Simulation von Nanostrukturen

Forschungszentrum Dresden Rossendorf

Klaus Morawetz

Universidade de Brasília

1. Was sind Nanostructuren ?
2. Gefühl für Größenordnungen
3. Herstellung und Anwendungen
4. Organische Feldeffekttransistoren (Material, Funktion)
5. Modellierung durch Hüpfen auf Gitterplätzen (Dichtefunktionaltheorie)
6. Transporteigenschaften (Leitfähigkeit, thermische Leitfähigkeit, Thermokraft)
7. Schüttel- oder Hüpftransport?

Chemnitz University

MPI for the Physics of Complex Systems

LPC/ISMRA

Arizona State University

Michigan State University

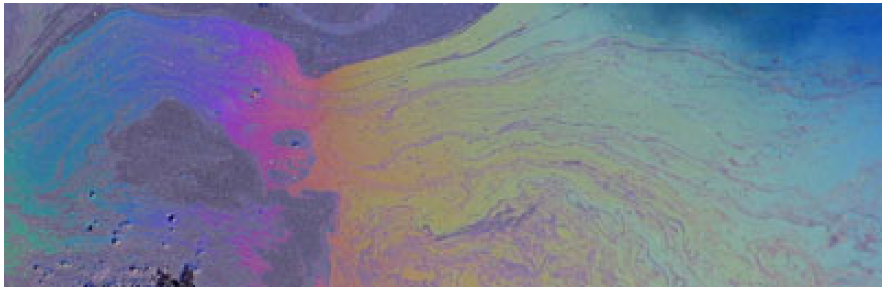
Tennessee Tech University

Rostock University

Nanostructures

The Lycurgus Cup, Late Roman, 4th BC, probably Rome, (the British Museum)

A dichroic glass cup changes colour when held up to the light. The opaque green cup turns to a glowing translucent red when light is shone through it. The glass contains tiny amounts of colloidal gold and silver, which give it these unusual optical properties.



oil-slick-rainbow

Tiger orange glass with cobalt blue shimmer

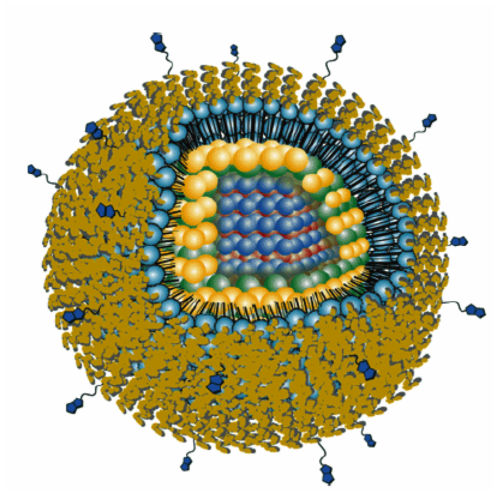
Price: $35.00

Nanocrystals

Quantum effect: Crystal size determines the color

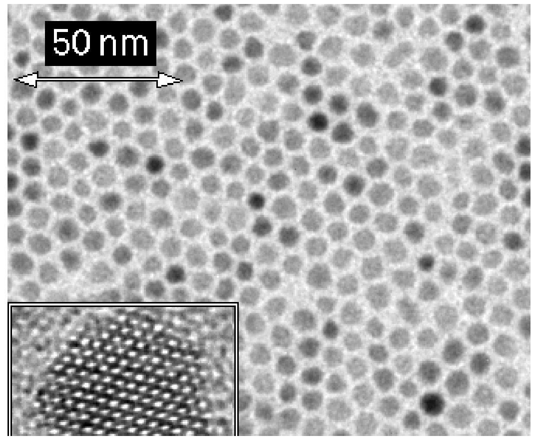
(blue-shifted when smaller)

CdSe Nanoparticles (Quantum Dots)



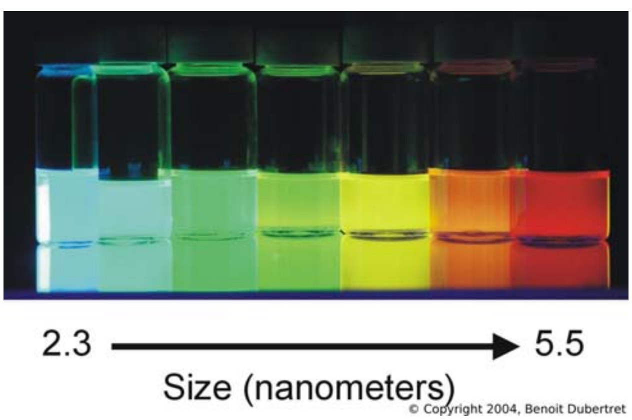
Schema von Quantum Dots

Beispiele als Teilchen im 3-D Kasten

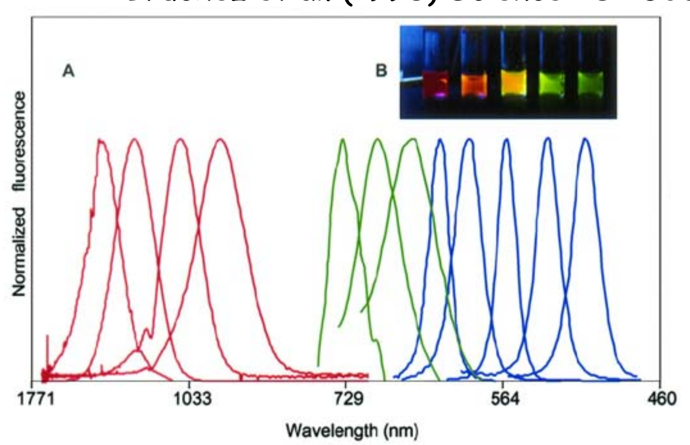


elektronenmikroskopische Aufnahme von Quantum Dots

http://www.chemie/uni-hamburg.de/pc/Weller



Bruchez et al. (1998) *Science* **281**:5385



Emissionseigenschaften von Quantum Dots sind von der Größe des Kastens abhängig

Spektren: (rechts nach links)

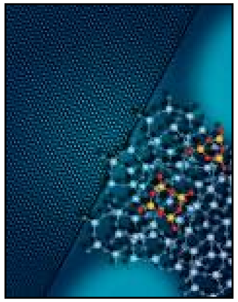
Blau: CdSe Nanocrystals mit ∅ = 2.1, 2.4, 3.1, 3.6, 4.6 nm

Grün: InP Nanocrystals mit ∅ = 3.0, 3.6, 4.6 nm

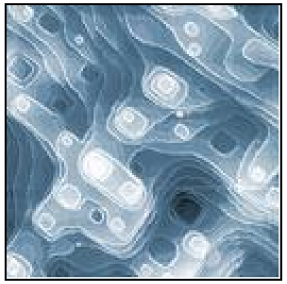
Rot: InAs Nanocrystals mit ∅ = 2.8, 3.6, 4.6, 6.0 nm

Some more recent nanostructures

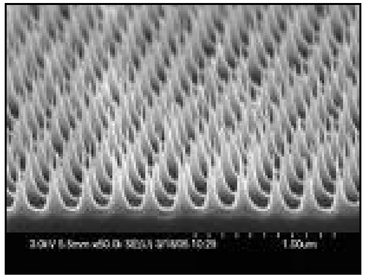
http://images.google.com/images?um=1&hl=de&client=firefox-a&rls=org.mozilla:de:official&q=Nanostructures&start=18&sa=N&ndsp=18



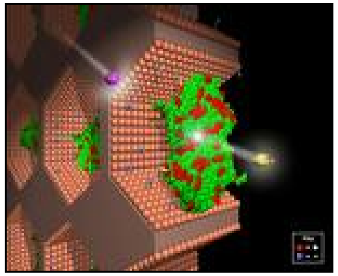
... porous, cube-like **nanostructure**.
www.sandia.gov



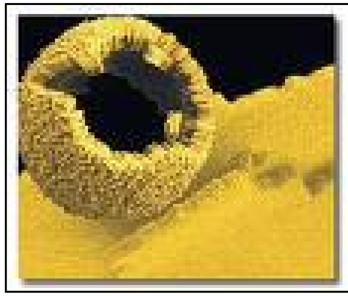
These **nanostructures** are usually **...**
iramis.cea.fr



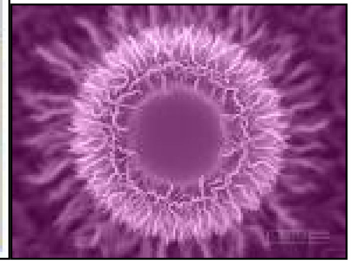
SEM images of silicon **nanostructures ...**
cjmems.seas.ucla.edu



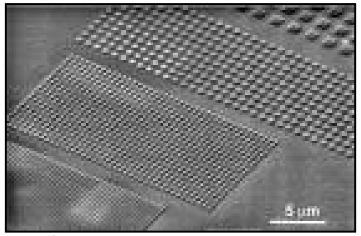
Synthetic **Nanostructures** Offer **...**
genomicsgtl.energy.gov



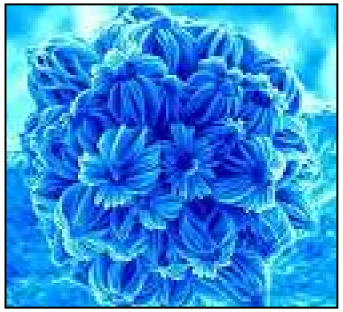
... of Gold Polymer **Nanostructures**
www.azonano.com



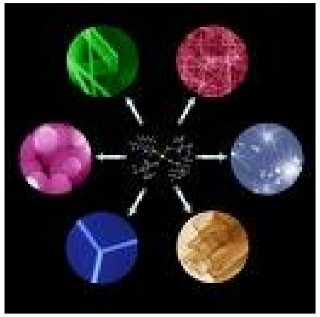
... carbon **nanostructures** grown on a **...**
www.mrs.org



... these **nanostructures** are still **...**
www.mpi-halle.mpg.de

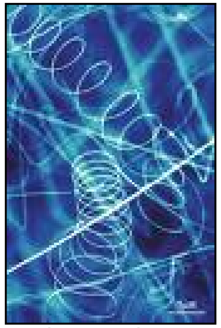


... Si composite **nanostructures**, **...**
blog.nanovic.com.au

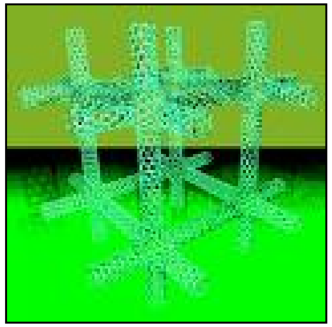


... use **nanostructures** to dazzle us **...**
www.impactlab.com

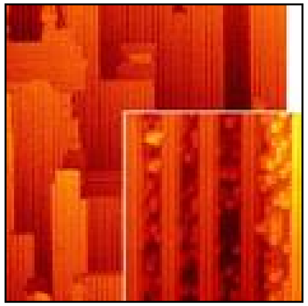
... self-assembled Sb **nanostructures ...**
www.phys.canterbury.ac.nz



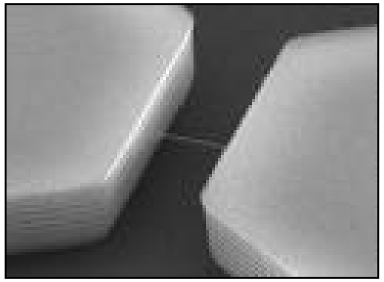
These unique **nanostructures** have **...**
www.solid-state.com



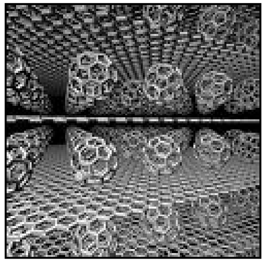
Nanostructure
publishing.royalsociety.org



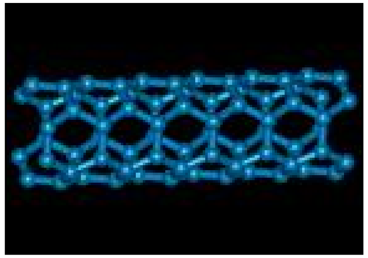
... of Bi **nanostructures** on Si (001).
www.omicron.de



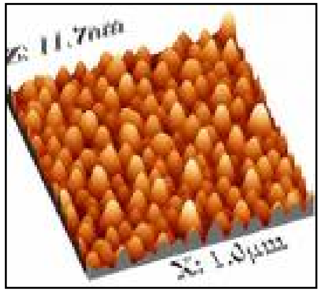
... of 1D **nanostructures** endow them **...**
www.cchem.berkeley.edu



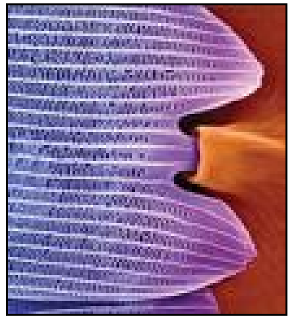
substructures to **nanostructures**
www.iaacblog.com



... carbon-based **nanostructures** with **...**
www.physics.purdue.edu.



Magnetic **nanostructures** delevoped by **...**
www.icmm.csic.es



... are often due to **nanostructures ...**
www.rsc.org

Understanding Size

- 1 meter

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

- 10 centimeters

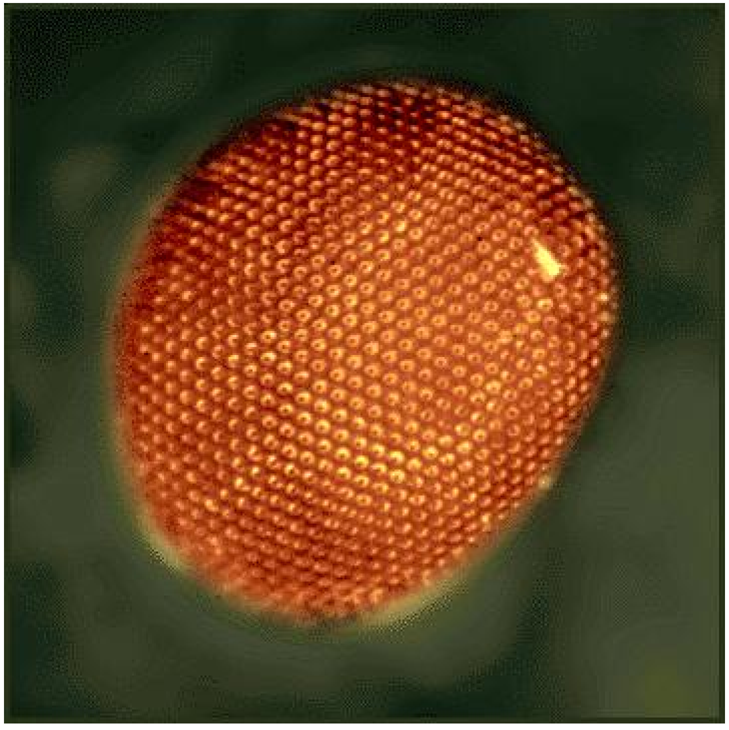
source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

- 1 centimeter

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

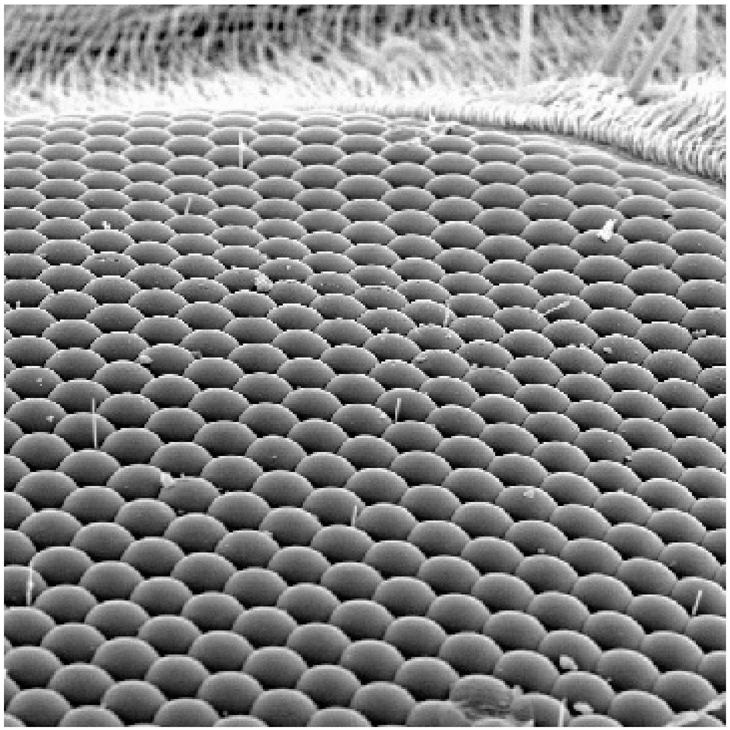


- 100 micrometers

The fly's eye is made of hundreds of tiny facets, resembling a honeycomb.

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

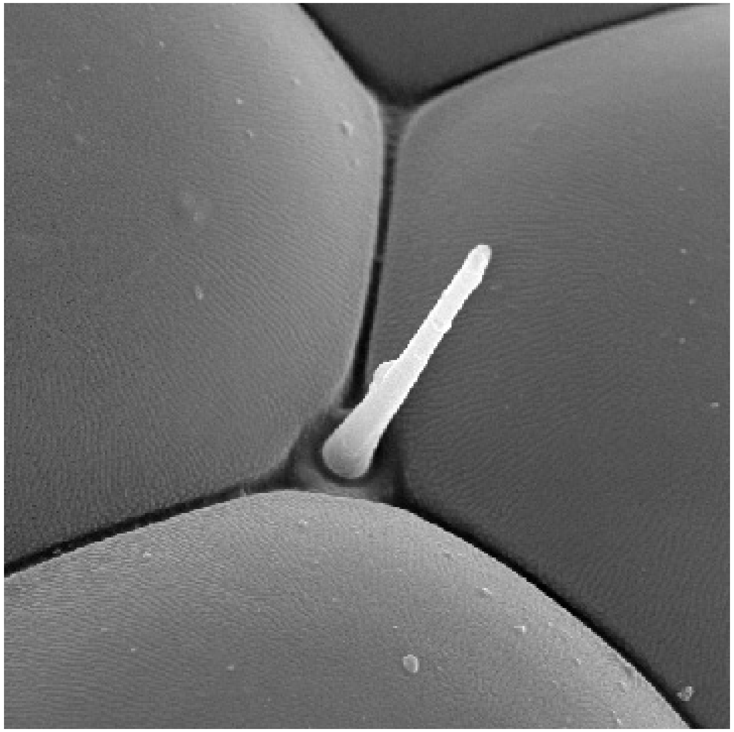


- 10 micrometers

The fly's eye is made of hundreds of smaller eyes. Each facet is a small lens with light sensitive cells underneath. This image was taken using an electron microscope.

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

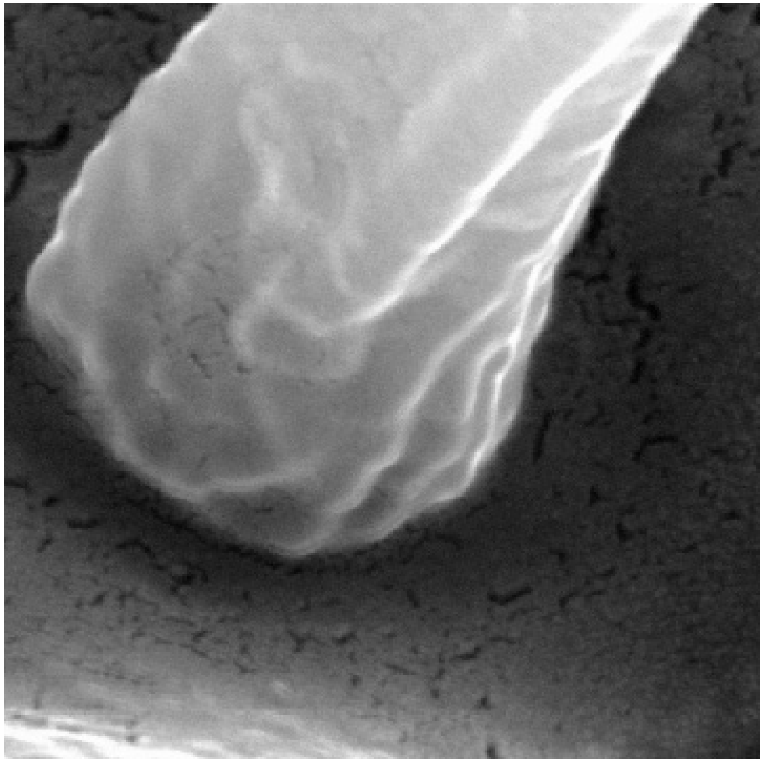


- 1 micrometer

In between the facets are bristles which give sensory input from the surface of the eye.

source: CERN
http://microcosm.web.cern.ch/microcosm

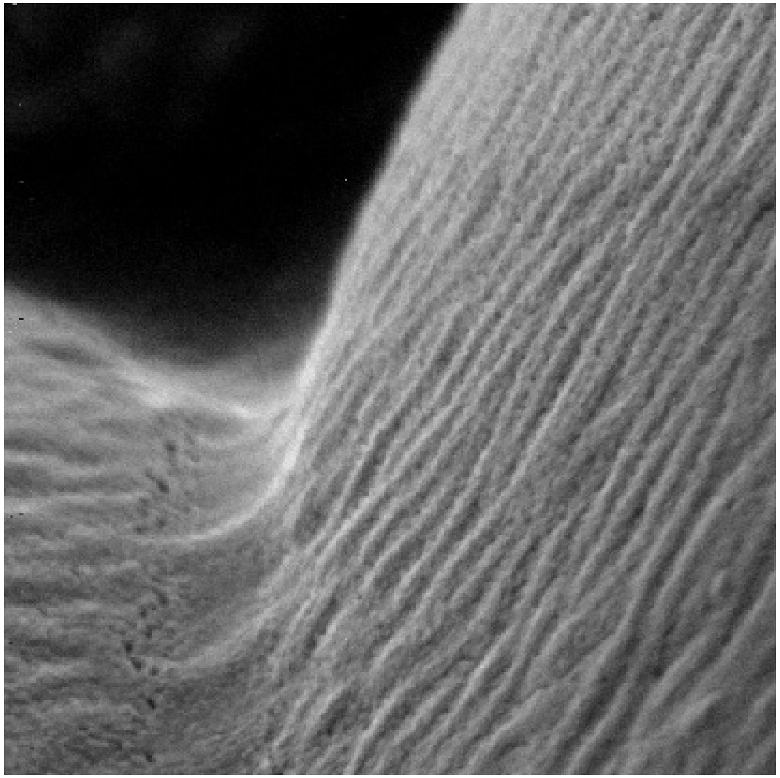
Understanding Size



- 100 nanometer

source: CERN
http://microcosm.web.cern.ch/microcosm

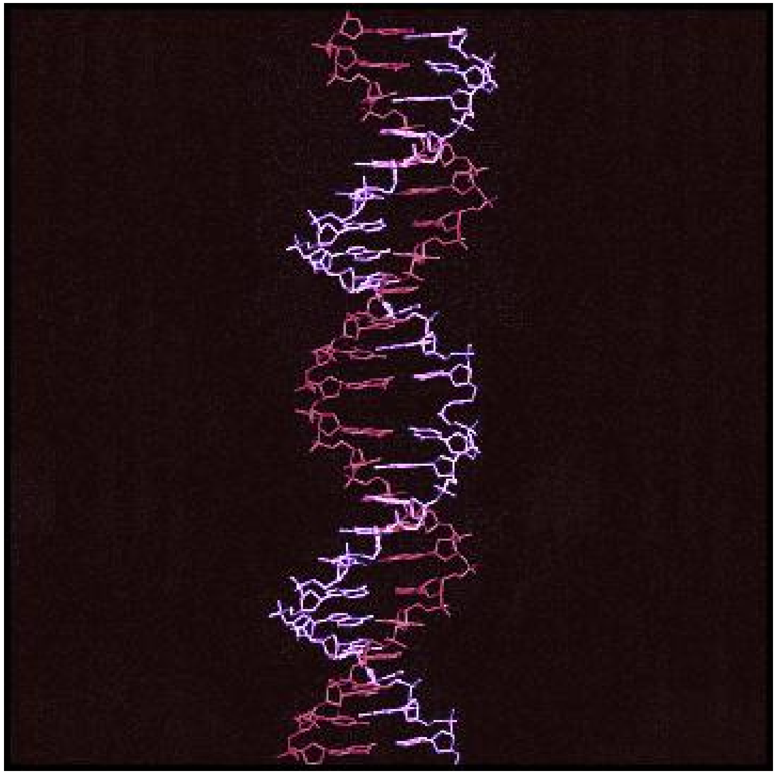
Understanding Size



- 100 nanometer

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size

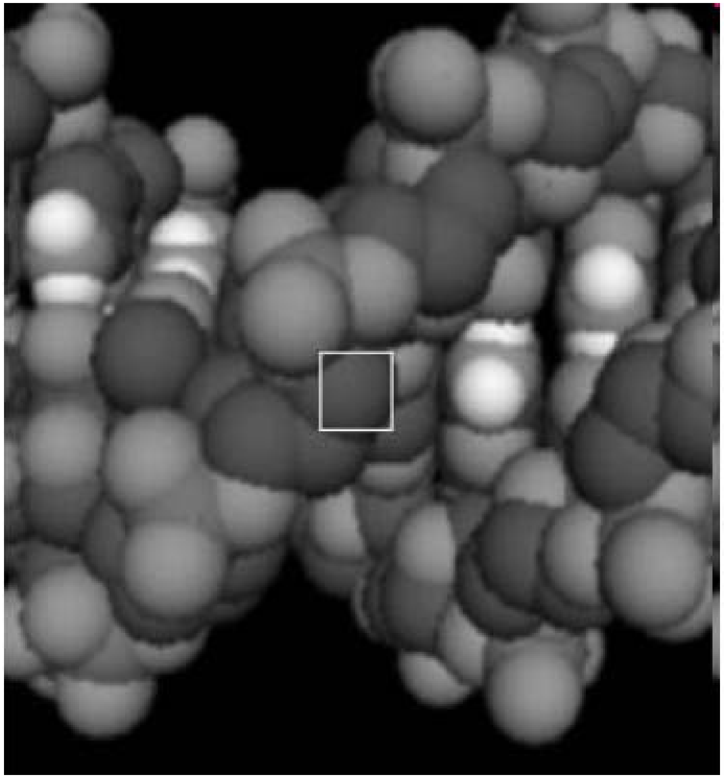


- 10 nanometer

At the centre of the cell is a tightly coiled molecule called DNA. It contains the genetic material needed to duplicate the fly.

source: CERN
http://microcosm.web.cern.ch/microcosm

Understanding Size



- 1 nanometer

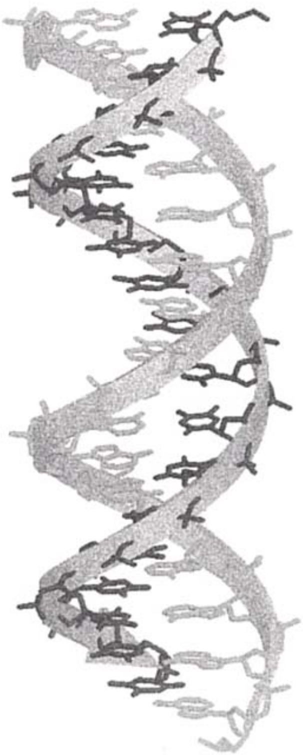
source: CERN
http://microcosm.web.cern.ch/microcosm

Biological Length Scales

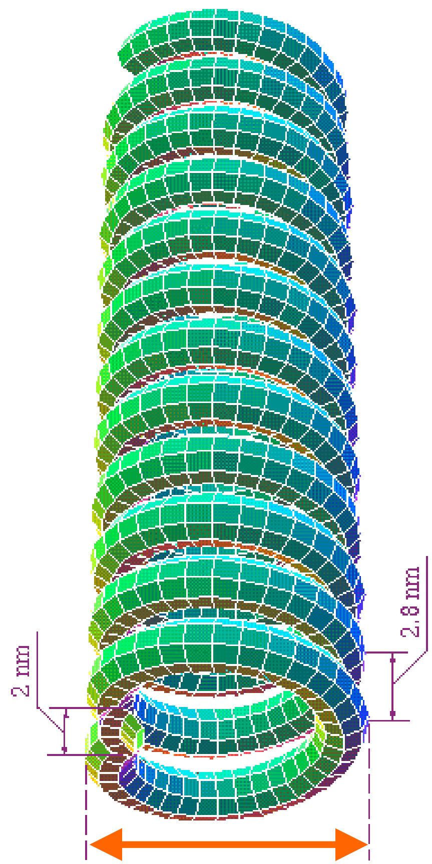
DNA

3.4 nm pitch

10 base pairs

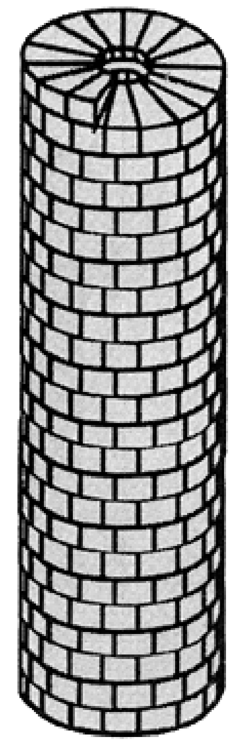


2 nm



11 nm

Virus (TMV)



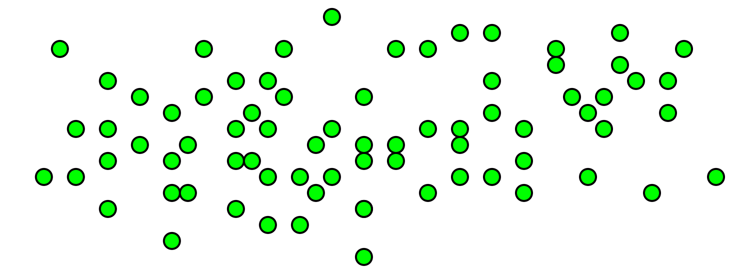
300 nm

18 nm

Franz J. Himpsel,University of Wisconsin Madison

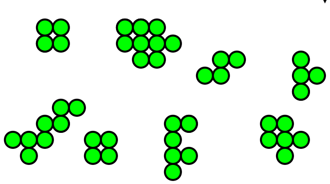
Nanostrukturen - Herstellung

"bottom-up"

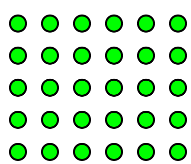


verteilte Monomere (10^{-9}m)

Aggregation



Cluster

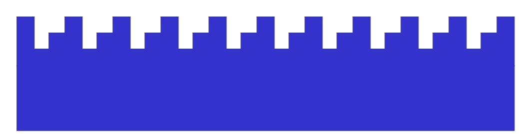


Übergitter

"top-down"

Einkristall (10^{-1}m)

Lithographie



Sibylle Gemming, FZD

Applications of nanotechnology

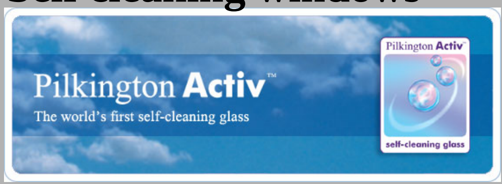
Medicine; diagnostics, therapy
Genomics; sequencing?

Nano-electronics
Actuators
Nanorobots
catalysis
…

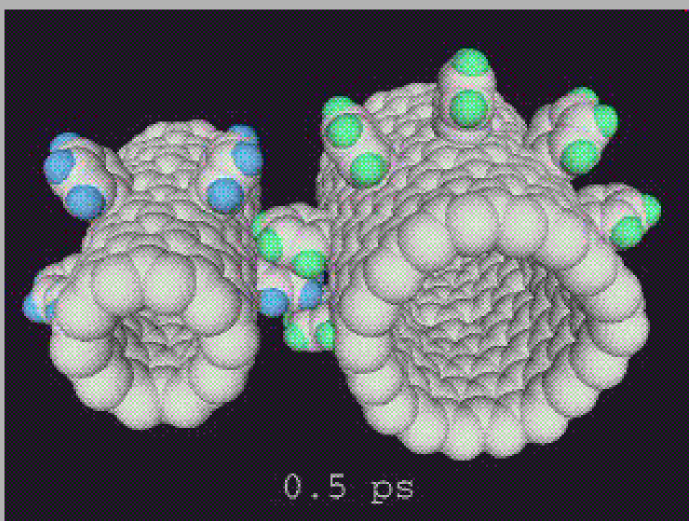
Nano-pants

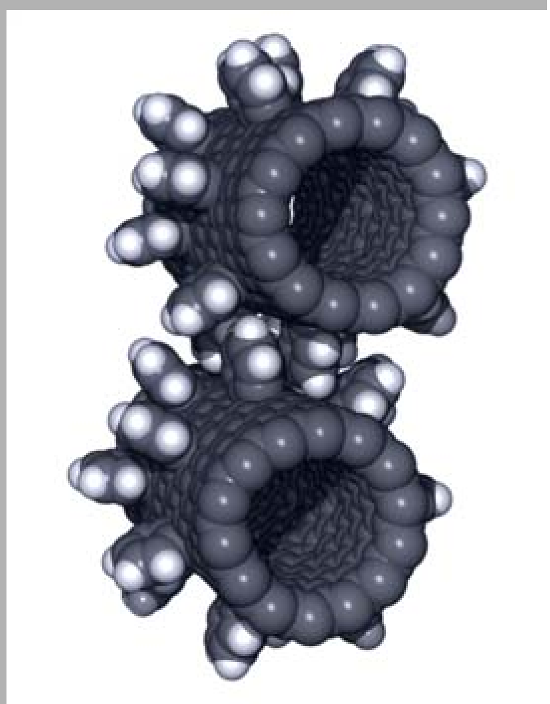
Ferrofluids

Self cleaning windows



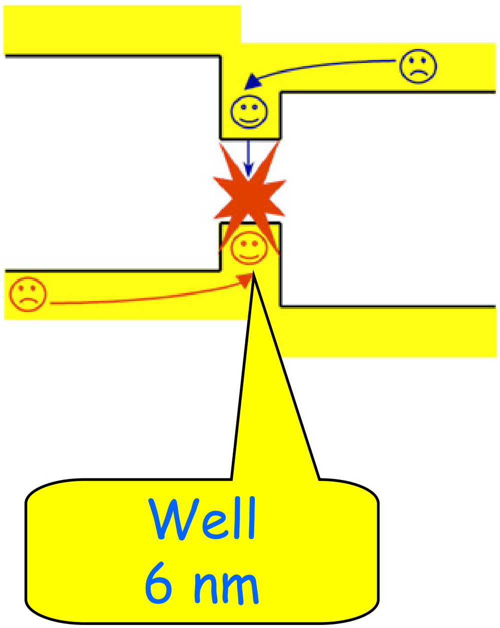
Nano-gear



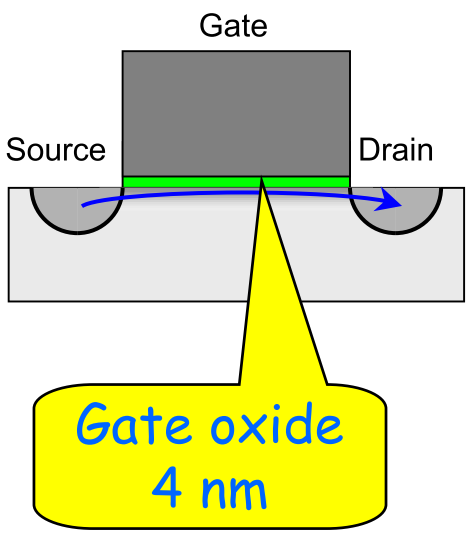


Nanotechnology on our Desktops

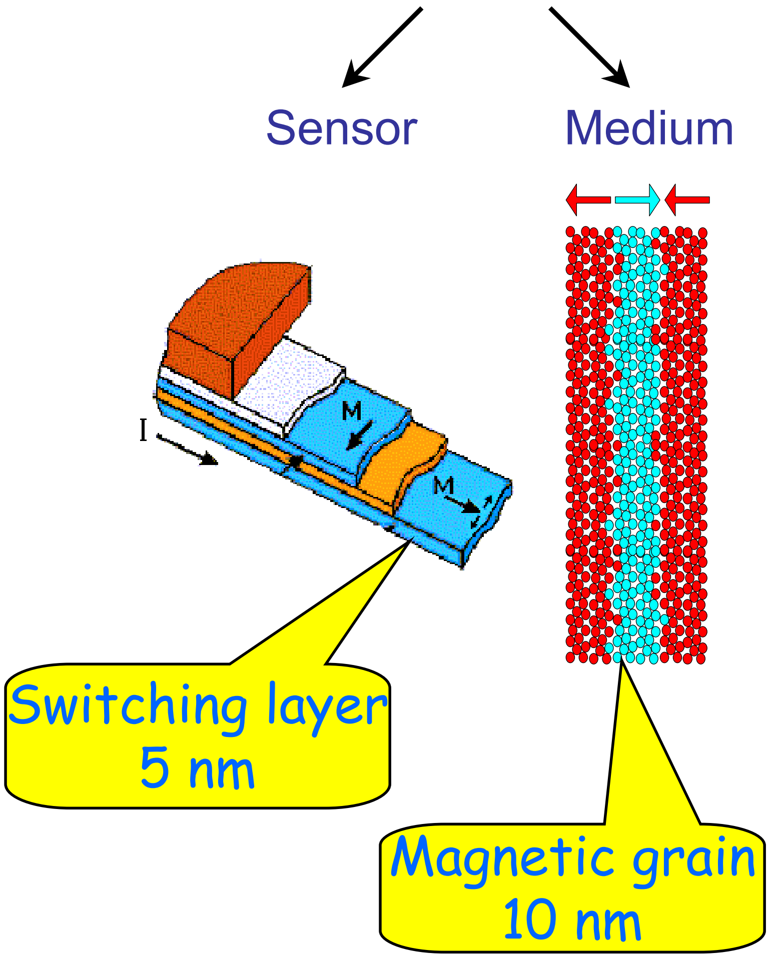
Quantum Well Laser



Transistor



Hard Disk



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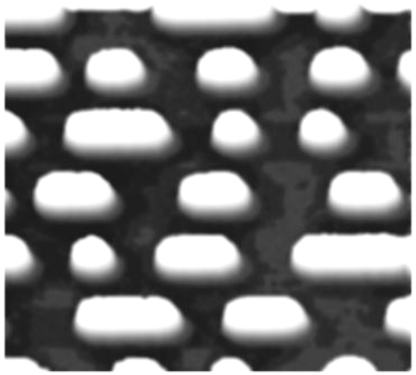
In Pursuit of the Ultimate Storage Medium :

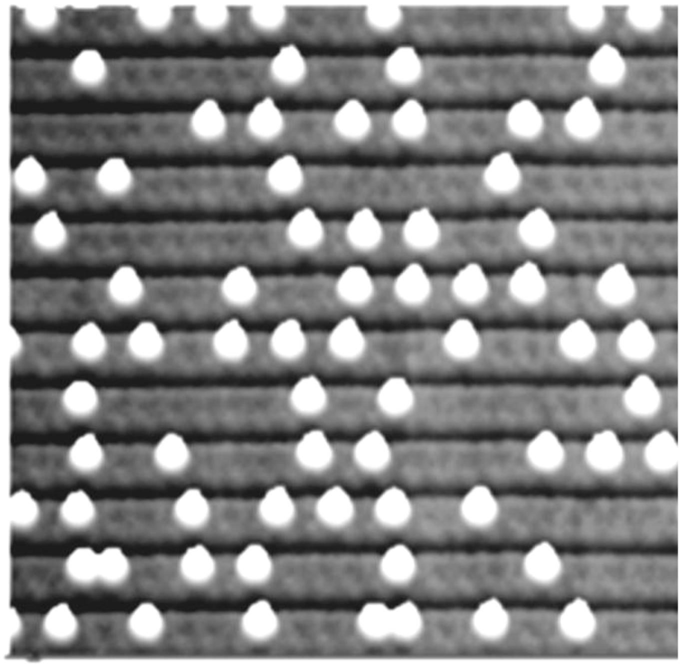
1 Bit = 1 Atom

CD-ROM



10 μm

Silicon Surface



1.6 nm Track

10 nm

Density × 1 000 000

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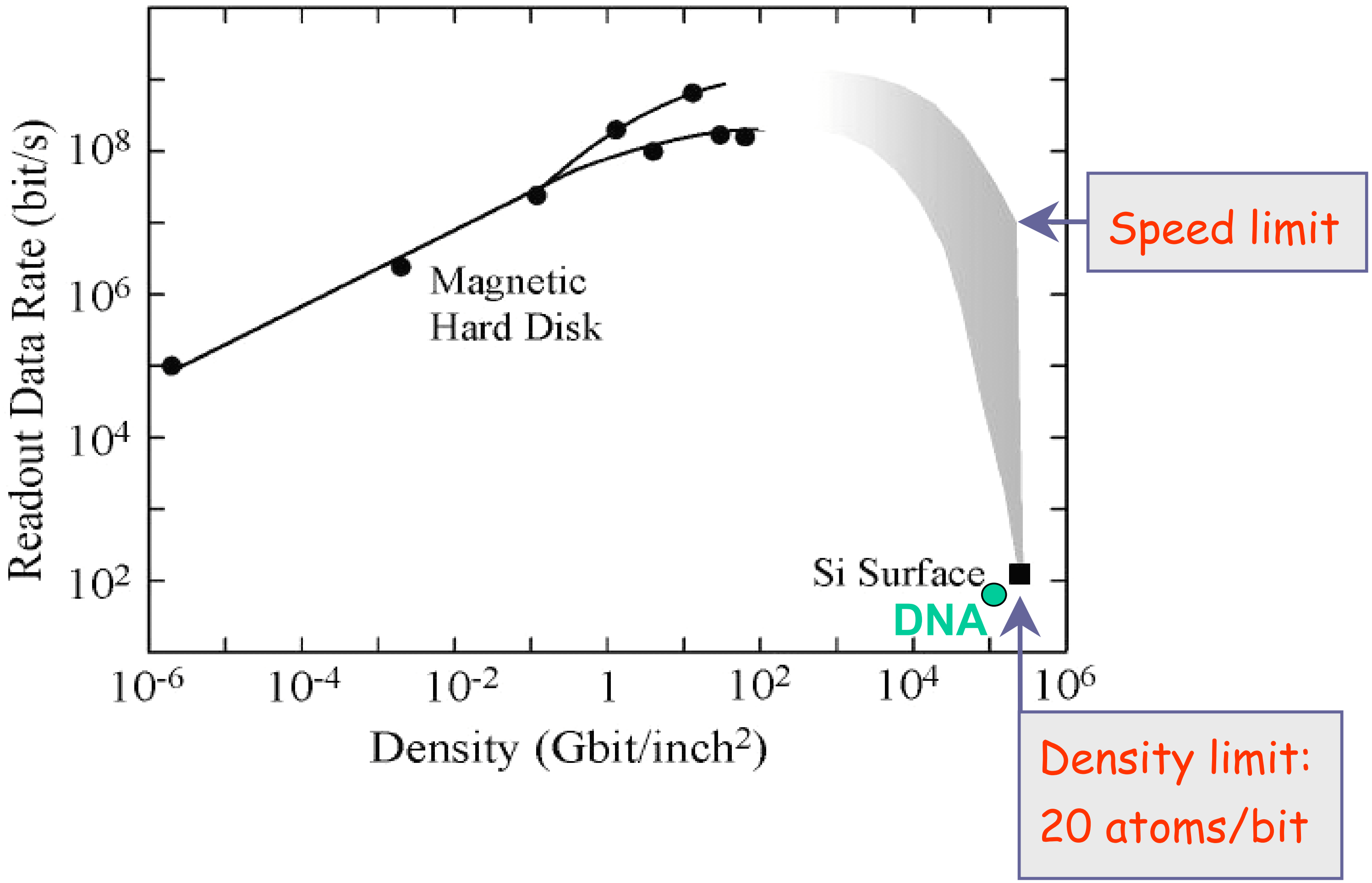
Speed versus Density



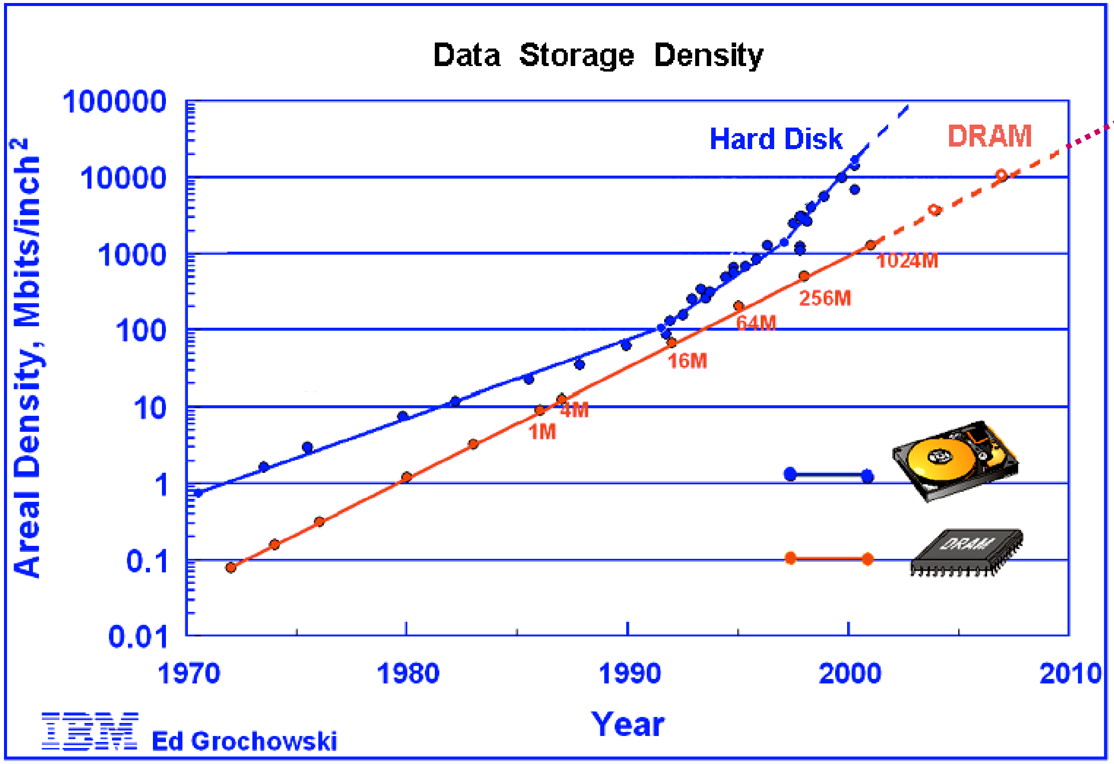
- Speed is sacrificed as density increases (less signal per bit)
- Density and speed in silicon are comparable to those in **DNA**

When will we be down to atoms ?

Using Moore's Law ...

250 Terabit/inch^2

Year 2038



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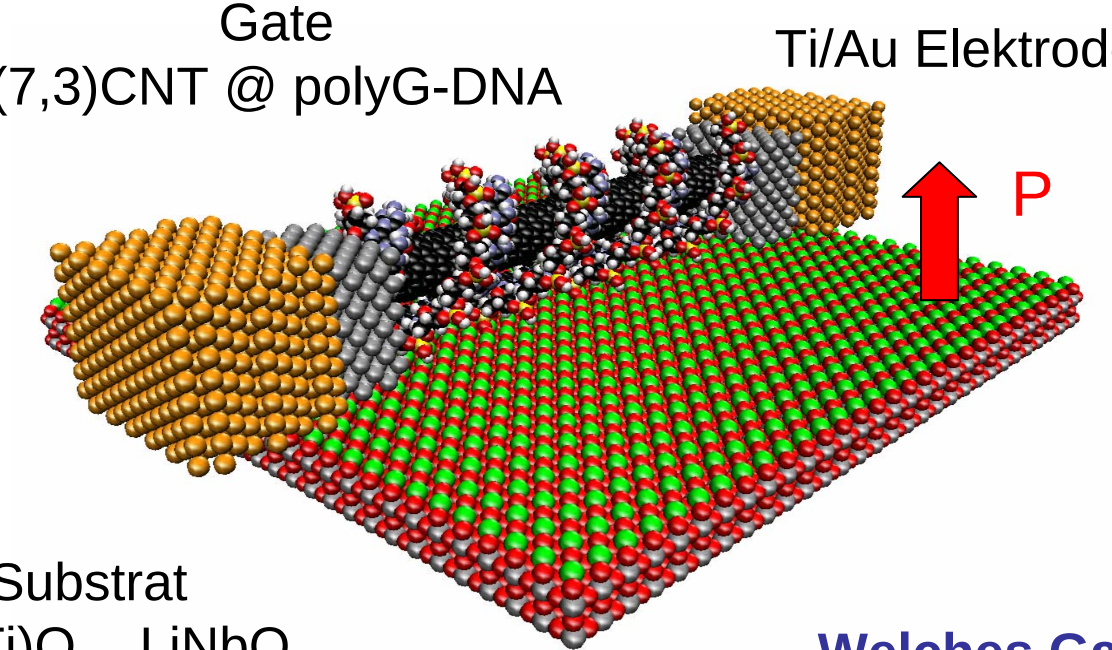
Nanoskaliger organischer ferroischer FET

FET-Prototyp



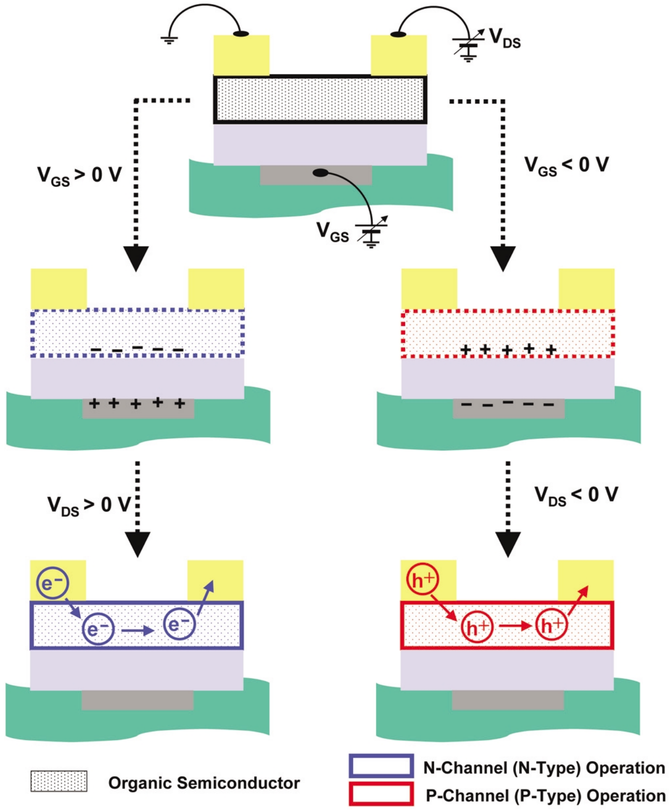
Ferroelektrisches Substrat
- $BaTiO_3$, $Pb(Zr,Ti)O_3$, $LiNbO_3$
- Oberflächen-Polarisation **P ~ GV/m**

Welches Gate ?

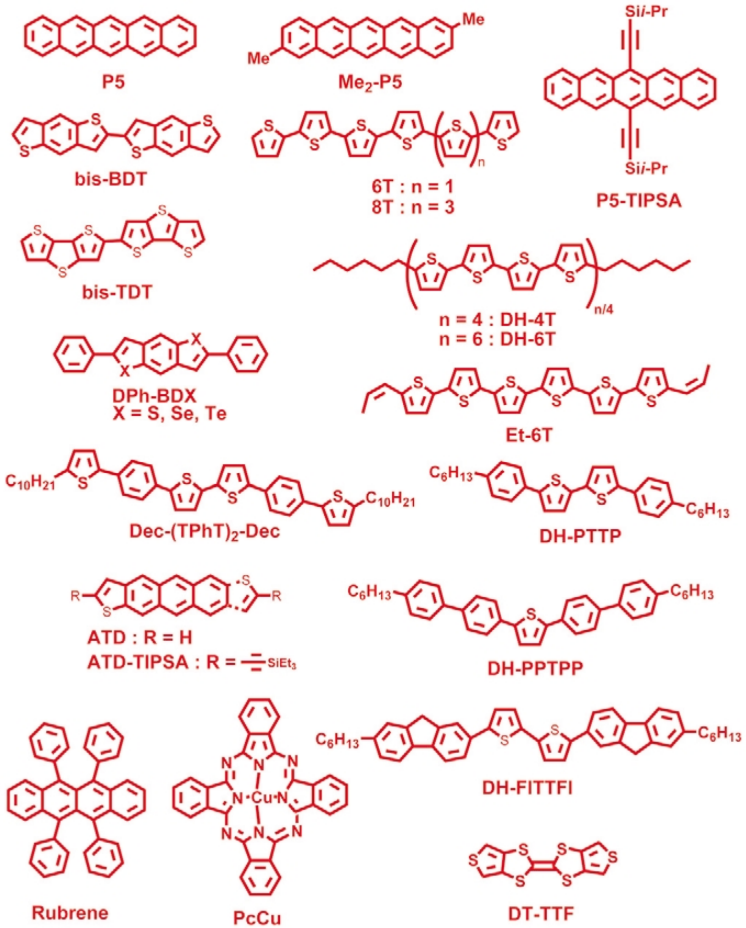
Welche Leitfähigkeit ?

Experimente: Eng, TU Dresden

Organic field effect transistors



p- and n-channel thin-film transistor operation



structures of molecular p-channel organic semiconductors

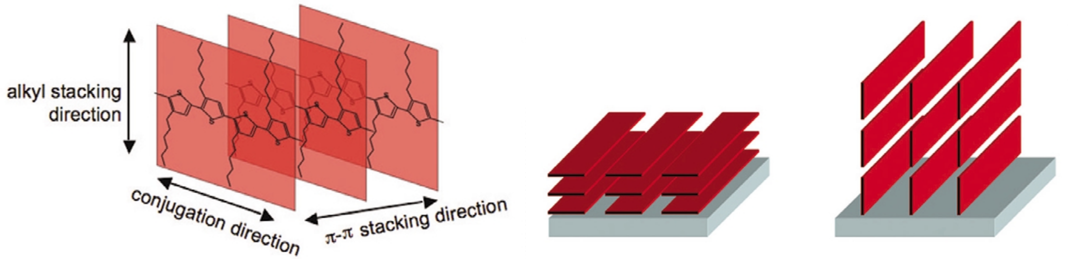
Semiconductor	(cm2/Vs)	Ion/Ioff
Rubrene (air, PMMA)	1.5-20	1.5-20
P5	1.5	10^8
P5 (PVP-CP)	2.9-3.0	10^5
P5 (Al_2O_3)	0.06-0.1	$\sim 10^6$
P5 (SiN_x)	0.2-0.4	$\sim 10^8$
P5 (Ta_2O_5)	0.24	10^4
P5 (Gd_2O_3)	0.1	10^3
P5 TiO2+PαMS	0.8	10^4
P5 (BZT or BST)	0.32-0.60	$\sim 10^5$
P5-precursor	0.01-0.2	$\sim 10^5$
P5-precursor	0.89	$\sim 10^7$
Me_4-P5	0.3	10^3-10^5
P5-TIPSA	0.17	$\sim 10^5$
6T	0.002	
8T	0.33	
DH-6T	0.05	10^3
DH-4T	0.06	10^6
Me_2-6T	0.02	
Et-6T	0.03-0.05	$> 10^5$
Bis-BDT	0.04	
Bis-TDT	0.05	$\sim 10^8$
DPh-BDX	0.01-2.0	$10^3 \rightarrow 10^7$
DH-PTTP	0.09	10^5
DH-PPTPP	0.02	10^4
Dec-(TPhT)$_2$-Dec	0.4	10^5
DH-FITTFI	0.1	10^4-10^5
ADT	0.1	
PcCu	0.02-0.1	$\sim 10^5$
DT-TTF	1.4	$\sim 10^5$
PcCuTa_2O_5	0.01	$\sim 10^4$
Bis-BDX	0.17-2.0	10^6-10^7

OFET performance of molecular p-channel semiconductors

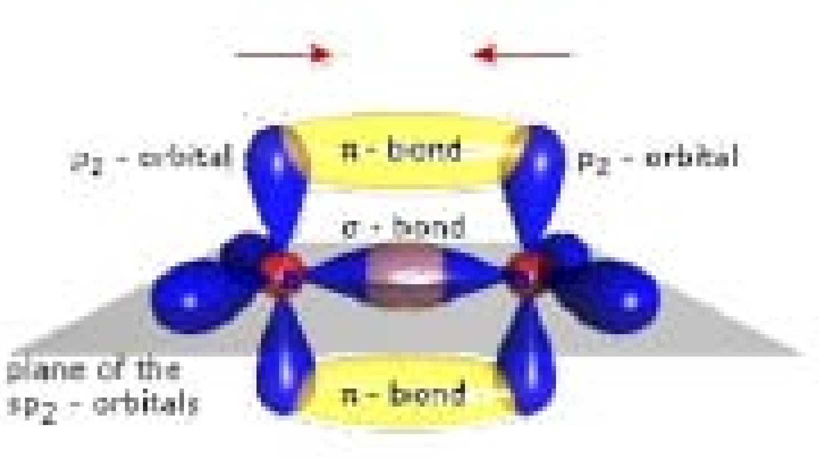
Antonio Facchetti, materialstoday 10,3 (2007) 28

Stacking

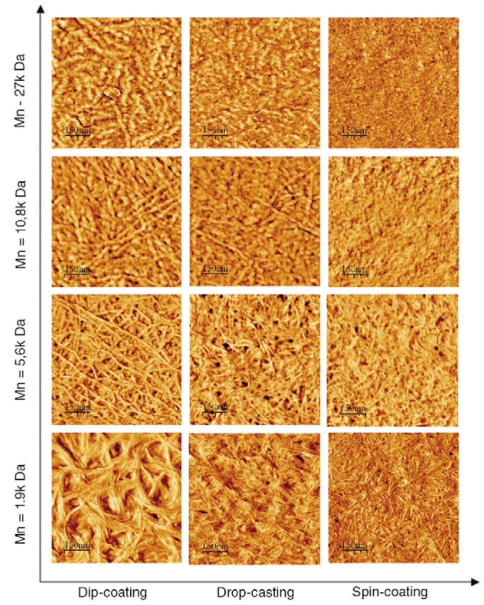
Alberto Salleo, materialstoday 10,3 (2007) 38



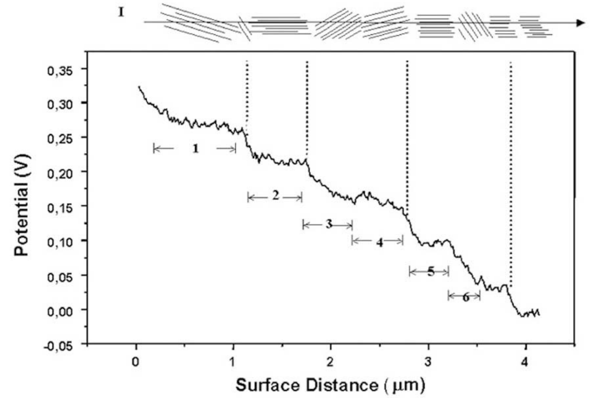
(a) Crystallite structure in polythiophenes. The conjugation direction and the p-p stacking direction are fast charge transport directions. (b) Plane-on (left panel) and edge-on (c) (right panel) texture of polymeric crystallites.



principle of delocalized π electrons



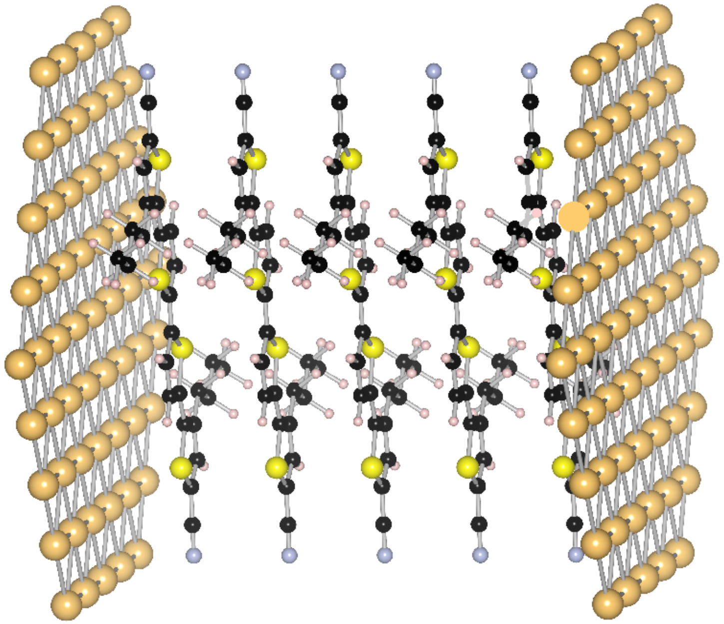
Tapping-mode AFM phase images obtained from P3HT fractions of different Mw and using different processing techniques

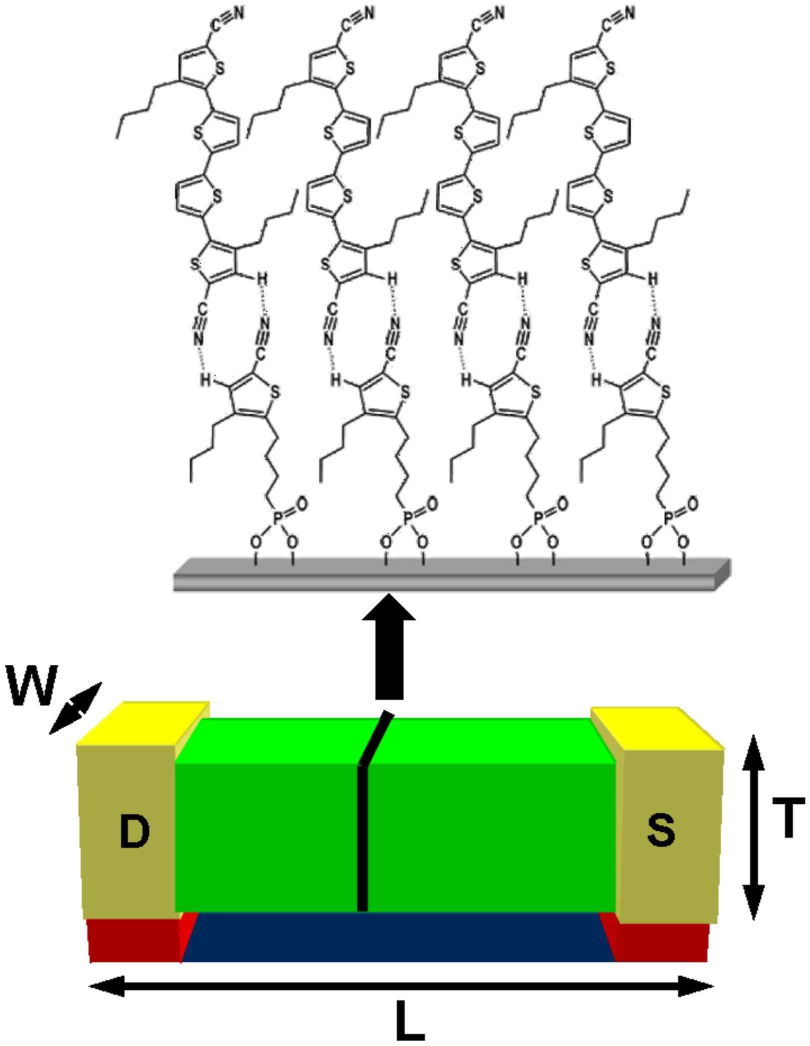


EFM measurement of the potential profile in a conducting polythiophene monolayer deposited between two electrodes

Transport in organic field effect transistors

Parallel stacking of thiophene molecules between 2 Au contacts



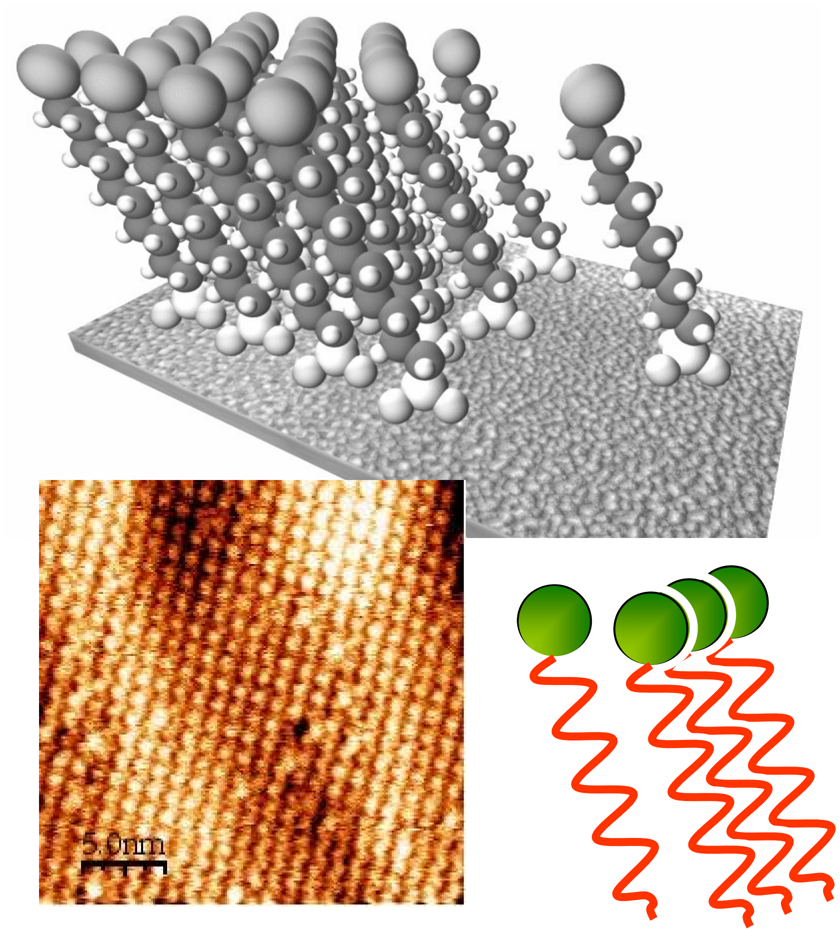


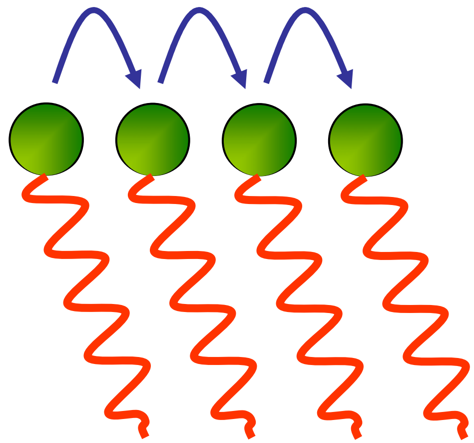
$W = 1000\mu$m, $T = 20$nm and $L = 10\mu$m

K. Haubner, et al., phys. stat. sol. (a), 2008 in press

Transportmechanismen

Selbstorganisierte QT-Schicht

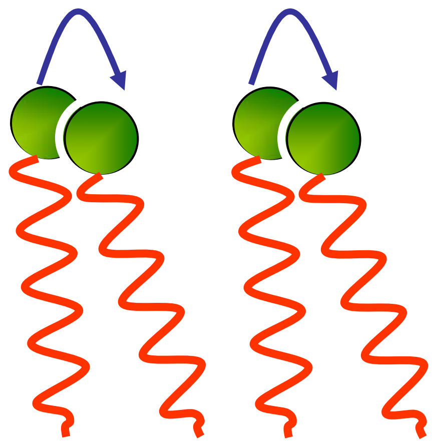




Hopping

klassisch
Master-Gleichung

semi-klassisch
Greens-Funktionen



Shuttling

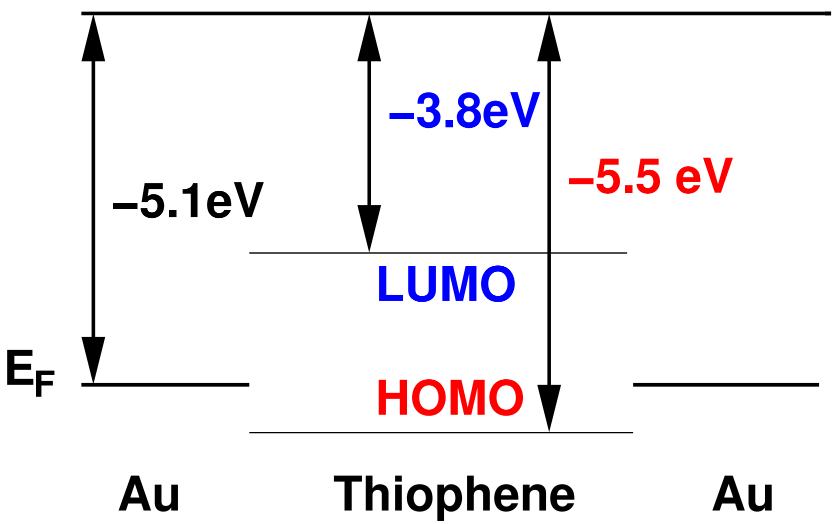
klassisch
elasto-mechanisch

Tight binding model for HOMO, LUMO transport

Hamiltonian

$$H = \sum_{i=-\infty}^{\infty} \left(|i\rangle v_i \langle i| + |i+1\rangle t_{i+1} \langle i| + |i-1\rangle t_i \langle i| \right)$$

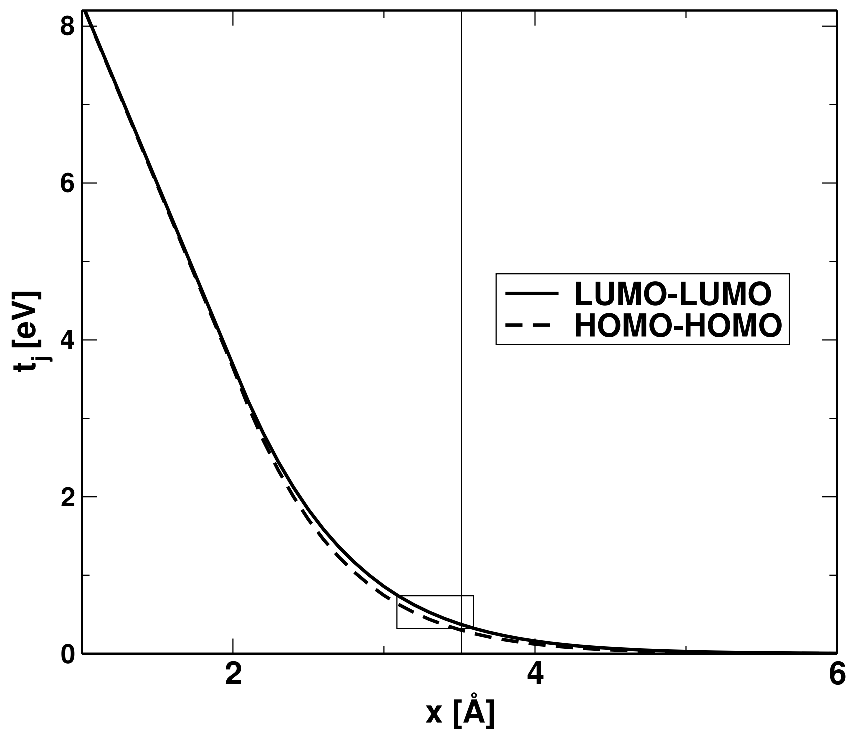
left leads: $j \leq 0$, right leads: $j \geq N+1$



fragment orbital approach with self-consistent charge density-functional based tight-binding (SCC-DFTB) method (Elstner1998,Porezag1995,Seifert1996)

$$T_{ij} = \left\langle \phi_i | \hat{H}_{KS} | \phi_j \right\rangle$$

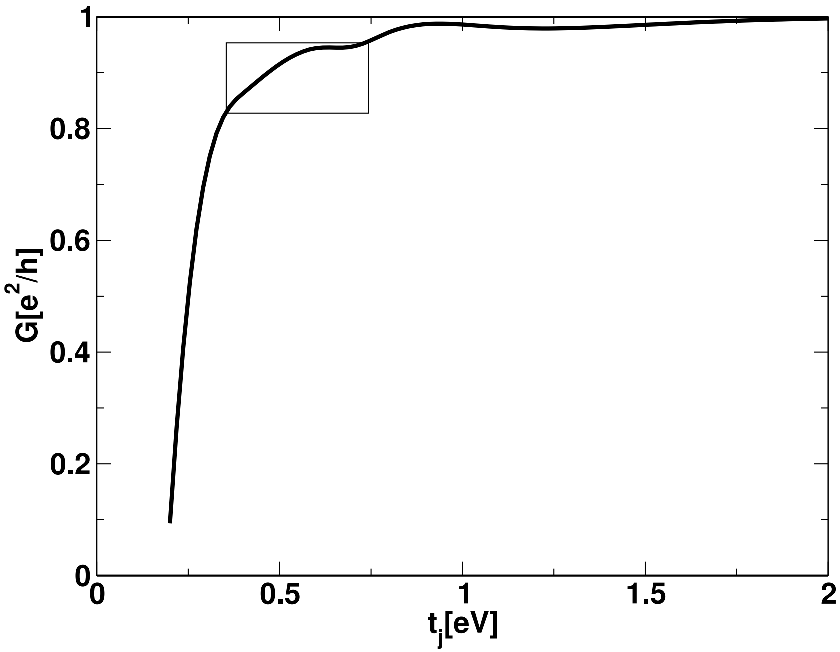
whith Kohn-Sham Hamiltonian H_{KS}



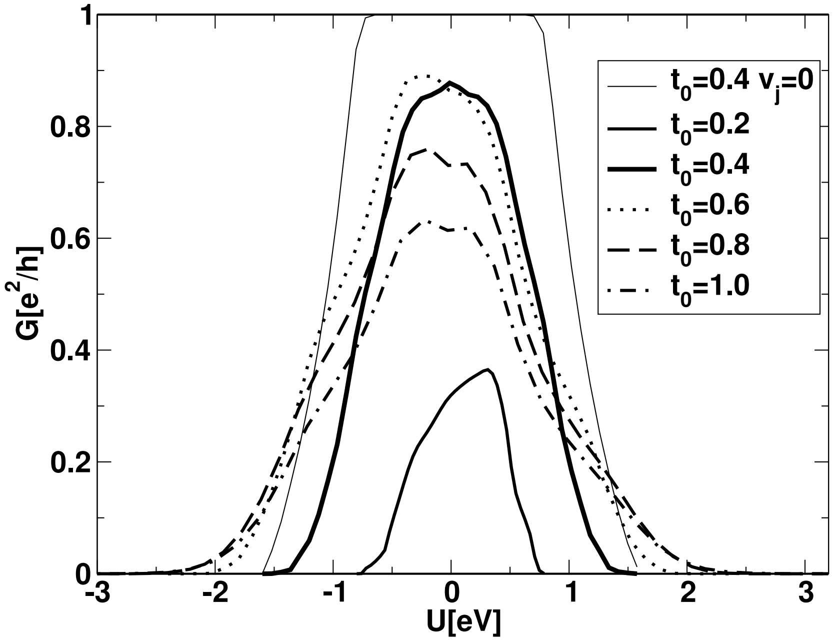
Currents with surface Green functions

Conductance

$$G = \frac{e^2}{U} \int \frac{dz}{2\pi\hbar} T_{N+1,0} (f_r - f_l)$$



20 Thiophene molecules

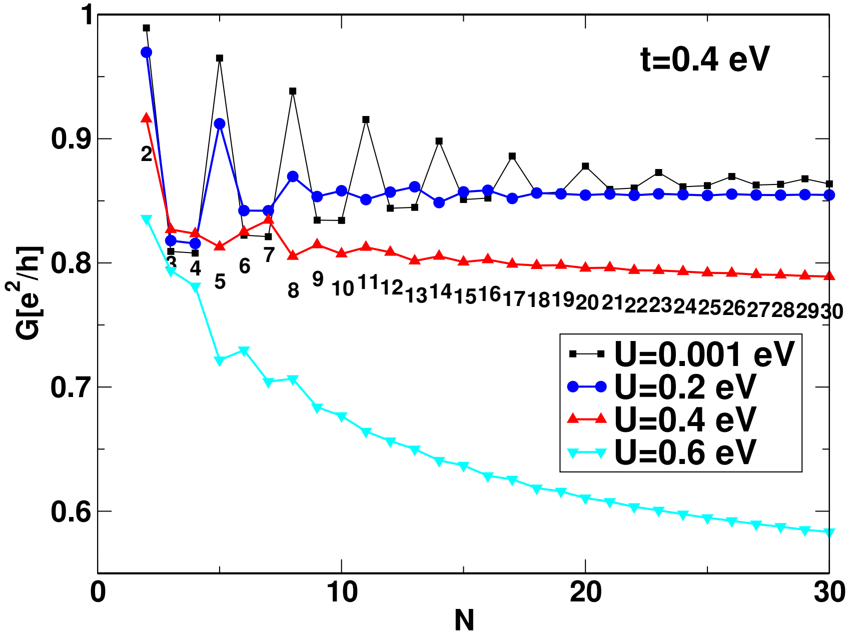


versus applied voltage bias for different hopping parameters from lead to thiophene, $v_0 = 0$, $v_j = -0.4$, reference curve $v_j = 0$

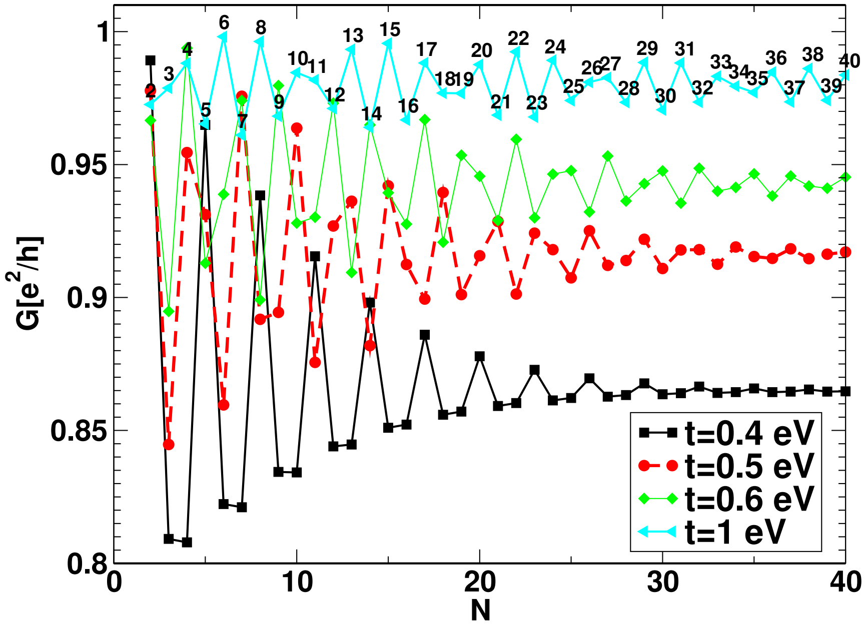
Current oscillation

Conductance

$$G = \frac{e^2}{U}\int \frac{dz}{2\pi\hbar} T_{N+1,0}(f_r - f_l)$$



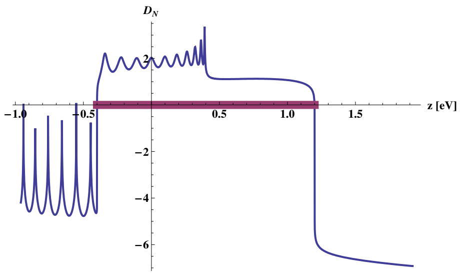
conductance versus number of thiophene molecules between Au contacts for different voltages



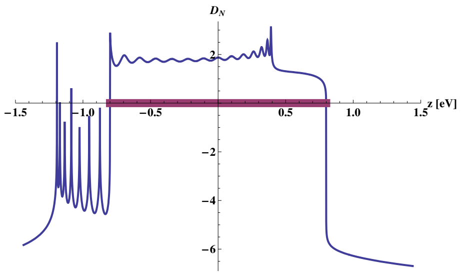
number of molecules between Au leads in linear response regime

Lead design, e.g by barrier

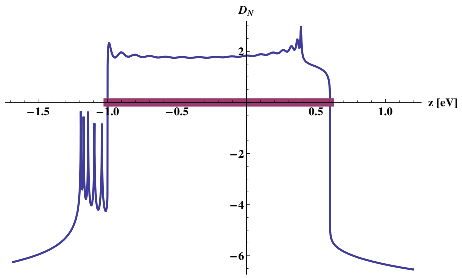
Density of states



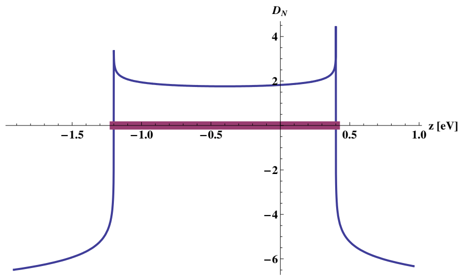
$v_0 = 0.4eV$



$v_0 = 0eV$

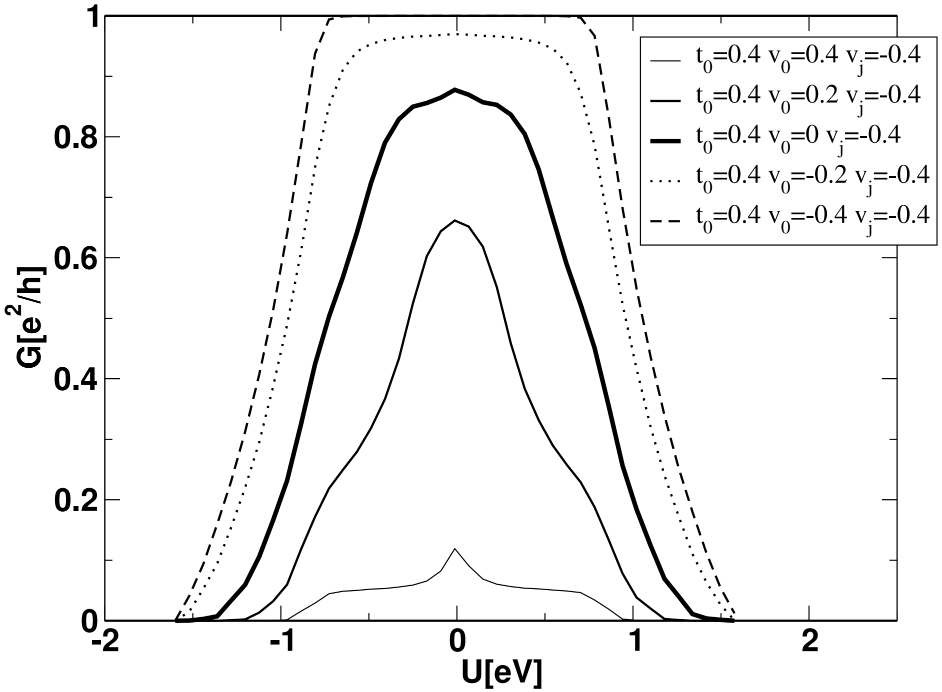


$v_0 = -0.2eV$

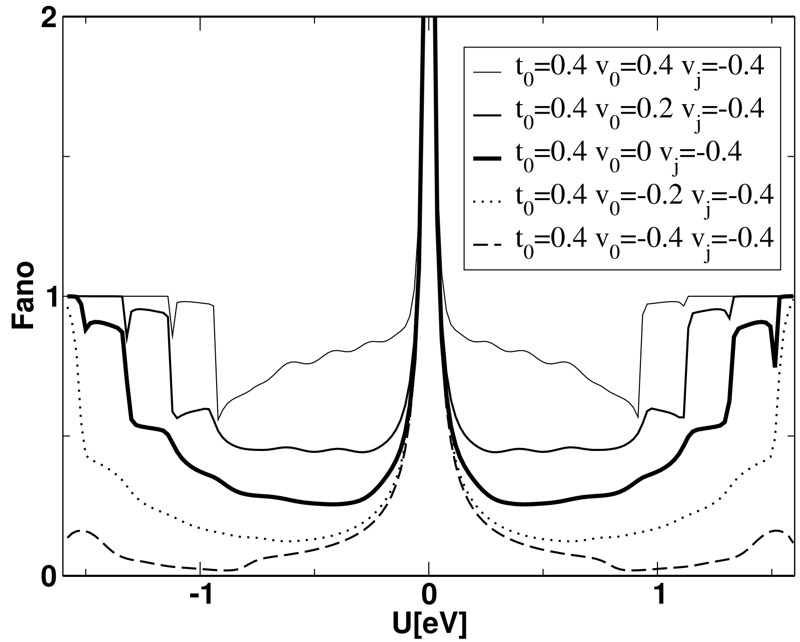


$v_0 = -0.4eV$

Conductance



Fano factor $\frac{\overline{\Delta J \Delta J}}{eJ}$



Thermoelectric properties

Temperature difference at right: $T_r = T + \Delta T/2$ and left lead: $T_r = T - \Delta T/2$

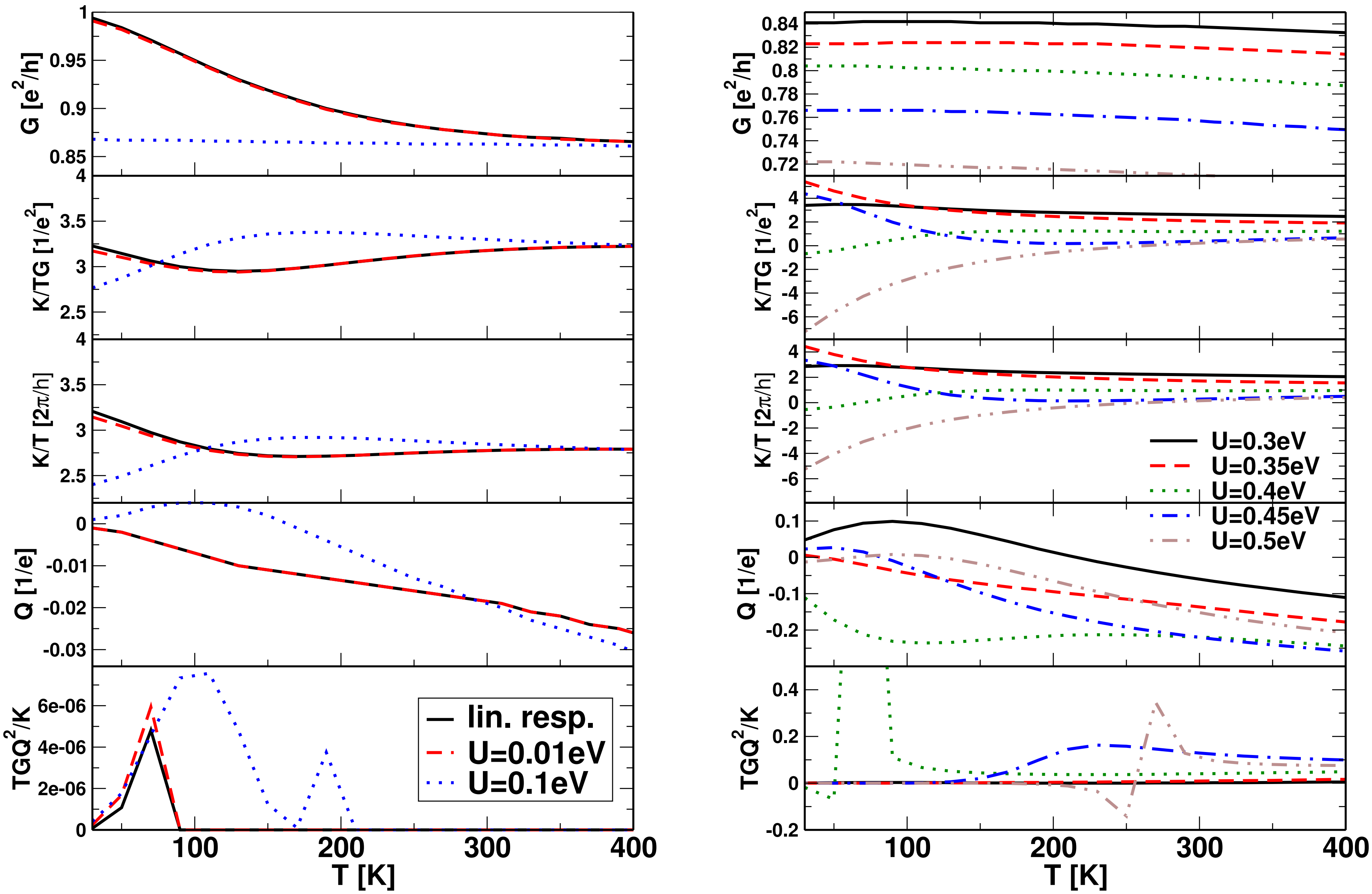
$$
\begin{aligned}
\text{particle current} \quad J &= L^{11}V + L^{12}\Delta T \\
\text{heat current} \quad J_q &= L^{21}V + L^{22}\Delta T
\end{aligned}
$$

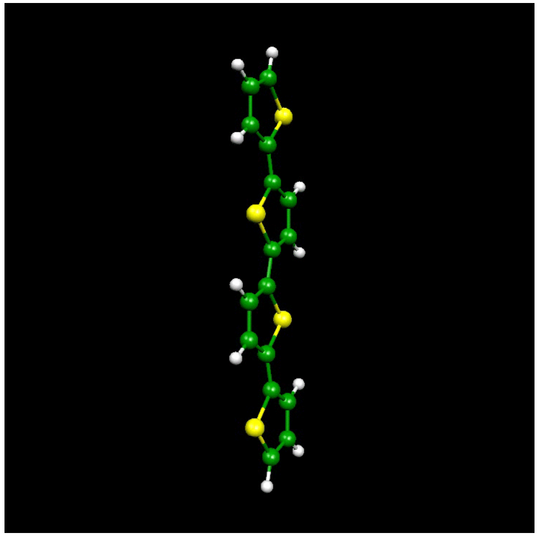
- conductance, $J = GV$: $G = L^{11}$
- thermoelectric power, $V = -Q\Delta T$ with $J = 0$: $Q = \frac{L^{12}}{L^{11}}$
- thermoelectric conductance, $J_q = K\Delta T$ with $J = 0$: $K = L^{22} - \frac{L^{21}L^{12}}{L^{11}}$
- figure of merit or ZT factor: $ZT = \frac{TQ^2G}{K} = \frac{T(L^{12})^2}{L^{11}L^{22} - L^{21}L^{12}}$

Conductance, heat conductance, thermopower, figure of merit

near the linear response

beyond linear response





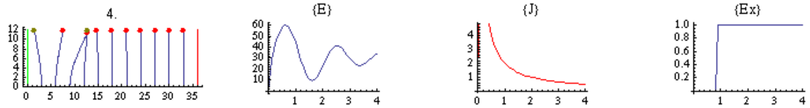
Diode effect in shuttling transport

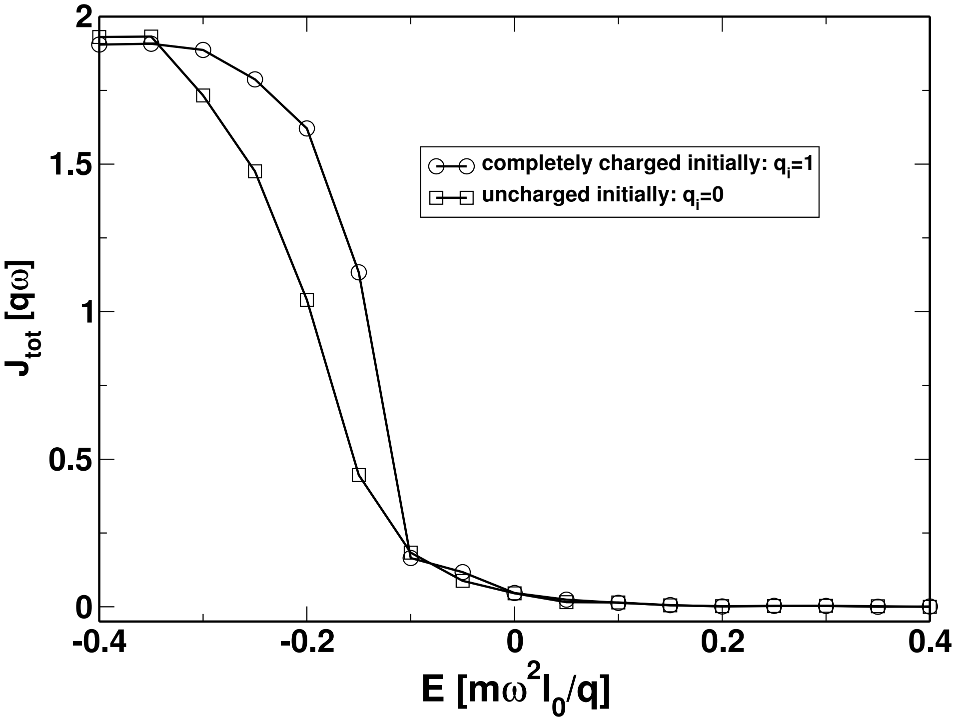
Parameter from DFT calculations:

k=1 N/m, m=5.49x10^{-22}g, ω=1.35/ps, l_0=0.1nm

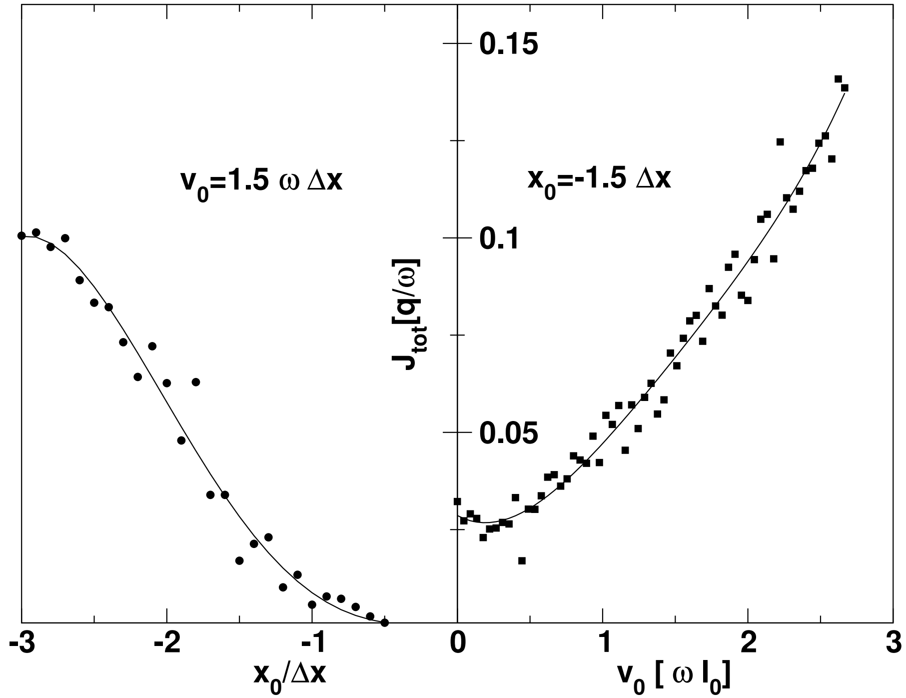
[E]=$m\omega^2 l_0/q$=6.2x10^8V/m, [J]=$q\omega$=21.6mA

initially charged





total current versus applied electric field



vs initial displacement (left), initial velocity (right)

Methoden – Kopplung von Längen-/Zeitskalen

‘Scale-Hopping‘ | **‘Scale-Bridging‘**

L / m

10^{-9}

10^{-6}

10^{-3}

10^{0}

Parameter-Transfer

First-principles Theorie
Quantenmechanik mit Elektronen

(Semi-)Empirische Theorie
Molekulardynamik (MD) mit Atomen

QM/MM
QM/QM‘
TUD

Ising/Heisenberg
Monte-Carlo (MC) mit Molekülen/Spins

Kontinuumstheorie
BCF-Phasenfeld mit Konzentrationen

PP/MC
RWTH

Zusammenfassung für Transport durch Hüpfen

- Transport der Elektronen durch organische Moleküle kann bequem durch Hüpfen von Molekül zu Molekül beschrieben werden
- Thermoelektrische Eigenschaften lassen sich durch die Geometrie, die Energiebarrieren der Kontakte, durch die Hüpfwahrscheinlichkeit sowie die Temperatur einstellen

Dank an die Zusammenarbeit (2 gegenwärtige Veröffentlichungen):

• New J. Phys. **10** (2008) 103014-1-8: *Current without bias and diode effect in shuttling transport of nanoshafts*, K. Morawetz ,S. Gemming, R. Luschtinetz, L. M. Eng, G. Seifert, A. Kenfack

• Phys. Rev. B **79**,4 (2009) in print : *Transport and noise in organic field effect devices*, K. Morawetz, S. Gemming, R. Luschtinetz, T. Kunze, P. Lipavský, L. M. Eng, G. Seifert, P. Milde