Chaotic Behavior Appearing in Dynamic Motions of Nanoscale Particles

M Ishikawa1, R Harada2, M Kato1, N Sasaki3 and K Miura1,2

1Innovation Plaza Tokai, Japan Science and Technology Agency, 23-1 Ahara-cho, Minami-ku, Nagoya 457-0063, Japan

2Department of Physics, Aichi University of Education, Hirosawa 1, Igaya-cho, Kariya 448-8542, Japan

3Department of Applied Physics, Faculty of Science and Engineering, Seikei University, 3-3-1 Kichijoji Kitamachi, Musashino-shi, Tokyo 180-8633, Japan

e-mail: kmiura@auecc.aichi-edu.ac.jp

Abstract. The case of one-directional motion, under which graphite and mica flakes are driven on an octamethylcyclotetrasiloxane (OMCTS) liquid surface, is presented. The dynamical forces needed to move these bodies increase linearly with the logarithm of scanning velocity, which are typical energy dissipation process. A transition from quasi-periodic to chaotic motions occurs in the dynamics of a graphite flake when its velocity is increased. The dynamics of graphite flakes pulled by the nanotip on an OMCTS liquid surface can be treated as that of a nanobody on a liquid. On the other hand, there do not appear chaotic motions in the dynamics of a mica flake because the contact area between a mica flake and an OMCTS liquid surface is larger than that between a graphite flake and an OMCTS liquid surface.

1. Introduction

At present, an understanding of the dynamics of a small body in a liquid is of great importance because it will enable the application for lubrication, molecular electronics and microfluid. This leads to the problem that is presently facing nanoelectrical mechanical systems (NEMS) and microelectrical mechanical systems (MEMS) because it becomes difficult to make the nanometer-scale body to move on a surface. In addition, when the size of body on the liquid is reduced to the nano- and micrometers, this becomes to be the problem of a small body in one direction under Brownian motion. However, there has little been study on this topic, because there are no applicable methods for investigating the dynamics of a small body in a liquid. We present the case of one-directional motion, under which a flake on a liquid surface is driven by a nanotip. This method has been applied for the studies on atomic friction of solid on solid [(Miura and Kamiya 2002), (Miura et al. 2003), (Miura et al. 2004)]. Here, we report the results of the one-directional motion of a flake on a liquid examined by this method. The force needed to drive a flake on a liquid surface is investigated as functions of loading force and scanning velocity. Friction forces and energy dissipation, which appears in the dynamics of a flake propulsive on a liquid, are discussed.
2. Experimental

Octamethylcyclotetrasiloxane (OMCTS), a molecule which consists of forty atoms in an ellipsoidal shape on average, as shown at the upper part of Figure 1, was used as the liquid material. Graphite and mica substrates were prepared by cleaving highly oriented pyrolytic graphite (HOPG) and muscovite mica blocks, respectively. An OMCTS droplet was dropped onto each of the graphite and mica substrates. Cleaved graphite and mica flakes with an area of 1 mm square and a thickness of several...
micrometers were placed on the OMCTS droplet, and then an atomic force microscope tip was brought into contact with the cleaved graphite and mica flakes. At this time, using a CCD camera, we always confirmed that the graphite and mica flakes are not immersed in the OMCTS droplet but float on it. Within ten minutes, lateral forces were measured at room temperature using a commercially available instrument (Seiko Instruments Inc., SPI-3700) because the OMCTS droplet quickly vaporizes and disappears. A rectangular silicon cantilever with a normal spring constant of 0.75 N/m was used. The zero normal force is defined as that at the position at which the cantilever is not bent. The friction forces were calibrated by the method reported in our previous papers [(Miura and Kamiya 2002), (Miura et al. 2003), (Miura et al. 2004)].

3. Load and velocity dependence of friction force

3.1. Graphite flake case

Figure 2 shows the lateral force loops needed to drive the graphite flake on the OMCTS droplet as functions of loading force and scanning velocity. All experiments were done within ten minutes of introducing the OMCTS droplet onto the graphite substrate because the OMCTS droplet rapidly volatilizes and is lost. The lateral force loops versus scan velocity exhibit fluctuating oscillations at a low scan velocity for each loading force. Namely, the behaviors of fluctuating oscillations seem to depend strongly on scan velocity whereas they are insensitive to loading force. The mean friction force at a loading force of 0nN increases only slightly linearly with the logarithm of the scan velocity, as seen at the bottom of Figure 2. The mean friction forces in relation to loading force at a scan velocity of 1024 nm/s are almost constant (friction coefficient is 0.003), as shown on the right-hand side of Figure 2.

In a friction experiment of a graphite flake on a graphite substrate where an AFM tip pushes the graphite flake, it has been known that the actual contact area between the graphite flake and graphite surface becomes very small and is on the order of a nanometer square, compared to the total area of the flake, 1 mm square, reflecting the prominent surface deformations of graphite, as shown in our previous paper (Miura et al. 2004), Guo et al.’s study (Guo et al. 2004) and Dienwiebel et al.’s study (Dienwiebel et al. 2004). In a similar manner to the experiment of a graphite flake on the graphite substrate, even in this experiment the contact size between the flake and the OMCTS droplet is thought to be of nanometer order, because the mean friction forces on the right-hand side of Figure 2, relative to loading force, is almost constant (friction coefficient is 0.003 and comparable to that (0.001) of a graphite flake on a graphite substrate). Furthermore, the emergence of fluctuations of the graphite flake at a low scan velocity supports the contact size between the flake and the OMCTS droplet being of nanometer order.

The Fourier spectra of Figure 2 are shown in Figure 3, where the vertical axis of the inset on the right-hand side is in units of dB. Peaks of these spectra consist of quasi-periodic ones of $m f_1 + n f_2$ (m, n: integer) where main peaks $f_1$ and $f_2$ are produced. The $f_2$ peak is the strongest at a low scanning velocity which gives high-frequency oscillations, however, as the scanning velocity increases, the $f_1$ peak becomes the strongest and the noise level increases, as shown by the arrows in the background of the inset on the right-hand side. This is the typical pattern of a transition from a quasi-periodic state to a nonperiodic (or chaotic) state (Rand et al. 1982). Thus, the dynamics of the graphite flake changes from quasi-periodic motion to chaotic motion as the scanning velocity increases.

Here the important point is that the change of the scanning velocity of the graphite flake reveals the different time-scaled dynamics of an OMCTS molecule. If the low scanning velocity of the graphite flake is comparable to the effective velocity of dynamics of the internal degrees of freedom of the OMCTS molecule, the graphite flake could detect mainly structural fluctuations derived from rotations, oscillations and stretches of the OMCTS molecule, which results in the $f_2$ peak corresponding to a
Figure 2. Lateral forces needed to drive a graphite flake on an OMCTS liquid as functions of loading force and scanning velocity, where the black and red lines indicate one direction and the opposite direction, respectively. The mean friction forces at a loading force of 0 nN are shown on the scale of the logarithm of the scan velocity at the bottom. The mean friction forces in relation to loading force at a scan velocity of 1024 nm/s are shown on the right-hand side.

scale of about 0.2 nm [a scan velocity of 64 nm/s in Figure 3]. Although it is interesting to confirm exactly which internal degree of freedom of the OMCTS molecule contributes to the $f_2$ peak, it is difficult to determine it under the present experimental setup. On the other hand, as the scanning velocity increases more, the graphite flake could detect mainly the stationary arrangement of OMCTS molecules. Compared to the scanning velocity of the graphite flake, the OMCTS molecule appears to
be fixed, which results in the $f_1$ peak corresponding to a scale of about 1 nm [a scan velocity of 1024 nm/s in Figure 3]. Thus, the interactions between the graphite flake and the OMCTS liquid consist of the combined ones of the two modes, $f_1$ and $f_2$. The competition between these modes, as a result, keeps viscosity (or friction) against one-directional motion of the graphite flake almost constant. It is interesting to note that at a higher scanning velocity, this system is not yet in the adiabatic state but in the nonequilibrium stationary state. Thus, as the scanning velocity increases, a transition to the chaotic state is necessary to lower the energy dissipation of this system in the nonequilibrium stationary state, which is derived from the minimum entropy production principle of Gransdorff and Prigogine (Grandsorff and Prigogine 1964).

**Figure 3.** Fourier spectra of the samples on the case of Figure 2 are shown, where the vertical axis of the inset on the right-hand side is in units of $dB$.
3.2. Mica flake case

Figure 4 shows the lateral force loops needed to drive the mica flake on the OMCTS droplet as functions of loading force and scanning velocity. In a similar manner to the graphite flake experiments, all experiments were done within ten minutes of introducing the OMCTS droplet onto the mica substrate because the OMCTS droplet rapidly volatilizes and is lost. The mean friction forces in relation to loading force for each scan velocity increase linearly; for example, friction coefficient is 0.03, as shown on the right-hand side of Figure 4. The lateral force loops versus scan velocity exhibit for each loading force. The mean friction force for each loading force increases linearly with the logarithm of the scan velocity, as seen at the bottom of Figure 4. This behaviour is clearly different from the graphite flake case. The linear increase of the frictional forces in relation to loading force in the mica case reveals that the contact area between the mica surface and the OMCTS liquid surface.

**Figure 4.** Lateral forces needed to drive a mica flake on an OMCTS liquid as functions of loading force and scanning velocity, where the black and red lines indicate one direction and the opposite direction, respectively. The mean friction forces at a loading force of 0 nN are shown on the scale of the logarithm of the scan velocity at the bottom. The mean friction forces in relation to loading force at a scan velocity of 64 nm/s are shown on the right-hand side.
increases linearly with increasing loading force. This indicates that the surface deformation of mica, which behaves like a hard plate compared to the graphite flake, is significantly smaller than that of graphite, which maintains a contact radius of 1 nm irrespective of loading force.

Keeping in mind the fact that this system consists of friction between the tip and the flake and between the flake and OMCTS, it was found that the friction from this system includes two different mechanisms. However, it can be concluded that the features of the friction of a flake on OMCTS are only those of friction between the flake and OMCTS, because they do not include a frictional force map of the tip on the flake. This indicates that the friction between the tip and the flake is greater than that between the flake and OMCTS.

4. Energy dissipation and friction

As shown at the bottoms of Figure 2 and Figure 3, the mean friction forces only slightly increase linearly with the logarithm of the scan velocity \( V \):

\[
F = \alpha + \beta \ln V .
\]  

(4.1)

This result can be interpreted within the framework of a modified Tomlinson model, taking into account the thermally activated process \([\text{Eyring 1935}], \text{(Briscoe and Evans 1982)}, \text{(Heslot et al. 1994)}\). Now, we consider the motion under an effective potential \( U_{\text{eff}}(x, y) = U_0(x) + V(x, t) \), where \( U_0(x) \) and \( V(x, t) \) describe the interaction potential between the flake and the OMCTS liquid surface, and the elastic energy stored in a cantilever, respectively. Thus, \( V(x, t) \) is given as \( 1/2k_{\text{eff}}(x-x_s(t))^2 \), where \( x \), \( x_s \), and \( k_{\text{eff}} \) are the position of the tip, the support position of the microscope and the effective spring constant, respectively. According to the formula derived by Heslot et al.\((\text{Heslot et al.1994})\), as soon as the work performed by the driving force for moving from the minimum of \( U_{\text{eff}} \) to the next maximum becomes much greater than the thermal energy \( \Delta E \), the friction force \( F \) can be given as

\[
F(x, t) = \frac{2}{a} \left\{ \Delta U_0(F_0) + \Delta E \ln \left( \frac{V}{V_0} \right) \right\} ,
\]  

(4.2)

where \( a \), \( \Delta U_0 \) and \( V_0 \) are the space between the minimums, the amplitude modulation of \( U_0 \) and the velocity at the minimum \( U_{\text{eff}} \), respectively. Here, it should be noted that \( \Delta U_0 \) is defined as a function of loading force \( F_n \) although Heslot et al. \((\text{Heslot et al.1994})\) defined it as a function of ageing time, because \( \Delta U_0 \) is related strongly to contact areas and then loading force becomes equivalent to ageing time in a physical meaning. In the case where scan velocity is kept constant, the difference \( \Delta F \) between the friction forces at different loading forces \( F_{n1} \) and \( F_{n2} \) is given as follows using equation (4.2):

\[
\Delta F = \frac{2}{a} \left\{ \Delta U_0(F_{n1}) - \Delta U_0(F_{n2}) \right\} .
\]  

(4.3)

In the case where the loading force is kept constant, the difference between the friction forces \( \Delta F \) at different scan velocities \( V_1 \) and \( V_2 \) is given as follows, using equations (4.1) and (4.2):
\[ \Delta F = \beta \ln \frac{V_1}{V_2} = \frac{2\Delta E}{a} \ln \frac{V_1}{V_2}. \]  

(4.4)

Using equation (4.3), the increase of $\Delta U_0$ per nanonewton loading force, $\mu a / 2$, is estimated to be approximately 0.002 eV/nN and 0.3 eV/nN for graphite flake and mica flake cases, respectively. Here, $\mu$ is a friction coefficient as $\mu = \Delta F / (F_{n1} - F_{n2})$. Using equation (4.4), the thermally activated energy contributing to this slip process, $\Delta E$, was estimated to be approximately $36 k_B T$ and $200 k_B T$, for graphite flake and mica flake cases using the relation $\beta = 2\Delta E / a$, respectively. The $\Delta E$ for graphite flake case is comparable to the chemical energy (approximately $20 k_B T$) released by a single adenosinetriphosphosphate (ATP) molecule in the molecular motor kinesin, where $k_B$ and $T$ are the Boltzmann factor and the absolute temperature, respectively. Hence, it is shown that the dynamics of a graphite flake pulled by the nanotip on OMCTS liquid can be treated as that of a nanobody on liquid.

5. Conclusion

Here, the case of one-directional motion, under which a flake is driven on a liquid surface, was presented. The dynamical forces needed to move these bodies increased linearly with the logarithm of scanning velocity. The energy dissipation of graphite and mica were estimated to be approximately $36 k_B T$ and $200 k_B T$, respectively. A transition from quasi-periodic to chaotic motions appears in the dynamics of graphite flakes propulsive on an OMCTS liquid. This means it possible to maintain a small resistance by chaotic motion when the velocity of a graphite flake is increased. This result reveals the dynamical motion of nanoscale-body on the OMCTS liquid irrespective of a graphite flake size because a contact size between the graphite flake and the OMCTS droplet is the order of nanometer. This study reveals that “viscosity and friction” are phenomena of the complex systems closely related to the nonequilibrium stationary state and “lubrication” arises through “chaotic motions” in the nonequilibrium stationary state.

Generally, the stick-slip oscillations occur in Surface Force Apparatus (SFA) experiments when the contact between the two surfaces is adhesive (or solid-like). Up to now, it has been reported by Drummond et al. (Drummond et al. 2002) that quasi-periodic oscillation appears in stick-slip oscillation on a micrometer scale in the SFA experiment, because the contact area in SFA experiments is of few tens of micrometers. They have measured a complex sequence of periodic regimes separated by aperiodic regimes. They have also pointed out that the number density of adhesive junctions could possibly explain such a complex dynamics. At first sight, the transition between periodic and aperiodic regimes obtained by Drummond et al. (Drummond et al. 2002) can be easily compared to that between quasi-periodic and chaotic regimes obtained by us. Furthermore, unlike measurements by Drummond et al. (Drummond et al. 2002), our measurements show no periodic oscillations. However we must be careful of making a direct comparison between them. The first difference between these two cases is the system: the adhesive solid-solid interface (hemi-fused state) by Drummond et al. (Drummond et al. 2002) and the solid-liquid interface (a solid nanobody on a liquid) in our experiment. The second difference is the scale of the time and space: the contact area is of micrometer order by Drummond et al. (Drummond et al. 2002) and of nanometer order in our experiment. Thus we meet difficulties in making a clear comparison with previous works. However, if the bonding between an OMCTS molecule and a graphite flake is assumed to be a single adhesive junction, it may be possible to find a correlation between two different systems and the key to universal understanding of complex dynamics with scaled time and space irrespective of the system.

References

[1] Briscoe BJ, Evans DCB 1982 Proc. R. Soc. Lond. A380 389.

[2] Dienwiebel M, Verhoeven G, Pradeep N, Frenken J, Heimberg J, Zandbergen H 2004 Phys.
Rev. Lett. 92 12601.

[3] Drummond C, Elezgaray J, Richetti P 2002 Europhys. Lett. 58 503.
[4] Eyring H 1935 J. Chem. Phys. 3 107.
[5] Gransdorff P, Prigogine I 1964 Physica 30 351.
[6] Guo W, Zhu CZ, Yu TX, Woo CH, Zhang B, Dai YT 2004 Phys. Rev. Lett. 93 245502.
[7] Heslot F, Baumberger T, Perrin B, Caroli B, Caroli C 1994 Phys. Rev. E49 4973.
[8] Miura K, Kamiya S 2002 Europhys. Lett. 65 610.
[9] Miura K, Kamiya S, Sasaki N 2003 Phys. Rev. Lett. 90 055509.
[10] Miura K, Sasaki N, Kamiya S 2004 Phys. Rev. B69 075420.
[11] Rand D, Ostlund S, Sethna J, Siggia ED 1982 Phys. Rev. Lett. 49 132.