Anisotropy in Friction and Molecular Stick-Slip Motion

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A fundamental study of friction by friction force microscopy on an organic bilayer assembly is presented. Frictional domains are observed with a real area of contact in the regime of the lattice spacings. Their frictional contrast is changing in respect with the sliding direction. Such a local anisotropic behavior of friction is shown to originate in different 2D crystal orientations. On the molecular scale stick-slip motion is observed which can be related to the macroscopic terms of static and dynamic friction.

Anisotropy of friction forces was reported between muscovite mica sheets as a function of the lattice misfit angle [1]. This study was based on the effect of the commensurability between contacting lattices under a load of about 10^{-3} N and an elastic contact zone of 0.25 μm. First, atomic force microscopy [2] (AFM) studies which were concerned with friction [termed friction force microscopy (FFM)] provided *stick-slip* motion on the atomic scale [3], and frictional inhomogeneities on the submicrometer scale [4] under loadings of 10^{-5} and 10^{-8} N, respectively. The area of contact has been reported to be on the nanometer scale but still large compared to the lattice spacings. The inhomogeneities in friction which were observed on an organic bilayer film of cadmium arachidate were not present in the simultaneously recorded topography image [4]. Because of the limitation of resolution it was not possible to decide if changes in interfilm or intrafilm coupling at the film-substrate interface or local different orientations of molecules (in domains) caused the additional frictional contrast.

We report here our observations of inhomogeneities in friction on a laterally anisotropic and highly ordered organic monolayer and relate it to the molecular arrangement of the molecules. The studied film fulfills four requirements which allow a very fundamental study of friction: (1) a high stability, (2) a highly anisotropic 2D symmetry, (3) a well defined structure and molecular smooth planes, and (4) boundaries which allow us to estimate the contact area. The results have been achieved under a load between 10^{-7} and 10^{-8} N and an elastic area of contact on the order of the lattice spacings. Because the magnitude of the lattice parameters and the area of contact are similar, a friction force study, which is independent on any collective phenomena such as lattice misfit, could be conducted the first time. Further, we discuss the observed *stick-slip* motion on the molecular scale under variation of the loading and the velocity, and define, based on this observation, static and dynamic friction.

Our experiments were conducted under ambient conditions with a commercially available AFM [5]. Friction has been measured simultaneously with topography by laser beam deflection [6]. Scanners of 20 and 1 μm, and triangular and bar shaped cantilevers with normal spring constants of 0.08 and 0.25 N/m, respectively, have been used. The torsional spring constant of the bar shaped cantilever is 610 N/m.

During the measurements, no apparent damage could be observed either by increasing the load or decreasing the scan velocity (see [6]) presumably due to the robustness of the sample material. The ability of the AFM to nondestructively collect lattice spacings has already been well documented [6]. The sample, a bilayer lipid film, is built up of 5-(4'-N,N-dihexadecylamino)benzylidene barbituric acid (*lipid*), Fig. 1. The film has been prepared on an aqueous subphase with a pH of 3 and transferred by Langmuir Blodgett technique on an oxidized silicon (100) substrate. A bilayer structure of a highly ordered, two-dimensional and lateral anisotropic structure with large lattice spacings of 0.6 and 1.1 nm with a lattice angle of 72° could be observed by AFM. This anisotropic structure is manifested in the row structure of 1 nm sketched in Fig. 1.

Domains of the same molecular structure, but with different alignments of the rows are aligned smoothly to each other forming a molecularly intact film. Only in the friction image can the domains be distinguished on the submicrometer scale as seen in Fig. 2(a). The boundary-free topography and smooth alignment is discussed elsewhere [7].

In the present work, we studied this inhomogeneity of friction in respect to the sample orientation and the scanning direction. In Fig. 2(a), the initial scan is presented providing a frictional inhomogeneity on the bilayer system of about 20% around a mean friction value of 29 nN under a loading of 63 nN. Rotating the sample [8], but still scanning in the same direction, gradually changes the contrast in friction. At a rotation angle of 90°, Fig. 2(b), the contrast is inversed; i.e., what was bright (high fric-
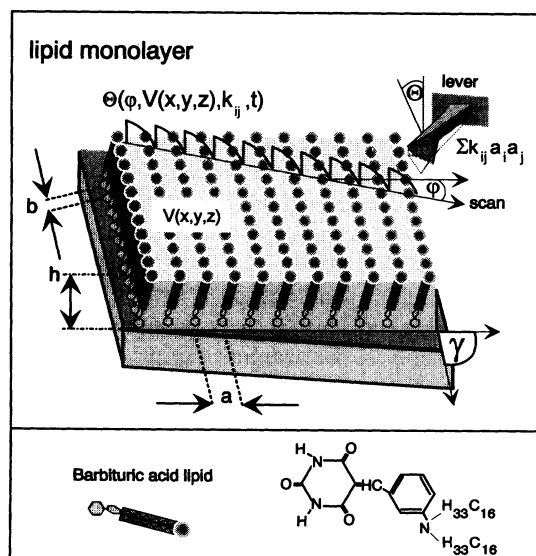
FIG. 1. Lipid monolayer structure [5-(4'-N,N-dihexade-cylamino)benzylidene barbituric acid (*lipid*)] of $h = 2.4$ nm in height. For the sake of simplicity only the monolayer has been sketched though the film consists of a bilayer. The spacings of the molecules are $a = 1.1$ nm and $b = 0.6$ nm with $\gamma = 72°$. The torsional movement of the cantilever Θ depends below a scan velocity of 100 nm/s on the scan direction φ, the strength of the interaction potential V, and the coupling constants k_{ij} between other oscillation modes a_i of the cantilever. The chemical formula of the barbituric acid lipid [14] is added below.

tion) before turned dark (low friction), and vice versa. From a more macroscopic point of view, this behavior could be related to the commensurability of the lattice of the tip plane in contact with the sample lattice [1,3]. Yet, high resolution images show that at the border of two domains the real area of contact is smaller than 2 nm, which is on the order of the lattice spacing, Fig. 3. Therefore, the anisotropy in friction observed here cannot be explained in terms of misfit angles of lattices in contact.

The distinction between commensurability and incommensurability is not applicable in this study as shown by examination on the molecular scale. Figure 3 is a magnification of the horizontally aligned boundary, seen in Fig. 2(b) on the lipid film, between the dark-gray (lower friction) area and the bright-gray (higher friction) area. Figure 3 is rotated 90° so that the left and right part corresponds to the bright and dark area in Fig. 2(b), respectively. The scan direction of Fig. 3 is vertical to the image.

Figure 3 shows two molecular arrangements of neighboring domains whose measured dynamic friction forces are 34 ± 3 and 25 ± 2 nN on the submicrometer scale of Fig. 2(b). Up and down scan (*friction loop*) reveal energy dissipation on the molecular scale, Figs. 4(a) and 4(b). The representative friction loops for scanning on the left
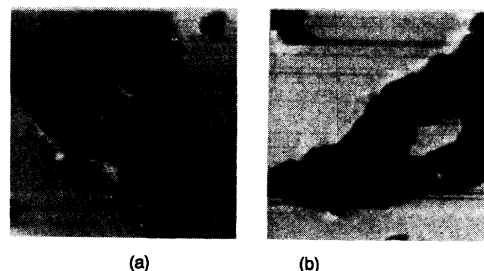

FIG. 2. (a) 6×6 μm^2 FFM image of the lipid film. The bright area (higher friction) is the silicon(100) substrate covered with a monolayer of a nonstructured lipid film. On top of this, a lipid bilayer island (*darker grays*, i.e., lower friction) shows domains of different frictional contrast (inhomogeneity). Inhomogeneities of friction can be observed only on such lipid bilayer islands. The variation of the frictional domains is in the range of 25 to 34 nN. (b) After a 90° rotation of the sample, the contrast in the frictional domains of the bilayer is reversed. The contrast of the surrounding bright area remained.

and right side of Fig. 3 provide an average friction force value of 32.5 nN [Fig. 4(a)] and 24 nN [Fig. 4(b)], respectively, which corresponds to the measured dynamic friction in Fig. 2(b). Dynamic friction observed on the submicrometer scale can therefore be defined as the mean value of *molecular stick-slip* motion. The maximum values of the molecular stick-slip motion in Figs. 4(a) and 4(b) of friction has been measured to be 60 and 50 nN. These values correspond to the static friction value measured at the turning points of each scan line. From Figs. 2 and 3 can be concluded that scanning along the molecular rows gives rise to lowest friction whereas scanning perpendicularly to the rows causes highest resistance against sliding.

The imaged rows in Fig. 3 enclose with the vertical scan direction an angle of 63° and 22° for the left and right sides, respectively. The left side provides a periodic length of the stick-slip motion of 1.1 nm [Fig. 4(a)] corresponding to the row distance of 1.0 nm. The right side provides a periodic length of the stick-slip motion of 0.55 nm [Fig. 4(b)] which is related to an interrow molecular distance b of 0.6 nm and a larger offset periodicity of 4.8
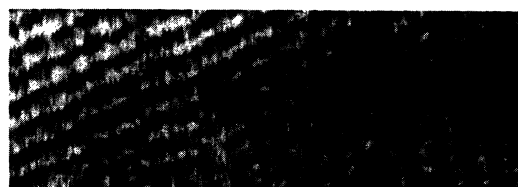

FIG. 3. 24×8.5 nm^2 FFM image. Two alignments of rows can be observed. In the left part of the image the rows are oriented 63° to the vertical scan direction. In the right part the rows are oriented 22° to the scan direction. The scan velocity is 36 nm/s.
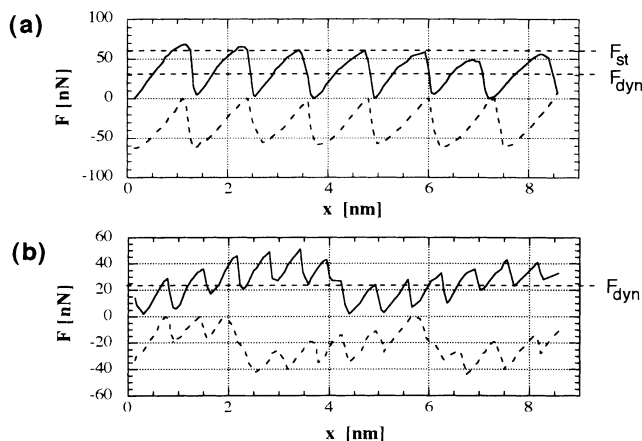
FIG. 4. Representative up and down scans (*dashed line*) of Fig. 3; also termed *friction loop*. (a) The frictional corrugations of the 63° oriented rows show 1.1 nm periodicity and are stick-slip in nature. The maximum value F_{st} has been measured to be 60 nN and can be related to the macroscopically measured static friction. The average value of friction F_{dyn} is 32 nN and corresponds to the observed dynamic friction. (b) The 22° oriented rows show periodicities are 0.55 and 4.8 nm, respectively. The average friction has been measured to 24 nN.

nm which can be related to the row distance under consideration of the scan angle. It is worth noting that the interaction potential is anisotropic on the molecular scale causing anisotropy in friction.

The movement of the cantilever, whose lateral spring constant is very important, is, as seen in Figs. 4(a) and 4(b), *stick-slip* in nature. As long as the second spatial derivative of the interaction potential between scanning tip and sample surface does not exceed the lateral spring constant, the cantilever will stick to the surface. But in the case the spring constant is reached, the cantilever slips to the next stable position, which is always observed to be related to the next molecule. The finite negative slope in the sliding regime of the *stick-slip* motion is given by the response time of the used electronics.

A very idealized approach [9] to the experimentally observed stick-slip behavior can be undertaken by considering the following equation of motion

$$I\ddot{\Theta} = -k\Theta + M(v_s - \omega r) \, ,$$

where I is the moment of inertia of the cantilever, Θ the angle of torsion, k the elastic spring constant of the system, and $M(v_s - \omega r)$ the frictional torque depending on the relative velocity which is given by the scan speed v_s and the product of the angular velocity ω and the length r of the tip. Because of the small mass of the cantilever, self-oscillations of the system are built up divided into two types of motion [10]. As long as the spring torque equals the friction torque, the cantilever motion ω varies slowly (stick regime). In the case friction and spring torques do not balance each other and hence the tip acceleration is very large, an instantaneous slip occurs (slip regime).

No differences in the stick-slip motion could be measured by varying the loading between 30 and 120 nN. Even though this range is not sufficient to inform definitely about the loading dependence of friction in the elastic region, it is important to consider that loading dependencies were always reported in terms of *lattice over lattice* sliding. Mate *et al.*, who discussed atomic-scale friction under loadings of 2 orders of magnitude larger than those discussed here, contemplated sliding graphite flakes along the graphite sample [3]. Under this aspect, the loading dependence of friction can be seen as a more collective phenomenon than a local quality of friction with a constant area of contact on the order of the unit cell of the sample lattice. Further it is worth mentioning that as long as measurements are conducted in air there is an intermediate liquid film between tip and sample. It is reasonable to assume that such films act as stress distributor for the high pressure between tip and sample.

Sliding velocities between 36 and 100 nm/s did not affect the stick-slip behavior of friction. At higher velocities than 500 nm/s, but still within the bandwidth and response time of the electronics (allows a sliding velocity of about 800 nm/s), the stick-slip motion becomes more and more disordered.

As described above, energy is dissipated by stick-slip motion of the cantilever tip under the influence of the interacting potential. Because of the softness of the cantilever, it can be assumed that no distortion of the sample lattice occurred during sliding. Excitations of vibrational modes in the sample can therefore be neglected. Tomanek, Zhong, and Thomas showed theoretically that dissipation occurs for soft cantilevers in the form of *stick-slip* motions [11]. His calculations were partially confirmed by Sokoloff's theoretical work [12], which considers built up strain in the opposite sliding bodies caused by a critical lateral interaction force—defined as static friction force. In his model, strain is built up until the resulting stress is able to overcome the maximum pinning force. Based on this model, the strain which is built up in the cantilever should release entirely or by some fraction.

It can be observed, Fig. 4, that the strain is released entirely for small sliding velocities. However, at higher velocities where the *stick-slip* behavior is more noisy, the strain is mainly built up only by some fraction. At very slow sliding velocities of around 18 nm/s, the cantilever can even overswing (negative value of the stick-slip motion). The overswing amplitude is very small indicating a strong damping of the torsional cantilever oscillation. Hereby the damping is mainly caused by van der Waals forces between tip and sample.

One approach to explain the velocity dependence of the strain release in the cantilever is to consider the inertia of the tip (in contact with the sample) in respect to the sample's relative movement. This classical approach of a

forced oscillation of a single degree of freedom system could be described by

$$I\ddot{\Theta} = -k\Theta + M(v_s - \omega r) + E(t),$$

where $E(t)$ represents an external periodic excitation determined by the molecular arrangement of the sample. This approach is interesting at larger scan velocities where the frequency of $E(t)$ is in the range of the resonance frequency of the damped cantilever.

Based on these experimental results, we propose a new approach in the atomistic dry friction theory by considering the fluctuations of the torsional movement of the cantilever with time [13]. We consider the fluctuations to be flat, thus allowing a discussion of a white-noise-driven system. In our experiment the tip can be considered to be on the size scale of single molecules and hence allows the discussion of fluctuations around only a few attractors. The distance from the attractors which can be described by a van der Waals potential determines the loading. In our on-going work, we hope to describe with this approach theoretically the velocity and loading dependence of friction in the low speed regime (nonresonance regime) and to test it experimentally with the here described system.

To conclude, it has been shown that anisotropy in friction can be explained by different molecular alignments of the molecular structure in respect to the scanning direction. This has been shown on the basis of *local friction* where the real area of contact is in the range of the lattice spacing. The macroscopic terms of static and dynamic friction could be related to quantities of the molecular *stick-slip* motion and theoretical assumptions of built up strain experimentally confirmed.

[1] M. Hirano, K. Shinjo, R. Kaneko, and Y. Murata, Phys. Rev. Lett. 67, 2642 (1991).

[2] G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. 56, 930 (1986).

[3] C. M. Mate, G. M. McClelland, R. Erlandsson, and S. Chiang, Phys. Rev. Lett. 59, 1942 (1987).

[4] E. Meyer, R. Overney, D. Brodbeck, L. Howald, R.Lüthi, J. Frommer, and H.-J. Güntherodt, Phys. Rev. Lett. 69, 1777 (1992).

[5] SPI3700 AFM, Seiko Instruments Inc., Chiba, Japan.

[6] A review of FFM: R. Overney and E. Meyer, MRS Bull. 18, No. 5, 26 (1993). A general review of the application of AFM to organic thin films: J. Frommer, J. Angew. Chem., Int. Ed. Engl. 31, 1298 (1992).

[7] R. M. Overney, H. Takano, M. Fujihira, G. Overney, W. Paulus, and H. Ringsdorf, in "Forces in Scanning Probe Methods," edited by H.-J. Güntherodt, D. Anselmetti, and E. Meyer, NATO ASI, 1–18 March 1994, Schluchsee, Germany (Kluwer Dordrecht, The Netherlands, to be published).

[8] Many commercial AFM instruments provide today the possibility of scan rotation. For friction force measurements, the scanner moves perpendicularly to the cantilever beam to achieve highest resolution. Variations of the angle of the scanning movement (scan rotation) causes alterations in the geometrical setup and changes the lateral bending (or torsion) of the cantilever. This intrinsic problem of scan rotation requires each time a new calibration of the friction force. To avoid this problem, we rotated the sample which is mounted on a rotating sample holder and maintained herewith the geometrical setup between scan direction and cantilever. The accuracy of a 90° rotation is about 0.5 μm which is in the range of the scanner and can be compensated by the piezo to locate the distinctive geometry of the original frame.

[9] This approach does not explicitly consider the molecular attractors of excitation of the sample. However, under the circumstances of self-oscillation of the system [$M'(v_s) < 0$], the sample molecular inhomogeneity can be simulated.

[10] A. A. Andronov, A. A. Vitt, and S. E. Khaikin, *Theory of Oscillators* (Pergamon Press, Oxford, 1966), Vol. 4, pp. 690–696.

[11] D. Tomanek, W. Zhong, and H. Thomas, Europhys. Lett. 15, 887 (1991).

[12] J. B. Sokoloff, Thin Solid Films 206, 208 (1991).

[13] M. I. Dykman, P. V. E. McClintock, V. N. Smelyanski, N.D. Stein, and N. G. Stocks, Phys. Rev. Lett. 68, 2718 (1992).

[14] R. Ahuja, P. L. Caruso, D. Möbius, W. Paulus, H. Ringsdorf, and G. Wildburg, J. Angew. Chem., Int. Ed. Engl. 32, 1033 (1993).
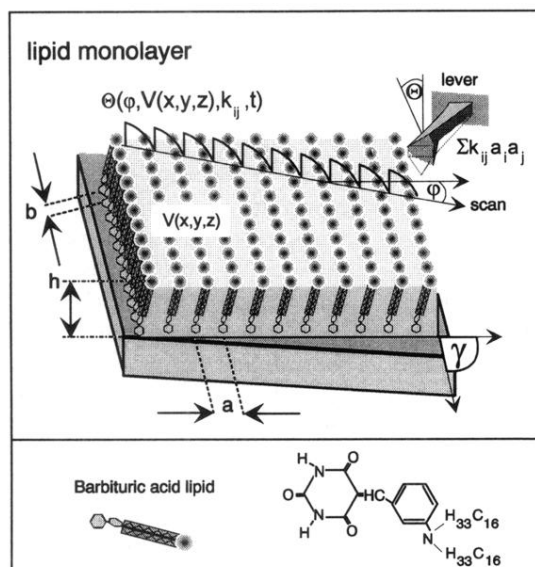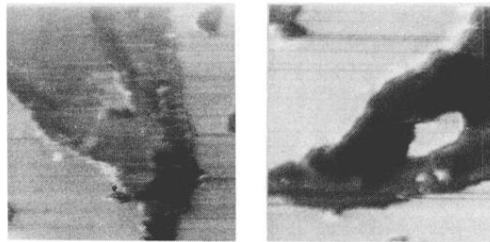
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(a)   (b)

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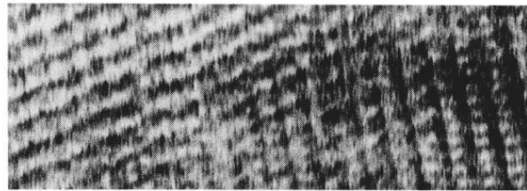
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