

The Need for Self-Assembly

Earlier we discussed Microfabrication:

A method for **simultaneously** making large numbers of IC / MEMS devices

It's very efficient and very cost-effective . . .

But use of projected light images → Sizes $> \lambda_{\text{light}}$ (deep UV ~ 0.05 micron)

In our last class I described methods of making things MUCH smaller

Atomic Force Microscope writing oxide patterns or melting polymer pits

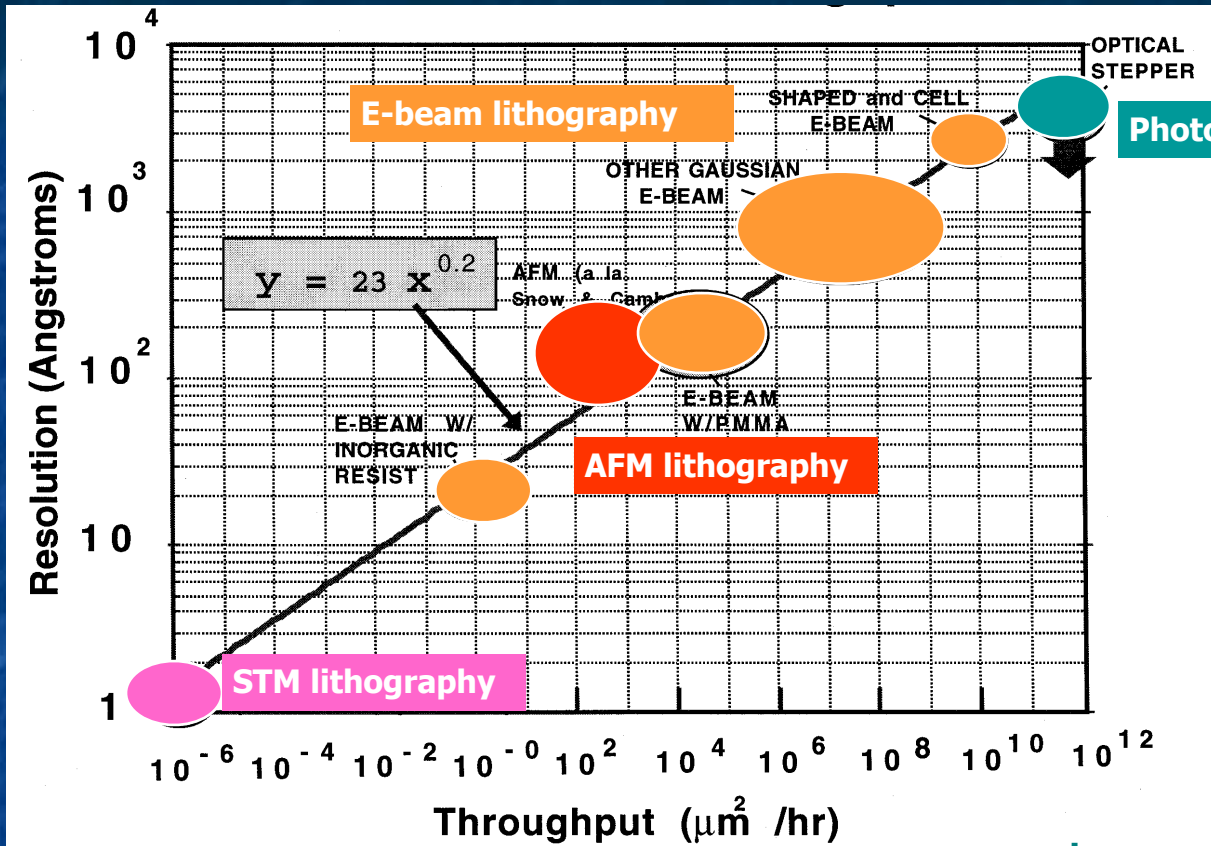
Scanning Tunneling Microscopes pushing atoms . . .

Electron Beams patterning photographic emulsions

But new techniques often fell on wrong side of science vs. technology boundary

Key figure (introduced in lecture 5) was:

Processing rate vs. lithography and its best resolution



Photolithography

- 3 billion years

- 3000 Years

- 30 Years

- 25 Hours

- 1/100 seconds

Processing time for 5x5 mm²
 1/10,000 the area **single** Si wafer

Producing a dilemma:

Microfabrication: Efficient but crude (on the nanoscale)

Nanofabrication using AFM or STM: Precise, but lifetime of universe to pattern one wafer

These are now often described as "Top Down Fabrication" techniques

TOP DOWN in that we 10^9 X larger humans are trying to directly control everything

That is, top down in a management sense

TOP DOWN in that we often start with LARGE things and try to whittle them smaller

E.G. microfabrication's deposition of whole layers → etch away unwanted portions

Alternative? "Bottom Up Fabrication"

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

But here we are still on a steep leaning curve!

Focusing on the second more difficult step, this bottom up process is 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

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

1) Trivial case – only one possible end state:

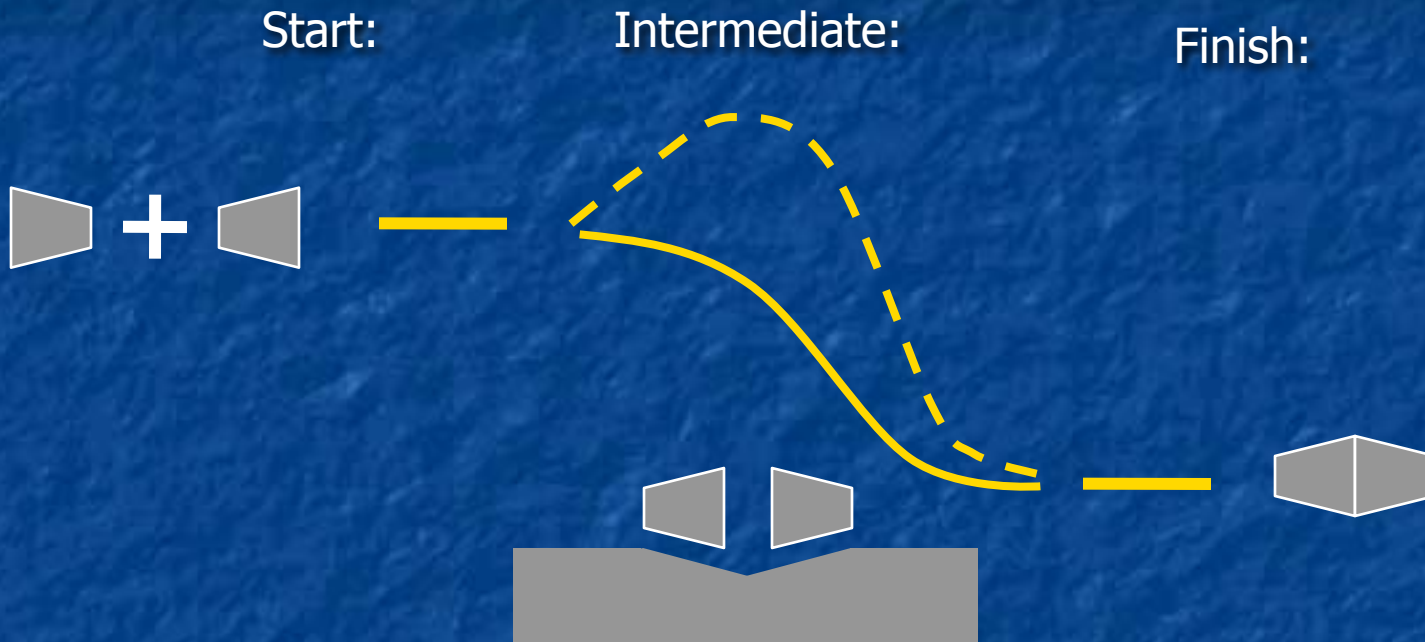


2) More realistic – many possible end states (but one slightly favored):



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

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



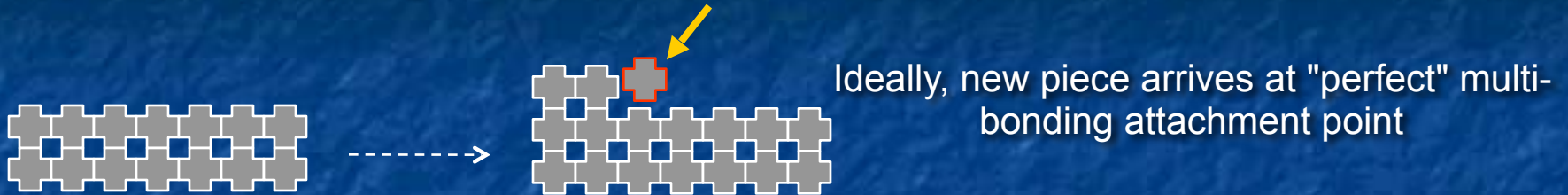
4) ENZYMES: **DRIVE** pieces to state that may even be at HIGHER ENERGY

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

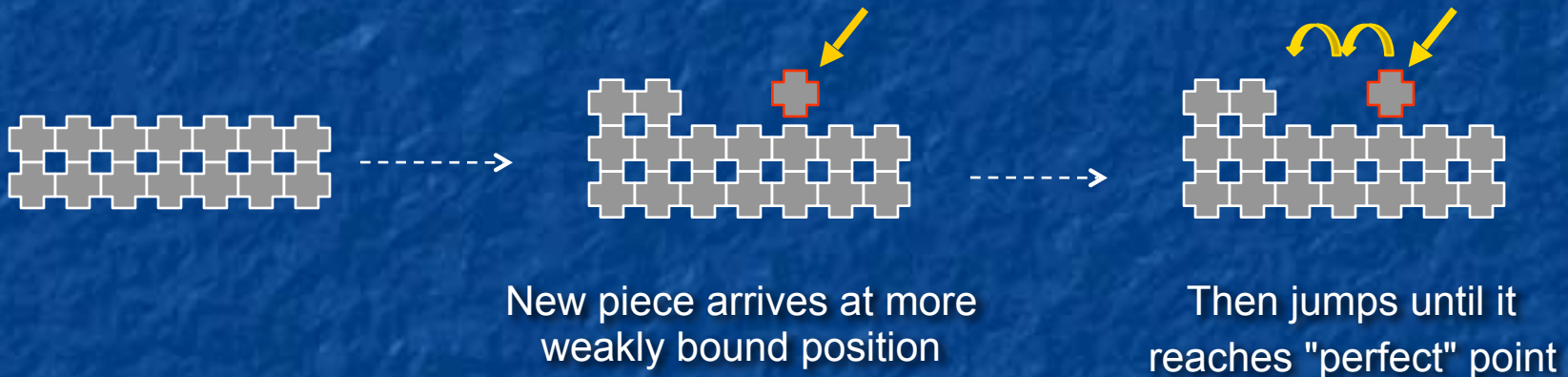
As occurs with many forms of DNA and protein "self-assembly"

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°C !

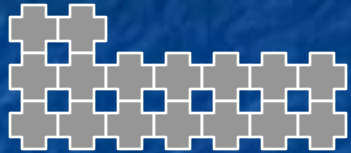
AS TEMPERATURE INCREASES: Vibrational frequency AND amplitude increase

   becomes    = increasing jumps

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

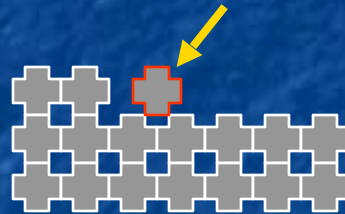
But there are other potential problems:

What happens if a second piece arrives too soon?

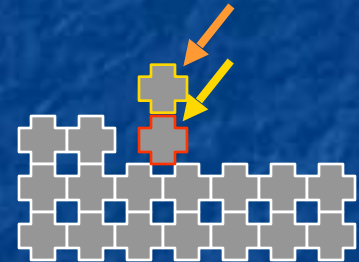


First piece aligns between "atoms"

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:

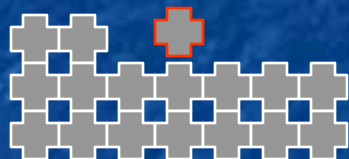
TURN UP THE TEMPERATURE, so that things "settle in" faster

Because vibrations and jumps will then all happen more quickly

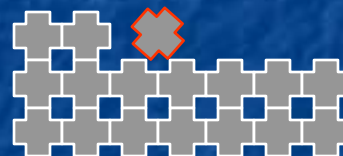
It's like doing everything in "fast forward"

Another Oops: Piece that is accommodated in alternative arrangement

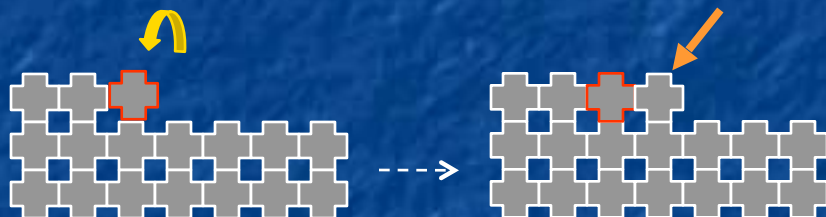
What we'd expected (or hoped for):



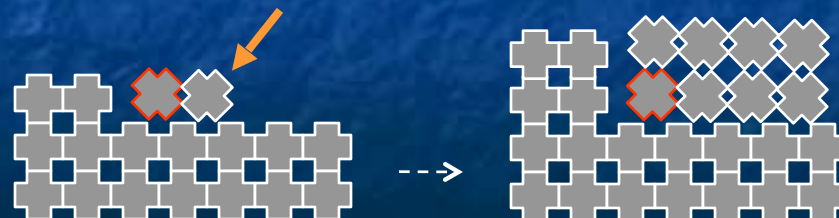
But at only slightly higher energy (nearly as likely):



Leading to assembly we'd hoped for:



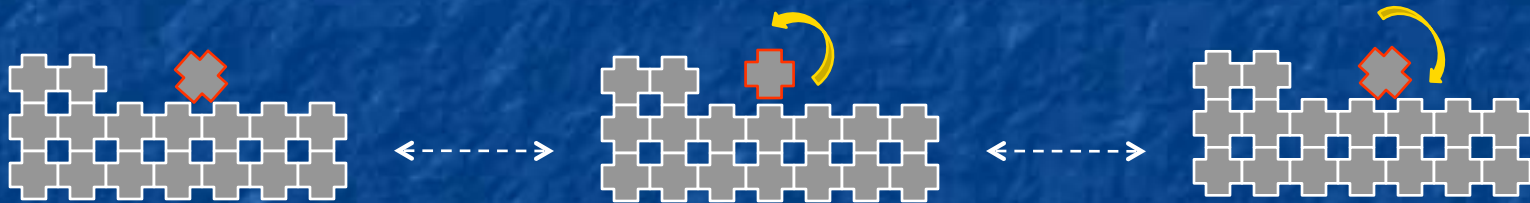
Or something VERY different:



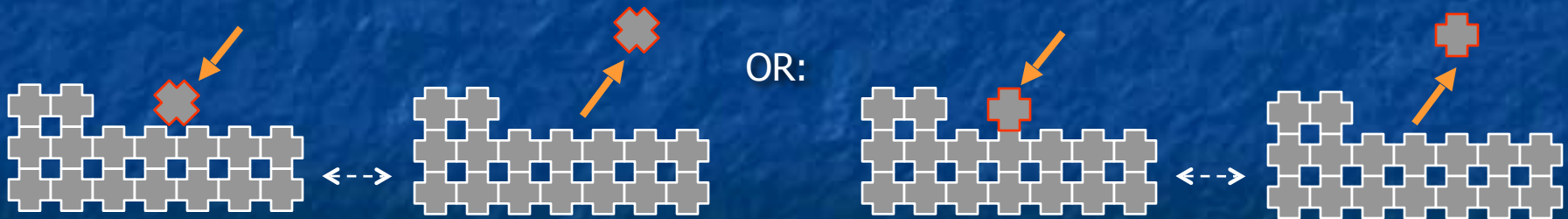
Key to dealing with this is exploitation of REVERSIBILITY

Temperature driven vibrations and jumps continuously . . .

ARRANGE AND REARRANGE:



ASSEMBLE AND DISASSEMBLE:

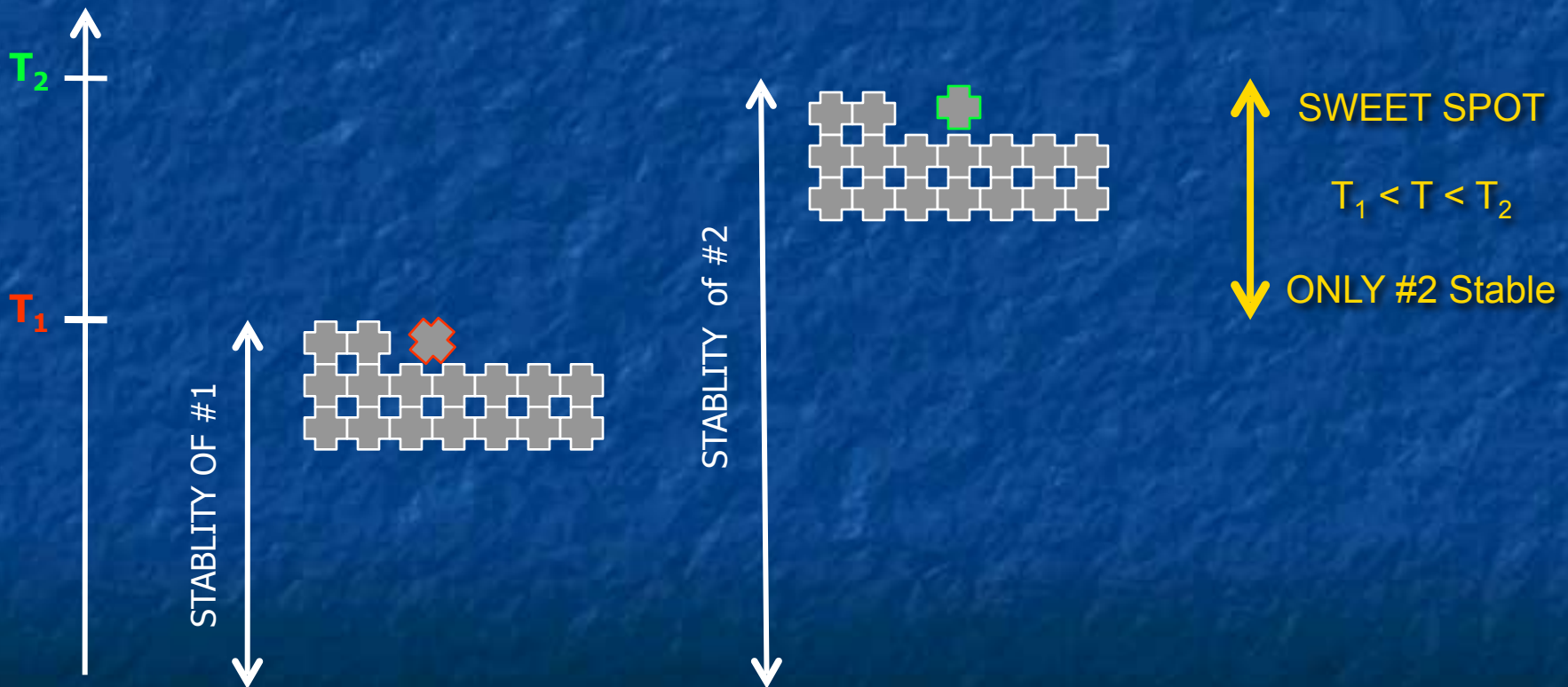


So things that are "done" are also being continuously "undone"

But lower energy configurations are "undone" less frequently / readily (they're more stable!)

IDEAL would be **sudden** loss of stability with increasing temperature:

TEMPERATURE



Unfortunately things are not quite that simple

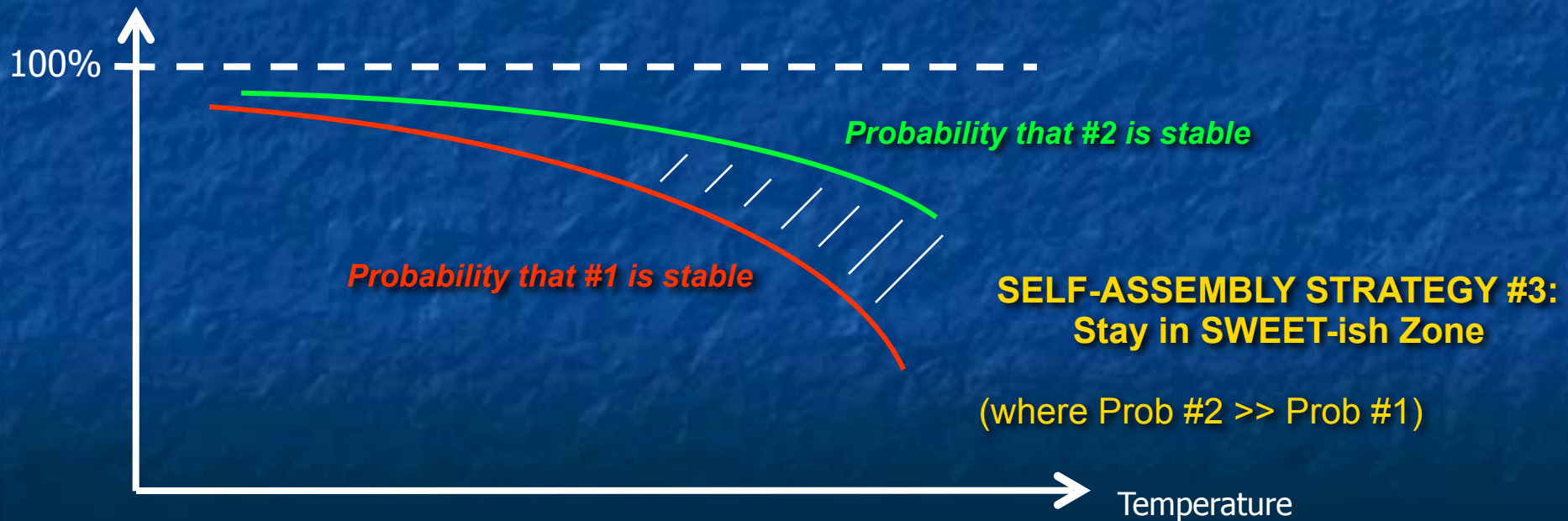
Generally, regions of stability and instability do not have sharp temperature boundaries

That can be played against each other to promote certain structures

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

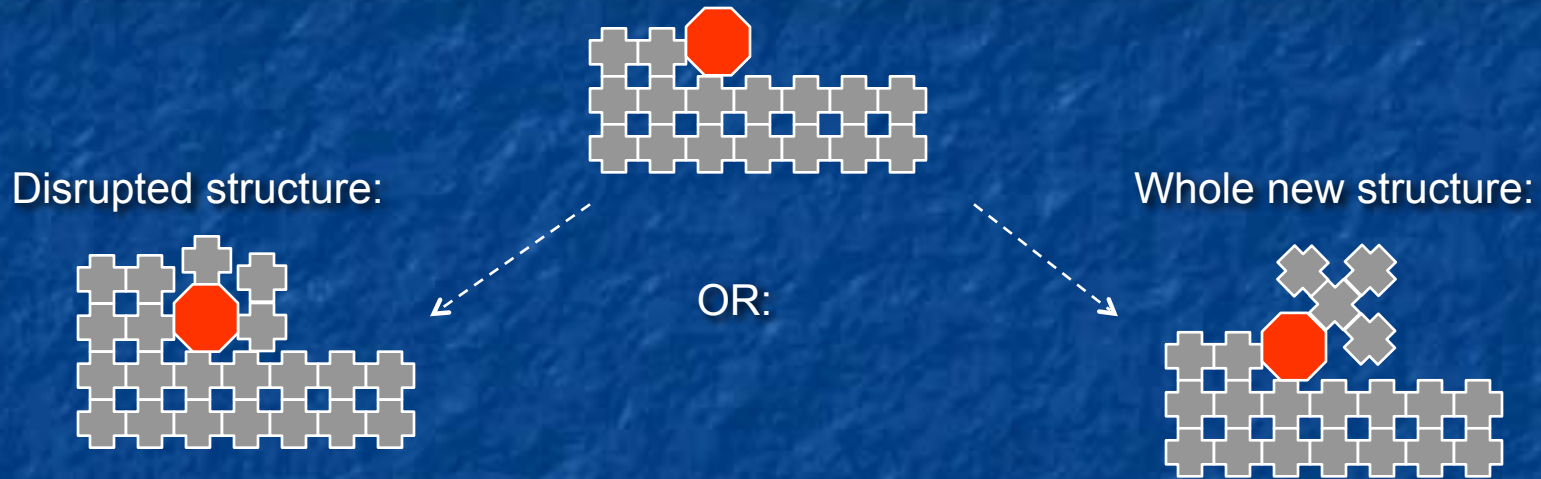
That is, involving factors like: $e^{-E/kT}$

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

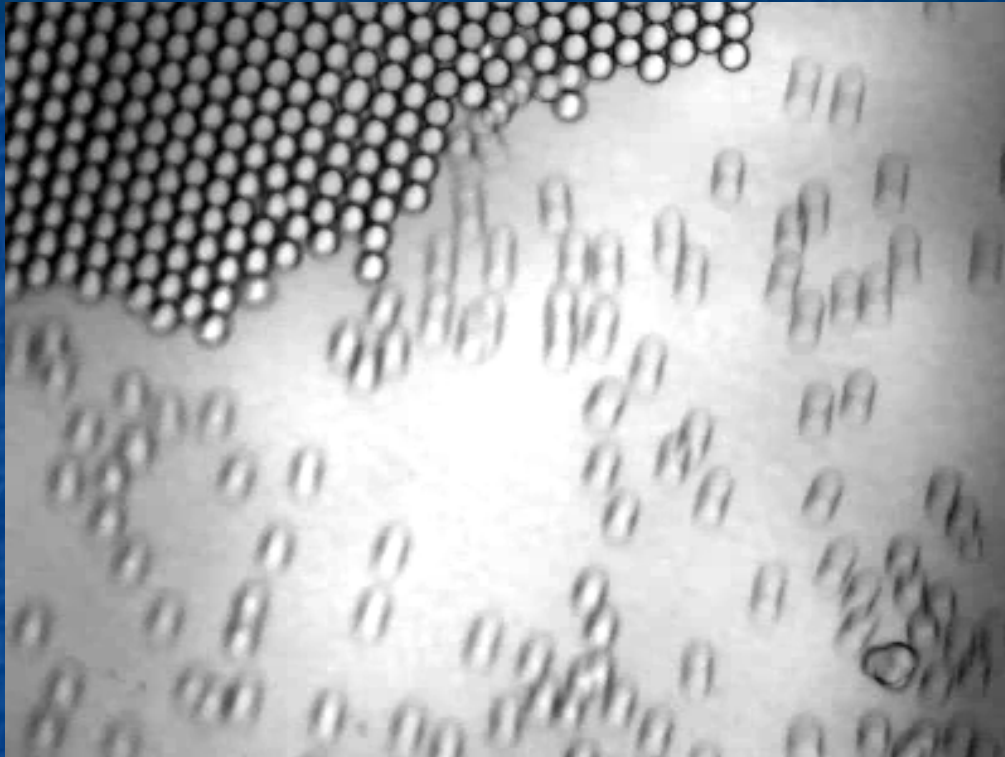
Sometimes possible with self-assembly from gas (i.e., some forms of crystal growth)

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

But this time where only impurity bonding becomes unstable

TIME FOR SOME EXAMPLES: Crystal growth of glass microspheres

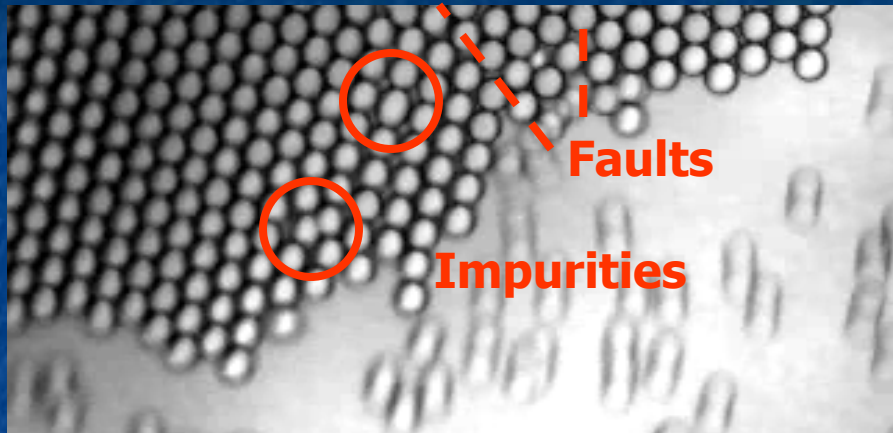


Supporting webpage with embedded animation:
[The Need for Self-Assembly - Supporting Materials - Animation_1](#)

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:

With 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!!

So 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

Another visualization of self-assembly: floating magnetized shapes

Crystal growth / self-assembly of floating plastic magnets:



Supporting webpage with embedded animation:

[The Need for Self-Assembly - Supporting Materials - Animation_2](http://www.mrsec.wisc.edu/Edetc/cineplex/self/text.html)

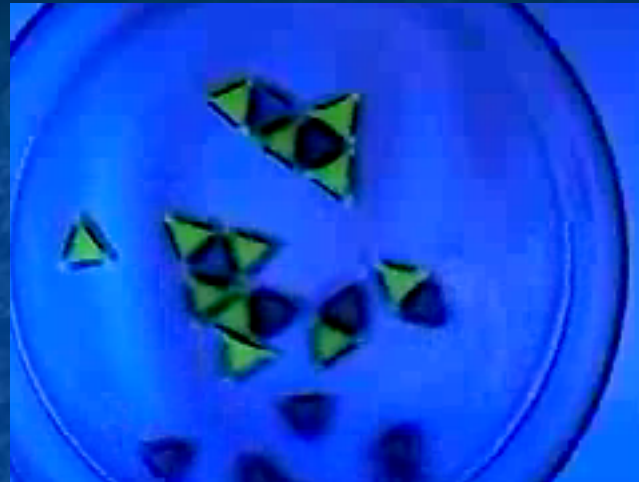
Note how it takes **many** tries to find the ideal / lowest-energy configuration

Facilitated by agitation (background energy) to knock it out of less desirable states

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

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

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



Problem? **Too much energy**

Triangles briefly condensed - but then jumped back off

But this DID have side advantage: It grew almost no “Bad” mis-bonded crystal

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

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

Confirming earlier self-assembly strategies:

Best self-assembly almost always produced by a subtle optimization of temperature and flux:

Temperature:

Low temperatures: Easier to reach, less likely to liberate impurities from elsewhere, and may best preserve desirable features of assembly

Moderate temperatures: Help newly arrived parts to quickly reach proper sites

High temperatures: Make it less likely that undesirable impurities will stick or that more energetic arrangements will persist

Flux (or flow):

Higher the flux, faster the parts already on surface must get into proper positions

So higher fluxes require use of higher growth temperatures

But higher flux **does** make presence of ambient impurities less important

Because they then constitute smaller fraction of arriving parts (atoms)

A neat example of naturally occurring self-assembly:

One that I only recently learned about!

Water, percolating down through rocks, leeches out (dissolves) silica (SiO_2)

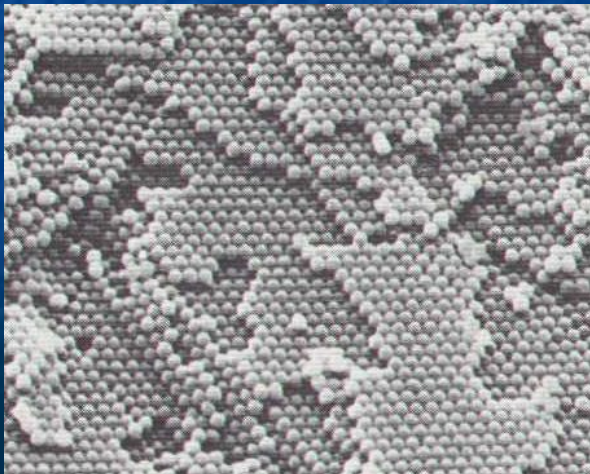
If the water then begins to dry up

Silica becomes supersaturated, and precipitates back out of solution

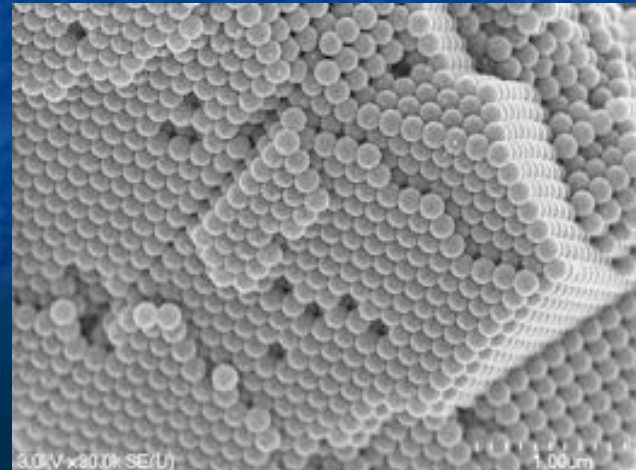
Under the right conditions, silica precipitates form uniform spheres, 100's of nm in diameter

If drying/precipitation is slow enough, spheres have time to get organized

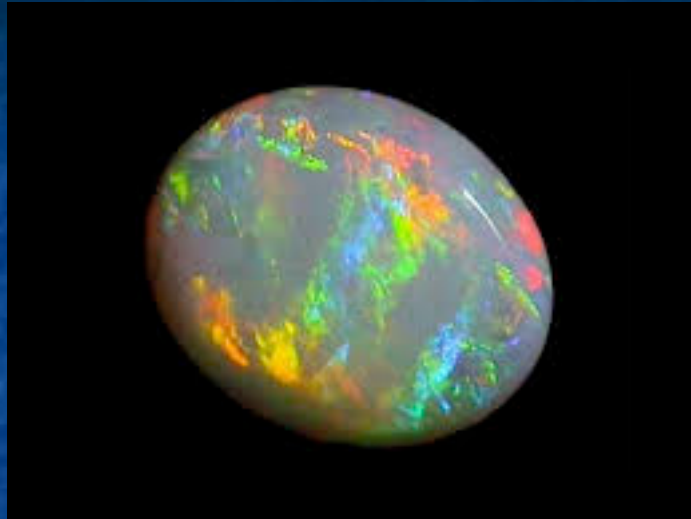
First into sheets:



And, eventually, into full 3D structures:



When 3D regions grow into one another, you get the gemstone **OPAL!**



Which is treasured for its "**iridescent colors**" (= colors that shift with viewing angle)

All because of **Wave Diffraction!**

Spheres are about the size of light's wavelength so they scatter light

Which adds constructively for one color (wavelength), in one direction

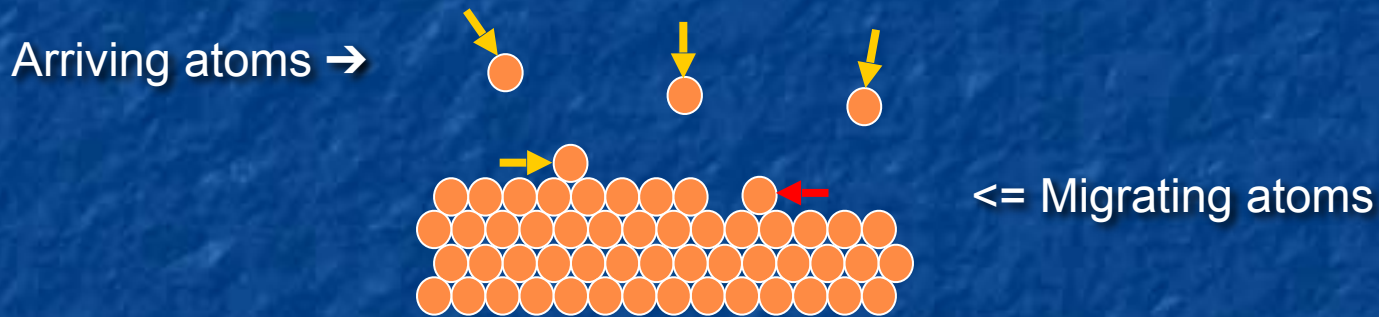
Or adds constructively for another color (wavelength), in another direction

In the lab, I did something similar with individual atoms via:

"Molecular Beam Epitaxy" (MBE)

Throw individual atoms across vacuum chamber (by evaporating them)

Let them land on mildly heated substrate (which allows them to still move around)

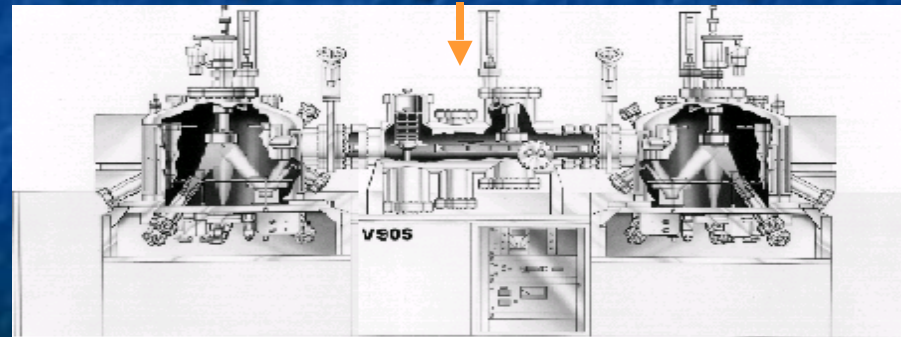


But it takes 1M\$ plus worth of vacuum equipment to make it this "simple"

My homepage view:



My full two growth chamber system:

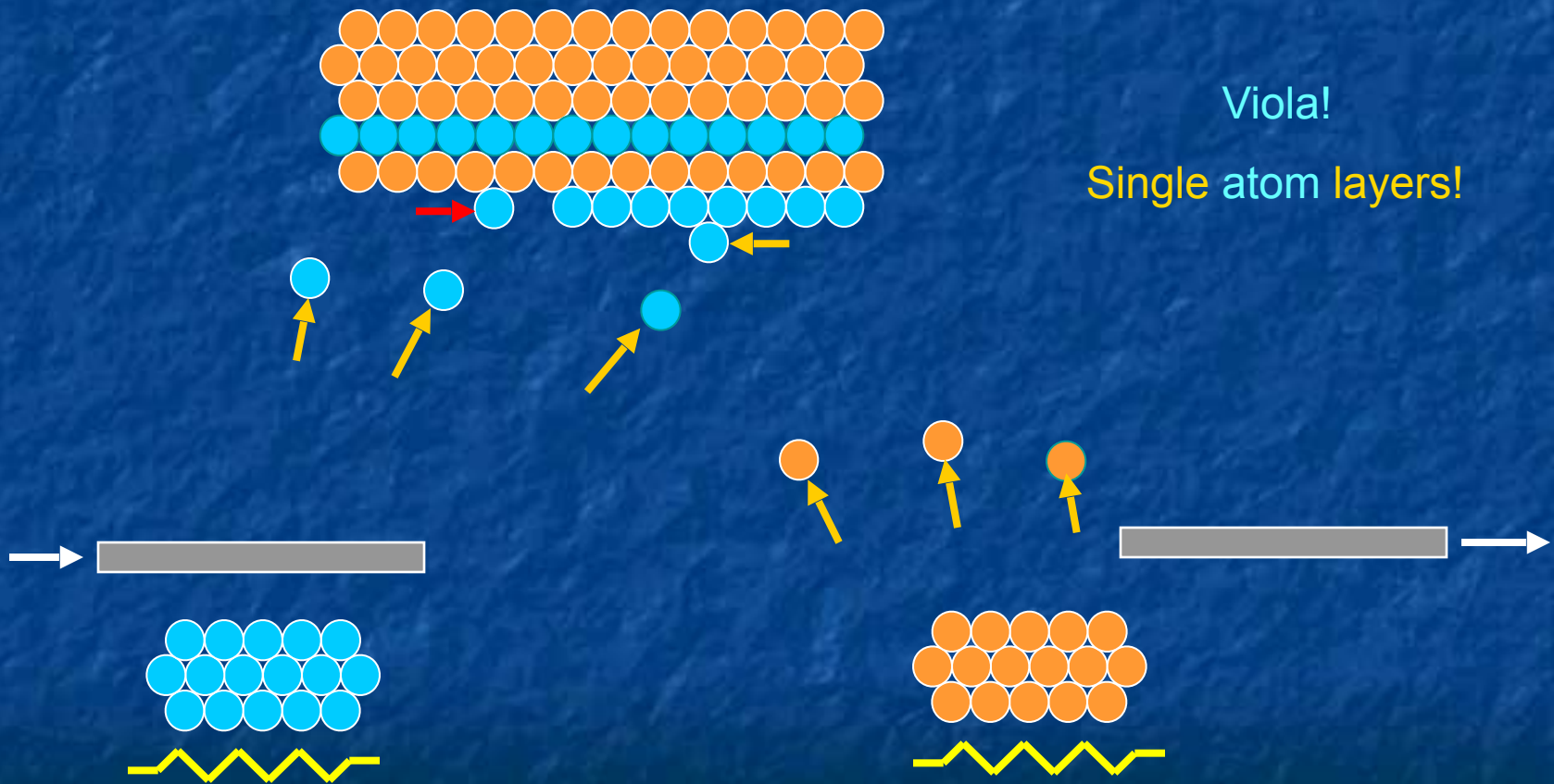


Arrow marks point where photo at left was taken

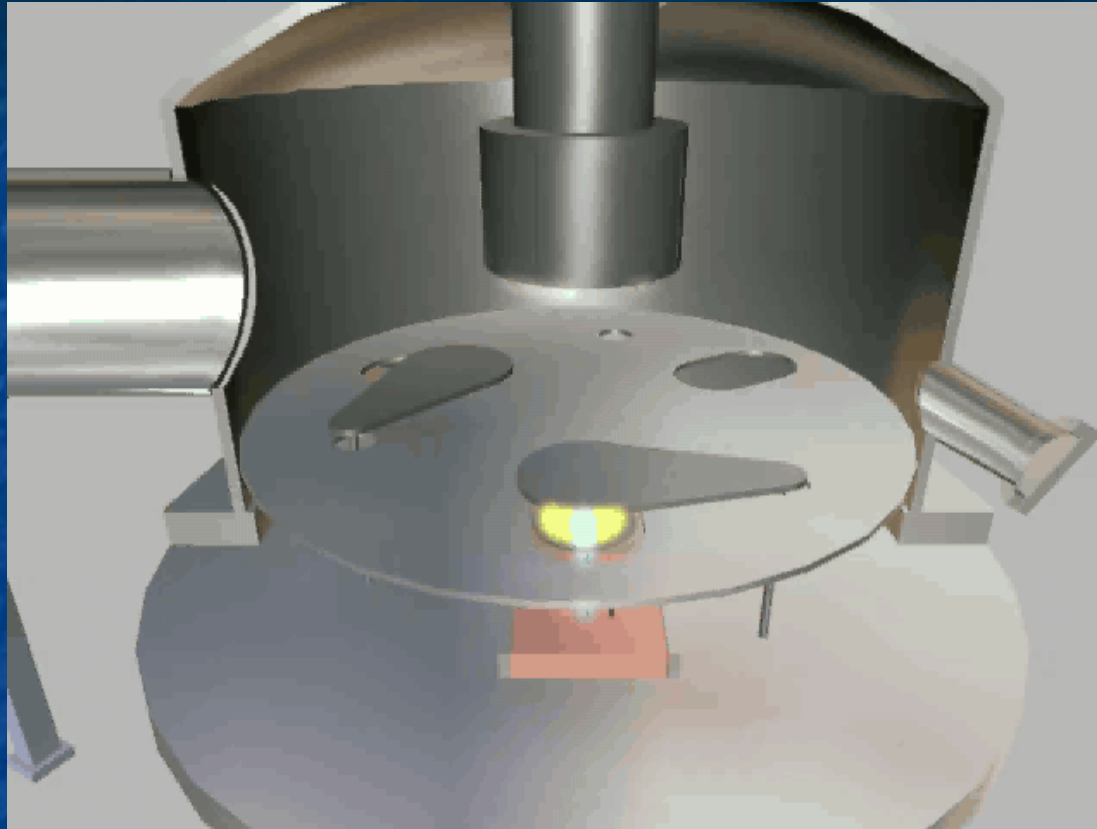
OK, but where's the ~~beef~~ nano?

Sure, "MBE" involves nano atoms, but how does this produce nano **structures**?

Flip upside down, install TWO evaporation sources, then alternate atoms:



Or more realistically:



Supporting webpage with embedded animation:
[The Need for Self-Assembly - Supporting Materials - Animation 3](#)

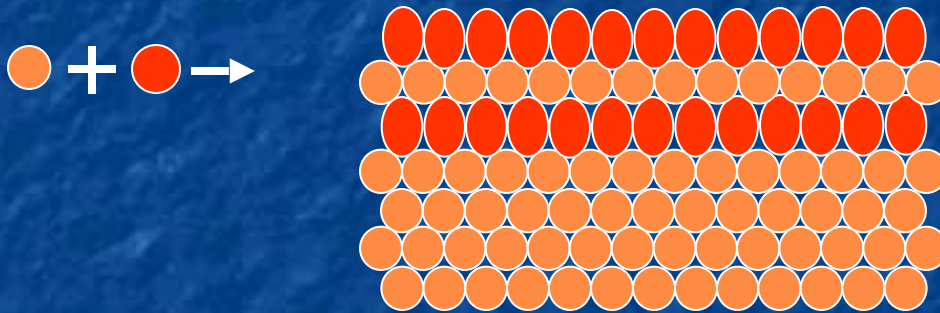
From WeCanFigureThisOut.org: <https://WeCanFigureThisOut.org/VL/MBE.htm>

A Hands-on Introduction to Nanoscience: WeCanFigureThisOut.org/NANO/Nano_home.htm

But what if you want 3D nano-structures?

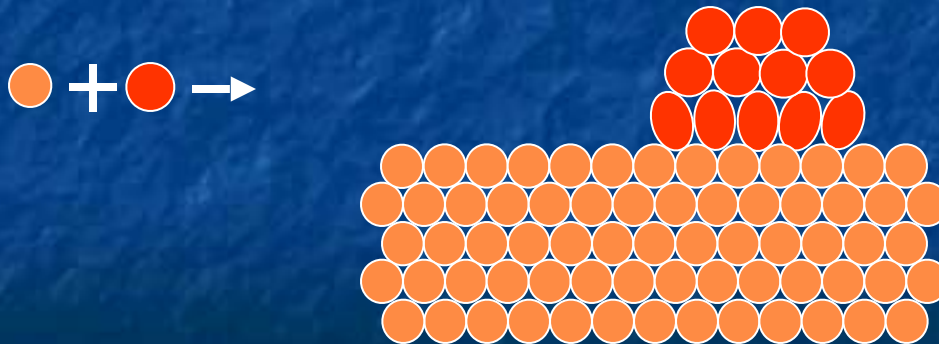
Try with atoms of different sizes: Smaller Si atoms and larger Ge atoms

Alternative #1: Larger Ge atoms squeeze to fit = **Strained Layer Epitaxy**¹



Favored at lower temperatures

Alternative #2: Arriving atoms exploit their surface mobility to segregate / island:



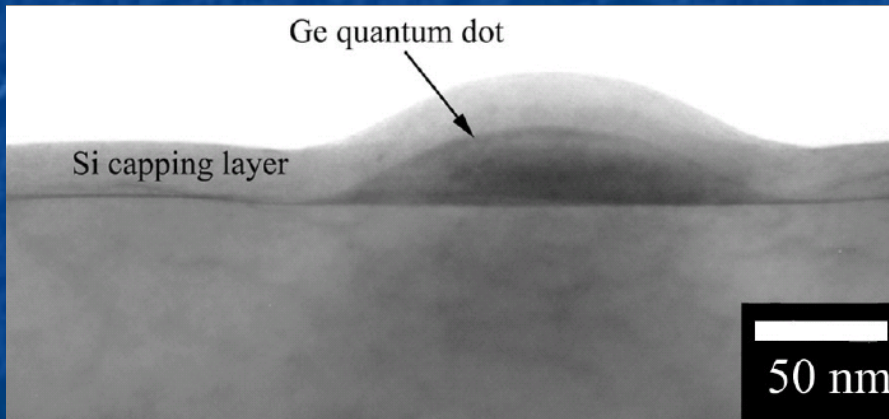
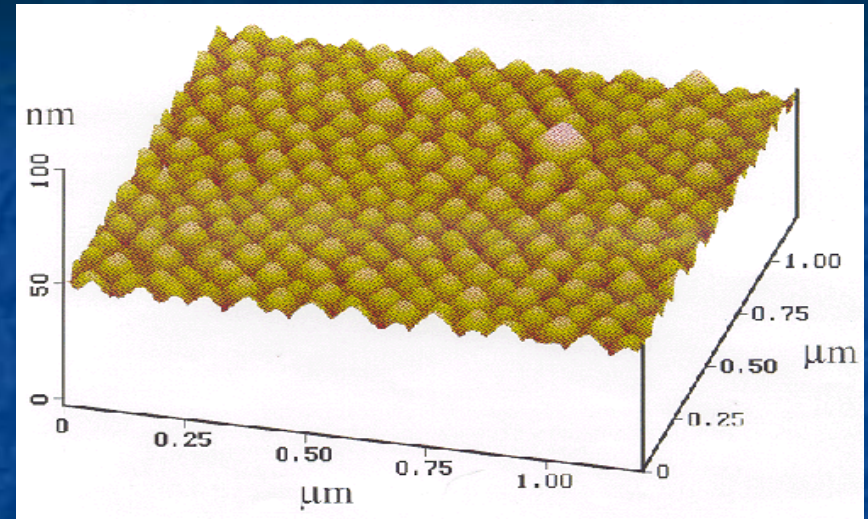
Favored at higher temperatures

¹ *Strained Layer Epitaxy of Germanium-Silicon Alloys*, John C. Bean, Invited Review, *Science Magazine* 230, 127-131 (1985)

Really do get such spontaneous 2D self assembly:

AFM image of slightly organized MBE Germanium islands on Silicon

(Stress-Induced Self-Organization of Nanoscale Structures in SiGe/Si Multilayer Films, C. Teichert, L.J. Peticolas, J.C. Bean, J. Tersoff and M.G. Lagally, Physical Review B 53 (24), 16334-7, 1996)

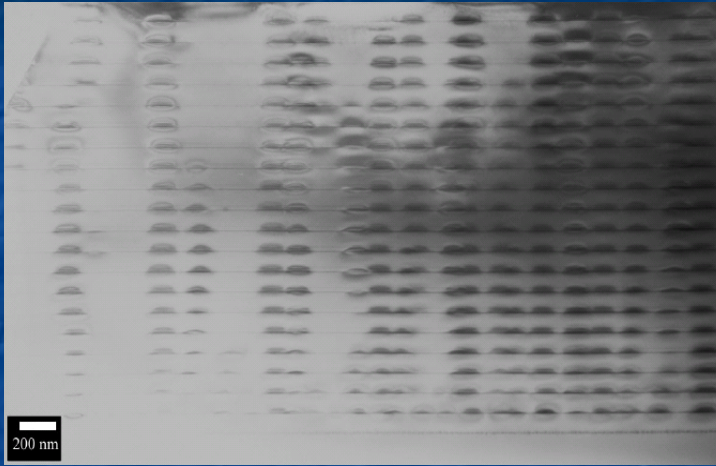


TEM cross-section of MBE Germanium island embedded in Silicon

"Analysis of the 3D relationship of Ge quantum dots in a Si matrix using focused ion beam tomography" A.J. Kubis, T.E. Vandervelde, J.C. Bean, D. Dunn, R. Hull, Nanoparticles and Nanowire Building Blocks-Synthesis, Processing, Characterization and Theory. 2p. 411 (2004), Materials Res. Soc.

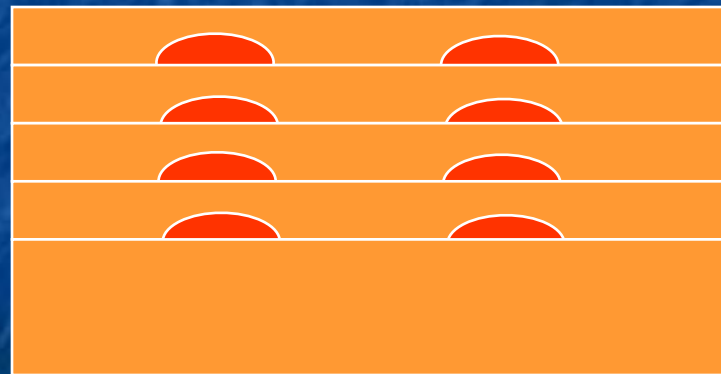
And this led to an even more complex 3D self-assembly:

TEM Cross-section of MANY layers of self organizing Ge dots embedded in Si:



"Analysis of the 3D relationship of Ge quantum dots in a Si matrix using focused ion beam tomography" A.J. Kubis, T.E. Vandervelde, J.C. Bean, D. Dunn, R. Hull, Nanoparticles and Nanowire Building Blocks-Synthesis, Processing, Characterization and Theory. 2p. 411 (2004), Materials Res. Soc.

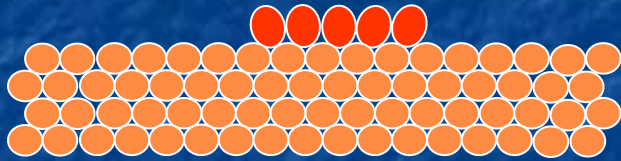
What you are seeing is this:



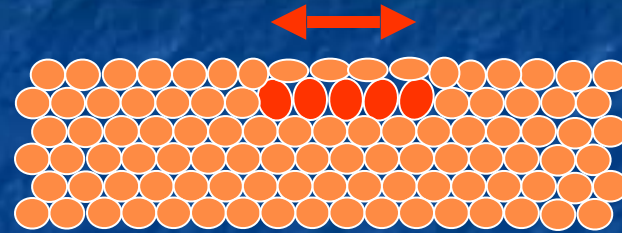
Ge islands growing atop Ge islands, growing atop Ge islands . . . WHY?

Explanation comes from variation of earlier figure:

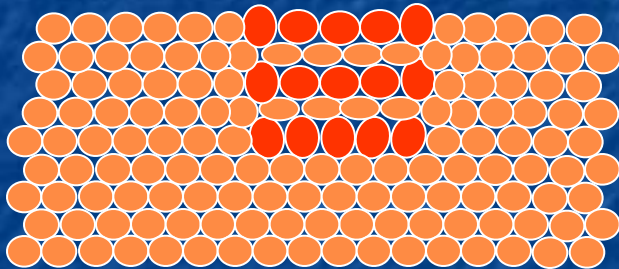
Bulging Ge island on Si:



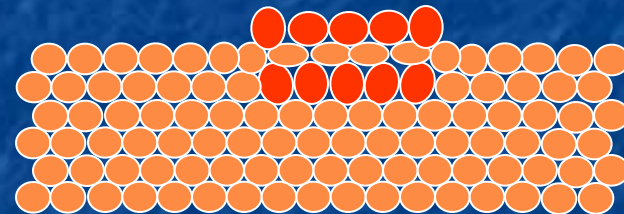
Stretches Si layer deposited above it:



And so on and so on . . .



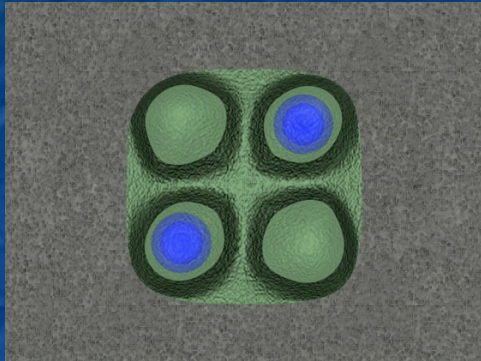
Attracting next layer of Ge atoms:



Explanation first published in: Stress-Induced Self-Organization of Nanoscale Structures in SiGe/Si Multilayer Films, C. Teichert, L.J. Peticolas, J.C. Bean, J. Tersoff and M.G. Lagally, Physical Review B 53 (24), 16334-7, 1996

Device-relevant forms of self-assembly?

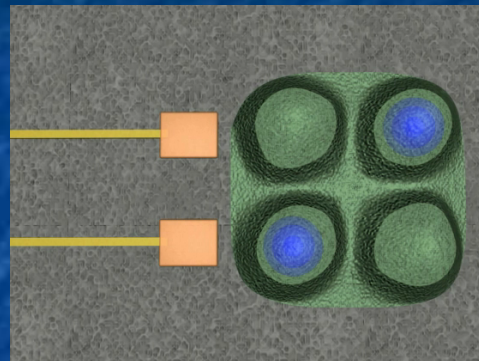
Consider proposal for nanoscale Quantum Cellular Automata:



Square array of Q-dots
with affinity for electrons

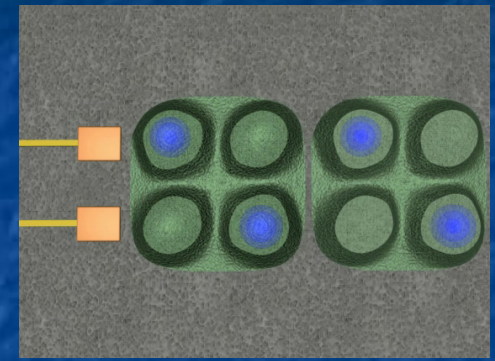
So small & close (~30 nm)
that charges repel

End up only holding two
charges



Two alternate charging
patterns => Digital 1 and 0!

Which can be manipulated
by input signal on wire.



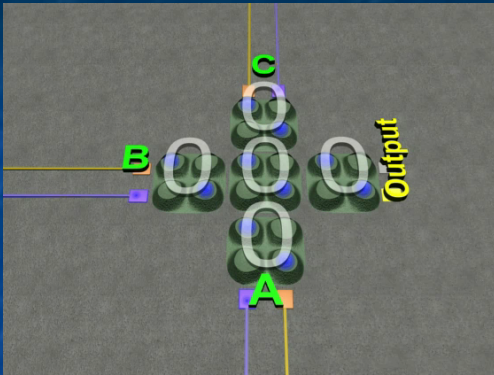
And charge configuration
will then propagate along
a "wire" of such QCA
elements!

Supporting webpage with embedded animation:

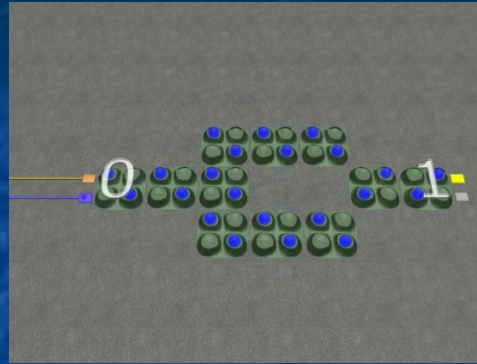
[The Need for Self-Assembly - Supporting Materials - Animations_4_6](https://wecanfigurethisout.org/VL/QCA_cells.htm)

(Source: WeCanFigureThisOut.org https://wecanfigurethisout.org/VL/QCA_cells.htm)

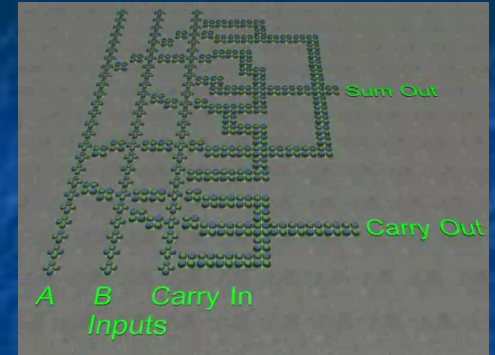
Self-assembled QCA's could be used in digital logic gates:



QCA Majority, AND, OR gate



QCA Inverter



QCA Binary Adder!

(Source: WeCanFigureThisOut.org https://wecanfigurethisout.org/VL/QCA_logic.htm)

I'll explain how these digital devices work in my Nanoelectronics lecture

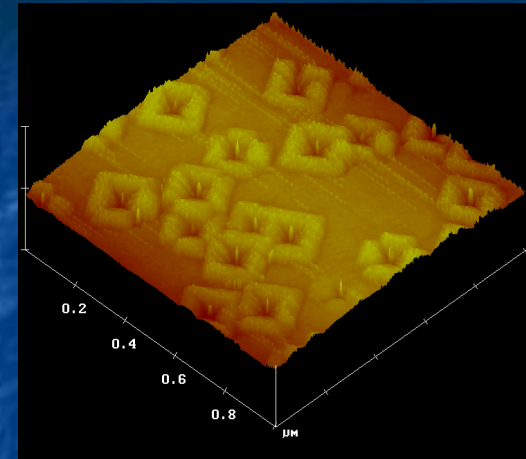
Today's question is: Can we con mother nature into self-assembling QCA's?

Well, we've made a good start:

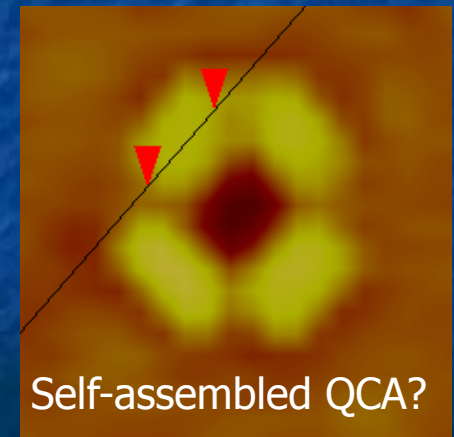
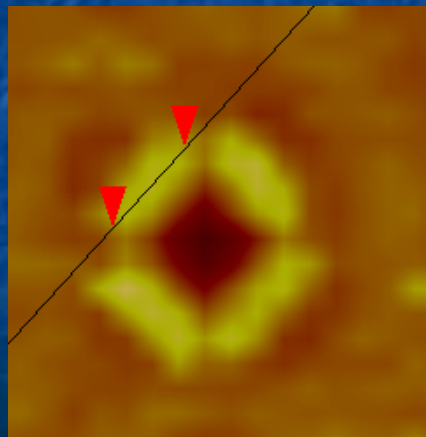
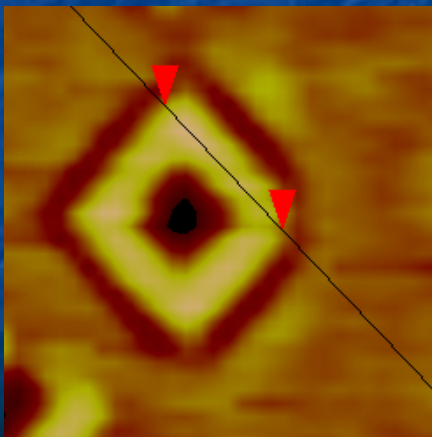
Self-assembled QCA dot like structures:

AFM image of MBE grown GeSi “quantum fortresses”

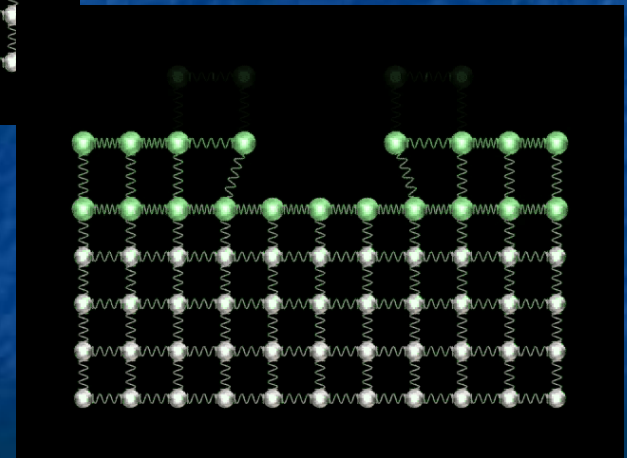
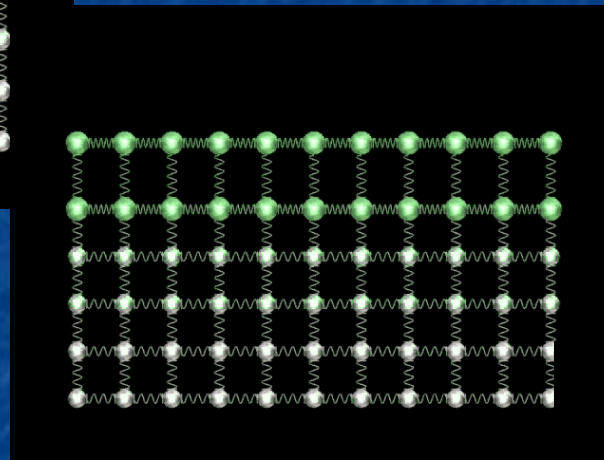
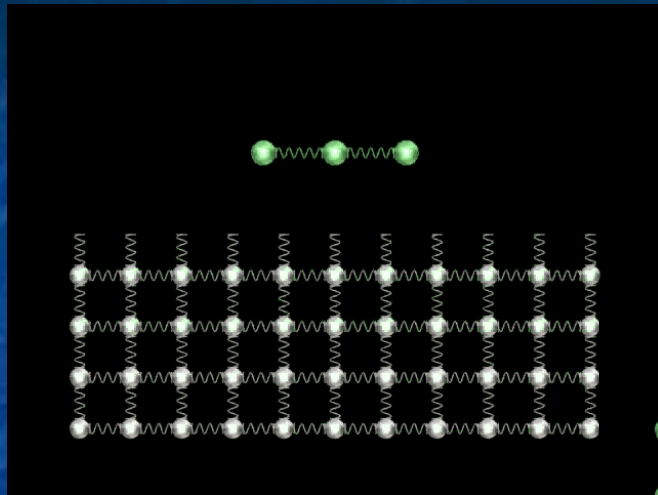
P. Kumar, T.E. Vandervelde, T. Kobayashi, J.L.Gray, T. Pernel, J. A. Floro, R. Hull, J.C. Bean, Applied Physics Letters 83, 5205-7 (2003)



Higher resolution top views of QF's grown under slightly different conditions:



How on earth did you get nature to do this?



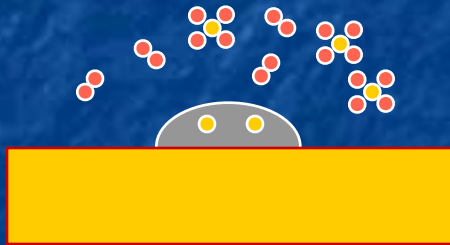
Supporting webpage with embedded animation:

[The Need for Self-Assembly - Supporting Materials - Animations_10_12](http://www.we-can-figure-this-out.org/NANO/Nano_home.htm)

Other unique forms of crystal self-assembly?

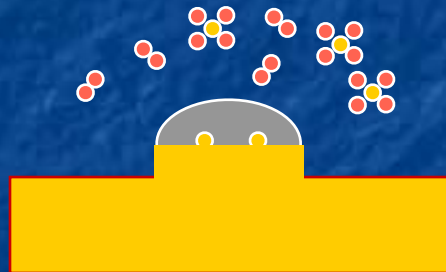


Heat metal dot on Si until melts.
Immerse in vapors of SiH₄.

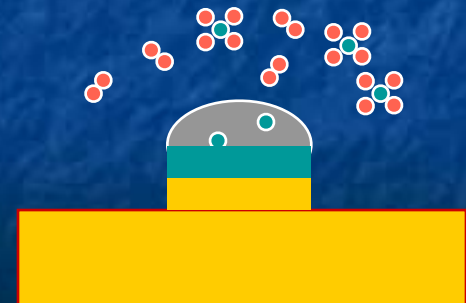


Si dissolves into molten metal
(forming eutectic)

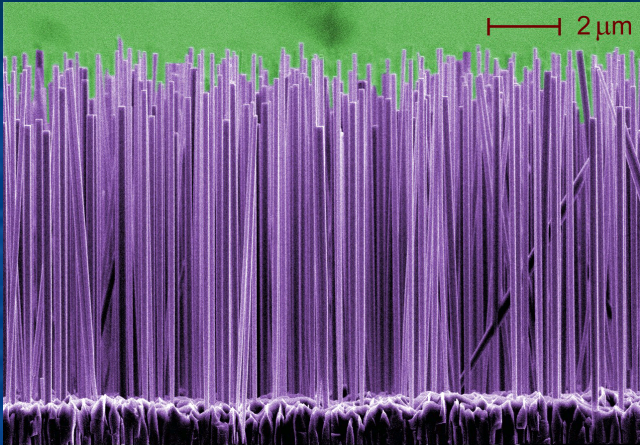
Then precipitates
onto Si surface



Now switch from SiH₄ to GeH₄ vapor:

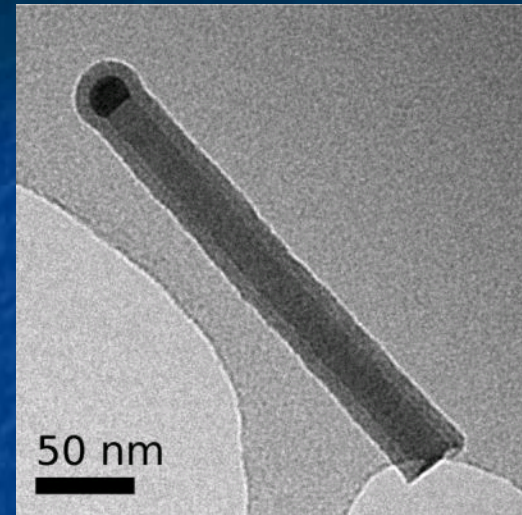


Are you pulling our leg? No:



Lorelle Mansfield -NIST:

http://www.nist.gov/public_affairs/techbeat/tb2006_0525.htm



U. Helsinki: www.micronova.fi/units/ntq/research/nanowires.php

Switch back and forth between gases:



Switch gases after metal removed:



Or do both!

Or how about self-assembly of gold nano particles:

From CytImmune Inc:



Supporting webpage with embedded animation:

[The Need for Self-Assembly - Supporting Materials - CytImmune](#)

What exactly did he do?

Basic Process:

Put gold chloride (HAuCl_4) into solution liberating Au^+ ions

Added sodium citrate "reducing agent" that de-ionizes the gold: $\text{Au}^+ \Rightarrow \text{Au}$

Some Au atoms then start to clump together into sub nanometer nuclei

Remaining Au atoms then pile on \Rightarrow almost uniform Au nanoparticles

Size = 5 to 100 nm depending on gold chloride to sodium citrate ratio

OR can controllably enlarge nanoparticles in second process:

Put above particles into fresh HAuCl_4 solution (creating new supply of Au^+ ions)

"Reduce" driving those ions to coat old nanoparticles, enlarging them

Is self-assembly ALL about crystal growth?

ABSOLUTELY NOT! In fact I am running out of crystal growth examples

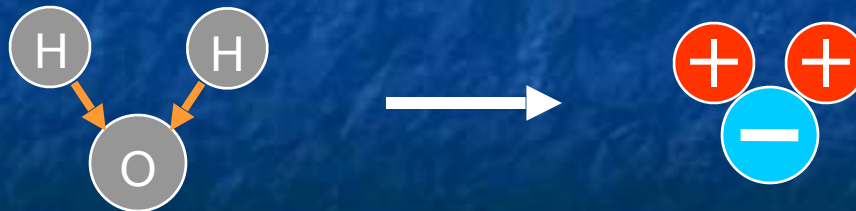
There are more numerous and more powerful examples in the wet world

A small sampler (with much more to follow in subsequent lectures):

Consider the peculiar properties of water:

Oxygen wants electrons much more than hydrogen

So charge distribution in water is not uniform - Molecule is "polarized"



Which means that water molecules like to organize (sort of):



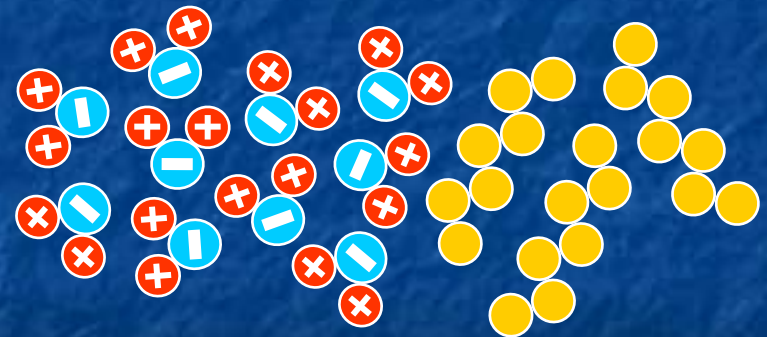
As liquid water jostles about, molecules tend to place (+) hydrogens next to (-) oxygens on neighbor

Energy reduced as opposite charges snuggle closer

“HYDROGEN BONDING”

(When solidifies, REALLY gets organized - Why it expands)

Screwed up if big non-polarized molecules (e.g. oils) inserted into mix:



Oils hold water molecules apart

So oil and water tend to segregate

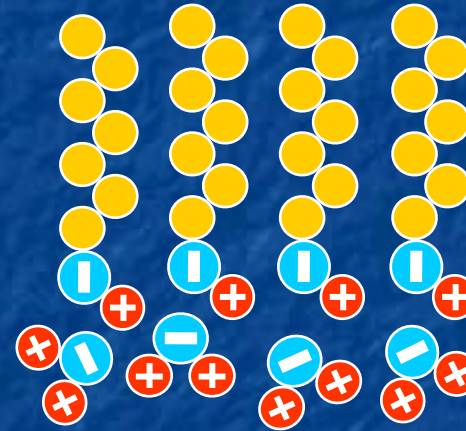
But what if add polarized end group to oil?



Then water IS attracted to ends:



Or even better:

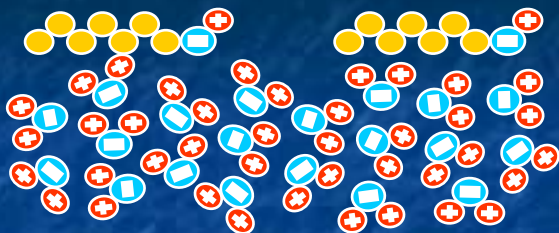


Long molecules organize:

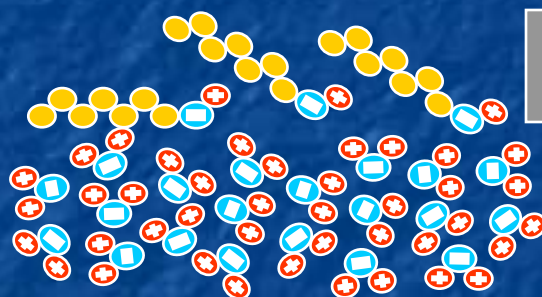
Hydrophillic (water loving) ends aligned in same direction

Becomes the low energy interface with the water

Use in complex self-assembly?

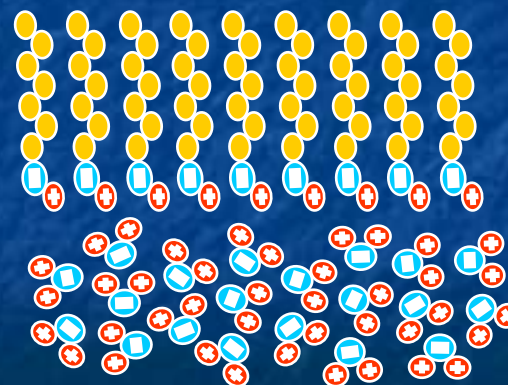


Float layer of oily molecules on top of water bath

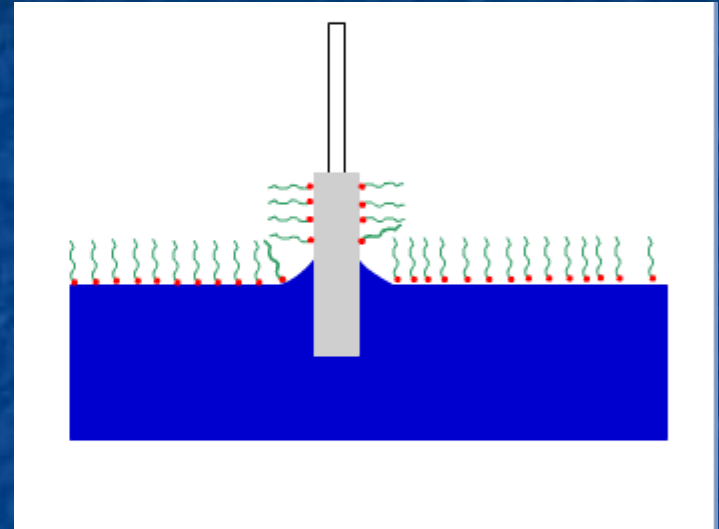
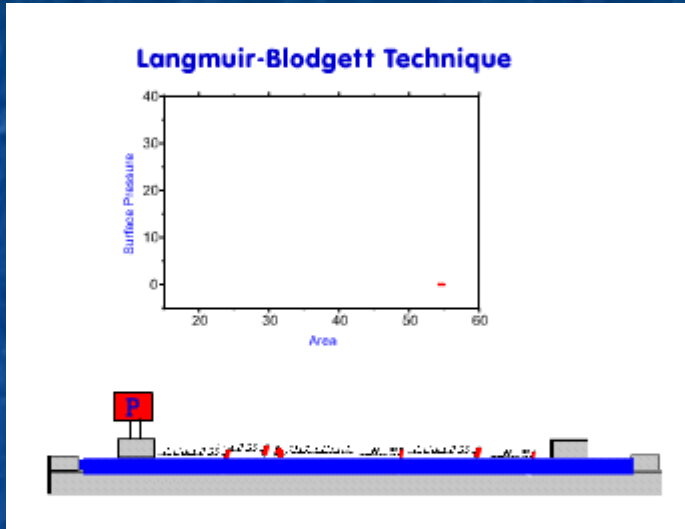


Move surface barrier inward to compress oil layer

Monitor surface tension by the pull on a sheet partially immersed in bath to sense when oils "self-assemble" side to side



Its called "Langmuir-Blodgett" film growth:

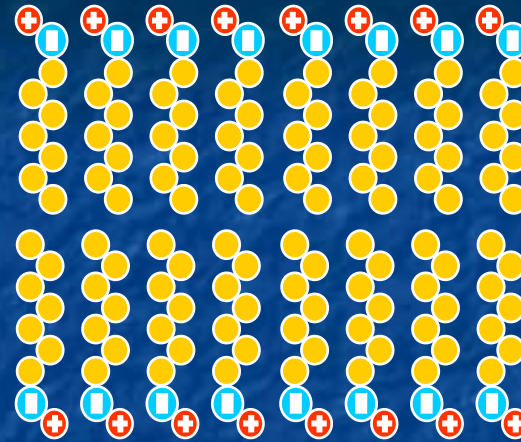


Courtesy of Professor Arend-Jan Schouten, Laboratory of Polymer Chemistry, University of Groningen, The Netherlands: <http://polchajs.fmns.rug.nl/files/jv/lb.html>

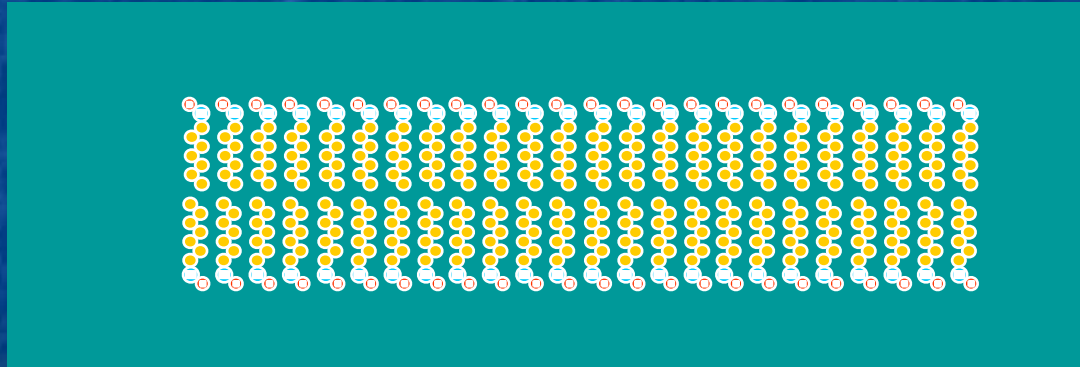
But there is an even better molecular arrangement!

Organize oils with special polarized ends so that they are tail to tail:

Called a "lipid bilayer" - Ring a bell?



Both sides of film are now "hydrophillic" so it's happy to be immersed in water:

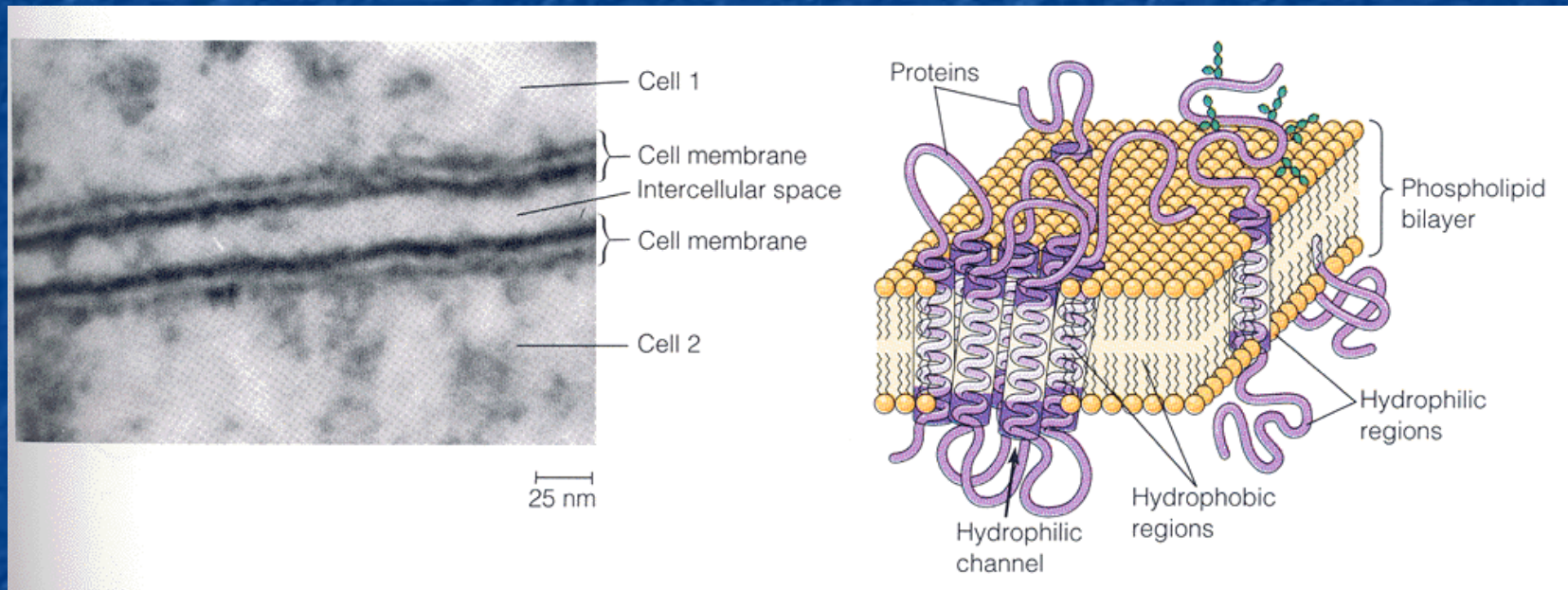


(OK, so I got tired of orienting dozens of tiny water molecules!)

Which gives . . . a cell membrane!

Which is constructed out of exactly such a “lipid bilayer” layer

And does not actually involve atomic bonding BETWEEN the lipid molecules!



Source: The World of the Cell, W.M. Becker, J.B. Reece and M.F. Poenie, Benjamin/Cummings Publishing, 3rd edition, page 27

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



Supporting webpage with embedded animation:

[The Need for Self-Assembly - Supporting Materials - Animation_15](http://mgl.scripps.edu/projects/tangible_models/movies)

From the Molecular Graphics Laboratory of Professor Arthur J. Olson of the Scripps Institute

http://mgl.scripps.edu/projects/tangible_models/movies

Or via computer animation:

From the “Auto Cell Project”

Supporting webpage with embedded animation:

[The Need for Self-Assembly - Supporting Materials - Animations_16_19](#)



Shows not only how molecular fragments might assemble, but how their assembled structure would then produce more of the ingredient fragments!

But there is much more than mere atomic/molecular self-assembly!

To really get into **PROGRAMMED** self-assembly we need to learn about:

Organic chemistry → DNA Replication → Et Cetera

Topics of lectures to follow!!

Credits / Acknowledgements

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This set of notes was authored by John C. Bean who also created all figures not explicitly credited above.

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