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On the Lifetime of Suspended Atomic Chains Formed from Stretched Metallic Gold Nanowires

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Metallic nanowires have been object of intense theoretical and experimental works in the last years. In spite of the large number of studies for such systems some fundamental aspects remain open and polemical questions. In this work we report preliminary results for the study of the final steps of Au suspended atomic chains (LACs) with different number of atoms as a function of temperature. We have carried out classical molecular dynamics simulations using tight-binding models with a second moment approximations. Our results suggest a more complex phenomenon than previously anticipated. The dynamics of chain rupture seems to be determined beyond thermodynamics contributions and the bond breaking patterns were observed to be chain-length dependent.

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1. INTRODUCTION

In the last years a great effort has been devoted to better understand fundamental aspects of nanostructures. Advances in experimental techniques have generated new and more detailed information about structures and dynamical processes at nanoscale.

Among nanostructures metallic nanowires (NWs) have received special attention due to the observation of very interesting new phenomena, as well as, by their potential technological application [1]. Since the pioneering theoretical investigations from indentation and tribology studies [2] followed by experimental realization from high resolution transmission electron microscopy (HRTEM) [3, 4], NWs remain one of most important subjects in nanosciences [1]. However, in spite of the large amount of theoretical and experimental works, some fundamental aspects about NW formation and stability remain open and polemical questions and unexpected findings continue to be produced [5, 6].

From the experimental point of view two major techniques have been used to study NW under mechanical stretching; HRTEM [3, 4, 7–10] and mechanically controllable break junctions (MCBJ) [7, 11, 12]. HRTEM experiments provide structural and dynamics information from real-time imaging and MCBJ can address electronic transport phenomena. There are fewer studies using other techniques, such as, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) [1].

Stretching NWs up to rupture limit can generate nanostructures of many different shapes and forms. Rod-like, helicoidal, tubular, and linear atomic chains have been reported from theoretical and experimental studies [1, 3, 5, 6, 13–18]. Many and diverse theoretical techniques [5, 15, 16, 19–22, 26–32] have been used to study these systems; continuous, mixed models with empirical potentials, and even *ab initio* ones. In this work we have theoretically investigated the lifetime of suspended atomic chains (LACs) formed from stretched gold NWs. Experimental LAC formation involves stochastic aspects which implies the need of considering many cases at different conditions (temperature, pulling velocities, crystallographic orientations, etc.). The large number of cases and size of the structures (hundreds of atoms) precludes the use of full *ab initio* methods due to the high computational cost. A natural choice to study these systems could be to use embedded atom potential (EAM) [31, 32] or tight-binding model with second moment approximations (TB-SMA) [33, 34]. EAM and TB-SMA have good records of well describing metallic structures. Our choice was to use TB-SMA by the reasons detailed in the methodology section.

2. METHODOLOGY

The problem of LAC formation is very complex. From the experimental point of view factors such as temperature, stress/strain values, grain crystallographic orientations, etc., play an important role determining NW morphology and dynamics formation. In order to investigate this problem from a theoretical point of view we need a methodology capable of reliably addressing these aspects, as well as, being cost effectively handling structures containing hundreds of atoms. As mentioned above our choice was to use TB-SMA. We have successfully used this methodology to study NW of different elements (Au, Ag, Pt, Cu) and even alloys (Au-Ag, Cu-Au) [5, 15–18]. Also, a recent comparative study of potentials to describe metallic nanostructures [35] showed that TB-SMA is a good and reliable choice.

TB-SMA methodology is based on moment theory [36, 37] within a tight-binding approximation [33, 34]. It has been successfully used to obtain fusion temperatures and

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cohesive energies of transition metals. It has also been used to study crystalline field effect and stacking fault energies of hexagonal closed packed (hcp), face-centered cubic (fcc) and body-centered cubic (bcc) metals [38–40].

The cohesive properties of transition metals is related to the density of states (DOS) of d-bands, but the thermodynamics structural properties are not very sensitive to details of the electronic DOS. The local DOS (LDOS) expansion in moments is possible calculating the electronic Hamiltonian terms along specific directions of the Brillouin zone [36, 37]. In particular, the first moment is associated with the center energy-band value (in general set to zero for pure systems) and the second moment is proportional to the mean DOS width value. Higher moments can be obtained using recursive methods [33, 39].

The cohesive energy E_c of the system can be written as [30]:

$$\begin{aligned} E_R^i &= \left[\sum_j A_{\alpha\beta} e^{-p_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)}\right] \\ E_A^i &= -\left[\sum_j \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)}\right]^{1/2} \\ E_c &= \sum_i \left(E_R^i + E_A^i\right) \end{aligned} \qquad (1)$$

- $r_0^{\alpha\beta}$ is the first neighbor distances in perfect crystalline lattice $\alpha\beta$ ($\alpha = \beta$ in pure systems and $\alpha \neq \beta$ for alloys);
- $r_{ij} = \mid \vec{r_j} - \vec{r_i} \mid$ is the distance between i and j atoms;
- $A_{\alpha\beta}$ is the repulsive energy term between atoms;
- $p_{\alpha\beta}$ describes the repulsive dependence on the relative interatomic distances and it is related to the system compressibility;
- $\xi_{\alpha\beta}$ represents the effective integral hopping;
- $q_{\alpha\beta}$ describes the dependence of the effective integral hopping on the relative interatomic distance.

For conservative systems the force (F) can be related to the potential energy as: $\vec{F} = -\vec{\nabla}U$, and the acceleration by $\vec{a} = -\vec{\nabla}U/m$. Once we have obtained the forces and accelerations, we can solve the temporal Newton's equations integrating the accelerations to obtain the velocities and positions. For TB-SMA models we can write [31]:

$$\begin{aligned} F_a &= -\frac{2Ap}{r_0} e^{-p(\frac{r_{ij}}{r_0}-1)} \\ F_b &= \left[\sum_L e^{-2q\left(\frac{r_{iL}}{r_0}-1\right)}\right]^{-1/2} \\ F_c &= \left[\sum_L e^{-2q\left(\frac{r_{jL}}{r_0}-1\right)}\right]^{-1/2} \\ F_d &= \frac{q\xi}{r_0} e^{-2q\left(\frac{r_{ij}}{r_0}-1\right)} \\ F_{ij} &= F_a + (F_b + F_c)F_d \\ F_i &= \sum_{j \neq i} F_{ij} \end{aligned} \qquad (2)$$

In order to integrate Newton's equations we have used the Velocity Verlet (VV) method [41–44] (Eqs. 3). The Verlet expressions were obtained from Fourier expansions and the associated errors in positions and velocities are in orders of Δt^4 and Δt^2, respectively.

$$\begin{aligned} \vec{r}(t+\Delta t) &= \vec{r}(t) + \vec{v}(t)\Delta(t) + (1/2)\vec{a}(t)\Delta t^2 \\ \vec{v}(t+\Delta t/2) &= \vec{v}(t) + (1/2)\vec{a}(t)\Delta t \\ \vec{a}(t+\Delta t) &= -(1/m)\Delta\vec{U}(\vec{r}(t+\Delta t)) \\ \vec{v}(t+\Delta t) &= \vec{v}(t+\Delta t/2) + (1/2)\vec{a}(t+\Delta t)\Delta t \end{aligned} \qquad (3)$$

From integration processes the velocities and positions were obtained and they define the system kinetic and potential energies for time $t+\Delta t$. Using a canonical ensemble (NVT, number of particles, volume and temperature are kept constant), the temperature is directly related to system kinetic energy from energy equipartition theorem (EET):

$$\sum_i^N \frac{1}{2} m_i \vec{v}_i^2 = \frac{3}{2} N k_b T \qquad (4)$$

where m_i and $\vec{v}_i$ are the mass and velocity of particle i, N is the number of particles, k_b is the Boltzmann constant and T the temperature.

To maintain the temperature constant during simulations we use a thermal bath, through scaling velocities periodically during the simulations, as indicated in Eq. 5. More sophisticated thermostats as Langevin, Berendsen Predictor-corrector, etc., can be used, but in general:

$$\vec{v_{in}} = \frac{T_T}{T_I}\vec{v_i} \qquad (5)$$

in this way the new velocity ($\vec{v_{in}}$) is obtained multiplying the old velocity ($\vec{v_i}$) by a factor that depends on the target temperature (T_T) and the instantaneous temperature (T_I) can be obtained from Eq. 4 isolating the temperature T.

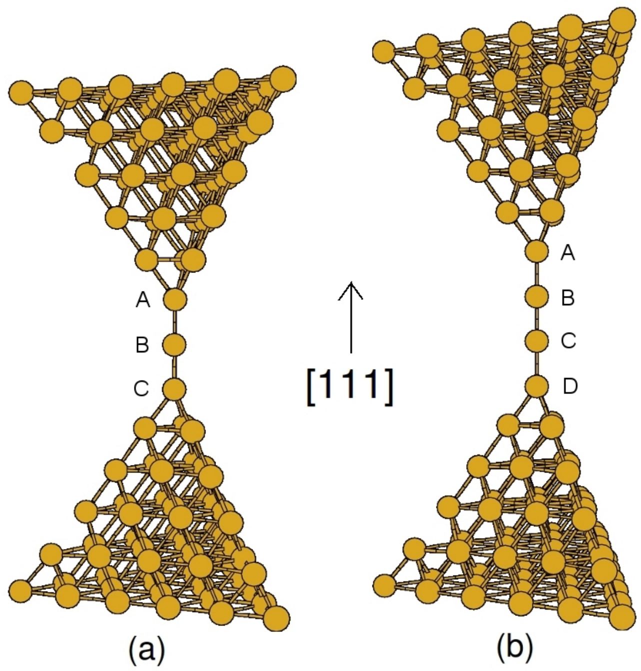

Figure 1: Formed NW (a) 3 atoms and (b) 4 atoms in chain.

In order to improve velocity calculations and to optimize simulations we have used the Verlet Neighbor List (VNL) [41, 43, 44]. The optimum time step value (Δt) to be used in the simulations is dependent on the investigated system. For metals, in general, the used time step is 2.0×10^{-15} s [30, 31]. For non-heavy atoms typical time steps are of the order of 0.5×10^{-15} s.

3. RESULTS AND DISCUSSIONS

In this work we report preliminary results for the problem of LAC lifetime formed from stretching Au NWs. In particular, we have analyzed how LAC lifetime is dependent on temperature and on chain-length. We restricted our analysis to the cases of LACs formed by 3 and 4 atoms (figure 1), or 1 and 2 atoms if we did not consider the atoms in the apexes as being part of the LACs. Although LACs with larger number of atoms have been reported by different groups [1, 7, 8], 3 and 4-atoms are the mostly found LACs. Also, here we only considered [111] NWs, since [111] is the crystallographic direction that statistically more LACs are observed [15].

We started from idealized structures assuming that the LACs were formed between two sharper lips along the [111] crystallographic direction, as shown in figures 1a and 1b, which contain 113 and 114 atoms, respectively. The starting configurations for the simulations are with the LACs already formed (containing 3 and 4 atoms). The choice for these specific structures were based on information obtained from previous theoretical and experimental works [1, 15]. These structures are then stretched until rupture/breaking. The instant of rupture/breaking is determined by monitoring in time the force profile obtained from the simulations. The stress is created in the NS structures increasing systematically the distance among the outmost NW layers. These outmost layers are kept frozen during the simulations in order to mimic and to preserve the [111] configuration. We used a pulling velocity of 1.0 m/s (0.5 m/s for each apex). We have considered two temperatures, 300 and 150 K (room and cryogenic liquid nitrogen temperatures). These values were chosen because LAC lifetime experimental data are available for these temperatures [45]. For more details about the simulation protocols, see [15, 18].

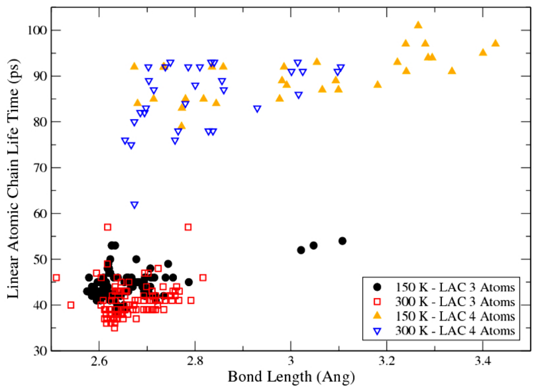

Figure 2: LAC lifetime for chains composed of 3 and 4 atoms.See text to discussions.

We have run 260 simulations for the structures shown in figure 1, 130 for each temperature. In figure 2 we present the results for LAC lifetime for the structures shown in figure 1.

In figure 2 we present the lifetime results of the 260 simulations as a function of the longest bond-length before rupture/breaking. The chain with 3 atoms are represented by circles and squares, for temperatures of 150 and 300 K, respectively. For the same temperatures the 4-atom chains are indicated by up and down triangles. As we can see from the figure for 3-atom chains the LACs tend to slightly last longer at 150 K. Also, at 150 K the bond-length rupture distances tend to be slightly larger than at 300 K. For 4-atom chains the lifetime distinction at 150 and 300 K is less clear but the rupture at larger bond-length values is more evident at 150 K, than in the case of 3-atom chains. These results are the first theoretical evidences that the temperature can play a much important role in the breaking mechanisms of metallic nanowires than previously anticipated. Further evidences of the importance of temperature can be evidenced by the bond-breaking patterns during the final stages of NW rupture. For 4-atom chains we observed that the rupture always occurs at the A-B or C-B bonds (see figure 1), but never at B-C bonds. Also, it seems that B-C dimerization bonds occur before NW breaking. The thermal energy difference from 150 to 300 K is too small (in comparison with the elastic energy contributions) to explain such differentiated dynamics. These preliminary results suggests that temperature variations affect the NW breaking beyond pure thermodynamics contributions and remain to be fully explained. Further studies with the use of more sophisticated methodologies are necessary in order to obtain a better understanding of these phenomena. Works along these lines are in progress.

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