UNI BASEL

Empa
Materials Science and Technology

Molecular and carbon-based electronic systems

Lecture 4

Molecular junctions: formation mechanisms, transport basics

Vorlesung Uni Basel, HS2018
28.03.2018

Topics for workshop

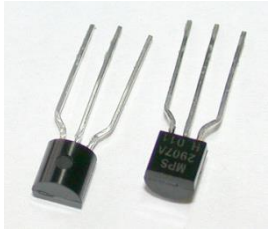
- **Select topic till** **31. March 2018** (send to oliver.braun@unibas.ch)
- Hand in presentation 9. May 2018 (send to oliver.braun@unibas.ch)
- Day of Presentation 30. May 2018

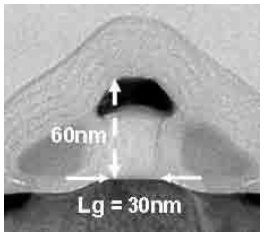
- **Hall effect in graphene**
- **Graphene properties studied by inelastic light scattering**
- **Graphene for molecular electronics**
- **Thermoelectric effects in Graphene based devices**
- **Graphene Nanoribbons**
- **Exotic transport regimes: Electron hydrodynamics**
- **Mass Sensing with Carbon Nanotubes**
- **Spin transport in Carbon-based devices**
- **NV centers in diamond**
- **Diamond Photonics**
- **Silicon nanowires for chemical /biosensing**
- **Single molecule electronic devices**
- **Nanoparticles arrays for junctions networks**
- **Density Fuctional Theory**
- **Single molecule deposition**
- **Organic solar cells, OLEDs**
- **New computing achitectures**

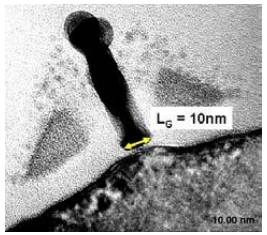
- single molecule electronics
- atomic contacts and conductance quantization
- contacting individual molecules : mechanically controllable break junctions
  - formation mechanisms: fluctuations, conductance plateaus
  - understanding transport through junctions: Landauer approach
  - conjugated compounds
- examples of spectroscopy in molecular junctions
  - current-voltage characteristics
  - force spectroscopy using conducting AFM
- outlook

context

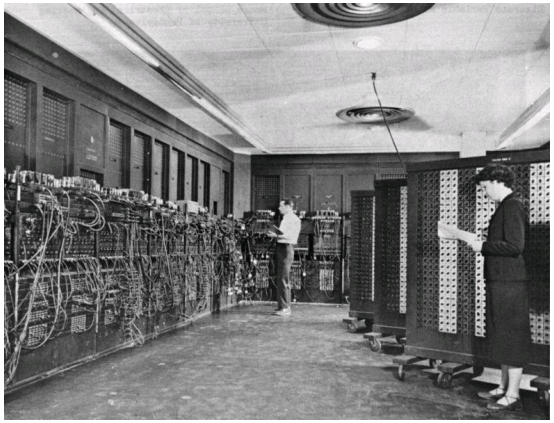
Bardeen, Brattain, Shockley







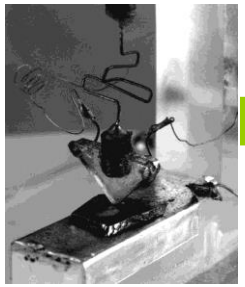
1947 … today



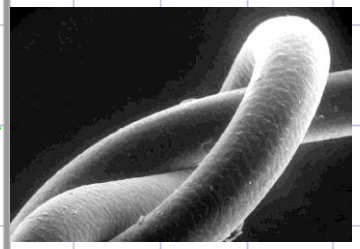
⇨***Building blocks (transistors) at nm scale***

(Volume reduced by 10^{12})

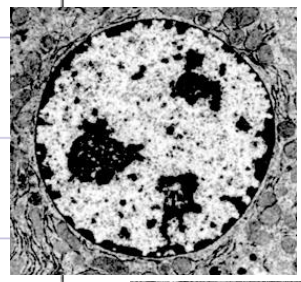
Molecular and carbon-based electronic systems



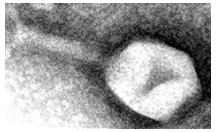
spider



hair



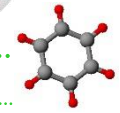
cell



virus

proteins

supramolecules



molecule

atom

minimum feature size

linear size of element (transistor)

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

IC
LSI
VLSI
ULSI

su r chemistry

chemistry

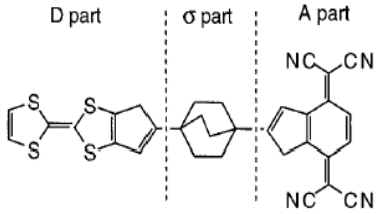
single (few) molecules electronics

1950 1960 1970 1980 1990 2000 2010 2020 2030 2040 2050

year

1940s Robert S. Mulliken:

concept of donor-acceptor charge transfer complexes



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

historical perspective < 1980

1960s Eley and Spivey *(Trans. Faraday Soc., 1962)*

"*It seemed therefore reasonable to suppose that a DNA molecule might behave as a 1D aromati*

"*...if it should pr*

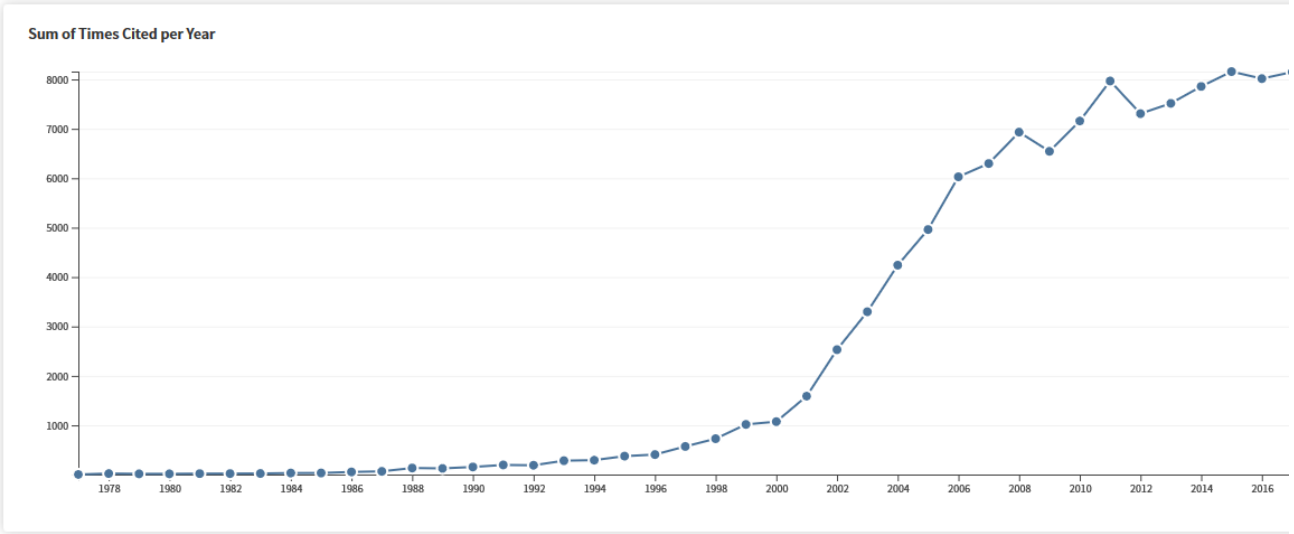
1970s B. Mann and H.

1st reproducible

A. Aviram, M. A

Chemical Physi

from molecular

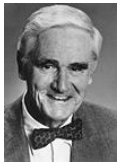


nb citations of Aviram, Ratner paper (WoS)

molecules …?

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 1996

"for the discovery of fullerenes"

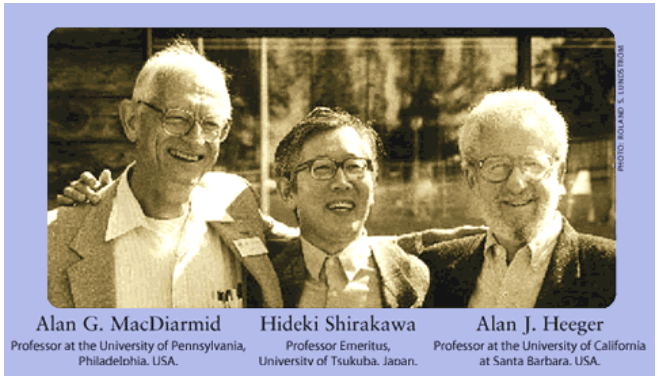
Robert F. Curl Jr.

Sir Harold W. Kroto

Richard E. Smalley

The Nobel Prize in Chemistry 2000

"for the discovery and development of **conductive polymers**"

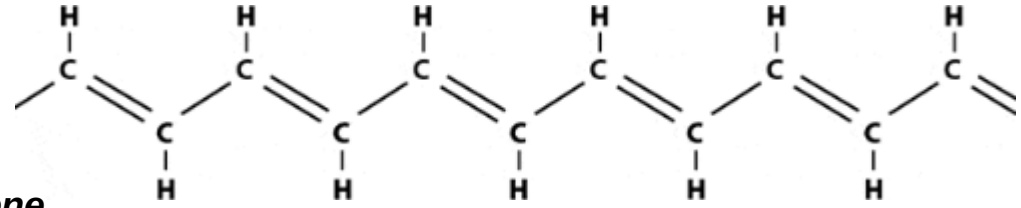


The Nobel Prize in Chemistry 1992

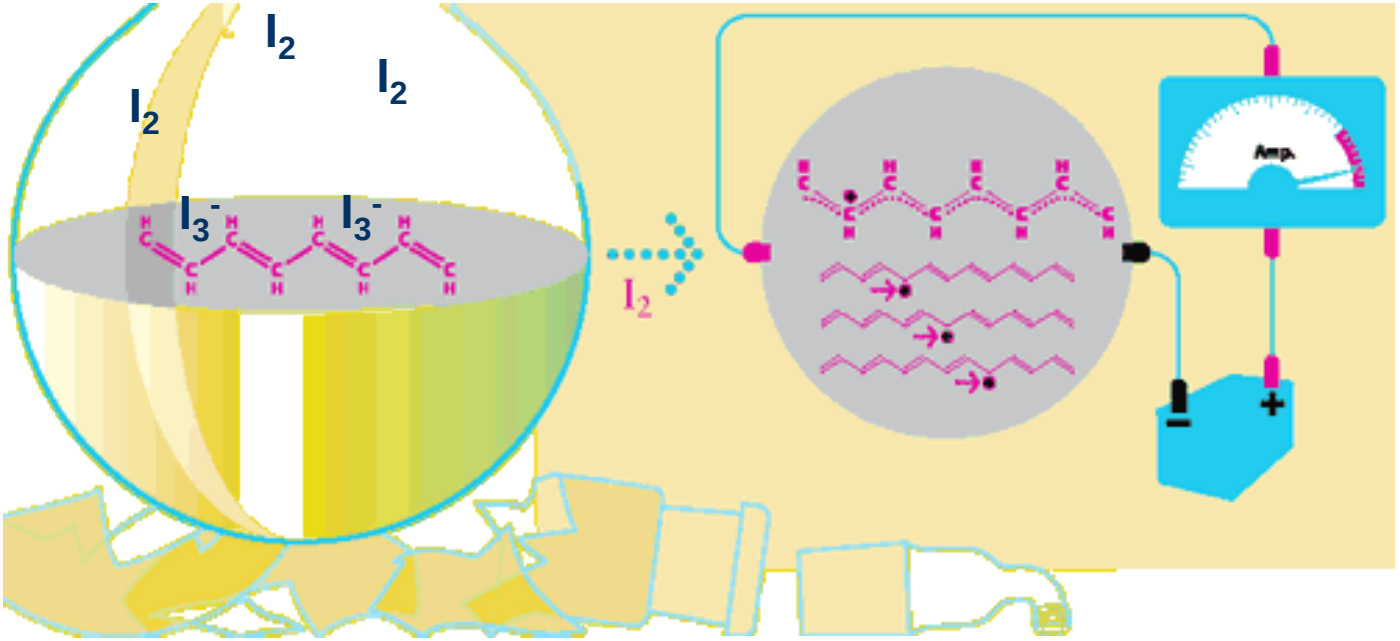
"for for his contributions to the theory of electron transfer reactions in chemical systems "

Rudolph A. Marcus

conducting polymers

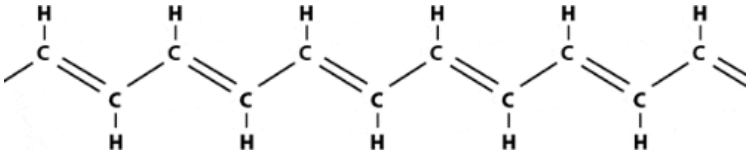


polyacetylene

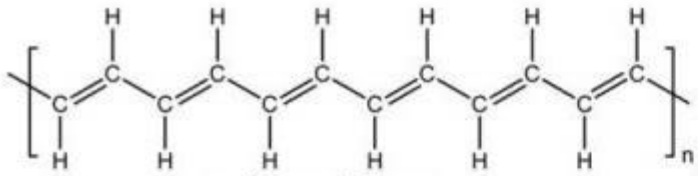


conducting polymers

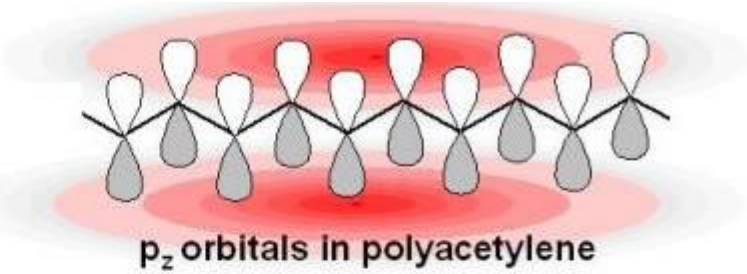
linear chain of atoms
(free electron model)



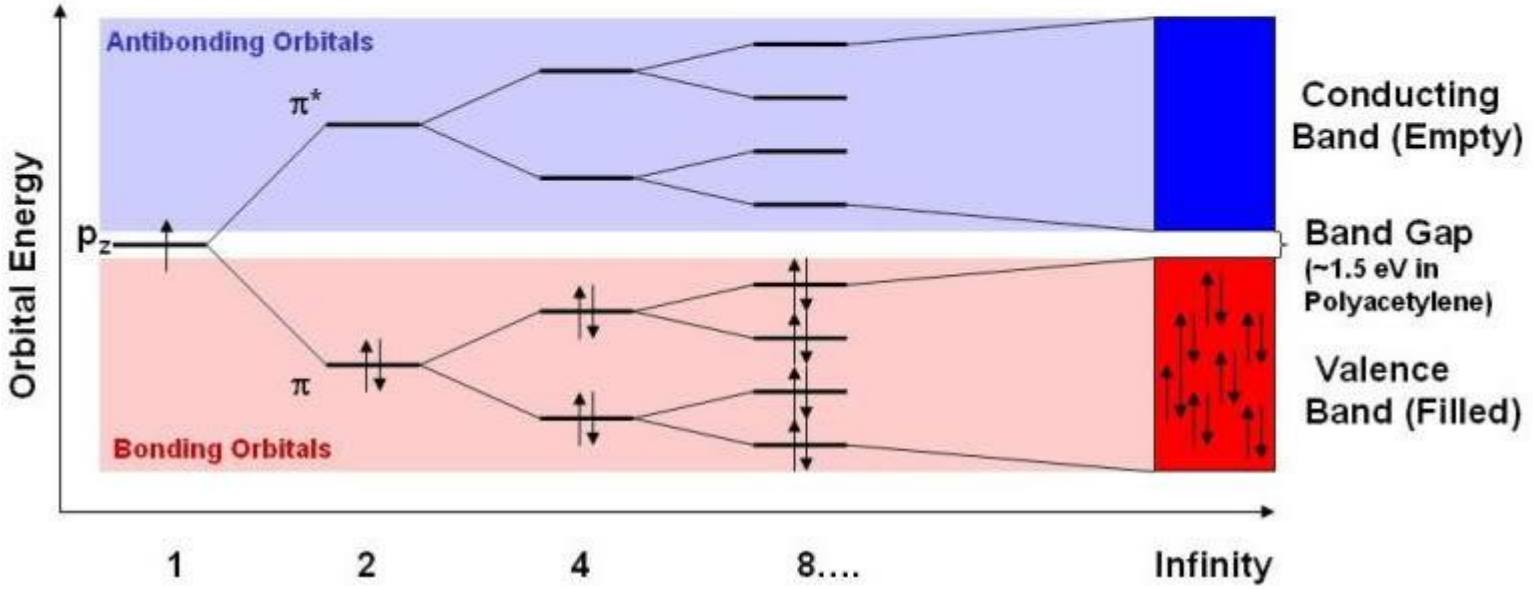
conducting polymers



polyacetylene –
an approximately linear structure



p_z orbitals in polyacetylene

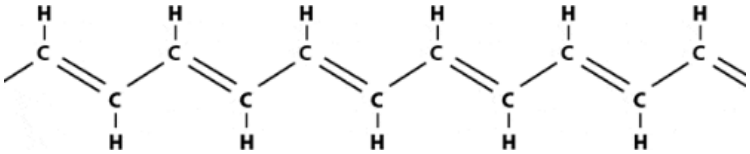


conducting polymers

linear chain of atoms
(free electron model)

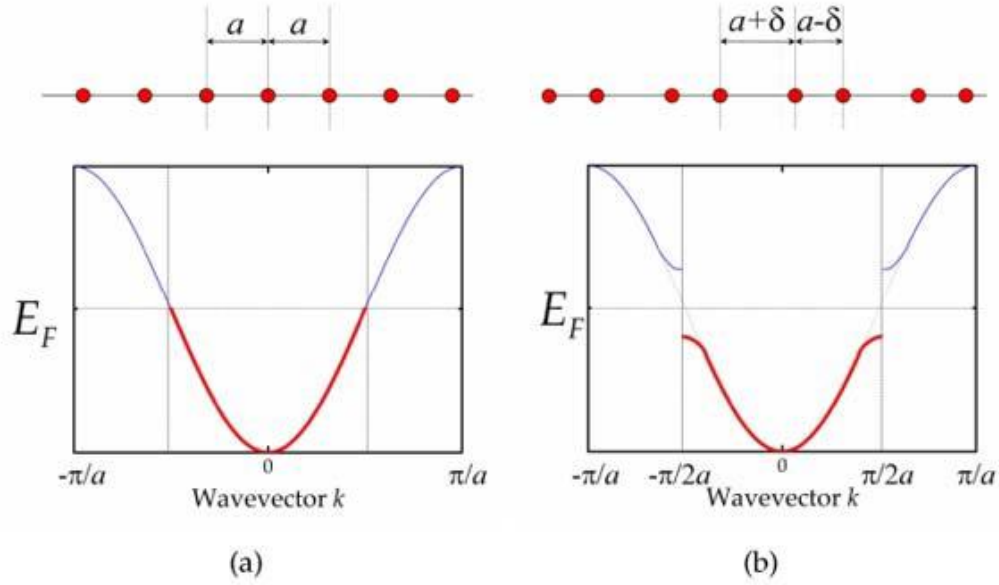
$$\Delta E = E_{LUMO} - E_{HOMO} = \frac{(N+1)h^2}{8mNa^2} \approx \frac{h^2}{8ma^2}\frac{1}{N}$$

⇨ ***vanishing gap for N large***



-pure polyacetyle: insulating (notes: gap)

- Peierls: 1 d atomic chain unstable
⇨ chain deformation, gap opening



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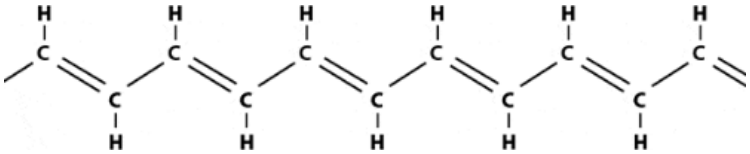
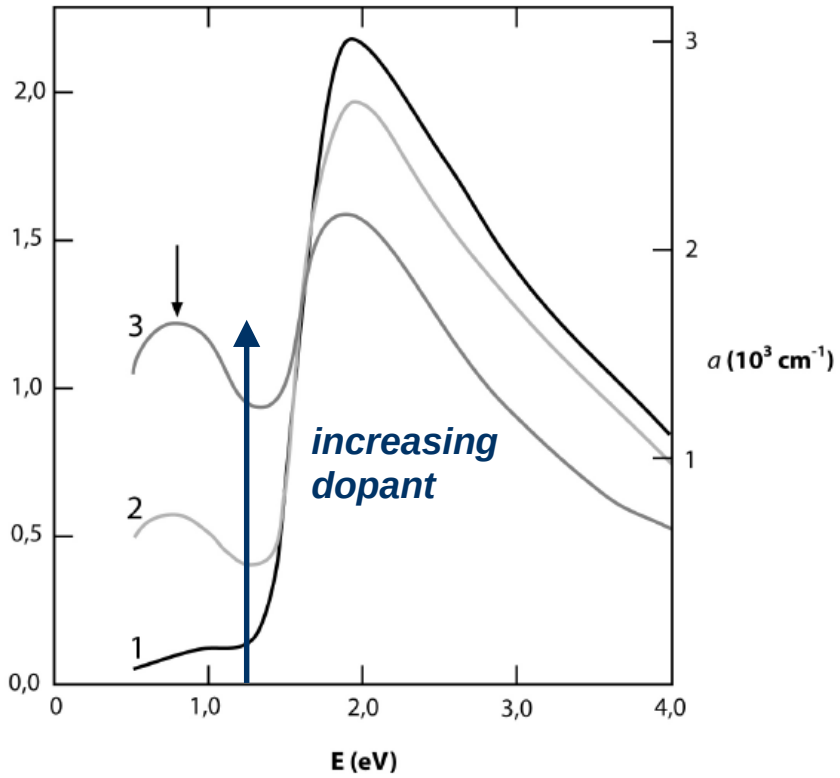


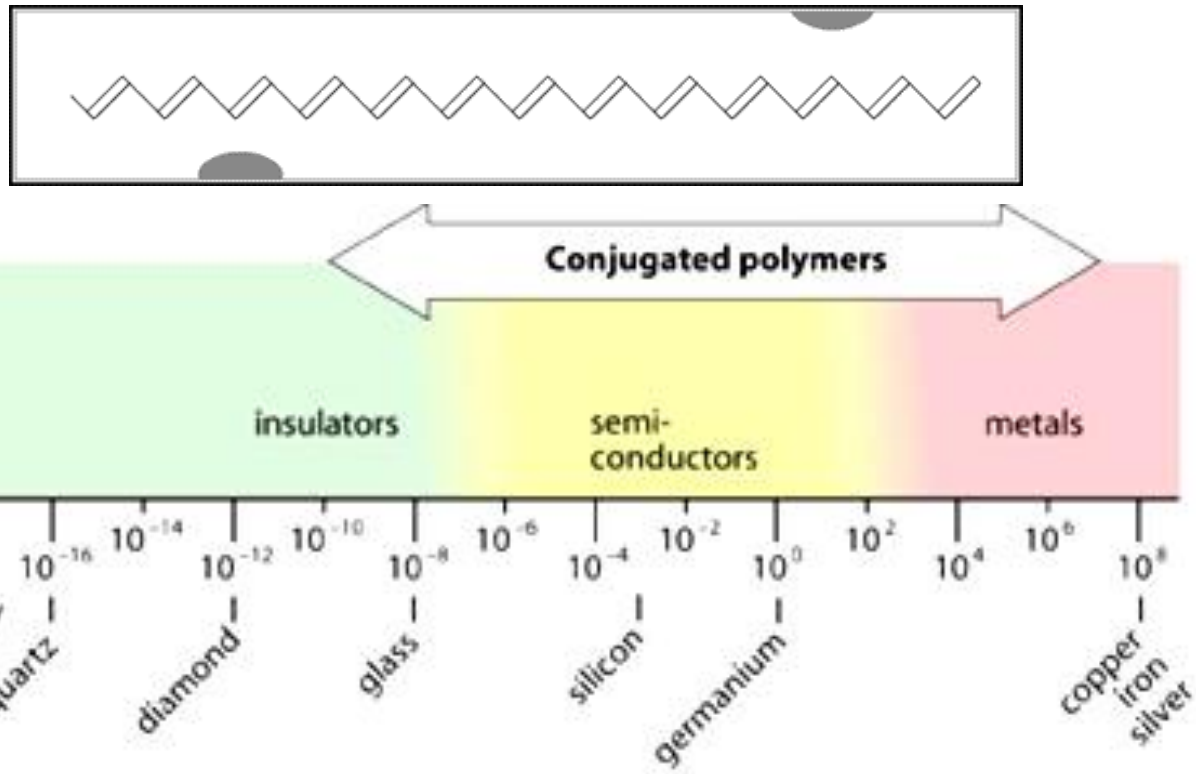
-pure polyacetyle: insulating (notes: gap)

- Peierls: 1 d atomic chain unstable
⇨ chain deformation, gap opening

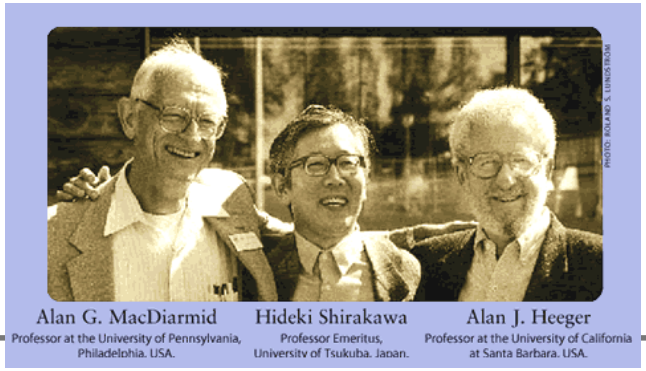
- dopant: mid-gap states, hole transport



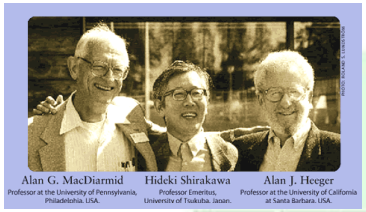
conducting polymers



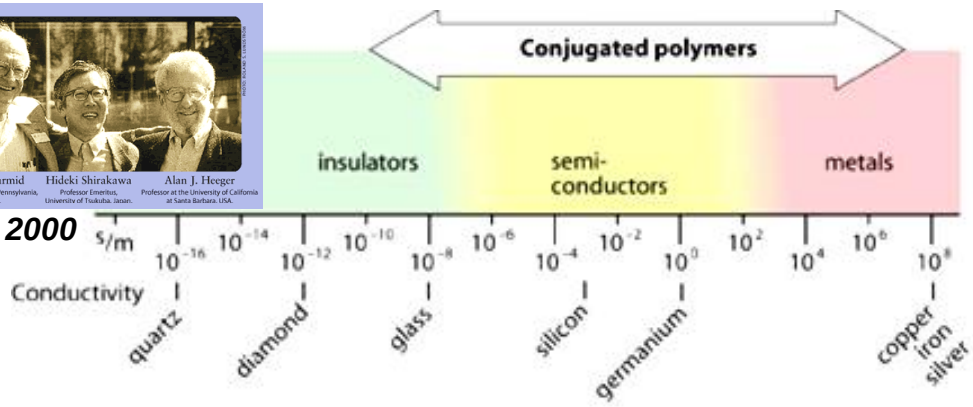
Nobel 2000
(chimie)



context



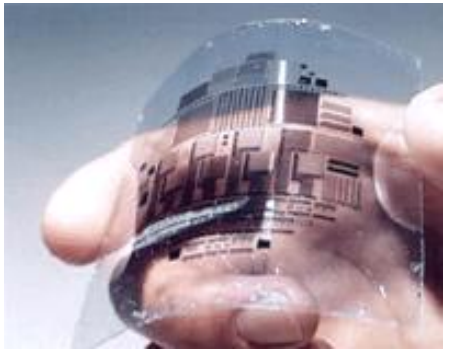
Nobel 2000



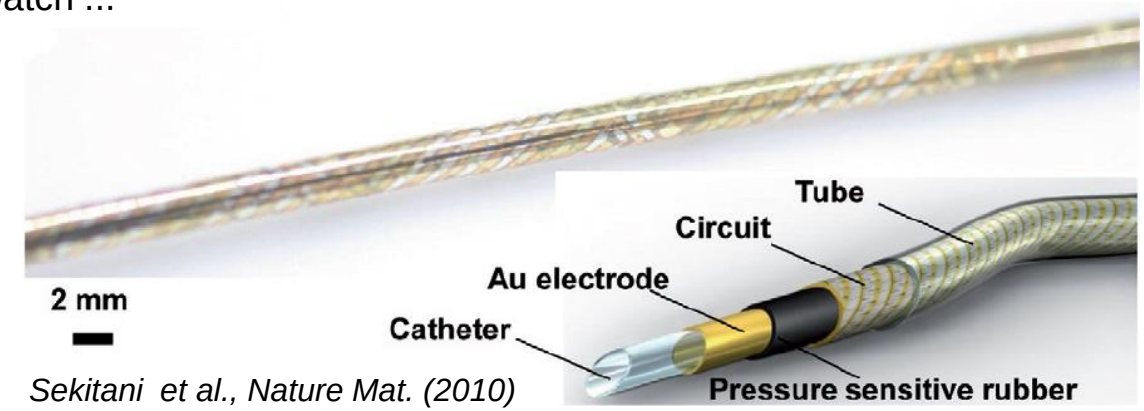
TV display
40" OLED
(EPSON, 2004)

press release, 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 ...



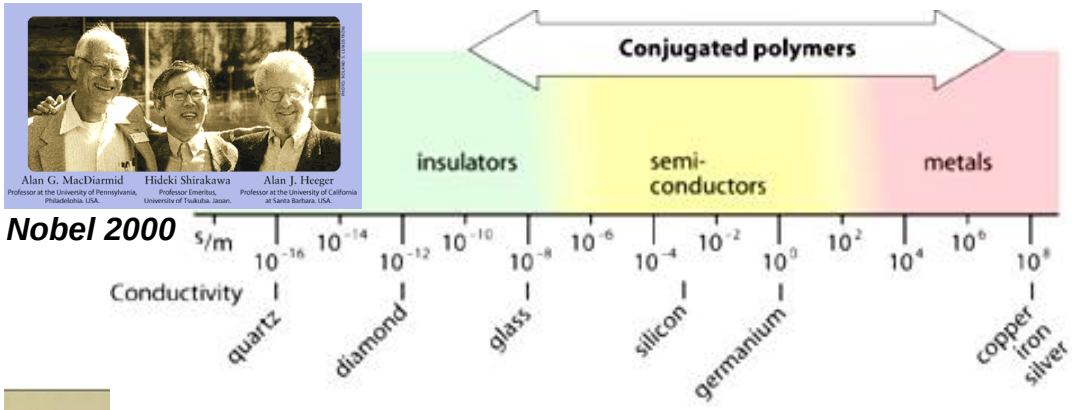
Low-cost organic electronics on plastic
Forrest, Nature (2004)

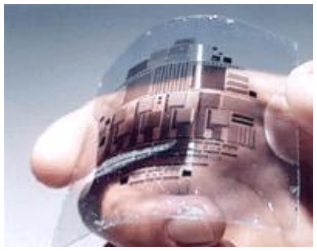


Sekitani et al., Nature Mat. (2010)

context

Nobel 2000





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TV display, 40” OLED

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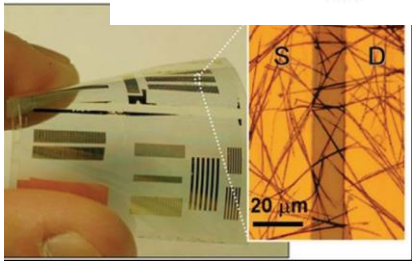
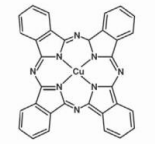
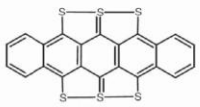


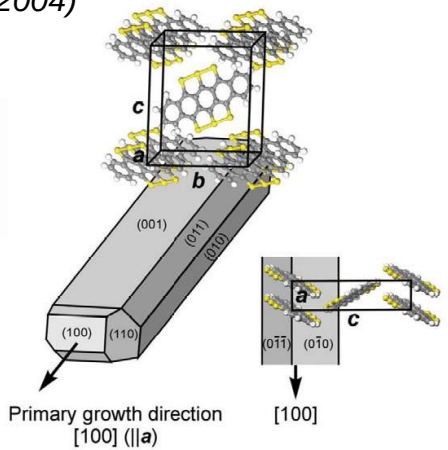
molecular crystals

(π-stacking)

~ 1D wires

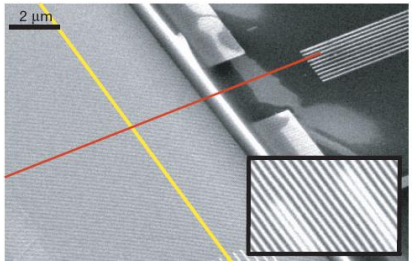






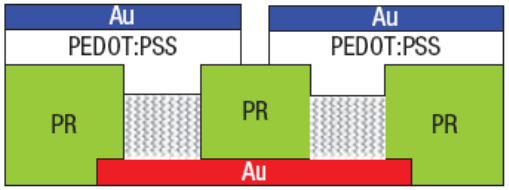
Organic nanowire transistors

Mat. Today (2008)



molecular mono-layers

(self-assembly)



160kb crossed-wire memory

Heat et al., Nature (2007)

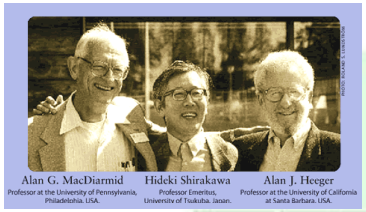
Organic ICs based on self-assembly (SAMFETs)

de Boer et al., Nature (2008)

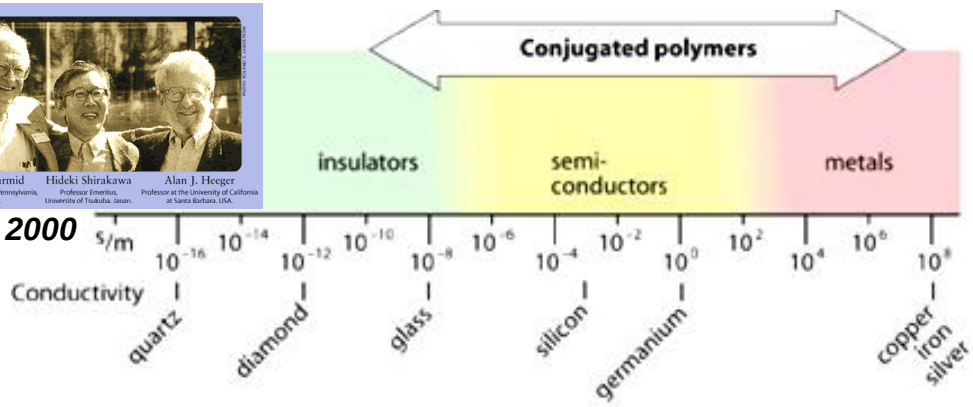
Large scale integr. of molecular junctions

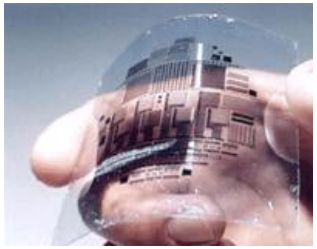
de Leeuw et al., Nature Nano (2008)

context



Nobel 2000





Low-cost organic electronics on plastic

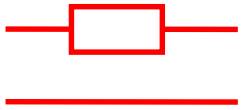
Forrest, Nature (2004)

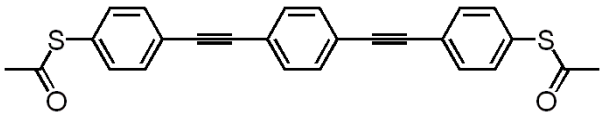
TV display, 40” OLED

(EPSON, 2004)

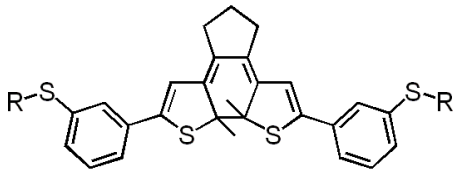
⇨ at the level of a few or even a single molecule ?

resistor
wire





switch



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 1mmol of (identical) molecule at a time, not one device
- molecules can be **active** (have a function)

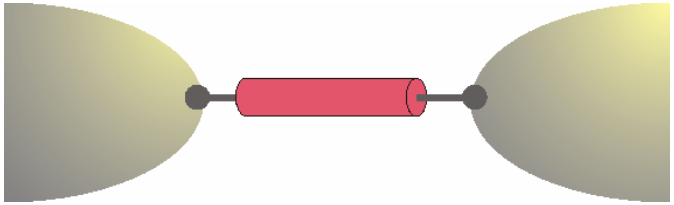
  stereochemistry (distinct stable geometric structures – isomers), **mechanical flexibility** (rotation axis), **photochemistry** (photochromism), **electrochemistry** (redox reactions)
  (self-)assembly (building of structures) and **molecular recognition** (switching, sensing)

-

- 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

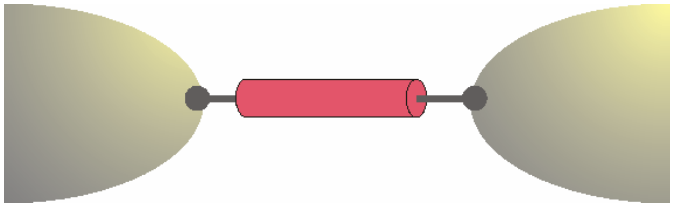
- electro-mechanical properties
  (e.g.: atomic, molecular switch)
- transport at μs, ns, ps, ...
- e-e and e-ph interactions
- heat flow (atomic & molecular level)
- spin dependent transport & selectivity
- exciton generation, separation
- interaction with EM field (plasmonics)
- coherence aspects
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

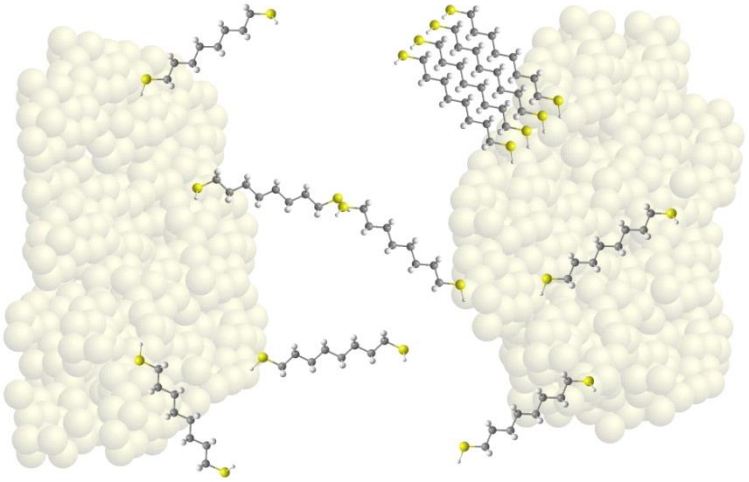
device aspects

- 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





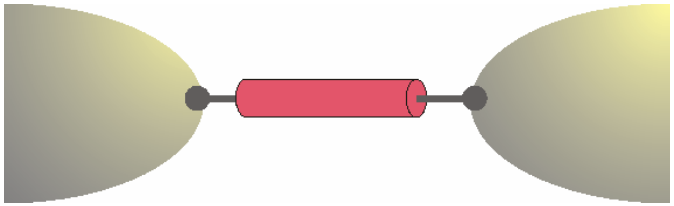
nanometer and molecular-scale junctions

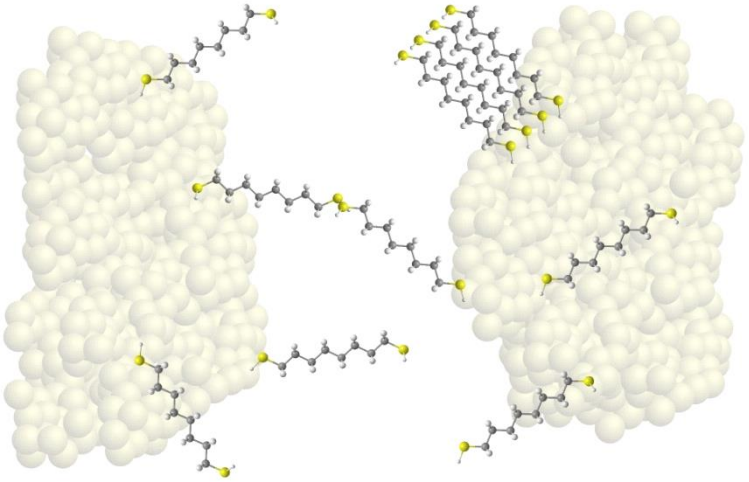
- structural disorder — *electrodes and junction geometry*
- interactions — *anchoring*, *self-assembly, polymerization*
- fluctuations — *mobility of (surface) atoms, molecular distortions, multiple local energy minima*

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





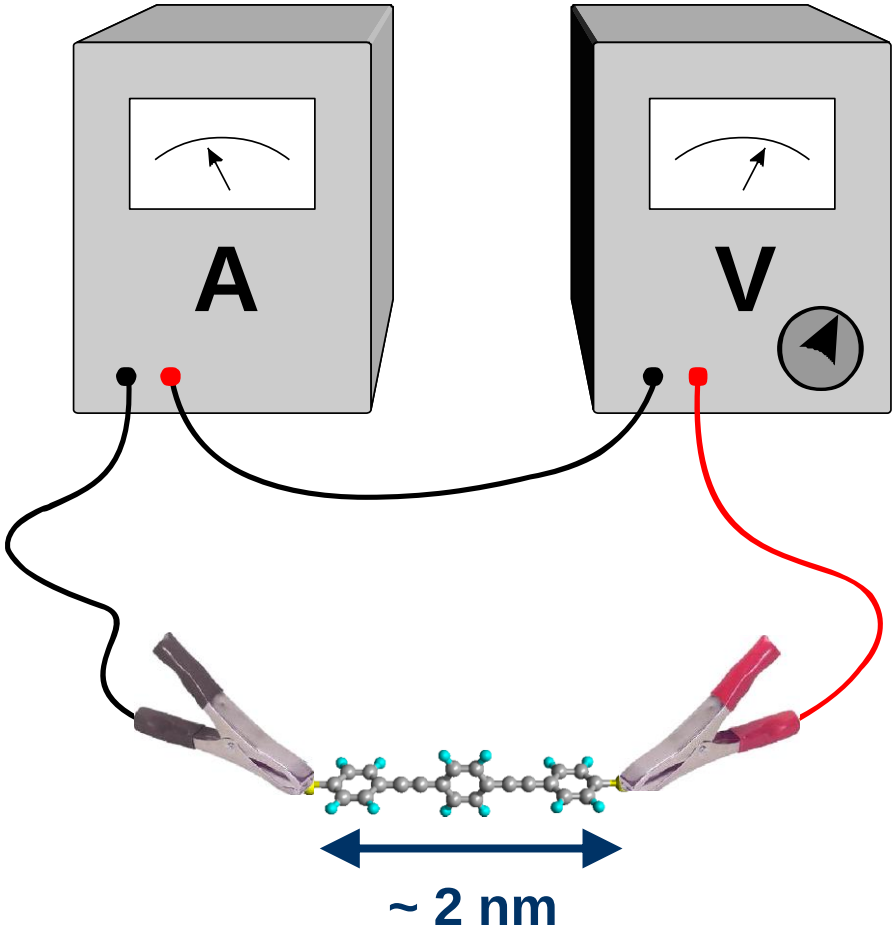
nanometer and molecular-scale junctions

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

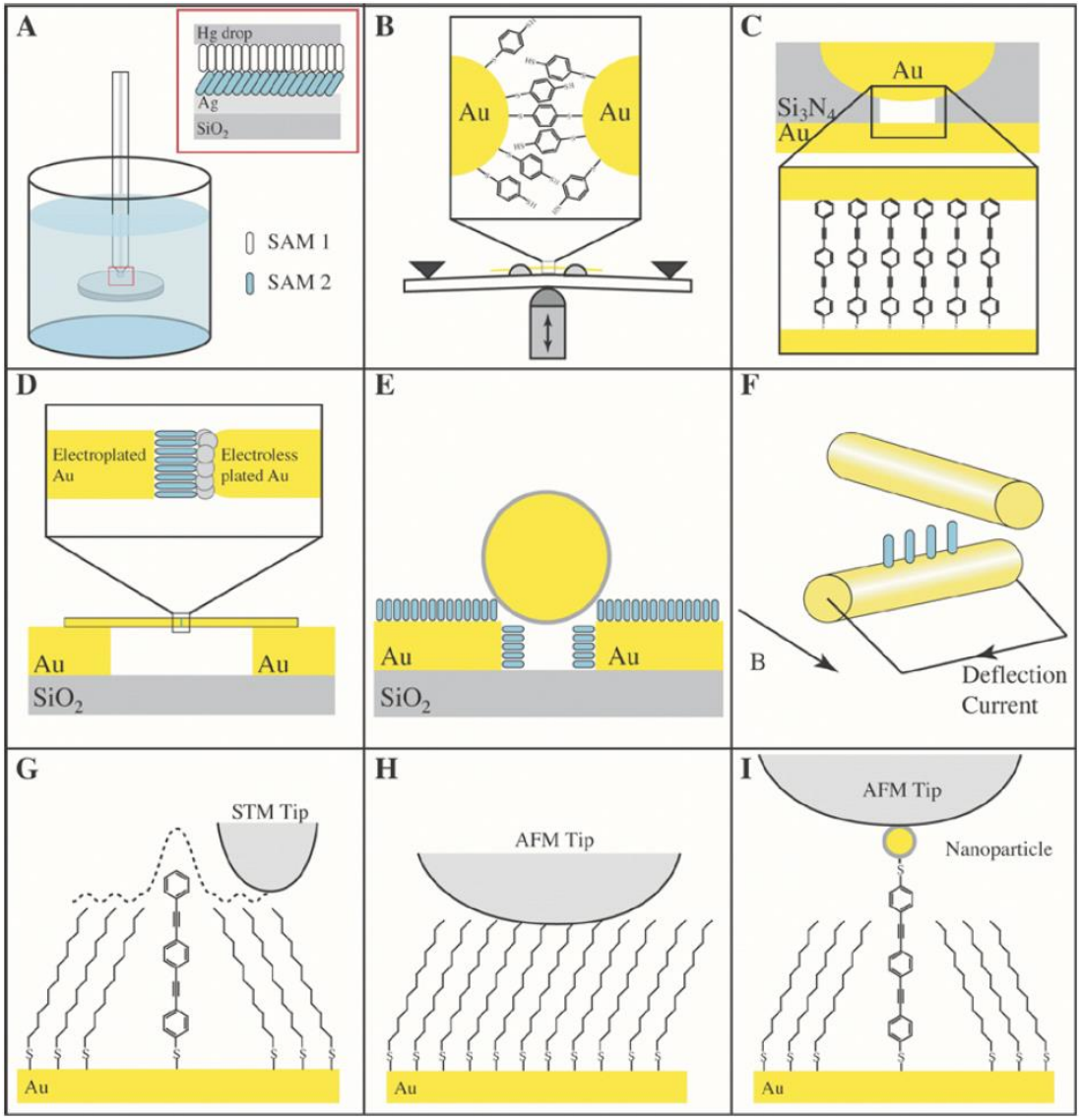
⇨ **junction formation** (and breaking up)**: dynamic process, variability**

- ***time scale(s)***
- ***local environment effect***
- ***local geometry and structure effect***

contacting a molecule



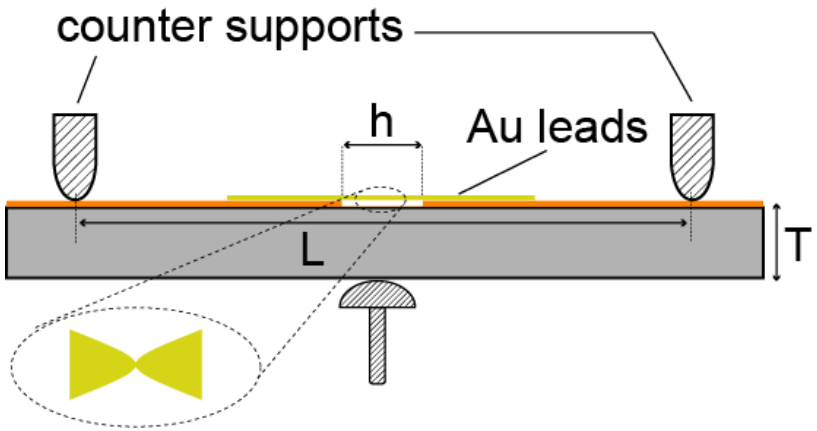
contacting a molecule: exp. techniques

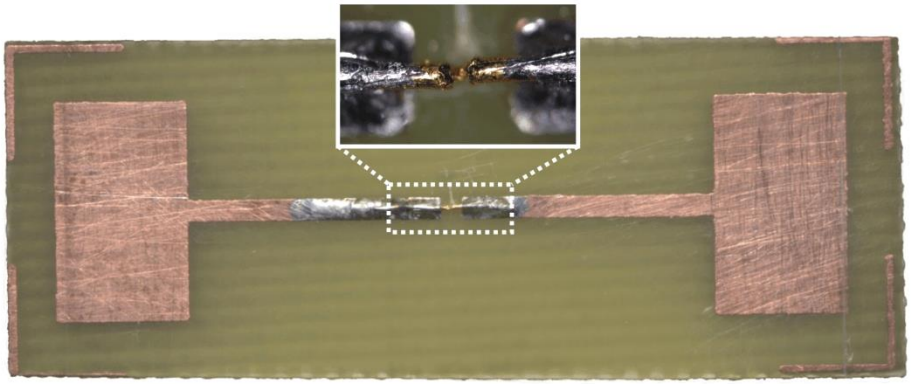


Mantooth, Weiss., Proc. IEEE, 2003

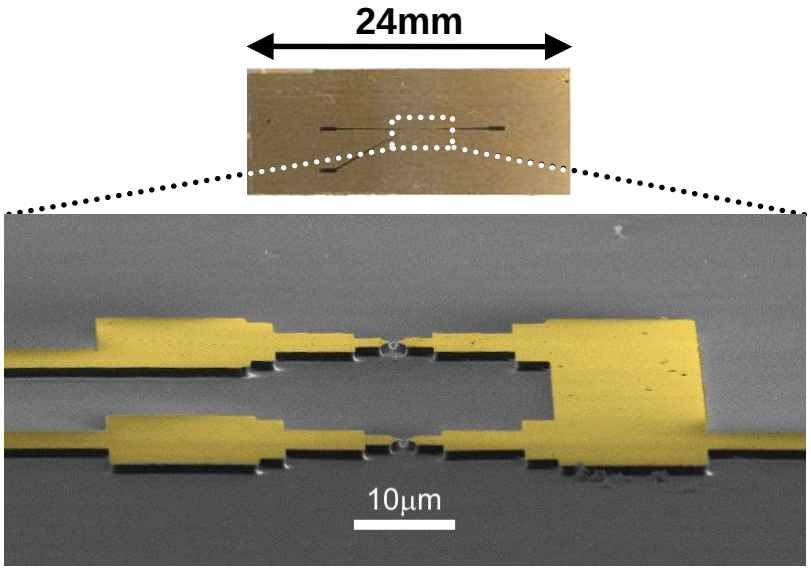
forming atomic contacts

break junctions: forming atomic contacts

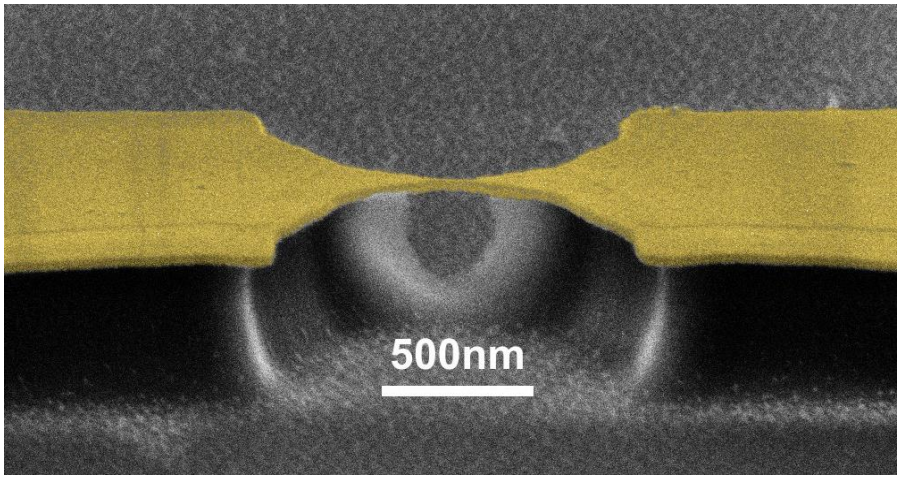




hand-made notched Au wire



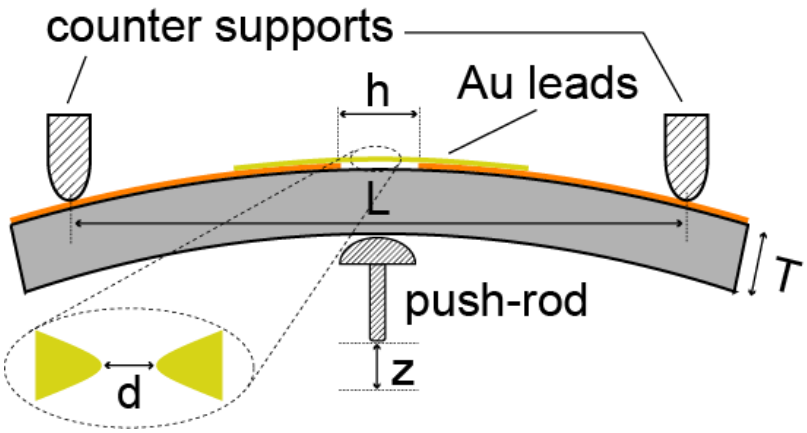
e-beam fabricated Au bridges

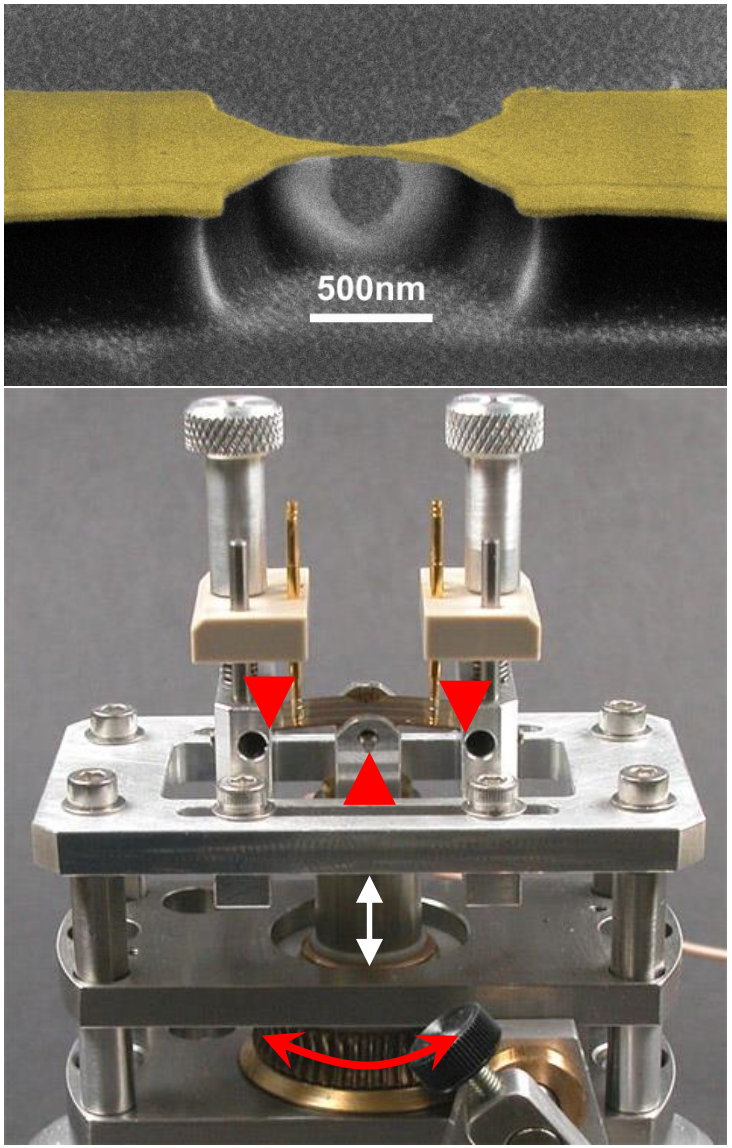


Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)

break junction: a draw bridge at the atomic scale

break junctions





elongation: $d = 6thz/L^2$

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

⇨ **$\Delta Z = 10\mu m \Leftrightarrow \Delta d \sim 3$ Å**

vertical speed: $v_z = 30\mu m/s$

⇨ **0.5 - 1.2 nm/s**

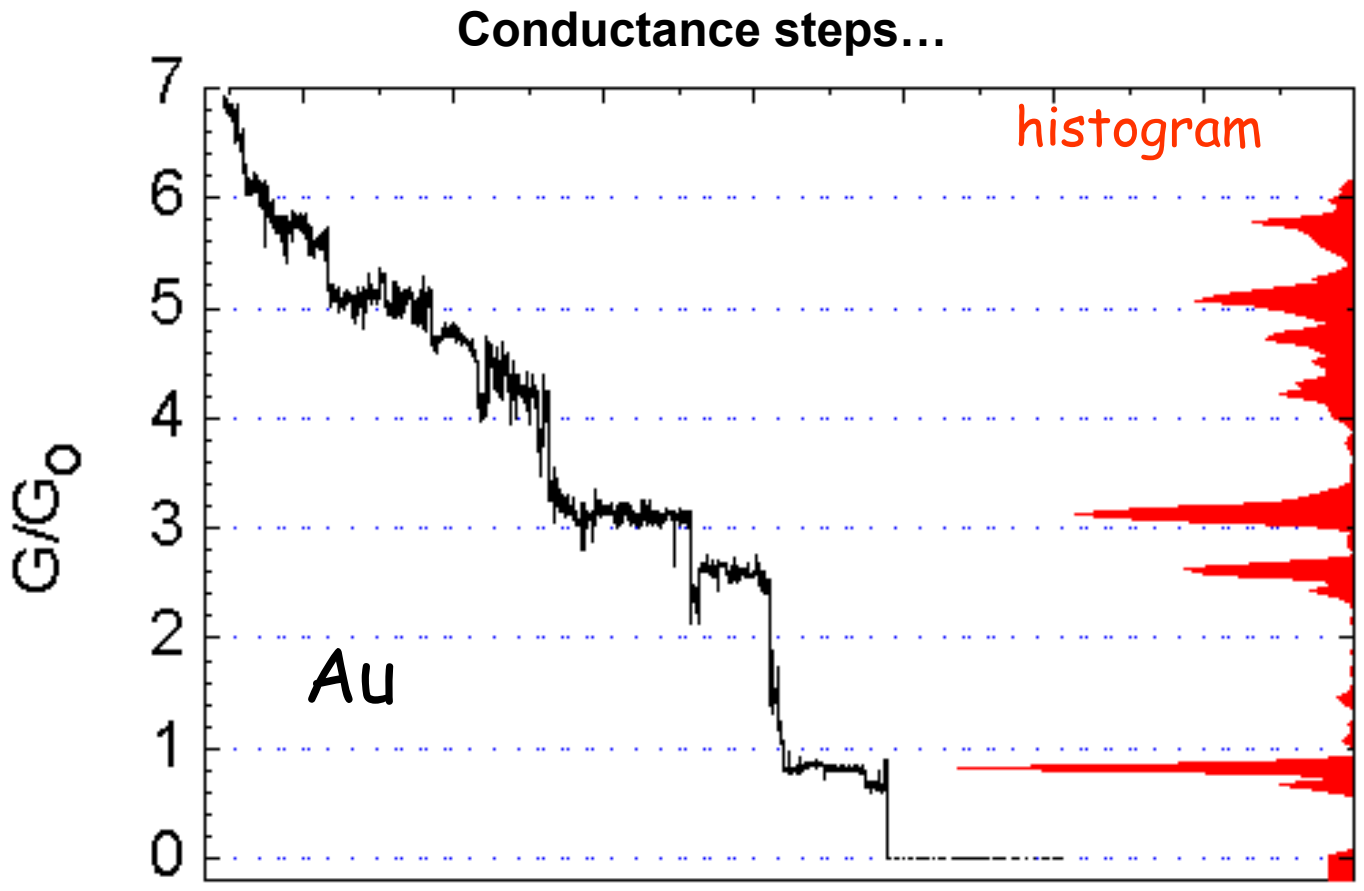
electrodes separation speed

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

Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)

break junctions

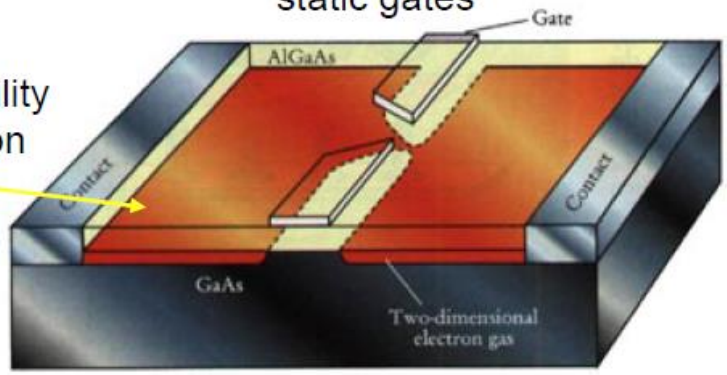
closed ⇨ open: contact to tunneling



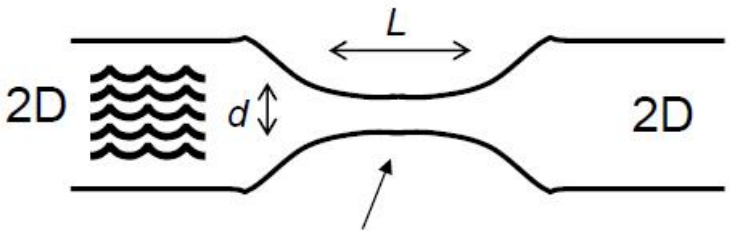
conductance quantization: 2DEG systems

Depletion by electro-static gates

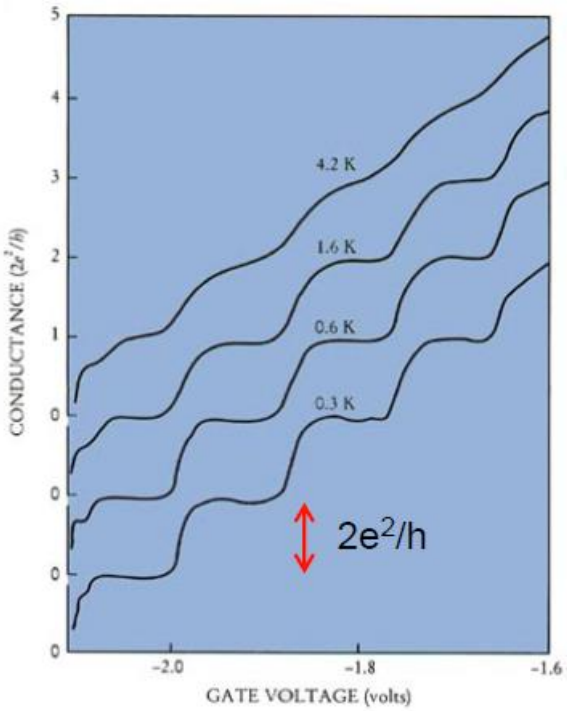
High mobility 2D electron gas ('ballistic')



'Quantum Point Contact'



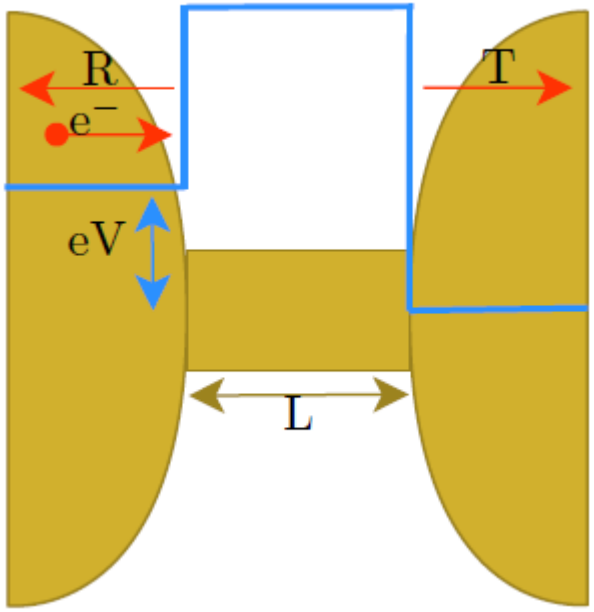
Narrow constriction; quasi-1D
(width d ~ Fermi wavelength λ_F)



Limited conductance $2e^2/h$ even without scattering, regardless of length L: "contact resistance"

$$G(E_F) = \frac{2e^2}{h}\sum_n T_n(E_F) \approx \frac{2e^2}{h}N(E_F)\ (T = 0\mathrm{K})$$

conductance quantization



electron mfp > L: ballistic regime

Fermi wavelength (Au)

GaAs: 200nm

$$\lambda_F \approx 5.2\mathring{A}$$

Energy modes splitting

GaAs: ≈1meV

$$\frac{\pi^2\hbar^2}{2m\lambda_F^2} \approx 1.4eV$$

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

Landauer, 1957
Landauer, Büttiker

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

see later

$$G_0 = \frac{2e^2}{h} \qquad G_0 \simeq (12.9k\Omega)^{-1}$$

conductance of a quantum coherent structure accommodating N channels

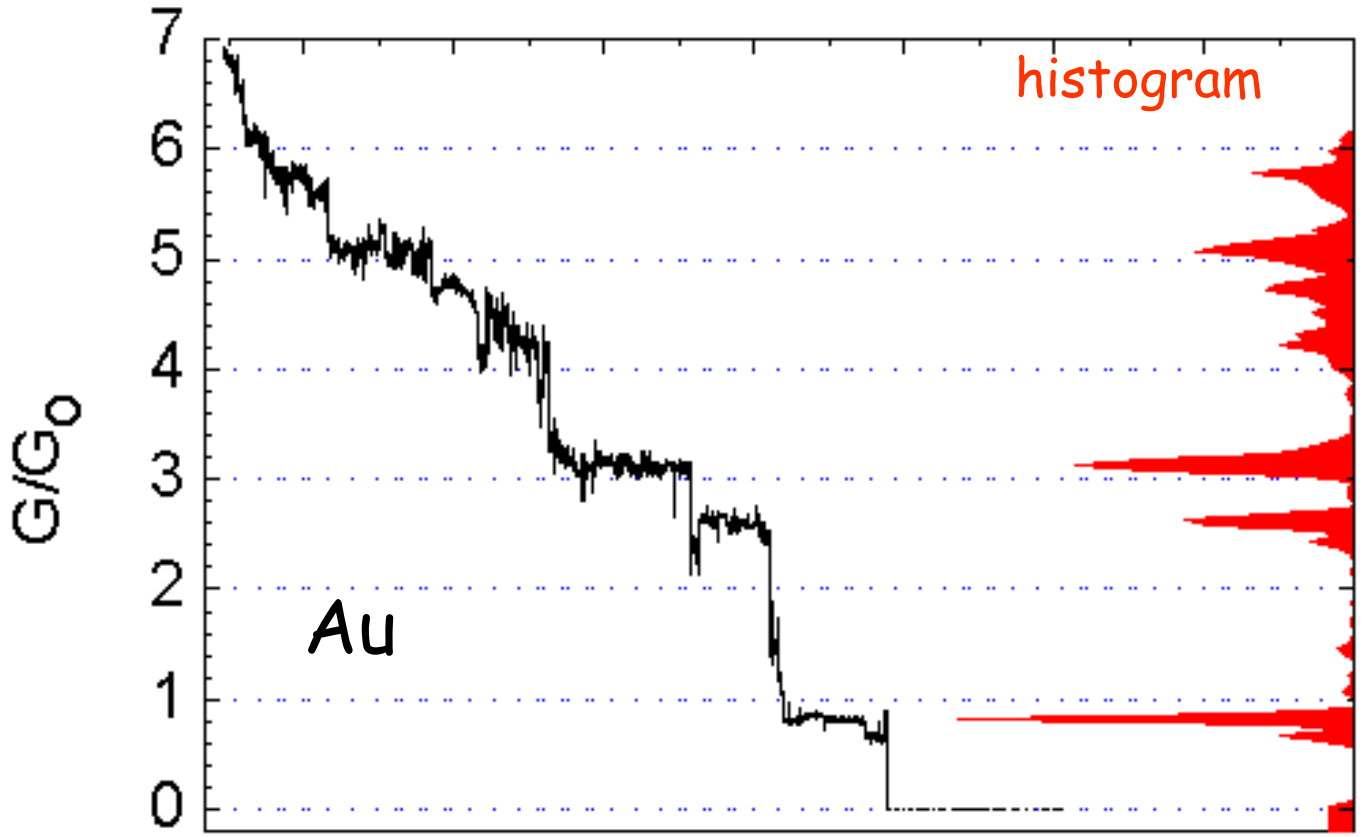
Tn: transmission probability through channel n

see e.g. Agrait, van Ruitenbeek, Phys. Rep. (2003)

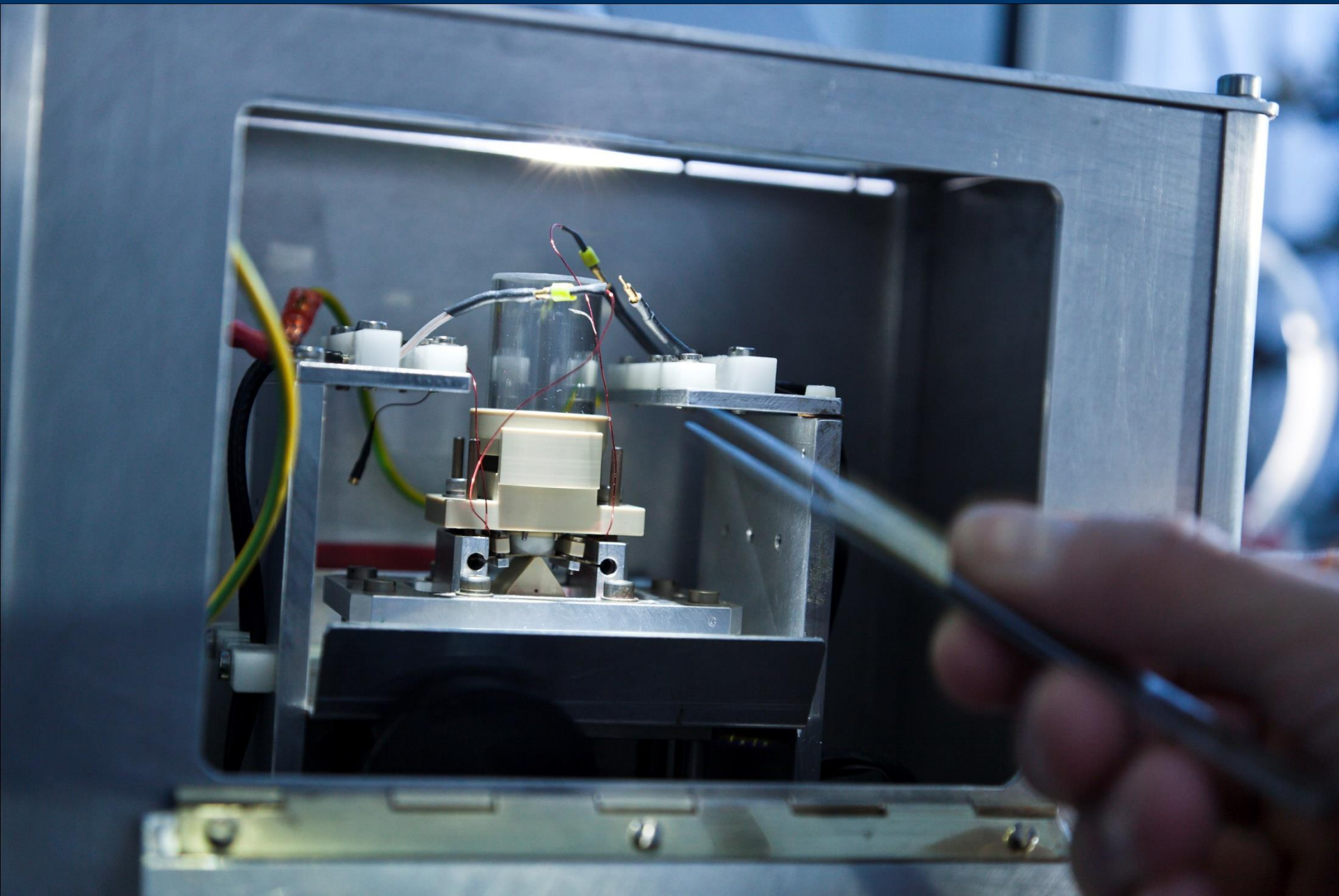
break junctions

Conductance quantization for Au contact

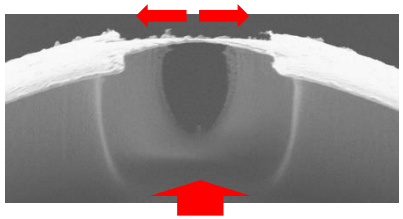
n = 1 with T = 1 ⇨ $G = \frac{2e^2}{h}\sum_n T_n = G_0 = \frac{2e^2}{h}$ = **77.5 μS**



break junctions in liquid environment

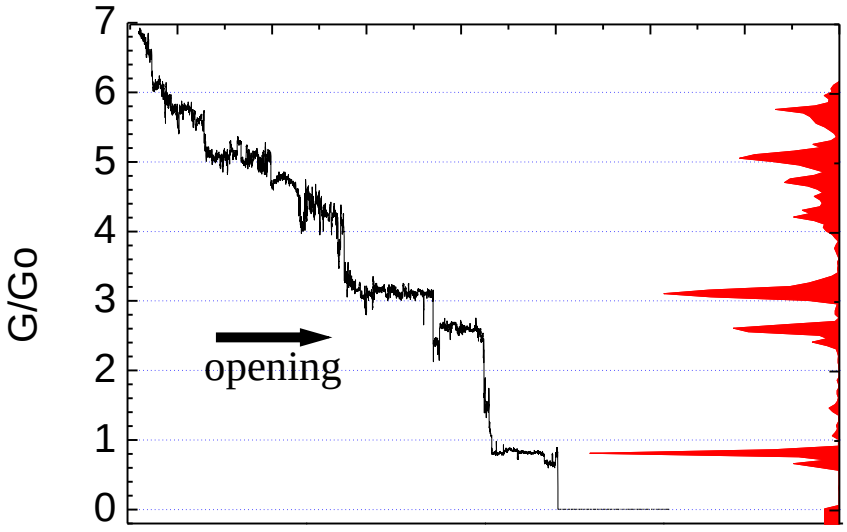


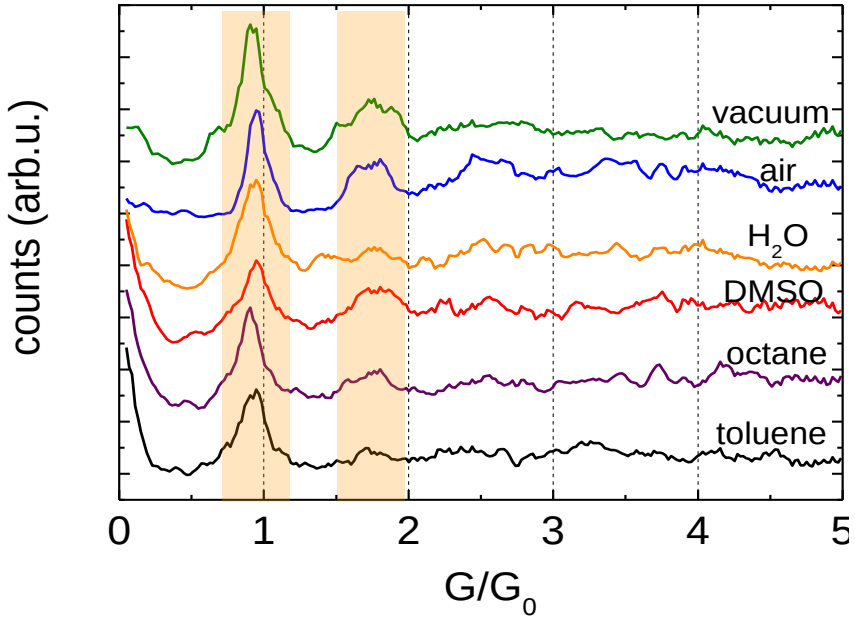
“high” conductance regime



$G \geq G_0 = 2e^2/h$
$=(12.9\ k\Omega)^{-1}$

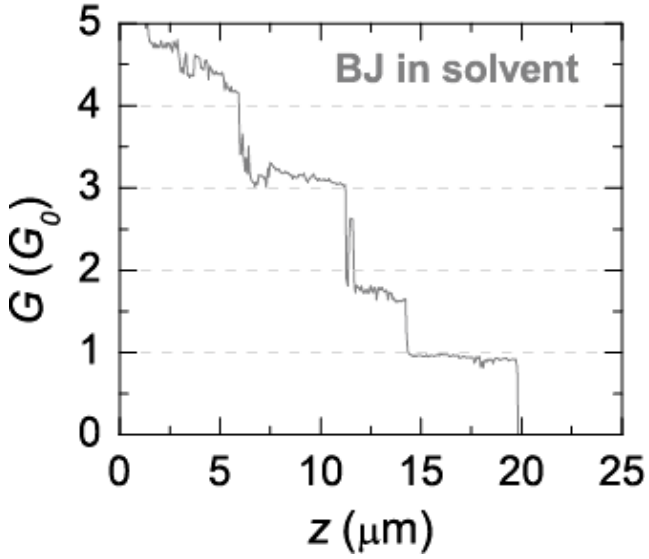
conductance histogram (counts)

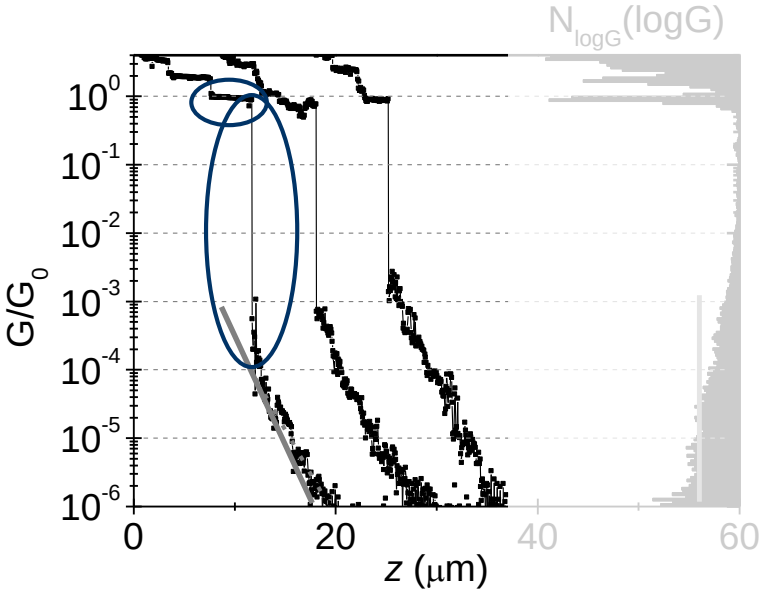




no significant differences between enviroments at high G

opening: conductance vs elongation



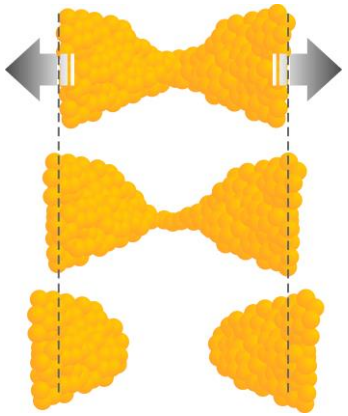


break junction opening
(solvent:THF/mesitylene 1:4 v/v)

conductance quantization, plateaus

$$G_0 = \frac{2e^2}{h} = 77.5\mu S$$

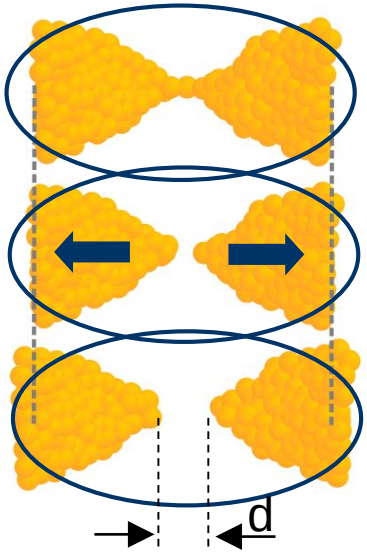
cf e.g. Agrait et al., Phys. Rep. 2003



- last Au G-plateau (~1G_0)
- breaking of Au bridge
- tunneling regime

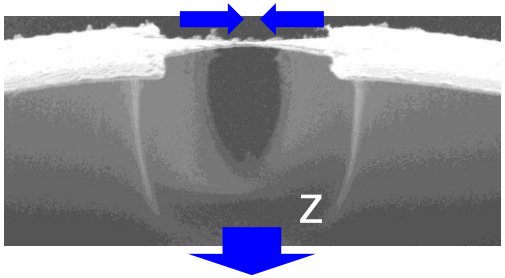
$$G \propto e^{-\beta d}$$

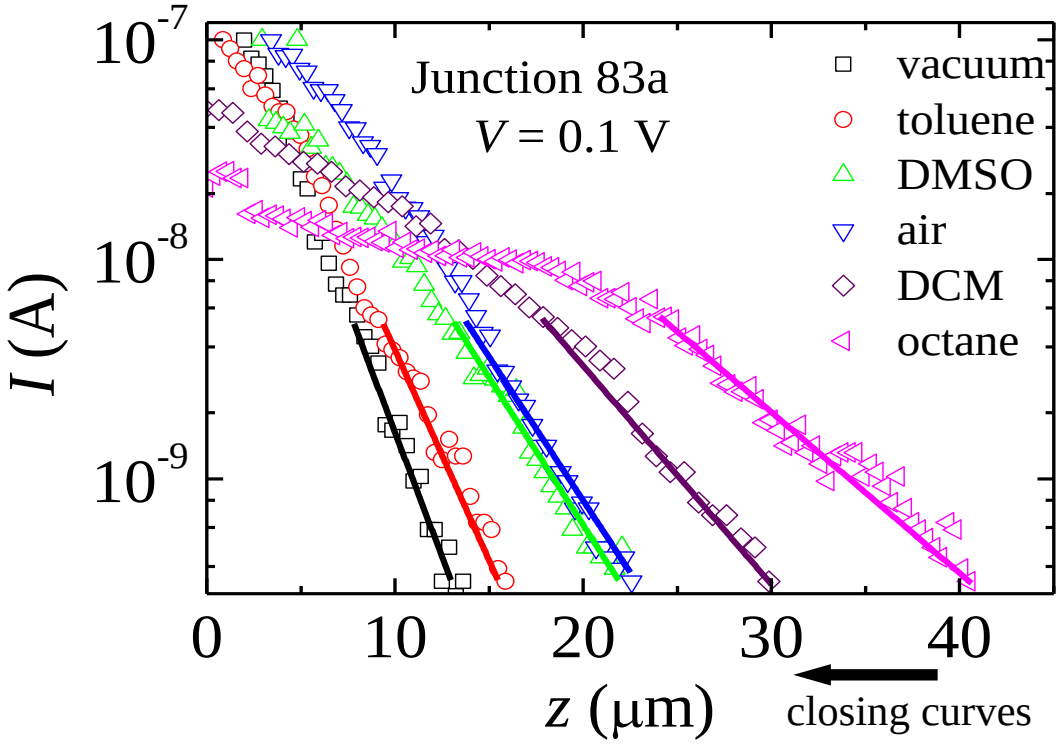
- statistics: histogram
  tunneling background
  ⇔ const.



tunneling regime

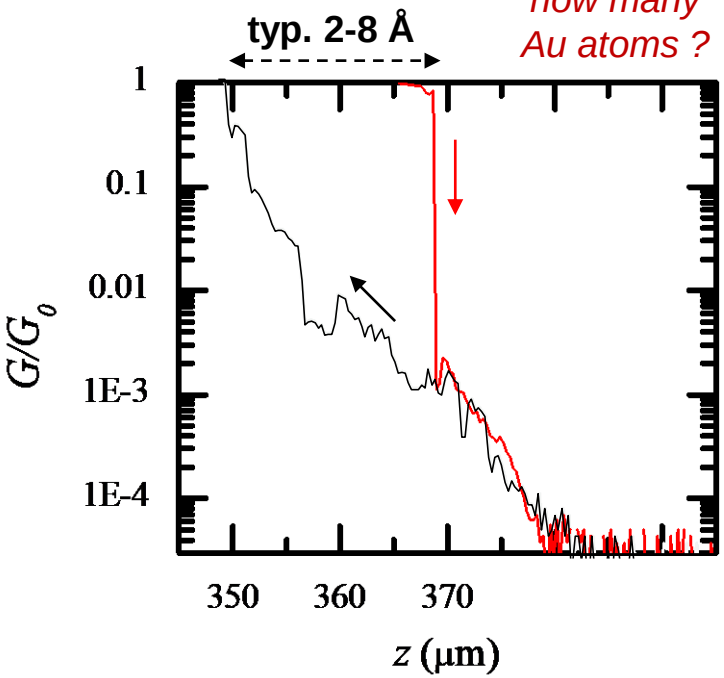
gap open,
close the
junction





opening-closing trace

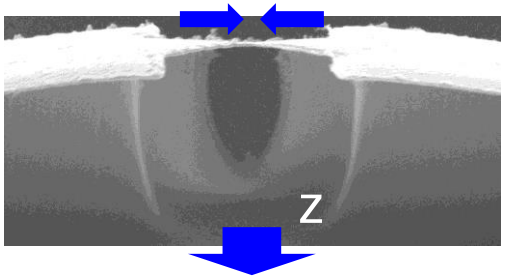
how many Au atoms ?



liquid ~ effective medium in first approx.

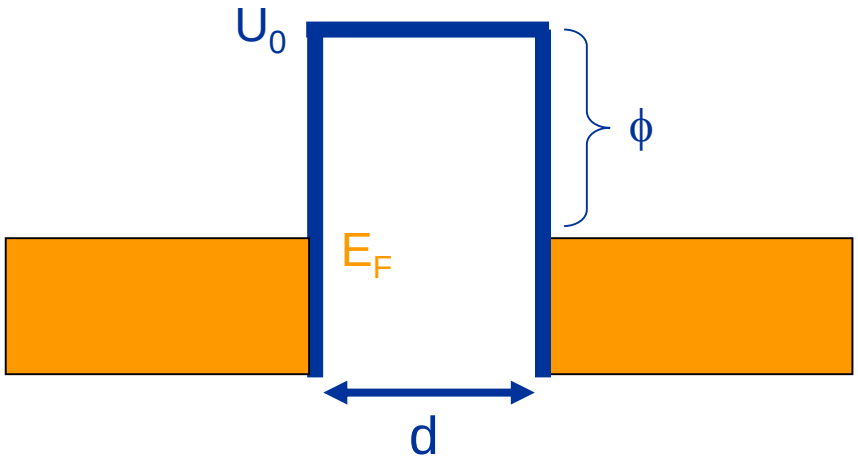
tunneling regime

gap open, close the junction



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

d=r·z r = reduction factor



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

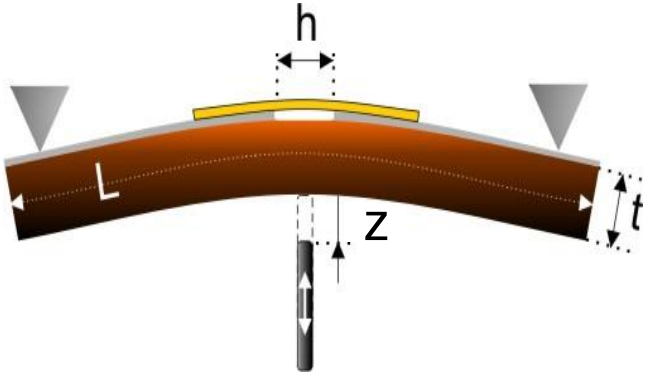
$$\rightarrow \quad I \propto e^{-Bz}$$

$\phi = U_0 - E_F$

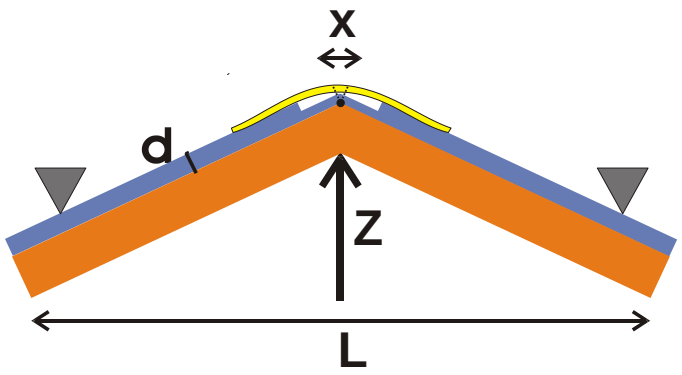
in vacuum: metal workfunction

in solvent: apparent barrier height

tunneling regime: attenuation factor



purely elastic: $r = 6\,t\,h/L^2 \sim 5 \times 10^{-6}$



"hinge" model: $r \approx 4\,d/L \sim 6 \times 10^{-4}$

In vacuum

$\phi_{vac} = 3.5 - 5$ eV ⇨ $r \sim 5 \times 10^{-5}$

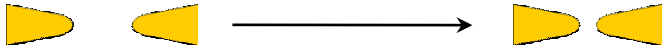
$$B = 2r\sqrt{2m\phi}/\hbar \qquad I \propto e^{-Bz}$$

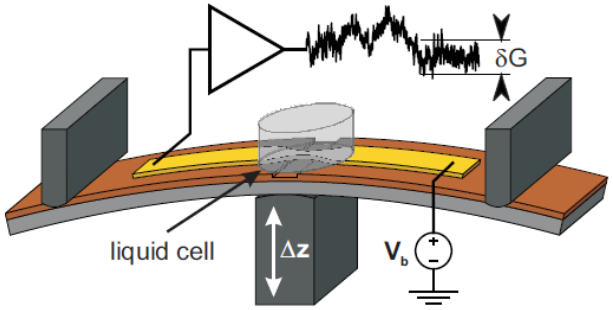
NB: plastic deformation of the substrate can affect r

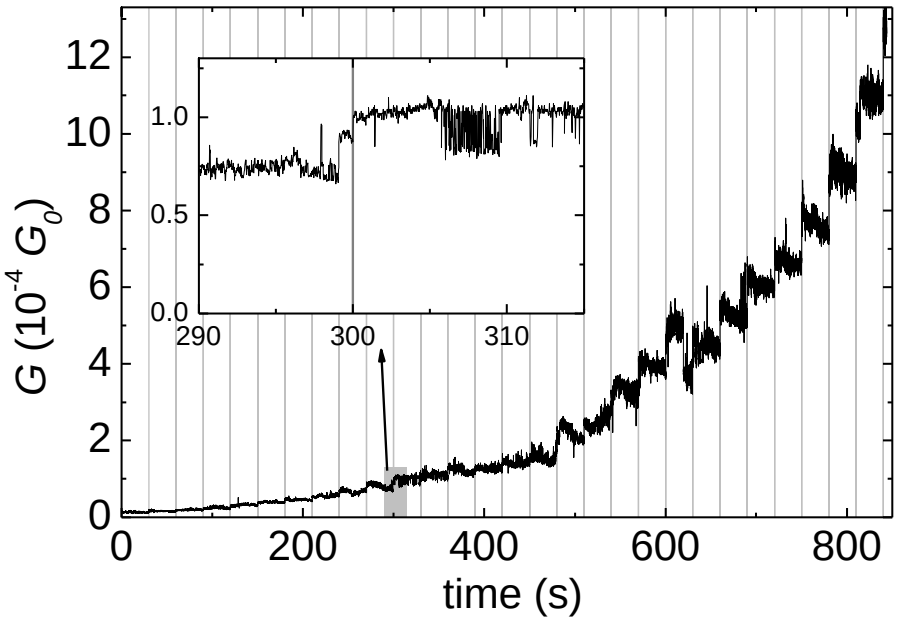
contacting simple molecules

dynamical behavior & fluctuations: solvent

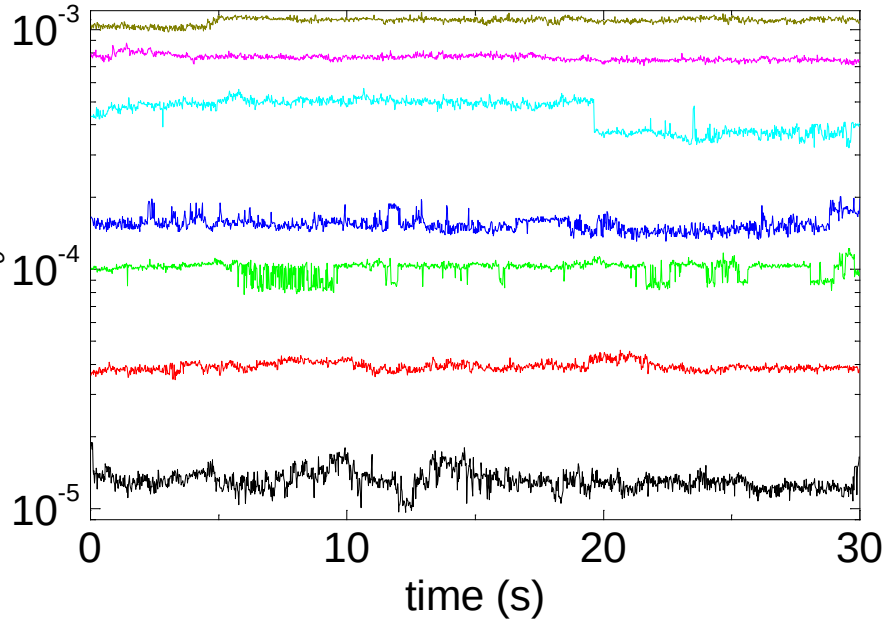
pure solvent (mesitylene)







full measurement

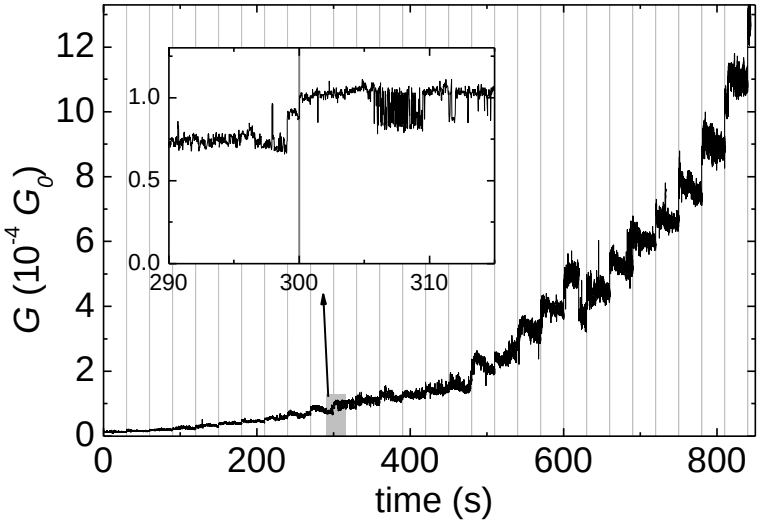


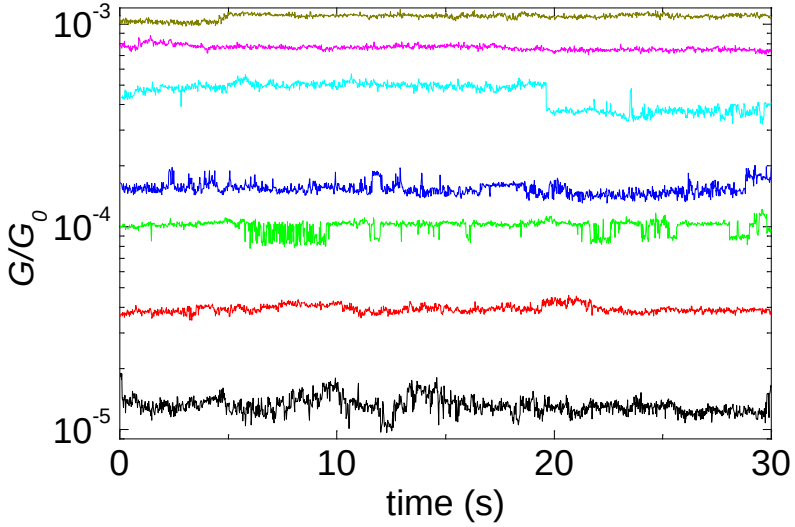
30 s intervals

J. Brunner et al., JPCM, 2014

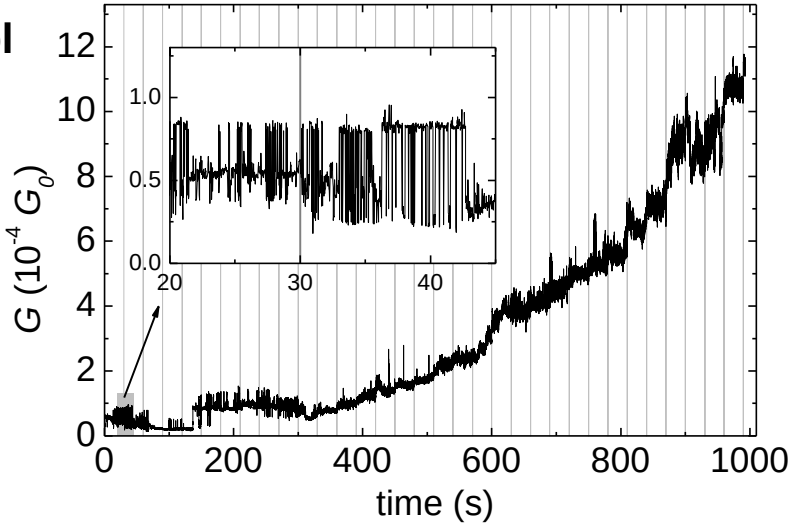
dynamical behavior & fluctuations: solvent + alkanedithiols

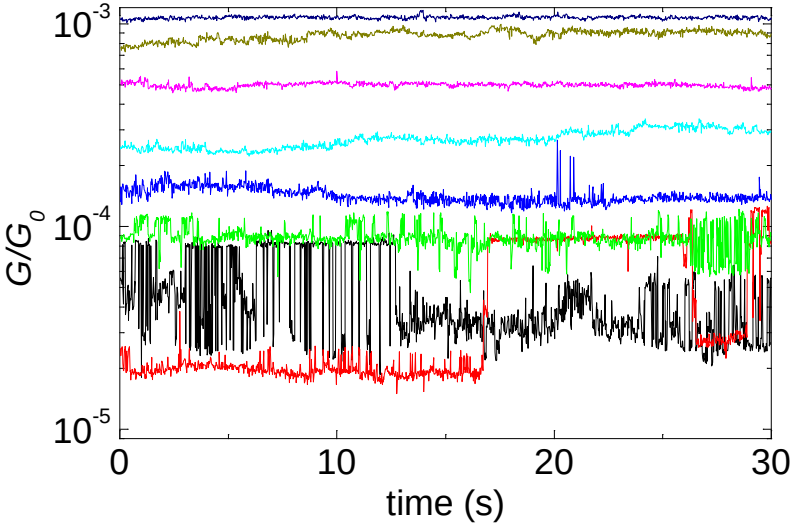
solvent





octanedithiol solution

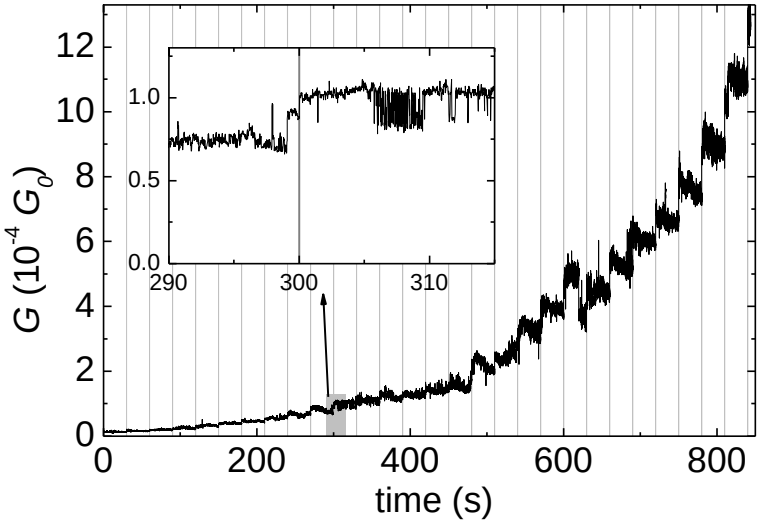


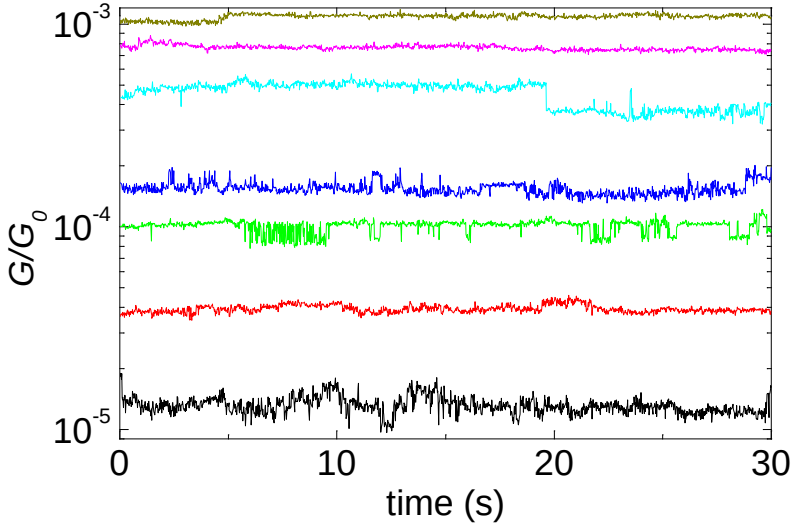


J. Brunner et al., JPCM, 2014

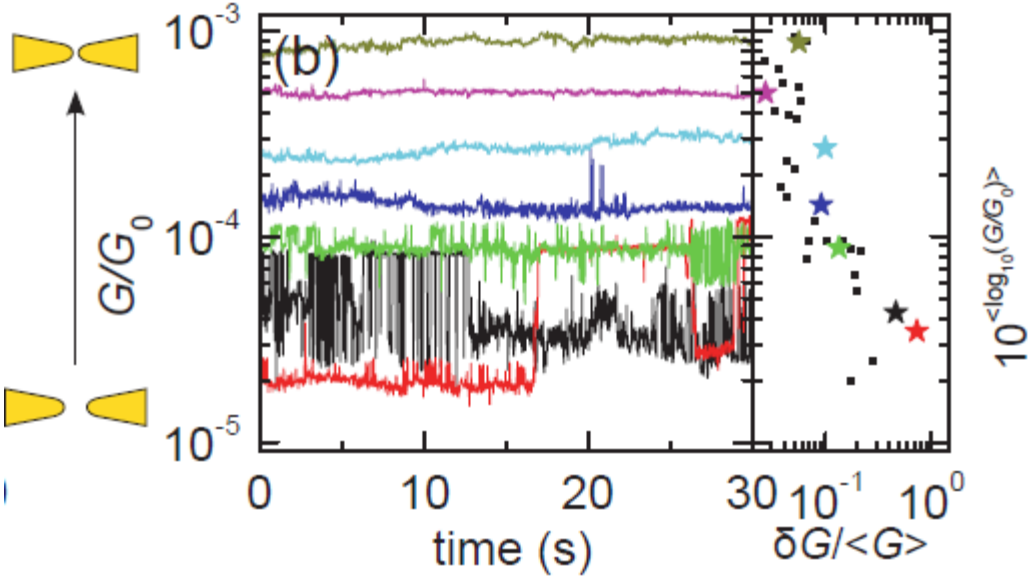
dynamical behavior & fluctuations: solvent + alkanedithiols

solvent





octanedithiol solution

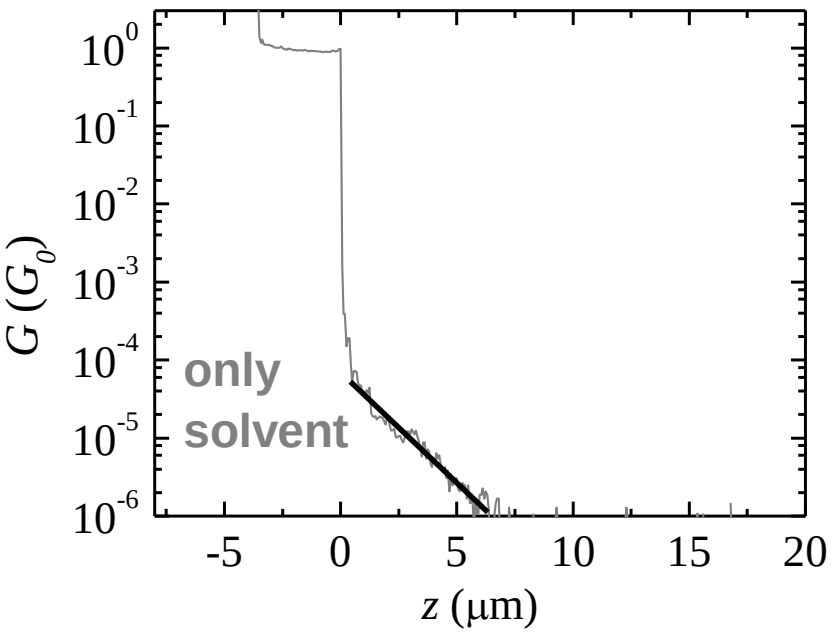


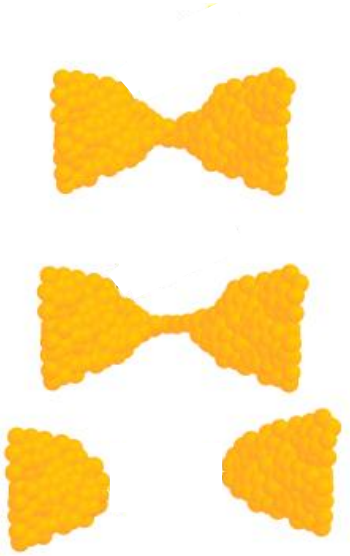
relative conductance fluctuation amplitude

$$\delta G_{\mathrm{rel}} = \delta G / \langle G \rangle$$

J. Brunner et al.

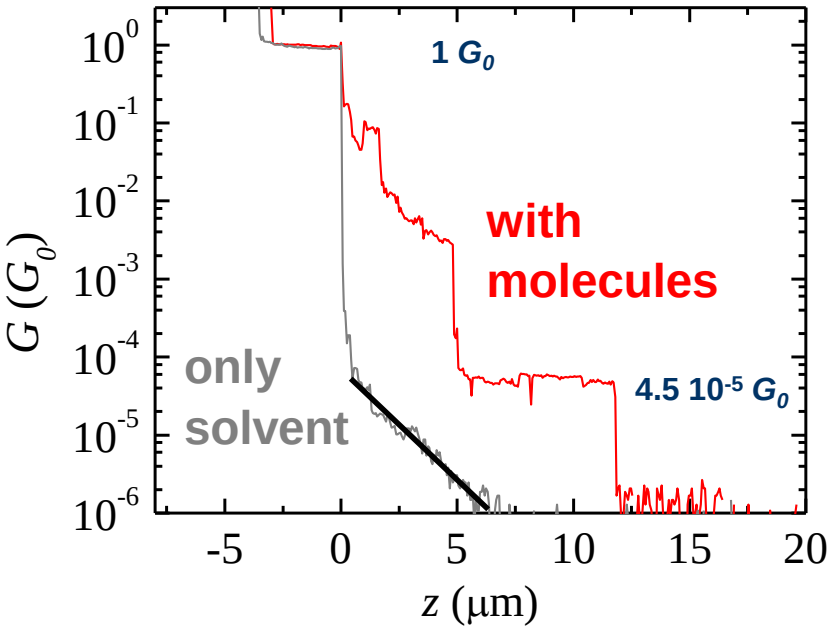
formation of a molecular junction: opening traces

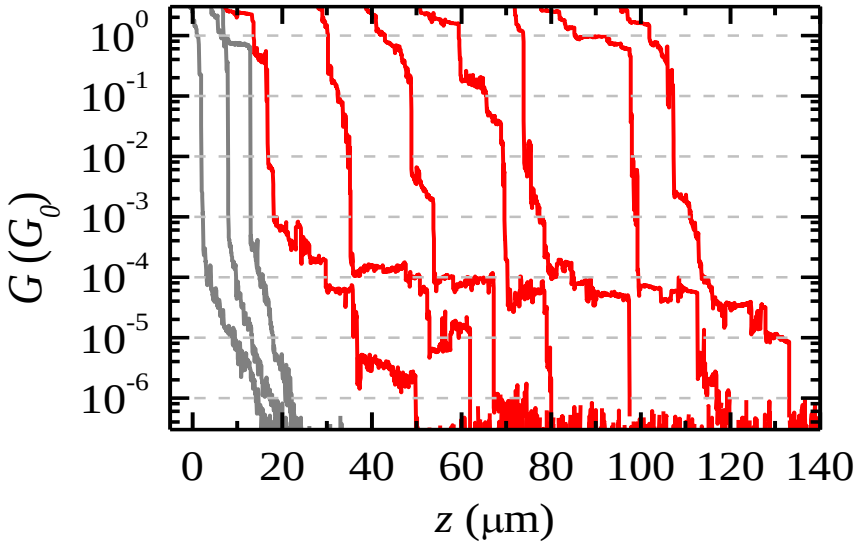




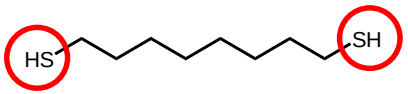
only solvent

signature of a molecular junction





example: alkanedithiols

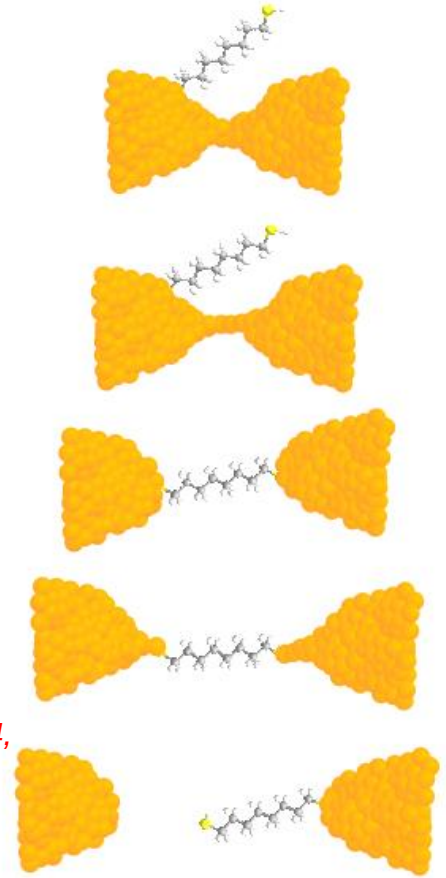


large HOMO-LUMO gap (few eV), ~ no solvent effect

molecular signature:

plateau *(at $G \ll G_0$)*

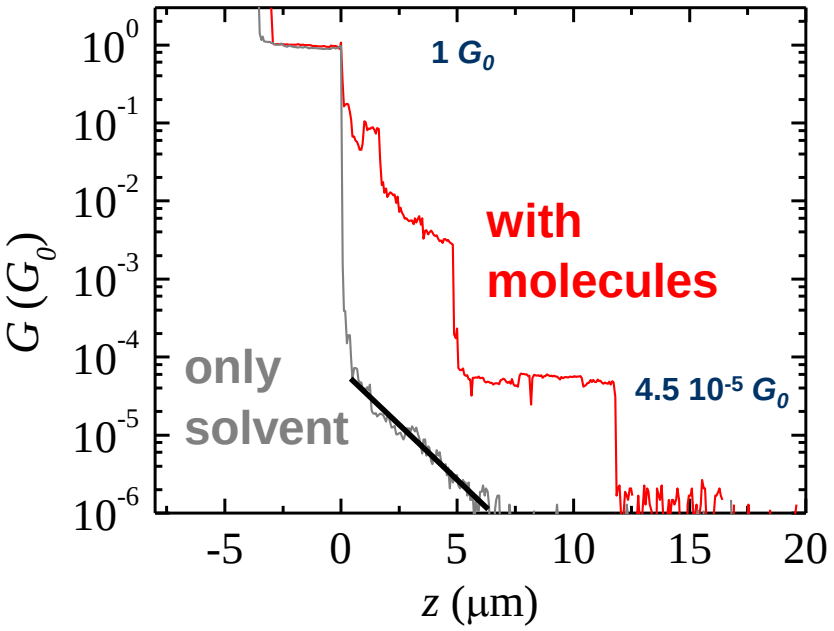
(Reichert et al., PRL 2002, Tao et al., Science, 2003, Nano Lett. 2004, JACS 2007)

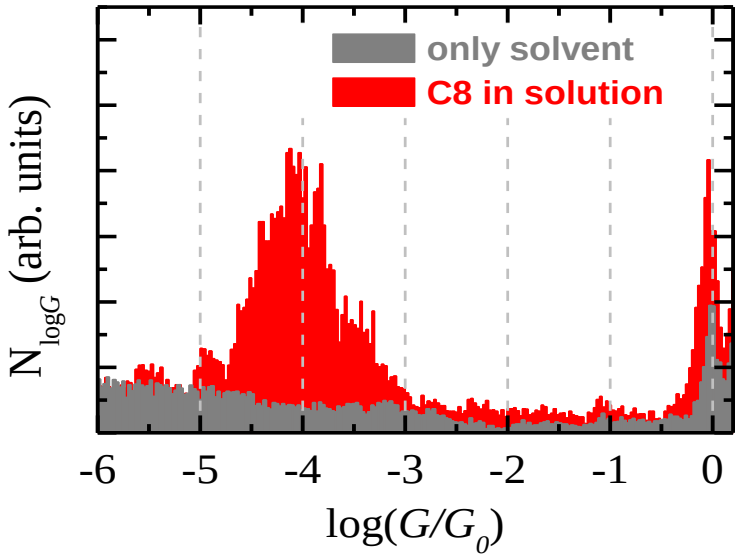


only solvent: Mesitylene

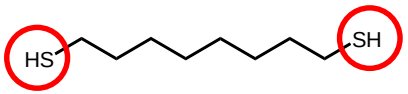
with molecules:0.1 M octanedithiol in Mesitylene

signature of a molecular junction

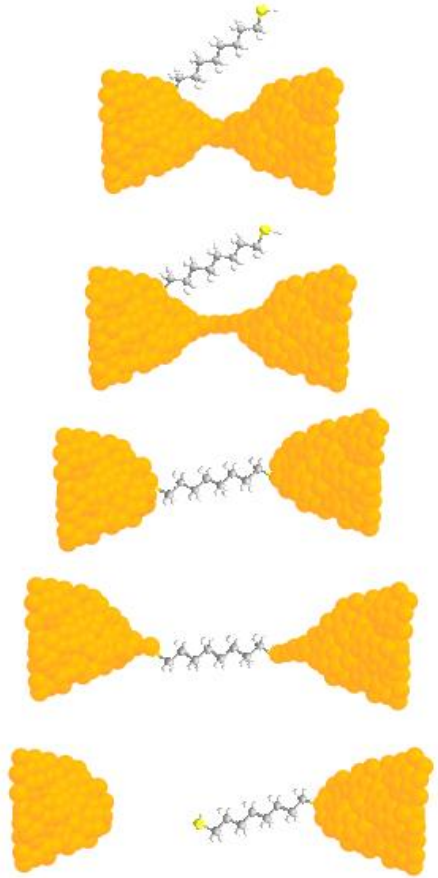




model system: alkanedithiols



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

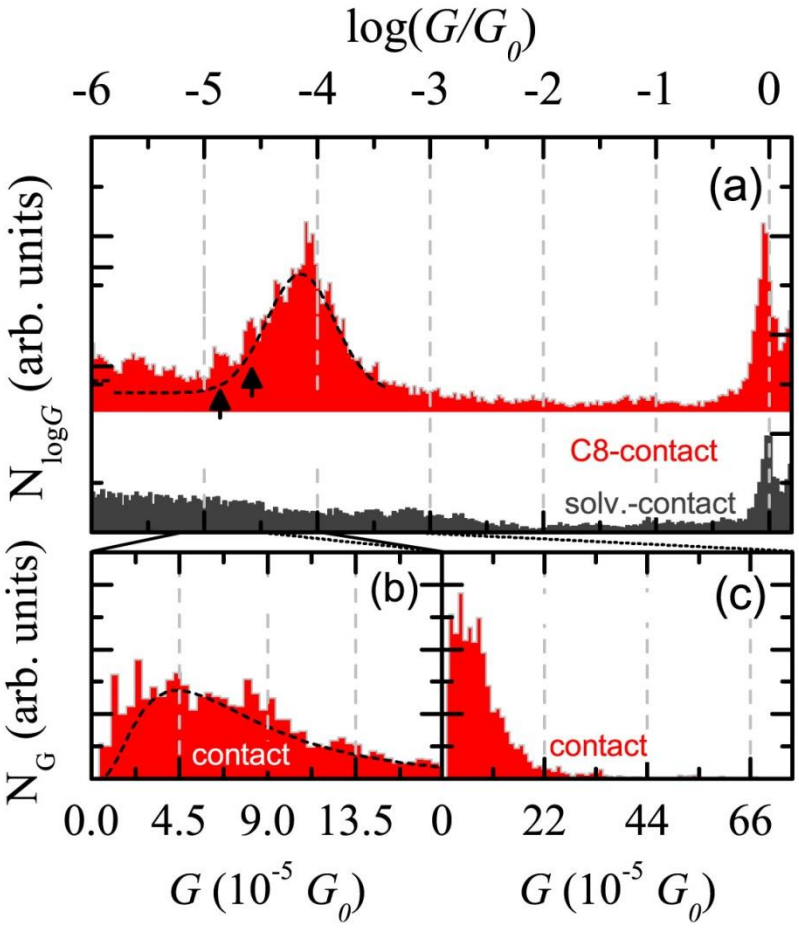


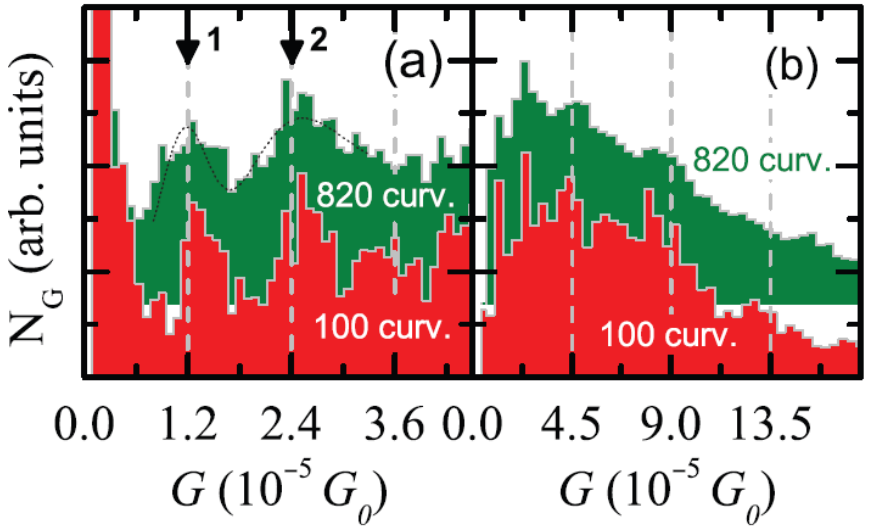
molecular signature:
plateau *(at $G \ll G_0$)*
⇔ ***peak in (log-G) histogram***

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

M.T. Gonzàlez et al., Nano Lett. (2006) & New J. Phys. (2008)

statistical analysis





Interpretation of peak shape in literature

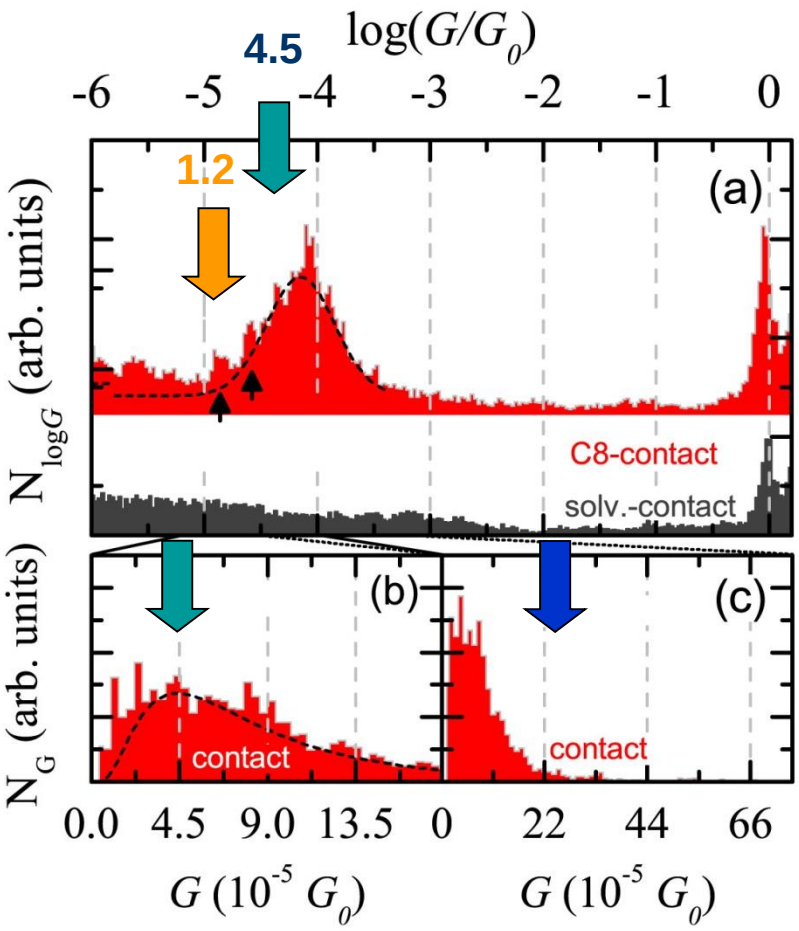
mean	single-molecule conductance
width	related to molecule-electrode adsorption chemistry
shape of peak	log-normal since tunnel process

Frisbie et al., JPC 2005, Brandbyge et al., NL 2009, R. Nichols et al., JPC 2009,

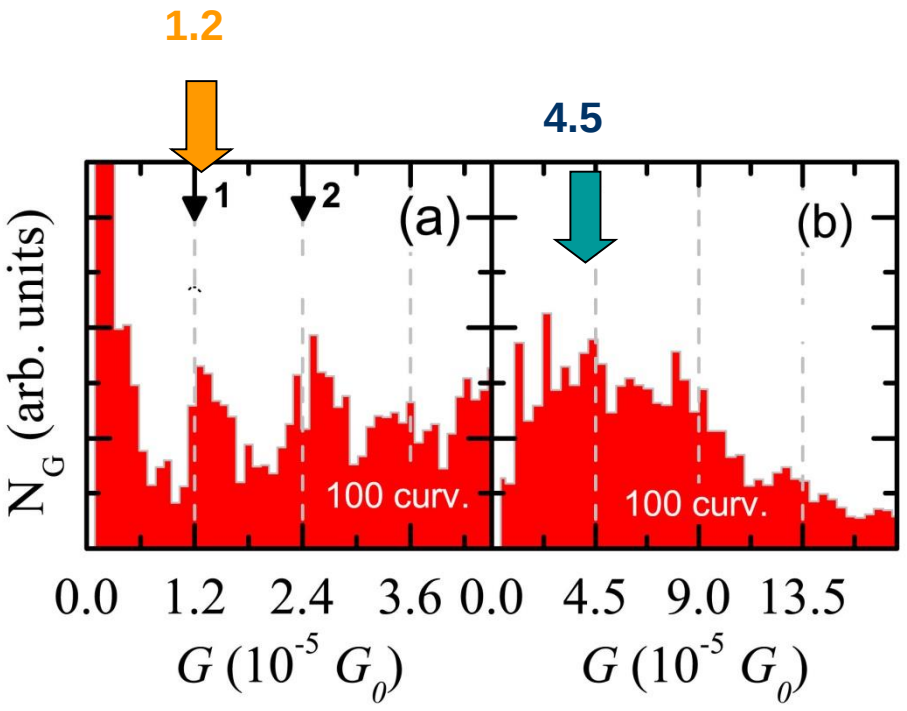
Reuter et al., NL 2012, JPC 2013 & 2015

T. Gonzàlez et al., New J. Phys. (2008)

statistical analysis

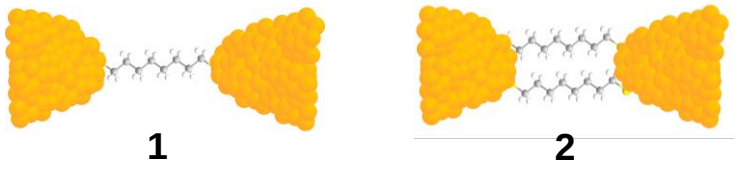


values at **1.2**, **4.5** and **25** 10^{-5} G_0



Interpretation of the different mean values

- anchoring geometry
- conformational states
- multiple bridges



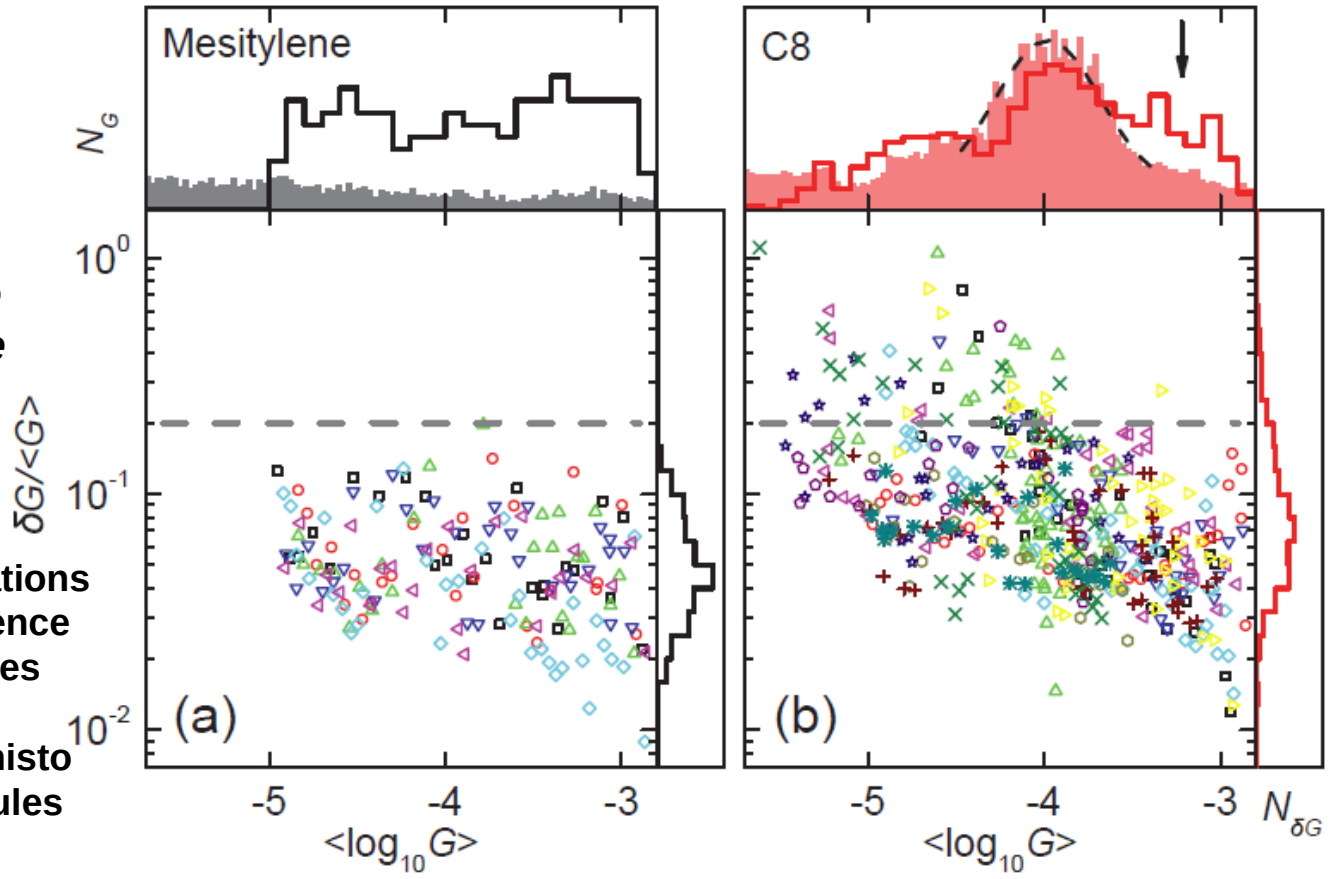
T. Gonzàlez et al., New J. Phys. (2008)

dynamical behavior & fluctuations: solvent + alkanedithiols

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

***outlined* histograms** from main panel data

relative conductance fluctuation amplitude



⇨**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.

understanding transport through molecules

Landauer approach to electron transport

Electronic transport as scattering problem

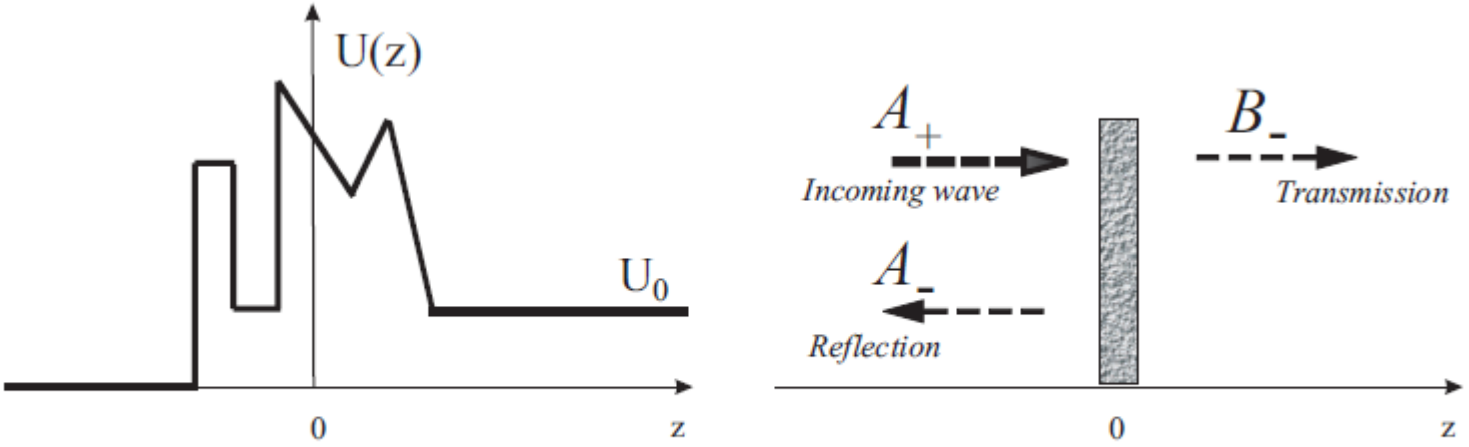
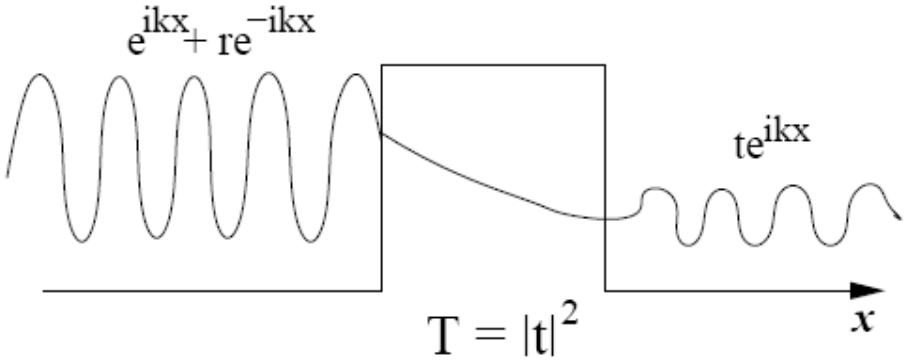


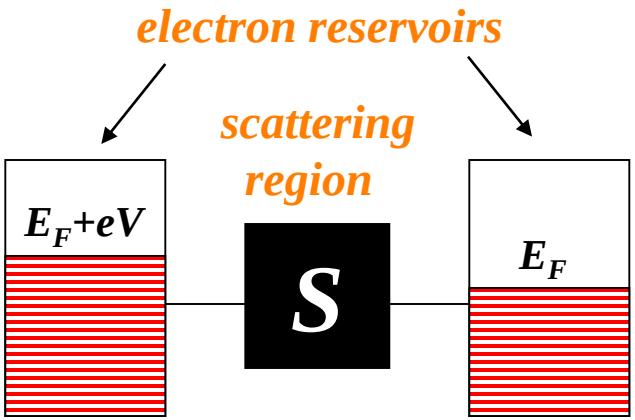
Fig. 1.2. One-dimensional potential. Reflection and transmission.

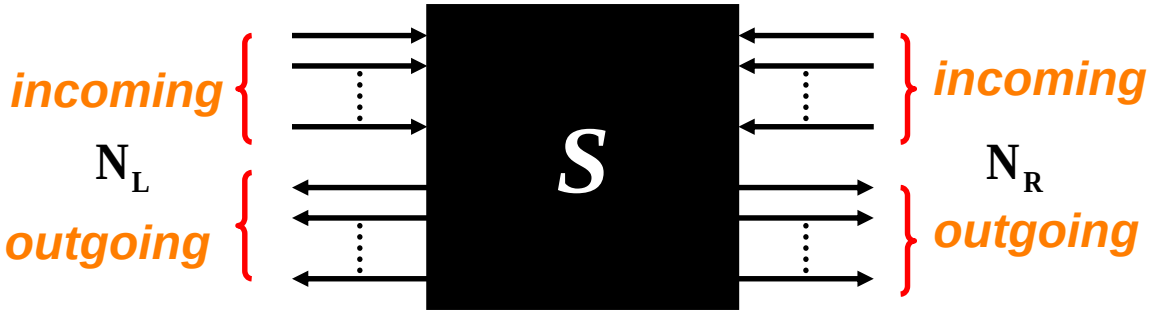
R. Landauer, IBM J. Res. Dev. 1, 223 (1957)

Landauer approach to electron transport

Electronic transport as scattering problem







$$G = \frac{2e^2}{h} T(E_F)$$

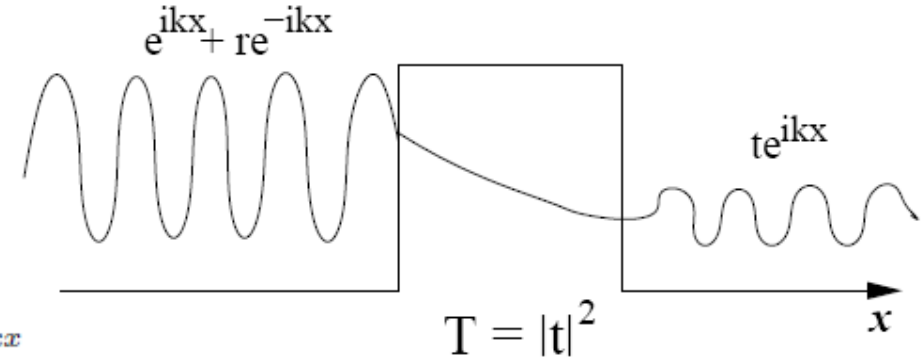
G = conductance
$T(E_F)$ = transmission at the Fermi energy

see Cuevas, Molecular Electronics, World Scientific

R. Landauer, IBM J. Res. Dev. 1, 223 (1957)

Landauer approach to electron transport

Electronic transport as scattering problem



one electron approach, 1D, phase coherent electrons in reservoir, thermal equilibrium plane waves (L: length of system): $(1/\sqrt{L})e^{ikx}$

electrical current density (calc. on right hand side of scattering potential) carried by one electron

$$J_k = \frac{\hbar}{2mi}\left[\psi^*(x)\frac{d\psi}{dx} - \psi(x)\frac{d\psi^*}{dx}\right] = \frac{e}{L}v(k)T(k) \qquad v(k) = \hbar k/m$$

group velocity

solid state device: sum over k (many electrons) and add Fermi distrib. for Left and Right reservoirs

$$J_{L\to R} = \frac{e}{L}\sum_k v(k)T(k)f_L(k)[1 - f_R(k)]$$

NB: Fermi func. account for shift of chemical potential upon applied bias voltage V

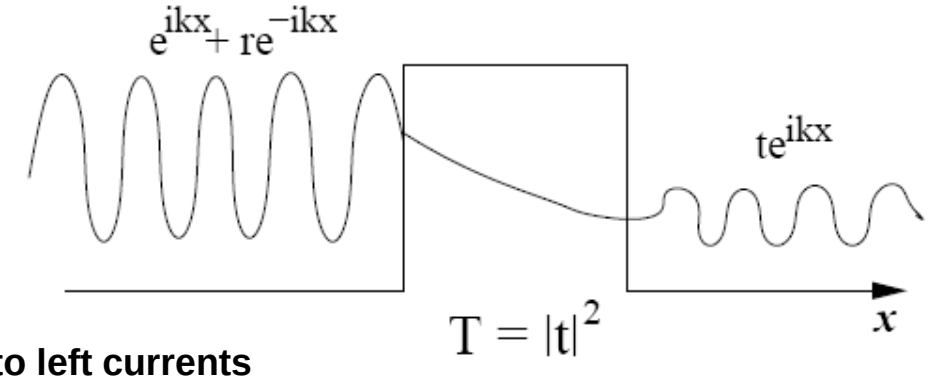
integrate $(1/L)\sum_k g(k) \to 1/(2\pi)\int g(k)dk$

variable change $dk/dE = (dE/dk)^{-1} = m/(\hbar^2 k)$ using $E = \hbar^2 k^2/(2m)$

conducting electrons: Fermi gas (non-interacting electrons)

Landauer approach to electron transport

Electronic transport as scattering problem



hence, we can write the **left to right** and **right to left currents**

NB: *the transmission probability is the same, no matter in which direction the barrier is crossed*

$$J_{L\to R} = \frac{e}{h}\int dE\, T(E) f_L(E)[1 - f_R(E)] \qquad J_{R\to L} = \frac{e}{h}\int dE\, T(E) f_R(E)[1 - f_L(E)]$$

total current through junction

NB: 1D situation: no difference between total current and current density

$$I(V) = J_{L\to R} - J_{R\to L}$$

spin →

$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, T(E)[f_L(E) - f_R(E)]$$

at low bias voltages (linear regime) and T=0

At T=0, $f_{L,R}(E)$ are step func. and

$$f_L(E) = 1 \text{ if } E < E_F + eV/2$$
$$f_R(E) = 1 \text{ if } E < E_F - eV/2$$

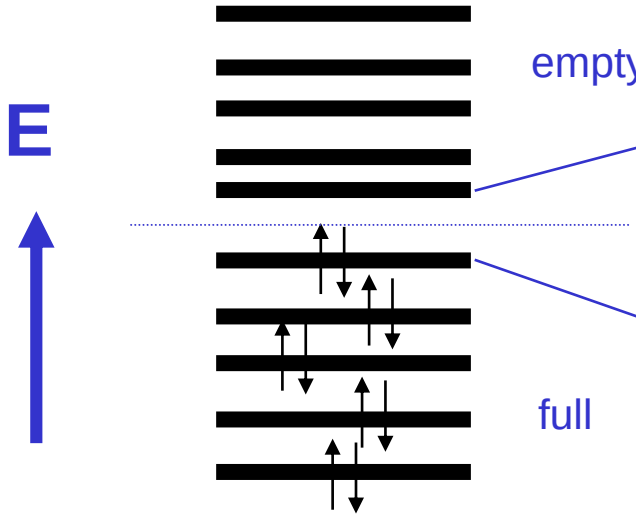
$$I = GV \quad \text{with} \quad G = (2e^2/h)T \qquad G_0 = \frac{2e^2}{h} \quad \text{conductance quantum}$$

and $T = T(E_F)$

$$G_0 \simeq (12.9k\Omega)^{-1}$$

molecular energy levels

(isolated) molecule
quantum system with spectrum of discrete energy states (molecular orbitals)



LUMO = lowest unoccupied molecular orbital

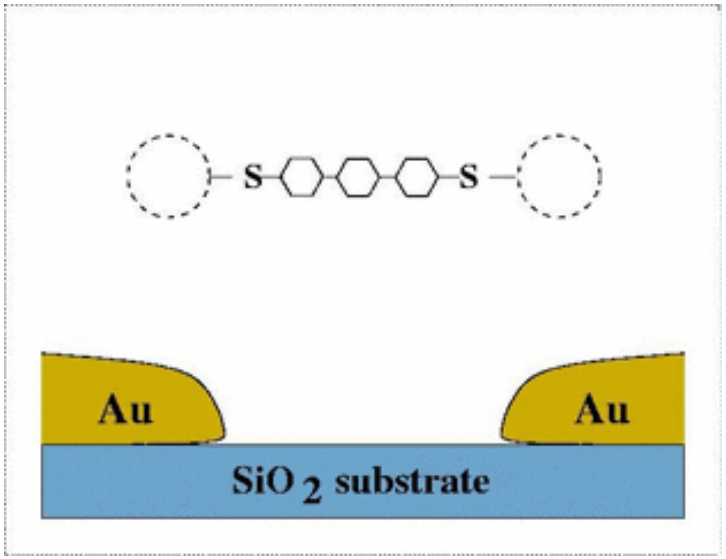
(HOMO-LUMO gap from light absorption)

HOMO = highest occupied molecular orbital

⇨ ‘Particle in a box’: molecule is small box

box smaller ⇔ levels more spaced ($\delta E > k_B T$)

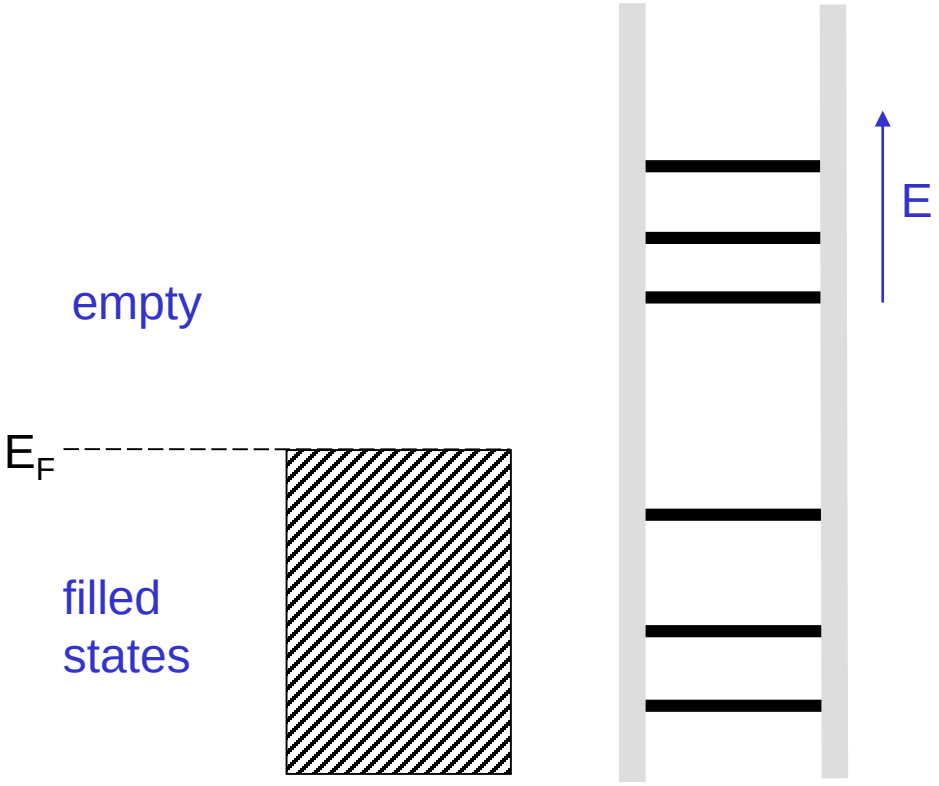
making contact…



Univ. Karlsruhe

Au: many levels: ~ continuous

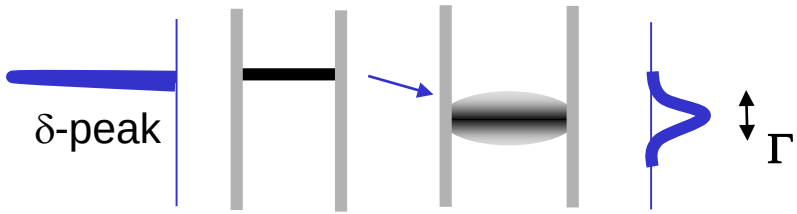
molecule: few discrete, levels



⇨ typ. 2 regimes: weak or strong coupling

"good" contact

energy levels



- **broadening**: Γ

  delta function

  ⇨ Lorentzian DOS

$$D(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_0)^2 + (\Gamma/2)^2}$$

$$\Gamma = \Gamma_L + \Gamma_R$$

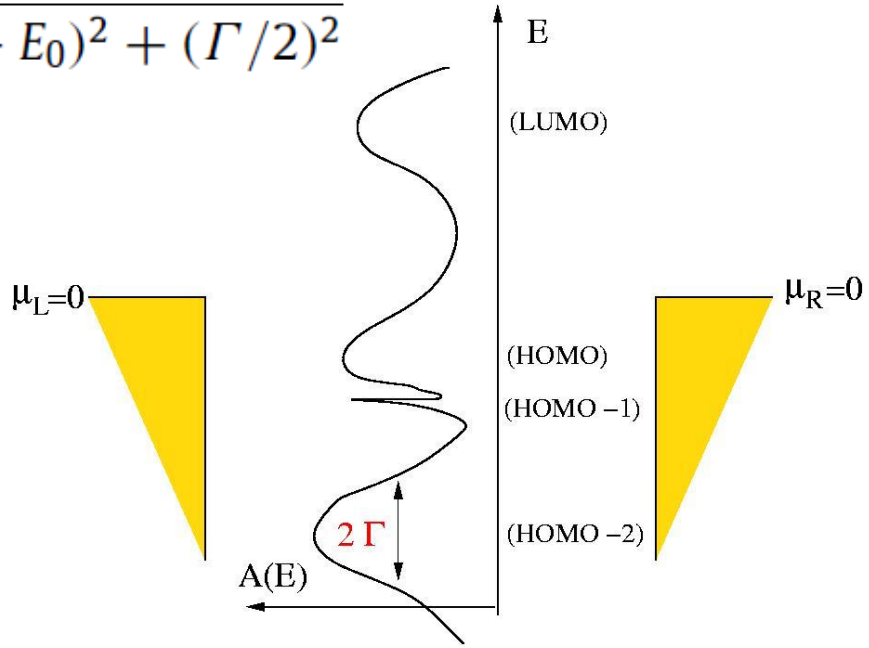
  relate Γ to typical resilience time τ:

  Heisenberg $\Delta E \, \Delta t > h$

  hence $\Gamma = h/\tau$

- **shift:** equil. ⇔ charge transfer

  typ. from electrode to molecule



"good" contact

current

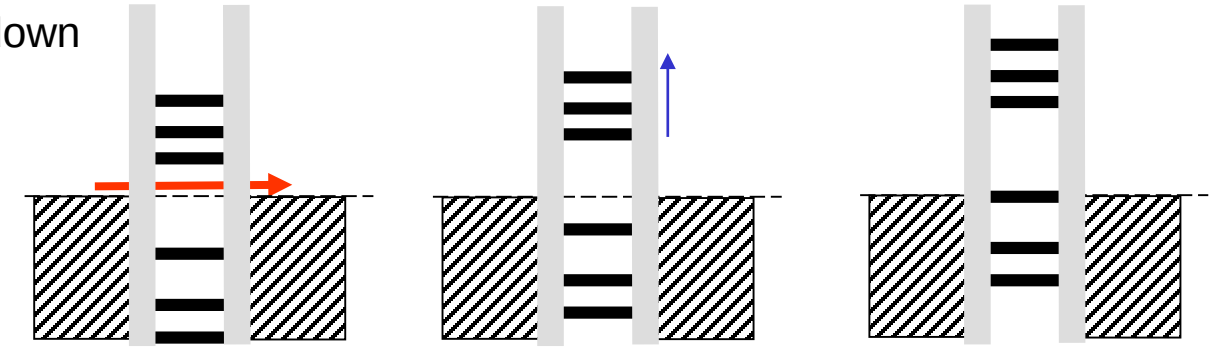
- **molecule seen as scatterer (Landauer)**
  ⇨ def. transmission function T(E)
  molecular orbitals ⇔ peaks in T(E)

$$I(E,V) = \frac{2e}{h} \int_{-\infty}^{\infty} \overline{T}(E,V)[f(E-\mu_2)-f(E-\mu_1)]dE$$

current ~ transmission probability x nb of states

- **at low bias:**
  E_F in HOMO-LUMO gap**, I and G=U/I small**

- **gating:** moving levels up/down

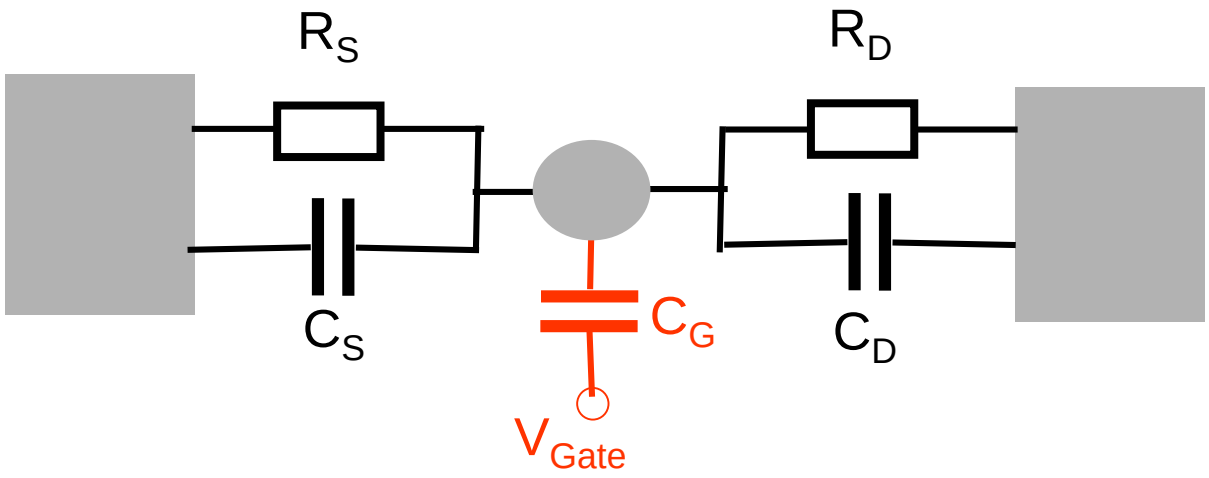


'Tunneling', small G

Level lines up, G ⇗

"bad" contact ⇨ capacitance

Equivalent circuit, **R large, C small**

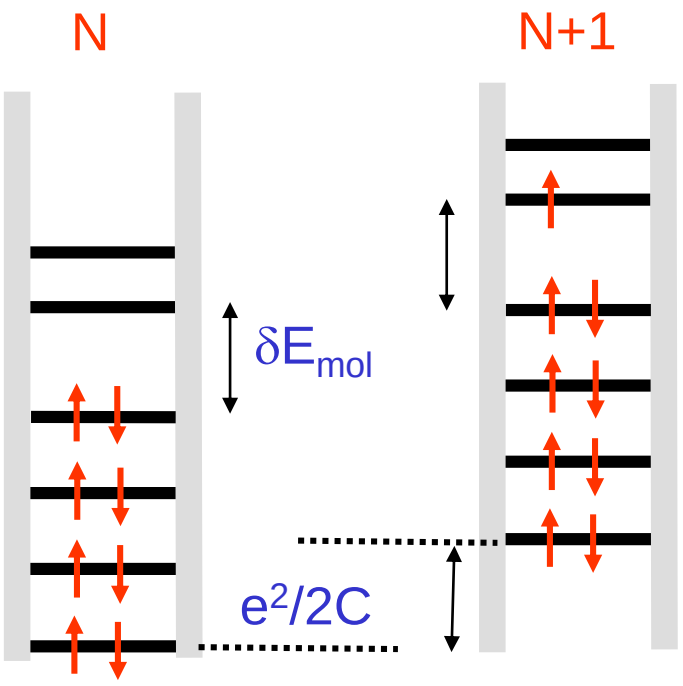


1. Residence time e^- : $\Delta t = R_t C$
2. Charging energy e^-: $E_C = e^2/2C$

Coulomb Blockade

If $E_C = e^2/2C \gg k_B T$

Then: Charging by one electron changes **all** energy levels!



Transport only if

$eV > \delta E_{mol} + \mathbf{e^2/2C}$

'Coulomb blockade'

contacts

too weak coupling: like semiconductors qdots

"boring" for molecular electronics…

rather work with a GaAs structure, more stable and reproducible

too strong coupling: loose molecular signature

… "boring" again!

⇨ **control coupling to preserve integrity of molecular orbitals**
in particular for **active** devices (otherwise, loss of functionality)