Molecular and carbon-based electronic systems

Lecture 5

Molecular junctions basics
• single molecule electronics

• atomic contacts and conductance quantization

• contacting individual molecules: mechanically controllable break junctions
  – formation mechanisms: fluctuations, conductance plateaus
  – understanding transport through junctions: Landauer approach
  – conjugated compounds

• examples of spectroscopy in molecular junctions
  – current-voltage characteristics
  – conducting AFM

• outlook
Building blocks (transistors) at nm scale

(Volume reduced by $10^{12}$)

Bardeen, Brattain, Shockley
Molecular and carbon-based electronic systems

- IC
- LSI
- VLSI
- ULSI

Minimum size of element (transistor)

- 1 mm
- 100 μm
- 10 μm
- 1 μm
- 100 nm
- 10 nm
- 1 nm
- 100 pm

Year

- 1950
- 1960
- 1970
- 1980
- 1990
- 2000
- 2010
- 2020
- 2030
- 2040
- 2050

Chemistry

Supramolecular chemistry

Supramolecules

Hair

Virus

Cell

Spider

Molecule

Atom
1940s  Robert S. Mulliken: concept of donor-acceptor charge transfer complexes

                       D part                   σ part                 A part
                       S          S          N C C N
                       S          S          N C C N

Albert Szent-Gyorgi:  proteins "might not be insulators"

historical perspective  < 1980

       "It seemed therefore reasonable to suppose that a DNA molecule might behave as a 1D aromatic crystal and show a p-electron conductivity down the axis."
       "...if it should prove possible to measure a single fiber..."

       1st reproducible transport meas. through organic layers

       A. Aviram, M. A. Ratner: molecular rectifier (theory)
       Chemical Physics Letters 29 (2), Nov.1974
       from molecular conduction to molecular electronics

nb citations of Aviram, Ratner paper
1985's – 2000's

The Nobel Prize in Chemistry 1987
"for their development and use of molecules with structure-specific interactions of high selectivity"

Donald J. Cram
Jean-Marie Lehn
Charles J. Pedersen

The Nobel Prize in Chemistry 1992
"for for his contributions to the theory of electron transfer reactions in chemical systems"

Rudolph A. Marcus

The Nobel Prize in Chemistry 1996
"for the discovery of fullerenes"

Robert F. Curl Jr.
Sir Harold W. Kroto
Richard E. Smalley

The Nobel Prize in Chemistry 2000
"for the discovery and development of conductive polymers"

Alan G. MacDiarmid
Professor at the University of Pennsylvania, Philadelphia, USA.

Hideki Shirakawa
Professor Emeritus, University of Tsukuba, Japan.

Alan J. Heeger
Professor at the University of California at Santa Barbara, USA.
conducting polymers

polyacetylene
conducting polymers

linear chain of atoms
(free electron model)

\[ \Delta E = E_{LUMO} - E_{HOMO} = \frac{(N + 1)\hbar^2}{8mN\alpha^2} \approx \frac{\hbar^2}{8m\alpha^2N} \]

- pure polyacetylene: insulating
- doped polyacetylene: conducting... why?

- Peierls: 1 d atomic chain unstable
  \(\Rightarrow\) chain deformation, gap opening

- dopant: mid-gap states, hole transport

\(\Rightarrow\) vanishing gap for \(N\) large

increasing dopant
conducting polymers

Nobel 2000 (chimie)

Alan G. MacDiarmid
Professor at the University of Pennsylvania, Philadelphia, USA.

Hideki Shirakawa
Professor Emeritus, University of Tsukuba, Japan.

Alan J. Heeger
Professor at the University of California at Santa Barbara, USA.
Nobel prize 2000

(...) In the future we will be able to produce transistors and other electronic components consisting of individual molecules - which will dramatically increase the speed and reduce the size of our computers. A computer corresponding to what we now carry around in our bags would suddenly fit inside a watch ...
Organic nanowire transistors
Mat. Today (2008)

molecular crystals
($\pi$-stacking)

Low-cost organic electronics on plastic

TV display, 40” OLED
(EPSON, 2004)

Organic ICs based on self-assembly (SAMFETs)
de Boer et al., Nature (2008)

Large scale integr. of molecular junctions
at the level of a few or even a single molecule?

resistor
wire

diode, memory device, ...

questions:
- contact
- stability
- (self-) assembly,
- scalability, …

reviews, e.g.: Liljeroth (2010), de Boer et al., (2008); Ratner et al; (2008); Cahen et al., (2008)
molecules: pros & cons

+ 
- 

• molecules are small: typ. 1-100 nm
• molecules have extended pi systems
  provides thermodynamically favorable electron conduit: molecules as "wires"
• molecules have discrete energy levels
  better confinement of the charges as in Si devices
• molecules can be designed/tailored
  by choice of composition and geometry, the transport, optical and geometrical properties can be adjusted
• molecules are identical
  chemists synthesize 1 mmol of (identical) molecule at a time, not one device
• molecules can be active (have a function)
  stereochemistry (distinct stable geometric structures – isomers), mechanical flexibility (rotation axis),
  photochemistry (photochromism), electrochemistry (redox reactions)
  (self-)assembly (building of structures) and molecular recognition (switching, sensing)
• reliable connection to the micro/macro-scopic world (contacts)
  and characterisation of a single molecule ?
• limited thermal and electrical stability
• what about the reproducibility of molecular devices ?
• how to fabricate/integrate many devices (upscaling) ?

see e.g.: Nitzan, Ratner, Science 2003; Heath, Ratner, Phys. Today, 2003
nanometer and molecular-scale junctions

"playground " for

**fundamental aspects**

- electro-mechanical properties (e.g.: atomic, molecular switch)
- transport at μs, ns, ps, ...
- e-e and e-ph interactions
- heat flow (atomic & molecular level)
- spin dependent transport & selectivity
- exciton generation, separation
- interaction with EM field (plasmonics)
- coherence aspects

only indirect evidence to date

**device aspects**

- control of molecule-electrode interface
- reliable 2-terminal switches (V-driven)
  conformational change, interference
- few molecules devices and monolayers, pores & crossbars (Sony, HP, NIST, IBM)
- carbon-based electronics
- upscaling, programmability

NB: variability, tunneling, power dissipation, cost, are current issues in CMOS tech.
molecular junction

- structural disorder
- interactions
- fluctuations

electrodes and junction geometry
anchoring, self-assembly, polymerization
mobility of (surface) atoms, molecular distortions, multiple local energy minima

typ. energies
- Au-Au, Au-S bond 0.7-1.5eV Kawai et al., APL 2008, Tao et al., JACS 2009, JL arrays
- surface Au-Au ~ 0.3eV
- benzene-benzene ~ 0.1eV Jorgensen et al., JACS, 1990
molecular junction

- structural disorder
- interactions
- fluctuations

electrodes and junction geometry
anchoring, self-assembly, polymerization
mobility of (surface) atoms, molecular distortions, multiple local energy minima

junction formation (and breaking up): dynamic process, variability
  - time scale(s)
  - local environment effect
  - local geometry and structure effect
contacting a molecule

~ 2 nm
contacting a molecule: exp. techniques

forming atomic contacts
break junctions: forming atomic contacts

break junction: a draw bridge at the atomic scale
break junctions

elongation: \( d = \frac{6thz}{L^2} \)

reduction factor: \( r = \frac{\Delta d}{\Delta z} \approx (1.6 - 4) \cdot 10^{-5} \)

\( \Rightarrow \Delta Z = 10\mu m \Leftrightarrow \Delta d \sim 3 \text{ Å} \)

vertical speed: \( v_z = 30\mu m/s \)

\( \Rightarrow 0.5 - 1.2 \text{ nm/s} \)

electrodes separation speed

atomic-scale metallic contacts with well controlled sub-nm gap

closed ⇒ open: contact to tunneling

Conductance quantization

histogram
conductance quantization

Fermi wavelength (Au)

\[ \lambda_F \approx 5.2 \text{Å} \]

GaAs: 200nm

Energy modes splitting

\[ \frac{\pi^2 \hbar^2}{2m\lambda_F^2} \approx 1.4 \text{eV} \]

GaAs: \( \approx 1 \text{meV} \)

\[ G = \frac{2e^2}{h} \sum_n T_n \]

\[ I = GV = \frac{2e^2V}{h} \sum_n T_n \]

\[ G_0 = \frac{2e^2}{h} \quad G_0 \approx (12.9k\Omega)^{-1} \]

\[ \ell > L \text{ ballistic regime} \]

\[ \text{conductance of a quantum coherent structure accommodating } N \text{ channels} \]

\( T_n: \text{transmission probability through channel } n \)

Conductance quantization for Au contact

\[ n = 1 \text{ with } T = 1 \Rightarrow G = \frac{2e^2}{h} \sum_n T_n = G_0 = \frac{2e^2}{h} = 77.5 \, \mu S \]
conductance quantization: 2DEG systems

\[ G(E_F) = \frac{2e^2}{h} \sum_n T_n(E_F) \approx \frac{2e^2}{h} N(E_F) \quad (T = 0K) \]
break junctions in liquid environment
"high" conductance regime

\[ G \geq G_0 = \frac{2e^2}{h} = (12.9 \ k\Omega)^{-1} \]

no significant differences between environments
**opening**: conductance vs elongation

**break junction opening**  
(solvent: THF/mesitylene 1:4 v/v)

- conductance quantization, plateaus
  \[ G_0 = \frac{2e^2}{h} = 77.5 \mu S \]
  cf e.g. Agrait et al., Phys. Rep. 2003

- last Au G-plateau (~1G₀)
- breaking of Au bridge
- tunneling regime
  \[ G \propto e^{-\beta d} \]

- statistics: histogram tunneling background ⇔ const.
tunneling regime

gap open, close the junction

Junction 83a

\[ V = 0.1 \text{ V} \]

\[ I (\text{A}) \]

\[ z (\text{mm}) \]

\[ 0 \quad 10 \quad 20 \quad 30 \quad 40 \]

\[ \begin{array}{c}
\text{vacuum} \\
\circ \text{toluene} \\
\triangle \text{DMSO} \\
\text{air} \\
\square \text{DCM} \\
\text{octane}
\end{array} \]

opening-closing trace

liquid \sim\text{ effective medium in first approx.}

typ. 2-8 Å
tunneling regime

gap open, close the junction

\[ I \propto \exp \left( -\frac{2d}{\hbar} \sqrt{2m\phi} \right) \]

d = r \cdot z \quad r = \text{reduction factor}

\[ B = 2r \sqrt{2m\phi / \hbar} \]

\[ I \propto e^{-Bz} \]

\( \phi = U_0 - E_F \)

- in vacuum: metal workfunction
- in solvent: apparent barrier height
tunneling regime: attenuation factor

purely elastic: \( r = 6 \frac{t h}{L^2} \sim 5 \times 10^{-6} \)

“hinge” model: \( r \approx 4 \frac{d}{L} \sim 6 \times 10^{-4} \)

In vacuum
\( \phi_{\text{vac}} = 3.5 - 5 \ \text{eV} \Rightarrow r \sim 5 \times 10^{-5} \)

\[
B = 2r \sqrt{2m\phi / \hbar} \quad I \propto e^{-Bz}
\]

NB: plastic deformation of the substrate can affect \( r \)
contacting simple molecules
dynamical behavior & fluctuations: solvent

pure solvent (mesitylene)

full measurement

30 s intervals

J. Brunner et al., to appear in JPCM, 2014
dynamical behavior & fluctuations: solvent + alkanedithiols

solvent

octanediethiol solution

J. Brunner et al., to appear in JPCM, 2014
dynamical behavior & fluctuations: solvent + alkanedithiols

solvent

octanedithiol solution

relative conductance fluctuation amplitude

\[ \delta G_{\text{rel}} = \frac{\delta G}{\langle G \rangle} \]
formation of a molecular junction: opening traces
signature of a molecular junction

example: alkanedithiols

large HOMO-LUMO gap (few eV), ~ no solvent effect

molecular signature: plateau (at $G \ll G_0$)

only solvent: Mesitylene
with molecules: 0.1 M octanedithiol in Mesitylene
signature of a molecular junction

**model system:**
alkanedithiols

large HOMO-LUMO gap (few eV), ~no solvent effect

molecular signature:
plateau (at $G \ll G_0$)
$\Rightarrow$ peak in $(\log G)$ histogram

- plateau in 20-60% curves
- conductance window $> 6$ orders of mag.

statistical analysis

interpretation of the different values
- anchoring geometry
- conformational states
- multiple bridges

values at 1.2, 4.5 and 25 $10^{-5} G_0$

dynamical behavior & fluctuations: solvent + alkanedithiols

filled histograms from opening conductance curves $G(z)$

outlined histograms from main panel data

relative conductance fluctuation amplitude

$\delta G / \langle G \rangle$

$N_G$

10

10

large-amplitude fluctuations only appear in the presence of Au-binding molecules

dominant peak in 1D histo signature of few molecules junction

J. Brunner et al.