Species fractionation in atomic chains from mechanically stretched alloys

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Abstract

Bettini et al. (2006 Nat. Nanotechnol. 1 182–5) reported the first experimental realization of linear atomic chains (LACs) composed of different atoms (Au and Ag). The different contents of Au and Ag were observed in the chains from what was found in the bulk alloys, which raises the question of what the wire composition is, if it is in equilibrium with a bulk alloy. In this work we address the thermodynamic driving force for species fractionation in LACs under tension, and we present the density-functional theory results for Ag–Au chain alloys. A pronounced stabilization of the wires with an alternating Ag–Au sequence is observed, which could be behind the experimentally observed Au enrichment in LACs from alloys with high Ag content.

Keywords: nanowires, molecular dynamics, alloys, HRTEM

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal nanowires have attracted great interest with the increasing miniaturization of electronic and mechanical devices [1], given their very interesting properties related to quantum transport [2]. From an experimental point of view, two techniques have been mostly used in nanowire research: Mechanically controllable break junctions (MCBJ) [3–5] and in situ high-resolution transmission electron microscopy (HRTEM) [5–11]. While an MCBJ is used to obtain the electronic properties of nanowires, HRTEM gives the structural information, providing the atomic resolution with real-time image acquisition. A combination of both techniques is frequently used in order to establish a correlation between the atomic arrangement and the quantum conductance [12]. Since 1997, these techniques have revealed the existence of some quite unexpected structures, such as: Extremely thin metal nanotubes with a square cross-section [13], helical multishell gold nanowires [14], single-walled metal nanotubes [15, 16], and the ultimate nanowires, linear atomic chains (LACs) [10, 17]. The stability of these structures has been inferred using statistics over a large number of observed structures (in HRTEM) and on conductance histograms for a large number of contact-breaking events (in MCBJs). These experimental analyses have shown the remarkable existence of stable (or metastable) nanowires for alkali [3] and noble metals [4].

There have been many theoretical studies of these structures, mostly using classical atomistic models, as well as the first principle ones [13, 18–20]. Of particular importance is the work by Tosatti et al. [21], who investigated the stability of these nanostructures, considering the metal wires connected to the atomic reservoirs at both ends, and determining the local minima (different metastable structures) as a function of the tension of the wire. Using this approach the authors were able to predict the stability of the magic sizes for Au nanowires.

Although metal nanowires have been the object of intense theoretical and experimental investigations, most of these studies were carried out for pure metals. The first
The considered geometries are presented in figure 1. The LAC was similar to the ones for Au rich nanowires [22]. From the classical molecular dynamics [22] it was concluded that this unusual behavior was a consequence of the Au enrichment at the region where the LACs were formed. The concentration of these nanowires changed significantly over time from the nominal initial values. They basically behaved as if they had a much high Au content than in their nominal composition. This behavior was addressed by Fao [23], who considered the enthalpy as defining the stability of these atomic chains under tension, in line with what was pioneered by Tosatti [21].

A grand canonical perspective, however, is the only adequate framework for studying the thermodynamic trends in these systems, has not been done to this date and will be the focus of this work.

The main objective of this paper is to determine the relative concentrations of two species (Ag and Au in this case) in LAC when in equilibrium with bulk alloys of any given composition. For this purpose the relevant free energy is defined and calculated from the first principles, analogously to what was done in [21] for single-species wires and tubes, which is generalized to a grand-canonical setting. The observed capability of the wires to change composition with respect to the bulk reservoir demands this kind of grand canonical treatment, beyond what was presented in [23].

In this way, with our approach we should be able to predict for specific bulk alloy concentrations, what the corresponding likely concentrations for LACs formed by stretching a nanowire will be. This is a general approach that can be applied to other systems and situations. It is important to remember, however, that this method takes an equilibrium viewpoint, which assumes atom exchange between the reservoirs and wire, and should only be taken as a determination of equilibrium trends. The kinetics of the formation process will very probably originate deviations from this limiting behavior. It is, however, important to know what the thermodynamic trends are, which is what we are addressing here.

2. Methodology

Density-functional theory (DFT) calculations were carried out for free-standing infinite nanowires by preparing arrays of tetragonal supercells were used with the wires aligned along the $x$-axis, with four atoms of Au or Ag and their binary alloys. The considered geometries are presented in figure 1. The LAC geometries were relaxed for a fixed supercell size, keeping the $y$ and $z$ sizes such that the minimum distance between the wires was 15.0 Å, while the $x$ direction was varied in increments of 0.05 Å, from 6.00 Å until the wire snapped. We considered LAC lengths of between 7 Å and 11 Å.

![Figure 1. Structural motifs for the atomic-wire compositions considered in this work. The dark (light) balls indicate Ag (Au) atoms. See text for discussions.](image)

The DFT calculations were performed with the Siesta method [24, 25], using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange and correlation [26]. Norm-conserving scalar-relativistic pseudopotentials [27] replaced the nuclei and core electrons, considering the normal core-valence separation for Ag and Au. Double-$\zeta$ polarized bases were used for the valence electrons [28]. Integrals in real space were performed on a mesh of 250 Ry cutoff [25]. The integration over the first Brillouin zone was carried out using the special $k$-points method [29] with $k$-meshes of $1 \times 1 \times 30$ and $10 \times 10 \times 10$ for the wire and bulk structures, respectively.

In order to calculate the nanowire stability for an alloy we generalized the string tension analysis to the different atomic species. The free energy $\Lambda$ we will seek to minimize is:

$$\Lambda = E_{LAC} - n_{Au} \mu_{Au} - n_{Ag} \mu_{Ag}$$

where $n_{Au}$ and $n_{Ag}$ represent the number of Au and Ag atoms in the LAC (for the case of AgAu alloys), and $\mu_{Au}$ and $\mu_{Ag}$ are the corresponding chemical potentials. It is the zero-temperature grand-canonical free energy (per unit cell) that gives the stability for a wire of unit-cell length $L$ (length of the cell along $x$). The analysis can also be done as a function of $F$, the force pulling the wire, in which case the relevant free energy would be [21]:

$$\Theta = \Lambda - FL$$

Here we will restrict ourselves to $L$-dependence and thus $\Lambda$. We will consider the low temperature limit, disregarding the entropy effects. The generalization of the present scheme to the finite temperature is costly but conceptually straightforward, either by including the entropy of harmonic vibrations [30] (for a fully quantum albeit harmonic treatment), or thermodynamic integration for the free energy [31], using molecular dynamics for classical nuclei, or with path-integral Monte–Carlo or molecular dynamics for quantum nuclei.

If we define:

$$n = n_{Au} + n_{Ag}; \quad \Delta n = n_{Au} - n_{Ag}$$

we can write:

$$\Lambda = E_{LAC} - n \bar{\mu} - \Delta n \Delta \mu$$
where:
\[
\bar{\mu} = (\mu_{\text{Au}} + \mu_{\text{Ag}})/2 \quad \text{and} \quad \Delta \mu = (\mu_{\text{Au}} - \mu_{\text{Ag}})/2.
\] (5)

The \( n \bar{\mu} \) term controls the energetics related to their having more or less atoms in the chain, regardless of the species, while the \( \Delta n \Delta \mu \) term controls the energetics related to swapping atoms of different species in a wire with a given number of atoms. We will confine ourselves here mainly to the latter behavior considering wires with a constant \( n \), and will consider the free energy:
\[
\Omega = E_{\text{LAC}} - \Delta n \Delta \mu = \Lambda + n \bar{\mu}.
\] (6)

The wire is formed through the atom exchange processes between the bulk of the contacts and the wire. The chemical potentials are thus defined by the bulk alloy out of which the wire is formed, which constitutes the effective reservoir. In particular, the relative chemical potential can be calculated as the statistical average energy changes when swapping any Au atom in the alloy with an Ag one [32]:
\[
\Delta \mu = \langle \Delta E(\text{Au} \rightarrow \text{Ag}) \rangle.
\] (7)

This was obtained by making random substitutions of Au with Ag in the disordered bulk alloy samples of different relative concentrations, relaxing the structures before and after the swap, and computing the energy difference. Although other underlying structures can exist [33], here we have only considered the face-centered cubic structure. We have taken an fcc supercell with 32 atoms in periodic boundary conditions, each atom being either Ag or Au, allowing for all possible orderings for every concentration considered. The original concentrations of Ag in Au were 0, 7/32, 13/32, 20/32, 26/32, and 1. The results are shown in figure 2. Both for \( \mu_{\text{Au}} \) and \( \mu_{\text{Ag}} \) the zero is defined for their respective pure bulk crystals6. The curve shows a mostly linear behaviour except at very low Ag concentrations.

3. Results

Figure 3 shows the free energy \( \Omega \) as a function of cell length \( L \), for the six atomic-wire configurations, as shown in figure 1, and for the different bulk composition of the lead alloys specified in the figure. Starting from the left, the regime up to \( \sim 7.7 \, \text{Å} \) corresponds to zigzag wires in which three consecutive atoms define quite an equilateral triangle, i.e. essentially a band with two rows of atoms and edge-sharing triangles. The regime at larger distances corresponds to the zigzag structures, as shown in figure 1, agreeing with what is known about Au wires [19], which gradually stretch with a growing \( L \), until they snap at \( L \)-values slightly above what is displayed. The transitions between regimes, which involve ‘bond’ breaking, are discontinuous and hysteretic, and thus will be quite dependent on the quantum and thermal fluctuations [30]. The experimentally observed LACs correspond to the intermediate regime.

6 This is for convenience with the numbers. The bare \( \Delta \mu \) coming from \( \Delta E^{\text{DFT}}(\text{Au} \rightarrow \text{Ag}) \) gives large numbers referring to the separate cores and electrons. Here we use \( \Delta E^{\text{DFT}}(\text{Au} \rightarrow \text{Ag}) + \mu_{\text{Au}}^b - \mu_{\text{Ag}}^b \), the two latter terms being the DFT energy per atom of bulk Au and bulk Ag, respectively. The same is done in the definition of \( E_{\text{LAC}} \).

Figure 3 shows that for most alloy concentrations the structure IV of figure 1, with Ag–Au alternation is most stable in the LAC regime, with higher stabilization for a higher Ag content in the bulk alloy. This implies that Ag-rich bulk alloys tend to produce wires with [Ag] tending towards 50%, i.e. the
wires will be Au enriched. These results agree with the mixed and Au enriched wires, as seen in the experimental atomically resolved micrographs, even through the experiments were done at room temperature. It seems likely that the differences between the Ag and Au atoms are too small for the vibrations at room temperature to make a significant difference in the thermodynamic trends. By reducing the Ag concentration in the alloy there is a transition to a situation in which the wire could change equilibrium concentration with stretching, as seen for 20%. For $L \sim 9.5 \text{Å}$, the wire would tend to be pure Au, thus depleting the Ag (although the configuration II with 25% Ag is close in energy, and indeed lower for the mechanically unstable shorter $L$). Upon stretching, though, the Ag/Au alternating wire dominates again, thus replenishing the Ag.

In summary, we have defined and calculated from the first-principles the grand-canonical zero-temperature of free energy governing the fractionation of two species between an alloyed atomic chain and the bulk alloy. We have applied this to Ag/Au alloy chains and explained the tendency for Au enrichment in LACs observed experimentally for Ag rich alloys.

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