Nanoscale Frictional Properties of Nickel with one-dimensional and two-dimensional materials

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Nanoscale Frictional Properties of Nickel with one-dimensional and two-dimensional materials.

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Abstract

When looking at the nanoscale, material interface interactions have been observed to exhibit particularly interesting properties. Our research looks into various combinations of carbyne and graphene atop a nickel block to look into the interface friction properties between them. Both the carbyne and graphene are tested using steered molecular dynamics (SMD) in shearing and peeling directions along the surface of the nickel block. These tests are then analyzed by comparing the magnitude of the acting force versus the displacement of the carbon allotrope sample across the nickel block. It is found that as the width of a carbon allotrope sample is increased the force required to displace the sample in the shearing and peeling directions increases as well. Also, as the width of the carbon allotrope sample increases the sample stiffness tends to increase. The results of the peeling test cases with regard to stiffness are inconclusive.

1. Introduction

1.1 Background

Tribology at the nanoscale has recently become a topic of great interest as it has exposed the potential for interfaces with much lower friction than previously thought possible. Since the discovery of the ultralow friction characteristics of graphite in 2004, efforts have been made to better understand the effects of superlubricity, as well as its limitations. Superlubricity occurs with a geometrical configuration such that there is a misalignment of lattice structures which does not encourage a stable stopping point to enable stick-slip motion. [1] One concern with friction, especially superlubricity, at the nanoscale is whether its observed properties are scalable. It has been found that some materials behave quite differently at the nanoscale than they do at the macroscale. As materials emerge with aspects of superlubricity at the nanoscale the question arises as to the applicability of these material properties at a larger scale. A recent study by Ma et al. was conducted to discover exactly this; to what extent can superlubricity still be observed. [2]

Both empirical and computational efforts have been made to explore the extent of superlubricity of carbon-based materials and their capabilities. One such study by Fuentes-Cabrera et al. first sought to look into the surface stability between graphene and nickel in various orientations including the top-fcc structure used in this study. [3] Carbon based materials such as graphene and other derivative materials of graphite attribute the low friction characteristics to low shear resistance between atomistic layers. [4] Graphene consists of the formation of a single sheet or 2D system of carbon atoms in a honeycomb like structure. This form has been found to be relatively simple and cheap to produce and exhibits superior mechanical properties such as electrical and thermal conductivity, elastic modulus, and intrinsic strength. [5]

In addition to graphene, other allotropes of carbon have been extensively studied to see if they too exhibit interesting or novel properties. These studies are fairly vast, showing that carbon can be synthesized to create many different allotropes including graphene, carbyne, carbon nanotubes, and more recently carbon nanolattices. [6] Carbyne is one such allotrope that consists of single carbon atoms formed into a one-dimensional chain with alternating single and triple bonds. The successful synthesis of a complete, viable carbyne chain has been elusive, however a
recent experiment successfully created a stable chain containing more than 6,000 atoms where the previous benchmark was set at a mere 44 atoms. [7, 8]

1.2 Objectives

It is important to understand the interface properties of carbon materials at the nanoscale as the superlubricity characteristics seen in graphite could potentially extend to these materials. The nature of the study by Dienwiebel et al. worked to show superlubricity between layers of graphite so graphene and carbyne may exhibit potential for superlow friction as well. [1] The goal of this research is to determine the frictional force characteristics of the one-dimensional carbyne and the two-dimensional graphene materials and its width dependence in relation to each other or lack thereof. Each sample will be subject to two different loading scenarios which include a shearing force case and a peeling force case. The peeling and shearing forces will be introduced to the system similar to the work of Ma et al. via tethered springs. [2] Comparisons will be made amongst three different width samples of graphene and one carbyne chain, each of the same length, to draw conclusions.

2. Methods

2.1 Sample Generation

The simulations are carried out on a Ni(111) block which is generated by LAMMPS. [9] LAMMPS is a molecular dynamics simulation code that utilizes parallel computations and can be used to generate and simulate various material types and test cases. The smaller samples of carbon allotropes containing anywhere from 50 to 4000 atoms are created using NanoEngineer-1. [10] NanoEngineer-1 is an extremely useful tool in generating small samples, but would be too exhaustive to use for the generation of a nickel block large enough to serve as a base for these simulations, which contains around 140,000 atoms. The final dimensions for the nickel block are around 500 Å x 18 Å x 150 Å (see Figure 1) surrounded by a vacuum space of 20 Å in every direction. Dimensions for the nickel block were based on the face centered cubic lattice structure in the rotated orientation such that the nickel is identified as Ni(111). The (111) surface is used for its ability to bond well with graphene in various orientations which can be seen in the study by Fuentes-Cabrera et al. [3]. Throughout the simulation, LAMMPS keeps track of the atom id, type, and coordinates amongst other identifiers that can be used for later steps in the simulation.
To begin the process of testing width dependence on frictional characteristics of one-dimensional and two-dimensional materials on a nickel block, the material systems for the computational simulation needed to be created first. Four test samples were created, each one consisting of graphene or carbyne on top of the nickel block. Three different graphene sheets 100 angstroms (Å) in length with a width of 24 Å, 48 Å, and 70Å (see Figure 2) were first created via a user-friendly molecular dynamics studio software called NanoEngineer-1. [10] The widths of each sample were chosen based on the bond length of graphene to ensure an even number of hexagonal rings, which was necessary to maintain stability. This stability in question is considered maintained if the sheet remains flat after initial relaxation in NanoEngineer-1 for ease of deposition onto the nickel block.

The carbyne sample was generated with enough atoms in a chain to be comparable in length to the graphene samples, while taking into account bond length between carbon atoms with single and triple bonds. This system setup can be seen in Figure 3.

Figure 1: Initialized nickel block generated using LAMMPS molecular dynamics simulator such that the top face aligns with the (111) plane.

Figure 2: Top view diagram of the system setup as it were for each of the eight simulations ran. The width (w) of the sample placed on top of the nickel block simulated includes 24 Å, 48 Å, and 70Å width samples as well as a single carbyne chain. The atoms above are singular carbon, hydrogen, and nickel atoms showing relative size and makeup of the samples shown.
Figure 3: Isometric view diagram of the system setup of a single carbyne chain atop the nickel block for simulations. The atoms above are carbon, hydrogen, and nickel atoms showing relative size and makeup of the samples shown.

With the graphene, carbyne, and nickel samples made the next step was to combine them into viable samples to be used for simulation. Using a Python 2.7 script the coordinates from the PDB files generated in NanoEngineer-1 and the coordinates from the LAMMPS dump files were combined into a usable data file to be used back in LAMMPS. The source code used for the combination of the two is available upon request. [11]

2.2 System Setup

Once the samples have been generated, the system is further set up by defining the interactions between atom types. In this system there are three different types of atoms including carbon, hydrogen, and nickel. Since there are three different types of atoms, a hybrid pair style was employed in order to account for the multiple potentials used. Each potential describes the pairwise interactions for atoms with one another which is essential in ensuring the simulation accurately reflects the correct characteristics. For self-interactions of carbon and hydrogen the AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential was used. [12] This potential gives the model reactive capabilities for short ranged interactions between carbon and hydrogen. For self-interactions of nickel the EAM (embedded-atom method) potential is used which describes pairwise interactions for metals and metal alloys. [13] All other interactions between dissimilar atoms or the remaining interactions between nickel and hydrogen are described using the standard 12/6 Lennard-Jones potential. [14]

2.3 Equilibration

All combined equilibration simulations were conducted using LAMMPS, but samples made in NanoEngineer-1 were pre-equilibrated within the software after creation. Time was recorded during the simulation in picoseconds, and all processes were identical for each subsequent simulation including graphene and carbyne. The system is first minimized using the Polak-Ribiere version of the conjugate gradient algorithm which dictates the minimization search direction. The iterations for the minimization stop when specified stopping criteria of energy and force are satisfied. The atoms within the system begin with an initial velocity of zero. After the minimization process, the system is equilibrated through time integration on Nose-Hoover style non-Hamiltonian equations of motion to generate position and velocities from the canonical ensembles. [15-18] The equilibration occurs over 160 ps starting at an initial temperature of 0K and ending around 300K. The bottom three layers of the nickel block are held fixed throughout the simulation and held consistent through the next steps of the simulation process. System accuracy is confirmed through visualization and inspection of relative atom distances compared to known bond length in a visualization tool called OVITO. [19]

2.4 Steered Molecular Dynamics

Once the system is fully equilibrated, steered molecular dynamics (SMD) is used to continue with the simulation. SMD allows the induction of conformational changes in systems to compute the potential mean force along the assumed reaction coordinate based on Jarzynski’s equality. [20] This SMD can be carried out multiple different ways; the chosen method in this
simulation is employing the use of a tether. The tether system setup example can be seen in Figure 4. When using a tether, the simulation attaches a virtual spring to a group of atoms (or a single atom) and pulls the other end of the spring at a constant velocity (or force). For these simulations, a tether was attached to the two front-most, center-most carbon atoms on the graphene samples and to the lead carbon atom of the carbyne chain. When more than one atom is selected to be tethered by SMD the center of mass of the selected group of atoms is used as the tether point. The position of the untethered end of the spring is then placed out in front of the sample to contract in such a way that induces a shear or above the sample in such a way that peeling of the sample occurs. The velocity and spring constant chosen and kept consistent throughout the simulations are 0.001 Å/ps (0.1 m/s) and 230.609 eV/Å² (3695 N/m).

Figure 4: Isometric view of the system setup showing how the steered molecular dynamics (SMD) tether was employed on the samples to induce a shearing or peeling force. The atoms above are singular carbon, hydrogen, and nickel atoms showing relative size and makeup of the samples shown.

2.5 Post-Processing

All systems were visualized in OVITO, but data extraction and analysis was done with Python 2.7 and MATLAB.[21] In LAMMPS, a data set was created to log a continuing pulling force calculation in the x, y, and z directions of the simulation. This file was read into MATLAB along with another similar dump tracking the x, y, and z positions of the tethered atoms to generate a force versus displacement graph for each simulation. The graphs were smoothed using the a built in MATLAB smoothing function and converted to be in units of nanonewtons (nN) for the pulling force.

3. Results and Discussion

3.1 Shearing of one-dimensional and two-dimensional materials

The following simulation results were simulated using SMD for approximately 0.2ns. During this time the forces experienced by the tethered spring reached up to 18nN before slipping occurs. The first simulation was run with a 24Å wide graphene sample. The force versus displacement graph can be seen below in Figure 5.
Figure 5: Tether shearing force versus displacement for the 24Å graphene sample

Figure 5 above shows that the shearing force versus displacement for the shearing system. The maximum force experienced by the spring attached to the graphene sample is about 6 nN before slipping and offloading of the spring occurs.

Figure 6: Tether shearing force versus displacement for the 47Å graphene sample
Figure 6 above shows that the shearing force versus displacement for the shearing system. The maximum force experienced by the spring attached to the graphene sample is about 13nN before slipping and offloading of the spring occurs. This is about double what is experienced by the 24 Å graphene sample.

Figure 7: Tether shearing force versus displacement for the 71Å graphene sample

Figure 7 above shows that the shearing force versus displacement for the shearing system. The maximum force experienced by the spring attached to the graphene sample is about 18nN before slipping and offloading of the spring occurs. This value is approximately three times what is experienced by the 24Å graphene sample.
Figure 8: Tether shearing force versus displacement for the carbyne chain

Figure 8 above shows that the shearing force versus displacement for the shearing system. The maximum force experienced by the spring attached to the graphene sample is about 1nN before slipping and offloading of the spring occurs.

Figure 9: Tether shearing force vs. sample displacement comparison
Figure 9 above shows all shearing simulation cases at once compared against each other. As we can see in this figure when focusing on the displacement between zero and two angstroms, as the width of the sample increases the force required to move the sample initially also increases. Also, the slope of the force versus displacement curve increases.

3.2 Peeling of one-dimensional and two-dimensional materials

Like the shearing simulations, the peeling simulations were conducted using SMD for approximately 0.2ns. During this time, the forces experienced by the tethered spring were progressively recorded as the sample was pulled up and away from the nickel block. The first simulation was carried out with a 24Å wide graphene sample. The force versus displacement graph can be seen below in figure 5.

![Figure 10: Tether peeling force versus 24Å graphene sample displacement](image)

Figure 10 above shows that the peeling force versus displacement for the peeling system. The maximum force experienced by the spring attached to the graphene sample is about 23nN before offloading of the spring occurs. This is the highest recorded response for all peeling cases.
Figure 11: Tether peeling force versus 47Å graphene sample displacement

Figure 11 above shows that the peeling force versus displacement for the peeling system. The maximum force experienced by the spring attached to the graphene sample is about 10 nN before offloading of the spring occurs.

Figure 12: Tether peeling force versus 71Å graphene sample displacement

Figure 12 above shows that the peeling force versus displacement for the peeling system. The maximum force experienced by the spring attached to the graphene sample is about 17 nN before offloading of the spring occurs.
Figure 13: Tether pulling force versus carbyne chain sample displacement

Figure 13 above shows that the peeling force versus displacement for the peeling system. The maximum force experienced by the spring attached to the graphene sample is about 2.75nN before offloading of the spring occurs.

Figure 14: Peeling force versus displacement comparison for all cases

3.3 Stiffness

Once all of the force versus displacement data had been collected and studied for both the shearing and peeling test cases, interaction stiffness could be extrapolated from the comparison graphs. Figure 15 shows the shearing case comparison in consideration of the force build up just
until the first slip occurred only. This tended to be within the first two angstroms of displacement, which can be seen in the figures below. Figure 16 shows the peeling case comparison in consideration of the force build up just until the tethered carbon atoms were completely peeled off of the nickel block. The difference in generating the peeling stiffness plot is that the comparison graph was zoomed in to correspond to exactly one angstrom of displacement due to non-uniformity in the peeling cases. By inspection the data was then subject to a linear curve fit, which led to the overall slope of each test case before slip, occurred. These slopes were then compared against the width of the sample and can be seen in Figure 17.

![Figure 15: Shearing force versus sample displacement graph before slip occurs](image1)

![Figure 16: Peeling force versus displacement up to 1Å of displacement](image2)
Figure 17: Data plot of test cast stiffness (a) for the shearing case versus width; (b) for the peeling case versus width

3.4 Discussion

The shearing simulations behaved as expected as the width of the sample is increased. The large build up of shearing force before offloading and slippage occur is most likely due to the interface between the nickel surface and the graphene sheet. Graphene lies on nickel (111) surface such that the individual atoms come to rest in the space between the nickel atoms. When the graphene is forced to move (i.e. shearing force induced) there is quite a bit of opposition to the movement as the carbon atoms are in a stable position. This justifies what can be seen in Figure 9 as the sample width increases the force required to move the sample also increases. As the width of the sample increases, so does the amount of atoms being displaced to the next stable position. Hence, the increased force required for slip motion, which can be seen in Figure 18 below.

Figure 18: Plot of the maximum shearing force exerted versus the sample width
In general, the peeling simulations behaved similar to the shearing simulations: as the sample width increased the force required to lift the sample of the nickel block also increased. However the smallest graphene sample case proved a notable exception. The smallest graphene sheet recorded a much larger magnitude of peeling force than even that of the largest sample simulated. By observation of these simulations using OVITO it seems that the hydrogen atoms on the perimeter of the graphene sheet are the determining factor of the force required to peel the sample off the nickel block, as shown in Figures 19a-e. It can be observed in Figure 14 that each of the curves has smaller peaks and troughs in them as they displace. These smaller spikes are shown to correspond to the separation of the lead hydrogen atoms separating from the nickel block as shown in Figure 19a and 19b. When referencing the lead hydrogen atoms it refers to the perimeter hydrogen atoms along the same side of the graphene sheet in which the spring is attached to. Here, all of the lead hydrogen atoms eventually separate which then causes the sides of the sheet to pull together to accommodate the continued vertical pull of the spring also shown in Figure 19c. It is at this point the force jumps up significantly because there are significantly more hydrogen atoms on these sides resisting the pull of the spring as well as the pull of the nickel atoms, which can be seen in Figures 19d and 19e. The sharp drop in Figure 10 corresponds to the breakaway from the nickel block shown in Figure 19f. This behavior is not observed in any of the peeling cases for larger graphene sheets, however, if the simulations of the larger sheets of graphene were allowed to run longer a similar effect may be seen after the lead hydrogen atoms are all separated from the nickel block.

![Figure 19: Time lapse images to show stages of peel](image-url)
pull in; (c) graphene lead hydrogen atoms come together; (d) graphene sheet perimeter hydrogen atoms fully closed and pulling up on nickel block just before release; (e) front view of same time image as (d); (f) graphene sheet release from nickel block and restoration of nickel atoms to original position

Superlubricity for the graphene sheets in accordance with a nickel surface was not immediately apparent in either the peeling test cases or the shearing. The interactions between graphene sheet and nickel observed in these simulations more closely resembles that of a stick-slip system for reasons discussed earlier. However, carbyne does exhibit an extremely low static frictional force and stiffness under the test conditions with nickel. Future work could expand upon the reasoning behind the lack of superlubricity as well as identify more trends in accordance to width.

4. Conclusions

We use SMD simulations to study the force displacement behavior of one-dimensional and two-dimensional materials under shearing and peeling loading conditions. The conclusions of our study are listed below.

1. As the width of graphene increases:
   • The shearing force required to move graphene increases
   • The peeling force required to peel graphene increases
   • The slope of the shearing force vs. displacement (stiffness) increases
2. The hydrogen atoms surrounding the graphene sheets play a role in keeping the material attached to the Ni surface when subject to a peeling force
3. The force needed to shear and peel carbyne is smaller than that of graphene
4. The stiffness of carbyne is lower than that of graphene in both peeling and shearing cases

We were not able to establish the idea of superlubricity for the graphene sheets in accordance with a nickel surface. However, carbyne does exhibit an extremely low static frictional force and stiffness under similar conditions. Future work could expand upon the reasoning behind the lack of superlubricity as well as identify more trends in accordance to width.

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6. References


