces vdW interaction)

$$\epsilon(\omega) = 1 + \sum_j \frac{a_j}{1 - i\omega\tau_j} + \sum_j \frac{b_j}{(\omega_j^2 - \omega^2) - i\gamma_j\omega}$$

↑ relaxation times ↑ resonance frequencies ↑ damping rates

$$U_{pp} \sim \frac{p_1 p_2}{r^3} \quad p_2 \sim \alpha E_1(r) \sim \frac{1}{r^3}$$

$$\Rightarrow U_{pp} \sim \frac{1}{r^6}$$

contributions greatest near optical/uv frequencies

van der Waals interaction

(between two spheres)

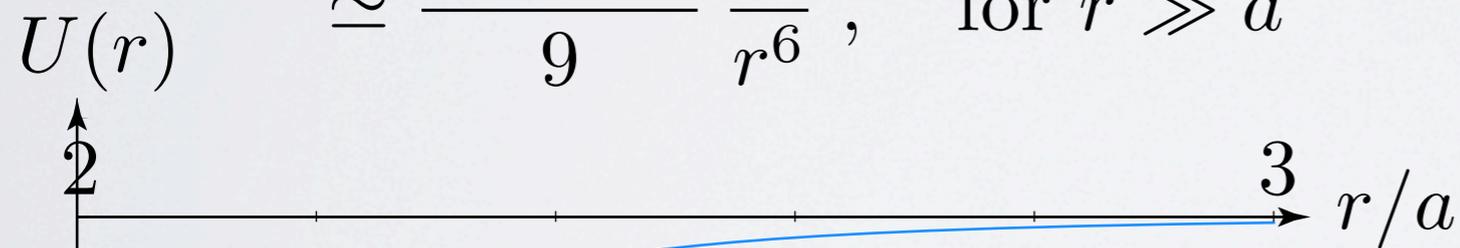
$$U(r) \simeq -\frac{A_{\text{Ham}}}{\pi^2} \int_{V_A} \int_{V_B} \frac{1}{r^6} dV_A dV_B \quad (\text{fluctuating induced dipole})$$

visible light travels
0.5 μm in one period

$$U(r) = \frac{A_{\text{Ham}}}{6} \left[\frac{2}{(r/a)^2 - 4} + \frac{2}{(r/a)^2} + \ln \left(1 - \frac{4}{(r/a)^2} \right) \right]$$

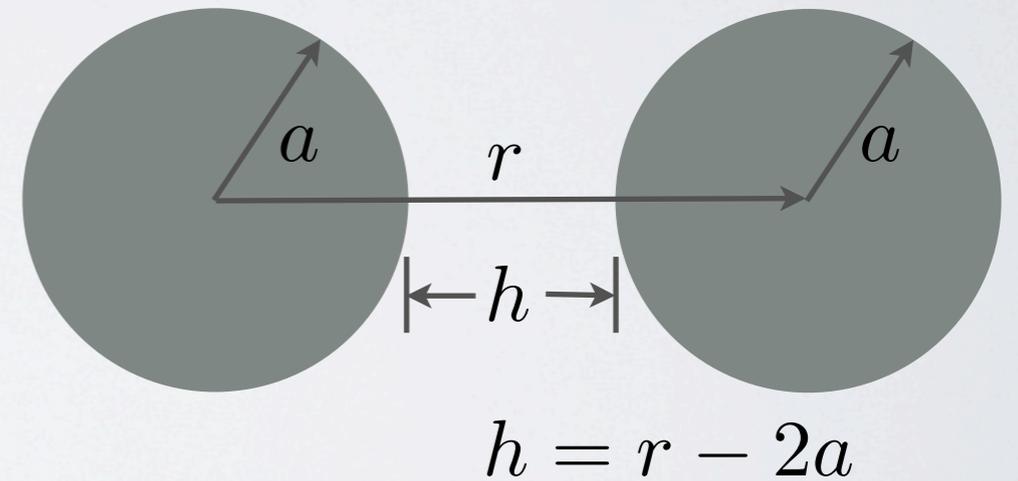
$$\simeq \frac{A_{\text{Ham}}}{12} \frac{a}{h}, \quad \text{for } h \ll a$$

$$\simeq \frac{16A_{\text{Ham}}}{9} \frac{a^6}{r^6}, \quad \text{for } r \gg a$$



$$\sim \frac{1}{r^6} \text{ or weaker}$$

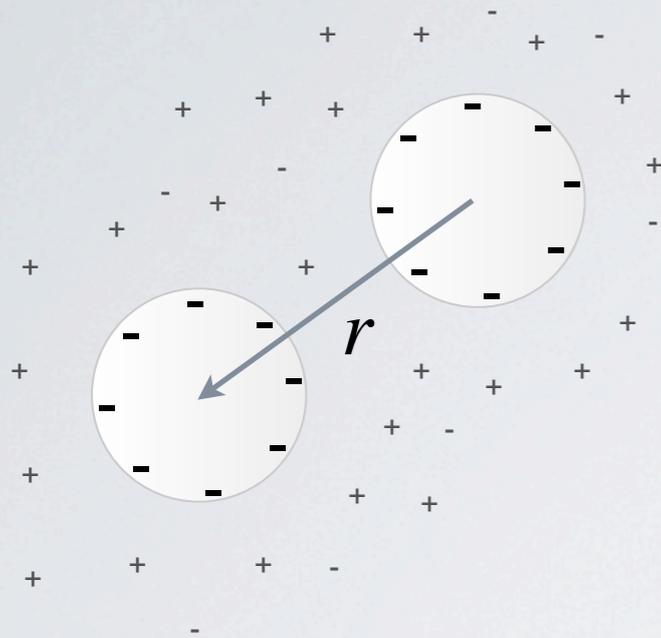
$$\sim \frac{1}{h} = \frac{1}{r - 2a}$$



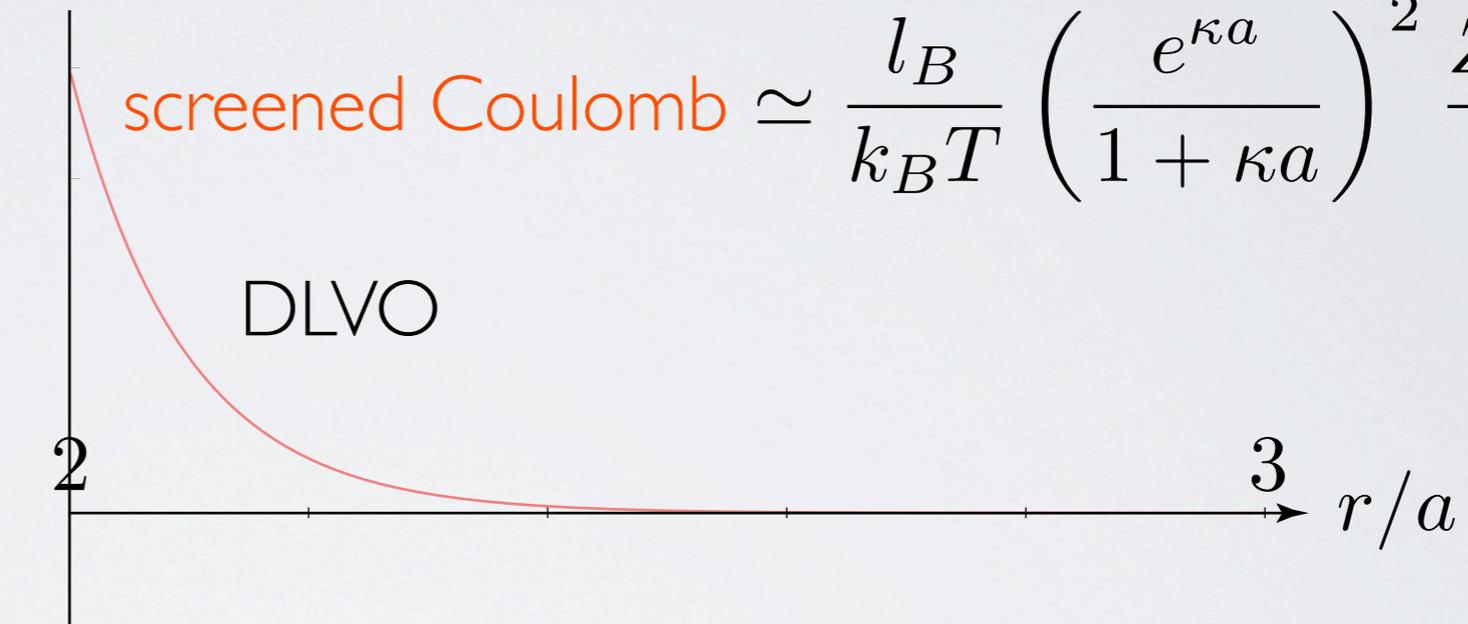
For 1 micron spheres at contact:

$$U(2a) \sim -10^3 k_B T$$

Screened Coulomb



$U(r)$



screened Coulomb $\approx \frac{l_B}{k_B T} \left(\frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{Z^2 e^{-\kappa r}}{r}$

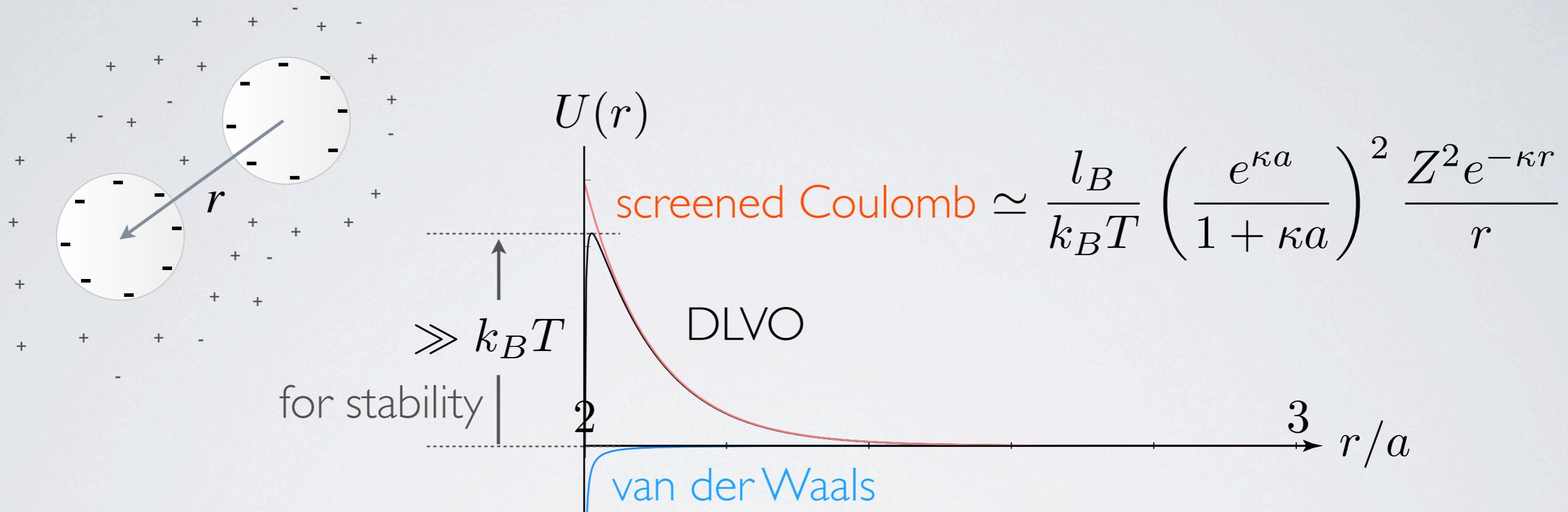
Bjerrum length

$$l_B = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\epsilon_r k_B T}$$

Debye screening length

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

Screened Coulomb + van der Waals (DLVO theory)



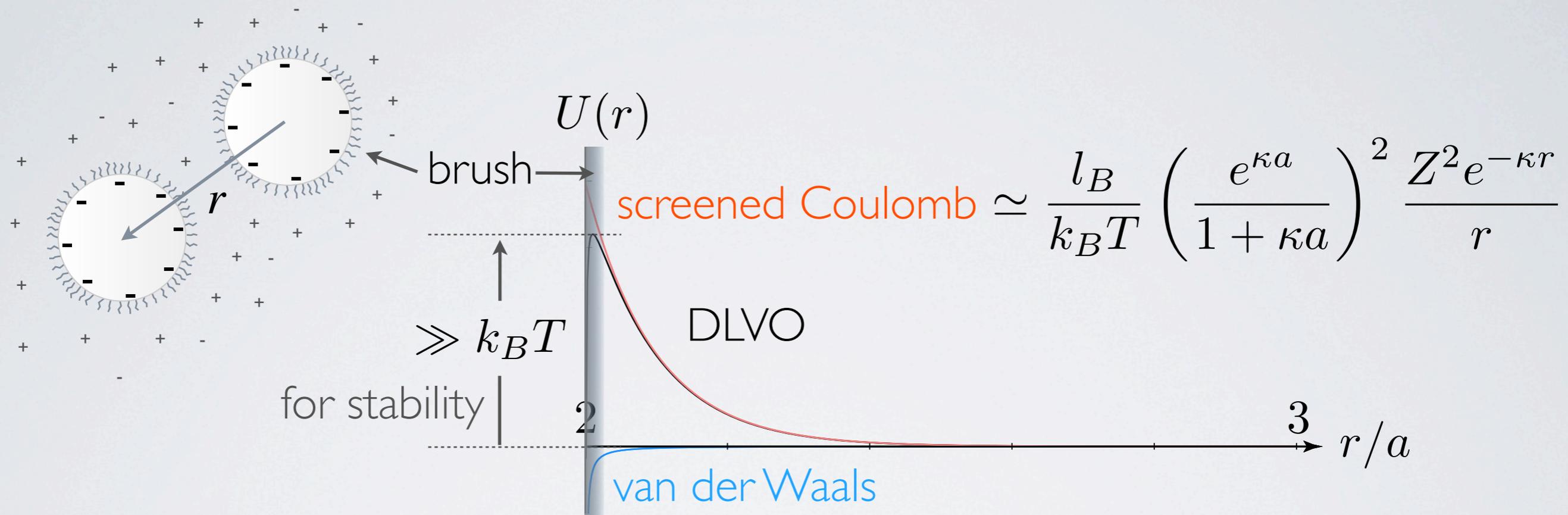
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Bjerrum length

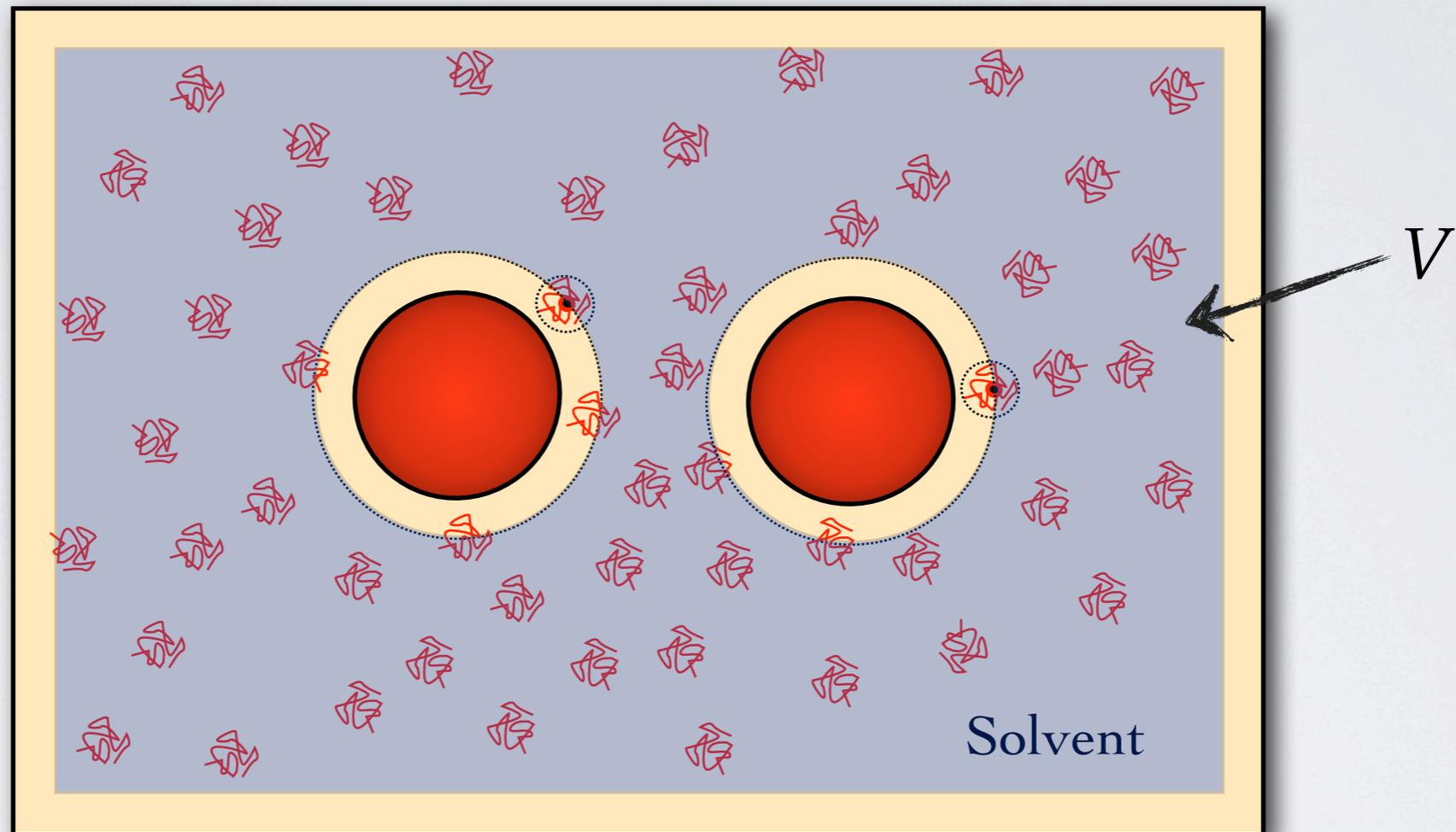
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Depletion interaction

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

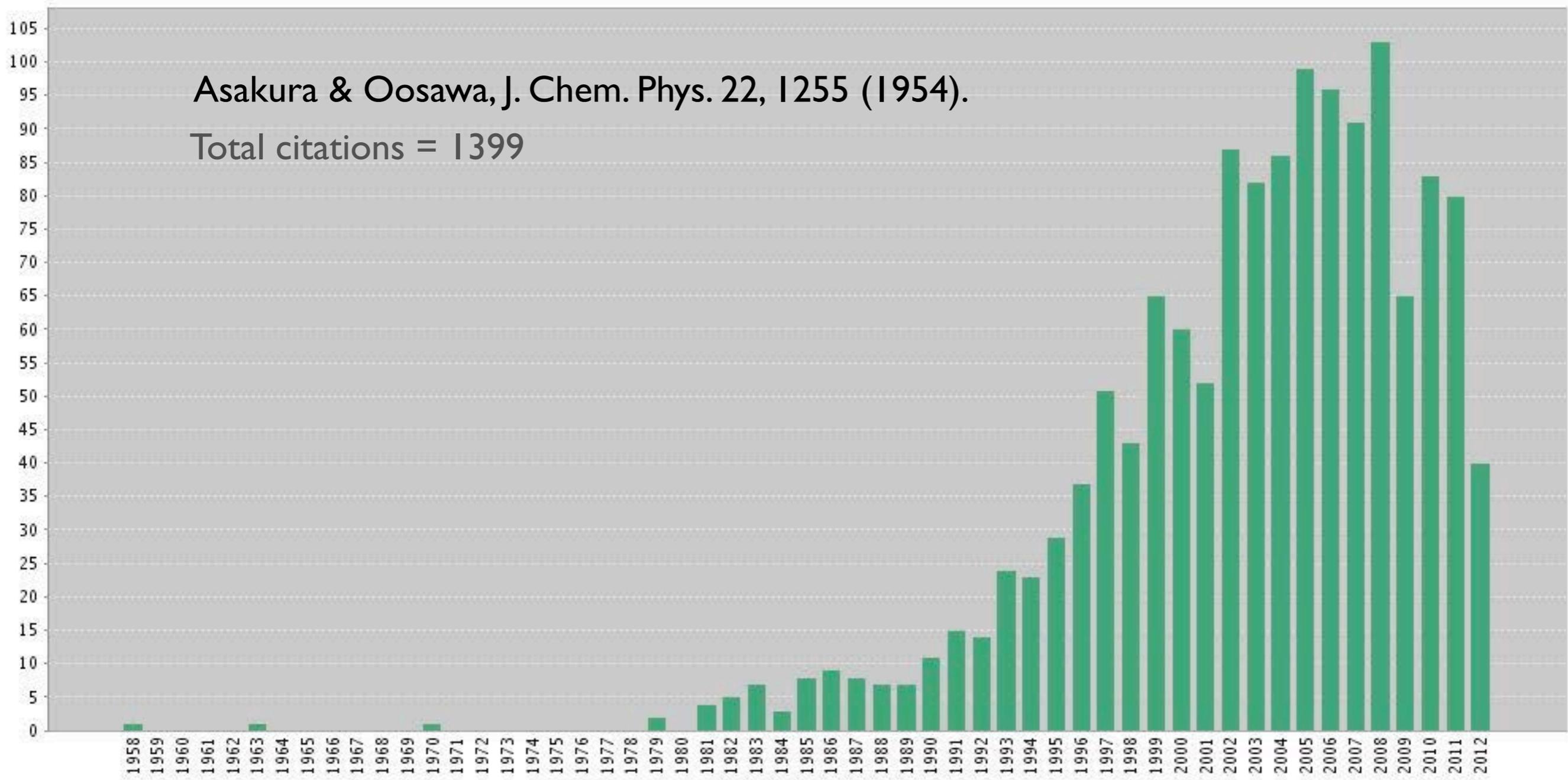


Citation time line

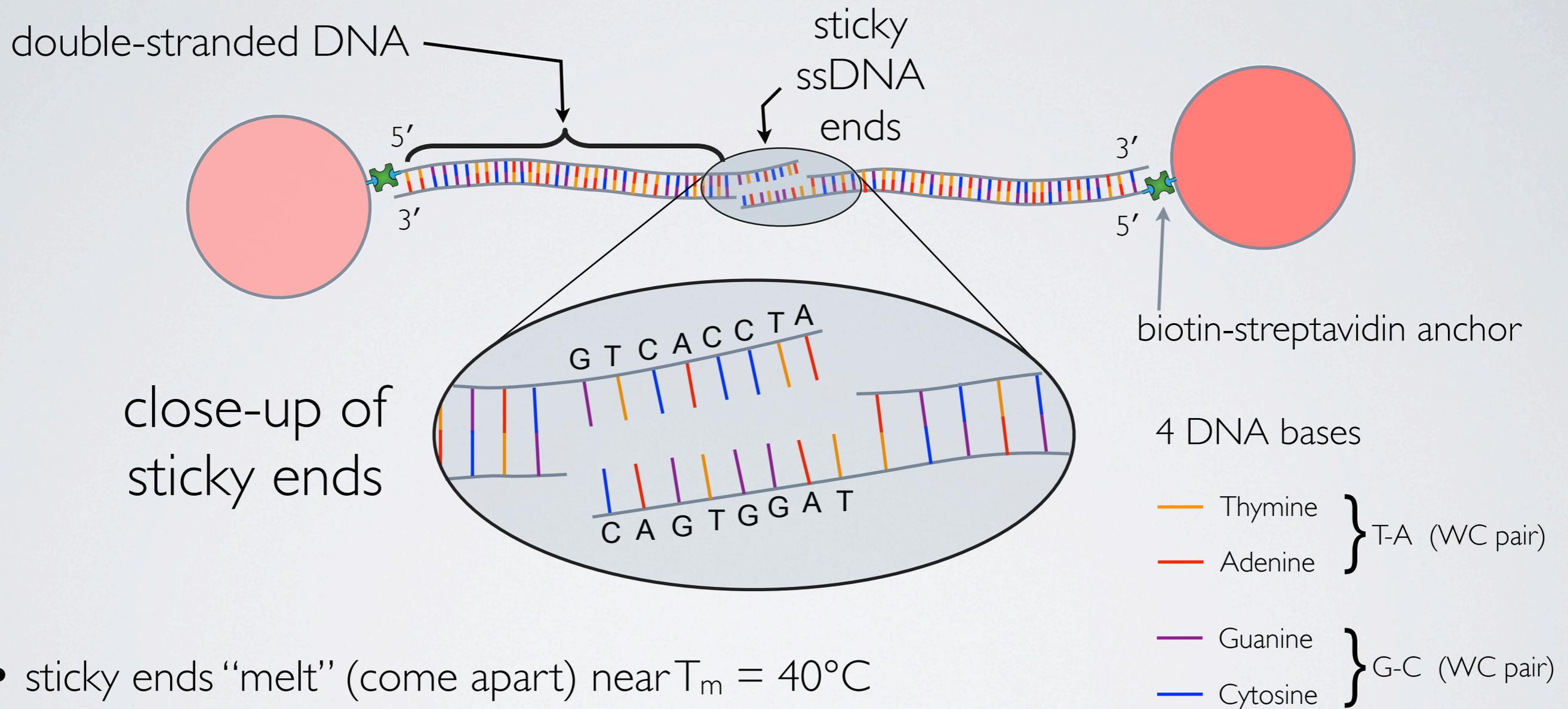
for original paper on the depletion interaction

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

Total citations = 1399



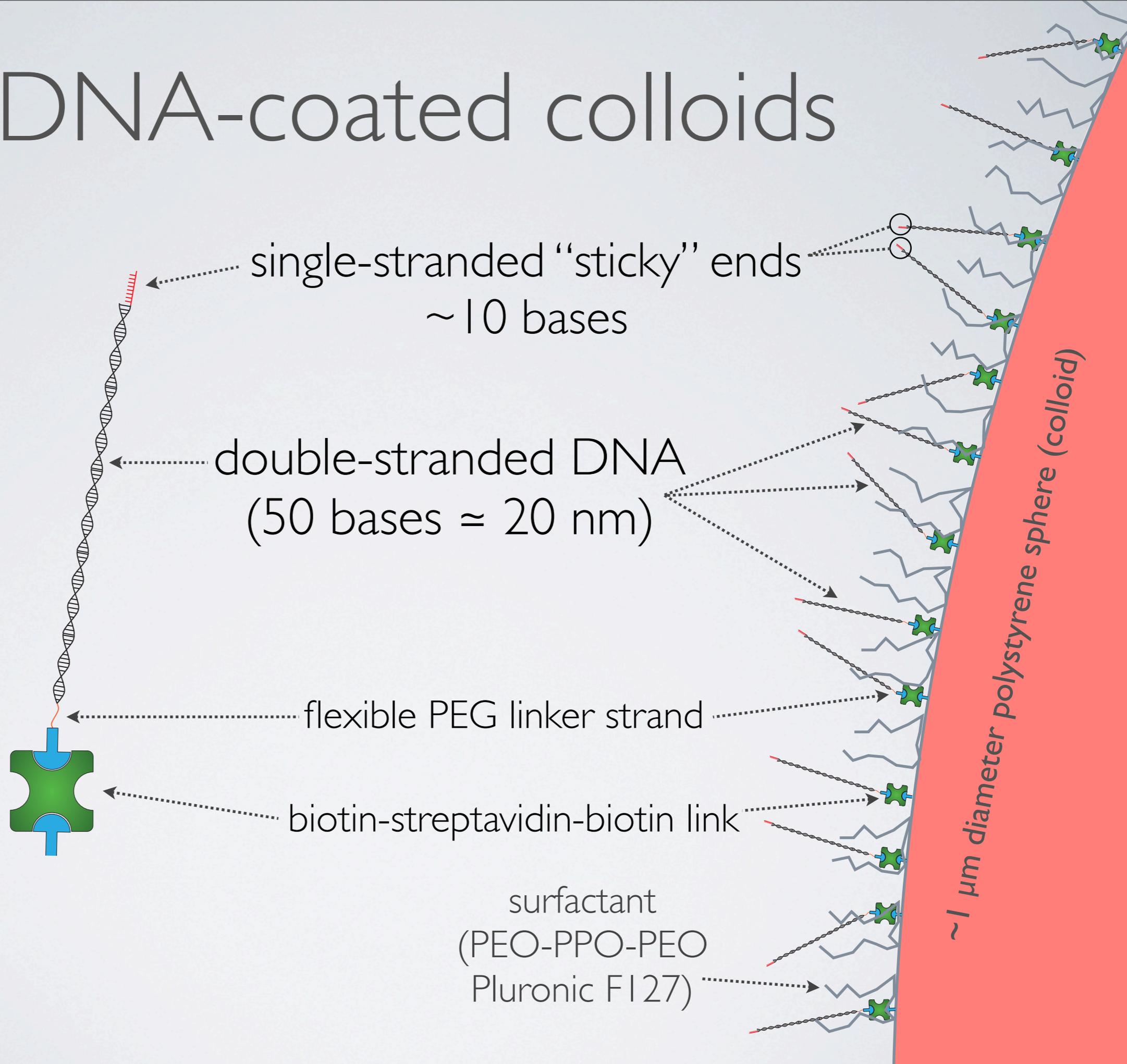
single-stranded DNA (ssDNA)



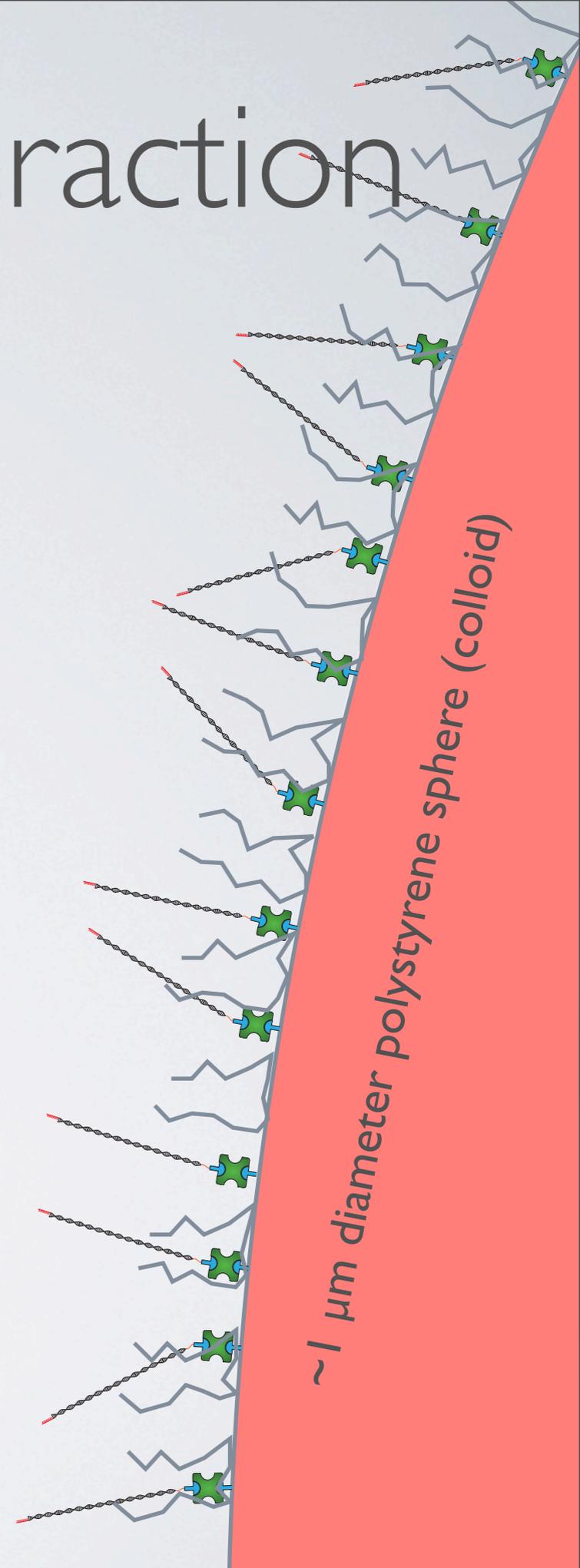
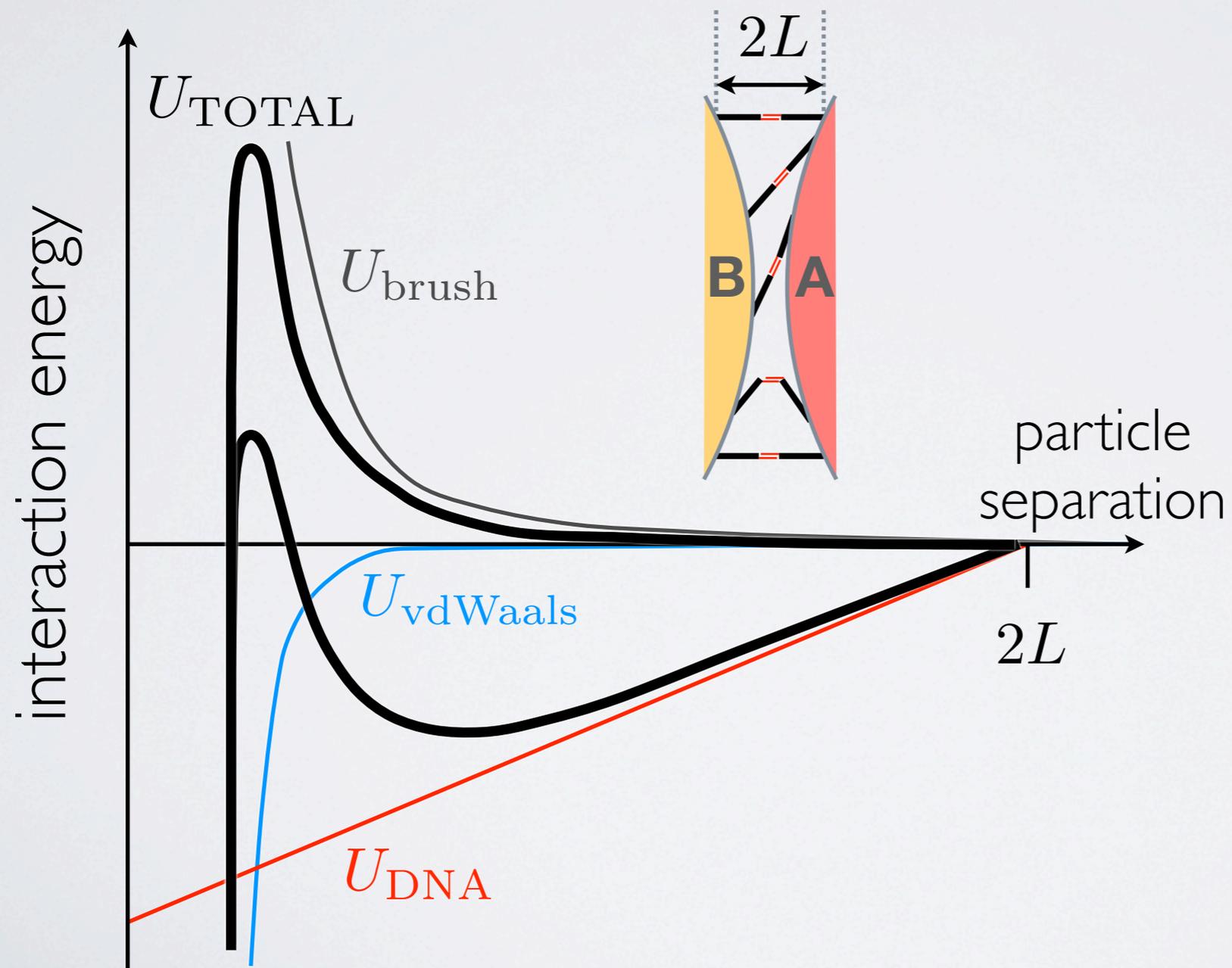
- sticky ends “melt” (come apart) near $T_m = 40^\circ\text{C}$
- T_m depends on number (and kind) of base pairs
- specificity – only complementary strands link:

→ can “program” sticky ends by sequence of bases \Rightarrow recognition

DNA-coated colloids



DNA hybridization interaction



Tomorrow

- Colloids with directional interactions
 - ▶ Pacman particles
 - ▶ Colloids with valence