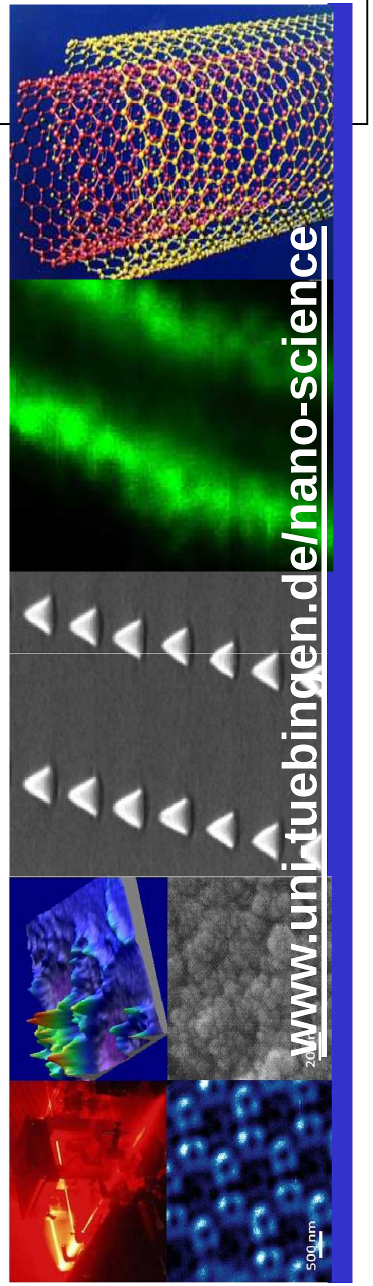
Introduction to Nano-Science I

Einführung in die Nano-Science I

Prof. Dr. Frank Schreiber (Studiendekan)
frank.schreiber@uni-tuebingen.de
Tel.78663, office C7A35
http://www.soft-matter.uni-tuebingen.de
MON & THU 15-17 in BioIII / N10-50



Outline

1. Who are we ?
2. What is nano-science ?
3. Why do we do nano-science ?
   → Fundamental questions
   → Applications
4. What is going to come ?
   → Tools and methods
   → Preparation
   → Effects
5. Organisation and logistics (Üner in the break)

Introduction to Nano-Science I

Who are we ?

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Tel.78663, office C7A35
http://www.soft-matter.uni-tuebingen.de

Biology

Prof. Dr. Klaus Harter

Dr. Üner Kolukisaoglu (Studienkoordination)

Physics

Dr. Fajun Zhang

Dr. Monika Fleischer

Chemistry

Prof. Dr. Reiner Anwander

Dr. Yucang Liang

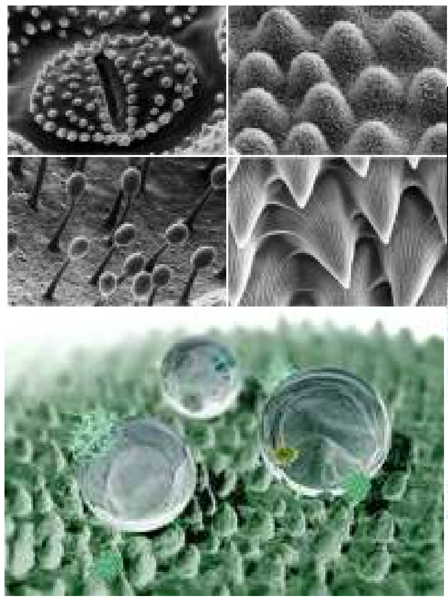
What is Nano-Science ?

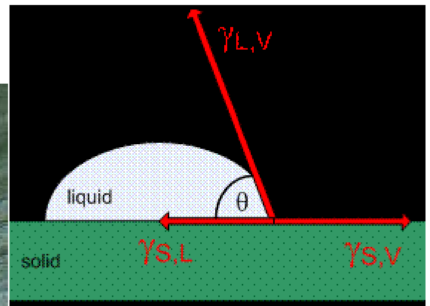
Introduction to Nano-Science I

What is Nano-Science ?

- "Nano-Science" summarises the scientific areas concerned with materials and effects on the nano-meter scale (1 nm=0.000000001 m) (note that "nano one dimension (i.e. thin films)" is enough to qualify)
- Interdisciplinary in nature (biology / chemistry / physics) (including applications and engineering)

An example:
Lotus effect





Introduction to Nano-Science I

What is Nano-Science ?

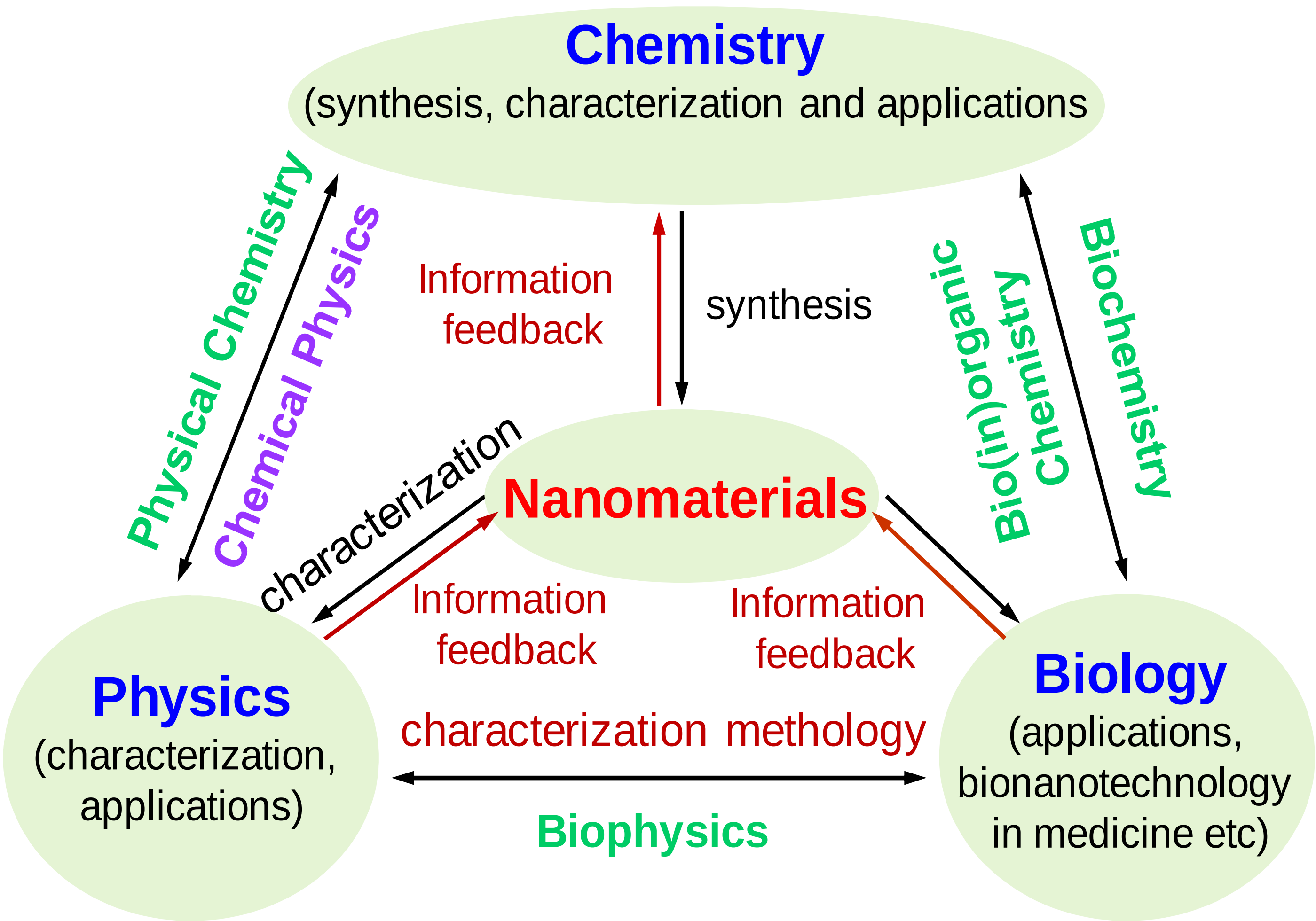


Figure prepared by Yucang Liang

Introduction to Nano-Science I

What is Nano-Science ?

General remarks

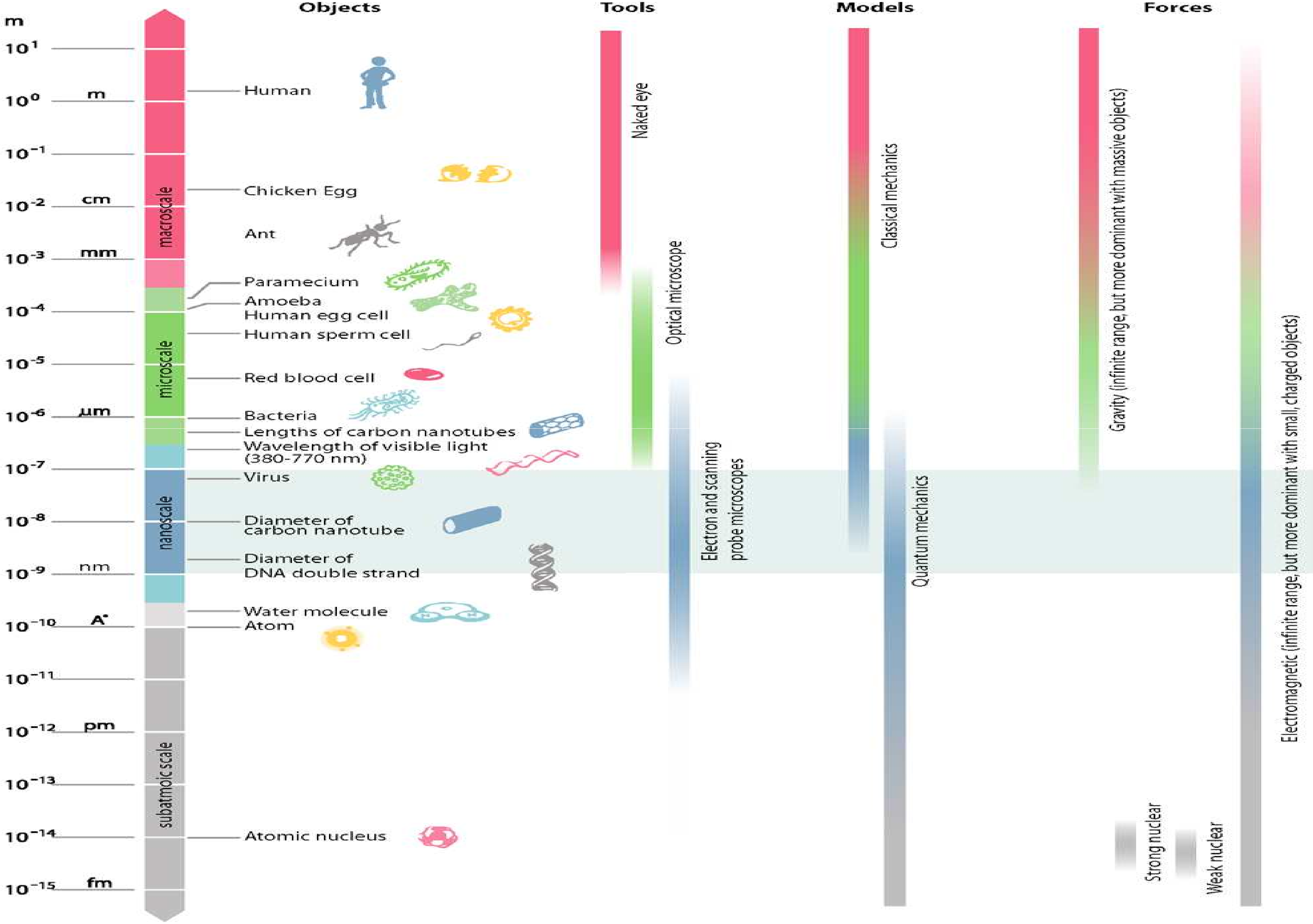
Consider relevant orders of magnitude

… length scales
… time scales
… energy scales
… temperature scales

Methods for Characterisation

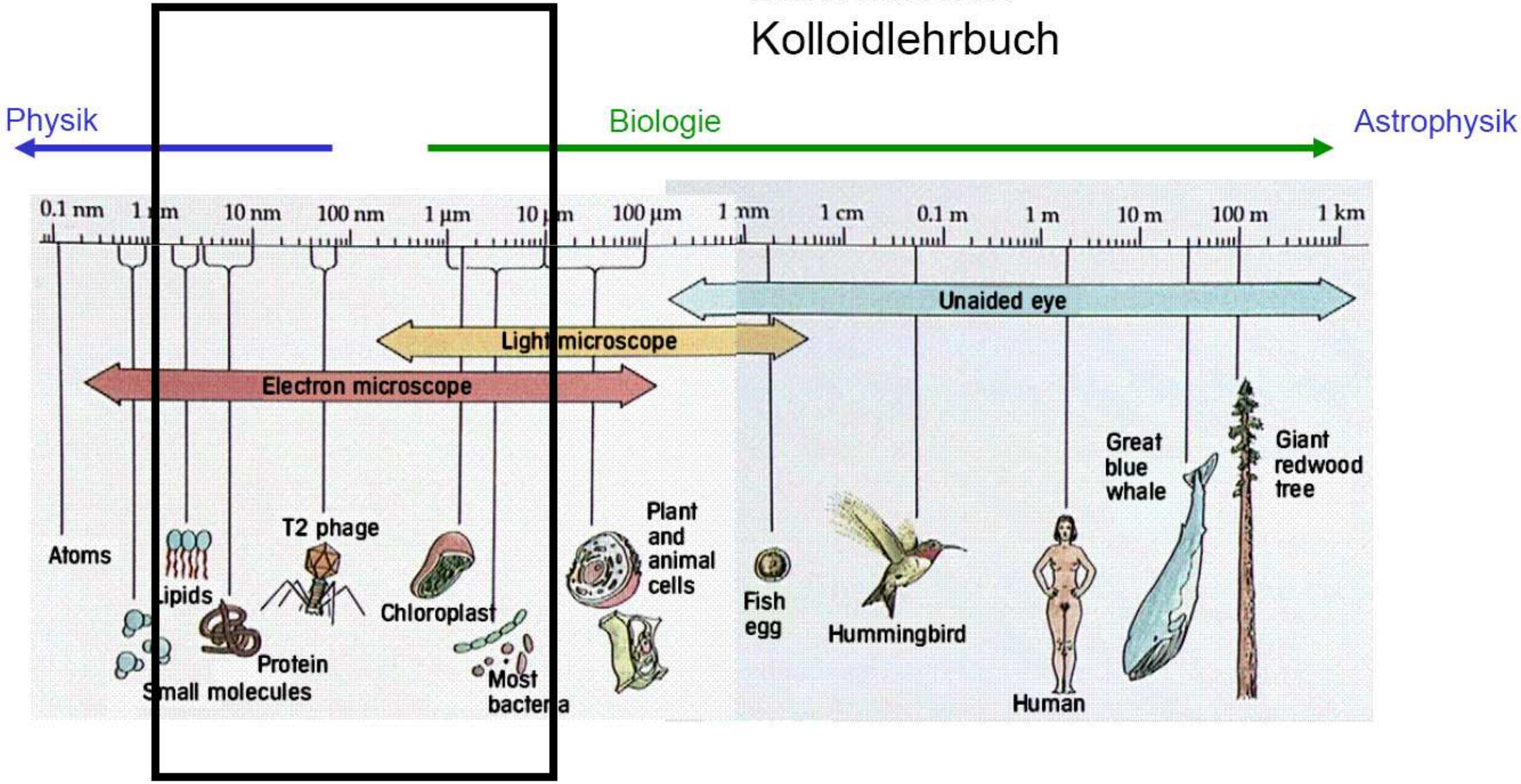
... microscopy
... scattering
... spectroscopy

Scale Diagram: Dominant Objects, Tools, Models, and Forces at Various Different Scales



Weiche Materie (Soft Matter)

Wolfgang Ostwald (1915):
Die Welt der vernachlässigten Dimensionen
Kolloidlehrbuch



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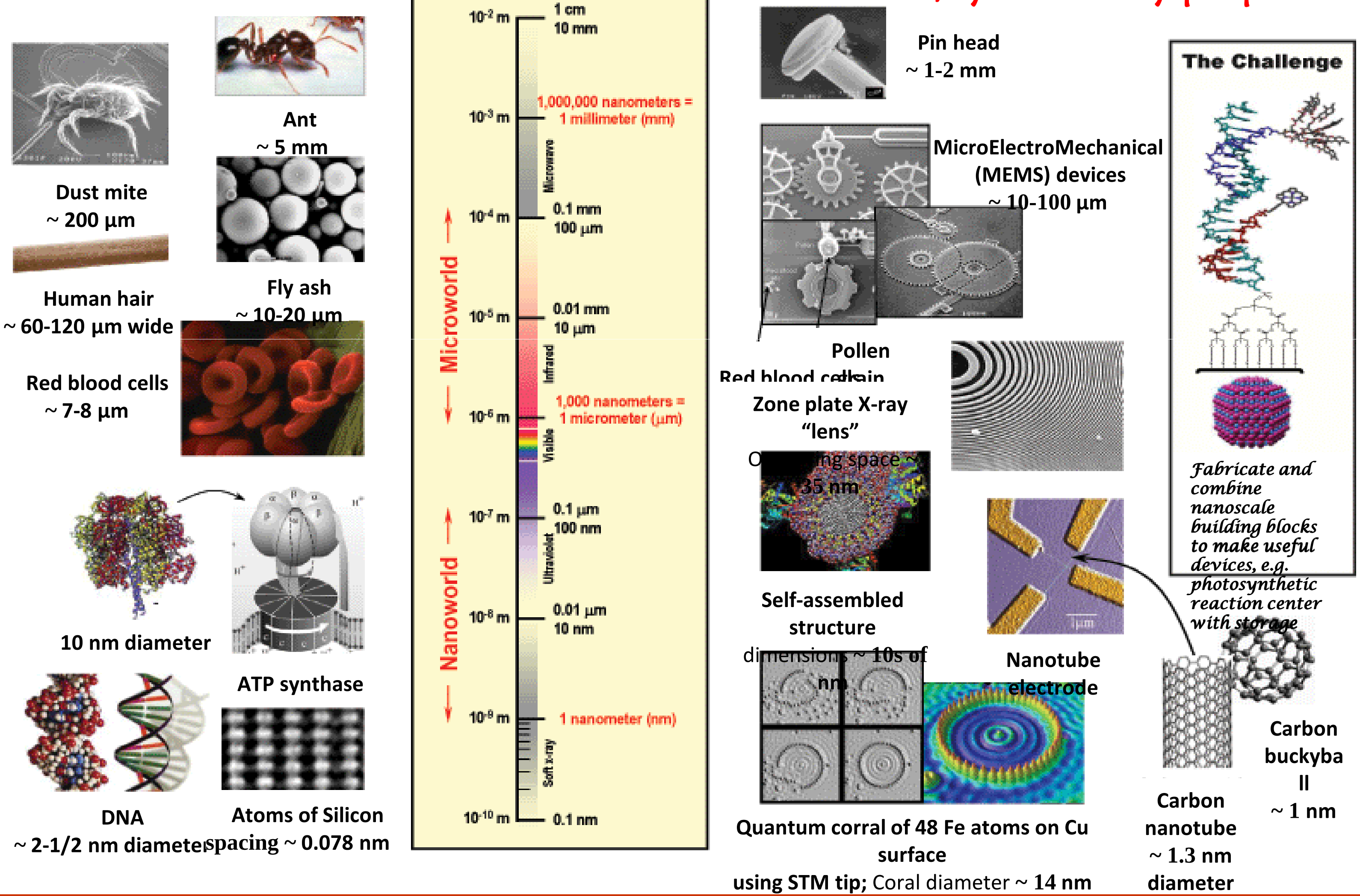
Introduction to Nano-Science I

What is Nano-Science ?

Available in Nature | Manmade/synthetically prepared



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Note that there are not only *length* scales,
but also *time* and *energy* scales

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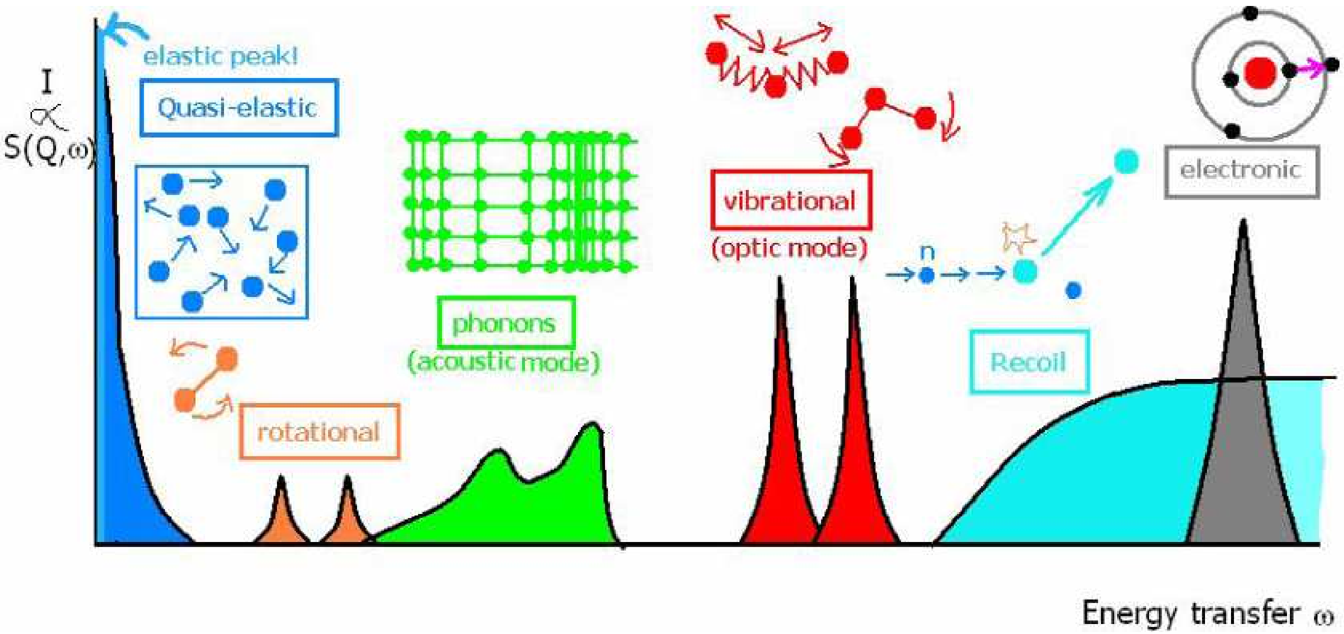
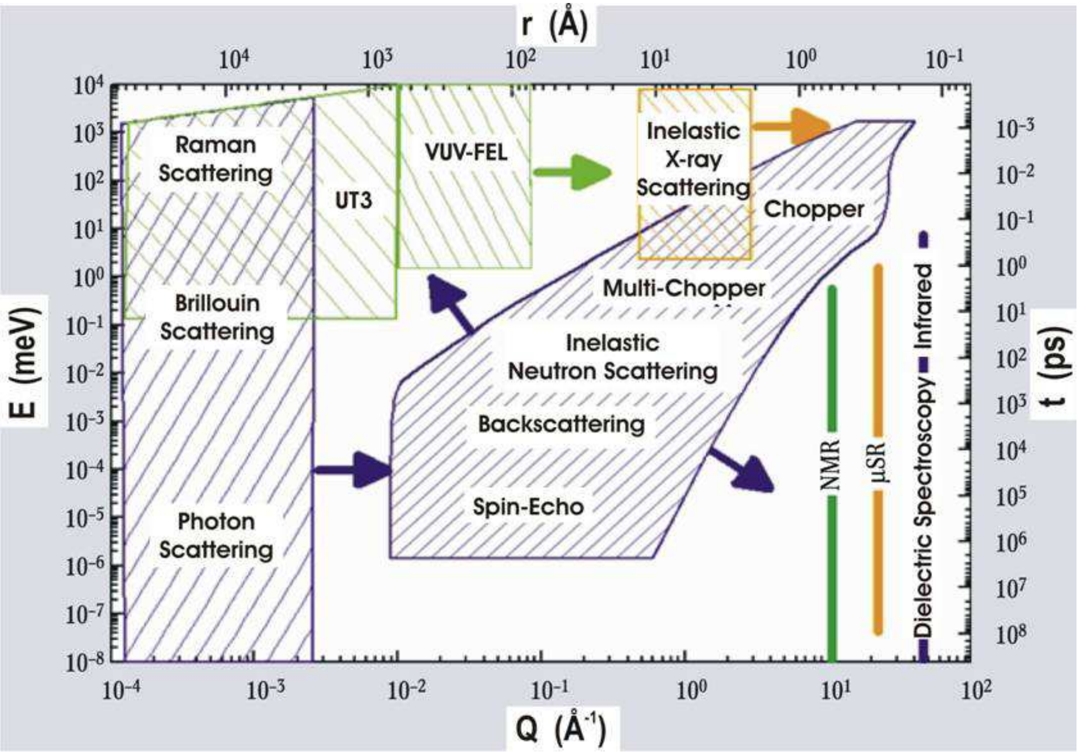


Note that there are not only *length* scales, but also *time* and *energy* scales



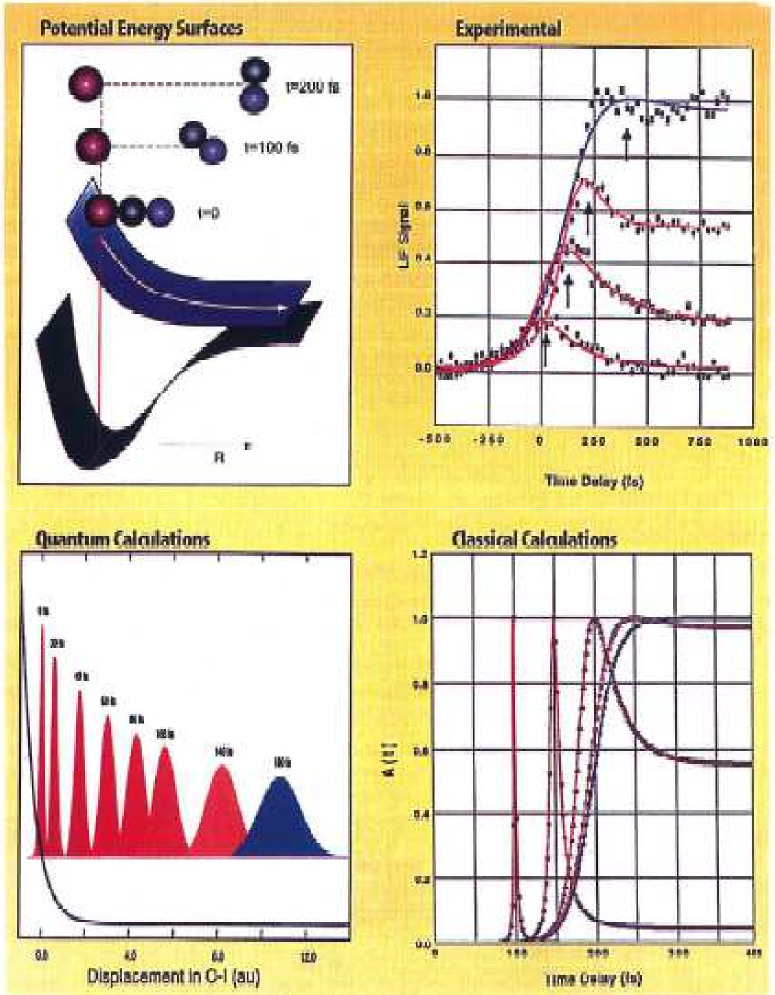
$$E = \hbar\omega = h\nu \quad \rightarrow h/t$$

i.e. order of magnitude: energy 1 meV → time scale ~1 ps

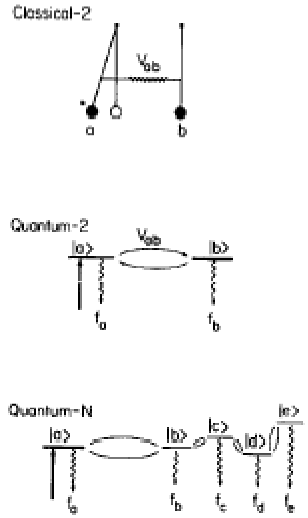
If you want to understand *function*,
you need to study *structure*

(added later by Zewail and others:)

… and *dynamics*.



$$\Psi(R,t) = \sum_i c_i \cdot \psi_i(R) \cdot \exp(-iE_i t/\hbar)$$



Ahmed Zewail

Nobel Prize 1999

in Chemistry

"for his studies of the transition states of chemical reactions using femtosecond spectroscopy "

Introduction to Nano-Science I

What is Nano-Science ?

Why do we do Nano-Science ?

Why do we do Nano-Science ?

Fundamental issues

& Applications

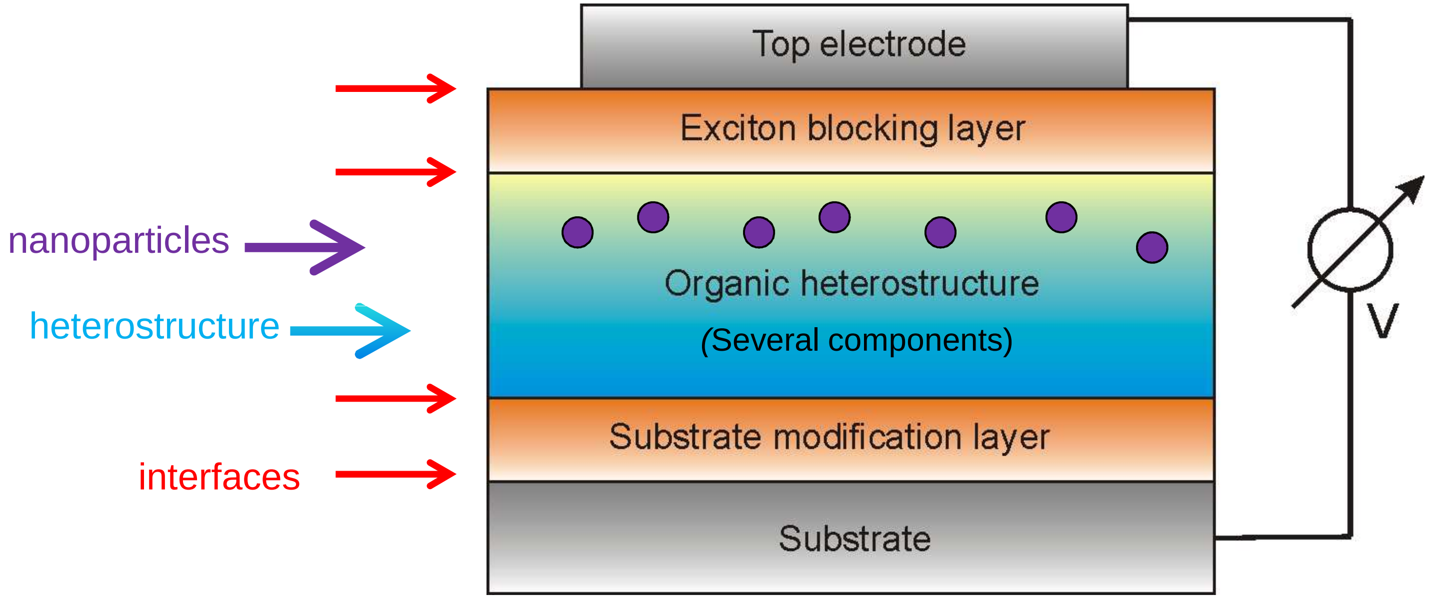
Fundamental issues

1. How do things work on the microscopic level ?
   → in solids ? (e.g, Do we understand crystallisation of proteins ?)
   → in chemistry ?
   → in biology ? (from Hamiltonians to Life ?)
2. Small is different ? … new effects ?
   → magnetic recording (perpendicular magnetisation)
   → giant magneto-resistance (GMR)
   → Mermin-Wagner-theorem ("magnetism breaks down in pure 2D")
   → melting point changes for small particles compared to bulk
   → limits of microelectronics ?
3. Small is different ? … new material properties ?
   → colour effects of nano-particles
   → quantum transport
   → …

Applications

1. New material properties, e.g.
   → small is different
   → new structures (e.g., open frameworks)
2. New effects, e.g.
   → magnetic recording (perpendicular magnetisation)
   → giant magneto-resistance (GMR)
   → colour effects
3. New sensing applications, e.g.
   → various microscopy techniques
   → field enhancement near nanoparticles
   (see section on nano-science and biology)
4. …

Example: Making Organic Photovoltaics Devices



→ This is a *very* complicated architecture !

→ There is lots of work for nano-scientists to improve this !

What is going to come in Nano-Science I ?

<u>Outline of the lecture is **_not really:_**</u>

1. Nano-Science and Biology
2. Nano-Science and Physics
3. Nano-Science and Chemistry

What is going to come in Nano-Science I ?

Outline of the lecture is ***rather:***

1. Making nano-materials:
   Top-down vs. Bottom-up
2. Making nano-materials:
   Nano-chemistry
3. Properties & applications of nano-materials:
   Gold nanoparticles as a prototype example
4. Nano-science and biology:
   Advanced microscopy tools and beyond

Making nano-materials:

Top-down vs. Bottom-up

(Fajun Zhang and Monika Fleischer)

Introduction to Nano-Science I

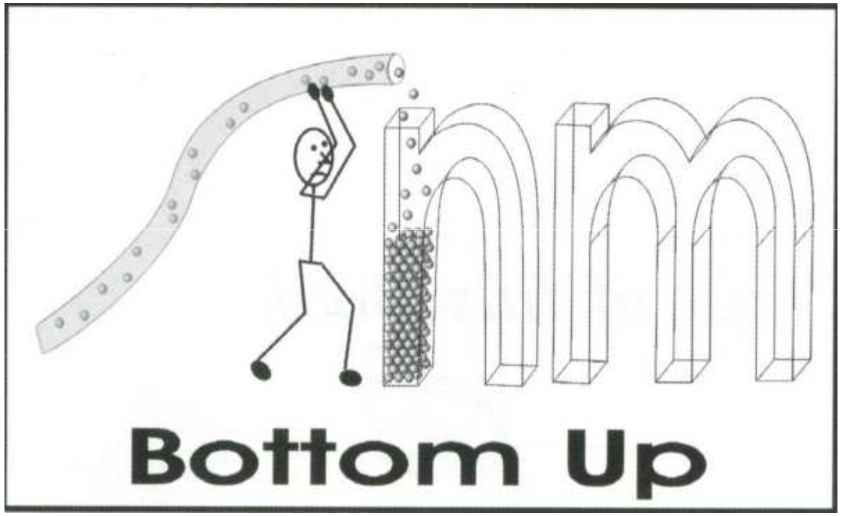
What is going to come in Nano-Science I ?

Making nano-structures

Manipulation of atoms on surfaces …

Smart chemistry …

Lithography and beyond …



"Bottom up" fabrication:

(Self organized) arrangement of atoms, molecules or particles, e.g. by chemical synthesis. Very small particles possible, limited control over shape and position.

"Top down" fabrication:

Fabrication of individual structures from extended material, often miniaturization of existing concepts. Good control over position and shape, downsizing limited.

Making nano-structures

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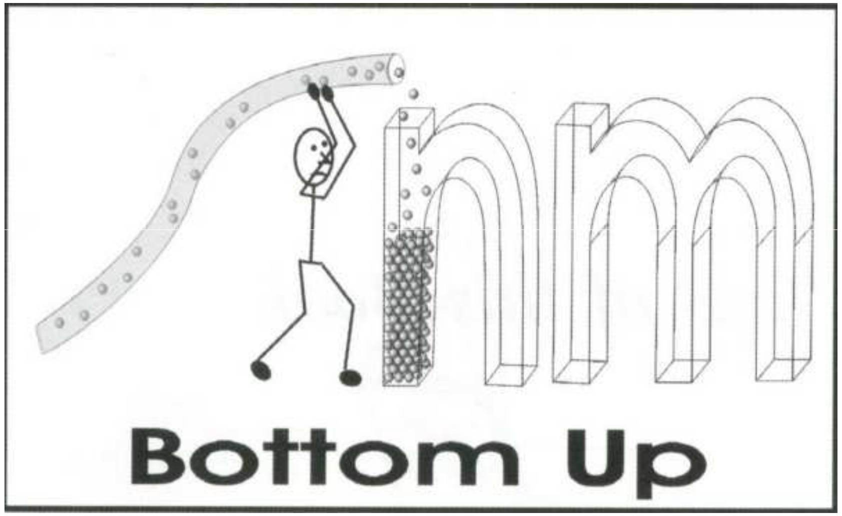

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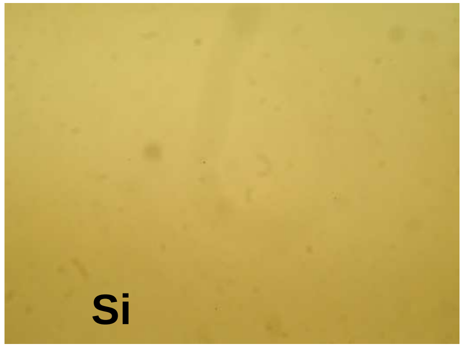
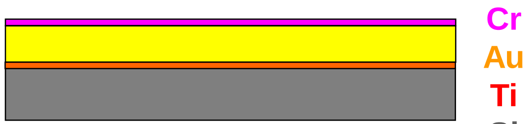
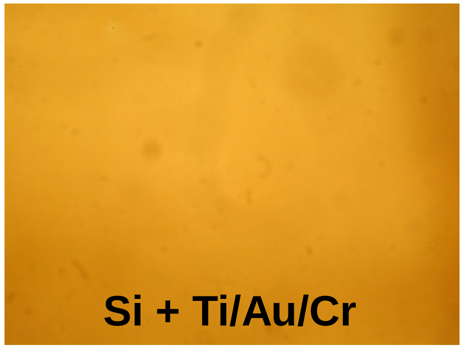
Fabrication process - example

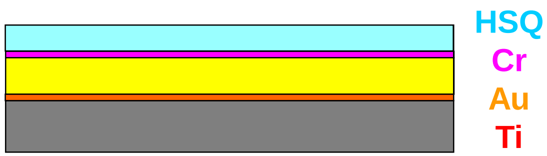
1) Silicon wafer



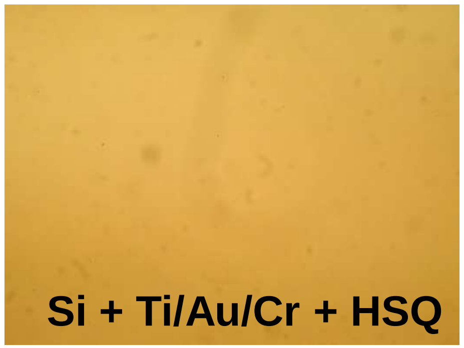


2) Evaporation of Ti, Au and Cr



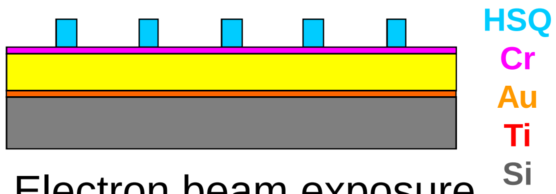


3) Spin-coating with HSQ negative e-beam resist

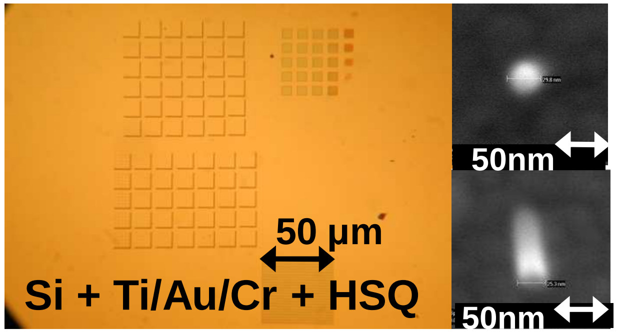


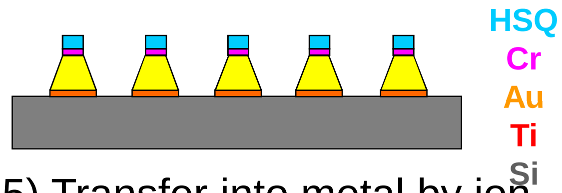
F. Stade et al., Microelectron. Eng. 84, 1589 (2007); M. Fleischer et al., Nanotechnology 21, 065301 (2010)

Fabrication process - example

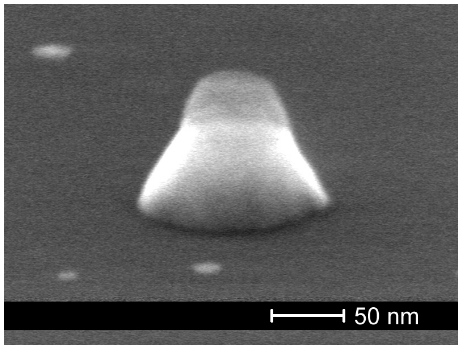


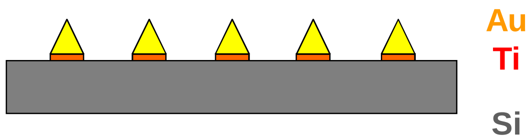
4) Electron beam exposure, development with TMAH



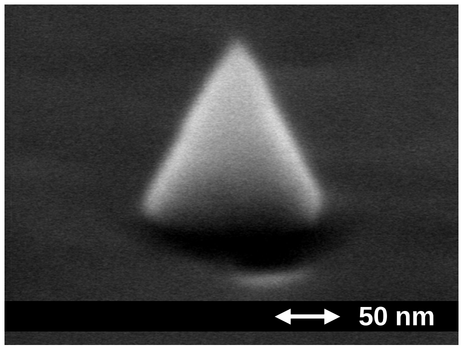


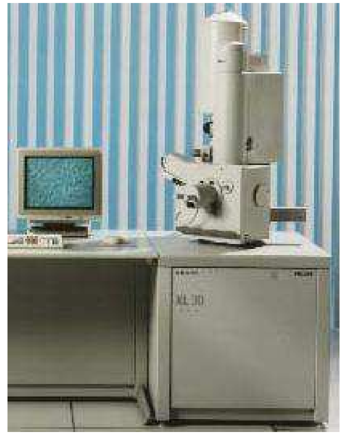
5) Transfer into metal by ion etching

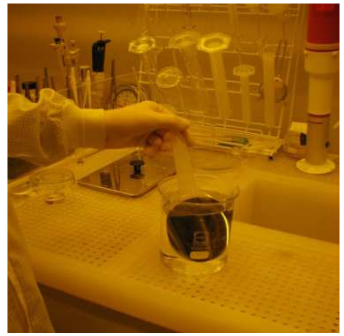




6) HSQ removal by further ion etching





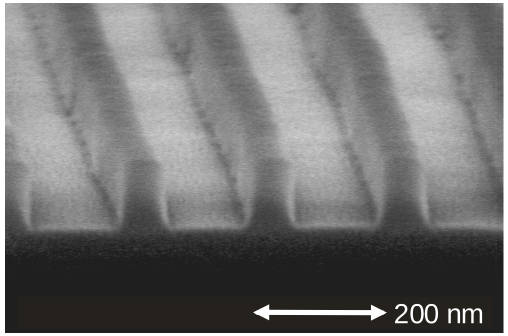


F. Stade et al., Microelectron. Eng. 84, 1589 (2007); M. Fleischer et al., Nanotechnology 21, 065301 (2010)

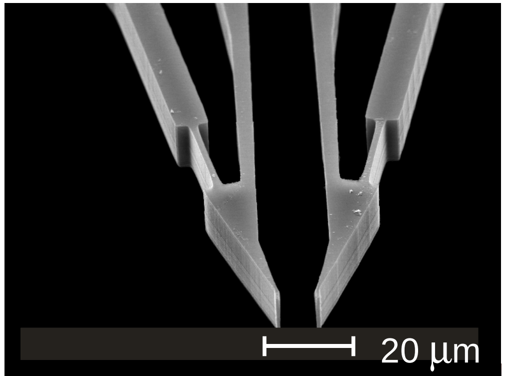
Functional micro- and nanostructures

Courtesy of Kern / Fleischer group, Tübingen

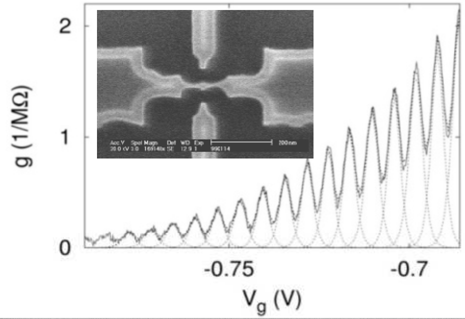
Resist characterization



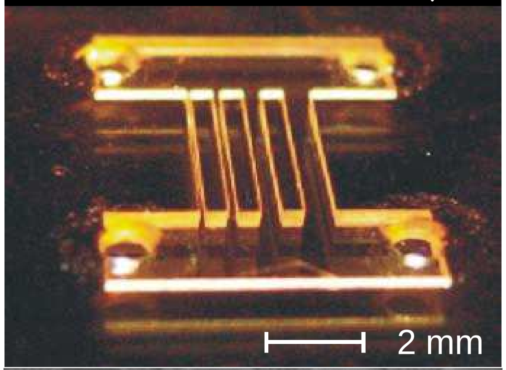
Microgrippers



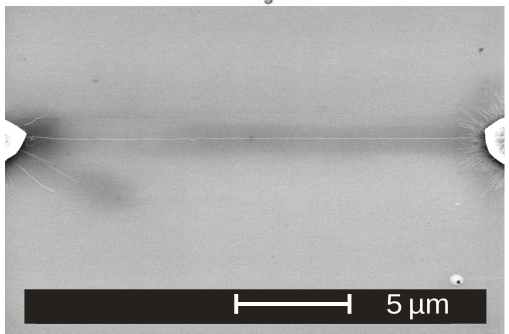
Single electron transistors



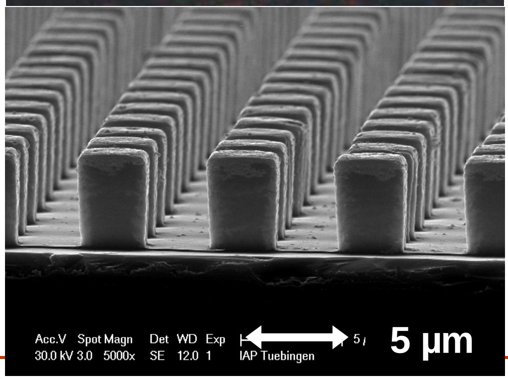
- Microfluidic channels



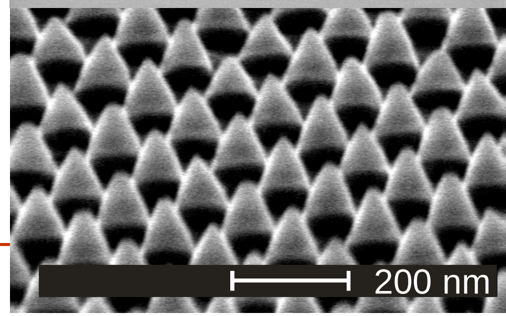
Carbon nanotubes ●



- Bio templates



Plasmonic nanostructures ●



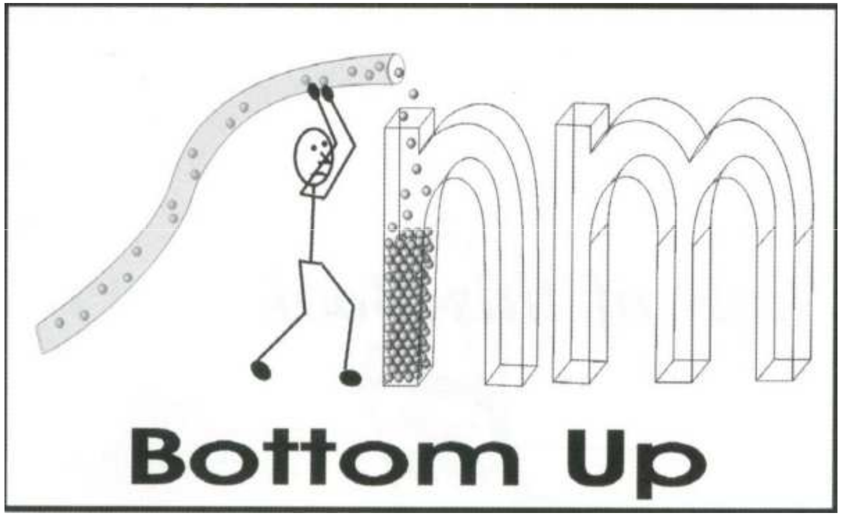
What is going to come in Nano-Science I ?

Making nano-structures

Manipulation of atoms on surfaces …

Smart chemistry …

Lithography and beyond …



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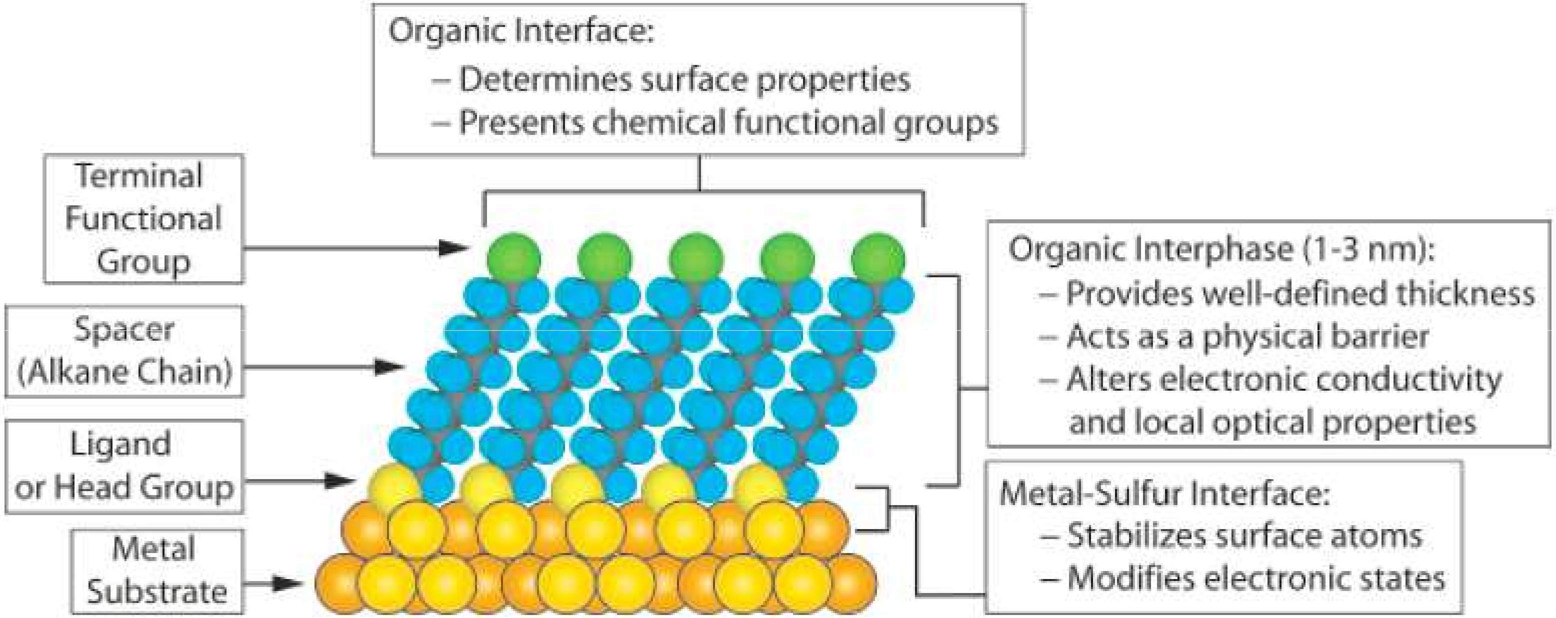
Surface modification by self-assembled monolayers (SAMs) as a form of nano-technology



Applications of SAMs

→ Tailoring wetting, adsorption, and growth

→ Docking of adsorbates, e.g. biomolecules

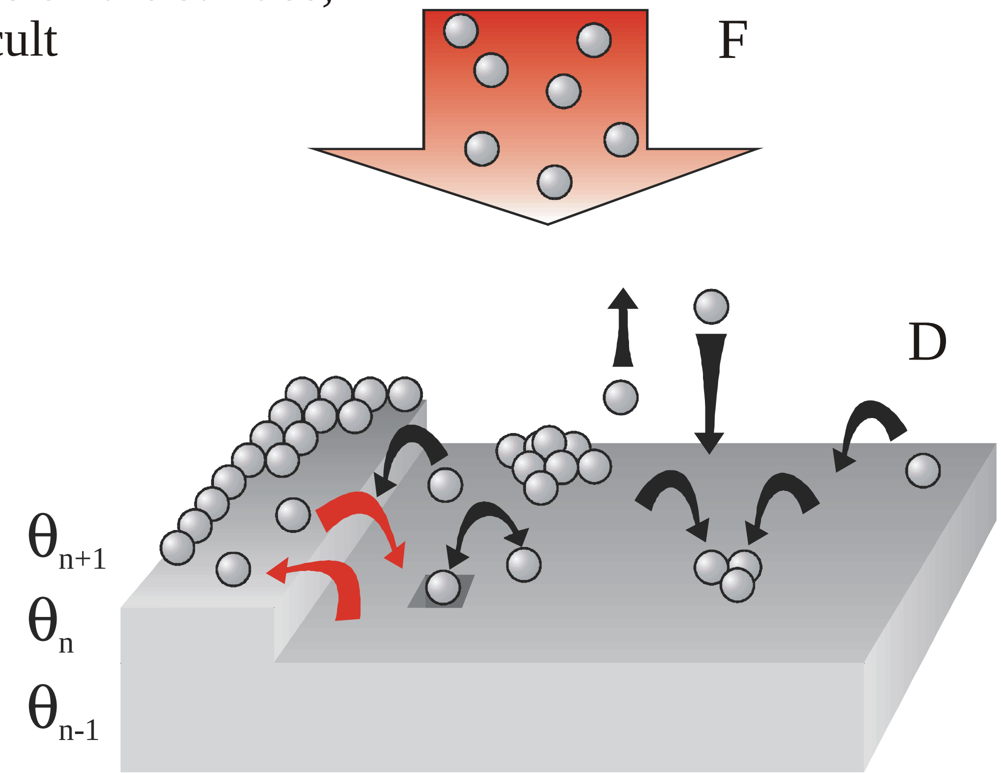
→ Corrosion protection

→ …

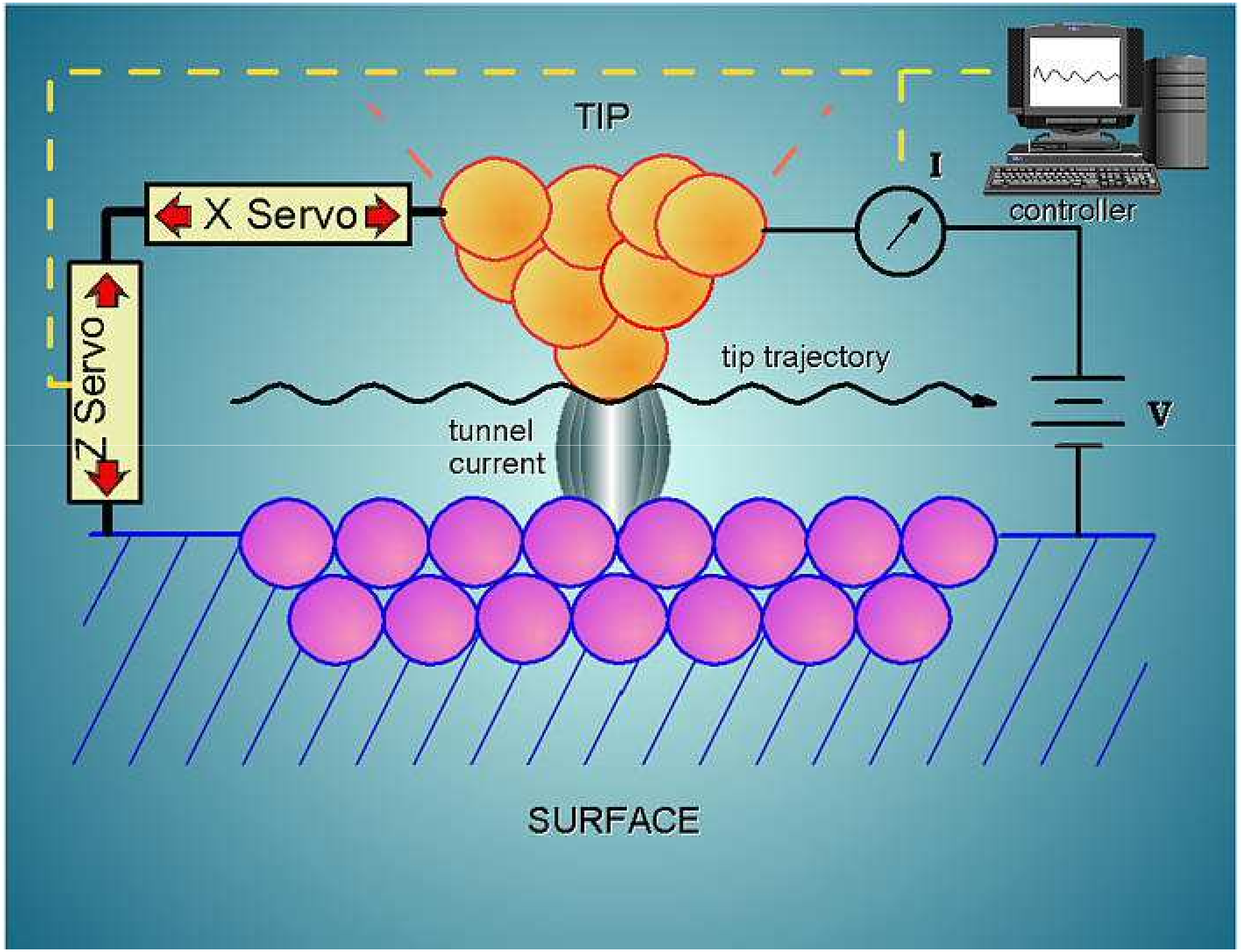
Love et al., Chem. Rev. 105 (2005), 1103
Schreiber, Prog. Surf. Sci. 65 (2000) 151

Growth of thin films

Many competing processes on the surface;
full description very difficult



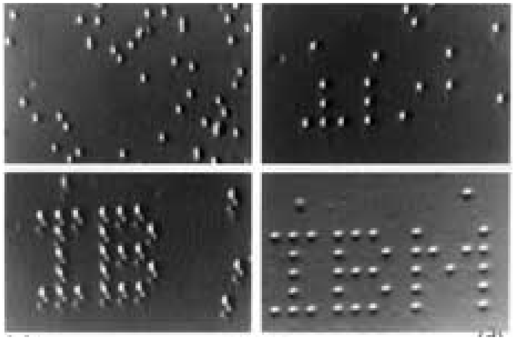
What is going to come in Nano-Science I ?

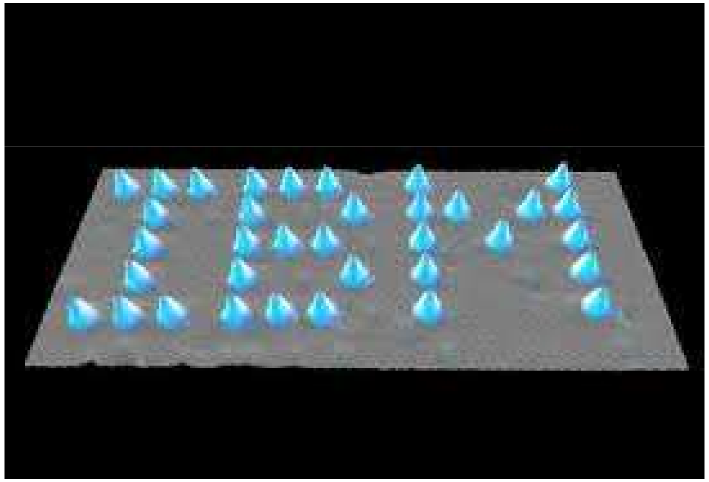


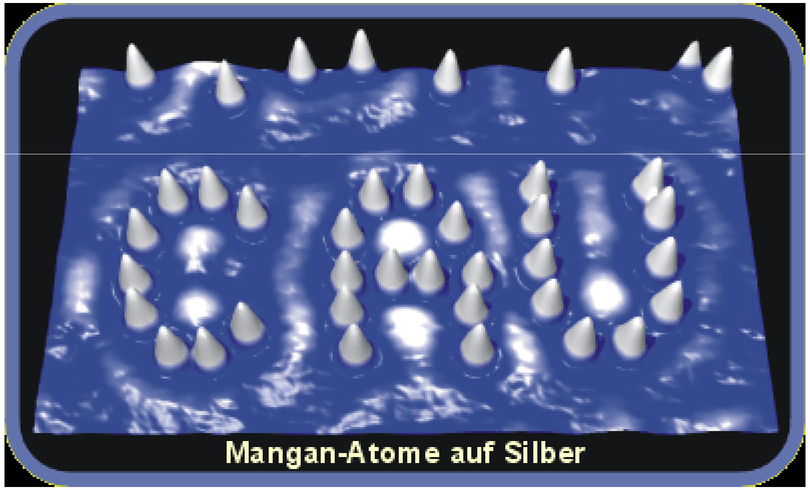
Principle of Scanning Tunneling Microscopy ,(STM)

Introduction to Nano-Science I

What is going to come in Nano-Science I ?



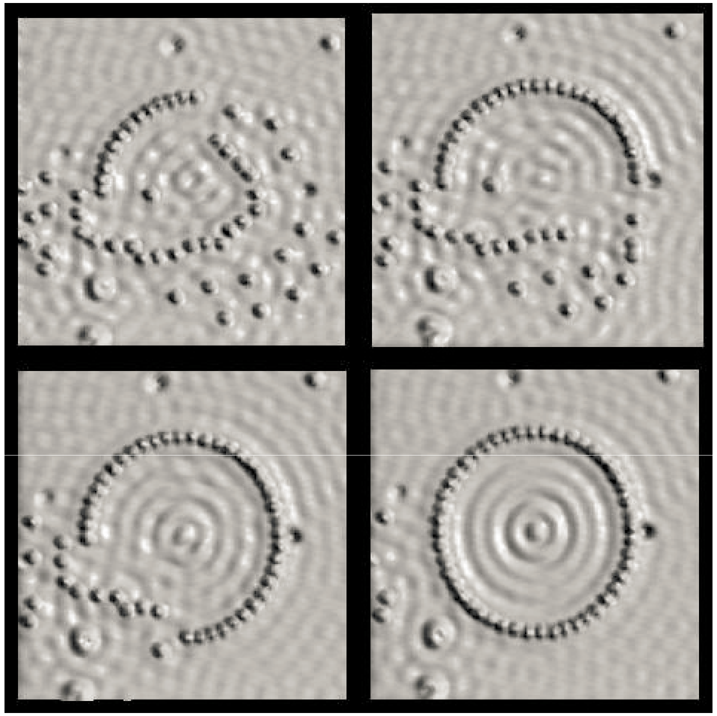


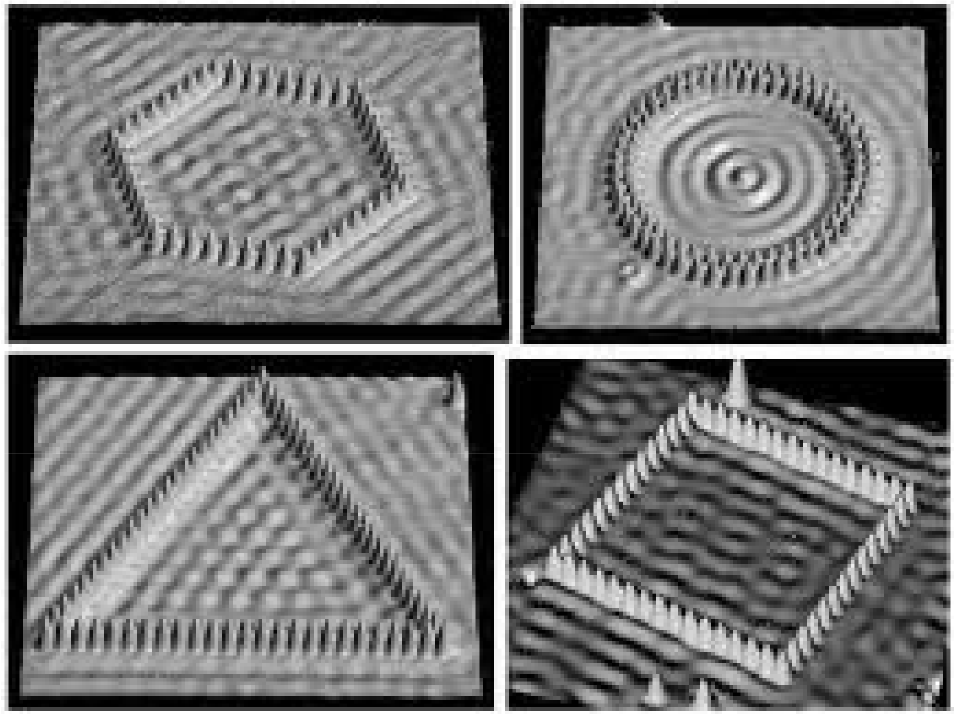


Images by Don Eigler (IBM)
Recorded by STM at low T
after manipulation of atoms
See also Don Eigler talk on YouTube

Images by Richard Berndt (Kiel)
Recorded by STM at low T
after manipulation of atoms

What is going to come in Nano-Science I ?



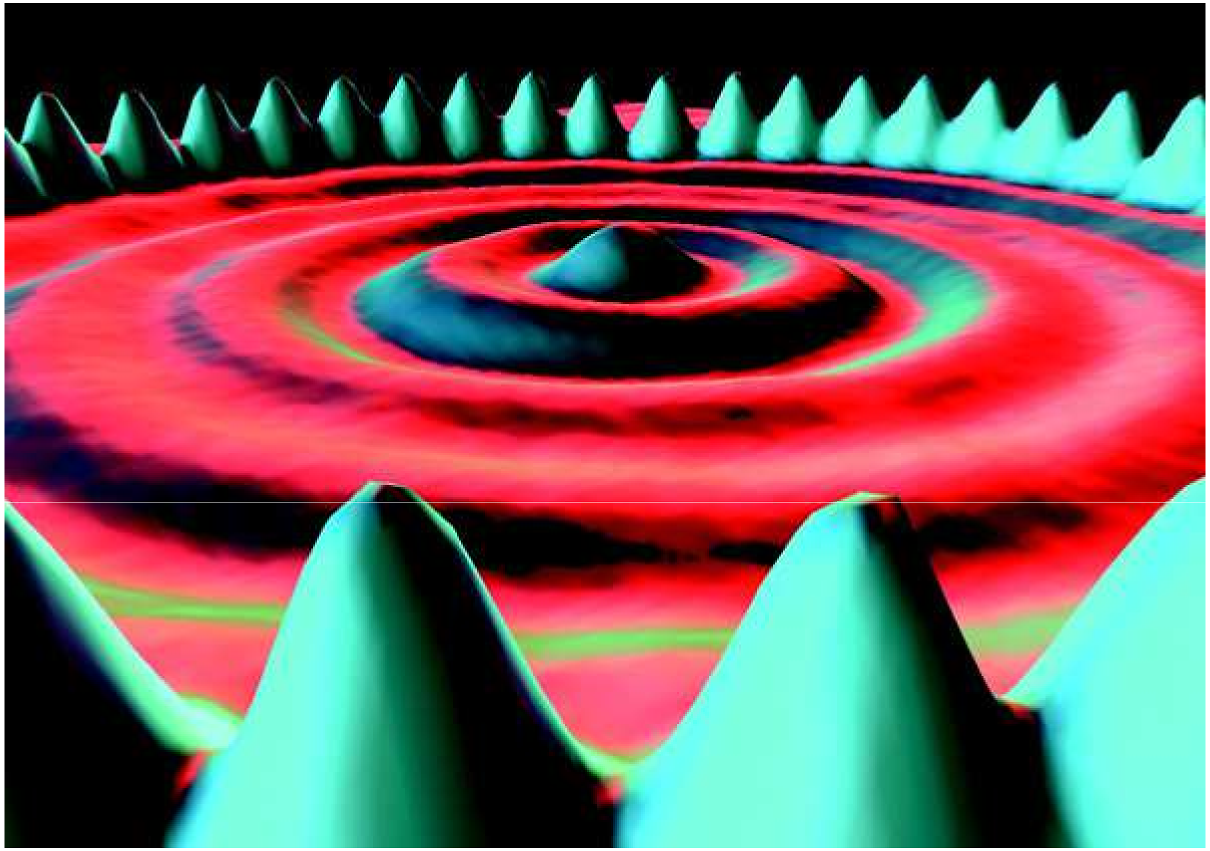


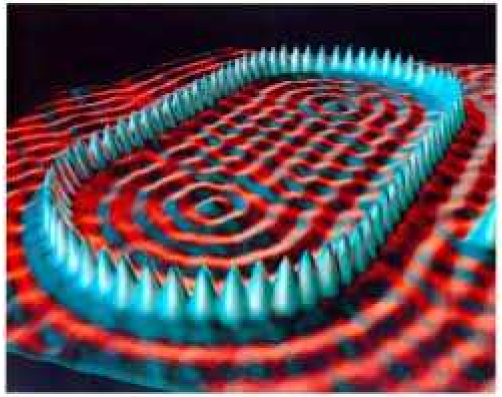
Images by Don Eigler (IBM)

Recorded by STM at low T after manipulation of atoms

TEDxCaltech - Don Eigler - Moving Atoms, one-by-one

http://www.youtube.com/watch?v=rd2dri9p_EI



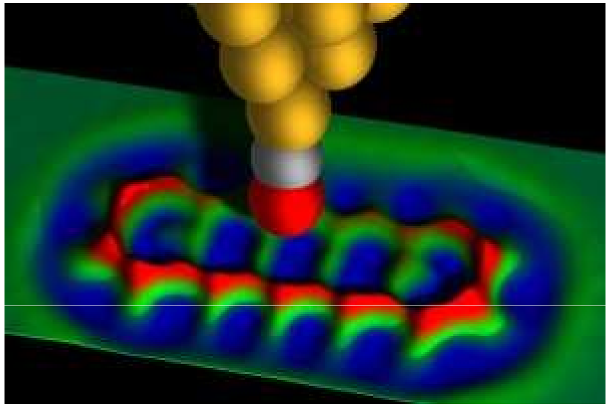


Images by Don Eigler (IBM)

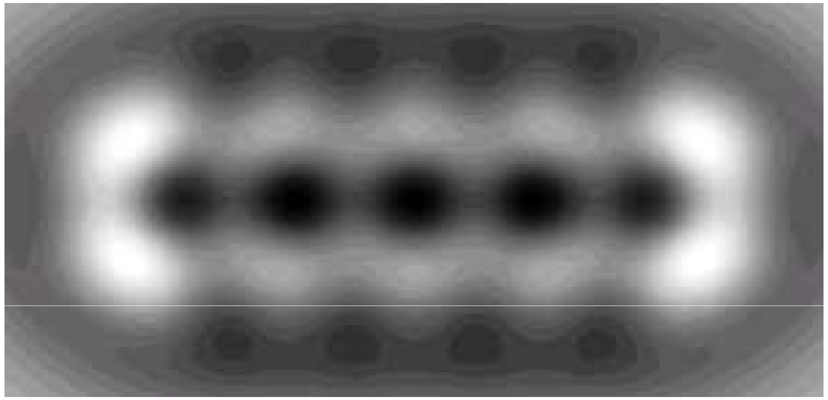
Recorded by STM at low T after manipulation of atoms

Here they have positioned 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. [Crommie, Lutz & Eigler]

Animation



STM data



Images by Gerhard Meyer (IBM)

Image of pentacene on surface, recorded by STM at low T

An example

→ for making nano-structures

→ for chemistry,

→ and for properties on the nano-scale

http://www.youtube.com/watch?v=jnLRl_74BZs

"IBM Scientists First to Image the Anatomy of a Molecule"

Introduction to Nano-Science I

What is going to come in Nano-Science I ?

Making nano-materials:

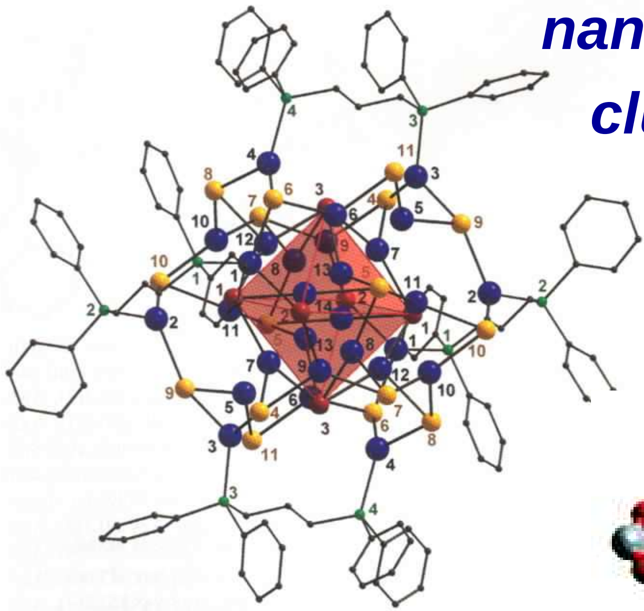
Nano-chemistry

(Reiner Anwander and Yucang Liang)

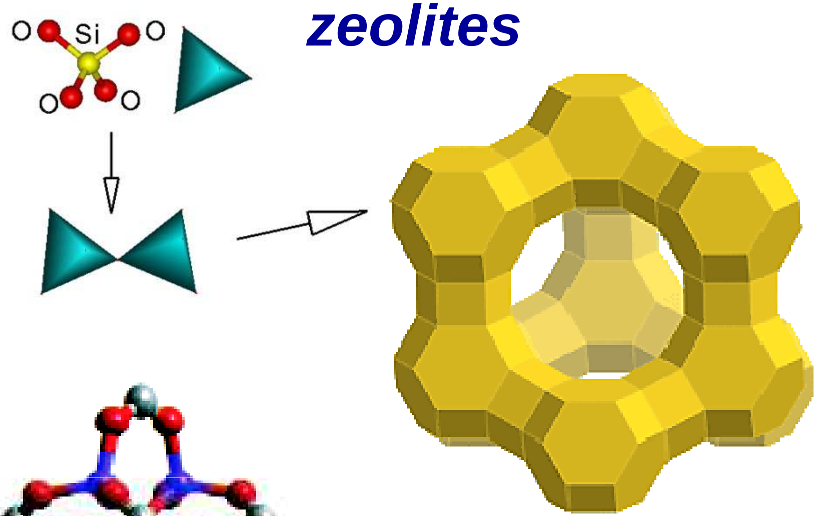
Introduction to Nano-Science I

What is going to come in Nano-Science I ?

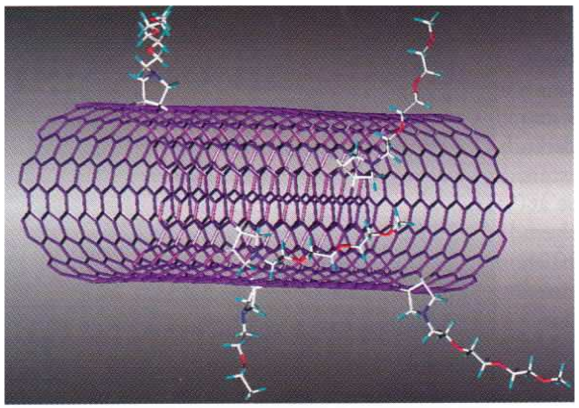
nano-sized clusters



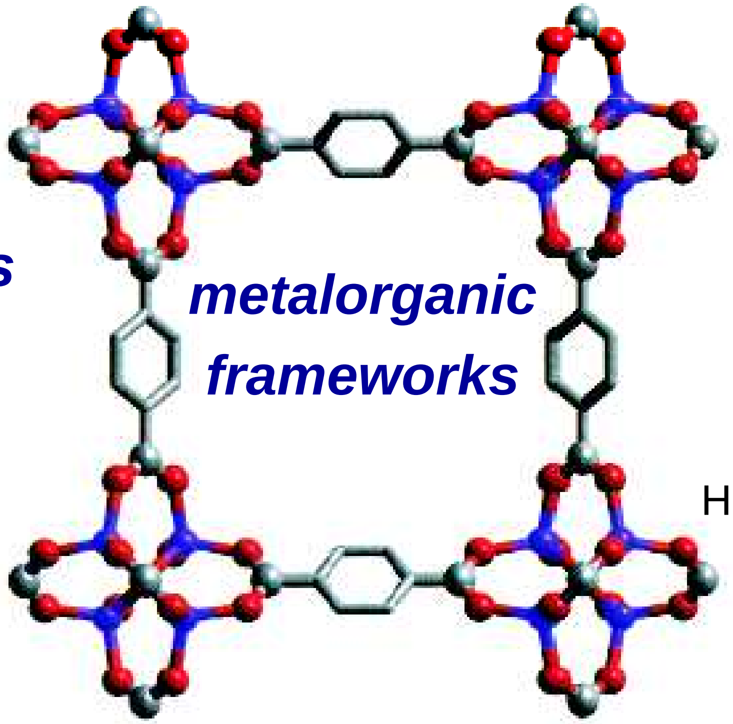
zeolites



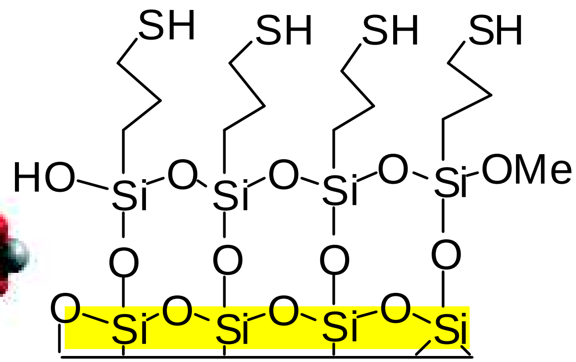
carbon „bucky“ tubes



metalorganic frameworks



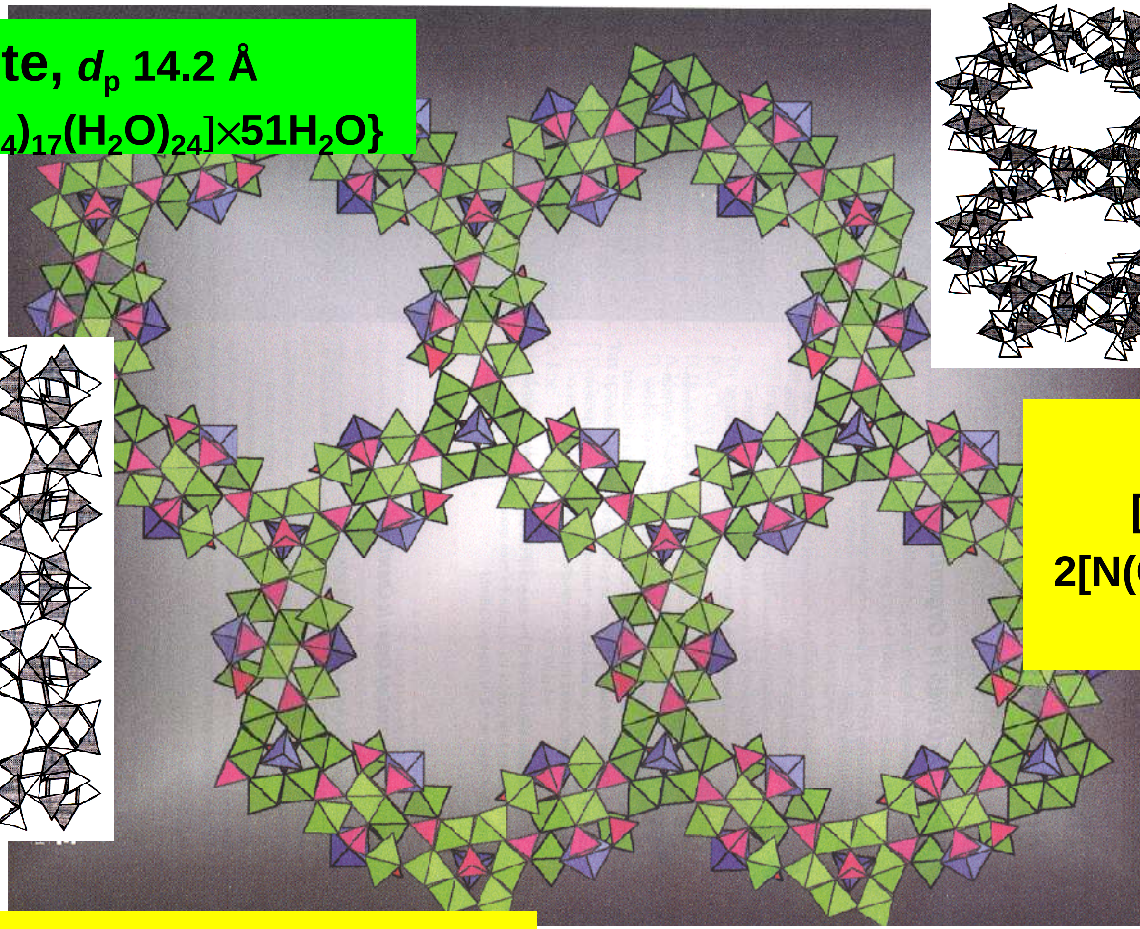
surface functionalization

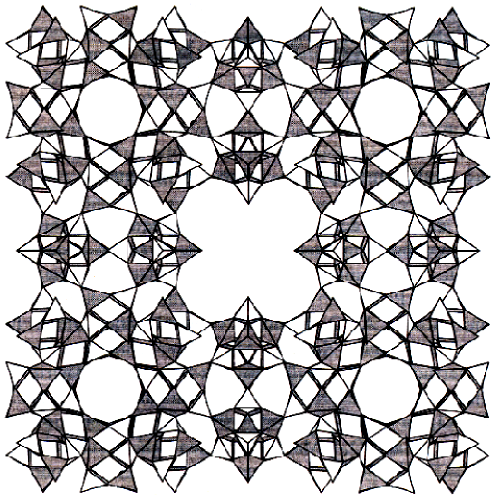


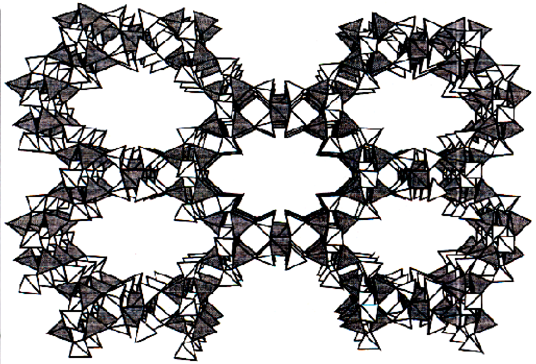
Open-Framework Inorganic Materials

New materials try to emulate nature`s open frameworks

cacoxenite, d_p 14.2 Å
$\{[AlFe_{24}(OH)_{12}(PO_4)_{17}(H_2O)_{24}]\times 51H_2O\}$







JDF-20
$[Al_5P_6O_{24}H]^{2-}$
$2[N(C_2H_5)_3H]^{+}\times 2H_2O$,
14.5×6.5 Å

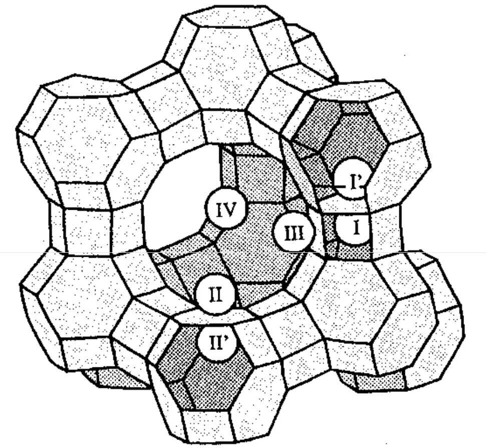
cloverite (CLO), gallophosphate, d_p 13.2 Å

Angew. Chem. Int. Ed. 1999, *38*, 3268–3292.

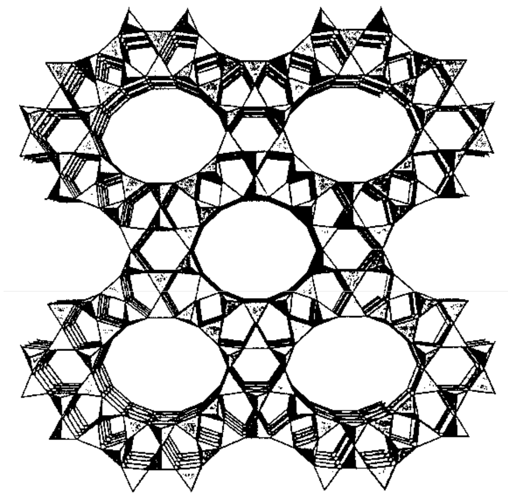
Introduction to Nano-Science I

What is going to come in Nano-Science I ?

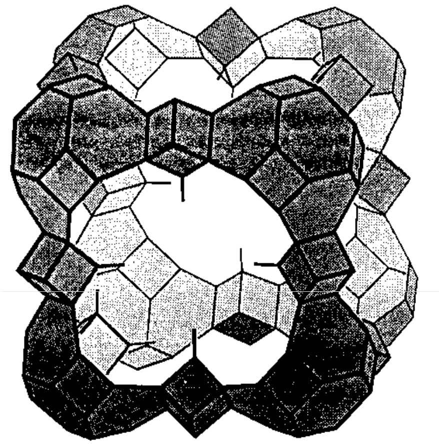
Crystalline, Microporous Supports – Zeolites and Zeotypes



Zeolite Y
12R-pores:
7.4 × 7.4 Å
supercage: *d* = 13 Å



Zeolite UTD-1
14R-pores:
7.5 × 10 Å



Cloverite ($GaPO_4$)
20R-pores:
6.0 × 13.2 Å
supercage: d = 30 Å

Introduction to Nano-Science I

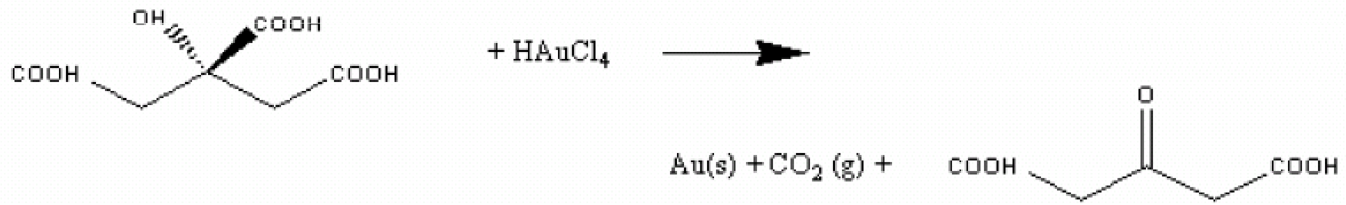
What is going to come in Nano-Science I ?

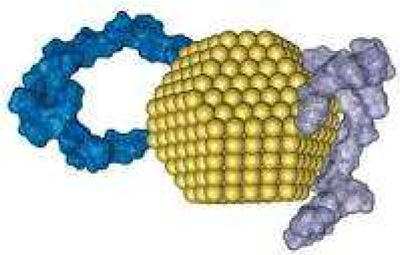
Synthesis of a quintessential nano-object:

Gold nano-particles

Method by Turkevich *et al.* (Reduction by citrate)

A STUDY OF THE NUCLEATION AND GROWTH PROCESSES IN THE SYNTHESIS OF COLLOIDAL GOLD
by J. Turkevich, P. C. Stevenson, J. Hillier
DISCUSSIONS OF THE FARADAY SOCIETY (11): 55 (1951)





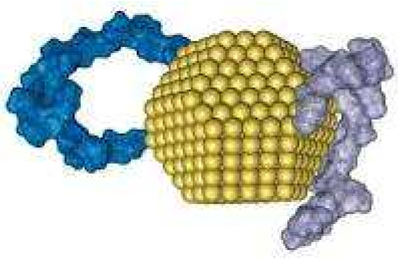
Gold chloride is dissolved in water while heating and stirring
Trisodium citrate dihydrate is dissolved in a small amount of water then added
Reflux for one hour, as citrate reduces Gold(III).

Citrate as reducing and stabilizing agent

What is going to come in Nano-Science I ?

Properties & applications of nano-materials: Gold nanoparticles as a prototype example

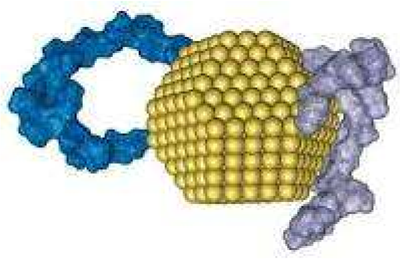
(Fajun Zhang)



Properties & applications of nano-materials: Gold nanoparticles as a prototype example

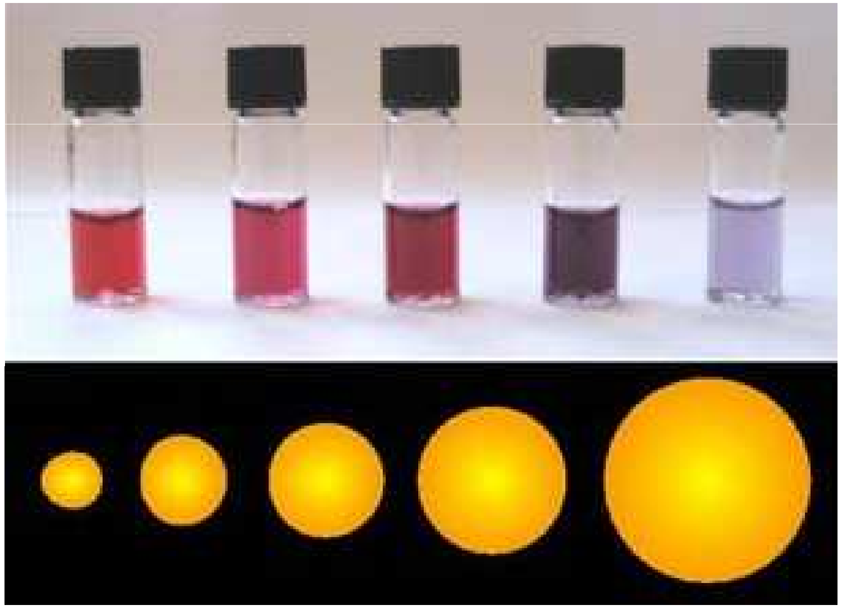
(Fajun Zhang)

1. Colour effects
2. Near-field effects
3. Scattering effects
4. Field enhancement e.g. in organic photovoltaics
5. Field enhancement e.g. for sensors
6. AuNPs as marker in biology



Tailoring of the Optical Properties of Gold Colloids

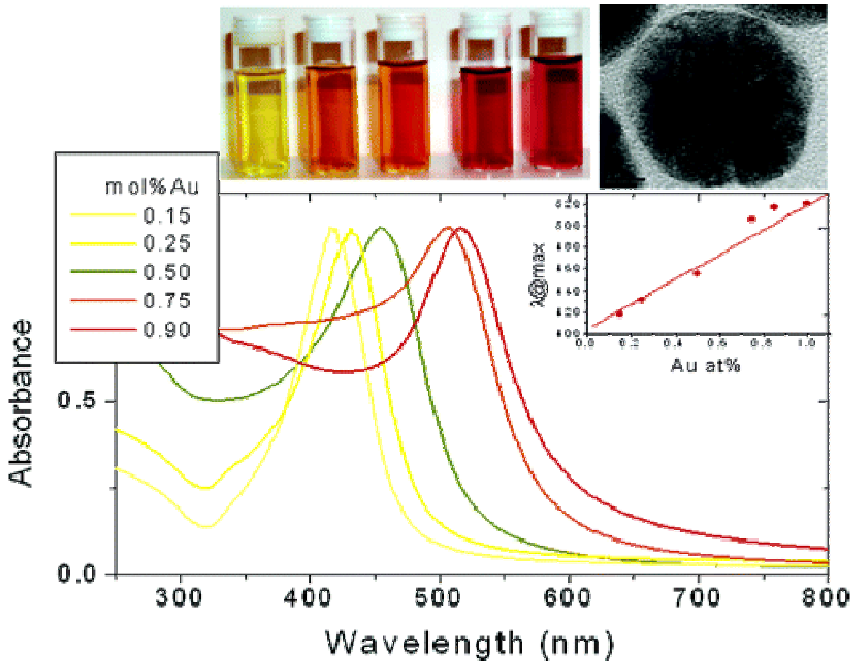
Au Nanoparticles: Colour as a function of size



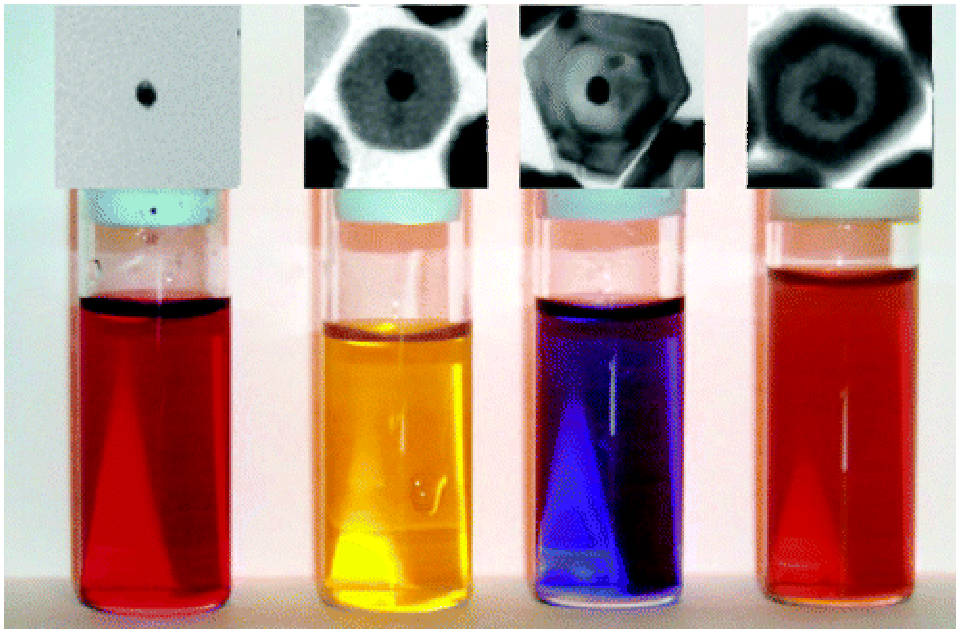
Sources: http://www.sharps-jewellers.co.uk/rings/images/bien-hccncsq5.jpg
http://www.foresight.org/Conferences/MNT7/Abstracts/Levi/

Tailoring of the Optical Properties of Gold Colloids

AuAg Bimetallic Nanoparticles: Alloys vs. Core-Shells



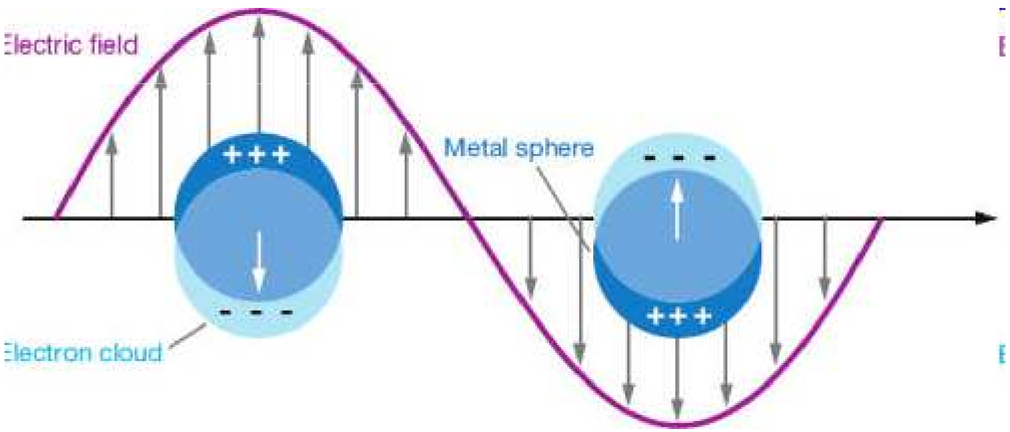
Variation in optical properties
(UV-vis spectra and color)
for AuAg alloy nanoparticle colloids
with varying compositions.



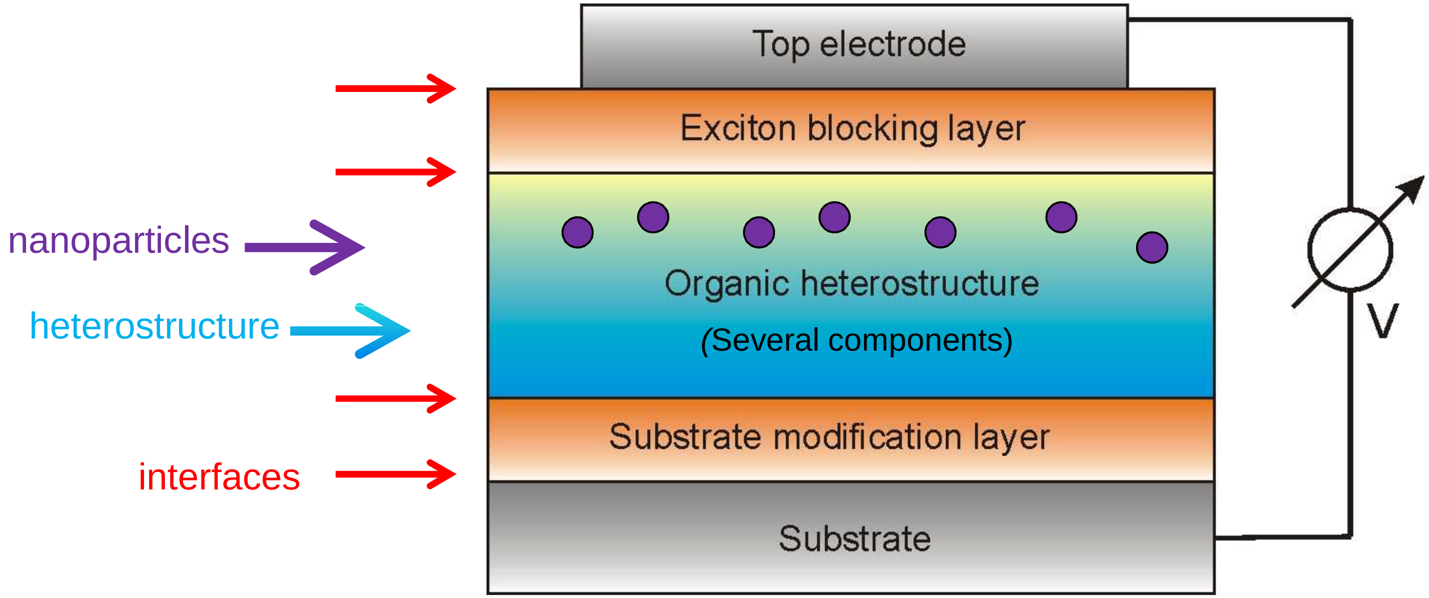
Aqueous dispersions of (from left to right)
Au, Au@Ag, Au@Ag@Au, and Au@Ag@Au@Ag NPs,
and the corresponding TEM images.
Au core size: 16 nm.

MPI Golm

- Surface plasmon resonance of metal NP
- Intensity enhancement (near field)



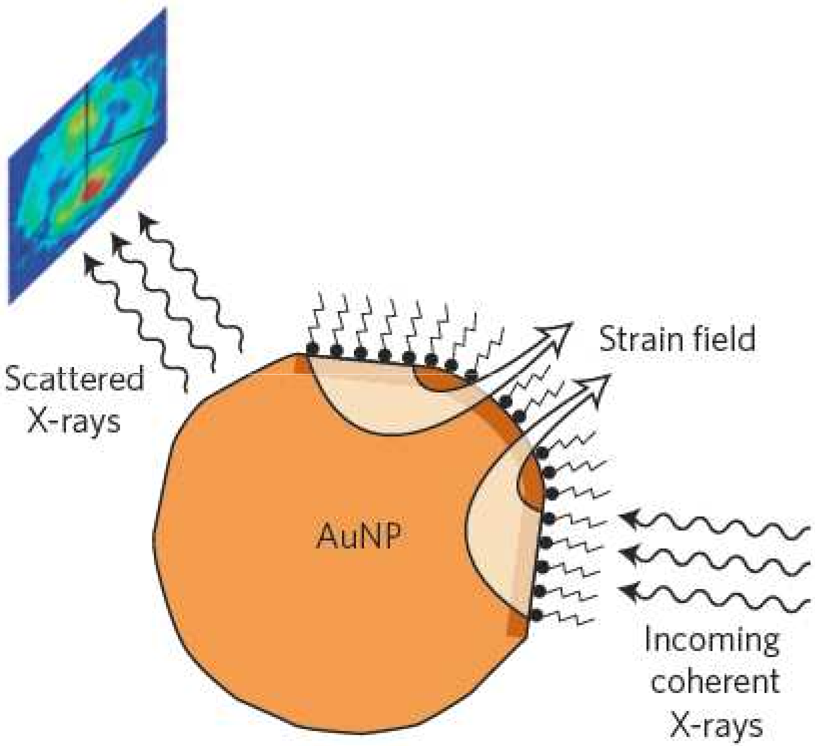
Example: Making Organic Photovoltaics Devices



→ This is a *very* complicated architecture !

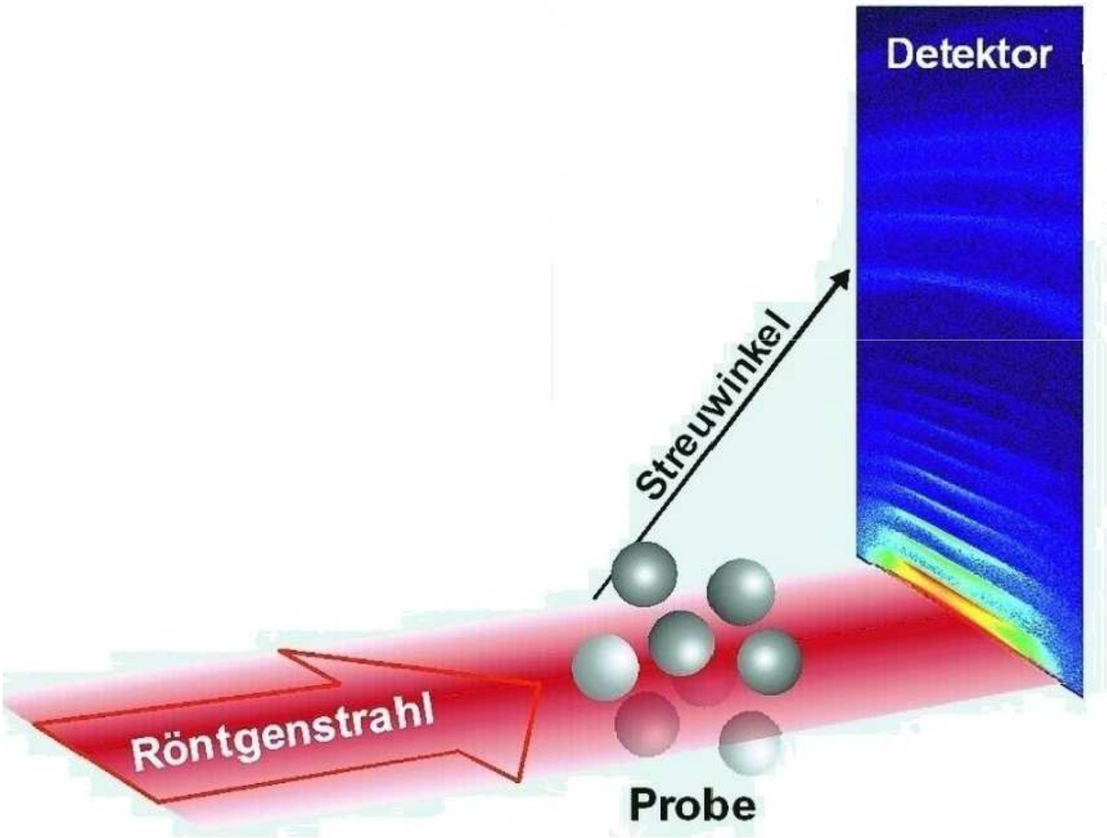
→ There is lots of work for nano-scientists to improve this !

What is going to come in Nano-Science I ?



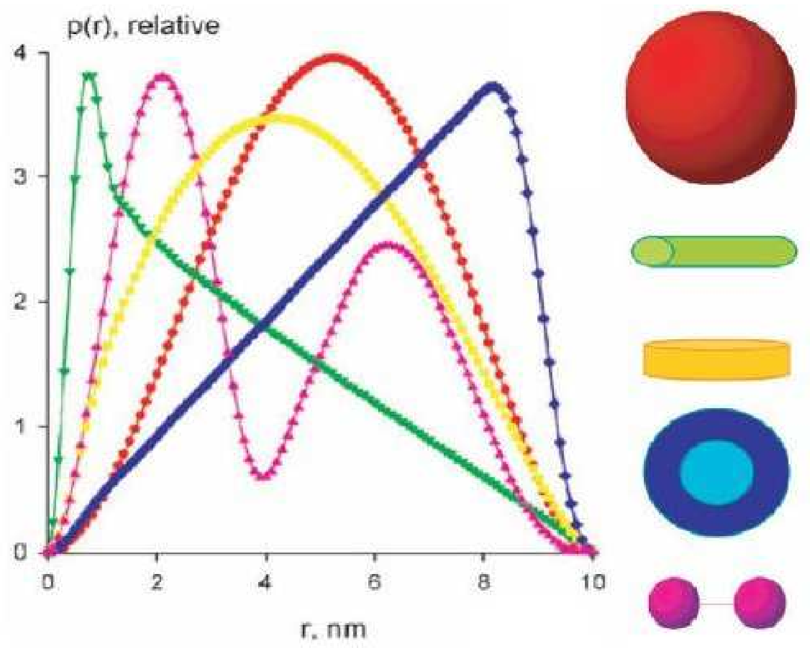
F. Schreiber, Nature Materials, 10 (2011), 813

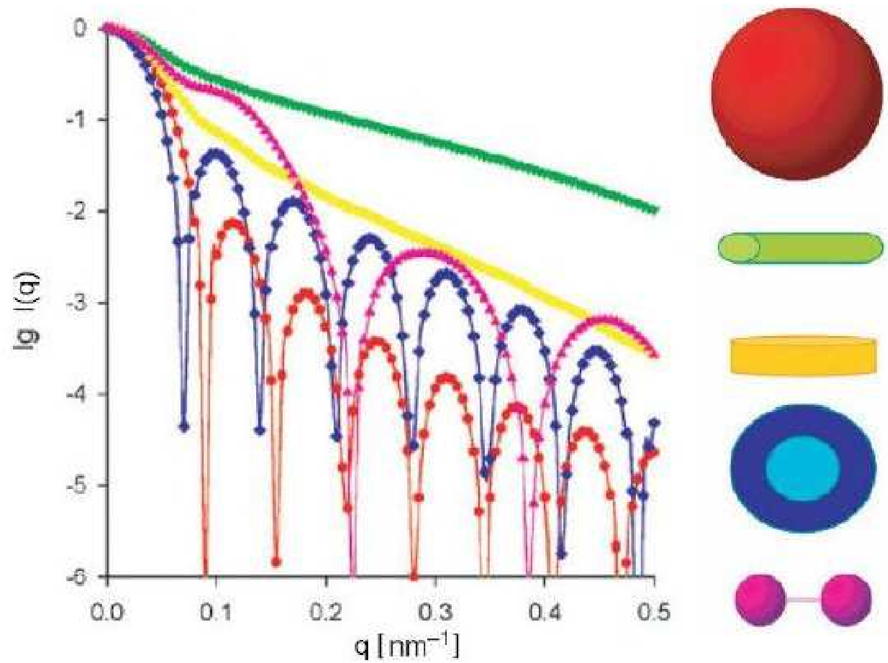
Small-Angle Scattering



$$p(r) = r^2 \gamma(r)$$

gemessene Intensität





What is going to come in Nano-Science I ?

Nano-science and biology:

Advanced microscopy tools and beyond

(Klaus Harter and Üner Kolukisaoglu)

… STED microscopy

… STORM (microscopy)

… FCS

… optical tweezers

Stimulated Emission Depletion (STED)-Mikroskopie

Vol 440|13 April 2006|doi:10.1038/nature04592 nature

LETTERS

STED microscopy reveals that synaptotagmin remains clustered after synaptic vesicle exocytosis

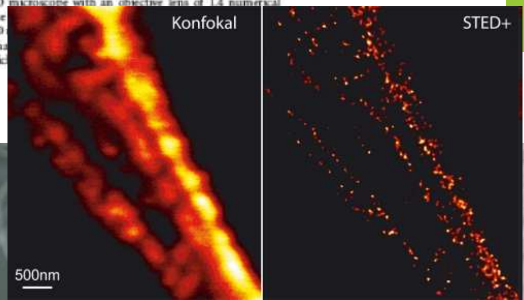
Katrin I. Willig[1*], Silvio O. Rizzoli[2*], Volker Westphal[1], Reinhard Jahn[2] & Stefan W. Hell[1]

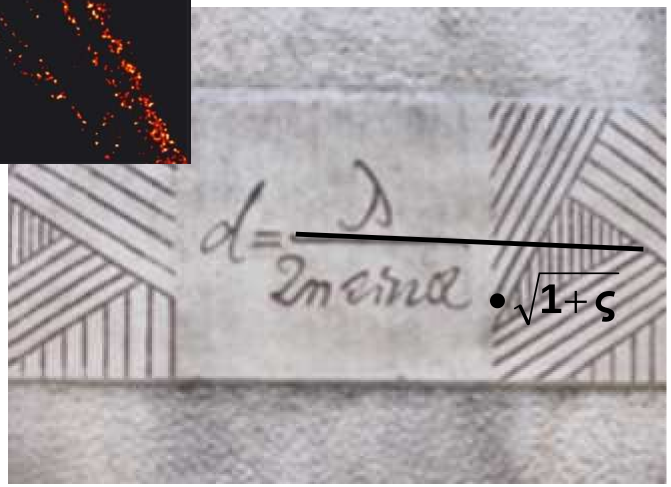
Synaptic transmission is mediated by neurotransmitters that are stored in synaptic vesicles and released by exocytosis upon activation. The vesicle membrane is then retrieved by endocytosis, and synaptic vesicles are regenerated and re-filled with neurotransmitter[1]. Although many aspects of vesicle recycling are understood, the fate of the vesicles after fusion is still unclear. Do their components diffuse on the plasma membrane, or do they remain together? This question has been difficult to answer because synaptic vesicles are too small (~40 nm in diameter) and too densely packed to be resolved by available fluorescence microscopes. Here we use stimulated emission depletion (STED)[2] ... spot where the doughnut beam is close to zero (Fig. 1a). Scanning with a narrowed spot across the sample readily yields subdiffraction images. With a sufficiently intense doughnut, the fluorescent spot of a STED microscope can, in principle, be sharpened down to the molecular scale[3,11,12].

To investigate synaptic vesicle recycling in cultured neurons, we built a STED microscope with an objective lens of 1.4 numerical aperture. The ... excited at 470 ... width-half-ma... 195 nm, whic...

STED benutzt stimulierte Emission zur Auflösungssteigerung

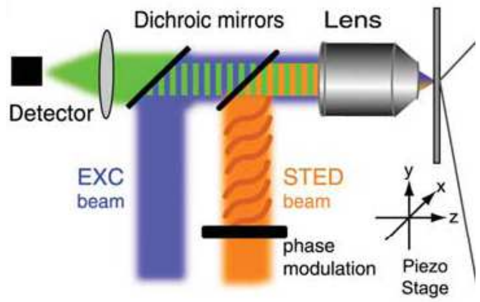
Die Abbesche Grenze gilt noch immer, der Ausdruck wird um einen Sättigungsterm erweitert

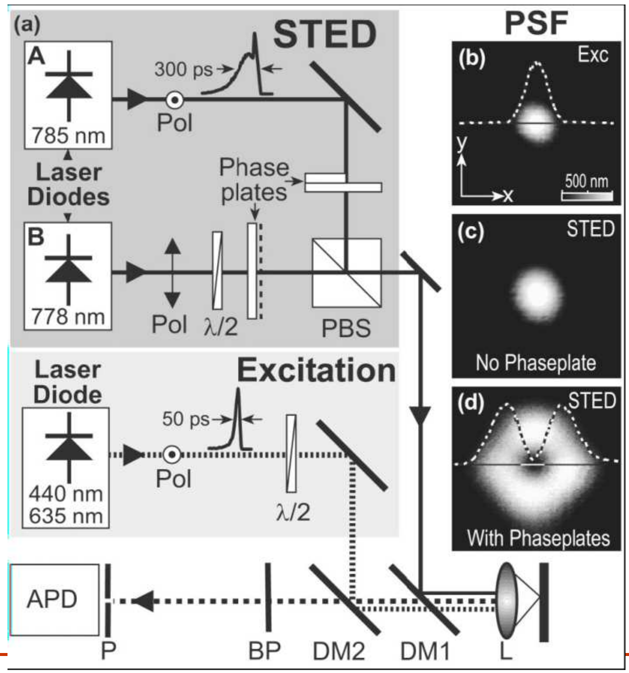


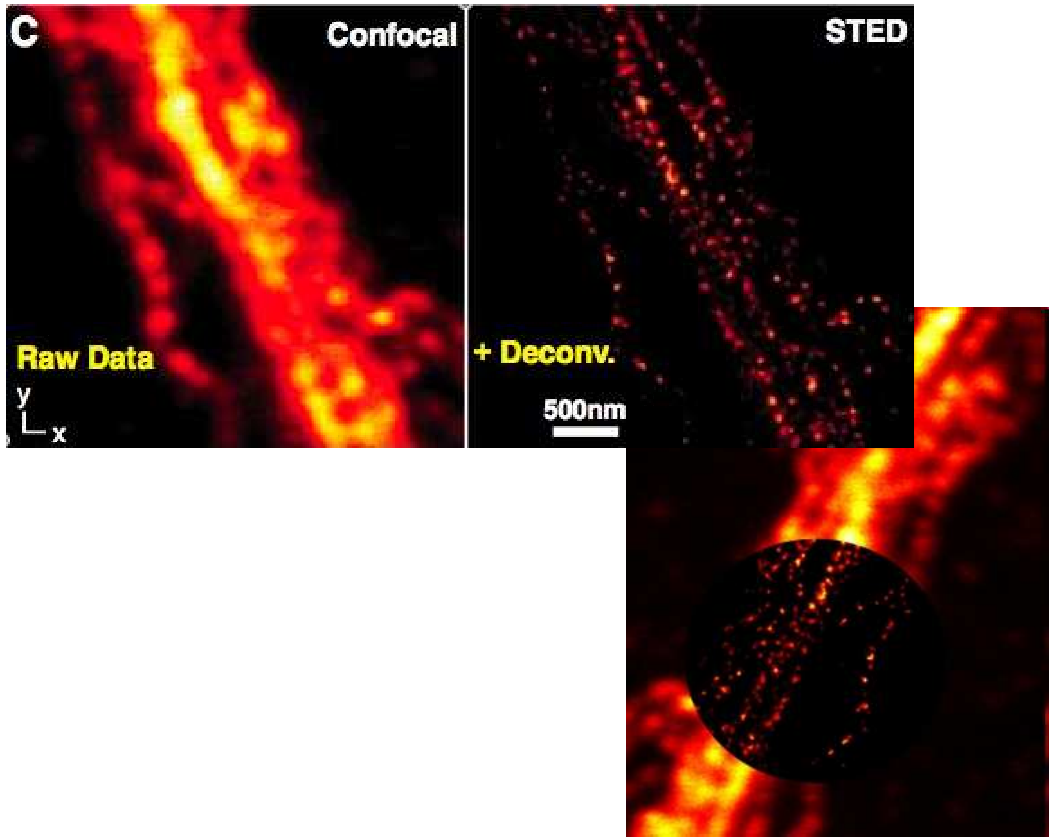


STED-Aufbau und Ergebnis

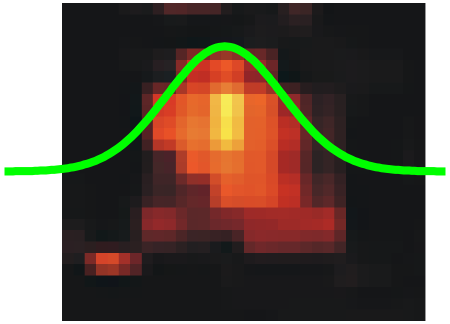
STED: Aufbau und Ergebnis







Stochastic Reconstruction Microscopy (STORM)



Einzelne Punkte können im konfokalen Bild mit wesentlich höherer Präzision lokalisiert werden, als zwei Punkte getrennt voneinander aufgelöst werden können.

Ein Punkt erscheint im Fluoreszenzbild in der Form der Point Spread Function (PSF):

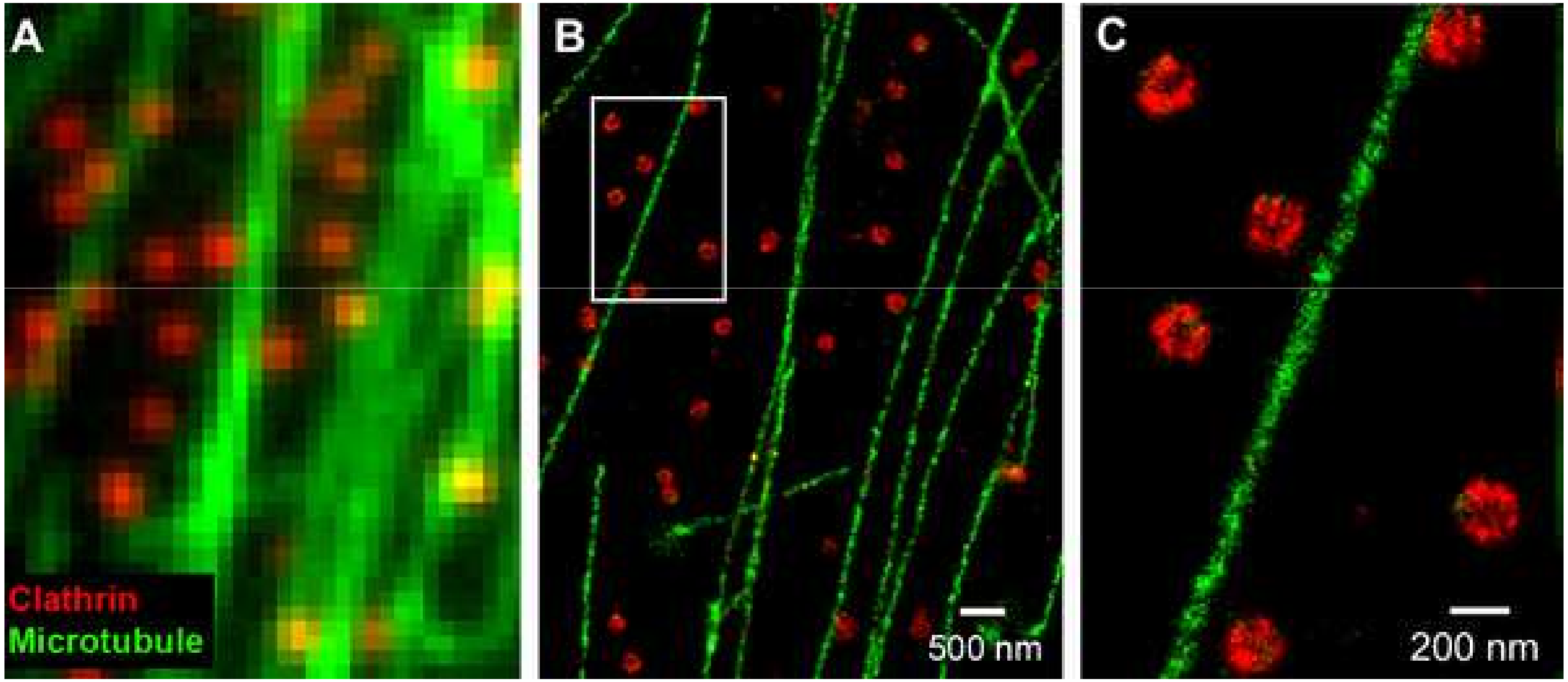
Einfachste Form: Gaussform der PSF: Maximum bestimmbar nach:

$$f_{\max} = \frac{1}{\sigma\sqrt{2\pi}}.$$

Positionsgenauigkeit nur Abhängigkeit von Photonenzählstatistik

STORM-Ergebnis

konfokal ***STORM***

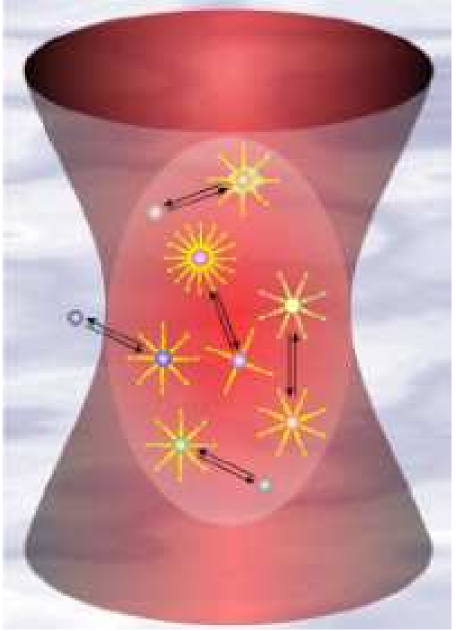


Fluorescence Correlation Spectroscopy (FCS)

Optische Messmethode, bei der Informationen aus <u>Fluktuationen</u> der <u>Fluoreszenzintensität</u> gewonnen werden

Methode entwickelt in 1972; prinzipiell sind alle Moleküldynamiken zugänglich, z. B.:

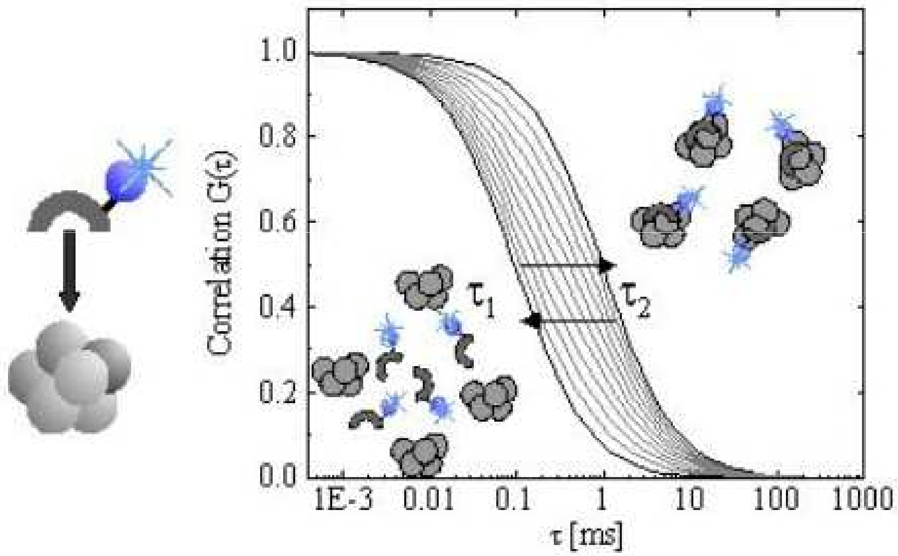
- ***Molekülbewegung***
- ***Konformationsumkehrungen***
- ***Chemische und photophysikalische Reaktionen***

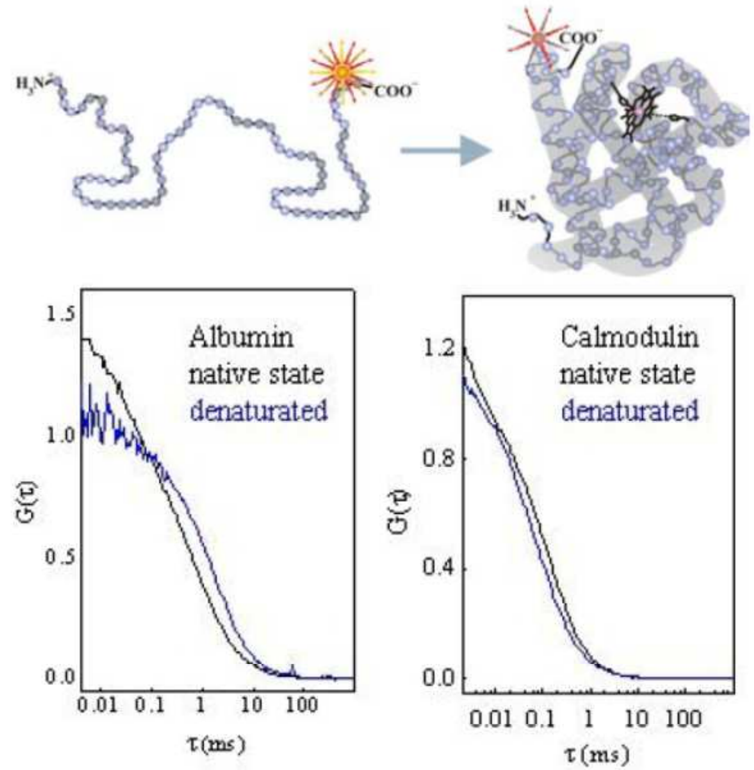


Aus: Schwille et al. Fluorescence Correlation Spectroscopy

FCS-Ergebnisse: In Vitro

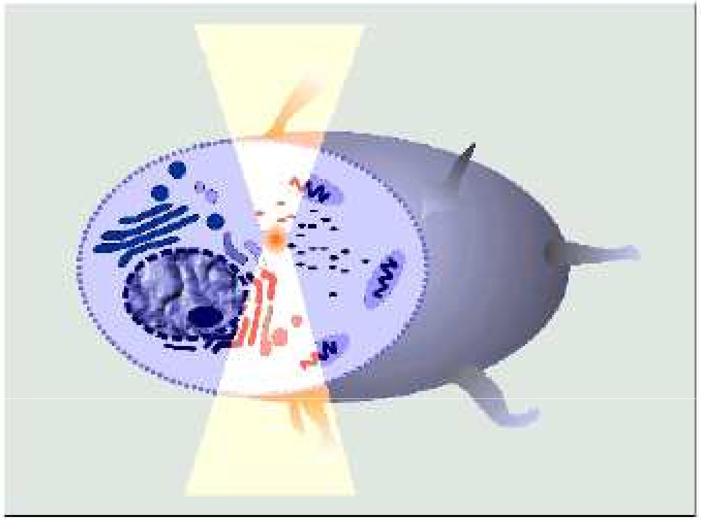
Diffusion Abhängig von Temperatur, Viskosität des LSM (beides konstant) und Größe / Form des diffundierenden Partikels

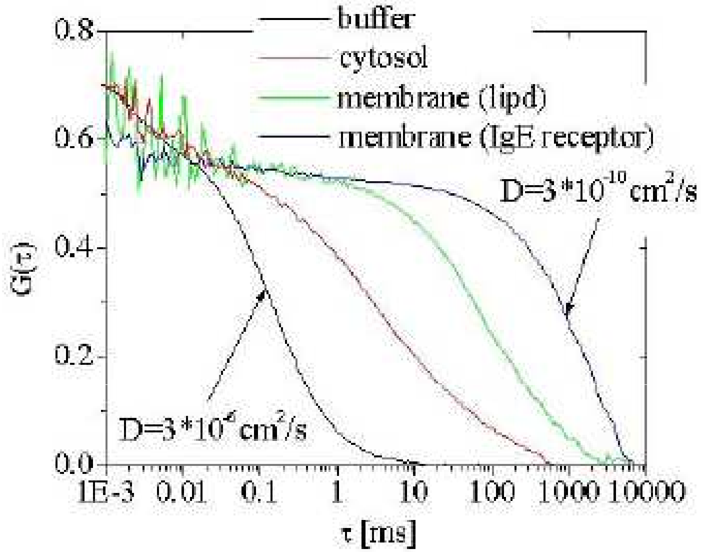




- Nachweis von Bindungsereignis, z. B. Protein/Antikörper-Interaktion
- Verfolgung von Konformationsänderungen

FCS-Ergebnisse: In Vivo





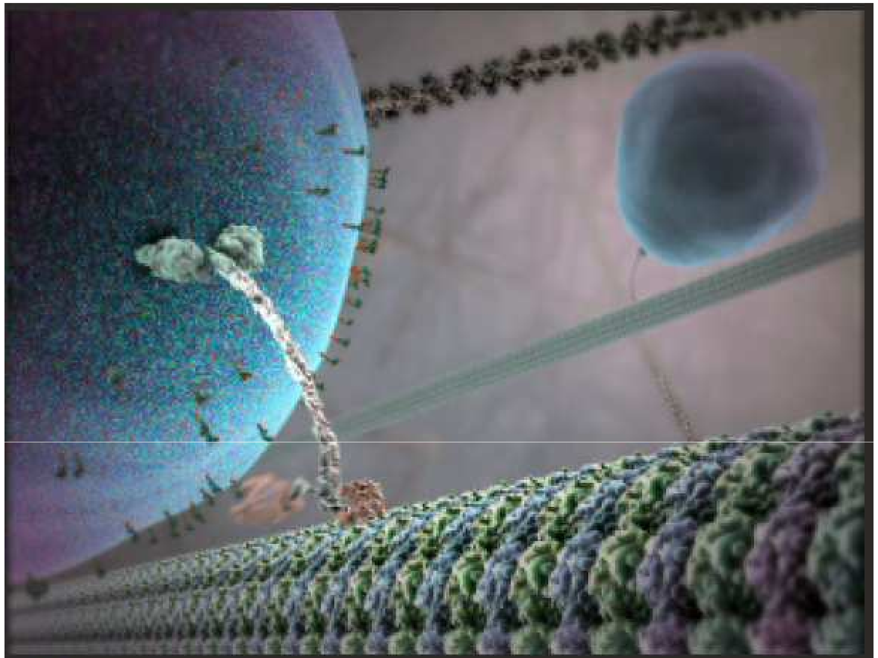
Subzelluläre Analytik:

- Proteinbeweglichkeit

- Viskosität

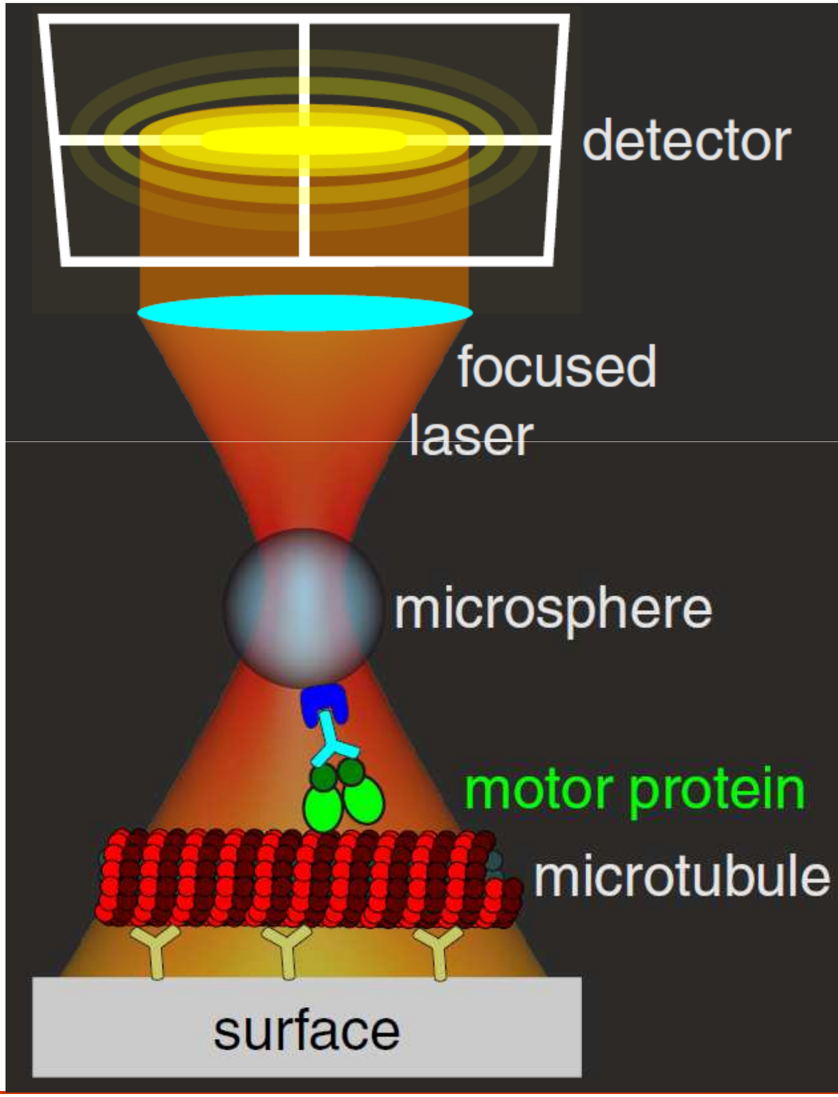
- Verteilung

Optical Tweezers: Werkzeuge zur Untersuchung von biomolekularen Motoren



Kinesin-1 (BioVisions, Harvard University)

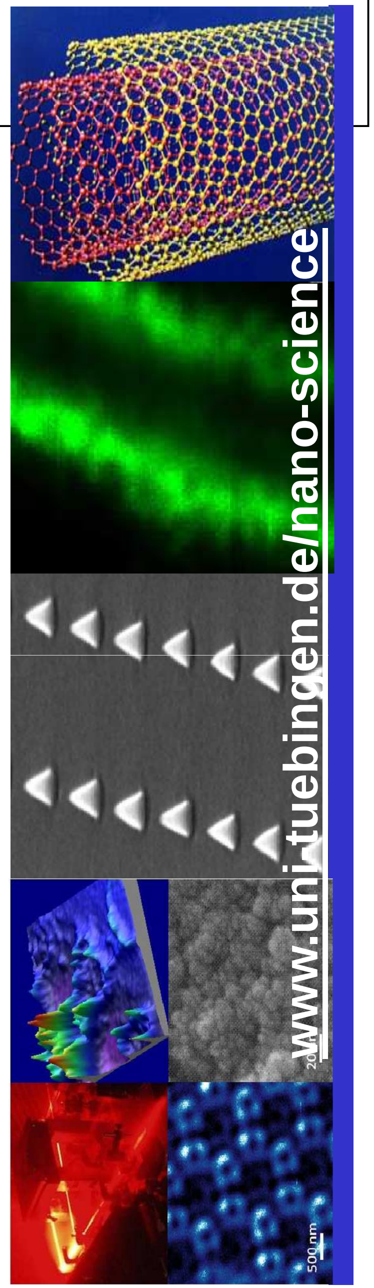
- Vesicle transport
- 8 nm steps,
  6-7 pN force,
  800 nm/s (no load)



Introduction to Nano-Science I

Einführung in die Nano-Science I

Prof. Dr. Frank Schreiber (Studiendekan)
frank.schreiber@uni-tuebingen.de
Tel.78663, office C7A35
http://www.soft-matter.uni-tuebingen.de
MON & THU 15-17 in BioIII / N10-50



Outline

1. Who are we ?
2. What is nano-science ?
3. Why do we do nano-science ?
   - → Fundamental questions
   - → Applications
4. What is going to come ?
   - → Tools and methods
   - → Preparation
   - → Effects
5. Organisation and logistics (Üner in the break)