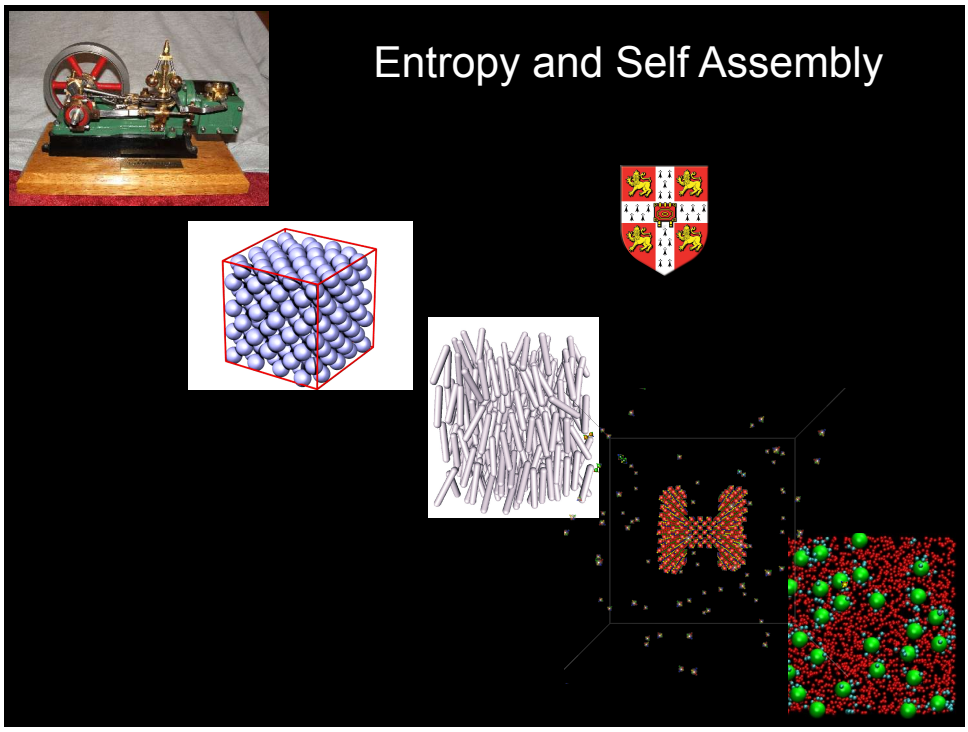


Holy grail of nano-structured materials:

To design “complex” three-dimensional structures that assemble themselves.

For instance: A self-assembling, three-dimensional integrated circuit.

QUESTION:

IS THERE A LIMIT TO THE COMPLEXITY OF SELF-ASSEMBLING `COLLOIDAL' STRUCTURES?

Short answer: I don't know.

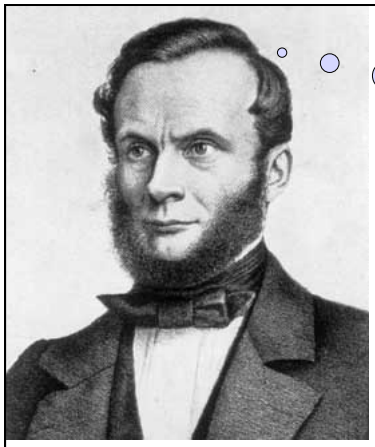
Longer answer:

1. **Complexity through packing**
2. **Complexity through specific interactions**

1. Complexity through packing

Order through disorder: the unexpected side of entropy

ENTROPY: the pre-history…



Rudolf Clausius

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

$dU = đq + đw$

$TdS = dU + PdV - \mu dN$

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

$\Rightarrow dS \geq 0$!!!

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

From heat flow to entropy…

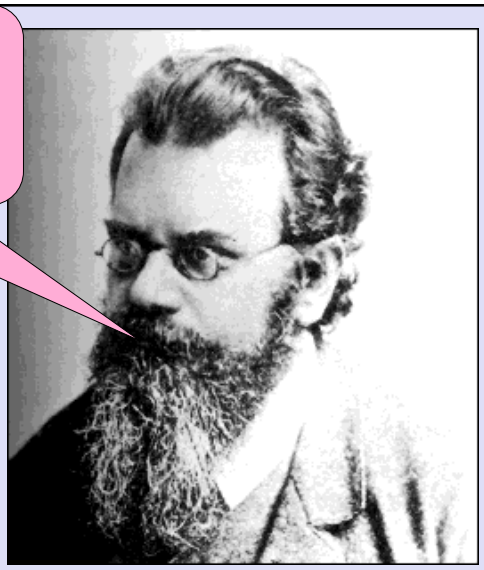
the birth of Thermodynamics

Clausius taught us that the entropy of a closed system never decreases, but…

What is Entropy?

Enters: **Boltzmann**

S=k ln W



Ludwig Boltzmann

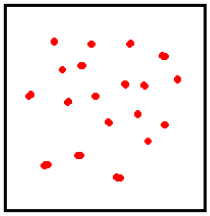
True…

… but not very popular

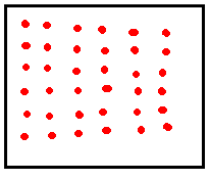
A more popular view of entropy:

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

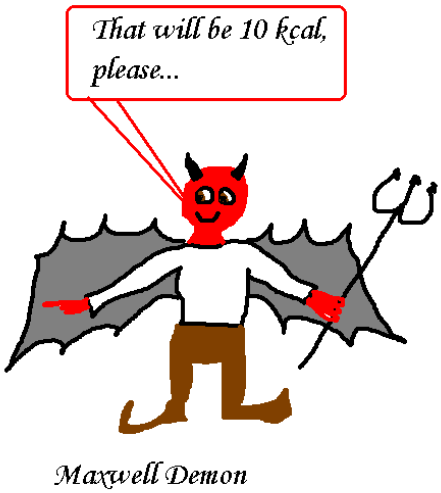
The "intuitive" version of the Second Law of Thermodynamics



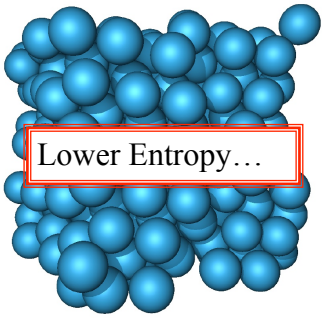
disorder



order

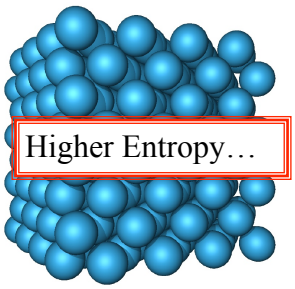


Maxwell Demon



Hard-sphere liquid

Hard-sphere freezing is driven by entropy !



Hard-sphere crystal

The 2nd Law is not violated.

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

..but entropic freezing is real:

ENTROPIC ORDERING IS VERY COMMON

FIRST EXAMPLE:

ONSAGER'S THEORY OF THE ISOTROPIC-NEMATIC TRANSITION

There are many more examples of entropic phase transitions…

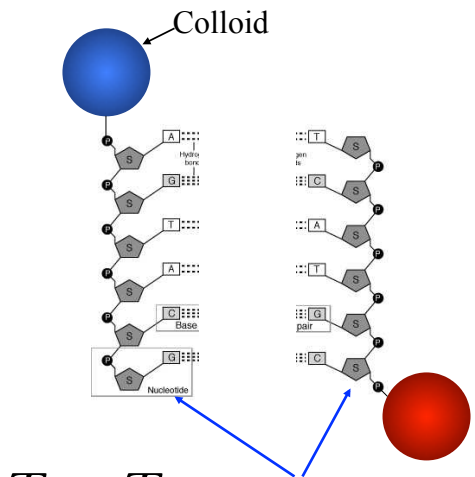
…yet, not all phase transitions are entropic.

Counter examples:

vapour-liquid condensation (argon, water, NaCl …)

1. Complexity through packing
2. **Complexity through specific interactions**

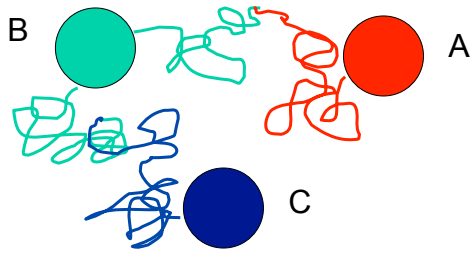
One popular idea:



$T > T_m$ ➡ DNA unbinding ("melting")

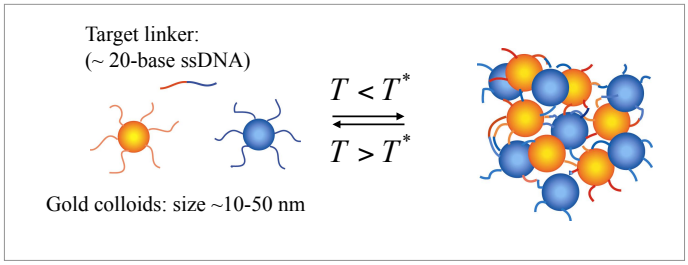
By choosing the appropriate DNA connectors, we can selectively switch on attractions between some colloids

e.g. AB and BC, but NOT AC



Background: ssDNA recognition

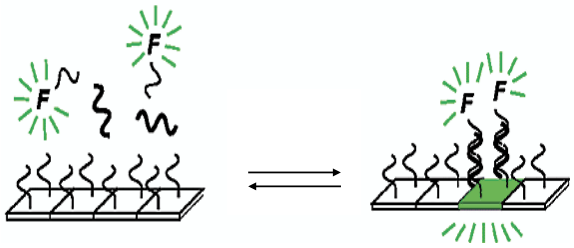
C. A. Mirkin et al., Nature, 382, 607 (1996)

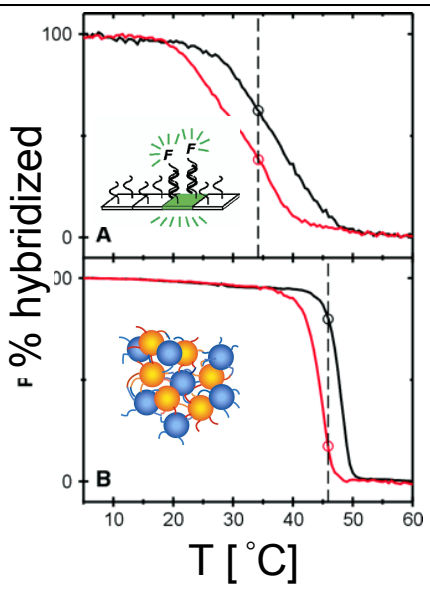


Single-stranded DNA fragments link ssDNA coated colloids and cause aggregation…

Alternative:

Fluorophore-based DNA-array:
1 linker per fluorophore.





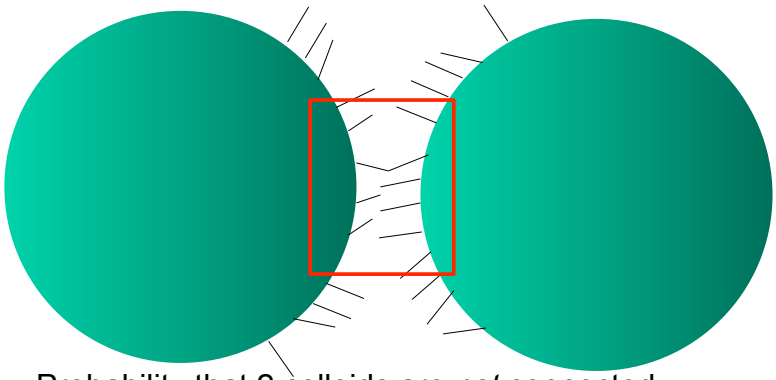
Fluorophore probes
(one bond ⇒
weak T-dependence)

Nanoparticle probes
(many bonds ⇒
strong T-dependence)

Complementary sequence
Single-base mismatched sequence

Cooperativity:

Now: N possible bonds

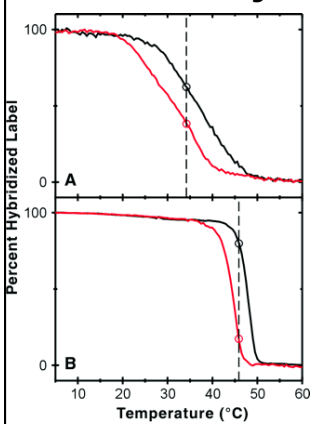


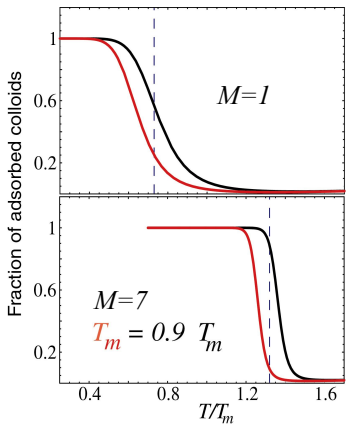
Probability that 2 colloids are *not* connected:

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

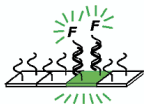
Changes steeply with Δf and N.

Simple (lattice) theory:

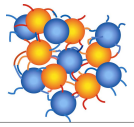




Fluorophore probes



Nanoparticle probes (higher selectivity)



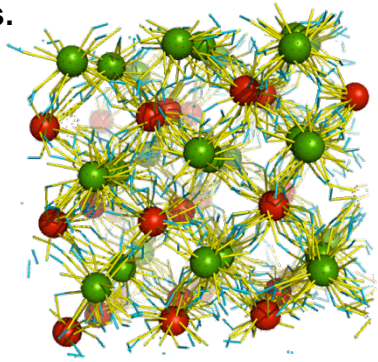
Experiment | **Theory**

Sharp dissolution profiles → High selectivity

END OF INTRODUCTION.

Attempts to build non-trivial crystal structures have had limited success.

Thus far only relatively "simple" binary and ternary crystals.



See e.g.: R. J. Macfarlane et al. Science 334, 204 (2011)

Why is complex self assembly difficult?

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

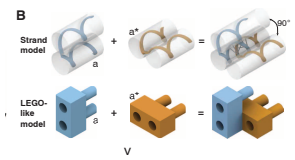
…compromise the kinetics of self assembly.

The material that forms is NOT the equilibrium phase.

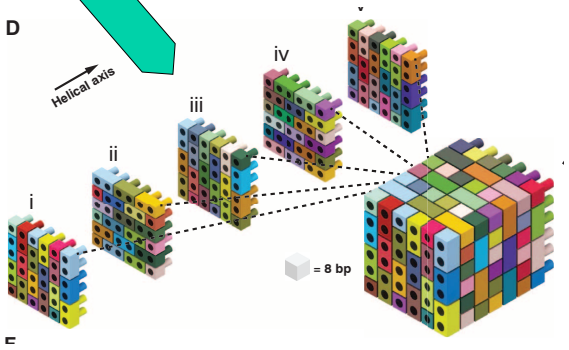
Strong temperature dependence is good for gene detection…but bad for self assembly because crystallisation can only happen in a very narrow "window".

THE GOOD NEWS IS THE BAD NEWS…

So, how about assembly of DNA `bricks'?



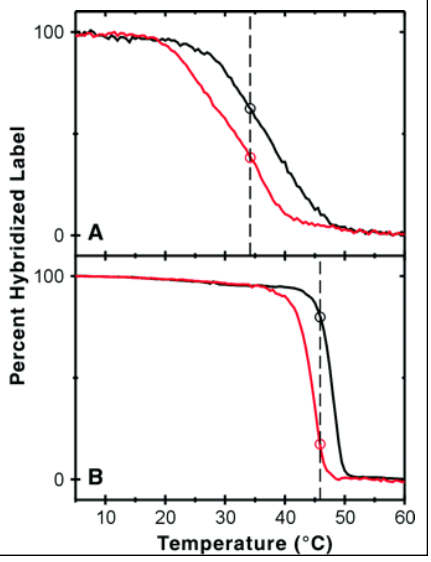
DESIGNED SHAPES MAY CONTAIN HUNDREDS OR THOUSANDS OF **DIFFERENT** DNA STRANDS



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

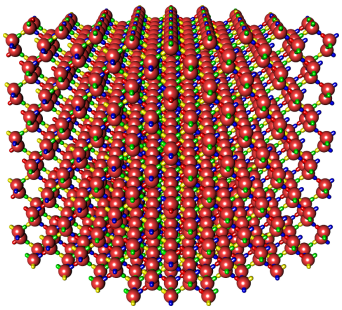
With colloids, we can barely assemble 2 different species.

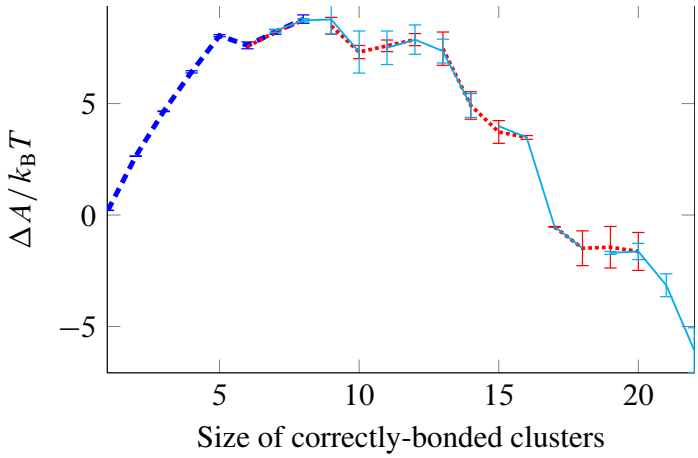
ANSWER:
THE BAD NEWS IS THE GOOD NEWS…



SIMULATIONS: 998 (!) different DNA `bricks'.

Every unit in the target structure is different.

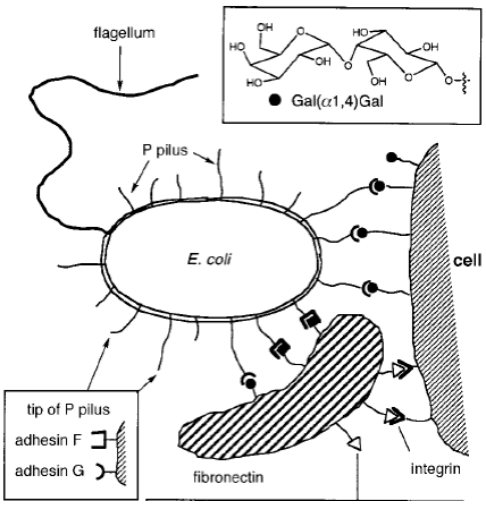




Formation of structures proceeds via nucleation and growth…

The bad news is the good news: part 2.

Multivalent binding in nature:
Example



Whitesides et al. Angew. Chem. Int. Ed. 1998, 37, 2754.

Multivalent binding - What are the advantages?

The literature says:

1. Increased binding strength
2. Graded signaling (not "ON-OFF")
3. Evolutionary efficiency: simpler to repeat same unit

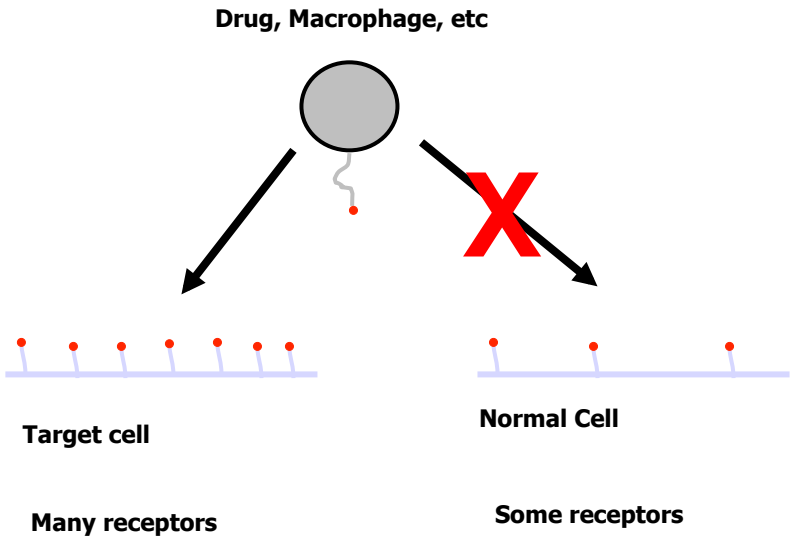
than creating a new one

4. Induction of specific geometries and conformations, etc.

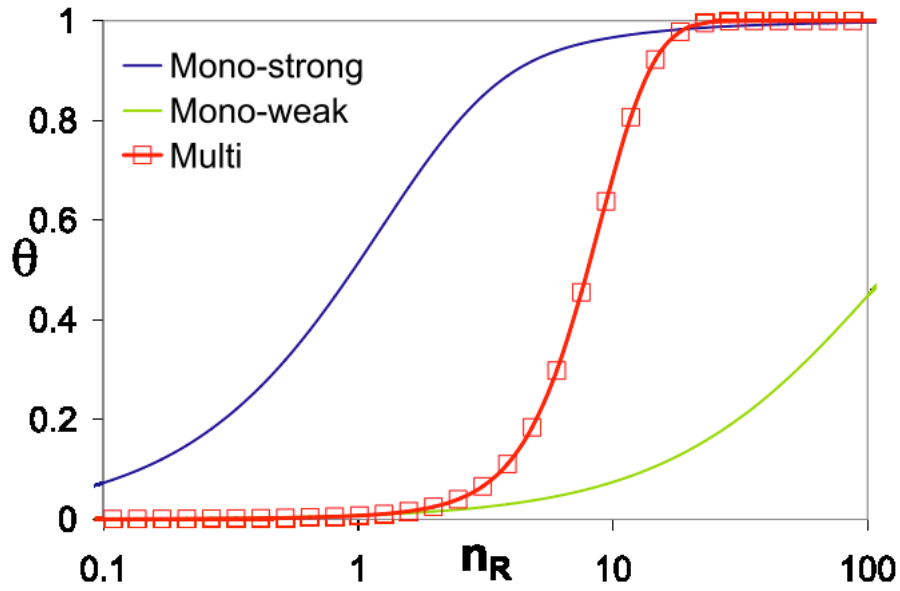
…and

Enhancement of the sensitivity to receptor concentrations

Binding Selectivity



θ = fraction bound adsorbate



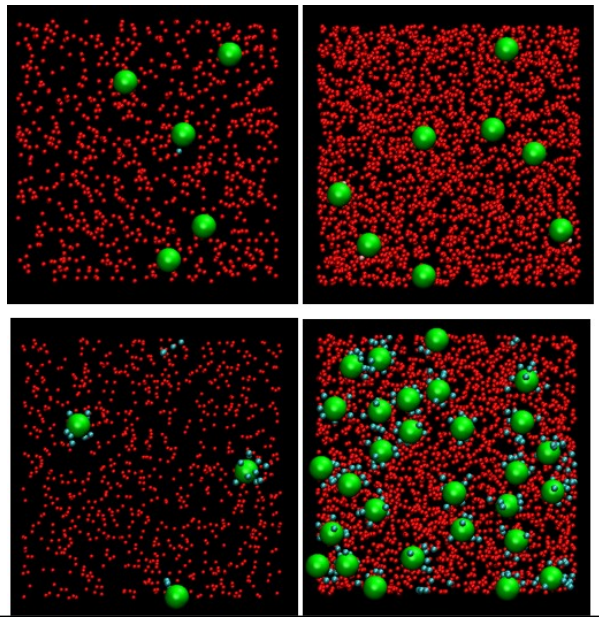
Surface density of receptors

Receptor concentration increases 3X

⇒

Monovalent nanoparticles (1 ligand)

Multivalent nanoparticles (10 ligands)



Complex self assembly:

1. The good news is the bad news
2. The bad news is the good news.

and

3. …entropy is more important than we thought