On the formation and the stability of suspended transition metal monatomic chains

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Abstract

We present a Tight-Binding Molecular Dynamics investigation of the stability, the geometrical and the electronic structure of suspended monatomic transition metal chains. We show that linear and stable monatomic chains are formed at temperature equal or smaller than 500 K for Au, 200 K for Ag and 4 K for Cu. We also evidence that such stability is associated with the persisting sd orbital hybridization along the chains. The study highlight fundamental limitations of conductance measurement experiments to detect these chains in the breaking process of nanowires.
Understanding physical properties such as the stability and ubiquity of suspended monatomic chains (SMCs) is an important step to exploit their abilities to transport spontaneously spin polarized electrons \[1, 2\] and to support high current densities \[3\]. In spite of different efforts \[4, 5, 6, 7, 8, 9, 10, 11, 12, 13\], a theoretical explanation for their relatively high stability and their characteristic linear chain structure remains elusive \[14, 15, 16, 17, 18\]. Moreover, rationalizing the possible formation of these chains in 3d and 4d transition metals continues being a challenge to scientists mainly due to a lack of agreement between results \[19, 20, 21, 22\].

Suspended monatomic chains (SMCs) are typically generated by electron beam irradiation of a suspended metal film \[1, 6, 9, 20, 21\] as well through a stretching nanowire procedure that makes use of a scanning tunneling microscope (STM) \[4, 5, 7\] or a mechanically controllable break junction (MCBJ) technique \[5, 19, 22\]. Despite of their popularity, these techniques suffer of inherent limitations that have made the unambiguous interpretation of the data a difficult task. On the one hand, SMCs formation experiments with electron beam irradiation and STM techniques are based on high-resolution transmission electron microscopy (HR TEM) observations, which are limited due to the poor time resolution (around thirty pictures per second) \[6\] and uncontrollable sample contaminations \[23\]. On the other hand, MCBJ is based on a not totally justified interpretation of the conductance data generated during the nanowire breaking process \[19, 22\]. Therefore, computational studies constitute an appealing complement that could pave the way for a coherent description of the experimental results.

In this letter, the formation and the stability of SMCs are investigated by stretching Au, Ag and Cu nanowires. Using the tight-binding molecular dynamics technique, we show that linear and stable SMCs are formed at temperature equal or smaller than 500 K for Au, 200 K for Ag and 4 K for Cu, and that such stability is associated with the persisting sd orbital hybridization along the chains. Additionally, a good agreement is found when numerical histograms of nanowire stretching lengths are compared to experiments.

For the molecular dynamics simulations, at each iteration step of 2 fs, we calculated the electronic structure by considering the total-energy tight-binding method introduced by Papaconstantopoulos and Mehl \[24\]. Comparisons with Density Functional Theory calculations revealed that this approximation is able to describe the SMC formation process \[13, 16\]. We used the Verlet algorithm to integrate the equations of motion of each atom. The temperature \(T\) was controlled with a Langevin thermostat. The dynamical evolution of the wire
under stress was simulated in the following way: for the initial configurations, we considered
a metal block containing 68 atoms obtained from a bulk face centered cubic (fcc) (111) layers
oriented along the z-axis and tapered to a narrowing in the middle. The atoms at the top
layer were frozen and through periodic boundary conditions along the z-axis, their images
were considered to form also the bottom layer of the wire. These frozen layers (the real at
the top and its image at the bottom) determine the bulk support of the wire during the
elongation process and were used to stretch the structure along the z-axis by increasing the
distance between them. The atoms inside these frozen slabs remained frozen during sub-
sequent stages of the simulation while the other atoms between them move and rearrange
into new configurations. We equilibrated the wire for about 20 ps. Then, as has been done
in previous classical studies[7, 8, 10, 11, 21, 25], a stretching velocity of 5 m/s was applied.
The stretching distance is defined as the increased distance between the real top layer and
its image at the bottom respect to the resulting nanowire configuration just before the first
atom-contact appears.

Figs. 1a-g show the last stage of a nanowire stretching process when an Au SMC is formed.
In all these configurations, the bond lengths between the atoms forming the chain range
from 2.5-2.9 Å, in good agreement with experiments[5, 9]. Along the chain, we computed
the orbital populations based on a Mulliken population analysis, while the cohesive energy
$E_{coh}$ of an $i$-atom was obtained by calculating $Tr(\rho H) = \sum |\rho|_{i\alpha,j\beta}|H|_{j\beta,i\alpha}$, where $\rho$ is the
density matrix and $H$ the hamiltonian. The above summation is over atom labels $j\neq i$
and state labels $\alpha, \beta$, and implicitly includes an integral over $k$ as well. We found that during
the nanowire stretching process, when the monatomic chain gains an extra atom (coming
from the apexes of the breaking nanowire as seen in Figs. 1a-g), the electron populations
abruptly redistribute within the chain, as reflected by the jumps in the d-orbital population
curves depicted in Fig. 1h. A similar effect was found for the s-orbital populations (data not
shown), in consistency with the sawtoothlike conductance signal observed in experiments
during the formation of Au SMCs[7]. Fig. 1h also shows that depending on the monatomic
chain regions, the d-orbital populations tend to decrease (increase) in the atoms located at
the top and bottom (at the middle) of the chains as the stretching distance is increased.
Finally, when this Au monatomic chain (consisting of 6 atoms) breaks, the the populations
abruptly increase in the central region an reach an approximate value of 9.92, a fact that
is supported by the drop to zero of the corresponding $E_{coh}$ (see Fig. 1i). Such threshold
value corresponds to the typical d-orbital population for an atom located in an extreme of an Au monatomic chain. Correlatively, after some relaxation of the broken chain, $E_{\text{coh}}$ for that atom jumps from 0 to the corresponding energy value of a single bonded Au atom ($\sim -1$ eV).

Although the maximum number of atoms contained in a monatomic chain depends on the stretching realization (as we will discuss below), the above observed abrupt increasing behavior for the d-orbital populations in the middle of the chain seems to be independent on the chain length and realization. The later is evidenced in Fig. 2 for two Au monatomic chains (black symbols) generated from different stretching process realizations leading to one chain of 4 atoms (black circles) and the other of 5 atoms (black triangles). As before, it is observed that $E_{\text{coh}}$ decreases when the d-orbital populations become equal to 9.92. The results in Fig. 2 also show that Ag (blue symbols) and Cu (red symbols) chains of 4 atoms exhibit a similar behavior. In these cases, when the chains break, the d-orbital populations result equal to 9.96 and 9.98 for Ag and Cu, respectively, a fact that may reflect the weaker sd hybridization in these elements. These results also indicate that during the stretching process, the loss of the sd orbital hybridization occurs in the lower atomic coordination region, where the atoms tend to completely fill their d-orbitals.

The stability of SMCs has been also examined here by stopping the nanowire stretching process before the chains break. In the molecular dynamics simulations, the later is achieved by fixing to zero the stretching velocity applied to the top and the bottom of the nanowire just when each chain realization reaches its respective maximum number of atoms. The chains are then allowed to relax at different $T$. Fig. 3 shows the d-orbital populations for Au (circles), Ag (squares) and Cu (triangles) at the middle of these chains as a function of time for $T$ around values where the chains become unstable. Note that these populations fluctuate around a constant value and that the amplitude of the fluctuations depend on $T$ and the atom type. We found that at 4 K, the structure of Au, Ag and Cu monatomic chains remained linear and stable for more than 10 nanosec. When $T$ is increased the amplitude of the fluctuations of the d-orbital populations increases, leading to an increase of the probability to break the monatomic chains by reaching the reported d-orbital population threshold values. The chains break when $T$ is increased to 600 K, 300 K and 100 K in the case of Au, Ag and Cu, respectively. In addition, for the high $T$ considered in this study, we found that the chains tend to adopt a zigzag structure. The later suggests that although this
zigzag shape for the chain corresponds to a minimum energy configuration (as predicted by DFT calculations [15, 18]), its experimental observation is not possible because the required energy to overcome the characteristic potential barrier between the linear and the zigzag chain configuration is equivalent to a temperature where these chains are unstable.

In MCBJ experiments, the conductance is monitored as a function of the stretching length, showing a steplike decrease as a nanowire is slowly broken [3, 5]. Since in monovalent transition metals each atom located at the nanowire neck is expected to contribute with one quantum unit of conductance $G_0 (=2e^2/h)$ [4, 6, 20], the length of the last conductance plateau (where $G$ is approximately equal to $G_0$) is usually associated to the chain length [5, 19, 22]. A large number of contact breaking cycles are typically performed in order to build histogram distributions of stretching lengths. At low $T$ and for 5d transition metals, such histograms exhibit a series of peaks, while a single strong peak is observed in 4d metals. The difference between 5d and 4d transition metal histogram distributions of lengths has been used to argue that only 5d transition metals exhibit SMCs [19, 22], a fact that contrast with the stability of Ag and Cu monatomic chains reported in this study. To investigate the source of such discrepancy, numerical histogram distributions of lengths were computed by considering different chain formations generated from a hundred numerical realizations of the breaking process on Au, Ag and Cu nanowires. A very good agreement between the resulting simulated histograms and those obtained experimentally [19, 22] is deduced from Fig. 4 (black curves). While for $T=4$ K, Ag and Cu exhibit only a single strong peak, the Au histogram shows two strong peaks as in the experiments, with a peak-peak separation consistent with the expected bond length of the Au atoms in the chain. In addition, the vanishing second peak as $T$ increases observed experimentally for Au [22] is also predicted by these calculations (see Fig. 4). This agreement between the simulations and the experiments provides strong confidence on the predictive ability of the theoretical approximation considered here.

The simulation data allows a degree of a detailed analysis not possible experimentally, as is the characterization of the different contributions of chains containing different number of atoms in the histogram distributions of lengths. Fig. 4 (colored curves) shows that in the case of Au, Ag and Cu, the first peak exhibited by these histograms are due to the contributions of chains with 2 (red curve), 3 (green curve) and 4 (blue curve) atoms, thus indicating that a stretching length (plateau length) of 2 Å can form indistinctively
short or long monatomic chains, depending on each breakage realization i.e. the particular nanowire evolution process. Therefore, the stretching length required to form a diatomic suspended chain (the two columns of atoms formed just before the monatomic chain starts to appear) should serve as an indicator of what will happen in the subsequent monatomic chain formation process. Thus, in the case of Ag, we found that when the stretching length associated with the diatomic chain becomes larger than 3 Å, a monatomic chain of 4 Ag atoms can be formed by just stretching a length of 2 Å. However, if the stretching length corresponding to the diatomic chain formation is smaller than 1 Å, a stretching length of more than 4 Å is required to form the same monatomic chain of 4 atoms. This result leads to the conclusion that the presence of a single strong maximum around 2 Å in the histogram length distributions cannot be interpreted as the absence of monatomic Ag chain formation as previously claimed[19, 22], and agrees with the HRTEM data that provides experimental evidence for the formation of Ag SMCs[20]. The importance of the history of the nanowire breakage process is also observed in the case of Au. Figs. 4c and 4d show how the formation of monatomic chains containing 4 Au atoms contribute to the high-intensity of the first and second maxima of these histogram length distributions. Moreover, Figs. 1a,g and 4e illustrate how the chain formation process can differ from one realization to another: while the structure depicted in Fig. 1a requires a stretching distance of 5 Å to form an Au chain of 6 atoms, the configuration depicted in the left panel of Fig. 4e requires only 2.2 Å to form a similar Au chain of 6 atoms.

The chain sizes and the critical temperature where these chains lose the stability will depend on the specific electronic configuration of each chemical species. The tendency of Au to produce longer stable monatomic chains can be understood in terms of the strong sd orbital hybridization that characterize this metal. The strength of this hybridization can be examined by comparing the orbital populations of an isolated Au atom (1 for s and 10 for the d-orbital), with the corresponding populations in the bulk phase (1.5 for s and 9.5 for d-orbitals), a fact that can be related with the well known strong relativistic effects in the last row transition metal elements[27]. For other transition metals, these s-orbital (d-orbital) populations are smaller (higher) as one moves up rows in the periodic table.

In summary, we show that at low T (4 K) Au, Ag and Cu exhibit linear and stable monatomic chains, and that these two last elements tend to form shorter chains. Particularly, compared to Au, the tendency of Cu to form shorter chains than agrees with a recent
Our findings show that the stability of the chains is associated with the persisting sd orbital hybridization along the chains, which is affected when the system is heated in an amount that depends on the particular metal species. We found that among these three elements, only Au monatomic chains are highly stable at room temperature. The present study not only provides a coherent interpretation of the differences found in monatomic chain formations between 3d and 4d, with respect to 5d transition metals, but also is consistent with the picture that the sp-character of some atoms like oxygen intercalated in monatomic metal chains would help the hybridization of d-orbitals, favoring longer chain formations, as recently suggested in experimental studies on controlled oxygen atmosphere.

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FIG. 1: (a-g) Schematic representation of the formation of a chain of 6 atoms when a nanowire is stretched. (h) d-orbital populations and (i) cohesive energy as a function of the stretching distance for the different chain regions labeled in figs. (a-g).

FIG. 2: (a) d-orbital populations and (b) cohesive energy as a function of the stretching distance for atoms located in the central region of Cu, Ag and Au chains. These curves correspond to chains containing a maximum number of 4 atoms (circle symbols) and 5 atoms (triangle symbols). In (a) the dotted segments denote the threshold value for the d-orbital populations where the chains break.

FIG. 3: Time evolution of the d-orbital populations of the atoms located in the central region of Cu, Ag and Au chains for different $T$. Cu and Ag chains contain 4 atoms while the Au chain contains 6 atoms. The dotted lines depict the typical threshold values where the chain breaks.
FIG. 4: (a) Cu, (b) Ag and (c) Au histogram distribution of stretching lengths (black curves) obtained from a hundred of realizations at $T$ equal to 4 K, and (d) 300 K for Au. The different contributions in these histograms of chains containing 2, 3, 4, 5 and 6 atoms are depicted by the colored curves. (e) Illustrates a situation where a stretching distance of 2.2 Å is enough to form an Au chain of 6 atoms.
Fig. 1

Stretching distance (Ångstroms)

Cohesive energy (eV)

1 and 2
3 and 4
5 and 6

9.7
9.8
9.9

G"RUELWDOSRSXODWLRQV
$WRPODEHOV

i

a b c d
e
f g

0 1 2 3 4 5 6

Stretching distance (Ångstroms)
Fig. 2

- Stretching distance (Å)
- Cohesive energy (eV)

Cu
Ag
Au

(a)
(b)
Fig. 4