Numerical study of friction of flake and adsorbed monolayer on atomically clean substrate

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Abstract. Frictional behaviors of flake and adsorbed monolayer on substrate can be observed by Frictional force microscope and Quartz crystal microbalance experiments and are typical problems in nano-friction. Computer simulations had been played important roles in understanding those behaviors, but in most of them the driving direction coincides with one of the crystal axes of the substrate. Here we report our numerical results of direction dependence of friction of flake and adsorbed monolayer. We found a new kind of dynamical phase transition in which flake and adsorbed monolayer change their structure relative to the substrate and make incommensurate structure to reduce kinetic frictional force after certain transition time. When the driving velocity is decreased the transition time tends to diverge at certain critical velocity for the flake. For the adsorbed monolayer the transition time tends to diverge at certain critical magnitudes of the external force or the interaction strength between adsorbates when they are decreased.

1. Introduction
Friction is one of the most important unresolved problem in science[1]. In macroscopic systems the famous Amontons-Coulomb’s law holds well. The mechanism of the law is, however, not established still now[2, 3, 4]. This is because that friction is affected by many factors, such as materials, surface conditions such as roughness, oxidation and contamination, and so on, all of which had been hard to control. Another reason is that the experimental method of friction had been very limited. These conditions of research of friction is now changing. Surface treatment technique, ultra high vacuum technique and many new experimental technique are progressing so much. Here we study one of the most simple case of friction, friction on atomically clean substrate. Frictional force microscope (FFM)[5, 6] and Quartz crystal microbalance (QCM) technique[7, 8, 9] enable to investigate friction of such systems experimentally and many interesting observations are reported. Numerical experiments also had been playing an important role in the study of friction of such systems. The pioneering works by Persson made clear that the adsorbed layer on atomically clean substrate shows structural phase transition by changing the magnitude of the driving force[10].

Here we extend the works by Persson paying special attention to the driving direction dependence. Hirano et.al. observed that the frictional force depends strongly on the driving direction or relative direction of crystal axes of two surfaces[11]. In the case that the ratio of two lattice spacings of two surfaces along the driving direction is rational, that is called commensurare case, the system shows large frictional force. On the other hand in the case that
this ratio is irrational, that is called incommensurate case, the frictional force becomes small because of the cancelation of the change of interatomic potential energy between two surfaces against translational motion. Theoretically it was also shown that finite static frictional force appears even in the incommensurate case for interatomic potential between two surfaces larger than a certain critical strength due to a kind of surface reconstruction[12, 13].

We investigate here two systems under various conditions. One is the atomic flake and 2nd adsorbed monolayer. It is shown that the systems changes their structure in order to make their motion easier, in other words, in order to make kinetic frictional force smaller after a certain transition time. The transition time tends to diverge at a certain critical velocity when the driving velocity is decreased for the flake. For the adsorbed monolayer the transition time tends to diverge at certain critical magnitudes of the external force or the interaction strength between adsorbates when they are decreased.

2. Flakes on atomically clean substrate
Here we put flake on an atomically clean substrate, both of which have same lattice structure and same lattice constant. In the ground state configuration the crystal axes of 2 surfaces coincide with each other and the system is commensurate. How the flake moves when we drive the center of the flake? One idea is that the system keeps commensurate structure in order to gain the interatomic potential energy between 2 surfaces. Another is that the flake rotates by itself to make incommensurate structure and reduce the frictional force. In order to clarify this problem, we investigate the dynamics of the flake numerically.

The model is as follows. The substrate is assumed to be rigid and makes periodic potential, which is sinusoidal along x and y direction, then the substrate has square lattice symmetry. The atoms in the flake moves in 2 dimensional space, interact each other via linear spring and make also square lattice of which lattice constant coincides with that of the substrate. The center of the flake is driven by linear spring, of which another end is pulled to a certain driving direction with a constant velocity. The equation of motion of i-th atom in the flake is expressed as,

\[ m \frac{d^2 \vec{r}_i}{dt^2} = -\eta m \frac{d\vec{r}_i}{dt} - \frac{\partial U(\vec{r}_i)}{\partial \vec{r}_i} - \frac{\partial V(\{\vec{r}'_j\})}{\partial \vec{r}_i} + \vec{F}_{\text{ext},i}. \]  

Here m is the mass of an atom in the flake, \( \vec{r}_i = (x_i, y_i) \) 2-dimensional position vector of i-th atom, \( \eta \) dissipation coefficient, \( U(\vec{r}_i) = U_0 \{2 - \cos(k_x x_i) - \cos(k_y y_i)\} \) the substrate potential, where \( k_a = 2\pi/a \) and a is the lattice constant, \( V(\{\vec{r}'_j\}) = \sum_{(i,j)} (k/2)|\vec{r}_i - \vec{r}_j - \vec{a}|^2 \) the interatomic potential in the flake via the linear spring, where the summation \((i,j)\) is taken for the nearest neighbor pairs, \( F_{\text{ext},i} = \delta_{i,0} k_f (v t \vec{e}_a - \vec{r}_0) \) the external driving force, where \( \delta_{i,0} = 1 \) for the atom at the center of the flake and vanishes for other atoms, v driving velocity and \( \vec{e}_a \) is the unit vector of the driving direction. Periodic boundary condition is adopted.

Fig.1 shows a time dependence of velocities of the flake along x and y directions, \( V_x \) and \( V_y \). The number of atoms in the flake is 49. The initial configuration is the ground state, in which the crystal axes of the flake and the substrate coincides with each other as shown in Fig.2. The angle between the driving direction and the x axis is 30°. At first the flake shows stick-slip motion only along x direction and then does along x and y directions keeping the commensurate structure. The stuck state is almost equivalent to the initial configuration and the system gains the substrate potential energy. After certain time the flake rotates and makes incommensurate structure with the substrate as shown in Fig.3. The time dependence of the frictional force is shown in Fig.4 for various driving directions. Here the frictional force is defined as the driving direction component of the pulling spring force, because it relates to the energy dissipation. The frictional force decreases after certain time. We define "transition time" as the time the frictional force decreases and becomes stationary after the application of external drive.
**Figure 1.** Time dependence of velocities of the flake along $x$ and $y$ directions, $V_x$ and $V_y$. The angle between the driving direction and $x$ axis is $30^\circ$. The number of atoms in the flake is 49.

![Initial configuration of the flake. Two crystal axes of the flake and the substrate coincide with each other.](image1)

**Figure 2.** Initial configuration of the flake. Two crystal axes of the flake and the substrate coincide with each other.

![Final configuration of the flake. The system becomes incommensurate.](image2)

**Figure 3.** Final configuration of the flake. The system becomes incommensurate.

**Figure 4.** Time dependence of the frictional force for various driving directions. The number of atoms in the flake is 49 and the driving velocity is 1.2. After certain time the system becomes incommensurate and then the frictional force becomes small.

![Time dependence of the frictional force for various driving directions.](image3)
transition time depends on the driving velocity and the system size. Fig. 5 shows the transition time as a function of driving velocity for the systems with number of atoms 9, 25 and 49. When the driving velocity is decreased, the transition time tends to diverge toward a certain critical velocity. Below the critical velocity the system keeps the commensurate structure in order to gain the substrate potential energy. Above the critical velocity, however, the system favors incommensurate structure in order to reduce the kinetic frictional force. The size dependence is not so strong. This behavior may relate to the slip diffusion of an adsorbed gold nanocluster discussed in ref. [14].

3. Adsorbed monolayer on atomically clean substrate

In the model examined in previous section atoms in the flake interact each other via linear spring. The model is so simple that we can observe essential behavior and mechanism rather easily. The flake in the model, however, never breaks and the model is idealized in some sense. In this section we investigate the behavior of the adsorbed monolayer on atomically clean substrate based on more realistic model. In the model atoms in the adsorbed monolayer interact with each other via the Lennard-Jones potential,

$$\nu(\vec{r}) = \epsilon \left[ (r_0/r)^{12} - 2(r_0/r)^6 \right].$$

(2)

The equation of motion of the $i$-th adsorbed atom is expressed as,

$$m \frac{d^2\vec{r}_i}{dt^2} = -\eta m \frac{d\vec{r}_i}{dt} - \frac{\partial U(\vec{r}_i)}{\partial \vec{r}_i} - \frac{\partial V(\{\vec{r}_i\})}{\partial \vec{r}_i} + \vec{f}_i(t) + \vec{F}_{\text{ext}}.$$ 

(3)

The equation of motion is same with that in the previous section except $V(\{\vec{r}_i\})$, $\vec{f}_i(t)$ and $\vec{F}_{\text{ext}}$. In eq.3 $V(\{\vec{r}_i\})$ is the sum of the Lennard-Jones potential eq.2 over all pairs of adsorbed atoms, $\vec{f}_i(t)$ is the thermal fluctuating force which obeys the fluctuation-dissipation theorem $\left< f_i^\alpha(t) f_j^\beta(t') \right> = 2\eta m k_B T \delta_{i,j} \delta_{\alpha,\beta}$, and the external driving force $\vec{F}_{\text{ext}}$ is applied to all adsorbed atoms directly. Hereafter we measure the spatial coordinate by $a/2\pi$ and time by

Figure 5. The transition time as a function of driving velocity for the systems with number of atoms 9, 25 and 49. The angle between the driving direction and the $x$ axis is $15^\circ$. When the driving velocity is decreased, the transition time tends to diverge toward a certain critical velocity.
\[ \tau = \frac{a}{2\pi} \sqrt{m/U_0}, \] and introduce \( \vec{r}_i = \frac{(2\pi/a)}{\vec{r}_i}, \tilde{t} = t/\tau \) and \( \tilde{\eta} = \eta\tau \). The obtained dimensionless equation of motion is expressed as,

\[ \frac{d^2 \vec{r}_i}{d\tilde{t}^2} = -\tilde{\eta} \frac{d\vec{r}_i}{d\tilde{t}} - \frac{\partial \tilde{U}(\tilde{r}_i)}{\partial \tilde{r}_i} - \frac{\partial \tilde{V}(\{\tilde{r}_i\})}{\partial \tilde{r}_i} + \tilde{f}_i(t) + \tilde{F}_{\text{ext}}, \]

(4)

where \( \tilde{U}(\tilde{r}_i) = 2 - \cos(\tilde{x}_i) - \cos(\tilde{y}_i) \) and \( \tilde{V}(\{\tilde{r}_i\}) = \sum_{(i,j)} \tilde{v}(\tilde{r}_i - \tilde{r}_j), \tilde{v}(\tilde{r}) = (\epsilon/U_0) \left[(\tilde{r}_0/\tilde{r})^{12} - 2(\tilde{r}_0/\tilde{r})^6 \right] \). We fix the value of \( r_0/a = 1.56 \).

We show the ground state configuration of the system for the case of strong substrate potential \( \epsilon/U_0 = 0.5 \) in fig.6, which is the initial configuration of our simulation. The number of adsorbed atoms is 450 and that in the substrate is 900. Hence the coverage \( \theta = 0.5 \). Periodic boundary condition is adopted. The left panel shows the whole system and the right one does the magnification of the part of the whole system. The open red circles show substrate atoms and blue crosses do adsorbed atoms, which sit just between the substrate atoms. The structure factor of the ground state configuration is shown in fig.7. It is to be noted that the lattice

**Figure 6.** The ground state configuration for the case of strong substrate potential \( \epsilon/U_0 = 0.5 \), which is the initial state configuration of our simulation shown in fig.8.

**Figure 7.** The structure factor of the initial configuration.

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Figure 8. $V_x$, $V_y$ and the direction of motion for the case of $\epsilon/U_0 = 0.5$. The angle between the driving direction and the $x$ axis is $15^\circ$ and $\tilde{F}_{\text{ext}} = 1.2$.

By applying external force to all the adsorbed atoms directly in the ground state configuration we investigate their dynamics. Fig.8 shows the $x$ and $y$ components of the velocity of adsorbed monolayer, $V_x$ and $V_y$, and the direction of motion in the case of strong substrate potential $\epsilon/U_0 = 0.5$ at 0°K. The angle between the driving direction and the $x$ axis is $15^\circ$ and $\tilde{F}_{\text{ext}} = 1.2$. Three time regimes appear. In the 1st time regime the adsorbed monolayer shows stick-slip motion only along $x$-direction. The configuration of adsorbed monolayer is same with that of the initial one. The whole atoms repeat stick-slip motion coherently. In the 2nd time regime $y$ component of velocity appears but oscillates around 0. In this regime sticking and slipping atoms coexist, that is, the motion becomes incoherent. As a result the amplitude of oscillation of $V_x$ decreases compared to that in the 1st time regime. The instantaneous structure factor is shown in fig.9. The 4-fold rotational symmetry survives, but new peaks appear compared to fig.7. Finally the system reaches to the 3rd time regime, where the direction of motion approaches to the driving direction and the absolute value of the velocity increases. The instantaneous structure factor in this time regime is shown in fig.10. Clear 6-fold rotational symmetry appears, which indicates that the system becomes incommensurate. As in the case of flake motion discussed in the previous section we can define the transition time also for the present system, which is the time between the instance of the application of the external force and the instance that the system changes its structure to incommensurate one. Fig.11 shows the transition time as a function $\epsilon/U_0$. The angle between the driving direction and the $x$ axis is $15^\circ$ and $\tilde{F}_{\text{ext}} = 1.2$. In the range $\epsilon/U_0 > 2.3$ the ground state configuration is incommensurate, hence the transition time is not defined. Interesting point is that the transition time tends to diverge at $\epsilon/U_0 \simeq 0.4$ from above. In the range $\epsilon/U_0 < 0.4$ the system keeps commensurate structure in order to gain the substrate potential energy.

The transition time also depends on the strength of the external force $\tilde{F}_{\text{ext}}$. Fig.12 shows the
transition time as a function $\tilde{F}_{\text{ext}}$. The angle between the driving direction and the $x$ axis is $15^\circ$ and $\epsilon/U_0 = 0.5$. The maximum static frictional force is about 1.0. The transition time tends to diverge at the maximum static frictional force.

4. Summary
We reported results of numerical experiments of flake and adsorbed monolayer on atomically clean substrate. Flake on the atomically clean substrate rotates to make incommensurate structure and reduce the frictional force after certain transition time above a critical velocity. Adsorbed monolayer also makes incommensurate structure and velocity larger and moves almost along driving direction after certain transition time for the weaker substrate potential than a critical strength. For the substrate potential stronger than a critical value, it keeps commensurate structure and moves along crystal axis. This change of structure as a function of the strength of substrate potential is similar to that discussed in refs.[12, 13] in some aspect, but has essential difference because it accompanies the change of rotational symmetry. The transition time tends to diverge at the maximum static frictional force and critical strength of the substrate potential. Adsorbed atomic island also shows similar behaviors.
Figure 11. The transition time as a function $\epsilon/U_0$.

Figure 12. The transition time as a function $\tilde{F}_{\text{ext}}$.

Therefore we can say that there is a kind of phase transition. Below a certain critical velocity for flake or above a certain critical strength of substrate potential for adsorbed systems, systems keep commensurate structure and move along the crystal axis of the substrate. In opposite side of critical points, systems spontaneously select configurations with smaller frictional force or larger velocity. Such a kind of phase transition is expected to be observed by QCM or FFM technique.

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