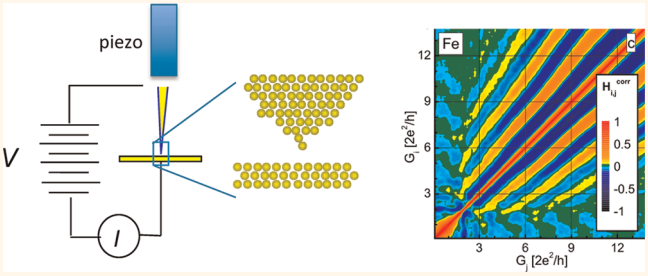
Mechanical Break Junctions: Enormous Information in a Nanoscale Package

Douglas Natelson*

Department of Physics and Astronomy, Rice University, 6100 Main Street, Houston, Texas 77005, United States

ABSTRACT



Mechanical break junctions, particularly those in which a metal tip is repeatedly moved in and out of contact with a metal film, have provided many insights into electronic conduction at the atomic and molecular scale, most often by averaging over many possible junction configurations. This averaging throws away a great deal of information, and Makk *et al.* in this issue of *ACS Nano* demonstrate that, with both simulated and real experimental data, more sophisticated two-dimensional analysis methods can reveal information otherwise obscured in simple histograms. As additional measured quantities come into play in break junction experiments, including thermopower, noise, and optical response, these more sophisticated analytic approaches are likely to become even more powerful. While break junctions are not directly practical for useful electronic devices, they are incredibly valuable tools for unraveling the electronic transport physics relevant for ultrascaled nanoelectronics.

The single biggest challenge in attempting to understand electronic conduction at the scale of single molecules is the assessment of the microscopic environment. It is clear that microscopic details matter enormously. In the simplest limit, tunneling varies exponentially with the separation of two metallic electrodes, such that a 0.1 nm change in the electrode spacing decreases conduction by a factor of e^2. Since the pioneering work by Landauer,[1] it has been known that conduction at the molecular scale can be considered in terms of quantum channels with transmittances, all of which should depend in detail on the overlap of electronic wave functions and hence the arrangement of atoms.

The problem is, as anyone who has attempted to work at this scale can tell you, it is very hard to see what you are doing. Even in scanning tunneling microscopy, the one clear case when you *can* see what you are doing, our knowledge is quite limited. While one may know the sample surface at the atomic level, the scanned probe tip is usually not characterized as well, and the best imaging typically takes place when the tip is far from any molecule of interest, so that tunneling conduction usually functions as a weakly perturbative probe rather than as a way of directly understanding the physics of interest in molecular-scale conductors "hardwired" to electrodes.

Mechanical break junction experiments have enabled a great deal of recent progress in characterizing conduction at the single-molecule level.[2] In one popular variation, a piezoelectric transducer brings a metal tip in and out of contact with an underlying metal film in an environment containing molecules of interest. Near the moment of breaking and junction formation, the tip/film junction is at the atomic scale. With a dc bias voltage applied to the tip, the current and transducer position are recorded as a function of time throughout the junction breaking and formation process. The most basic version of the analysis of this experiment then compiles histograms of the measured values of the conductance, $G \equiv I/V$. Junction configurations that are the most mechanically stable last the longest time and, thus, contribute the most to the histogram at the particular value of conductance that is favored by that arrangement of atoms and molecules. The result is a histogram with pronounced peaks at certain conductance values (Figure 1). For metals with conduction dominated by s electrons, such as gold, these peaks are located near integer multiples of $G_0 \equiv 2e^2/h$, the quantum of conductance.[3] In that case, the peak at 1 G_0 is largely due to junction configurations with a single, nearly perfectly transmitting quantum channel. In the absence of molecules, such

* Address correspondence to natelson@rice.edu.

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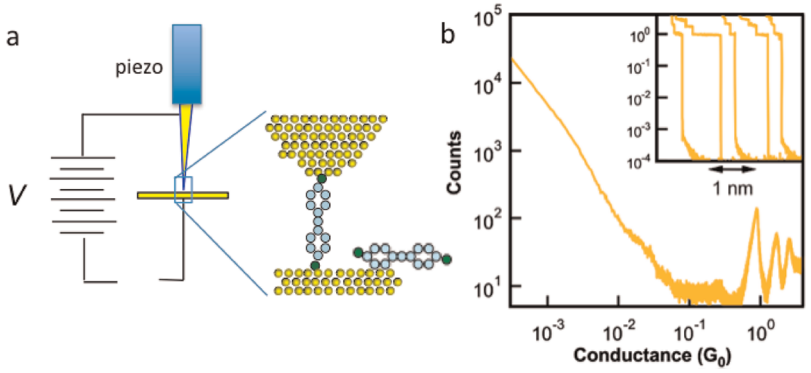

Figure 1. Break junction measurements in a scanning tunneling microscope configuration. (a) Piezoelectric actuator moves a metal tip in and out of contact with a conducting film substrate (or moves a substrate in and out of contact with a conducting tip), while the tip–film conductance is monitored. Conductance traces *vs* time are recorded, and a histogram is made that shows the relative frequency of occurrence of different conductance values. (b) Typical histogram for clean gold–gold junctions. Reproduced with permission from ref 4. Copyright 2008 The Institute of Physics.

peaks are all that are seen, with the histogram being essentially featureless and smooth at conductances lower than G_0.

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In the presence of molecules designed to bind with both the tip and the film, however, additional peaks show up at (most commonly) lower values of conductance. Through careful, systematic studies[5,6] of the peak conductances as a function of variation in the molecular structure, it has been confirmed that the most pronounced of these peaks represent junction configurations where a single molecule is bridging the (transiently formed) gap between the tip and the film. These experiments have been very enlightening. For example, these histogram measurements demonstrate that off-resonant conduction (when no molecular electronic level lies within the "bias window" between the tip and film chemical potentials) decays exponentially with molecular length for short molecules (a result seen previously *via* scanning tunneling microscopy[7] and conducting atomic force microscopy in molecular ensembles).[8] This is the expected situation when conduction is *via* what chemists call "superexchange" and what physicists call "co-tunneling", when the molecule acts like an effective tunnel barrier. Depending on whether the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) is closer to the electronic chemical potential (Fermi level) of the metal electrodes, transport can be hole-like or electron-like, respectively. Figure 2 presents a schematic of the relevant energy scales in such a junction. This length scaling also makes it possible to delineate between the contribution of the molecular "backbone" and that of the molecule/metal contacts,[9] as shown in Figure 3.

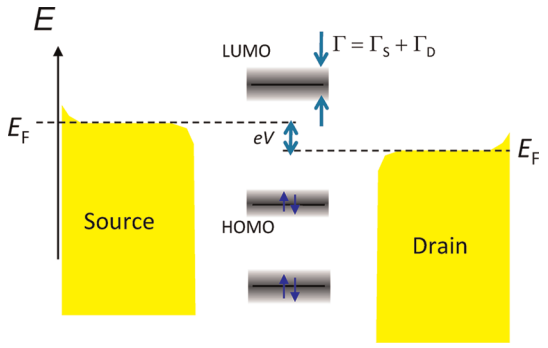

Figure 2. Some energy scales relevant for single-molecule junctions. The chemical potential for electrons in the metal electrodes is conventionally called the Fermi level, E_F, and is identical for the two electrodes in the absence of an applied bias voltage. A molecule bridging the electrodes has a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO). The widths of those levels, Γ, are determined by the wave function overlap between the molecular states and the electronic states in the metal. In most break junction experiments, transport is off-resonance, meaning that no electronic level lies between the Fermi levels of the electrodes.

The strength and definition of the molecular conductance peaks are related to the mechanical stability of the junction configuration and the robustness of the conductance as a function of geometric distortion of the junction. For example, if the overall junction conductance is strongly dominated by the metal–molecule contact, and if the wave function overlap between the electronic states in the metal and those in the molecule is strongly altered by tweaking the angle at which the molecule is bound to a particular metal site, then one might expect rather broad conductance histogram peaks, as the junction conductance varies

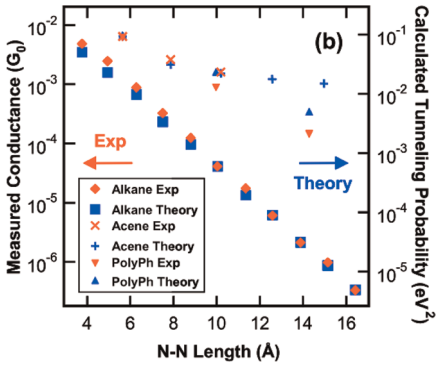

Figure 3. Electronic conduction as a function of molecular length for two different classes of molecules. The exponential decay of conduction with molecular length shows that in this off-resonant, small-molecule limit, transport is through cotunneling/superexchange, with the molecule acting as an effective tunnel barrier. Extrapolation back to zero molecular length gives an effective conductance of the metal/molecule contact. Reproduced with permission from ref 4. Copyright 2008 The Institute of Physics.

widely over a small range of tip motion. Conversely, a conductance that depends only weakly on molecular orientation would contribute to a relatively narrow peak since the conductance would not vary much over that same range of tip displacement. The combination of experimental results as a function of molecular terminal functional groups and detailed, realistic, density functional theory calculations has been of great help in understanding such effects, offering explanations for why molecular conductance peaks tend to be better defined with amine-terminated molecules on Au than the thiol-terminated molecules, for example.[10]

As revealing as these simple histogram analyses are, this approach ignores a great deal of information latent in the data being collected. The histogram is a complicated ensemble average over many junction configurations. The data, however, contain the particular time history of individual trajectories of junction formation and breaking. In this issue of *ACS Nano*, Makk *et al.* present[11] a clear, comprehensive look at cross-correlation techniques to extract this additional information. Rather than one-dimensional (1D) histograms, the authors consider different variants of two-dimensional (2D) analysis.

In addition to conductance, experimenters also record the voltage applied to the piezoelectric actuator that moves the tip relative to the surface. This voltage is a proxy for the tip−surface displacement, provided that there is a procedure for determining, in a given sweep, the point at which the metallic contact is broken and free-space tunneling begins. (The mechanical hysteresis inherent in both piezoelectric materials and the actual metal interface means that one cannot simply pick a reference piezoelectric voltage for this purpose.) For many materials, including Au, this is relatively straightforward. Examining histograms of conductance and elongation can reveal a great deal, including the formation of atomic chains (Figure 2) and reorientation and bond rupture in molecular junctions.[12,13] Although not plotted this way, looking at the evolution of junction elongation with applied bias voltage across the junction has offered one avenue of inferring current-driven ionic heating.[14] Heating the ionic degrees of freedom should generally make elongated junctions less stable, leading to rupture at shorter elongation distances.

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More to the point, 2D histograms can cross-correlate the occurrence of certain conductance values as junctions are broken.[15] Makk *et al.*[11] elucidate the procedure, including normalization, for constructing 2D histograms that highlight particular types of recurring phenomena (Figure 4). Each conductance trace r obtained while breaking a junction is binned into n conductance bins G_i, where i runs from 1 to n, with $N_i(r)$ counts appearing in bin i of trace r, for example. It is then possible to compute correlations between the bins. For example, one can consider the quantity $N_i \cdot N_j$ and its average over all the traces, which gives the cross-product histogram. One can construct and normalize "covariance" histograms that look at deviations away from averaged correlations. Makk *et al.* spell out the expected form of such histograms when, for example, particular conductance plateaus are anticorrelated in their appearance, or when there is a recurring spacing of conductance plateaus, even if the absolute magnitude of the plateau conductances varies from trace to trace. These analyses, backed up by experimental examples of their realizations, demonstrate convincingly that the future is bright for this approach, in terms of squeezing as much information as possible out of such a conceptually simple experimental method.

With the addition of further measurable quantities besides basic conductance and inferred elongation, these methods should become even more powerful. Over the last several years, additional experimental probes have been combined with the break junction technique. These include thermopower, noise, and optical response, which we discuss briefly below and show schematically in Figure 5.

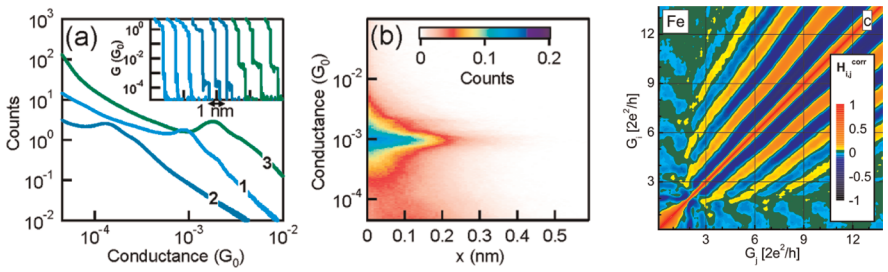

Figure 4. Examples of two-dimensional (2D) histograms of the type explained by Makk *et al*. (a) One-dimensional conductance histograms for three particular molecules, with an inset showing breaking traces as a function of tip–sample distance. (b) Two-dimensional histogram of conductance as a function of distance for molecule 1 of (a). Adapted with permission from ref 10. Copyright 2009 American Physical Society. (c) Two-dimensional correlation histogram for atomic-scale Fe junctions. The distinctive diagonal stripes seen in this histogram indicate that breaking traces of Fe junctions tend to show regularly spaced conductance plateaus with a common spacing from trace to trace, though the particular values of conductance vary. Adapted from ref 11. Copyright 2012 American Chemical Society.

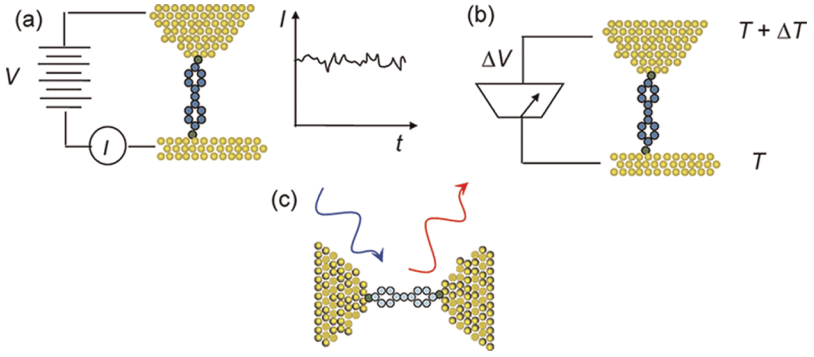

Figure 5. Additional measurement modalities being combined with repeated break junction conductance experiments. (a) Current noise, rather than just conductance. (b) Thermopower, looking at the voltage generated in the presence of an applied temperature gradient. (c) Optical spectroscopic response.

Makk *et al.* elucidate the procedure for constructing two-dimensional histograms that highlight particular types of recurring phenomena.

Thermopower Measurements. One topic of great interest has been the ultimate nanoscale limits of thermopower.[16,17] A temperature gradient ΔT imposed across a material leads to the establishment of a voltage difference ΔV. The thermopower $S \equiv \Delta V/\Delta T$ as $\Delta T \rightarrow 0$ and there is no net flow of current. In a macroscopic material in an "open circuit", the voltage difference appears to produce a countervailing flow of charge, canceling out thermally driven current. Apart from its appeal in the realm of possible power generation, thermopower is a sensitive probe of the density of states of the system of interest. Differences in the density of states (and effective mass and mobility in bulk materials) between charge carriers strongly influence the thermopower. Single-molecule junctions provide a great testbed for the ultimate limits of these ideas since electronic transport takes place primarily through only a very small number of (often only one) electronic levels. The magnitude and sign of the thermopower are thus very sensitive to the relative alignment of the HOMO/LUMO and the Fermi level of the electrodes. Thermopower is thus a powerful though challenging scientific tool for accessing this information. Break junction measurements examining multiple- and single-molecule thermopower have already begun.[18–20] Examining the detailed dependence of thermopower on junction configuration *via* 2D analysis techniques should prove fruitful, particularly in connection with theoretical analysis based on electronic structure methods.

Noise Measurements. Similarly, measurements of current noise—fluctuations about the average rate of charge flow through nanoscale systems—can contain much more information than ordinary measurements of conductance. Almost 100 years ago, Schottky[21] showed that the discreteness of charge and the assumption of independent electrons leads to current noise directly proportional to the average current and the electronic charge. Since the 1980s, researchers have recognized that such non-equilibrium "shot" noise is a means of examining both the detailed quantum channels that allow transmission through a nanoscale device and the correlations between electrons. Measurements in individual mechanical break junction configurations at low

temperatures have demonstrated the quantum nature of conductance, showing strong suppression of such noise in the presence of fully transmitting quantum channels[22] and allowing the assessment of the number of channels at work in certain molecular junctions.[23] Recent advances have made it possible to measure noise, albeit without much averaging, with sufficient speed that data may be acquired during the repetitive junction experiments discussed here,[24] even at room temperature. Given the expectation that shot noise can be modified significantly by electron-vibrational coupling, and that this coupling evolves with junction configuration, the above 2D analysis techniques should be able to examine physics previously obscured by ensemble averaging.

Optical Measurements. Finally, there have been recent advances combining optical measurements with break junctions. Optical spectroscopy is enormously useful, but many complications arise in trying to apply it to individual atoms or molecules in junctions, including local heating and the challenges of efficient illumination or collection of light. Immediate proximity to the metal electrodes (tip and surface in a STM geometry) can quench fluorescence and other luminescence processes due to nonradiative relaxation mechanisms. However, plasmon excitations localized right at the nanogap between the two electrodes can lead to tremendous enhancement of local electromagnetic fields. These enhanced fields enable single-molecule Raman sensitivity,[25−28] and radiative decay of electrically excited plasmons allows simultaneous studies of light emission as a function of junction conductance.[29] The ability to perform nanojunction optical measurements rapidly, on the time scale associated with the repetitive junction experiments discussed here, would open up many possibilities. Given the complicated nature of the experimental environment (*e.g.*, hot electrons due to optical excitation, plasmon excitations in the metal, potential photon-assisted processes involving molecules), however, great care may be needed to unravel the underlying physics.

CONCLUSIONS AND OUTLOOK

This is a bright time for measurements in nanojunctions. Analyses like those of Makk *et al.*[11] vividly demonstrate how much information is latent in conductance traces obtained with break junctions. Expanding these experiments to include other measured quantities promises a wealth of new insights, particularly with advances in state-of-the-art theoretical methods to aid in the interpretation of the results. While no one is going to build technologically useful nanoelectronic devices based on atomic- and molecular-scale break junctions, there is no doubt that the physics at work in these systems will one day be directly relevant to charge transport and heat dissipation in ultrascaled nanoelectronics—amazing for an experimental approach that started off with such conceptual simplicity.

Conflict of Interest: The authors declare no competing financial interest.

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