Ab initio simulations of the mechanics and electrical transport of Pt nanowires

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Abstract

Based on first principles, theoretical studies of atomic-scale platinum contacts are presented. A short monatomic wire freely suspended between tips is seen to vibrate as its tensile load increases. The main vibration mode is transversal for lower tensions and longitudinal for higher tensions up to the breaking of the nanowire. The computed conductance exhibits oscillation in the sub-picosecond regime that can be well correlated to the mechanical oscillations of the nanowire. Both the values for the maximum tensile load and the average conductance agree well with available experimental measurements.

Keywords: Platinum nanowires; Density functional theory; Non-equilibrium greens functions; Ballistic conductance; Conductance quantization; Molecular dynamics simulations

1. Introduction

When two pieces of material are taken into contact, nano-scale asperities at the surfaces give rise to the formation of a series of disordered “nano-scale point contacts”. Upon pulling the pieces apart, these nano-scale point contacts break one after another, such that the mechanical contact is definitely lost when the last one disappears. In the last decade, many studies have been focused on the formation, mechanical evolution and electrical characterization of single nano-scale point contact. In particular, due to its importance in fields such as tribology, wear, friction, and electrical quantum transport, the physics of metal nanowires has been studied intensely [1].

In this work, we will focus on monatomic Pt nanowires for which various experimental studies have been carried out at different temperatures and under different environments [2–7]. In particular, an interesting transition, a shift of the first peak of the conductance histogram, was observed as a function of the bias voltage applied [5,7].

The given interpretation is that the shift marks a geometric transition point where single-atom Pt contacts replace longer monoatomic chains. Thus, single atom contacts are expected to present a conductance value of ca. 1.8$G_0$ ($G_0 = 2e^2/h$ being the quantum unit of conductance) while for longer chains (not defined how long) there is a broad peak centered slightly below 1.5$G_0$ [7].

Theoretical calculations of Pt monatomic wires and their eventual magnetization were presented by Delin and Tosatti in 2003 [8]. They concluded that at 0 K and for ideally long monatomic wires there should be a permanent magnetic moment of about 0.6$\mu_B$. The energy gain of the ferromagnetic state is about 8 meV. The conclusion is that magnetization could be observed at very low temperature or with some high field applied. From their results, it is not expected, however, that magnetization could be observed at room temperature and zero magnetic field.

Many are the remaining questions, among them we can mention just a few: (i) what is the most stable atomic configuration of a tip-wire-tip system for monatomic Pt wires? (ii) Does the tensile load influence the vibration mode of the monatomic wire? (iii) How do thermal vibrations influence the conductive properties of Pt monatomic wires? (iv) The chemical reactivity of the...
monatomic wires and its effects on their mechanical and conducting properties are still to be analyzed.

The last question, that of the chemical reactivity and influence of impurities in the Pt chains, will be the focus of our future work, in the present, we will provide some clues to answer the rest.

2. Method

For the theoretical analysis, we have performed room temperature first principles molecular dynamics (MD) simulations of the breaking process of tip suspended monatomic Pt wires under tensile stress. At each time step, the forces are calculated from a Born–Oppenheimer density functional (DFT) self-consistent calculation of the electronic structure of the instantaneous configuration of the nuclei. The core electrons are approximated by standard scalar relativistic norm-conserving pseudopotentials [9], and the valence density is expanded in a basis set of numerical pseudoatomic orbitals [10]. Owing to our goal of room temperature simulation, since the magnetization is expected to be null (in the scalar relativistic approximation) or weak [8], and in order to speed up the computations, no spin polarization has been allowed or searched. The function used for the exchange and correlation was a generalized gradient approximation [11]. In good agreement with previous calculations, test calculations with the same functional and basis sets yield the following relaxed distances: 2.78 Å for the bulk and 2.42 Å for the infinite undimerized monatomic linear wire. The conductance was computed by attaching, as electrodes, semiinfinite Pt nanowires as thick as the extreme layers and in the same 111 orientation. The self-consistent solution for DFT scattering states was achieved by non-equilibrium Green’s functions (NEGF) computation techniques and using the same local basis sets as in the cluster MD simulations. This was computed as implemented in the software package ATK [12].

3. Results

The starting configuration is that labeled as “time 0 ps” in Fig. 1 (left-most panel) consists of two 111 tips, of 10 Pt atoms each, plus two atoms in between forming an initially straight monatomic-wire-between-tips configuration. The interatomic distances are: 2.7 Å between atoms in the tips, corresponding to the relaxed isolated tip configuration, and 2.45 Å for the interatomic distances in the wire, corresponding to an slightly compressed wire. From there, both extreme layers are kept frozen and controllably pulled apart at a relative velocity of 0.25 mA˚/fs.

Upon starting the simulation, and due to the mechanical and thermal energy, the wire and the mobile atoms at the tips start vibrating. We found that the vibration mode and the frequency depend on the strain of the wire. Initially, the vibrations are mainly transversal to the wire axis, where the tip-apex atoms and the immediately lower layer follow lateral movements very markedly. See, for example, the remarkable left-right-left displacements exhibited by the four mobile atoms of the upper tip as a whole (see frames for times: 3.0, 3.6 and 4.06 ps, respectively). Upon further stretching, the longitudinal vibrations become dominant. From 4.26 to 4.8 ps one of these longitudinal vibrations is in charge of definitively breaking the bond, and the monatomic wire.

While the overall kinetic energy fluctuates around a constant due to the controlled-temperature dynamics, a general increase of the potential (Kohn–Sham) energy can be seen in Fig. 2. This is due to the external force acting on the system; the extreme layers are being pulled apart. The average slope up to the breaking point at ca. 4 ps, see the dashed line in Fig. 2, yields the time averaged (during 4 ps) tensile force over the system: 2.8 nN in the present simulation.

The zero-bias ballistic conductance as a function of time shows strong oscillations that correlate, in frequency (being the dominant harmonic at 6 ps⁻¹) and intensity, to the mechanical vibrations of the wire (see Fig. 3). Naively, one might expect that conductance quantization effects would
promote a steady evolution of the conductance with a value close to one quantum unit. However, the high sensitivity of the conductance to the mechanical vibrations indicates that conductance quantization is not taking place overall. Indeed, our analysis of the conduction channels shows that there are three partially open channels; one of them (s–d$^2$) quite saturated, accounting for most of the current, while the other two present a much lower transmission, which is dependent very sensitively on the geometry of the contacts.

The correlation between the conductance oscillations (CO) and the geometry oscillations (GO) is trivial from the following reasoning: from one frame to the next the only thing that changes (in our model) is the geometry. So any change in the conductance is necessarily a result of a geometrical variation. Differential changes in the geometry

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**Fig. 2.** Upper panel; time evolution of the Kohn–Sham potential energy of the system depicted in Fig. 1. A general increase of the potential energy can be seen due to the external force acting on the system. Lower panel; externally applied force (positive sign means tensile load), computed as a running average derivative with a window of 1 ps (solid line) and 4 ps (dashed line). The average force is tensile and of the order of 2.8 nN.

**Fig. 3.** Conductance as a function of time for three increasingly better basis sets: SZ, DZ, and DZP. It can be seen how the results of DZ and DZP do not differ significantly, so we consider the computation converged with respect to the basis set. The oscillations can be correlated to the mechanical vibrations (or the energy vs. time oscillations seen in Fig. 2). The high sensitivity to atomic configuration (particularly at the contacts) of two partially open channels yields this sub-picosecond conductance oscillations. The average value of the plateau is 1.2$G_0$ in good agreement with observation.
give differential changes in the conductance with a given slope (quite high most of the time as can be seen in the conductance vs. time curve), these changes are of course reversible; undoing the geometry variations takes us back to the previous conductances values through the same conductance curve. Now, note the periodic nature of the GO where (practically) the same configurations are adopted periodically. Thus, it is obvious that: (i) The CO will follow the GO; (ii) The only possibility for the CO to have a different frequency is for it to be higher than the frequency of the GO. And the latter case, that the CO are of higher frequency than the GO, is not taking place as can be concluded by simple observation and comparison of the CO and GO plots (the sampling of the conductance vs time curve was steadily increased until all the peaks were resolved by at least two points). Therefore, as it is not higher, it is apparent that GO and CO have the same frequency, as we wanted to proof.

That the amplitude of the CO correlates to the amplitude of the GO can be deduced to be true for small geometrical variations (since the conductance changes are linear at first order). However, it is not so obvious for larger geometry variations since the conductance, specially close to conductance quantization plateaus, might be highly non linear. Nevertheless, this correlation can be seen empirically as we show in the following.

Note that geometrical variations beyond the harmonic limit are difficult to parametrize because the number of possible variables is large (inter-atomic distances, dihedral angles, etc.). However, in this case it is reasonable to think that the geometrical variations that most influence the conductance are those pertaining to the central region; the four central atoms. Therefore, let us characterize the geometry of the system by a very simple parameter; the sum of the three inter-atomic distances in the central 1D monatomic wire: d [14]. In Fig. 4, we have plotted the time dependence of the amplitude of the oscillations of d (solid line) [15]. As can be seen, the curve has several broad peaks centered at ca. 0.7, 1.4, 2.2, 3.1 and 3.9 ps. All these peaks (but the last) correspond with peaks in the plot of the amplitude of the CO (dashed line). Note that there are other peaks in the amplitude of the CO, these might be due to other geometrical fluctuations not well characterized by the simple parameter d. In spite of d’s simplicity, a high degree of correlation between curves is clearly seen, from which we can conclude that the conductance is not quantized (or just weekly so).

4. Discussion

For metals, but mostly so for 5d metals owing to relativistic effects, the binding energy per bond increases with decreasing coordination. Thus, the lower-coordinated first atom of the wire would have a (roughly three times) stronger bond with the tip-apex atom, than the latter with the tip. It has been argued that the metal bonding in 5d elements is such that one single atom from the monatomic wire would be able to “pull out” the tip-apex atom even though it counts with a greater number of “bonds”. Therefore, we were expecting that upon stretching, one of the apex atoms would be incorporated to the monatomic wire. But this has not been the case in the present simulation. Is our model too incorrect? Should we include spin polarization in the calculations? Or we just have been unlucky this time? The answer is that the model (meaning DFT and the theoretical approximations used) is not that incorrect and we have not been unlucky. We simply chose somewhat unrealistic, even though very common, initial geometry and constrains. We believe that the selection of the initial configuration—in particular the ⟨111⟩ tips
orientation, and the reduced number of mobile atoms—is the main cause for the failure to “pull out” a new atom into the monatomic chain. Using the same theoretical approximations, simulations with larger number of mobile atoms and starting from fully annealed configurations, where the tips have not been assumed to be \( \langle 111 \rangle \), yield otherwise; monatomic wires naturally “grow” out of thicker contacts [13], in correspondence with experimental observations. In fact, even though atoms have not been “pulled out into the wire” in the present simulation, there are clear indications that it has been almost the case. The marked lateral oscillations of the whole mobile atoms at the tips clearly indicate that the bonds between atoms of the monatomic wire are stronger than the bonds between the tip-apex atom and the surface. The simulation shows that—by pulling from the monatomic wire—all four mobile atoms at the tip are slightly “pulled out”, such that the potential energy barrier to lateral displacements (of the whole mobile part) is overcome! In this sense, a single bond can “lift” vibrations of the whole mobile atoms at the tips clearly indicate that the bonds between atoms of the monatomic wire are stronger than the bonds between the tip-apex atom and the surface. The simulation shows that—by pulling from the monatomic wire—all four mobile atoms at the tip are slightly “pulled out”, such that the potential energy barrier to lateral displacements (of the whole mobile part of the tip) is overcome! In this sense, a single bond can “lift up” other four and remain intact while the tip atoms laterally vibrate for lengths of ca. 1.5 Å. These marked lateral vibrations of the contacts are indeed related to the fluctuations seen in the conductance as we have discussed earlier.

5. Summary and conclusions

In conclusion, the atomic structure and electrical and mechanical properties of atomic-size Pt wires have been studied theoretically using first principles techniques. We have shown how a short monatomic wire freely suspended between tips vibrates as its tensile load increases. We found that the main vibration mode changes with tensile load; it is transversal for lower tensions and longitudinal for higher tensions. The zero bias ballistic conductance has been computed all along the simulation and it has been shown that it exhibits oscillations in the sub-picosecond regime. These oscillations can be well correlated to the mechanical vibrations of the nanowire. The maximum force supported by the monatomic wire in the present simulation is ca. 2.8 nN, while the conductance is seen to oscillate around 1.2 \( G_0 \). Both the values for the maximum tensile load and the average conductance agree well with available experimental measurements. We have seen how the zero-bias ballistic conductance shows strong time dependent oscillations that correlate, in frequency and intensity, to the mechanical vibrations of the wire. These can be understood as a consequence of the high sensitivity to atomic configuration of the contacts of two partially open conduction channels.

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[13] Jose A. Torres, unpublished data.
[14] Mathematical definition of \( d \). Let us number atoms as follows; number 1 is the atom at one of the tip’s apex. The next atom (towards the center) is atom number 2. The next is atom number 3. And the next atom (located in the other tip’s apex) is number 4. Then, the definition of the geometrical parameter \( d \) is simply: \( d = d_{12} + d_{34} \) where \( d_j \) is defined as the distance between atoms with indexes \( i \) and \( j \).
[15] We define and compute the amplitude of the oscillations of \( d \) as follows; first a running average of \( d \) with a time window of 0.3 ps has been computed. Then, the square of the difference between \( d \) and this running average has been computed. Which has been further running-averaged (with a window of 0.15 ps) to yield the results shown in Fig. 4. To compute the amplitude of the conductance oscillations, exactly the same prescription has been performed.