The Bleeding Edge – Part I:

Emerging Applications of Nano<u>mechanics</u>

It's called bleeding edge because it's science trying to make the leap into technology

And those of us working in such fields often feel bloodied in such attempts!

We can't possibly cover the whole "bleeding edge" in one day

Today I'll highlight just 3 areas where nanomechanics might bring radical change:

1) **Walking on the walls:** Exploiting nano surface effects

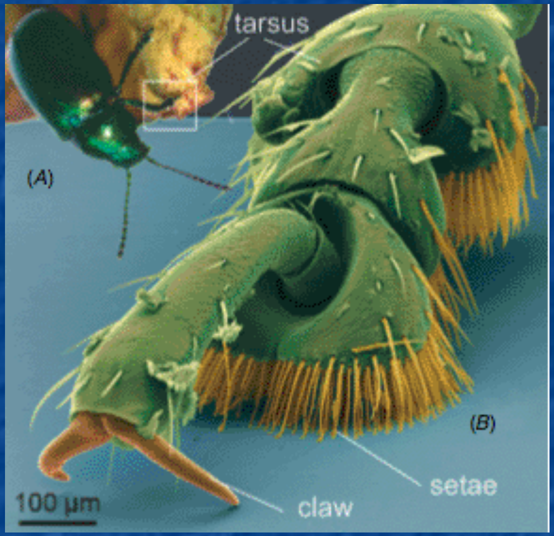
2) **DNA Erector Sets:** The key to non-biological self-assembly?

3) **The Beanstalk:** A real stairway to the heavens?

1) ***Walking on the walls:*** *Exploiting nano surface effects*

Looking for ideas we can hijack from nanoscale mother nature

This looks like it has got possibilities:

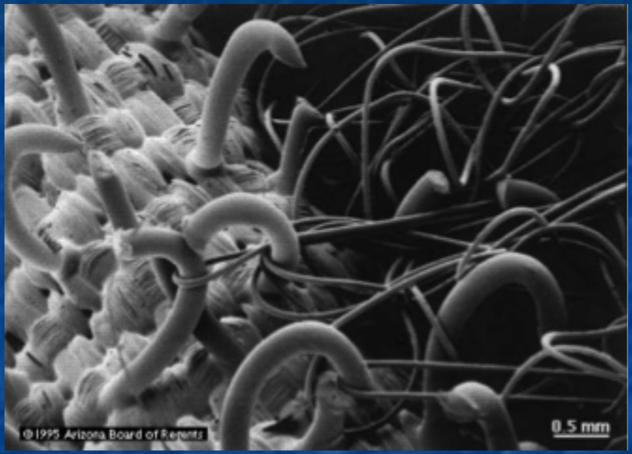


(from "Insects did it first: a micropatterned adhesive tape for robotic applications"
Gorb et al., Bioinpiration & Biometrics 2 (2007))

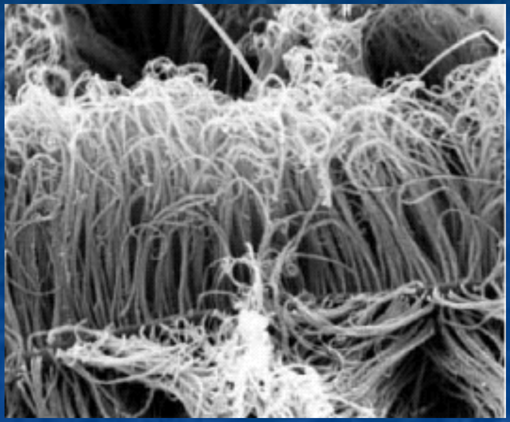
Can we emulate insect wall walking (or at least exploit their tricks?)

How MIGHT insects be walking on walls?

Velcro?



Nano-Velcro:



(from Hope Chik's presentation on the "INEM Nano Attach Project")

No, can't be what insects use because it IS attachment via hook AND loop

Insects could grow hooks (or loops) on their feet

But could then only climb surfaces with loops (or hooks) . . . very limiting

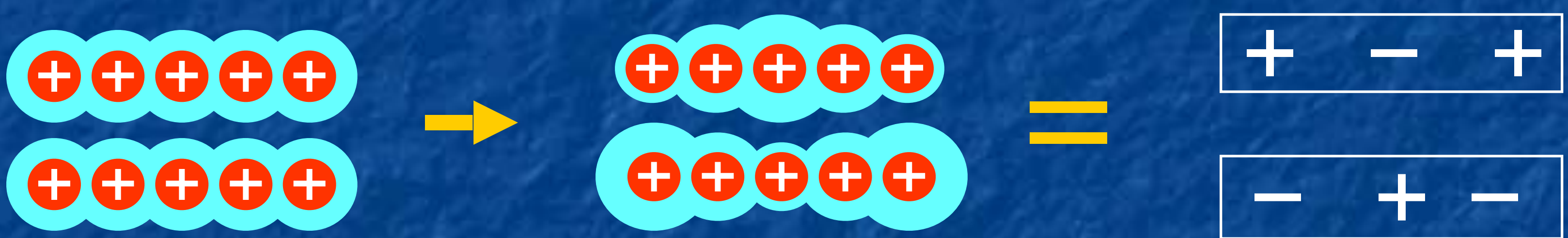
Better possibility might be a nanoscale surface effect

Effect #1: Van der Waals bonding (a.k.a. “induced dipole bonding”)

Electrons on molecules (especially longer ones) can slosh back and forth

This disrupts local charge balance setting up regions of + or -

Counter-charged nearby molecule is then attracted:



(see also my note set on Molecular Self-Assembly

But VDW attraction occurs only over VERY short distances

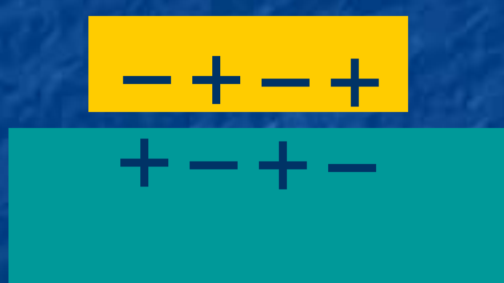
Because, despite charge sloshing, molecules are still net electrically neutral

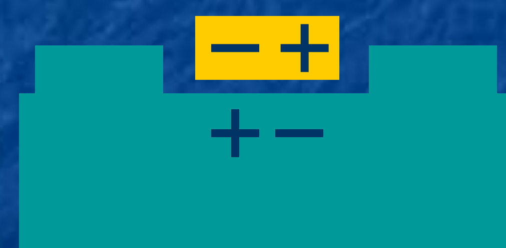
So moving away from local + / - charge imbalance, forces begin to cancel

Result: For strong VDW forces, molecules must be within ~ one nanometer

But how do solid or semi-solid surfaces fit that closely together? They must be:

a) Smooth on nanoscale OR b) One piece must be ~ nanoscale





Suggesting that insects might need VERY TINY feet!

And/Or insects might exploit “surface tension”

Surface tension is also based on attraction between charge dipoles

But water's molecular dipole is permanent (unlike transient VDW charge waves)

Water molecules move/rotate to bring negative oxygen's near positive hydrogen's

Interior water molecules are happy

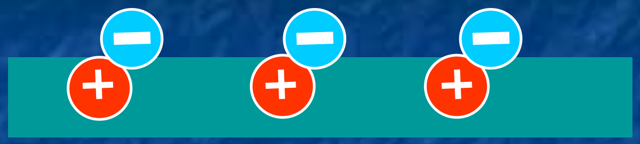
Many molecules at edge of droplet are not!

(e.g., prevalence of + charge on surface)

To minimize unhappy surface molecules, minimize surface area => “surface tension”

To attract such water droplets to surfaces, we'll need:

Surfaces that also have polarized charge (a.k.a. “hydrophillic” surfaces)



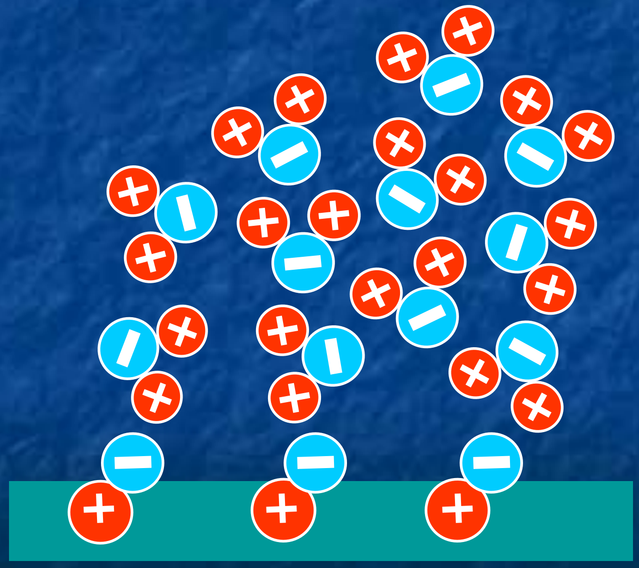
Oxidized surfaces naturally have such polarized oxygen-to-other bonds

And they're VERY common in oxidizing atmosphere: glass, metal surfaces . . .

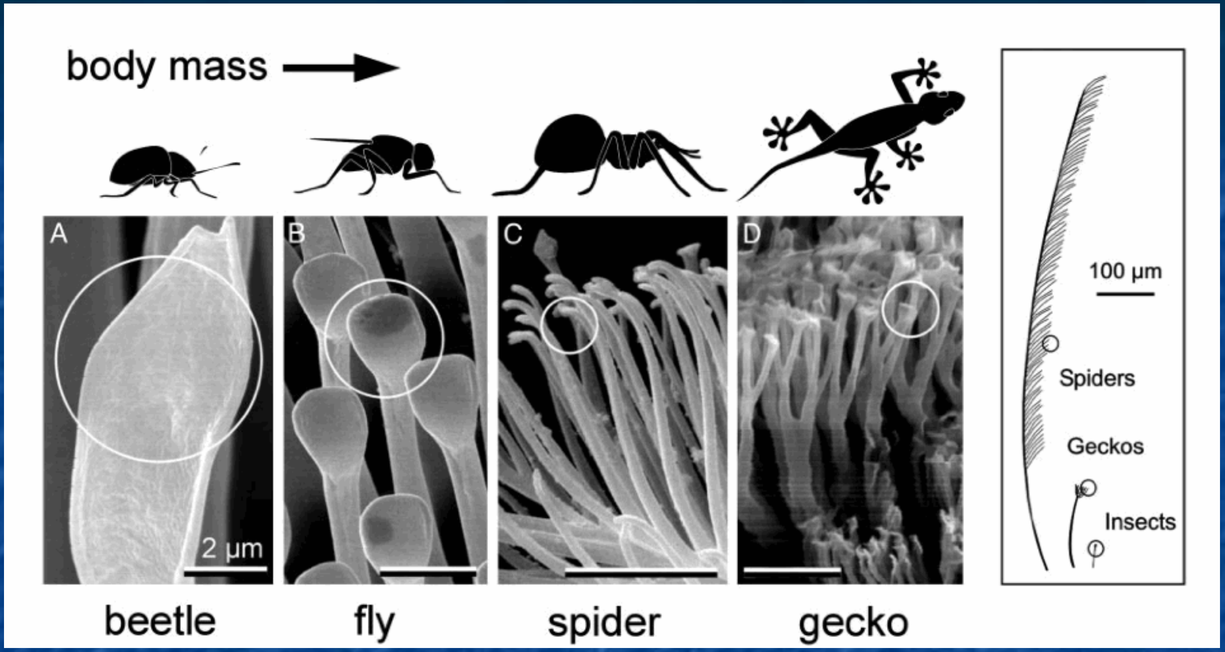
With only a few rotations, water molecules

on bottom of earlier water droplet are

now QUITE happy near oxide surface:



So we'd guess that insects must have sweaty little polarized feet



("From micro to nano contacts in biological attachment devices," Arzt et al., PNAS 100(19) 2003))

And this turns out to be correct:

Small insects: Compliant pads (to shape themselves to rough surfaces) + sweat

Medium insects: Multiple pads per leg + sweat

Spiders and lizards: Lots of pads (hair) per foot - but dry / no secretions

And applying this new found knowledge:

We get wall climbing robots:

Supporting webpage with full Stickybot movie:
Bleeding Edge Nanomechanics - Supporting Materials - Stickybot

NASA's planned use for Son of Stickybot:

The International space station gets hit by ~3000 micrometeorites per year!

Astronaut EVA’s to inspect after each of these would be costly and dangerous

Today’s fix: Proliferation of steerable cameras mounted on ISS surface

And they are working on a rocket-powered flying inspection robot

Modeled on the Star War’s light saber-training bot - "MIT SPHERES:"

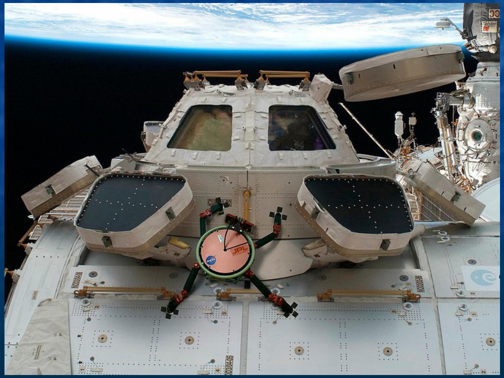
But NASA believes long-term solution could be bots **crawling** over surface

Clinging by means of Stickybot’s Van der Waals attracted mini-haired feet:

So they hired one of the Stanford Stickybot

graduate students to develop "LEMUR"

(here represented only via computer graphics):



Source: http://www.airspacemag.com/space/orbital-inspectors-180953376/?page=1&no-ist

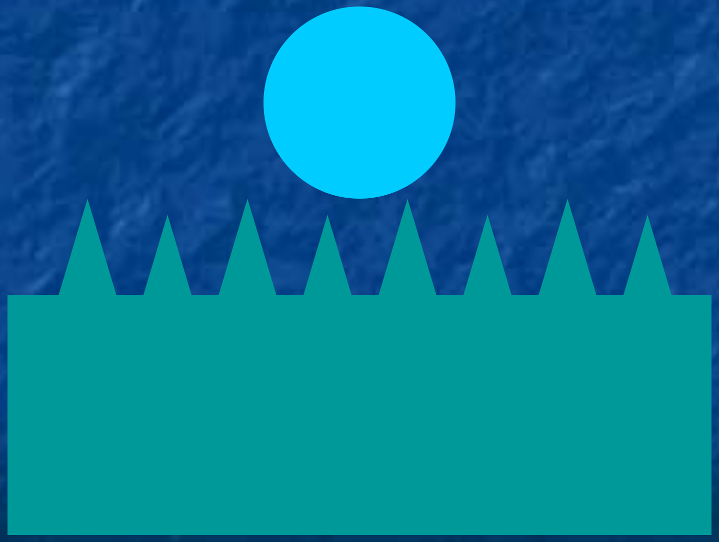
We can also turn our knowledge around to get

SUPER HYDROPHOBIC SURFACES

What would be required to make surfaces **unattractive** to water?

1) Materials w/ NON-polarized surfaces

2) Rough surfaces minimizing close contact required for Van der Waals bonding



Or as shown in this computer animation of "The Lotus Effect"

Supporting webpage with full Lotus Effect movie:
Bleeding Edge Nanomechanics - Supporting Materials - LotusEffect

(Source: William Thielcke, Hamburg Germany)

But does reality work as well?

Yes. And you'll get to try this out for yourself in the lab!

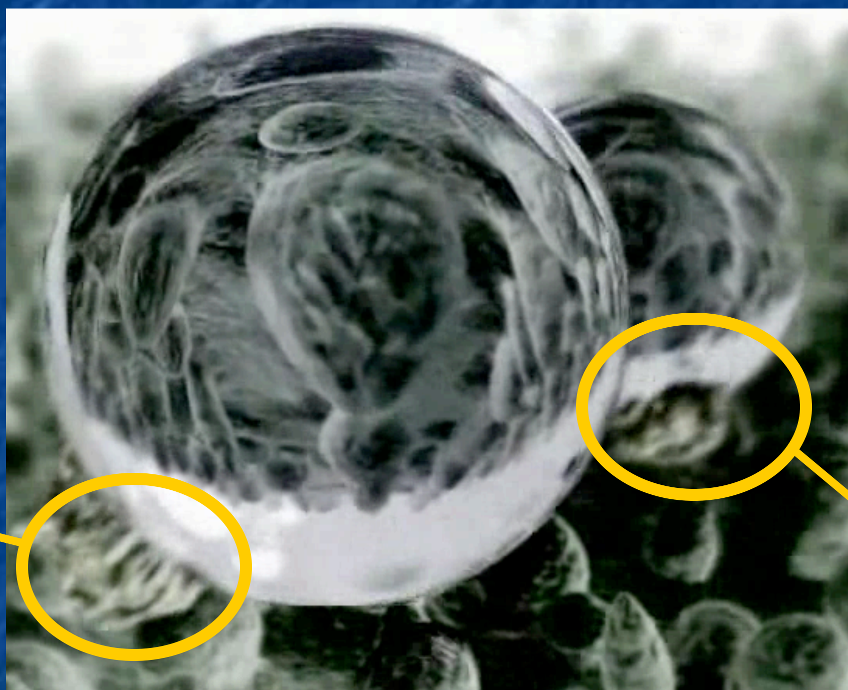
Supporting webpage with full YouTube video:
[Bleeding Edge Nanomechanics - Supporting Materials - Hydrophobicity]

(Source: Neil Shirtcliffe, Nottingham Trent University / YouTube)

OK it's fun to watch, but is it useful?

If dirty water flows quickly off surfaces, it will not dry there (leaving dirt behind)

Further, as shown in animation, droplets can pick up and carry away earlier dirt:



That’s why it is called

“The Lotus Effect”

It’s a way plants keep

leaf surfaces clean!

APPLICATIONS: Self-cleaning windows, paints, photovoltaic solar energy panels . . .

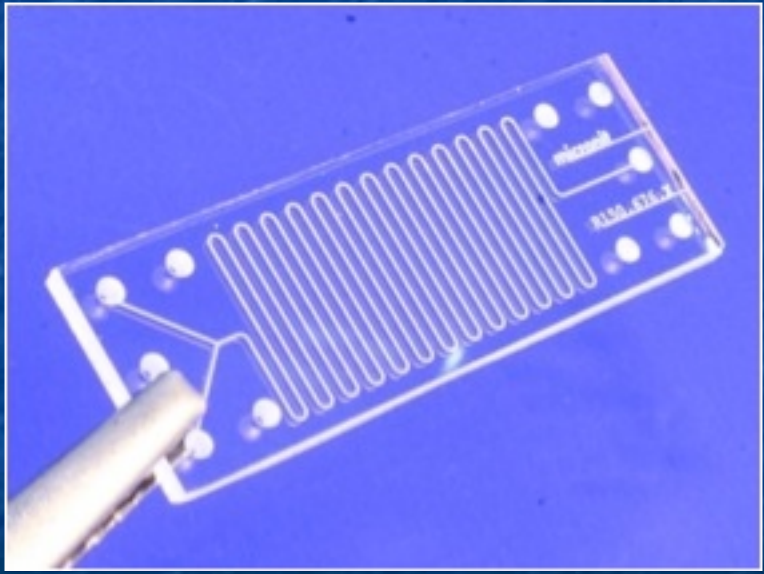
Also, why then bother with plumbing?

There are many times when we'd like a whole analytical chemistry "lab on a chip"

This might now be possible without building mini test tubes and beakers!

We could instead could just PRINT patterns using super hydrophobic inks

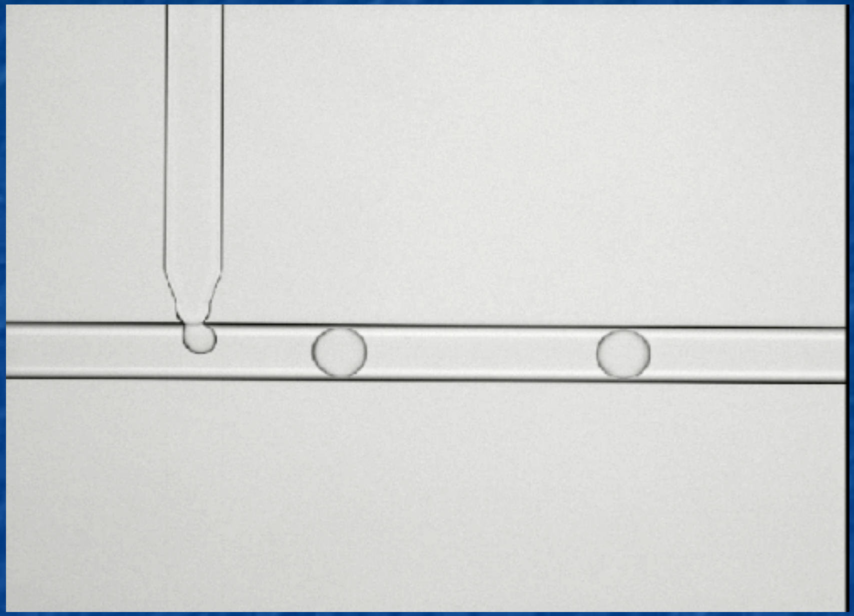
Forcing water to then flow ONLY where there was no ink

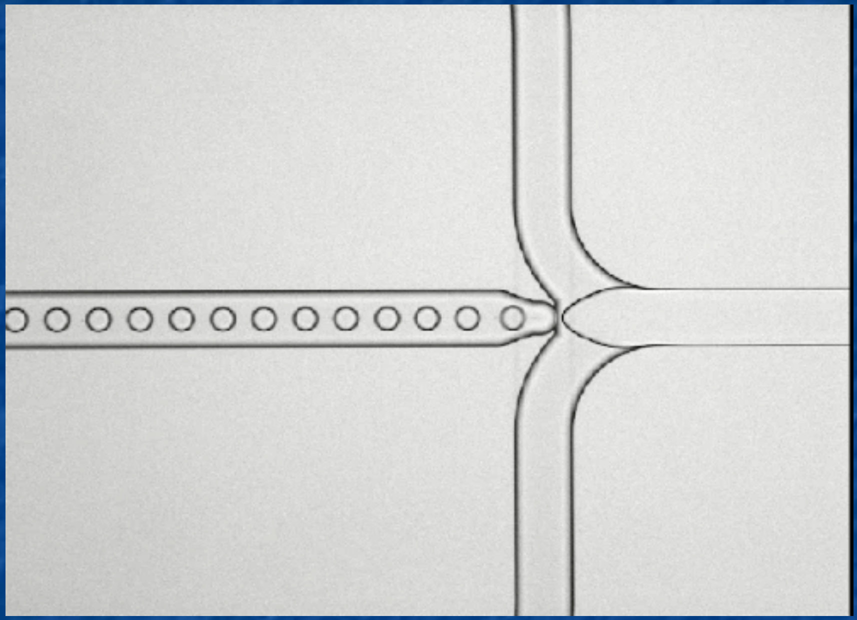


(Source: Wikipedia Commons - Micronit Microfluidics Inc.)

Actual operation of micro "lab on a chip" components

Via combination of micro-machined channels and hydrophobic surface treatments:





Supporting webpage with lab on a chip videos:
[Bleeding Edge Nanomechanics - Supporting Materials - Lab on a chip]

(Source: Micronit Microfluidics Inc.)

Or, how about a deterrent to "guys behaving badly" (in Hamburg Germany):

Walls in the red light district are being painted with hydrophobic coatings:

(before) (after)

Link to video: http://www.slate.com/articles/video/video/2015/03/hydrophobic_paint_public_urinators_germany_rigged_walls_video.html

2) DNA Erector Sets: *The key to non-biological self-assembly?*

Recurring obstacle to conversion of nanoscience into complex nanotechnology

is our inability to make more then a few expensive prototypes

We **hope** to find a solution in SELF-ASSEMBLY, but we are not sure how

One particularly exciting possibility is use of DNA outside of living organisms

Key observations:

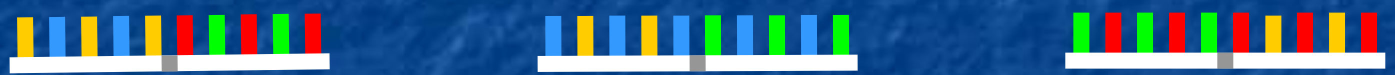
Off-the-shelf equipment can now create programmed DNA strands

Complementary DNA segments separate (“denature”) w/ mild heat (~90 ˚C)

Then naturally recombine upon cooling

What if one strand is coded to complement parts of two others?

Create the following three synthetic DNA single strands:



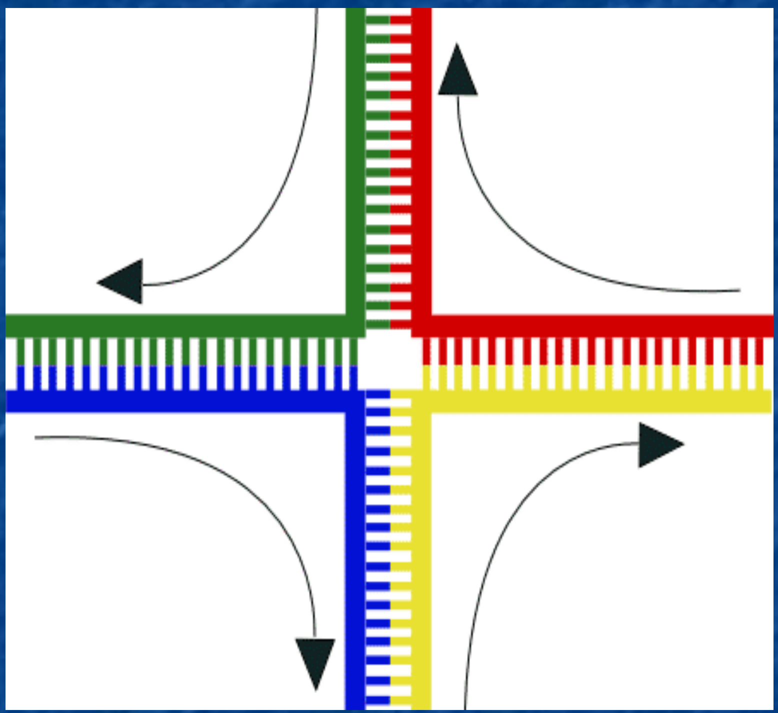
What is going to happen if they are mixed together then cooled?

~ 90 ˚C

< 80 ˚C

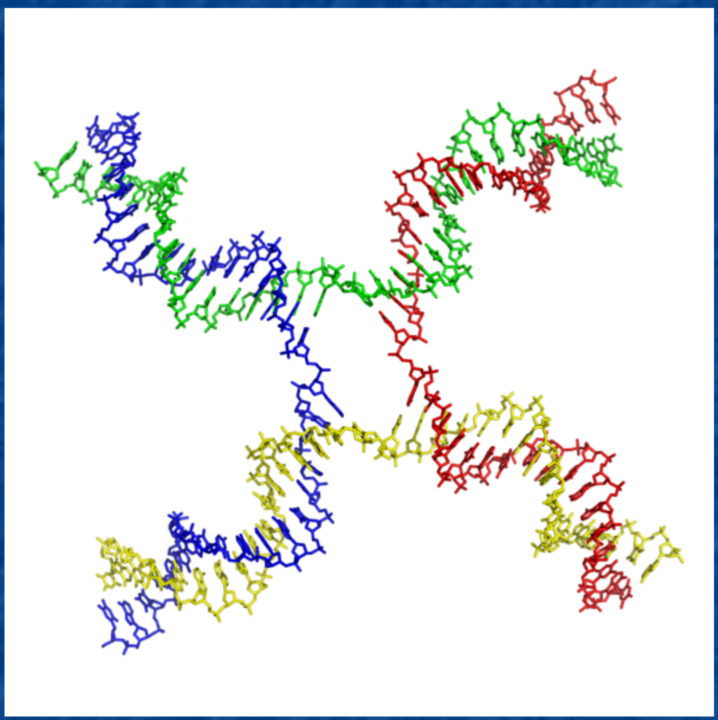
And it is just about that simple:

Start with four encoded strands, cool in solution to assemble together:



Four single strands of DNA combine to form "Holliday" X junctions (Wikipedia Commons)

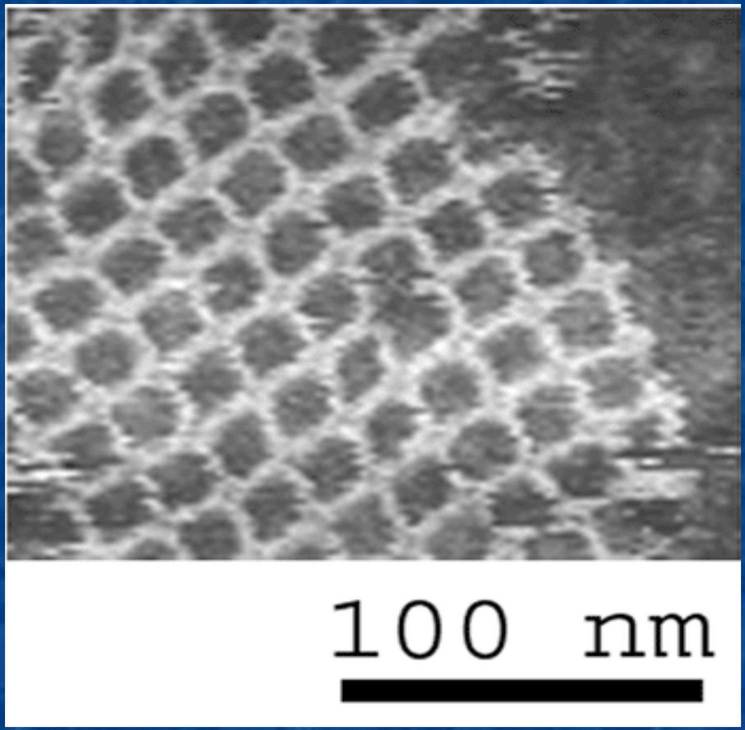
Although the atomistic reality is a bit more twisted:



Resulting 3D DNA structure (Richard Wheeler - Wikipedia Commons)

As confirmed by high resolution electron microscopy:

Each node of this nanoscale mesh was fabricated as shown on preceding slide:



The pioneer of this field,

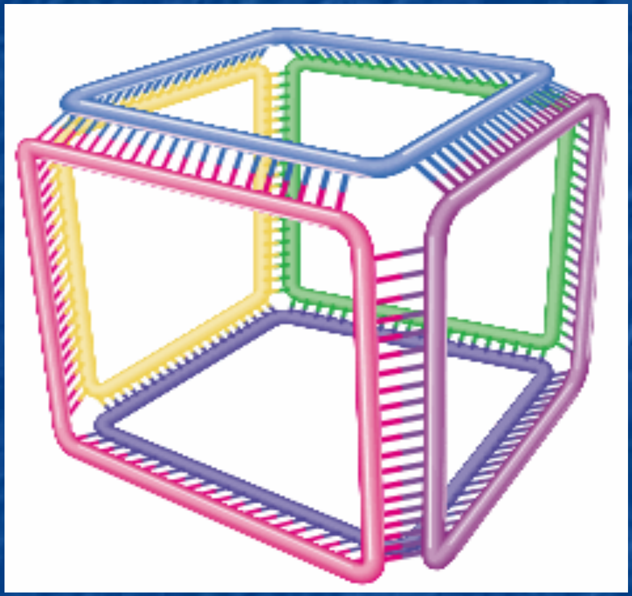
Ned Seeman of New York Univ.

assured me it is really ~ that easy!

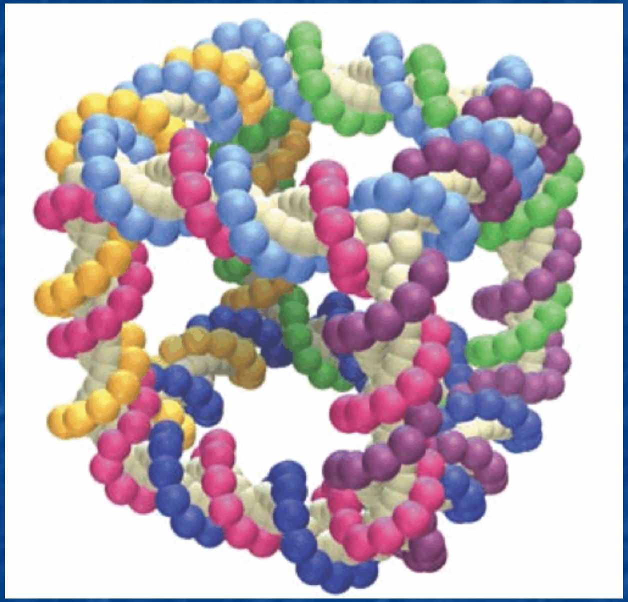
(Thomas H. LaBean & Hao Yan - Wikipedia Commons)

Ned Seeman has taken it into 3D:

Schematic of 3D box:



Complete DNA structure:



Based on the work of Ned Seeman, New York University

(See Ned Seeman papers at Bleeding Edge Nanomechanics – Supporting Materials - DNA Scaffolding)

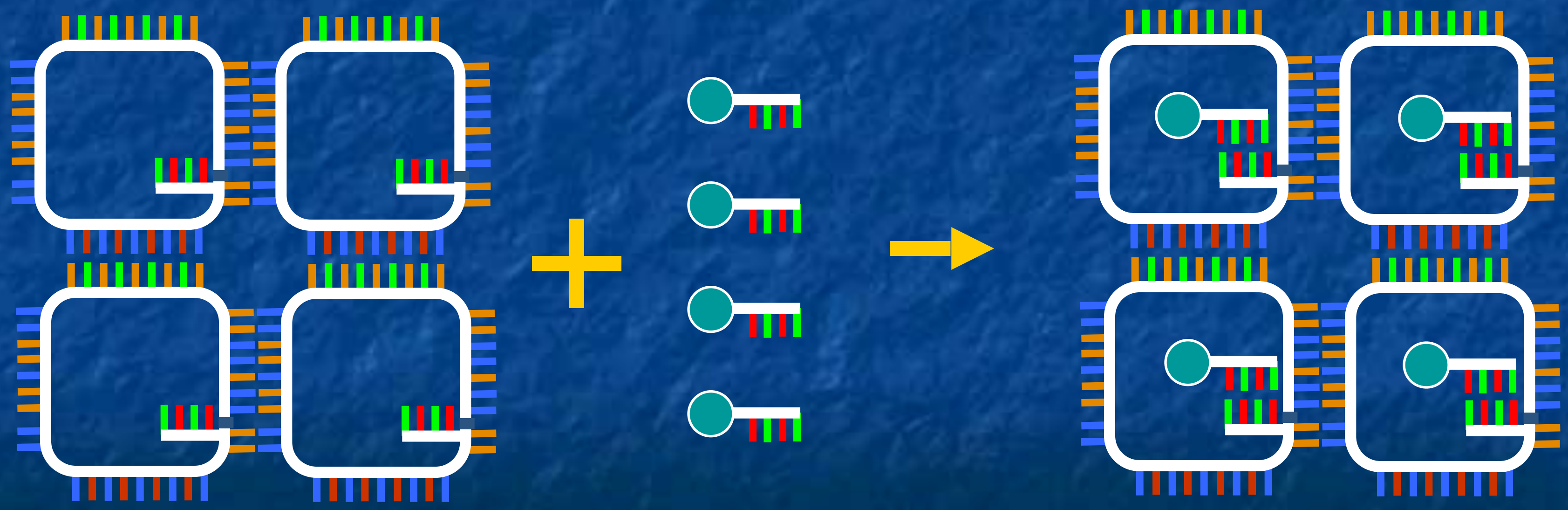
Why as an electrical engineer does this excite me?

Possibility of Using DNA self-assembly to:

1) Arrange DNA boxes into scaffolds

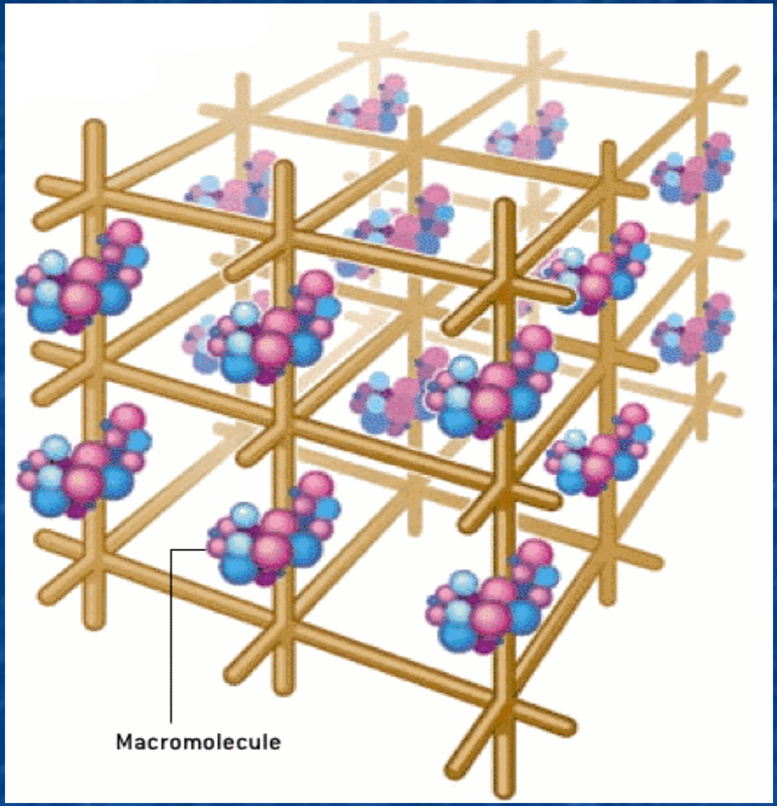
2) But with extra **single strand** DNA "address label" ends in each box

3) Then add quantum dots with complementary single strands => **Q-Dot arrays!**



Or in 3D:

Based on DNA scaffold, Q-dots self-assemble into programmable 3D arrangement:



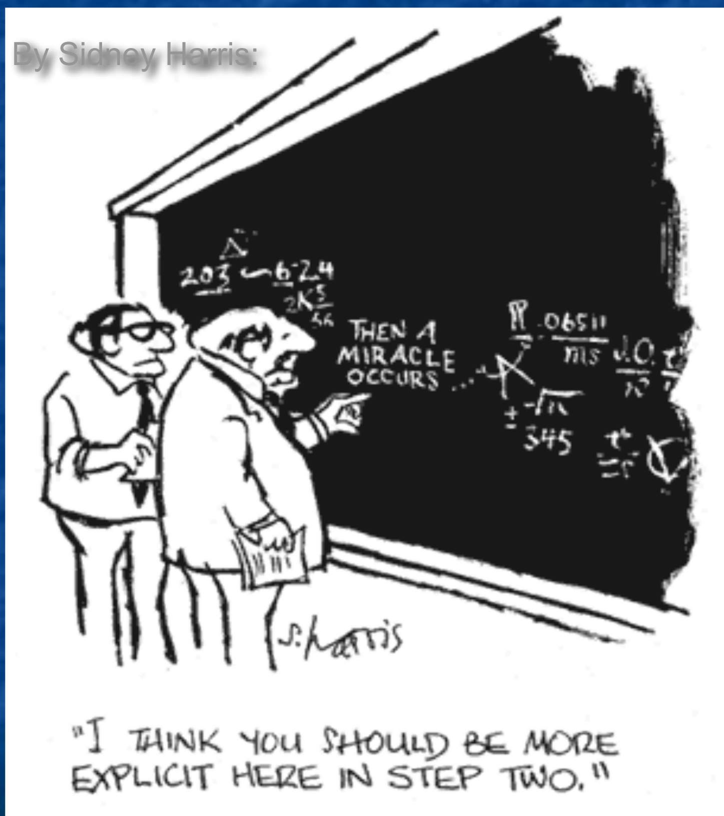
("Nanotechnology and the Double Helix" Scientific American 2007)

Different DNA scaffolds => Different 3D Q-dot structures!

But is this just another artwork fantasy?

Along the lines of this classic cartoon

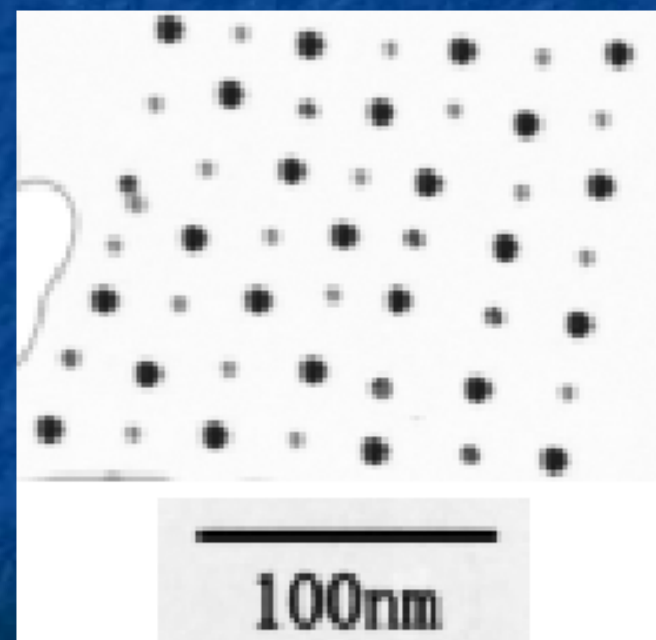
lampooning scientists' wishful thinking?



No!

Here's an electron micrograph Ned Seeman

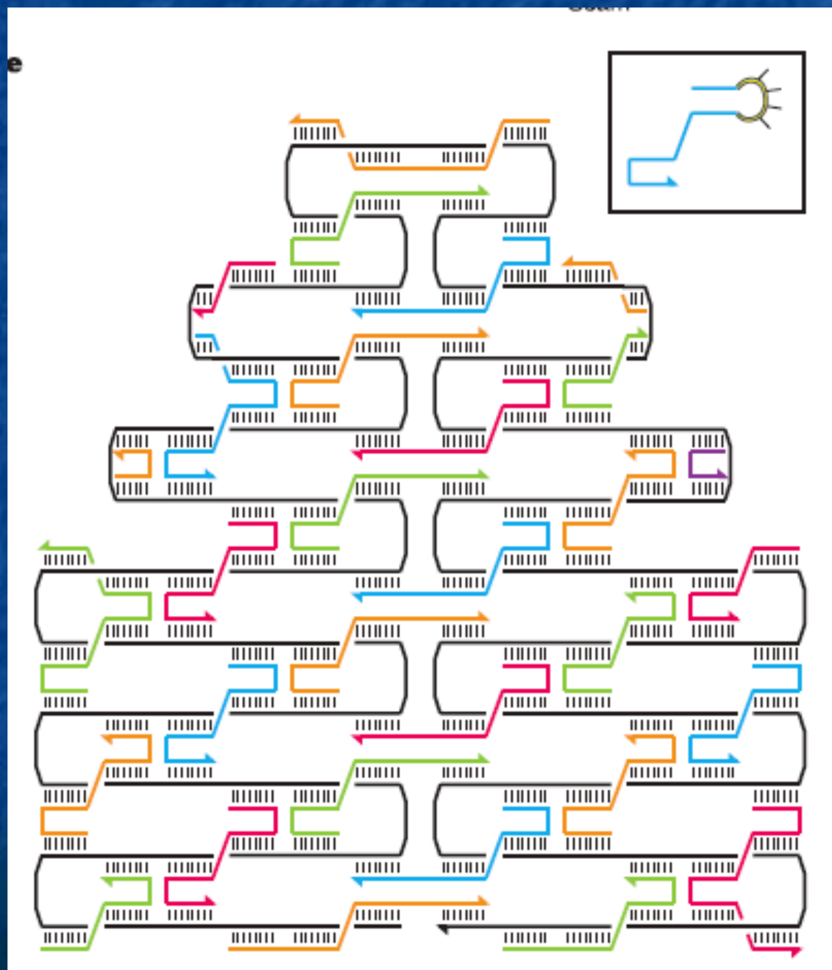
sent me of such DNA organized Q-dot array:



An alternate approach based on DNA rafts:

Lay out long, standard, well-known strand of bacterial DNA in desired shape (black line)

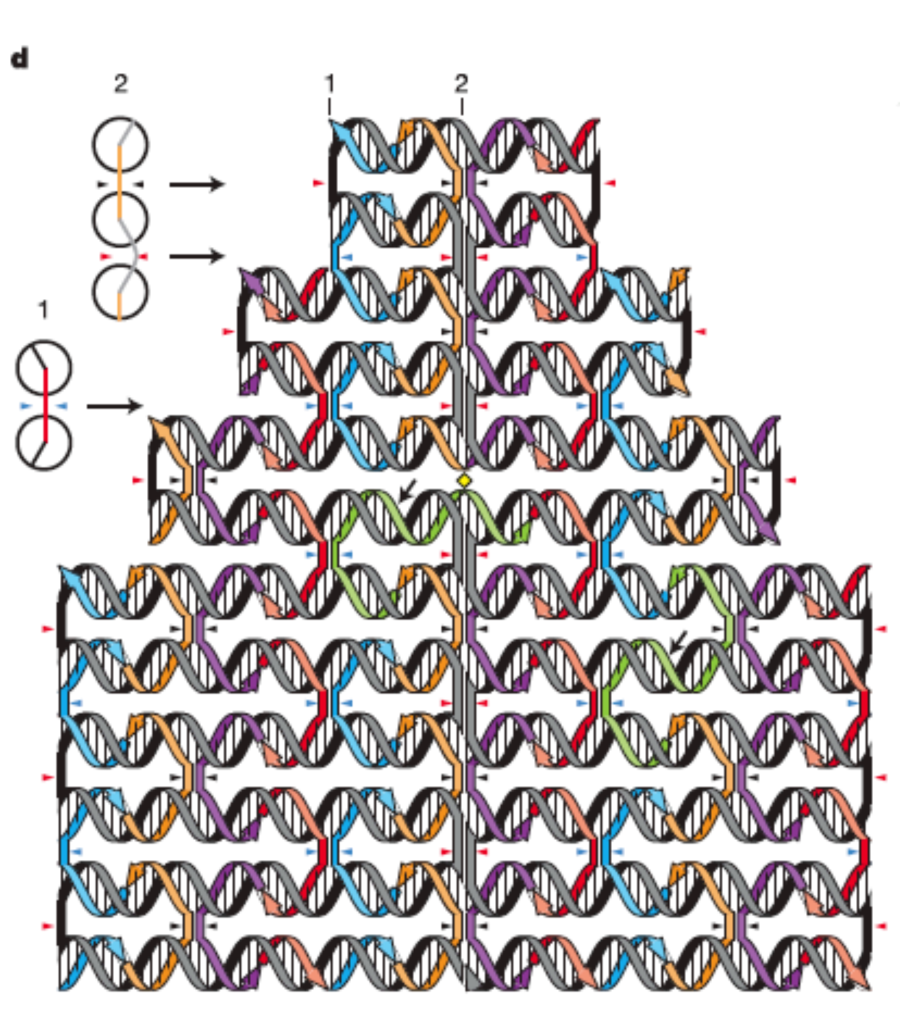
Link its turns together with short engineered complementary strands



"DNA Origami"

(See Paul Rothemund paper at [Bleeding Edge Nanomechanics – Supporting Materials - DNA Origami])

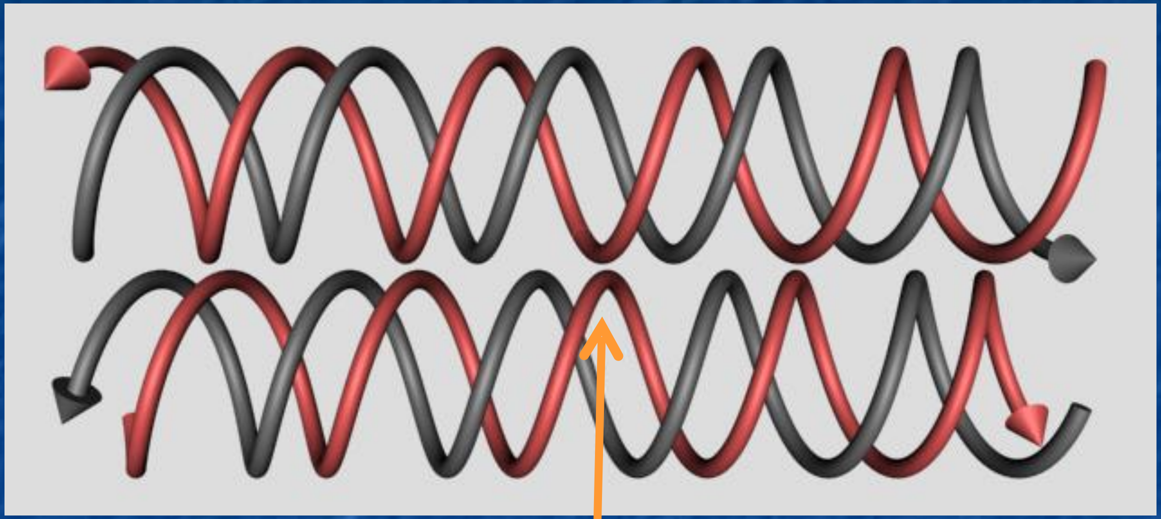
Or in 3D, taking DNA spiral into account:



Sounds easy? Think again!

The dirty little details

Step 1 (in design process) – DNA double strand folded back on itself:

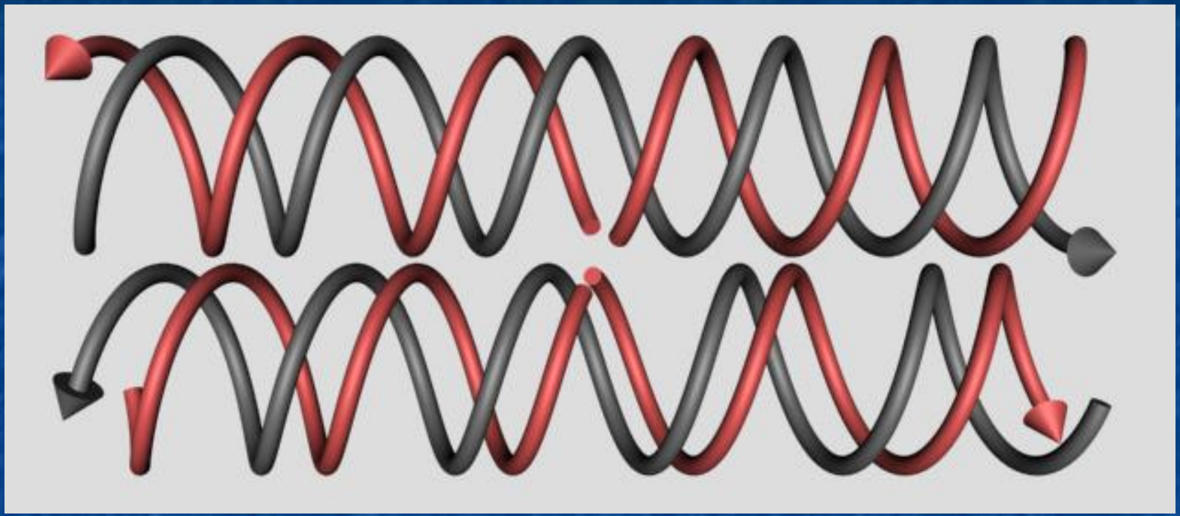


Natural point to make a new link

Place where red (secondary / non-master) strand comes into close alignment

The dirty little details (cont'd)

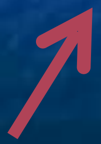
Step 2 – Cut secondary strand at this point:



But how should severed strands now be cross-connected?

New connections MUST take into account direction (5' => 3') of DNA backbone

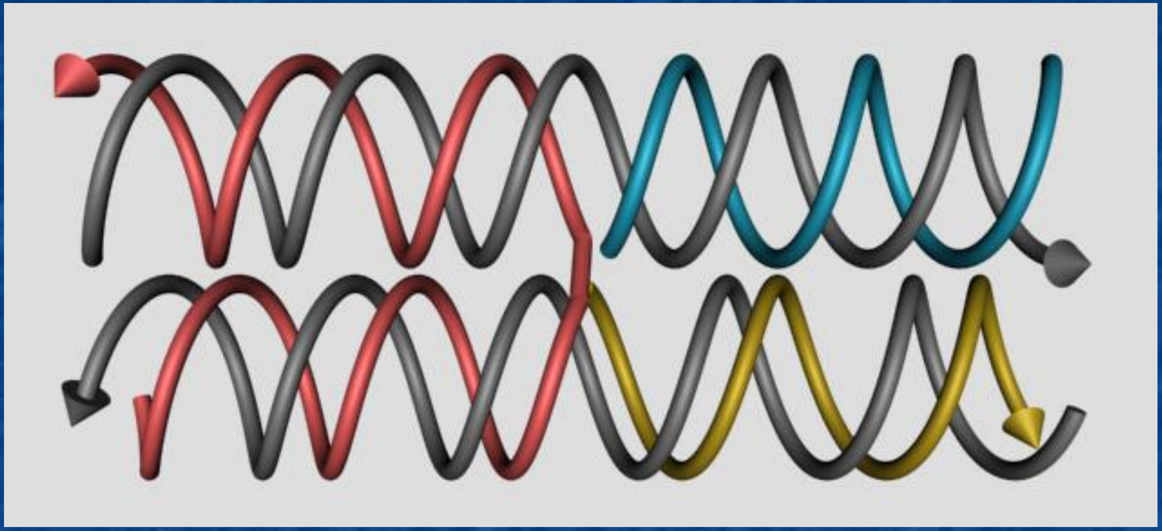
Making sure that connection maintains this progression (see arrows)

NO! 

YES! 

The dirty little details (cont'd)

Step 3 – Connect up what becomes a "staple" cross-connection segment:

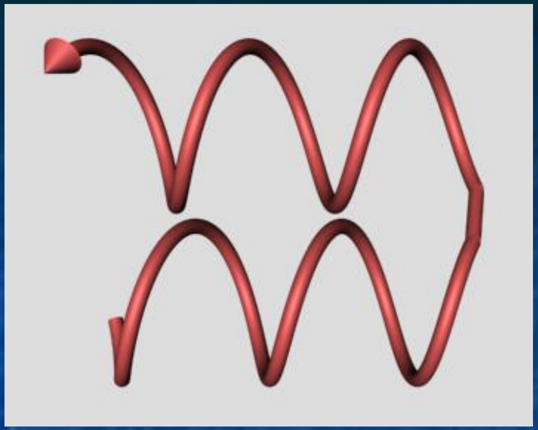


New red = Staple segment

Blue & Yellow = non-staple segments

OR if merge blue/yellow at appropriate point, they could become second staple

Oh, but I forgot something major:



We can't just arbitrarily link strands!

Backbone units of (phosphate + ribose) must repeat every 1/10 turn

Position of cuts and reconnections MUST maintain this repetition

So can one indeed add short (single phosphate-ribose) link as I show above?

THAT ribose would have to do without an attached base

It that feasible? Or must link be deleted, pulling DNA strands very tightly together?

This problem must be solved, one way or another, to get to final step:

Step 4 – Choose BASES on colored segments to complement
opposing BASES on black bacterial master strand

Sounds like design might require one heck of a computer program

Which might explain why its inventor, Paul Rothemund in NOT a biologist

Nor is he a nanoscientist (at least, not a conventional one)

Rothemund IS in fact a Computer Science professor

But then does he only **plan** (a.k.a. "model") such things?

And should we really trust that those plans are viable?

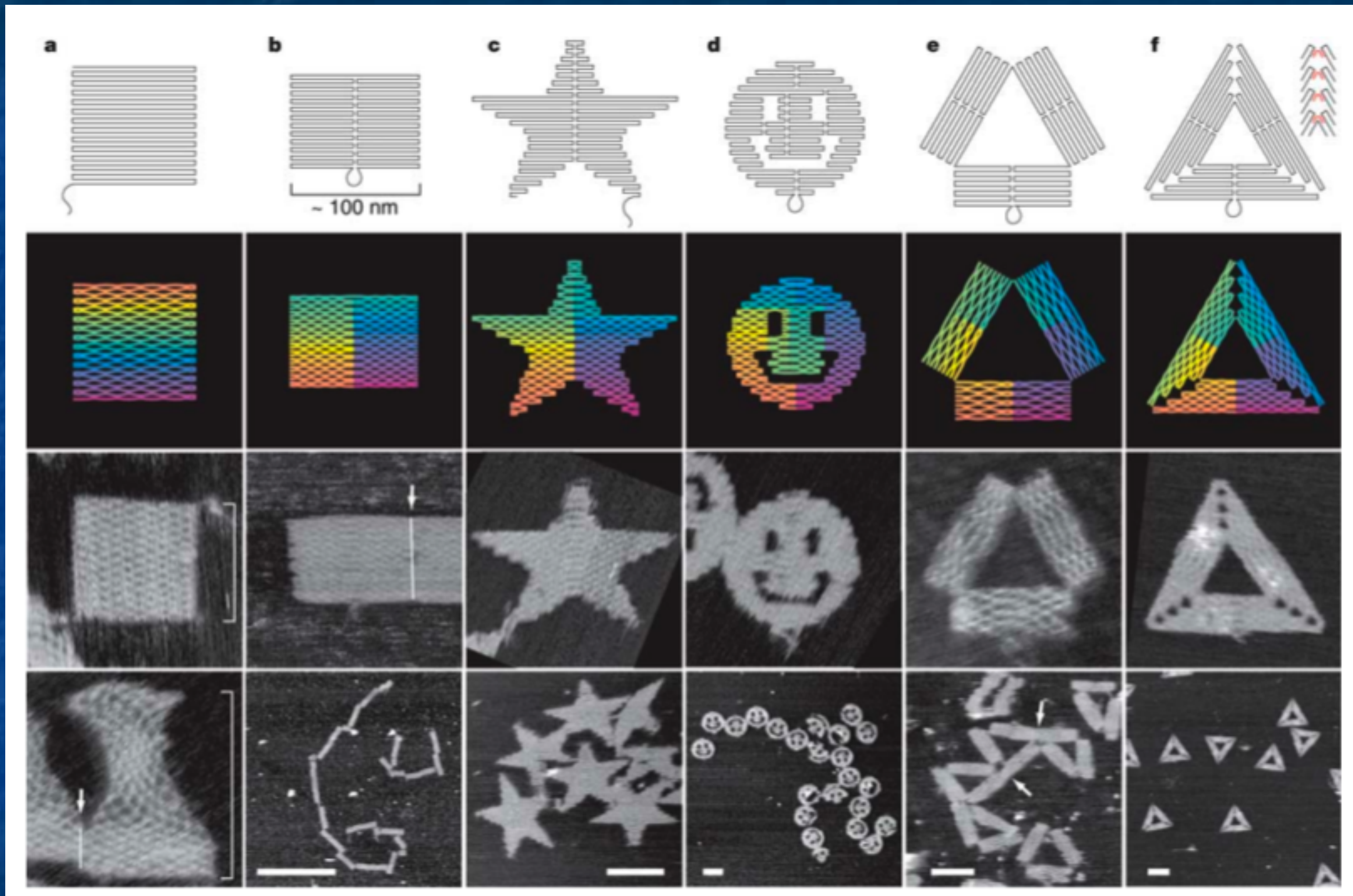
That his programs get all of the above details right?

And that proposed bending of DNA is actually feasible?

Here's the proof: He also **makes** these things:

Figures

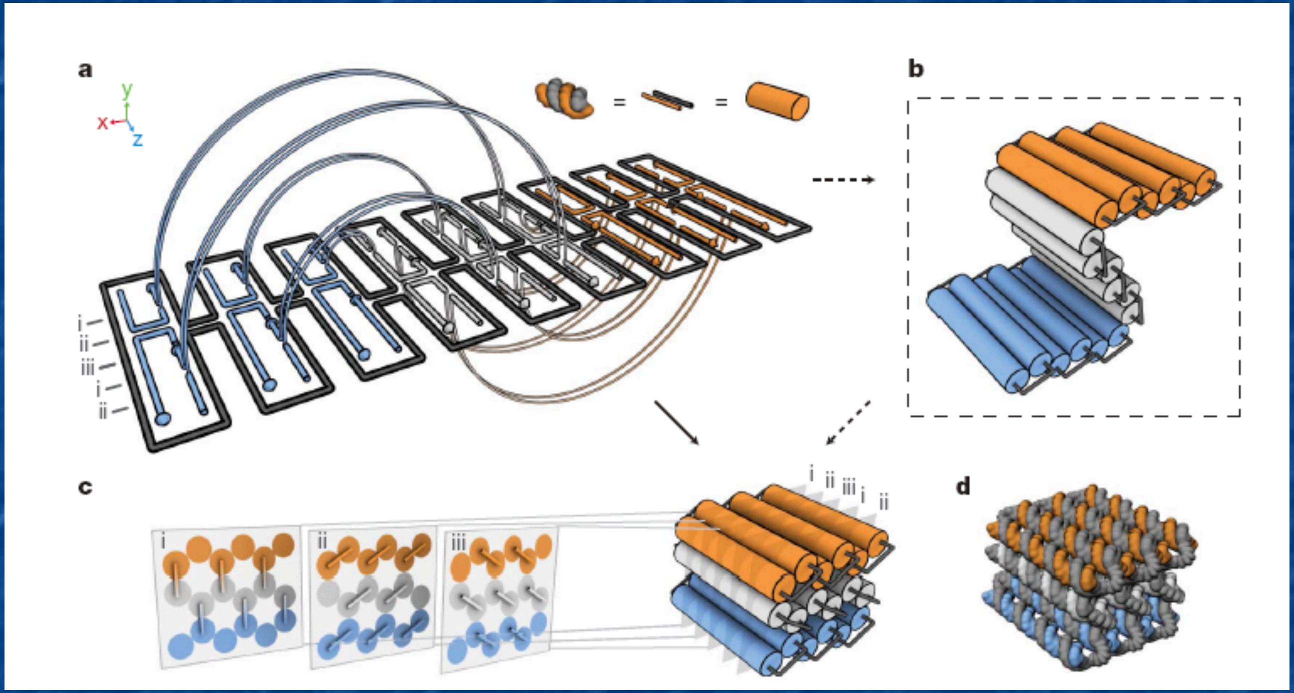
Data



Source: Folding DNA to create nanoscale shapes and folding patterns, P.W.K. Rothemund, Nature 440, p297 (2006)

*And flat DNA rafts can also be **folded** into 3D shapes:*

Start with planar DNA Origami raft, the add cross links to fold the raft into a 3D shape:



Take **one whole week** for very SLOW cooling

Giving time for raft to fold and unfold,

Allowing links to bump into one another and connect up!

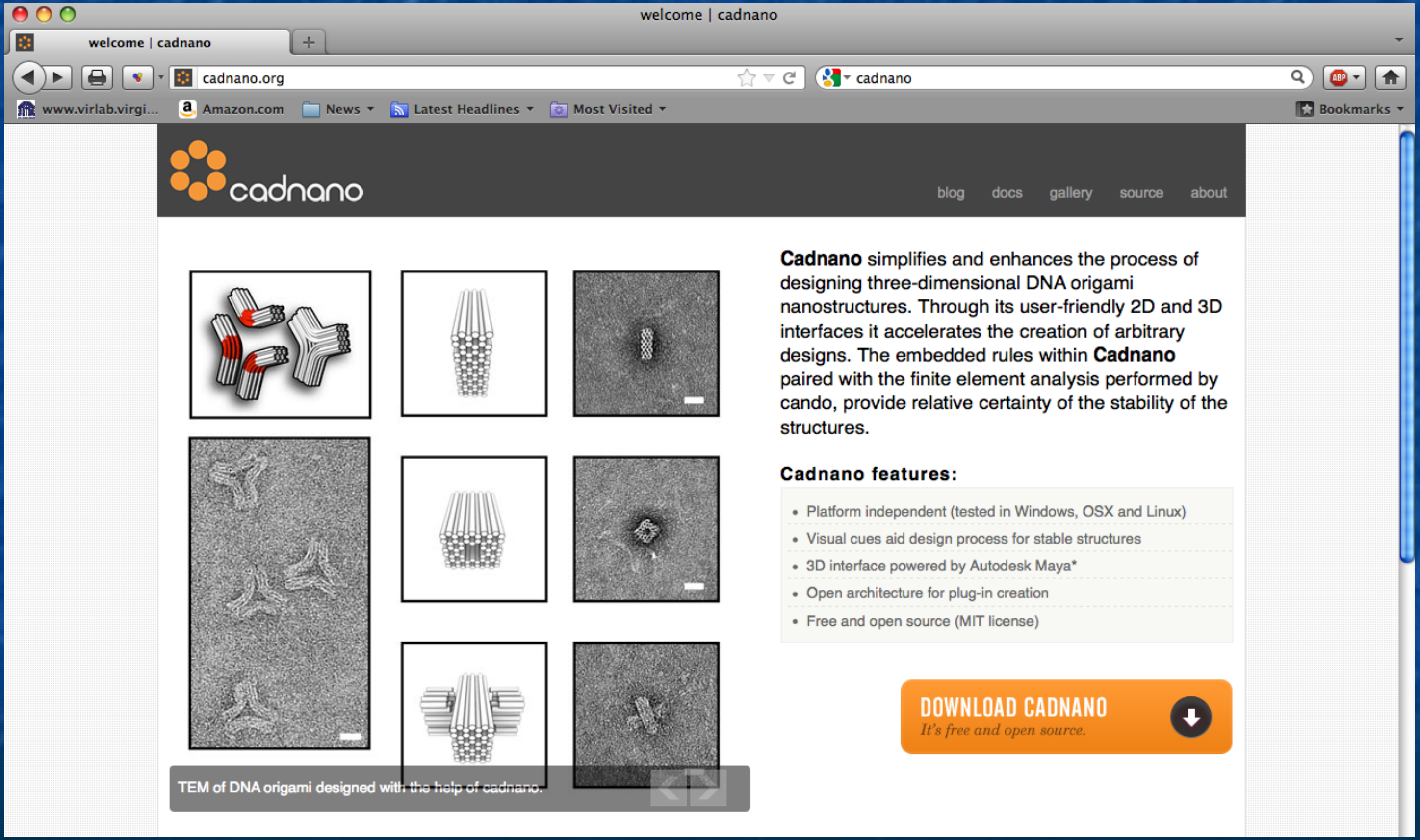
(See Shawn Douglas paper at Bleeding Edge Nanomechanics – Supporting Materials - DNA Origami)

NOW do you understand why EE professors like me are studying DNA?

The design programming sounds REALLY complex

But there is now a free, downloadable, do-it-yourself DNA Origami design program!

Developed by the Dana Farber Cancer Lab & Harvard's Wyss Institute



www.cadnano.org

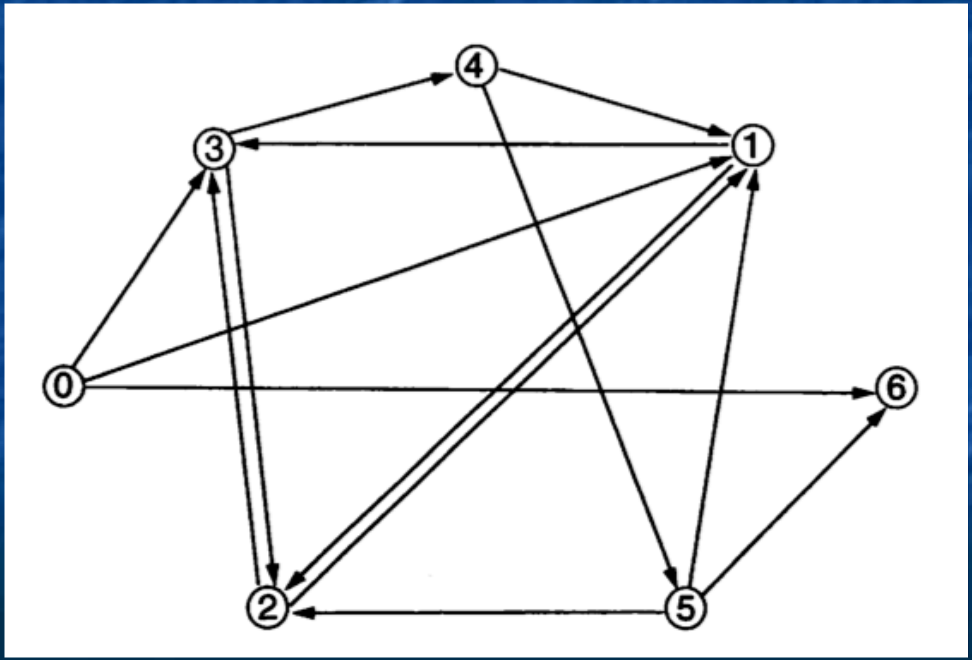
There is a somewhat related effort to use DNA to "compute"

Generally, to compute solutions to "combinatorial" problems

For instance, finding the most effective complex routes

Where there is a HUGE range of possible route segments

Classic problem is how to go through a large number of points via fewest lines

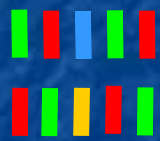


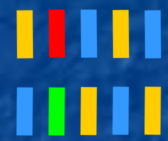
But some complete routes are a LOT shorter than others!

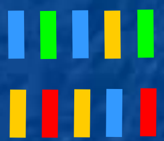
Computers can't cope with humongous number of possible routes!

Because number of routes increases as **factorial** of number of connecting points (n!)

So, instead, associate each possible point ("node") with a DNA base pair sequence:

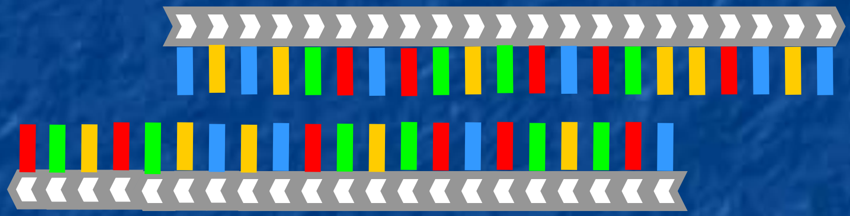
Node 1: 

Node 2: 

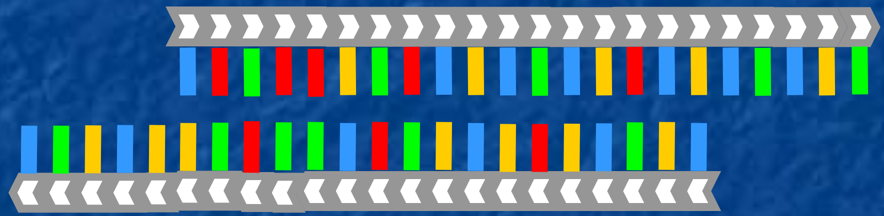
Node 3: 

Then create a DNA segments with "sticky ends" coded to each node:

">1-2>"

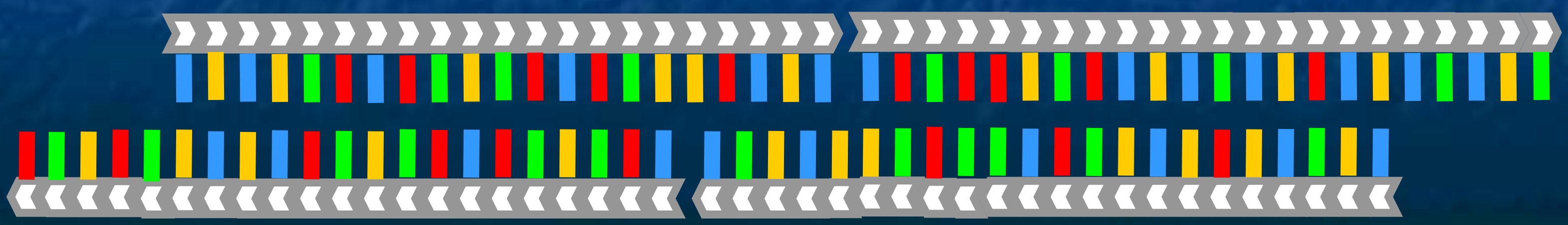


">2-3>"



Coded "sticky ends" **will** then drive **those** "connectors" to connect **those** nodes:

Node 1: Node 2: Node 3:



Now synthesize connectors for EVERY possible connection

For the earlier route drawing you'd need at least these connectors:

>0-1>, >0-3>, >0-6>, >2-1>, >2-3>, >3-4>, >4-1>, >4-5>, >5-1>, >5-6>

Then make a huge number of copies of each connector

As you will see in our DNA lab, you can just use "PCR multiplication"

Mix everything together, heat above 90°C, then slowly cool:

You'll connect long strings of DNA, representing EVERY possible route

Sort those strings by length, using standard "gel electrophoresis" technique

Shortest one has smallest number of connectors

Decode its connectors' identity and positions => Shortest possible route!

Seminal publication (and route figure) was by Aldeman (in 1994)

Copy, plus some explanatory notes, are posted on [Supporting Webpage]

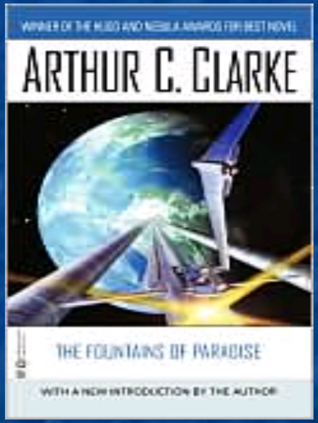
3) The Beanstalk: A real stairway to the heavens?

I used to have lecture on the huge flaws in many nano science fiction stories

But, strangely, Nano may soon make one of Sci-Fi's BIGGEST ideas possible:

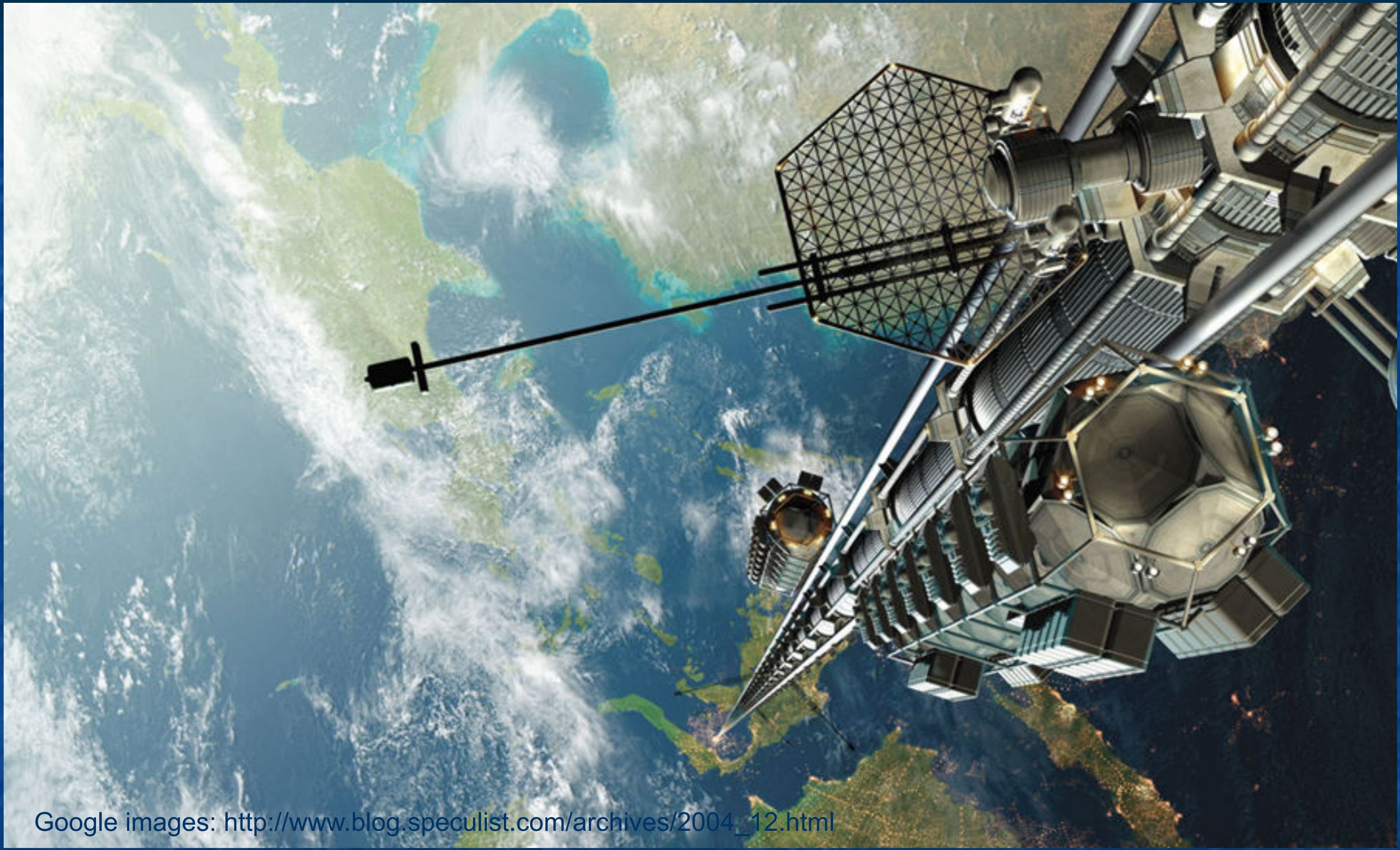
The “Beanstalk”

Proposed by Arthur C. Clarke in his 1979 novel "The Fountains of Paradise"



But what is a Beanstalk?

This is a Beanstalk:

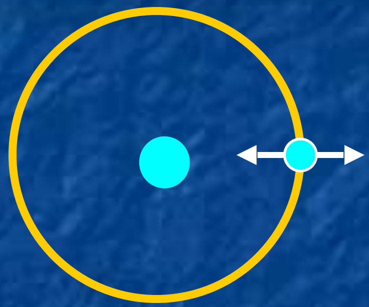


Google images: http://www.blog.speculist.com/archives/2004_12.html

Also known as a “Skyhook” or as a “Space Elevator”

It's actually an old idea . . . But with a BIG problem

It was proposed by Russian scientist Konstantin Tsiolkovsky, in 1895



Satellite's orbit = balance between centrifugal force & gravitational force

Higher it goes, weaker the gravity, slower the orbit required

Near-earth orbit (R ~ 6,500 km) ~ 90 minutes

Moon orbit (R ~ 385,000 km) ~ 30 days

35,786 km orbit = one day → Over equator, stays above fixed point = "Geosynchronous Orbit"

Tsiolkovsky: Satellite is happy, earth is happy, tie together with rope + elevator

Problem: Rope is not happy, all but top of it is moving too low and slow to orbit

Load on rope => Good fraction of its own 35,000 km length => SNAP!

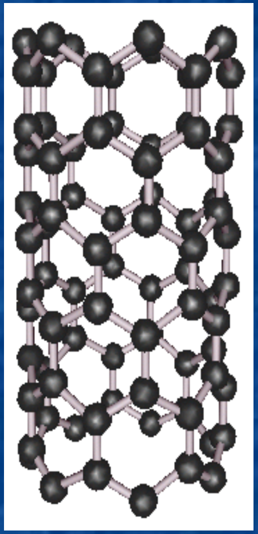
So you'll need incredibly LIGHT yet STRONG rope!!!

Analysis by U. Washington Physics Prof. John G. Cramer:

In his December 2001 Alternate View column in Analog Magazine (link to cached copy)

Tension at top of rope = 92 Giga Pascals = 13.3 MILLION pounds per square inch!

But he also estimates that: Carbon nanotube (CNT) rope might attain strength 50% larger!



HOWEVER: 36,000 km long single carbon nanotubes cannot now be grown

Even ONE continuous METER is beyond our current capability

So Cramer invoked rope woven from short fibers (like normal rope)

This assumes bonds <u>between</u> CNTs are as strong as bonds <u>within</u> CNTs

That's NOT the case with normal fibers, nor presently the case with CNTs

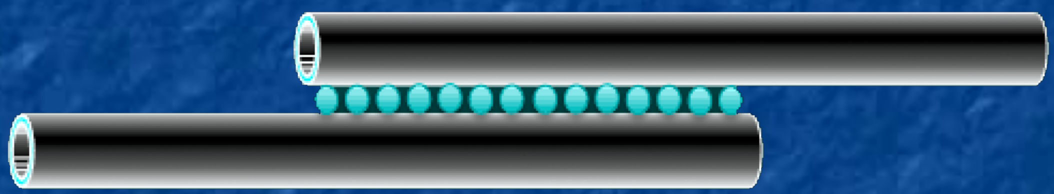
So how MIGHT this be done?

My thoughts about ways of linking carbon nanotubes

Scheme 1) Splice together with larger nanotubes:

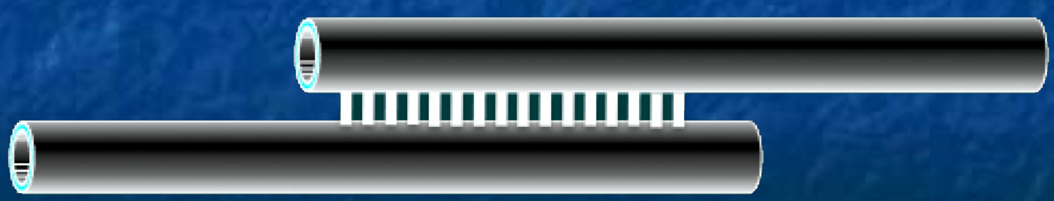
Might pull this off **once** (= enough for another AZOnano headline?) . . . but a gazillion times?

Scheme 2) Bond together via intermediate atoms or molecules:



But carbon-other bonds are SO much weaker than carbon-carbon bonds!!

Scheme 3) Bond together the carbon atoms on adjacent nanotubes

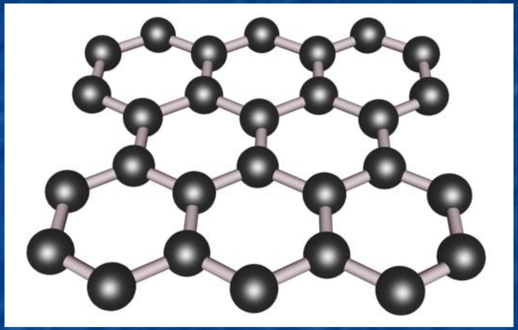


Let's explore this one a bit more deeply:

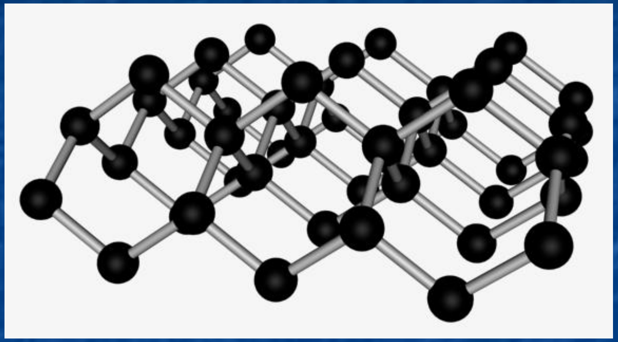
Direct carbon to carbon nanotube binding:

Need to go from carbons bonded with 3 neighbors to bonding with four neighbors

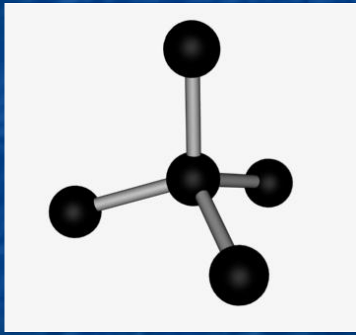
Graphene
(3 neighbors):



Diamond
(4 neighbors):

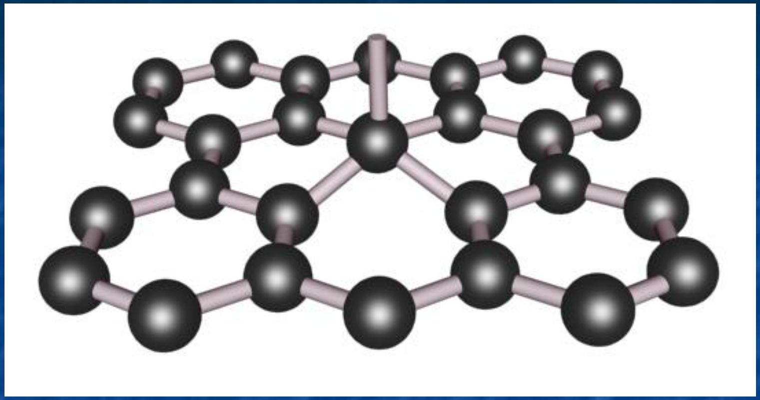


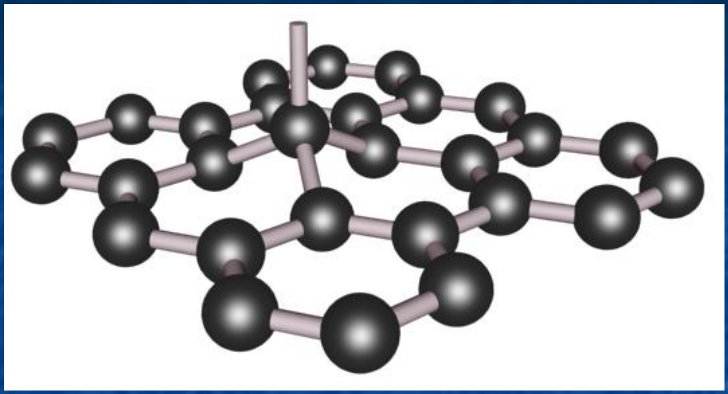
Both DO have exceptionally strong bonds! Take a closer look at diamond:



Need to incorporate some of these structures into the surface of graphene:

Diamond bonding inserted into graphene sheet:





Bonds DO bend fairly easily, so that part might be plausible

But it is MUCH harder to stretch bonds (as I did in these figures):

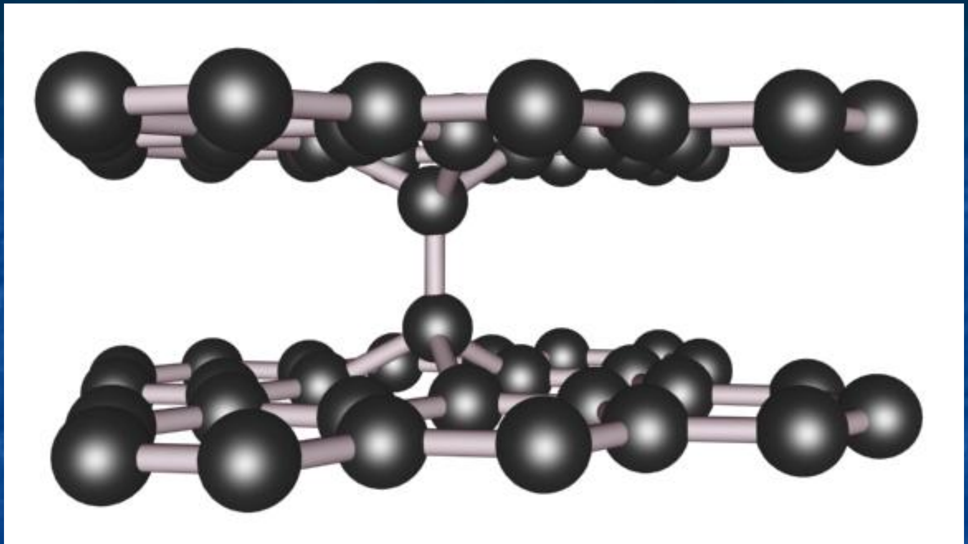
So I don't know if depicted configuration is energetically feasible

And I worry about disruption of graphene's "resonant bonding" (use of 4^{th} electrons)

But assume this IS energetically feasible and CAN be induced:

Need to go from carbons bonded with 3 neighbors to bonding with four neighbors

Possible result:



So this might provide a way of linking short carbon nanotubes together

But Cramer's estimate of CNT strength = 3-10 times larger than figure I got from other experts

However numbers ARE in the ballpark, and "experts" have been wrong or superseded before

(i.e. I wouldn't invest in beanstalk / skyhook yet, but not sure I'd bet against it either)

Conclusions

Discussed (only!): Walking on the walls

DNA Erector Sets

Beanstalks / Skyhooks

Only a few of many “bleeding edge” mechanical applications of nanotechnology

Nevertheless, range of potential applications is already stunning

Next week: Bleeding edge of nano<u>electronic</u> applications

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.