Outline – Nanotechnology part

I. Motivation:

- Nanotechnology, in general. Feynman lecture from today.
  Status of CMOS technology, End of Moore's law
- Small is different!
  Important length scales, quantum effects, fluctuations
  Different fields: electron transport, optics, mechanics, N/MEMS, microfluidics, biology,…

II. Scanning probe microscopes

- STM
- AFM
- MFM, Kelvin probe, …

III. Electron microscopy

SEM, TEM, FIB

IV. Nanostructures with top-down

- Lithography: photo, electron
- Vacuum techniques
- Thin film deposition, MBE, ALD
- Stamp techniques, FIB

Outline – Nanotechnology part

IV. Novel nanomaterials

V. New concepts in electronics

Spintronics, memristors, quantum electronics

VI. MEMS

VII. Surface analytical methods

SIMS, SNMS, XPS, AES

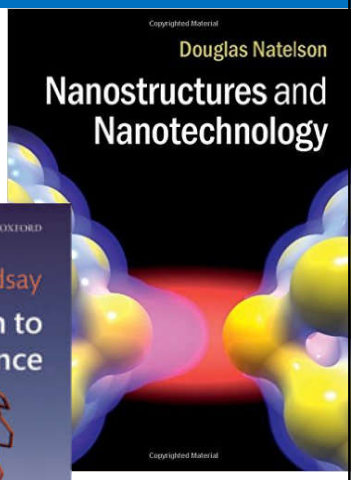
VIII. Modern optical techniques in material science

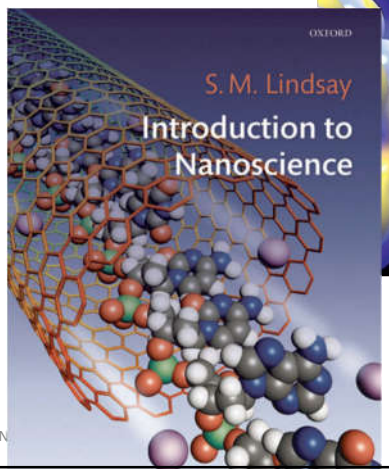
…

Nanotechnology and material science - 2017

Literature

- D. Natelson:
  Nanostructures and Nanotechnology
  Cambridge University Press (2015)
  ISBN-13: 978-0521877008
- S. M. Lindsay:
  Introduction to Nanoscience
  Oxford Uni. Press. (2010)
  ISBN: 978–0199544202
- T. Ihn: Semiconductor Nano-structures, Oxford Uni. P.
  ISBN-13: 978-0199534432
- Scientific papers
  see citations
- Wikipedia





Nanotechnology today, Following Feynman's ideas 1959

„There is plenty of room at the bottom"
There are several ideas, predictions from the talk of Feynman (1959), which have been realized. He has envisioned the birth of nanotechology and realized the great potential at nanoscale.

Examples from Feynman's suggestions:

- **Electron beam litography (EBL)**

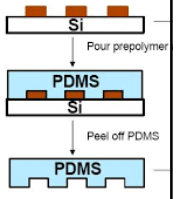
Using electron beams, demagnified in an electron microscope, to write small features: *"We can reverse the lens of an electron microscope in order to demagnify as well as magnify . . . This, when you demagnify it 25,000×, it is … 32 atoms across."* Sub 10nm accessable. → See top-down techniques

R (Up) principle of EBL

(Bottom) Principle of soft litography

- **Soft litography ('98)**

"We would just have to press the same metal plate again into the plastic and we would have another copy." Stamping technology, leaving an imprint of the nano-features on the surface of the stamp. The stamp can then be used to print out multiple copies of the original (laboriously manufactured) nano-structure very rapidly. → See micro fluid.



After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology today, Following Feynman's ideas 1959

„There is plenty of room at the bottom"

- **Focused ion beam (FIB)**

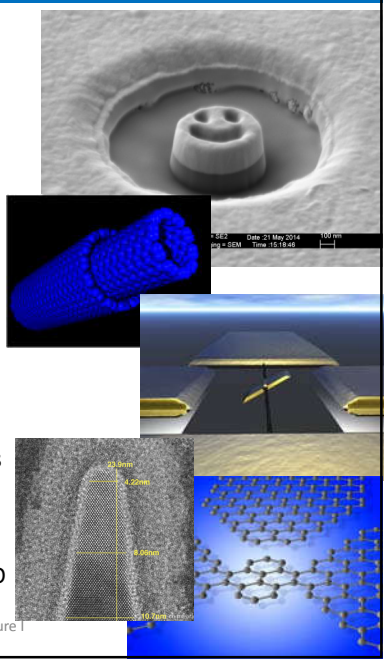
Use ions to etch structures. *"A source of ions, sent through the lens in reverse, could be focused to a very small spot."* Today it is used for nanoscale milling machine. (E.g. TEM preparation, etc…) → See top down techniques

- **Machines at the nanoscale**

"Consider the possibility that we too can make a thing very small, which does what we want—that we can manufacture an object that maneuvers at that level! " E.g. motor that rotates on a carbon nanotube shaft. Tiny molecular/biomotors have been constructed, but which operate on very different principles from the motors humans build.

- **Miniaturizing computer components → supercomputers**

"For instance, the wires could be 10 or 100 atoms in diameter . . .. If they had millions of times as many elements, they could make judgments . . . ." See COMS presently, 14nm node or results of molecular electronics, also achived possibilites as Deep Mind in GO (2016).

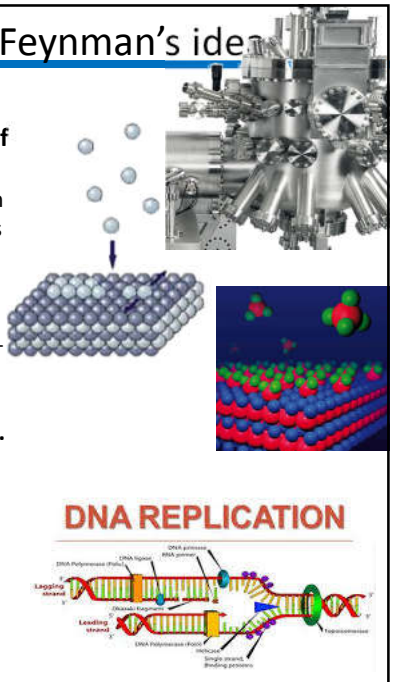


After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology today, Following Feynman's ide

„There is plenty of room at the bottom"

- **Making atomic scale structures by evaporating layers of atoms (MBE, ALD):**
  "So, you simply evaporate until you have a block of stuff which has the elements . . . What could we do with layered materials with just the right layers?" **Molecular beam epitaxy** (MBE) layers of atoms are formed by projecting hot vapors onto a substrate in UHV. Different types of atoms can be projected to form layered structures with nanometer thickness. → See top-down. **Atomic layer depostion** (ALD): grow e.g. oxides layer-by-layer → See bottom-up
- **Manufacturing: machines that make machines and so…**
  "I let each one manufacture 10 copies, so that I would have a hundred hands at the 1/16 size." This idea, of making small machines, that make more even smaller machines etc. (Gray goo) Is not realised, but exponential growth through copying copies is what lies behind the amazing polymerase chain reaction, the biochemical process that yields macroscopic amounts (micrograms) of identical copies of just one DNA molecule. → see example later

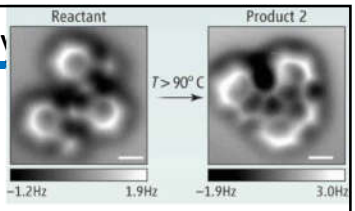


After Lindsay: Intro. to Nanosicence Section 1.3

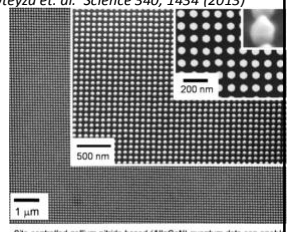
Nanotechnology today, Following Fe

„There is plenty of room at the bottom"

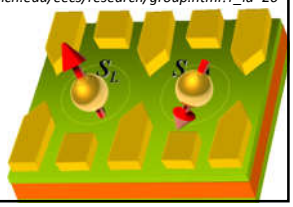
- **Doing synthesis of complex organic molecules by "pushing atoms together":** *"We can arrange atoms the way we want."* With the invention of STM, we can image molecules and even induce reactions by pushing → See tools of nano
- **Resonant antennas for light emission and absorption:** *"It is possible to emit light from a whole set of antennas, like we emit radio waves."* This is the modern field known as "nanophotonics." For example, arrays of nanoparticles can be used to guide light. → See optics part
- **Using quantum phenomena in electronic devices:** *"We could use, not just circuits, but some system involving quantized energy levels, or the interaction of quantized spins."* Quantum mechanics offers us completely novel ways to do computations. Massive parallel computing based quantum entanglement. Field of Quantum Computing. QuantumManifesto 2017-2027. →See new concept in electronics



(Up) STM image of covalent bond structure of a chemical reaction on surface, Oteyza et. al. Science 340, 1434 (2013)

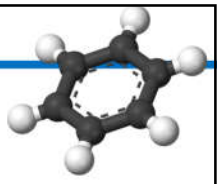


https://www.cse.umich.edu/eecs/research/group.html?r_id=26&g_id=66

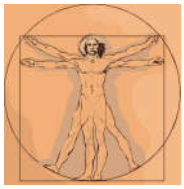


After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology



Nanotechnology:
Manipulation of matter with at least one dimension sized from 1 to 100 nanometers
Multidisciplinary field including physics, chemistry, biology and engineering.
Various applications: nanoelectronics, biomaterials, nanomedicines, energy production…, toxicity.



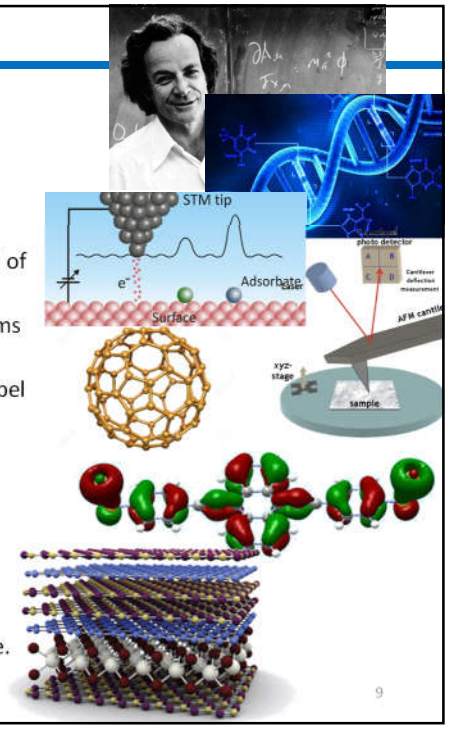
How small is nano?
Incredibly different scale: 1nm = 10^{-6}mm Thus a 1cm^3 = 10^{21} nm^3 Converstion between macro and nanoworld is ~ Avogadro-number
E.g. Caesar's last breath: 15th March -44. 1l of gas = 0.05mol of N_2 . Earth atmosphere has a mass of 10^{18}kg with 80% of N_2. I.e. it has 10^{20} mol of N_2. If N_2 from Ceasar's last breath diffused evenly through the atmosphere, we inhale all the time 10 molecule of Caesar's last breath!

Size matters in other way as well… - Length scales
Electronics, optics, mechanics, fluidics, bio …
First example: Electronics
- Present status of CMOS
- Length scales in electron transport

Other examples…

History of nanotechnology

1959 An inspiration of Nano. Feynman famous talk There's Plenty of Room at the Bottom
1970 First sequencing of DNA
1974 N. Taniguchi has used first ‚nano-technology'
1981 STM unprecedented visualization (later manipulation) of individual atoms and bonds, (low cost tool) [Nobel 1986]
1986 AFM opened a way to explore chemical and bio systems as well
1985 Discovery of fullerenes → carbon nanostructures [Nobel 1996]
1990 DFT calculations get accurate by better exchange and correlation interactions. Various program packages. [Courses of A. Gali, L. Szunyogh, J. Pipek]
2004 Graphene as the first 2D crystal extracted → van der Waals heterostructures [Nobel 2010]
Today nanotechnology is a common platform for modern physics, biology and chemistry. ‚Like' plastic in everyday life.



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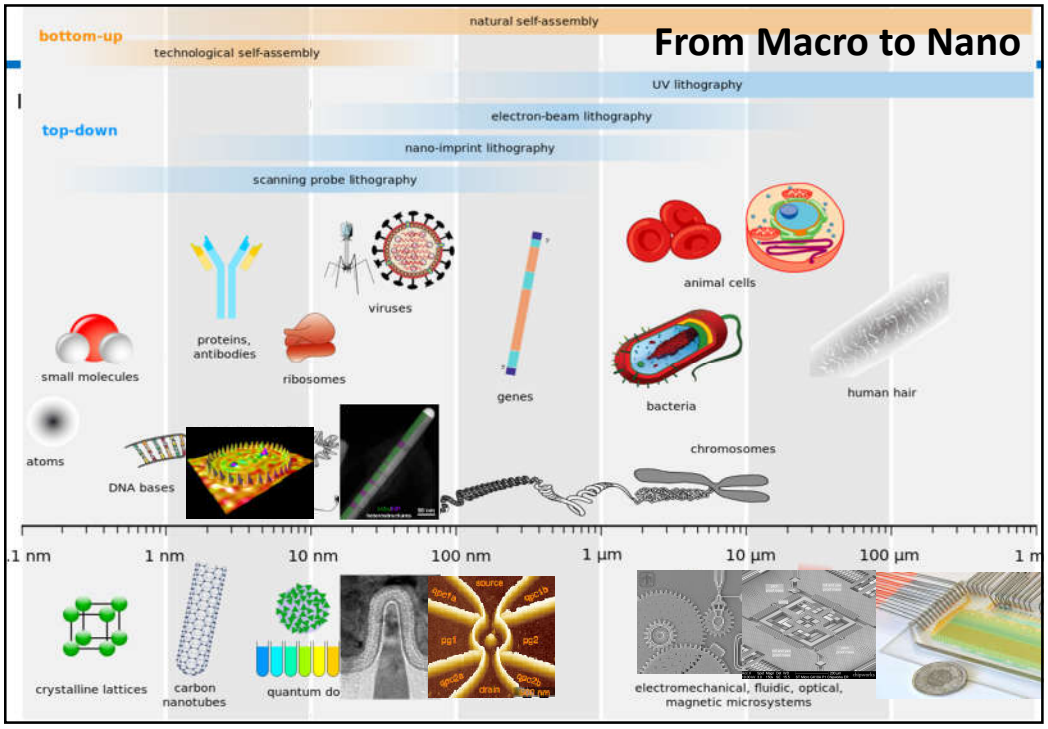
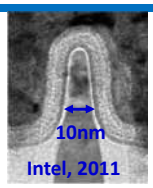
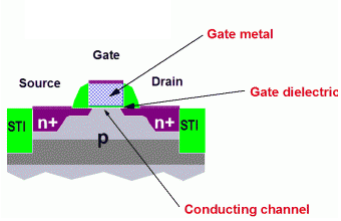


Intel MosFET

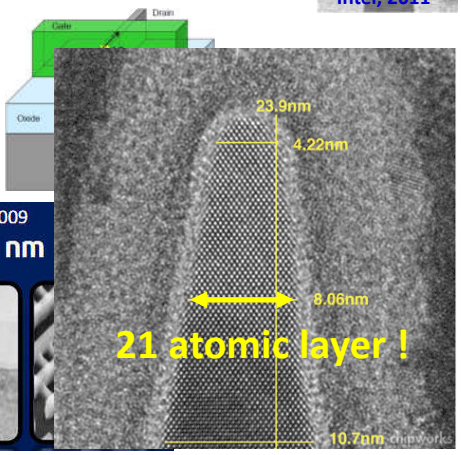
Bottleneck is leakage

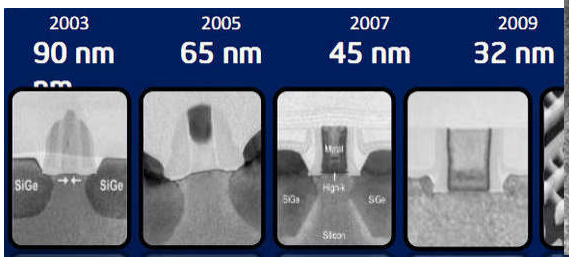


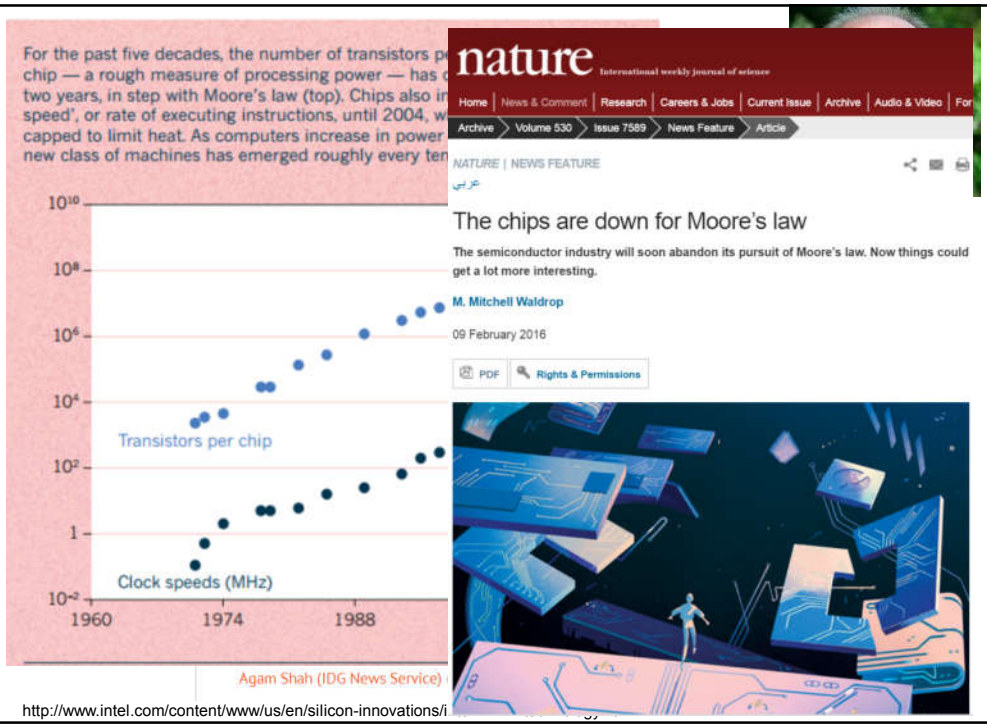
Conventional MOSFET design



22nm 3D Tri-gate technology

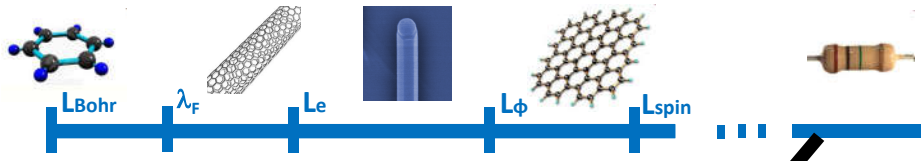






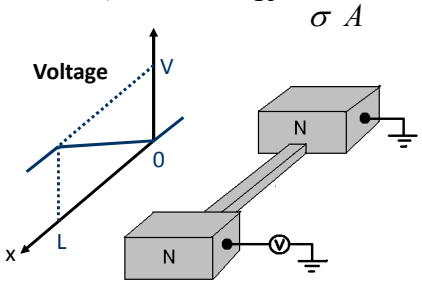
http://www.intel.com/content/www/us/en/silicon-innovations/i

Length scales in electronics



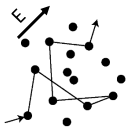
Macroscopic conductor

Ohm's law, Resistance $R = \frac{1}{\sigma}\frac{L}{A}$



Drude – model (1900)

$$\left[\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t}\right]_{\text{scattering}} = \left[\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t}\right]_{\text{electric field}}$$



average drift velocity

$$\frac{m\mathbf{v}_\mathrm{d}}{\tau_\mathrm{m}} = e\mathbf{E} \Rightarrow \mathbf{v}_\mathrm{d} = \underbrace{\frac{e\tau_\mathrm{m}}{m}}_{\text{mobility }(\mu)}\mathbf{E}$$

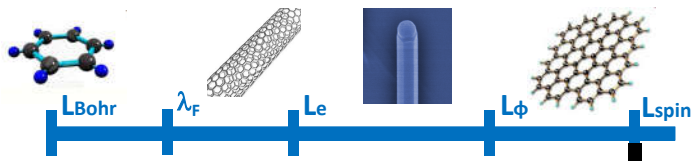
$$\mathbf{j} = ne\mathbf{v}_\mathrm{d} = ne\mu\mathbf{E} \Rightarrow \sigma = ne\mu = \frac{ne^2\tau_\mathrm{m}}{m}$$

L_e : elastic scattering length, distance between scattering events. $l_e = v_F\tau_m$

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

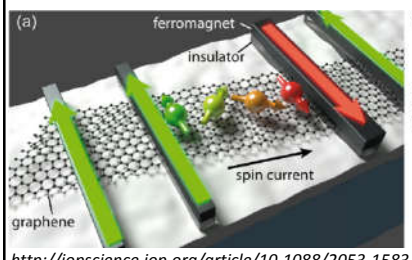
Length scales in electronics

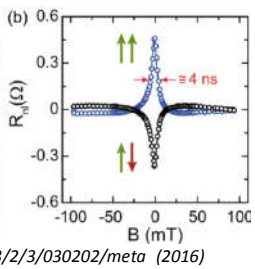
See Wikipedia: Spin valves, GMR effect



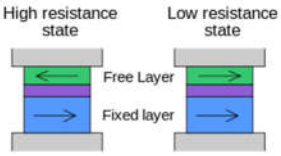
Spintronics

L_{spin}: spin relaxation length.
When size is < L_{spin} , the spin information of electron is not lost during travelling through.





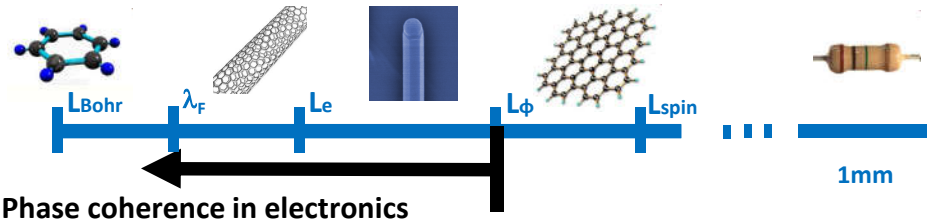
http://iopscience.iop.org/article/10.1088/2053-1583/2/3/030202/meta (2016)



(Up) Spin valve devices used in hard disk reader head as a spintronics device (Left) Graphene based spin valve, where ferromagnetic leads with magnetization pointing up (green) and down (red) are used to inject spin polarized current, which propagates thorough graphene for several μm distances. (b) Influence of perpendicular B field, measured in non-local geometry.

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

Length scales in electronics

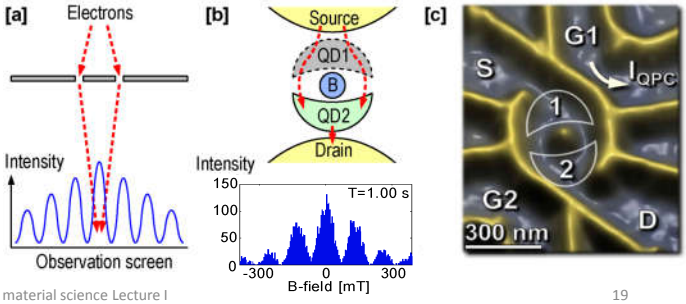


Phase coherence in electronics

L_ϕ: Phase coherence length When size is < L_ϕ phase coherent processes could take place. E.g. quantum interference.

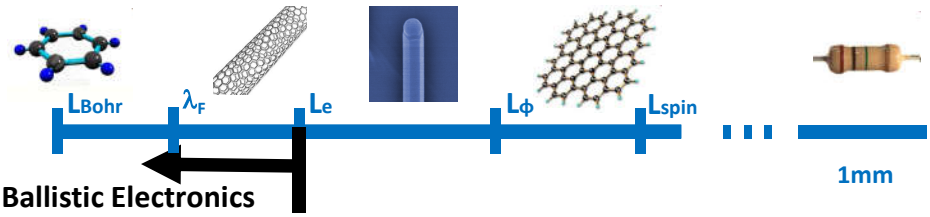
S. Gustavson, T. Ihn, K. Ensslin ETH Zurich

(a) Typical optical interference setup with two slits. (b) An analog interferometer for electrons. There are two paths where electrons can get from source to drain electrode. Phase difference between the two paths is induced by magnetic field. (i.e. Aharonov- Bohm effect) (c) Realization of the interferometer device in 2DEGs with AFM lithography. Intensity corresponds to the transferred electrons, it is measured by QPC.



See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

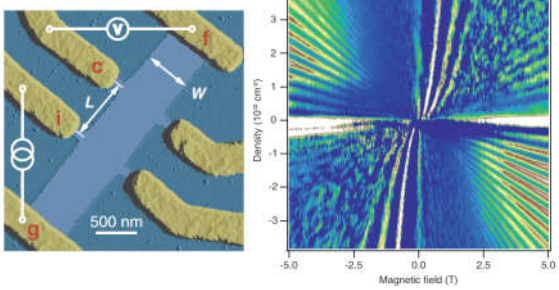
Length scales in electronics



Ballistic Electronics

L_e: Elastic mean free path When size is < L_e , electrons propagate via the system without scattering. They have ballistic motion.

(Left) Ballistic graphene device, where graphene is stacked between hBN layers. Contacts are yellow, graphene is smooth blue region with a width of w.
*(Right) **Transfer magnetic focusing in graphene.** Electrons follow a circular trajectory in magnetic field, which sends electrons from contact to the other when the cyclotron radius properly set.*



T.Taychatanapat et. al. , Nature Physics 9, 225 (2013)

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

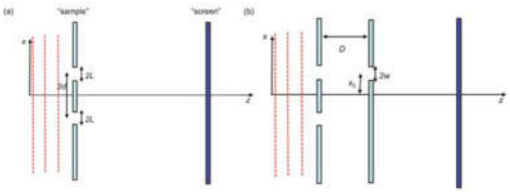
Near-field scanning optical microscopy (NSOM)

Resolution of optical microscope limited by λ
Nano objects can effect EMF on scale << λ
E.g. small opening with d<< λ. But evanescent field still gets through. NSOM probe this.
See example: a) Double slit experiment → diffraction pattern
b) Add an extra small sub-λ aperture (w<< λ) close by (i.e. z<< λ) and move its position → Double slit with sizes <<λ can be resolved.

Tip, aperture or particle in the near field of the sample can scatter the evanescent component into propagating component that survives to far field.

Contrast is system dependent.

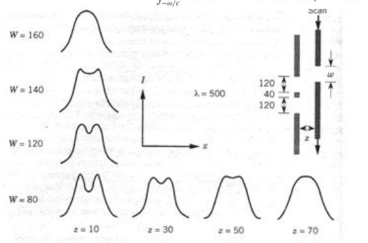
Principle of operation: small aperture very close to a double slit



Diffraction pattern for a double slit (Fourier transformation of slits)

$$F(k_x, z=0) = \int_{d-L}^{d+L} E_0 \exp(ik_x x)\mathrm{d}x + \int_{-d-L}^{-d+L} E_0 \exp(ik_x x)\mathrm{d}x$$
$$= 4E_0 \cos(k_x d)\frac{\sin(k_x L)}{k_x},$$

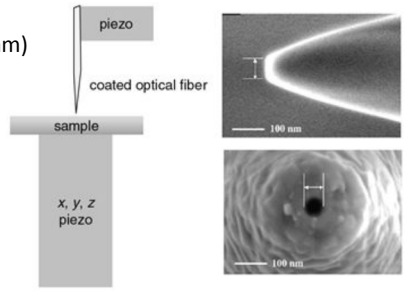
$$E(x,z) = \int_{-\infty}^{+\infty} \mathrm{d}k_x [F(k_x, z=0)\exp(-ik_x x)]\exp(ik_z z)$$
$$\approx \int_{-\omega/c}^{\omega/c} \mathrm{d}k_x [F(k_x, z=0)\exp(-ik_x x)\exp(i\sqrt{k^2 - k_x^2}z)],$$



Near-field scanning optical microscopy (NSOM)

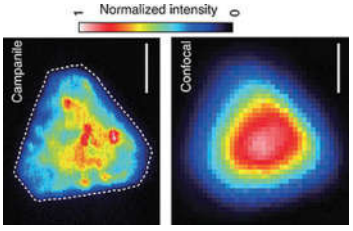
Setup:
- Coated optical fiber with a subwavelegth aperture (∝10nm)
- Piezo positioning of the sample to achieve nm lateral resolution
- Tip-sample distance is kept constant by tuning fork like AFM configuration

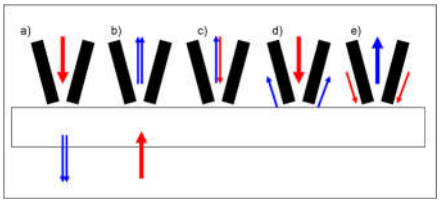
Various operation modes:
a) Illumination b) Collection c) Illumination/collection
d) Reflection e) Reflection/collection f) Aperture less modes (e.g. tip, metal particle)….
Used for biology, photonic crystals, plasmonic structures



(Top left) Setup of NMOS, (Top right) End of optical fiber tip (Bottom) NMOS operational modes

Method provides relative information.





Example: Comparison of photoluminescence maps recorded from a MoS_2 flake using NSOM with a campanile probe (left) and conventional confocal microscopy (righ). Scale bars: 1 μm

Micro-fluidics ‚Lab-on-chip'

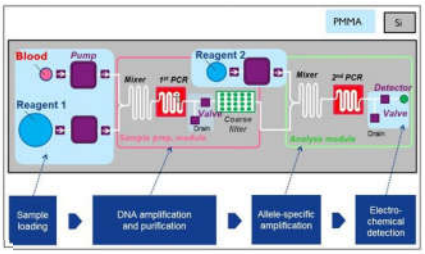
Simple example**: inkjet printers** micron scale droplets of ink through a microfabricated array of orifices.

Future goal, "lab-on-a-chip" technologies:
More complex systems, enabling the circulation, routing, mixing, and storage of small quantities of fluids on demand, microfluidic systems can perform complex chemical and biochemical procedures using much more reduced amounts of analytes or reactants than traditional, "full size" bench approaches.
If mass production is cheap --> revolutional medical diagnostics (e.g. DNS check similar to pregnant test)

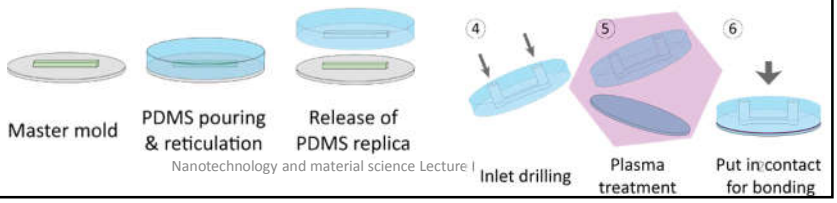
Typically based on planar semiconductor fabrication (similar to MEMS) or recetly soft lithographic techniques involving PDMS. **Replica molding of various PDMS layers** on top. → cheap thus revolutional for LOC.

See http://www.meddeviceonline.com/doc/silicon-a-material-with-huge-potential-for-lab-on-chips-0001
http://www.elveflow.com/microfluidic-tutorials/microfluidic-reviews-and-tutorials/the-poly-di-methyl-siloxane-pdms-and-microfluidics/

(Top) lab-on-chip (LOC) devices that can be used at the "point of need." (Bottom) Sscheme of a silicon based LOC device for Blood testing



(Bottom) Fabrication of PDMS based microfluidics



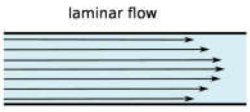
Micro-fluidics ‚Lab-on-chip'

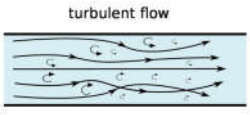
Reynold number (Re): ratio of inertial force and viscous forces
- Re large : turbulent flow, -Re small: laminar flow

Macroscopic world is in the **large Re** limit.
Cosequences: Two examples:
- mixing coffee with milk is fast
- during swimming we can coast. (Momentum is enough to overcome comparatively weak viscous drag forces)

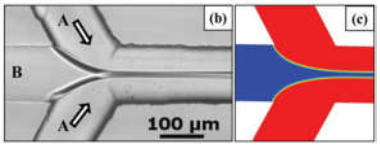
Micro and nano world is in **low Re** limit.
- Laminar flow → no turbulances. Mixing fluids is based on slow diffusion at interface. → challanging to mix fluids efficiently in micro-fluidic systems. Challanges for chemical or bio reactions
- Swimmig for a bacterium. Its size ~1µm, initial velocity v ~30µm/sec, Re~ 10^{-5} . Coasting distance: 1nm!

(Top) While a macro scale swimmer can coaat in water micron scale one can not!





(Left) Velocity profile of low Re, laminar flow typical in microfluidics system. And of high Re turbulent flow.
(Bottom) Special microfluidic arrangements for mixing liquids, which based on flow focusing. A liquid of interest may be "squeezed" down hydrodynamically to small (tens of nanometers) transverse dimensions. This small flow width leads to diffusive mixing times across the flow down to the microsecond regime



See Natelson Section 10.1 and 10.6, 10.7

Magnetic separation at nanoscale

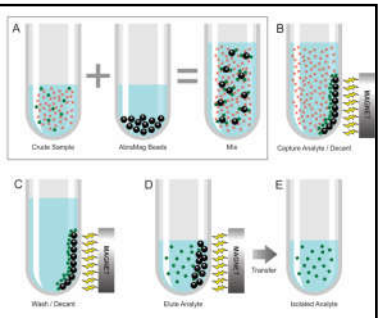
A multiple example showing differences at nanoscale

It is used for capturing or purifying e.g. proteins, antibodies, or DNA from diverse biological samples.

Principle: Targeted analyte connects to functionalized magnetic particles and removed by magnetic field gradient. Micron sized magnetic beads are widely used in biology

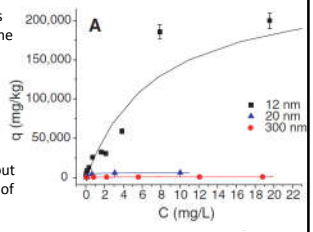
Recently magnetic nanoparticles can be synthesized chemically. Much larger surface! → Increased efficincy.

However **issues at nanoscale**: force of B field ~ volume, viscous force ~ diameter, fluctuations i.e. Brownian motion ~k_BT/d. → Nanoscale is not preferable.
Still it works for 10nm scale particles with better sensitivity. . Reasons: a) Single domain particles -> large stray field ~M_{sat}/d and b) large interparticle force which order neighbouring particles → collective response of particles



(Up) Principle of magnetic separation. Functional magnetic beads are added to mixture under investigation (A) Mix beads (black spheres) with crude sample (red Xs) containing desired analyte (green squares); (B) capture analyte-bound beads with magnet; (C wash away crude sample components; (D) elute analyte from beads; (E) transfer to new tube.
http://www.abraxiskits.com/products/magnetic-beads/

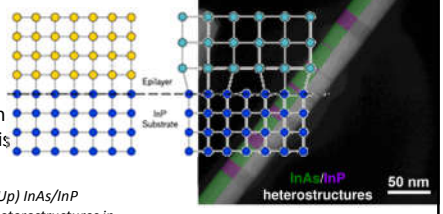
(Down) Arsenic adsorption studies with nanocrystalline (12 nm) and commercially available (20 and 300 nm) Fe3O4. 1000 times less 12nm scale NP is required to filter out the same amount of arsenic.



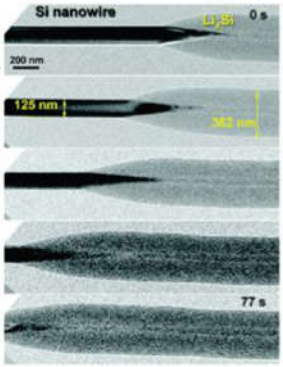
See Natelson Section 7.7
Cafer T. Yavuz Science 314, 964 (2006) DOI: 10.1126/science.1131475

Mechanics at nanoscale

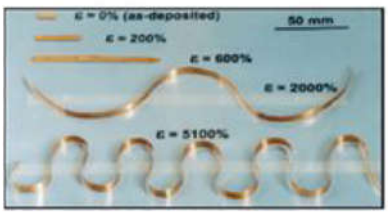
Examples:
Easier to accommodate strain at nanoscale…
- Novel heterostructures: Possible to relax lattice mismatch at nanoscale. E.g. InAs/InP heterostructures
- Huge strain before failure E.g. intercalation of lithium into silicon NWs for potential chargable battery option. Strains up to 200% is possible! Nanowires can respond much more reversibly to the distortions associated with lithiation and delithiation



(Up) InAs/InP heterostructures in nanowires, possible due to lattice mismatch relaxing at nanoscale. (Right) Si nanowire as its size increasing during Li intercalation over 200%. A reversible process.



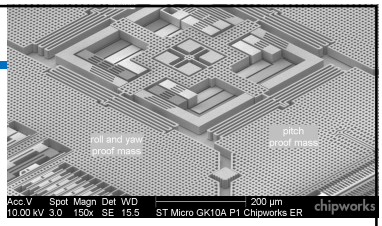
Superplasticity
Plastic deformation happens with displacement of dislocations When grain size smaller than the length scale of formation/ propagation of dislocations (i.e. at the nanoscale) → different plastic deformation properties. Grain bonderies dominate.



Superplasticity of nanocrystalline Cu: When grain size becomes small, significant fraction of atoms are at grain boundaries, remarkable deformations can be possible. See elongation over 5000%.

See D. Natelson Section 9.1.4 27
L. LU et al. ADVANCED ENGINEERING MATERIALS 2001, 3, No. 9, 663

NEMS/MEMS systems

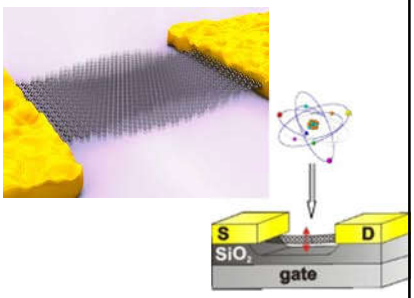


Nano/micro electro mechanical systems
Various applications: automative systems,sensing, electronics etc.
Huge market.

Planar techniques for semiconductor manufacturing.
Limited fabrication paths and materials

Used for: cantilevels, Inertial sensing, mass sensing, inkjet head, …

NEMS goals: ultimate limit of mass (or force) sensing, e.g. to detect a molecule by its mass.
Resonance freq: f=√D/m → To increase mass sensitivity: m↘ , D↗ and also Q should be large.
Use: Carbon nanotubes or graphene
Achived resolution 1.7 yg (1 yg = 10^{-24} g) (2012) Mass of one proton.



Chastle Nature Nanotecnology **7**, 301–304 (201

See D. Natelson Section 9.4

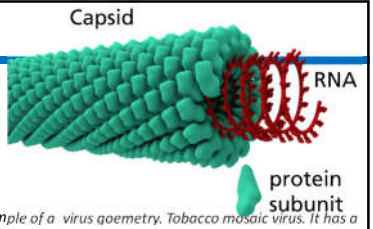
BioNanoTechnology

Biology operates truly at the nanoscale
There are nanoscale machines in our cells, e.g. they fabricate complex structures (molecules), they can act as motors, pumps, transducers to mechanical energy. Biological systems can build up complex structures from nano to macro scale.

Typical objects and their sizes
Viruses: E.g. Tobacco mosaic virus 18nm in diameter and 300nm long
Cells: their wall are at the ~10nm scale
Ion transporters, pumps etc.

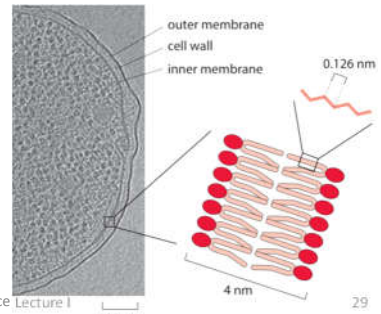
Molecules and their interaction governed by electrostatic, van der Waals, hydrogen bonding & hydrophobic interactions at k_BT.

(Left) Sodium-potassium pump: It is an enzyme, which pumps sodium (Na) out of cells while pumping potassium (K) into cells, both against their concentration gradients.It as active element using energy from ATP. One of its application: nerve conduction.



(Up) Example of a virus geometry. Tobacco mosaic virus. It has a helical protein shell (called capsid), which encloses the genetic material (RNA).

(Down) Electron micrograph of a cell, with its wall. The membranes consist lipid bilayers. Red circle denotes the hydrophilic head, the pink lines represent the hydrocarbon chains forming a tight hydrophobic barrier excluding water, polar or charged compounds



Source: Wikipedia
http://book.bionumbers.org/what-is-the-thickness-of-the-cell-membrane/

See D. Natelson Section 11.1