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Friction force studies on layered materials using an Atomic Force Microscope

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Abstract

We have studied friction force versus normal load on the nanometer scale on three layered materials which are expected to exhibit different mechanical properties: 2H-MoS_2, 2H-$NbSe_2$, α-MoO_3. Different behaviours have been observed, such as plastic deformation and local wear. Under well-defined conditions there exists an analogy between nanoscopic experimental results and macroscopic friction results predicted by models (Amontons' law for instance). It is then possible to extract mean values of the friction coefficient on the nanometer scale. We are interested in friction measurements under atmospheric conditions which correspond to real sliding conditions. The influence of parameters such as surface pollution and scan speed appears to be determinant for the reliability of the results.

Keywords: Atomic force microscopy; Friction; Single crystal surfaces; Tribology

1. Introduction

Atomic force microscopy (AFM) is known as a convenient tool for imaging surfaces up to atomic resolution. Thanks to its conception, AFM is also an excellent tool for probing fundamental forces, Van der Waals and electrostatic forces for instance, and more particularly friction forces. Recently, AFM has brought a new understanding in fundamental mechanisms of friction and adhesion on the atomic scale [1–6]. But it could also be powerful for the comprehension of friction phenomena (wear and degradation) on the nanometer scale [7], which is of great interest for industry. From this point of view, investigation on layered materials [1,8,9] constitutes a model case for these problems, and it is of interest to perform friction studies on these prototype surfaces under atmospheric, i.e. real, conditions.

2. Principles of friction force measurements using AFM

By scanning the AFM probe (a sharp tip mounted on a flexible cantilever) over a surface, the interactions between the tip and the surface induce cantilever deflections recorded by deviation of a laser beam as shown in Fig. 1. These deflections contain both topographic and frictional information about the surface.

According to several models [10] (Amontons'

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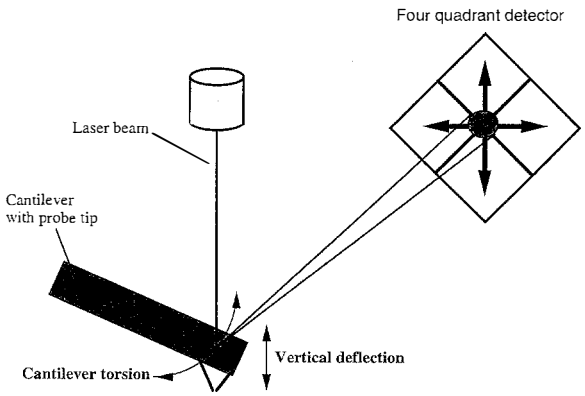


Fig. 1. Schematic description of the cantilever movement detection: tip displacements lead to movement of the laser beam reflected on the cantilever. This movement is detected on the four quadrant photodiode.

law, JKR model, etc.), the friction force F_f is dependent on the normal load F_n.

In addition, on the nanometer scale the friction force intensity depends also on further parameters such as surface pollution [11,12], which modifies the characteristics of the tip/surface interface, surface roughness [13], which causes normal load variations, or tilt of the probed surface out of the AFM scan plane [14], which leads to variation of the signal level read on the microscope detector.

3. Experimental measurements of F_f

In AFM the intensity of the normal load F_n applied to the tip is easily obtained by multiplying the cantilever deflection Δz by its normal spring constant Γ_z (in our case a V-shaped silicon nitride cantilever, 193 μm in length, normal spring $\Gamma_z = 0.03\ \mathrm{N\ m^{-1}}$):

$$F_n = \Gamma_z \cdot \Delta z. \tag{1}$$

This normal load is in the range of a few 10^{-8} N, and contains both the interfacial adhesive force and the externally applied force normal to the surface [15].

During lateral scanning (perpendicular to the longitudinal axis of the cantilever), cantilever torsion occurs due to friction force at the tip/surface interface. For a flat surface (i.e. atomically smooth), the detected signal depends mainly on the friction phenomenon (Fig. 2). Nevertheless, due to sample roughness, the lateral scan leads to a mixed signal where a component resulting from sample topography is superimposed on the real friction signal. Roughness can also affect local values of F_n and, consequently, the friction coefficient [13]. To minimize this phenomenon, it is necessary to investigate surfaces with the minimum of roughness and, when comparisons are desired, to compare surfaces with similar roughnesses. Following these requirements, cantilever torsions are mainly produced by the friction force resulting from the applied normal load and tip movement.

For such a lateral mode it could be tempting to use, in analogy with Eq. (1), a very simple relationship between cantilever torsion angle and friction force:

$$F_f = \Gamma_t \cdot \theta \tag{2}$$

where Γ_t represents the torsional spring constant of the cantilever, and θ the angle of torsion. Nevertheless, such a procedure is not trivial using a commercial atomic force microscope (Nanoscope III, Digital Instruments). Indeed, Γ_t depends only on cantilever and tip geometry and material constants (E, G, ν) of the cantilever [16]. This constant Γ_t could be obtained by calculation [17] or experimental calibration [18]. But the measurement of θ and consequently the measurement of F_f intensity is connected to the microscope setup (geometry,

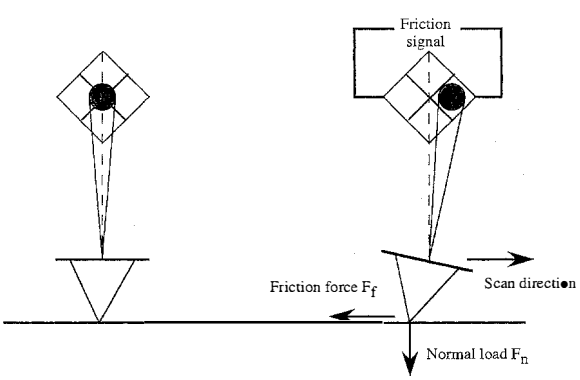


Fig. 2. Schematic representation of a tip submitted to a friction force during a lateral scan.

sensitivity of the photodiodes). Therefore, it is clear that we need an accurate method to calibrate our F_f measurements and to extract friction contributions from the torsion signal detected during a lateral scan.

Ruan and Bhushan [19] have proposed an original method to calibrate the atomic force microscope for these measurements, using both usual (parallel to the longitudinal axis of the cantilever) and lateral scanning. In usual scanning, the atomic force microscope is already calibrated to measure vertical deflections of the cantilever and consequently the forces applied to the tip (Eq. (1)). In this direction, the friction force is superimposed on the normal force, and the measured signal contains both topographic and frictional information (Fig. 3). Therefore, upon operating on very flat surfaces where the topographic signal is negligible with respect to the friction signal, we can obtain meaningful F_f values. As we expect the same friction force at the tip/surface interface during a usual scan as during a lateral scan, we can link the friction signal V_f (in volts) detected upon laterally scanning to the values extracted from the usual scan. This method leads to a relationship:

$$F_f = k \cdot V_f. \tag{3}$$

However, to obtain an exact value of k it is important to suppress the topographic contribution of the signal. The topographic signal is independent of scan direction, as opposed to the friction signal which has an algebraic intensity depending on the scan direction. By subtracting two AFM pictures recorded in the forward and backward scan directions, we could then obtain a mean value of the true friction signal.

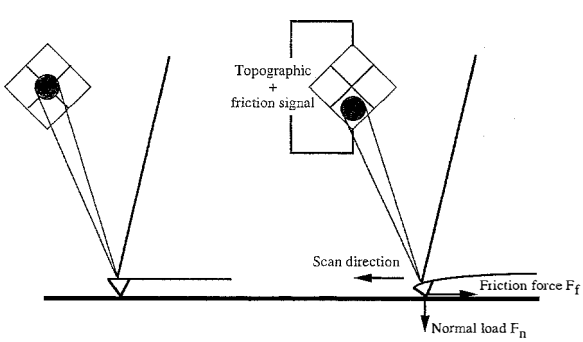


Fig. 3. Superimposition of topographic and frictional information during a usual scan.

In our case, the calibration carried out on a flat (111) silicon single crystal (less than 0.1 nm RMS) gives $k = 2 \pm 0.2 \times 10^{-9}$ N V^{-1}. [1]

4. Different frictional behaviours for lamellar materials

We study here three layered materials, 2H-MoS_2, 2H-$NbSe_2$ and α-MoO_3 [20], which have their general bidimensional structure in common, but differ in their interlayer cohesion because of their electronic (d^2 Mo for MoS_2, d^1 Nb for $NbSe_2$ and d^0 Mo for MoO_3) and crystallographic structures (hexagonal with different unit cell parameters for MoS_2 and $NbSe_2$, orthorhombic for MoO_3). Upon considering Van der Waals gaps [21], MoS_2 is expected to have the lowest and MoO_3 the highest interlayer cohesion. For these reasons we expect different frictional behaviour for these three materials during AFM scans.

For our tests, samples are all single crystals freshly cleaved along their highest density plane. It is noteworthy that these surfaces are all atomically smooth at the beginning of the experiments (RMS in the range of 0.1 nm). They are investigated by AFM in air, under the experimental conditions described above. All the experiments presented below are performed with the same tip[2] on a 1 μm × 1 μm square area at 1 μm s^{-1} scan speed. During the tests we make F_n variable, firstly increasing to a maximum value and then decreasing to the initial value, in order to put in evidence reversible and irreversible phenomena due to friction (wear for instance). We present hereafter graphs showing the variation of F_f vs. F_n for the three samples. We present also pictures recorded by AFM in topographic mode at the end of each friction acquisition series.

2H-MoS_2 is known to be a good lubricant on

[1] NanoscopeIII AFM, Digital Instruments, V-shaped silicon nitride cantilever of 193 μm length with $\Gamma_z = 0.03$ N m^{-1}.

[2] V-shaped cantilever of 193 μm length with $\Gamma_z = 0.03$ N m^{-1}.

the macroscopic scale because of its low interlayer cohesion. Fig. 4(a) shows that there is no correlation between F_f and F_n following a known friction model, except in the first steps where F_f vs. F_n is more or less linear according to Amonton's law.[3] Moreover, the topographic picture of Fig. 4(b) exhibits a surface where the investigated area during friction measurements is darker (meaning at a lower level) than the unaltered surface. The area corresponding to the presented results is delimited by a line, other darker areas correspond to preliminary experiments.

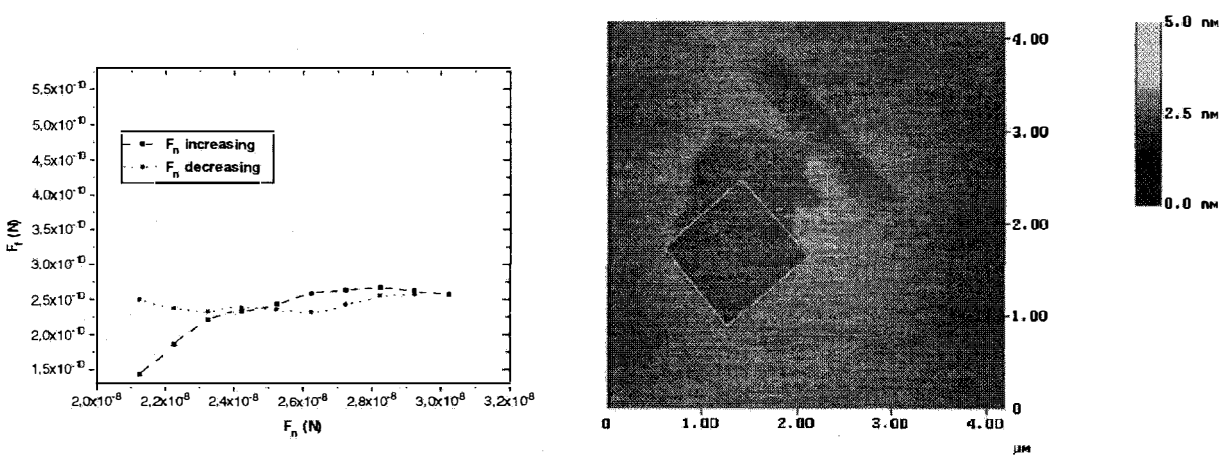
These facts lead us to think that the MoS_2 surface has been modified during the experiment beyond a threshold value of F_n (2.3×10^{-8} N). This modification could be explained by a plastic deformation (depression) of the material under the tip stress, because we have not seen on the surface profile (Fig. 5) any material rejected out of the investigated area.

In the case of 2H-$NbSe_2$, which has a higher interlayer cohesion than MoS_2 (Fig. 6(a)), when F_n increases, F_f measurements are incoherent with large variations of intensity due to subsidiary phenomena. Interestingly enough, as soon as F_n decreases after the first normal loading, the relationship between F_f and F_n becomes linear, in full agreement with Amontons' law. After this first experiment we carried out several load/unload cycles showing a linear relationship F_f vs. F_n, even if F_n is increasing again. The topographic picture after the first experiment (Fig. 6(b)) exhibits a surface with several holes in the investigated area (delimited by a line), and many material fragments scattered out of the investigated area during topographic picture recording on a larger size. The mean depth of the holes, in the range of 10 Å (Fig. 7), roughly corresponds to the thickness (6.7 Å) of one layer of $NbSe_2$.

This clearly indicates a local wear during the first F_n increase, and after the sweeping away of layer fragments which disturb the microscope regulation, we obtain a linear relationship between F_f and F_n on a surface which remains unchanged with a constant RMS even if we perform further friction measurements with the same F_n range.

This phenomenon of wear on $NbSe_2$ has been observed previously by Lieber and Kim [22].

For α-MoO_3, during the load/unload cycle of F_n, the relationship between F_f and F_n is linear



(a) (b)

Fig. 4. (a) F_f vs. F_n during friction test on a 2H-MoS_2 single crystal. (b) AFM picture recorded after the friction test, exhibiting a depression of the surface.

[3] Amontons' law defines a constant coefficient of friction $\mu = F_f/F_n$.

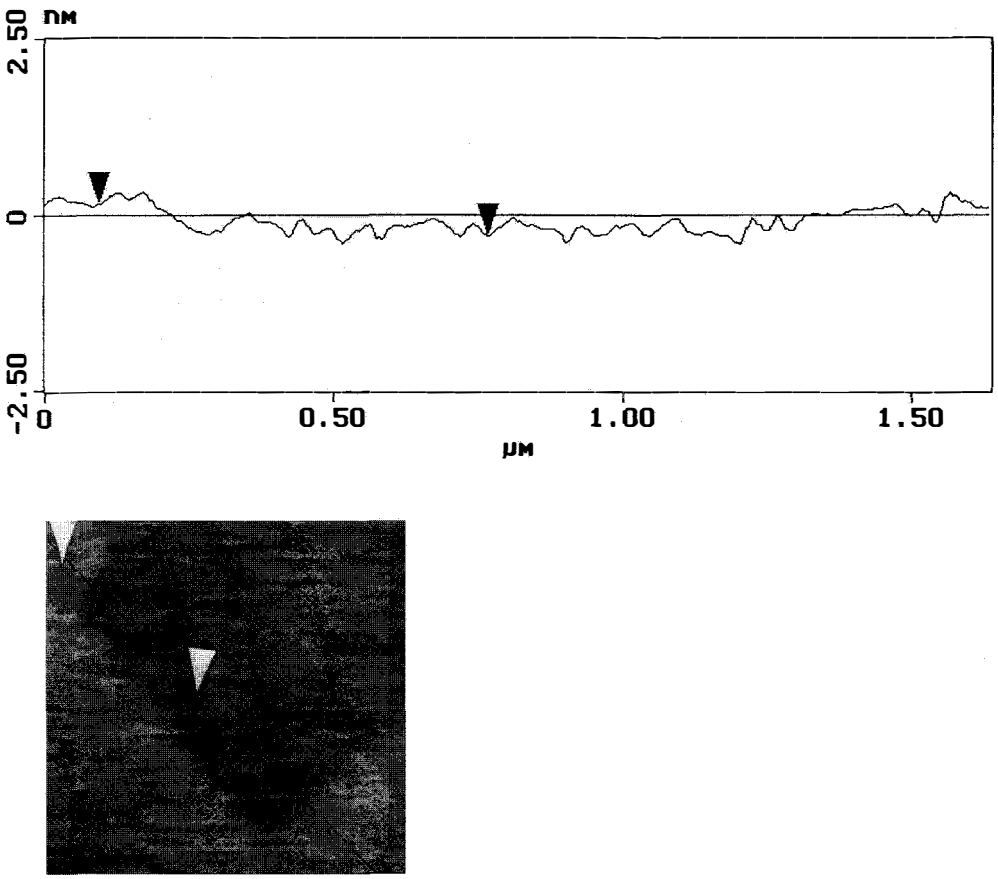


Fig. 5. AFM surface profile in the depressed area of the 2H-MoS_2 single crystal after the friction test. The vertical distance between the two cursors is 4.7 Å.

according to Amontons' law, Fig. 8(a). Furthermore, it is obvious that the surface is kept unaltered during AFM scans, Fig. 8(b). We correlate this observation with a strength of interlayer interaction higher in MoO_3 than in MoS_2 or $NbSe_2$.

From our experiments it appears that when surfaces are unaltered during the measurements, as in the MoO_3 case, friction behaviour on the nanometer scale could be compared to classical behaviour on the macroscopic scale.

During AFM friction measurements on MoO_3, the linear evolution F_f vs. F_n follows the Amontons' law, which defines a constant coefficient of friction μ. This law is verified when the true area of a contact is proportional to F_n. This is often true on the macroscopic scale, where contact areas are rough. In this configuration, when F_n increases, new asperities are created by plastic and elastic deformations, increasing the true contact area. On the nanoscopic scale, a single elastic contact results in an $F_f \propto F_n^{2/3}$ law [12]. We interpret our observation of a linear relationship F_f vs. F_n as evidence of the rough nature of the tip/surface contact. It allows us to extract a mean friction coefficient value of 0.022 for the investigated surface on the nanometer scale.

Although some phenomena, such as ploughing or surface deformation, act on the nanoscopic scale, they are negligible with respect to those acting at the macroscopic scale [2]. This explains

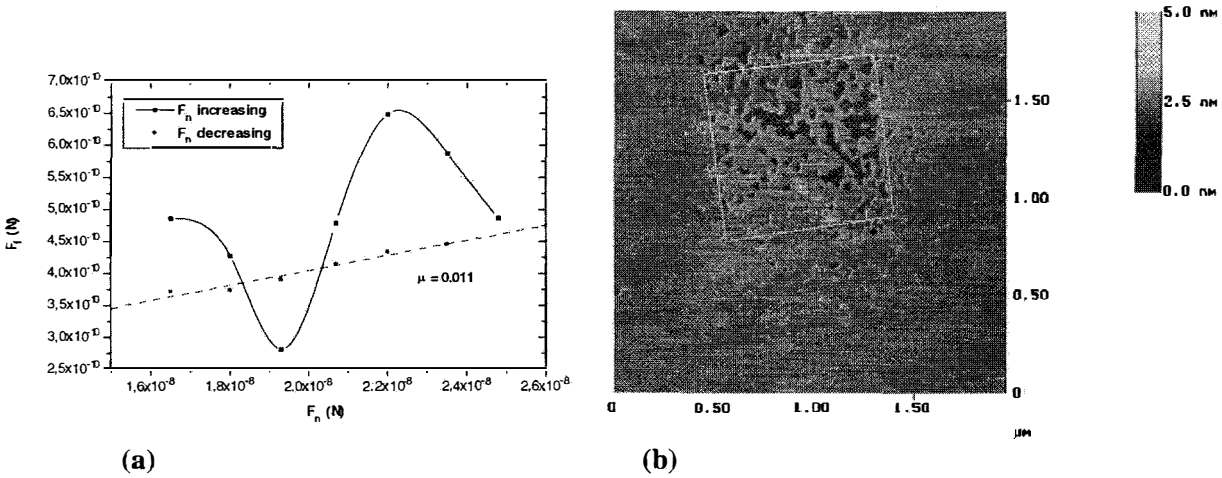


Fig. 6. (a) F_f vs. F_n during friction test on a 2H-$NbSe_2$ single crystal where measurements for increasing F_n are incoherent. A mean value $\mu = 0.011$ is extracted for decreasing F_n. (b) AFM picture recorded after the friction test, exhibiting a local wear of the surface.

why the nanoscopic values of μ are small compared to the macroscopic ones, as already observed for many materials [19,23,24].

5. Importance of parameter control

The investigation of the frictional behaviour on the nanometer scale appears to be very delicate, and some parameters are susceptible to play a role of utmost importance. In particular, the question immediately arises of surface pollution in air. When this phenomenon is significant, friction measurements on the nanometer scale may be totally incoherent.

For instance, it is known that on silica there is an important condensation of water and other pollutants on the surface when kept in air. Following our experimental protocol, on an initially cleaned and dried silica surface, several force measurements at various times give different results, indicating that there is a growing layer of pollutants on the surface. Consequently, the tip/surface interface is continuously changing and force measurements remain impossible. When the surface is saturated by water, measurements are also impossible, because during a continuous scan the tip modifies the layer adsorbed on the surface. With a lower scan speed, an interface equilibrium would be obtained, and coherent measurements performed.

If measurements are coherent in air (with MoO_3 for instance), it does not mean that the surfaces are unpolluted, but that there is a dynamical equilibrium of the tip/surface interface including pollutant layer on the surface, pollutant meniscus around the tip, and material fragments pulled off from the surface and from the tip.

Obviously, in these conditions, friction measurements are not really characterising the investigated surface, but a system resulting from the adsorption of pollutants on the material surface.

As far as MoO_3 is concerned, the linear dependence of F_f vs. F_n indicates the relatively low degree of pollution of the surface. Indeed, in the case of an important pollution, the capillary condensation of pollutants in contact asperities should induce a transition from a rough to a single asperity contact, and therefore to an $F_n^{2/3}$ dependence of friction [12].

Besides the importance of the thickness and of the dynamic stability of the pollution layer, we would like to define the role of two other parameters, the tip/surface interface composition and the scan speed, able to modify the value of μ for a given system.

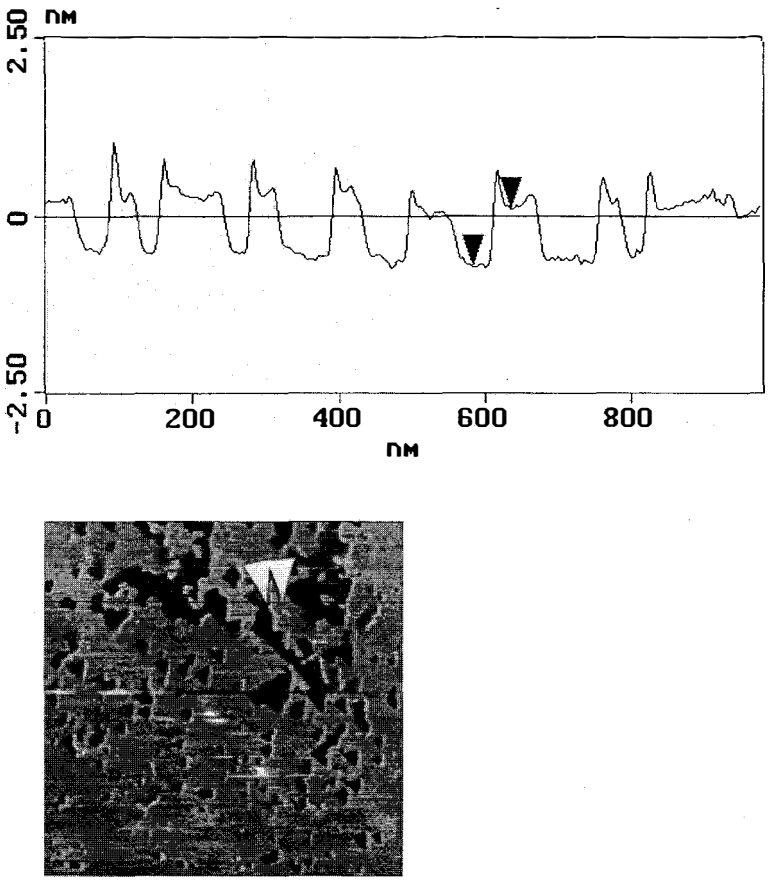


Fig. 7. AFM surface profile in the depressed area of the 2H-$NbSe_2$ single crystal after the friction test. The vertical distance between the two cursors is 8.1 Å.

We have realized friction experiments with MoO_3 in argon, Fig. 9. Despite the expectation of a lower stage of pollution in argon, we observe a larger tip/surface adhesive interaction in our force measurements, which is generally due to a pollutant meniscus around the tip.

The linear dependence F_f vs. F_n is preserved, indicating that the thickness of the adsorbed layer cannot be responsible for the strengthening of the adhesive interaction.

Furthermore, we obtain a friction coefficient value of 0.014, close to the μ value in air with respect to the uncertainty of measurements (see k value in Section 3).

Therefore, despite the expectation of a lower adhesion of F_n due to a lower degree of pollution, at first glance there is no significant difference between studies performed in air and in argon.

Nevertheless, if the measurements are realized in a proof cell filled alternately with air and argon, large and reversible increases of the friction signal intensity are observed with argon (Fig. 10) due to modification of the composition of the tip/surface interface. Hence, it appears that, although there is no significant difference between studies performed in air and in argon, the modifications of the interface composition during experiments have a profound effect on friction measurements on this scale.

In another series of experiments carried out on MoO_3, varying the scan speed is shown to induce variations of the friction signal for a constant

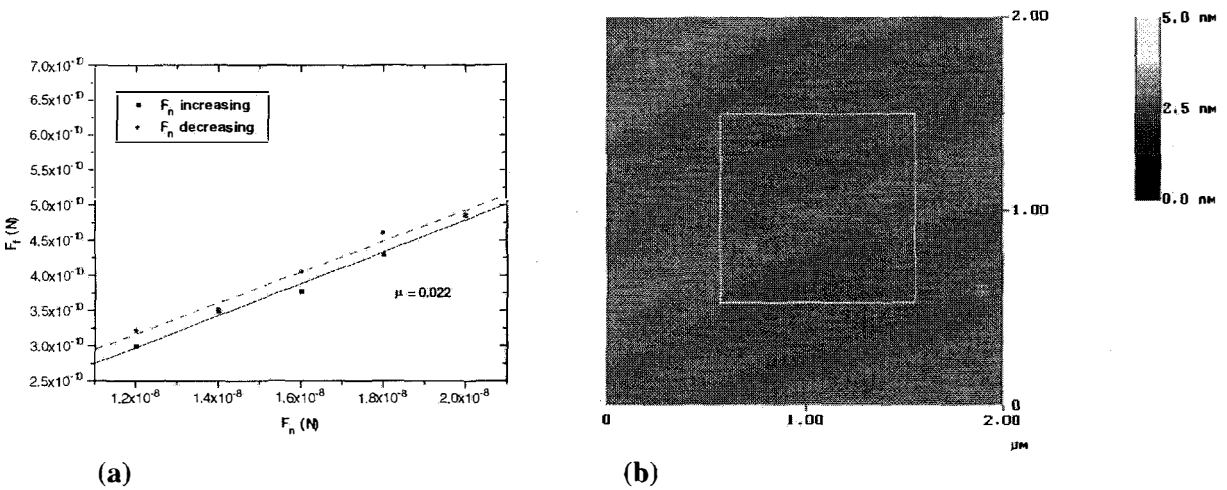


Fig. 8. (a) F_f vs. F_n during friction test on an α-MoO_3 single crystal. A mean value of $\mu = 0.022$ is extracted. (b) AFM picture recorded after the friction test, showing no significant alteration of the surface.

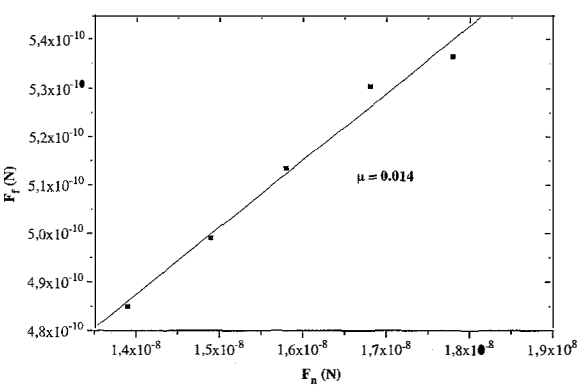


Fig. 9. F_f vs. F_n during friction test on an α-MoO_3 single crystal in an argon atmosphere. A mean value of $\mu = 0.014$ is extracted.

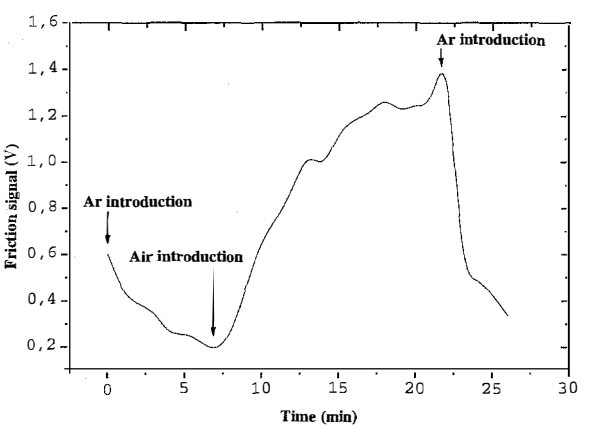


Fig. 10. Evolution of the friction signal for a constant value of F_n correlated to atmosphere changes during a test on an α-MoO_3 single crystal. The microscope is set in a proof cell filled alternately with argon and air.

value of F_n (Fig. 11), in discrepancy with Amontons' law (friction does not depend on sliding speed [10]), without variation of the topographic information (consistent pictures and constant RMS). Such a result could be explained by a modification of the tip/surface interface, and especially of the meniscus around the tip, related to the scan speed. Furthermore, before acquisition it is necessary to let the microscope scan for 5 min at least. During this period we can note a constant decrease of the friction signal, certainly due to a balancing of the sliding system.

6. Conclusion

Friction measurements on the nanometer scale have been performed with AFM. Some problems of an instrumental nature, such as cantilever and detector calibration, may occur and hinder us from obtaining reliable results. Also, depending on the nature of the investigated sample (roughness in particular), the surrounding atmosphere and the scanning parameters (scan speed for instance), the

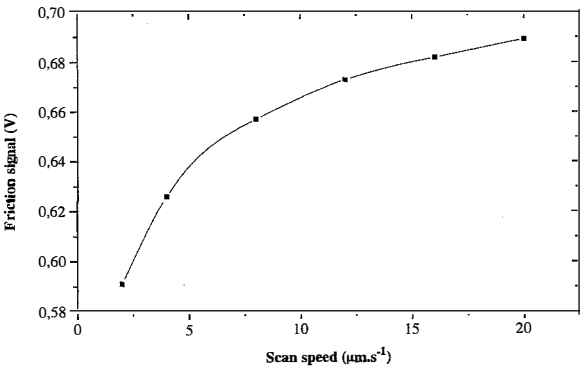


Fig. 11. Evolution of the friction signal for a constant value of F_n correlated to variation of scan speed during a test on an α-MoO_3 single crystal.

experimental results may or may not be meaningful. Therefore, well-defined experimental protocol and choice of parameters (e.g. atmosphere composition and scan speed) is absolutely necessary to overcome these unreliability difficulties. Under such conditions, there appears to be an accord between nanoscopic experimental results and macroscopic friction results predicted by models (Amontons' law for instance). As a matter of fact, some parameters of our experiments could be compared to those of macroscopic sliding. For instance, scan speed (a few micrometers per second) and strain due to the tip (about 200 MPa calculated using the Hertz model) are close to parameters of fretting on the macroscopic scale. The interest of friction measurements with AFM is to focus on phenomena such as local wear, which are not accessible with macroscopic apparatus.

In the prototype surfaces investigated here, depending upon the layered system: 2H-MoS_2, 2H-$NbSe_2$, α-MoO_3, different behaviours such as plastic deformation, local wear or unaltération have been observed. Many phenomena related to friction measurements on this scale are not yet well understood. Nevertheless, upon offering an unrivalled way to discriminate rapidly between surfaces handled under real conditions and, in the absence of wear, to qualify them in terms of nanoscopic friction coefficients, AFM appears to be a promising tool for nanotribology in both laboratory and industrial environments.

References

[1] C.M. Mate, G.M. McClelland, R. Erlandsson, S. Shiang, Phys. Rev. Lett. 59 (17) (1987) 1942.
[2] M. Hirano, K. Shinjo, Phys. Rev. B 41 (17) (1990) 11837.
[3] W. Zhong, D. Tomanek, Phys. Rev. Lett. 64 (25) (1990) 3054.
[4] M. Hirano, K. Shinjo, R. Kaneko, Y. Murata, Phys. Rev. Lett. 67 (19) (1991) 2642.
[5] G.J. Germann, S.R. Cohen, G. Neubauer, G.M. McClelland, H. Seki, D. Coulman, J. Appl. Phys. 73 (1) (1993) 163.
[6] J. Krim, Scient. Am. 10 (1996) 48; Comm. Cond. Mater. Phys. 17(5) (1995) 263.
[7] B. Bhushan, J.N. Israelachvili, U. Landman, Nature 374 (13) (1995) 607.
[8] R. Nisman, P. Smith, G.J. Vansco, Langmuir 10 (1994) 1667.
[9] J. Kerssemakers, J.T.M. De Hosson, Appl. Phys. Lett. 67 (3) (1995) 347.
[10] D. Tabor, Surf. Sci. 2 (1974) 149.
[11] M. Bingelli, C.M. Mate, Appl. Phys. Lett. 65 (4) (1994) 415.
[12] C.M.J. Putman, M. Igarashi, R. Kaneko, Appl. Phys. Lett. 66 (23) (1995) 3221.
[13] J.A. Ruan, B. Bhushan, J. Appl. Phys. 76 (9) (1994) 5022.
[14] D.F. Ogletree, R.W. Carprick, M. Salmeron, Rev. Sci. Instrum. 67 (9) (1996) 3298.
[15] J.N. Israelachvili, Intermolecular and Surface Forces, 2nd edn, Academic Press, New York, 1992.
[16] J.M. Neumeister, W.A. Ducker, Rev. Sci. Instrum. 65 (8) (1994) 2527.
[17] J.E. Sader, Rev. Sci. Instrum. 66 (9) (1995) 4583.
[18] G.Y. Chen, R. Warmack, T. Thundat, D. Pallison, A. Huang, Rev. Sci. Instrum. 65 (8) (1994) 2532.
[19] J.A. Ruan, B. Bhushan, Trans. ASME 116 (1994) 378.
[20] F. Levy (Ed.), Physics and Chemistry of Materials with Layered Structures, vol. 2, Reidel, New York, 1976.
[21] J.A. Wilson, D. Yoffe, Adv. Phys. 18 (1969) 193.
[22] C.M. Lieber, Y. Kim, Thin Solid Films 206 (1991) 355.
[23] B. Bhushan, A.V. Kulkarni, V. Kointar, M. Boehm, L. Odoni, C. Martelet, M. Belin, Langmuir 11 (1995) 3189.
[24] J.A. Ruan, B. Bhushan, J. Appl. Phys. 76 (12) (1994) 8117.