

# Due strategie per la nanofabbricazione

## Top-down

Sfruttando strumentazioni complesse e 'grandi' si possono costruire oggetti sempre più piccoli

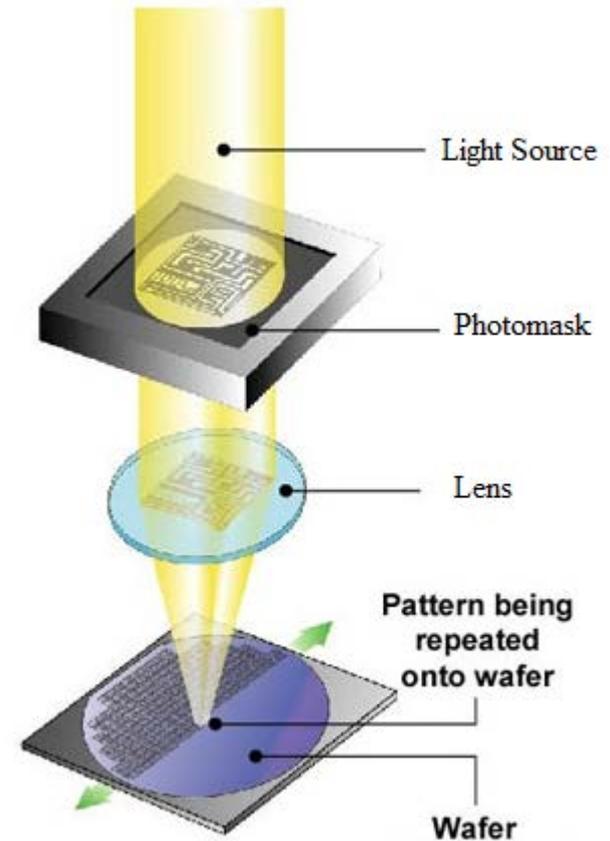
(ad esempio usando la litografia, le microscopie a sonda, le pinzette ottiche, *gli assemblatori molecolari*)

## Bottom-up

Si può codificare l'informazione dell'assemblaggio in mattoni intelligenti, molecole o gruppi di molecole che poi autonomamente si trovano, si riconoscono e formano strutture via via più grandi e complesse. (*come agitare un sacco di mattoni e aprendolo trovarci dentro una casa costruita*)

# Photolithography

- Photolithography is a common micro-fabrication technique used to transfer an image from a photomask to the surface of a substrate by using ultraviolet light.
- The components needed for Photolithography are light source, photomask, lens and wafer.



# *Bottom Up Fabrication*

1) START with nanoscale things

*Researchers have made a LOT of progress with this*

2) Then try to find a way to get them organized in useful ways

Focusing on the second more difficult step, this bottom up process also called:

***SELF - ASSEMBLY***

*(that is, figure out a way to get mother nature to do the hard part)*

Nanoscale self-assembly has been going on for BILLIONS of years

Challenges are to figure:            WHERE it has been going on (*we can't SEE it directly*)

Which forms of self-assembly might be useful

# Definition

- The **spontaneous** organization of **individual components** into an **ordered structure** without human/supernatural intervention.
- **Self-assembly** is the fundamental principle which generates structural organization on all scales from molecules to galaxies. It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns.
  - From Wikipedia, the free encyclopedia

# Common features of self assembly

- **Self-assembly reflects information coded** (as shape, surface properties, charge, polarizability, magnetic dipole, mass, etc.) **in individual components**; these characteristics determine the interactions among them. The design of components that organize themselves into desired patterns and functions is the key to applications of self-assembly.

# Common features of self assembly (cont'd)

- **The components must be able to move with respect to one another.** Their steady-state positions balance attractions and repulsions. Molecular self-assembly involves noncovalent or weak covalent interactions (van der Waals, electrostatic, and hydrophobic interactions, hydrogen and coordination bonds). In the self-assembly of larger components--meso- or macroscopic objects--interactions can often be selected and tailored, and can include interactions such as gravitational attraction, external electromagnetic fields, and magnetic, capillary, and entropic interactions, which are not important in the case of molecules.

# Common features of self assembly (cont'd)

- Because self-assembly requires that the components be mobile, **it usually takes place in fluid phases or on smooth surfaces**. The environment can modify the interactions between the components; the use of boundaries and other templates in self-assembly is particularly important, because templates can reduce defects and control structures.

# Common features of self assembly (cont'd)

- **Equilibration is usually required to reach ordered structures.** If components stick together irreversibly when they collide, they form a glass rather than a crystal or other regular structure. Self-assembly requires that the components either equilibrate between aggregated and non-aggregated states, or adjust their positions relative to one another once in an aggregate.

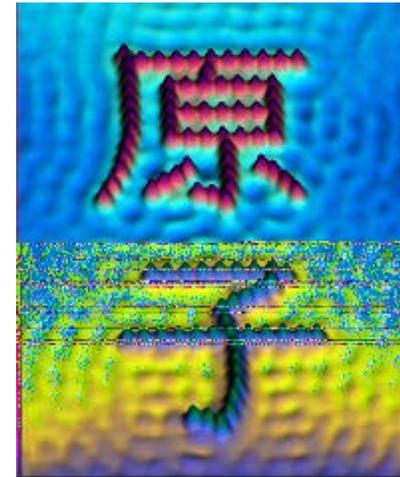
# Why do we have special interests in self assembly?

- humans are attracted by the appearance of order from disorder.
- living cells self-assemble, and understanding life will therefore require understanding self-assembly. The cell also offers countless examples of functional self-assembly that stimulate the design of non-living systems.
- self-assembly is one of the few practical strategies for making ensembles of nanostructures. It will therefore be an essential part of nanotechnology.

# Advantages of self assembly

- **Practicality**

it carries out many of the most difficult steps in nanofabrication--those involving atomic-level modification of structure--using the very highly developed techniques of synthetic chemistry.



Crommie et al, Science, 1993

Directed assembly of nano-structures is time-consuming and impractical.

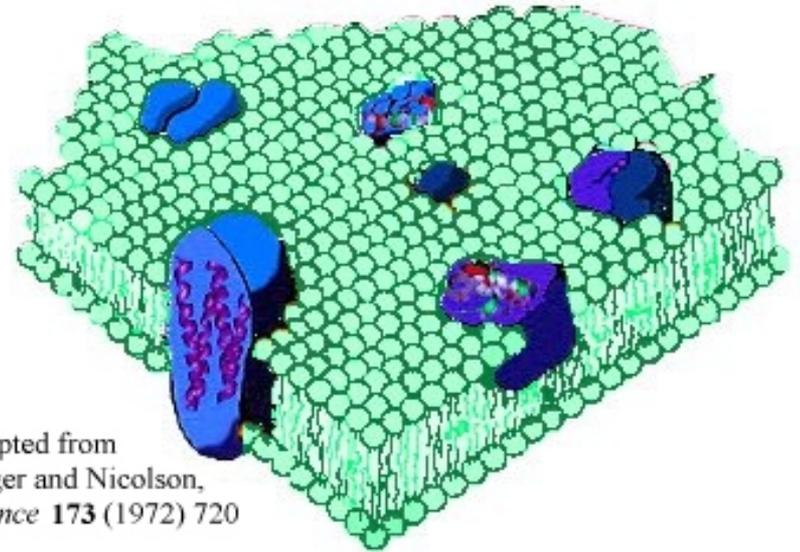
Creating complex 3D structures on nanometer scale may be "impossible" using directed assembly.

# Advantages of self assembly

- it draws from the enormous wealth of examples in biology for inspiration: self-assembly is one of the most important strategies used in biology for the development of complex, functional structures.

And

- it can incorporate biological structures directly as components in the final systems.



# Driving forces of self assembly

- Assembly by capillary forces
- Assembly by electrostatic forces
- Assembly by magnetic forces
- Assembly by van der Waals
- Assembly by hydrophobic interactions
- Assembly by hydrogen and coordination bonds
- But, attention! There is no covalent bonds!



**Weak  
bonds**

## **Bottom Up Fabrication**

*Una visualizzazione del self-assembly: forme geometriche magnetiche galleggianti (la crescita di un cristallo)*



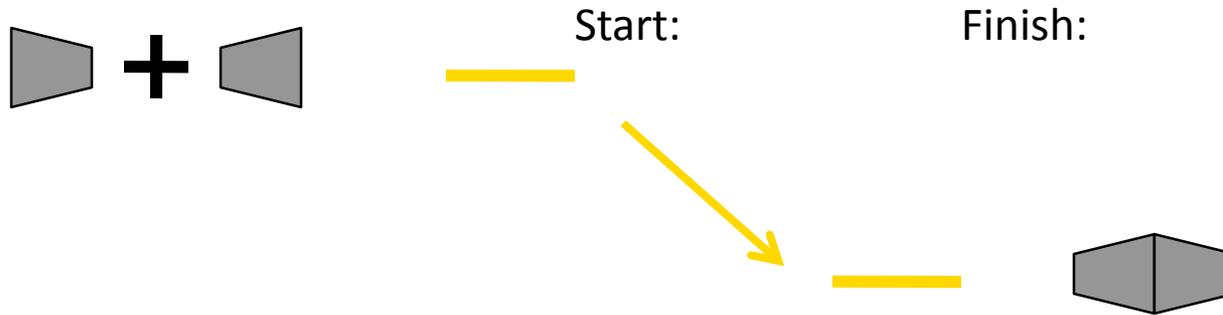
[video](#)

Notate come siano necessari numerosi tentativi per trovare la configurazione ideale a minima energia.

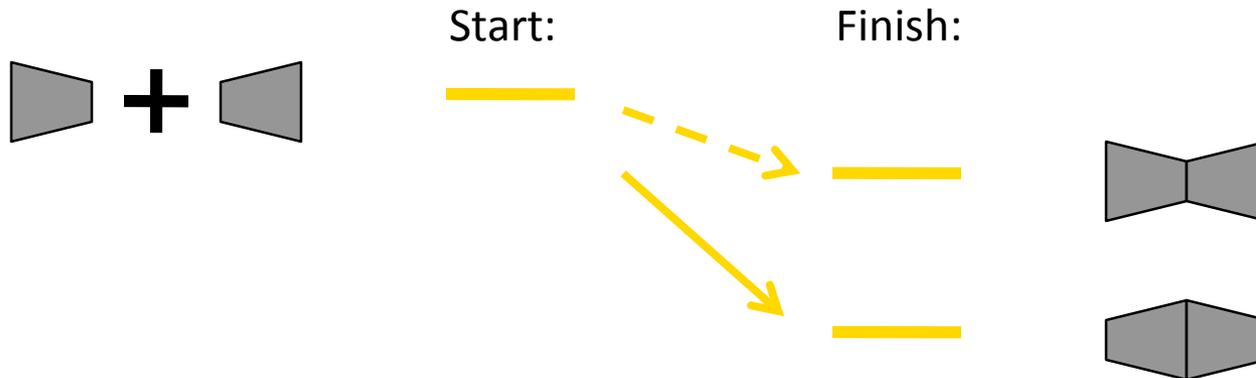
È facilitato dall'agitazione (energia) che permette di smontare gli stati non desiderati (meno stabili).

*SELF-ASSEMBLY (most often) = Lower energy through organization*

1) Trivial case – only one possible end state:

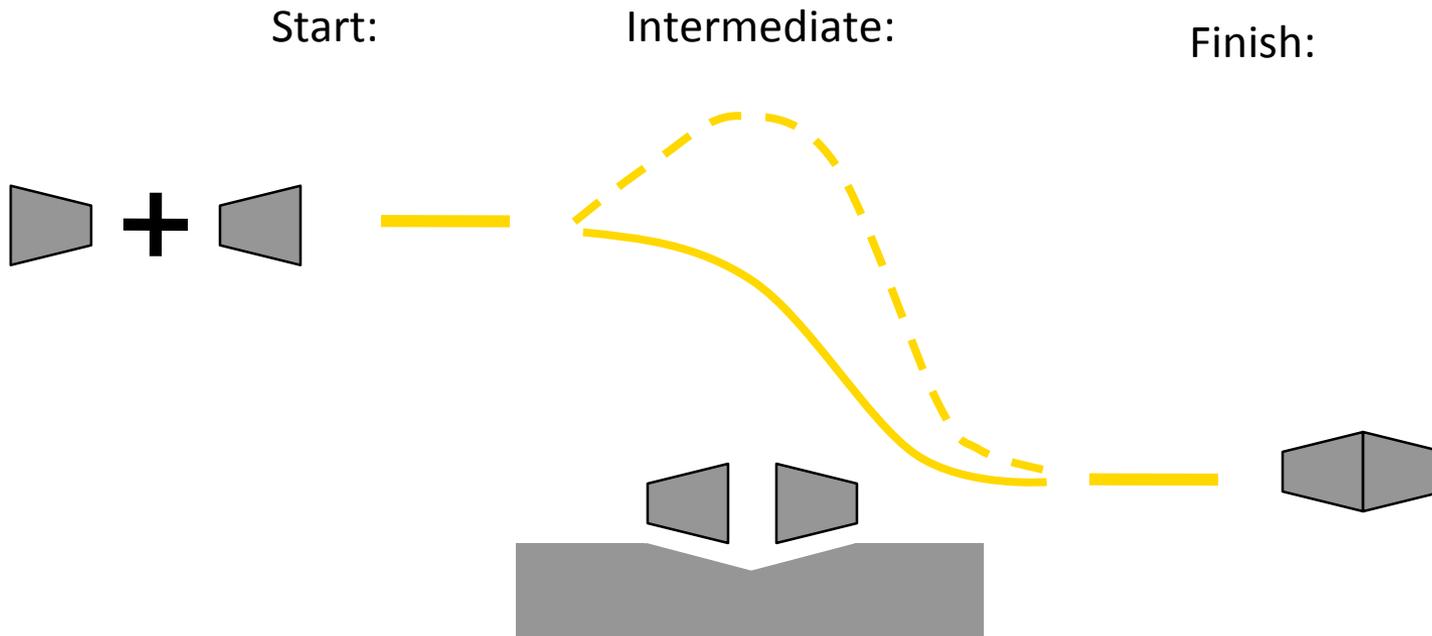


2) More realistic – many possible end states (but one slightly favored):



Or helped by catalysts and enzymes ("Semi Self-Assembly?")

3) CATALYSTS: **GUIDE** parts toward final LOWER ENERGY state:



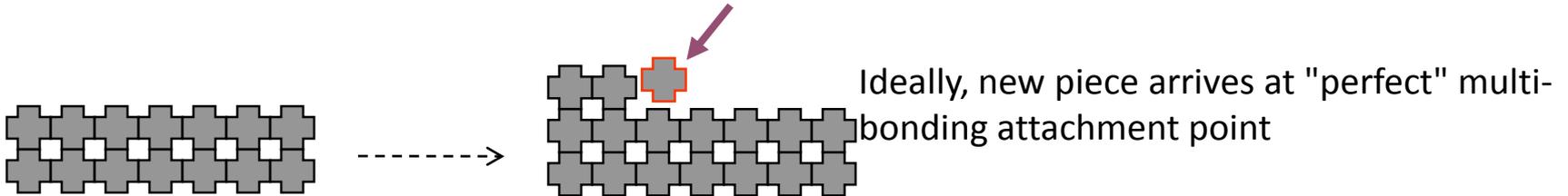
4) ENZYMES: *DRIVE* pieces to state that may even be at HIGHER ENERGY

Using force/energy provided by enzyme (e.g., fueled by ATP → ADP)

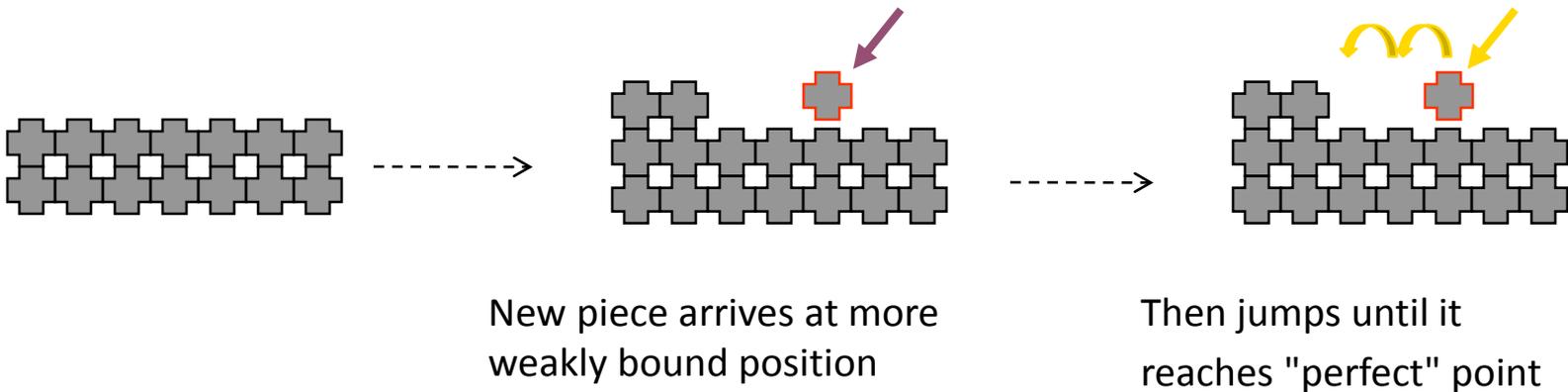
*As occurs with many forms of DNA and protein "self-assembly"*

*Looking more deeply:*

Say that we want to "grow" (i.e. self-assemble) more of the structure at the left:



More complicated (but realistic) scenario:



*This takes more time, especially because jump DIRECTION is likely RANDOM:*

SO new piece actually wanders about until it STUMBLES upon "perfect" point

*Sounds like that might take a heck of a long time!*

What it *actually* takes is a whole lot of jumps (for wandering to finally pay off)

So elapsed time depends on time per jump (or jump frequency)

Relevant quantity is atomic vibration frequency = "Debye Frequency"

Because some fraction of vibrations () produce jumps ()

But Debye frequencies are HUGE:

For Silicon (at  $\sim 400^\circ\text{C}$ )\*\*  $\sim 2\text{-}20$  THz (i.e.  $2\text{-}20 \times 10^{12}$  times per second)

*Debye vibrational frequencies are even HUGE at  $25^\circ\text{C}$  !*

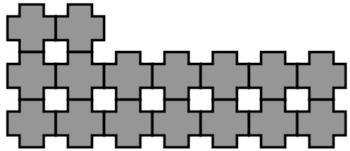
AS TEMPERATURE INCREASES: Vibrational frequency AND amplitude increase

 becomes  = increasing jumps

*Implying, instead, that self-assembly could progress VERY rapidly!*

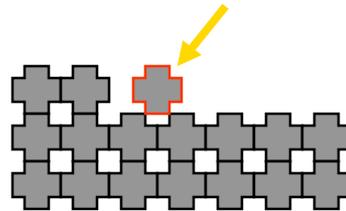
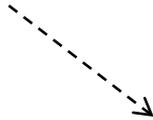
*But there are other potential problems:*

What happens if a second piece arrives too soon?

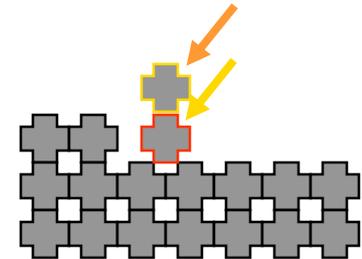
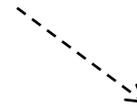


First piece aligns between "atoms"

Given a short bit of time it would wiggle over to full bonding position



But before that can occur, second piece arrives to sit atop it



Self-assembly is getting into big trouble:

First piece is now buried, no longer independent, semi-locked into (wrong) position!

## *SELF-ASSEMBLY STRATEGY #1:*

**SLOW DOWN**, reducing arrival rates, giving each new piece time to settle in

How do you "reduce arrival rates?"

- In self-assembly from solution, reduce concentration of reactants
- In self-assembly from gas, reduce partial pressures of reactants

## *SELF-ASSEMBLY STRATEGY #2:*

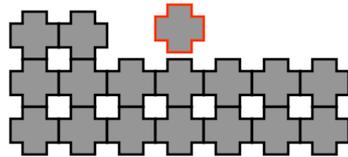
**TURN UP THE TEMPERATURE**, so that things "settle in" faster

Because vibrations and jumps will then all happen more quickly

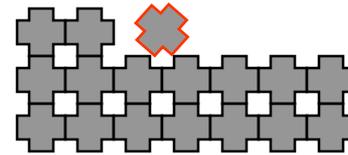
*It's like doing everything in "fast forward"*

*Another Oops: Piece that is accommodated in alternative arrangements*

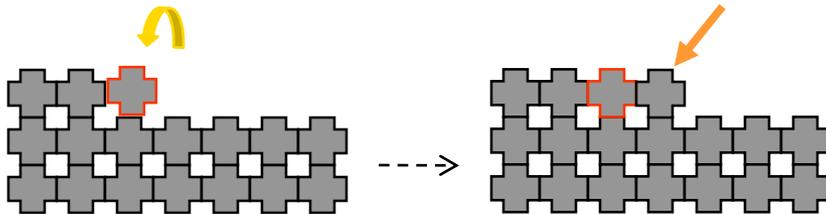
What we'd expected (or hoped for):



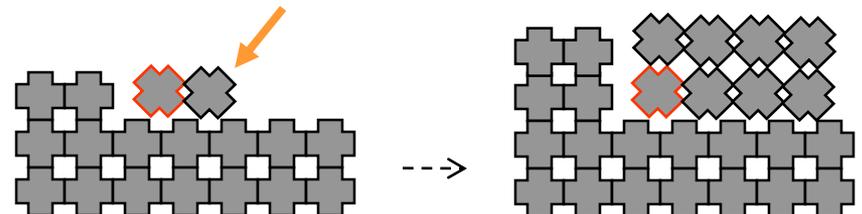
But at only slightly higher energy (nearly as likely):



Leading to assembly we'd hoped for:



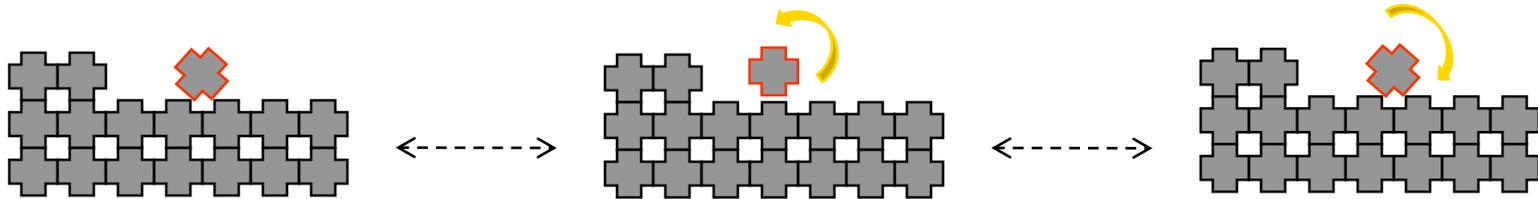
Or something VERY different:



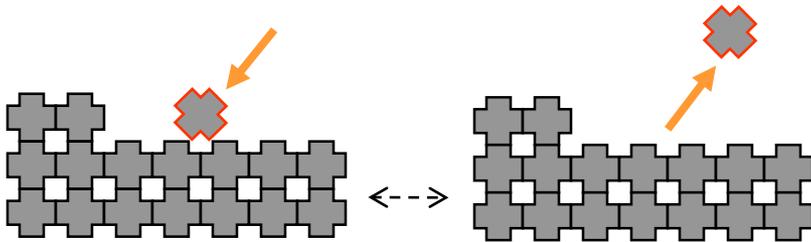
*Key to dealing with this is exploitation of REVERSIBILITY*

Temperature driven vibrations and jumps continuously . . .

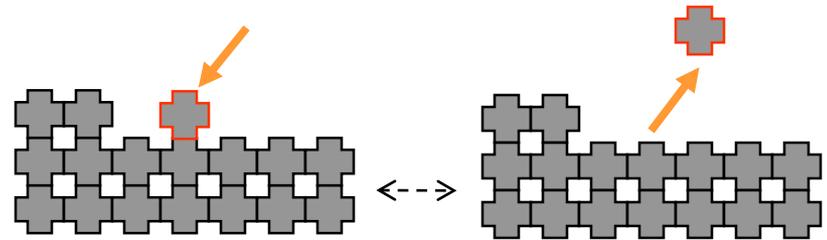
ARRANGE AND REARRANGE:



ASSEMBLE AND DISASSEMBLE:



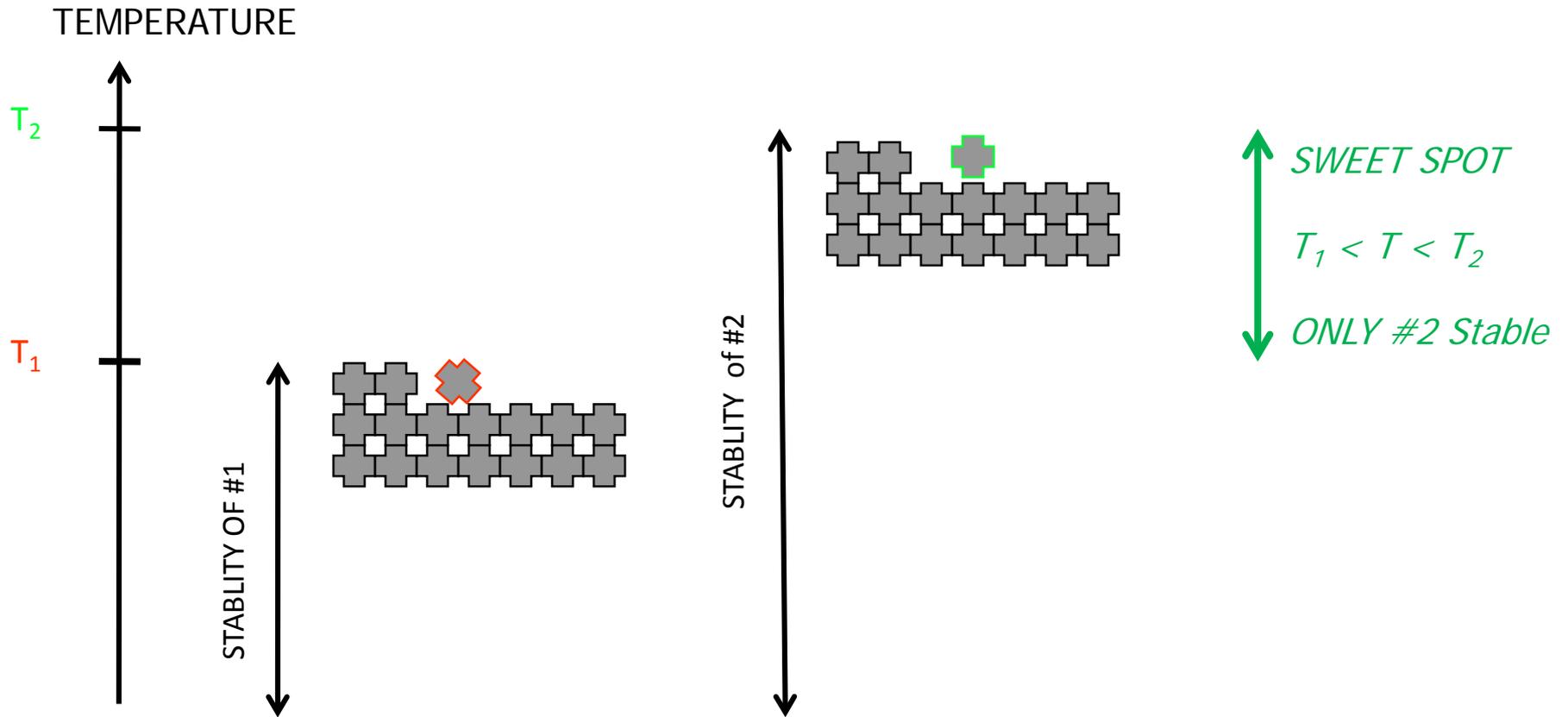
OR:



*So things that are "done" are also being continuously "undone"*

But lower energy configurations are "undone" less frequently / readily (i.e., are more stable)

IDEAL would be sudden loss of stability with increasing temperature:



## *Unfortunately things are not quite that simple*

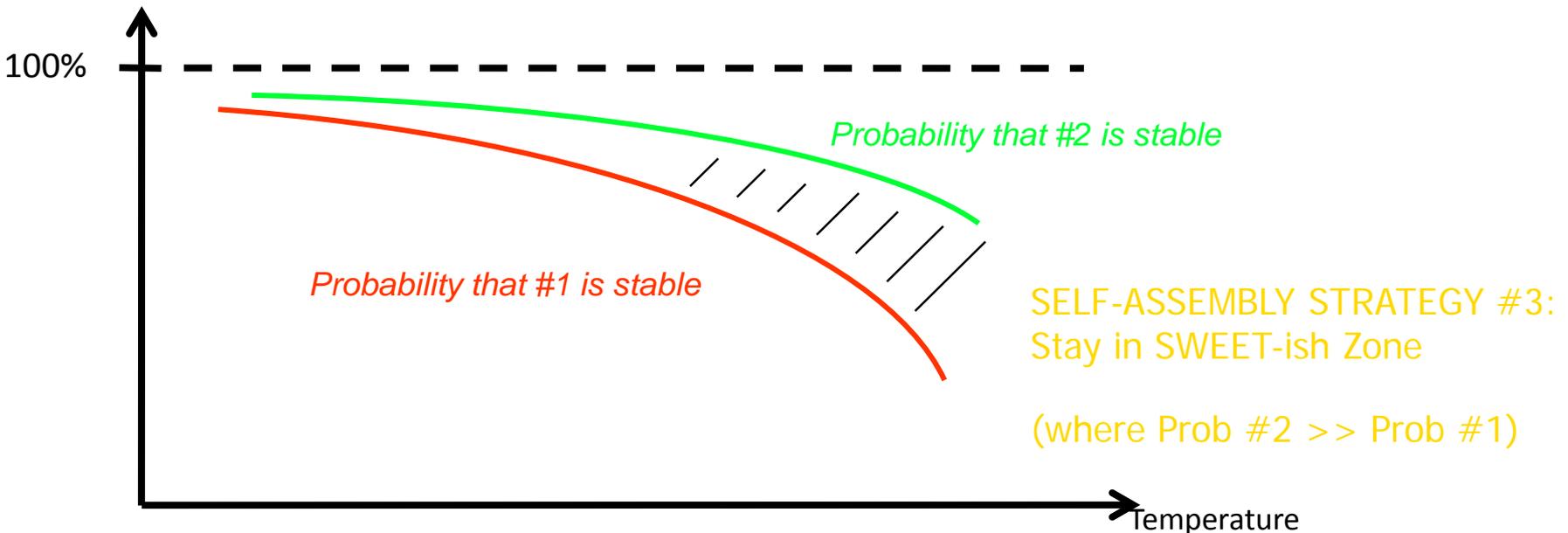
Generally are not sharply temperature-bounded regions of stability and instability

That can be played against each other to promote certain structures

Stability is instead PROBABILISTIC, governed by "Arrhenius" / "Boltzmann" / "Fermi" behavior:

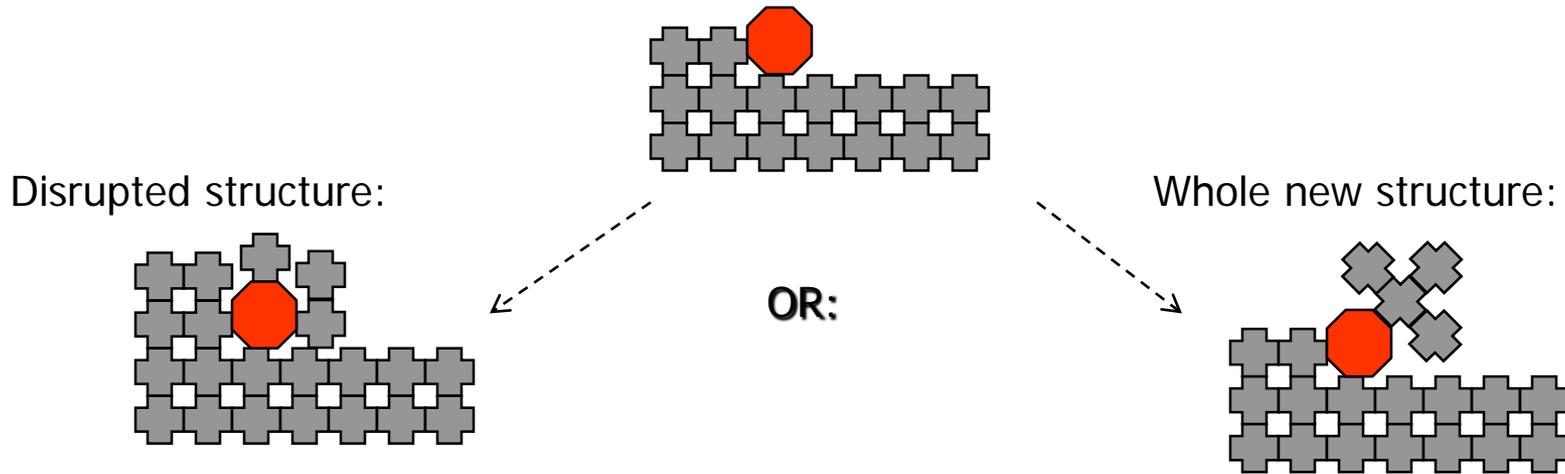
That is, involving factors like:  $e^{-E_1/kT}$

Yielding probability plots of stability similar to this (for  $E_2 > E_1$ ):



*And then there are impurities to deal with:*

"Impurity" = anything else you really hadn't planned on being present:



SELF-ASSEMBLY STRATEGY #4: Get rid of almost all impurities

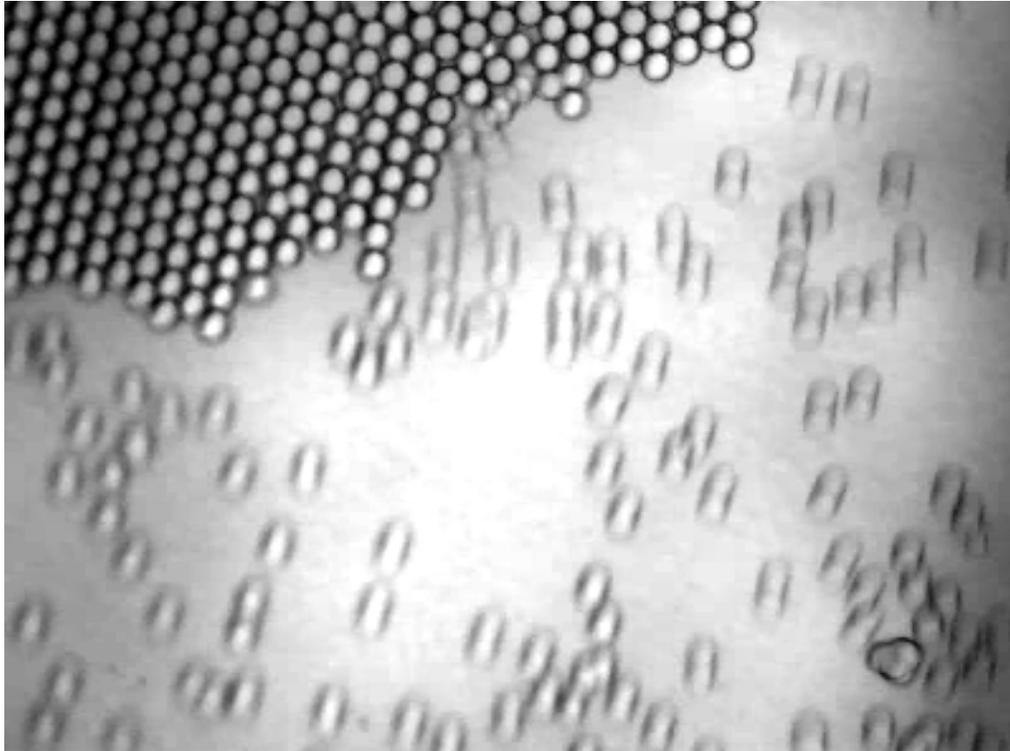
Sometimes possible with self-assembly from gas (i.e., some forms of crystal growth)

Hopeless with aqueous growth (i.e., chemistry, where must later refine out mistakes)

SELF-ASSEMBLY STRATEGY #5: Again try to find a "SWEET-ish" temperature zone

Possible only if bonding of impurity is less stable

*EXAMPLE: Crystal growth of glass microspheres*



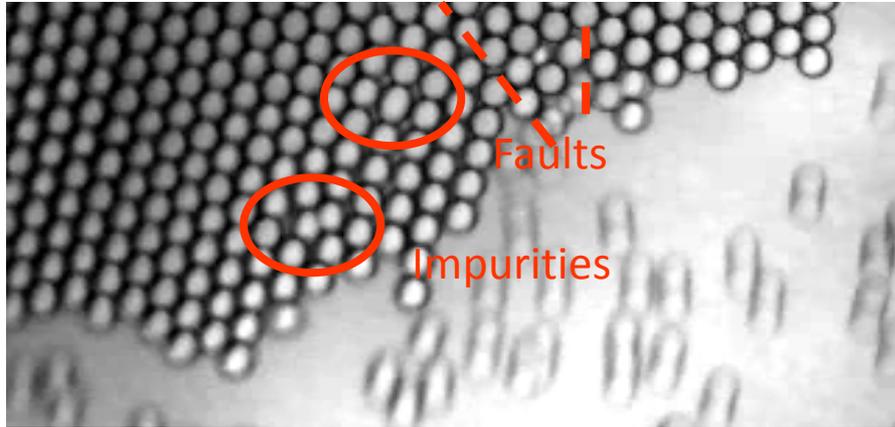
[video](#)

Source: Interdisciplinary Education Group, NSF MRSEC project of the University of Wisconsin.

<http://www.mrsec.wisc.edu/Edetc/cineplex/self/text.html>

*That was a less than perfect example of self-assembly:*

MANY faults in the crystal (involving 0.1 to 1% of "atoms"):



In semiconductor crystals, fewer than 1 in  $10^{12}$  atoms can be out of place!!

What was the problem with above crystal growth?

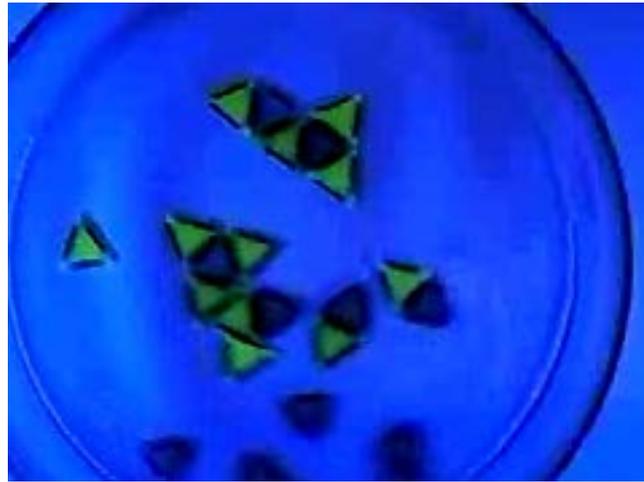
New atoms arrived way TOO quickly

Allowing no time for: Crystal to expel impurity atoms

Or to try to repair flawed crystal

In this case obvious solution = Turn down flux / Dilute concentration of reactants

*But this time didn't get much overall crystal growth!*



Problem this time? Too much energy

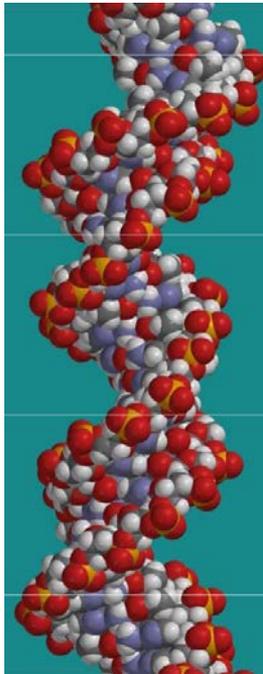
Triangles briefly condensed - but then jumped back off

But DID have side advantage: Grew almost no "Bad" mis-bonded crystal

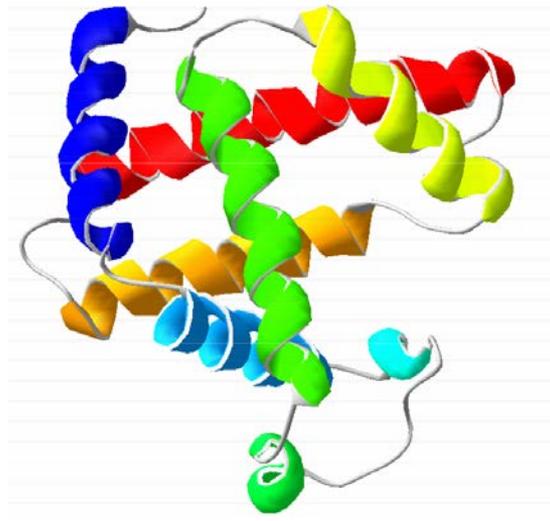
Mis-bonded atoms held so weakly that they re-evaporated VERY fast

Solution this time: Slow things down = Reduce temperature of the system

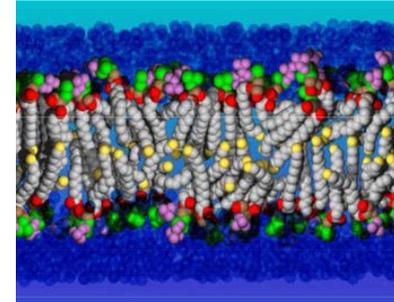
## Solo alcuni esempi di autoassemblaggio nei sistemi viventi



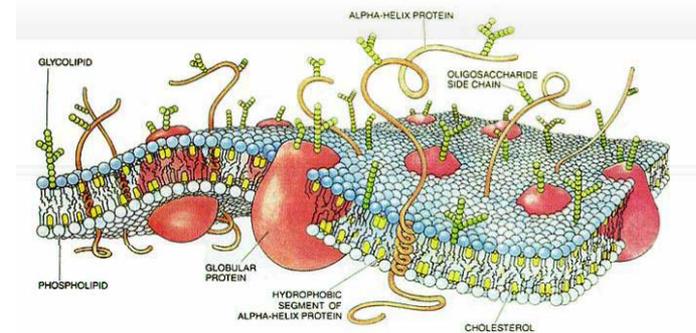
DNA double-helix



Protein: A representation of the 3D structure of myoglobin  
“Protein folding”



Lipid bilayer



Cell Membrane

# *But how does nature actually assemble such things?*

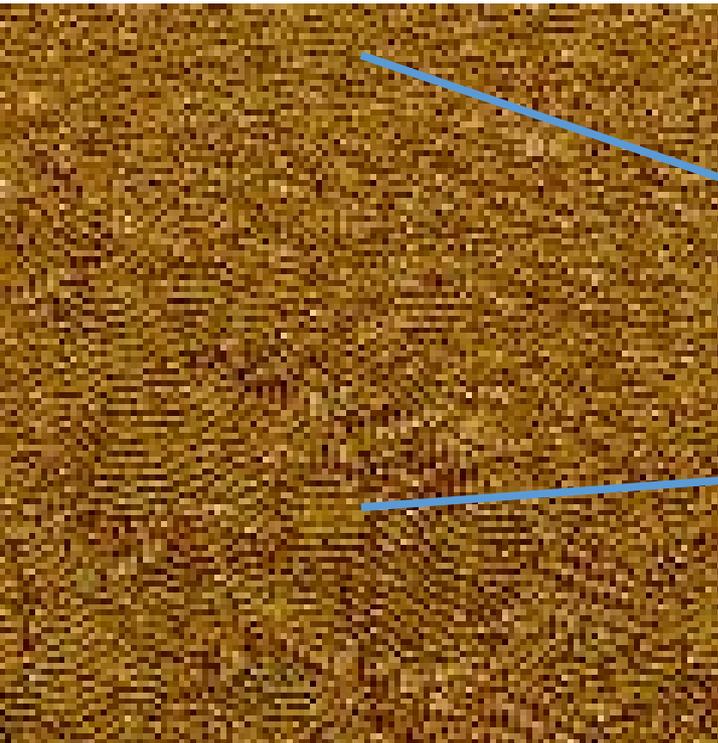
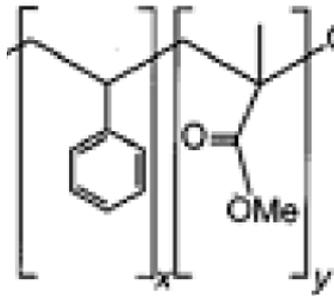
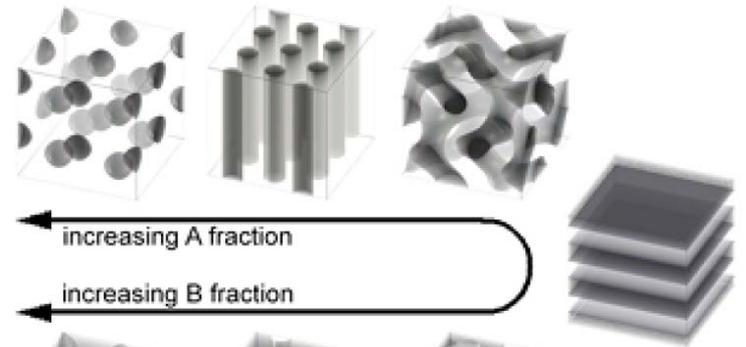
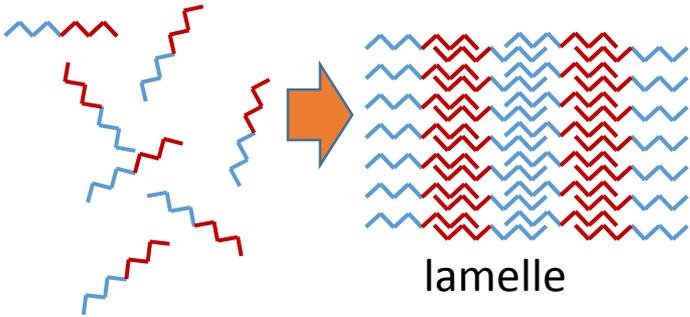
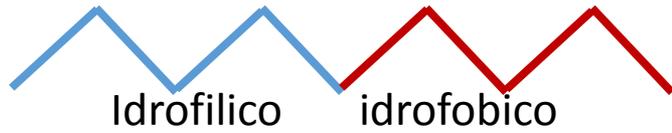
Demonstration of how a virus shell might assemble:  
Uses plastic subunits with embedded magnets to simulate bonding



[video](#)

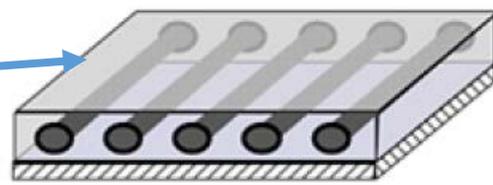
[http://mgl.scripps.edu/projects/tangible\\_models/movies](http://mgl.scripps.edu/projects/tangible_models/movies)

# Autoassemblaggio di copolimeri a blocchi (2 blocchi diversi)

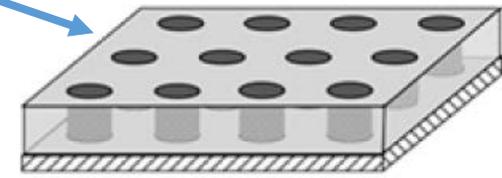


With surface neutralization using random copolymers:

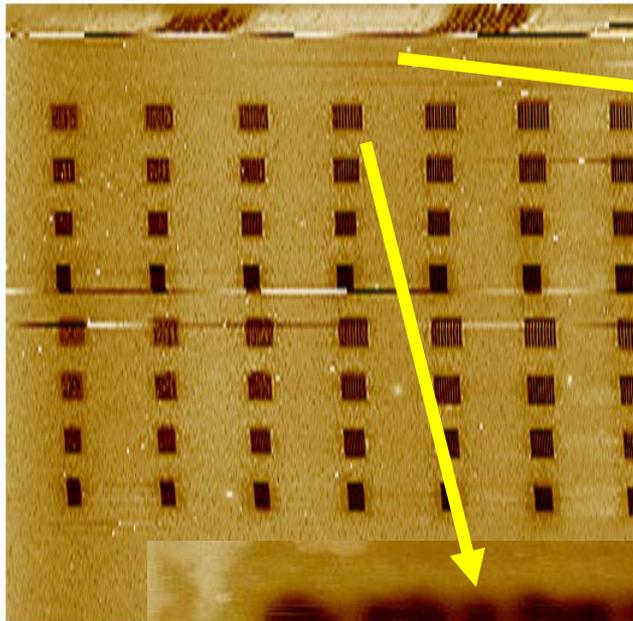
|| **Cylinders**



⊥ **Cylinders**

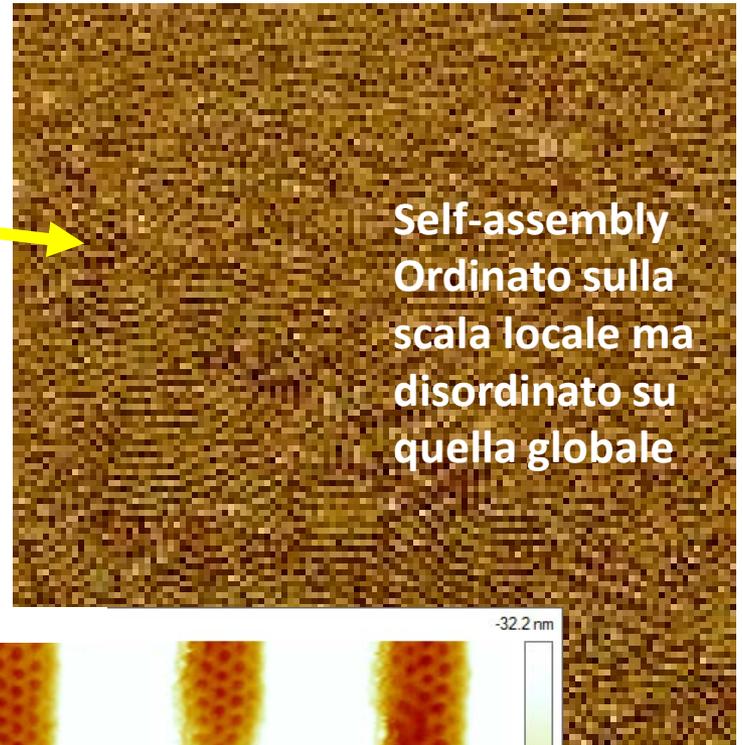


# Top-down+bottom-up: nanolithography (EBL or FIB) + self-assembly of block copolymers

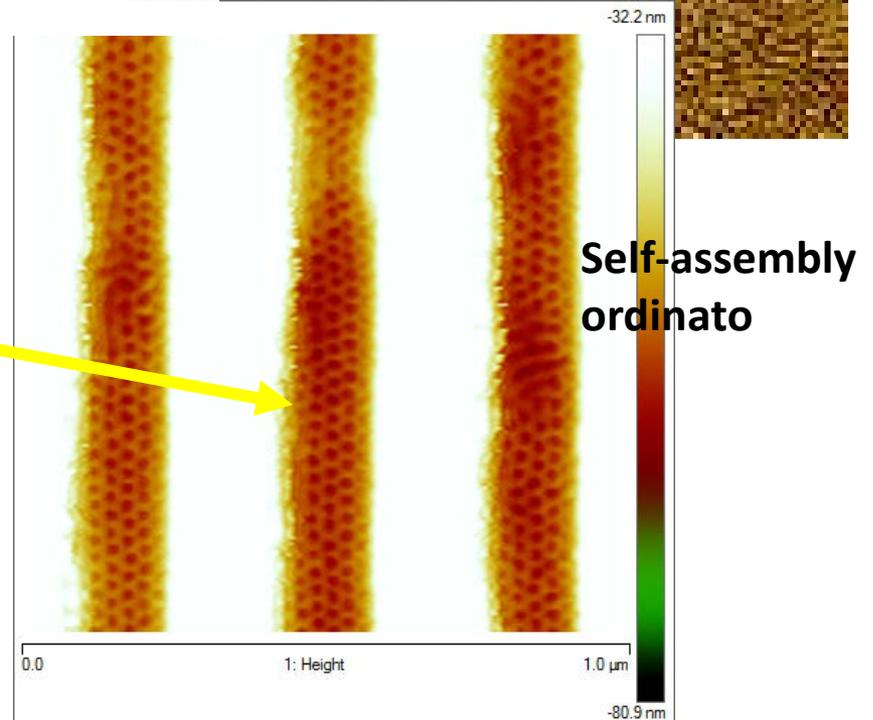
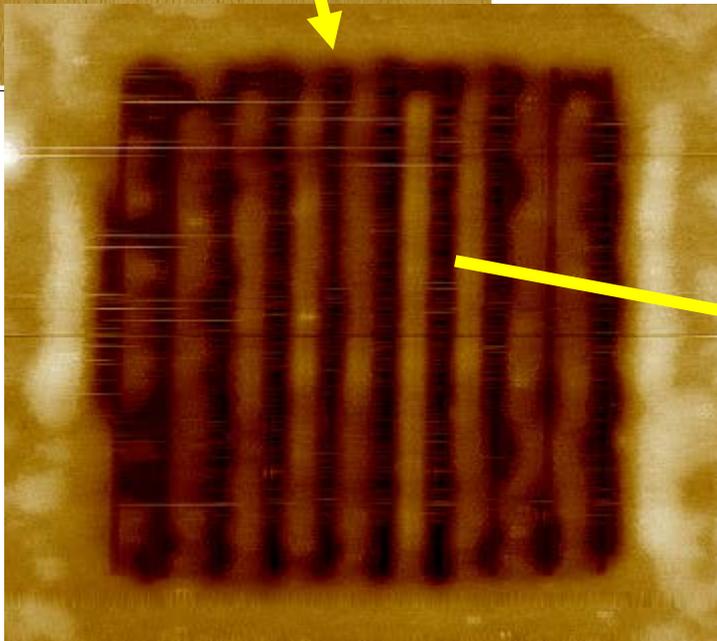


23.7 nm

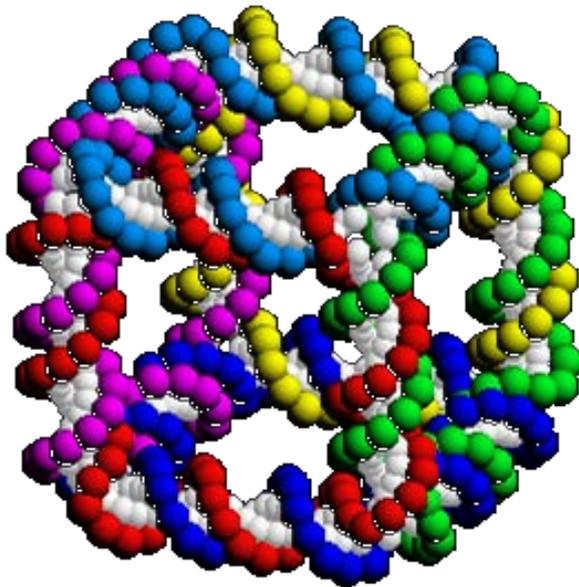
-58.4 nm



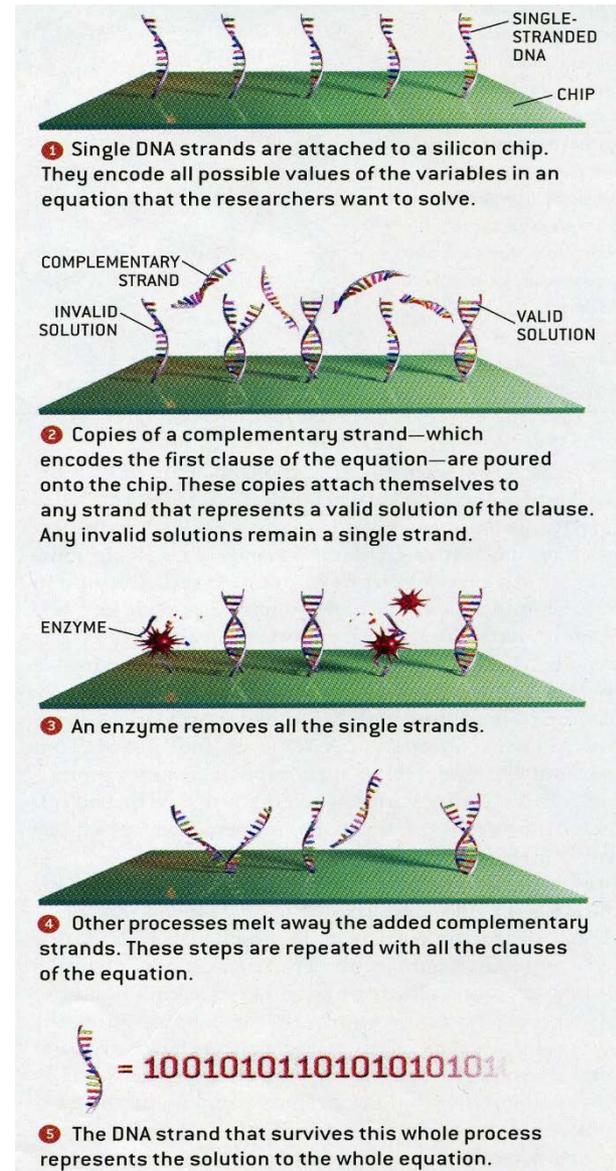
0.0



Una certa varietà di costruzioni, dispositivi e calcoli si possono fare con gli acidi nucleici: l'autoassemblaggio di questi è prevedibile con una certa facilità sfruttando le regole dell'appaiamento secondo Watson e Crick



DNA cube (Ned Seeman)



DNA computing (Adleman)