Flying Colloidal Carpets

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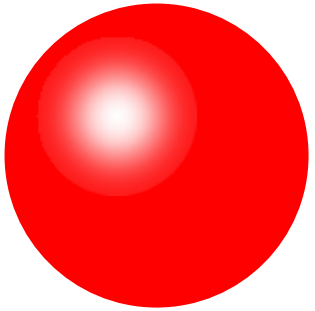
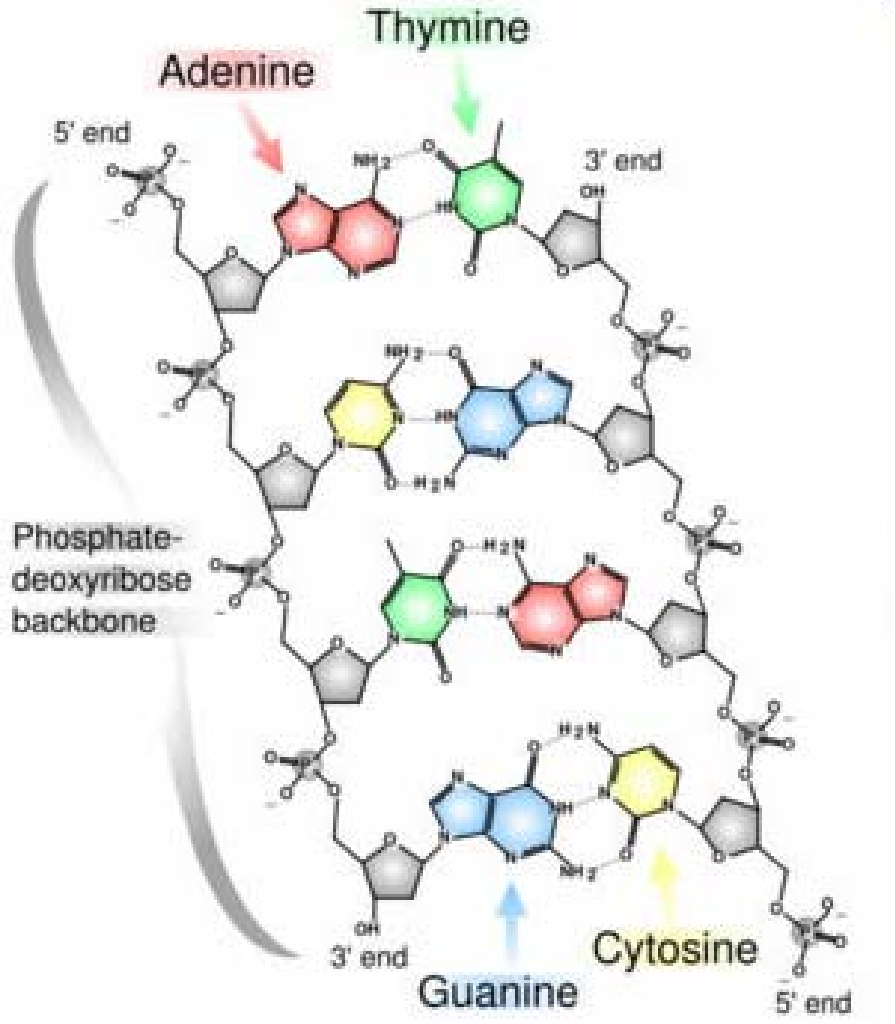
Introduction

Driving programmable self-assembly of colloids with the help of DNA.



Why DNA?



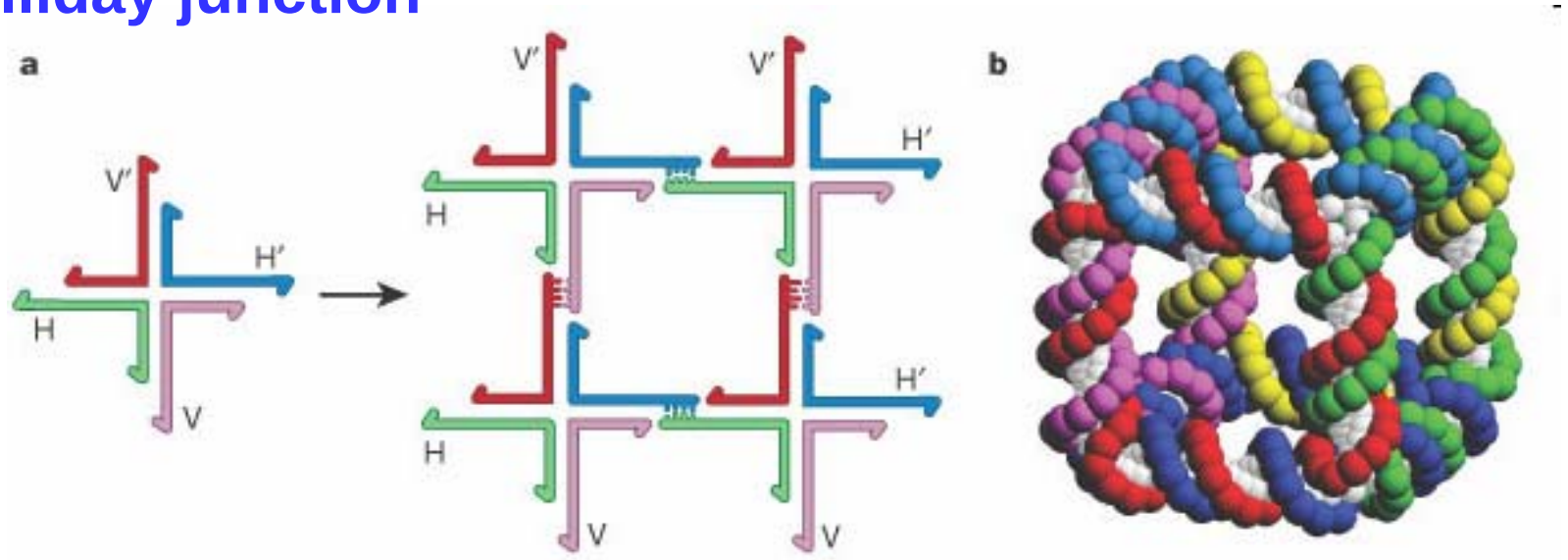
- **2** phosphate-sugar chains
- Running anti-parallel (3’ and 5’ end)
- Held together via H-bonds between **GC** & **AT** base pairs

Double-stranded DNA is highly specific

DNA self-assembles

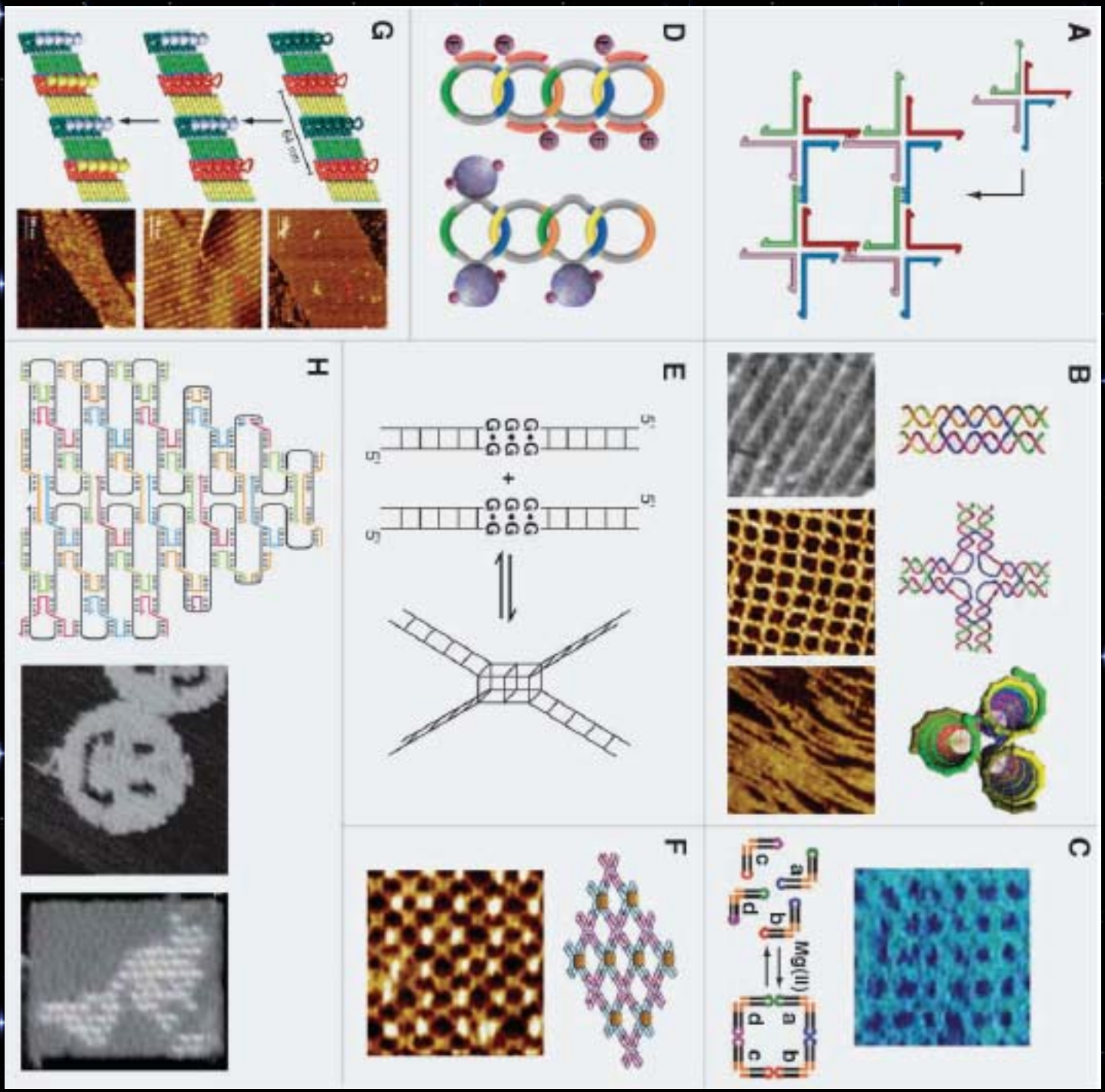
Designing DNA tiles:

Holliday junction



N. C. Seeman, Nature, 2003, 421, 427–431.

Faisal A. Aldaye, et al., *Science* 321, 1795 (2008)

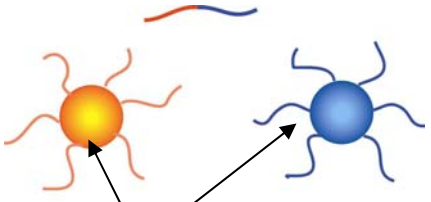


Why DNA + Colloids?

T-Reversible binding

DNA-nanoparticle array:

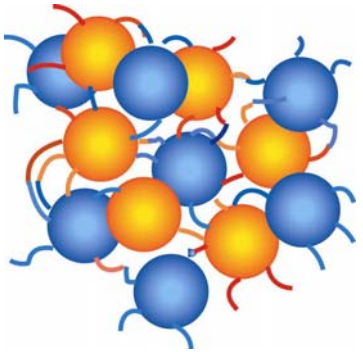
Target linker:
(~ 20-base ssDNA)



$$T < T^*$$

$$\rightleftharpoons$$

$$T > T^*$$



Gold colloids: size ~10-50 nm

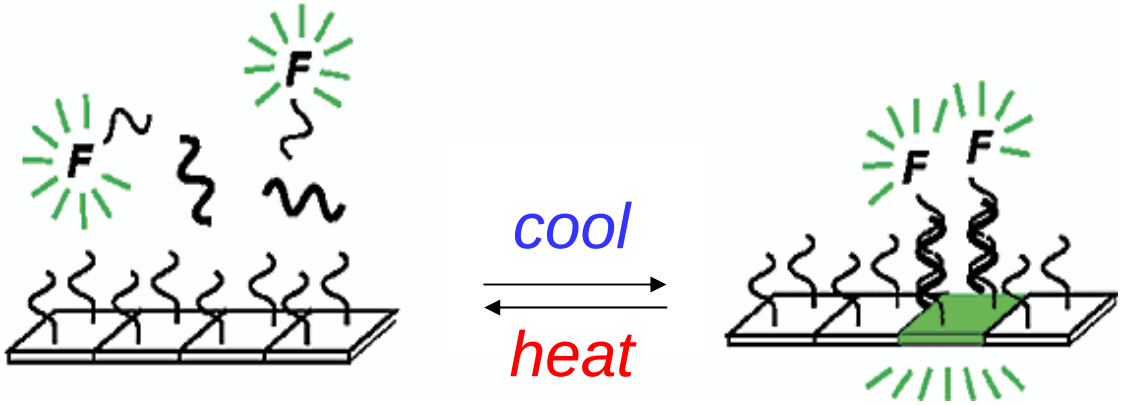
C. A. Mirkin et al. (2000, 2003)

Mirkin et al., Nature (London) 382, 607 (1996).

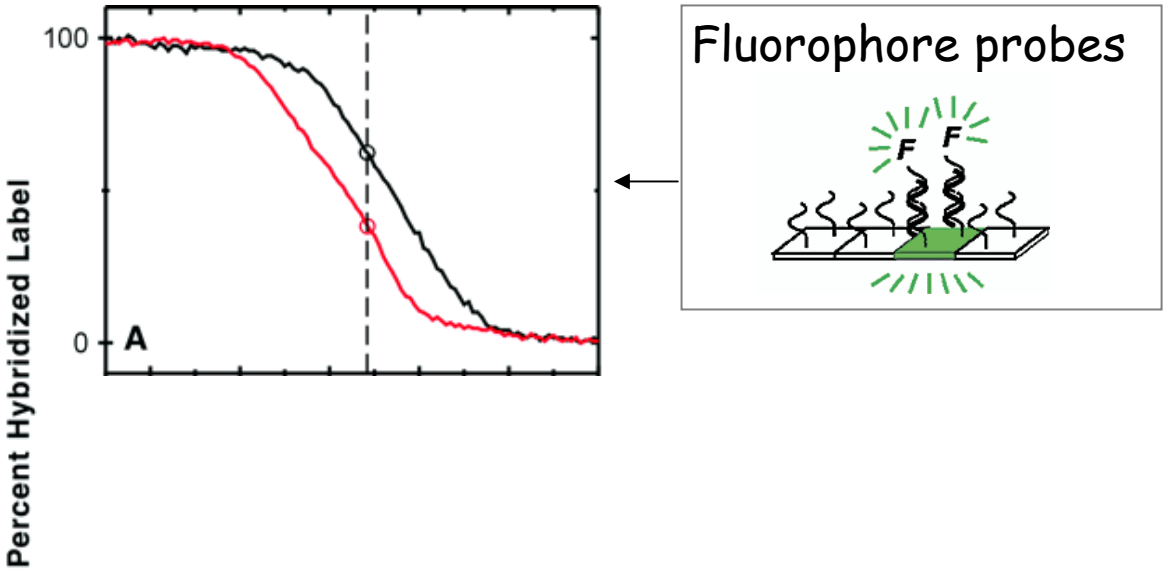
Alivisatos et al., in the same issue

Sensing base-pair mismatches

Fluorophore-based DNA-array:



Sensing base-pair mismatches



Complementary sequence

Single-base mismatched sequence

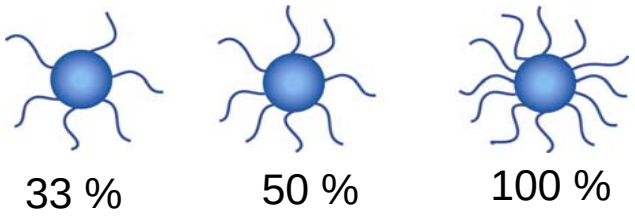
C. A. Mirkin et al. (2000)

Lukatsky & Frenkel, PRL (2004)

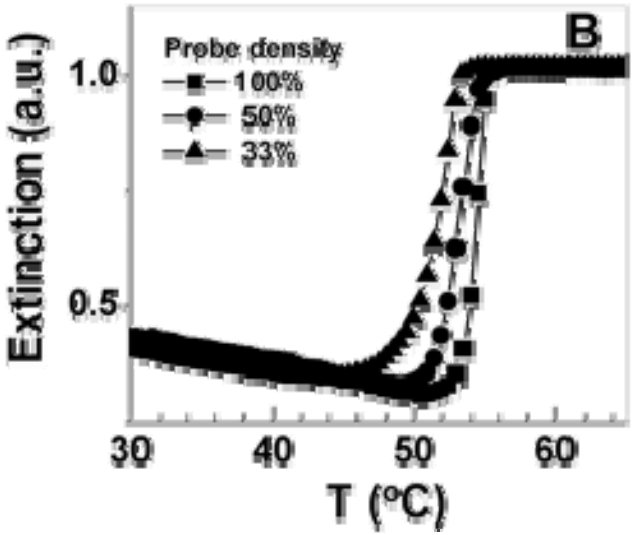
Sharp dissolution profiles → High selectivity

Sensing base-pair mismatches

ssDNA grafting density:



33 % 50 % 100 %



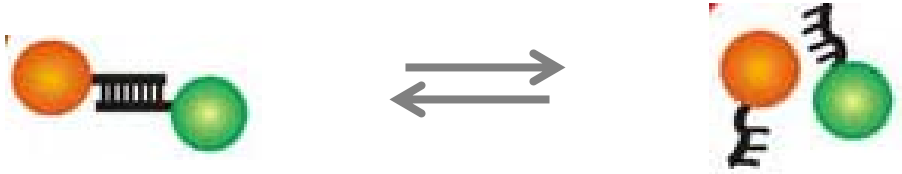
Adsorption @ λ = 260 nm

Higher ssDNA coverage density → Sharper dissolution profile

Higher ssDNA coverage density → Higher dissolution temperature

C. A. Mirkin et al. (2003)

What is the Physics behind?



If ***N*** ≡ max. no. of H-bonds

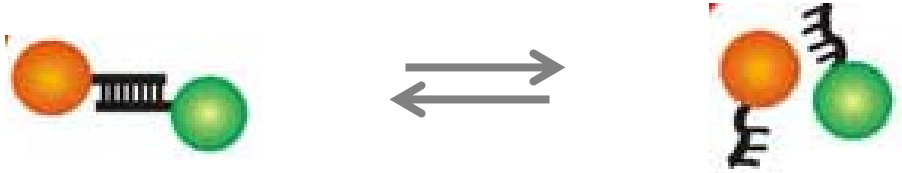
And ***Δf*** ≡ free energy difference between bound and unbound single DNA-pairs

➡ Probability that a single DNA pair is unbound

$$P_u(1) = \frac{1}{1 + e^{-\beta \Delta f}}$$

Geerts and Eiser, review in *Soft Matter* (2010)

Sharp Melt Transition



when $\Delta f = 0$: $$P_u(1) = \frac{1}{1 + e^{-\beta \Delta f}} = \frac{1}{2}$$

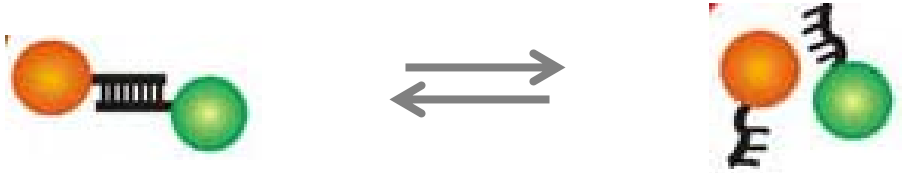
➡ 50% of the DNA pairs are bound

However, this is not the point where the two colloids will unbind!

For that to happen, ***ALL*** DNA pairs should be unbound.

Geerts and Eiser, review in *Soft Matter* (2010)

Sharp Melt Transition



Probability that all strands are unbound is

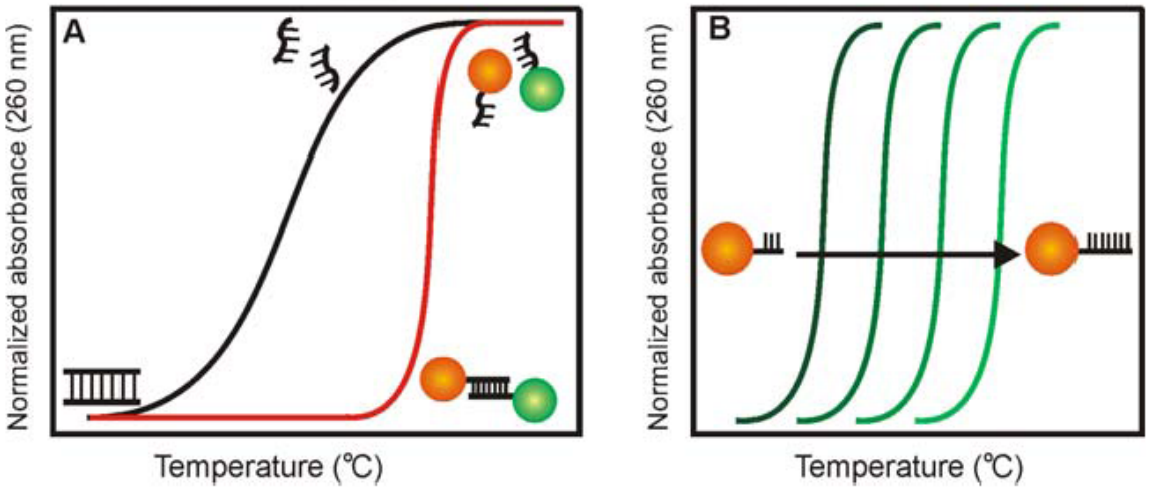
$$P_u(N) = P_u^N(1)$$

or $P_u(N) = \left(\frac{1}{1+e^{-\beta\Delta f}}\right)^N \approx \exp(-Ne^{-\beta\Delta f})$

step function for $N \to \infty$

Geerts and Eiser, review in *Soft Matter* (2010)

Entropically driven Melt Transition



- as ***N*** increases, the probability (@ ***T*** = const.) that a pair of colloids is unbound decreases exponentially

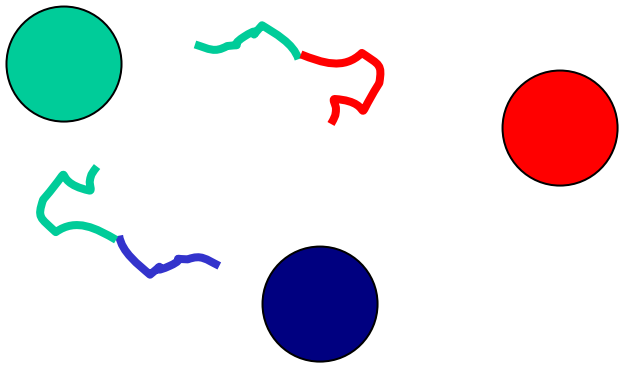
- and T_{melt} where there is a 50% chance that the colloids are bound is **~ ln*N***

Geerts and Eiser, review in *Soft Matter* (2010)

Building New Materials

Attractions between different species (A,B,C, etc) can be selectively **switched on** by the appropriate DNA-linker

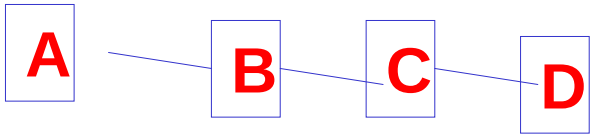
(e.g. AB and BC, but NOT AC)



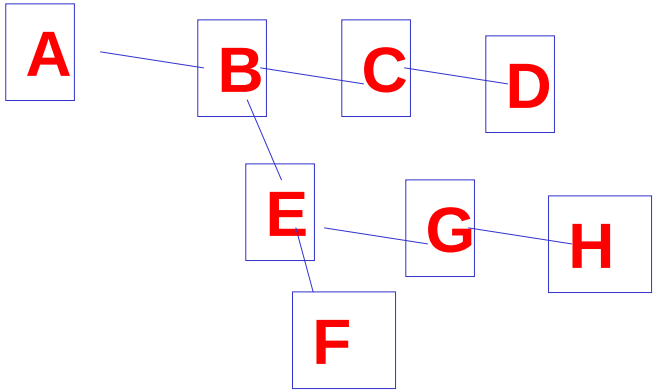
Building New Materials

In principle, we can design any interaction topology we like…

e.g.



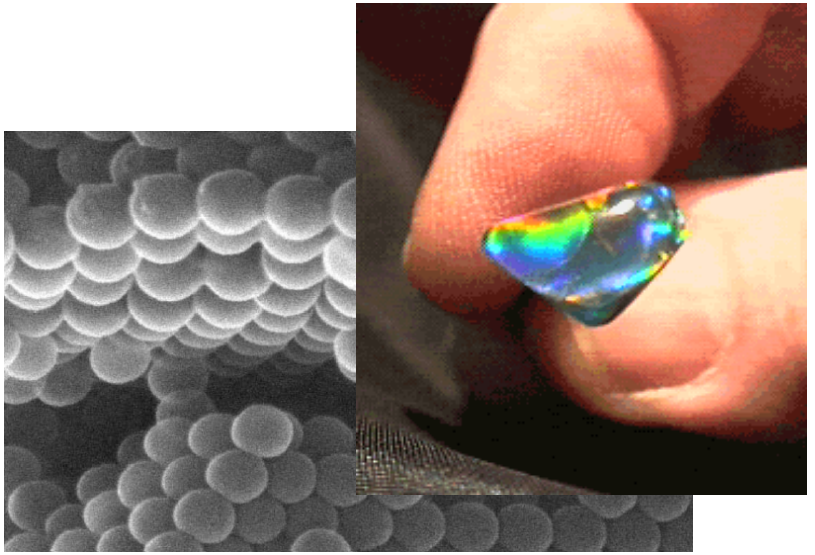
or



But the sharp melt curve causes experimental difficulties.

Holy GRAIL

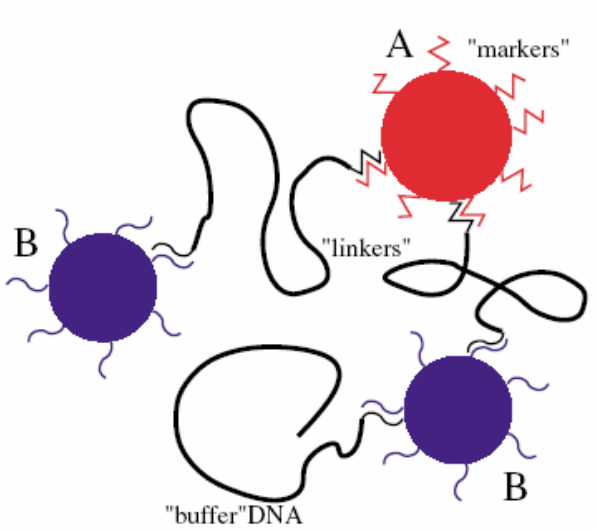
Making ordered subunits (clusters) that subsequently assemble into higher order structures

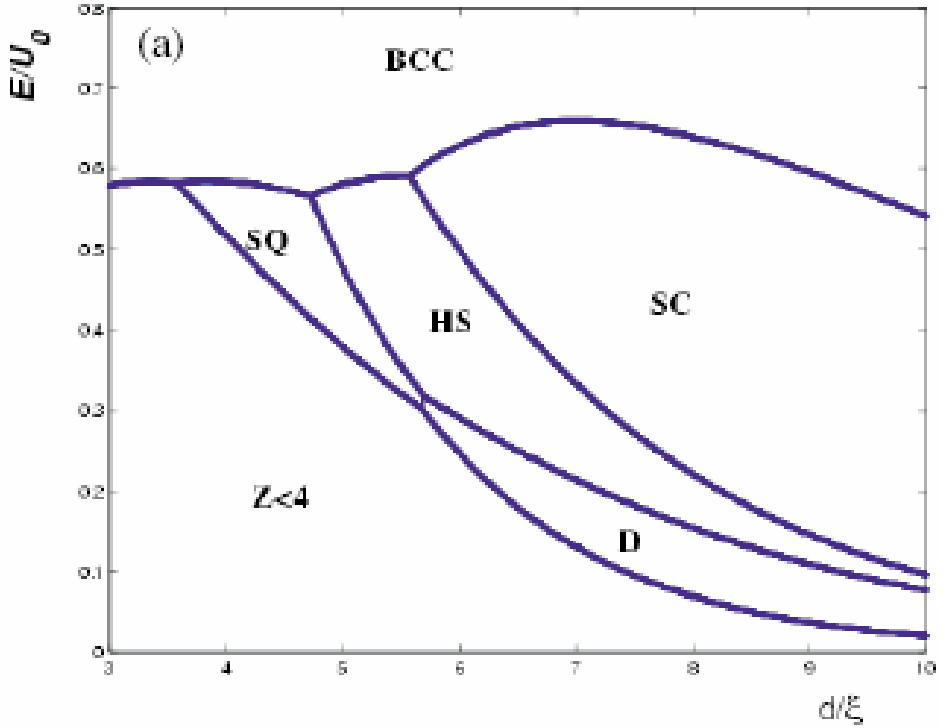


Building new materials

Tkachenko *PRL* **89** 148303 (2002) & arXiv: cond mat/0504407 v1 (2005)

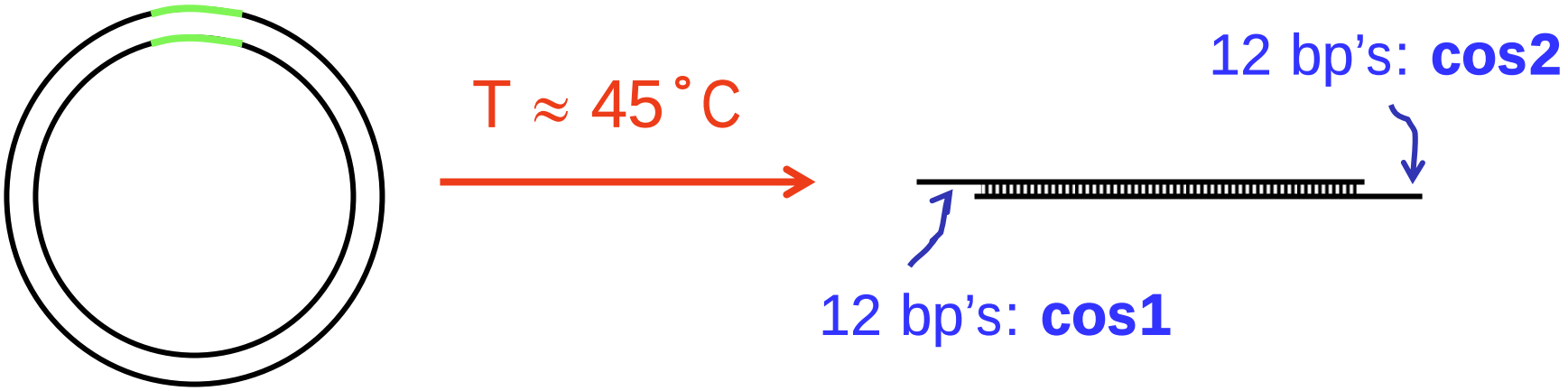
Calculated phase diagram: exponential potential



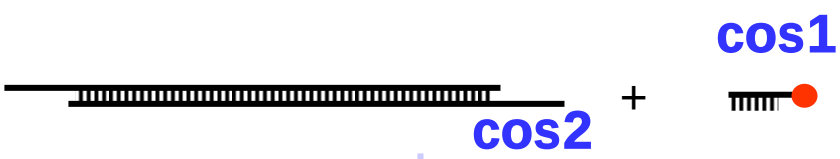


We are using very long DNA spacers

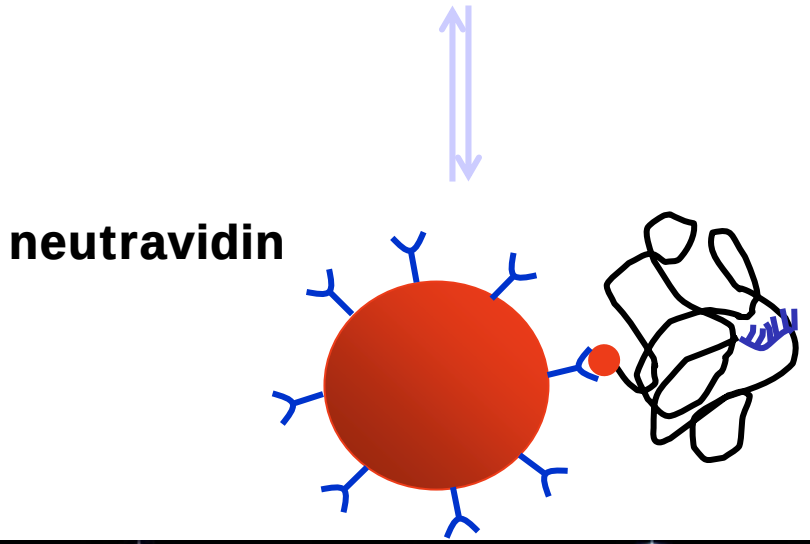
λ-phage DNA: 48500 base pairs (bp)



We are using very long DNA spacers



***Ligation* : covalent bonding**



Tris-HCl buffer in density matching sucrose solution (pH8).

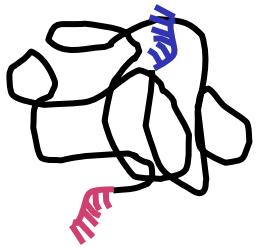
Ionic strength = 50 mM

Debye length ~ 10 nm

Sizes involved

$\mathcal{R}$ = 0.5 μm

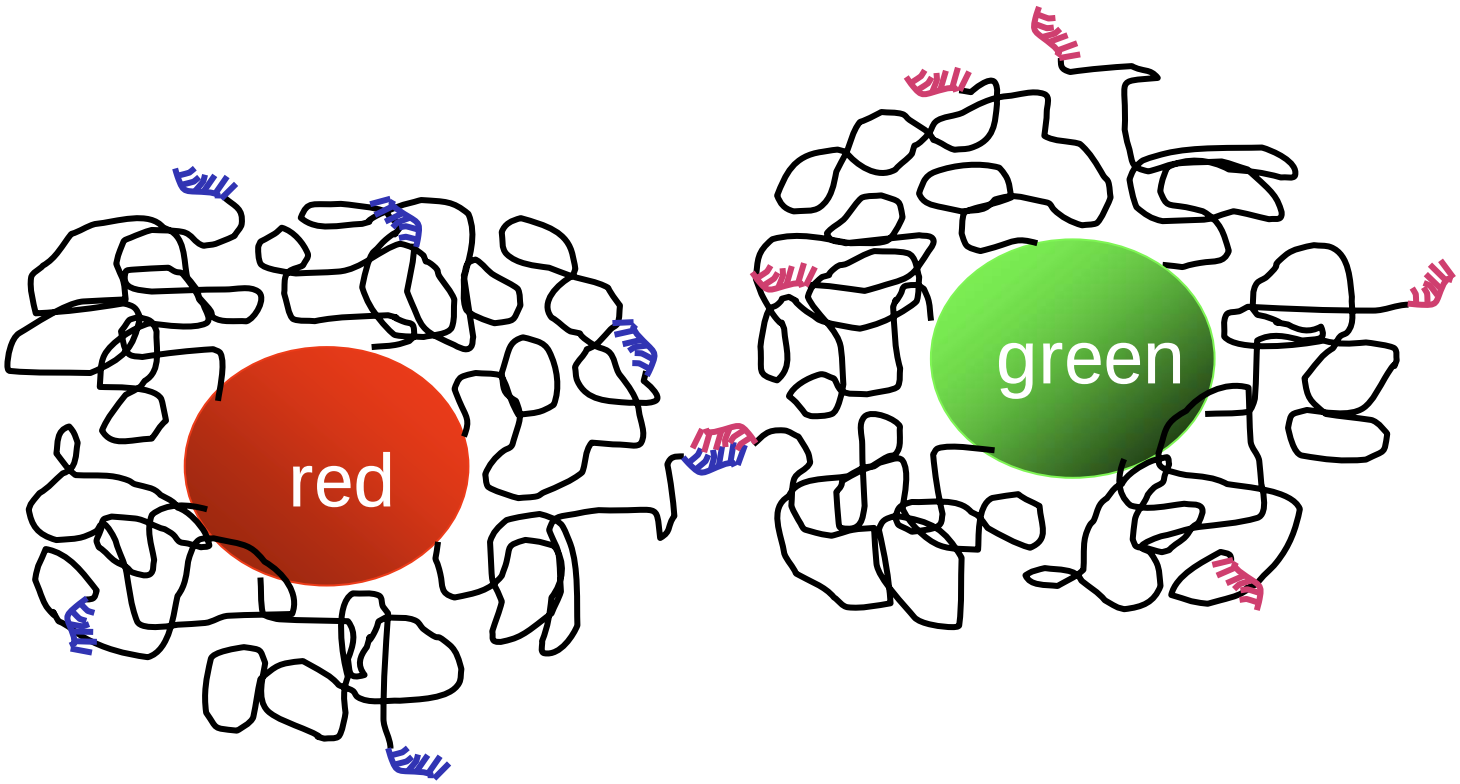
Open λ-DNA:



radius of gyration

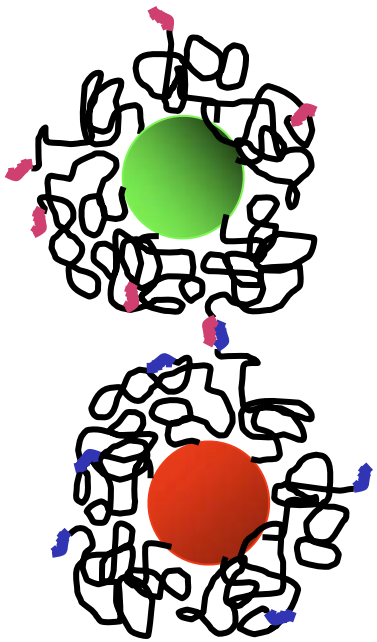
$$R_g = bN^{0.58} \approx 0.8\mu m$$

We are using very long DNA spacers



~ 10 λ-DNA arms per bead

Interactions involved



Van der Waals ~ - 300 k_BT @ 1nm separation

$$V_{vdW} = -\frac{A}{6}\left(\frac{2R^2}{(r^2-4R^2)} + 2\frac{R^2}{r^2} + ln(\frac{r^2-4R^2}{r^2})\right)$$

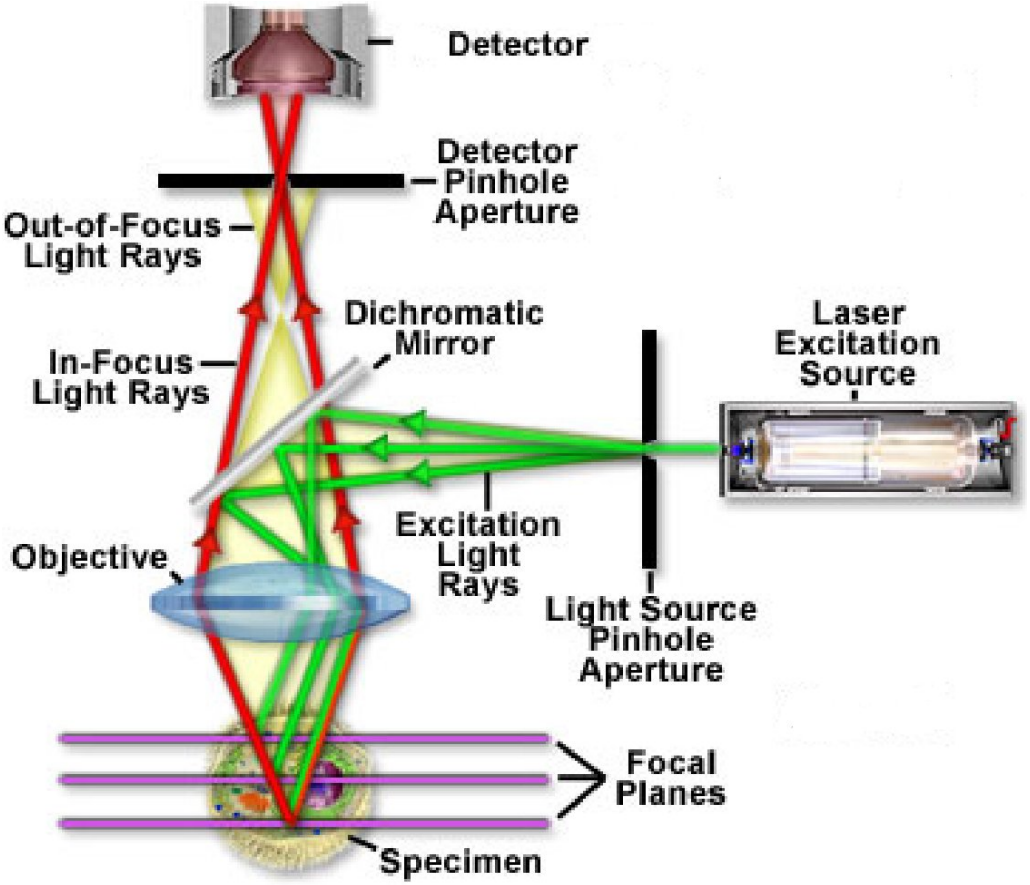
Coulomb repulsion ~ 80 k_BT @ 1 nm separation

DNA binding ~ - 25 k_BT

DNA steric repulsion – we do not know

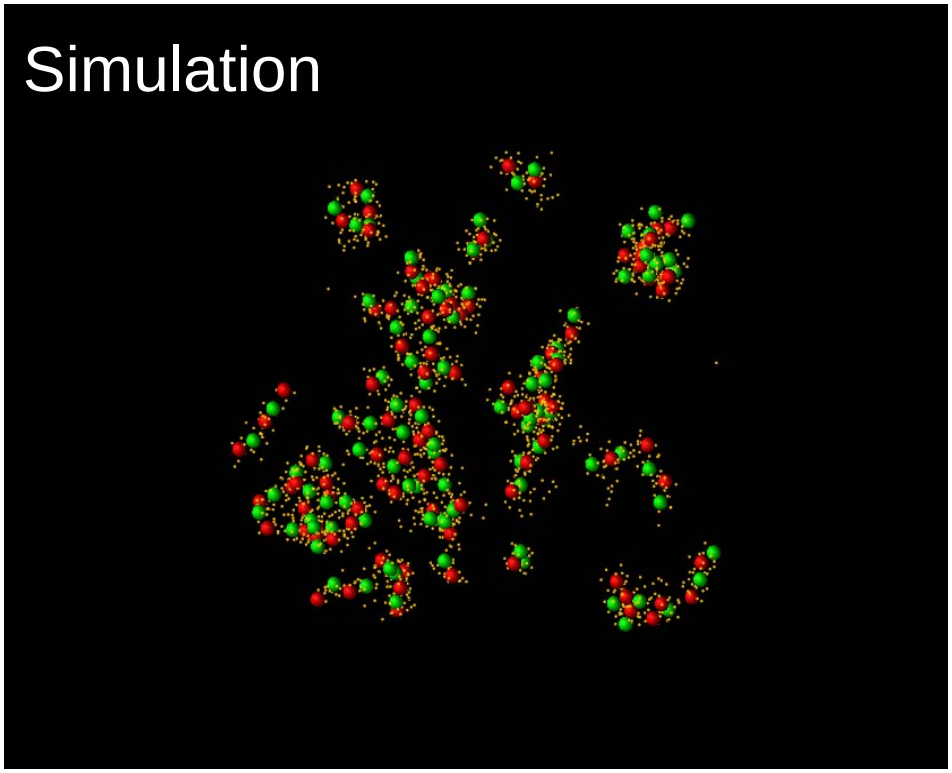
How do we image the Colloids?

Confocal Microscopy



http://www.microscopyu.com

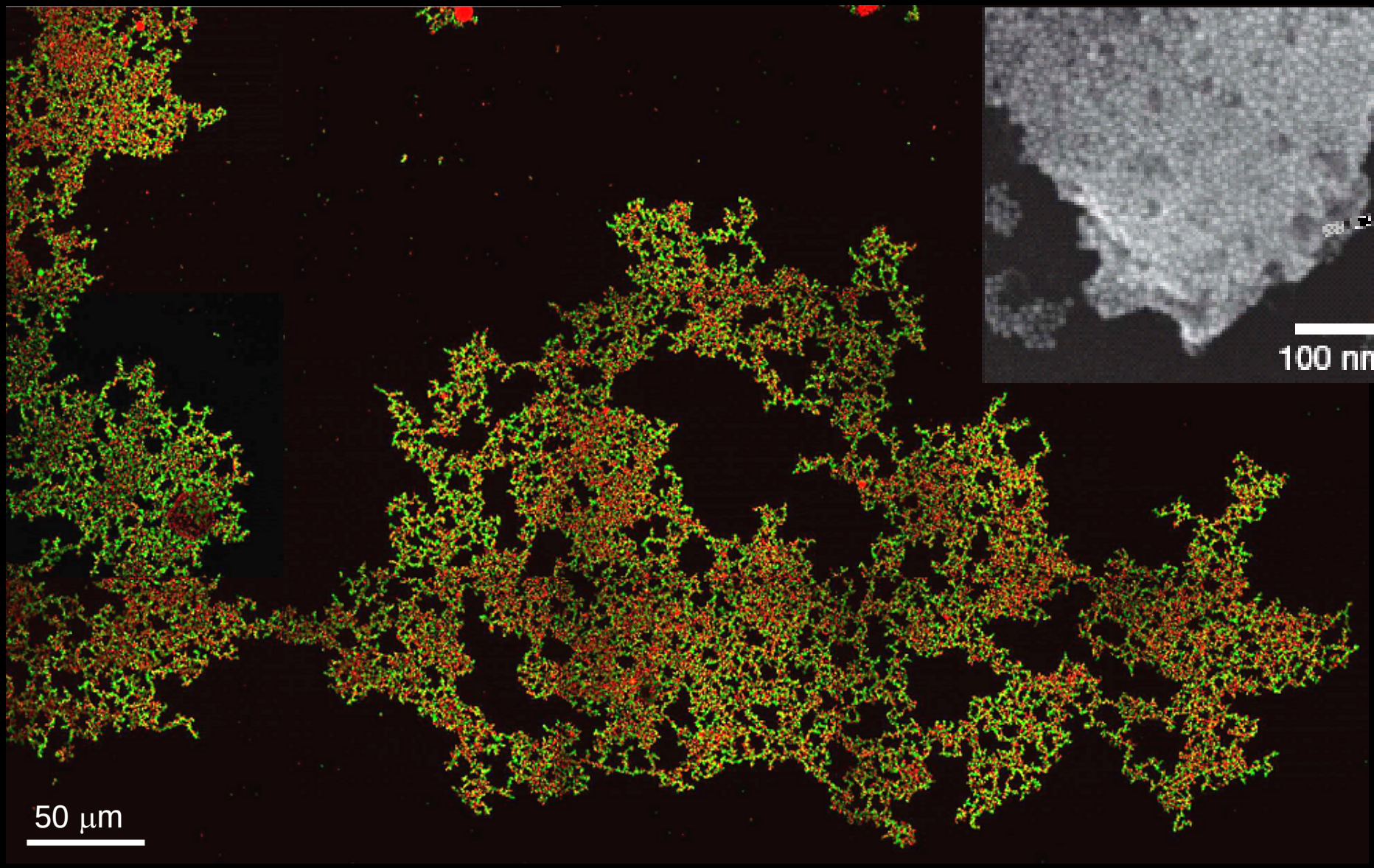
We are using very long DNA spacers



T. Schmatko, B. Bozorgui, N. Geerts, D. Frenkel, E. Eiser, W.C. Poon, Soft Matter, 3, 703 (2007).
B. Bozorgui, D. Frenkel, *PRL 101,* 045701 (2008)

Self-limiting cluster growth.

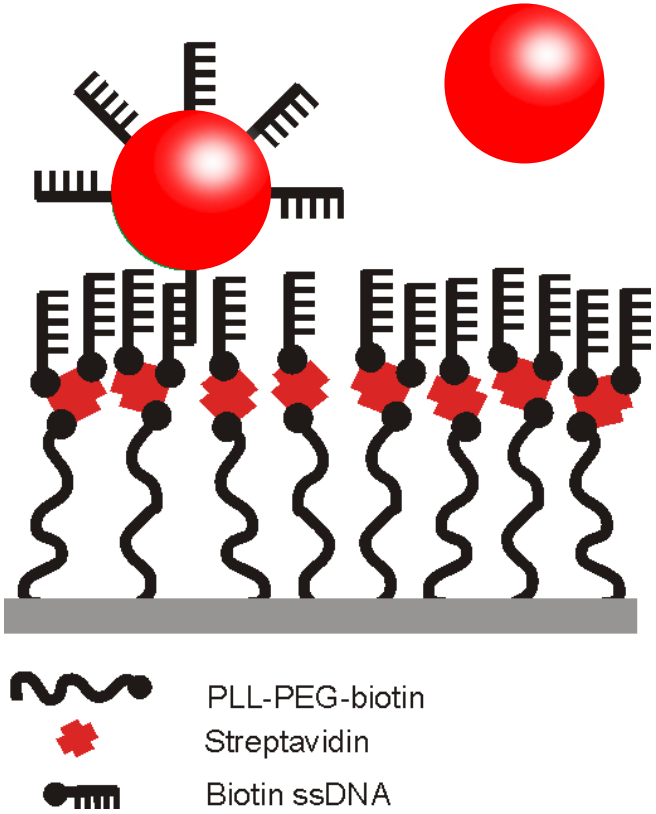
Using shorter dsDNA spacers

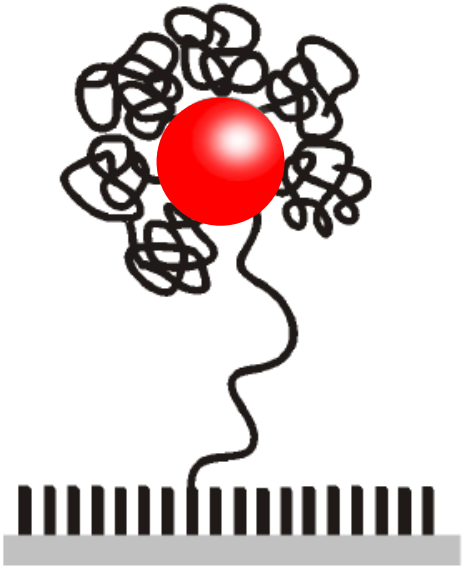


N. Geerts, T. Schmatko, E. Eiser, *Langmuir* (2008)

… now consider 2D aggregation…

2D Aggregation

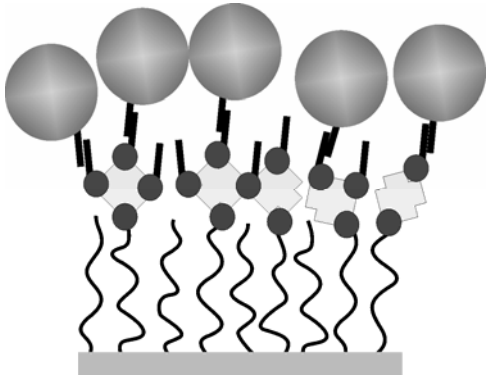


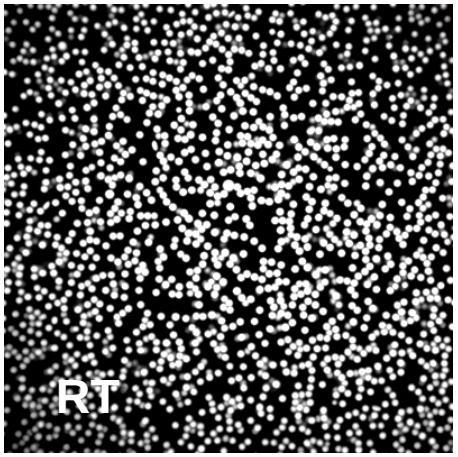


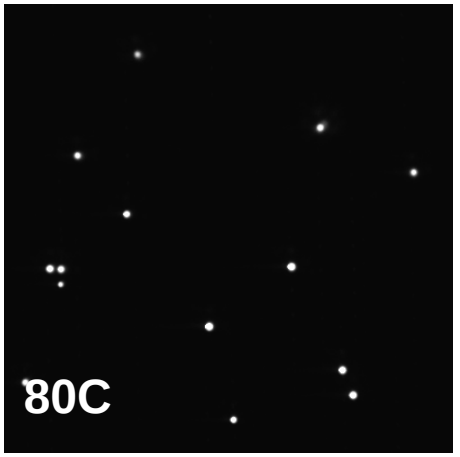
λ-DNA with complementary cos1-overhang

Testing DNA Melting

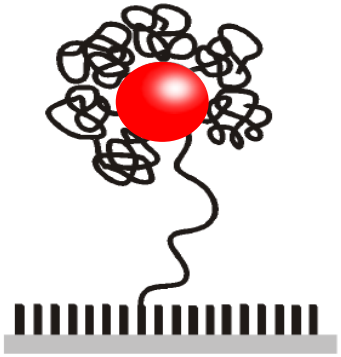
…using short ssDNA linkers on Colloids

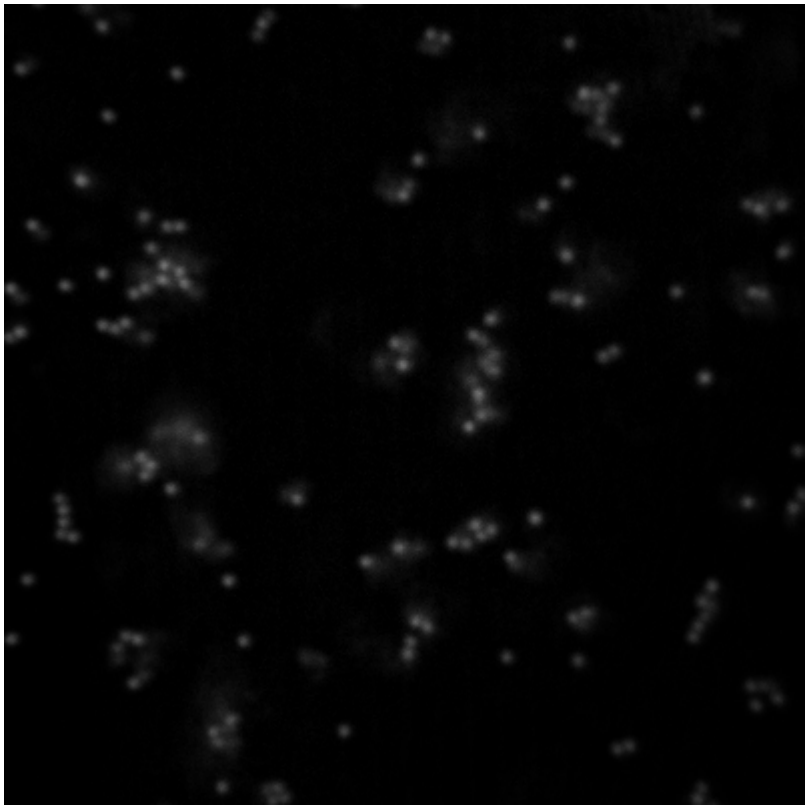




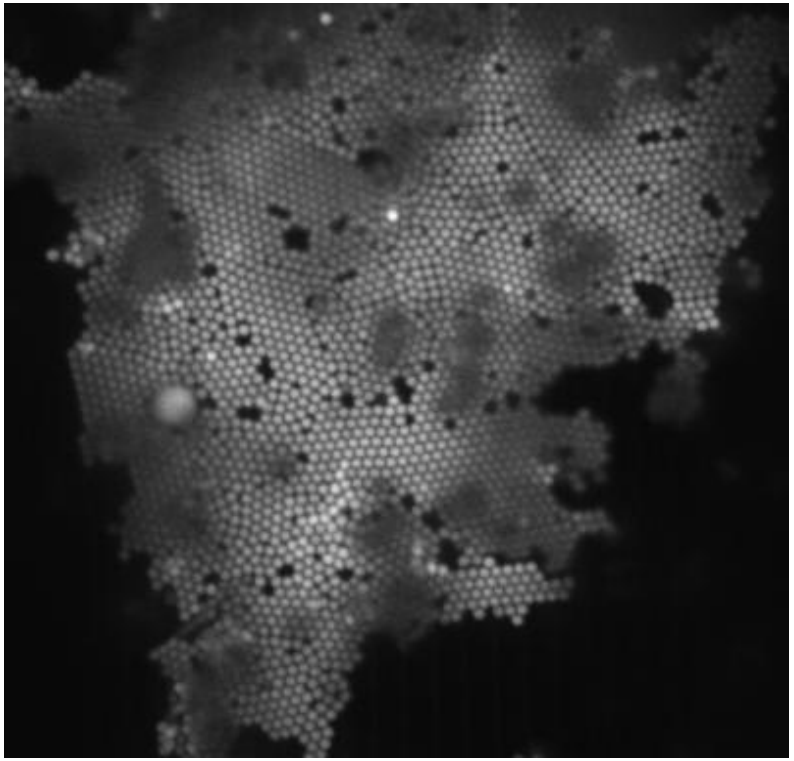


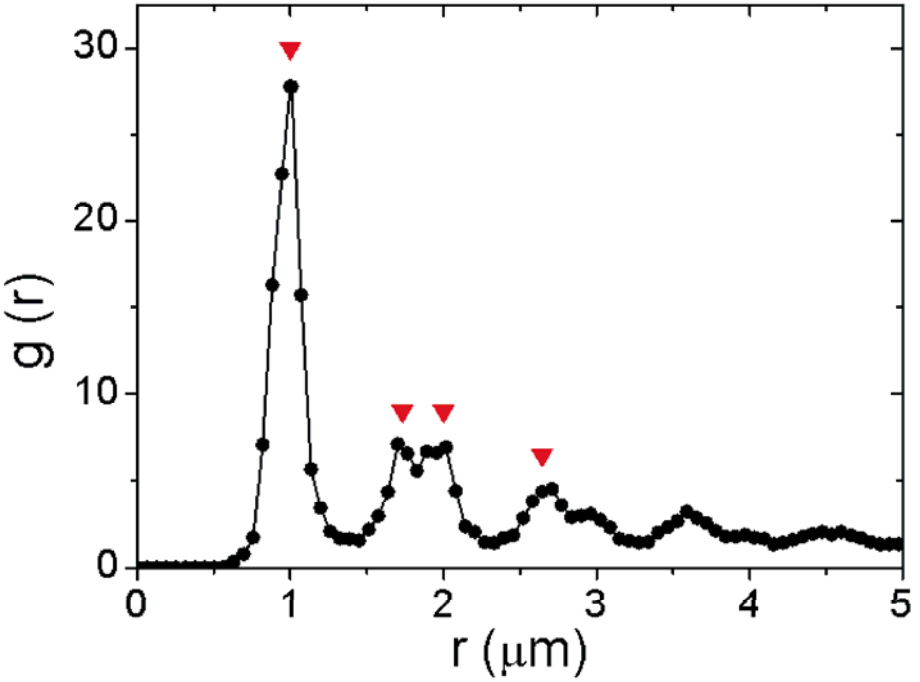
Flying Colloidal Carpet @ RT



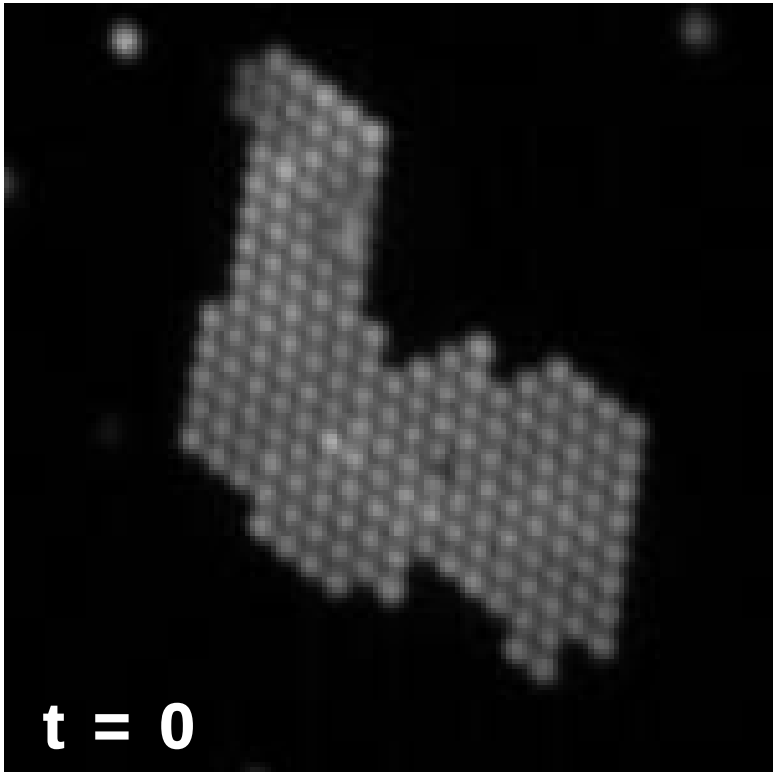


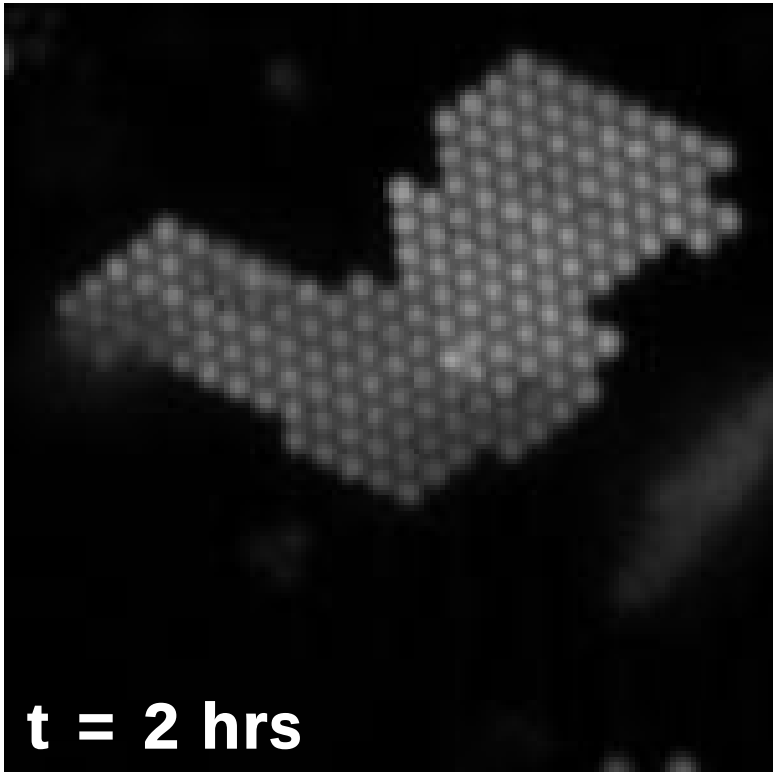
Pair-Correlation Function



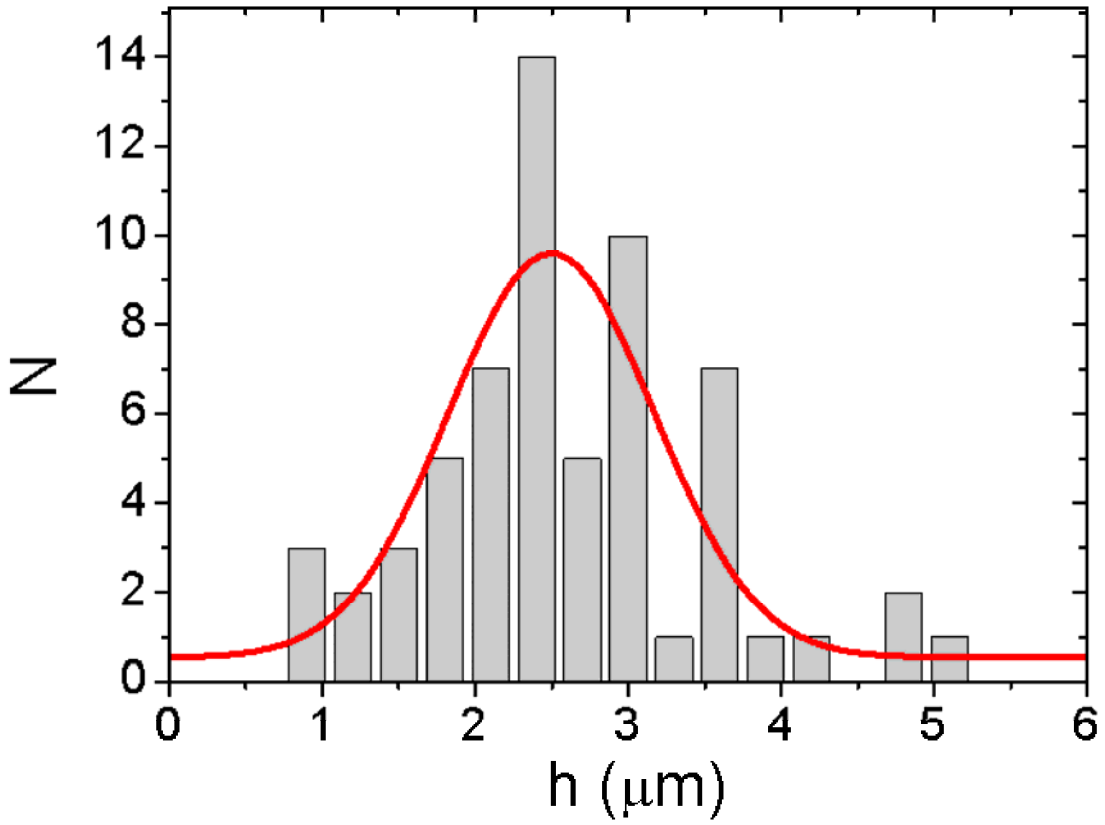


Carpets are Not Stuck



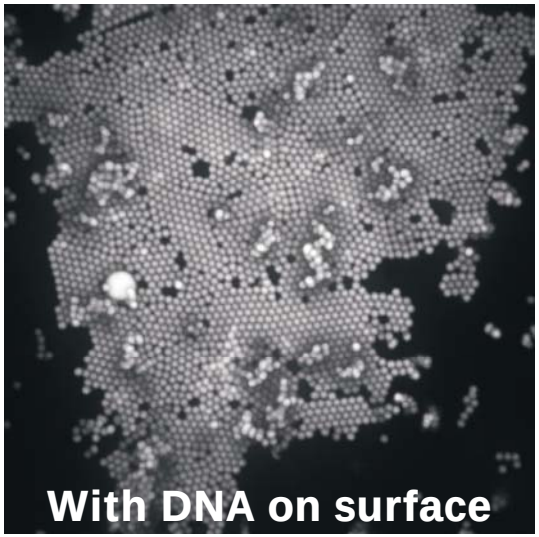


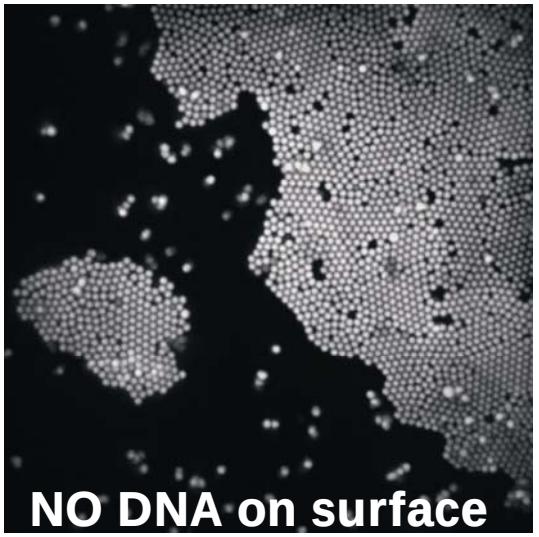
Cruising Altitude

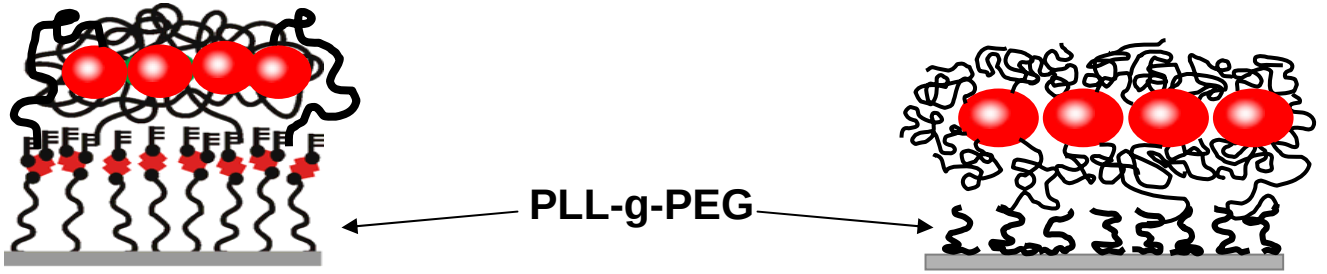


Crucial Ingredients

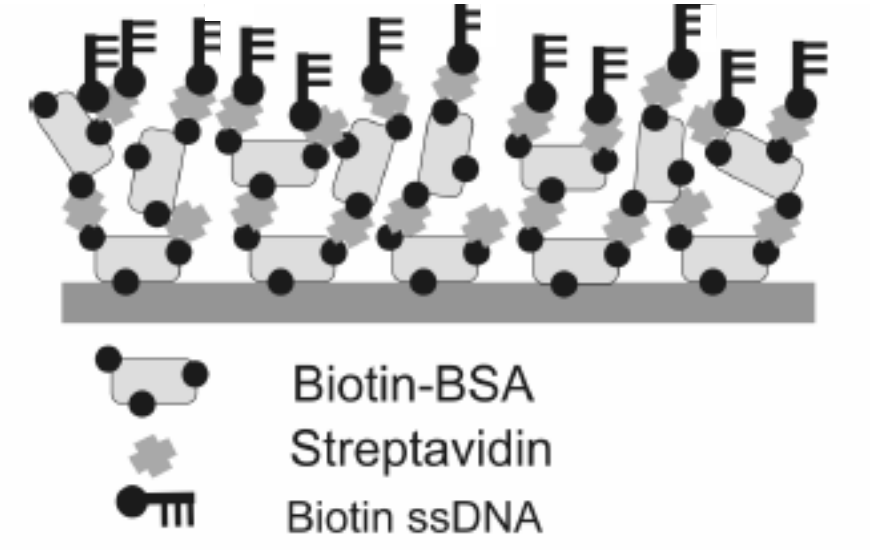
Anchoring to the surface

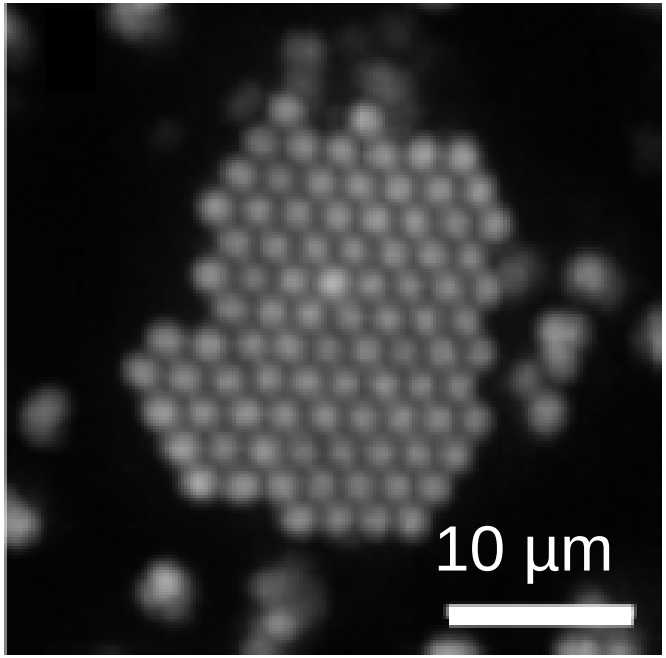






What is the role of PEG?

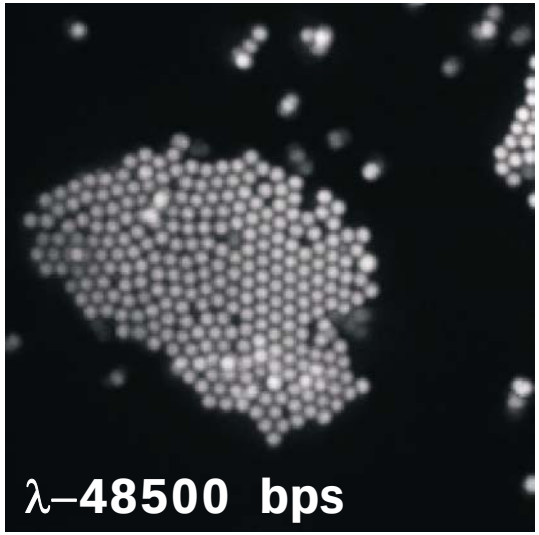




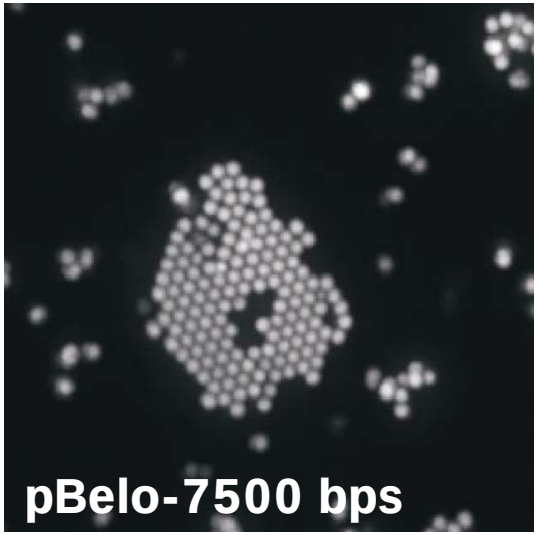
No PEG present → purely negatively charged coating,
but with short-range hybridization attraction.

Crucial Ingredients

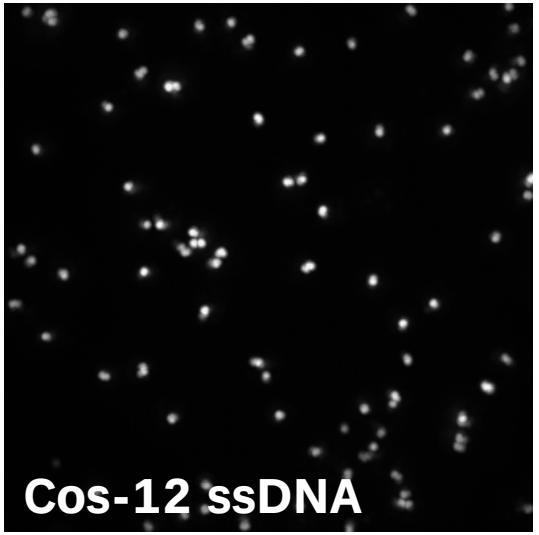
Length of the dsDNA spacer.



$R_G \approx 800$ nm



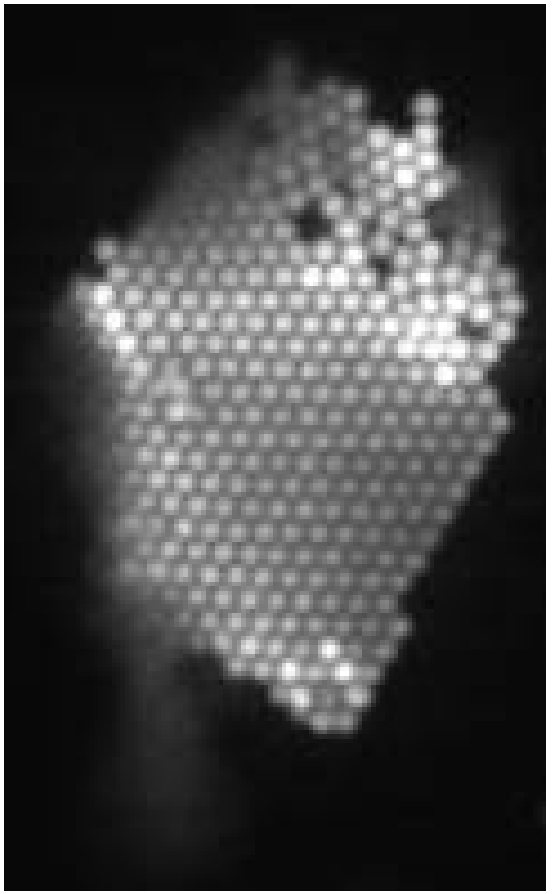
$R_G \approx 200$ nm



no spacer

This shows that:

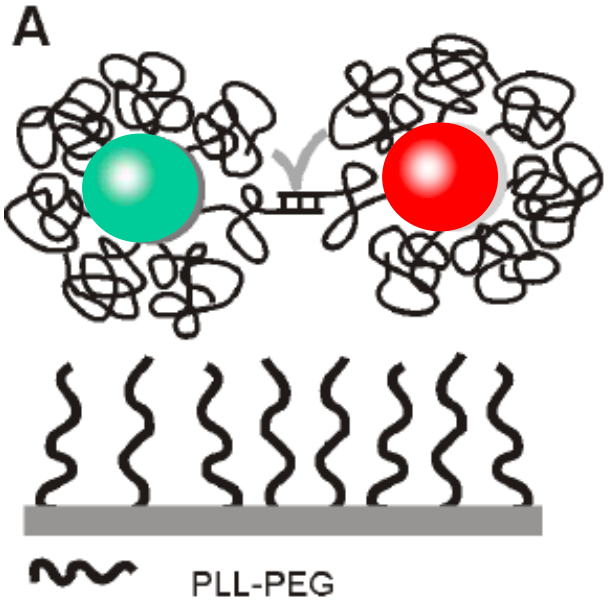
- 2D-crystallization is **NOT** due to specific colloid-substrate interactions
- Depends on **LONG** polymeric spacer
- **Weak attraction** to the substrate
- Once formed they are **Stable also in Bulk**.



Geerts and Eiser, *Soft Matter* (2010) 6, 664–669

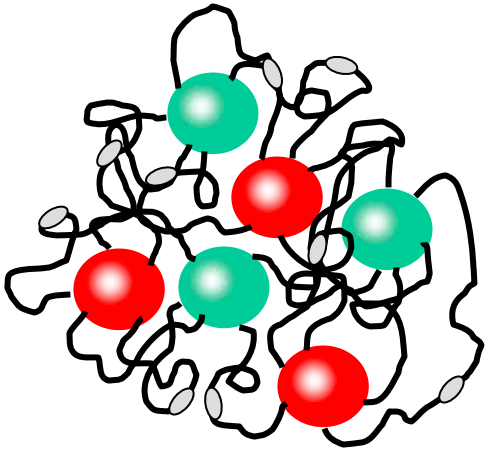
Effect of Colloid-Colloid binding

Allow binding between red and green colloids



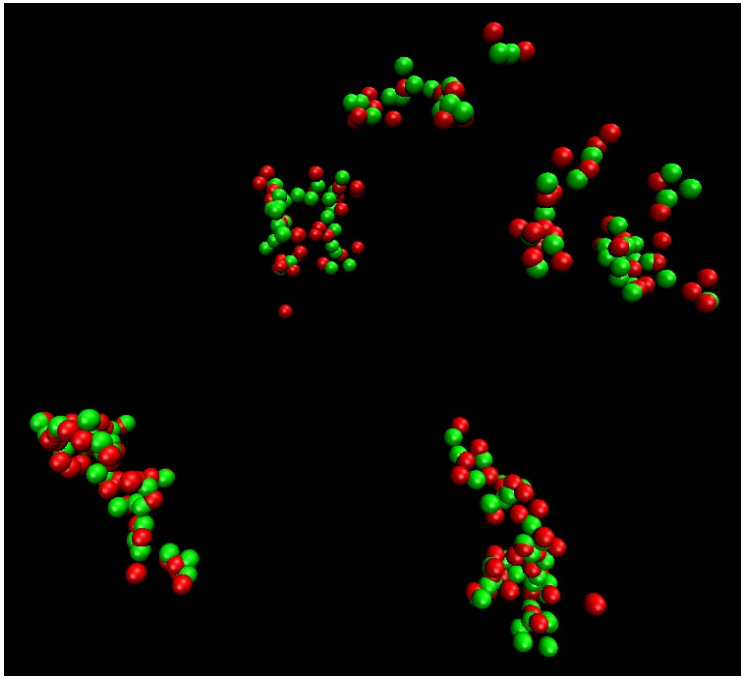
Geerts, Jahn, Eiser, *JPCM* (2010), 22, 104111

Remember - in bulk



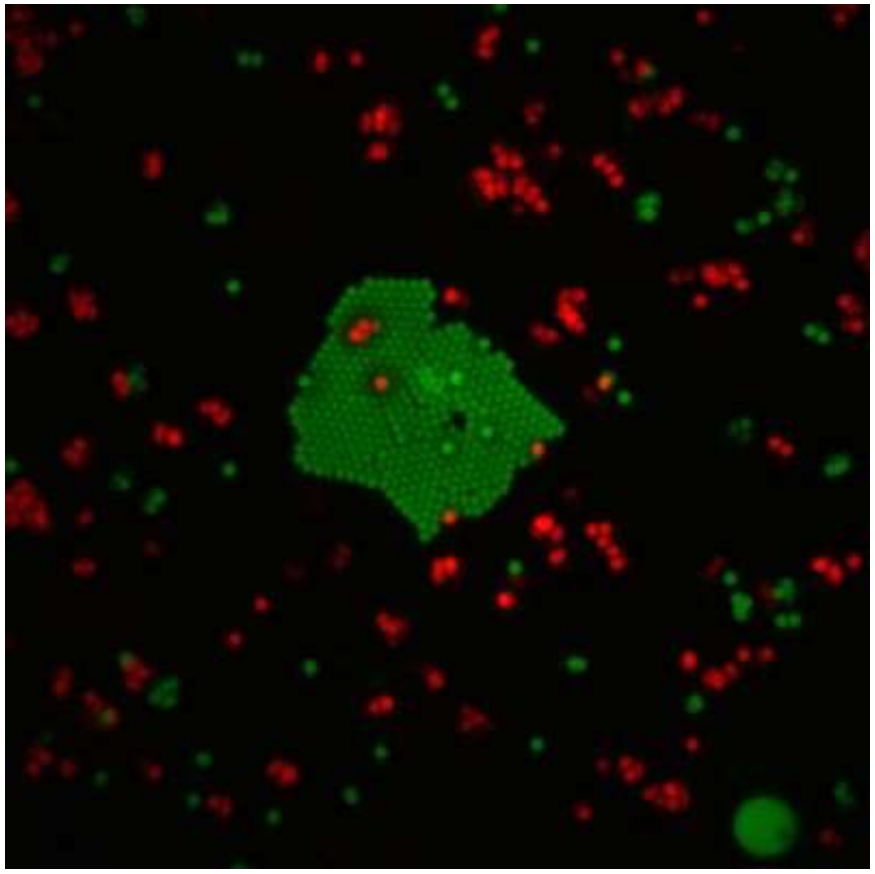
dsDNA-5'-GGG CGG CGA CCT-3'
3'-CCC GCC GCT GGA-5'-dsDNA

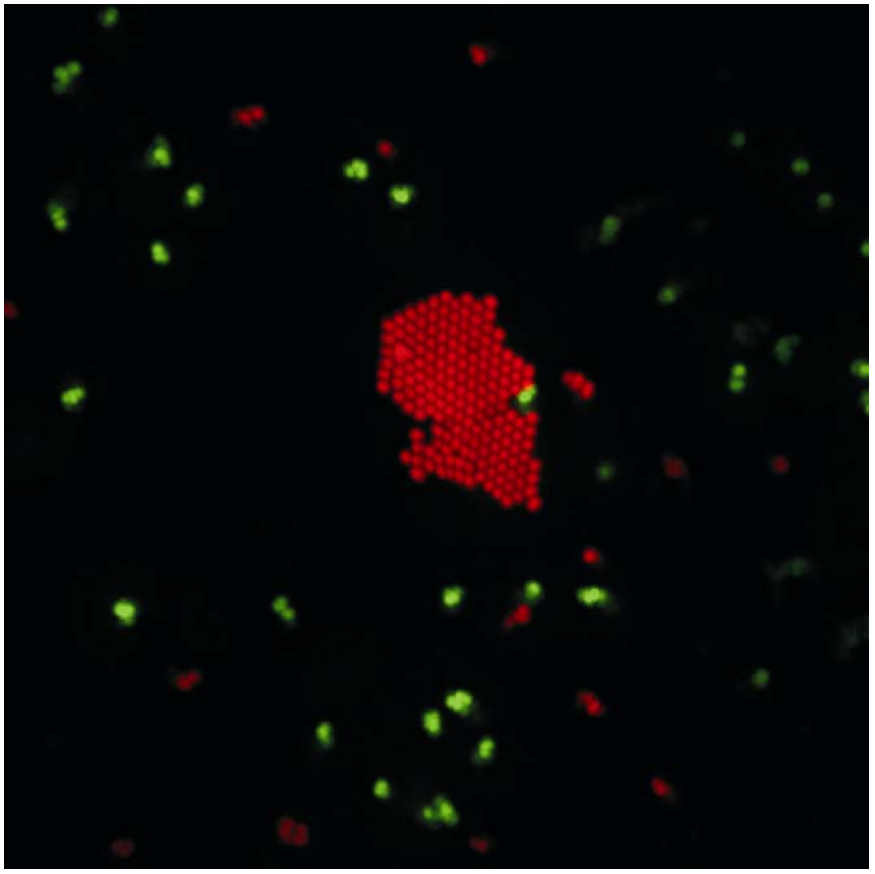
double-stranded DNA



No sticky surface present!

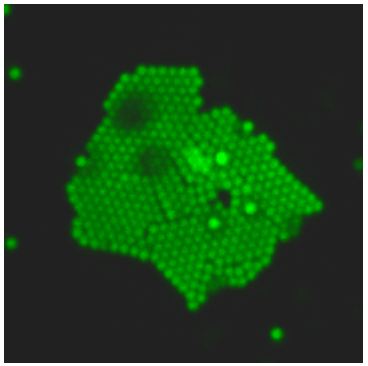
Surprise!





Geerts, Jahn, Eiser, *JPCM* (2010), 22, 104111

Why Fractionated Crystals ?



Radial distribution function tells us:

Green colloids are **~ 10%**
smaller than the red ones.

→ **Size-fractionated crystallization.**

Barrat and Hansen (1986) *J. Physique* **47**, 1547

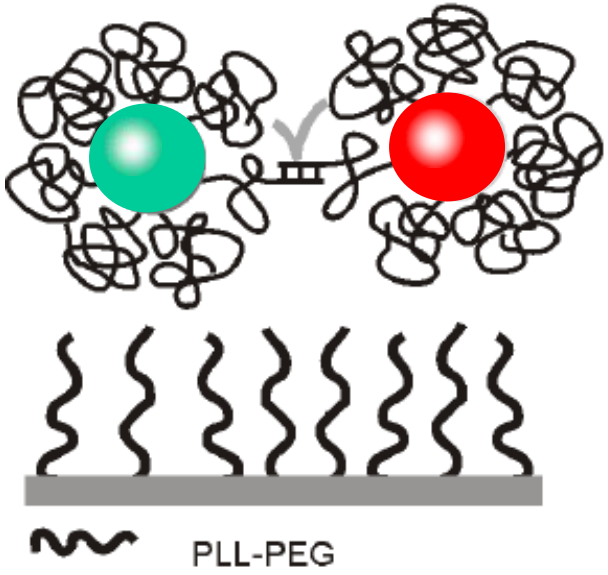
Rae and Haymet (1988) *J. Chem. Phys*. **88**, 1114

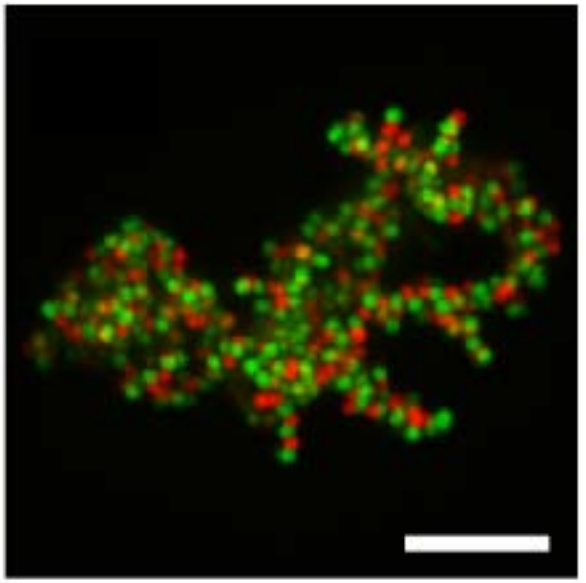
Pronk and Frenkel (2004) *Phys. Rev. E* **69**, 066123

2D versus 3D

Competition between the interactions

Using shorter DNA-polymer spacers (***R_g* ≈ 200 nm**)

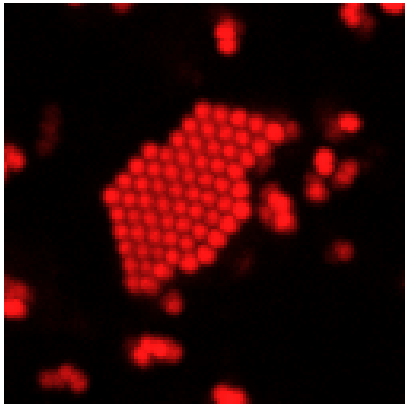


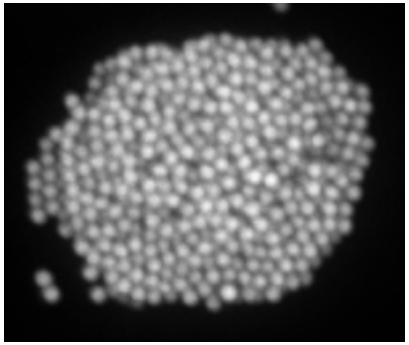


pBelo-DNA with
complementary cos-overhangs

Geerts, Jahn, Eiser, *JPCM* (2010), 22, 104111

Summary



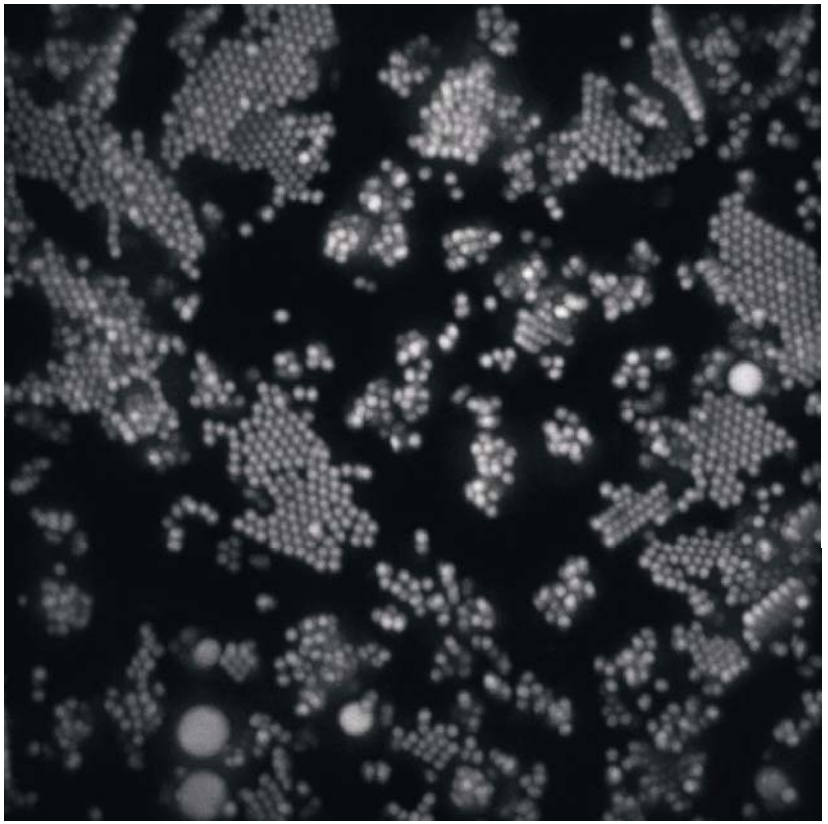


- **Highly specific and reversible self-assembly** is possible with **short** DNA
- **programmable self-assembly**
- **But DNA is also a perfect, monodisperse & very long polymer that brings about completely new physics**.

***Important for*: Biosensors, Photonics, Nano-devises….**

Thank you for listening.

Small Carpets do not Merge



What about depletion forces?