Nanotechnology

a personal overview

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Outline

- why nanotechnology
- historical introduction
- basic NT concepts
- “natural” nanomachines
- a survey on applications
- IIT Nano(bio)tech Facility: current situation

Why work on such a small scale?

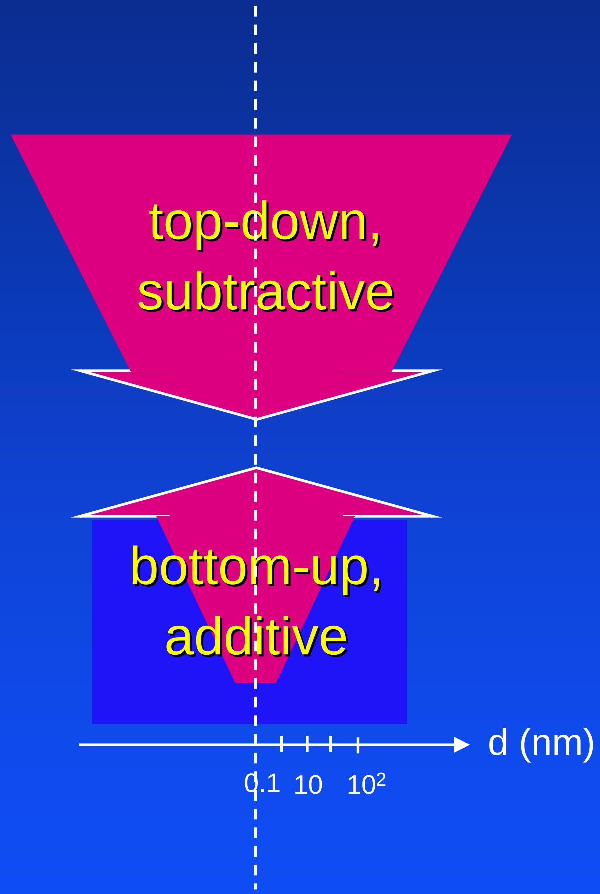
To <u>optimize properties</u> readily exploited:

increasing speed

mechanics: lower response time, higher resonance frequency

electronics: shorter signal paths, lower parasitic RCL, lower power dissipation

optics: faster (and higher density) storage, modulation, switching, routing



To investigate <u>novel properties:</u>

approaching wavelength scales,
increasing surface / volume ratio

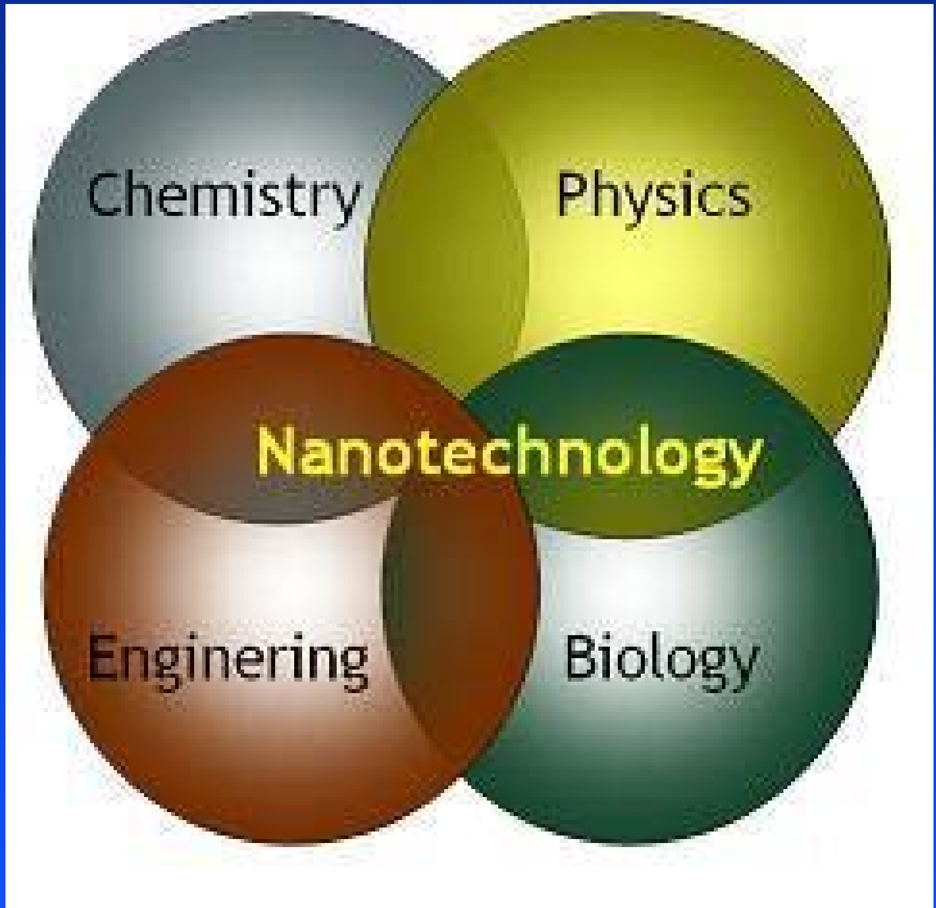
materials: decreasing crystallite size (mechanical strength, magnetic storage), nanoparticles for catalysis or optics

electronics: quantum effects

optics: near-fields, quantum communication

Eames "Powers of ten", Scientific American Books '82
Bonner, From bacteria to whales, '07

A great challenge: Interdisciplinarity

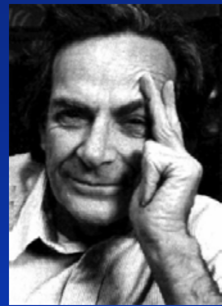


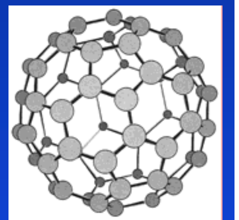
- problem of communication between individuals
- problem of coordination among institutions on international scale, on the model of e.g.
  - Human Genome Project
  - Space Program
  - particle accelerators
- discipline "under construction" delay with synthesis, e.g. no such a DB as for proteins (Brookhaven Natnl Lab)

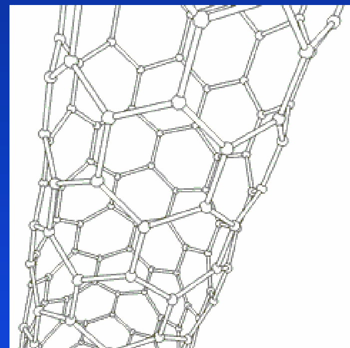
S.C: Florman "The existential pleasures of engineering" St. Martin's '76
C. & R. Eames "Powers of ten", Scientific American Books '82

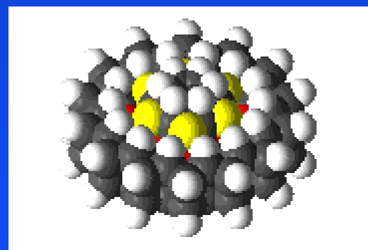
Milestones of Nanotechnology

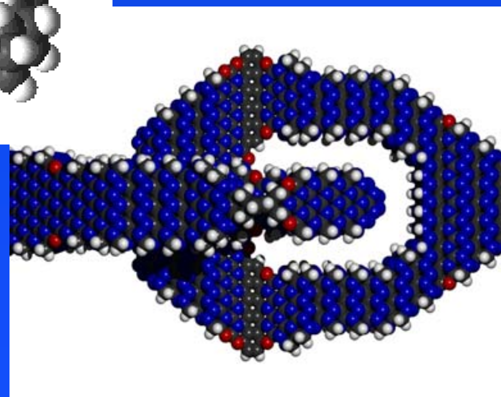
- 1931 M.Knoll, E.Ruska:
  Electron Microscope
- 1953: Watson & Crick:
  DNA structure
- 1959 Feynman's Talk
- 1974 N.Taniguchi:
  first used 'Nanotechnology'
- 1981 Binnig, Rohrer: STM, 1986
  McClelland, Quate AFM:
  Near-Field probing concept
- late 80's: Drexler's NT:
  atom-by-atom 'assembler'
- '85: Smalley's fullerenes,
  '91?: Iijima (NEC): C-nanotubes
- 90's: Supramolecular chemistry:
  Ghadiri's peptides,
  Lehn's molecular jigsaws,
  Stoddard's moelcular train,
  Seeman's DNA lattice,…





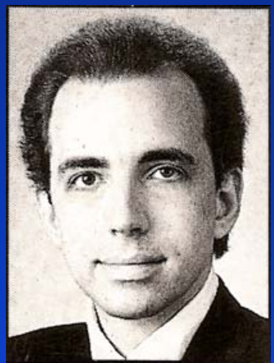




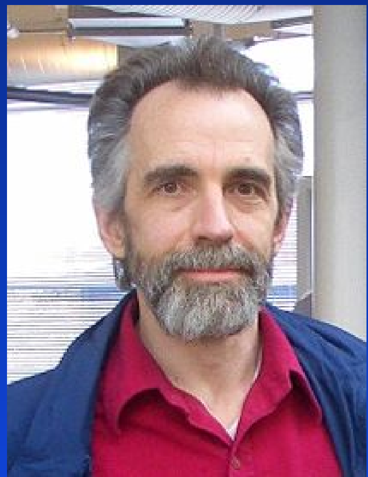


"Mr Nanotech": Kim Eric Drexler

1985



2007



- graduated @ MIT
- originally interested in human colonization of space

- '86: "Engines of Creation", founded the Foresight Institute, *www.foresight.org*
- '91: "Nanosystems", founded IMM, *www.imm.org*

FORESIGHT NANOTECH INSTITUTE
Advancing Beneficial Nanotechnology

iMM
Institute for Molecular Manufacturing

- Impossible to foresee technological developments >50 yrs ahead, also due to change in society
- Best view: by SF, (Verne, H. G. Wells, F. Pohl, Henlein, Asimov, Clarke)

- How to stack atoms?
- If possible, what about the consequencies in 50 yrs?
  → more changes than since the Middle Age !
- (In the last 50, not so much: TV < radio < telephone, airplane < car)

Molecular Nanomachines

"Engines of Construction" PNAS 78, 5275 '81

- Coal vs diamond,
  sand vs computer chips,
  cancer vs healthy tissue:
  the structure of matter is important
- How to change it: technology

- Bulk technology:
  like ~30,000 yrs ago:
  - chipping flint,
  - cooking clay,
  - cooking rocks,
  - cooking ceramics/steel/Si
    (slicing, burn patterns, …)
- Molecular NanoTechnology:
  manage individual building blocks
  @ nanoscale, i.e. molecules

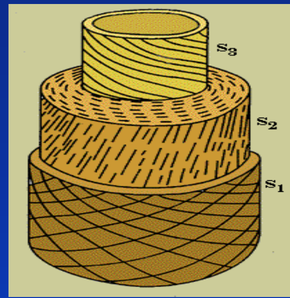
- Passive molecular patterns:
  - air: no shape, no volume: sparse, free molecules;
  - water: no shape, defined volume:
    molecules move together;
  - Cu: defined shape, defined volume: can change
    by hammering as atoms slip, yet remain bound;
  - glass: shattered, as atoms don't slip but separate;
  - rubber: net of kinked spring-like molecules

- Active molecular patterns:
  molecular n-machines
  …

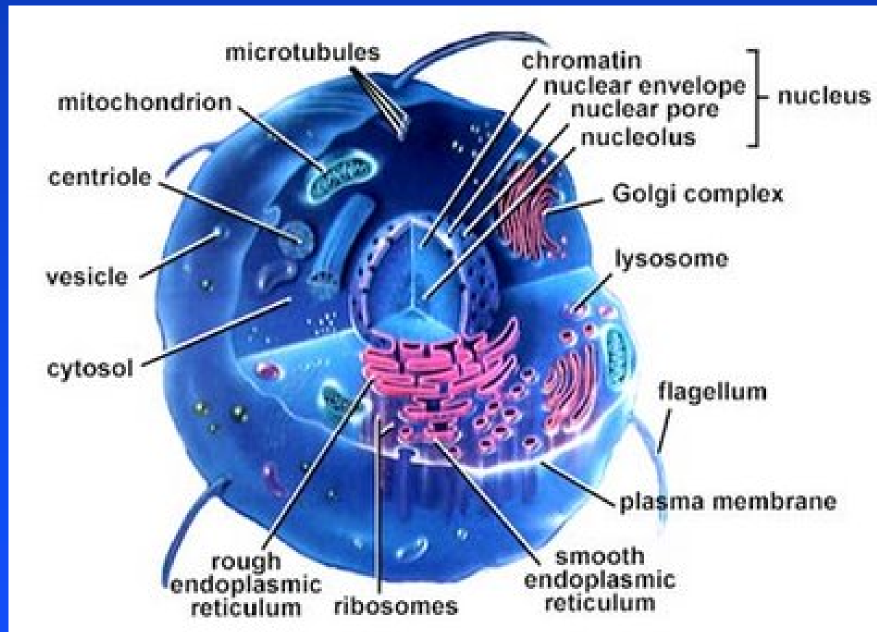
A look at bio-systems

macro-scale:

- Gordon's '78 "Structures, or why things don't fall down": "Nature is a better engineer than man" best ship masts: entire tree trunks



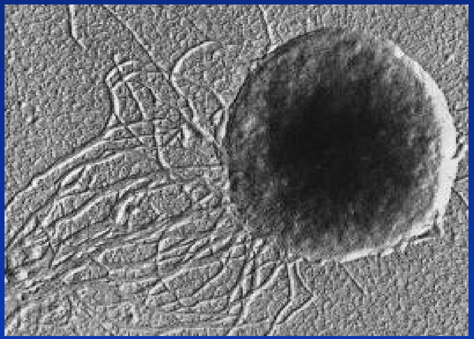
micro-scale:



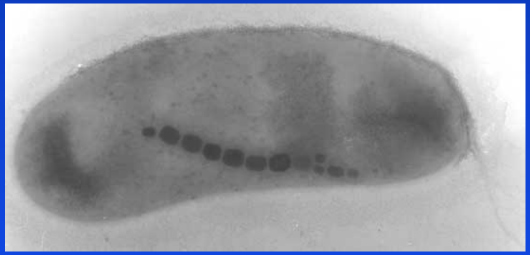
- cells: compartments which allow the chemical reactions of life
- protected by a lipid double layer membrane
- eukaryote cells (man, cat, yeast) have nucleus containing most DNA
- + other compartments: endoplasmatic reticulum, mitochondrion, …
- walls build themselves: self-organization, & doors are opened/closed (ionic channles)

Amazing micromachines: the cells…

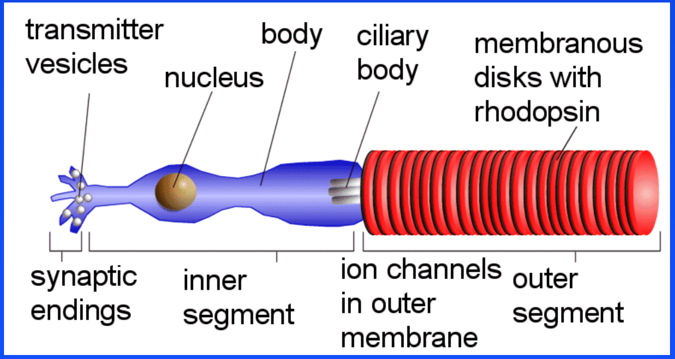
- archaea bacterium: methanococcus jannaschii:
  - first isolated '83 from 2600 m below sea near hydrothermal vents
  - autotrophic: N fixation, use H in H_2 form, take C from CO_2
  - from its genome: >1700 hi heat-stable proteins discovered, 56% completely unknown



- '75 Blakemore: magnetotactic bacteria: built-in compass of magnetite crystals
  - before O_2 appeared (not for the first 1.5 G yrs), Fe sulfides & oxides could have played similar roles in combustion of nutrients, or magnetite could just be a reservoir of Fe (~ferritin)

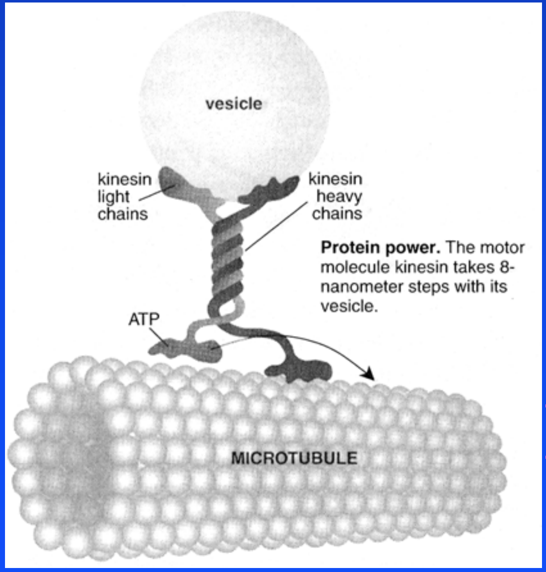


- retina's rods & cones: CCD-like signal conversion film
  - part of the brain (evolved from its cells)
  - cones: ~3 M, middle, colors, low sensitivity
  - rods: ~1 G, edges, colorblind, hi sensitivity: single photon, within 1 s



… Amazing nanomachines: the proteins

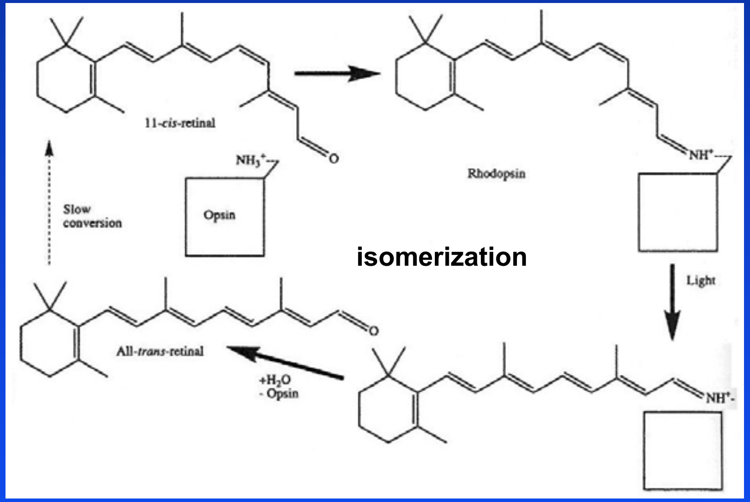
- *e.g. a motor:*
- in cells, microtubules: 25 nm wide train tracks for moving molecular equipment: help drive chromosome dance on cell division, guide migration of small membrane-bound vesicles, carrying to/from nerve terminals enzymes that synthesize neurotransmitters
- kinesin move along microtubules in 8 nm steps (viewed by optical tweezers)



Protein power. The motor molecule kinesin takes 8-nanometer steps with its vesicle.

+ tubulin
+ hemoglobin
…

- *e.g. a molecular computation element:*
- Robert Birge: light-harvesting molecule bacterio-rhodopsin can be read (interrogated) & written (flipped) by different lasers → 18 GB memory

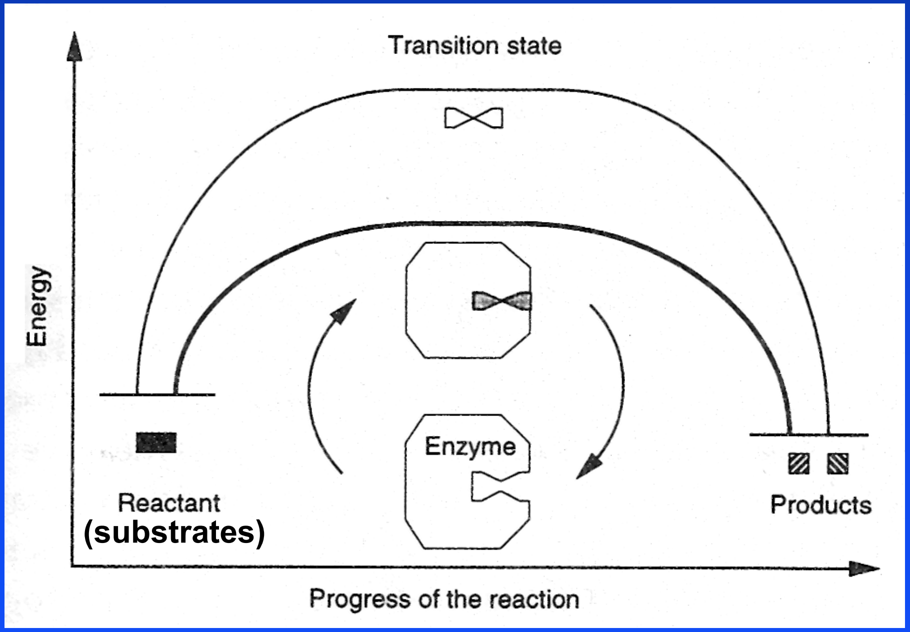


- Jonhatan Lindsey: porphyrin → processing element (switch)
- Prasanna de Silva: anthracene derivative fluoresces due to both H and Na channels → AND gate

Steve Block Science 27 Aug '93 1112
R. Birge "Protein-based computers" Sci. Am. 272, 90 '95
P. De Silva "A molecular photoionic AND gate based on fluorescent signalling" Nature 364 42 '93

Enzymes help us do the job

- *e.g. natural catalists: enzymes*
- most proteins are enzymes
- ~4,000 biochemical reactions catalyzed by enzymes

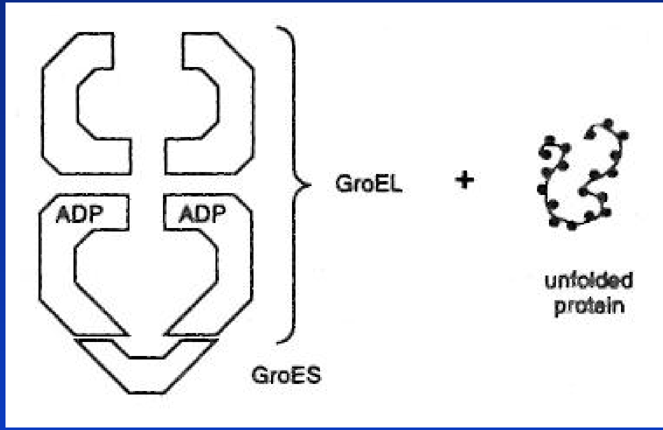


- not only accelerate reactions, but select them among all possible ones
  → used by cell to direct its production processes
- enzymes can couple reactions, helping synthesis of proteins by taking energy from cleavage of small molecules
- e.g. nitrogenase provides life: builds NH_3 from N_2, H @ ambient T, P
- DNA helicase, polymerase, ligase replicate DNA
- common enzyme apps:
  - stain removal
  - washing powders
  - curdling milk
  - cosmetics
  - hair perms
  - sugar production (degradation of starch)
  - pharmaceuticals, food processing, …

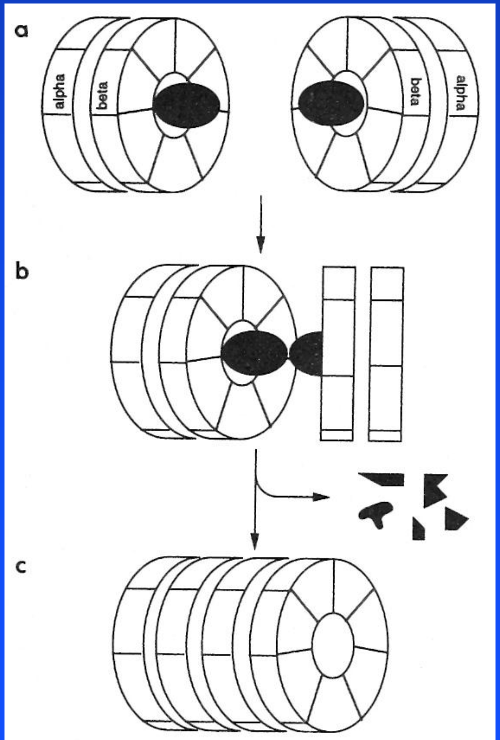
+ beer, bread, wine: *Biotech "the old way"*

More protein tasks

- ‘70s: people began refolding proteins in test tubes: yet only a fraction succeeded
- efficiency in the cell: even less,
  due to binding sites exposed to other chains
- → molecular “chaperones” family of proteins:
  e.g. DnaK in E.Coli
- the protein is passed on from 1 kind chaperone to the next: assisted folding → barrel-shaped protein complex: chaperonin-60



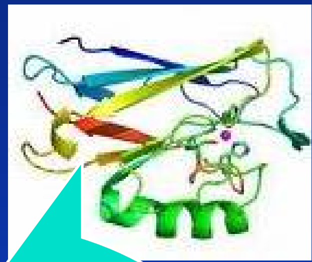
- cell: can deconstruct into aa the proteins damaged or no longer needed
- marking: a small protein: ubiquitin
- molecular factory: proteasome
- function similar to protein-degrading enzymes secreted by cells (e.g. digestive trypsin & chymotrypsin), yet intracellular
- e.g. ‘92: Baumeister (MPI Munich) found proteasome of archaebacterium Thermoplasma acidophilum:
  2 rings of 7 beta units sandwiched between
  2 rings of 7 alpha units
- proteins can only enter if carry ubiquitin & are fully unfolded: sieve effect



cell nanomachine production

proteins

- are active:
  fold to objects with functions
- Enzymes: assemble & disassemble
  proteins & DNA
- Hormones: (stick to proteins and) modify
  cell behavior
- are made by bacteria
  programmed by genetic engineers

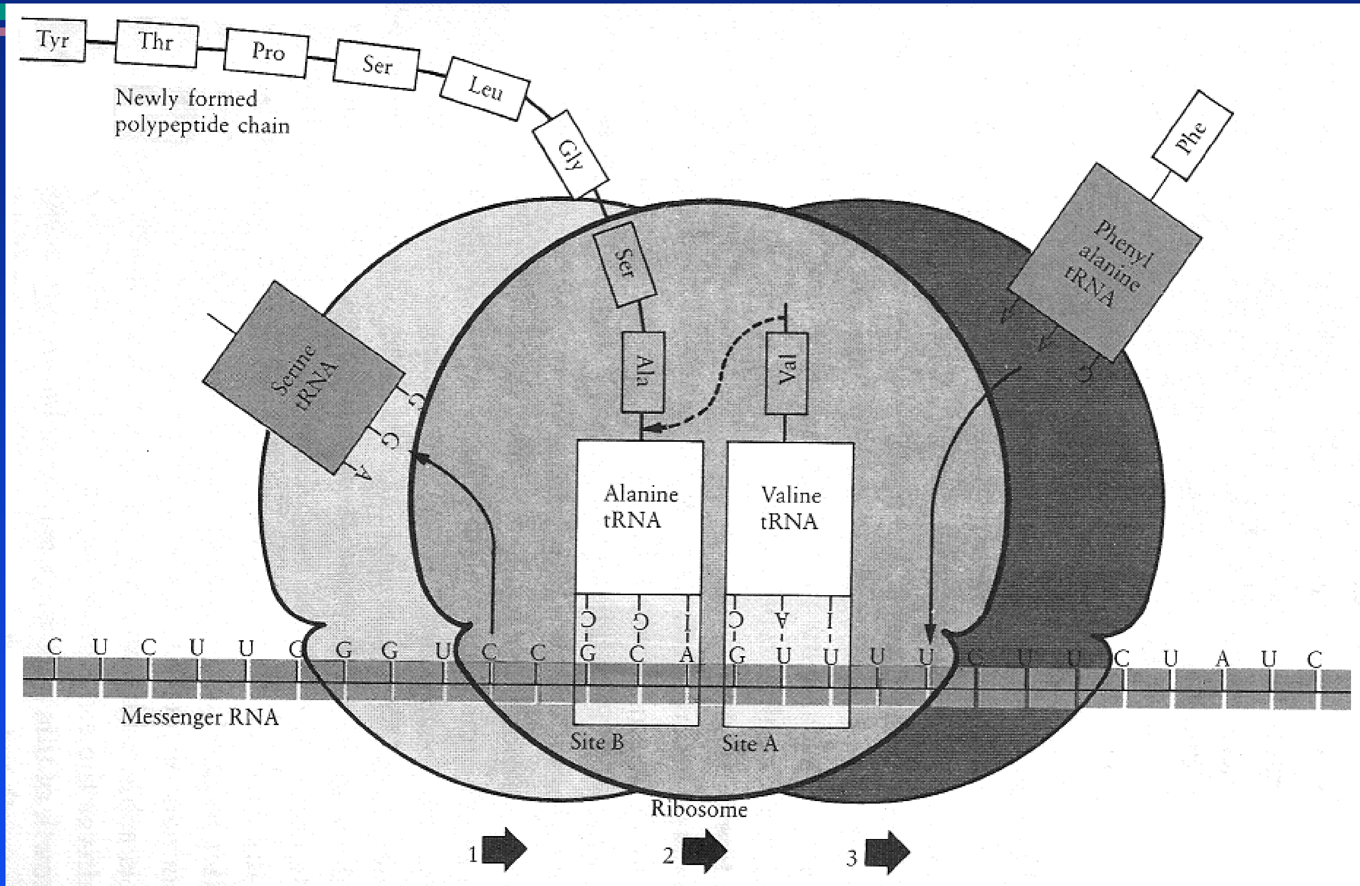


- first enzymes transcribe DNA
  copying its info into RNA tapes
- then based on RNA strands
  the *ribosomes* build proteins

DNA

- string of lumpy beads, like proteins
- not strong like Kevlar,
  not colorful like a dye,
  not active like an enzyme,
  but can drive ribosomes:
  molecular tape with stored info

Ribosome: a natural Assembler



- protein & RNA complex ~4200 kD, "molecular factory" (limited assembler & replicator)
- RNA is read 3 "letters" at a time
- info is used to assemble floating amino acids (peptides, 10 to <30 atoms) into a polypeptide chain
- folding → protein

- almost all living tissue is built from 20 aminoacids
- the mechanisms that control folding of the chain into a bio-active 3D form → challenge of molecular biologists, a reverse-engineering problem
- even ribosome itself self-assembles again

Artificial, universal nano-assemblers

- “second generation nanomachines” built of more than proteins, tolerating acids, vacuum, freezing or baking
- working on all reactive molecules used by chemists, but in a programmed way
- “able to place atoms in almost any reasonable arrangement”

early steps taken already:
- Genetic engineering
- Biotechnology
- SPM

“STM placing tool”, Binnig Rohrer Physica 127B 37 ‘85

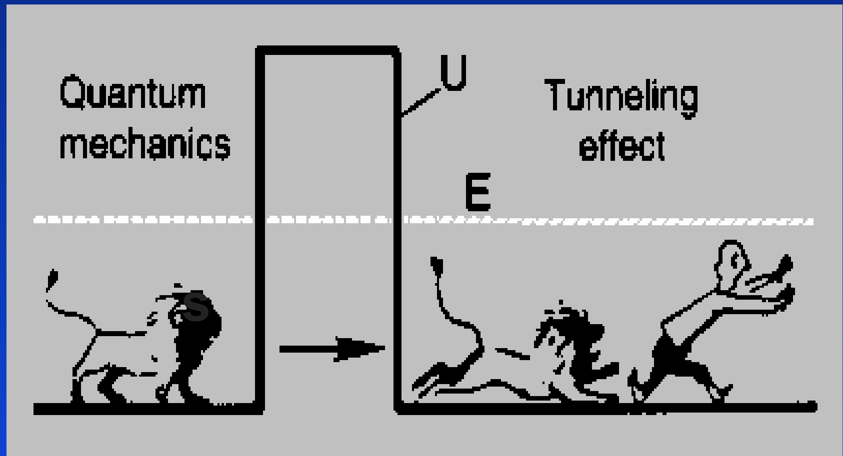
n-computers could be made,
to control n-assemblers:
- mechanical (100,000 times slower but on 10^{-6} distance, so 1/10 delay),
- electronic
- n-disassemblers: useful to learn & copy !

non-optical SPM: STM and AFM

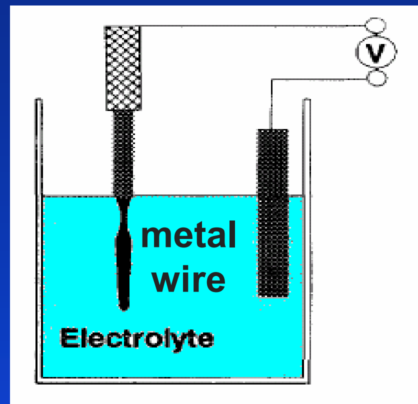
principle :

$I \sim e^{-2k\,s}$

$s \leq 1$ nm



probe :



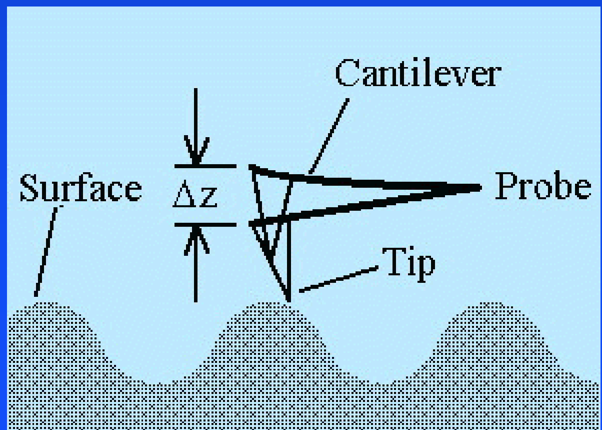
Au in HCl

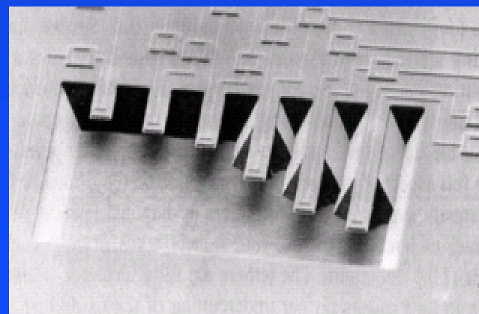
W in NaOH / KOH

$Pt_{0.8}Ir_{0.2}$ in molten $NaNO_3$

$F = -k\,\Delta z$

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$$

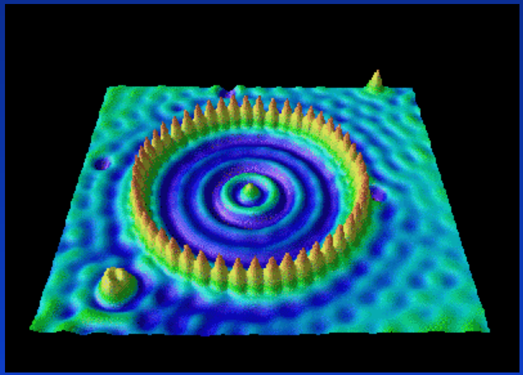




microfabricated Si / Si_3N_4

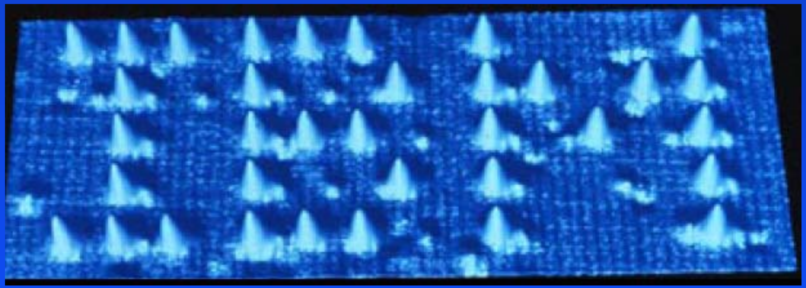
Early atomic manufacturing by SPM

- STM made & imaged "Quantum corral" of 48 Fe on Cu crystal
  → demonstrated 1942 de Broglie's wave character of particles



M.F.Crommie et al., Science 262, 218 (1993)

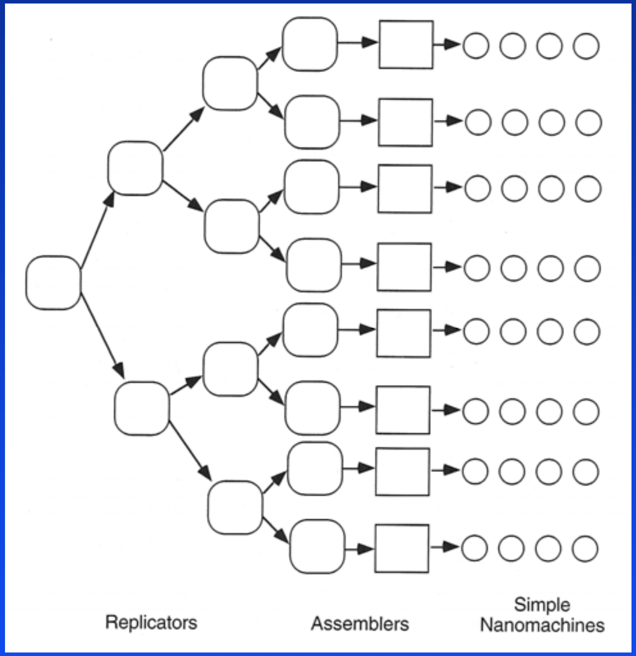
- '90: English IOP launched "Nanotechnology"
  & IBM miniaturized advertisement
  Xe on Ni



Shedd – Russell "The STM as a tool for nanofabrication" Nanotechnology 1, july '90

NT: a 2-weeks revolution ?

- by “hand” the earliest ones
- by “bulk” industrial processes next
- by “assemblers” later on (not replicators)
- yet, e.g. 10 M assemblers (built in several yrs !) will still take ~2 weeks to fill 1 cm^3 ! (~1 trillion nanomachines)
- by themselves (“replicators”) will be too risky !!
- use limited replicators at some intermediate stage



$n(t)=2^{t/\tau}$: the “Chinese population” problem !

Fantastic NanoTechnology !

- assembling speed:
  no problem due to replication
- abundance:
  lot of extraterrestrial
  room & materials
- positive-sum society:
  by cooperation
- medical nanomachines
  killing viruses, cancer cells, …
- biostasis by crio-preservation
- no pollution: not made
  & old one eaten by disassemblers

- "magic" trillions micro-robots,
  the size of a human cell or bacterium
- can link into a "lattice"
- we can use them to fill empty space
  (displacing some air), & program to be
  a "sustaining" medium:
  to move things, simulate real objects, …

J. Storrs Hall

Utility Foglets !

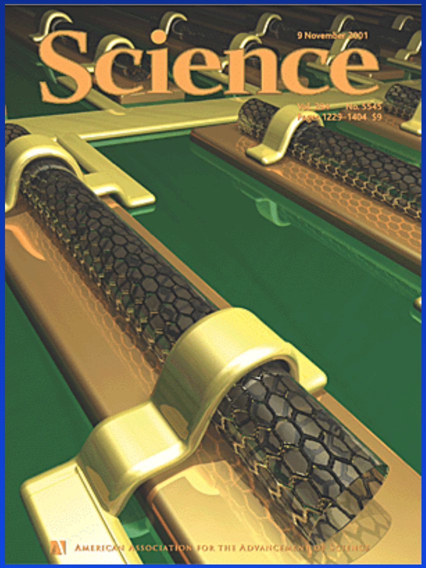
Forward, J. Spacecraft & Rockets, 21, 187 '84

Suda, Kito, Adachi "Long term frozen cat brain in vitro" Nature 212 268 '66

Popularized Science Fiction view of NT

www.foresight.org

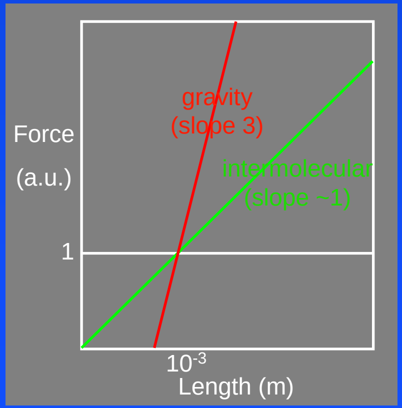
Scientific American september 2001



Science november 9, 2001

Problems:

- energy supply, communication, ...
- testing & debugging will need huge parallel processing
- scalability, molecular fluctuations due to thermal noise, *'sticky'* and *'fat'* fingers



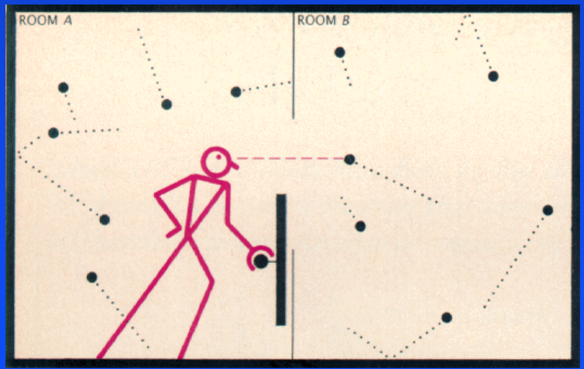
Reynolds Number:

R_e ~ (Inertial force)
/ (viscous force)

spermatozoon	**~ 1×10^{-2}**
blood in brain	**~ 1×10^{2}**
blood in aorta	**~ 1×10^{3}**
swimming man	**~ 4×10^{6}**
whale	**~ 3×10^{8}**

Nanomachines & thermodynamics

- Maxwell's Demon:
  1867 riddle: thought experiment
  contradicting 2nd law of thermodynamics:
  "in the universe total disorder
  can't decrease with time"
- $S = k\ ln\Omega$
- 1929, Szilard: the Demon should collect info about particles, & computer science: information is negative entropy
- at some point the Demon should delete accumulated info → increase entropy back



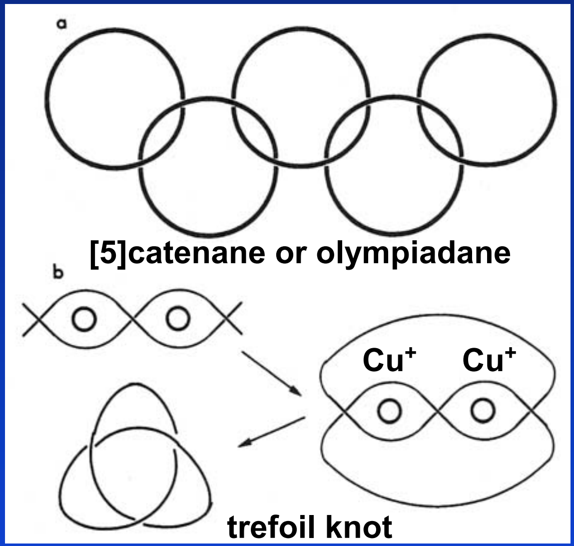
- best today computers:
  >Gx entropy strictly required
  to manage the respective info
- best limit case:
  every time a bit is erased
  kT *ln*2 Joules are dissipated
- 10,000 1 GHz conventional logic gates dissipate ~27 nW,
  → 1 m^3 dissipates 27 MW !

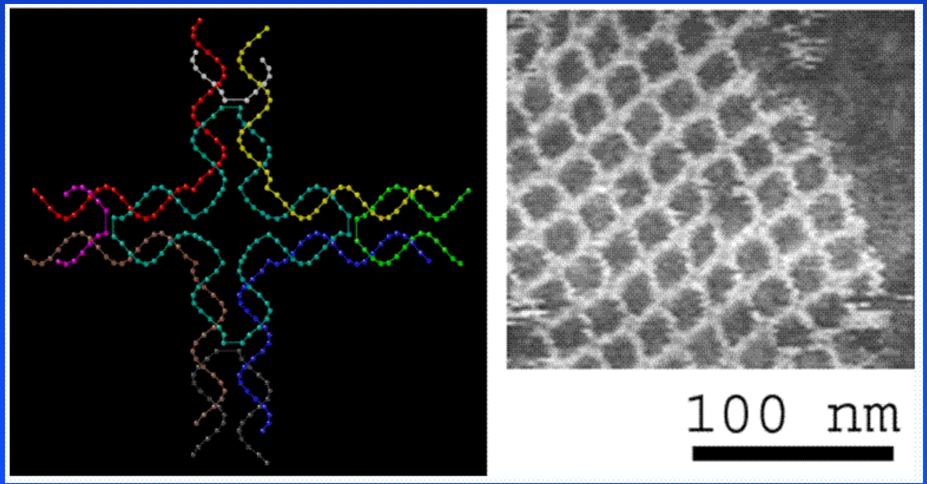
- assembler are like demons:
  produce entropy as heat
  → this would disrupt
  just created structures!
- nanocomputer containing foglets will never work

1) let fast molecules pass left-to-right, and slow ones right-to-left
   → more heat on the right: why not?
2) let just all particles go only in one direction
   → higher P on that side: why not?

From molecules to Supramolecules

- Topology: science of spatial relationships: stretched but maintain connectivity
- supramolecular chemistry locking: non-covalent
- Stoddard (U Birmingham): ~40 paper in a series: “molecular meccano”





(A) DNA “tile” of four branched junctions oriented at 90° intervals, “building block” for the assembly in (B). Each tile is 9 DNA oligonucleotides.
Strong M: *Protein Nanomachines.* PLoS Biol 2/3/2004: e73

- DNA: “dull” molecule compared to proteins
- can use as “brick”, as we have all the tools:
  - can be edited with comparable ease (restriction enzymes)
  - can be available in large quantities (PCR)
  - can be characterized fast (automatic sequencing)
- Seeman & Chen NY U ‘90: cube
- Seeman & Zhang ’94: truncated octahedron, 1440 nucleotides, MW~800 kDa,
- Seeman: DNA trefoil, Borromean rings, …. (AFM)

Molecular Electronics

Towards the ultimate (?) miniaturization by using *single organic molecules* as electronic switches and storage elements

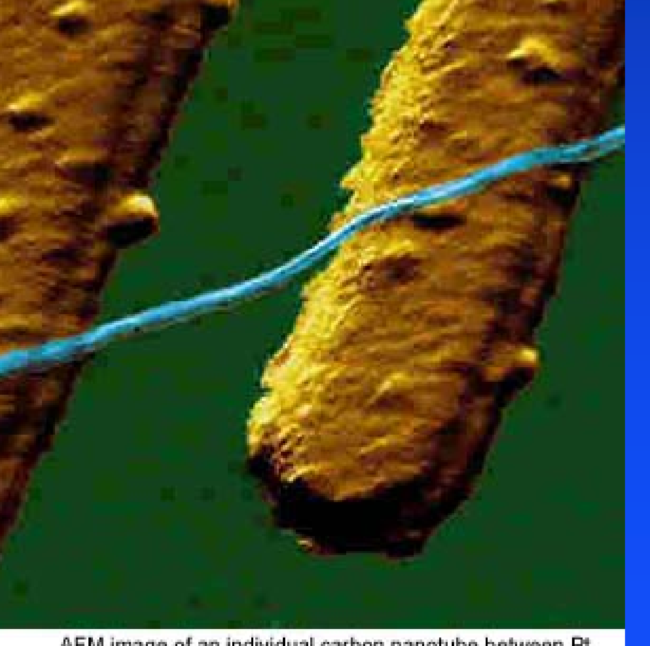
electronic properties can be adjusted via the chemical structure

size, speed, power consumption, cost

individuals absolutely identical

Hybrid molecular electronics

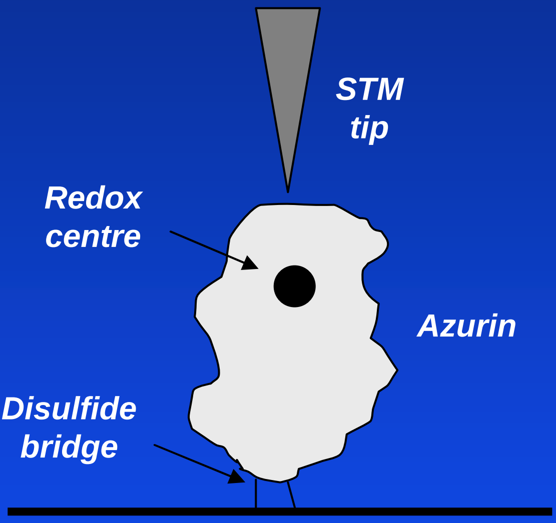
Mono-molecular electronics

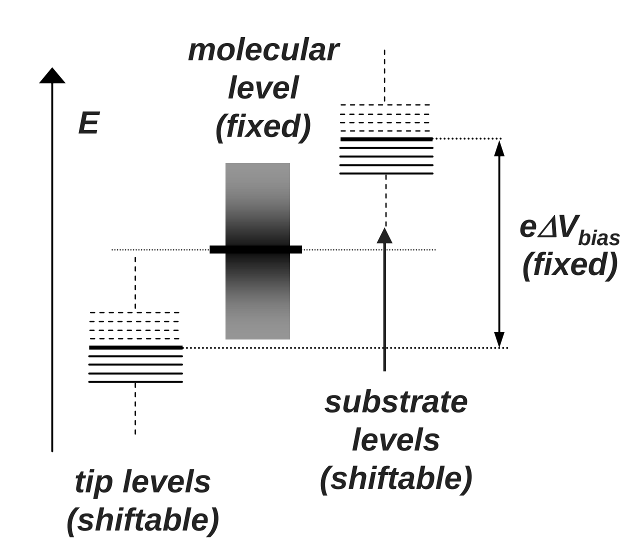


AFM image of an individual carbon nanotube between Pt electrodes spaced by 50 nm. Tans et al., *Nature* **386** (1997) 474.

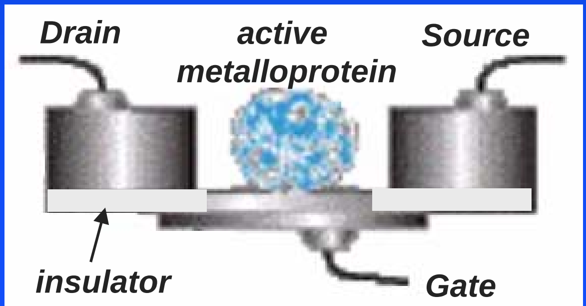
Nano-Bio-Electronics

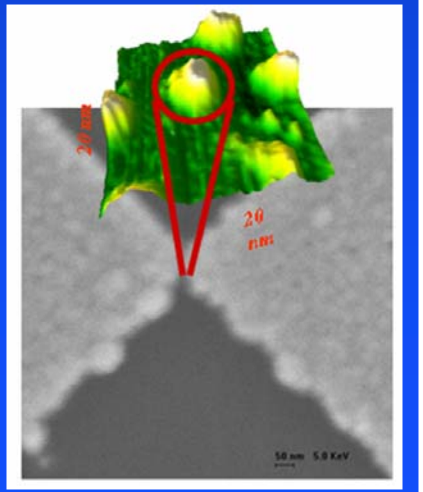
the redox system must be electrostatically decoupled from the electrode and from the tip so that a change in the electrode potential entails a concomitant relative shift of the Fermi level





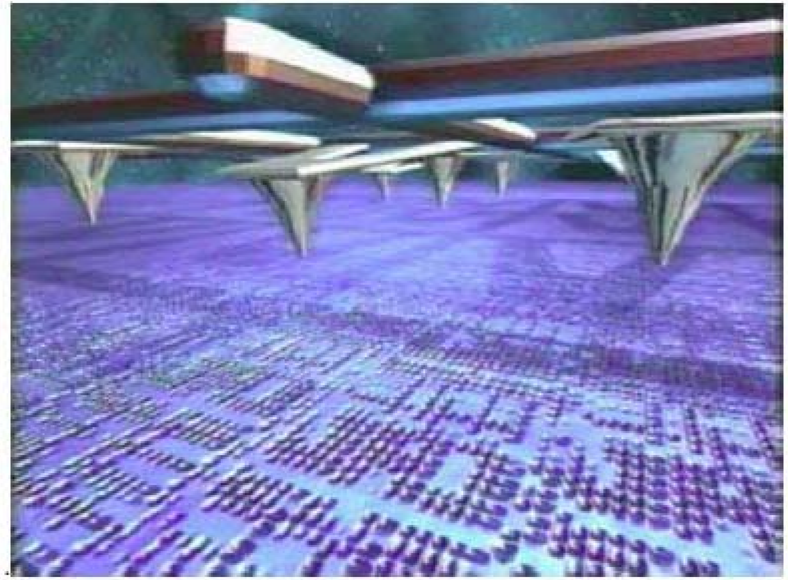
Facci et al. Ultramicr. 89, 291 (2001)





redox center insulated by the protein structure

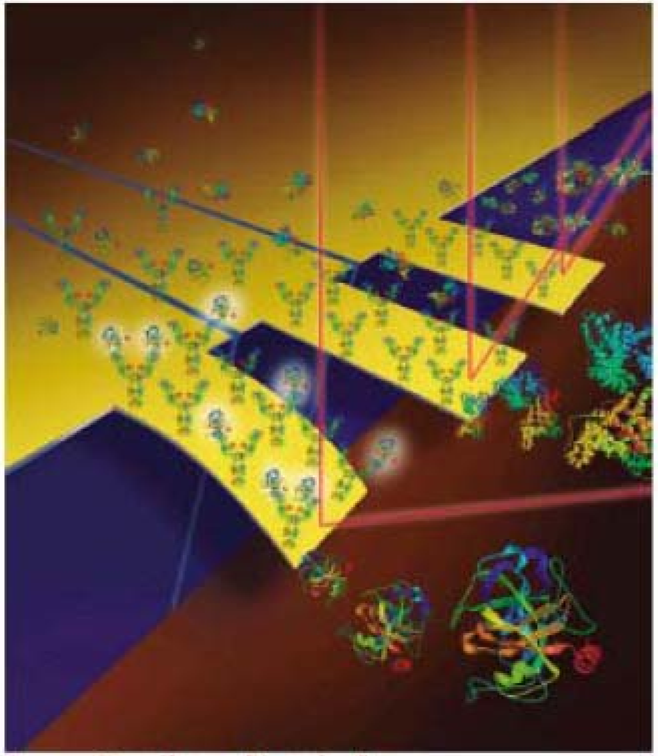
AFM advanced actuators / sensors



Millipide storage device using an array of AFM tips
Image courtesy of IBM.

C

- **computer memory** prototype
- bits written in a thin polymer by a MEMS device
- promises 1 Tb/in^2, =4x current magnetic storage
- 64x64 probes demonstrated @CeBIT '05
- works @ 300°C !!!
- too expensive



Laser-Cantilever Protein Sensor.
Image courtesy of Kenneth Hsu/UC Berkeley
& the Protein Data Bank

- **biosensor** prototype
- based on molecular recognition
- e.g. cantilevers coated with antibodies to PSA, a prostate cancer marker protein found in blood
- 2001 experiment: on 1 cantilever at a time

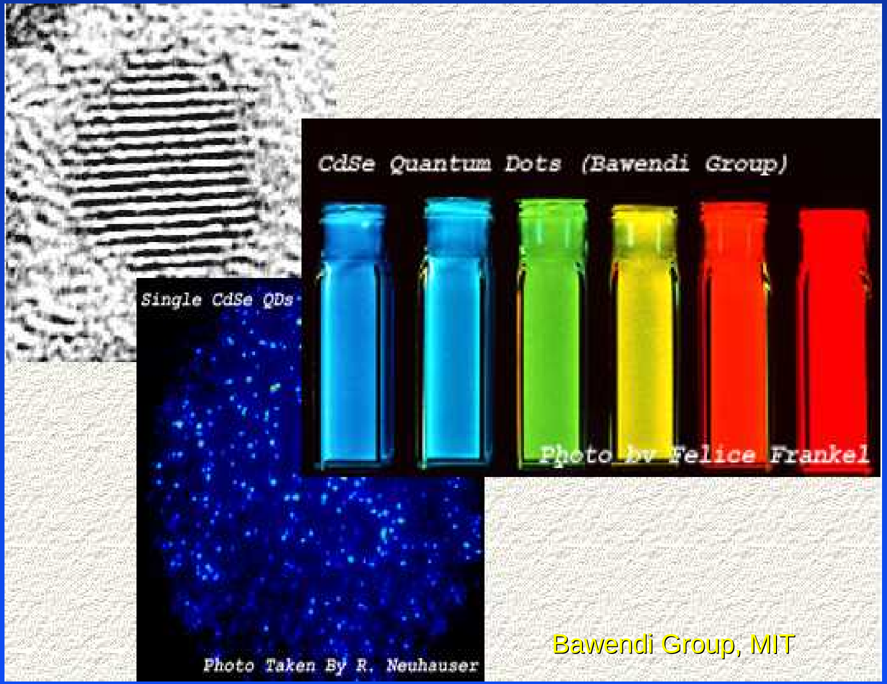
Quantum Dots Photonics

quantum dot size = the energy determining parameter

$$\lambda_e = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2m_0}}\frac{1}{\sqrt{m_m E}} = \frac{1.225}{\sqrt{m_m E(eV)}}$$

Al	λ_e=0.36 nm
GaAs	λ_e=21.2 nm
2D GaAs	λ_e=47.3 nm

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda_e^{\ 2}}, \Delta E \propto \frac{1}{\lambda_e^{\ 2}}$$

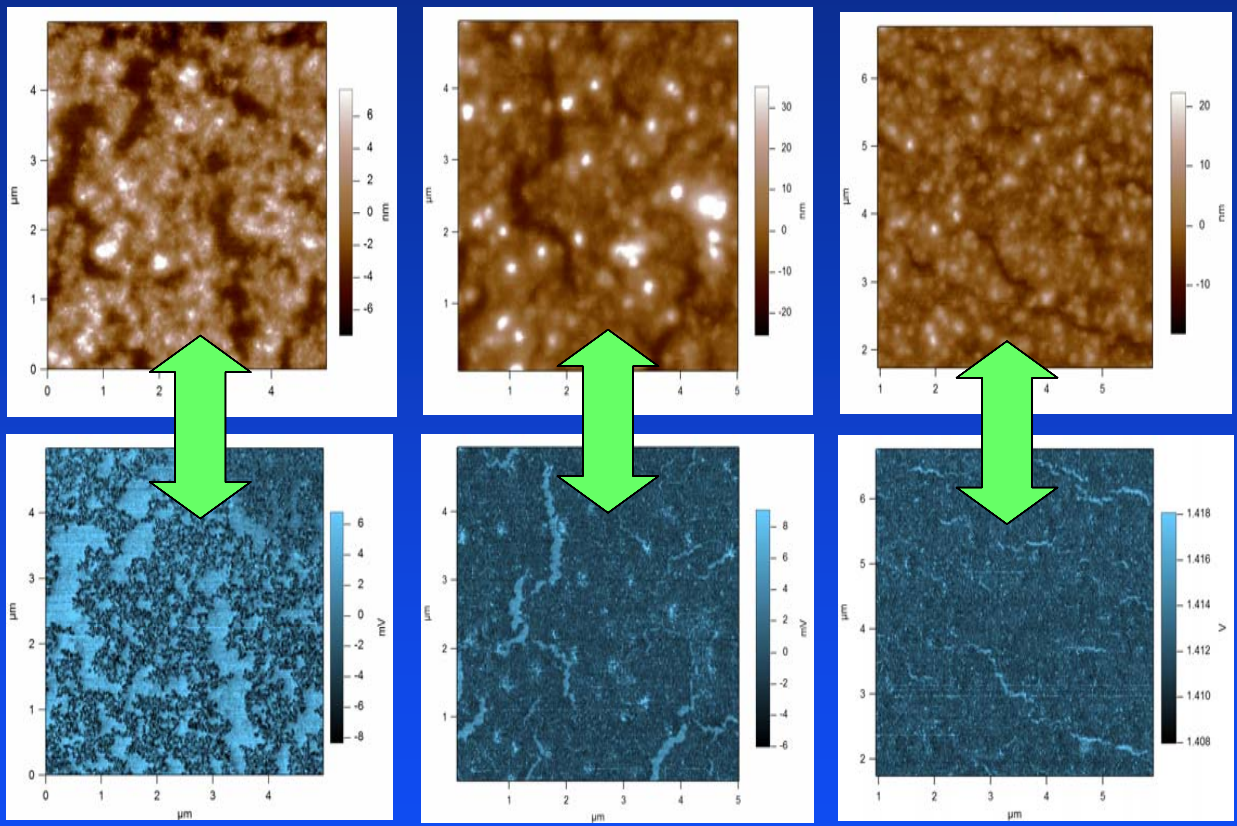


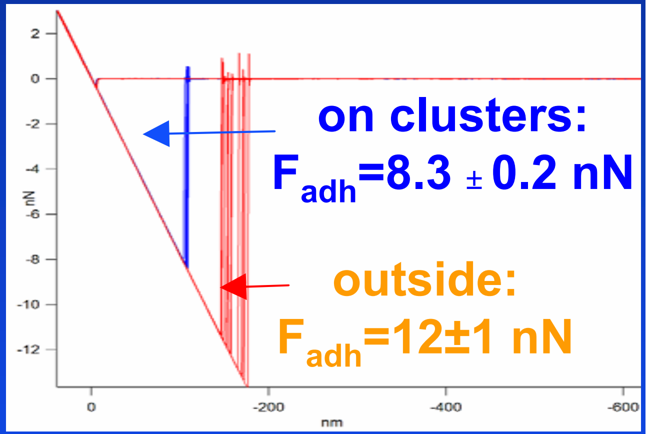
II-VI as CdSe, III-V as GaAs, Si, Ge,...

e.g. Klimov "Optical gain & SE in n-crystal QD" Science 290, 314 (00)

IIT: AFM of TiO_2 nanorods - PEMMA composites

10% TiO_2	15% TiO_2	20% TiO_2



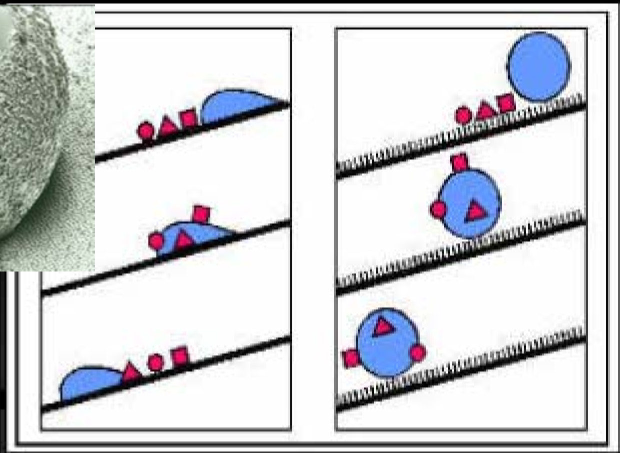


Force-distance curves on different regions

Lateral force in Contact AFM shows a strong negative contrast on the clusters, i.e. a lower friction or adhesion compared to the PEMMA nearby. Force measure-ments confirmed the lower adhesion, in agreement also with the hydrophobic character of the capped nanorods.

Superfici auto-pulenti: Effetto loto

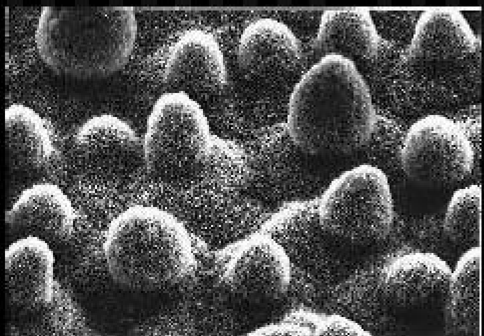
10 μm



W. Barthlott, Univ. of Hamburg

Su una superficie liscia le particelle contaminanti sono solo spostate dal movimento delle goccioline d'acqua (sinistra).

Su una superficie rugosa esse aderiscono alla goccia e rotolano via dalla foglia che rimane pulita (destra).



Cera epicuticolare

REM recording of a holographically produced self-cleaning surface.
© Fraunhofer ISE

Applicazione dell'effetto loto al tessile

nano~tex

Le fibre di cotone sono ricoperte da una "peluria" (nano-whiskers) che rende la loro superficie simile alla pelle di pesca.

Il processo consiste in (i) immersione in una sospensione di nano-whiskers e (ii) trattamento termico.

La peluria crea un cuscino d'aria che assicura l'"effetto loto" .

Clarity Defender Automotive-Glass Treatment

This product provides an invisible barrier for windshields, which repels rain and helps prevent snow, ice, bugs and tar from sticking. This is Valley View, Ohio-based Nanofilm's new product, Clarity Defender. A Clarity Defender treated windshield increases driver vision 34% on a rainy night, thereby adding approximately one second to driver response time. At 60 mph, that's an extra 88 feet of pavement. Clarity Defender is the first of an automotive-product line being launched in 2005 by Nano-Film, which we featured last December for their coating technologies in sunglasses.

Temptative conclusions

- Drexler assemblers:
  probably impossible

+ Biotechnology:
  partially successful

= supramolecular chemistry:
  not that useful so far

+ nanostructured materials
  can be fancy

- standard lithography
  close to the limit

+ novel fabrication methods
  based on weak interactions
  i.e. self assembly

keep going with:

• biological inspiration
• chemical synthesis
• physical manipulation
  & analysis

thank you
for your attention