Gold-atoms motion on mechanically controllable break junctions contacts

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September, 2006

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1 Introduction

Since the discovery of the transistor, the size of the components in integrated circuits (IC) has been shrinking continuously. The speed and performance increase of IC chips are based on the minimum printable feature size. The rate of progress is described by Moore’s law which states that the number of transistors per square centimeter roughly doubles every two years. A technological barrier that might slow down Moore’s law’s progress is imminent. The IC has reached a size where quantum effects start to play a role. Several solutions are studied and one of the proposed lines of research is Molecular Electronics, where molecules are used as building blocks in the construction of electronic circuits.

Molecular electronics introduces a new concept to IC. Instead of researching for new lithographical methods to minimize the IC (a top-down approach) the IC is built by already miniaturized elements - molecules (bottom-up approach).

Besides their main benefit of being small, molecules offer additional advantages such as a cheap production, ability to self-assemble on a surface and their structure is systematically designable.

Technological advances made it possible to address and investigate small groups of molecules or even single ones. Several methods to characterize their electrical properties were found - each with its advantages and disadvantages.

One of the preferred techniques is the break junction (BJ) technique [1, 2]. It offers a simple way to create a tunable gap between atomic-size electrodes. Measurements using BJ have been done with different molecules in vacuum [3, 4]. Recently, there have been some measurements in liquid environment using a STM break-junction configuration [5, 6, 7, 8] and mechanically controllable break junction (MCBJ) [9]. The work in liquid is particularly interesting because it allows to explore the possibility to perform electrochemical gating in single molecule junctions [10].

An important issue in single-molecule devices, is the role of the metal-molecule contact [11, 12]. The quality of these contacts can dominate the whole behavior of the junction. Experiments in simple molecules (alkanedithiols), using BJ setups [13, 14] have shown variations in the conductance of molecular junctions that relate to the way in which the molecule is held by electrodes.

In break junctions, the electrodes tips end in a few atoms, which can move and change their configuration during the molecule-metal link formation.
In this work we explore the gold-atoms motion in MCBJ tips in different environments. We study vacuum, air, and solvents of different polarity. The variation of the junction’s conductance, after the gold bridge breaks, is explored in consecutive measurement cycles, under different breaking conditions and along time. This work expands previous studies \cite{[15]} done in this group, where preliminary measurements of the tunneling regime in BJ were done in different solvents. It means to serve as a control experiment for further electrical characterization of single molecules.

2 Principles of MCBJ

2.1 The mechanism

MCBJ is a technique to create \emph{atomic contacts}, where a neck-shaped nanowire is stretched in a controlled manner in order to reduce its diameter down to a single atom, until breakage occurs and a gap opens. A very useful feature for \emph{atomic contacts} is that the breaking process creates sharp electrode tips (atomic sized). In addition, the distance between the electrodes is tunable (see section 2.4). Therefore, MCBJ prove to be excellent devices for single molecule measurements.

The principle of the MCBJ is very simple. A metal wire with a constriction is fixed on top of an elastic substrate. The constriction is in a freely lying section on top of the surface. The substrate is bent, straining the wire. The strain is concentrated in the suspended section and causes the wire to break at the constriction (weakest point). This results in two electrodes which can be brought back into contact by relaxing the force on the substrate.

The principle of a MCBJ is illustrated in Fig.1.
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Figure 1: Mechanically controllable break junction set-up. A Au wire with a suspended constriction is fixed on an elastic substrate. The substrate is bent by pressure on three points. A push rod that moves up/down (z direction) is under the middle of the substrate (below the suspended constriction). Counter supports from each side of the push rod are pressing from above (stationary). The distance between the counter supports is $L$. The substrate thickness it $t$. The suspended constriction length is $u$. While bending the beam, the wire breaks and the distance between the resulting electrodes can be adjusted by moving the push-rod. A zoom of the broken wire indicates the inter-electrode distance $d$.

2.2 The output

The conductance $G$ is measured as a function of $z$ displacement (see Fig.2). As the push rod is pressed up, $G$ decreases while the junction breaks gradually (an opening curve is produced). As the push rod is lowered, $G$ increases while the gap between the electrodes closes (a closing curve is produced). A measurement cycle is an open-close curve.

We can point out two main $G$ regimes: A tunneling regime ($G < G_0$) and a true metallic contact regime ($G > G_0$). $G_0 = 2e^2/h$ is the conductance quantum, $e$ is the electron charge and $h$ the Planck’s constant.

In the true metallic contact regime, the $G$ behavior of structures with dimensions much smaller than the phase coherence length is given by the Landauer expression:

$$ G = G_0 \sum_n \tau_n $$
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Where $\tau_n$ is the transmission of the $n$-th channel of conductance. For the case of few-atom contacts from monovalent metals like Au, Ag, Cu and for the alkali metals, each atom in the junction contributes with one fully open channel [16, 17] resulting in $\tau_n = 1$ and $G = nG_0$. Thus, in our case we can present the $G$ graphs as $G/G_0$ graphs and see the number of connected Au atoms in our junction.

The expression for the tunneling $G$ at low bias through a square barrier is:

$$G \propto \exp[-2d\sqrt{2m\phi}/\hbar]$$

Where $\phi$ is the barrier height, $m$ is the electron mass and $d(z)$ the distance between the two extremities of the Au contacts.

Fig.2(a) shows 3 measurement cycles measured by us (in air). The red (black) lines show the closing (opening) curves where $z$ decreases (increases) and $G$ increases (decreases). When addressing the tunneling regime, a semi-log scale is preferred. Thus, the tunneling behavior is easily identified as a line of slope proportional to the barrier height. This can be seen in Fig.2(b) where the same data as Fig.2(a) is shown.

![Figure 2: $G/G_0$ vs. vertical displacement of the push-rod $z$ while opening/closing (black/red) a Au junction in vacuum (sample 03b). (a) Linear scale. (b) Semi-log scale.](image)

The structural rearrangement of the contacts is varying each time they are pressed together and opened again. Therefore, the $G$ traces are different
in each cycle. However, some trends are reproducible in the opening and closing curves. In the opening curves (black) we see plateaus at $\sim n \times G_0$ corresponding to a junction formed by $n$ atoms in parallel. The most pronounced plateau is of the order of $1G_0$. Often the plateaus are not located at exactly integer quantum values. Such deviations are attributed to back scattering on defects near the contact. The opening curves describe a period in which the wire stretches elastically, with a smooth, approximately linear force increase while the cross section and the conductance decrease. After a certain elongation, when the tension in the wire has reached a high level, the system becomes mechanically unstable and the atoms rearrange themselves into a different structure (with smaller contact diameter) [18]. This is accompanied by a sharp decrease in the force and in $G$ (of the order of $1G_0$). The pattern is repeated until the wire eventually breaks.

After the junction is broken ($G < G_0$), another sharp decrease is observed. It corresponds to the retraction of the Au atoms on the newly created electrode tips. At larger gap distances, the Au atoms retraction relaxes and tunneling behavior is seen ($G(z)$ decreases exponentially with increasing $z$). This has also been demonstrated in MD simulations [19, 20, 21, 22].

In the closing curves, at start the junction is open ($G < G_0$) and transmission happen by tunneling ($G$ increases exponentially with $z$ decrease). When the two metal surfaces are closed a jump to contact occurs. Afterwards the conductance increases in a staircase-like manner but with less plateaus than in the opening curve. The first contact is usually of the order of several $G_0$ and only rarely at $1G_0$. This sudden jump-to-contact mechanism has been studied theoretically and the picture that has emerged is the following [23, 24]: When two surfaces are brought close to each other, the system becomes unstable at a certain critical distance of a few angstroms, and the surfaces suddenly jump into contact. This is called “adhesive avalanche” and involves a collective motion of many atoms. Another mechanism, called “diffusion-to-contact”, is suggested [25]. Here contact formation occurs by a thermally activated sequence of atomic hops.
2.3 Analysis tools

2.3.1 Conductance Histograms

Since the atomic-scale contact configuration is different for each opening and closing cycle, each $G$ trace is unique. Therefore, a statistical analysis of the data is needed in order to identify reproducible features and favorable configurations. Constructing $G$ histograms from a large set of $G$ curves gives the probability $N_G(G)$ to measure a certain value $G$. The peaks in the histogram correspond to $G$ values of the preferred atomic configurations of the system. Fig. 3 shows $G$ histograms from one of our junctions in vacuum. Fig.3(a) shows the statistics for opening the junction. Fig.3(b) for closing it.

![Figure 3: $G$ histograms in vacuum, collected from 100 measurements of $G(z)$ while (a) opening and (b) closing the junction (sample 07b). Bin width: 0.02 $G_0$.](image)

The most striking feature in Fig.3(a) is the peak at $1G_0$ as expected for monovalent wires [17]. It results from the formation of a chain of gold atoms during the last stage of contact breaking. There are two other clear peaks near $2G_0$ and $3G_0$, both clearly shifted to somewhat lower values compared to exact multiples of $G_0$. As mentioned in the previous section, this shift is attributed to backscattering of the electrons. Fig.3(b) exhibits only little features. At $G < G_0$ an accumulation of points
in the tunneling regime is seen, where $N_G \propto 1/G$ [9]. The fact that we don’t see any peaks in the true metallic regime, shows that every time the junction jumps into contact, it connects differently with no preferred configuration.

In order to analyze the tunneling regime, one can also plot histograms of $\log(G/G_0)$. The exponential behavior is presented by a uniform distribution of $\log$ values [9] (i.e. $N_{\log G}(\log G) = \text{const.}$). Fig. 4 shows two examples of $\log(G)$ histograms from one of our junctions in mesitylene.

Figure 4: $\log(G/G_0)$ histograms in mesitylene, collected from 50 measurements of $G(z)$ while (a) opening and (b) closing the junction (sample 02a). Bin width: $\Delta \log(G/G_0) = 0.005$.

In Fig. 4(a) (opening curves) the exponential behavior is present from -4 to -2.4 (shown by the red line). The $1G_0$ peak is seen explicitly. Left of the peak there is a lower area (-2 to -0.3) which has sparse counts because of the fast retraction of the Au atoms. We propose that, the inter-electrode gap $d(z)$ in this region becomes $d(z+M)$ where $M$ is the retraction of the Au atoms (most pronounced after breakage). This work researches this phenomenon. In Fig. 4(b) (closing curves) the exponential behavior is also present from -4 to -2.4 (shown by the red line). There is a decrease in counts over $1G_0$ (another evidence of the jump-to-contact mechanism). The region between -2 to 0 shows an non-uniform distribution with higher probability. This effect is explained in ref.[26] as a result from a layer of molecules that is trapped between the contacts. At short inter-electrodes separations, the
molecules block the Au atoms from contacting, resulting in a higher count of Log\(G\) values because the contacts move more slowly towards each other. This effect is not existing in vacuum measurements. Therefore, we define the -4 to 2.4 regime as “pure tunneling regime”.

### 2.3.2 Histograms as an averaging tool

The histograms contain the measured data in a way that enables us to average the curves. We write \(N_z\) as the respective probability of measuring a certain value of \(z\). \(N_z\) is a constant: \(N_z(z) = \frac{R}{\nu_z}\) (where \(R\) is the data acquisition rate and \(\nu_z\) is the velocity of the vertical push rod). Thus, we get the relation:

\[
N_G(G) dG = N_{logG}(logG) dlogG = -N_z(z) dz
\]

and for each bin size \(dz\) we can calculate the slope:

\[
\frac{dG}{dz} = -\frac{N_z}{N_G(G)}  \tag{4}
\]

\[
\frac{dlogG}{dz} = -\frac{N_z}{N_{logG}(logG)} \tag{5}
\]

and construct an averaged curve \(G(z)\) by numerical integration of the histogram. Fig.5 shows 5 input curves (black) and the produced average curve (red) by this method.

![Figure 5](image_url)

*Figure 5: An example for curve averaging using histograms. 5 input curves (black) and the produced average curve (red) are shown in (a) normal scale (b) semi-log scale.*
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2.4 Attenuation Factor

Assuming that the bending is elastic, the gap size \( d \) is proportional to the displacement \( z \). The ratio \( z/d =: r \) is called the reduction factor and \( 1/r =: a \) the attenuation factor. We get:

\[
d = a(z - z_0)
\] (6)

The inter-electrode separation \( d \) can give important information when measuring molecules. Therefore, it is desirable to determine the exact value of the attenuation factor \( a \).

For an elastically homogenous system, the attenuation factor can be derived based on geometrical considerations. Using the standard elastic beam theory [27] for our system (a beam with supported ends), leads to an attenuation factor \( a_g = 6tu/L^2 \). Another possible derivation is to compare the curvature of the beam with the curvature of a segment of a circle, leading to \( a_g = 4tu/L^2 \). Thus, depending on the approach, \( a_g \) can differ by a factor of 1.5. Based on our geometry with values \( t=0.3 \) mm, \( u \sim 390 \text{nm} \) and \( L=20 \) mm we estimate \( 1.1 \times 10^{-6} \leq a_g \leq 1.7 \times 10^{-6} \).

To verify this formula, measurement cycles are performed, and the results in the pure tunneling regime addressed (see Fig.6).

![Figure 6: Measurements cycles in vacuum from ref.[15]. The black line is the slope \( B \) obtained from a linear fit to \( \log(G) \), i.e. \( \log(G) = -Bz + \text{const} \)](image)

From eq.2 and eq.6 we get:

\[
\ln(G) \propto -Bz + \text{const.}
\] (7)
where

\[ B = 2a \sqrt{\frac{2m\phi}{\hbar}} = 1.025[eV^{-0.5}A^{-1}]\sqrt{\phi a} \] (8)

Hence, the slope of \( \ln (G) \) vs \(-z\) is given by \( B \propto a\sqrt{\phi} \). The measured \( B \) in vacuum is taken and \( \phi_{vac} \) is fixed to the established value of 3.5-5.0 eV [28]. In ref.[15] \( a \approx 5 \times 10^{-5} \), which is one order of magnitude larger than the geometrical \( a_g \). Such deviation was explained by the fact that, although the formula for \( a_g \) is widely used, it ignores the fact that the substrate can plastically deform [1]. The presence of plastic deformations is confirmed by a residual bending of the substrate, seen after several loading and unloading cycles.

Another work [29] explains that the polyimide (see section 3.1) flows in the vicinity of the junction due to inhomogeneous stress. Due to this inhomogeneity the bending mechanism changes and \( a_g \) should be corrected by a significant factor \( \xi = 2 - 4 (a = \xi \times a_g) \). Nevertheless, this correction could still not explain the factor of 10 difference between the experimental value and the geometrical one.

Further conclusions can be extracted from the results of this work (see section 4.2).

### 3 Sample preparation and description of the setup

The sample preparation process is very similar to the process done by L. Grüter in ref. [26]. A microfabrication technique is used to define the break junction metal bridge. A sheet of stainless steel covered with an insulating polyimide layer serves as flexible substrate. The top of the substrate is patterned with e-beam lithography and metal is evaporated through the obtained mask. The last step includes an isotropic dry etching to free the narrow bridge from the polyimide resulting in a freestanding metallic bridge (see Fig.7).
3 SAMPLE PREPARATION AND DESCRIPTION OF THE SETUP

![SEM image of a microfabricated break junction (our sample 03a). The suspended constriction is of size $a \sim 380\text{nm}$](image)

3.1 Substrate preparation

As substrate serves a 0.325 mm thick stainless steel sheet. The sheets are cut in $6.5 \times 6.5$ cm pieces. Then a $\sim 3\mu m$ polyimide layer (Pyralin PI2610, HD Microsystem) is spun on the substrate. The wafers are baked in the oven at 160°C for 30 minutes. A second layer of polyimide is spun on the substrate to reduce the probability of shorts through the polyimide. After another baking at 160°C for 30 minutes the substrate is annealed for one hour at 380°C and $10^{-5}$ mbar. Finally, the coated substrate is cut by laser in $23.7 \times 9.3$ mm samples.

The polyimide is used for three reasons. First, it serves as an insulating layer between the metallic pattern on the top of the polyimide and the substrate and second, it planarizes the stainless steel surface. Finally, the polyimide can be dry etched to get a free standing bridge (see section 3.2.4).

3.2 Electron-beam lithography and metal deposition

3.2.1 Principle

Electron-beam (e-beam) lithography is a standard method in microelectronics for patterning a substrate. The substrate is spin-coated with an organic resist, which is polymerized in the oven. The exposure to the electron beam leads to a change in the solvability of the affected area. With a positive resist the exposed area is dissolved during the development, whereas negative resist is further polymerized by the exposure and the unexposed area can be dissolved.
3.2.2 Electron-beam lithography

A scanning electron microscope (SEM) is used to pattern the resist. The mask is designed on the computer and transferred to the microscope. The resolution is given by the size of the beam and the proximity effect. A standard positive resist (PMMA, Polymethylmetacrylate 950 K from Allresist) is diluted with additional chlorobenzene to decrease the resist thickness (≈ 600 nm), spin coated on the substrate (4000 rpm, 40 s) and baked in the oven at 175°C for 40 minutes. It is exposed using a LEO Supra 35 scanning electron microscope. The stage and the pattern generation is controlled with the software Proxy-writer. The development is done in a solution of MIBK (4-Methyl-2-pentanone) : IPA (Isopropanol) 1:3 for 45 s. The sample is then rinsed for 30 s in IPA to stop the development process.

3.2.3 Metal deposition

After development the resist layer serves as a mask for the metal deposition. This step takes place in a vacuum chamber (PL500 from Balzers) at $10^{-6}$ mbar. The sample is mounted on a tilt able sample holder allowing evaporation at different angles. In addition, the sample holder can be cooled with liquid nitrogen to improve the adhesion of the metal (evaporation starts when the sample is under 0°C. The metal is thermally evaporated by an electron gun. The thickness of the evaporated film is controlled with a calibrated quartz resonator. A 10 nm Ti film in an angle of $30^\circ - 35^\circ$ is evaporated first for better grip of the Au to the substrate (the angle is to avoid getting Ti in the bridge). Then a 50 nm Au is evaporated for the bridge perpendicular to the sample. Once the metallic film is evaporated, the sample is immersed in acetone to remove the PMMA mask.

3.2.4 Plasma etching

In the final step, the polyimide is isotropically dry etched to obtain a suspended central metal bridge. This is done by Reactive Ion Etching (RIE) in a PlasmaLab 80 plus (Oxford) under the following rf plasma conditions: a flow of 80% of oxygen and 20% of $CHF_3$ at a pressure of 0.1 torr and a power of 100W for 3-3.15 min. The final device is inspected with a Scanning Electron Microscope (LEO Supra 35) (see Fig.7). On a substrate, two junctions with a central constriction of 80-250 nm width are fabricated in
parallel (see Fig.8). The resistance of a junction ranges typically $300 - 500 \Omega$.

![Figure 8: SEM image of a microfabricated break junction (our sample 03). (a) A picture from the side showing 2 junctions. (b) A picture from above showing the dimensions of the Au bridge.](image)

### 3.3 The setup

The sample is mounted in the setup with a three-point bending mechanism, sketched in Fig.1. A picture of the mounted sample is shown in Fig.9(a). The distance between the two counter supports is $L = 20 \text{ nm}$. The vertical displacement of the push-rod is driven by a stepper motor (Phytron GLD) via a coupling gear, allowing for displacement amplitudes $z$ up to a few millimeters. One substep is equivalent to $\Delta z = 3.125 \text{ nm}$ (from section 2.4 this results in $\Delta d = a_d \Delta z \rightarrow 5 \text{ fm} \leq \Delta d \leq 10 \text{ fm}$). The motor is controlled by the PC through a serial port RS 232. The motor speed is $31.2 \mu \text{m/s}$.

To perform measurements in liquid, a cell as shown in Fig.9(a) was used. It is formed by a portion of a Viton tube enclosing a volume of $250 \text{ µl}$. The cell includes an inlet and outlet port (Teflon tubes) allowing the exchange of fluids in the course of the measurements. A tight contact of the cell to the sample surface is ensured via a spring.

The measurements are performed on one bridge at a time, using clamped connectors attached over an Indium layer (introduced for better connectivity). A standard data acquisition boards (National Instruments) is used to apply a constant bias voltage and to record the current in the junction. The current was measured with the help of a current-voltage converter, which can automatically adjust its gain between 0.1 and 100 V/µA. An external resistance $R = 1 \text{k} \Omega$ is used to limit the current in the circuit. The grounding of the measurement setup is provided via the DAQ board source whereas the input is floating, see Fig.9(b). The entire setup is isolated from the grounded support. To avoid ground loops, an isolation between the lateral shield of
the setup and the grounded isolation of the BNC connectors, as sketched in Fig. 9(b). During the measurements we shielded the setup with an aluminum cover. The typical conductance fluctuations were of $\pm 7.5 \times 10^{-6} \frac{G}{G_0}$ at $V_{bias}=0.1V$.

We used two different measurement setups. They differ only by their DAQ cards resolution (16 and 12 bits). Thus, using the automatic current-voltage converter with the 16 (12) bit card, $I$ as high as 100 $\mu$A can be recorded with a resolution of 3 nA (50 nA), while maintaining a resolution of approximately 3 pA (50 pA) for $I$ below 0.5 nA. This allows us to register the conductance variation during the whole process, starting from the fused Au junction with high conductance values, $G > G_0$, down to $G \sim 10^{-5}G_0$.

Figure 9: (a) Detailed view of the substrate mounted in the three point bending mechanism (white triangles) with a liquid cell pressed against the substrate. (b) Break junction measurement setup with grounding schematics.
4 Measurements of atomic contacts in liquid environment

4.1 Experiment

We use the break junction setup with the integrated liquid cell to explore the influence of different solvents on the electronic properties of atomic contacts and to study the behavior of the retracting Au atoms in these solvents. For this we use a feedback process similar to ref.[10], where our measurement cycle consists of bending the substrate until a given lower $G$ value is reached, and relaxing the force on the substrate until a given upper $G$ is reached.

We define “measurement cycle without contact” (nc) as a measurement cycle where the upper and lower $G$ limits are $< G_0$. In this type of measurement, the junction is broken and the electrodes are not allowed to contact again. We define “measurement cycle with contact” (c) as a measurement cycle where the upper $G$ limit is $> G_0$ and the lower one $< G_0$. In this type of measurement, the junction is broken and contacted repeatedly.

This way we are able to try several measuring routines (different number of measurement cycles, with and without contact and different voltages) in an attempt to characterize the behavior of the retracting Au atoms in different solvents. Our assumption is that the retracting Au atoms should relax after a large number of measurement cycles (nc) causing the tunneling behavior to be defined mainly by the solvent of choice. We performed similar amounts of measurement cycles (c) to compare the effect.

As solvents, we use mesitylene, dichloromethane (DCM), dimethylsulfoxide (DMSO), tetrahydrofurane (THF), toluene and combinations of these solvents. These were chosen since they are potential organic solvents for molecules relevant in molecular electronics. In addition, these solvents cover a broad range of polarities. We also compare the results with reference measurements obtained in vacuum and air. Appendix I shows tables of the measurement sequence for each substrate.
4 MEASUREMENTS OF ATOMIC CONTACTS IN LIQUID ENVIRONMENT

4.2 Results

4.2.1 General notes

Our measurements produce graphs as we saw in Fig.2(a). Each measurement sequence contains a given number of measurement cycles. For exploring the retraction of the Au atoms and the solvent effect, we are interested in the regime where there is a gap between the two Au tips, i.e. the tunneling regime. Therefore, presenting the results in a semi-log scale is useful, where this regime’s exponential behavior can be seen as a line of constant slope (as seen in the closing curves of Fig.2(b)).

![Figure 10](image)

*Figure 10: 3 opening/closing (black/red) measurement curves on a junction in Vacuum (sample 03b). (a) Linear scale. (b) Semi-log scale. In a green line the offset $G$ is presented.*

Fig.10 shows the same results in a different scale. We see that our $G$ does not reach zero. It stops at an offset value $(1.4\times10^{-5}G_0)$. This offset is caused by an offset current introduced by the current-voltage converter. The offset value is mildly dependant on temperature. The offset value for $V_{bias}=0.1V$ was ranging $1 \times 10^{-5} - 4 \times 10^{-5} G/G_0$.

We chose not to subtract this offset from the results. It is not affecting the slope received in the semi-log scale (just shifts the curve), and allows us to explore the leakage current in the solvents. In our measurements we did not see significant leakage current effects, but it can be high with more polar
The fluctuation around the offset value are of the order of $\pm 5 \times 10^{-6} G/G_0$ at $V_{bias}=0.1V$. This represents the noise in our system.

Fig. 11 shows a typical measurement sequence in mesitylene. 200 cycles (nc) were measured consecutively. Each color represent a batch of 50 curves, measured in this order: black-red-green-blue. One can clearly see a slope change along time in the tunneling regime.

In small gap sizes an increasing “slope bending” is seen. For the closing curves (see Fig. 11(a)), we think that this behavior is due to molecule layering (see section 2.3.1). For the opening curves (see Fig. 11(b)), this behavior was not researched and is probably caused by the Au tips being notched into the molecule layer and trying to break free out of it. This approach is strengthened by the fact that this phenomena is rarely observed in (c) measurements. There, the Au junction is closed and while it breaks the Au atoms rearrange to a more favorable configuration and are not forced to attach to the molecule layer and break free from it. Therefore, our analysis of the tunneling behavior starts on larger gap sizes with $G$ values $< 10^{-3}$ (pure tunneling regime).

Figure 11: Measurement cycles (nc) in Mesytilene on sample 06a. 200 curves were measured consecutively. Each color represent a batch of 50 curves in this order: black-red-green-blue. (a) closing curves. (b) opening curves. In the insets, the first curve of each batch is shown to emphasize the change over time.
In order to study the slope change with time in the tunneling regime, we came up with the following analysis: We divided the curves into batches of 10. Out of each batch a histogram was created, and from it an average curve calculated (see section 2.3.2). On the averaged curves (in semi-log scale) we fitted linear lines to characterize the exponential behavior matching for this batch. The lines were fitted to the pure tunneling regime (see section 2.3.1), well over the noise level, i.e. $3 \times 10^{-5} G_0 \leq G \leq 5 \times 10^{-4} G_0$. To see the evolution of slope values with time, we plotted the fitted slopes together. Fig. 12 presents such a process.

![Figure 12: Analysis process:](image)

For each sample, consecutive measurement sequences were measured. The final output of their analysis is presented on the same graph with different background color. Thus, we can see the evolution in time along different sequences (sample history).
4.2.2 Attenuation factor in vacuum

Our measurements in vacuum in the tunneling regime showed a distinct exponential behavior. There was no molecule layering between the junction tips, and the pure tunneling regime extended up to \( \sim 10^{-1} G_0 \) both in the opening and closing curves (as shown in Fig.2).

Substrate 03b results in vacuum are presented in Fig.13. We present opening(closing) results with open(closed) symbols. The red line represents the slope \( B_g \) given by the geometrical attenuation factor \( a_g \) following eq.8 (the line shows the \( B_{\text{slope}} \) range given by \( \phi_{\text{vac}}, a_g \)). The orange line shows the wider \( B_g \) range due to the \( \xi \) range (see section 2.4).

The first measurement sequence (brightest background), shows the slopes obtained from 50 consecutive measurement cycles (c). The later measurement sequences were each of 20 measurement cycles (nc).

One can easily see the difference between the opening/closing slopes in the measurement cycles (c). The closing curves slopes are lower and closer to \( B_g \). This is probably because the opening curves, where the junction is broken every cycle, are causing the Au atoms to rearrange and retract (faster retraction = higher slope values). In the closing curves, the Au atoms already had time to rearrange and the Au retraction is less prominent (lower slope values).

In the later measurement cycles (nc) the bridge is broken in the beginning of every measurement sequence, and is not reconnected until its end. One sees that the opening/closing slopes are decreasing gradually (during the measurement sequences and between them) and reach a saturation value similar to \( B_g \).

We propose that, during each measurement sequence, the Au atoms have time to rearrange and their mobility decreases, causing a decrease of \( B_{\text{slope}} \). Between the measurement sequences \( B_{\text{slope}} \) decrease is due to the fact that when the junction is newly broken, the contact tips are sharper and the bridge is closed, even though the motor \( G \) limits are \(< G_0 \). During the measurement sequences (nc) the Au tips become less sharp because of the Au retraction. Thus, the first measurement sequence (nc) still behaves like a sequence (c) but in the last three sequences (nc) the bridge is no longer closed as the tips have dulled with repeated measurement cycle (nc).

These two effects, caused by the Au mobility, are decreasing with time in measurement sequences (nc) (the tips have time to rearrange to a more stable configuration), until the fast retraction in the opening curves (after breakage) disappears and the closing and opening curves produce the same
4 MEASUREMENTS OF ATOMIC CONTACTS IN LIQUID ENVIRONMENT

slope \( B \approx B_g \).
The calculated attenuation factor from the last point (closing curve) is \( 2.7 \times 10^{-6} \) (using \( \phi_{\text{vac}} = 5eV \)) which is 1.6 times the geometrical value \( a_g = 1.7 \times 10^{-6} \), but this offset is easily explained by plastic deformation of the substrate (\( \xi = 2 - 4 \)) (see orange line). This is the first time that measurements show values that agree with the geometrical calculations, stressing the importance of the Au mobility in the BJ setup.

![Sample 03b measurements in vacuum](image.png)

**Figure 13:** Results of sample 03b in vacuum. The closed(open) points are from the analysis of the closing(opening) curves. Each measurement sequence has a different background. The red lines represents the slope \( B_g \) (the line shows the \( B_{\text{slope}} \) range given by \( \phi_{\text{vac}}, a_g \)). The orange line represents the slope \( B_g \) that results from adding \( \xi=2-4 \) range.

4.2.3 Solvent influence

We measured each sample in several solvents (see Appendix I). The pure tunneling regime showed a distinct exponential behavior. After the first few curves (\( \geq 20 \)) we saw curve bending for small gaps, suggesting molecule layering between junction tips. Therefore, the slope was calculated only from the pure conductance regime.
The behavior we saw in vacuum, where the slopes in measurement cycles (nc) are descending to a saturation value was happening here too. This indicates that the mobility \( M \) of the Au atoms decreases also in solvents.
Fig.14(a) shows the resulting slopes from our measurement sequences on sample 06a in mesitylene. In every sequence (including (c)) the slope values
decrease with time. The junction is closed between sequences, and the slope values go up once more. The opening curves slopes are always larger than the closing ones (as in vacuum) until the saturation value of $B \approx 0.1 \mu m^{-1}$ is reached.

Our explanation is that the interaction of the Au tips with the solvent dulls the Au tips. Thus, the slope values decrease in the measurement (c) also. Once the saturation value is reached, the contacts are more stable (the tips are more blunt and the Au atoms are less influenced by the solvent). When the tips are closed together and broken again (between sequences), some Au atoms are stretched outwards from the blunt contacts. They create a sharper tip that wears down once more (seen by the higher slope values between sequences). Fig.14(b) shows the resulting slopes from our measurement sequences on sample 06a in several solvents represented in several colors.

To study the saturation slope value in different solvents, we took the slopes we deemed as fitting to this behavior and presented them in Fig.15(a) (sample 06a). The slopes seen for the solvents are varying around the same value, while the value in Air is far off. This is despite the fact that the mass of the molecules and their density in each solvent is different (as seen in the table below).
4 MEASUREMENTS OF ATOMIC CONTACTS IN LIQUID ENVIRONMENT

<table>
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<th>Solvent</th>
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<th>Molar mass</th>
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To summarize the behavior of different samples, we took the mean value of the saturation slopes from each sample in each solvent. We normalized those values by the mean saturation value in air.

Fig. 15(b) shows the normalized mean saturation levels. We see that the values achieved in vacuum and air are the highest. The solvent results are a factor $\sim 0.1$ smaller than the air/vacuum ones. Usually the vacuum values are higher than air, but in the case of sample 03b, more measurements were done in vacuum and a lower and a more stable saturation value achieved.

As we picked the saturation values, only 3 samples had air saturation values to normalize the results. This also explains the small number of different solvents measured in each sample, as the samples did not survive many saturation measurements in different solvents.

This behavior is suggesting that the type of the solvent has no effect, and that only the non/existence of a solvent plays a role. The interaction of the Au contacts with the medium dulls their tips. In air/vacuum less erosion takes place until the Au atoms rearrange, while in solvents a blunter tip is formed.

Figure 15: (a) Hand-picked saturation slopes (slopes from different measurement sequences that reached saturation behavior) of sample 06a in air,toluene,chloroform,mesitylene (black,red,green,blue). (b) Normalized saturation levels from each sample in each solvent.
Similar work has been done in ref.[15] where the first 10 measurements cycles (c) in each sample and solvent were taken (not the saturation values). In order to compare our results, we present in Fig.16 the normalized slope values of the first 10 closing curves (c) in each of our sample and solvent. We see similar behavior to the one shown in ref.[15], except that our toluene and DMSO values are lower than those of air. This change is due to the fact that our samples had longer measurement cycles. Thus, the contacts eroded and the solvent values are closer to the saturation level.

We propose that the solvent-to-solvent variation in this kind of measurement is due to the Au retraction $M$ that is different from solvent to solvent. The junction is newly broken and the tips are sharp. The Au atoms retract and rearrange while interacting with the surrounding molecules (different between solvents). Thus, in the first measurement cycles this effect is important but as the Au atoms rearrange to a more stable configuration (blunter tips), $M$ is less dominant and we see no solvent-to-solvent variation (see Fig.15).

![Normalized (c) slopes](image)

**Figure 16:** Normalized slope values levels from the first 10 cycles in each sample and each solvent.

### 4.2.4 Sample variation

In Fig.14(b) we saw that the time variation of the slope values (caused by the Au mobility) is of the same order as the solvent-to-solvent variation. We explored in the same way the sample-to-sample variation (caused by geometrical differences). Fig.17 shows measurements done by Roman Huber in mesitylene:THF-3:1. These are 100 measurements cycles (c) that serve as a
control group for the molecule measurements. We see that the time evolution causes cross-overs between the different sample values. This suggests that the Au mobility has an effect of the same order of the sample variation.

![Figure 17: Control group measurements (c) of several samples in THF:Mesitylene-1:3. Each time a 100 curves are done.](image)

5 Conclusions

This work demonstrates the importance of the motion of the Au atoms in understanding the $G$ vs. $z$ curves under $1G_0$.

It has been shown that the slope of these curves (in semi-log scale) can decrease in one order of magnitude (and, hence the attenuation factor) when the junction is kept open and the motion of the Au atom relaxes. This can account for the observed differences between the experimental and theoretical ‘a’.

The relaxation of the motion of the Au atoms is seen also in solvents. Each solvent has initial different effect on the motion of the Au atoms and thus, of the measured slope (as seen in [26]). The change with time, as the Au atoms motion decreased, was of the same order of the initial effect of the solvent variation. Once the Au motion relaxed all the solvent showed similar slopes.

When comparing the slopes in air/vacuum to those in the solvent we see a distinct difference. This due to the fact that the Au atoms rearrange in their medium until they reach a shape that is more stable and less influenced by the medium. The interaction of solvents with the contacts creates duller tips and higher friction causing the lowered slope.
As it was shown in previous work [26], the sample to sample variation is significant, but of the same order of the time dependance caused by the motion of the Au atoms.

An important trend that we saw, is the small-gap curve bending. This effect increased with time and was apparent in both opening and closing curves. It might play an important part in the rearrangement of the Au atoms and the blunting of the contact tips.

Many parameters play a role in the behavior of the Au break junctions (molecule layering/solvent of choice/sample variation). We saw that to study their effect, one must first let the motion of the Au atoms decrease as it is of the same order of the other phenomena.

6 Outlook

The ability to properly calibrate the control over the gap size $d$ from the offset $z$ is far from reached. Many parameters play a role in the function of $d(z)$. In order to study these effects, I propose that:

- A deeper research of the small-gap regime in different solvents is needed to understand the effects of molecule layering.
- Write a simulation of MCBJ in solvent. Perhaps this could shed light on the dynamics that affect the junction and how to reduce their variance.
- Perform the measurements under a SEM. To see the effect of the breakage on the junction in vacuum, and see why the attenuation factor “relaxes” after a while.
I would like to thank this opportunity to peek into the molecular electronics world. A special thank to Phd. M.Teresa González, that guided me all along this work with a lot of patience to my rebellious notions. And to, Songmei Wu and Roman Huber that every time I needed someone to “hold my hand” were there to instruct. Thanks.
8 Appendix I: Sample measurement sequence

Sample 02a measurements: (Voltage: 0.3V, Date: 9.5.06)

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Sample 02b measurements: (Voltage: 0.3V, Date: 9.5.06)

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Sample 03b measurements: (Voltage: 0.3V, Date: 22-23.5.06)

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0.1V
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References


REFERENCES


