Structure and stability of finite gold nanowires

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Finite gold nanowires containing less than 1000 atoms are studied using the molecular dynamics simulation method and embedded atom potential. Nanowires with the face-centered cubic structure and the (111) oriented cross-section are prepared at T = 0 K. After annealing and quenching the structure and vibrational properties of nanowires are studied at room temperature. Several of these nanowires form multi-walled structures of lasting stability. They consist of concentric cylindrical sheets and resemble multi-walled carbon nanotubes. Vibrations are investigated by diagonalization of the dynamical matrix. It was found that several percents of vibrational modes are unstable because of uncompleted restructuring of initial fcc nanowires.

Clusters and wires characterized by the nanometer length scales are constituents of nanocrystalline materials and components of nanoscale electronic devices. These nanostructures show physical and chemical properties different from the bulk. Metallic nanowires are usually fabricated using electron-beam lithography. The scanning tunneling microscopy experiments recently gave us a new way of producing nanostructures. In these experiments formation of metallic nanocontacts between the tip and the substrate was observed. For such nanowires quantization of conductance was found. It was shown that similar nanowires are formed between two vibrating macroscopic wires in contact. The formation of nanowires and their physical properties, such as the electrical conductance, are influenced by elastic, structural, and vibrational properties of materials involved. These properties are also important for applications. Elastic in-stabilities of metallic nanocontacts were already studied by molecular dynamics (MD) simulations.

It is well known that bulk gold crystallizes in a face-centered cubic lattice. Several studies have shown that icosahedra are preferred structures for small metallic nanoparticles (< 5 × 10^3 atoms). Metallic nanowires are not forming spontaneously under cluster preparation conditions. This shows that their cylindrical structure is artificial and less stable than an icosahedral shape of metallic clusters. In the laboratories, under special conditions, nanowires of gold and other metals are prepared and their cylindrical shapes seem to be rather stable. Nevertheless, these nanowires should transform into more stable structures on a time scale at which substantial mass transport could occur. Depending on the number of atoms, the most stable structure is either a fcc crystal, or an icosahedral nanoparticle. Therefore, it is important to analyze the properties of nanowires on various time and length scales to understand the effects of an imposed cylindrical geometry on their internal structure and stability. These properties are difficult to study experimentally. Recently, special gold nanowires (“nanobridges”) were formed by electron-beam irradiation of a gold (001) oriented thin film. The structures of these nanowires, which are induced and stabilized by the substrate, were investigated by electron microscopy. The study of the properties of free nanowires is even more demanding. In contrast, computer simulations are suitable for such investigations.

Vibrations of bulk materials are measured by neutron and X-ray scattering, Raman, and infrared spectroscopy. The He scattering and electron energy loss spectroscopy (EELS) methods are used to study surface vibrations. Raman scattering is also applied in studies of vibrational properties of some clusters, for example of semiconductors. In addition, vibrations of argon, water, and ammonia clusters (in the size range between 25 and 4600 atoms) were recently studied experimentally by the He scattering technique in a crossed beam arrangement. Vibrational spectra of semiconductor and carbon nanowires are measured by Raman scattering, but this technique cannot be used for metallic nanowires because of specific selection rules. Vibrational properties of various metallic and non-metallic nanoparticles are also investigated theoretically, either by diagonalization of the dynamical matrix, or by calculating the Fourier transform of auto-correlation functions in a MD simulation. The computational methods are for now the only techniques that can be used for investigations of vibrational properties of metallic nanowires.

In this work structural and vibrational properties of the finite Au nanowires are investigated. Several wires containing from 386 to 991 atoms are studied at T = 300 K. The MD simulation method based on a well-tested embedded atom potential is used to produce nanowires. Vibrations are studied by diagonalization of the dynamical matrix. The tight-binding MD method was recently applied in the study of finite carbon nanotubes. The MD method was also used for calculation of several properties of infinite wires, where periodic boundary conditions were applied along the wire axis. For example, ab initio MD simulations of infinite Si wires were used in the studies of optoelectronic properties of porous silicon. Ab initio simulations were also applied to analyze the growth mechanisms for boron-nitride nanotubes. Infinite carbon nanotubes were investigated by classical
The melting behavior of thin, infinite Pb wires was studied by a classical MD simulation [28], as well as mechanical properties of the SiSe simulation [29], and also A recent classical MD study of Pb and Al ultra-thin infinite wires at $T = 0$ K has shown that several unusual structures appear, for example icosahedral and helical forms [31]. In comparison with all these infinite wires, finite metallic structures studied here represent the smallest nanowires obtained in the laboratories. In addition, from theoretical point of view a finite nanowire is a special version of a cluster whose properties deserve an investigation.

The experiments have shown that formation of nanowires is pronounced for gold [1][3]. In this work the MD simulation method is used to prepare gold nanowires. It is well known that when classical many-body potentials of the embedded atom type are used in simulations, a satisfactory description of metallic bonding is obtained [22]. In this simulation a such many-body potential for gold was employed [3]. This potential was chosen because of its proven accuracy in various MD simulations for bulk, surfaces [24], and clusters [2].

These simulations started from crystalline nanowires with the fcc(111) oriented cross-section at $T = 0$ K. Nanowires were prepared in an ideal fcc structure by including all particles whose distance from the nanowire axis is smaller than a chosen radius. A basic cylindrical MD box consisted of $N_z = 12$ layers. The cross-section with the maximal radius of 0.9 nm was used. The total number of moving particles in this MD box was 386. Laterally larger nanowires having radii of 1.2 nm and 1.4 nm were also studied, as well as nanowires with $N_z = 18$ and $N_z = 24$ layers. The prepared ideal samples were first relaxed at $T = 0$ K. Then MD boxes were heated to 600 K. This was followed by a quench to $T = 0$ K and heating to $T = 300$ K. In this procedure no substantial change of the temperature, or during time evolution. Initially heating to 600 K was done, although the proper simulated annealing and quenching technique used in simulation of metallic structures requires higher temperatures ($\sim 0.75$ of the bulk melting temperature, i.e., 1000 K –1100 K for gold). This was done to prevent melting and collapse into a drop, but to give to the atoms a possibility to find some local minima while keeping a cylindrical shape of a nanowire. A similar kind of a constrained dynamical evolution of atoms should also occur for fabricated nanowires. Otherwise, under real equilibrium conditions depending on the number of atoms, fcc or icosahedral structures appear. A time step of $7.14 \times 10^{-15}$ s was used in simulations. Long runs of $10^6$ time steps (i.e., 7.1 ns) were performed to check a stability of the structures. It was found that the procedure used for heating and equilibration of nanowires gives good results. The structures of lasting stability were obtained. The shapes of these finite nanowires after quenching were also compared with infinite (111) oriented gold wires with similar cross-sections. In these infinite wires periodic boundary conditions were applied along their axes. Apart from slightly rounded ends for smaller finite wires and more disordering along the vertical direction for all finite wires, no other differences in external shapes of MD boxes were found at investigated temperatures.

As a result of simulation at $T = 300$ K several multi-walled cylindrical structures were obtained. This can be seen from Figs. 1 and 2. Although a multi-walled structure exists already after $10^4$ time steps, to check its stability the simulation was carried out up to $10^6$ time steps. All multi-walled structures are preserved on this time scale. In the cross-sections presented in Figs. 1 (b) the hexagonal symmetry of the fcc(111) surface, which existed in an initial sample at $T = 0$ K, is replaced by the rings. The curved sheets make the concentrical walls of a nanowire. The central core is surrounded by the three coaxial cylindrical shells. The walls of these shells, i.e., the curved sheets, are disordered (Fig. 1 (a)). Figures 1 and 2 show that the “caps” at the ends of a nanowire are flat and that the angle between these flat parts and the lateral wall is nearly 90 degrees. This is in contrast to the multi-walled carbon nanotubes usually capped with semispheres, or polygons [30]. However, it was found that the gold nanowire with the smallest number of atoms has rounded caps and smooth edges between the cap and the lateral wall. Other bigger gold nanowires possess flat ends such as these shown in Figs. 1 and 2. These flat caps, as well as the edges between them and lateral walls are disordered on the atomic scale. It was found that the formation of multi-walls becomes less pronounced when the radius of nanowire increases. For example, in two nanowires with $R = 0.9$ nm three shells are formed, whereas in a nanowire with $R = 1.2$ nm only two cylindrical walls exist. All nanowires are internally filled. Such “the Russian dolls” arrangement for carbon nanostructures, both clusters and wires, was recently the subject of many studies [36][37]. Multi-walled cylindrical forms were also found for the layered crystals of WSe$_2$ and MoSe$_2$ [38]. In order to check the stability of these structures simulation was actually carried out up to very long time of $3 \times 10^6$ time steps (21.3 ns). It was found that multi-walled cylindrical structures are preserved. However, between $10 \times 6$ and $2 \times 10^6$ time steps nanowires start to rotate about their axes. For very long simulation time the mass transport within the wire goes in a such direction that changes its moment of inertia and the angular velocity. The interplay of rotation and vibrational properties of nanoparticles is rather involved, as for example shown for vibrations of rotating cluster by Jellinek and Li [39]. The simulation time of $10^6$ time steps (7.1 ns) is already much longer than an average simulation time in other MD studies of clusters. Therefore, the approach of Ref. [40] where the analysis was stopped before noticeable rotation was detectable, is taken. The rotation of nanowires certainly also has some structural consequences. Centrifugal forces make the wall-structure more pronounced. Figure 2 (a) shows the only example of nanowire where the shells do not form, although
the fcc(111) cross-section structure of an initial sample is lost. Therefore, the formation of a multi-walled structure depends on the specific size and geometry, i.e., the radius and the length for a particular nanowire. The structure shown in Fig. 3 (a) is cylindrical and was formed already on a short time scale (<10^4 time steps) and did not change substantially up to 10^6 time steps. However, in further simulation this shape changes towards an icosahedral structure, as shown in Fig. 3 (b). The appearance of the outer (111) facets is obvious. The initial structure of this nanowire was untypical: the diameter was slightly (0.1 nm) bigger than the length. Therefore, a such evolution from a cylinder to an icosahedral is not surprising. Other nanowires with the diameter smaller than the length are multi-walled and remain in their cylindrical forms.

Vibrational modes of nanowires were investigated by diagonalization of the dynamical matrix. The averaged coordinates of atoms obtained in the MD run were taken as an input. The elements of the force constant matrix for the potential used were calculated. Then a such matrix was diagonalized. In this way the vibrational frequencies were found and from them the density of states was obtained. The calculated spectrum was smoothed by convolution with a Gaussian function. Vibrational frequencies were found and from them the density of states was calculated using the fitted force constant models [41]. It was found that the maximal frequency is ~7 THz. Therefore, the maximal frequencies calculated here for cylindrical multi-walled nanowires are higher than for the fcc bulk lattice. Figure 3 (b) shows that the structure of two peaks, present in the bulk density of states of gold [11] and most fcc metals [12], appears for gold nanowires containing less than 700 atoms. However, the peaks do not have the same size and shape as for the fcc bulk gold. The peaks in Fig. 3 (b) are shifted to lower frequencies in comparison with the vibrational density of states of the bulk. It was found that several percents of the total number of vibrational modes are unstable (i.e., for their frequencies is: \( \omega^2 < 0 \)). Two examples of a change in the number of unstable modes are shown in Table I. A similar instability of vibrational modes (so-called soft phonons with \( \omega^2 < 0 \)) was discussed for surface reconstruction [43] and displacive transitions in crystals [44]. The presence of small number of such modes for nanowires is a sign of their uncompleted structural evolution. Similar morphological changes between different solid phases on a rapid time scale were recently discovered in small CdSe nanocrystals [17].

In summary, MD simulations and lattice dynamical calculations for several finite gold nanowires at room temperature are presented. The interactions were described by a realistic embedded atom potential for gold. Vibrational properties were investigated by diagonalization of the dynamical matrix. It was found that cylindrical shapes with a multi-walled structure were preserved after a long simulation time of 7.1 ns. A nanowire whose initial configuration was such that a diameter was slightly bigger than the length evolved towards an icosahedral shape. An unusual multi-walled structure of metallic nanowires appears because of the imposed geometry. Some preliminary simulations have shown that a multi-walled structure also exists in infinite (111) oriented gold wires with similar cross sections. The potential for gold employed in this simulation [13] was already used in many studies of surfaces [45] and nanoparticles [33], and a good agreement with experimental results was obtained. Therefore, from a confirmed realibility of the potential we should expect that similar multi-walled structures exist in fabricated gold nanowires. In a MD study of Al and Pb infinite ultra-thin (110) and (100) oriented wires at \( T = 0 \) K some two-shell and three-shell structures were found [47]. Computer simulations and X-ray reflection studies showed that the liquid-vapor interface of metals is layered [14]. The layered structure propagates into the bulk liquid for a distance of a few atomic diameters. It was found that the driving force for such layering is the variation of electron density in the surface zone of a metal [16]. Similar phenomena also give rise to contractive surface reconstructions. This type of surface reconstruction is very pronounced in gold. The potential for gold employed in this work reproduces correctly both phenomena: layering at the liquid metal surface [17], and reconstruction for all surface orientations [8]. Therefore, the layering effects present in graphite sheets which form carbon nanowires [36], and in the layered crystals of \( W_2S_2 \) and \( MoS_2 \) [38], also exist in gold. Since the layering decreases with the distance from the surface, it is expected that multi-wall structures disappear when the radius of a nanowire is more than a few atomic diameters. The results of simulation show that a multi-wall structure becomes less pronounced when the radius of a nanowire increases. A jellium model calculation for energetics and quantized conductance of finite sodium nanowires recently appeared [18]. A discrete set of magic wire configurations was found in analogy with the shells in other finite-size fermionic systems, such as atomic nuclei, metallic and \(^3\)He clusters. Therefore, the finite size of metallic nanowires increases the tendency for the formation of multi-walled structures present also because of the layering effect.

All these metallic multi-walled wires, as well as similar structures discovered in experiments for carbon nanowires and nanoparticles [34,37], and for \( W_2S_2 \) and \( MoS_2 \) [38], show that such multi-walled morphologies might be quite common for materials at nanometer length scales.

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TABLE I. Time dependence of the number of unstable vibrational modes for two nanowires (in % of the total number of modes). The nanowire \( A \) has the radius \( R = 1.2 \) nm, the length \( L = 2.6 \) nm, and the number of atoms \( n = 689 \), whereas for the nanowire \( B \) initially is: \( R = 1.4 \) nm, \( L = 2.7 \) nm, and \( n = 991 \). The nanowire \( B \) after \( 10^6 \) time steps evolves towards an icosahedral structure (see Fig. 3). The nanowire \( A \) and all other investigated nanowires are multi-walled.

| Nanowire | Time steps | \( 150 \times 10^3 \) | \( 200 \times 10^3 \) | \( 500 \times 10^3 \) | \( 10^6 \) |
|----------|------------|----------------------|----------------------|----------------------|----------------------|
| \( A \)  |            | 1.9                  | 2.1                  | 2.9                  | 1.9                   |
| \( B \)  |            | 2.5                  | 3.2                  | 3.9                  | 3.4                   |

FIG. 1. Nanowire of 588 atoms, the length 4 nm, and an average radius of 0.9 nm, after a simulation time of 7.1 ns: (a) side view, (b) cross section. The trajectory plots refer to a time span of \( \sim 7 \) ps and always include the total thickness of the whole MD box.

FIG. 2. The density plot for a nanowire shown in Fig. 1. A snapshot of morphology is included.

FIG. 3. (a) Cross section for a nanowire of radius 1.4 nm, length 2.7 nm, and 991 atoms, after a simulation time of 7.1 ns. In an initial structure of this nanowire the diameter is slightly bigger than the length. (b) Side view of the same sample after 21.3 ns. During simulation a transformation towards an icosahedral morphology occurs.

FIG. 4. Vibrational density of states for nanowires of radius \( R \), length \( L \), and number of atoms \( n \): (a) \( R = 0.9 \) nm, \( L = 5.4 \) nm, \( n = 784 \), (b) \( R = 1.2 \) nm, \( L = 2.6 \) nm, \( n = 689 \).
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