

An investigation into the atomic planes of nanowires of FCC metals

*Thesis submitted for partial fulfillment of the requirements for
the degree of*

Bachelor of Science (Research)

in the Undergraduate Department

by

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Abstract

Nanowires are slender structures characterized by a length extremely longer than the diameter. 1D nanostructures constitute an important component of the nanotechnology industry owing to their wide range of applications such as sensing, actuation, cantilever bending, nanoelectronics, photovoltaics etc.^[2-9] Gold nanowires in particular are widely used as building blocks for sensing devices in chemistry and biochemistry domains owing to their unusual optical, electrical and mechanical properties.^[10]

A detailed understanding of the structure and stability of the nanostructures is critical to design applications. While doing structural studies of single crystalline Gold nanowires using Atomic resolution imaging, an interesting relaxation was revealed, wherein the atoms in the closed packed plane normal to the growth direction are displaced in the axial direction leading to a wrinkling of the atomic plane whose normal points in the direction of the wire axis. This is particularly observed in (111) planes when the wire axis is oriented along [111]direction^[11].

In the current study, the LAMMPs (*Large-scale Atomic/Molecular Massively Parallel Simulator*) code has been used to look into the relaxed structure of nanowires.

At first, I have tried to reproduce the results for pure Au single crystalline nanowires as given in [1]. Next the simulation was done for other FCC metals like Silver(Ag), Platinum(Pt), Copper(Cu) and Aluminium(Al).

Highlights:

- Relaxation was done for pure Au nanowires using LAMMPs.
- Relaxation was done for pure Pt, Au, Cu, and Al nanowires with the same geometry.

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Acknowledgement:

I take this opportunity to express my deep gratitude and sincere thanks to my thesis advisor Prof. N. Ravishankar, for his support and guidance without which this work would not have been possible. Research aside, I learnt a lot from him about the way of conducting life, first of which is humility or the act of staying humble and approachable even after being such a renowned professor. and his unconventional & original approach towards learning are some other things which I appreciate about him and look to learn from.

Secondly I would like to thank my co-advisor prof. S. Karthikeyan for his suggestions and help in doing this project. It was only through him that I got to meet Sarthak who introduced me to the LAMMPs software which was crucial for this project. Again research aside, I learnt several things from him too. Kindness, resourcefulness and the undying enthusiasm to start new initiatives are some of the things which I appreciate about him and would like to learn from.

I would like to thank my senior Sarthak Jadhav for introducing me to LAMMPs^[16]. On my first meeting with him, he patiently explained to me the syntax of the input script which made things pretty easier for me later on. The patience which he displayed while explaining to me is something which I appreciate about him and would like to learn.

I would also like to thank my friend Hitesh for introducing me to OVITO^[17] which made visualisations easier.

My sincere thanks to the Undergraduate Department of IISc for providing great opportunities for learning in the last year of my stay here.

Last but not the least, I am forever grateful to my parents for their support and encouragement throughout.

Introduction:

The one dimensional nanostructures in the form of nanowires, rods, belts etc are being extensively studied owing to their wide range of applications. To design these applications a proper understanding of the structure, morphology and chemistry is required.

Unlike the bulk solid case, as we move into smaller and smaller regimes such as nanowires and nanorods, the majority of the atoms lie on the surface, so surface effects such as capillary forces or surface tension etc. become significant and their effects cannot be ignored. The coordination number of the surface atoms is lower than those in the bulk. So they tend to adopt spacings that are different from the bulk. They do this in order to obtain minimum energy configuration. This spacing mismatch between bulk and the surface atoms leads to development of surface stresses. These surface stresses are compensated by generation of stresses which are felt within the bulk of the solid.

Here we explore one such interesting effect of surface stress on the structure of ultra-thin Au nanowire where the flat close packed (111) planes normal to the axis of the nanowire undergo wrinkling to form saddle shaped surfaces. This has previously been experimentally observed, studied and reported in [\[1\]](#) (Roy A. et al, 2014).

In this study we try to replicate the results obtained for pure Au nanowire by [\[1\]](#)(Roy A. et al, 2014) using LAMMPS(*Large-scale Atomic/Molecular Massively Parallel Simulator*)[\[16\]](#) software.

After replicating the results for pure Au nanowire, the aim was to look into other systems. We aimed at looking into alloy systems of Au-Ag or Au-Pd initially. But due to unavailability of their potential files in the LAMMPS[\[16\]](#) repository, we changed direction to study the same for Pt systems and subsequently Au-Pt system wherein the wrinkling was observed for various compositions of the Au-Pt binary alloy systems and coaxial systems(with Au core-Pt cladding and vice versa).

Literature survey:

Background:

Gold nanowires(GNWs) form an integral component of the nanotechnology industry because of their excellent physicochemical properties such as high current densities, high signal to noise ratio and low double layer capacitance. These properties when combined with the fact that the majority of their atoms lie on the surface makes them an excellent candidate for sensing applications. They are used extensively for manufacturing sensing devices in the chemistry and biochemistry industries. Some known applications include pressure sensors, DNA detectors, interconnects and nanoelectrodes.^[10]

The development of wet chemical methods for the synthesis of stable ultrathin Au nanowires both in solution phase and substrates has really opened up new frontiers for investigating the structures and properties of ultrathin systems in great detail.^[11-15]

Observation:

Using Transmission Electron Microscopy(TEM) when the imaging of the synthesized nanowires was done, it revealed some intriguing insights into the structure of the Au nanowires. In the study reported by [1](Roy A. et al, 2014) when the Au nanowire was grown on a graphene substrate with the growth axis being [111], the atoms on the plane normal to the axis ie (111) showed significant out of the plane displacements. This was observed when the imaging was done with electrons incident along a direction close to a <110> direction.

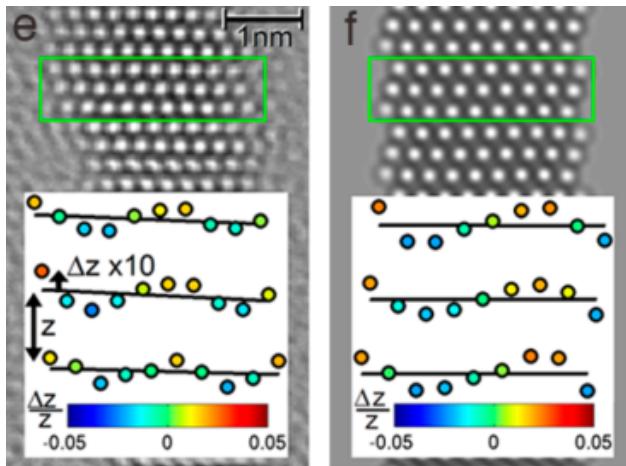


Fig 1:

TEM image of Au nanowire by [1](Roy A. et al, 2014)

Inorder to quantify the atomic displacements of individual (111) planes, the parameter ($\Delta z/z$) was used where Δz denotes the deviation in the axial direction from the best fit plain flat lattice and z denotes the interplanar spacing. The color coding is done as per the value of the same parameter.

Role of surface stresses:

In lower dimensional structures such as ultrathin nanowires in the present case, since the majority of the atoms lie on the surface, the surface effects such as capillary forces or surface tension cannot be neglected. The coordination number of the surface atoms is less than that of those in the bulk. Or in other words, the surface atoms are bonded to fewer neighbours. So they try to bring down the surface energy by adopting spacings that are quite different from those of the bulk. This deviation from the ideal lattice positions leads to a spacing mismatch between the surface and the bulk atoms which leads to development of both surface stresses and compensating stresses that are felt within the bulk of the material. When the bulk or the core is very small such as that in the current case of ultrathin Au nanowire, the effects can be quite significant. The wrinkling of the (111) planes can be attributed to these surface stresses.^[1]

The wrinkling caused due to relaxation can result in significant changes in both the electronic structure as well as the electrical transport that could have important implications for applications like sensing and actuation^[1].

In the current study we use Molecular Dynamics simulator LAMMPS^[16], to study the results given in the paper [1](Roy A. et al, 2014) which investigates the wrinkling in Au nanowire. Then, we move on to study the same in other FCC metals. After that we study how the wrinkling relates to material properties.

Methods:

The MD (molecular dynamics) simulations are performed using LAMMPs (*Large-scale Atomic/Molecular Massively Parallel Simulator*)^[16]

Simulation Setup:

Initialisation:

For carrying out the simulation:

- First the simulation region was specified.
- Next periodic boundary conditions were applied along the z direction. This was done because the axis of the nanowire will be aligned along this direction.
- The geometry of the nanowire and its orientation with respect to the lattice was specified. This was done by specifying what lattice directions orient along x,y and z directions of the simulation box.
- Next the atom(s) type(s) was(were) specified. The location of the potential file documenting the interaction between the atoms was specified.
- External Pressure was set to 0

Minimization:

Once the initial structure, boundary conditions and the interaction potentials are set, the next step is to call the ‘minimize’ function which would take the structure as input and then would keep perturbing the atomic coordinates in successive iterations with the objective of minimizing the potential energy of the system. This is achieved by using the cg (Conjugate Gradient descent) algorithm. This is done until the termination conditions are reached.

Termination :

When either of maximum force or energy difference between two successive iterations is less than the tolerance value, the minimization is stopped. At that point the configuration will hopefully be in local potential energy minimum.

For our case force tolerance and energy tolerance were set to 10^{-15} (eV/Å for force and unitless for energy).

Output:

After termination the final relaxed configuration was written in a text file using dump command. This file contained the atomic coordinates of all the atoms in the relaxed structure.

Next the information from the output file was extracted, filtered and analysed by writing python scripts. In some cases MATLAB was used for plotting and analysis.

Ovito^[17] software was used to visualise the relaxed structure.

For this study we required the initial structures for the cases given below:

1. Pure Au, Ag, Cu, Pt and nanowires with their axis oriented along a $<1\ 1\ 1>$ direction of the FCC lattice.
2. Pure Au, Pg ,Cu, Pt and Al nanowires with their axis oriented along a $<0\ 0\ 1>$ direction of the FCC lattice.

A brief description of how the initial structures were obtained for each case is given below:

1. Pure Au nanowires with their axis oriented along a $<1\ 1\ 1>$ direction of the FCC lattice.

For this case the x, y and z axis of a cylindrical region were oriented along orthogonal directions belonging to $<1\ 1\ 2>$, $<1\ 1\ 0>$ and $<1\ 1\ 1>$ family of directions of the FCC lattice respectively. After that the atoms were filled in the region following lattice periodicity. Due to hexagonal symmetry of the $\{1\ 1\ 1\}$ family of planes which are normal to the wire axis, the cross sections were either hexagonal (*bounded either by $\{1\ 1\ 0\}$ planes or the $\{1\ 1\ 2\}$ planes*) or near circular (*bounded by a combination of $\{1\ 1\ 0\}$ and $\{1\ 1\ 2\}$ planes*) depending on the radius of cylinder which determines where the cylinder cuts the lattice.

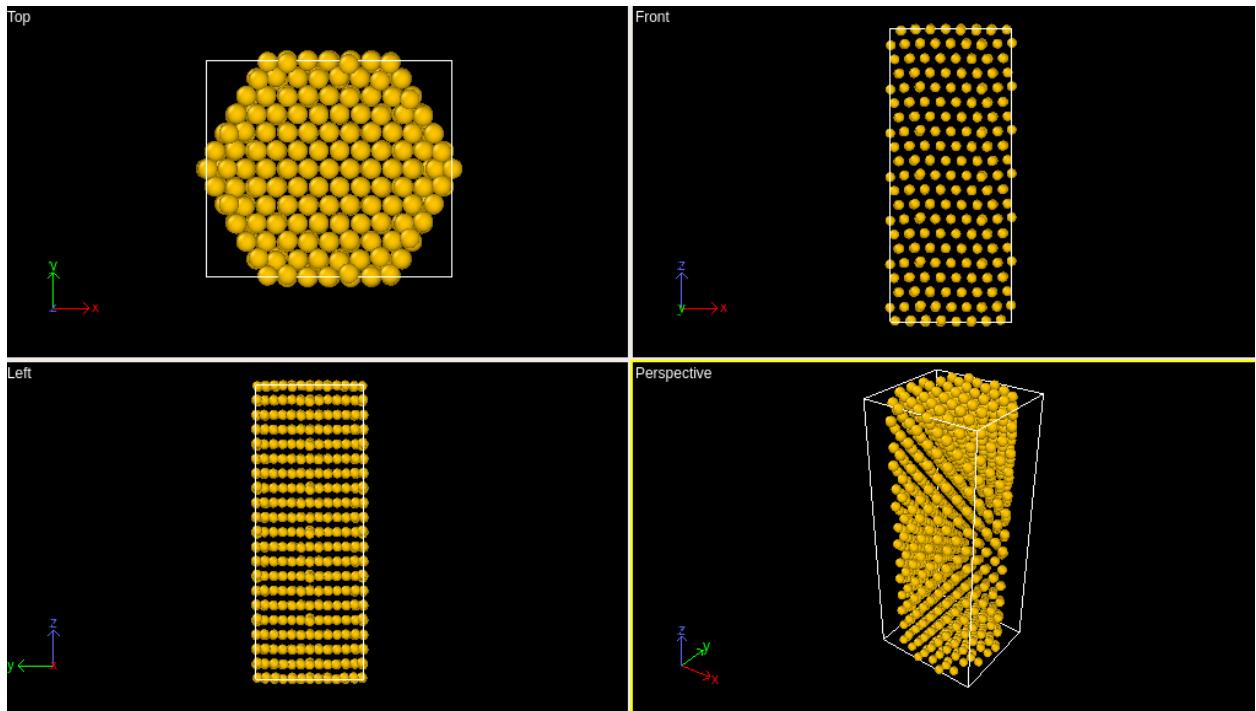


Fig 2:

The above image shows the relaxed structure of a gold nanowire with hexagonal cross section ($-1\bar{1}1$) bounded by $\{1\bar{1}2\}$ facets. For this case the x, y and z axis of a simulation region were oriented along $[-112]$, $[110]$ and $[-11-1]$ directions of the FCC lattice.

2. Pure Au nanowires with their axis oriented along a $<001>$ direction of the FCC lattice.

For this case the x, y and z direction of the simulation box are oriented along three orthogonal directions belonging to the $<100>$ family of the FCC lattice. After that the atoms are filled in the region obeying lattice periodicity.

Due to four fold symmetry of the (100) planes, when the atoms are filled in the box, a square cross section is obtained.

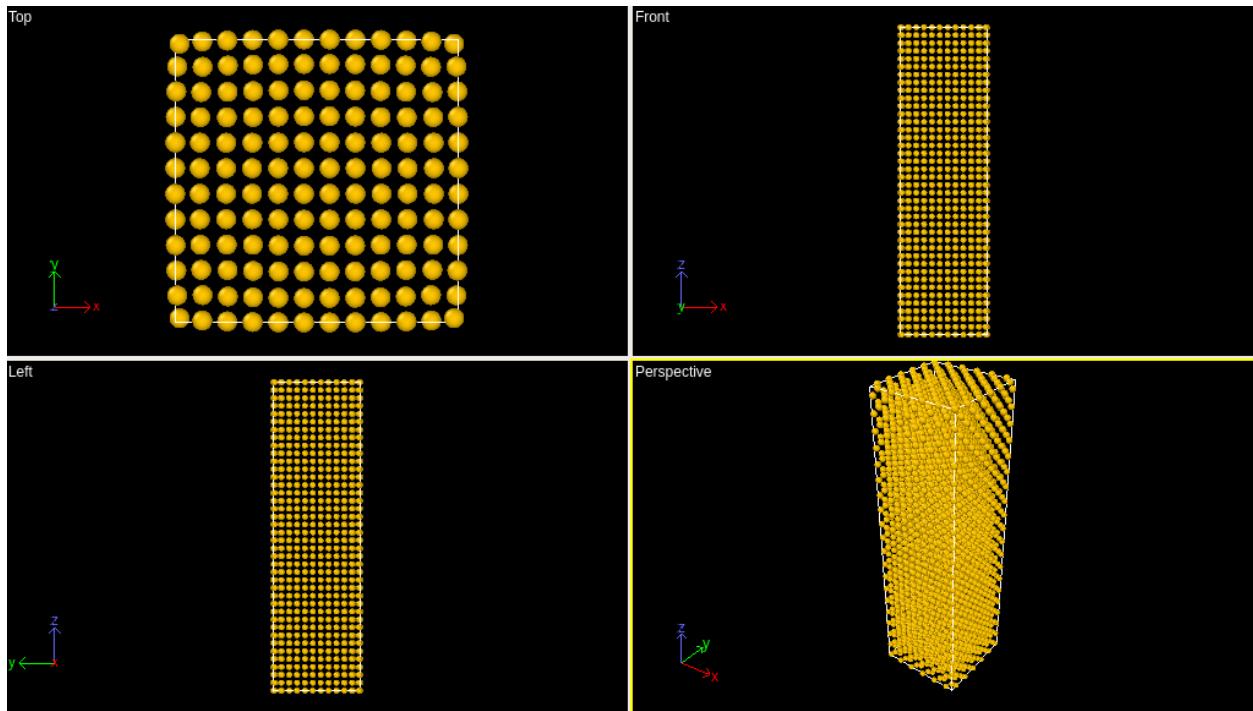


Fig 3:

The above image shows the relaxed structure for a gold nanowire, with axis pointing along [0 0 1] direction of FCC lattice.

Results & discussion:

Part 1

First the relaxation was done for pure Au and pure Pt nanowires of different diameters (2nm, 3nm, 4nm, 6nm and 10nm), whose axes were oriented along [-1 1 -1] direction of the FCC lattice.

Since FCC has ABC stacking for {1 1 1} planes, atoms of a particular stack or cross-sectional layer were selected from each of the wires for analysis and comparison.

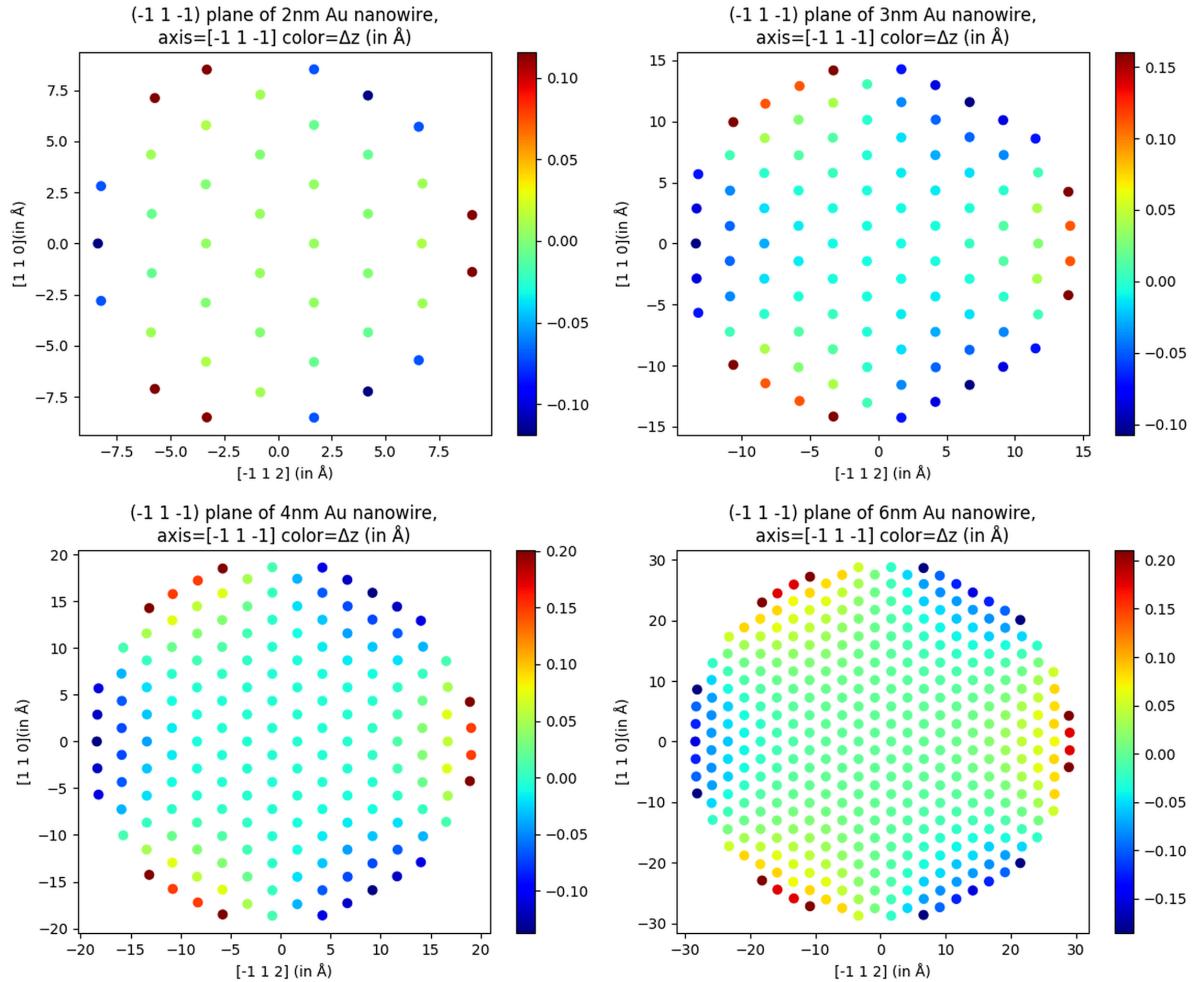


Fig 6:

In the above figure the atoms of a particular $(-1\ 1\ -1)$ plane are plotted for pure Au nanowires of different diameters. The colour coding is done according to Δz which represents the displacement of individual atoms from the best fit flat plane in Å.

Similarly when we do the same for pure Pt nanowire, we get the following:

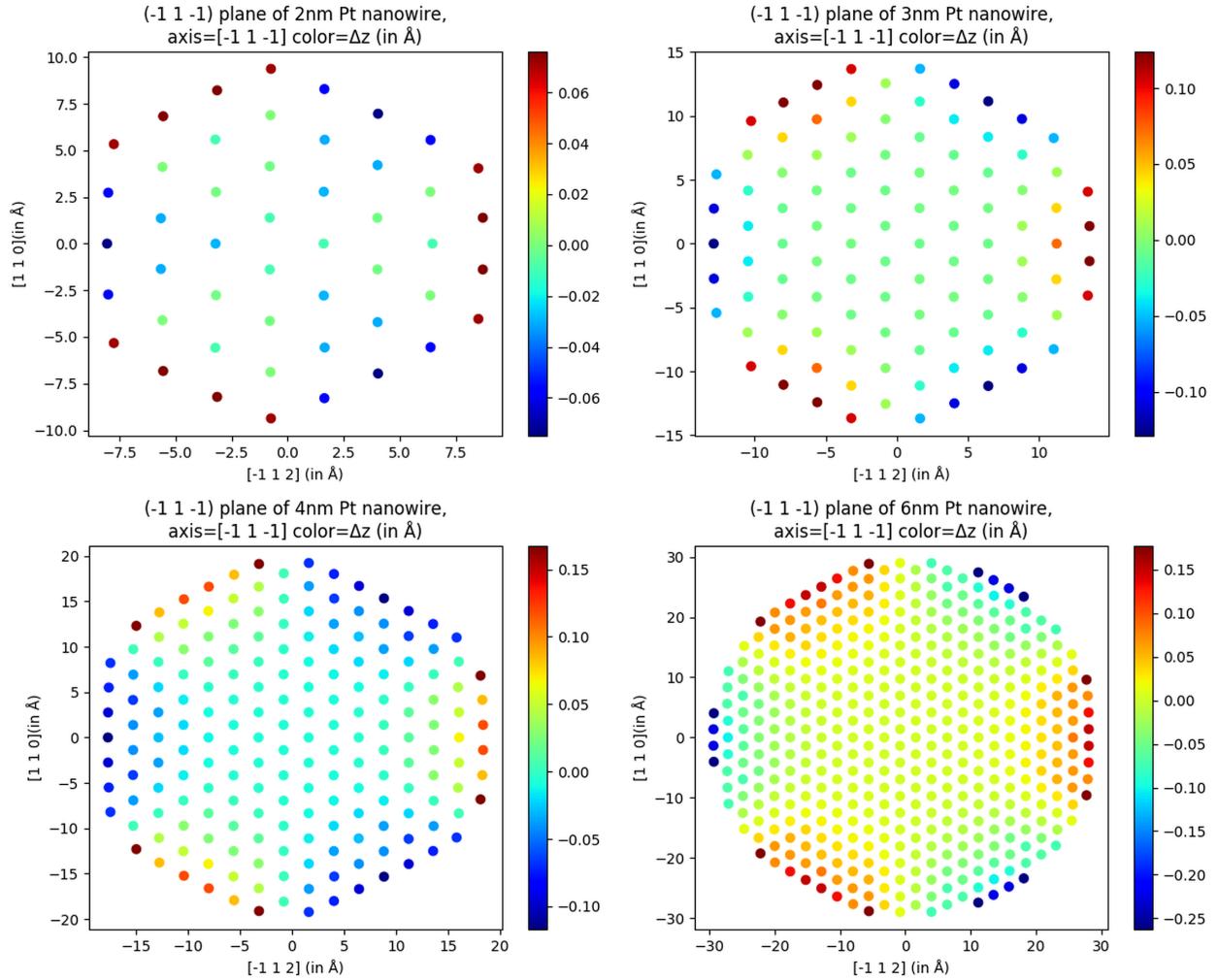


Fig 7:

In the above figure the atoms of a particular $(-1\ 1\ -1)$ plane are plotted for pure Pt nanowires of different diameters. The colour coding is done according to Δz which represents the displacement of individual atoms from the best fit flat plane in Å.

From the above results for Au and Pt nanowires it is clear that wrinkling of $\{1\ 1\ 1\}$ planes normal to the axis of the wires, happens. It is also evident (especially from the case of thicker nanowires) that the core regions of the wire are essentially flat. The variations become prominent towards the surface, suggesting that it can be a surface effect as was discussed in the literature survey.

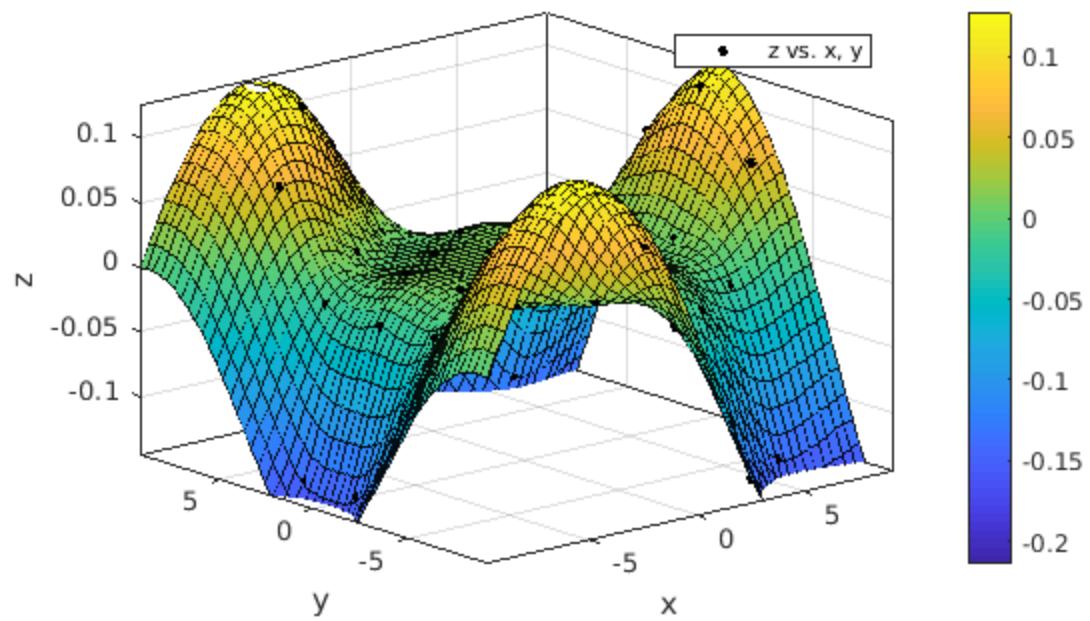


Fig 8:

The above image is obtained by performing a surface fit to the atoms of the (111) plane of a relaxed pure Au nanowire. This shows the wrinkling of flat (111) planes on relaxation which was reported by [\[1\]](#) (*Roy A. et al, 2014*)

On relaxation, the axial and the radial lattice constants of the nanowire deviated from the ideal. The axial lattice constant was calculated from the d spacing of the (111) planes which was obtained by dividing the axial length (l_z) of the simulation box by the number of (111) planes in the box.

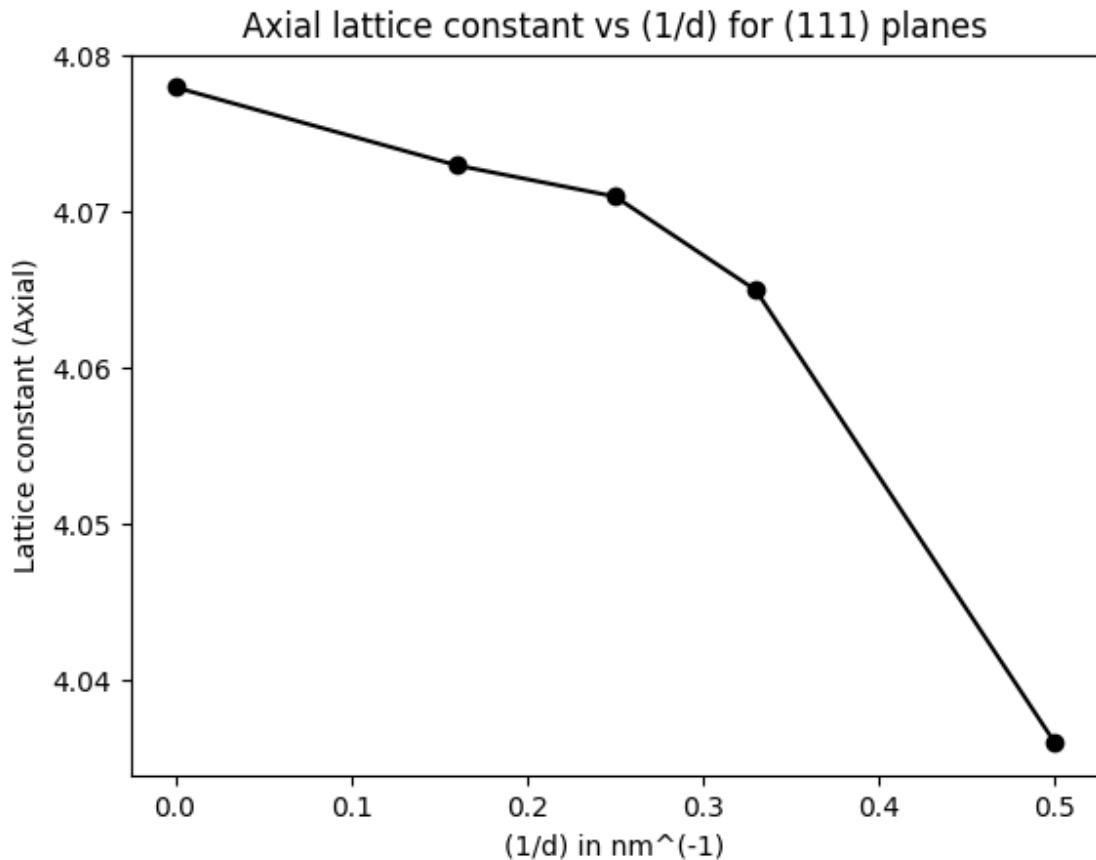


Fig 9:

In the above figure, the axial lattice constant of Pure Au nanowire is plotted with respect to the inverse of the diameter, for wires of different diameters. The decreasing trend shows that the axial lattice constant becomes smaller or axial contraction happens as we decrease the thickness of the nanowire. This was reported by [11] (Roy A. et al, 2014).

Axial lattice constant vs $(1/d)$ for (111) planes
for Pt nanowires

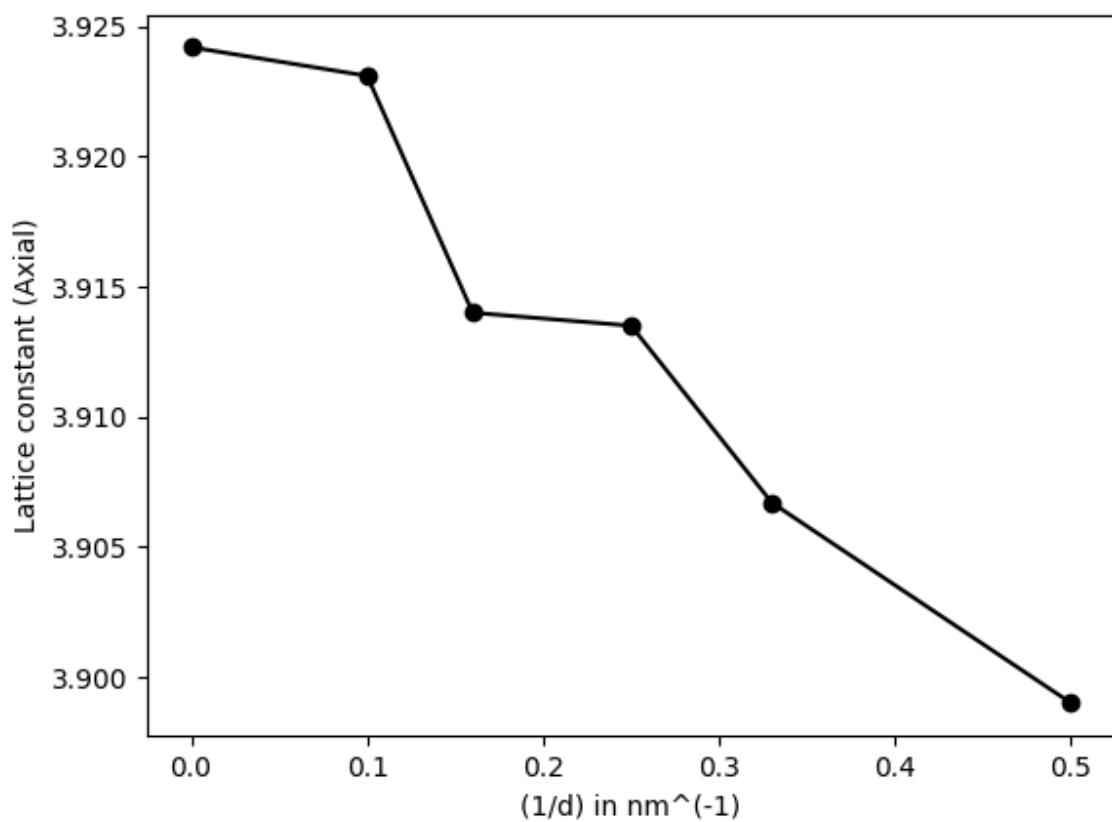


Fig 10: In the above figure, the axial lattice constant of pure Pt nanowire is plotted with respect to the inverse of the diameter; for wires of different diameters. Here too the same trend is followed as the previous.

Part 2

Here we compare the results of the relaxation for two nanowires of similar thickness (2nm) but with their axes pointed along [0 0 1] and [-1 1 -1] directions.

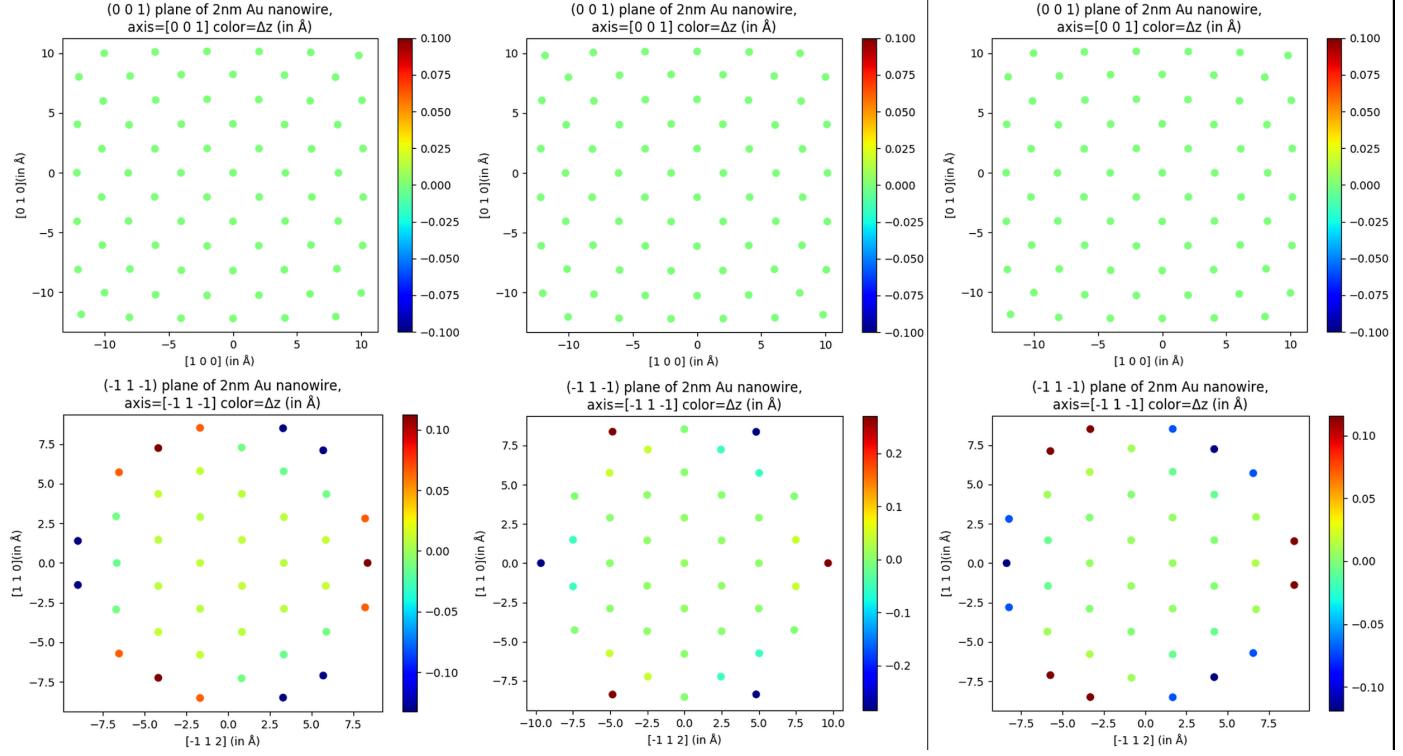


Fig 11:

In the first row we plot the Δz (atomic displacements of the individual atoms (from the best fit flat plane)) of three stacks of parallel (001) planes which are normal to the wire axis. In the second row we plot the Δz (atomic displacements of the individual atoms (from the best fit flat plane)) of three stacks(ABC) of parallel (111) planes which are normal to the wire axis.

We also find similar results from the simulation of pure Pt nanowires. Which is reported below.

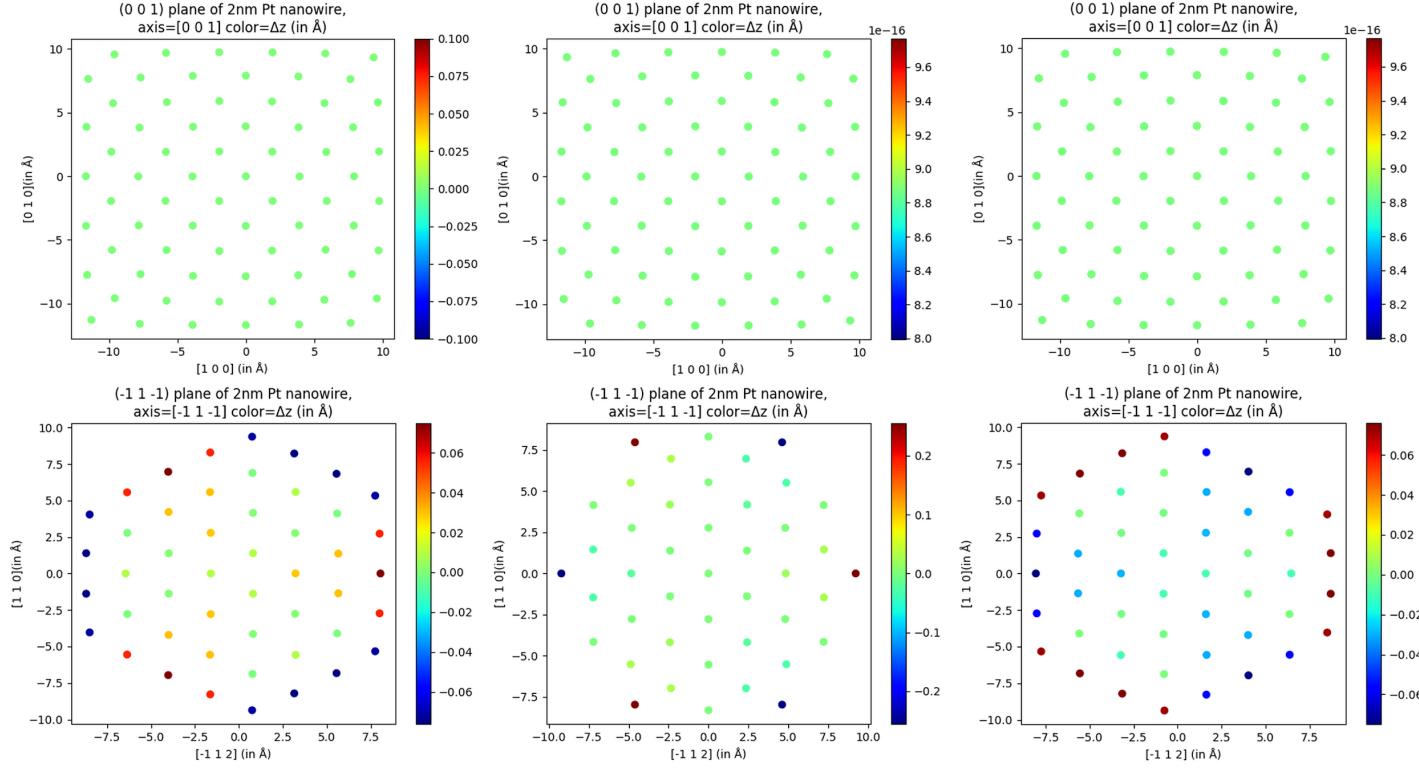


Fig 12:

In the first row we plot the Δz (atomic displacements of the individual atoms (from the best fit flat plane)) of three stacks of parallel (001) planes which are normal to the wire axis. In the second row we plot the Δz (atomic displacements of the individual atoms (from the best fit flat plane)) of three stacks(ABC) of parallel (111) planes which are normal to the wire axis.

From the above figures it is evident that the (001) planes, unlike the (111) planes, don't undergo wrinkling. This was reported by [1](Roy A. et al, 2014) where they linked it to anisotropy arguments.

Table 1

Wire axis	Bounding planes	Modulation seen
{1 1 1}	<112> or <110>	Yes
{1 0 0}	<1 0 0>	No

The table summarises the results of previous figures.

Part 3

The results of the simulation for coaxial Au-Pt systems is shown below.

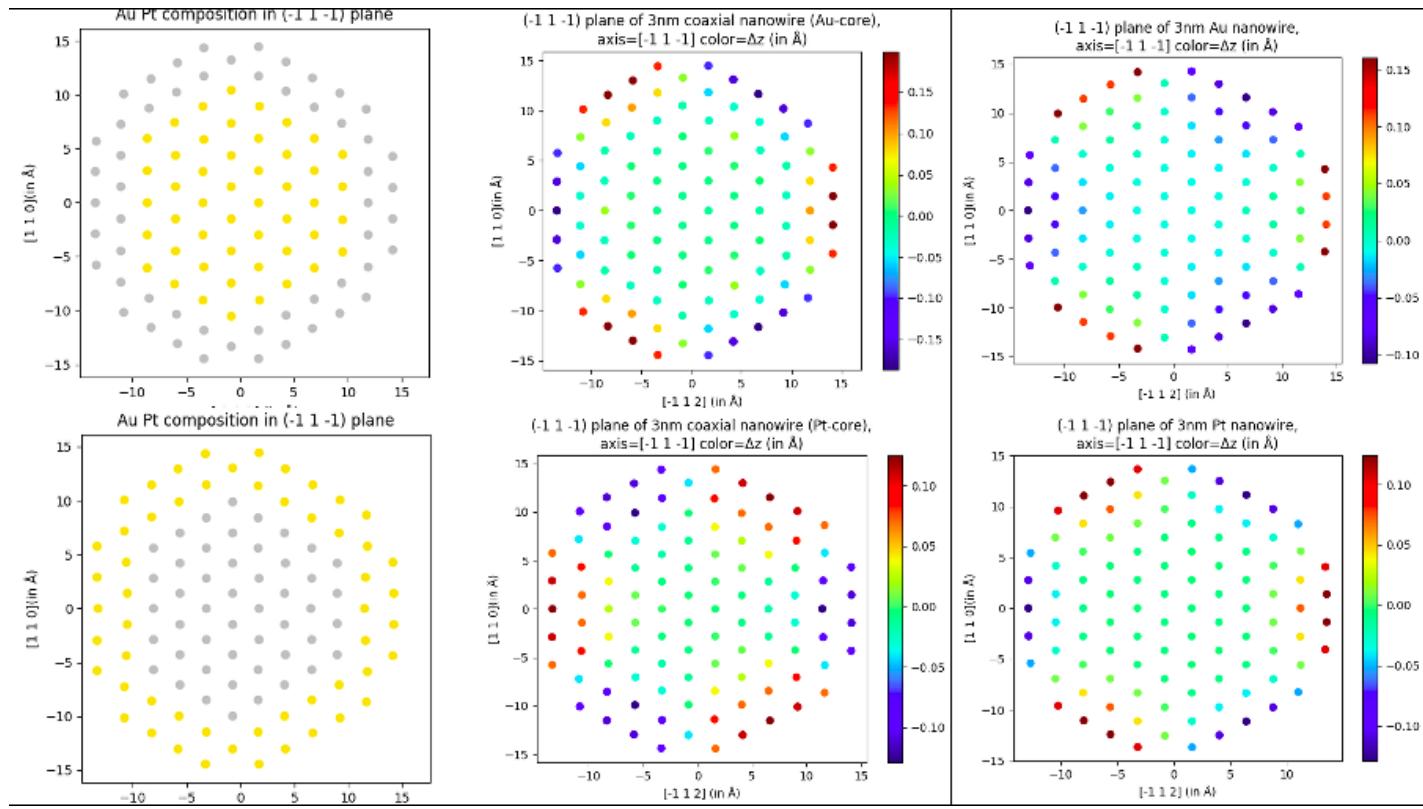


Fig 13:

In the above figure atoms of a particular (111) planes are plotted for comparison:

Top(left to right): 1. Composition profile of the coaxial nanowire with Au-core, Pt-cladding 2. Plot of Δz (atomic displacements of the individual atoms (from the best fit flat plane)) for Au-core coaxial nanowire. 3. Δz plot for pure Au nanowire for comparison.

Bottom(left to right): 1. Composition profile of the coaxial nanowire with Pt-core, Au-cladding 2. Plot of Δz (atomic displacements of the individual atoms (from the best fit flat plane)) for Pt-core coaxial nanowire. 3. Δz plot for pure Pt nanowire for comparison.

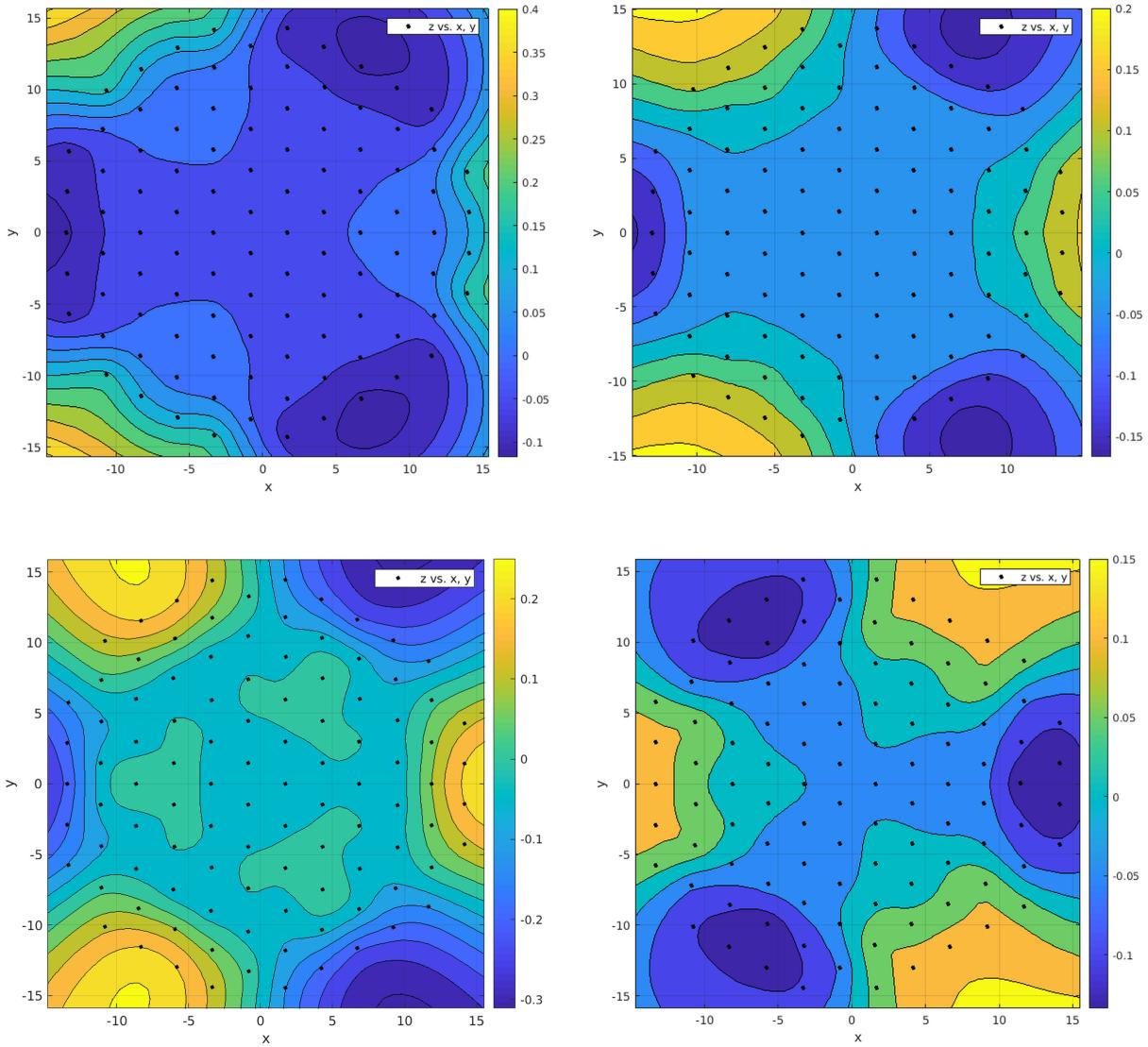


Fig 14:

(clockwise from top left): 1. Contour plot for Δz which shows displacements of the (111) plane of a pure Au nanowire(3nm dia) in the axial direction. This is plotted to serve as reference for comparing results of coaxial systems which are given below 2. Δz plot for pure Pt 3. Δz plot for coaxial nanowire with Au-core,Pt cladding. 4. Δz plot for coaxial nanowire with Pt-core, Au cladding.

It is interesting to note the formations of islands in the interior of the Au-core,Pt-cladding nanowire. This was consistently seen in wires of other diameters while doing the simulations.

Part 4

Next we present the results of relaxation on a nanowire made of Au60-Pt40 alloy.

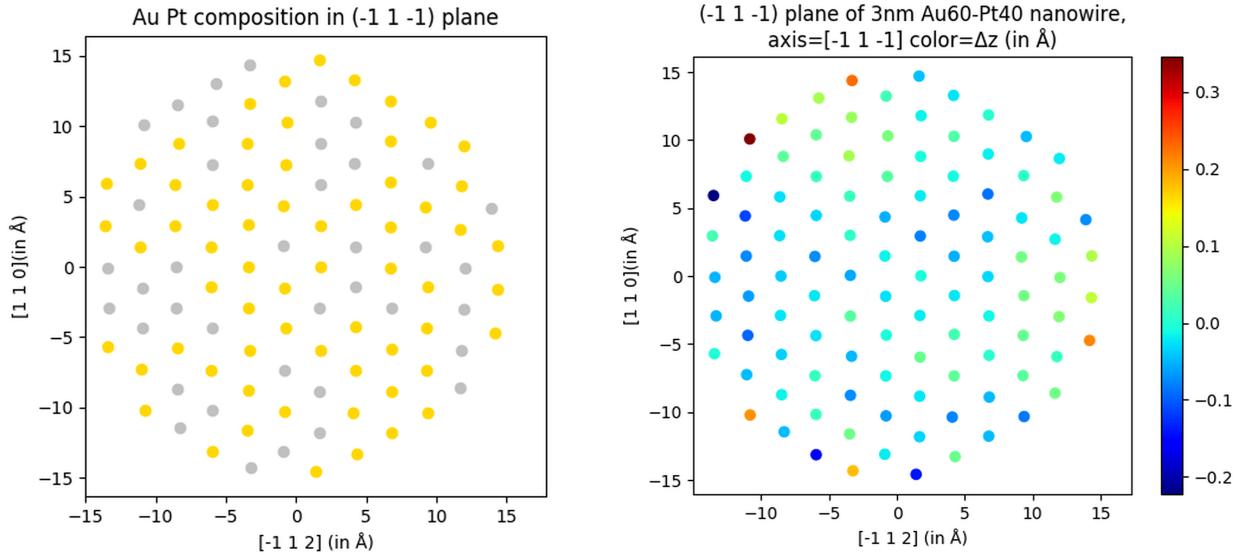


Fig 15:

- (left) It shows the composition profile of a particular (111) plane of an Au60-Pt40 nanowire,
- (right) It shows the Δz (axial displacement in angstroms) profile of the atoms to quantify the wrinkling.

It is evident that there is no symmetrical wrinkling pattern in the above case of nanowires of Au-Pt random alloy.

Work planned & problems faced:

Initial plan of work was to reproduce the results for pure Au nanowire given in the paper [1](
Roy A. et al, 2014) by performing MD simulations using the LAMMPS code. Not only this was
done but the results for pure Pt nanowire were also obtained.

After its completion the next plan was to do simulations for the Au-Pd and Ag-Au systems,
which would then have been investigated experimentally. But unfortunately the potential files for
those systems were not available in the repository. The only nearby system whose potential file
was available was Au-Pt. So I changed direction to investigate the various cases for this system
which included nanowires made of Au-Pt random binary alloys and coaxial nanowires (Au-core,
Pt-cladding and vice-versa).

So the work which I was looking forward to doing in the time lost due to COVID-19 pandemic
was maybe experimentally trying to work with pure Pt and Au-Pt nanowires for which I have
obtained the results of the simulation.

Conclusions:

Since I first reproduced the results of paper [1](Roy A. et al, 2014). The conclusions would be similar.

- Upon relaxation the initially planar {1 1 1} planes undergo wrinkling to form saddle-like surfaces.
- The dependence of the axial lattice parameter on radius shows a dependence on the thickness of the wire. And also the region near the core remains more or less planar. So it suggests that the wrinkling is a surface effect.
- Unlike the {1 1 1} planes, the {1 0 0} planes do not undergo any wrinkling. This can be suggestive of the cause of wrinkling being anisotropic nature of surface stress as discussed by [1](Roy A. et al, 2014).
- The appearance of islands in the core of Au-Pt coaxial nanowire can be something worth exploring.

Future Work:

- Experimental attempts can be made to verify the results of the simulation for pure Pt and Au-Pt coaxial systems.
- Nanowires of other elements and lattice structures can be studied.

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