How Small is Important

by Paul O’Brien
Professor of Inorganic Materials, The Department of Chemistry, and The Manchester Materials Science Centre

How small can you get?

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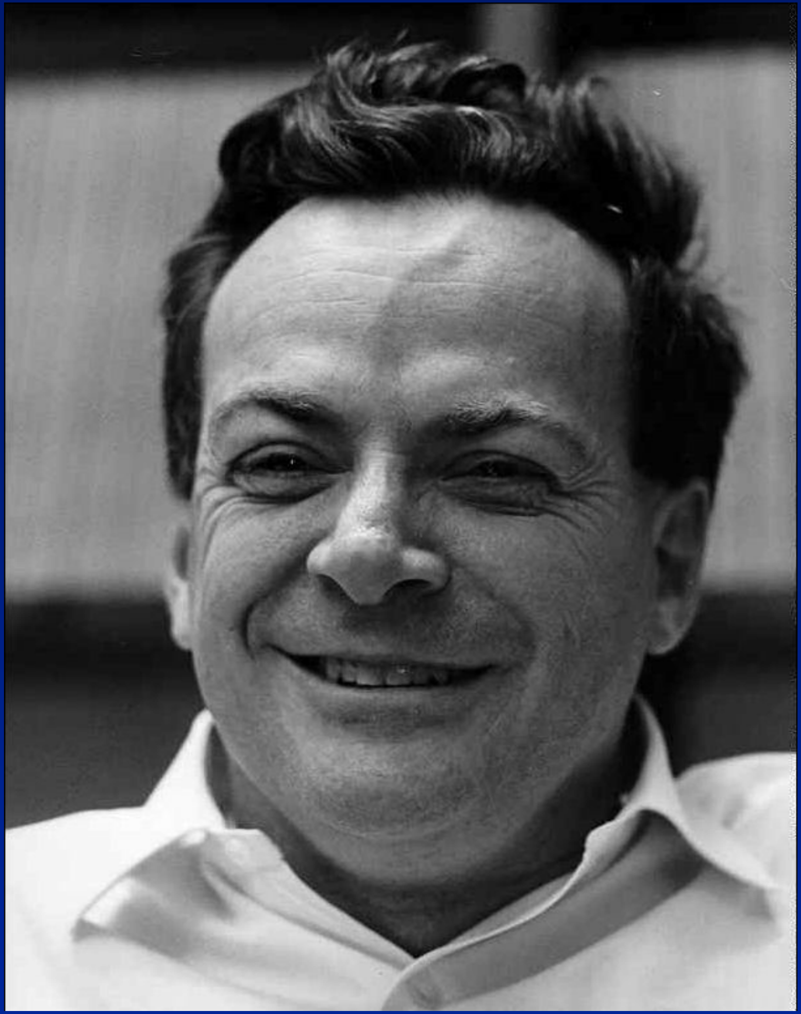
How small can you get?

How small can you get?

MANCHESTER
17/02/06



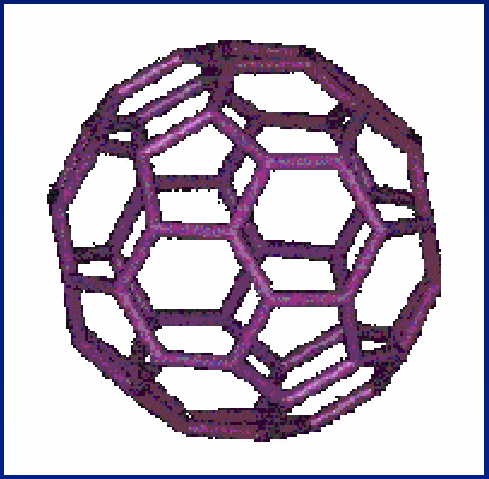
In the early 1950s Richard Feynman published and article entitled :
‘There is plenty of room the bottom’

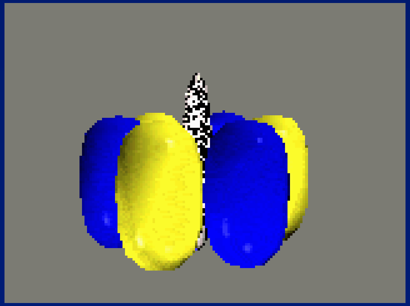
He also issued an interesting *and expensive (to him) challenge*

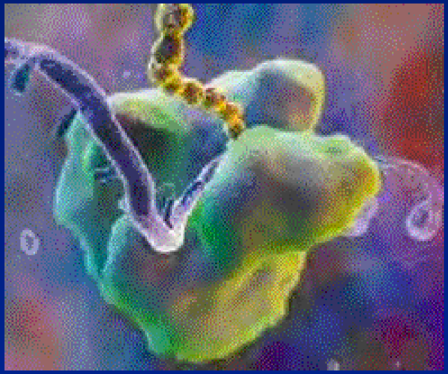
- *The first was rapidly solved*
- *The second shortly before his death in 1988*

DART

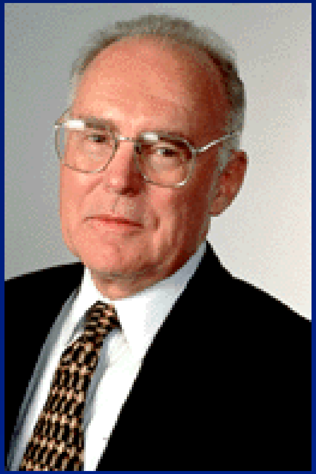
Discovery







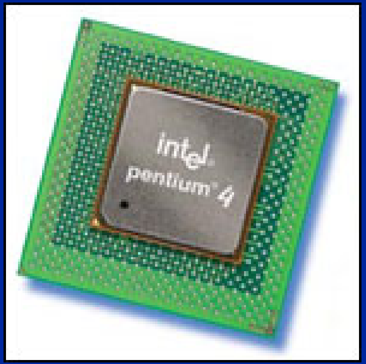
Reason



Access

Scanning
Tunneling
Electron
Microscopy

Technology



Moore's Law: Chip Power Doubles Every 18 (24) Months

20 Years of Mesoscopics

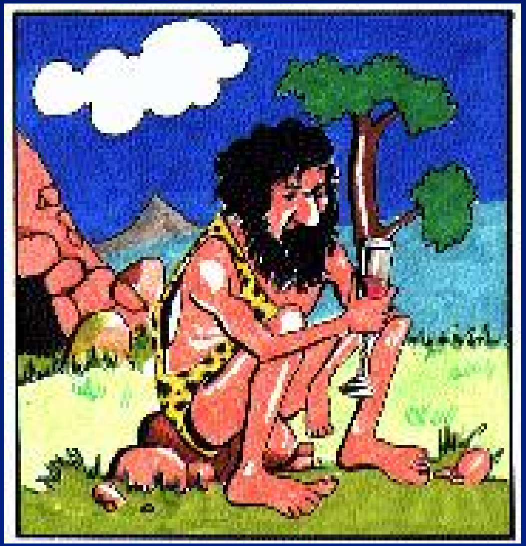
Year	Processor Name	Number of Transistors	Minimum Feature Size
1971	4004	2300	10 micron
1974	8008	3500	10 micron
1975	8080	6000	6 micron
1976	8085	6500	3 micron
1978	8086	29000	3 micron
1982	80286	134,000	1.5 micron
1985	80386	275,000	1.5 micron
1989	Intel486	1.2 million	1 micron
1993	Pentium	3.1 million	800 nanometer
1997	Pentium II	7.5 million	350 nanometer
1999	Pentium III	9.5 million	250 nanometer
2000	Pentium IV	42 million	180 nanometer

Continuous Improvement of the Same Approach:

Making a Master Mask and Its Replication by Photolithography

2002	2005	2008	2011	2014
130 nm	100 nm	75 nm	50 nm	35 nm

BOTTOM-UP APPROACH

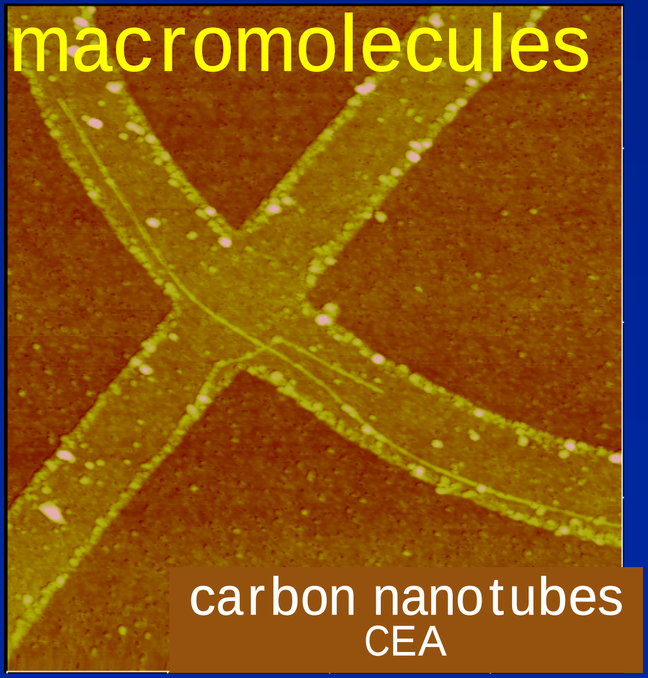


Long Track Record in Nanotechnology:

glass-making in Mesopotamia 4,500 BC

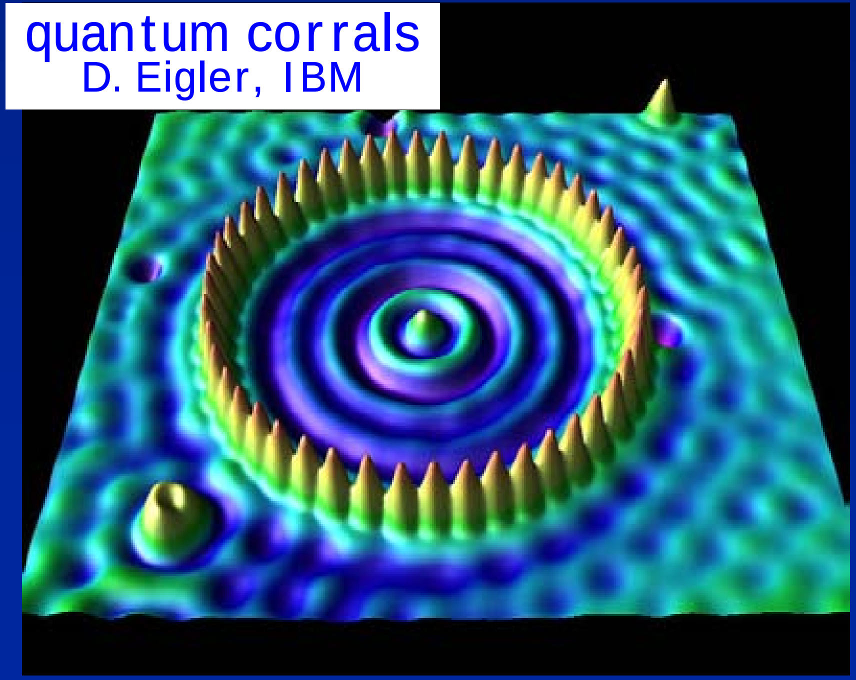
Recent Advances

making macromolecules



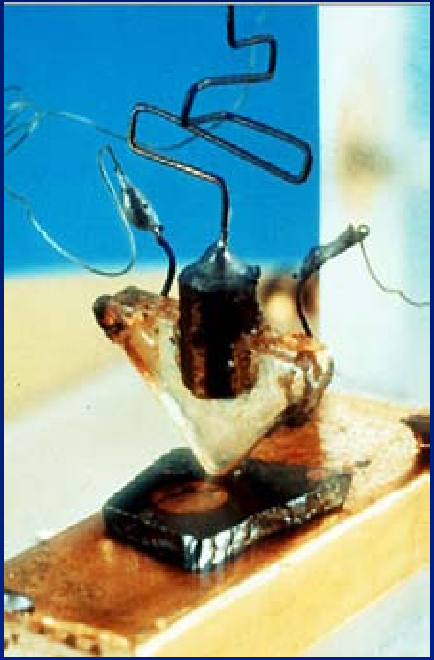
carbon nanotubes
CEA

atomic assembly

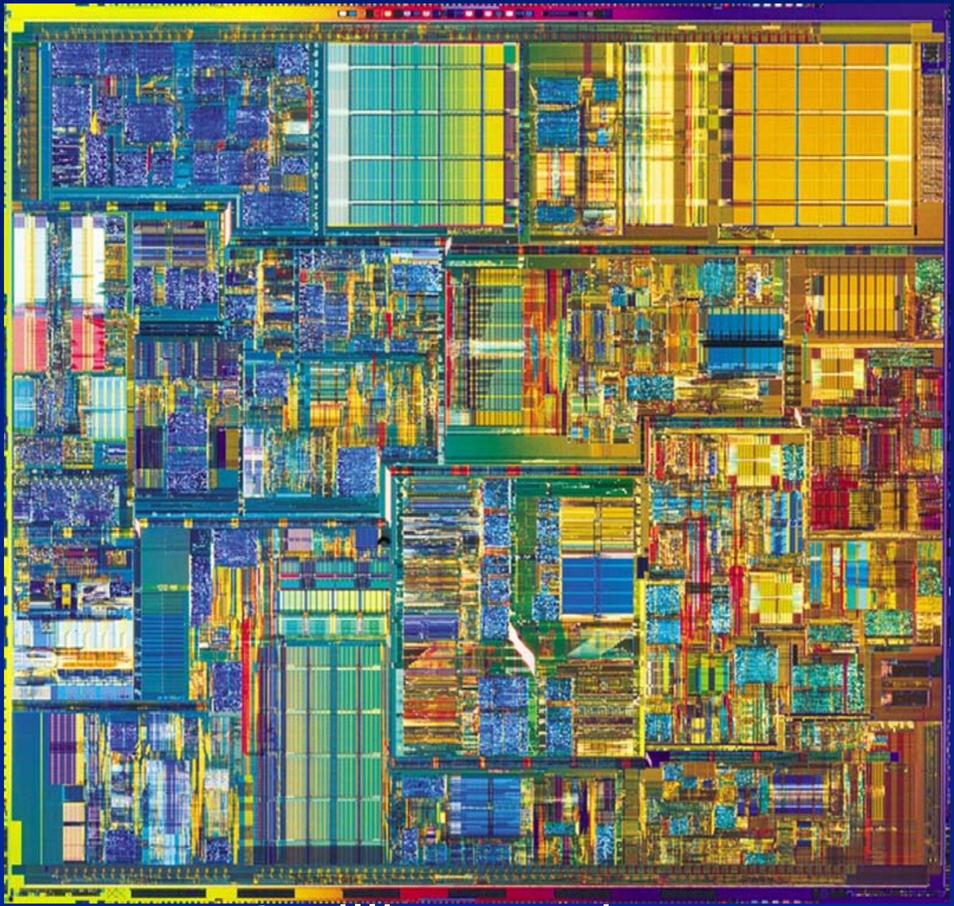


quantum corrals
D. Eigler, IBM

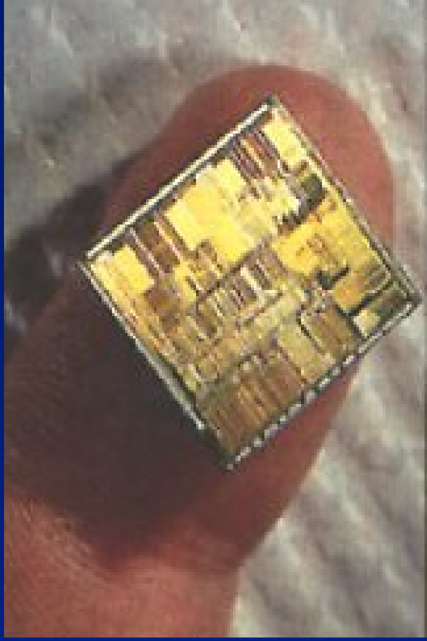
TOP-DOWN APPROACH



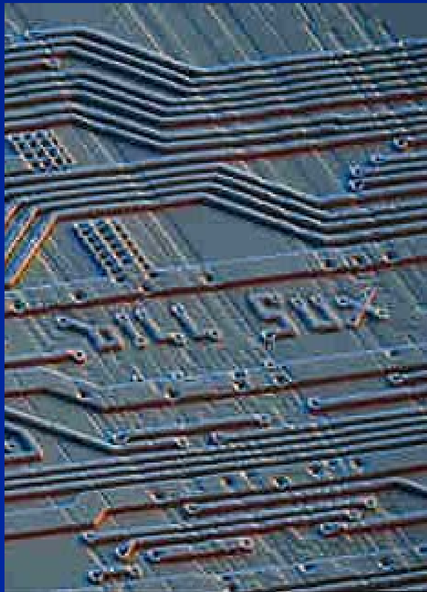
1947:
first transistor



42 million transistors
features down to 180 nm



2000:
Pentium IV

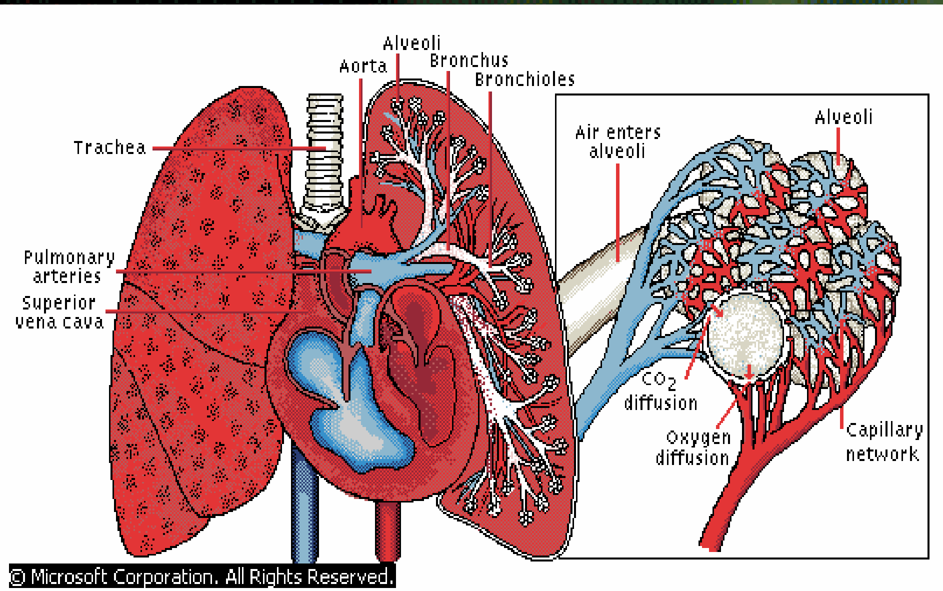


Structure of the Talk

- Size just as a concept (length, area and volume)
- Size and the structure of matter (atoms, molecules)
- Size and the control of properties
- Size and engineering limits

Size does matter

‘What a curious feeling I must be shutting up like a telescope’



Alveoli
Aorta
Bronchus
Bronchioles
Trachea
Pulmonary arteries
Superior vena cava
Air enters alveoli
Alveoli
CO_2 diffusion
Oxygen diffusion
Capillary network
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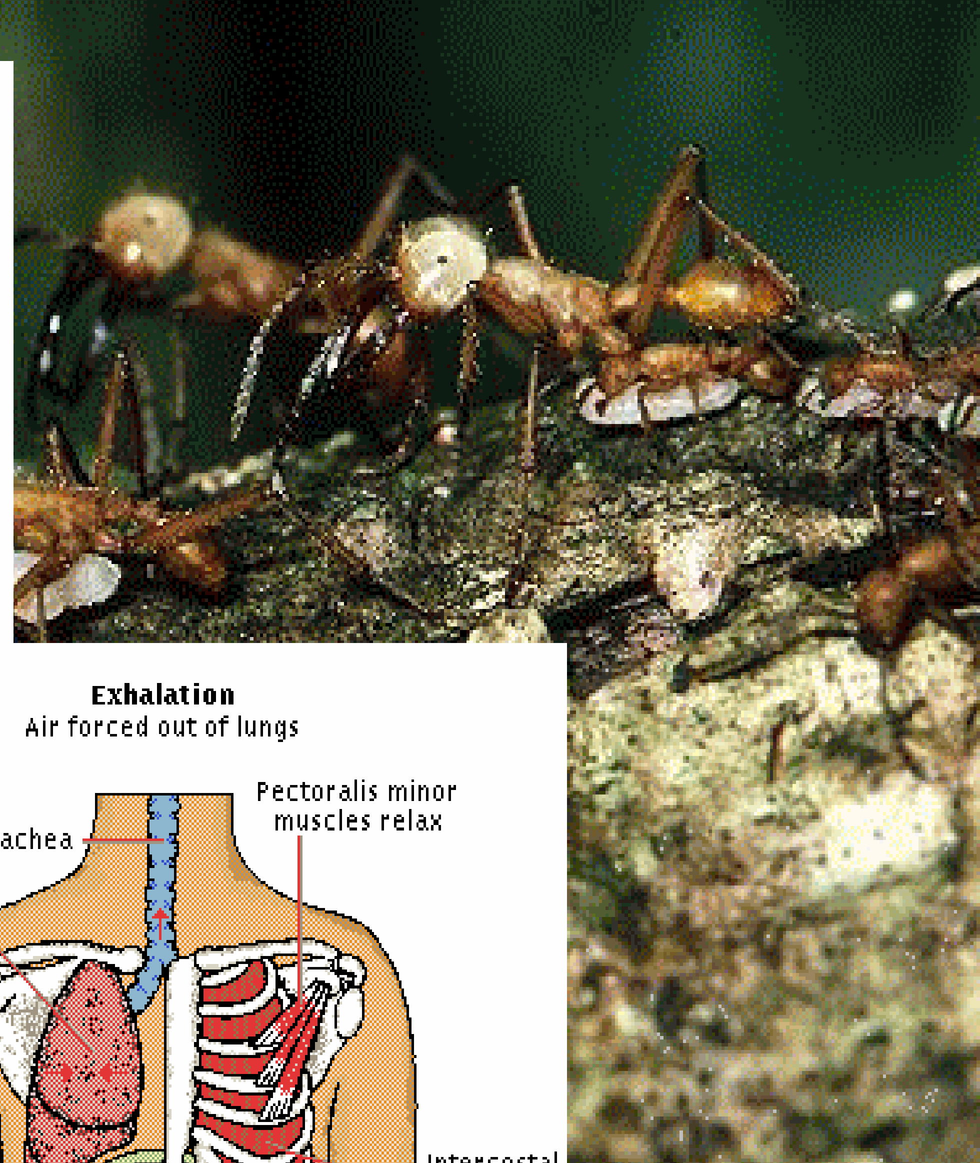

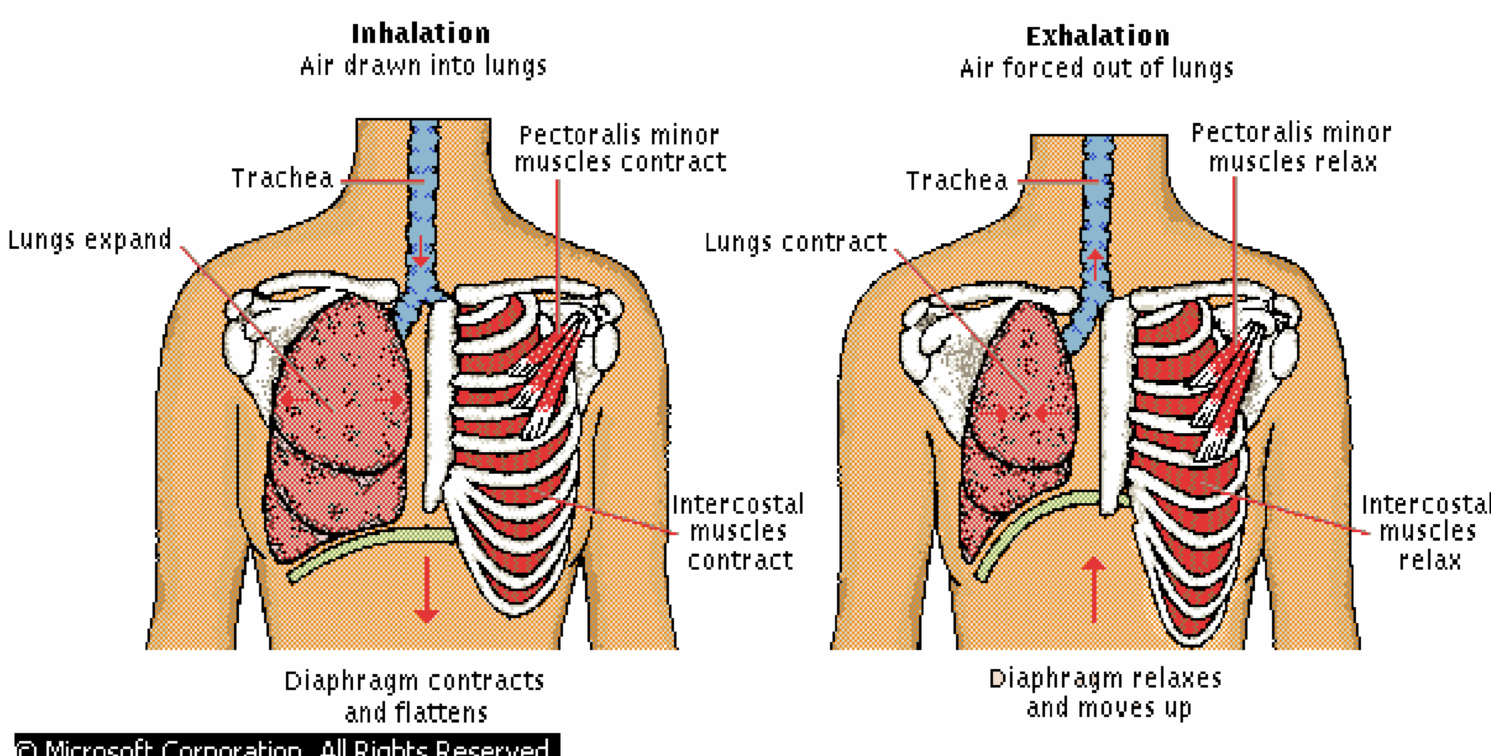

Inhalation
Air drawn into lungs
Trachea
Pectoralis minor muscles contract
Lungs expand
Intercostal muscles contract
Diaphragm contracts and flattens
Exhalation
Air forced out of lungs
Trachea
Pectoralis minor muscles relax
Lungs contract
Intercostal muscles relax
Diaphragm relaxes and moves up
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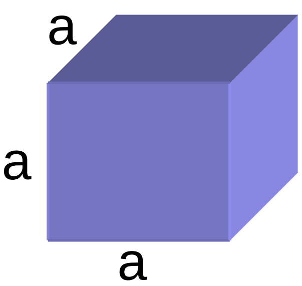
High surface to volume, a simple model

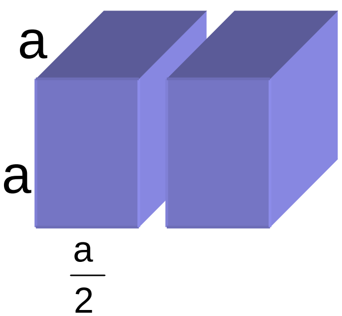


Surface area

$SA_{3D}=6a^2$

Volume

$V=a^3$

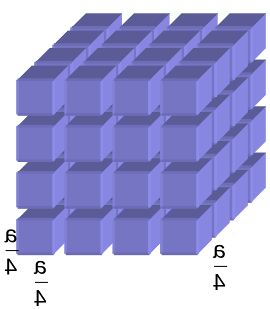


Surface area

$SA_{3D}=8a^2$

Volume

$V=a^3$

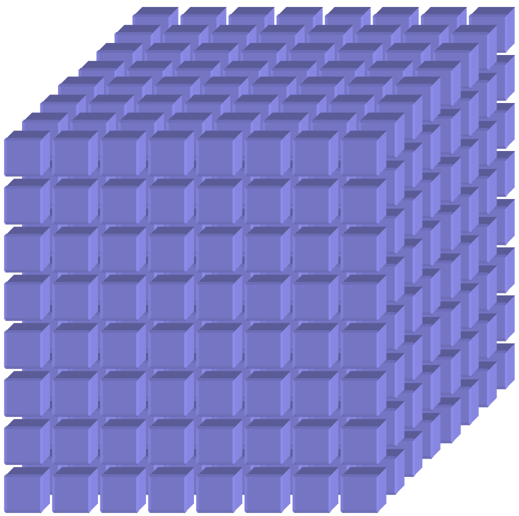


Surface area

$SA_{3D}=24a^2$

Volume

$V=a^3$



Surface area

$SA_{3D}=48a^2$

Volume

$V=a^3$

Physical Limitations

How Small Can We Really Get?

“To see a World in a grain of sand,
and Heaven in a wild flower,
Hold Infinity in the palm of your hand,
and Eternity in an hour.”

Auguries of Innocence

W. Blake

How much in the palm of a hand?

- Lets say we have a heap $.04 \times .04 \times .04\ m^3$

- $.0000064\ m^3$ or $6.4 \times 10^{-5}\ m^3$

- with a density of 2.65 (sand is silica)

- it comes to 170 grams of material

How big is a grain of sand?

We can see them so lets say 0.01mm

(actually that’s very very fine sand)

Think of a ruler !

The volume of each grain would be *ca* $1 \times 10^{-15\ m}$

How Many Grains?

The volume of each grain would be 1 x 10^{-15} m

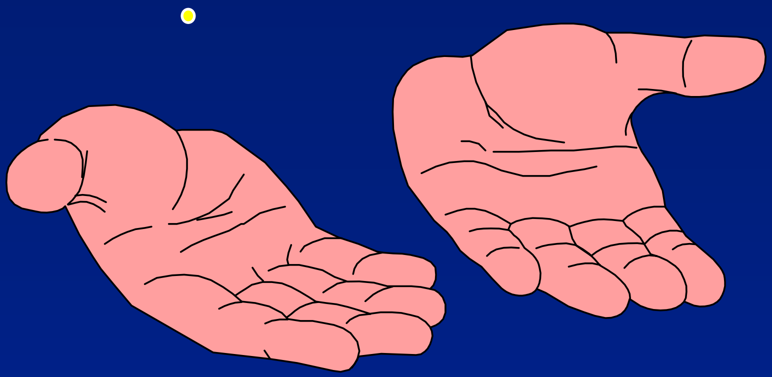
The pile is 0000064 m^3 or 6.4 x 10^{-6} m^3

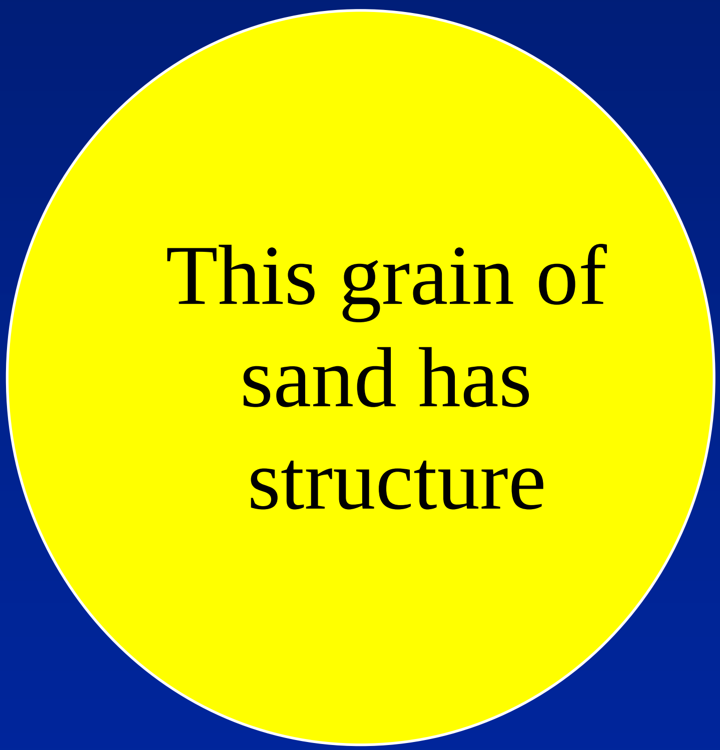
So we hold in the palm of our hand

6400 million grains of sand
(6.4 x 10^{10})…64 giga bits

A large number but not infinity!

The concept of the atom





It is made of atoms

How many molecules in a grain?

Sand is mainly SiO_2

With a molecular mass of ca 60
a mole weighs 60 gm

The weight of an individual molecule
is $60/N_o = 9.6 \times 10^{-23}$ gm

We have ($2.65 \times 10^{-9} \div 9.6 \times 10^{-23}$ gm) molecules

Which Hand holds the More Information?

6.4 x 10^{10}

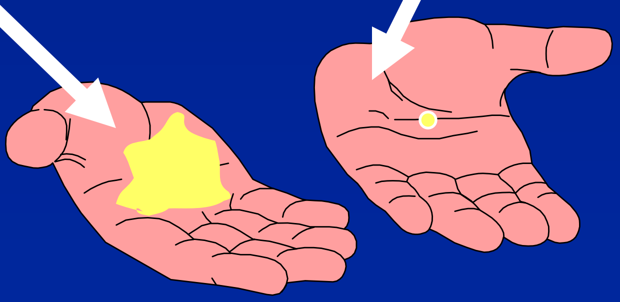
6400 million

64 giga bits

2.66 x 10^{13} molecules

ie SiO_2 units

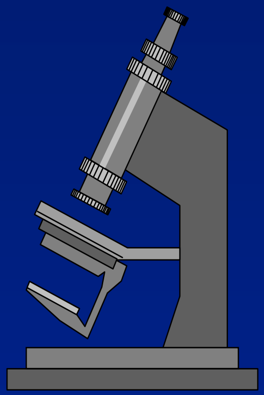
26.6 terra bits



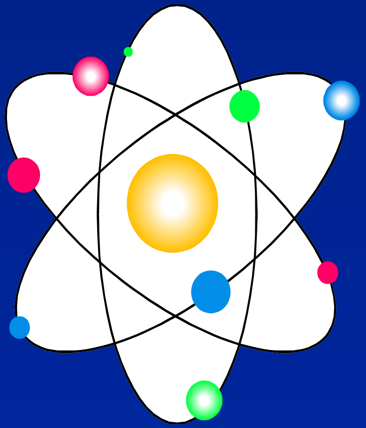
It depends on how we can read

The atomic concept places constraints on the system

These are classical



Things we can see

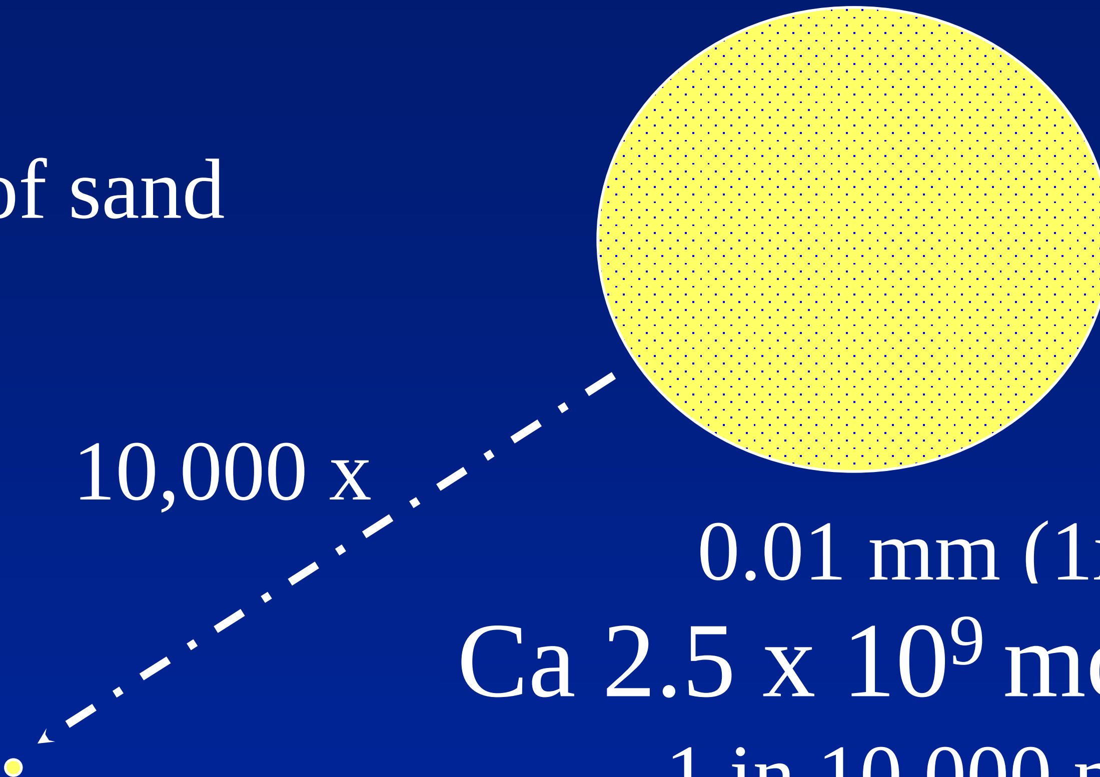


And also non classical

The world of Quantum Mechanics
……………………..of atoms!!!

How much is on the surface?

Our Grain of sand



10,000 x

0.01 mm (1x 10^{-5} m)

Ca 2.5 x 10^{9} molecules

1 in 10,000 molecules

5 nm (5 x 10^{-9} m)

Ca 6350 Molecules

2 in 100 i.e 2%

How Small Can We Make the Grains?

Because of high surface areas conventional powders methods reach their limits at 10^{-6} m (1 micron)

Smaller particles can be made but special methods are needed!

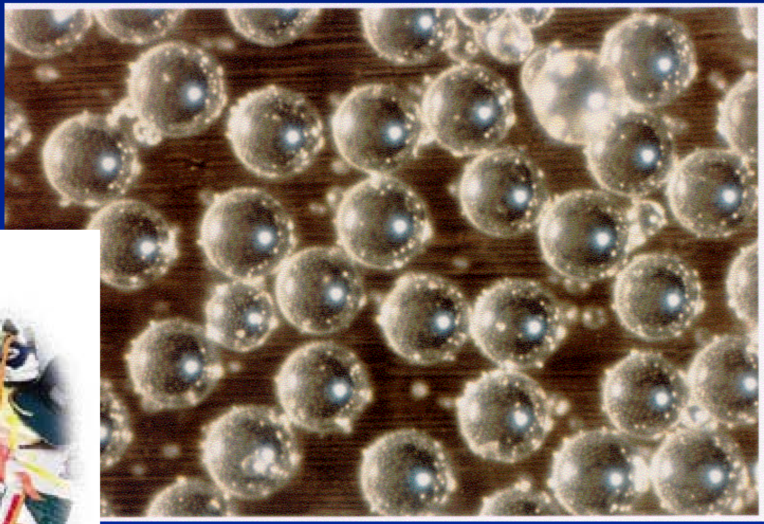
And nature has in store for us a surprise
But first lets look at some pictures

What are lost dimensions?

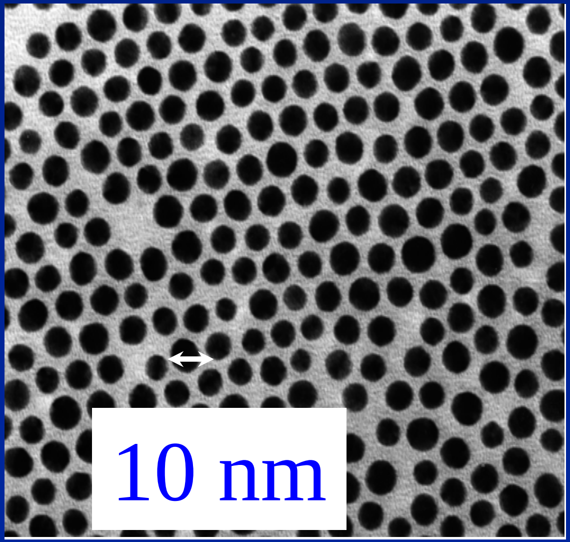
1850

Industrial Development and
a History of Precise Size Control

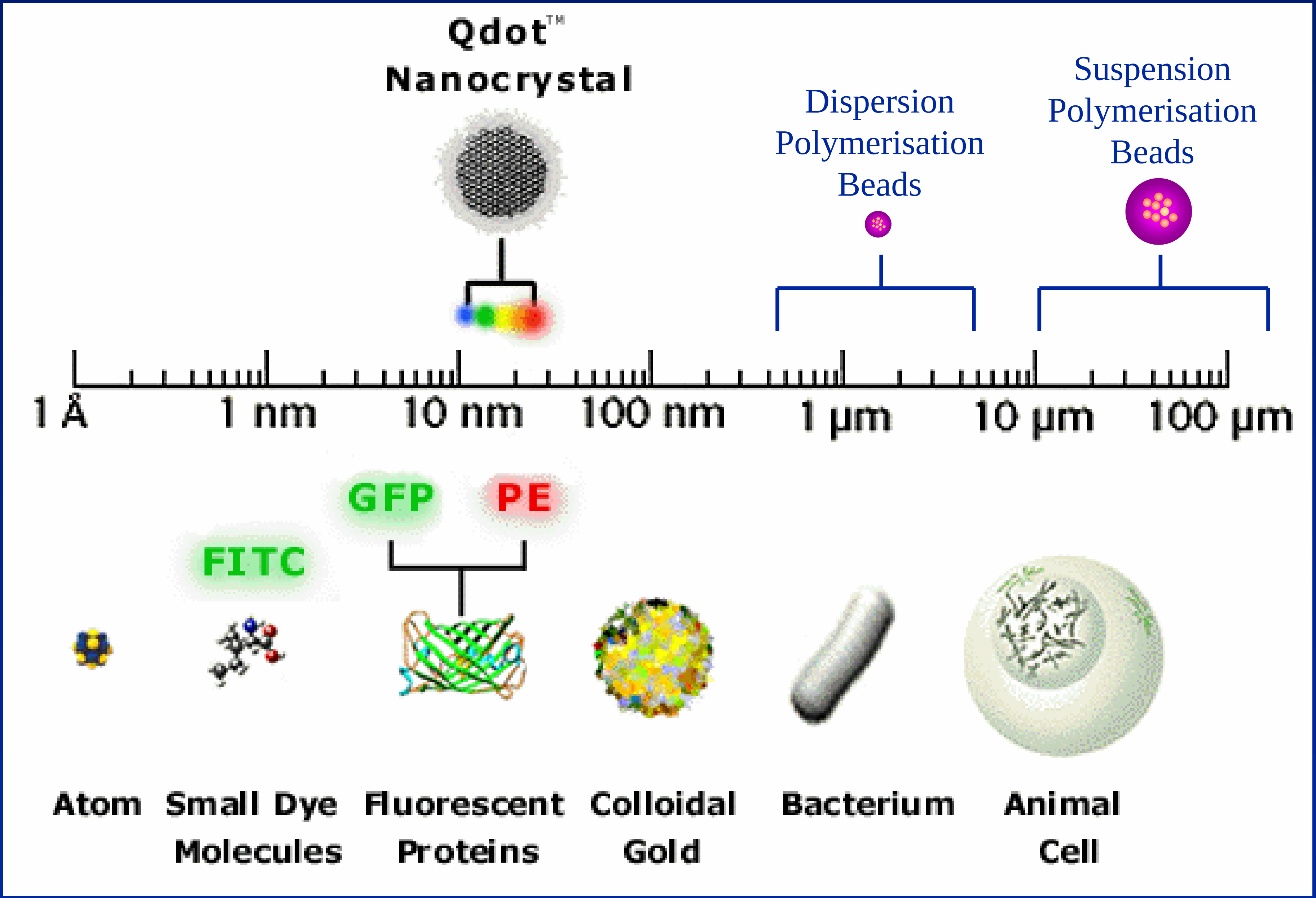
1980



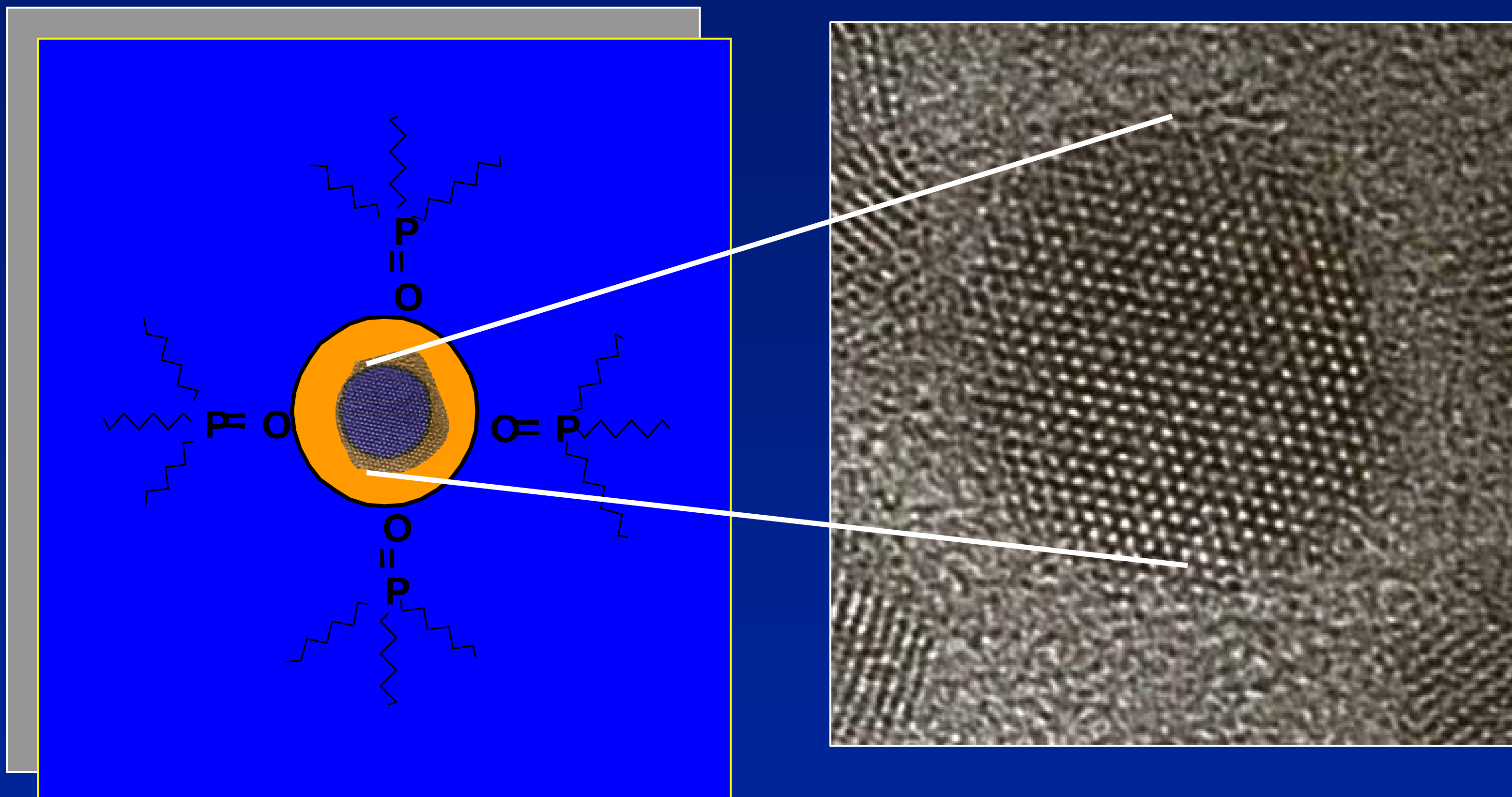
2005/6



Ball Bearings for the 21st Century!

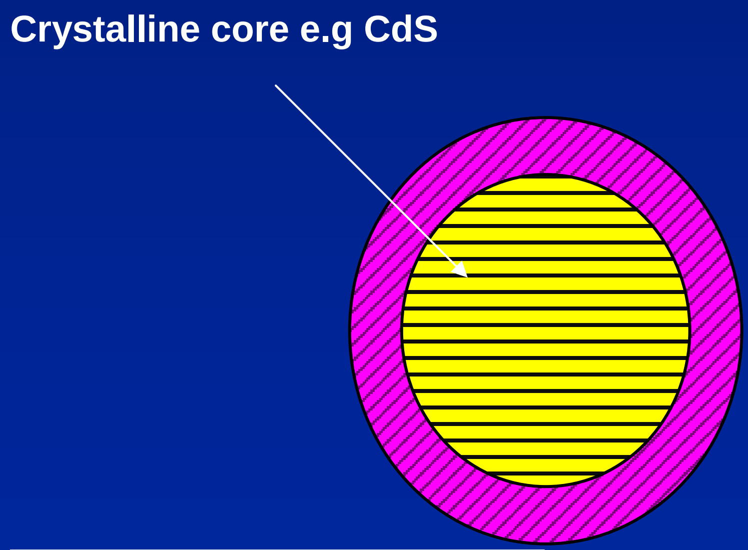


Qdot™
Nanocrystal
Dispersion
Polymerisation
Beads
Suspension
Polymerisation
Beads
1 Å
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
GFP
PE
FITC
Atom
Small Dye
Molecules
Fluorescent
Proteins
Colloidal
Gold
Bacterium
Animal
Cell

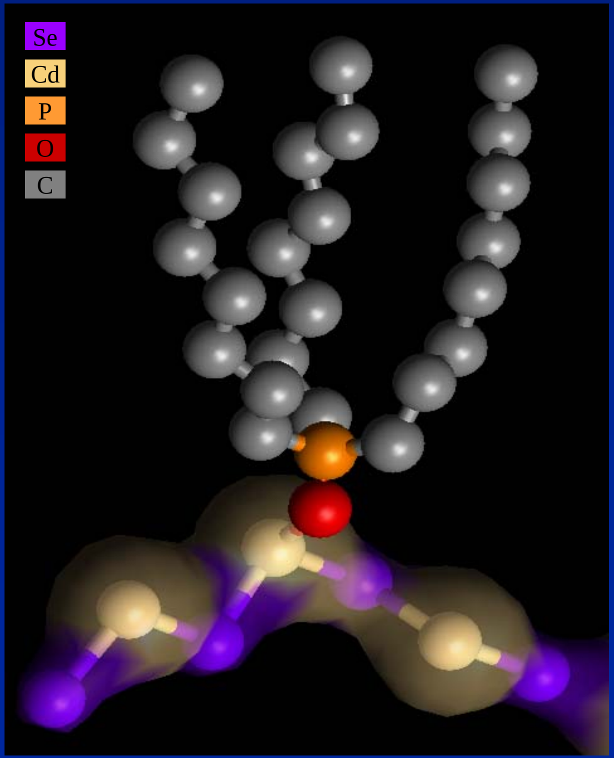

P
O
P
O
O
P
O
P

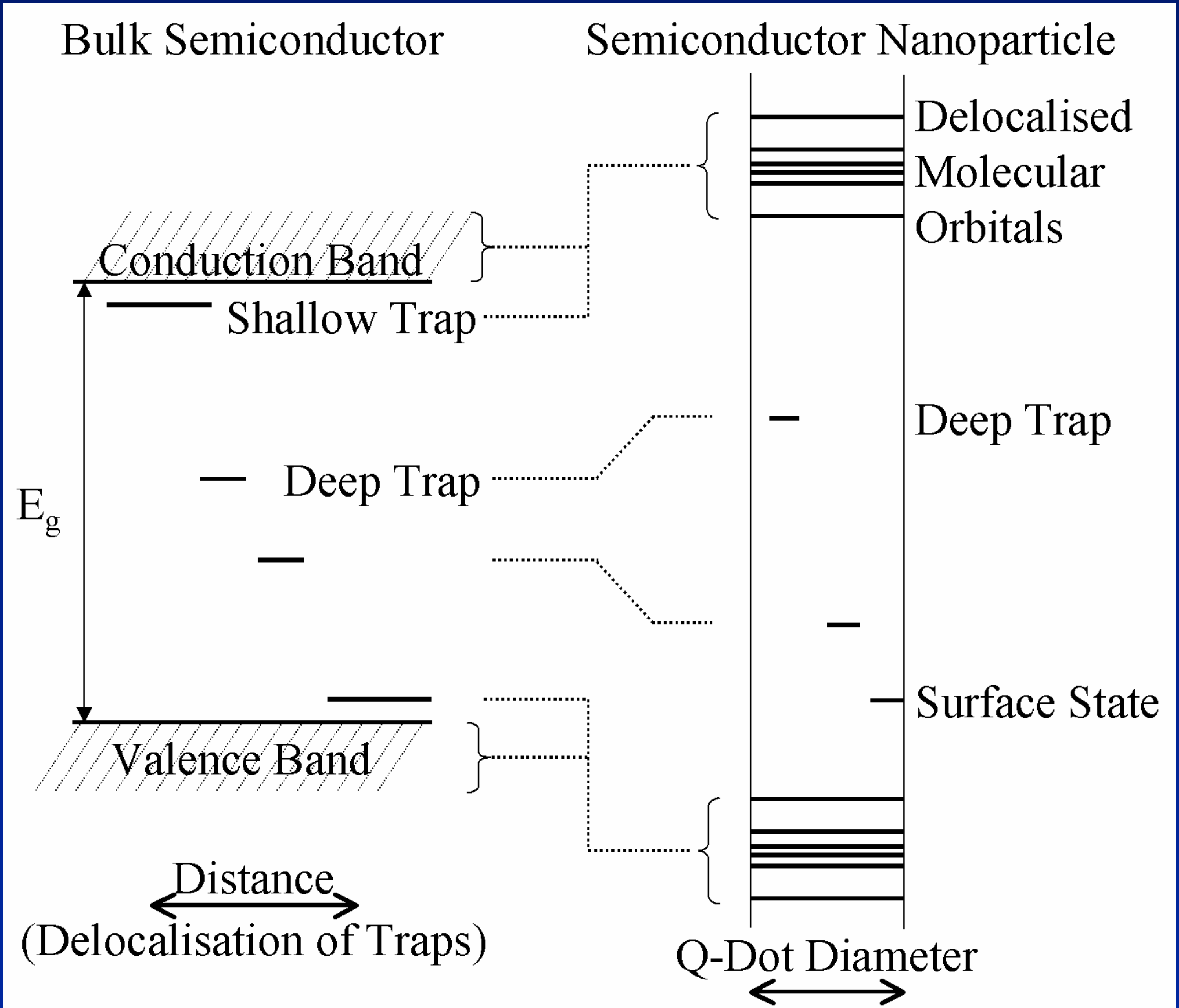
Development of quantum dot manufacturing technology

- **It is possible using our IP to manipulate the optical, electronic, magnetic and catalytic properties of these materials to those required.**
- **Nanopaticles have unique chemical, physical and electronic properties from those of the corresponding bulk material and are a new range of materials.**

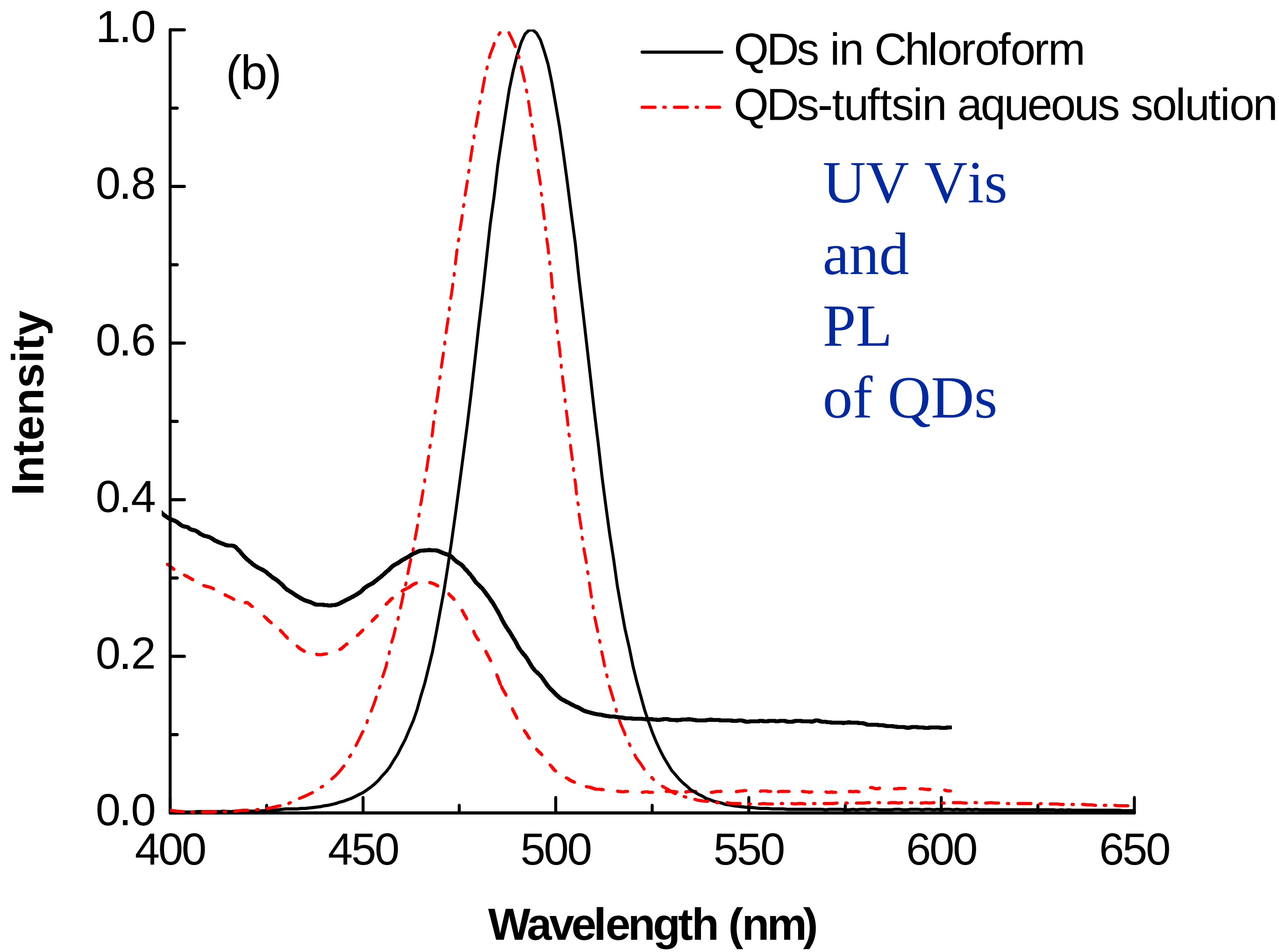


'Metal Organic Dot'



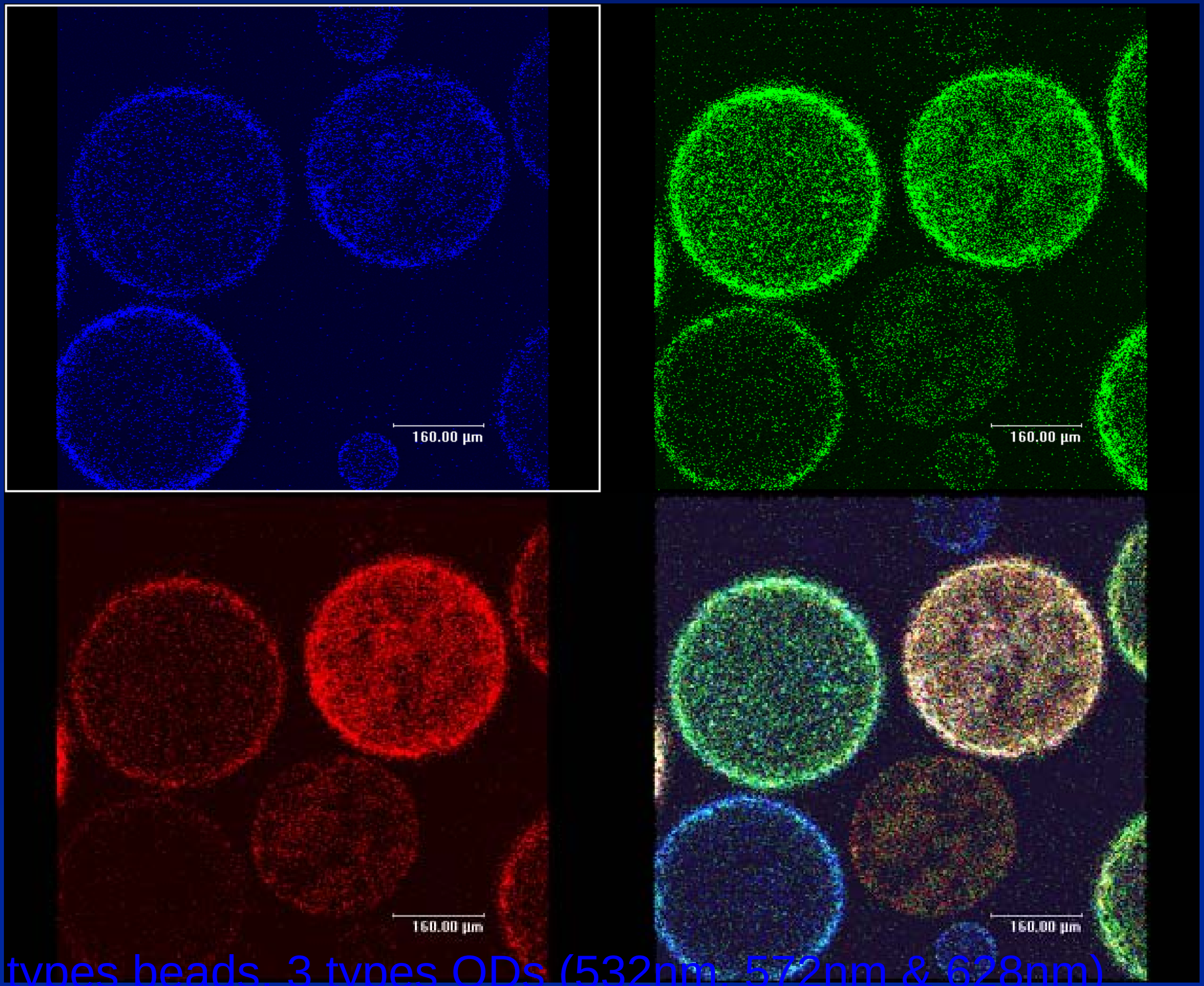

Bulk Semiconductor
Semiconductor Nanoparticle
Delocalised
Molecular
Orbitals
Conduction Band
Shallow Trap
Deep Trap
Deep Trap
E_g
Surface State
Valence Band
Distance
(Delocalisation of Traps)
Q-Dot Diameter


400
500
600
700
Wavelength (nanometers)

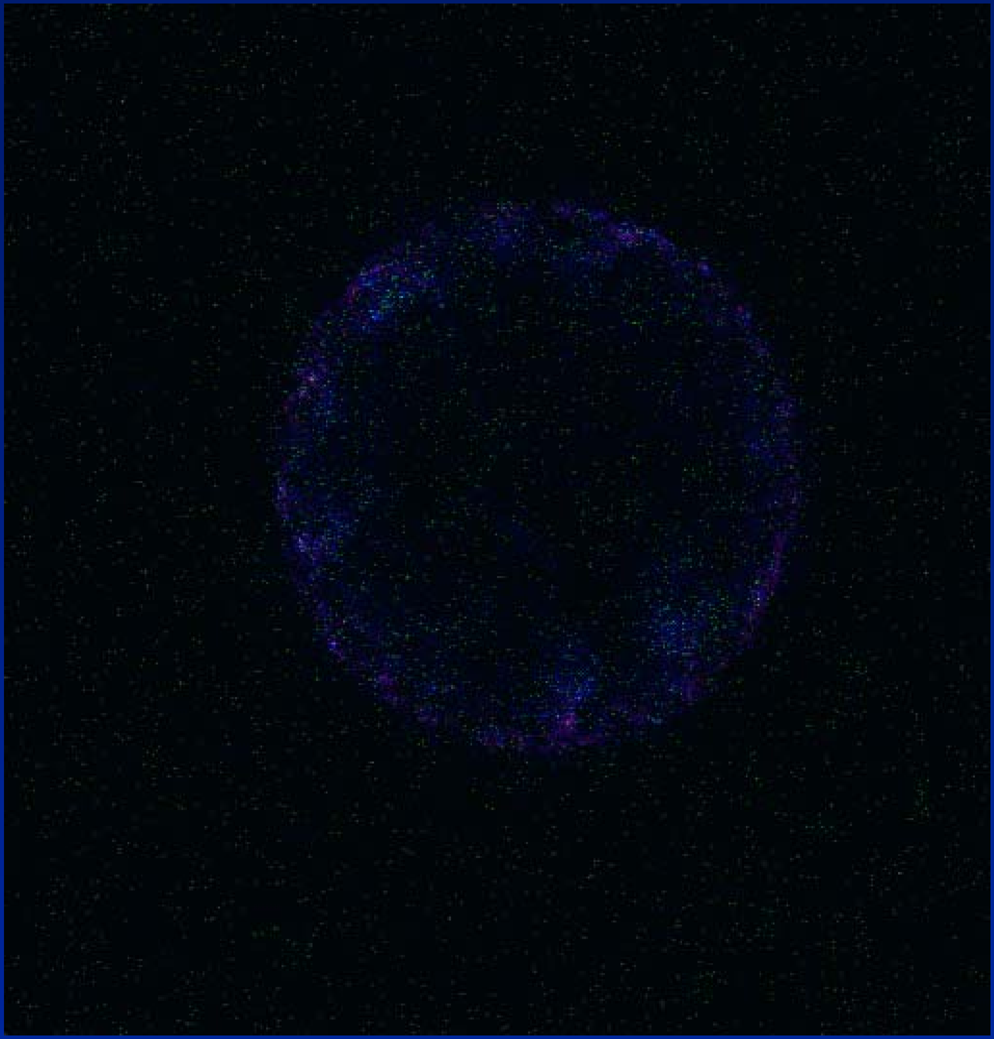

(b)
QDs in Chloroform
QDs-tuftsin aqueous solution
UV Vis
and
PL
of QDs
Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650

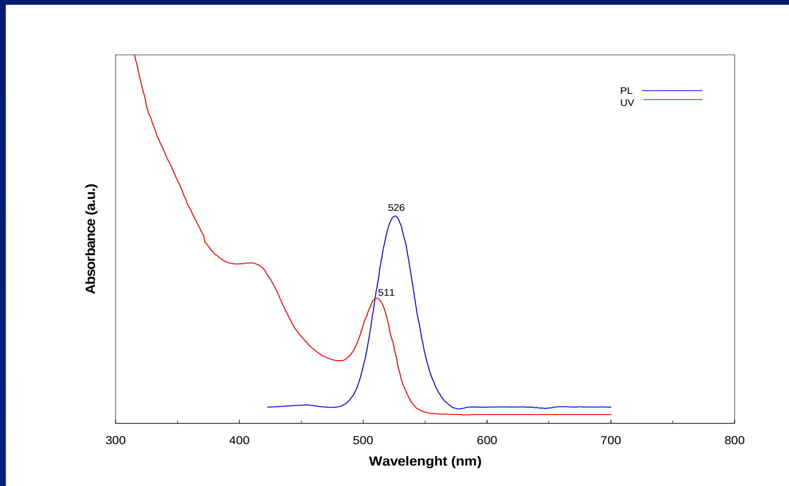
Nanoco “Production Quantities of Quantum Dots”

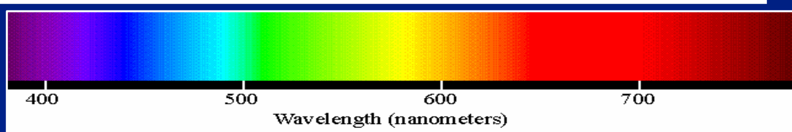
Identification of Beads by Fluorescence Profiles



4 types beads, 3 types QDs (532nm, 572nm & 628nm)



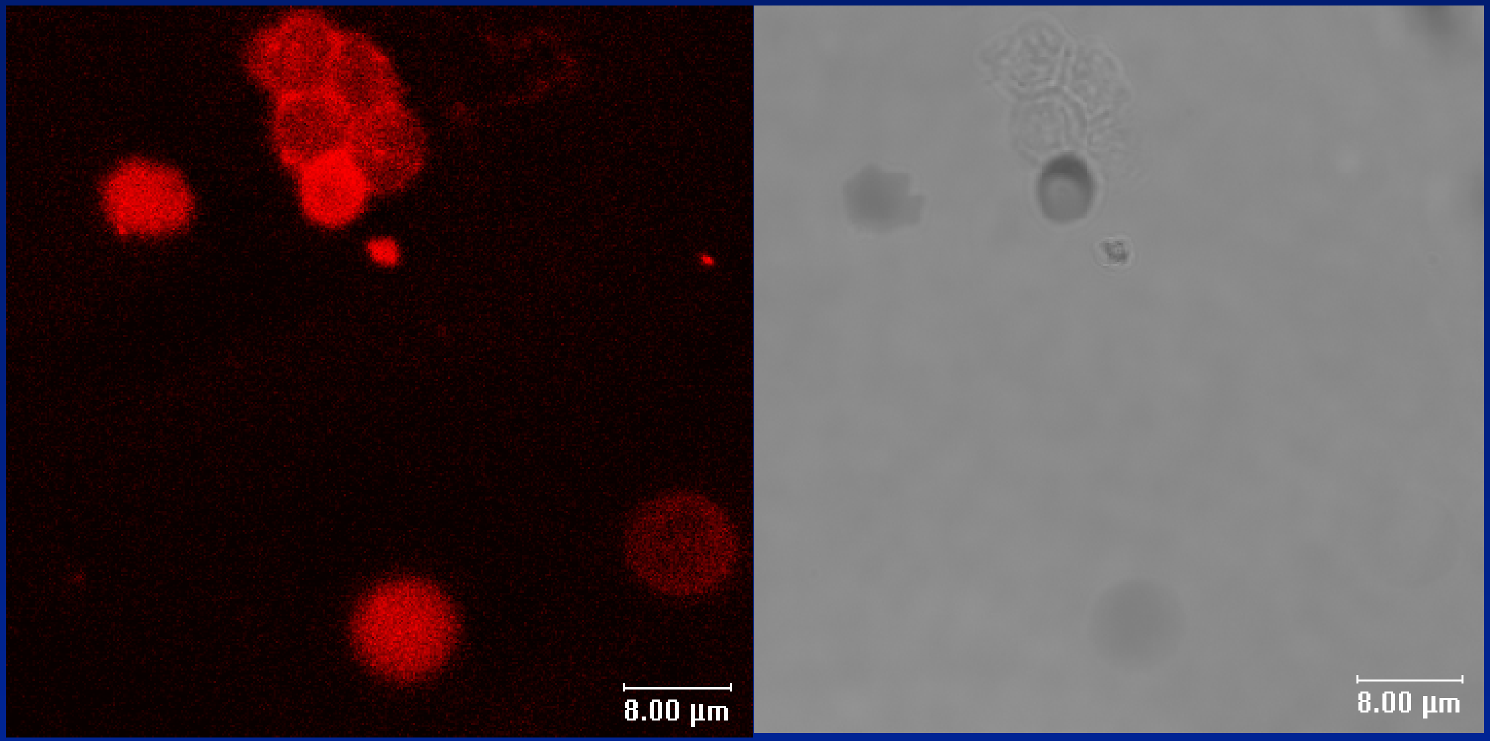




- Quantum dots absorb light over a wide wavelength range but have narrow emission spectra.
- The solutions, all contain the same semiconductor material (CdSe) but are different colours because unlike bulk CdSe, when below a certain size limit, we can control the electrical properties of the particles, by simply changing their size.

Large scale preparation of quantum dots

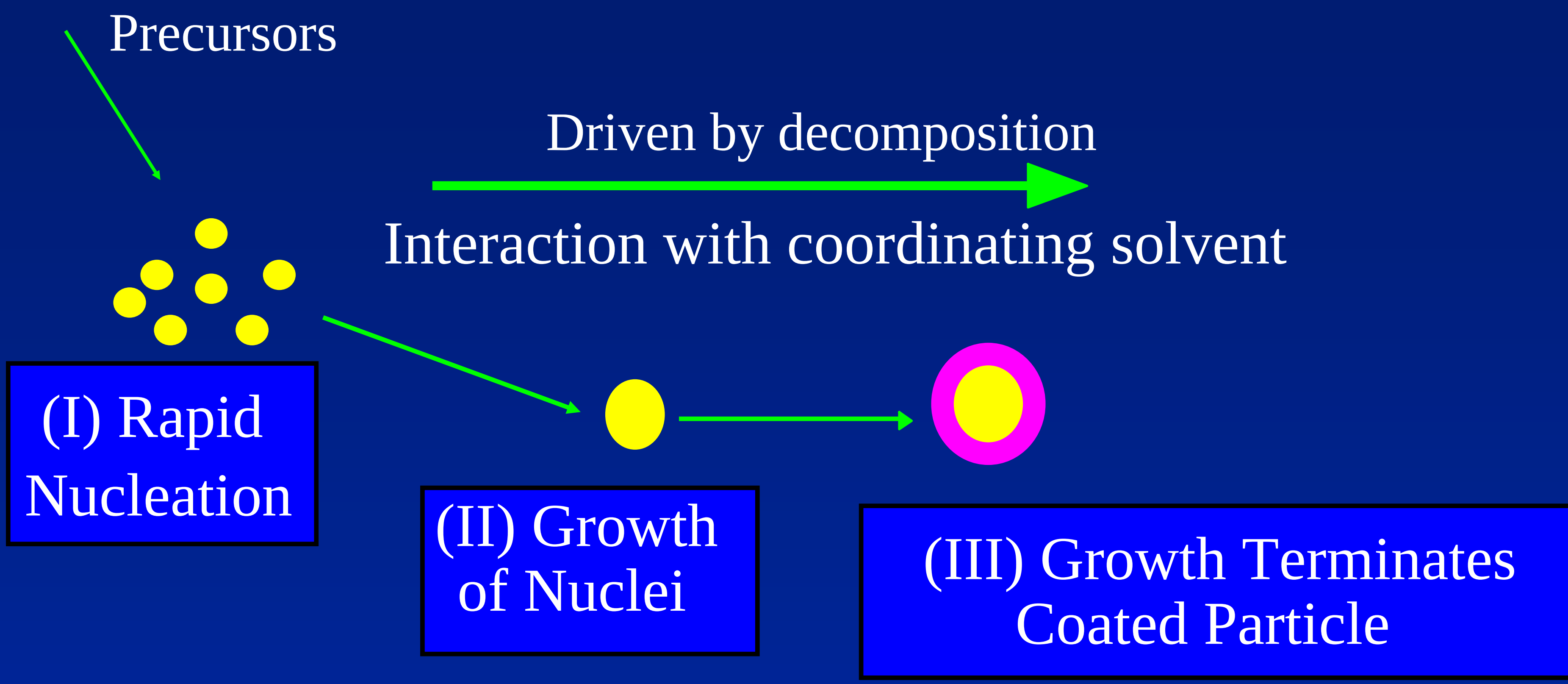
Lymphocyte Cells



Confocal pictures of different size 615nm

CdSe/ZnS QDs labeling Lymphocyte Cells

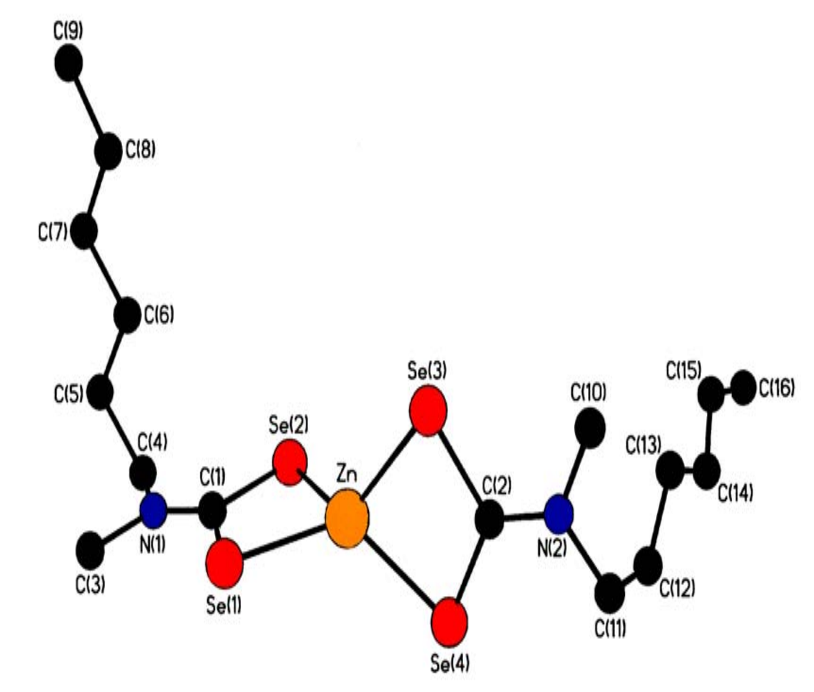
- Bis(3-aminopropyl) terminated Poly(ethylene glycol) ($H_2N-(CH_2CH_2O)_n-NH_2$) or DHLA-PEG were used to modify the surface of QDs to obtain QDs aqueous solution.
- The above QDs aqueous solution were conjugated with Tutfisn peptide and used to label macrophage and lymphocyte cells.



Requirements for Nanoparticulate Synthesis

. $Cd(Se_2CNRR')_2 \longrightarrow CdSe$

O'Brien et al Chem Comm, 1998 1849, ibid 1999, 1573.



Patent Family
UK patent application No. 9518910.6
PCT application WO 97/10175.
US patent No. 09/043,258 (Granted)
EP patent application No. 96927134.5

$Me_2Cd + TOPSe \longrightarrow CdSe$

The NanoCo Process

Current applications

- Biological screening
- Imaging
- Sunscreen

1 - 5 Years

- Light emitting diodes
- Chemical\biological sensors
- Flat panel displays
- Solar cells

6 - 10 Years

- Solar cells
- Date storage
- Security application/ Bar coding

10 – 30 Years

- Single electron devices
- Quantum computing

- Replacement for luminescent dyes and inorganic materials
- Better optical and electronic efficiencies
- More stable (photo-bleaching)
- More versatile (tune from UV to near IR)

A Crowd-Bulk Behaviour Size Dependence

A Smaller Group e.g. The Team

5-aside

7's

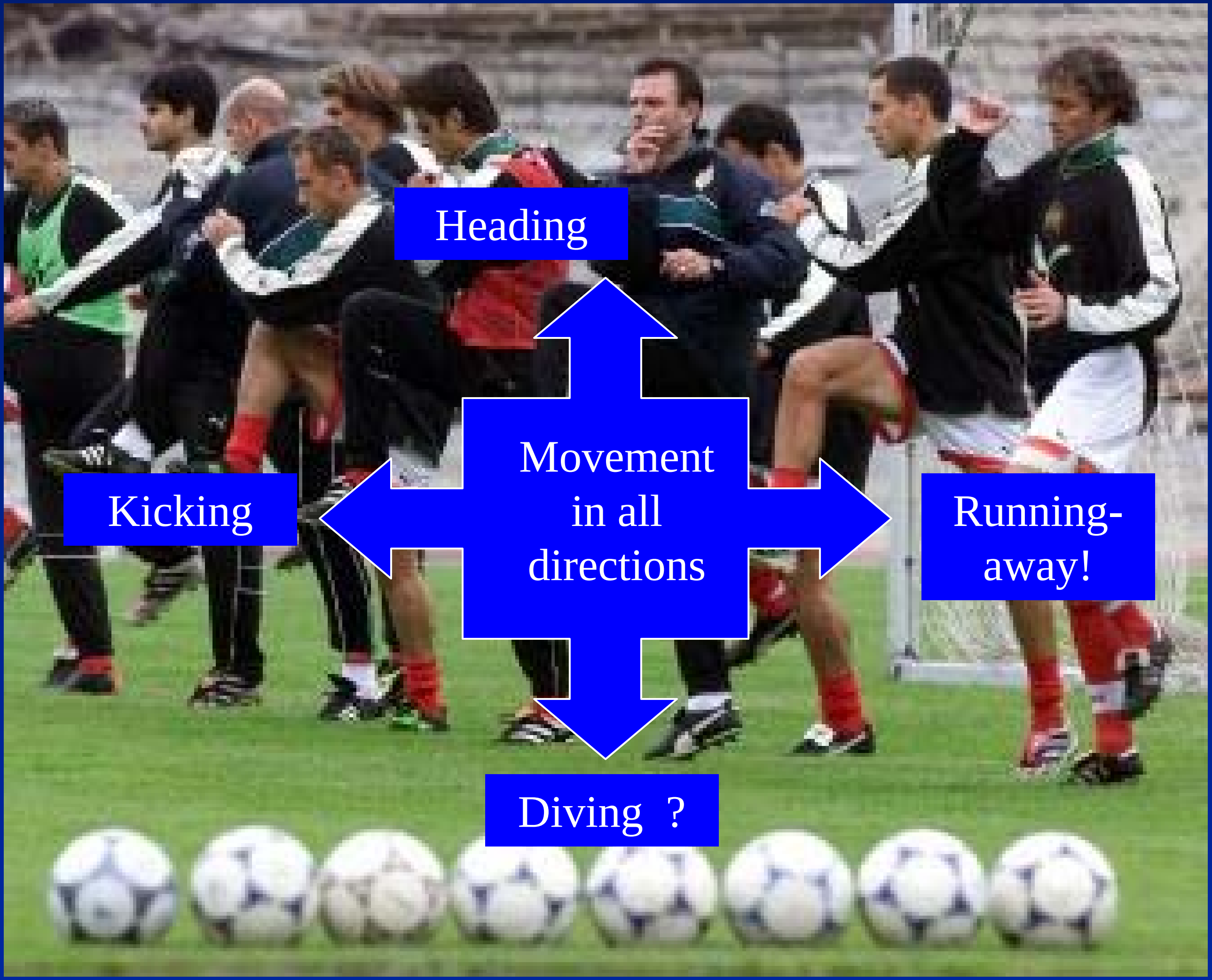
Volleyball

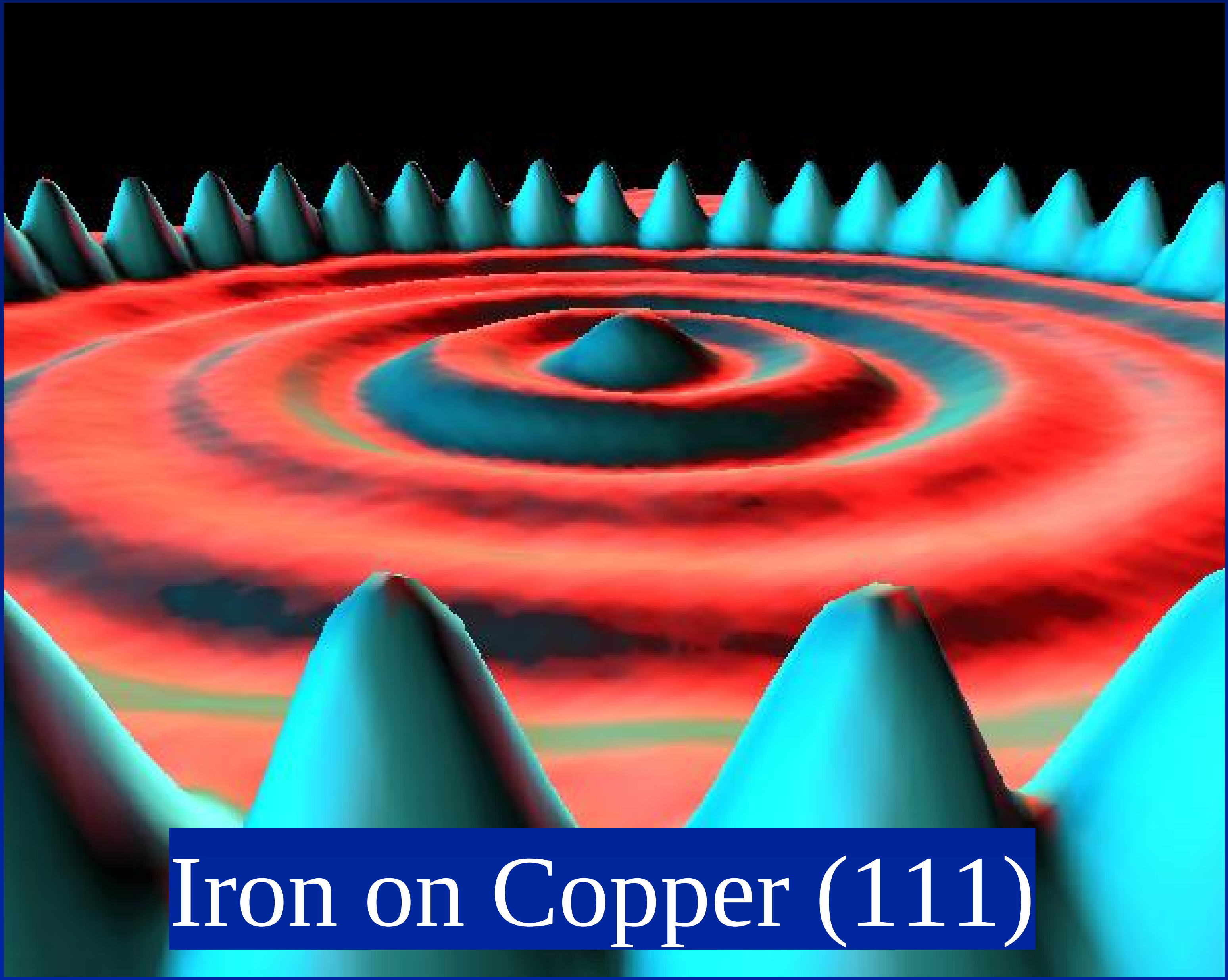
Soccer

Rugby

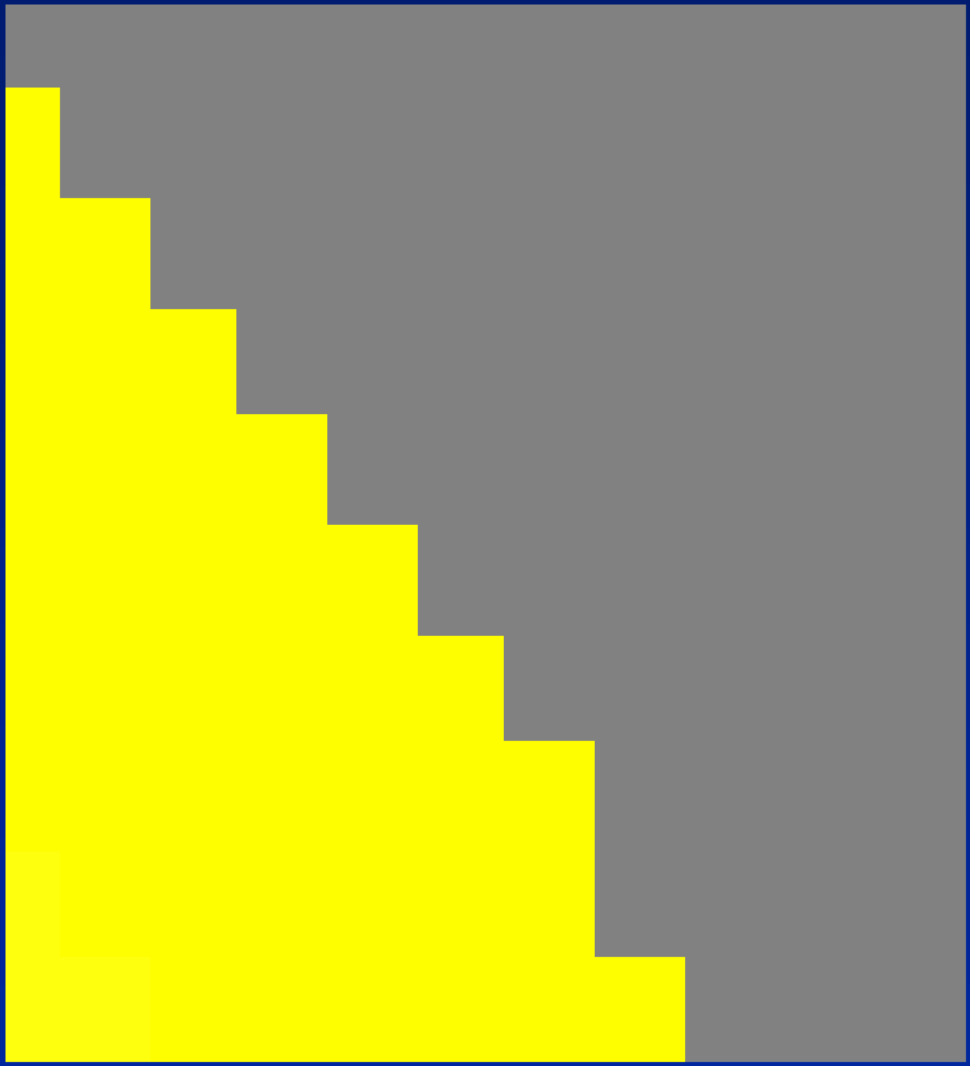
Union

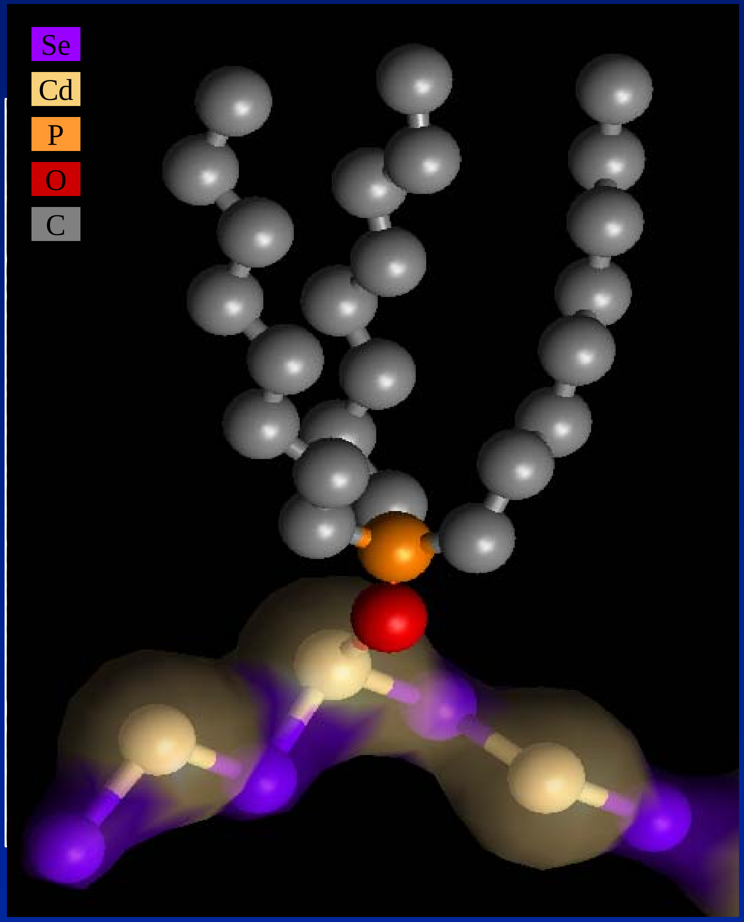
League

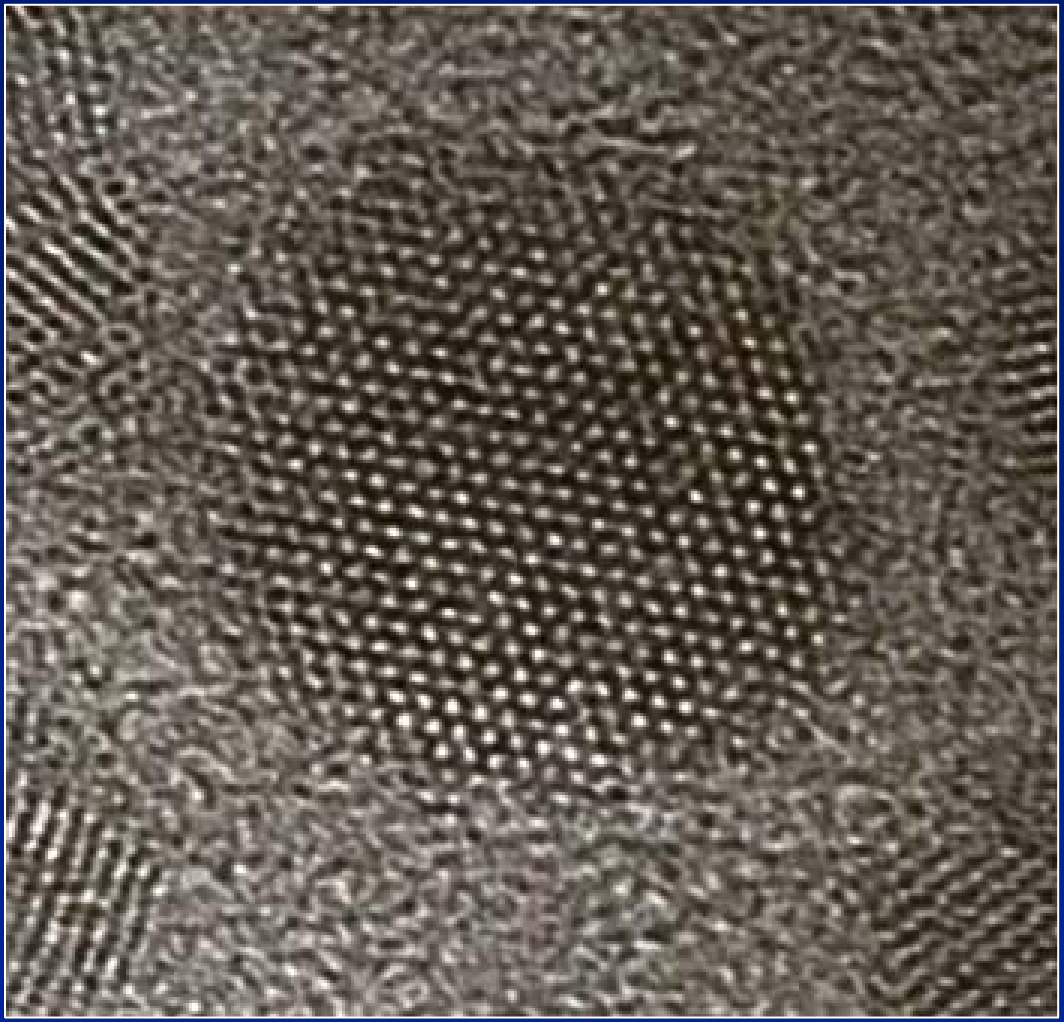



Iron on Copper (111)

Quantization



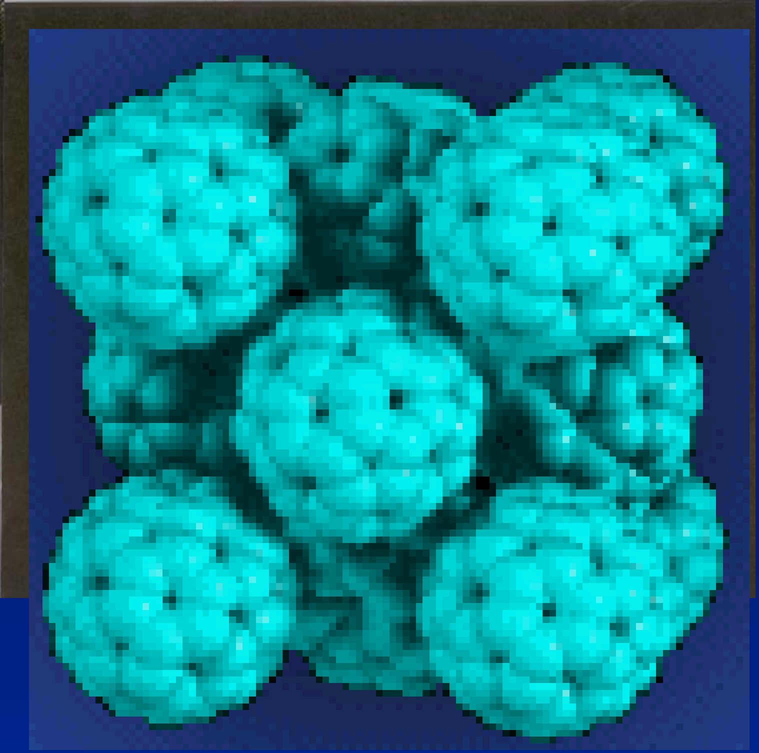




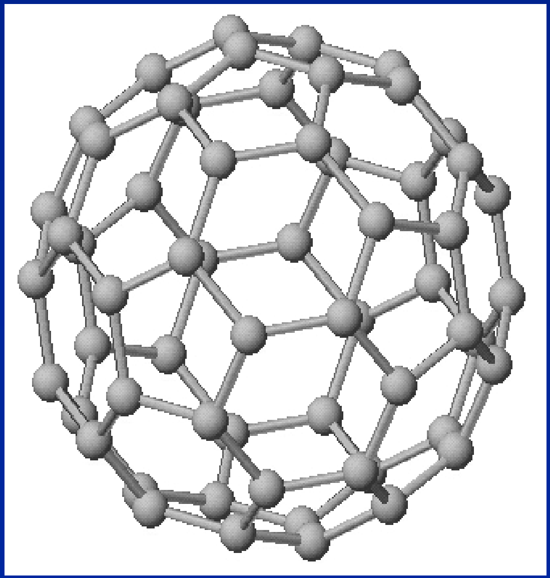
Single quantum dot of CdSe (ca. Diameter = 5 nm).

Building a bridge from the molecule to the particle!

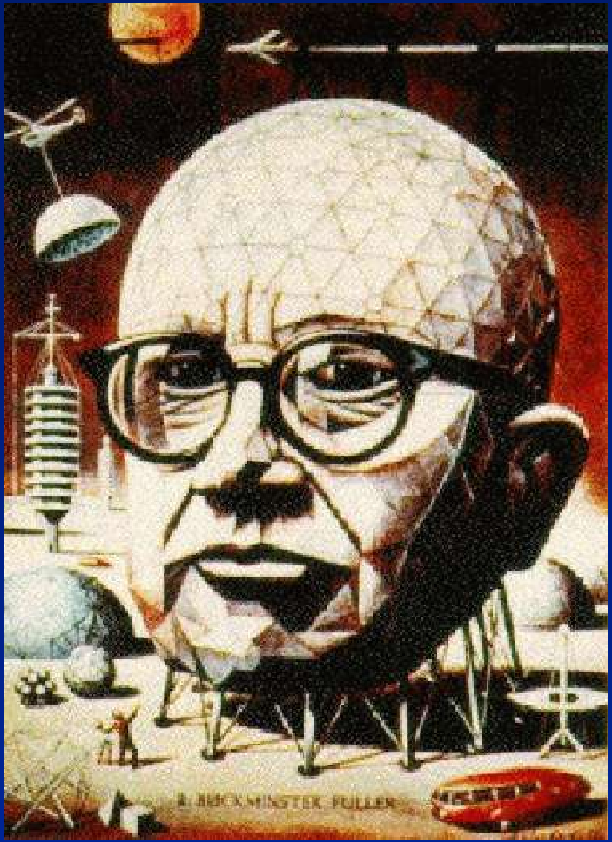
With a football!

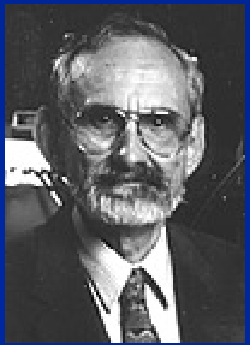


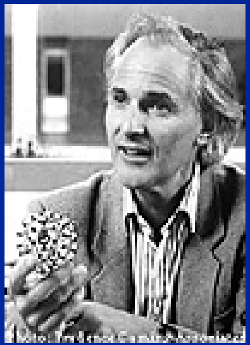
C_{60} Bukminster Fullerane

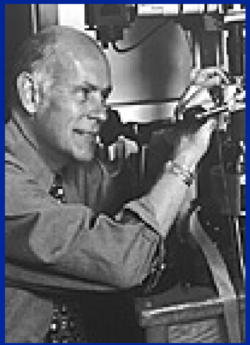


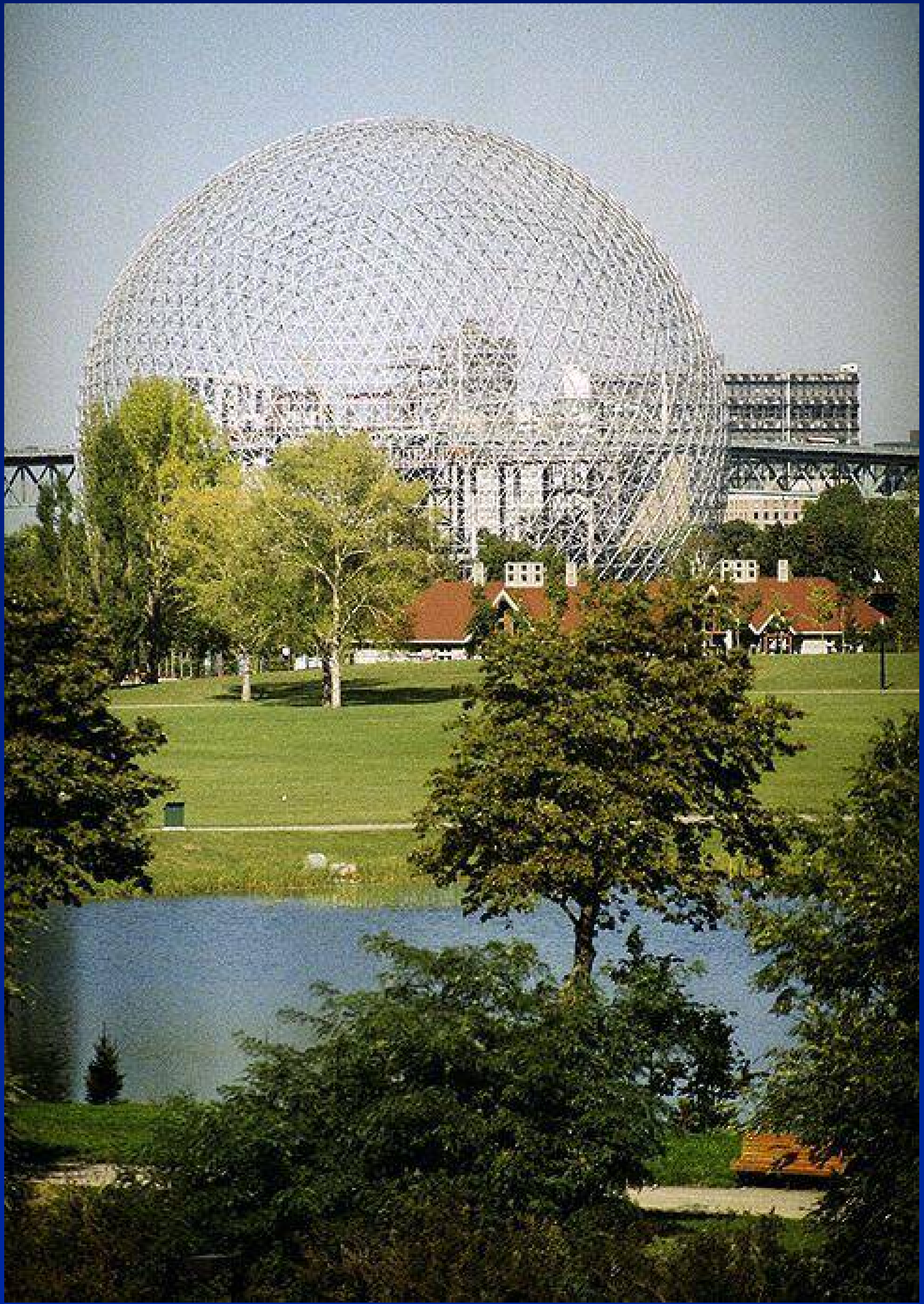
60 atoms of Carbon in
a sphere

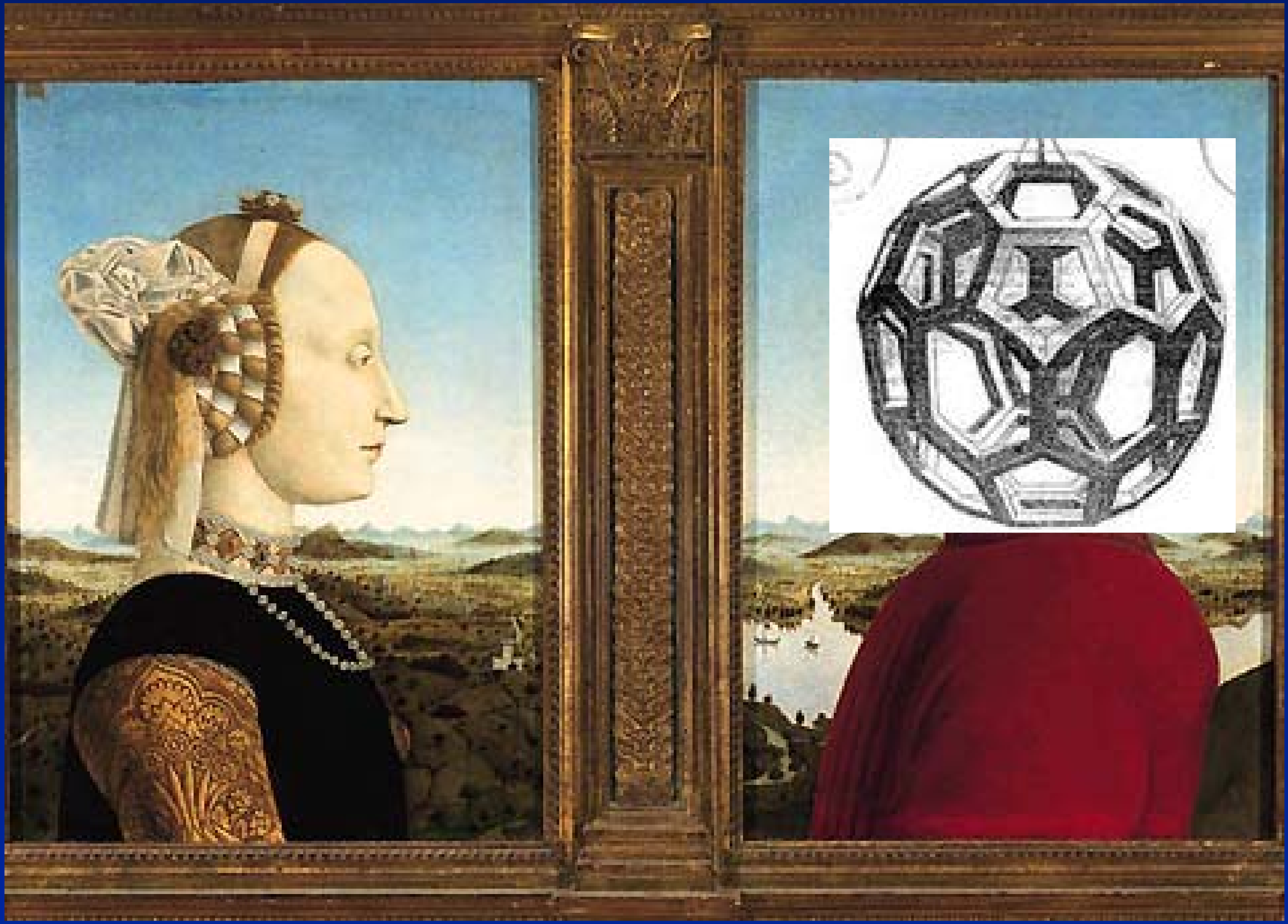

R. BUCKMINSTER FULLER











Federigo da Montefeltro and Battista Sforza (1465, Uffizi, Florence)

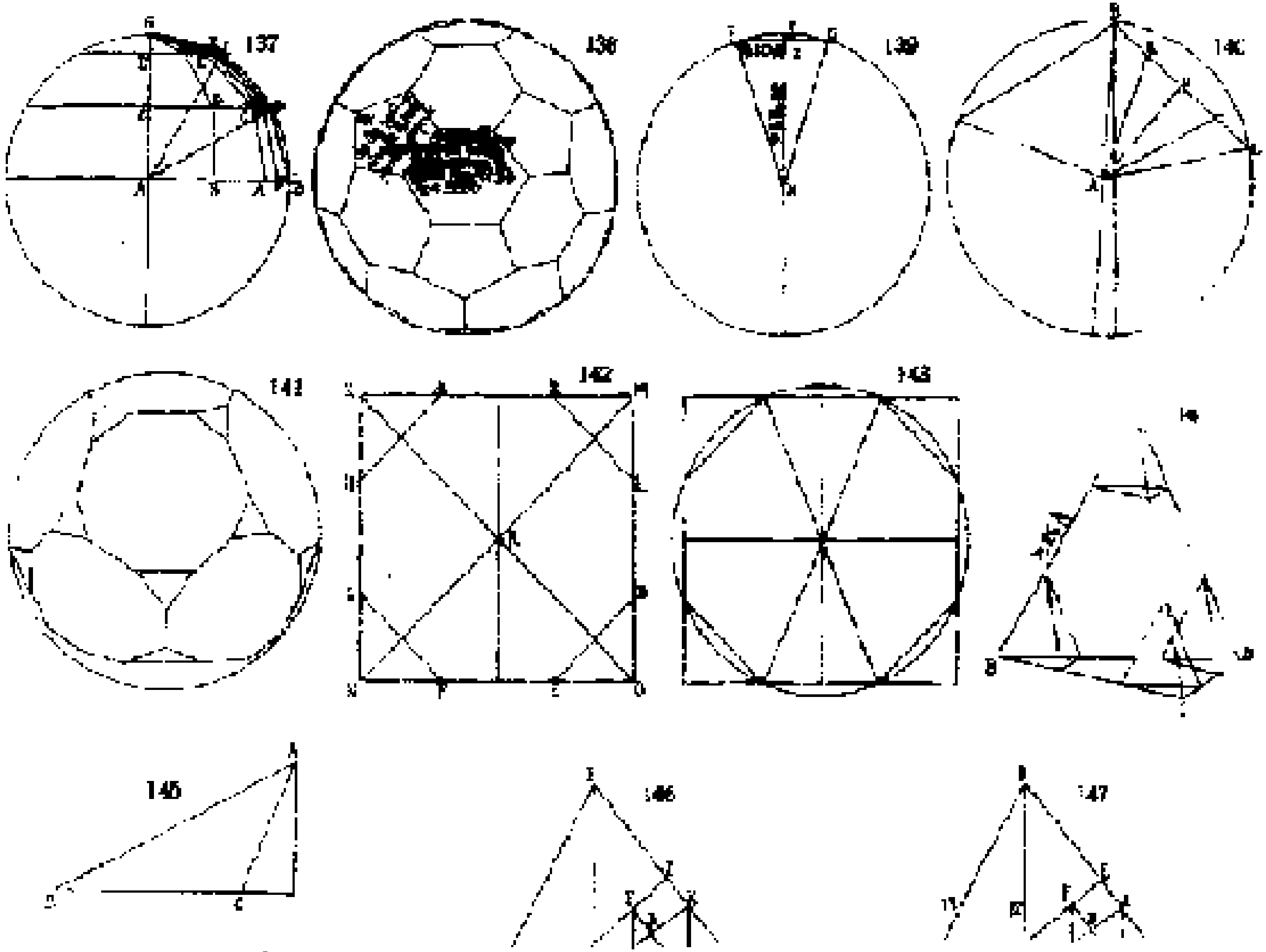
Piero della Francesca: De quinque corporibus regularibus

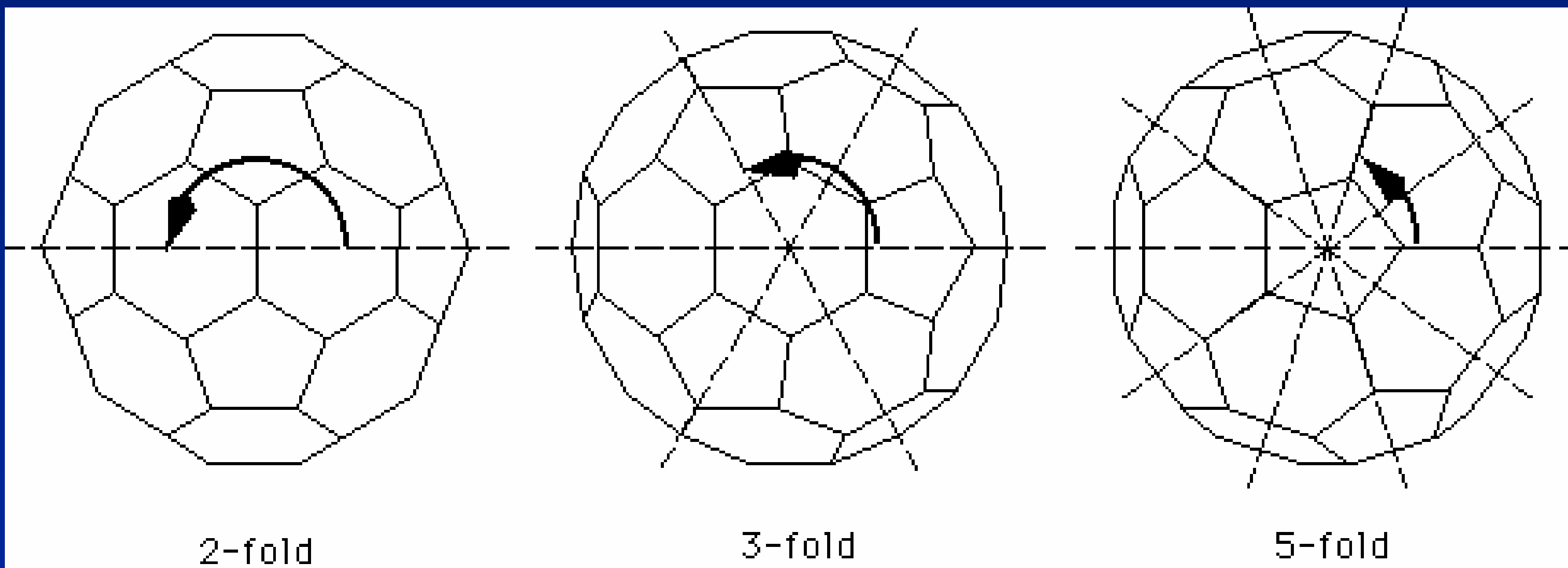
~1480

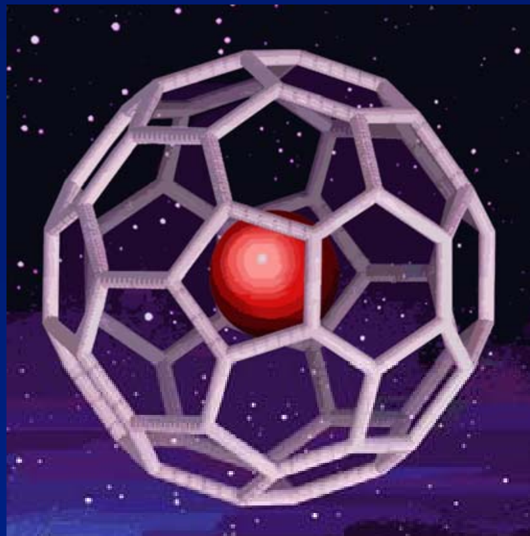
Vatican Library

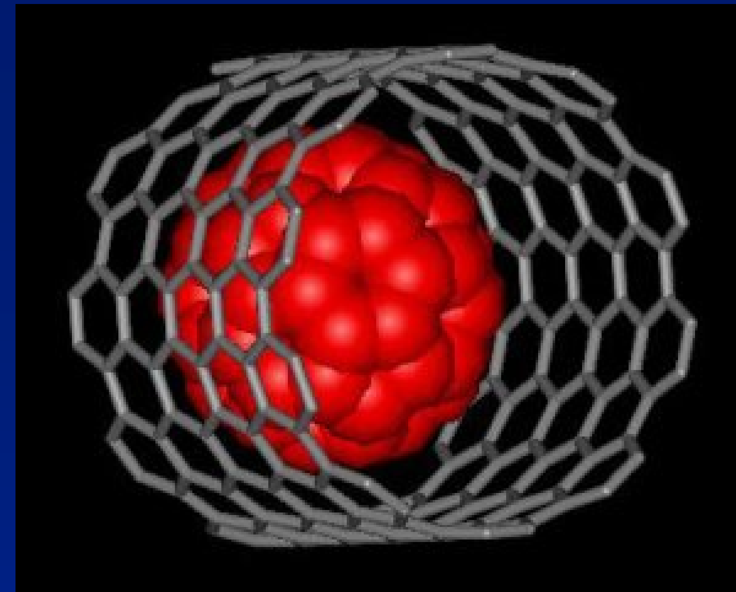
ATTI DEI LINCEI - ... - Serie V. Vol. XIV.

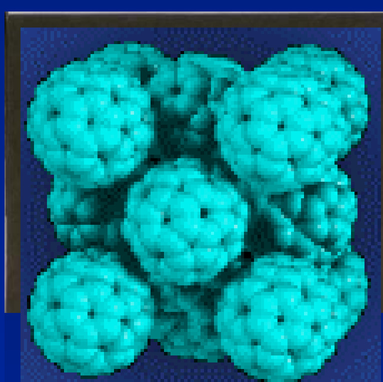
MANCINI ... TAV. II.



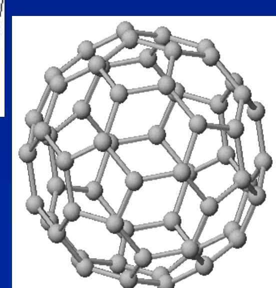

2-fold
3-fold
5-fold





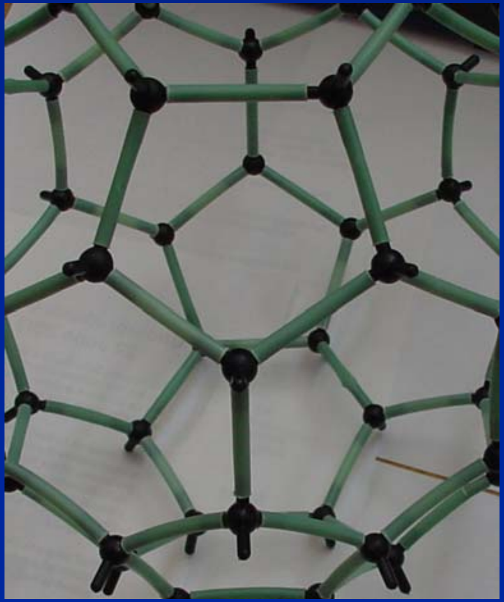


C_{60} Bukminster Fullerane

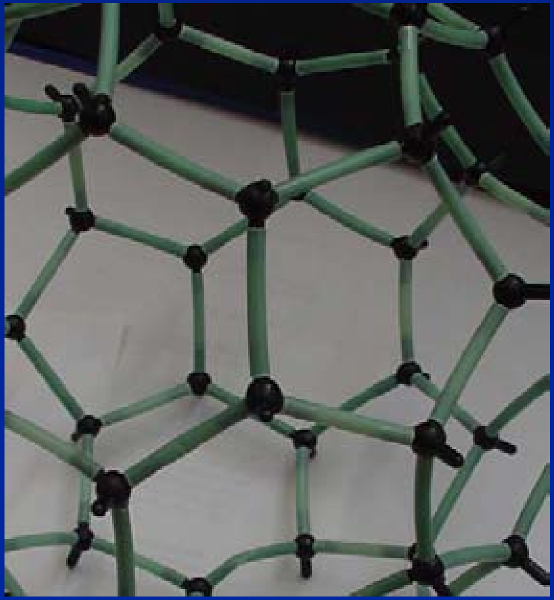


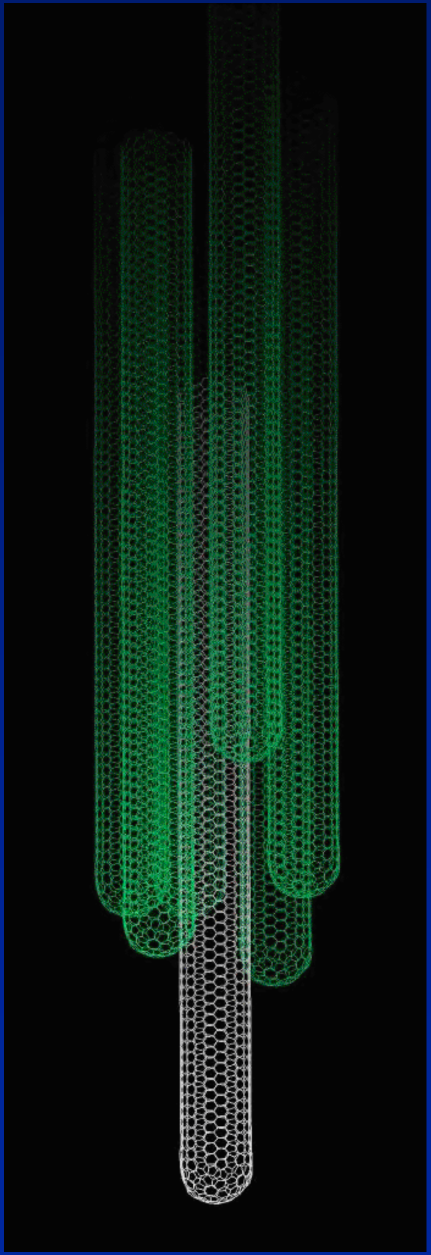
60 atoms of Carbon in a sphere

Imperial College

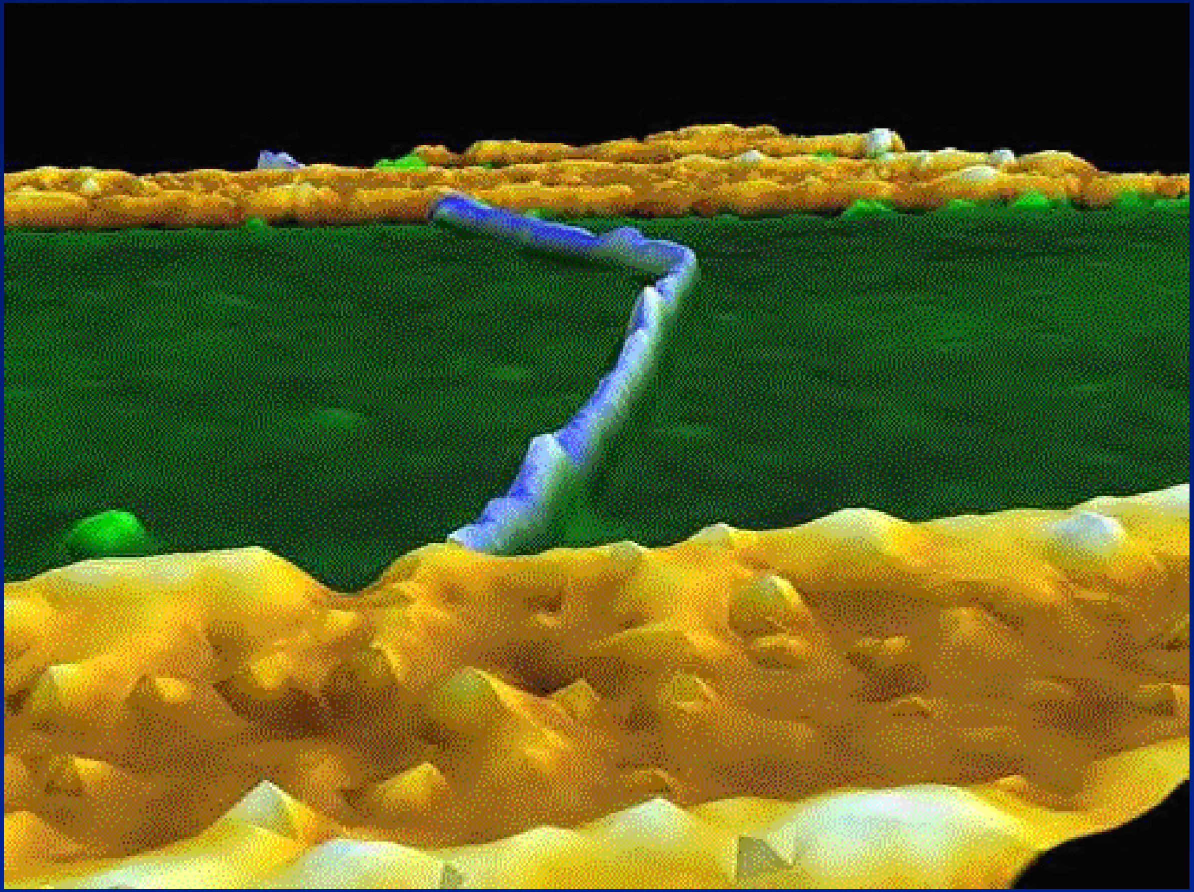


Build your Bucky Ball



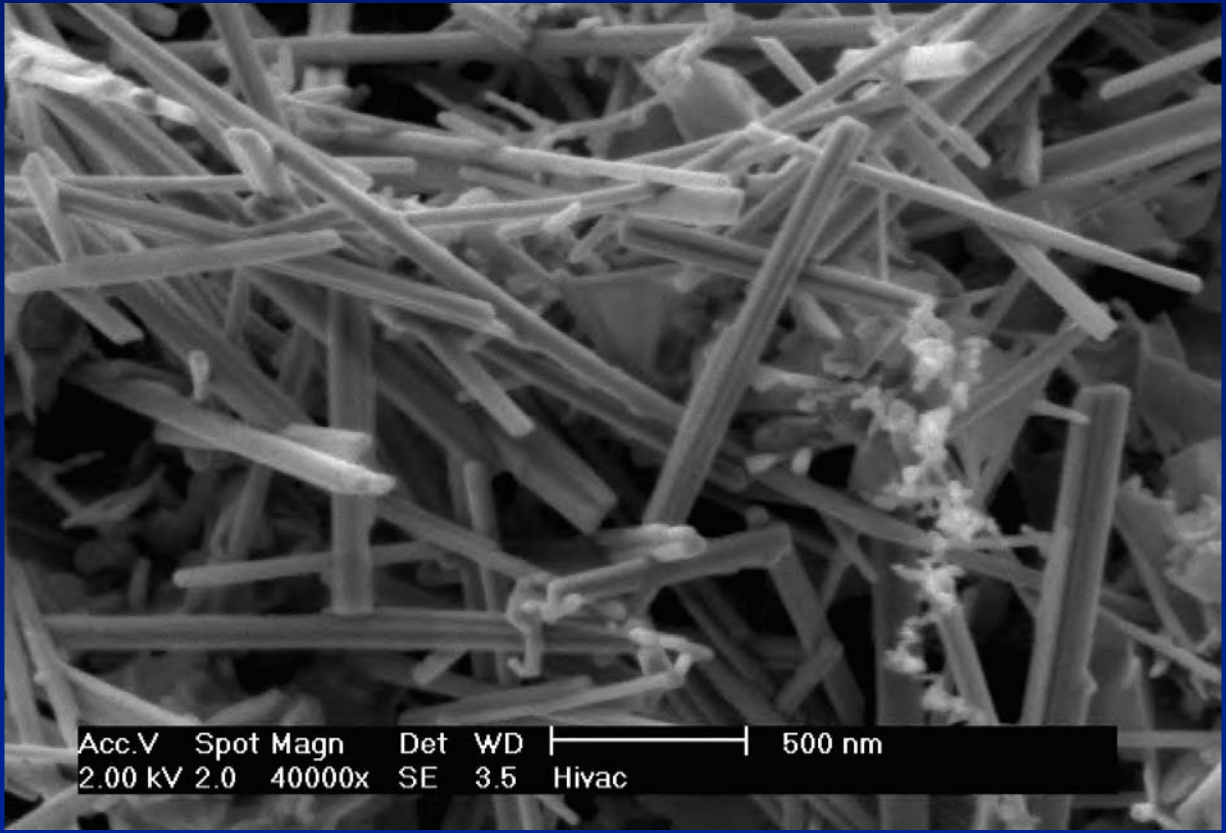


Single Walled tubes

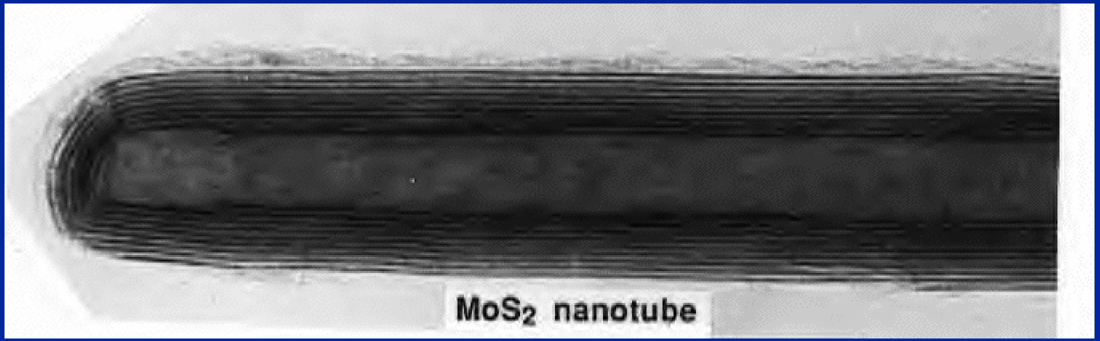


Kinks in carbon nanotubes:
Different conduction environments for electrons moving along the tube. The nanotube wire on one side of the kink This intramolecular versatility will help the designers of nanocircuits. The atomic force microscope image, showing a kinked nanotube draped across three electrodes, was recorede by Cees Dekker and his colleagues at Delft University in The Nether Lands.

reported by Yao et al., *Nature*, 18 November 1999



Inorganic Nanotubes
Prof Tenne
Weizmann



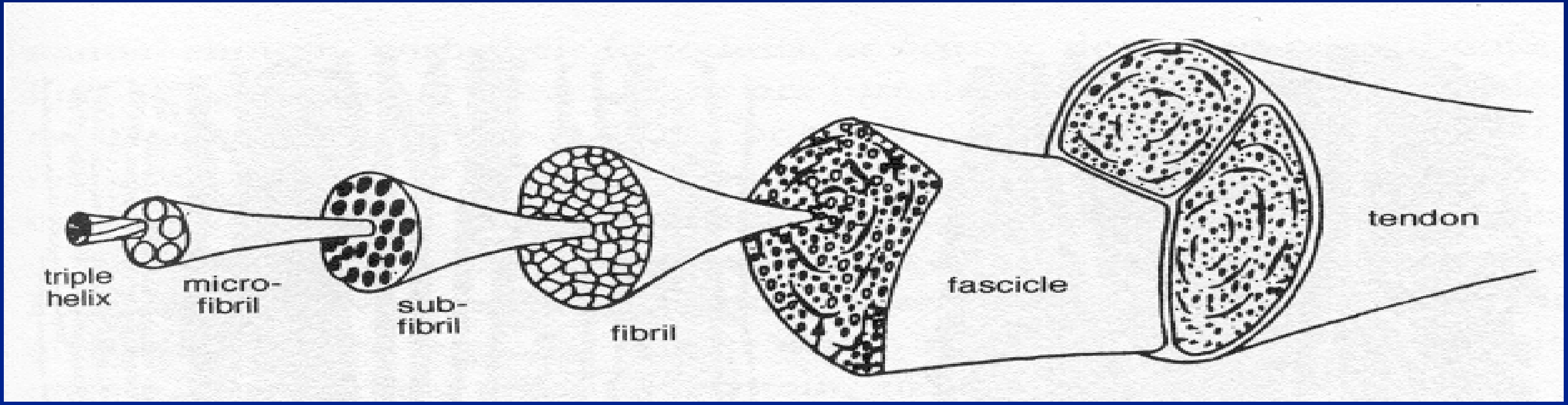
Biological Perspectives

We have already thought about respiration

- Dissolution
- Delivery
- Implants
- Biocomaptibility

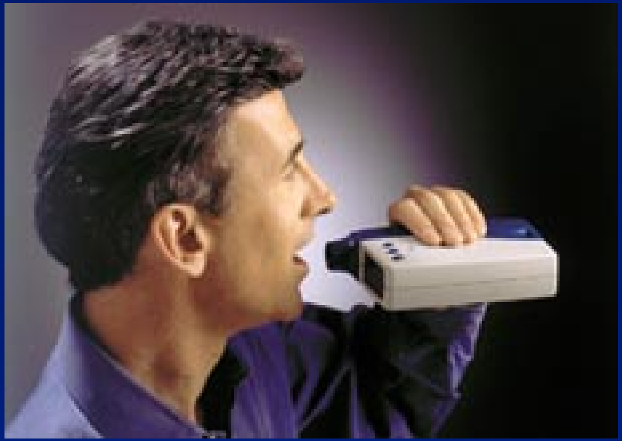
Influence of nanotechnology

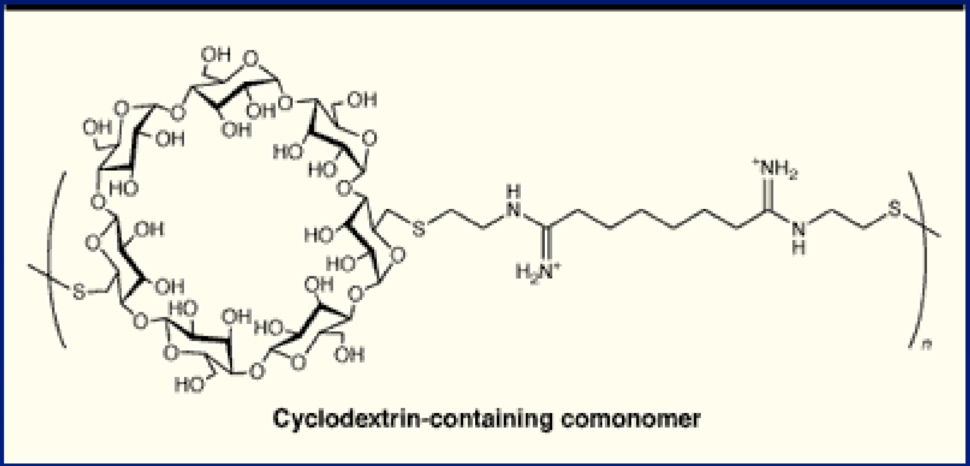
Where ever we go- Biology was there first?..Function and Form

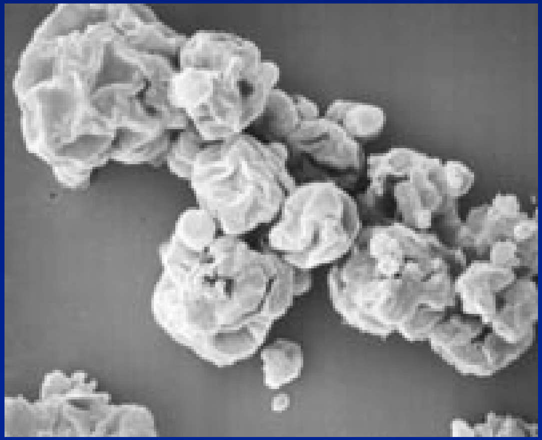


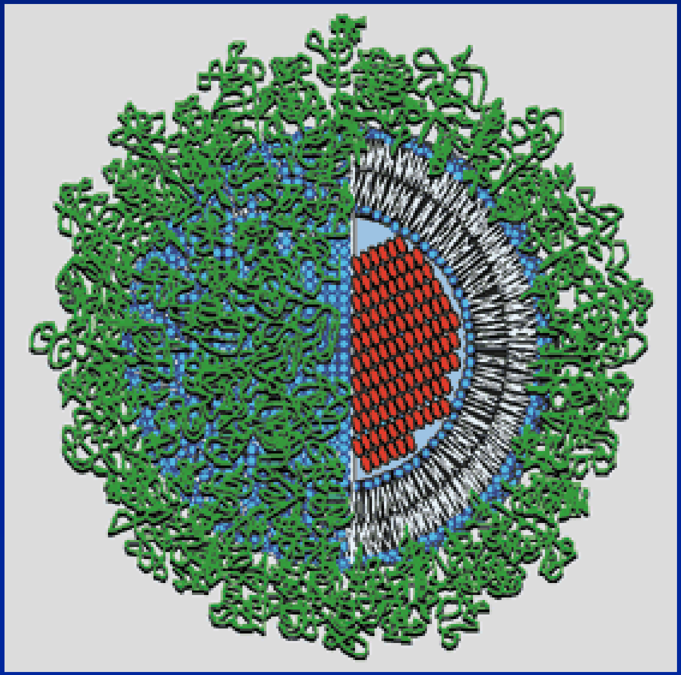
- In nature a very large range of material properties are obtained from a limited number of materials by varying the micron scale structure
- Ligaments, Cartilage, Tendons are all made from Collagen in different forms

Chemical Engineering News Sept 18th 2000





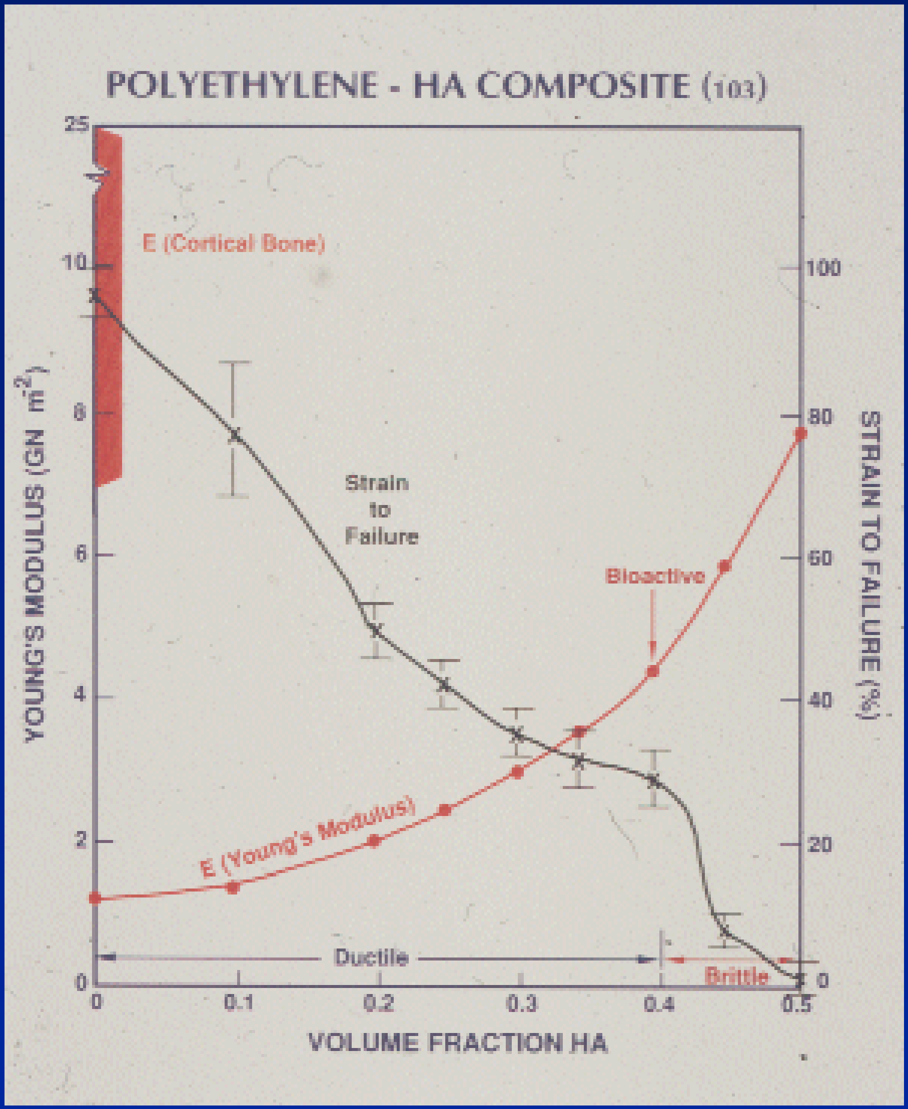




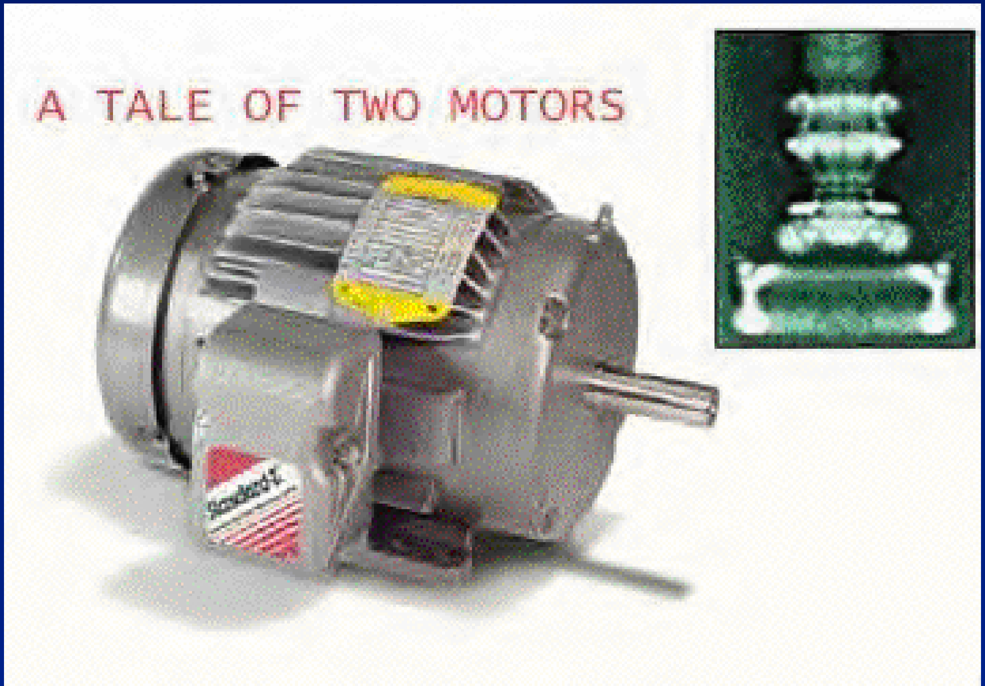
Chemical Engineering News Sept 18th 2000

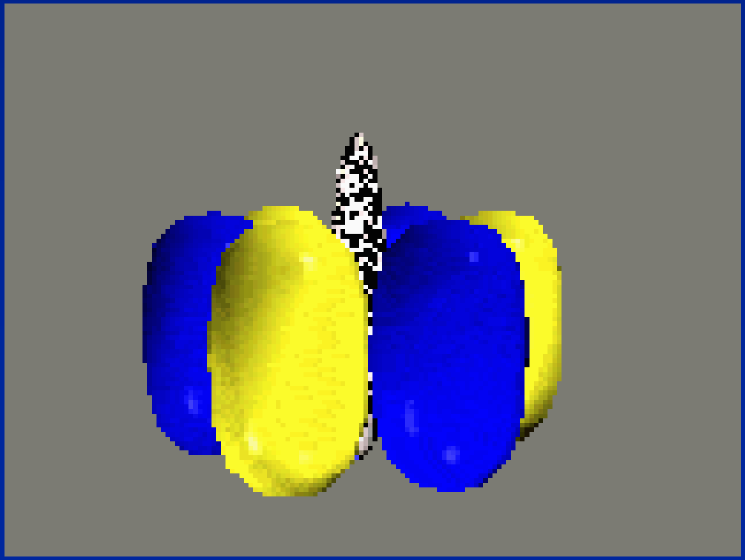
Implants Hench Definitions

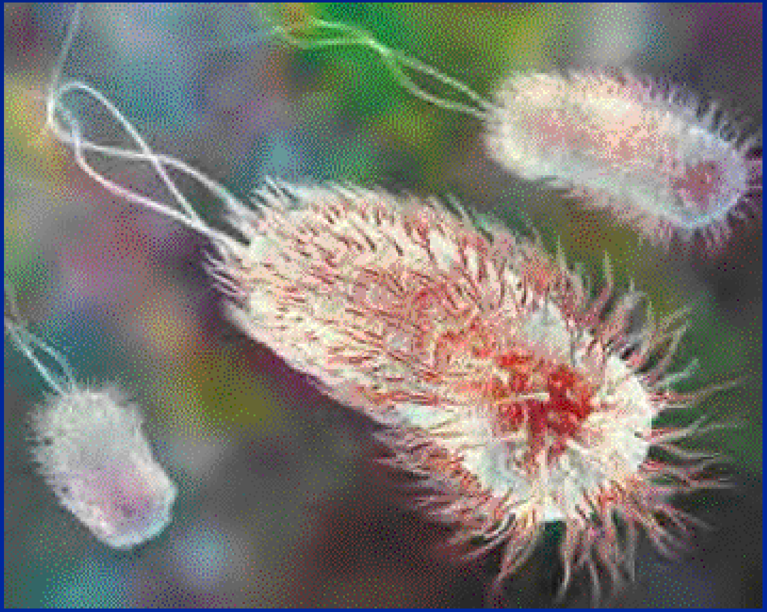
- Inert- Mechanical interaction only
- Porous- Fixation by by biological in growth
- Bioactive- Chemical bonding implant and host
- Resorbable- dissolves chemically or by cell action

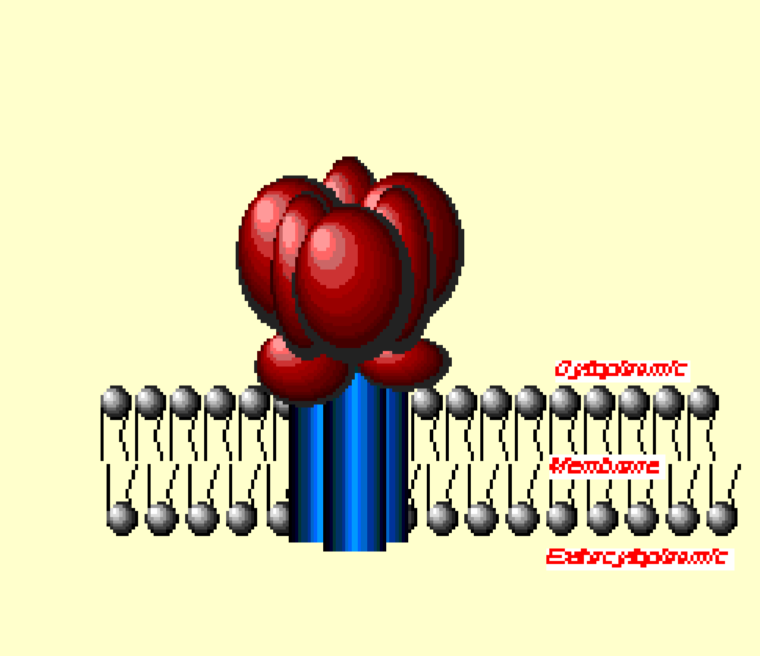


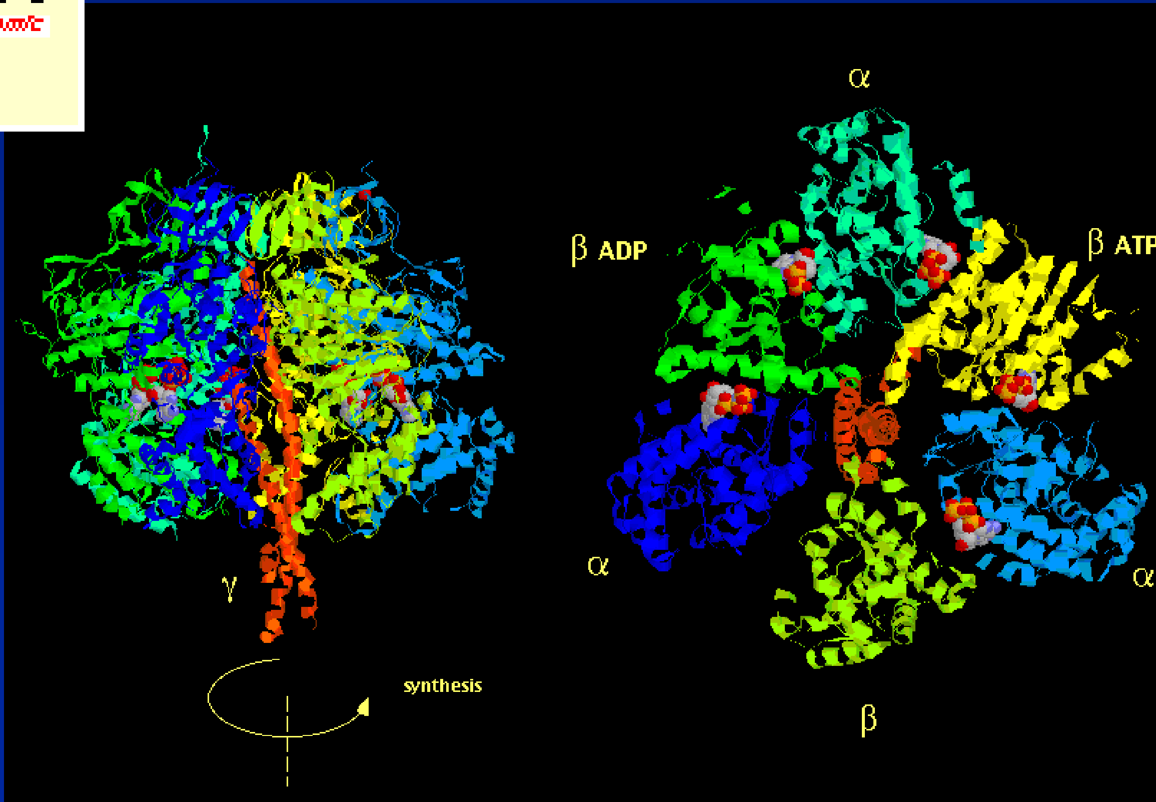
From Hench ICSTM 2000

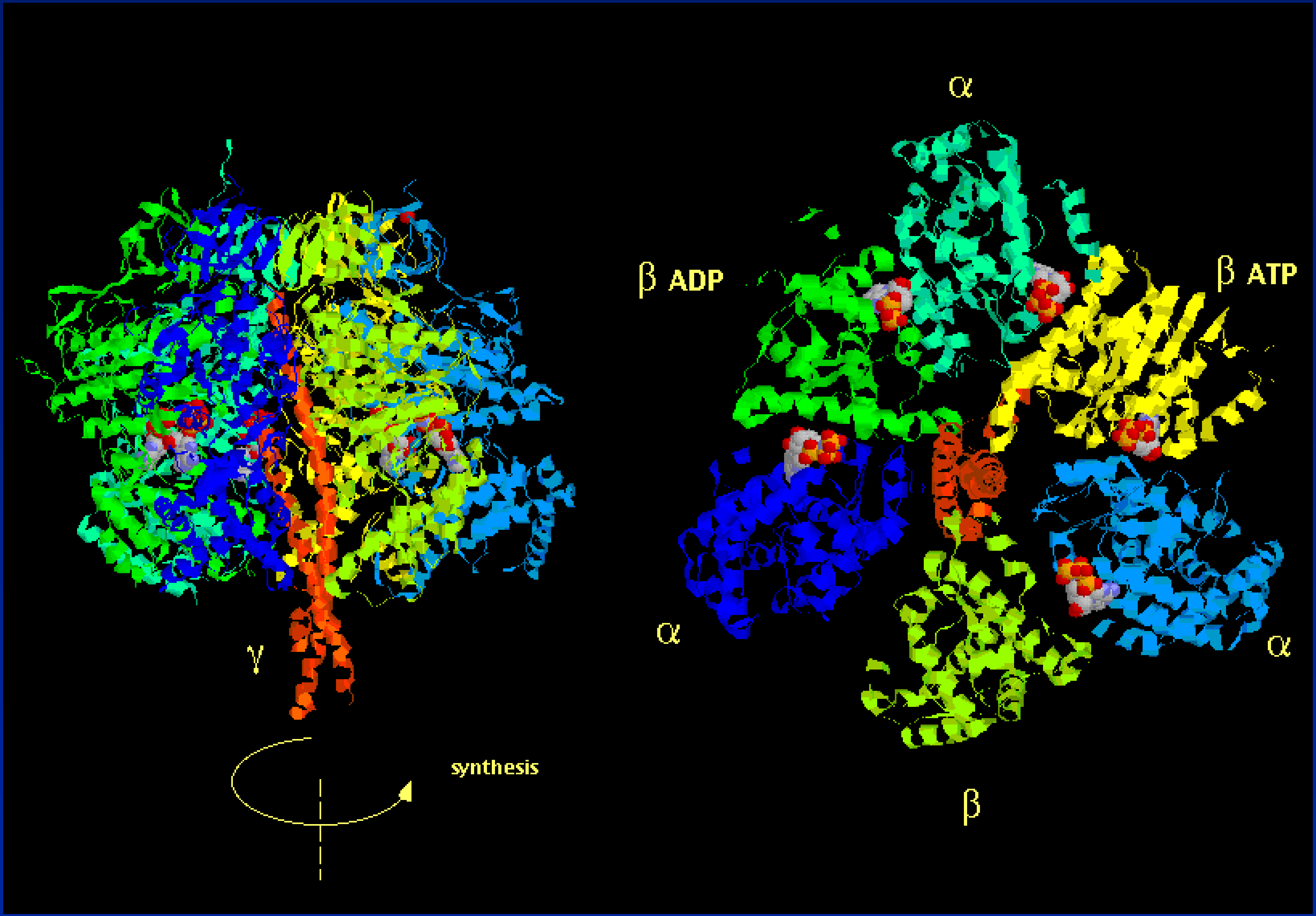

A TALE OF TWO MOTORS



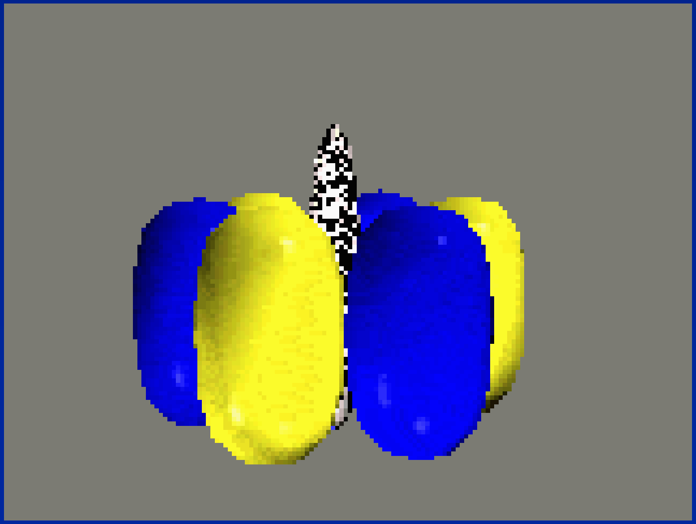


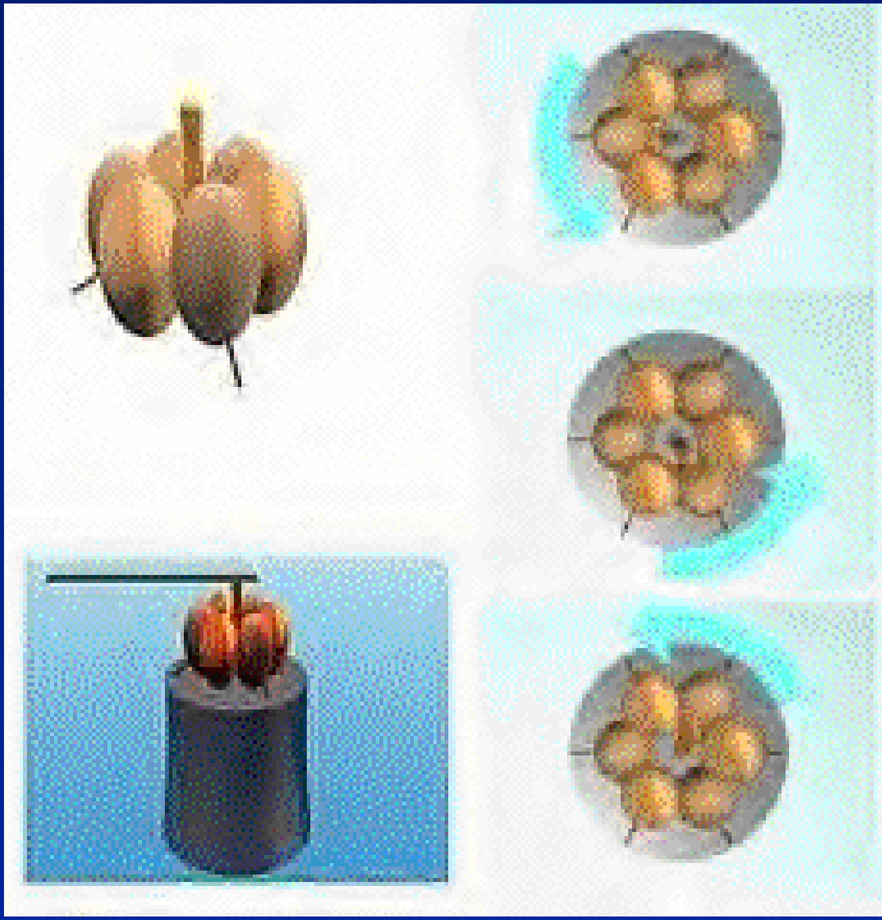

Cytoplasmic
Membrane
Extracytoplasmic


α
β ADP
β ATP
γ
α
α
synthesis
β



α
β ADP
β ATP
γ
α
α
synthesis
β



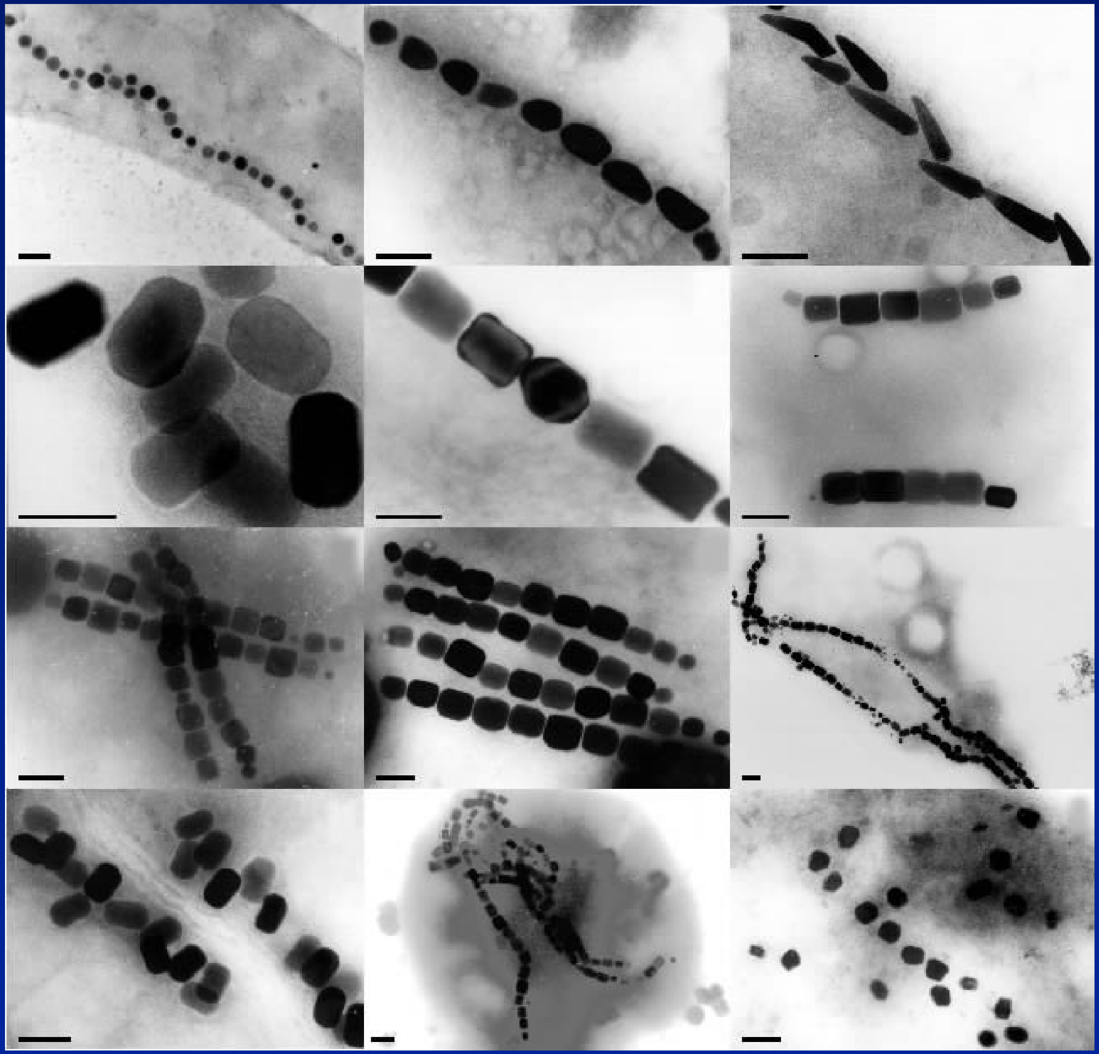


$$2\,H_2O_2 \longrightarrow 2H_2O + O_2$$

J. Am. Chem. Soc., **126** (41), 13424 -13431, 2004.
Web Release Date: September 21, 2004 **Catalytic Nanomotors: Autonomous Movement of Striped Nanorods** **Walter F. Paxton, Kevin C. Kistler, Christine C. Olmeda, Ayusman Sen,* Sarah K. St. Angelo, Yanyan Cao, Thomas E. Mallouk,* Paul E. Lammert, and Vincent H. Crespi***

$$2\ H_2O_2 \longrightarrow 2H_2O + O_2$$

$$H_2O_2 + AH_2 \longrightarrow A + 2H_2O$$



Diversity of magnetosome crystals found in various magnetotactic bacteria from different environments (bar represents 0.1 micrometer). Most of the bacteria shown have not been isolated in pure culture.

The Effect of Size on Intrinsic Properties

The relationship between:

- length, area and volume
- *information and space*

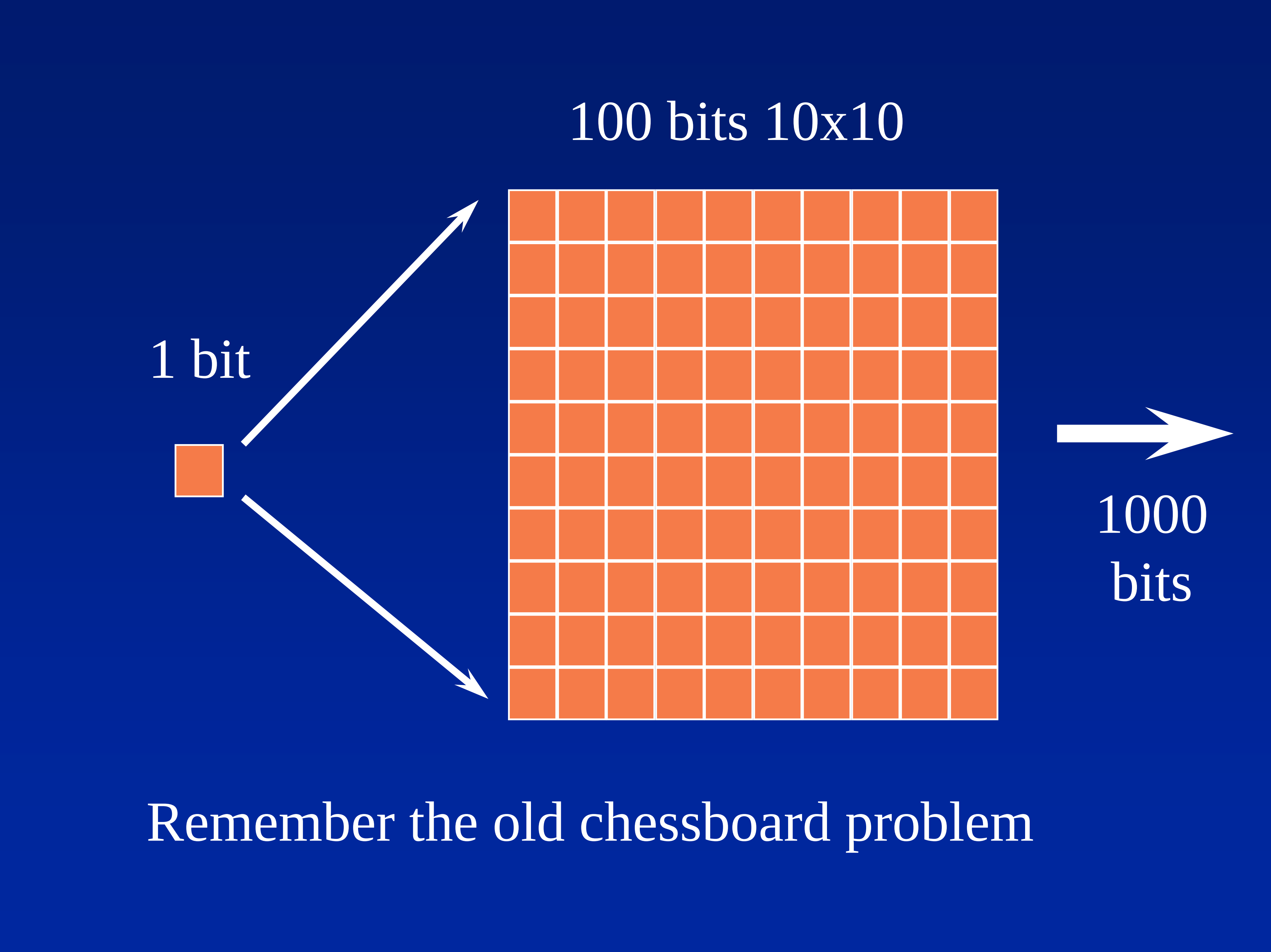
Then let us look at what is possible

Let Us First Investigate the Effect of Size on Intrinsic Properties

The relationship between:

- length, area and volume
- *information and space*

Then let us look at what is possible


100 bits 10x10
1 bit
1000
bits
Remember the old chessboard problem

ERROR WON’T FIT

ERROR WON’T FIT

ON SCREEN!!!

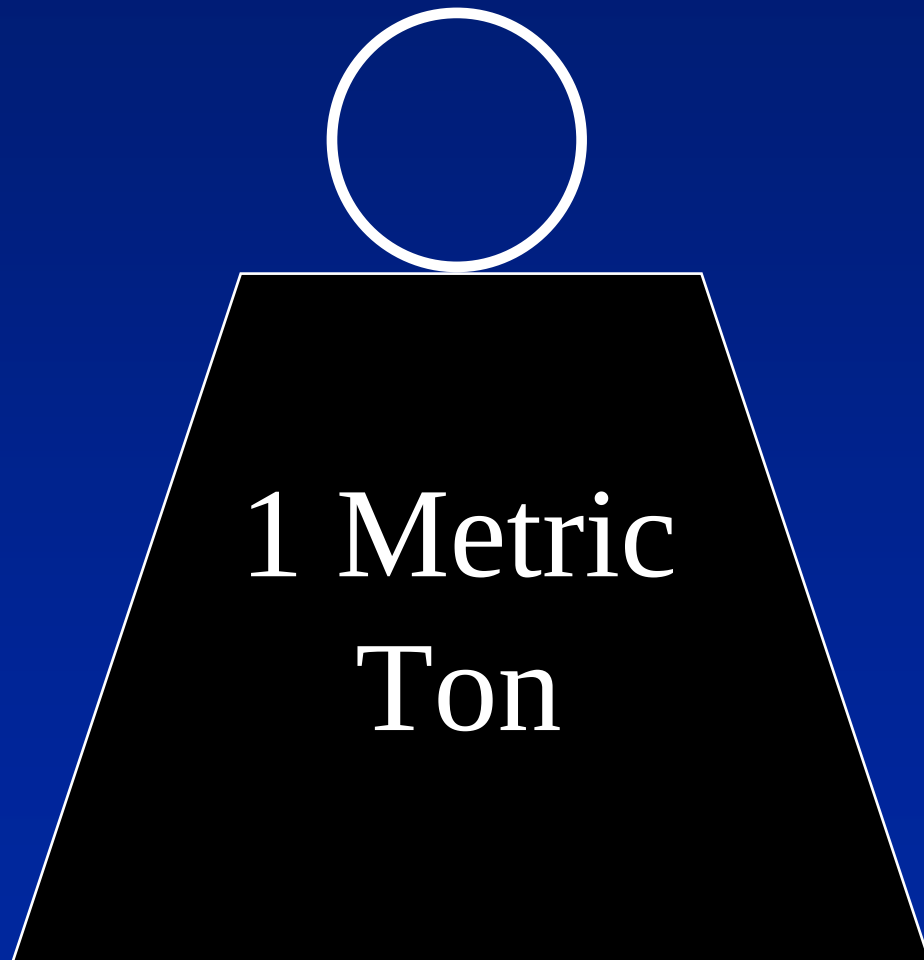
ERROR WON’T FIT

ON SCREEN!!!

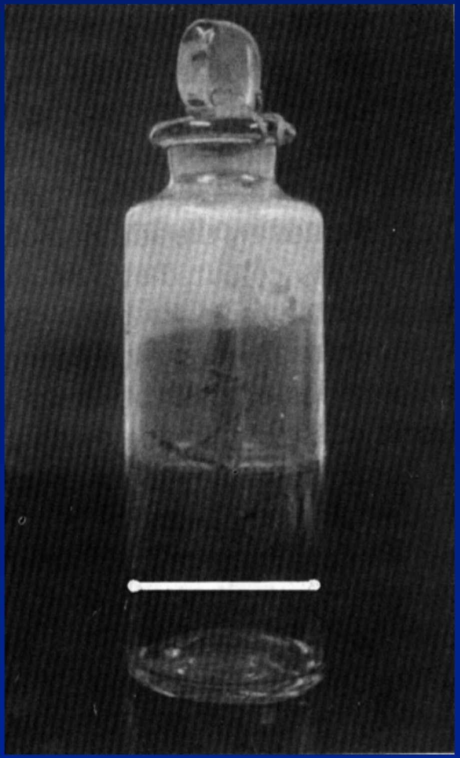
ERROR WON’T FIT

ON SCREEN!!!

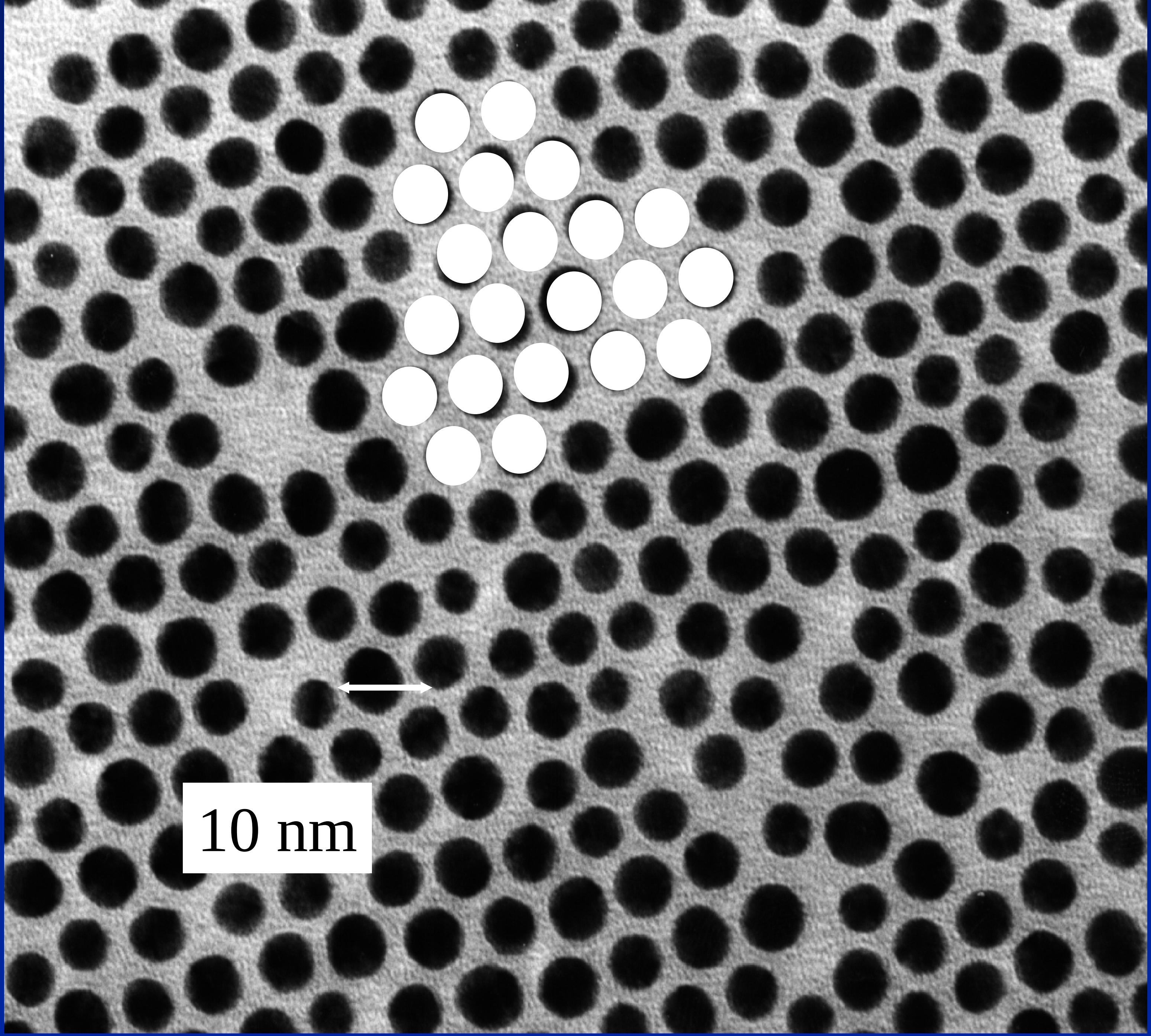
- Hard Disc ca 100g per giga bit




FOR A
LAPTOP!!!



Michael Faraday in the 1860s made Colloids of Gold


10 nm

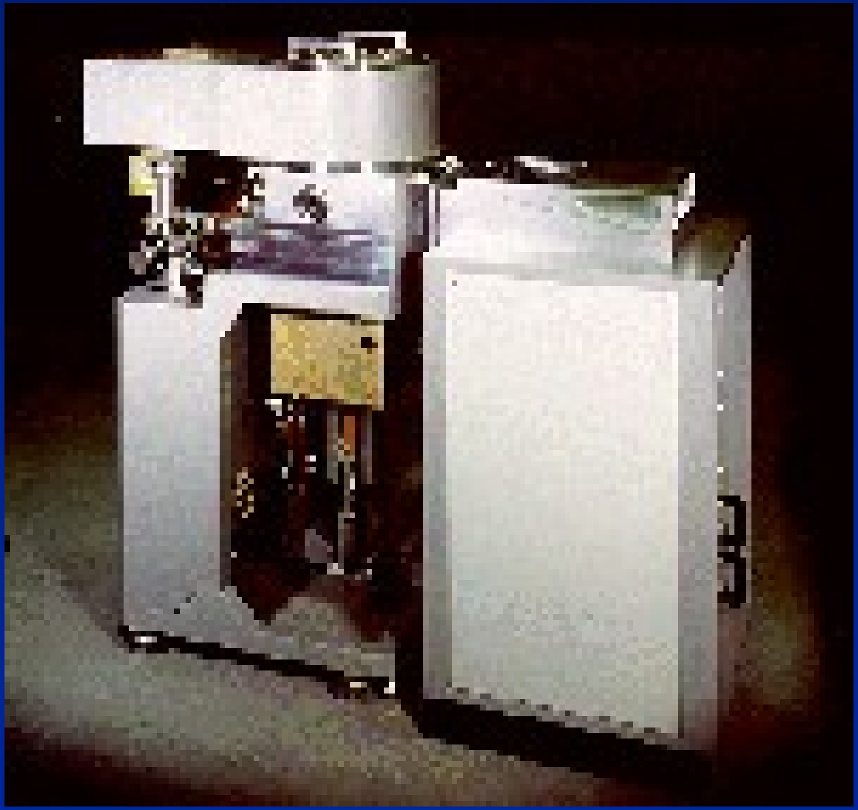
How Small Can we Make Machines?

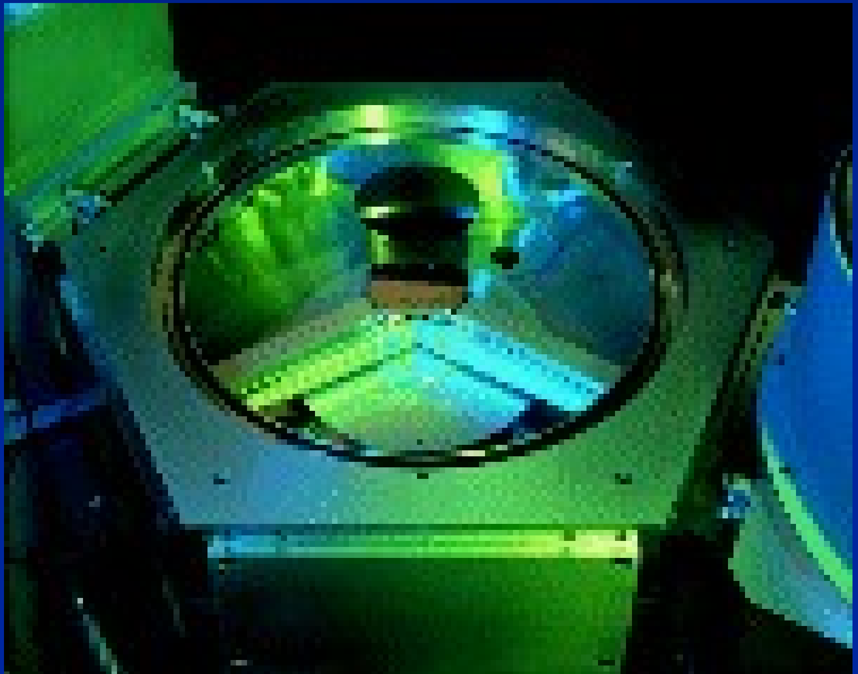
The process depends on chemistry for the manipulation often of silicon.

Into turbines, rotors, accelerometers…….

These are small 100-1000 nanometre parts

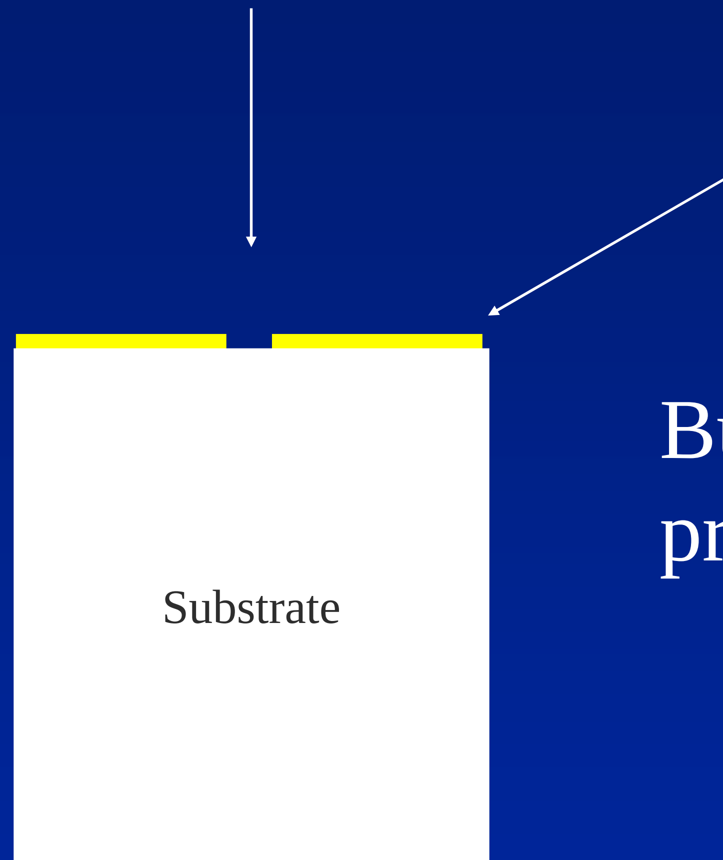
How to Engineer at the scale of Nanometres?





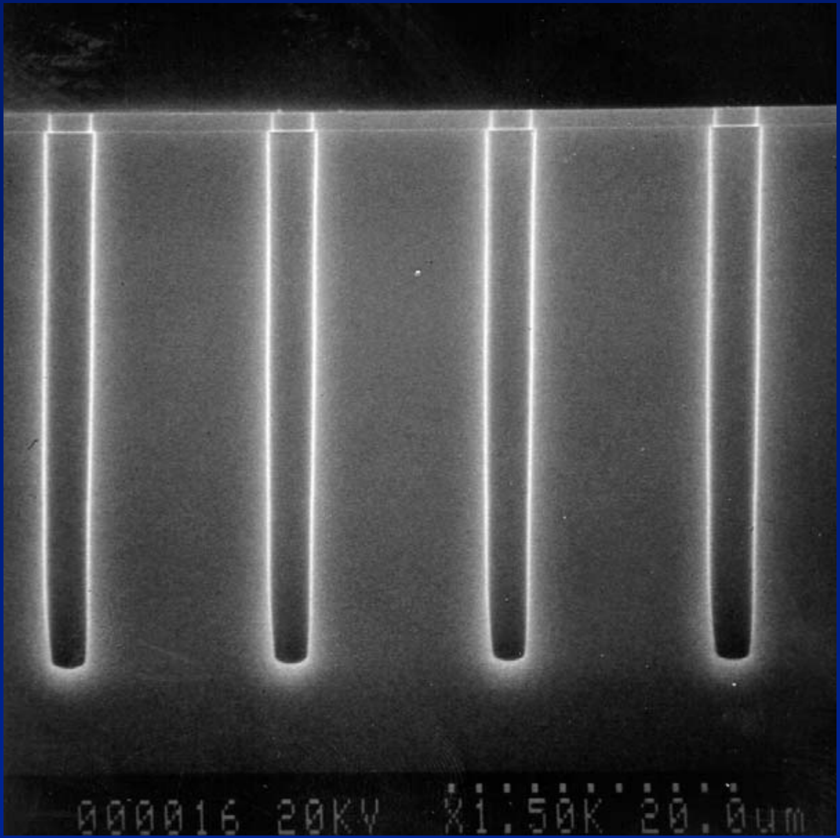
A Chemical to dissolve lower layer

A physical mask

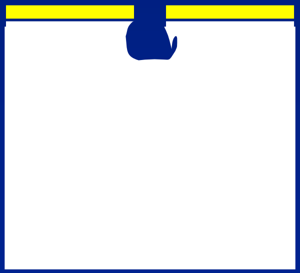


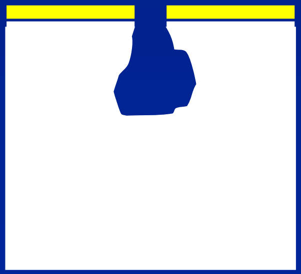
But there is a problem !

Chemical Etching as Route to Structures

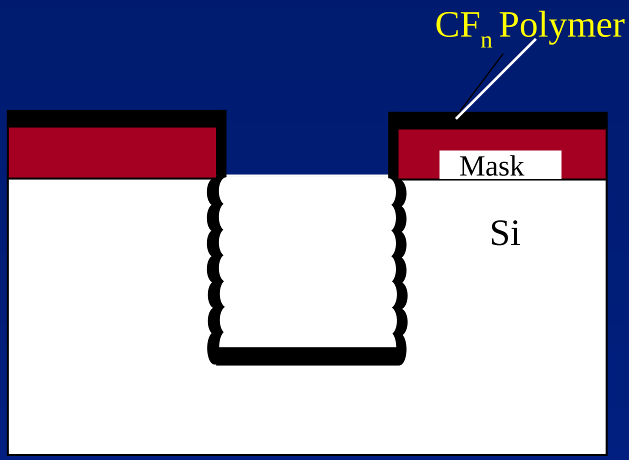


The problem with a
simple etch method
is to do with anisotropy

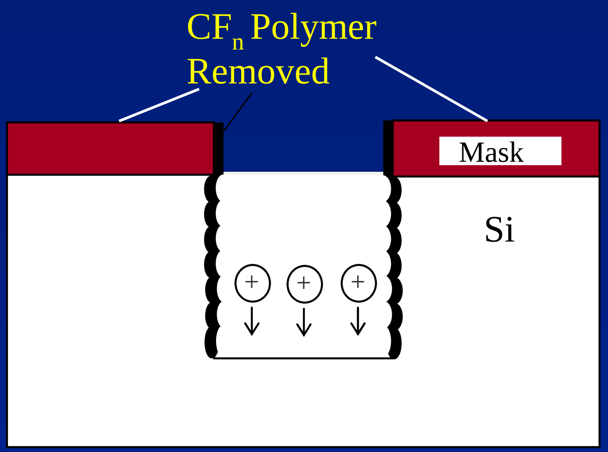




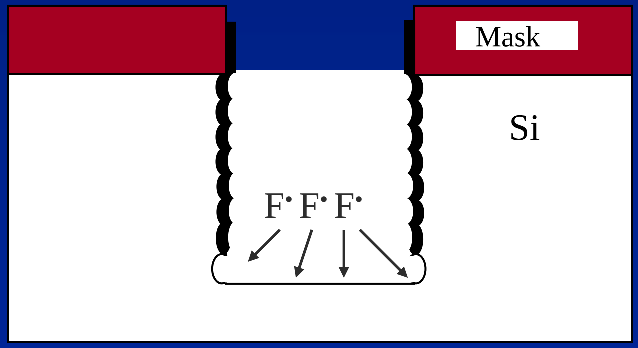
Anisotropy is Inevitably Lost !
The problem can also be a solution
Cutting out gear wheels etc.



CF_n polymer from C_4F_8 plasma, deposited on all surfaces

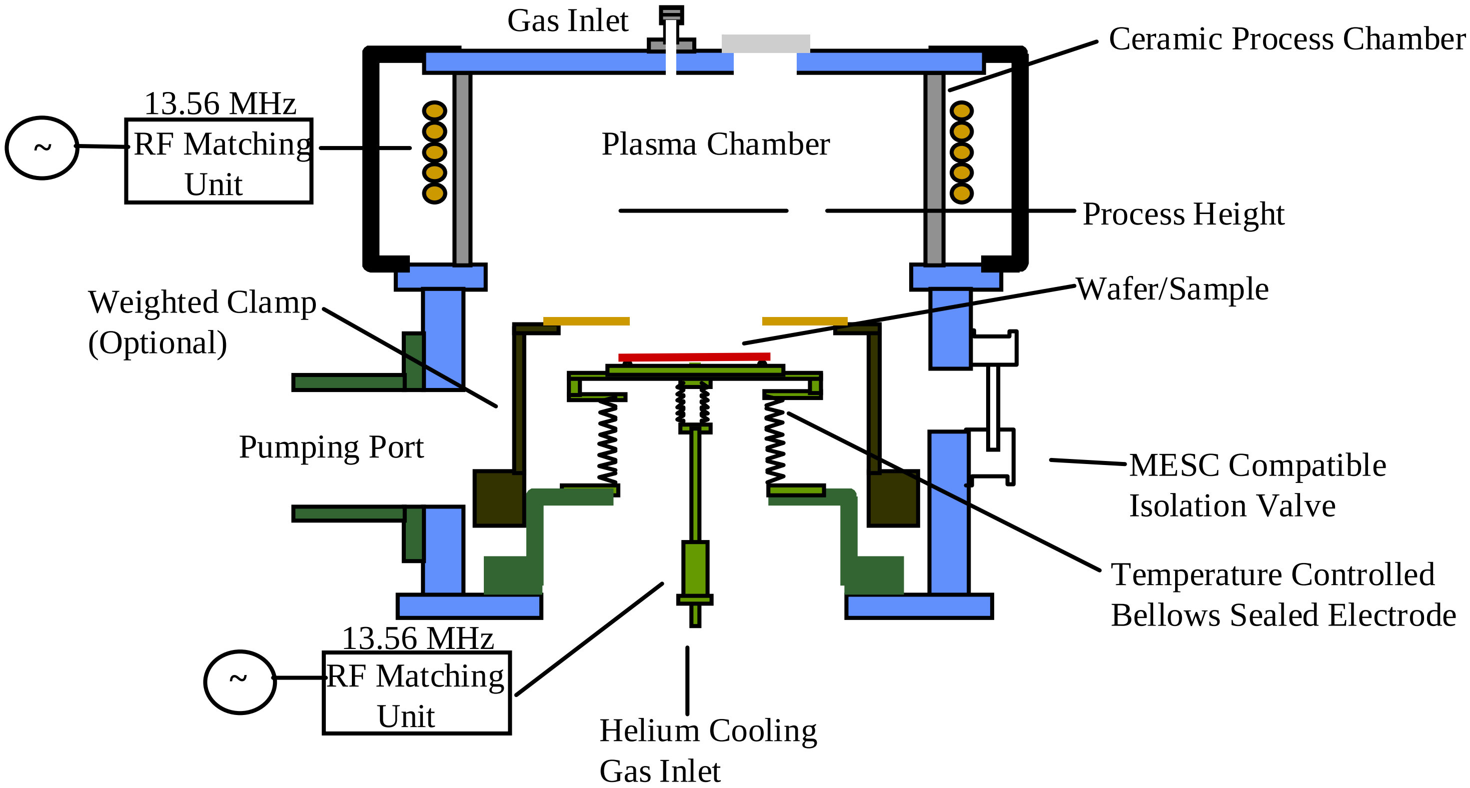


Due to directionality, polymer is removed from base at much higher rate than from side-walls.

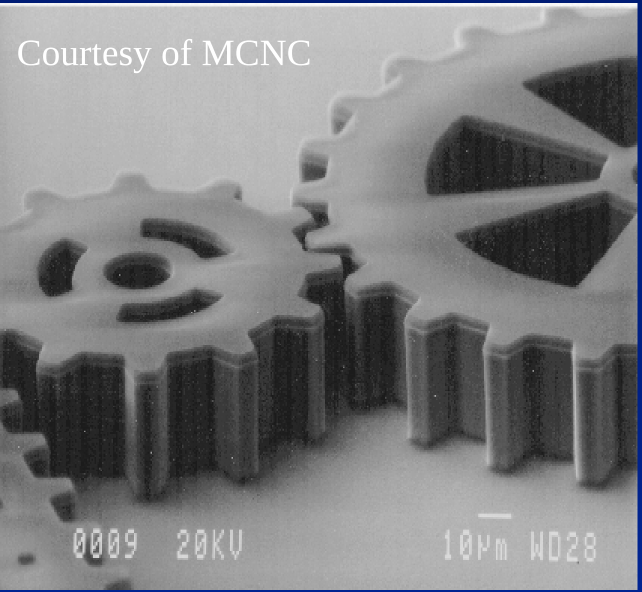


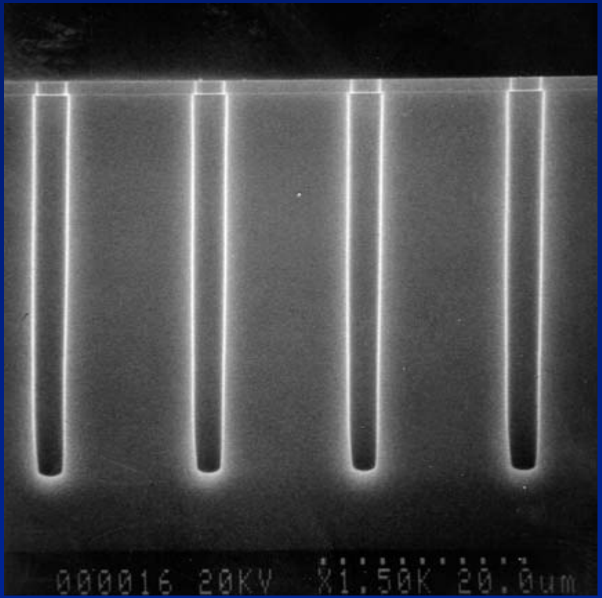
Exposed Si surfaces are then etched by fluorine species, from the SF_6 plasma.

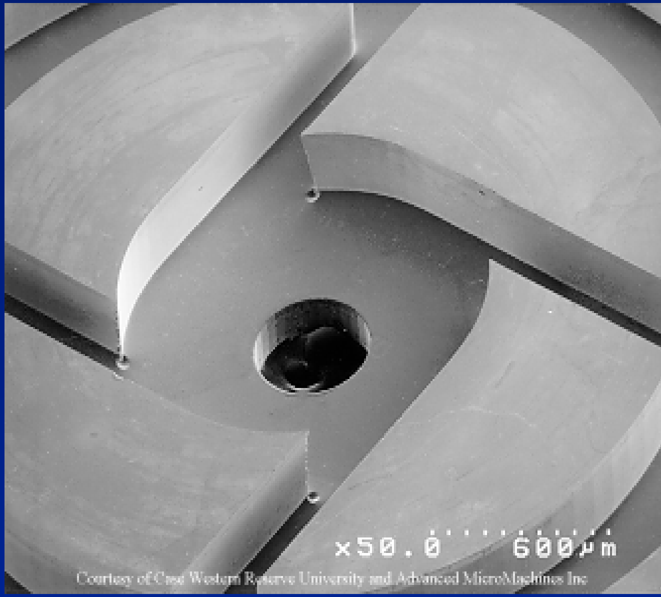
Advanced Silicon Etch Process


Gas Inlet
Ceramic Process Chamber
13.56 MHz
RF Matching Unit
Plasma Chamber
Process Height
Wafer/Sample
Weighted Clamp (Optional)
Pumping Port
MESC Compatible Isolation Valve
Temperature Controlled Bellows Sealed Electrode
13.56 MHz
RF Matching Unit
Helium Cooling Gas Inlet

Applications for anisotropic silicon etch technology



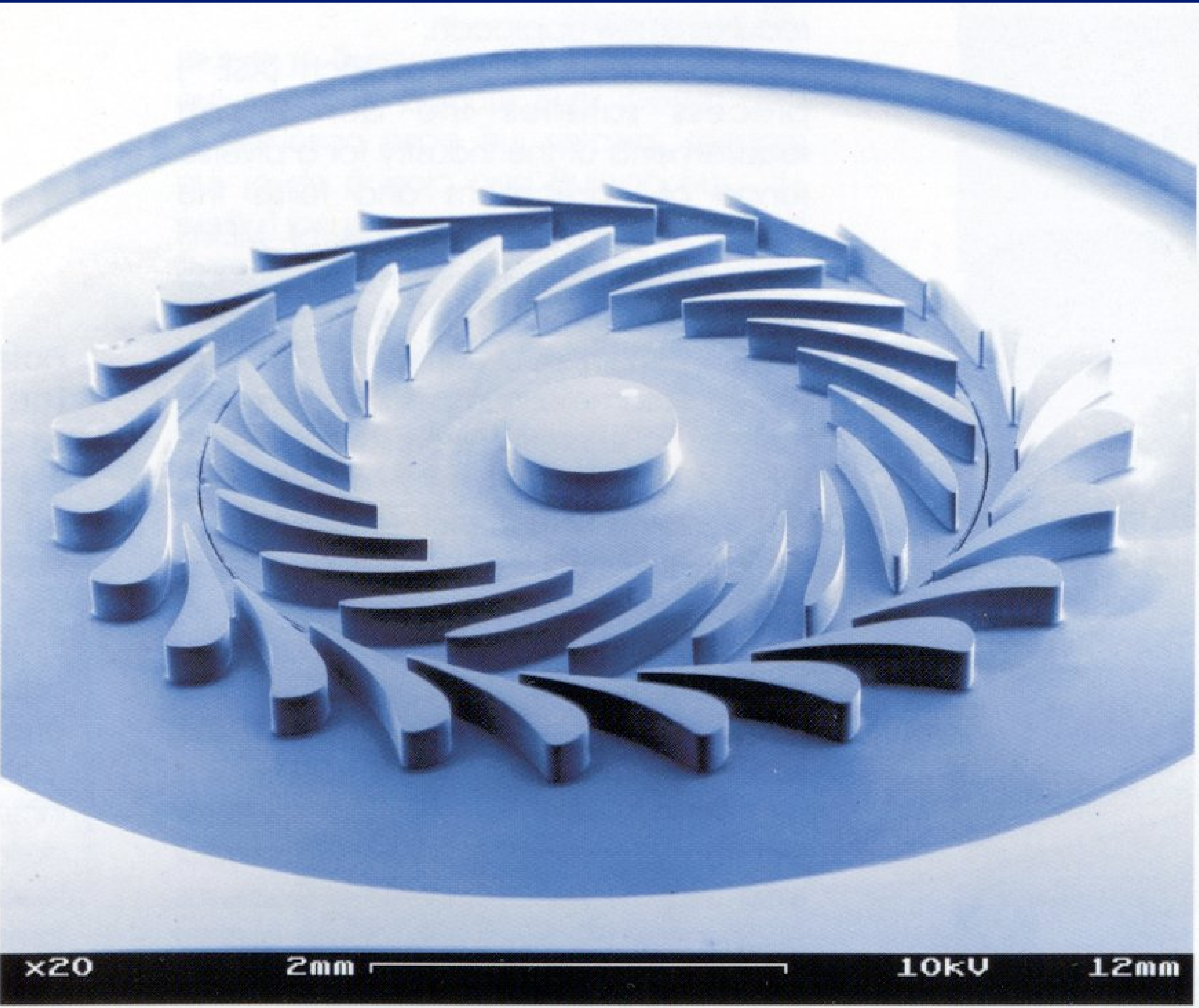




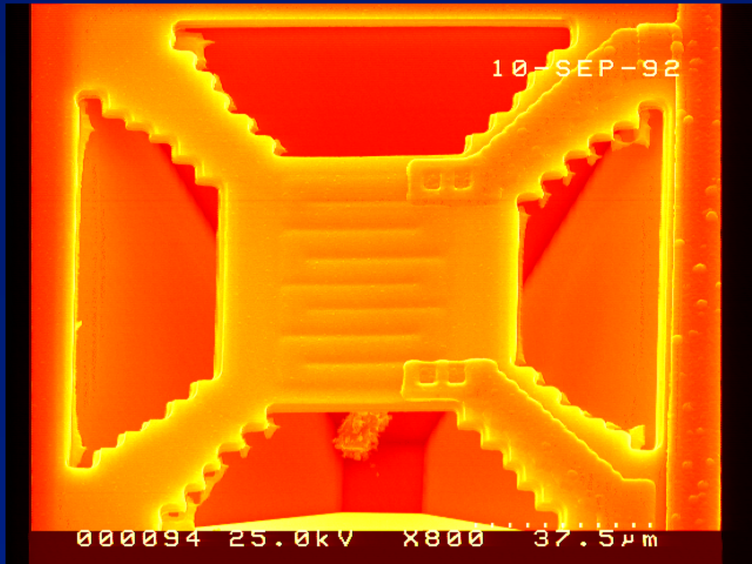
•Vertical features etched in silicon are required for micro-electro mechanical systems, optical applications, micro-fluidic devices, and semiconductor applications.

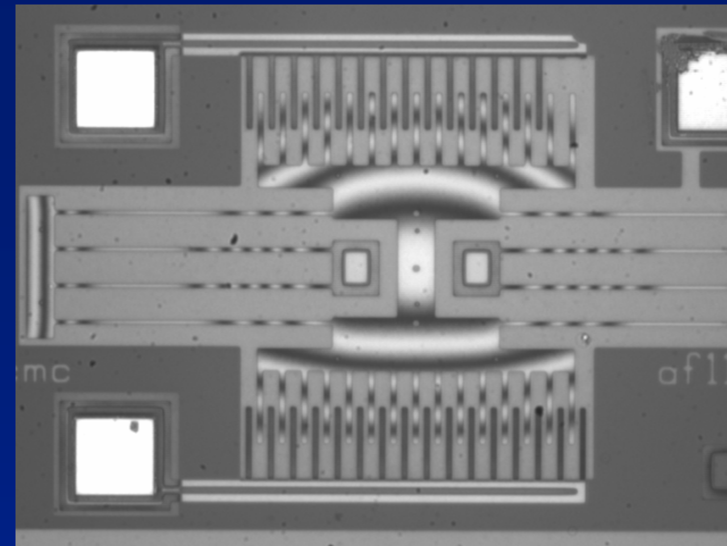
• As geometries of device components become smaller, the requirement to dry etch silicon with vertical profiles becomes important.

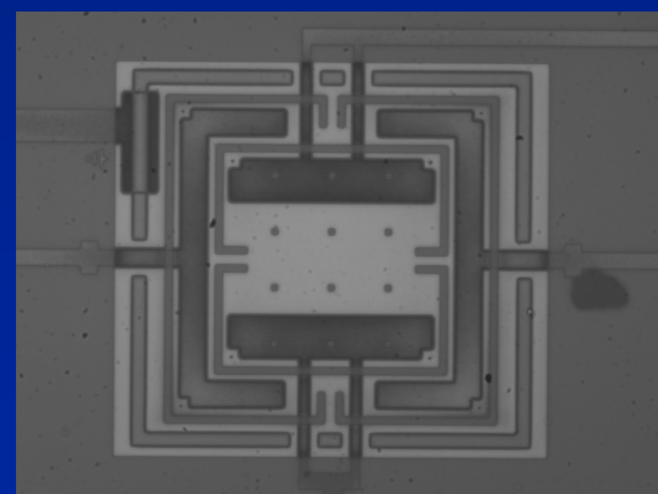
• Increasing aspect ratios often result in enhanced device performance.

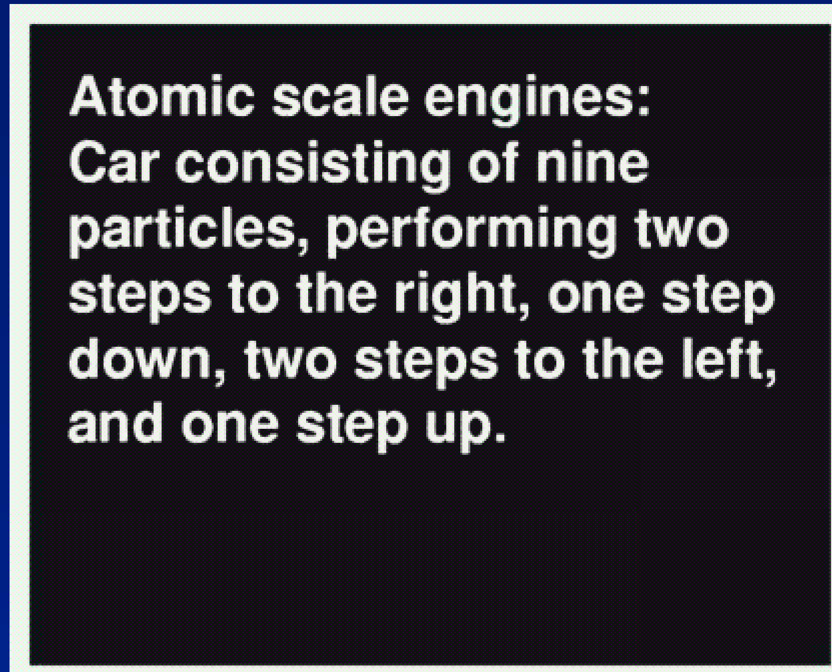


Micro-Turbine (courtesy of MIT)


10-SEP-92
000094 25.0kV X800 37.5μm

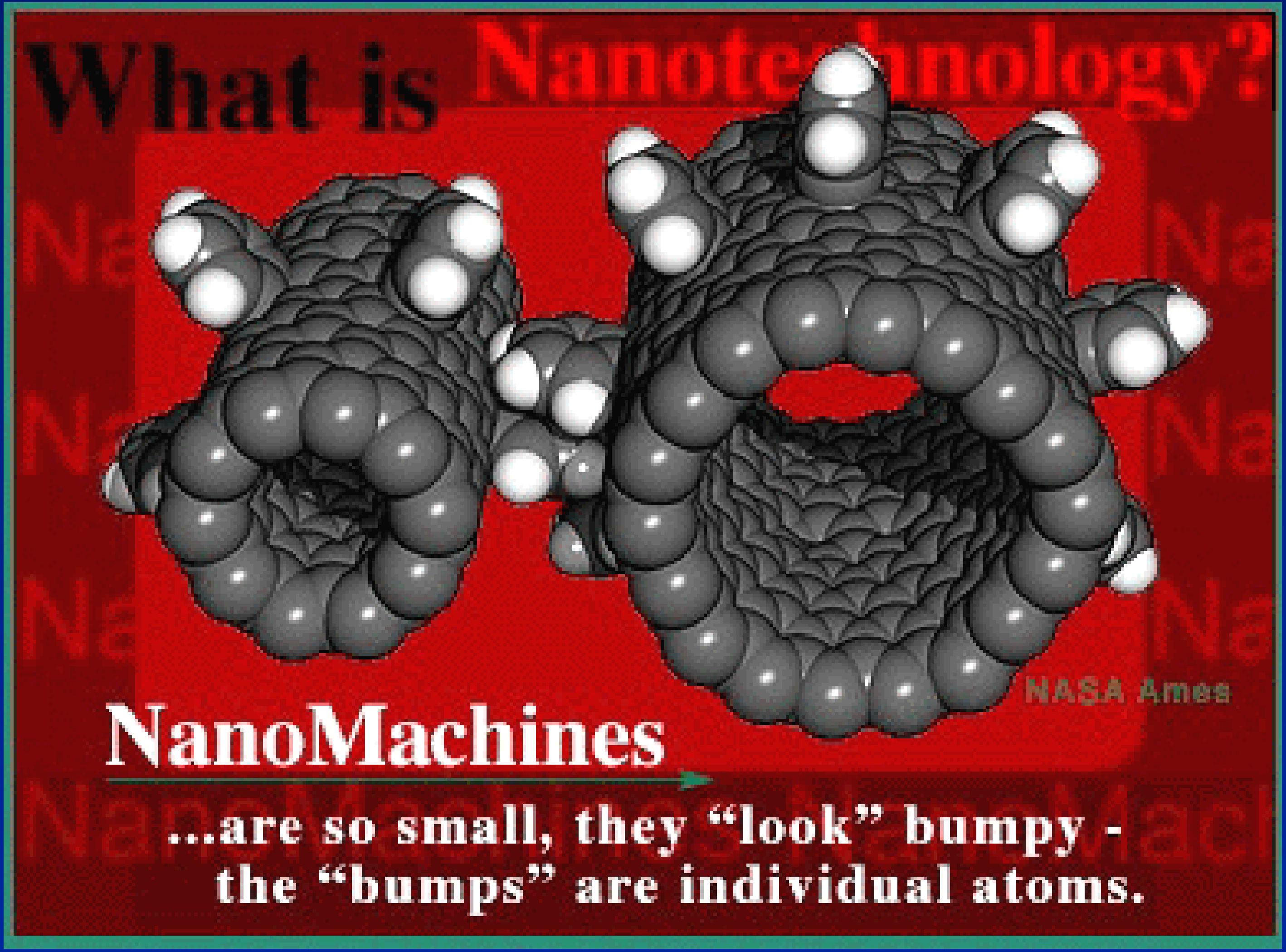

af11





A short movie showing how a molecular "locomotive" will possible work. The structure, consisting of two beads connected by a chromophore molecule which has the property of stretching or relaxing when struck by light from an outside source.

Reported by: Porto et al., *Physical Review Letters*, 26 June 2000.

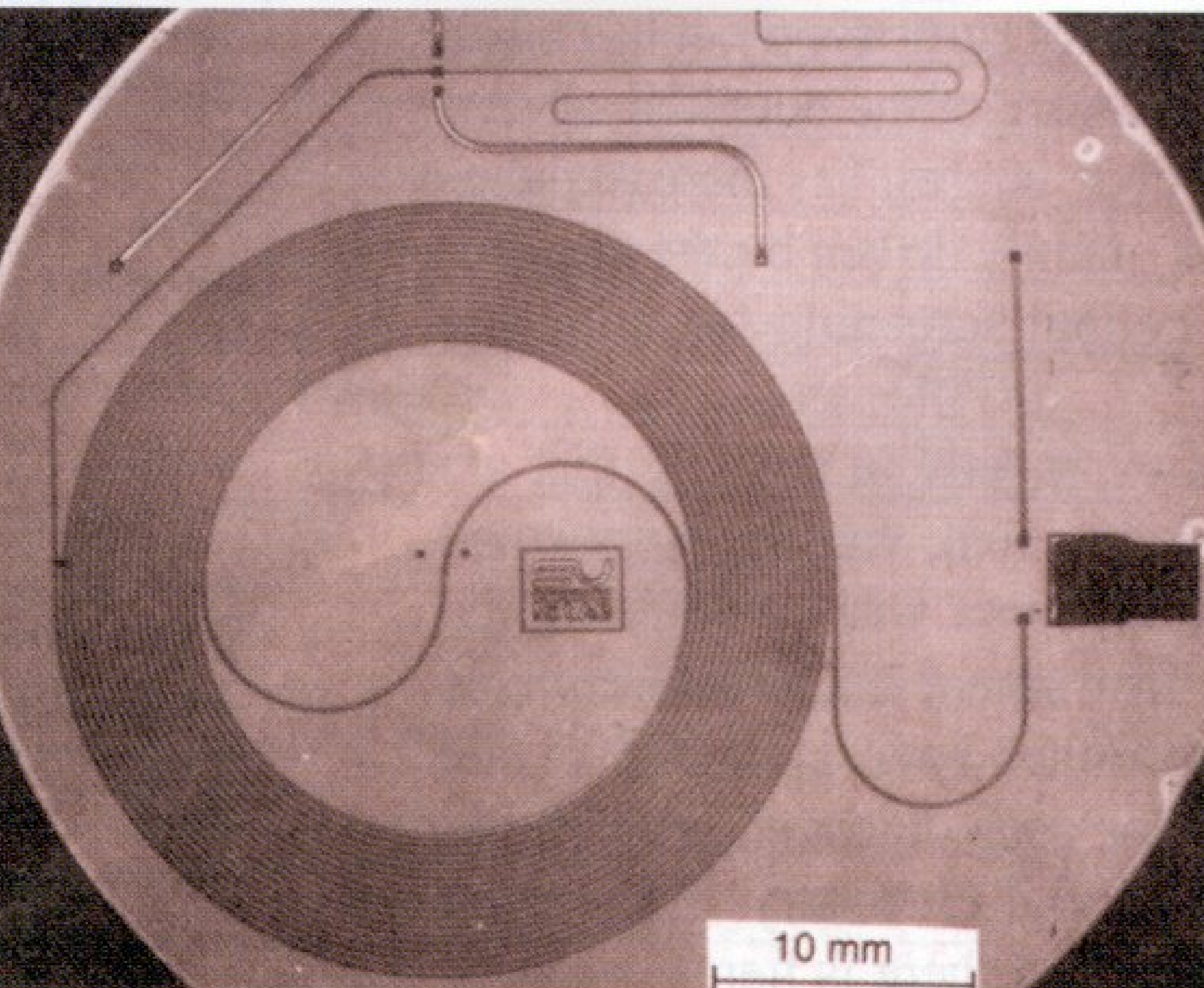

What is Nanotechnology?
NASA Ames
NanoMachines
...are so small, they "look" bumpy -
the "bumps" are individual atoms.

What will these machines do?

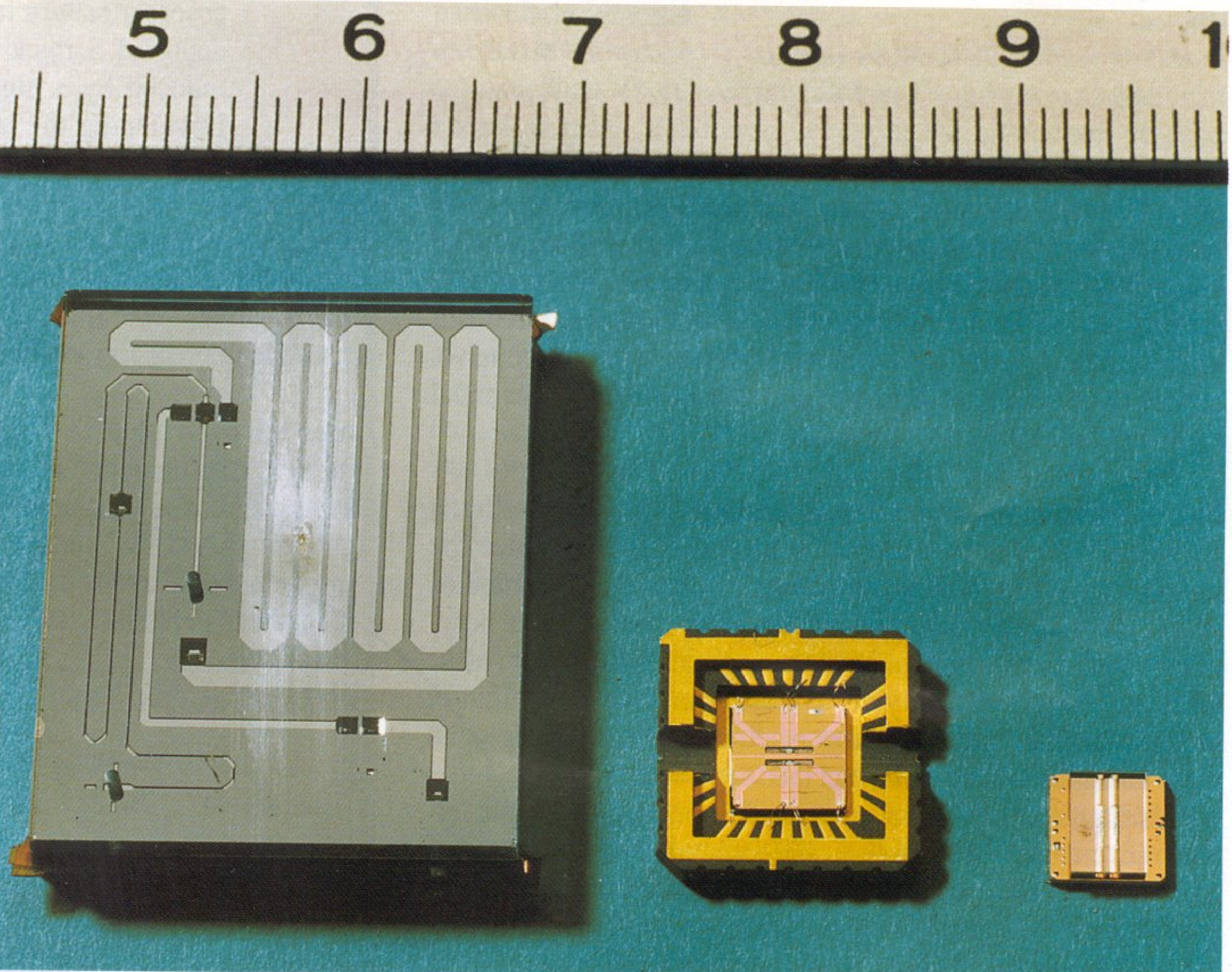
Analyse?

Process?

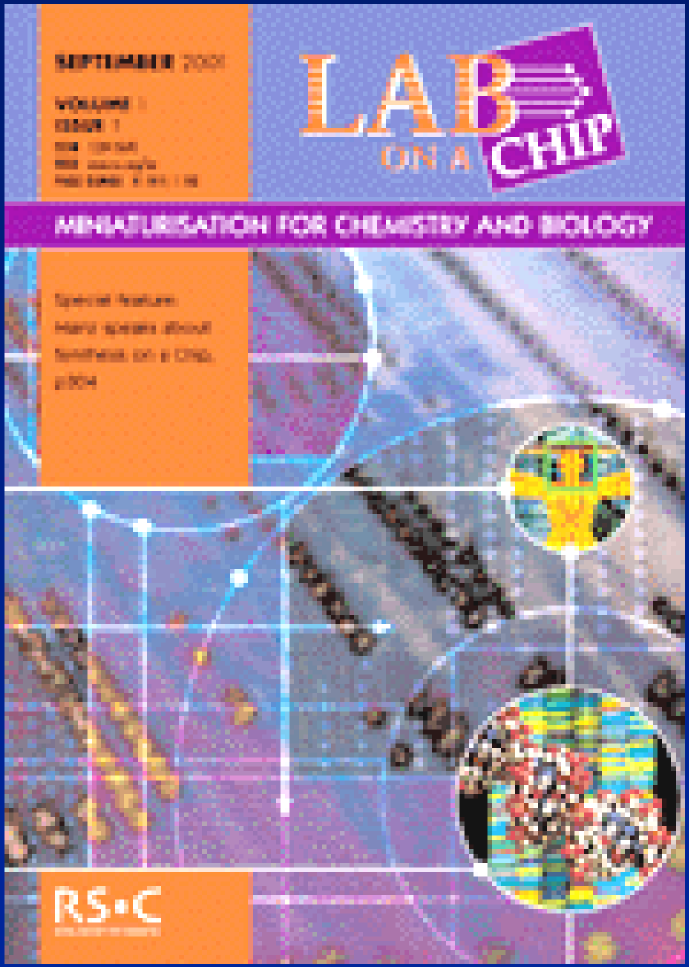
Diagnose?



Early work: the Stanford University gas chromatograph



Lab-on-a-chip technology: the future of chemistry is getting smaller

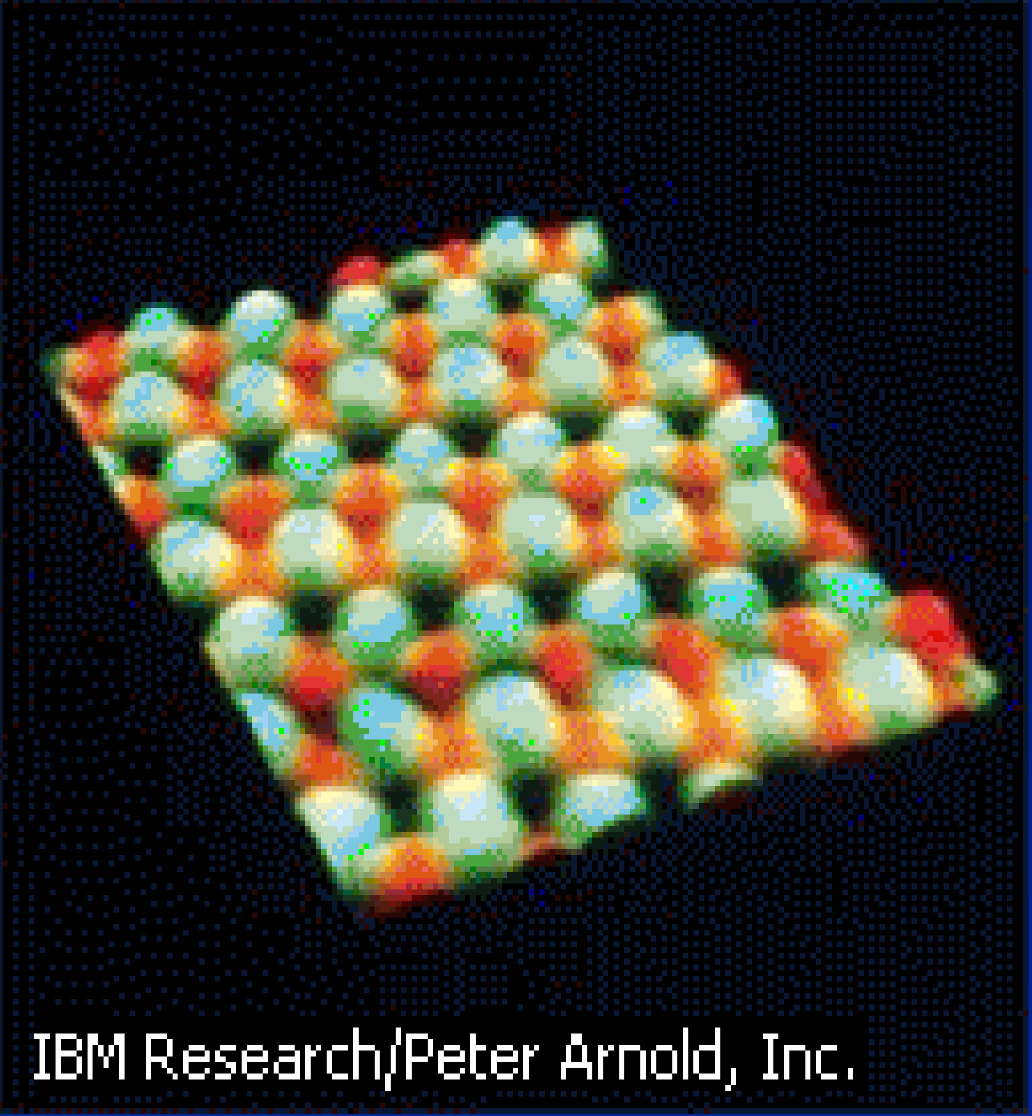


- Systems by Agilent
- Journals by RSC

What are the current limits to size?

Feynman’s 2nd Challenge

Are these absolute limits?

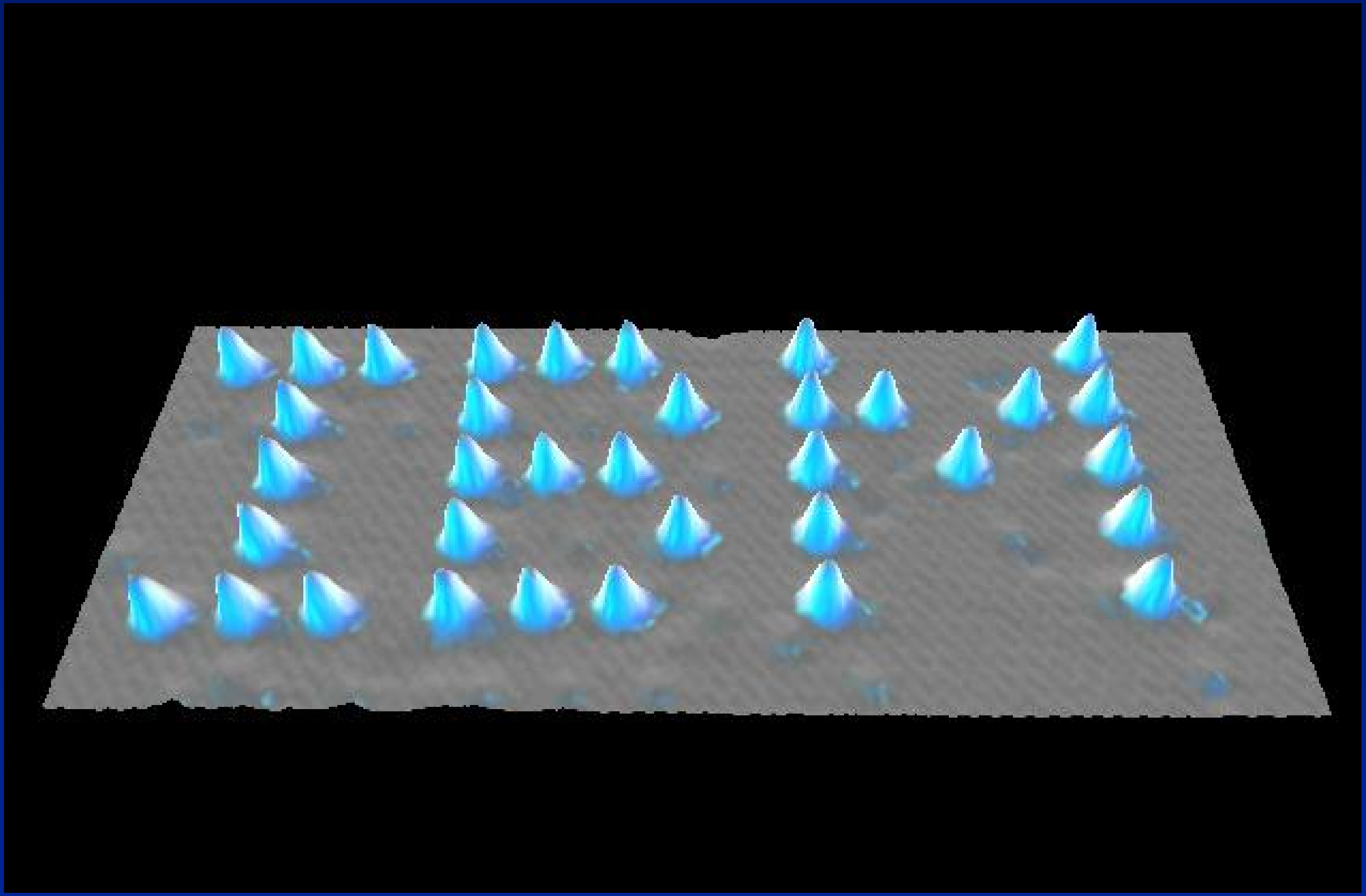


STEM

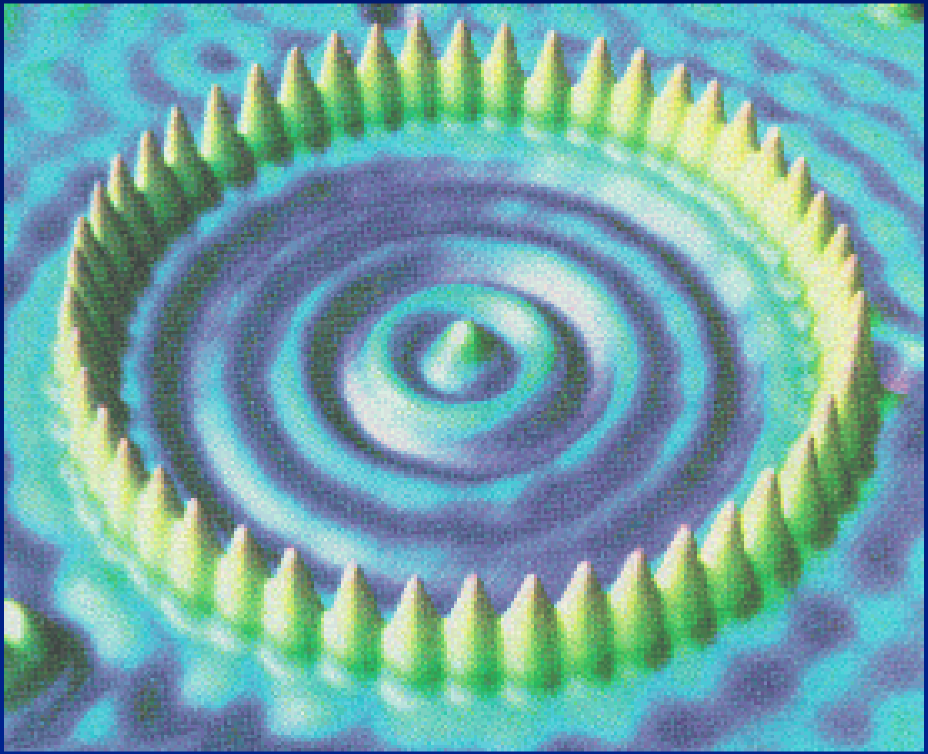
Scanning Tunneling Electron Microscopy

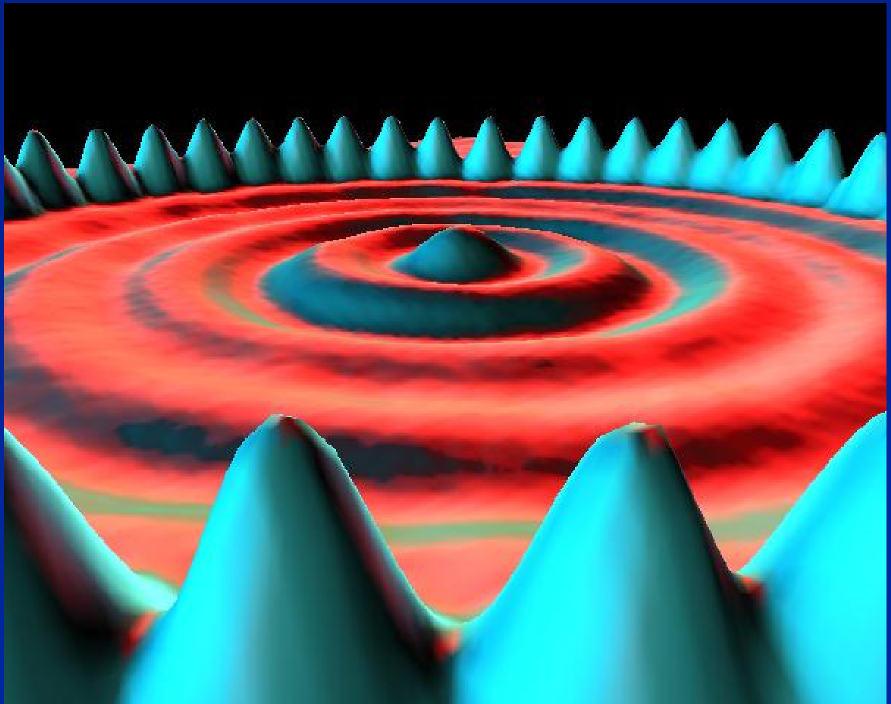
The scanning tunnelling electron microscope (STM) is a remarkable device invented in the 1980s by G. Bennig and H. Rohrer t

Individual atoms of the element germanium (Ge) can be seen. The microscope maps an atomic-scale surface by detecting an electric current flowing from the surface to the point of a fine metal probe.



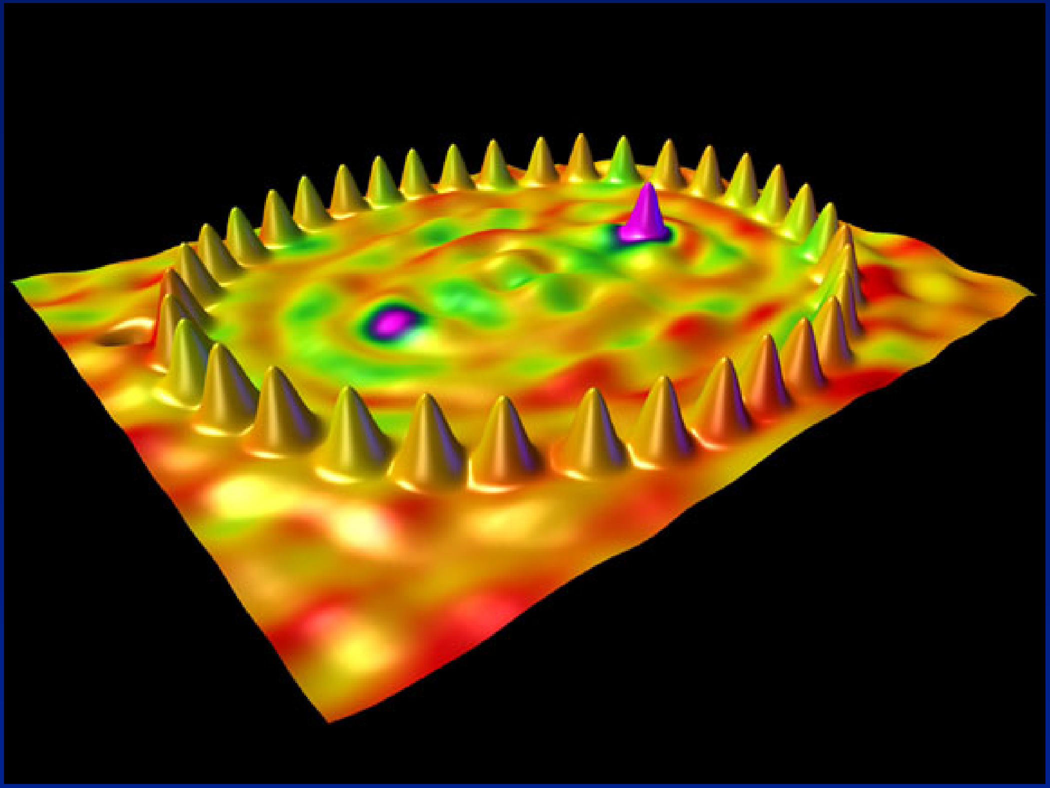
In 1990, D. M. Eigler and E. K. Schweizer of IBM used an STM to rearrange atoms on a surface. On a clean surface of nickel metal they used the tip of the STM to pick up individual Xenon atoms and move them around on the surface, with atomic precision.





Title : Quantum Corral
Media : Iron on Copper (111)

The density distribution of surface state electrons created in the artists a compulsion to have complete control of not only the atomic landscape, but the electronic landscape also. Here they havepositioned 48 iron atoms into a circular ring in order to "corral" some surface state electrons and force them into "quantum" states of the circular structure. The ripples in the ring of atoms are the density distribution of a particular set of quantum states of the corral. The artists were delighted to discover that they could predict what goes on in the corral by solving the classic eigenvalue problem in quantum mechanics -- a particle in a hard-wall box.



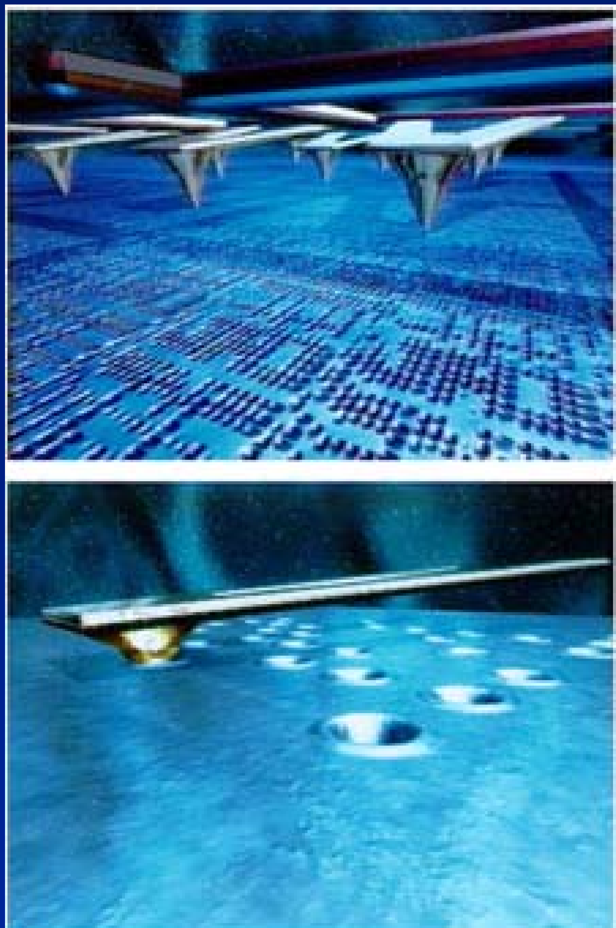
36 cobalt atoms in an elliptical "quantum corral"

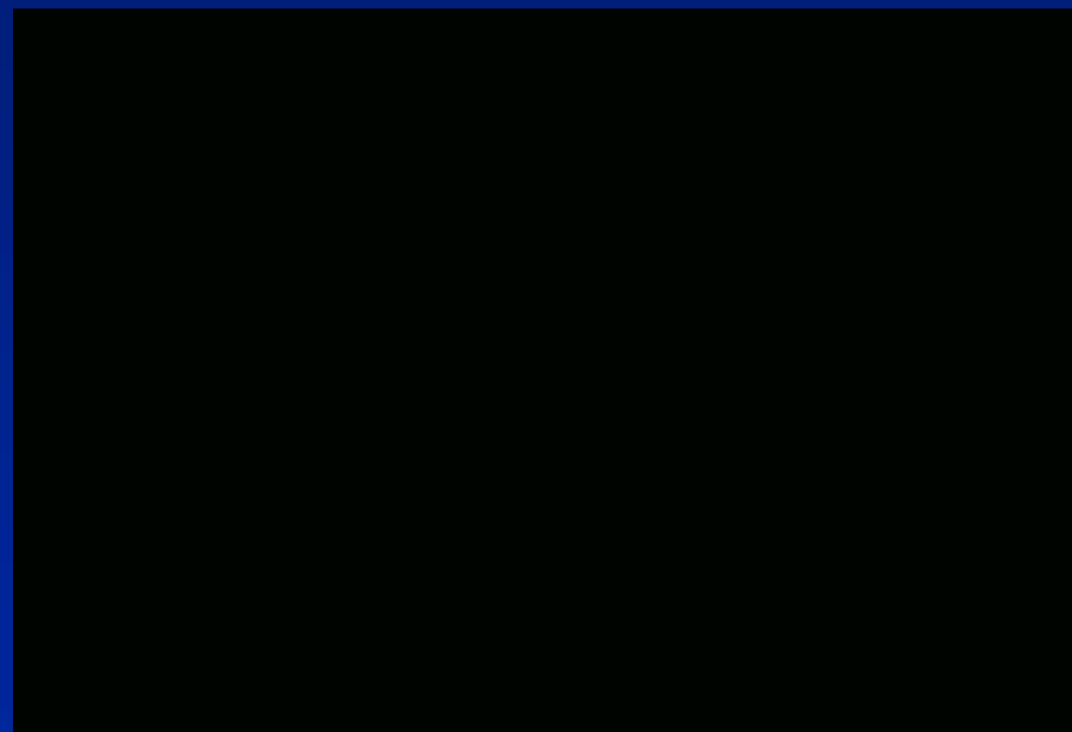
Electron waves moving in the copper substrate interact both with a magnetic cobalt atom carefully positioned at one of the foci of the ellipse and apparently with a "mirage" of another cobalt atom (that isn't really there) at the other focus.

(Courtesy of IBM.)

reported by: Manoharan et al., in *Nature*, 3 February 2000

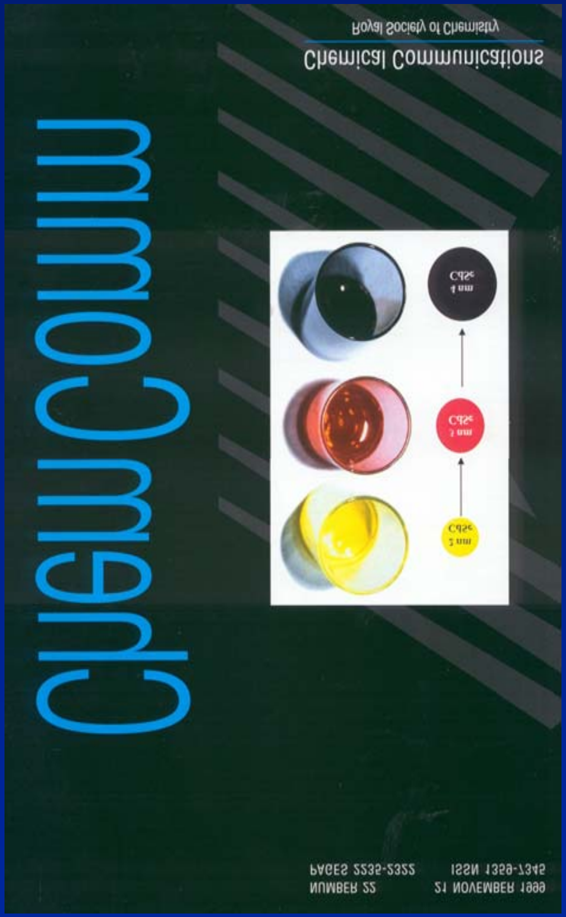
Store the equivalent of
25 DVDs on a surface
the size of a postage stamp !



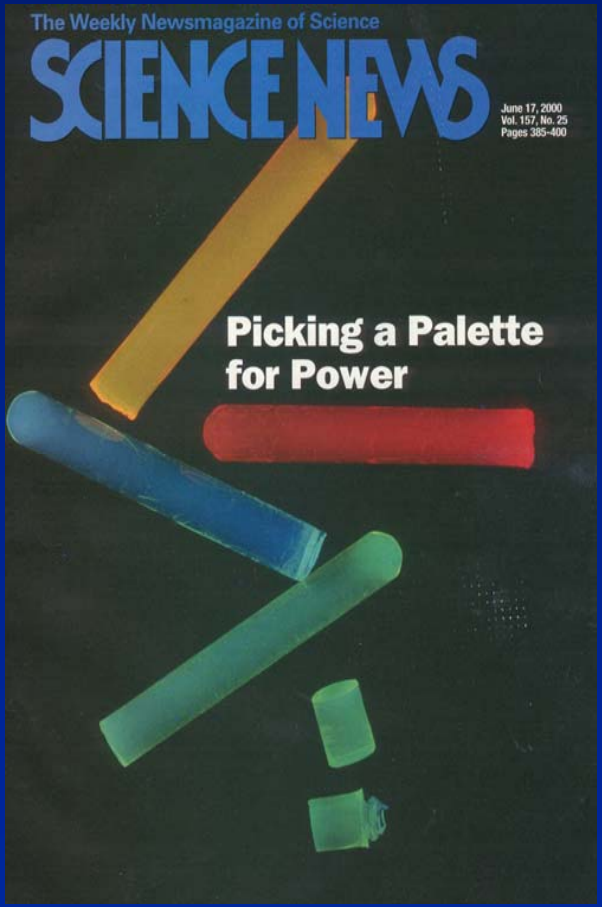


IBM's "Millipede" concept: an array of 1024 tips is scanned as a whole over a thin polymer film that is used as a storage medium. Each tip can be addressed infividually by a time-multiplexing system adapted from DRAM technology.

Why Now?

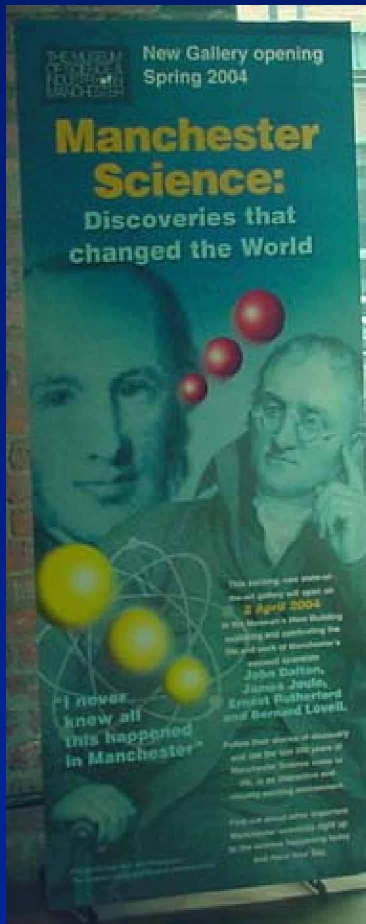


Royal Society of Chemistry
Chemical Communications
ChemComm



The Weekly Newsmagazine of Science
SCIENCE NEWS
June 17, 2000
Vol. 157, No. 25
Pages 385-400
Picking a Palette for Power

IPO REVIEW (ALAS)
CHIPS
RED HERRING
THIS COULD CHANGE EVERYTHING
NANOMATERIALS
NANOMEDICINE
NANOOPTICS


New Gallery opening
Spring 2004
Manchester Science:
Discoveries that changed the World
"I never knew all this happened in Manchester"


QUANTUM DOTS
These minute, light-sensitive nano particles are tens of thousands of times smaller than a human hair. These may be the cornerstones of the nanotechnology revolution.
© Images by kind permission of Manchester University


MICHAEL CONNELLY
CHASING THE DIME
PREY
MICHAEL CRICHTON
BESTSELLING AUTHOR OF JURASSIC PARK
LOONEY TUNES
Giga Pets
AFM
Interferometer Optics

10 things we'll know by this time next year

What will be the big scientific hits and misses of the next 12 months? Alok Jha looks ahead

Thursday January 8, 2004

The Guardian

1. How to make better cancer drugs

2. All about quantum dots

It may not sound like much, but these miniscule particles have not been nicknamed the ball bearings of the 21st century for nothing; before ball bearings were invented, there was no use for them and now they're everywhere. Sciebbntists say it will be the same with quantam dots.

Paul O'Brien, a chemist at Manchester University who helped to set up NanoCo, says the dots could replace inks or dyes in biological screening programmes. And further down the line, they could be used in security - bank notes could have barcodes made from the dots that would be very difficult to copy.

Until now the dots could only be produced in small batches and then only using dangerous chemicals. But this year NanoCo, a company spun out of the university, hopes to produce large quantities of them without using toxic materials.

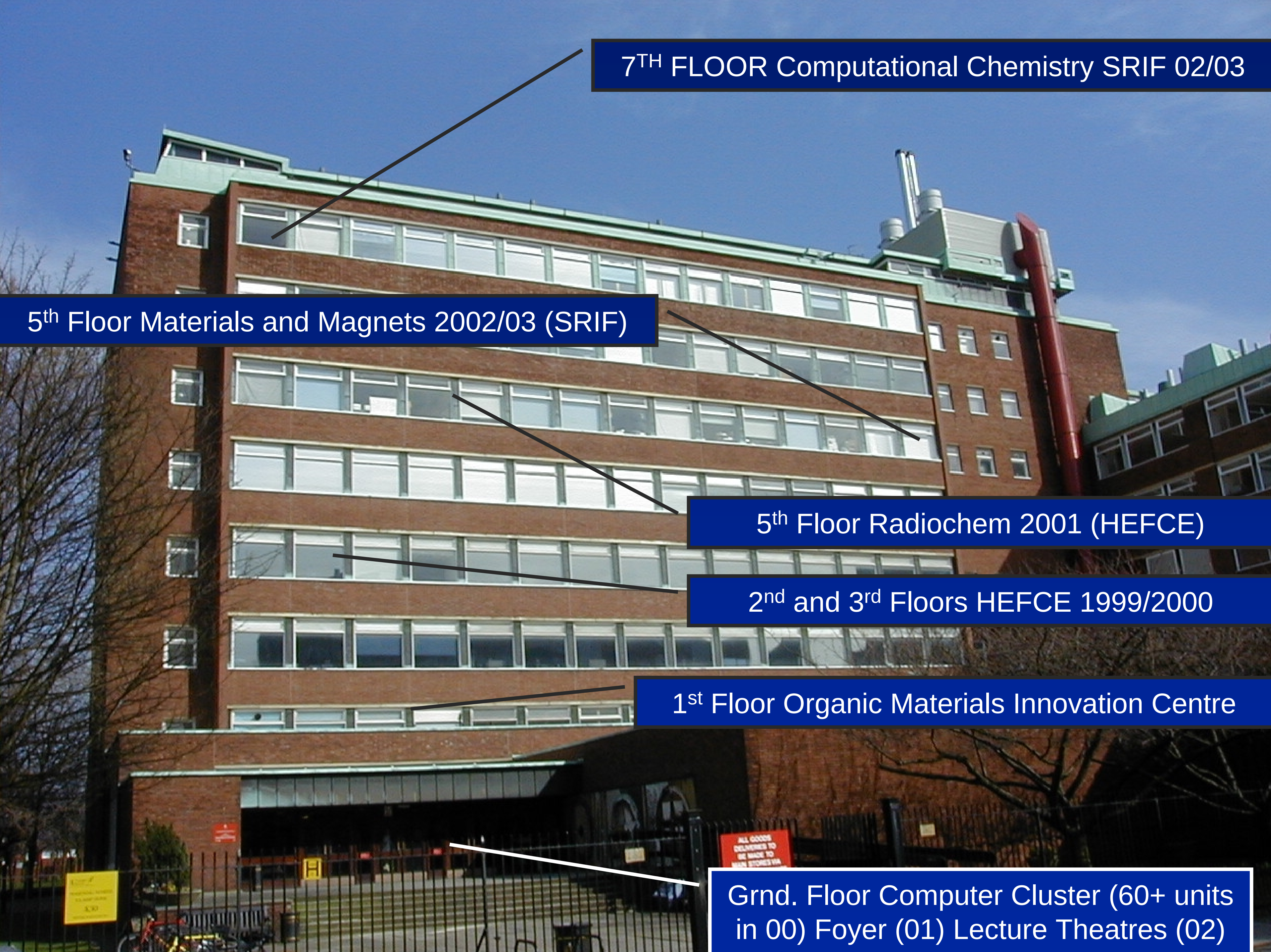
A New University for the 21st Century

- Established on 1st October 2004
- Royal Charter granted on 22nd October 2004
- 34 000 students from over 150 countries (1/3 postgraduate)
- 2000 academic staff & 1200 research staff
- £504M turnover (2004-5)
- £300M capital investment programme

MANCHESTER
1824

The University
of Manchester

Combining the strengths of UMIST and
The Victoria University of Manchester


7TH FLOOR Computational Chemistry SRIF 02/03
5th Floor Materials and Magnets 2002/03 (SRIF)
5th Floor Radiochem 2001 (HEFCE)
2nd and 3rd Floors HEFCE 1999/2000
1st Floor Organic Materials Innovation Centre
Grnd. Floor Computer Cluster (60+ units in 00) Foyer (01) Lecture Theatres (02)

November 2004/Volume 1/Number 11

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News review

FUNDING Good news for chemists at Manchester

Manchester merger completed

Multi-million pound boost for Manchester's School of Chemistry

HM the Queen was preparing to join freshers in Manchester, UK, for the official launch of The University of Manchester just as this issue went to the press. The institution, formed by the union of UMIST and the Victoria University of Manchester, will support 34 000 students, making it the largest single-site university in the UK. Its inauguration marks the first time that two British research-led universities have joined together.

The move has given rise to one of the largest chemistry departments in the UK, supporting around 60 researchers, over 200 postgraduates, over 600 undergraduates (second only to the University of Oxford), 6000m^2 of refurbished lab space and a two-year £13 million building project to include a suite of brand new teaching labs.

The new School of Chemistry is home to several research centres with extensive industry and research council support, including the British Nuclear Fuels (BNFL) centre for radiochemistry and the recently opened Organic Materials Innovation Centre, an independently-managed partnership between industry and academia. The new university overall has the third largest number of current EPSRC grants and the largest current value of BBSRC grants.

Strategic targets, outlined by head of school Paul O'Brien, include consolidating the school's position as a top 5* or equivalent UK chemistry school (5* may disappear in the next Research Assessment Exercise); forging stronger links with business and industry; increasing research spinout and commercial activity; and regional, national and international strategic research planning for new and emerging science and technology. In 2001, the last RAE before the two universities joined forces, the Victoria University of Manchester scored five in chemistry, while UMIST scored four. *Bea Perks*

INDUSTRY

Fantastic plastic

BASF wish you plastic dreams

German-owned chemicals company BASF has put out a call to specialists and 'interested amateurs' to enter a competition to suggest exciting ideas for new plastics, applications for plastics or processes for producing plastics.

The competition is not only open to people who work with plastics, says Thomas Fritzsche, a plastics sales manager at BASF. Anyone and everyone with an idea is welcome.

'Don't limit yourself by

ISSN 1473-7604

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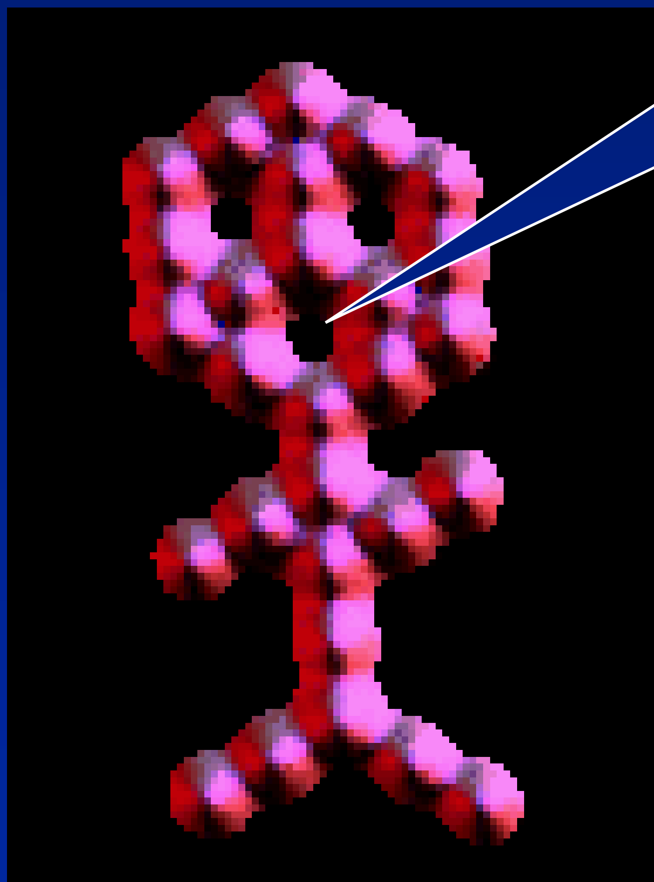
- **A GOOD START!**
- THES
- Chemistry World
- BBC1 Politics Show
- UniLife



Goodbye and Thanks for Listening