Monte Carlo simulation of nanowires of different metals and two-metal alloys

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Nanowires of different metals and two-metal alloys have been studied by means of canonical Monte Carlo simulations and the embedded atom method for the interatomic potentials. For nanowires of gold, a relatively stable three-atom-wide chain was observed. The presence of one-atom-wide linear atomic chains is not stable in any case. For two-metal alloy nanowires, the metal with a higher surface energy tends to locate in the inner region of the nanowire. © *2011 American Institute of Physics*. [doi:10.1063/1.3549900]

I. INTRODUCTION

During the last decade, metal nanowires have received enormous attention. This interest is founded in the important role that they promise to play in nanotechnology, where they may serve as contacts to single molecules, as sensors, as catalysts, or just as tips that may function as probes in scanning techniques.

We are interested in the formation and stability of nanowires. From the vast literature on such wires, we would like to mention a few works that are directly related to ours. Ugarte *et al.*[1–4] have experimentally studied the formation of linear atomic chains of some metals, such as copper[2] and alloys of silver and gold.[3,4] They have also researched into the atomic arrangement and electrical transport properties of gold and platinum.[5] Other related experimental studies are seen in Refs. 6 and 9. There are several studies on nanowire formation conducted by means of molecular dynamics simulation. Pu *et al.*[10] have done research on the formation of gold nanowires and have made a comparative analysis of different semiempirical methods for energy calculations. One of the methods employed is the embedded atom model, which is the one that we use in the present work. In addition, Sankaranarayanan *et al.*[11] have studied the formation of nanowires of alloys of palladium and platinum. Sørensen *et al.* have analyzed the structure of nanowires of gold and nickel.[12] Park and Zimmerman have found a structure for gold,[13] which is very similar to the one obtained in the present work.

In this work, we present the study, by means of canonical Monte Carlo simulations, of nanowires of these, and some other metals and alloys starting from a group of atoms between two planes with a given orientation. Monte Carlo simulations have some advantages over molecular dynamics simulations presented in previous works. Even though there is no absolute time scale in ordinary Monte Carlo, we can simulate events that take longer periods of time than those that can be covered by molecular dynamics. In particular, the simulations can be performed long enough to obtain equilibrium, which is always a problem in *ab initio* molecular dynamics. Also, a larger number of particles can be considered without too much computational cost.

For pure metals, we have found that one-atom-wide linear atomic chains are not stable in any case. For the case of gold, a particular structure was found, which is not present in other pure metals. The main contribution of the present work is in the study of several bimetallic nanoalloys. In all the studied cases, the two metals mix with each other, but the metal with higher surface energy shows a preference to locate in the inner region of the nanowire.

The outline of the paper is as follows: In Sec. II we describe the model along with the simulation scheme. In Sec. III we present the results. Finally, we shall draw a few general conclusions.

II. MODEL AND SIMULATION METHOD

A. The model

The model consists of a group of atoms of the metal investigated arranged in the form of a wire with a width of several atomic diameters, sandwiched between two fixed planes of the same metal with a particular orientation, as initial condition (see Fig. 1). In the case of bimetallic alloys, the composition of the mobile atoms is 50% of each species, and the two fixed planes are composed of one of the two metals. The spatial distribution consists of a set of parallel planes with the lattice parameter of the metal corresponding to the fixed planes.

Then, a canonical off-lattice Monte Carlo simulation (that is, a Monte Carlo simulation in the canonical ensemble and with movements of atoms in the space without any lattice restriction) is performed in order to reach the ensemble equilibrium. Once the equilibrium has been reached, the external planes are slightly separated and a new simulation is performed for this new situation. This procedure is repeated several times, until breaking of the wire is observed.

B. Energy calculations

We employ the embedded atom method (EAM) to calculate the total energy of the system at each step of the

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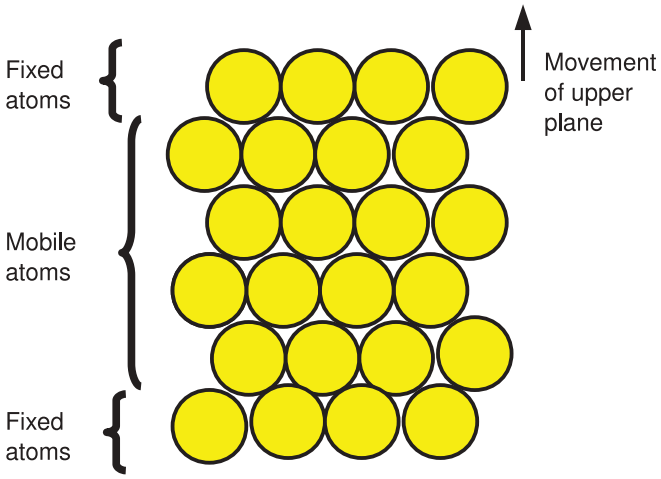

FIG. 1. Schematic representation of the model. Initial state: several layers of mobile atoms between two layers of fixed atoms.

simulation.[14] In order to make this paper self-contained, we briefly summarize the main points.

The EAM is a semiempirical method which considers that the total energy U_{tot} of an arrangement of N particles may be calculated as the sum of energies U_i corresponding to individual particles,

$$U_{\text{tot}} = \sum_{i=1}^{N} U_i, \tag{1}$$

where U_i is given by

$$U_i = F_i(\rho_{h,i}) + \frac{1}{2}\sum_{j\neq i} V_{ij}(r_{ij}). \tag{2}$$

F_i is called the embedding function and represents the energy necessary to embed atom i in the electronic density $\rho_{h,i}$ at the site where this atom is located. Thus, the attractive contribution to the EAM potential is given by the embedding energy, which accounts for many-body effects. The repulsion between ion cores is represented through a pair potential $V_{ij}(r_{ij})$, which depends on the distance between the cores r_{ij}.

The EAM has been parametrized to fit experimental data, such as elastic constants, dissolution enthalpies of binary alloys, bulk lattice constants, and heats of sublimation.[14]

C. Canonical Monte Carlo simulation

As mentioned above, the atoms of the two external planes are fixed while those in between are mobile. We take the z-direction as perpendicular to these planes. The Monte Carlo simulation consists in the movement of the atoms between the two external planes, until equilibrium is reached. Then, the top plane is slightly separated (0.1 Å in this case) and a new simulation is performed. Each simulation step consists in an attempt to move all the internal atoms, according to the Metropolis algorithm. For each plane distance, we performed 20 000 Monte Carlo steps; this was sufficient to reach equilibrium. Each trial (attempt to move one particular atom), consists in the selection of a position near the current position of the particular atom and an attempt to displace from the initial position to the proposed one. The new position is located in a cubic box of 1 Å of side, centered at the initial position and the probability of selection of a particular place is uniformly distributed in the box.

The probability of accepting the new position is given by

$$P = \min\left\{1, \exp\left[-\frac{\Delta E}{k_B T}\right]\right\}, \tag{3}$$

where k_B is the Boltzmann constant, T is the temperature (300 K in this case), and ΔE denotes the total energy difference of the system between the final and the initial positions of the atom.

In the case of bimetallic alloys, we start with half of the mobile planes of one kind and half of the other kind of metal and then 20 000 interchange Monte Carlo steps are performed in order to obtain an initial distribution of atoms according to the most energetically convenient configurations.[15,16] Each interchange trial consists in the random selection of two atoms and an attempt to interchange their positions, with an acceptance probability given by the Metropolis scheme. This initialization is followed by the standard Monte Carlo procedure described above.

III. RESULTS AND DISCUSSION

As a first example, we consider a nanowire of gold. Figure 2 shows six different stages of the simulation of a gold nanowire with a total of 96 atoms (6 parallel planes of 16 atoms as initial condition). As it can be noticed in the third picture, a nanowire of approximately three atoms of width is formed which presents a certain stability. As separation between the external planes increases, the breaking of the nanowire can be observed. In this simulation, a linear monoatomic chain is only observed just before breaking, and it is not stable.

Figure 3 shows an analysis of the evolution of the total energy for the simulation of a nanowire of gold, a nanowire of copper, and a bimetallic nanowire of gold and silver with 100 orientation of the planes. The total energy is calculated as the average energy of the system over the 10 000 last MC steps for each distance of the planes. The left side shows the

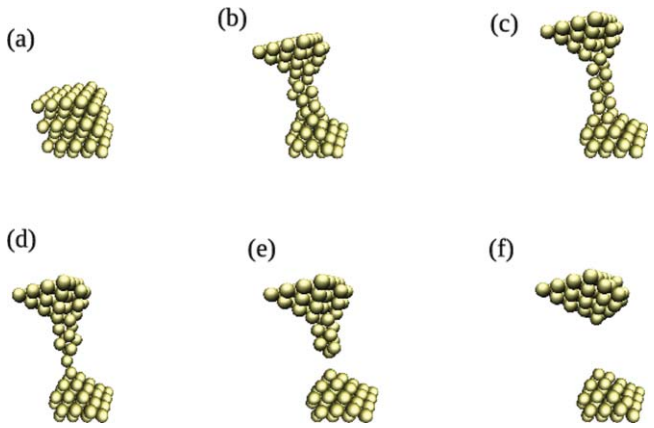

FIG. 2. Different stages in the simulation of a gold nanowire, with 96 atoms and a 100 orientation of the external planes.

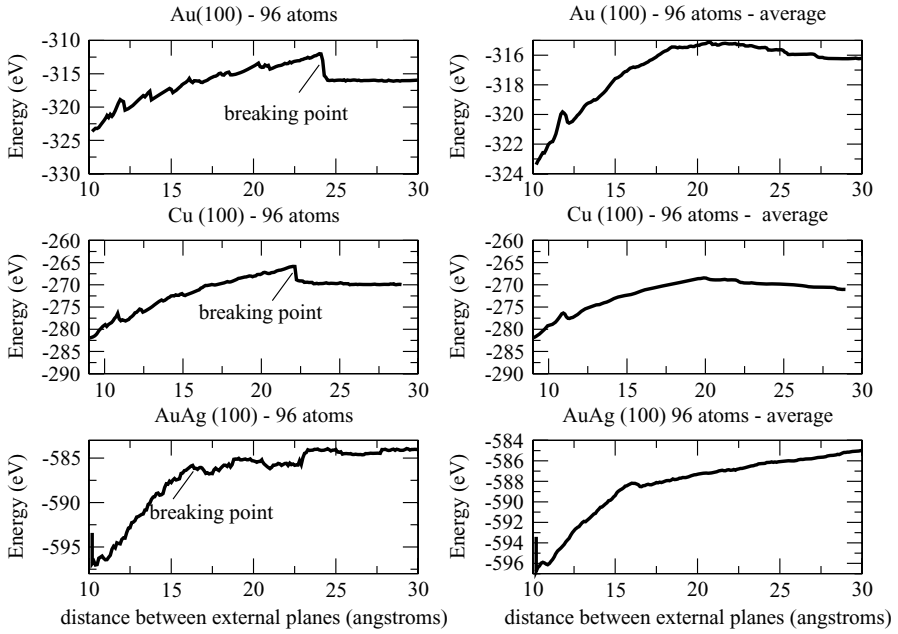

FIG. 3. Average total energy for a single simulation (left) and the average over 20 simulations (right) for nanowires of gold, copper and a binary nanowire of gold and silver, with 100 orientation of the planes.

resulting energy for a single simulation and the right side shows the average energy for 20 simulations. As regards the total energy, it can be noticed that the energy increases while the separation of the planes increases. In the case of monometallic nanowires, when the nanowire breaks, there is a drop in the energy, which then remains almost constant.

Figure 4 depicts eight different stages of the simulation of a gold nanowire with a total of 256 atoms (16 parallel planes of 16 atoms). As it can be seen in the sixth picture, a large nanowire with a definite structure is formed, with a width of approximately three atoms. This is similar to the structure found in Fig. 2 for a nanowire of 96 atoms, but it is longer due to the larger size of the system. Figures 6(a) and 6(b) show a portion and a cross section of this nanowire in order to better understand the structure. A similar structure for gold was found in previous works[13] by means of molecular dynamic simulations and EAM potentials. Having found the same structure through different techniques serves to validate the simulation method.

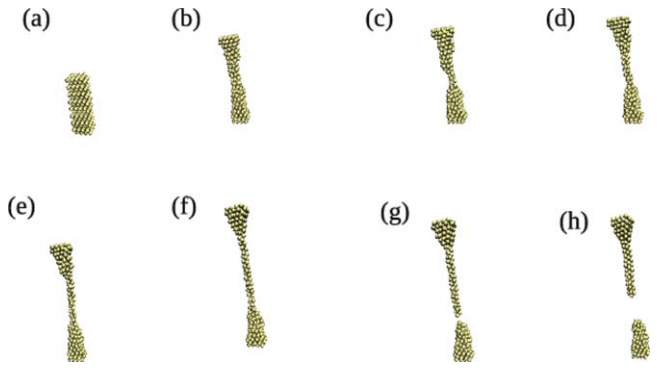

FIG. 4. Different stages in the simulation of a gold nanowire, with 256 atoms and a 100 orientation of the external planes.

Figure 5 shows nanowires of different pure metals before breaking, in this case, for systems with a total of 256 atoms. The studied metals are (from left to right) gold, silver, copper, palladium, and platinum. The orientation of the external planes is 100 (up) and 111 (down). It can be seen that in the case of gold, we have the formation of an approximately three-atom-wide nanowire for both orientations of the planes [see also Figs. 6(a) and 6(b)]. In the case of silver, the nanowires are not stable, we have an amorphous cluster and a thin section arises where the nanowire will be broken. The same situation is observed for copper and platinum for the orientation 100 of the planes. For copper and platinum with orientation 111 of the planes, we can observe the formation of thicker nanowires than those of gold. Figures 7(a) and 7(b) show a portion and a cross section of the copper nanowire, with the indicated structure. Figures 7(c) and 7(d) show a small portion of the platinum nanowire that appears just

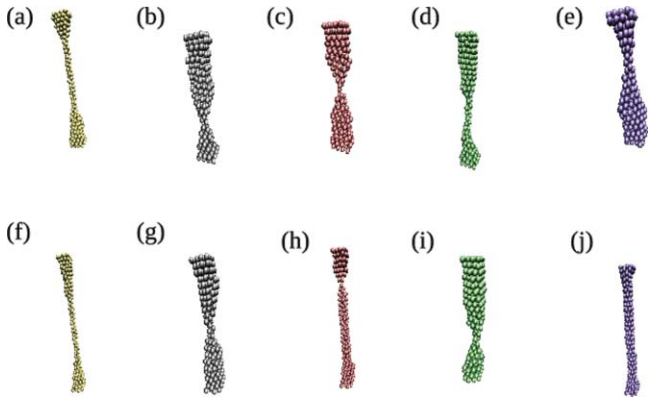

FIG. 5. Images of the simulated nanowires just before breaking, for several metals (gold, silver, copper, paladium, and platinum from left to right) and two orientations of the external planes (up: 100, down: 111). The total number of atoms is 256 in each case.

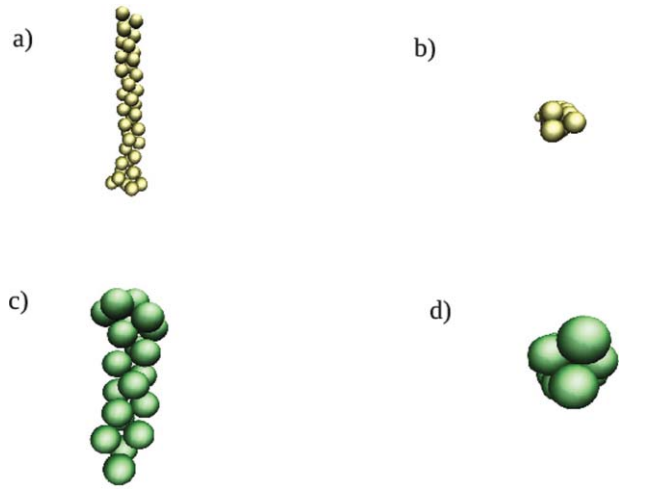

FIG. 6. Small portion (a) and cross section (b) of a gold (100) nanowire. Small portion (c) and cross section (d) of a palladium (100) nanowire.

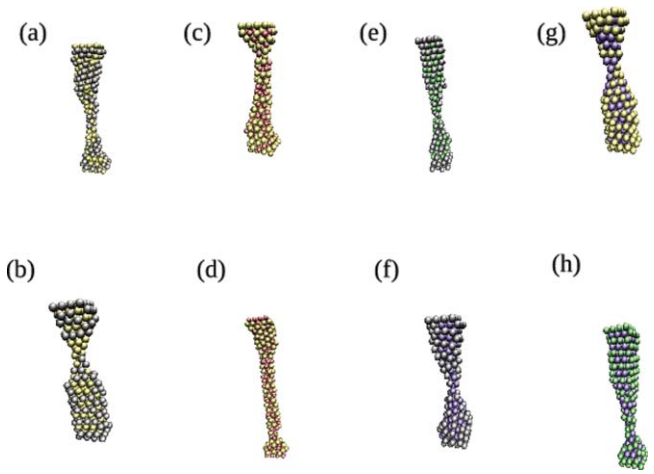

FIG. 8. Images of nanowires of two-metal alloys, just before breaking, for systems with a total of 256 atoms. Silver and gold between 100 planes of gold (a), silver and gold between 100 planes of silver (b), copper and gold between 100 planes of gold (c), copper and gold between 100 planes of copper (d), silver and palladium between 100 planes of silver (e), silver and platinum between 100 planes of silver (f), gold and platinum between 100 planes of gold (g), and palladium and platinum between 100 planes of palladium (h).

before breaking. This small portion is similar to the structure of gold nanowires, but it is less stable. Finally, for palladium, a small nanowire can be seen in some region of the system [Figs. 6(c) and 6(d)], but not as definite as the one observed for gold. In most cases, linear monoatomic chains only appear just before breaking and are just one- or two-atom long.

We have also studied nanowires of two-metal alloys: gold and silver, gold and copper, gold and platinum, silver and palladium, silver and platinum, and platinum and palladium. Four possibilities have been considered for each case: two orientations of the external planes (100 and 111) and two compositions of the external planes (one or the other of the involved metals). In all cases, the lattice parameter of the system for the initial configuration was set equal to the lattice parameter of the metal forming the external planes. Eight of these systems are shown in Fig. 8 for the case of 256 atoms (we only show here examples with 100 orientation of the planes).

The only systems, which present a definite structure, are the alloys of gold and silver (with external planes of gold) and gold and copper (with external planes of copper). These two systems are also analyzed in Fig. 9. In the case of gold and silver [see Figs. 9(a) and 9(b)], the structure is not as sharp as in the case of pure gold. It is an intermediate case between the well-defined structure of gold and the amorphous one of silver. In the case of copper and gold with the external planes of copper 100 [see Figs. 9(c) and 9(d)], we can notice that the structure is very similar to that of pure copper but with well mixed atoms of copper and gold.

Perhaps the most remarkable characteristic is that in all cases the metals involved mix with each other, but there is a slight tendency for one of them to be in the inner region and

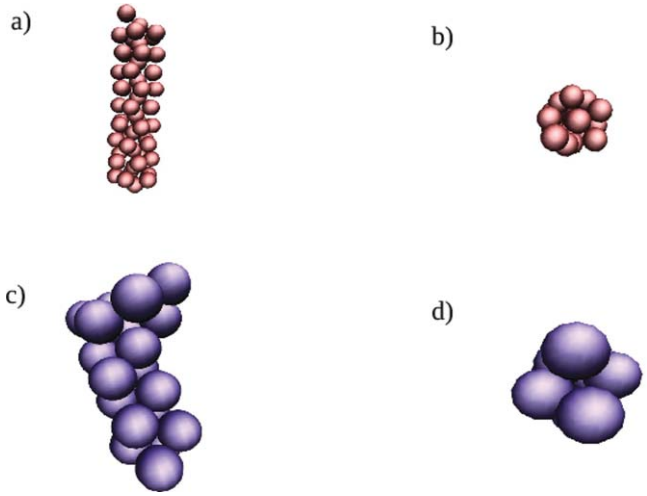

FIG. 7. Small portion (a) and cross section (b) of a copper (111) nanowire. Small portion (c) and cross section (d) of a platinum (111) nanowire.

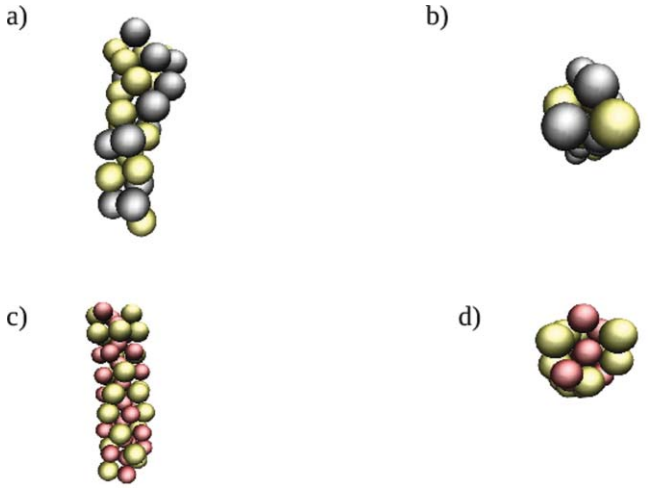

FIG. 9. Small portion (a) and cross section (b) of a gold–silver (100) nanowire. Small portion (c) and cross section (d) of a copper–gold (100) nanowire.

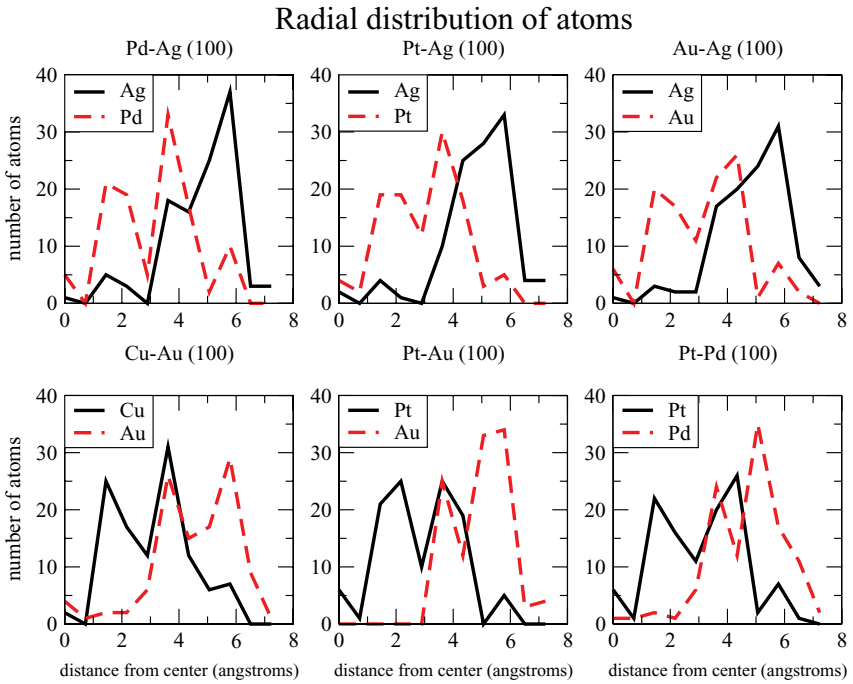

FIG. 10. Number of atoms of each species as a function of the distance to the central axis of the nanowire for six different systems (two-metal alloy nanowires).

the other one to be in the outer region of the nanowire. In order to quantify this observation, the number of atoms at discrete intervals of distance from the center of the nanowire has been counted. Figure 10 shows the radial distribution of each kind of atom for six of the studied systems, for the situation of the nanowire just before breaking.

For instance, taking the case of gold and silver, it can be seen that gold atoms tend to be near the center, whereas silver atoms tend to be in the outer region. This is true for the four systems involving silver and gold (with the two orientations and the two compositions of the external planes). Notice that gold has a higher surface energy than silver (see Table II). The same analysis can be done for the other systems. The case of copper and gold is somewhat particular in the sense that the distribution with copper inside and gold outside is not so clear in all the cases (not shown here). Table I summarizes the tendency for the metals of each of the alloys studied. In the case of silver and palladium, the atoms of the later tend to be located in the inner region and its surface energy is higher than that of silver. In the case of silver and platinum, the tendency is for the latter to be in the inner region and it has higher surface energy, too. Platinum also has higher surface energy than gold and than palladium, and in both cases it is located in the inner region of the nanowire. A generalization can be made in the sense that metals with higher surface energy (see Table II) tend to locate in the inner region of the nanowire.

TABLE I. Observed tendency for metals to be inside for different alloys.

Alloy	Pd–Ag	Pt–Ag	Au–Ag	Cu–Au	Pt–Au	Pt–Pd
Metal inside	Pd	Pt	Au	Cu	Pt	Pt

The characteristic behavior of the pair of metals according to the relative surface energies was also studied in other kinds of systems, such as nanoclusters[18,19] and surface processes.[20] But, to the best of our knowledge, however, this is the first time that the general tendency for atoms to arrange inside or outside a nanowire according to their surface energy is reported for nanowires.

IV. CONCLUSIONS

Nanowires of different metals and two-metal alloys were simulated by means of the canonical off-lattice Monte Carlo method. The embedded atom method was employed for the interatomic potentials.

For nanowires of gold, an interesting and stable structure was observed, of approximately three atoms wide. For the studied metals (gold, silver, copper, platinum, and palladium), the presence of monoatomic linear atomic chains is not stable.

For two-metal alloy nanowires, the metals mixed with each other, but a general tendency has been observed. In all cases, the metal with a higher surface energy tends to be located in the inner region of the nanowire.

TABLE II. Surface energies of the low-index faces from Ref. 14 and the experimental average surface energies from Ref. 14 and 17 in units of ergs/cm^2.

Metal	Ag	Au	Cu	Pd	Pt
(111)	620	790	1170	1220	1440
(100)	705	918	1280	1370	1650
(110)	770	980	1400	1490	1750
Experimental (average face)	1240	1500	1790	2000	2490

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