Ab-Initio Simulation Of The Formation Of Gold Nanowires With Impurities

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Metallic monoatomic nanowires have attracted much attention in recent years [1] both because they present new physical phenomena and because of their possible applications in nanotechnology. Gold in particular has been found to form specially long and stable monoatomic chains, observed by high resolution transmission electron microscopy (HRTEM) [2–4]. These observations have repeatedly found distances of up to 5 Å between the gold atoms of the chains, much longer than in bulk gold (2.9 Å) or in the gold dimer (2.5 Å). This suggests that there may be unobserved light-atom impurities that act as bridges in the bonds between the gold atoms. These impurities presumably affect the mechanical and electronic properties of the chain, and several experimental and theoretical studies have been performed to study their effects. The theoretical simulations typically consider an ideal chain [5, 6], sometimes connected to pyramidal tips [7–10], with an impurity atom placed by hand at some plausible position. To study their structure and stability, molecular dynamics (MD) simulations and/or geommetry relaxations have been also performed, using classical potentials [11] or tight-binding forces [12–14]. Apart from the limited accuracy and reliability of these methods, the main drawback of this procedure is that the presence of the impurity is simply assumed, and no description is obtained of how, when, or with what probability it migrates to its assumed position.

To overcome these limitations, we have simulated, using *ab initio* MD, the formation and growth of gold chains with a variety of impurities, without any assumption on their initial positions. The forces are calculated using density functional theory (DFT), as implemented in the SIESTA method [15, 16], with the generalized gradient approximation (GGA) for exchange and correlation. To accelerate the MD we use a combination of cheap and expensive forces [17]. The cheap forces use the non-selfconsistent Harris functional and a minimal basis set, and they are evaluated every one-femtosecond time step. The MD trajectories are corrected periodically (every 10 fs) with the expensive forces, calculated with the selfconsistent Kohn-Sham functional and a well converged basis set.

To avoid any bias on the initial chain structure and impurity position, we start from an amorphous geommetry, obtained by quenching a thick liquid column of 50-150 gold atoms, plus one or two impurity atoms placed at random substitutional positions early in the liquid simulation. The columns are stretched during 4-18 ns until they break, generally after forming a monoatomic chain of several atoms. To facilitate the flow of atoms, and the evolution of the structure towards stable configurations, a relatively high temperature of ~ 600 K was maintained by periodically rescaling the velocities during the simulation. Since we use periodic boundary conditions, no atoms are priviledged to participate in the chain. In principle, the impurity can also diffuse to or away from the chain, once this is formed, although no such diffusion was observed in practice.

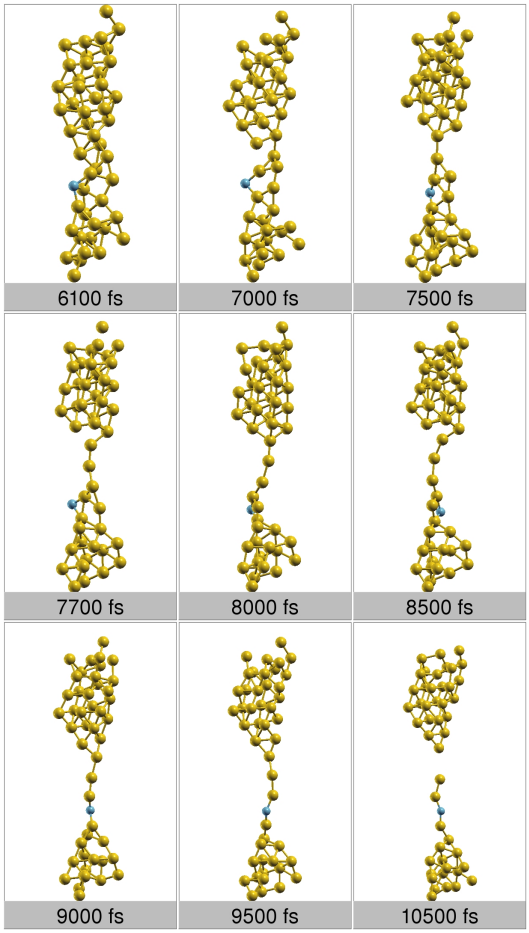

FIG. 1: Formation and growth of a monoatomic gold chain with a sulphur atom impurity.

For each of the species considered as impurities, $\sim 10-15$ simulations were performed at different temperatures and elongation speeds. Figure 1 shows one of these simulations. Figure 2 shows, for each species, the fraction of simulations that ended with the impurity in the monoatomic chain. Hydrogen always evaporated before

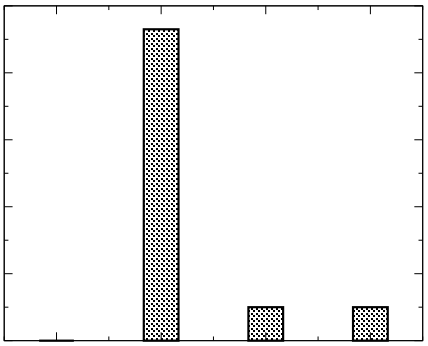

FIG. 2: Probability that impurities of various species participate in the monoatomic chains before they break. Hydrogen did not participate in any of the fifteen simulations performed with it. Carbon and oxygen ended in the chain in one of ten simulations each. Sulphur was in the chain in twelve out of thirteen simulations.

the chain formation. Carbon ended in one simulation as one of the extreme atoms of the chain or, more properly, as one of the vertex atoms of the tip, bonded to the gold chain and to two tip atoms. In another simulation, an oxigen impurity formed part of the chain itself. Sulphur was the only impurity found consistently to be in the monoatomic chain in most of the simulations. And, in one of these simulations, the chain had no less than 15 atoms! Furthermore, the mean distance between the two gold atoms bonded to sulphur is 5.0 ± 0.2 Å, in good agreement with HRTEM measurements.

In conclusion, we have simulated the formation of monoatomic gold chains in the presence of different impurities (H, C, O, and S). We find that, among them, sulphur is by far the most likely candidate to end up bridging the long gold-gold distances observed by HRTEM.

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