UNI BASEL

SWISS NANOSCIENCE INSTITUTE
EINE INITIATIVE DER UNIVERSITÄT BASEL UND DES KANTONS AARGAU

*Molecular and carbon-based electronic systems*

# ***Lecture 5***
# ***Molecular junctions basics***

**Vorlesung Uni Basel, HS2017**

- single molecule electronics

- atomic contacts and conductance quantization

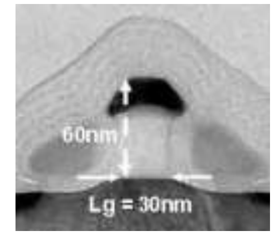
- contacting individual molecules : mechanically controllable break junctions
  - formation mechanisms:  fluctuations, conductance plateaus
  - understanding transport through junctions: Landauer  approach
  - conjugated compounds

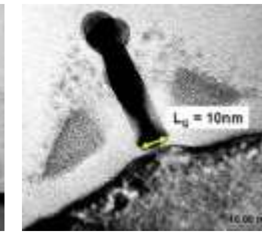
- examples of spectroscopy in molecular junctions
  - current-voltage characteristics
  - conducting AFM

- outlook

# context

Bardeen,
Brattain,
Shockley



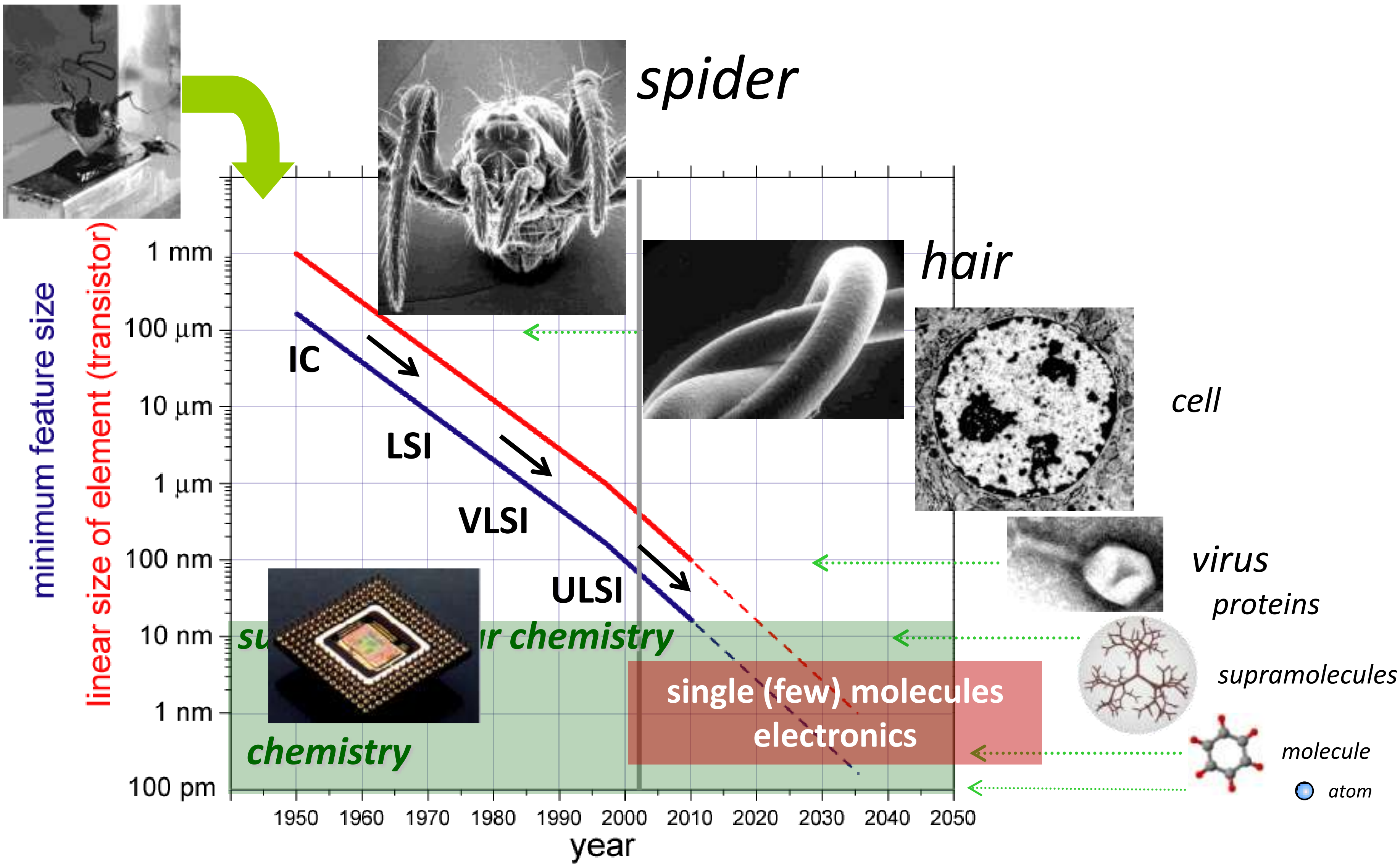

**1947 … today**



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

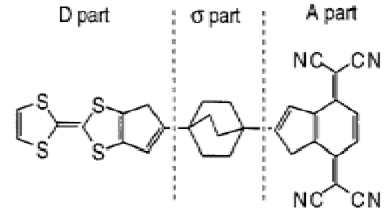
***(Volume reduced by $10^{12}$)***

# *Molecular and carbon-based electronic systems*



**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 aromatic crystal and show a p-electron conductivity down the axis*."

"*...if it should prove possible to measure a single fiber*…"

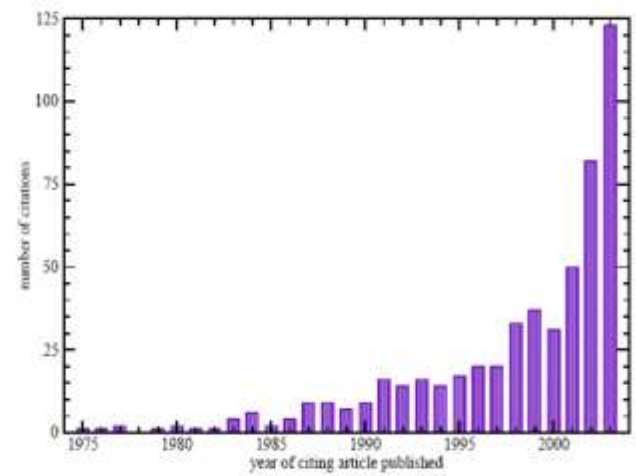
**1970s** B. Mann and H. Kuhn *(J. Appl. Phys., Oct. 1971)*

1st reproducible transport meas. through organic layers

A. Aviram, M. A. Ratner: **molecular rectifier** (theory)

*Chemical Physics Letters 29 (2), Nov.1974*

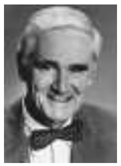
from molecular conduction to ***molecular electronics***




**nb citations of Aviram, Ratner paper**

# exponential development 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

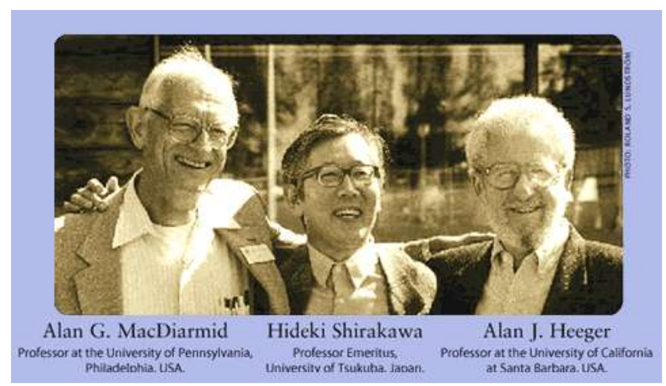
## The Nobel Prize in Chemistry 1996
"for the discovery of fullerenes"


Robert F. Curl Jr.


Sir Harold W. Kroto


Richard E. Smalley

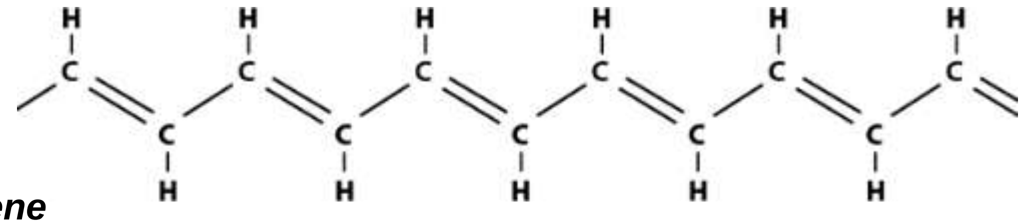
## The Nobel Prize in Chemistry 2000
"for the discovery and development of conductive polymers"

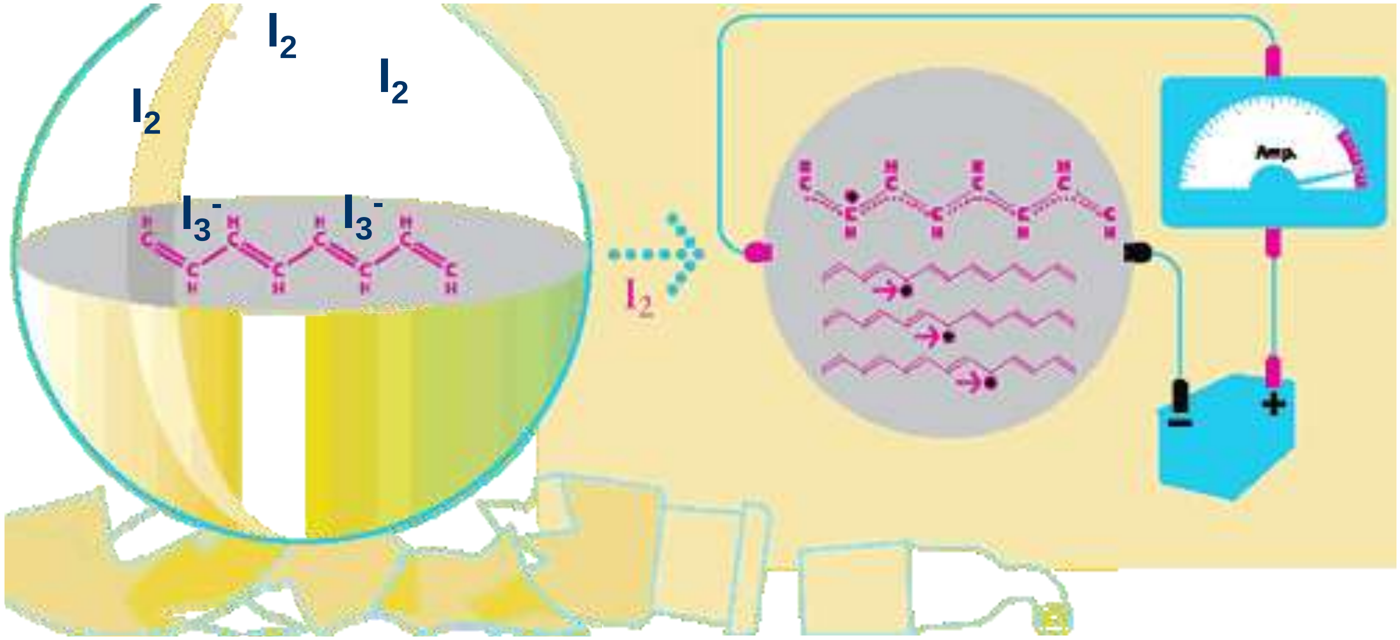



## The Nobel Prize in Chemistry 1992
"for for his contributions to the theory of electron transfer reactions in chemical systems "


Rudolph A. Marcus

# conducting polymers

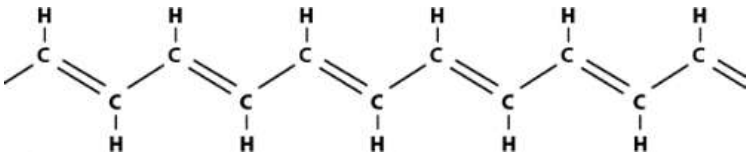


# conducting polymers

**linear chain of atoms**
(free electron model)

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

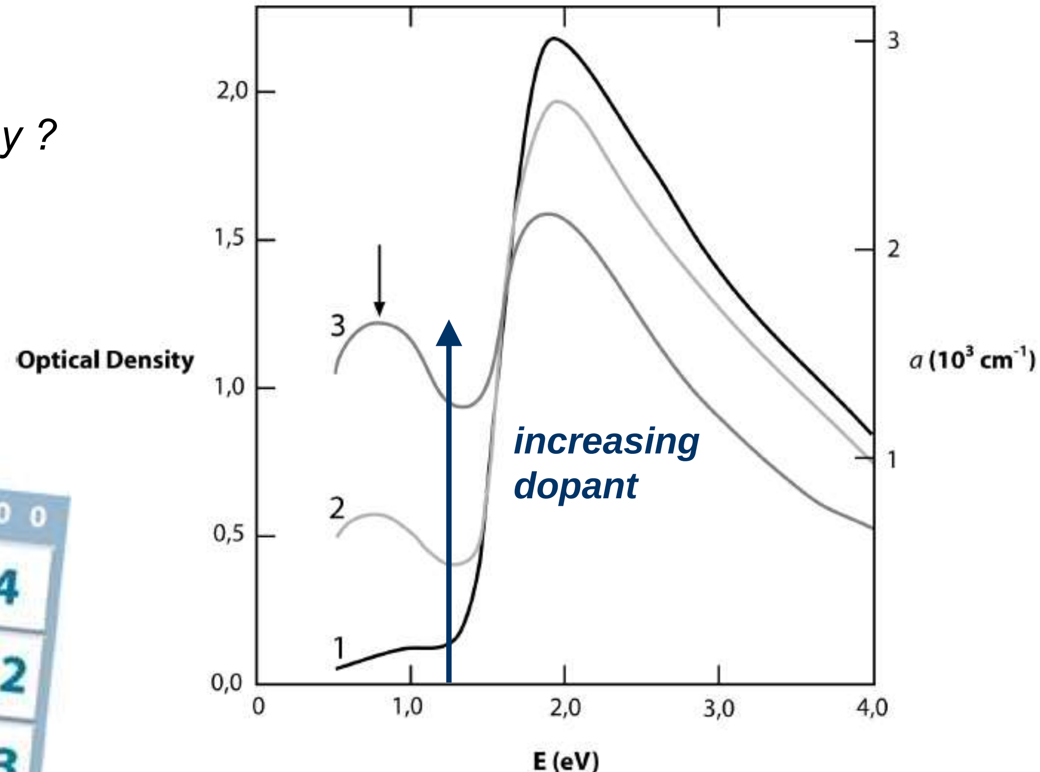


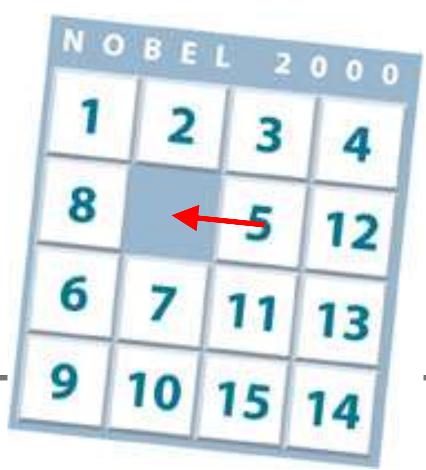
***⇨ vanishing gap for N large***

*- pure polyacetyle: insulating*
*- doped polyacetylene: conducting… why ?*

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

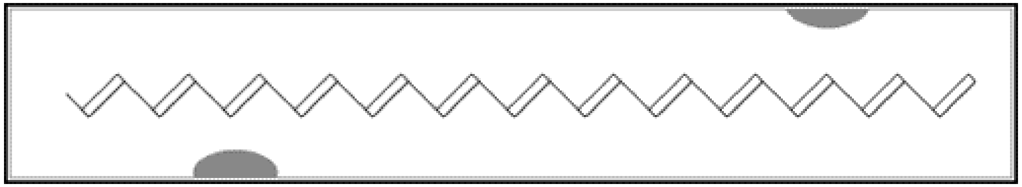
*- dopant: mid-gap states, hole transport*

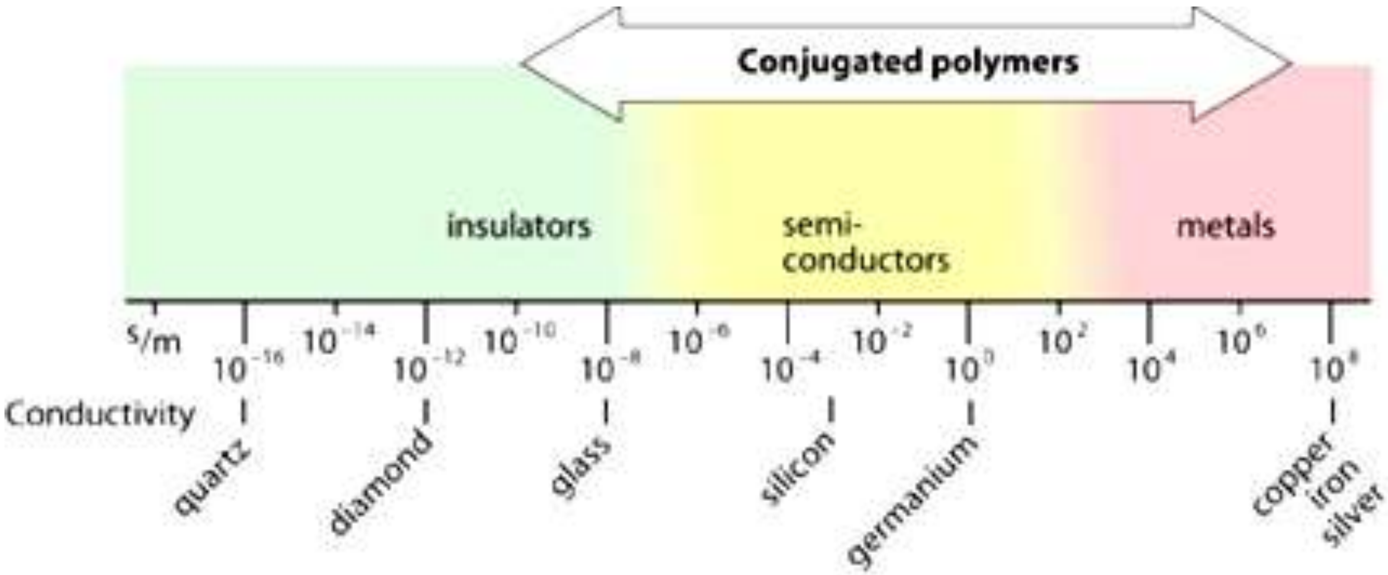


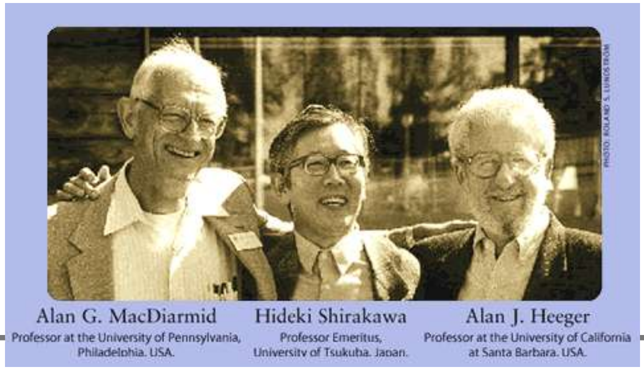

***nobelprize.org***

# conducting polymers

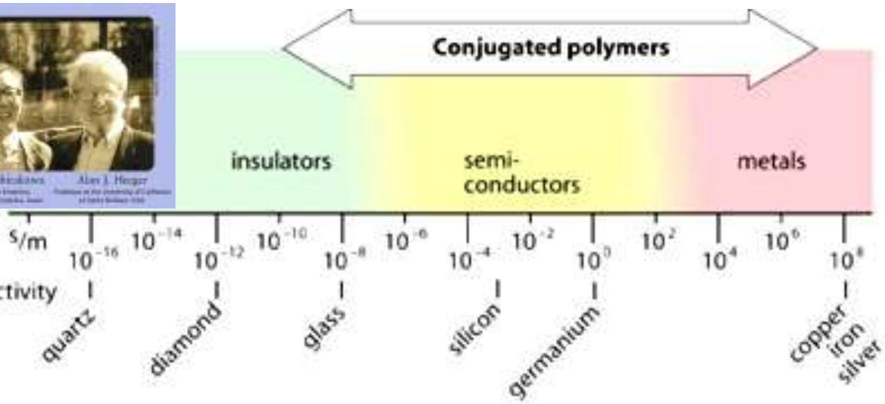





**Nobel 2000**
(chimie)



*Nobel 2000*

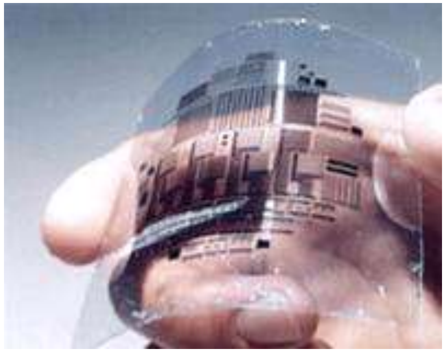


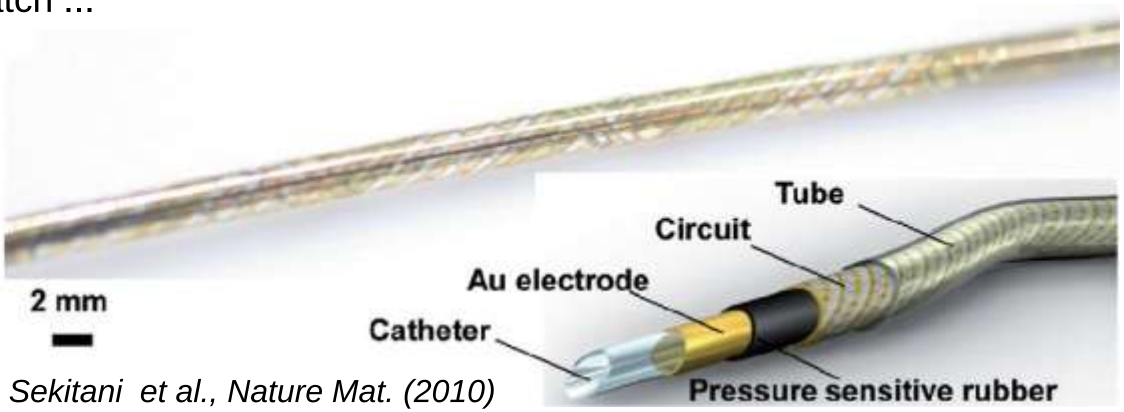

**TV display**
**40” OLED**
*(EPSON, 2004)*

***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)*

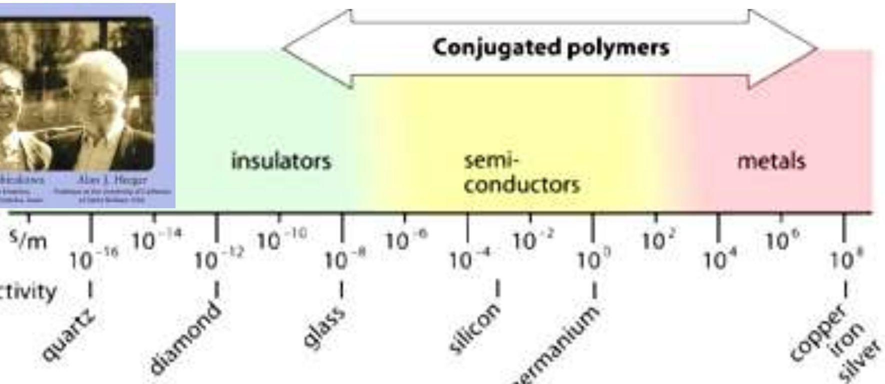


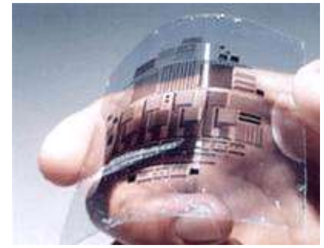



*Sekitani et al., Nature Mat. (2010)*

# context

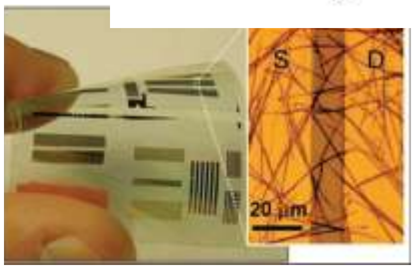

***Nobel 2000***



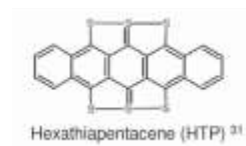



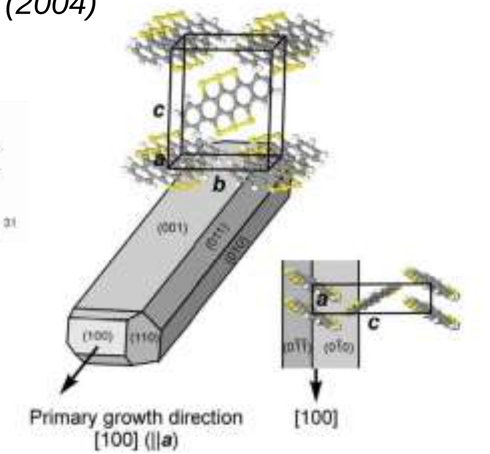
**Low-cost organic electronics on plastic**
*Forrest, Nature (2004)*

**TV display, 40" OLED**
*(EPSON, 2004)*

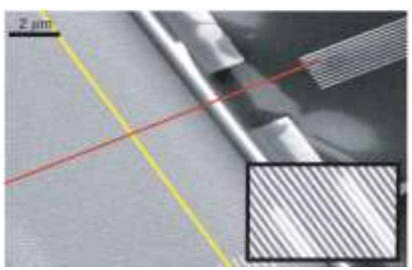



***molecular crystals***
*(π-stacking)*

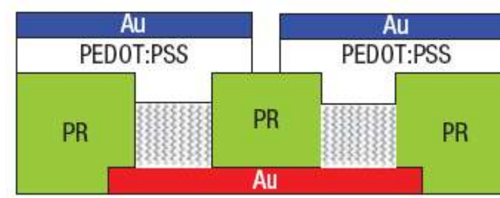

**Organic nanowire transistors**
***Mat. Today (2008)***




***molecular mono-layers***
*(self-assembly)*

**160kb crossed-wire memory**
***Heat et al., Nature (2007)***

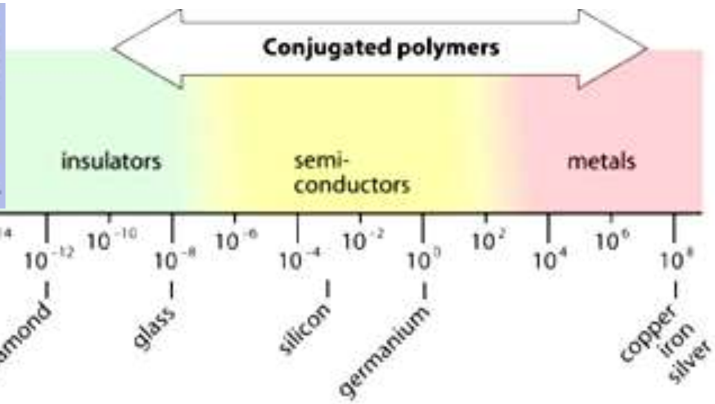
**Organic ICs based on self-assembly (SAMFETs)**
***de Boer et al., Nature (2008)***

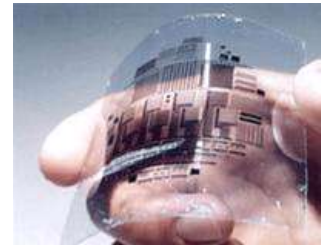



**Large scale integr. of molecular junctions**
***de Leeuw et al., Nature Nano (2008)***

# context

*Nobel 2000*



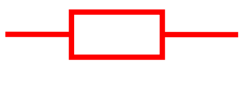



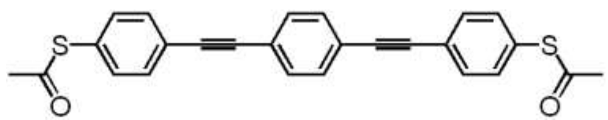
**Low-cost organic electronics on plastic**
*Forrest, Nature (2004)*

**TV display, 40” OLED**
*(EPSON, 2004)*

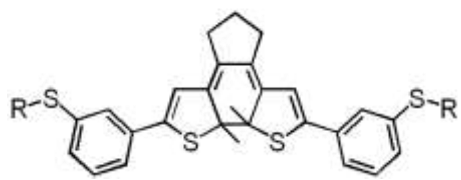
**⇨ at the level of a few or even a single molecule ?**

***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)

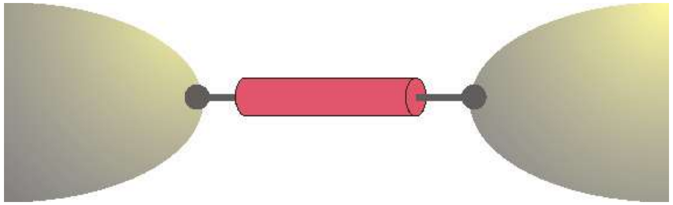
  **stereochemistry** (distinct stable geometric structures – isomers), **mechanical flexibility** (rotation axis), **photochemistry** (photochromism), **electrochemistry** (redox reactions)
  **(self-)assembly** (building of structures) and **molecular recognition** (switching, sensing)

-

- 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**

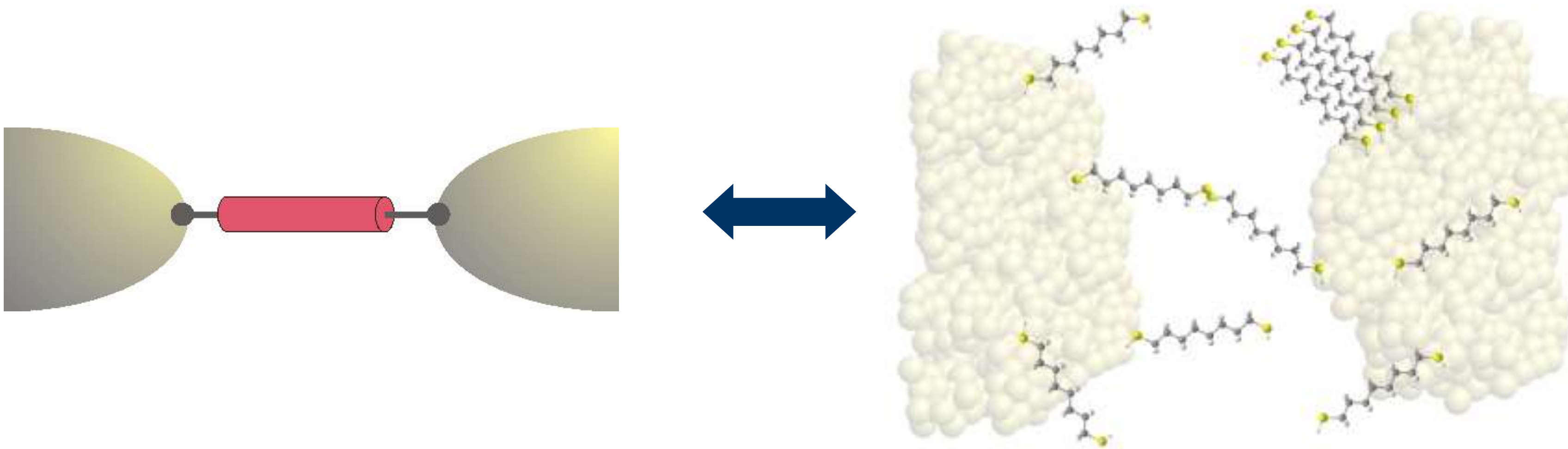
***fundamental aspects***

- electro-mechanical properties
  *(e.g.: atomic, molecular switch)*
- transport at $\mu$s, 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



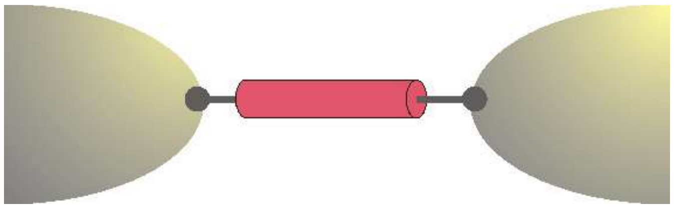
**nanometer and molecular-scale junctions**

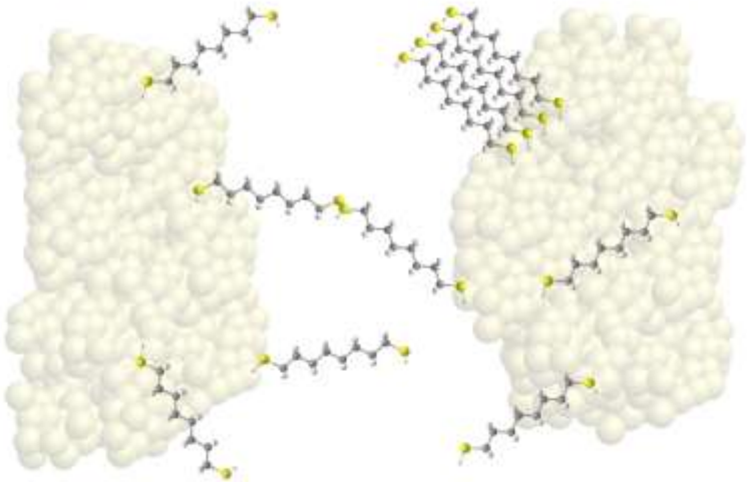
| | |
|---|---|
| - structural disorder | *electrodes and junction geometry* |
| - interactions | *anchoring*, *self-assembly, polymerization* |
| - fluctuations | *mobility of (surface) atoms, molecular distortions, multiple local energy minima* |

**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





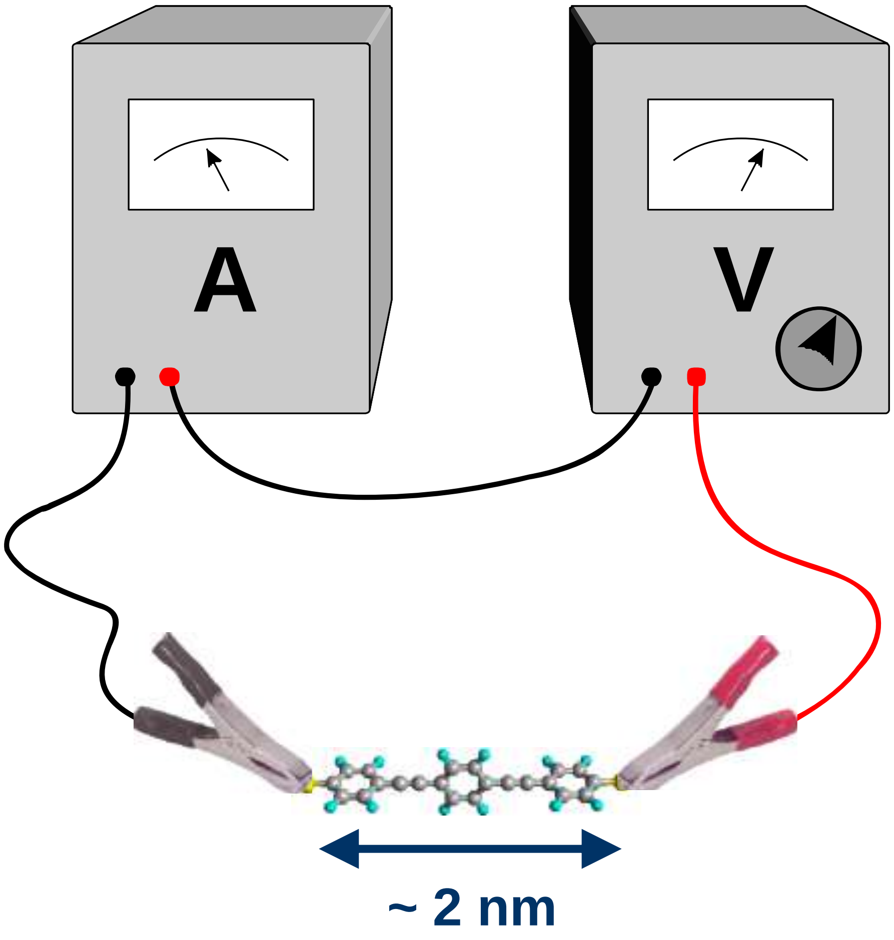
**nanometer and molecular-scale junctions**

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

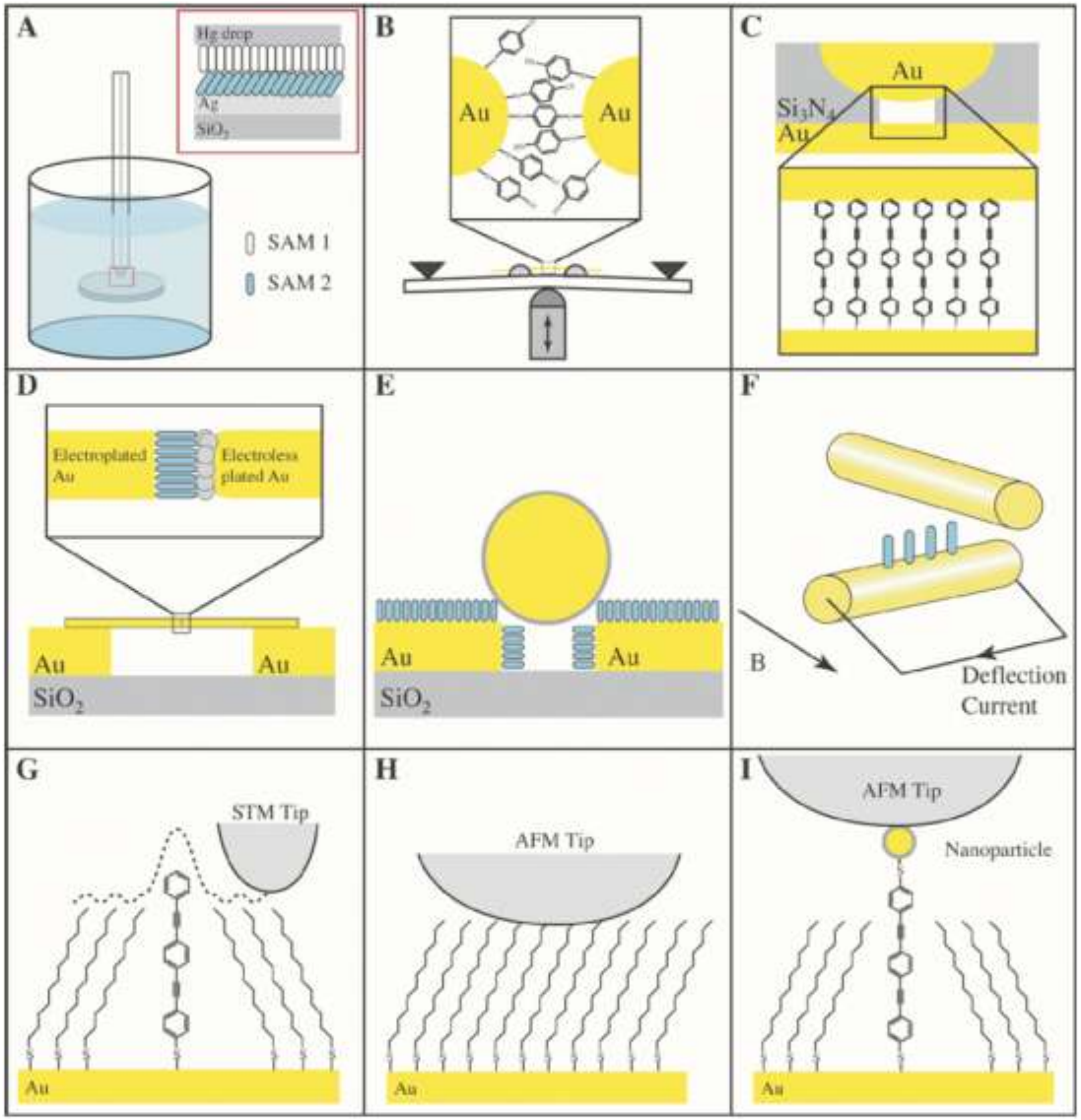
⇨ **junction formation** (and breaking up)**: dynamic process, variability**

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

# contacting a molecule



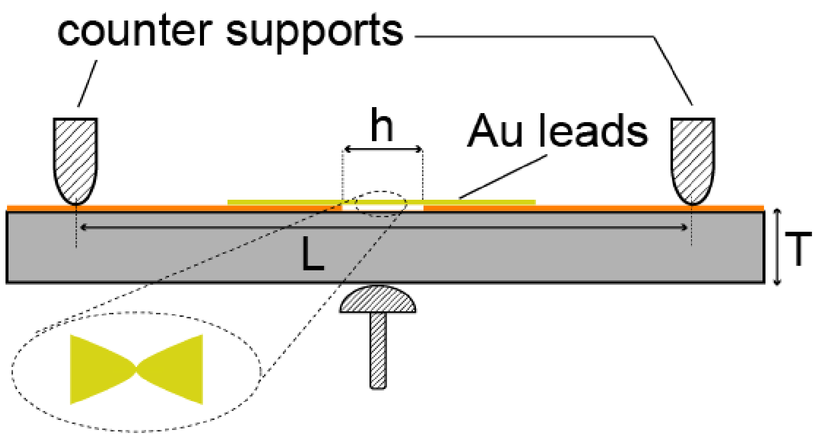
# contacting a molecule: exp. techniques

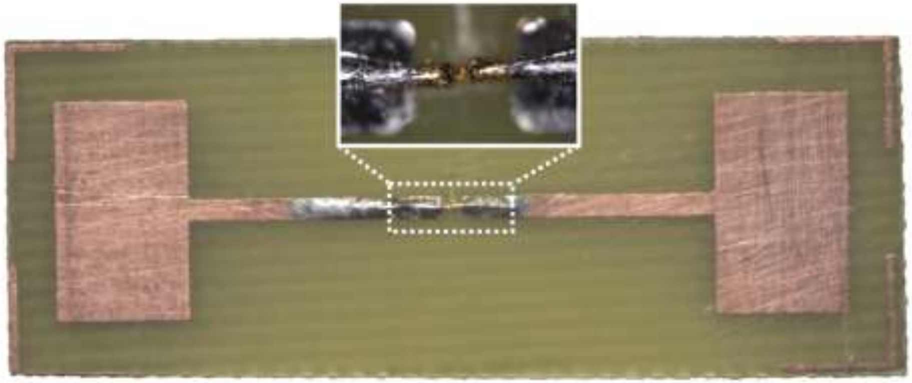



***Mantooth, Weiss., Proc. IEEE, 2003***

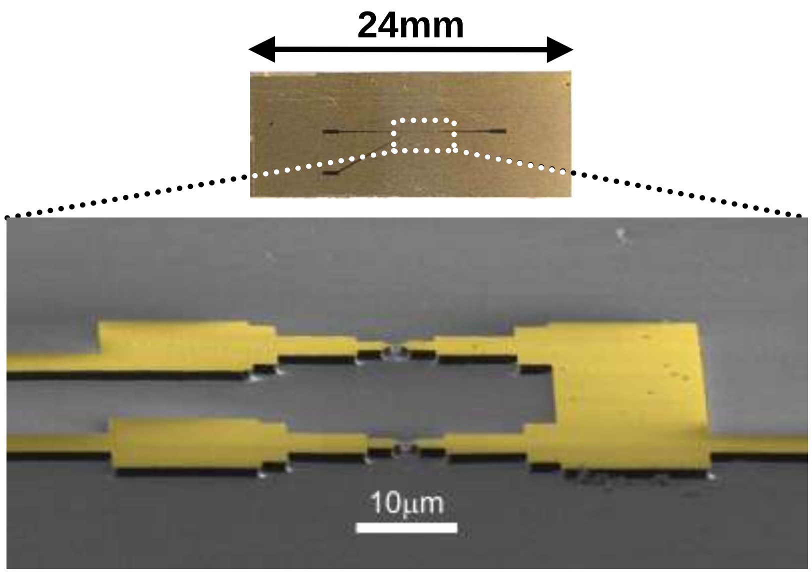
# forming atomic contacts

# **break junctions:** forming atomic contacts

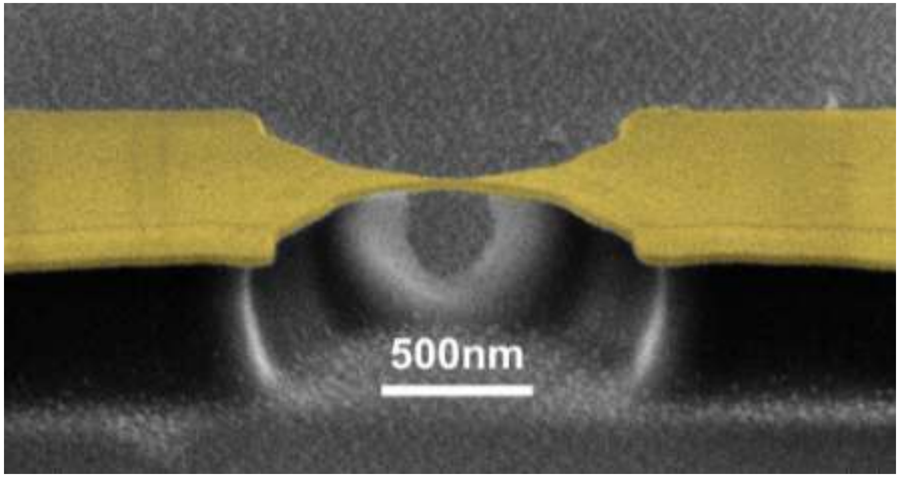


*hand-made notched Au wire*



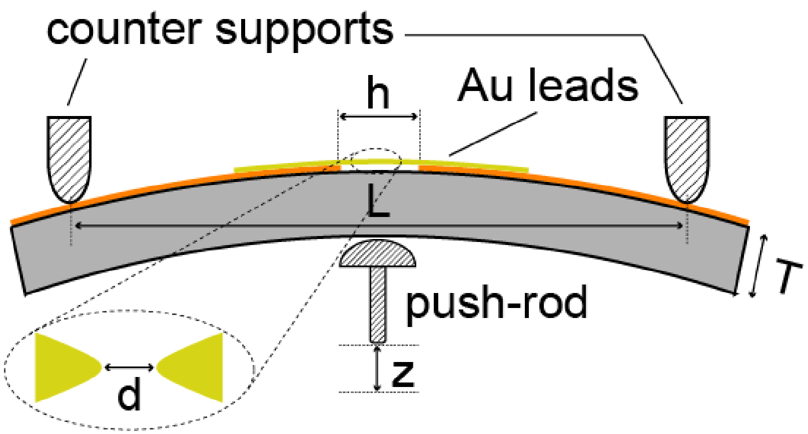

*e-beam fabricated Au bridges*

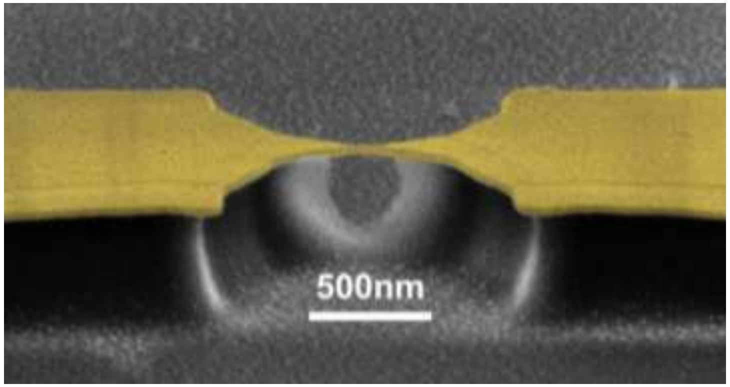


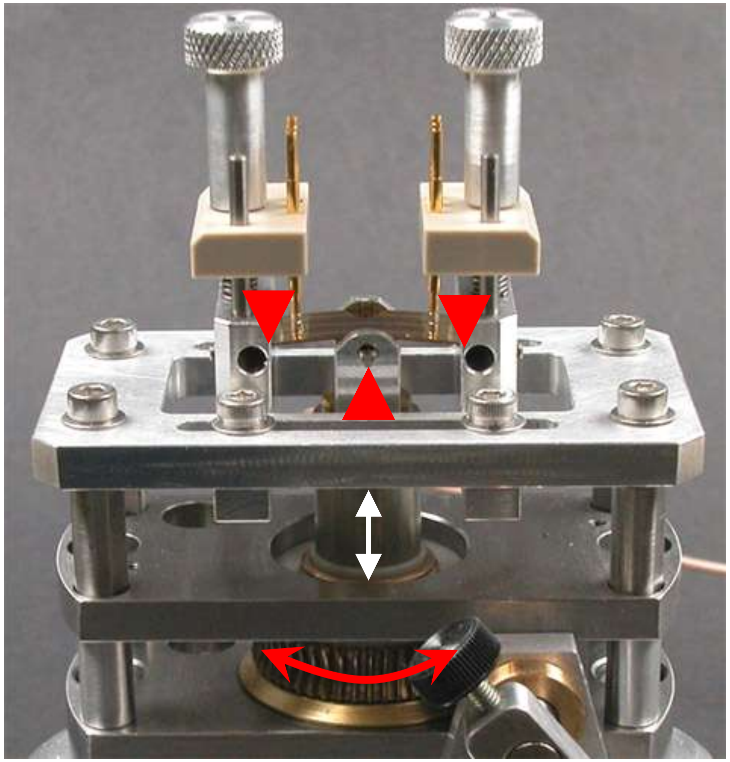

*Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)*

# break junction: a draw bridge at the atomic scale

# break junctions



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

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

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

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

⇨ **0.5 - 1.2 nm/s**

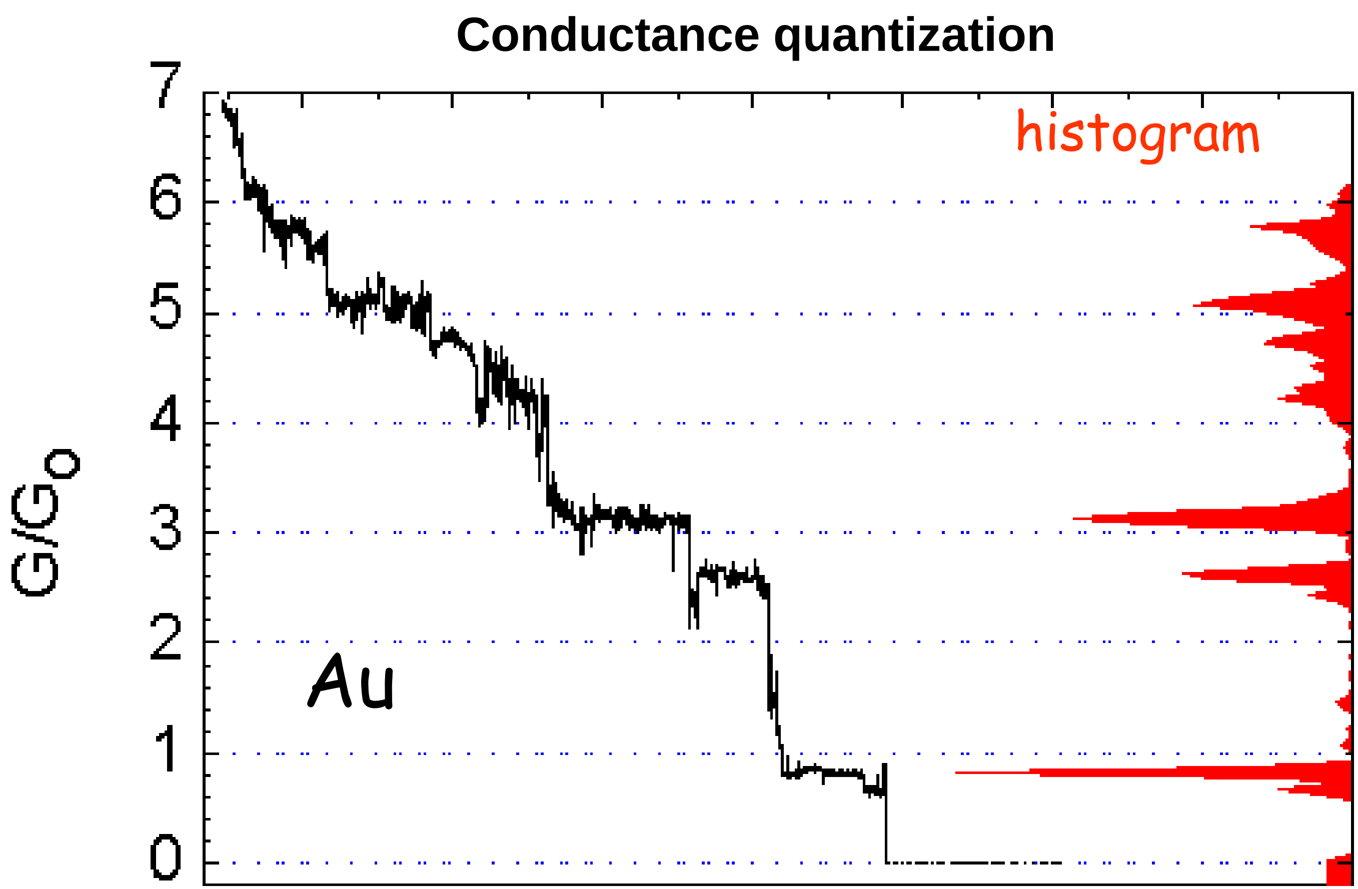
***electrodes separation speed***

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

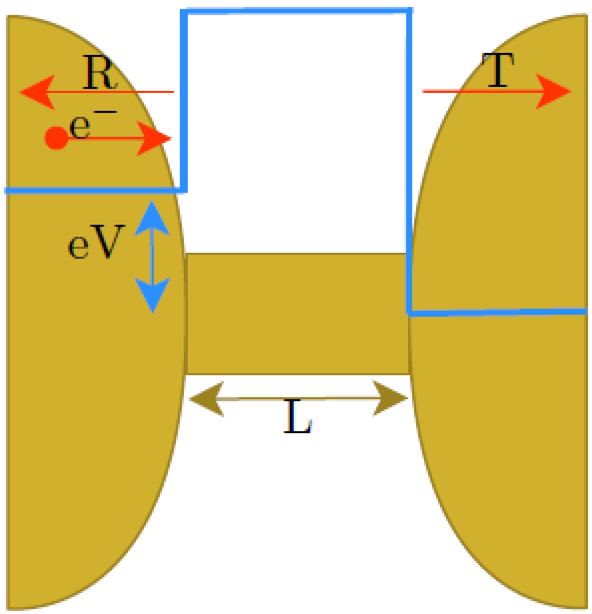
*Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)*

# break junctions

closed ⇨ open: contact to tunneling



# conductance quantization




$\ell > L$ ballistic regime

Fermi wavelength (Au) $\lambda_F \approx 5.2\mathring{A}$

*GaAs: 200nm*

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

*GaAs: ≈ 1meV*

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

*Landauer, 1957*
*Landauer, Büttiker*

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

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

conductance of a quantum coherent structure accommodating N channels

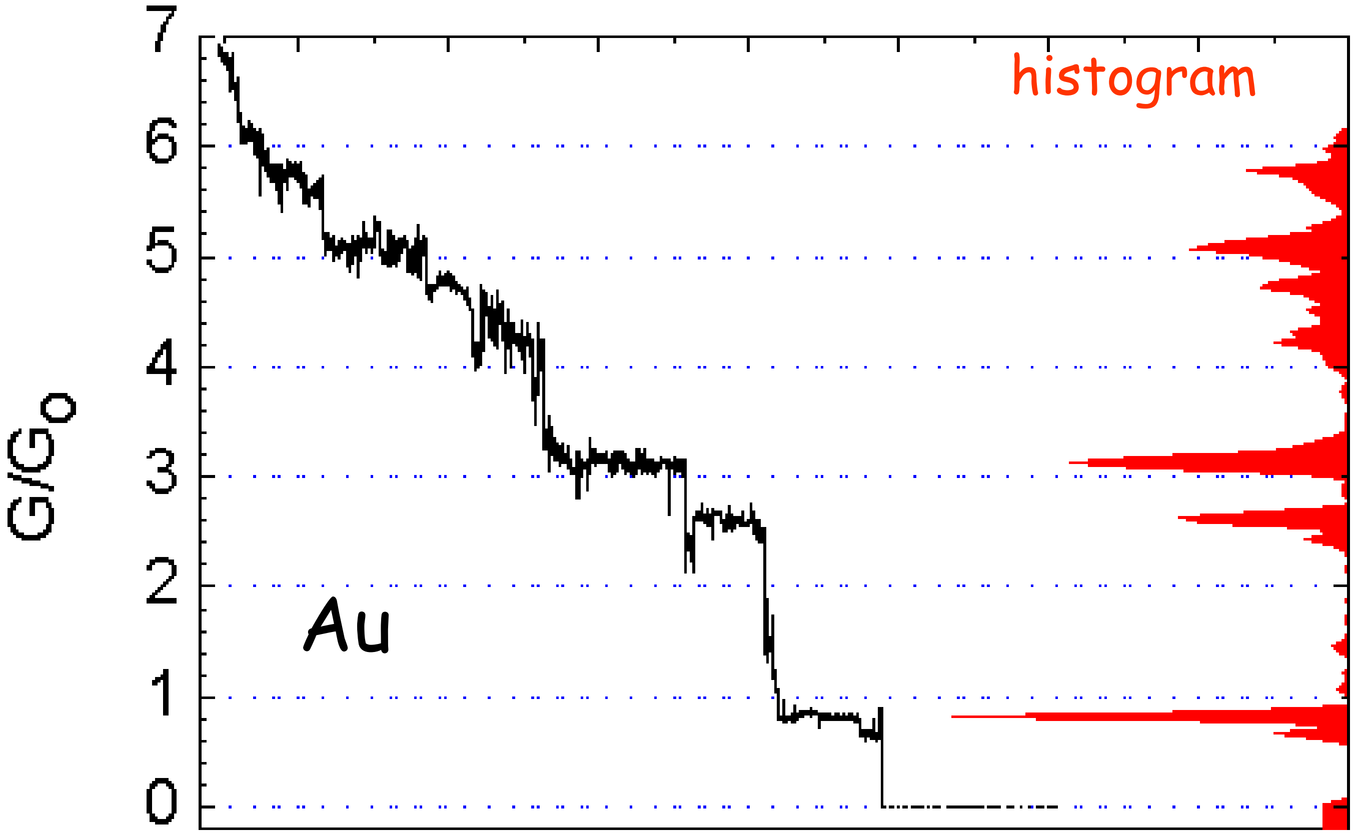
*Tn: transmission probability through channel n*

***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

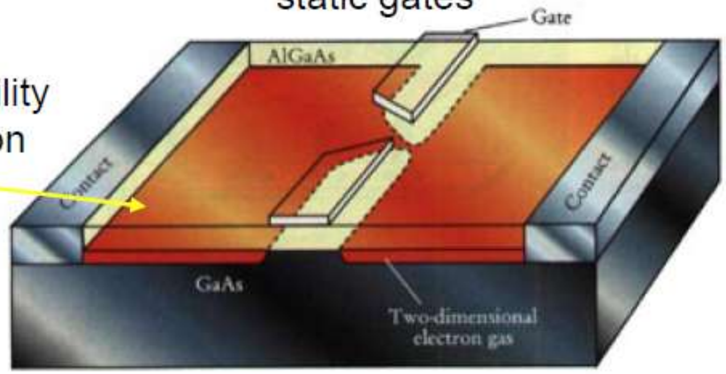


# conductance quantization: 2DEG systems

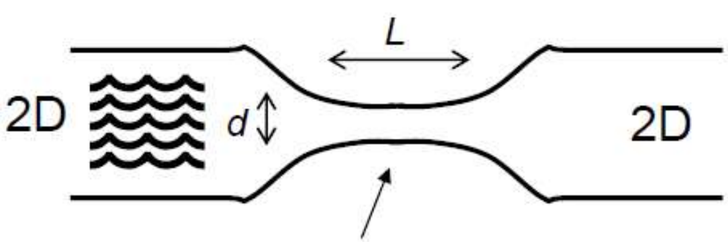
$$G(E_F) = \frac{2e^2}{h} \sum_n T_n(E_F) \approx \frac{2e^2}{h} N(E_F) \; (T = 0\mathrm{K})$$

Depletion by electro-
static gates

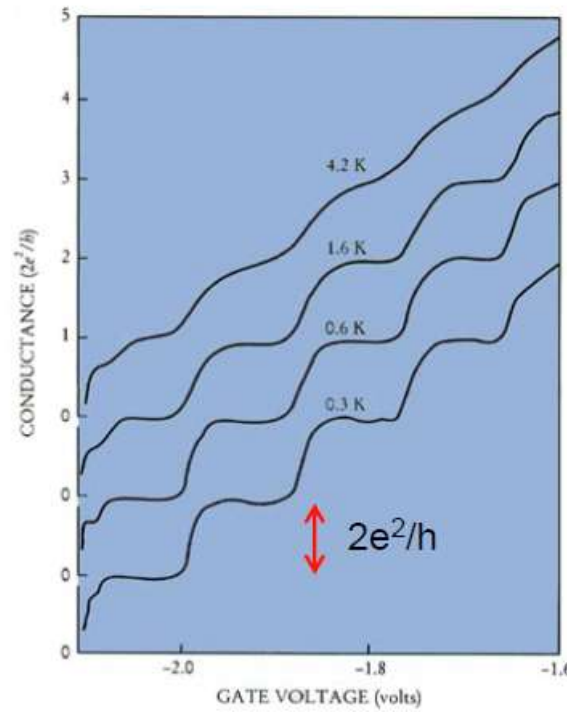
High mobility
2D electron
gas
('ballistic')




**'Quantum Point Contact'**

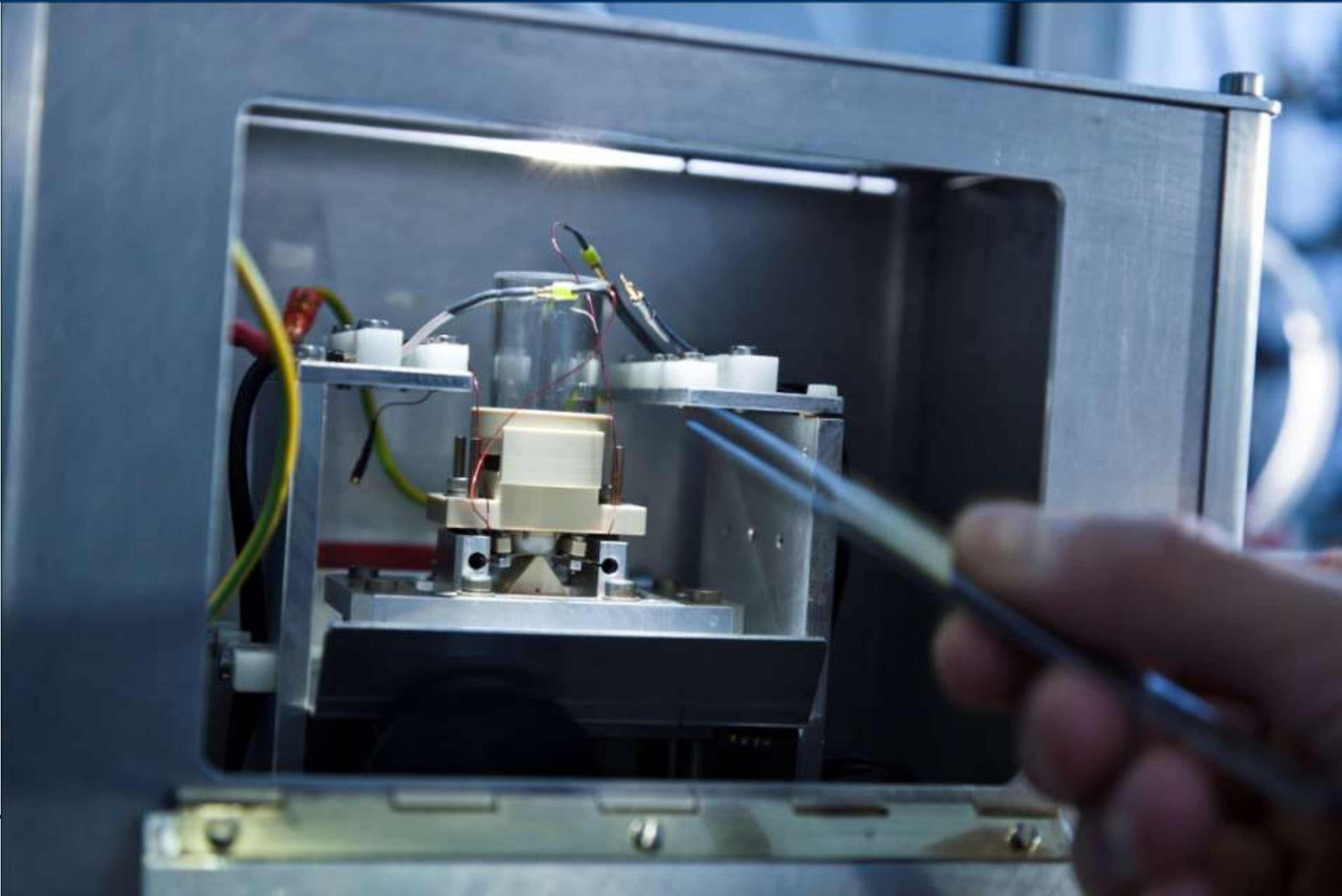



Narrow constriction; quasi-1D
(width $d$ ~ Fermi wavelength $\lambda_F$)



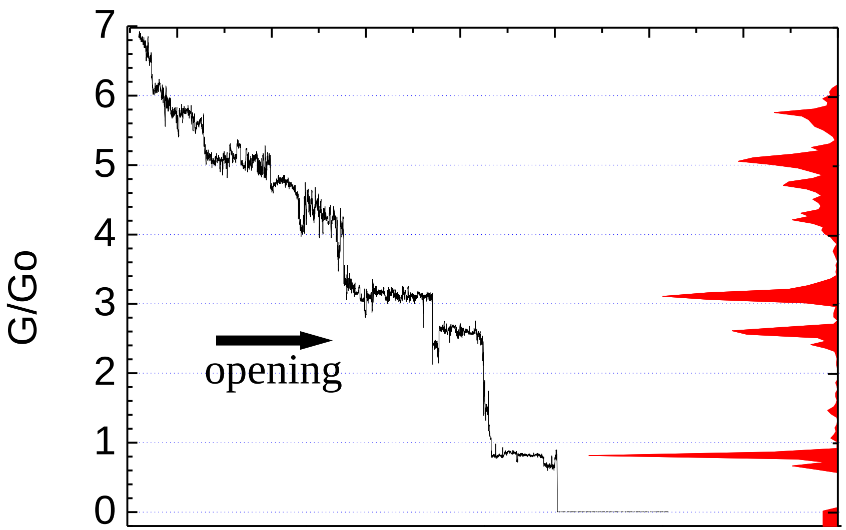

Limited conductance $2e^2/h$
even without scattering,
regardless of length $L$:
"contact resistance"

# break junctions in liquid environment



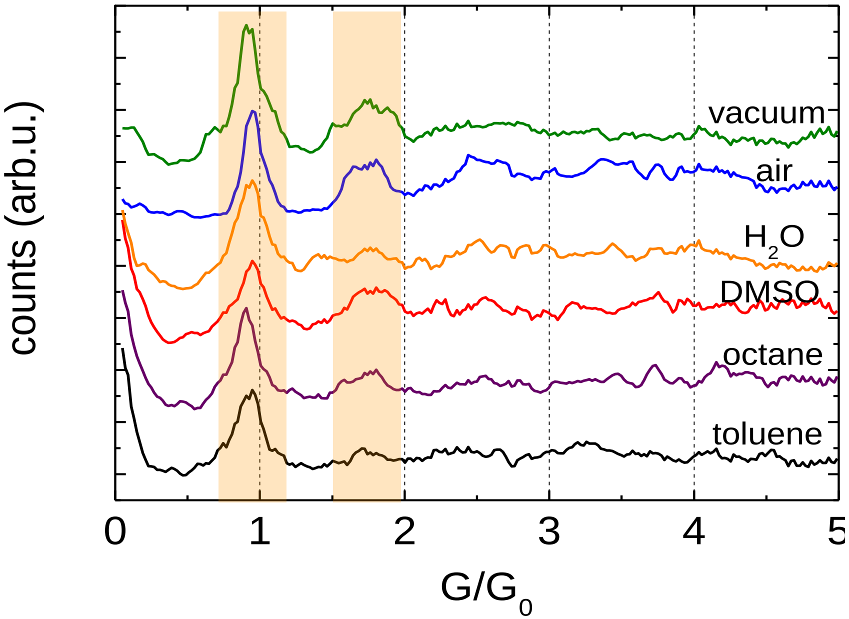
# “high” conductance regime

conductance histogram (counts)



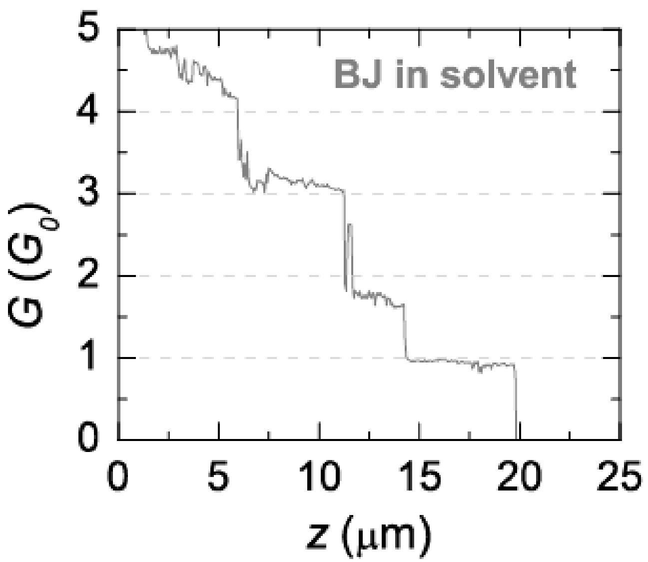

$G \geq G_0 = 2e^2/h$

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




*no significant differences between enviroments*

# **opening**: conductance vs elongation

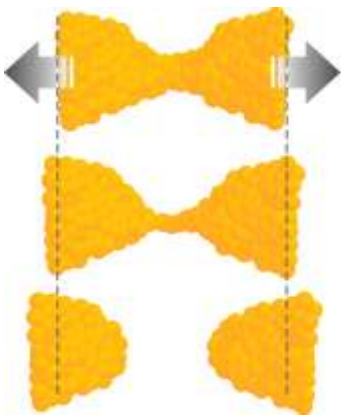


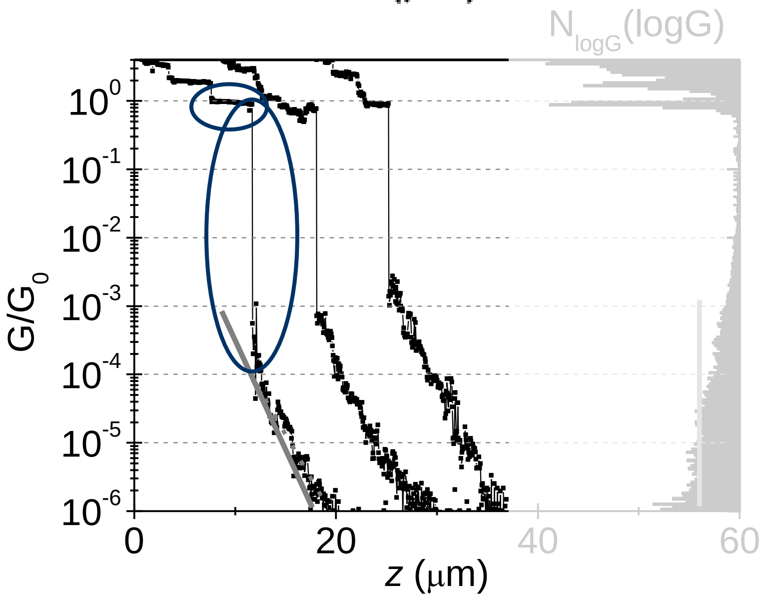

***break junction opening***
***(solvent:THF/mesitylene 1:4 v/v)***

conductance quantization, plateaus

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

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

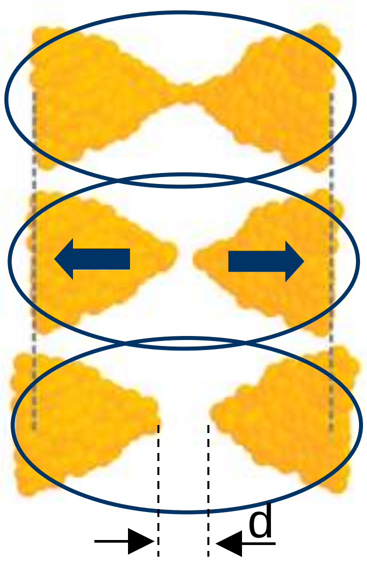





- last Au G-plateau (~$1G_0$)
- breaking of Au bridge
- tunneling regime

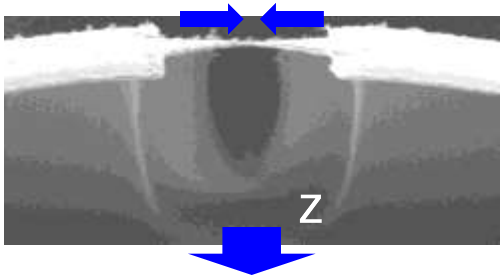
$$G \propto e^{-\beta d}$$

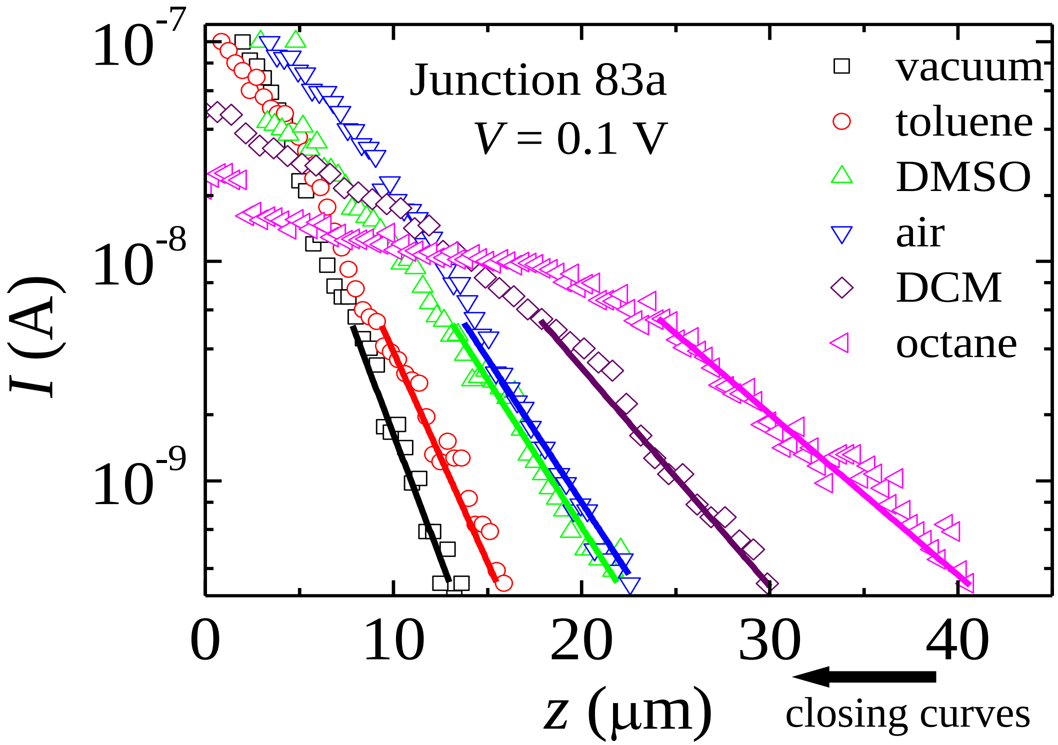
- statistics: histogram
  tunneling background
  ⇔ const.



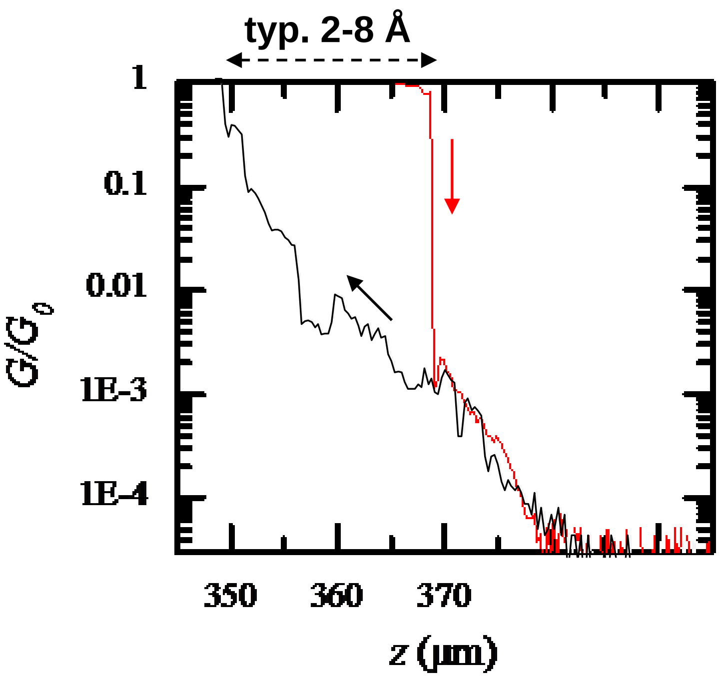
# tunneling regime

gap open, close the junction



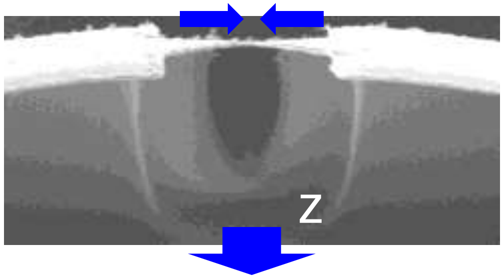

*opening-closing trace*




***liquid ~ effective medium in first approx.***

# tunneling regime

gap open, close the junction

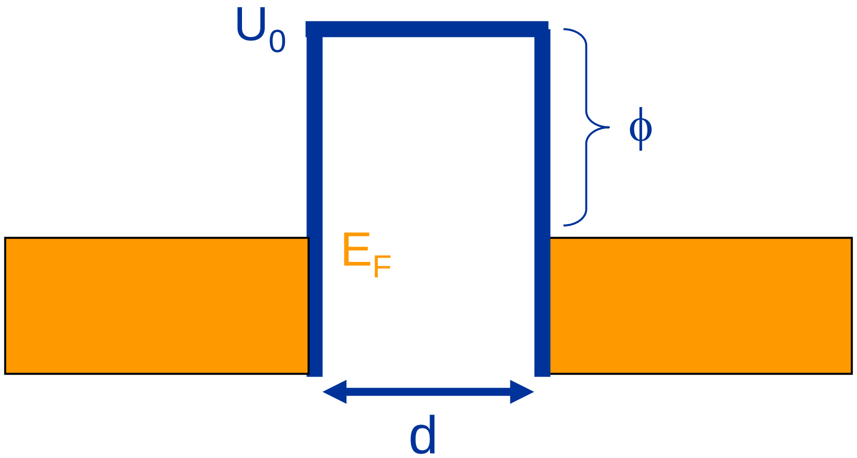



$$I \propto \exp\left(-\frac{2d}{\hbar}\sqrt{2m\phi}\right)$$

d=r·z     r = reduction factor

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

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

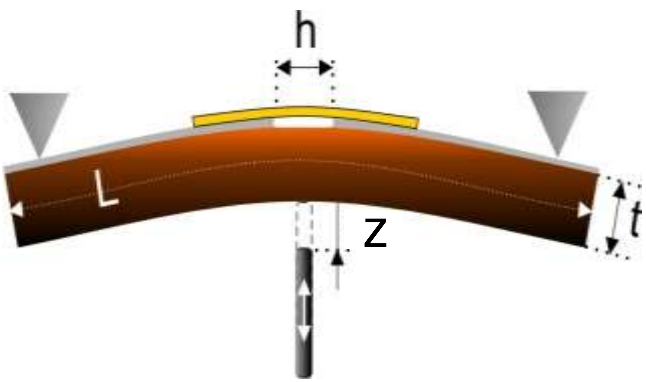



$\phi = U_0 - E_F$

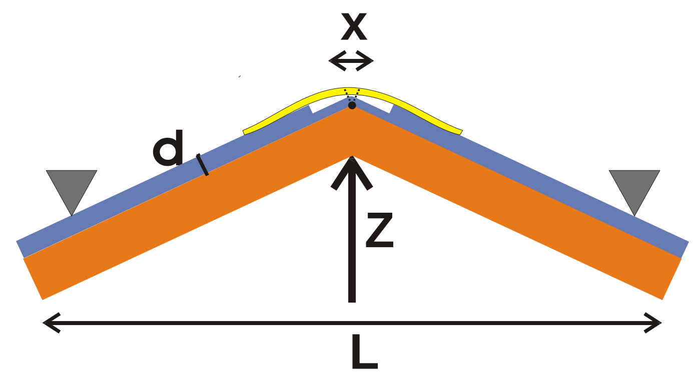
in vacuum: metal workfunction

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

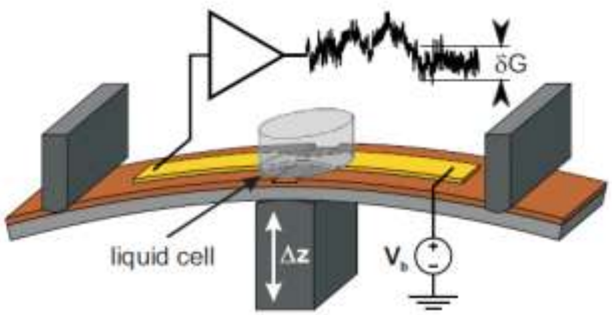
$\phi_{vac} = 3.5 - 5$ eV $\Rightarrow$ $r \sim 5 \times 10^{-5}$

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

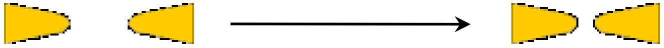
*NB: plastic deformation of the substrate can affect r*

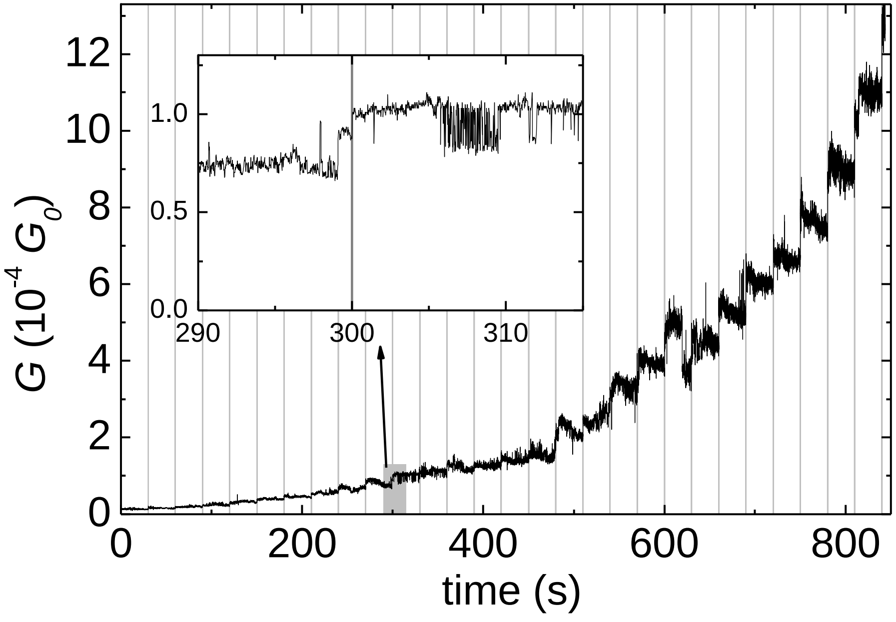
# contacting simple molecules

# dynamical behavior & fluctuations: solvent

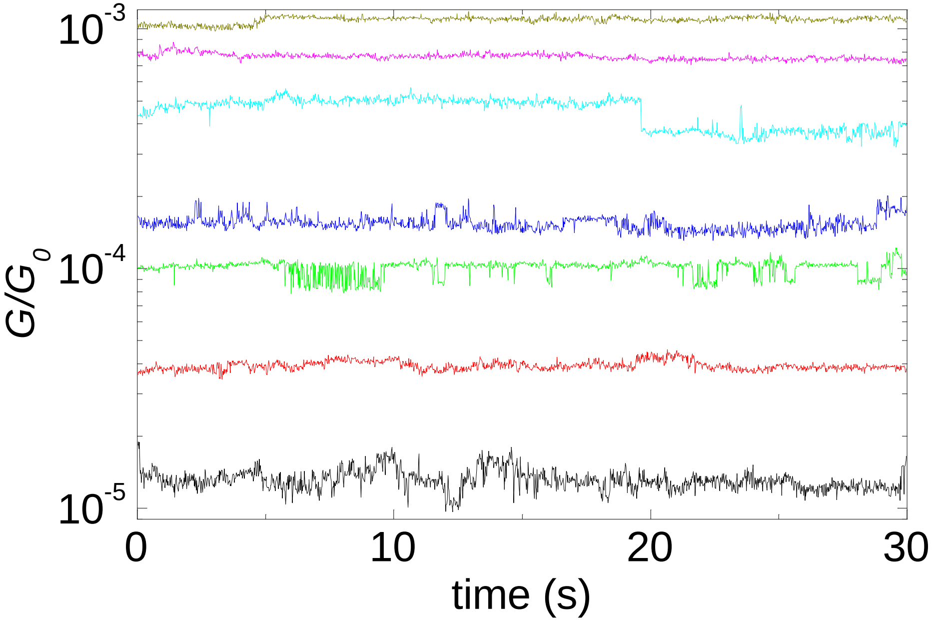



**pure solvent (mesitylene)**






***full measurement***

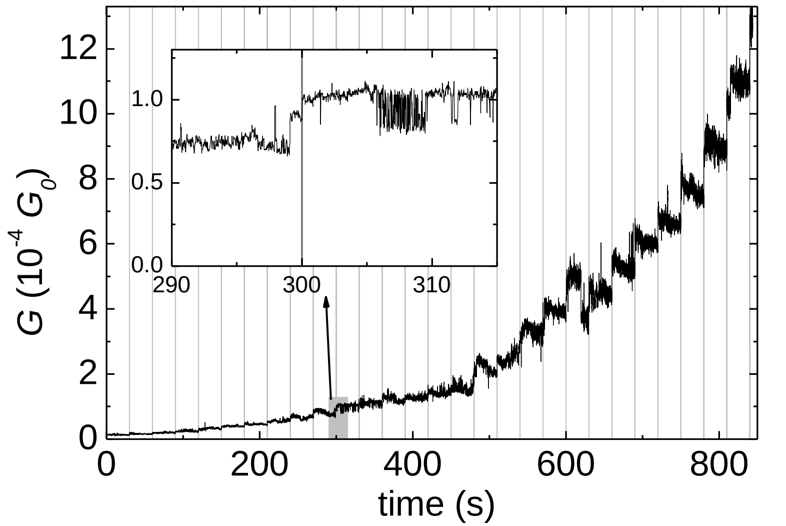


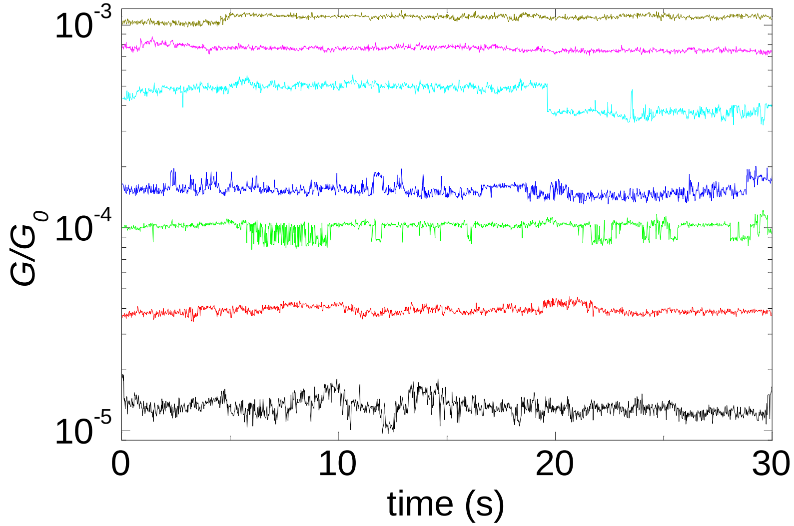

***30 s intervals***

***J. Brunner et al., to appear in JPCM, 2014***

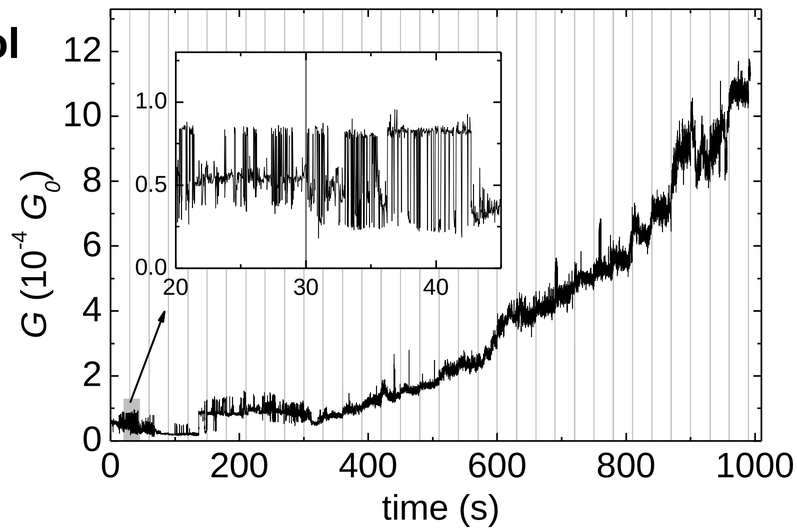
# dynamical behavior & fluctuations: solvent + alkanedithiols

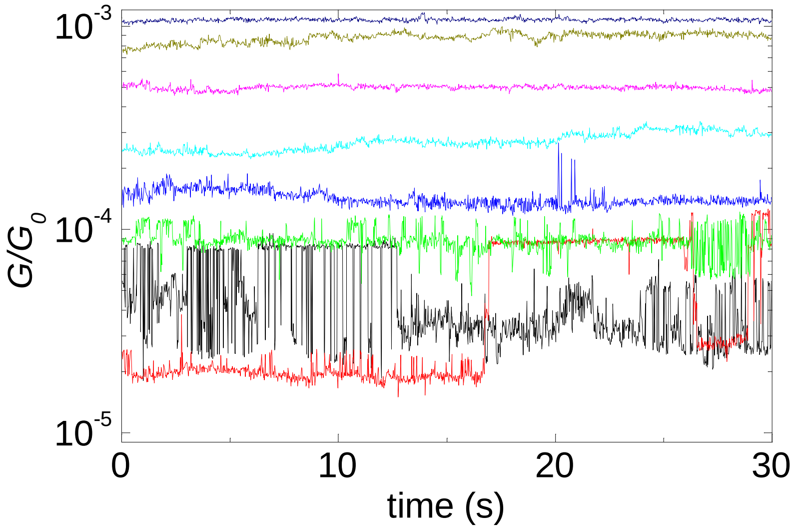
**solvent**




**octanedithiol solution**

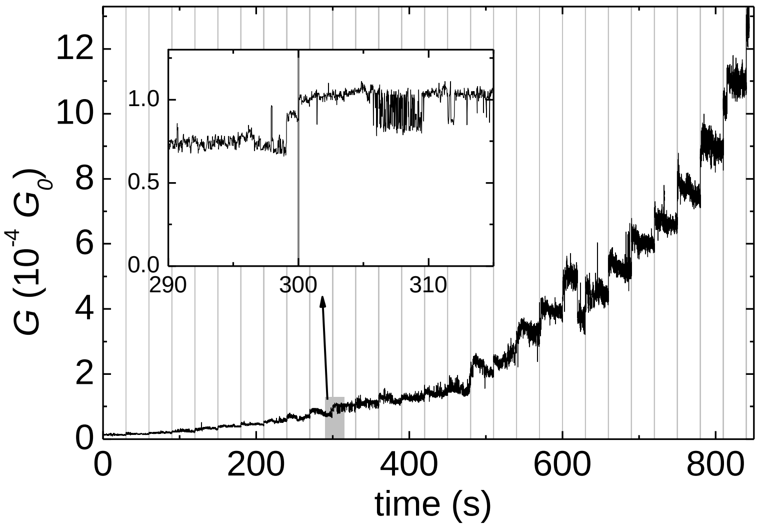


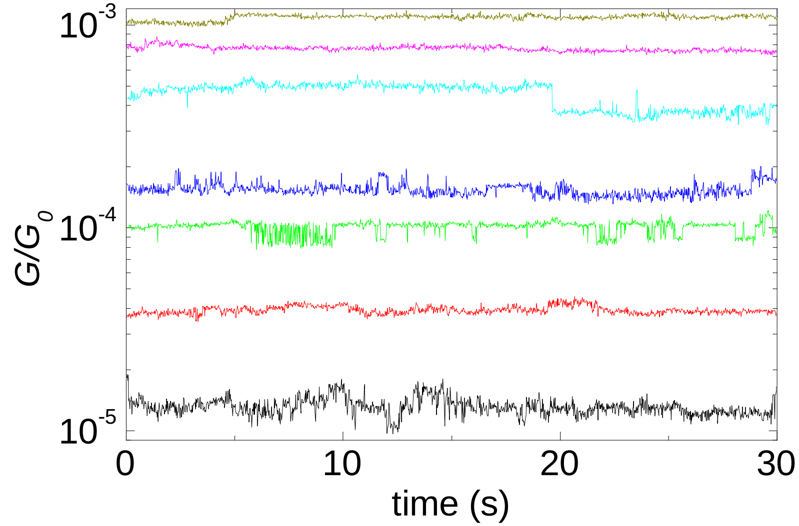




*J. Brunner et al., to appear in JPCM, 2014*

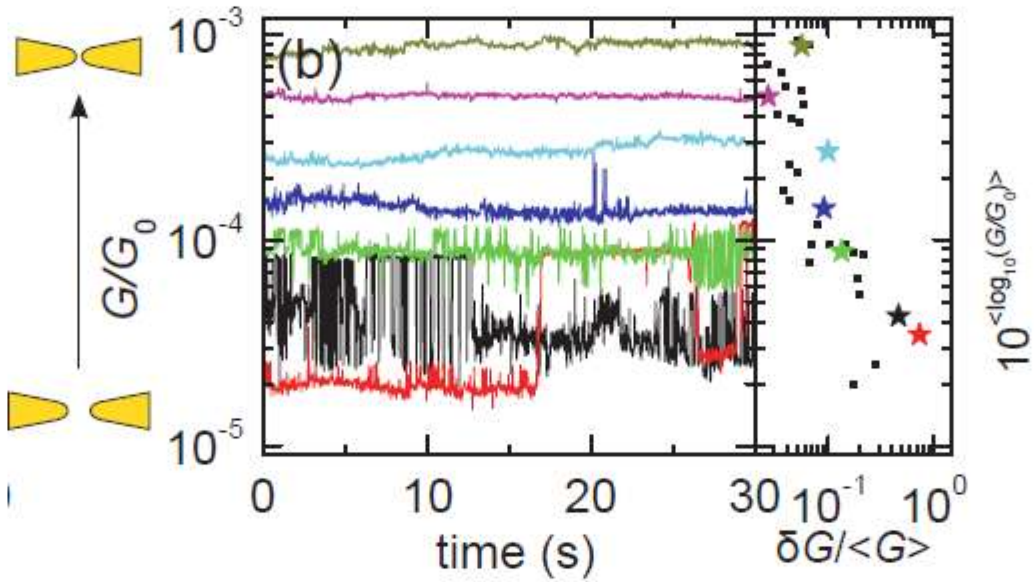
# dynamical behavior & fluctuations: solvent + alkanedithiols

**solvent**




**octanedithiol solution**

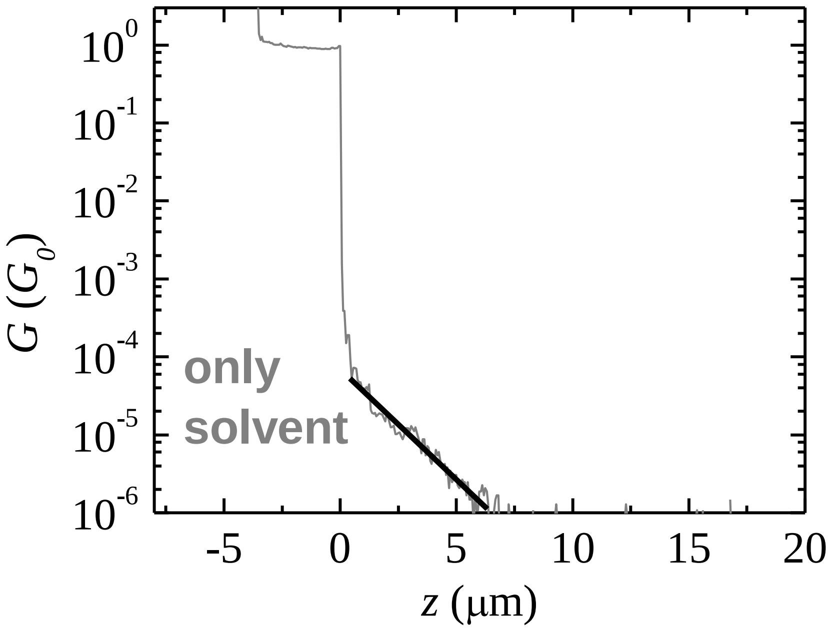


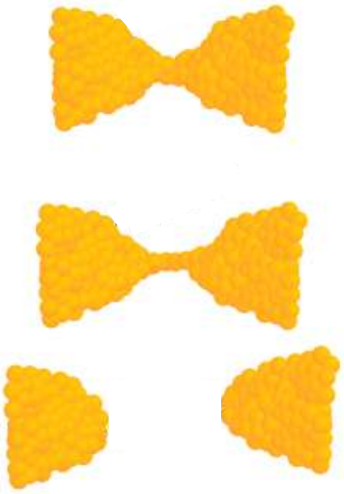

***relative conductance fluctuation amplitude***

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

***J. Brunner et al.***

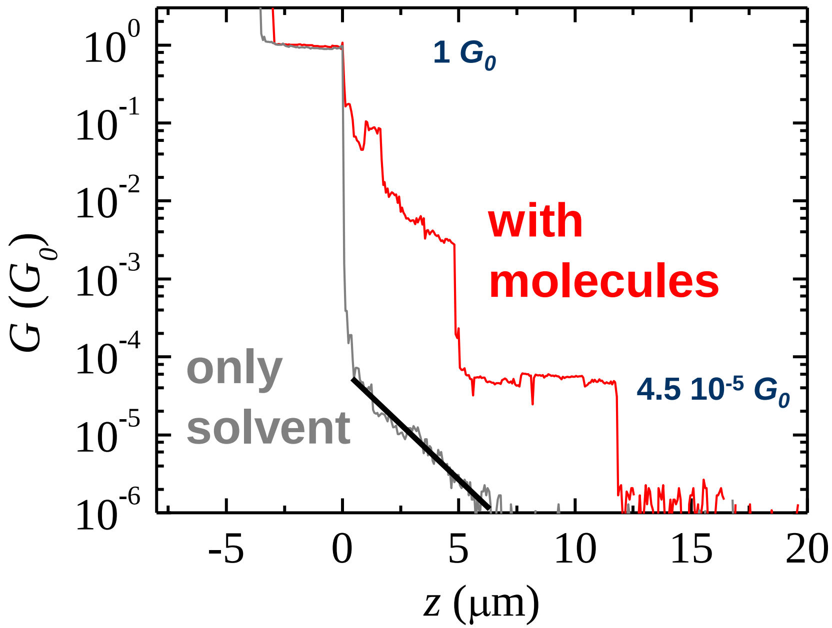
# formation of a molecular junction: opening traces

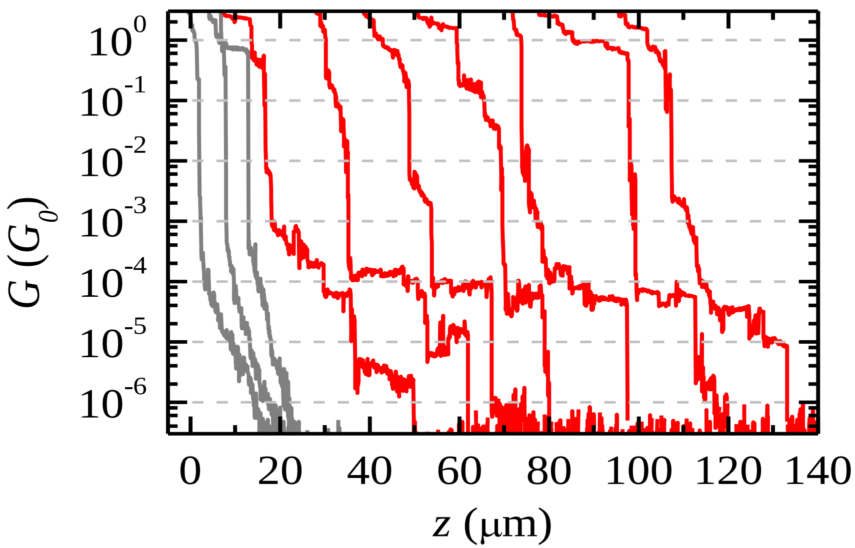


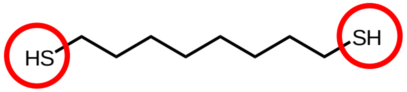
only solvent

# signature of a molecular junction

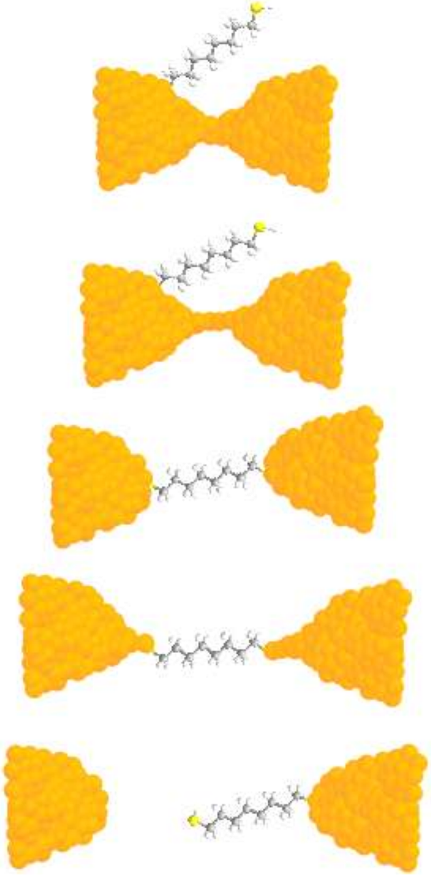



***example: alkanedithiols***




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



**molecular signature:**

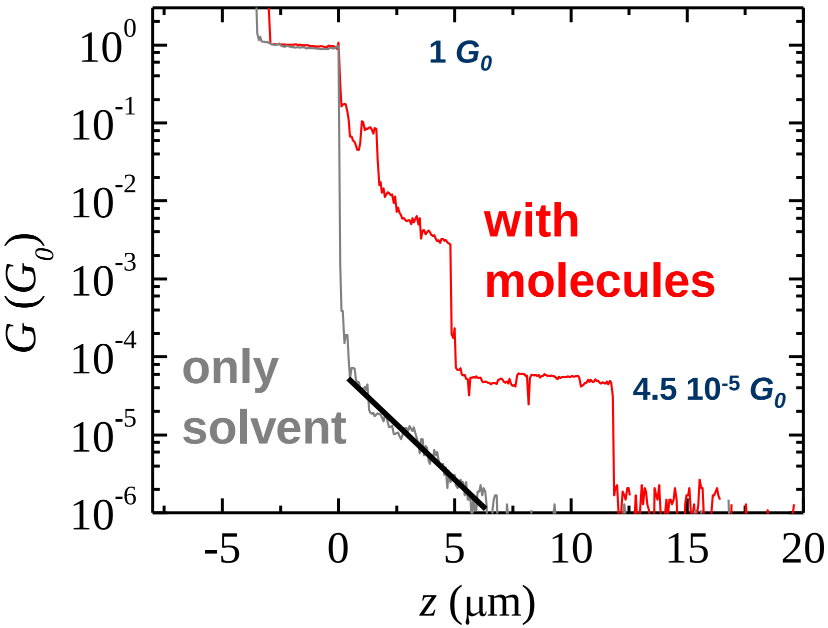
***plateau*** *(at $G \ll G_0$)*

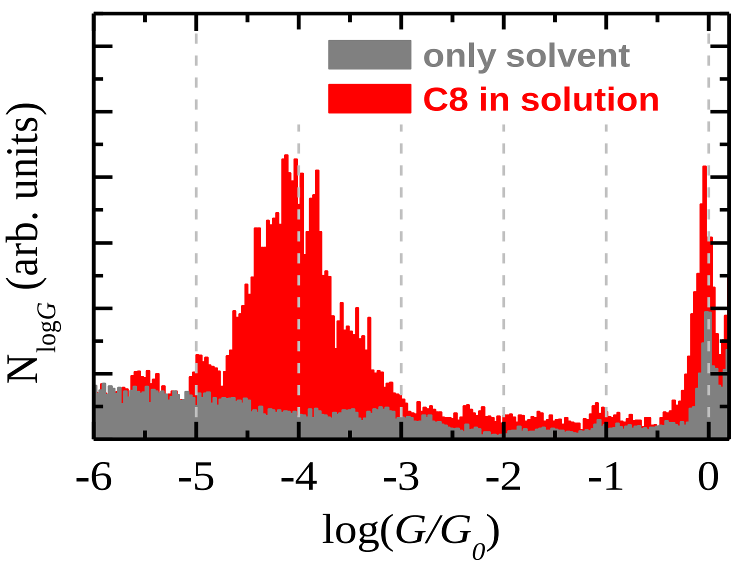
*(Reichert et al., PRL 2002, Tao et al., Science, 2003, Nano Lett. 2004, JACS 2007)*

only solvent: Mesitylene

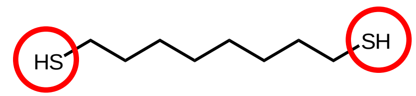
with molecules:0.1 M octanedithiol in Mesitylene

# signature of a molecular junction

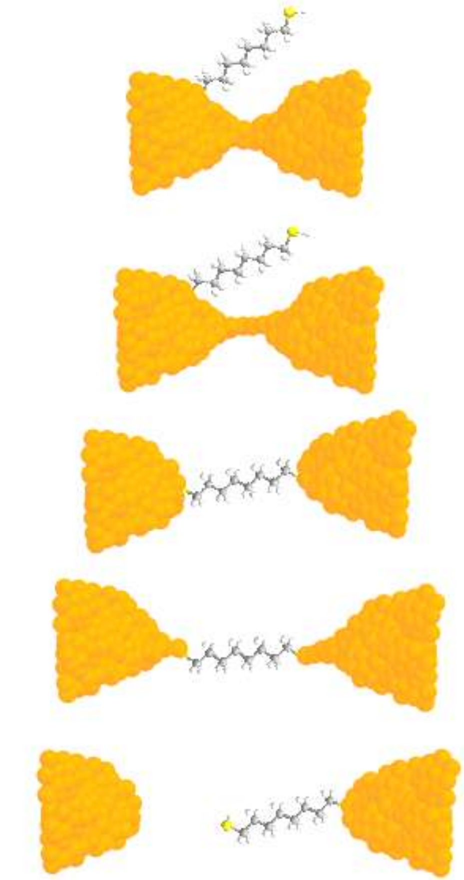



***model system: alkanedithiols***




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

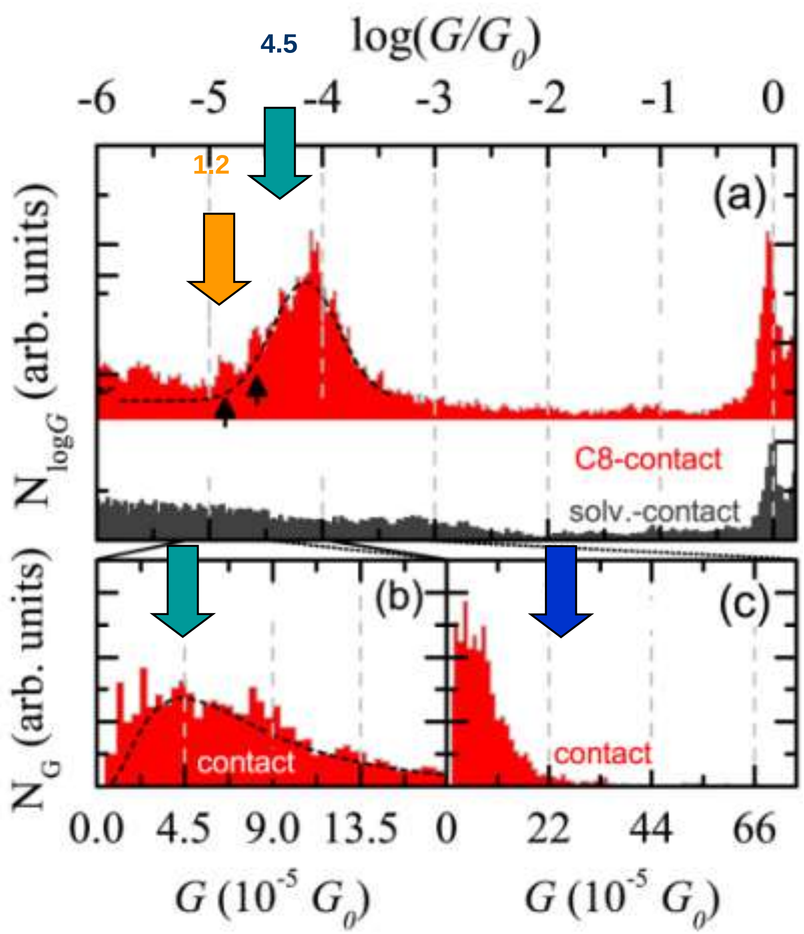


**molecular signature:**
***plateau*** *(at G « $G_0$)*
⇔ ***peak in (log-G) histogram***

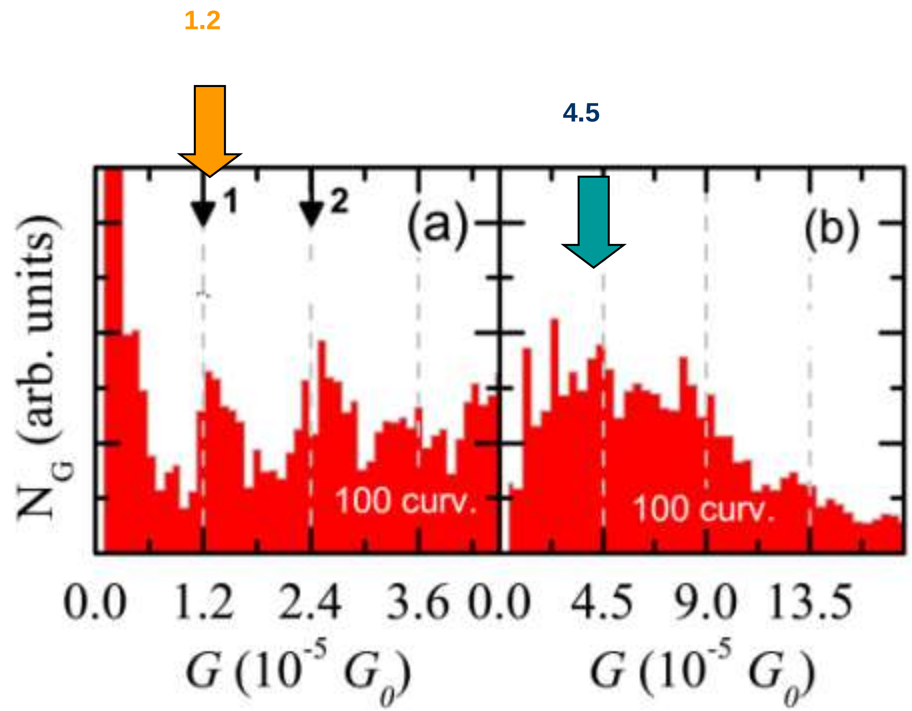
- ***plateau in 20-60% curves***
- ***conductance window > 6 orders of mag.***

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

# statistical analysis




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




**interpretation of the different values**

- anchoring geometry
- conformational states
- multiple bridges

**1** **2**

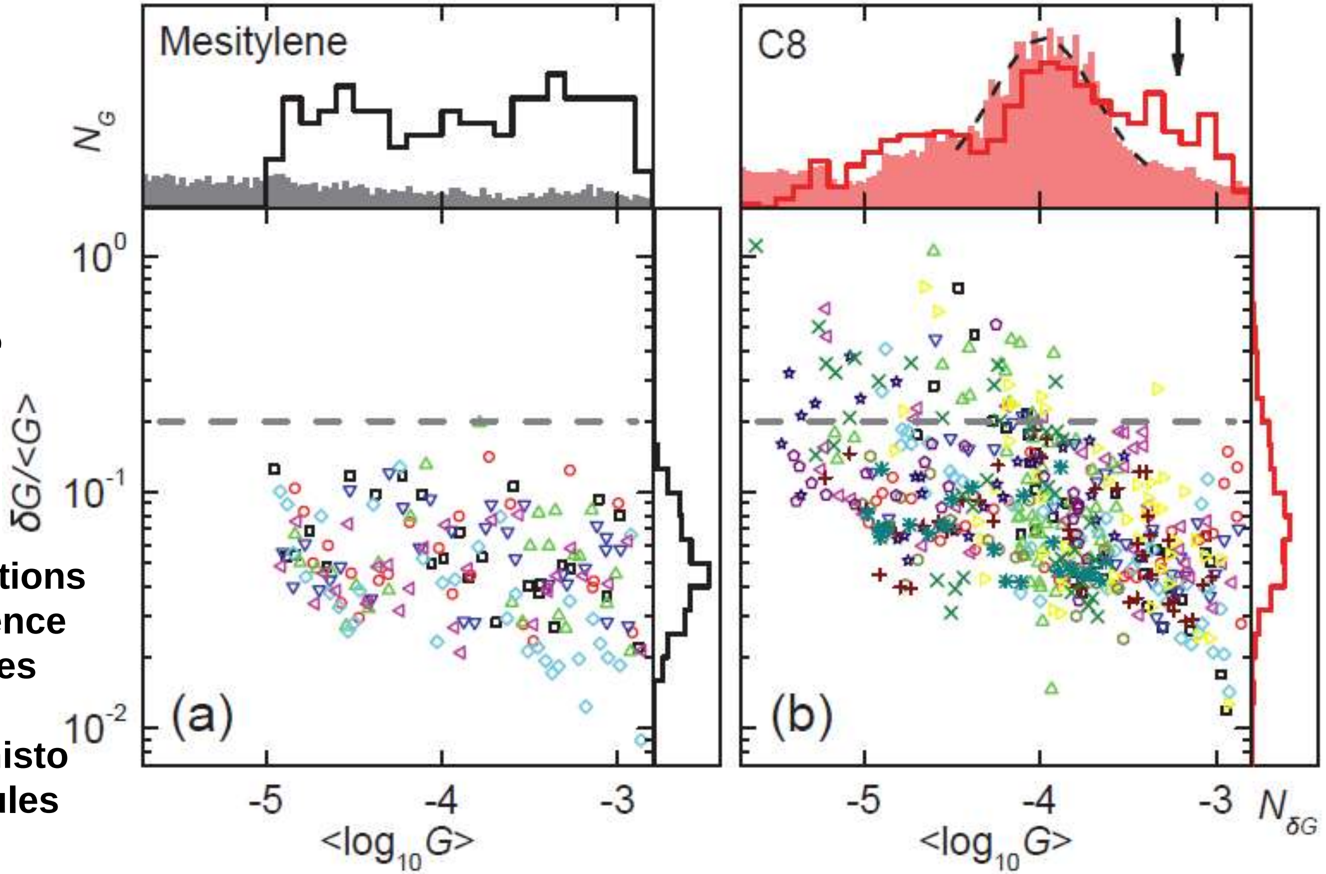
***T. Gonzàlez et al., New J. Phys. (2008)***

# 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.***