

## Structure and stability of finite gold nanowires

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Finite gold nanowires containing fewer than 1000 atoms are studied using the molecular-dynamics simulation method and the embedded-atom potential. Nanowires with a face-centered-cubic structure and (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 multiwalled structures of lasting stability. They consist of concentric cylindrical sheets, and resemble multiwalled carbon nanotubes. Vibrations are investigated by diagonalization of the dynamical matrix. It is found that several percent of vibrational modes are unstable because of an uncompleted restructuring of initial fcc nanowires. [S0163-1829(98)01944-4]

Clusters and wires characterized by 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.<sup>1</sup> Scanning tunneling microscopy experiments recently gave us a way of producing nanostructures. In these experiments formation of metallic nanocontacts between the tip and the substrate was observed.<sup>2</sup> For such nanowires, a quantization of the conductance was found. It was shown that similar nanowires are formed between two vibrating macroscopic wires in contact.<sup>3</sup> The formation of nanowires and their physical properties, such as the electrical conductance, are influenced by elastic, structural, and vibrational properties of the materials involved. These properties are also important for applications. Elastic instabilities of metallic nanocontacts were already studied by molecular-dynamics (MD) simulations.<sup>2,4-9</sup>

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 ( $<5 \times 10^3$  atoms).<sup>10</sup> Metallic nanowires do not form spontaneously under cluster preparation conditions. This shows that their cylindrical structure is artificial and less stable than an icosahedral shape of metallic clusters. In 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.<sup>11</sup> 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.

In this work, structural and vibrational properties of 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 a study of finite carbon nanotubes.<sup>12</sup> The MD method was also used for the 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 studies of the optoelectronic properties of porous silicon.<sup>13</sup> *Ab initio* simulations were also applied to analyze the growth mechanisms for boron-nitride nanotubes.<sup>14</sup> Infinite carbon nanotubes were investigated by classical and *ab initio* simulations.<sup>15</sup> The melting behavior of thin, infinite Pb wires was studied by a classical MD simulation,<sup>16</sup> as well as mechanical properties of the SiSe<sub>2</sub> wires under strain.<sup>17</sup> A recent classical MD study of Pb and Al ultrathin infinite wires at  $T=0$  K has shown that several unusual structures appear, for example icosahedral and helical forms.<sup>18</sup> In comparison with all these infinite wires, finite metallic structures studied here represent the smallest nanowires obtained in the laboratories. In addition, from a theoretical point of view, a finite nanowire is a special version of a cluster whose properties deserve investigation.

Experiments have shown that formation of nanowires is pronounced for gold.<sup>1-3</sup> 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.<sup>19</sup> In this simulation such a many-body potential for gold was employed.<sup>20</sup> This potential was chosen because of its proven accuracy in various MD simulations for bulk, surfaces, and clusters.

These simulations started from crystalline nanowires with a 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. A 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 and 1.4 nm were also studied, as well as nano-

wires with  $N_z = 18$  and 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 cylindrical shape of nanowires was observed, either with the temperature or during time evolution. Initially, heating to 600 K was done, although a proper simulated annealing and quenching technique used in the simulation of metallic clusters requires higher temperatures ( $\sim 0.75$  of the bulk melting temperature, i.e., 1000–1100 K for gold). This was done to prevent melting and collapse into a drop, but to give the atoms a possibility to find some local minima while keeping the 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 the stability of the structures. It was found that the procedure used for heating and equilibration of nanowires gives good results. 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 multiwalled cylindrical structures were obtained. This can be seen from Figs. 1 and 2. Although a multiwalled structure already exists after  $10^4$  time steps, to check its stability the simulation was carried out up to  $10^6$  time steps. All multiwalled structures are preserved on this time scale. In the cross sections presented in Fig. 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 form the concentric 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  $90^\circ$ . This is in contrast to the multiwalled carbon nanotubes usually capped with semi-spheres, or polygons.<sup>21</sup> 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 larger gold nanowires possess flat ends, such as those 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 multiwalls becomes less pronounced when the radius of the 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. The “Russian dolls” arrangement for carbon nanostructures, both clusters and wires, was recently the subject of many studies.<sup>21,22</sup> Multiwalled cylindrical forms were also found for the layered crystals of  $WS_2$  and  $MoS_2$ .<sup>23</sup> In order to check the stability of these structures, simulation was actu-

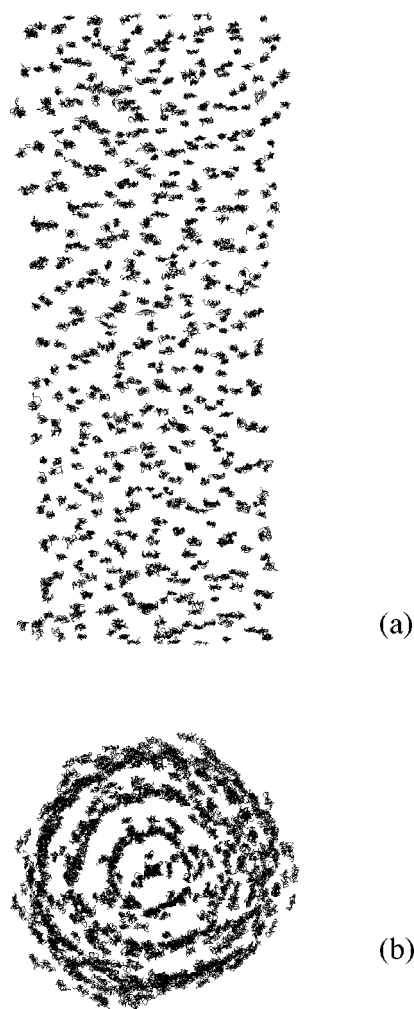


FIG. 1. Nanowire of 588 atoms, with length 4 nm and an average radius of 0.9 nm, after a simulation time of 7.1 ns: (a) side view; (b) cross section. The trajectory plots refer to a time span of  $\sim 7$  ps, and always include the total thickness of the whole MD box.

ally carried out up to very long time of  $3 \times 10^6$  time steps (21.3 ns). It was found that multiwalled cylindrical structures are preserved. However, between  $10 \times 6$  and  $2 \times 10^6$  time steps, nanowires start to rotate about their axes. For a very long simulation time the mass transport within the wire goes in a direction that changes its moment of inertia and the angular velocity. The interplay of rotation and vibrational properties of nanoparticles is rather involved, as shown, for example, for vibrations of rotating cluster by Jellinek and Li.<sup>24</sup> 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. 25, 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. The formation of a multiwalled structure depends on the specific size and geometry, i.e., the radius and the length for a particular nanowire. Nanowire of radius 1.4 nm and length 2.7 nm changes toward an icosahedral structure. The initial structure of this nanowire was untypical: the diameter was slightly (0.1 nm) larger than the length. Therefore, such an evolution from a

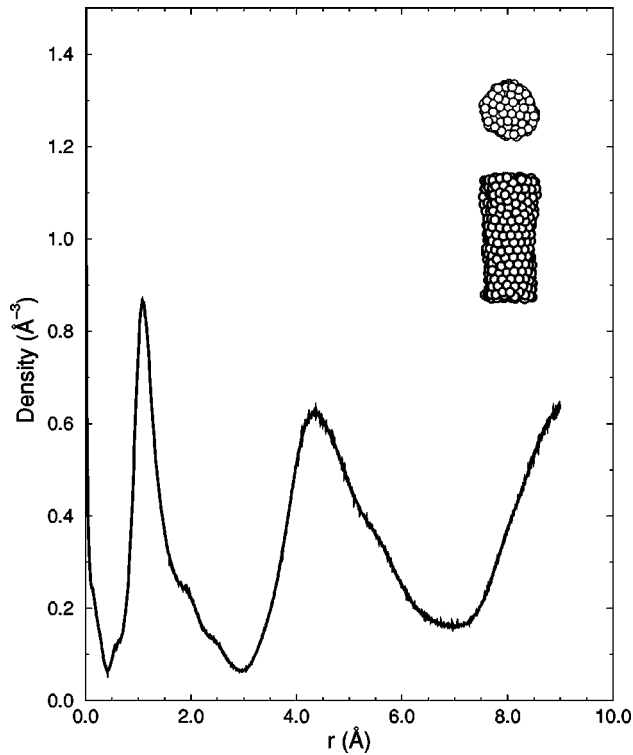


FIG. 2. The density plot for a nanowire shown in Fig. 1. A snapshot of the morphology is included.

cylinder to an icosahedron is not surprising. Other nanowires with a diameter smaller than the length are multiwalled, 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 such a 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 densities of states for two nanowires after  $10^6$  time steps are shown in Fig. 3. The values of maximal frequencies and the shapes of densities of states do not change substantially in time. The frequency peak at  $\sim 3.5$  THz becomes more pronounced when the radius of a nanowire increases. The maximal frequencies were found to approach 6 THz. The phonon-dispersion relations for the fcc bulk gold were measured by neutron scattering, and the vibrational density of states was calculated using the fitted force-constant models.<sup>26</sup> It was found that the maximal frequency is  $\sim 4.7$  THz. Therefore, the maximal frequencies calculated here for cylindrical multiwalled 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<sup>26</sup> and most fcc metals, 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 percent of the total number of vibrational modes are unstable (i.e., for their frequencies,  $\omega^2 < 0$ ). Two examples of a change in the number of unstable

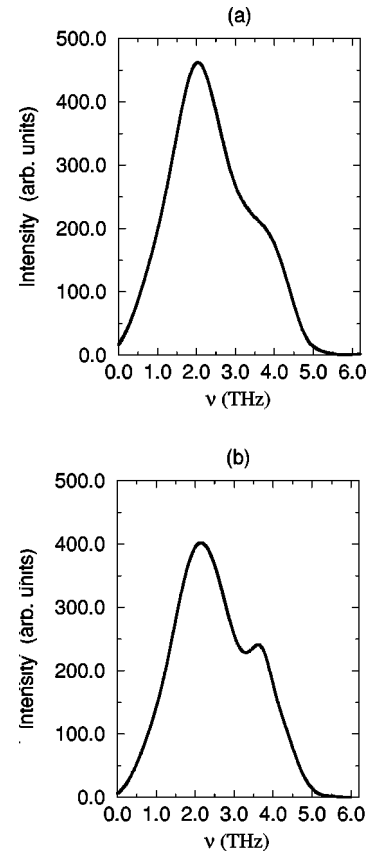


FIG. 3. Vibrational density of states for nanowires of radius  $R$ , length  $L$ , and number of atoms  $n$ : (a)  $R=0.9$  nm,  $L=5.4$  nm,  $n=784$ . (b)  $R=1.2$  nm,  $L=2.6$  nm, and  $n=689$ .

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<sup>27</sup> and displacive transitions in crystals.<sup>28</sup> The presence of a 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.<sup>29</sup>

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 multiwalled structure were preserved after a long simulation time of 7.1

TABLE I. Time dependence of the number of unstable vibrational modes for two nanowires (in percentage of the total number of modes). Nanowire *A* has a radius  $R=1.2$  nm, a length  $L=2.6$  nm, and a number of atoms  $n=689$ , whereas for nanowire *B* the dimensions initially are  $R=1.4$  nm,  $L=2.7$  nm, and  $n=991$ . Nanowire *B* after  $10^6$  time steps evolves toward an icosahedral structure). Nanowire *A* and all other investigated nanowires are multiwalled.

Nanowire/time steps	$150 \times 10^3$	$200 \times 10^3$	$500 \times 10^3$	$10^6$
<i>A</i>	1.9	2.1	2.9	1.9
<i>B</i>	2.5	3.2	3.9	3.4

ns. A nanowire whose initial configuration was such that its diameter was slightly larger than its length evolved toward an icosahedral shape. An unusual multiwalled structure of metallic nanowires appears because of the imposed geometry. Some preliminary simulations have shown that a multiwalled structure also exists in infinite (111)-oriented gold wires with similar cross sections. The potential for gold employed in this simulation<sup>20</sup> was already used in many studies of surfaces and nanoparticles, and a good agreement with experimental results was obtained. Therefore, from the confirmed reliability of the potential we should expect that similar multiwalled structures exist in fabricated gold nanowires. In a MD study of Al and Pb infinite ultrathin (110)- and (100)-oriented wires at  $T=0$  K, some two- and three-shell structures were found.<sup>18</sup> Computer simulations and x-ray reflection studies shown that the liquid-vapor interface of metals is layered.<sup>30</sup> 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 a layering is the variation of electron density in the surface zone of a metal.<sup>30</sup> 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 correctly reproduces both phenomena: layering at the liquid metal surface,<sup>31</sup> and reconstruction for all surface

orientations.<sup>20</sup> Therefore, the layering effects present in graphite sheets which form carbon nanowires,<sup>21</sup> and in the layered crystals of  $WS_2$  and  $MoS_2$ ,<sup>23</sup> also exist in gold. Since the layering decreases with the distance from the surface, it is expected that multiwall structures disappear when the radius of a nanowire is more than a few atomic diameters. The results of the simulation show that a multiwall structure becomes less pronounced when the radius of a nanowire increases. A jellium model calculation for the energetics and quantized conductance of finite sodium nanowires recently appeared.<sup>32</sup> A discrete set of magic wire configurations was found, in analogy with the shells in other finite-size fermionic systems, such as atomic nuclei, and metallic and  $^3He$  clusters. Therefore, the finite size of metallic nanowires increases the tendency toward the formation of multiwalled structures, also present because of the layering effect.

All these metallic multiwalled wires, as well as similar structures discovered in experiments for carbon nanowires and nanoparticles,<sup>21,22</sup> and for  $WS_2$  and  $MoS_2$ ,<sup>23</sup> show that such multiwalled morphologies might be quite common for materials at nanometer length scales.

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- <sup>1</sup>H. Hegger, B. Huckestein, K. Hecker, M. Janssen, A. Freimuth, G. Reckziegel, and R. Tuzinski, *Phys. Rev. Lett.* **77**, 3885 (1996).
- <sup>2</sup>J. I. Pascual, J. Mendez, J. Gomez-Herrero, A. M. Baro, N. Garcia, U. Landman, W. D. Luedtke, E. N. Bogachek, and H. P. Cheng, *Science* **267**, 1793 (1995).
- <sup>3</sup>J. L. Costa-Krämer, N. Garcia, P. Garcia Mochales, and P. A. Serena, *Surf. Sci.* **342**, L1144 (1995).
- <sup>4</sup>M. R. Sorensen, K. W. Jacobsen, and P. Stoltze, *Phys. Rev. B* **53**, 2101 (1996).
- <sup>5</sup>T. N. Todorov and A. P. Sutton, *Phys. Rev. Lett.* **70**, 2138 (1993).
- <sup>6</sup>R. M. Lynden-Bell, *Science* **263**, 1704 (1994).
- <sup>7</sup>U. Landman, W. D. Luedtke, B. E. Salisbury, and R. L. Whetten, *Phys. Rev. Lett.* **77**, 1362 (1996).
- <sup>8</sup>H. Mehrez and S. Ciraci, *Phys. Rev. B* **56**, 12 632 (1997).
- <sup>9</sup>R. N. Barnett and U. Landman, *Nature (London)* **387**, 788 (1997).
- <sup>10</sup>T. P. Martin, *Phys. Rep.* **273**, 199 (1996).
- <sup>11</sup>Y. Kondo and K. Takayanagi, *Phys. Rev. Lett.* **79**, 3455 (1997).
- <sup>12</sup>M. Menon, E. Richter, and K. R. Subbaswamy, *J. Chem. Phys.* **104**, 5875 (1996).
- <sup>13</sup>F. Buda, J. Kohanoff, and M. Parrinello, *Phys. Rev. Lett.* **69**, 1272 (1992).
- <sup>14</sup>X. Blase, A. De Vita, J. C. Charlier, and R. Car, *Phys. Rev. Lett.* **80**, 1666 (1998).
- <sup>15</sup>M. Buongiorno Nardelli, B. I. Yakobson, and J. Bernholc, *Phys. Rev. B* **57**, R4277 (1998).
- <sup>16</sup>O. Gülseren, F. Ercolessi, and E. Tosatti, *Phys. Rev. B* **51**, 7377 (1995).
- <sup>17</sup>W. Li, R. K. Kalia, and P. Vashishta, *Phys. Rev. Lett.* **77**, 2241 (1996).
- <sup>18</sup>O. Gülseren, F. Ercolessi, and E. Tosatti, *Phys. Rev. Lett.* **80**, 3775 (1998).
- <sup>19</sup>M. S. Daw, S. M. Foiles, and M. I. Baskes, *Mater. Sci. Rep.* **9**, 251 (1993).
- <sup>20</sup>F. Ercolessi, M. Parrinello, and E. Tosatti, *Philos. Mag. A* **58**, 213 (1988).
- <sup>21</sup>S. Iijima, *Nature (London)* **354**, 56 (1991); *MRS Bull.* **19**, 43 (1994).
- <sup>22</sup>D. Ugarte, *Chem. Phys. Lett.* **198**, 596 (1992).
- <sup>23</sup>R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature (London)* **360**, 444 (1992); L. Margulis, G. Salitra, R. Tenne, and M. Talenker, *ibid.* **365**, 113 (1993).
- <sup>24</sup>J. Jellinek and D. H. Li, *Chem. Phys. Lett.* **169**, 380 (1990).
- <sup>25</sup>J. Jellinek, T. Beck, and R. S. Berry, *J. Chem. Phys.* **84**, 2783 (1986).
- <sup>26</sup>J. W. Lynn, H. G. Smith, and R. M. Nicklow, *Phys. Rev. B* **8**, 3493 (1973).
- <sup>27</sup>A. Fasolino and E. Tosatti, *Phys. Rev. B* **35**, 4264 (1987).
- <sup>28</sup>N. Boccara and G. Sarma, *Physics (Long Island City, NY)* **1**, 219 (1965).
- <sup>29</sup>C. C. Chen, A. B. Herhold, C. S. Johnson, and A. P. Alivisatos, *Science* **276**, 398 (1997).
- <sup>30</sup>S. A. Rice, J. Gryko, and U. Mohanty, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986), p. 255.
- <sup>31</sup>O. Tomagnini, F. Ercolessi, S. Iarlori, F. D. DiTolla, and E. Tosatti, *Phys. Rev. Lett.* **76**, 1118 (1996).
- <sup>32</sup>C. Yannouleas and U. Landman, *J. Phys. Chem. B* **101**, 5780 (1997).