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Molecular Dynamics of Tribological Processes at Interaction of Cu and Au Nanoparticles with Graphene Sheet

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This work has a goal to study the behavior of metal nanoparticles on the graphene layer. After processing obtained data we have studied dependence of friction force on contact area of nanoparticle, in all cases it is linear. This conclusion is confirmed by real experiment results. Dependence of friction force on lateral coordinate of center of mass of nanoparticle has a sawtooth form.

Keywords: Molecular Dynamics, Graphene, Nanotribology, Metal Nanoparticles.

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1. INTRODUCTION

There are some well known experiment techniques in this area of science. First one is a friction force microscope and the second one - surface force apparatus. These techniques have several disadvantages: friction force microscope can not measure the actual contact area of particles it moves, and both methods are not able to take measurements of contact area between seven hundred and several thousand square nanometers [1].

The first step towards theoretical description of friction of metal nanoparticles adsorbed on a graphite surface is work [2] where the shear of silver and nickel nanoparticles on graphene surface was studied. Authors used classical molecular dynamics method. The main conclusions of [2] are: the value and shape of the dependence of friction force on the lateral component of nanoparticle's center of mass coordinate depends on the type of metal. Linear dependence of the average friction force value on contact area for Ag nanoparticle was obtained. The sawtooth shape dependence of the friction force on the lateral component of the center of mass coordinate for Ni nanoparticle was found.

This work is a next step of studying metal nanoparticles adsorbed on the graphene layer.

Main goal is to make the same simulations using other metals, such as gold and copper, and see if there is a connection between same dependencies but different materials. In this way we could compare results and make conclusions about correctness of previous calculations, how different materials influence the friction force and parameters of systems.

There is a hypothesis about dependence of friction force on short-range order of atoms [2]. If the distance between nearest neighbor metal atoms is close to the graphite constant lattice, local commensurability can take place. As a result, it can lead to a sawtooth dependence form for friction force. We can observe such behavior on the example of nickel nanoparticles.

We used Cu and Au nanoparticles where the distance between nearest neighbor atoms are 0.2556 nm and 0.2885 nm, respectively. Another factor that can influence friction force is a shear force value - F_S. It is applied to all atoms located on the left side to the center of mass of nanoparticle to move it on the surface of graphene. We simulated a friction process of Au nanoparticle with different values of F_S to find out if it is a case and F_S actually effects on friction force.

Many papers describing experiments with nanoparticles can be found [1-5]. Unfortunately most of them had no purpose to study the tribological properties of nanoparticles in detail.

Some experiments [1, 5, 6] studying the tribological properties of antimony nanoparticles formed on highly oriented pyrolytic graphite showed interesting results. Linear dependence of friction force on contact area of nanoparticle was found. But the most interesting is an unexpected property of nanoparticle that was shown: there is a sensible gap between the value of shear force applied to move nanoparticle with contact area less than 10^4 nm^2 and nanoparticle with bigger contact area.

In the last work [6] authors made an unusual assumption. They proposed a theory called "frictional dualism". Main idea is that some particles with contact area starting from 10^4 nm^2 and further demonstrates relatively low friction, while other particles with the same contact area show finite values of friction force. The full explanation of this effect was not given.

All that was said above gives us feeling of incompleteness and encourage for further research. Investigation of tribological properties of Au and Cu nanoparticles adsorbed on the graphene layer is one of the steps leading to fundamental understanding of the phenomena that occur at extremely small contact area.

2. MODEL

We have used molecular dynamics method for modeling the process of friction in this work (see [2] and the literature cited therein). Au and Cu nanoparticles were objects of study. Sizes of particles are between 10 and 30 thousands atoms. Vacuum conditions were maintained. Atoms on the edges of graphene layer were fixed (Fig. 1). Periodic boundary conditions were used.

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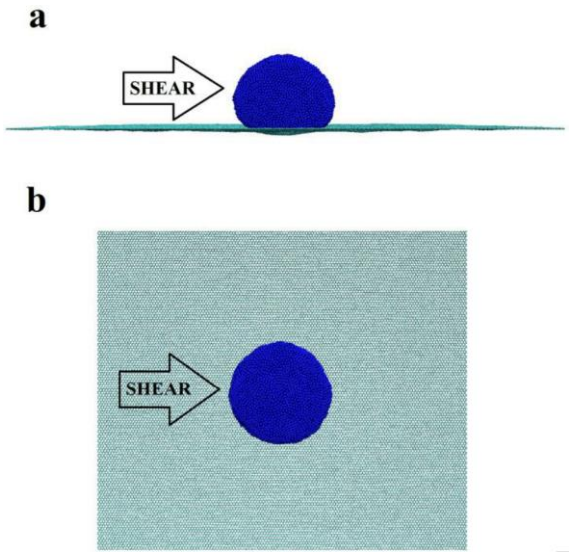

Fig. 1 – Snapshots of Cu nanoparticle including 25000 atoms from different sides (left (a), top (b)).

Embedded atom method was used to simulate interaction between metal atoms [3]:

$$V_{eam} = \frac{1}{2}\sum_{i,j,i\neq j} \Phi_{ij}\ r_{ij}\ + \sum_i F\ \rho_i\ , \qquad (1.1)$$

where Φ_{ij} is the function of pair energy, r_{ij} is the nearest-neighbor bond length between the atoms i-j, $F(\rho_i)$ is the embedded energy function, and ρ_i is the electron density.

Harmonic potential was used for modeling carbon atoms behavior [4]:

$$V_C = \frac{1}{2}\sum_{i-j} \mu_r (r_{ij} - r_0)^2 + \frac{1}{2}\sum_{i-j-k} \mu_\theta r_0^2\ \theta_{ijk} - \theta_0\ ^2 + \frac{1}{2}\sum_{i-\ j,k,l} \mu_p \left(\delta z_i - \frac{\delta z_j + \delta z_k + \delta z_l}{3} \right)^2 , \qquad (1.2)$$

where the indices of the summation i-j, i-j-k, and i-(j, k, l) represent the nearest-neighbor bonds, bond pairs, and bond triples, respectively. The first and second terms correspond to the bond stretching and the bond bending energy, respectively. θ_{ijk} denotes the angle between the bond i-j and the bond j-k within the same honeycomb net plane. The third term is the bending energy of the local planar structure due to the normal displacement of the i-th atom from the coplanar position with respect to the three neighboring atoms j, k, and l; δz_i denotes the normal displacement of the i-th atom from the initial position.

Interaction between metal and carbon atoms is based on Lennard-Jones potential [2, 4]:

$$V_{LJ} = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], & r < r_c, \\ 0, & r \geq r_c, \end{cases} \qquad (1.3)$$

where r is the distance between two atoms, r_c is the cutoff distance, ε and σ are constant parameters.

2.1 Computer Modeling

The code of program is written using NVIDIA CUDA library, which allowed us to use graphics processing unit (GPU) and significantly increased the speed of computations. Neighbor list algorithm [7] and special atom placement algorithm were used. Verle method was used to integrate equations of motion with a time step 0.2 fs.

2.2 The Process of Modeling

The process of modeling itself can be divided into two parts.

1. Obtaining a nanoparticle.
2. Shear of a nanoparticle.

In the first part the layer of metal atoms is placed onto the graphene sheet. Interaction energy between atoms of metal is stronger than between metal and carbon atoms. The metal layer starts to fold into nanoparticle. At this time energy is released, the temperature of system is growing. At some point we use Berendsen thermostat to cool nanoparticle and graphene layer.

The second part is the most informative one. After nanoparticle is formed, it is sheared. Shear force is applied to all atoms located on the left side to center of mass of nanoparticle. The force increasingly grows until the velocity of nanoparticle is 3.55 m/s. After that shear force remains constant, nanoparticle is moving with constant acceleration.

During the experiment different system parameters are measured: potential energy, temperature, size of nanoparticle, friction and shear forces, velocity of center of mass of nanoparticle.

3. RESULTS

We can see typical time dependencies of Cu nanoparticle parameters in Fig. 2.

It is easy to notice in the beginning of shear that V_X and X_{CM} are linearly and quadratically increasing with time. It indicates the movement with constant acceleration under the action of the shear force F_S. However, the friction force F_f is not constant and has a sawtooth form (Figs. 3 and 4), which shows that process of nanoparticle movement has a stick-slip character [8].

We can observe a different signs of values of friction force F_f which means that friction force changes the direction during the process of shear.

The dependence of friction force on the contact area of nanoparticle, as was mentioned in previous experiments [1, 6, 9], is linear. Nevertheless we used two different shear forces to ensure that the form of dependence is linear and the shear force does not influence it. To make that possible we used two different values of shear force increasing step: 0.0001 pN and 0.00001 pN.

Fig. 2 – Time dependencies of temperature T, lateral coordinates of center of mass X_{CM}, velocity V_X, shear force F_S, friction force F_f and lateral sizes L_X, L_Y for Cu nanoparticle which consists of 19000 atoms.

As is shown in Figs. 5 and Fig. 6, the dependence of friction force on contact area, as well as the dependence of shear stress on contact area is linear. Also it is shown that the form of dependence does not change with shear force. It allows us to confirm the results of previous experiments about linearity of dependencies.

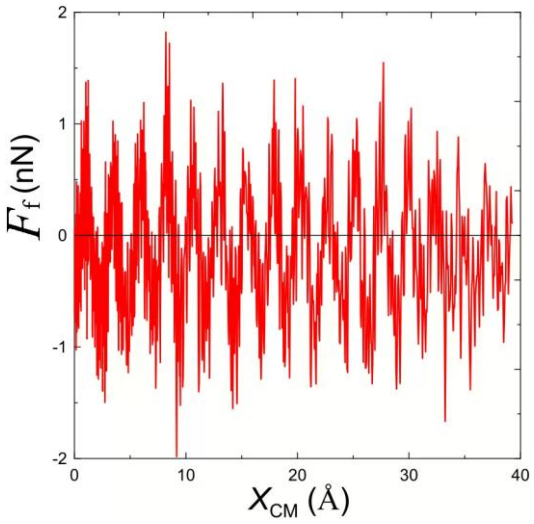

Fig. 3 – Dependence of friction force F_f on lateral component of center of mass coordinate for Au nanoparticle consisted of 10000 atoms

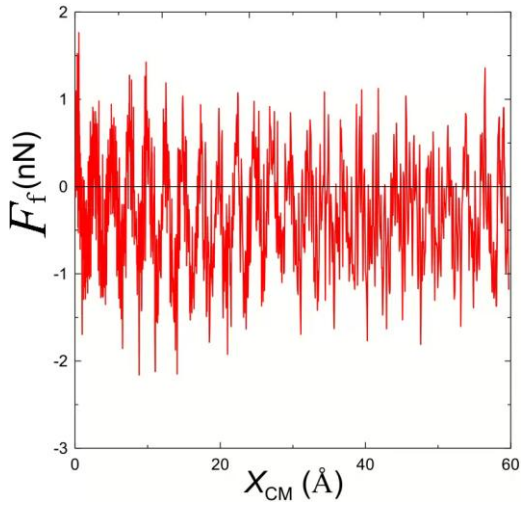

Fig. 4 – Dependence of friction force F_f on lateral component of center of mass coordinate for Au nanoparticle consisted of 25000 atoms

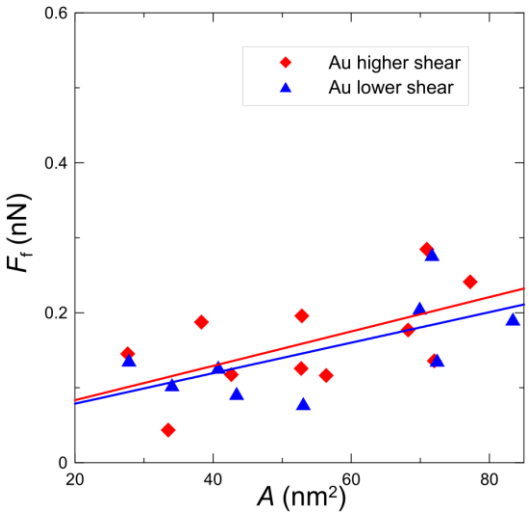

Fig. 5 – Dependence of friction force F_f on contact area for different shear forces

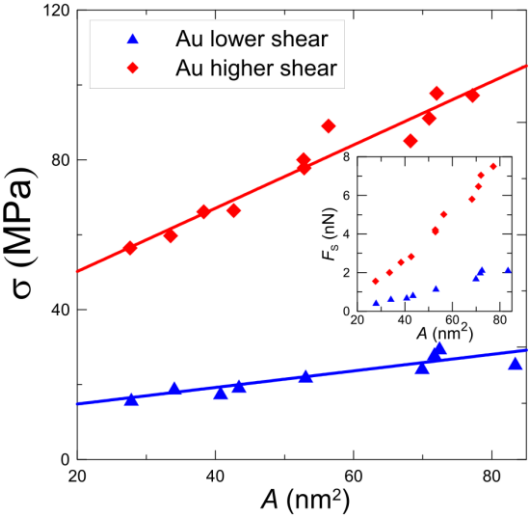

Fig. 6 – Dependence of shear stress on contact area for different shear forces

Speaking about the impact of size of contact area is usually believed that the adhesive interaction is proportional to contact area [2]. However, in our calculations Cu nanoparticles which have less contact area than the Au nanoparticles, show greater values of friction force. This fact can be connected to quantitative differences in the atomic structure of materials, which leads to different surface energies of nanoparticles. Smaller distance between the nearest neighbors in Cu nanoparticle, as described above, may lead to structure where number of atoms which will be located on one surface area is bigger than the number of Au atoms located on the same area. Obviously, it brings us to a higher surface energy and a stronger adhesion.

In addition, metal atoms located higher than the bottom layer can give a significant contribution to the adhesion to these relatively small nanoparticles. It can happen because they are located in action range of the Lennard-Jones potential. Thus, considering the disordered structure of nanoparticles, and the deformation of graphene, we can conclude that the metal atoms, located further than the surface layer, can give a significant contribution to the adhesion. For Cu atoms such contribution should be several times larger than for Au atoms. So the friction may depend not only on the contact area of nanoparticle, but also on characteristics of nanoparticle itself, and particularly on structure of the nanoparticle.

4. CONCLUSIONS

After processing obtained data we have studied the dependence of friction force on contact area of Cu and Au nanoparticles, in all cases it is linear. The dependence of shear stress on contact area is linear also. The form of these dependencies does not change with shear force. This conclusion is confirmed by real experiment results [1, 6, 9]. Dependence of friction force on lateral coordinate of nanoparticle center of mass has a sawtooth form for both types of atoms.

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REFERENCES

1. E. Gnecco, E. Meyer, *Fundamentals of friction and wear on the nanoscale* (Berlin: Springer-Verlag: 1998).
2. A.V. Khomenko, N.V. Prodanov, *J. Phys. Chem.* **114**, 19958 (2010).
3. X.W. Zhou, H. Wadley, R. Johnson, D. Larson, N. Tabat, A. Cerezo, A. Petford-Long, G. Smith, P. Clifton, R. Martens, T. Kelly, *Acta Mater.* **49**, 4005 (2001).
4. N. Sasaki, K. Kobayashi, M. Tsukada, *Phys. Rev. B* **54**, 2138 (1996).
5. M. Sitti, M. Hashimoto, *IEEE/ASME Trans. Mechatron.* **5**, 199 (2000).
6. D. Dietzel, C. Ritter, T. Mönninghoff, H. Fuchs, A. Schirmeisen, U.D. Schwarz, *Phys. Rev. Lett.* **101**, 125505 (2008).
7. J.A. Anderson, C.D. Lorenz, A. Travesset, *J. Comp. Phys.* **227**, 5342 (2008).
8. A.V. Khomenko, N.V. Prodanov, *Condens. Matt. Phys.* **11**, 615 (2008).
9. C. Ritter, M. Heyde, M. Stegemann, K. Rademann, U.D. Schwarz, *Phys. Rev. B* **71**, 085405 (2005).