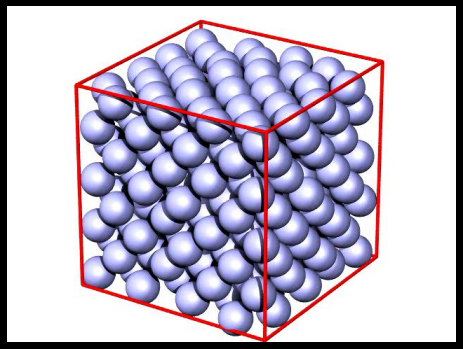
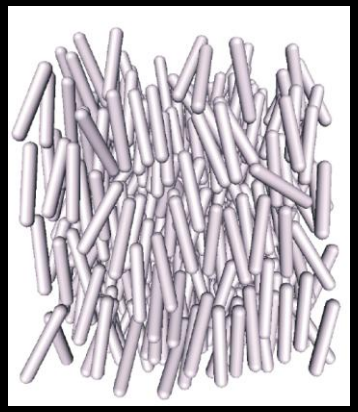
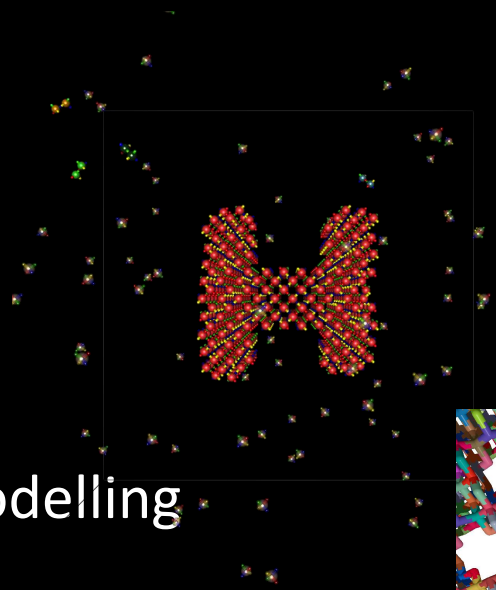
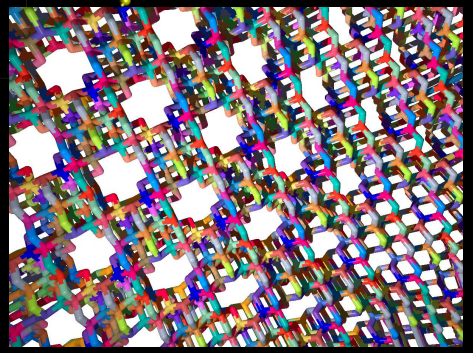

ON THIS SITE
MARCH 13,
1839
NOTHING HAPPENED

Numerical Design of Pathways for Addressable Self-assembly









Daan Frenkel

Predictive Multiscale Materials Modelling

4-12-2015

Will Jacobs

Aleks Reinhardt

They did the work

MODELLING COLLOIDAL MATTER:

Particle sizes: 10 nm to 1 microns.

Even a single colloid may contain hundreds to millions of atoms.

Consequence: atomistic modelling is only used for the smallest (nano) colloids.

MODELLING COLLOIDAL MATTER:

Two colloids may be very similar, but they are never the same.

Unlike atoms or simple molecules, colloids are polydisperse.

Colloids are (almost) always described by coarse-grained models that are not derived from atomistic (let alone quantum) simulations.

The shape of inter-colloidal potentials can be tuned into regimes that are **never** observed for atoms (e.g. very short-ranged attraction => no liquid-vapour transition).

Forces between colloids can be purely entropic:

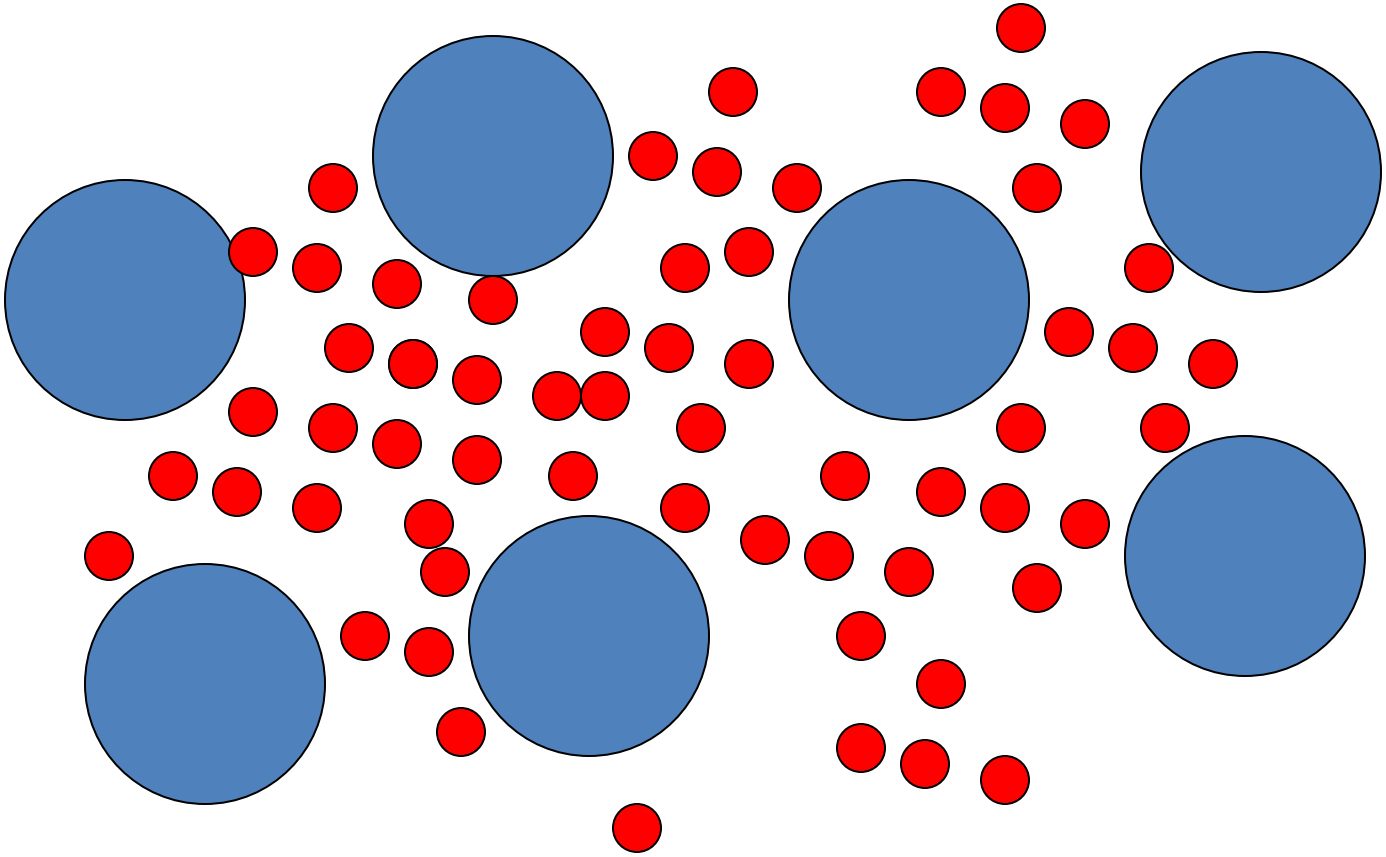
1. Excluded volume
2. “Depletion forces”
3. “Steric stabilisation”

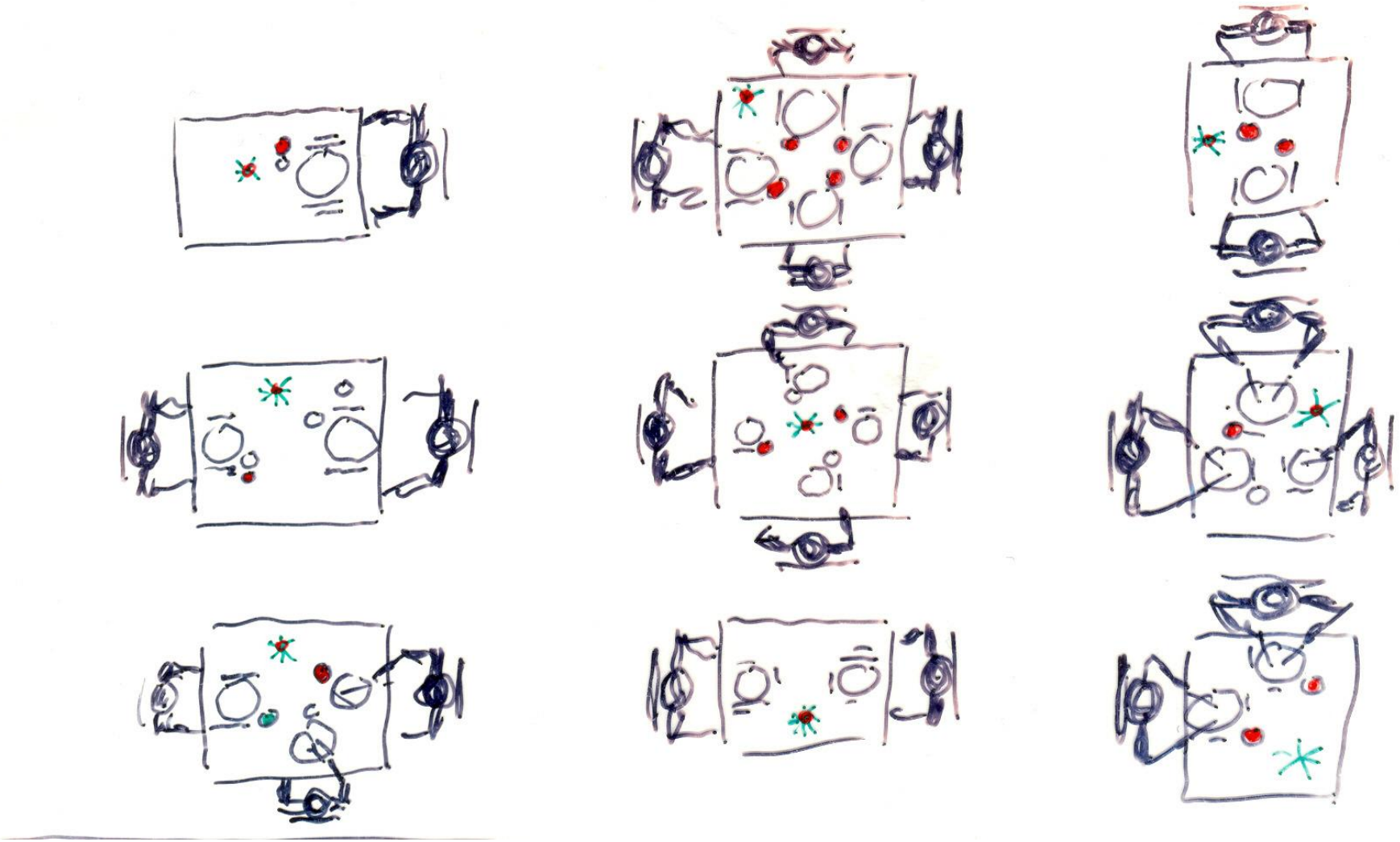
Depletion forces.

Typically:
(large) Colloid + (small) Polymer (`depletant’)

DEPLETION FORCES:

atomistic detail hardly matters

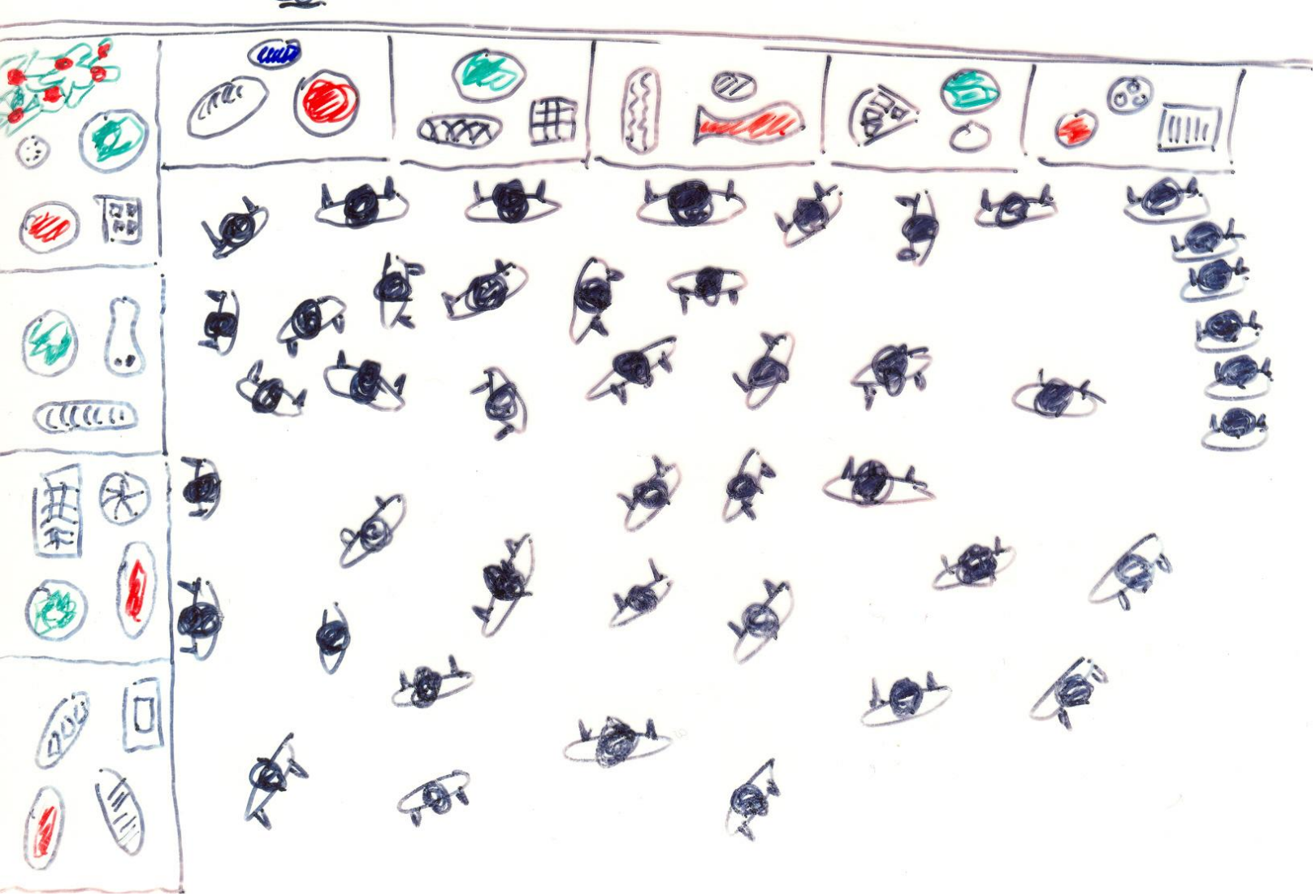




Colloids = tables

Polymers = guests

1. Low polymer concentration (quiet evening)



Colloids = tables

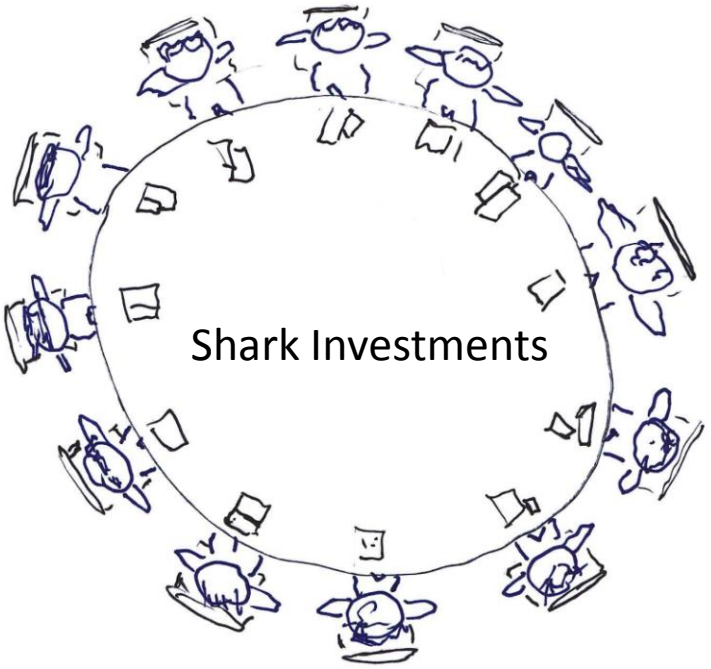
Polymers = guests

2. High polymer concentration (crowded reception)

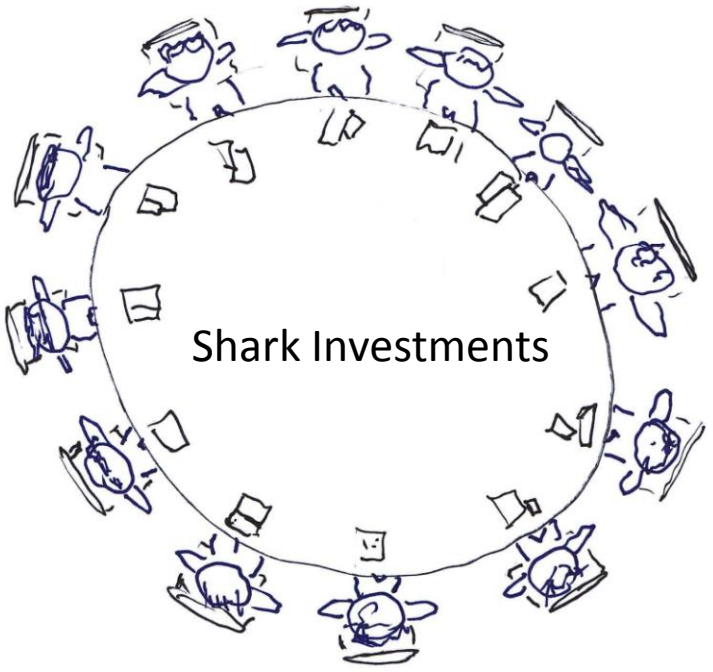
Steric stabilisation: molecules `grafted' onto colloids inhibit close approach

Human example: Failed Board merger

The attempted merger of BARRACUDA TRADING Inc and SHARK INVESTMENTS PLC



The attempted merger of BARRACUDA TRADING Inc and SHARK INVESTMENTS PLC



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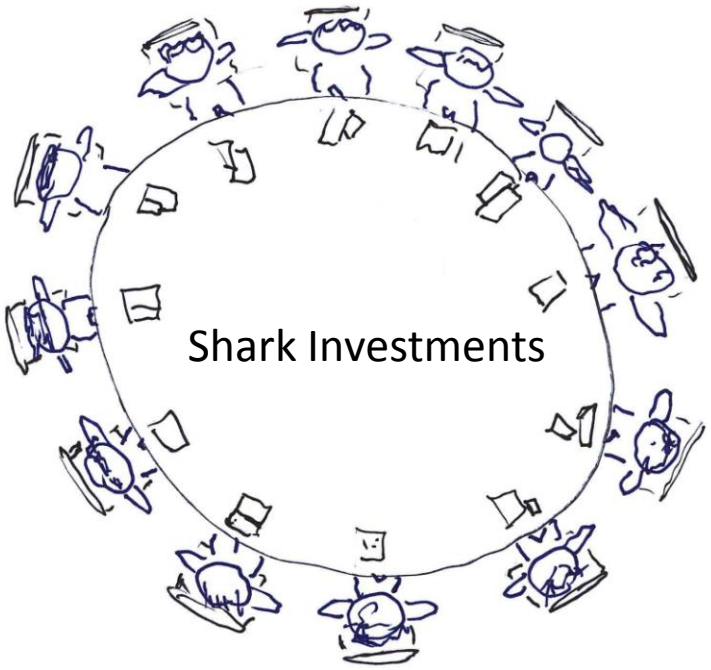

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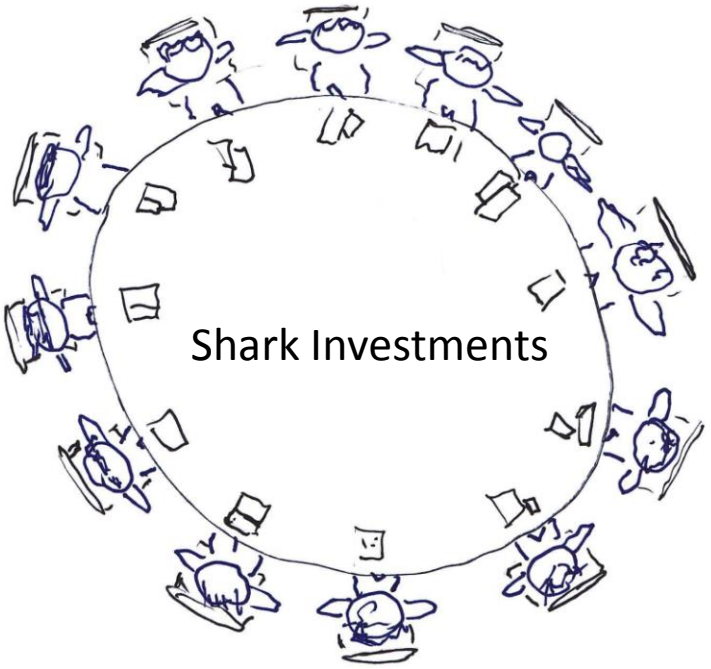


Self-Assembly

What is so interesting about self assembling materials?

My (rough) answer:
To eliminate the need for `manufacturing' nanoscale structures that perform a non-trivial function.

What kind of functions?

1. Photonic, plasmonic, magnetic (etc) **bulk** properties.
2. Nano-scale devices that can do `**logical**' operations.
3. …

What kind of structures are required?

1. Photonic (etc) **bulk** properties:
   - Complex structures, few building blocks.
2. Nano-scale `**logical**' devices:
   - Simple structures, **many different building blocks (`addressable complexity')**

Example of structures with addressable complexity

1. Protein complexes
2. (functionalised) `DNA-brick' structures

1. `Structural' Complexity through packing
2. `Addressable' Complexity through specific interactions

1. Structural complexity through packing

Order through disorder: the unexpected side of entropy

ENTROPY: the pre-history…

Thermodynamics

1st Law: $\Delta U = Q + W$

2nd Law: Heat does not spontaneously flow from cold to hot.

(0th Law: If $T_A = T_B$ and $T_A = T_c$, then $T_B = T_C$)

But then Clausius appeared…

Die Energie der Welt ist konstant; die Entropie der Welt strebt einen Maximum zu.

$dU = đq + đw$

$TdS = dU + PdV - \mu dN$

$\eta = w/q_1 = (q_1 - q_2)/q_1$

Rudolf Clausius

$\Rightarrow dS \geq 0$!!!

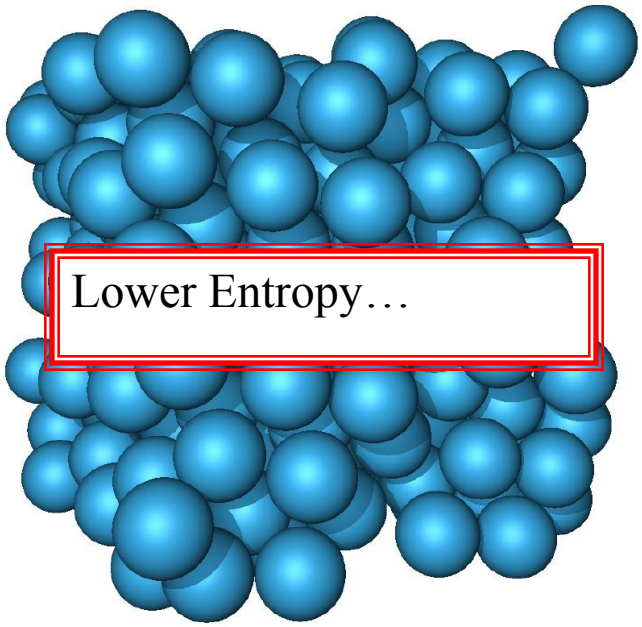
…in other words, the entropy of a closed system never decreases!!!

…but what is entropy?

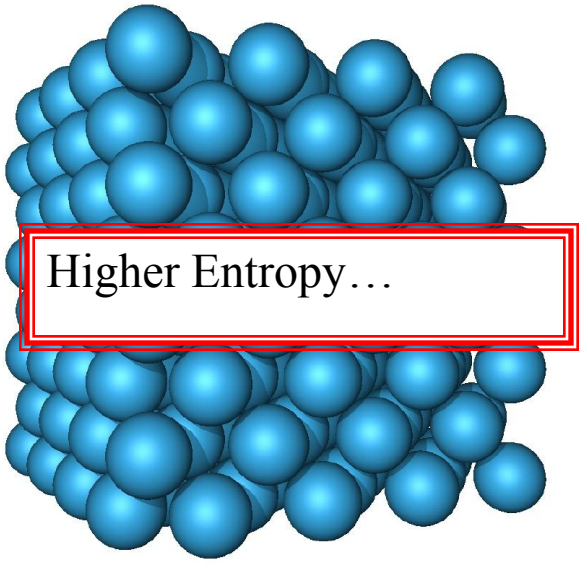
During a spontaneous change in a closed system, the DISORDER increases ….

Computer simulations (1957)

Hard-sphere liquid



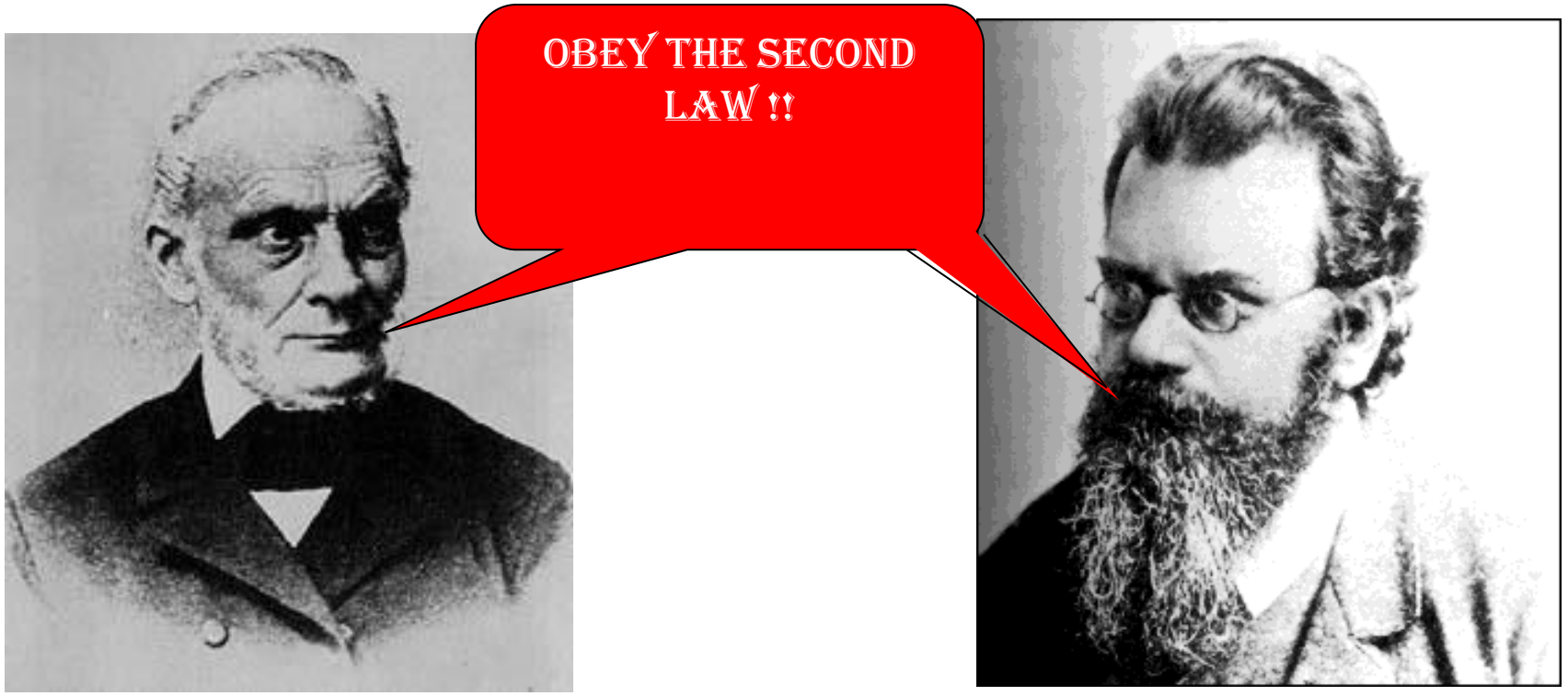
Hard-sphere freezing is driven by entropy !



Hard-sphere crystal

Is hard-sphere freezing against the

SECOND LAW OF THERMODYNAMICS ???



CLAUSIUS **BOLTZMANN**

"For the 2nd Law I will burn at the stake" (Heinz London)

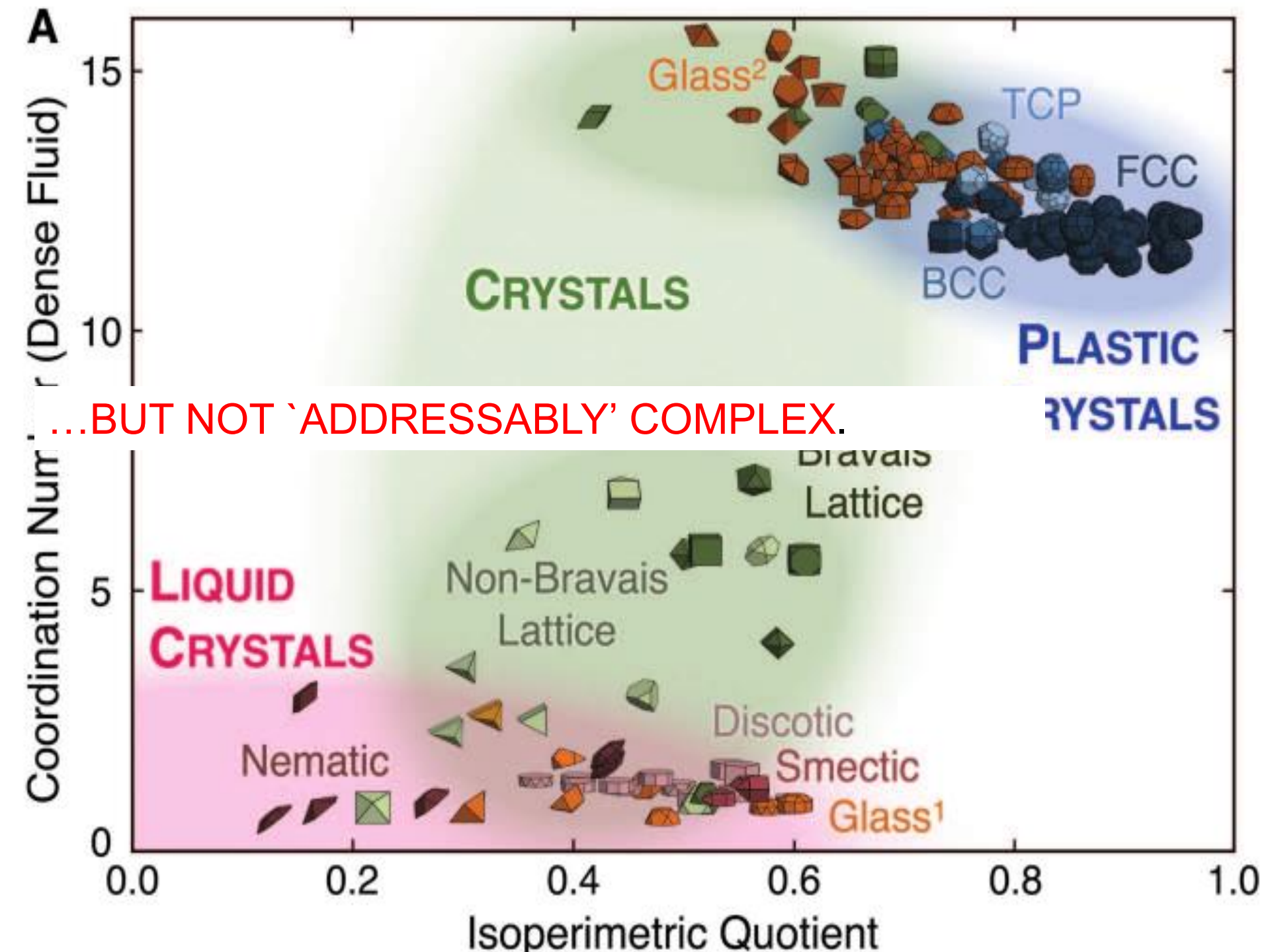
The 2nd Law is not violated.

In 1957, the Alder/Wood simulations of entropic freezing created quite a stir…

..but entropic freezing is real:

1986: Hard-sphere colloids really freeze

Pusey and van Megen ***Nature*** **320 340 (1986)**



…BUT NOT `ADDRESSABLY' COMPLEX.

1. `Structural' Complexity through packing

2. `Addressable' Complexity through specific interactions

One popular idea to make complex structures:

BOX 1:

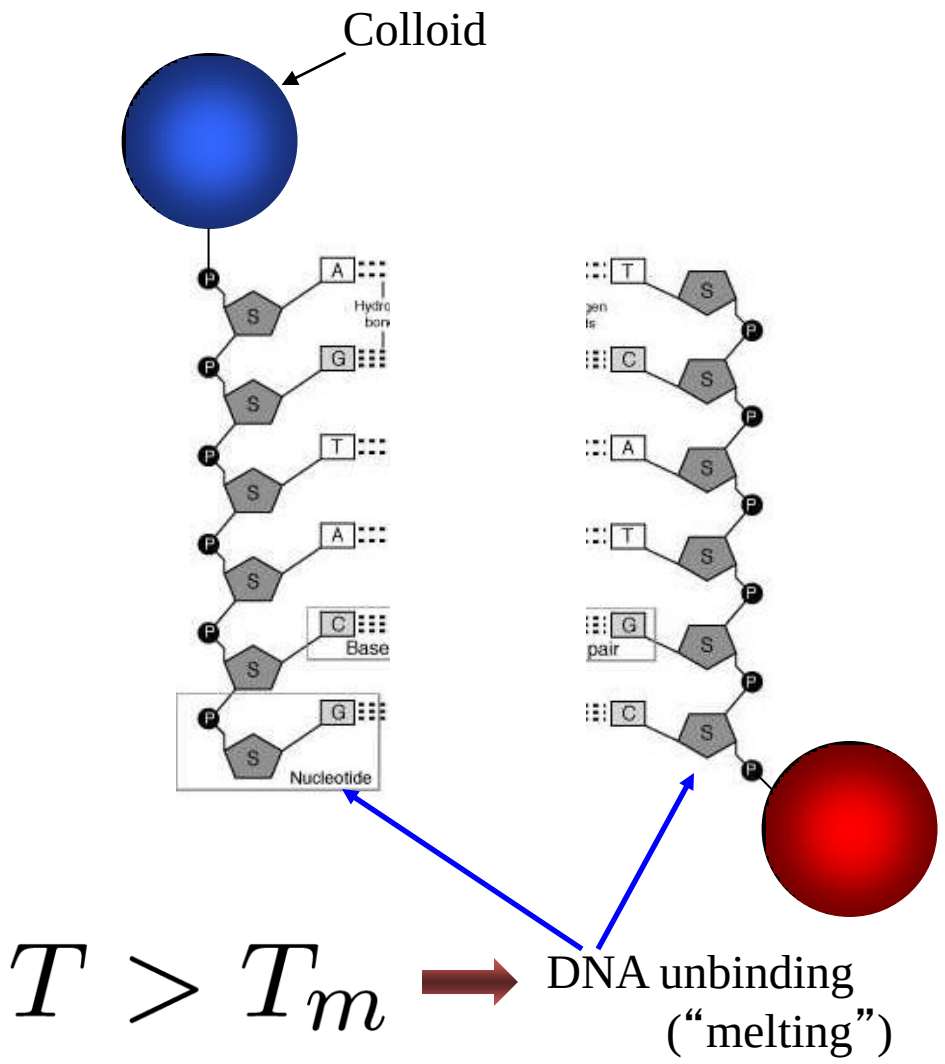
`Why DNA?'

Because it is selective and has a short `innovation cycle'

BOX 2:

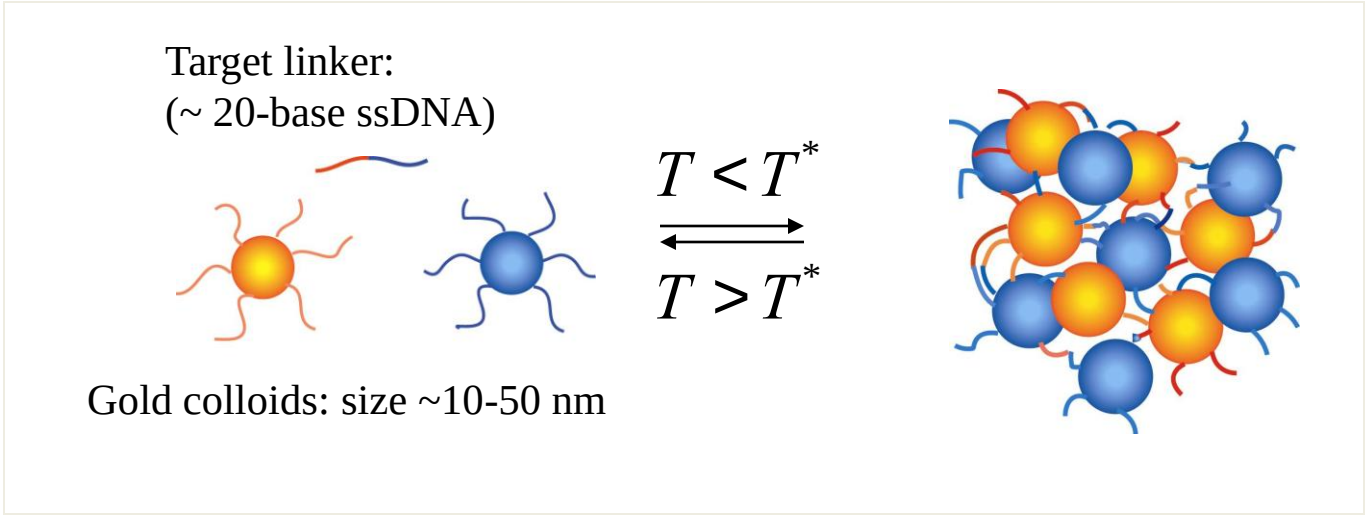
`Why not DNA'

Because it may be the wrong material for the task.

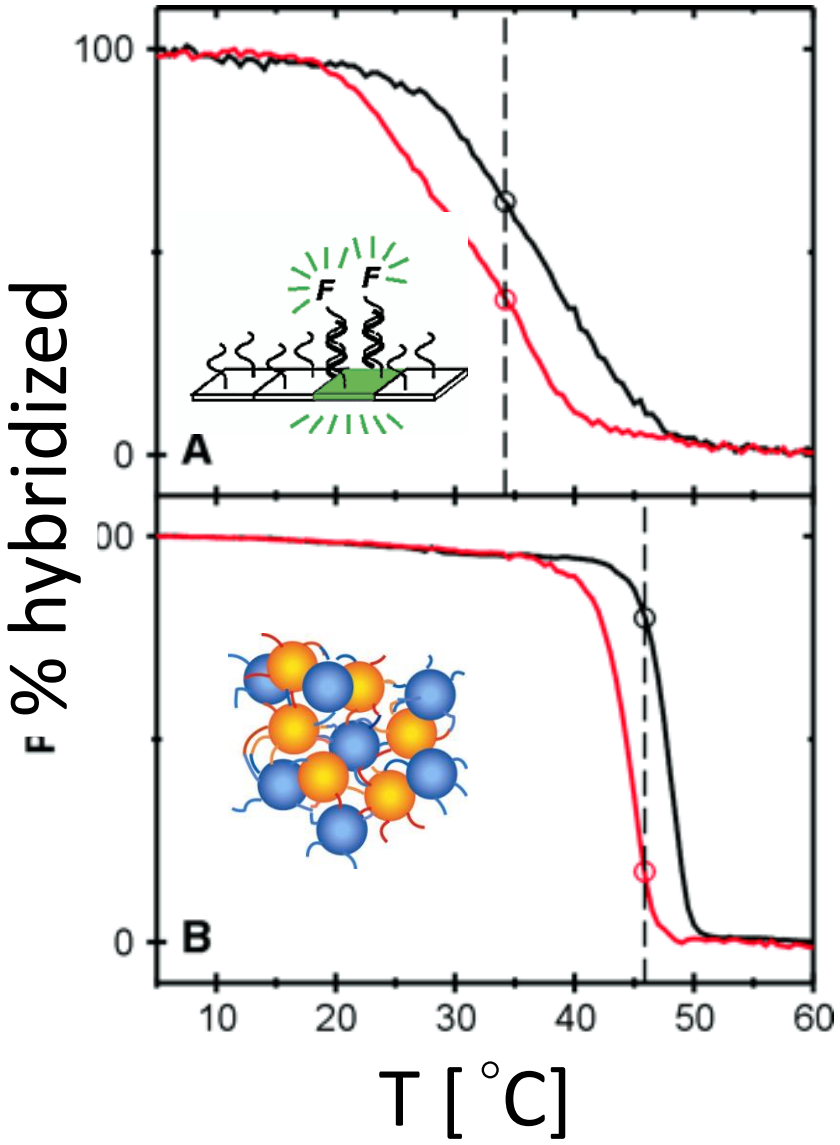


Background: ssDNA recognition

C. A. Mirkin et al., Nature, 382, 607 (1996)



Single-stranded DNA fragments link ssDNA coated colloids and cause aggregation…

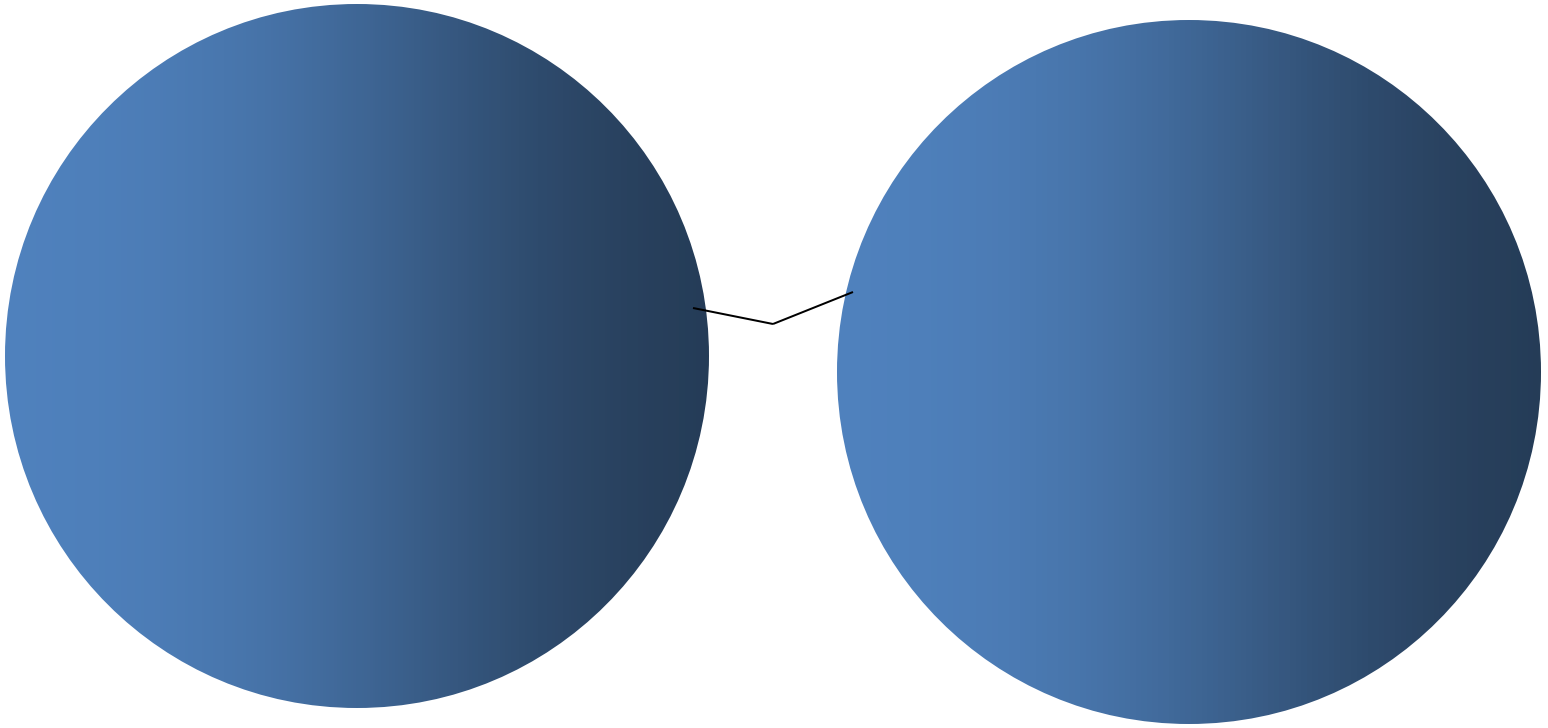


Fluorophore probes
(one bond ⇒
weak T-dependence)

Nanoparticle probes
(many bonds ⇒
strong T-dependence)

Complementary sequence

Single-base mismatched sequence

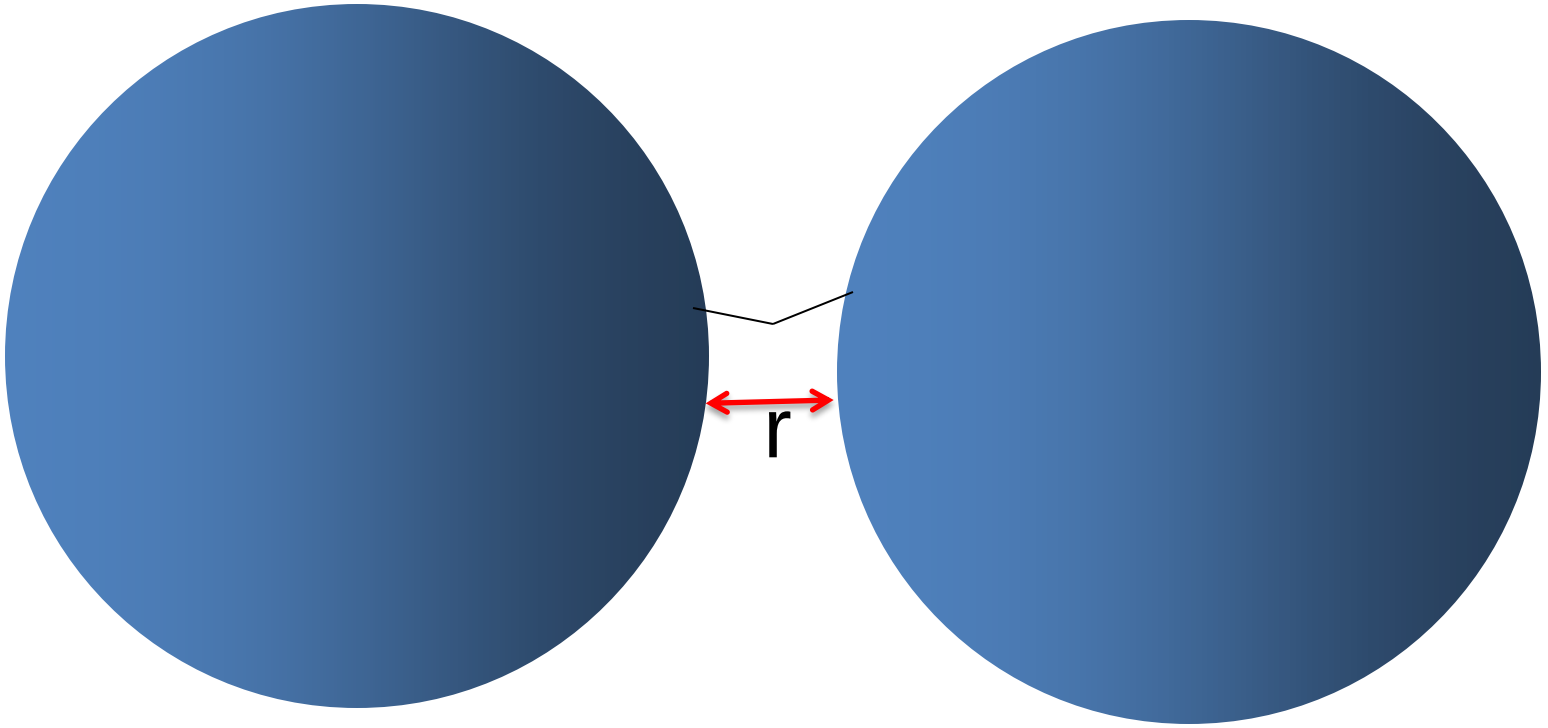


Colloids may be bound or unbound

$$e^{-\Delta f / kT} \equiv \frac{P_{\text{bound}}}{P_{\text{unbound}}}$$

This defines the binding free energy Δf

First consider 1 bond: binding free energy Δf

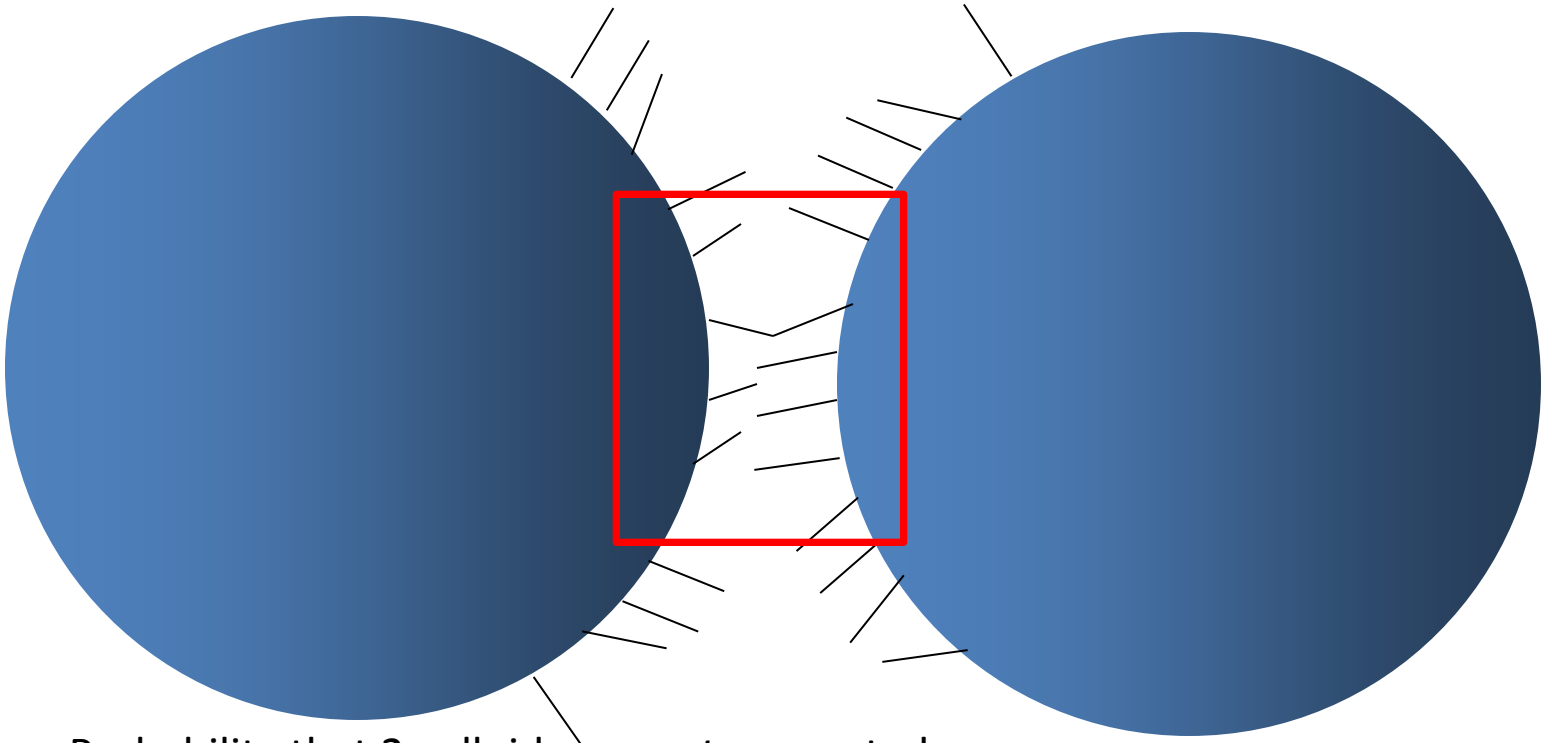


Probability that 2 colloids are *not* connected:

$$P_{\text{unbound}}(r) = \frac{1}{1 + e^{-\Delta f(r)/kT}}$$

Cooperativity:

Now: N possible bonds

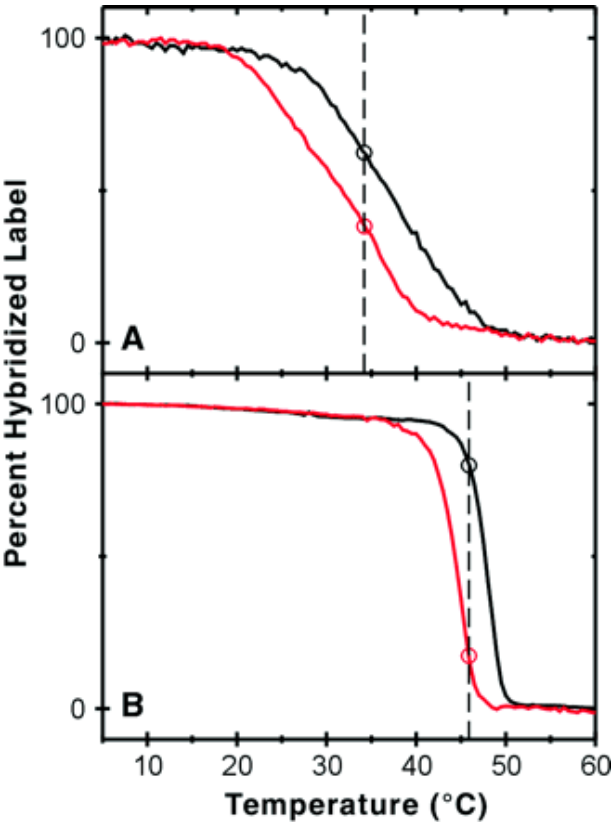


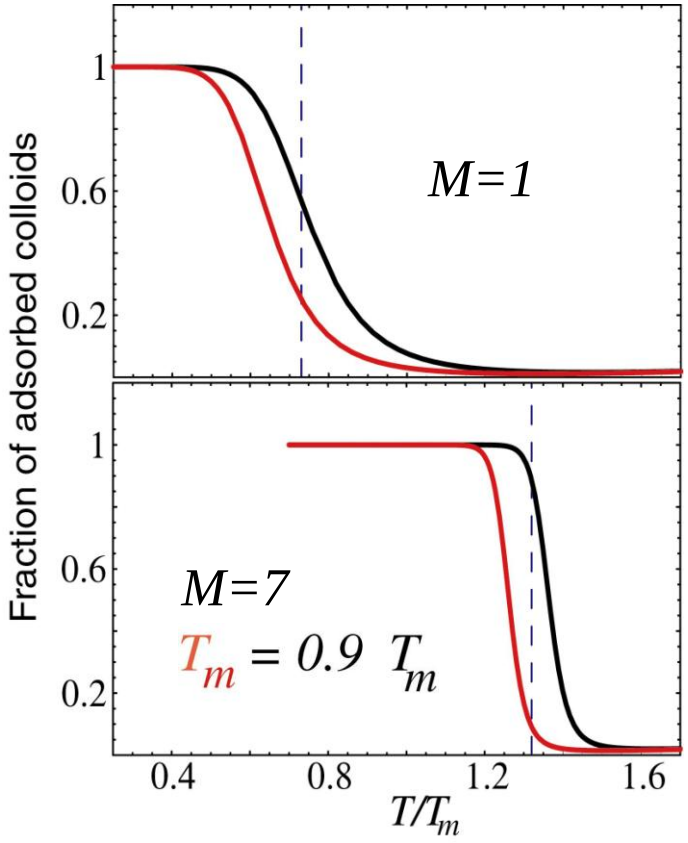
Probability that 2 colloids are *not* connected:

$$P(0) = \left(\frac{1}{1 + e^{-\Delta f / kT}} \right)^N$$

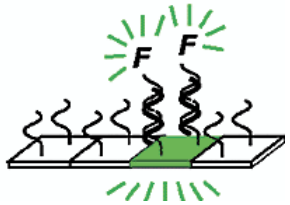
Changes steeply with Δf and N.

Simple (lattice) theory:

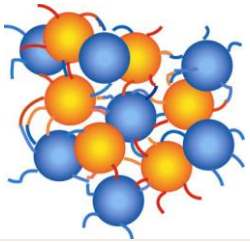




Fluorophore probes



Nanoparticle probes (higher selectivity)



Experiment

Theory

Sharp dissolution profiles → High selectivity

Simulations can be used to identify the factors that limit DNA-mediated colloidal self assembly.

But first, we need a working (i.e. validated) coarse-grained model
(atomistic models are hopeless)

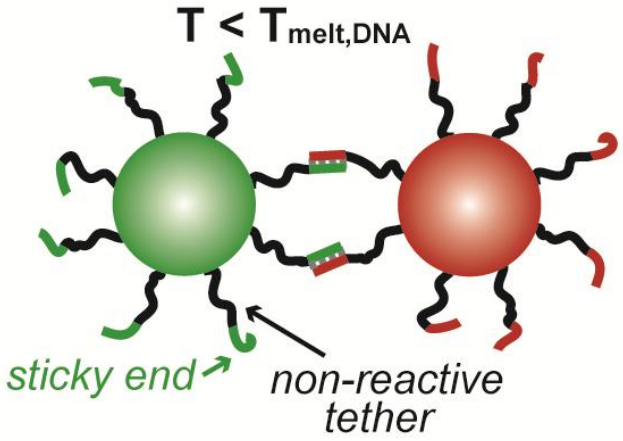
Basic `coarse-graining' approach:

- Use experimental input wherever possible
- In particular: use `SantaLucia (phenomenological) rules for DNA hybridization strength
- Colloids are (hard) spheres
- DNA chains modelled as:
  - Short polymers

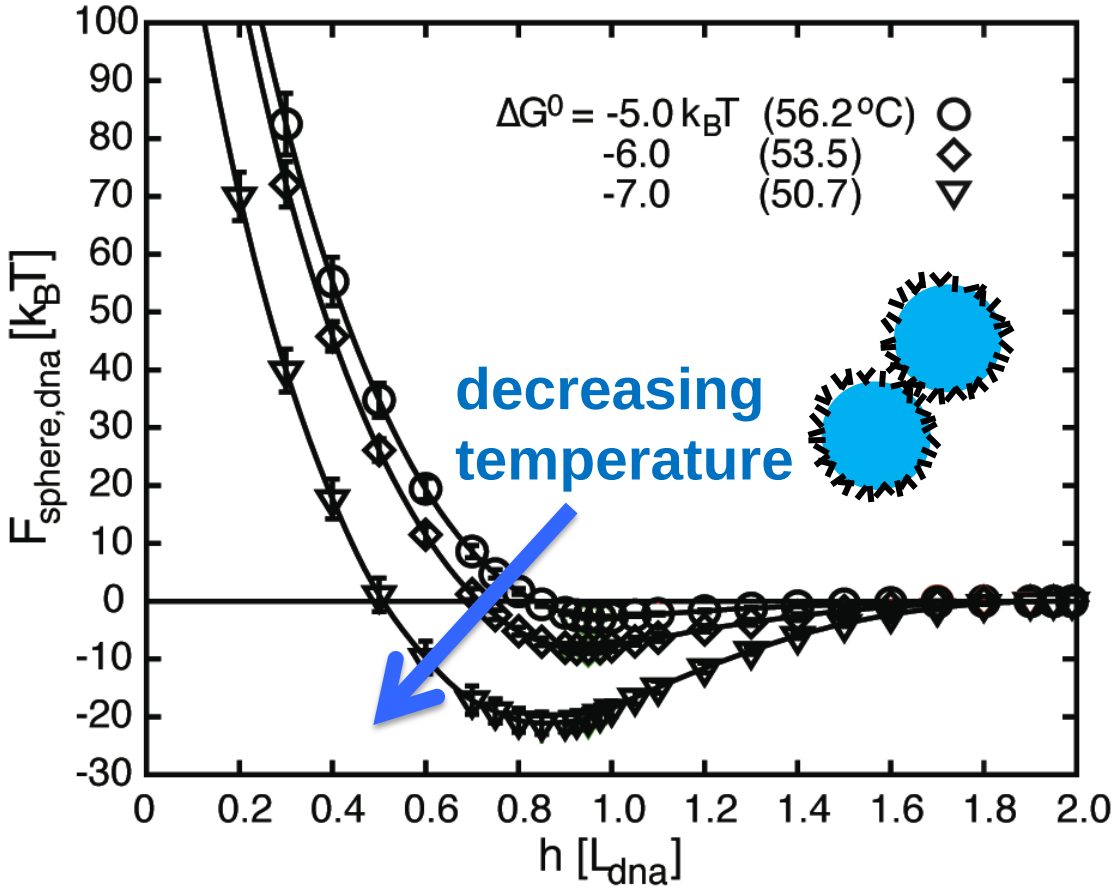
Micron –size colloids + short (rigid) DNA strands

Very narrow temperature window for equilibrium

self-assembly and crystallization due to multi-bond interactions



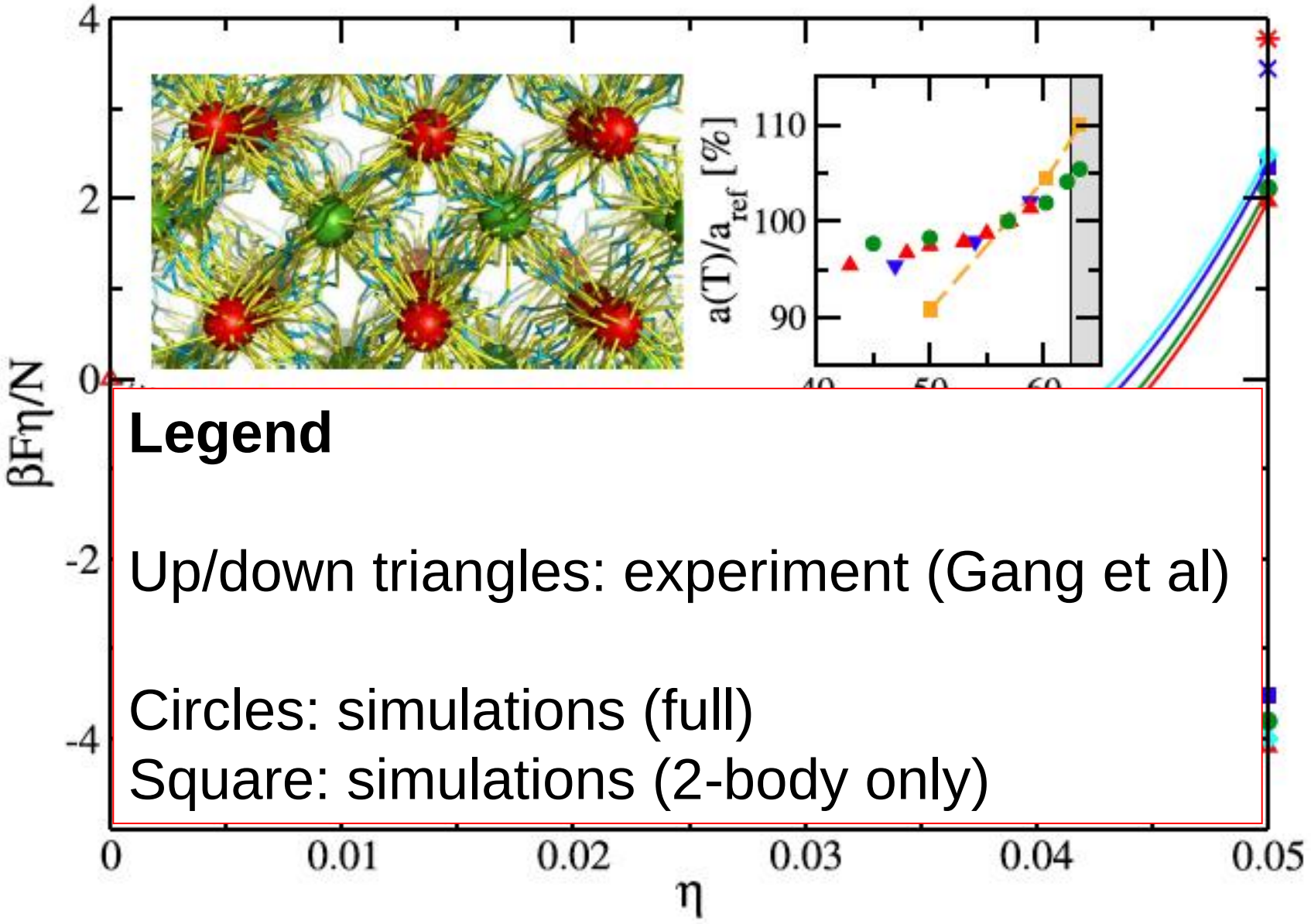
$N_{bonds} = 5 – 500$



Leunissen, Frenkel, ***J. Chem. Phys. 134, 084702 (2011)***

DNA-coated nano-colloids: Comparison to experiment

Melting temperature to within 1 ° C


4
2
0
-2
-4
βFη/N
0
0.01
0.02
0.03
0.04
0.05
η
a(T)/a_ref [%]
110
100
90
Legend
Up/down triangles: experiment (Gang et al)
Circles: simulations (full)
Square: simulations (2-body only)

Why is complex self assembly difficult?

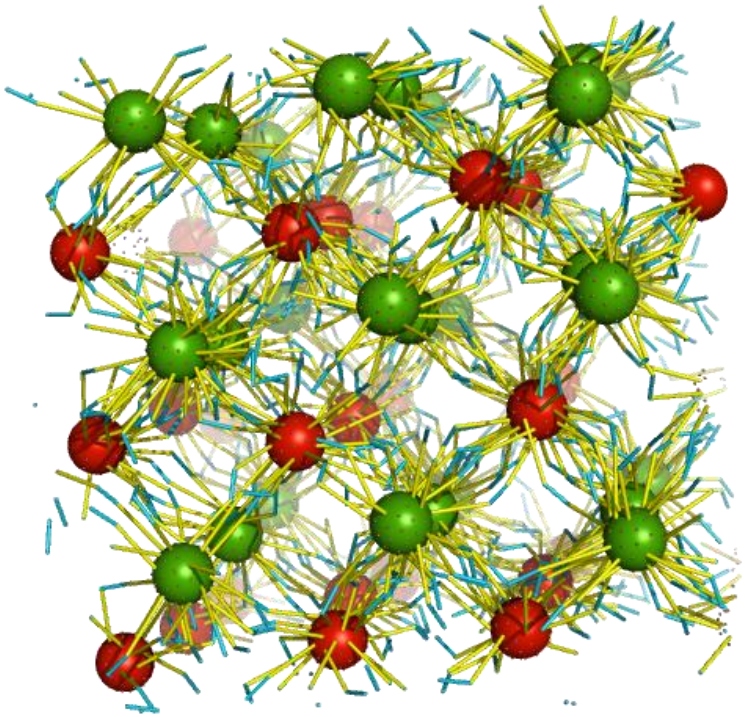
The same factors that make DNA-coated nano-colloids good "gene-detectors" …

…compromise the kinetics of self assembly.

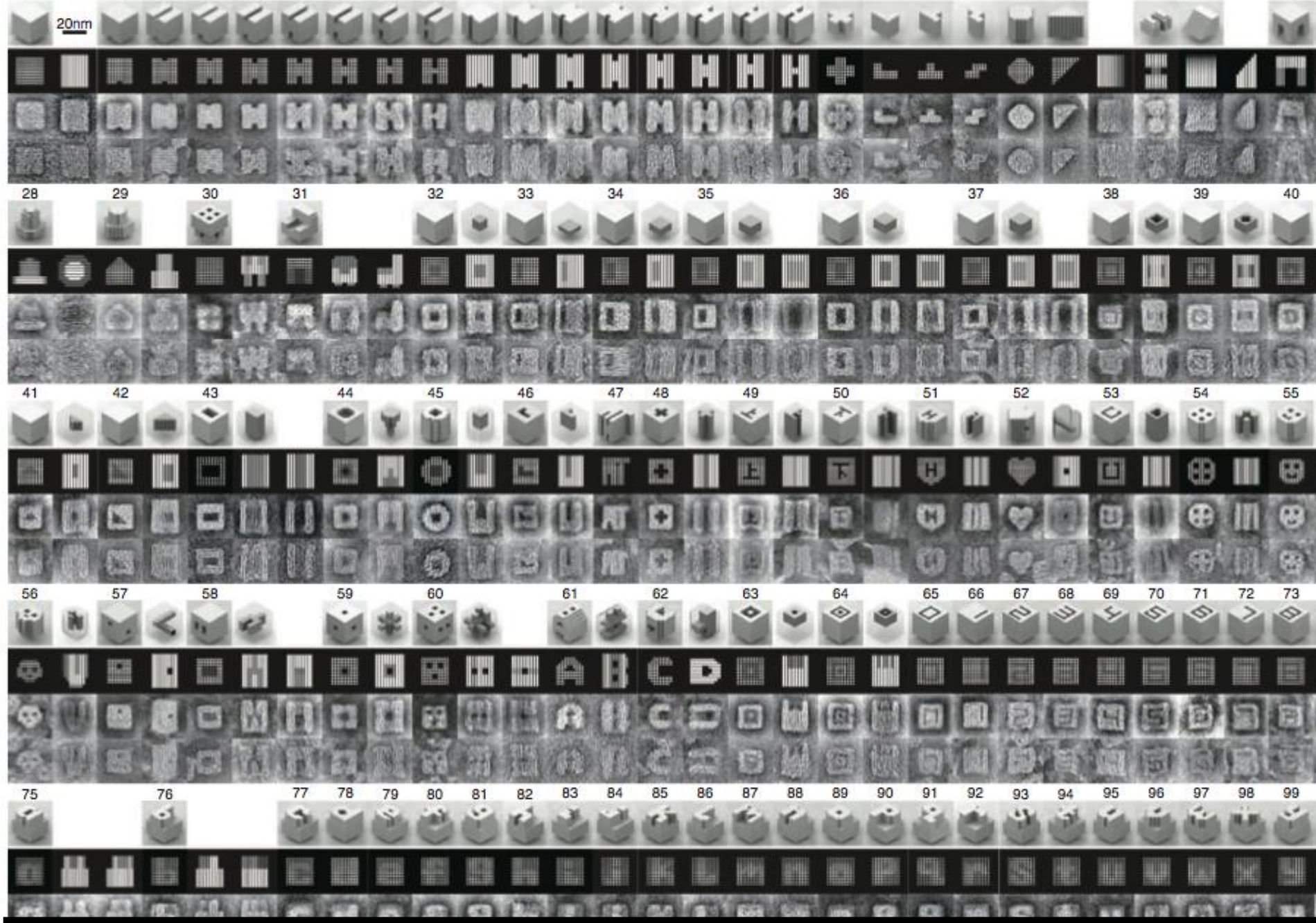
The material that forms is NOT the equilibrium phase.

For some, a great disappointment….

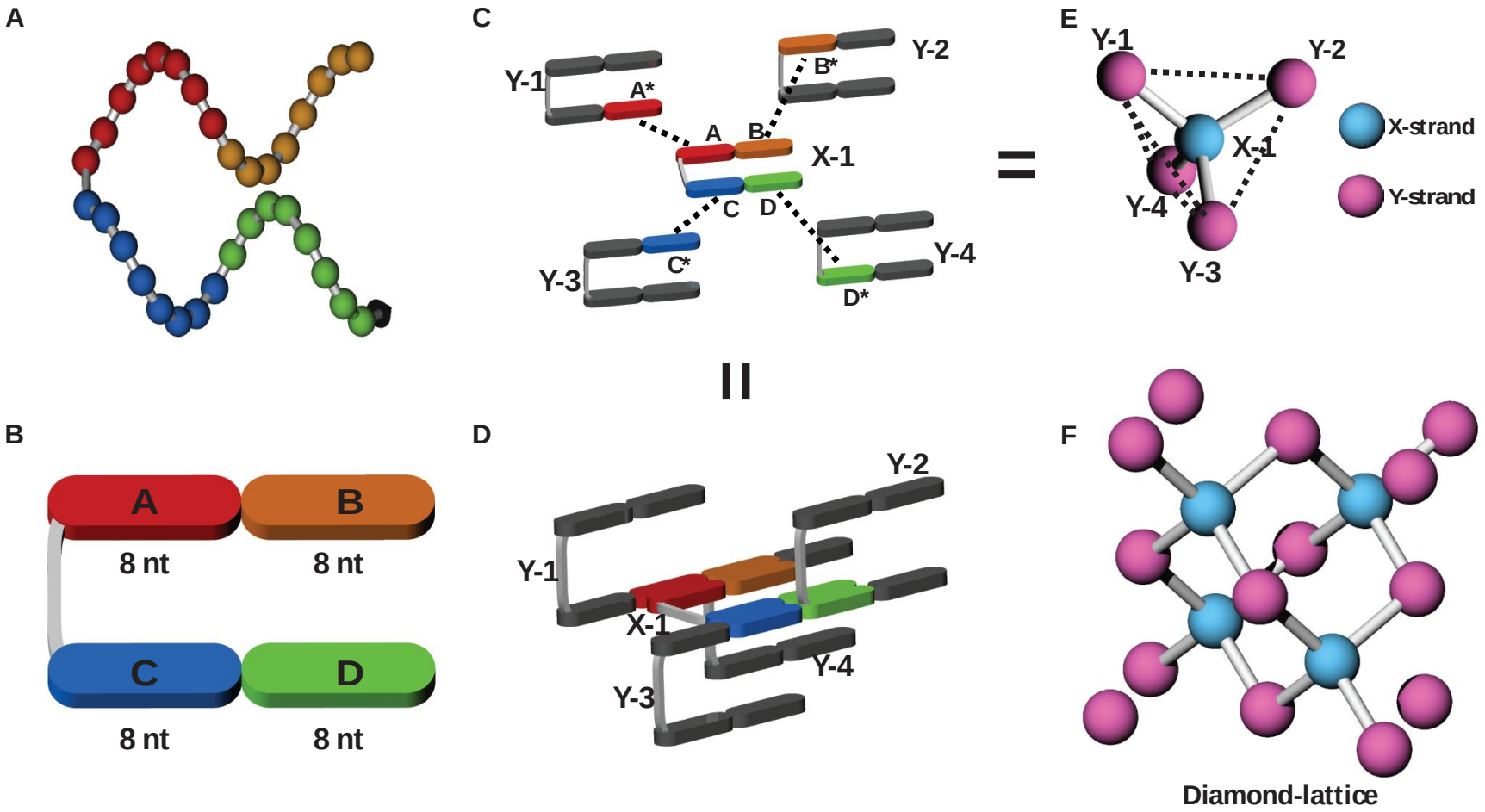
Thus far mainly `structural' complexity – small number of distinct building blocks



Gang, Manoharan, Pine, Crocker, Brujic, Mirkin – and many more.



Y. Ke, L. L. Ong, W. M. Shih, and P. Yin, Science 338, 1177 (2012)

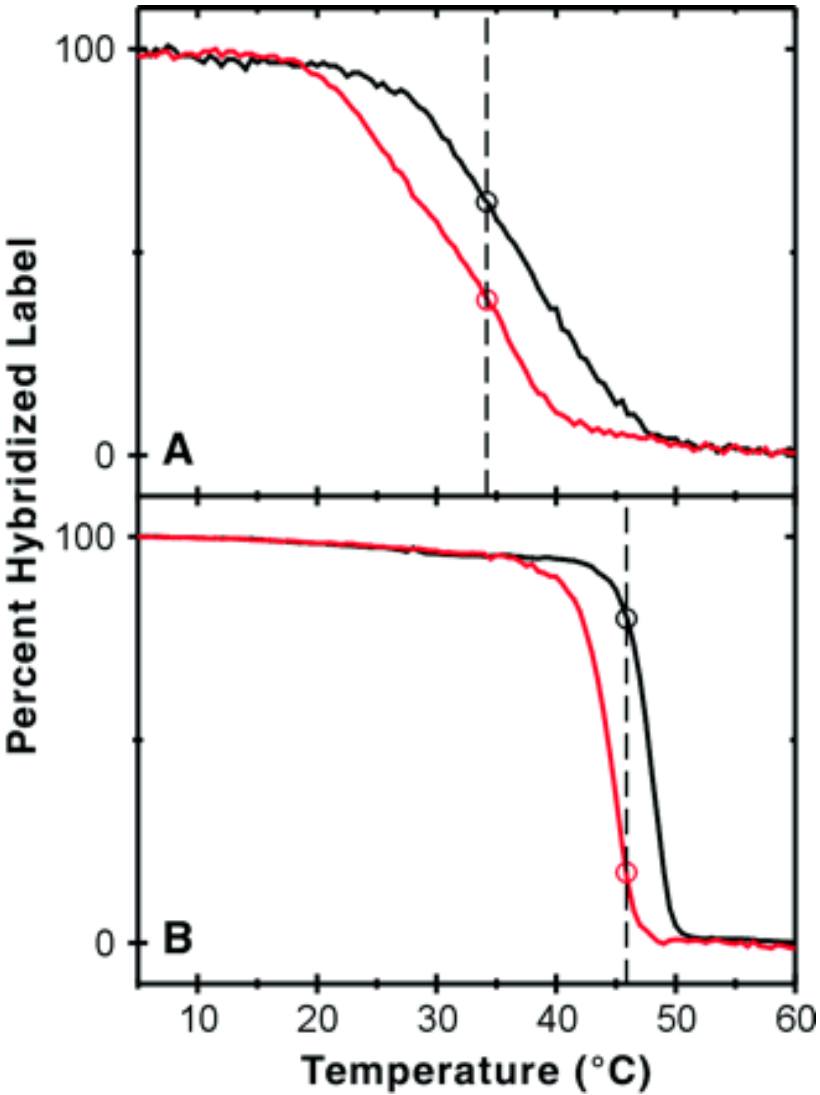


DESIGNED SHAPES MAY CONTAIN HUNDREDS OR THOUSANDS OF **DIFFERENT** DNA STRANDS

How is it possible to assemble thousands of different DNA strands?

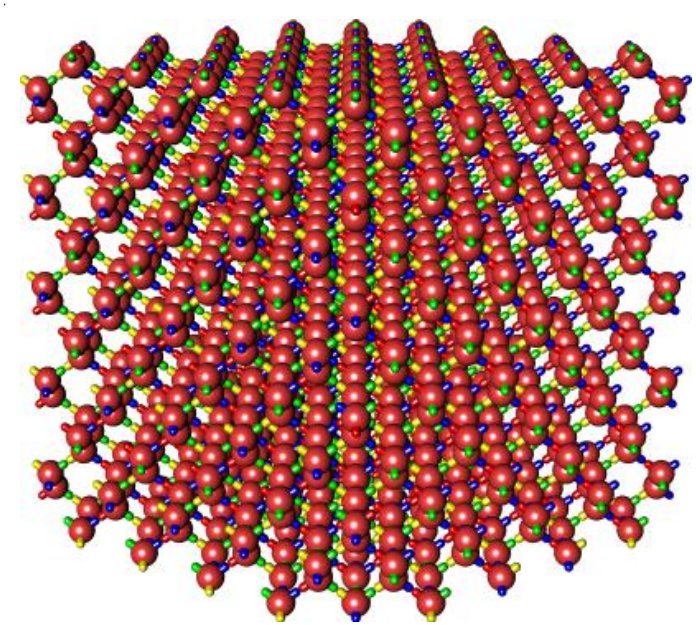
With colloids, we can barely assemble 3 different species.

ANSWER:
Only few bonds per particle



SIMULATIONS: **998** different DNA `bricks'.
Use **experimental** interactions (SantaLucia).

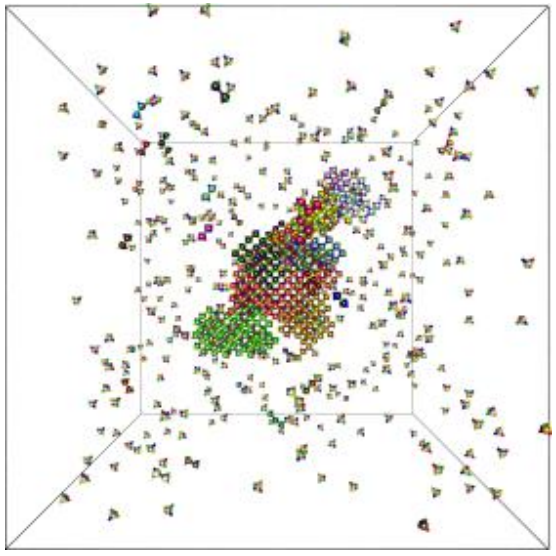
Every unit in the target structure is different.



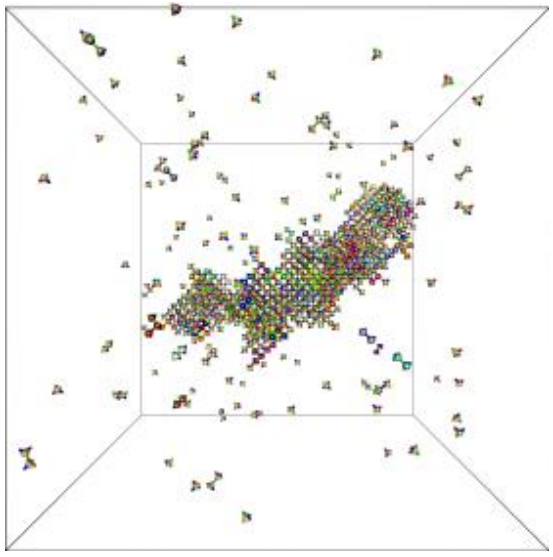
Color code:

RED:
correctly placed

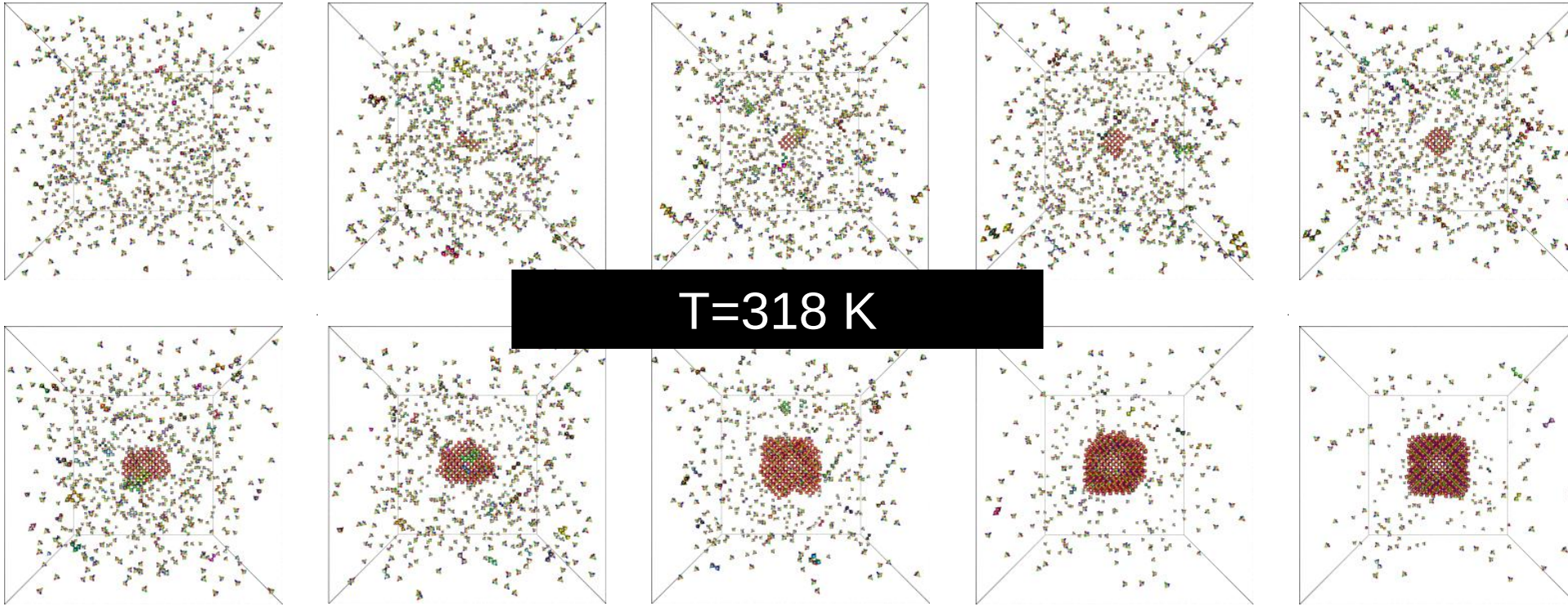
Other color:
incorrectly placed

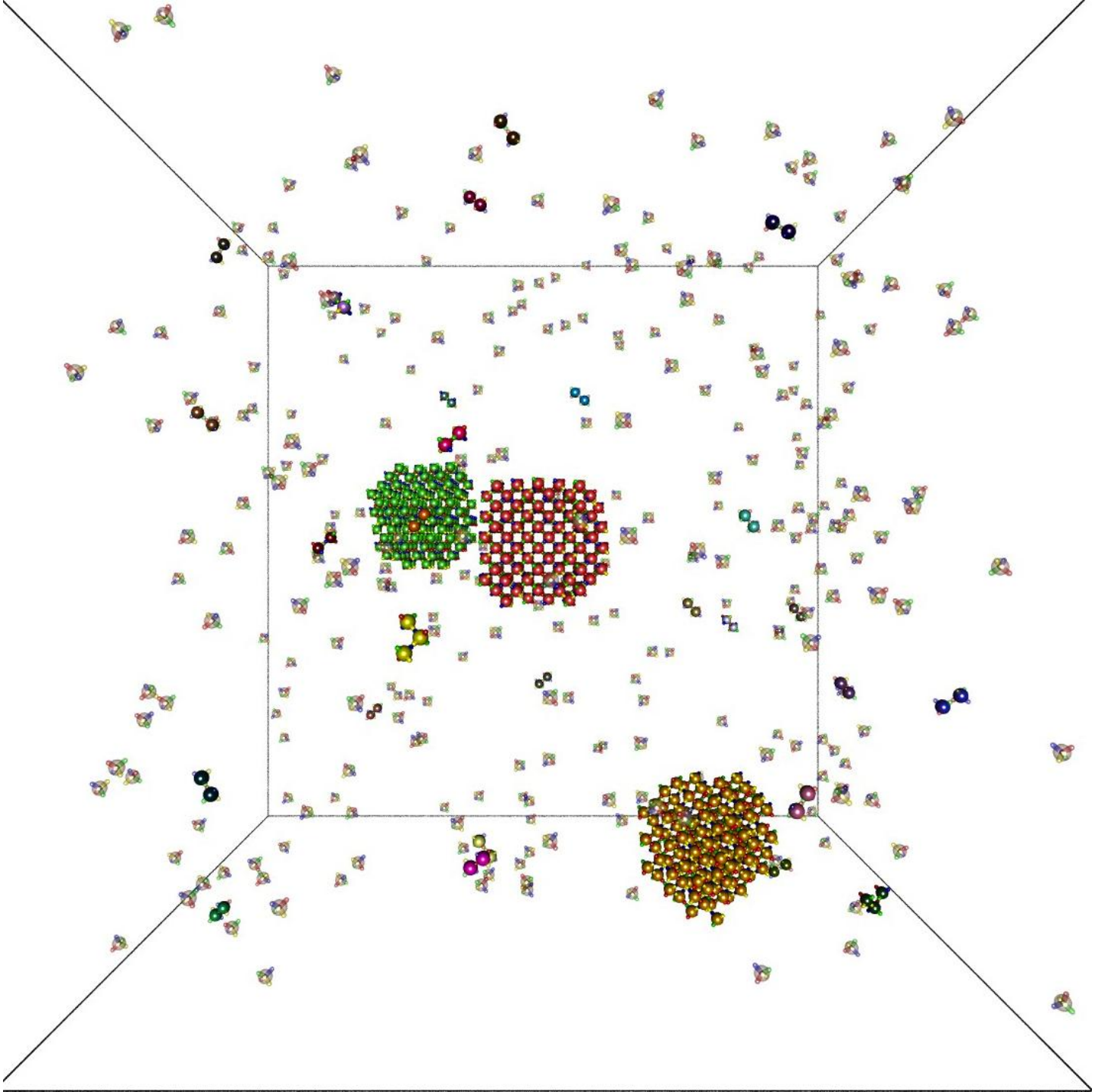


$T = 316\,\mathrm{K}$

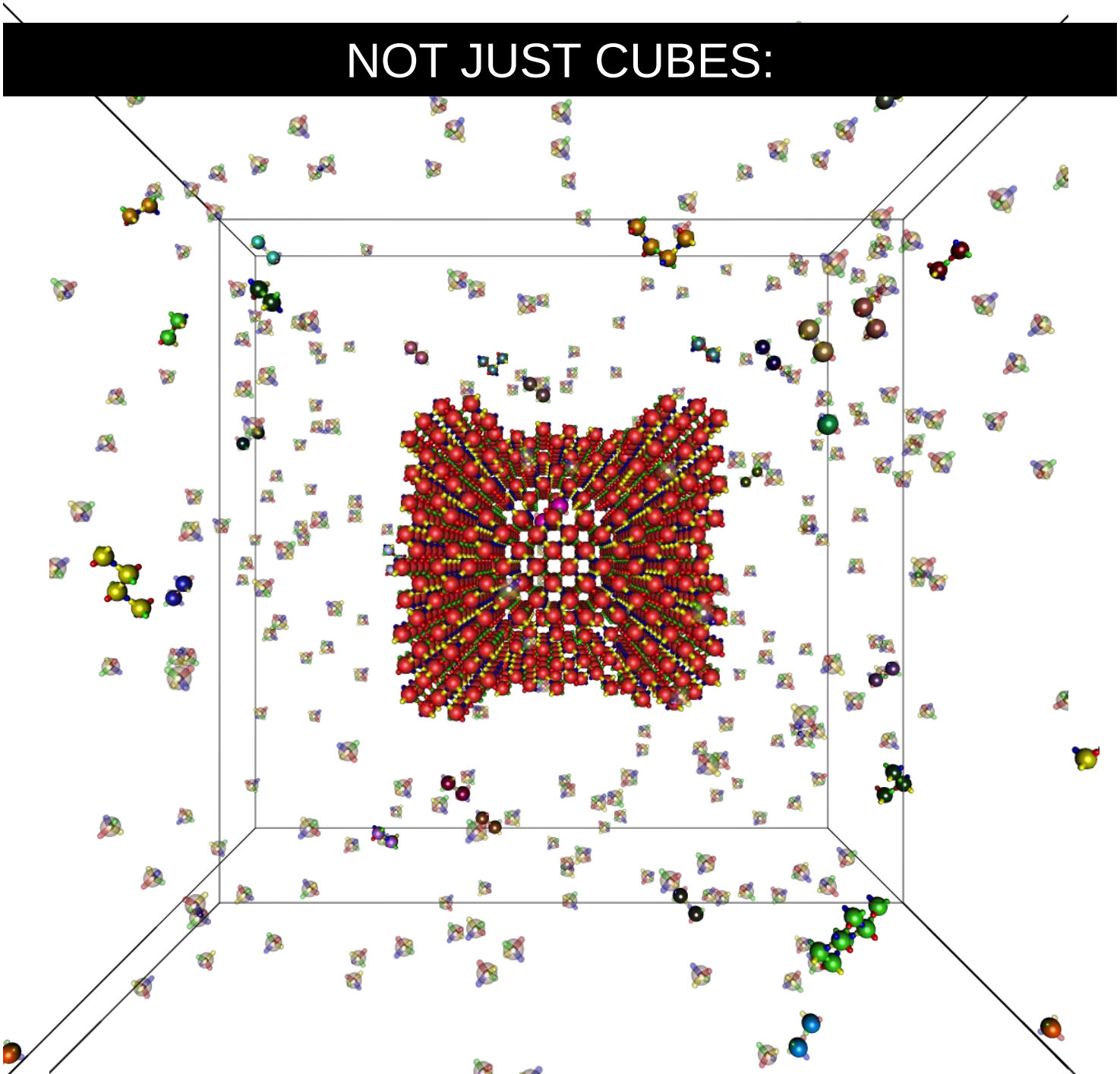


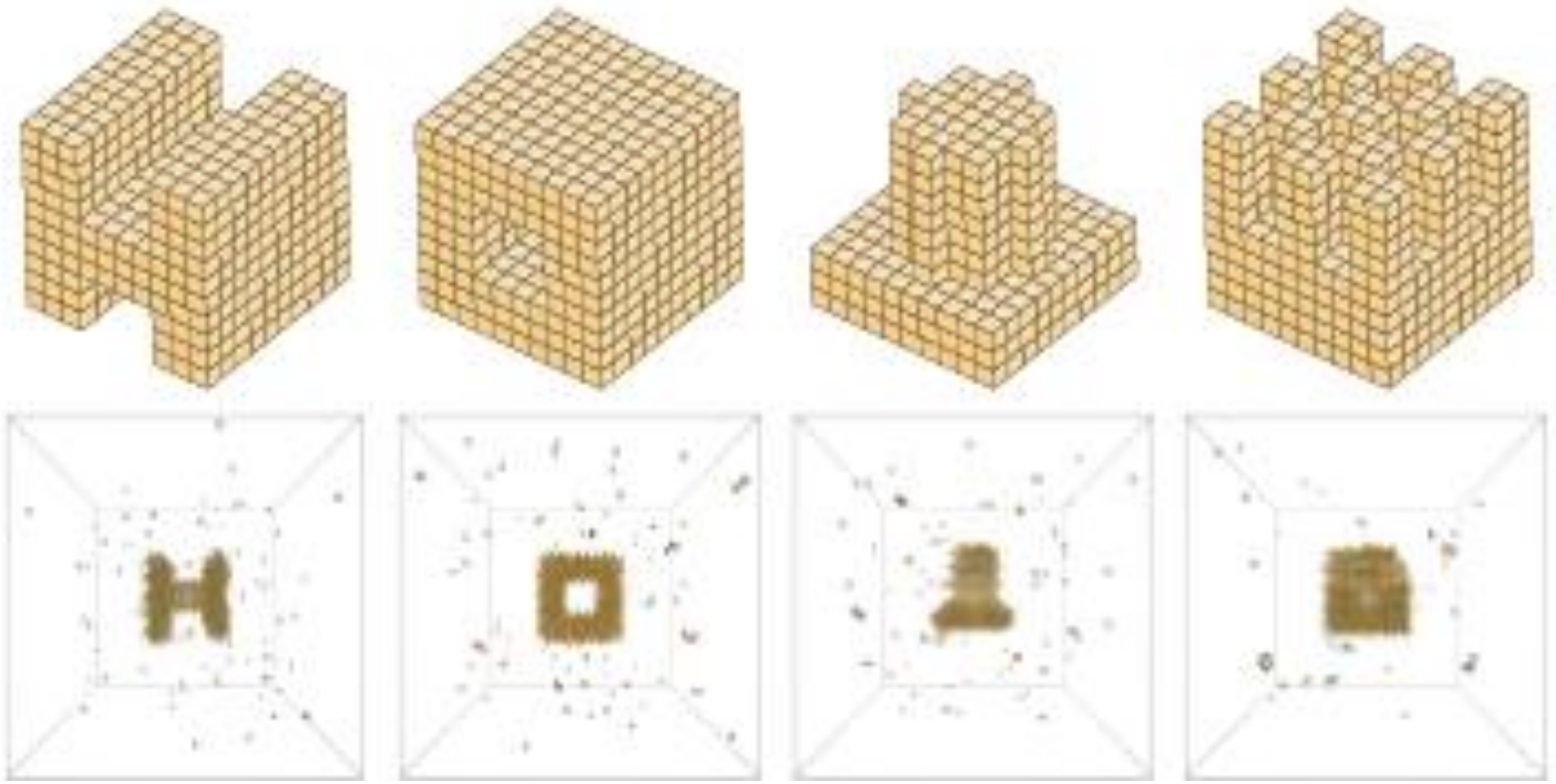
$T = 300\,\mathrm{K}$

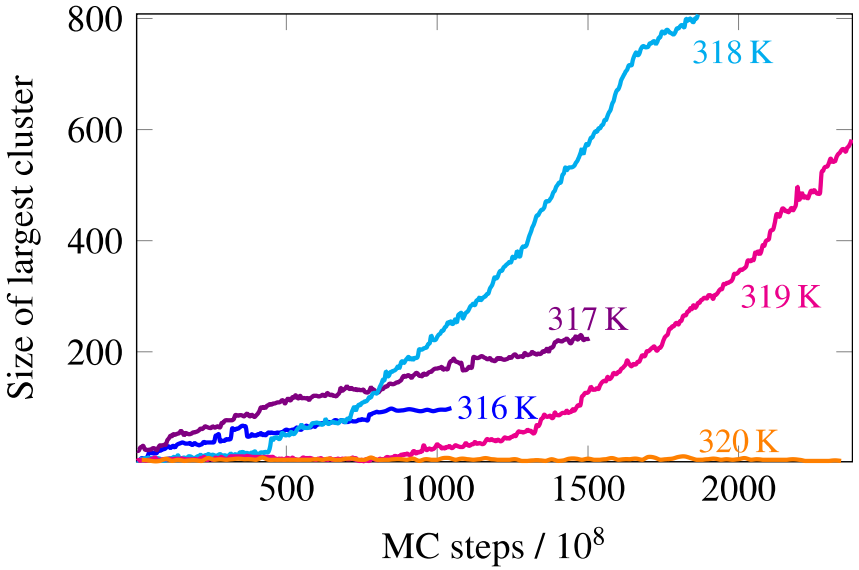




NOT JUST CUBES:

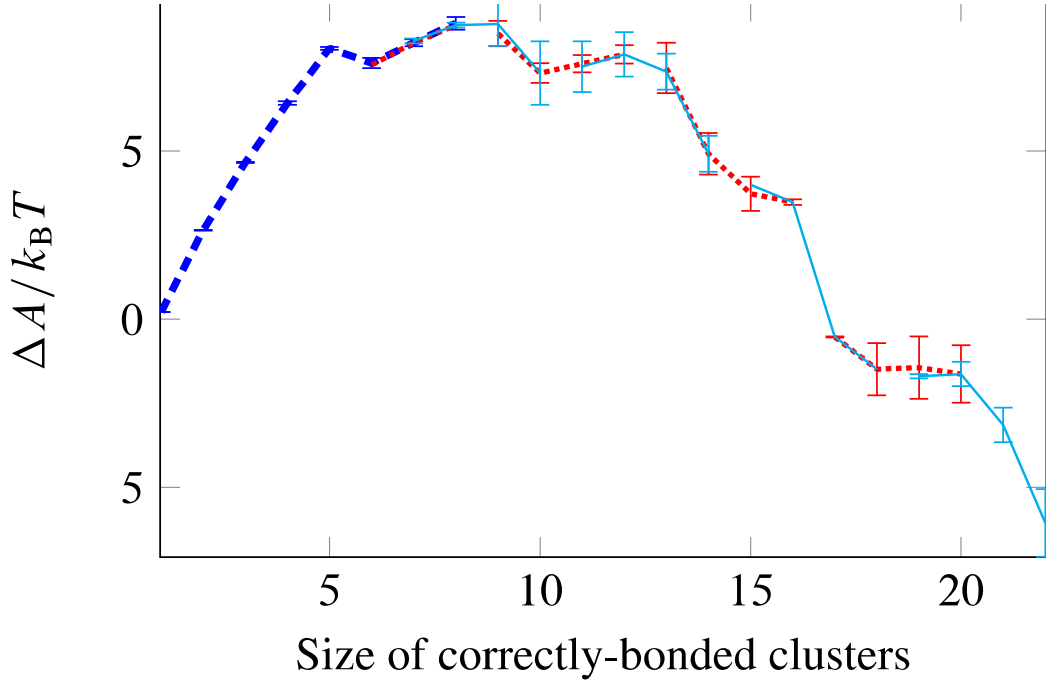






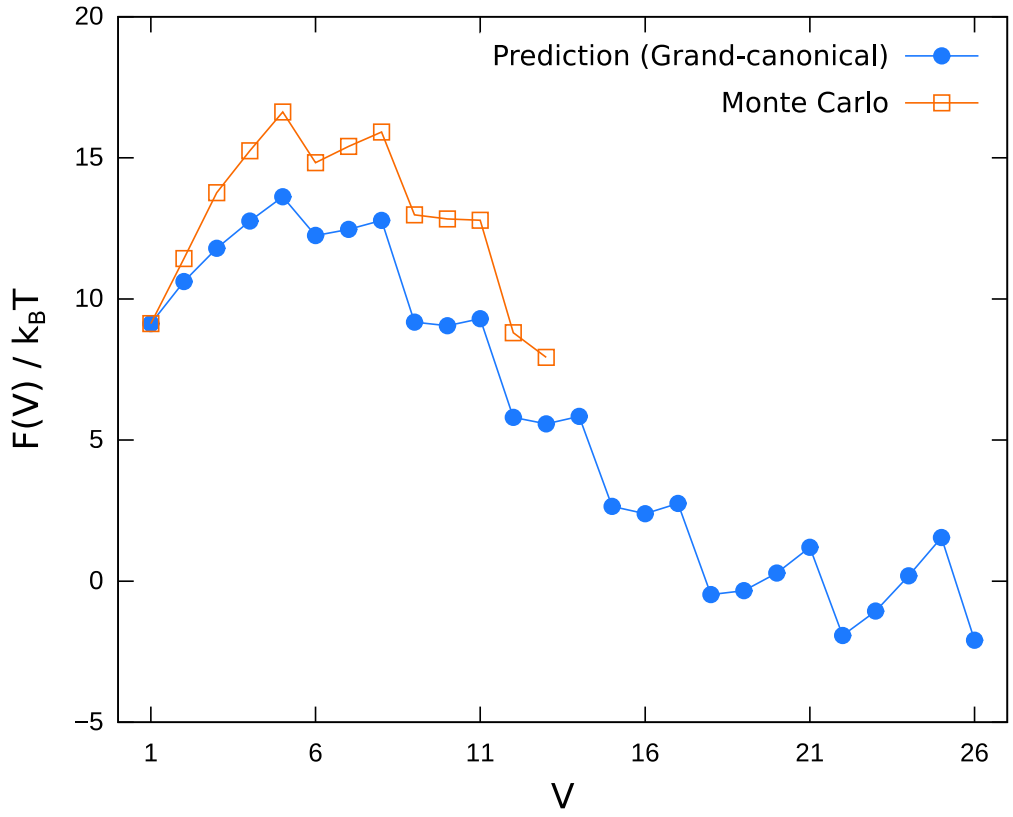
Narrow temperature window for successful self assembly

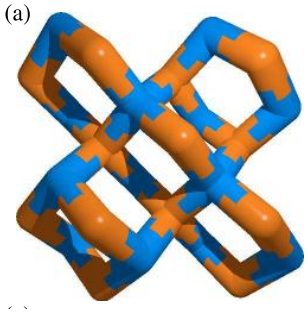
Does structure formation proceed via nucleation and growth?



Aleks Reinhardt & DF, PRL 112, 238103 (2014)

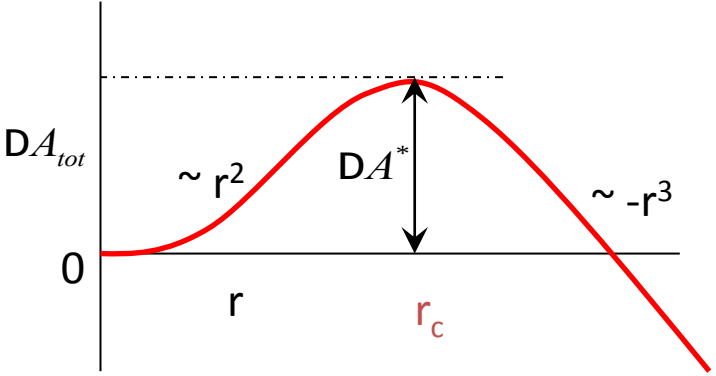
A simple theory (Will Jacobs) can reproduce the observed structure of the free energy barriers



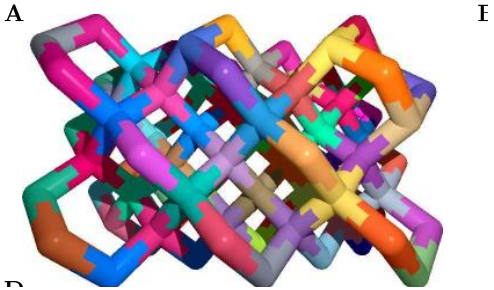


We can now **design** the lowest free-energy route to self assembly.

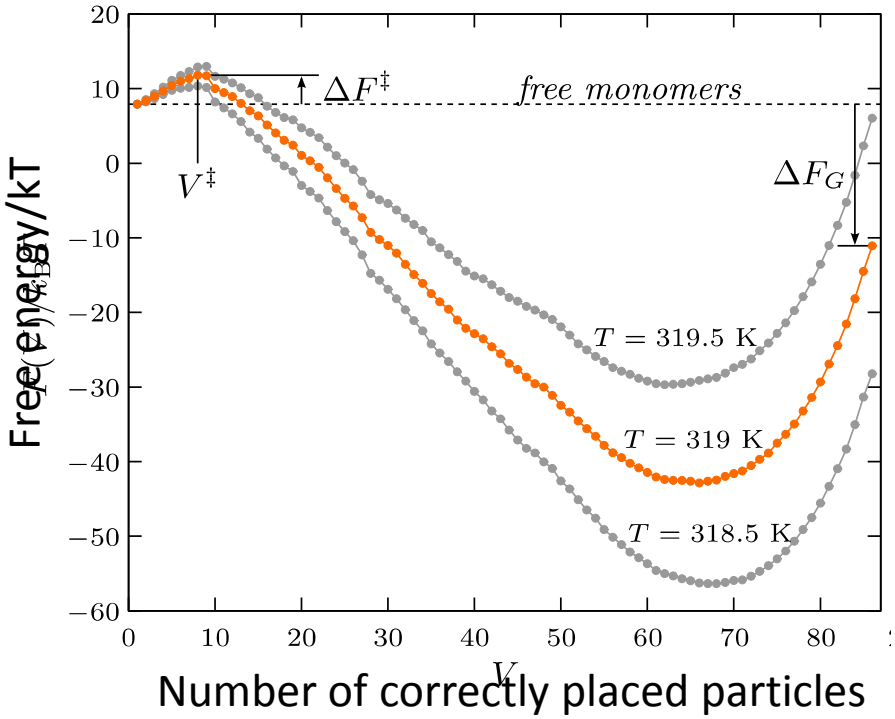
The kinetics of formation of DNA-brick structures is very different from crystal nucleation.

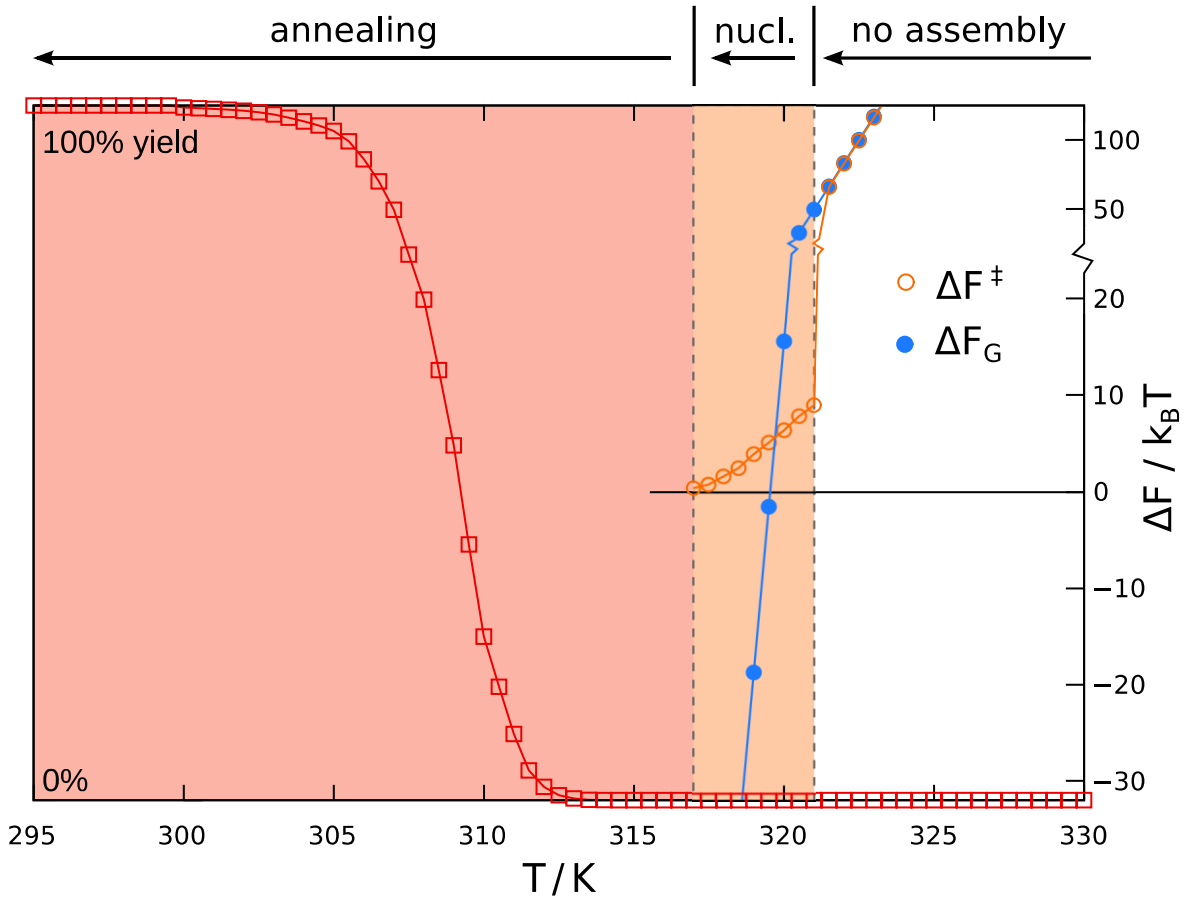


Classical Nucleation: once nucleated, it grows



DNA bricks: nucleation and growth do not happen under the same conditions



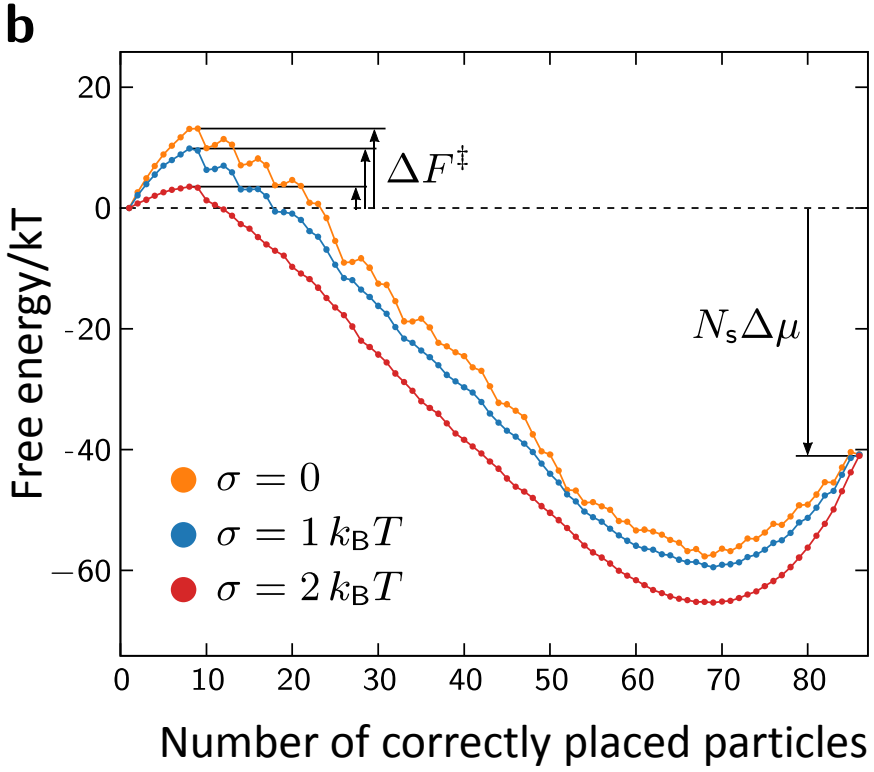


Simulations imply a **protocol** for self-assembly

DNA pairs have a spread of interaction strengths.

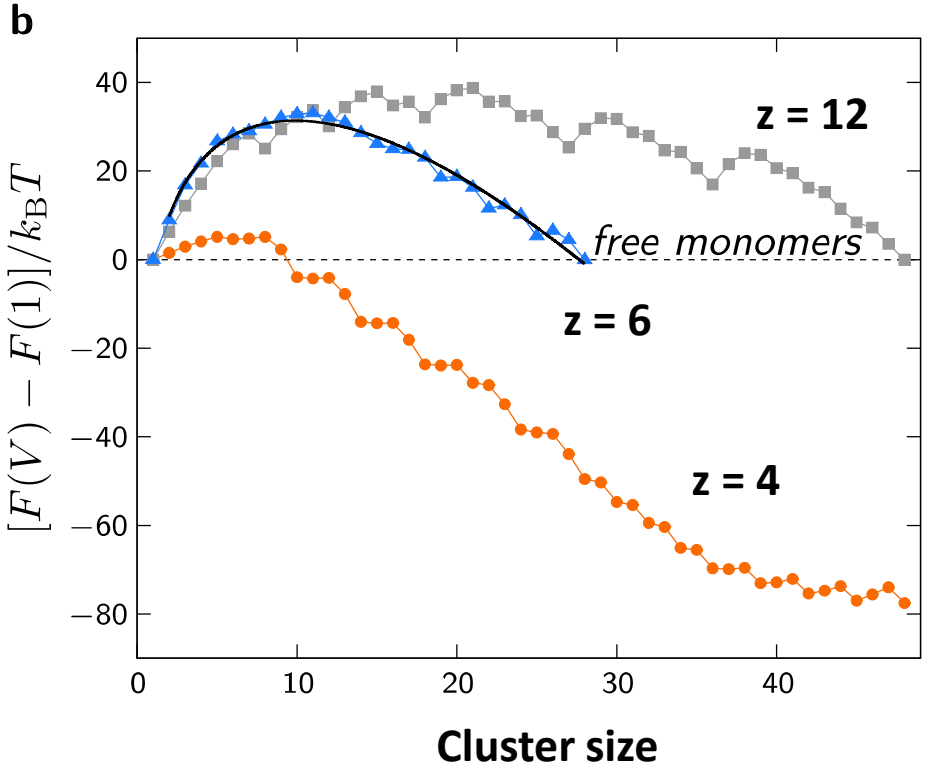
Would self assembly work better if we make all interactions equal?

Distribution in interaction strengths **facilitates** nucleation

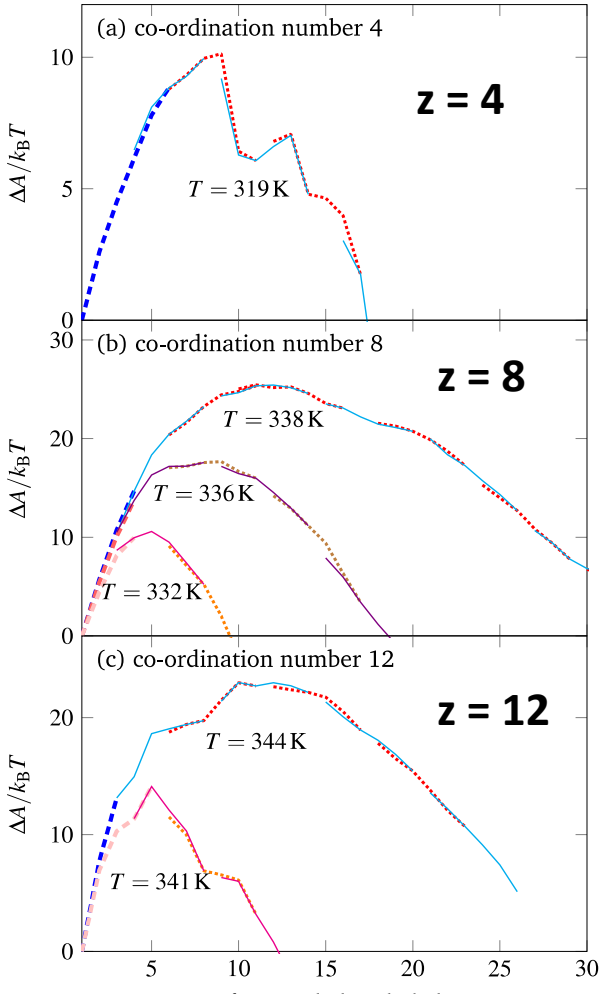


Lattice-coordination number matters…

Higher coordination numbers: more like bulk crystallization.



THEORY

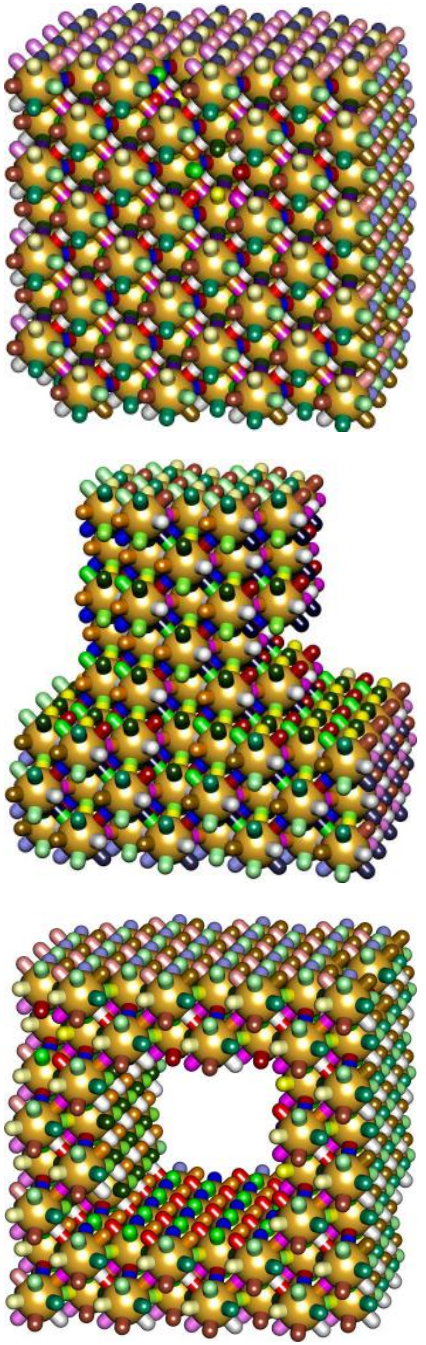


SIMULATIONS

So: brick structures can also form successfully with higher coordination numbers (colloidal `bricks'?).

However: point defects may be an issue.

Coordination number: 12

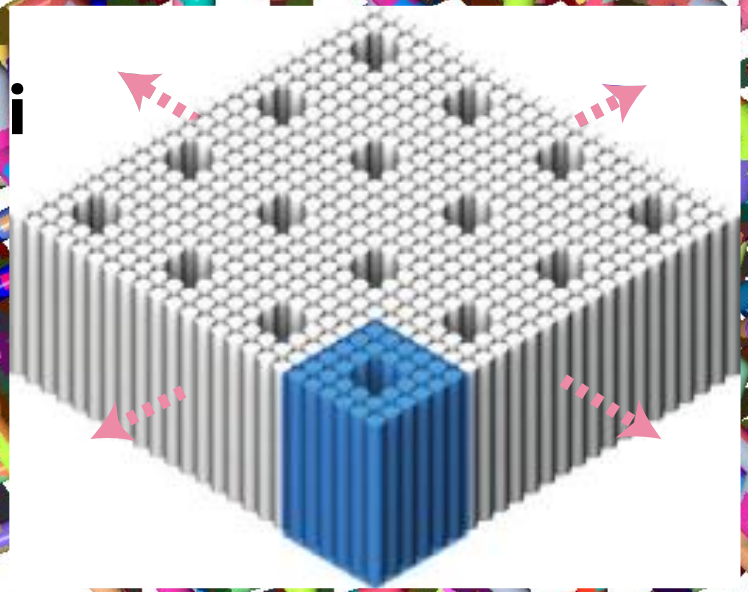


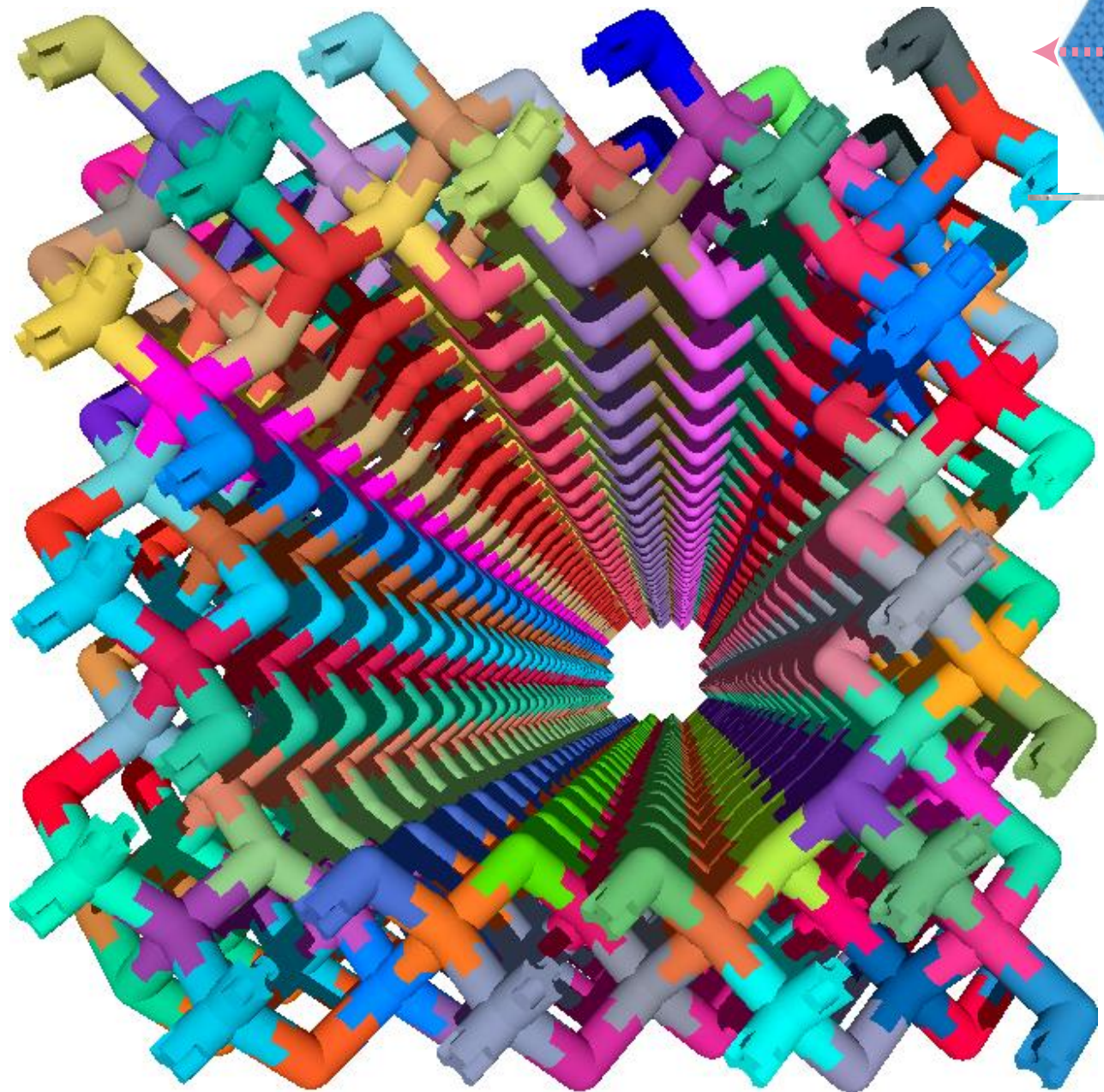
Designing complex, periodic patterns
(Y. Ke et al., Nature Chemistry 6, 994 (2014))

It requires many distinct building blocks to self-assemble a complex pattern.

Simpler examples:

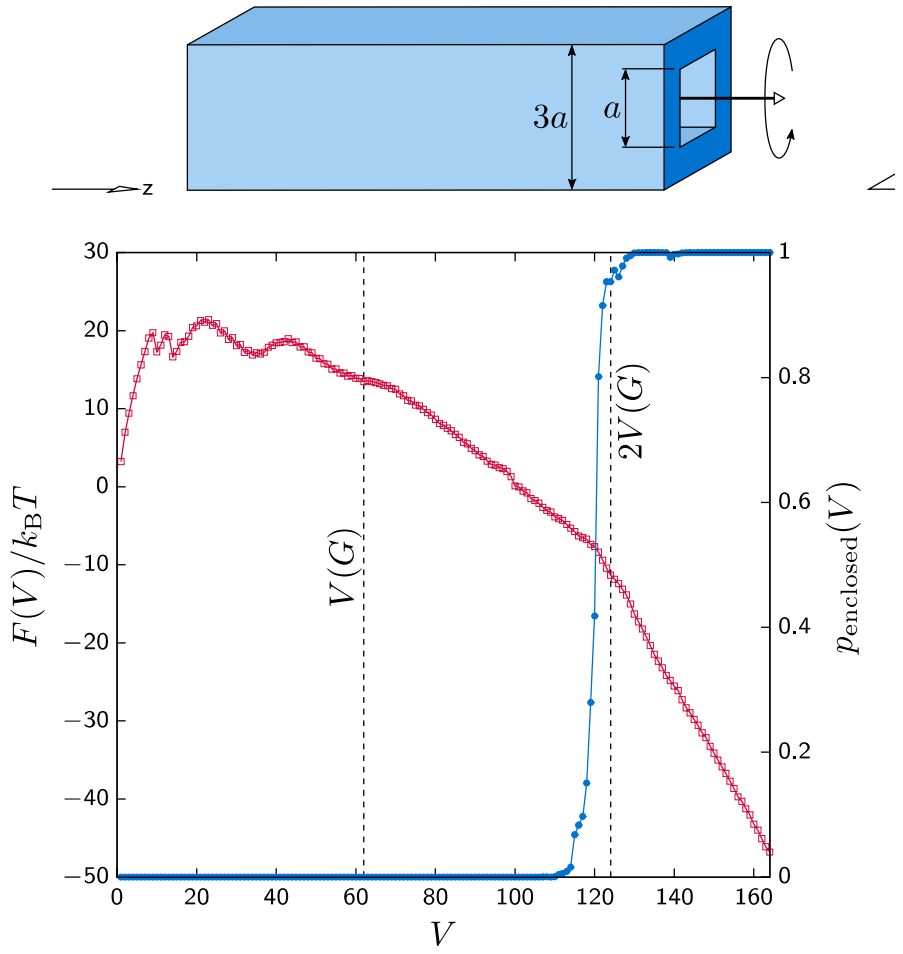
i






20 nm

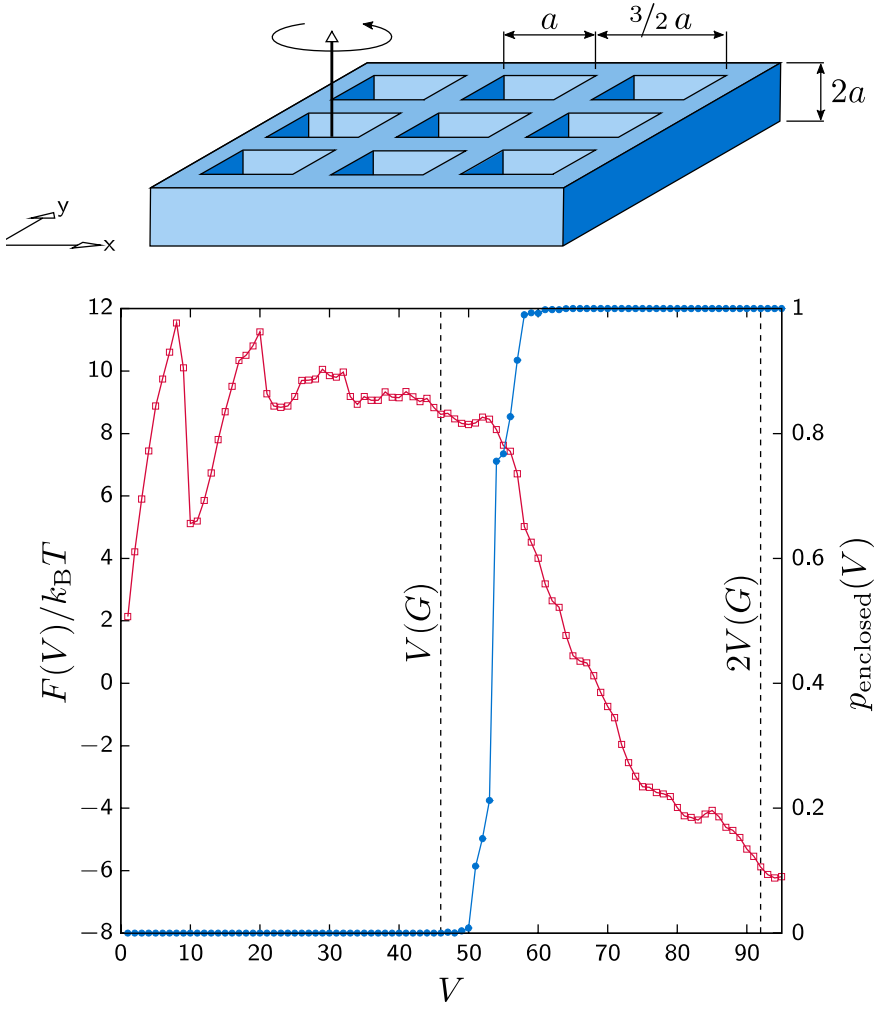
The structure that nucleates may not be representative of the bulk structure.



The critical nucleus does not enclose the central hole.

It forms well inside the `growth' regime.

The structure that nucleates may not be representative of the bulk structure.



Nucleation proceeds via metastable intermediates.

The target unit cell forms well inside the `growth' regime.

Controlling complex self assembly:

1. **Addressable** Complexity: designing pathway and protocol are key.
2. We now have the **numerical tools** to predict/design the optimal protocol to create addressable complexity – **not just for DNA**
3. … I cannot foresee all applications, but they probably will be taxed

Thank You !