Chimia 56 (2002) 562–565

ISSN 0009–4293

Nanotribology

Enrico Gnecco, Roland Bennewitz, and Ernst Meyer*

Abstract: The study of friction and wear processes on the nanometer scale is related to the development of the atomic force microscope, where laser beams and piezoelectric elements are used to detect the motion of a micro tip across a surface in a controlled way. Friction on the nanometer scale has peculiar characteristics which are not revealed by macroscopic tools. Well-known concepts such as the coefficient of friction and the independence of friction from the scan velocity must be modified. The load dependence of friction is based on the non-linear relation $f \propto F_N^{2/3}$; the velocity dependence is determined by thermally activated processes. The environment plays also an important role and different humidity conditions may lead to different friction, due to the formation of capillary necks in the contact area. A practical use of the atomic force microscope is to check the quality of surface preparation by comparing the responses of materials under different friction and wear conditions. Interesting applications are given by magnetic storage devices and micro-electromechanical systems.

Keywords: Atomic force microscopy · Friction · Wear

The term *tribology* comes from the ancient Greek word *tribos*, which means *to rub*. It was used for the first time in 1966 by Peter Jost, and, in current use, it refers to the study of friction, wear, lubrication, and contact mechanics. *Nanotribology* encompasses the same topics but it focuses on processes occurring on the nanometer scale. Nanotribology aims to realize two important tasks: (i) to give insight into the microscopic origin of friction and wear, and (ii) to exploit the knowledge so acquired for the optimization of micro devices. Considering the spreading tendency towards miniaturization in the data storage and microelectronics industry, the economic impact of such research is easily imaginable. As an example, it is estimated that about $200 billion per year are wasted in the U.S. due to ignorance of tribology [1]. A significant part of this sum could be saved by improving our knowledge of friction and wear on the small scale. The macroscopic results of tribology cannot be directly extrapolated to the micro and nanoworld. If the linear size of a component is reduced by a factor 10, the area of the surface is reduced ten times less than the volume, which implies that the resistive forces, proportional to the area of sliding, are reduced ten times less than the inertial forces, proportional to the volume of the component. Of course, classical tools in tribological research, such pin-on-disc tribometers, are not so useful when dealing with contacts formed by a few atoms.

The observation of tribological processes down to the nanometer scale was made possible by the *atomic force microscope* (AFM), introduced by Binnig, Quate and Gerber in 1986 [2]. A sketch of the microscope is shown in Fig. 1. The instrument reveals the forces acting on a tip sliding on a surface by means of a laser beam reflected on the rear of a micro cantilever that supports the tip. The normal force between tip and surface causes the vertical deflection of the cantilever, and the friction force causes its torsion. If the deflection is kept constant by a feedback loop, friction can be monitored at a given load while scanning. In such a context, the AFM is also referred to as the *friction force microscope* (FFM). Due to the precision of the piezoelectric elements that control the relative displacement, nanometer resolution is often achieved in a controlled atmosphere or under ultra-high vacuum (UHV) conditions. M. Mate and coworkers first measured friction with atomic features between a tungsten tip and a graphite surface in air in 1987 [3]. Forces of a few tens of micronewton were detected with interferometric techniques. Nowadays, commercial AFMs can easily reveal frictional forces in the sub-nano–newton range, which is of great interest for the development of nanoscience and related technologies.

The contact between two macroscopic surfaces involves thousands of micro asperities. The AFM tip sliding on the underlying sample represents a single asperity a few nanometer in size. The mechanics of a single contact differs from that of a multiple contact. If the tip has a spherical termination the friction force, *f*, is related to the applied normal force, F_N, by the Hertzian relation $f \propto F_N^{2/3}$ [4], which seems to be in contradiction with the well-known Amonton's law, $f \propto F_N$. However, Amonton's law is recovered when statistical distributions of single asperities are considered [5].

Correspondence: Prof. E. Meyer
University of Basel
Department of Physics
Klingelbergstrasse 82
CH–4056 Basel
Tel.: +41 61 267 3724
Fax: +41 61 267 3784
E-Mail: Ernst.Meyer@unibas.ch

CHIMIA 2002, 56, No. 10

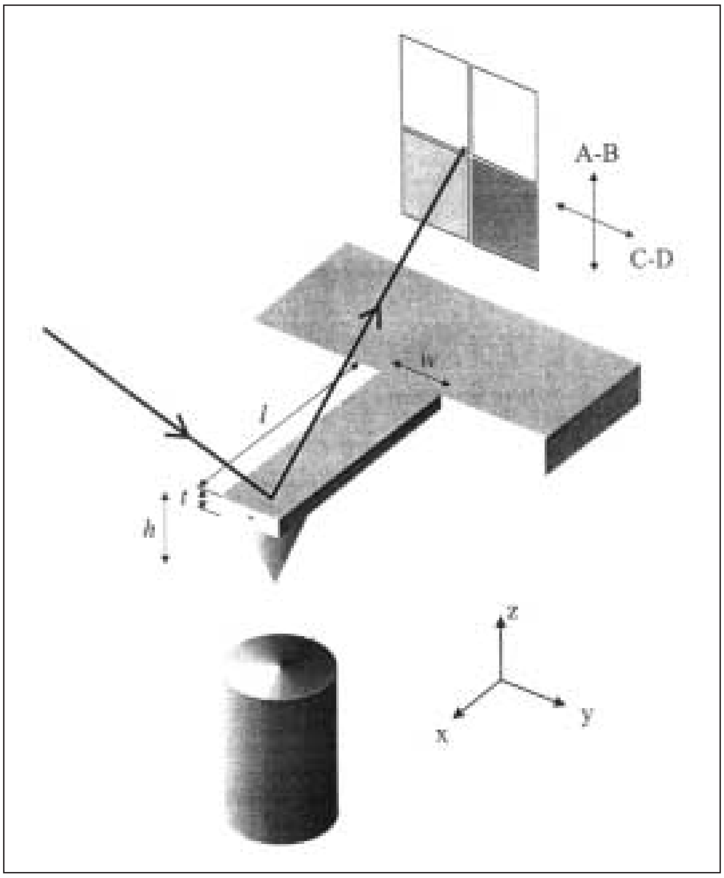

Fig. 1. Schematic diagram of a beam-deflection AFM

Experiments on graphite, diamond, amorphous carbon, ionic crystals, and metals revealed that adhesive forces play an important role in the contact between tip and surface [4][6–9]. These effects are considered in extended Hertzian models, which agree well with the experimental data in extreme cases where elastic deformation or, conversely, adhesion dominates [10][11]. Even the classical Coulomb's law of friction, which states that friction is independent of the sliding speed, is not fulfilled in AFM experiments, where relative velocities lie in the nm/s to μm/s range. In such a case logarithmic dependencies of friction on velocity are found due to thermally activated processes occurring in the contact regions. The chemical bonds in the contact area may be suddenly broken by thermal vibrations, an effect which is enhanced at low speeds, where it provokes a slight decrease of friction. This behavior was observed on ionic crystals and metals in UHV [12][13] and recently also on hydrophobic surfaces in controlled humidity [14]. In contrast, hydrophilic surfaces exhibit a different behavior, where friction decreases with velocity, due to the formation of capillary bridges, which hinder the detachment of the surfaces.

In a well-defined environment, the frictional response of the AFM depends, of course, on the surface under investigation. Although chemical identification is not possible by frictional mapping, useful information is drawn in particular cases. Fig. 2a shows a friction map detected on a silicon sample covered by two monolayers of a Langmuir-Blodgett film [15]. The two materials react differently to the stress exerted by the tip, and the uncovered regions of the substrate are easily recognized in the friction map. This kind of information is not revealed by the corresponding topography (Fig. 2b), which proves the material-specific contrast achieved by friction force microscopy.

On the atomic scale friction maps are far from uniform, as they reproduce the structure of the surface lattice. Fig. 3a shows a friction force map obtained with a silicon tip sliding on sodium chloride in UHV. A single scan line across the surface shows a saw tooth behavior with the periodicity of the lattice (Fig. 3b). When the scan direction is inverted the lateral force is also re-

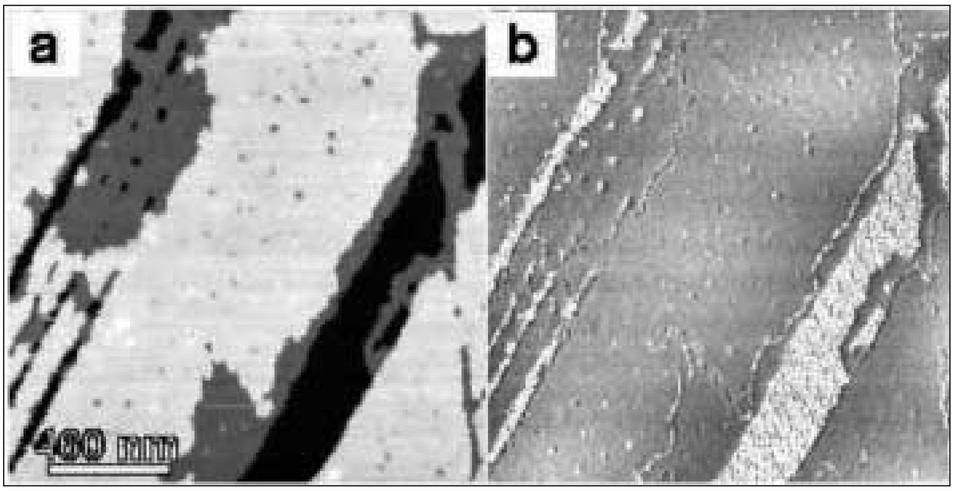

Fig. 2. (a) Topography and (b) friction image of two bilayers of Cd-arachidate on a silicon wafer.

versed. The area of the *friction loop* so obtained corresponds to the energy dissipated in a complete scan. A mean energy of about 1 eV per 'tooth' was dissipated in the case of Fig. 3. These features are the direct consequence of the *stick-slip* movement of the tip, which, driven by the cantilever, jumps periodically from a given equilibrium position on the lattice to the next one. Due to the thermal activation, jumps occur at different angles of torsion. A simple explanation of the atomic stick-slip relies on the Tomlinson model [16]; an analytical discussion of the model, which includes thermal effects, is given in [17].

The Tomlinson model loses its validity if plastic deformation and wear take place, which can occur even at loads of a few nanonewtons. In some cases the same tip can be used both to scratch and image the damaged surface [18]; for example, we have observed debris of potassium bromide in UHV recrystallized in mounds with the same lattice distance and orientation of the original surface (Fig. 4). The AFM revealed that this kind of wear consisted of a continuous abrasion of the surface, rather than of a series of abrupt rupture events; a quantification of the energy dissipated in the wear process is also possible. Fig. 5 shows five pits obtained by vibrating the AFM tip on KBr with different loads. For example, the second pit corresponds to the removal of 850 couples of ions, whereas the energy dissipated to produce it could break 2850 atomic bonds, as estimated from the areas of the friction loops acquired by scanning. Thus, only a minor part of the work done by the tip went into wear (about 30%).

A different kind of energy dissipation is observed when the AFM is operated in non-contact mode (NC-AFM), *i.e.* the cantilever is excited close to its resonance frequency and the energy required to keep the oscillation amplitude constant is monitored [19]. The origin of dissipation in NC-AFM is not clear, although it is recognized that Joule dissipation has a primary role at long distances. Very recently, energy dissipation was measured when the torsional oscillation of the cantilever is excited [20]; in future it is not excluded that the energy losses observed with FFM and NC-AFM will be considered in an unified framework.

Besides AFM, other experimental techniques are relevant in nanotribology, *i.e.* the *surface force apparatus* (SFA) and the *quartz crystal microbalance* (QCM). The SFA consists of a pair of mica sheets which

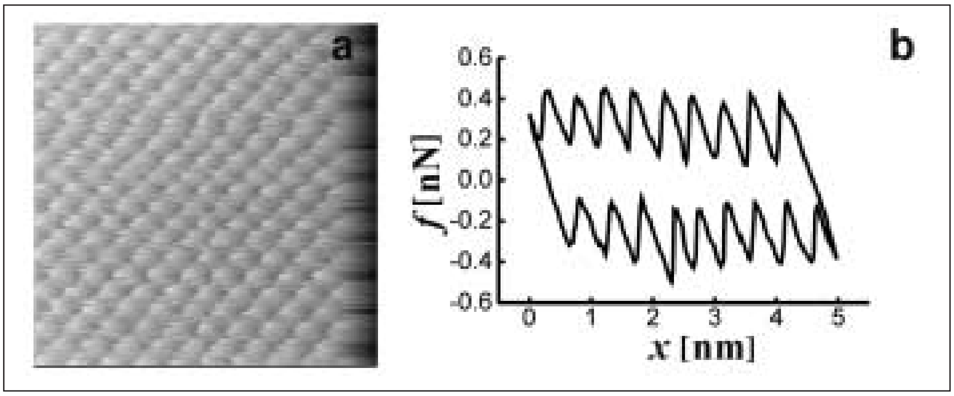

Fig. 3. (a) Lateral force map of NaCl(100) at F_N = 0.65 nN and ν = nm/s. (b) Friction loop formed by two scan lines measured forwards and backwards, respectively.

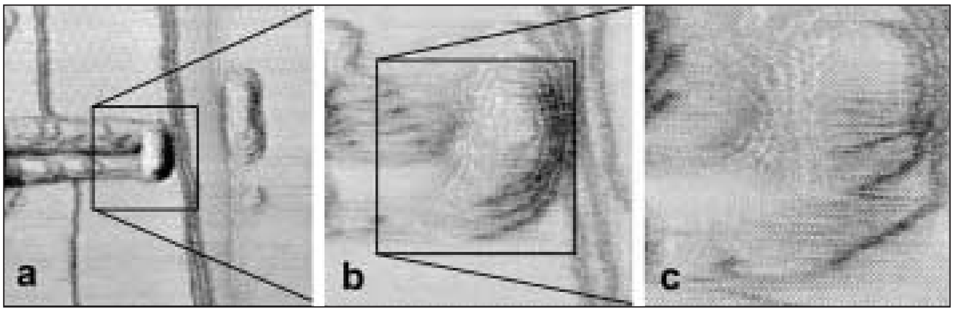

Fig. 4. (a) Lateral force images acquired at the end of a groove produced by 256 scratches with F_N = 20.9 nN and ν = 300 nm/s. Frame sizes: (a) 115 nm, (b) 39 nm, (c) 25 nm.

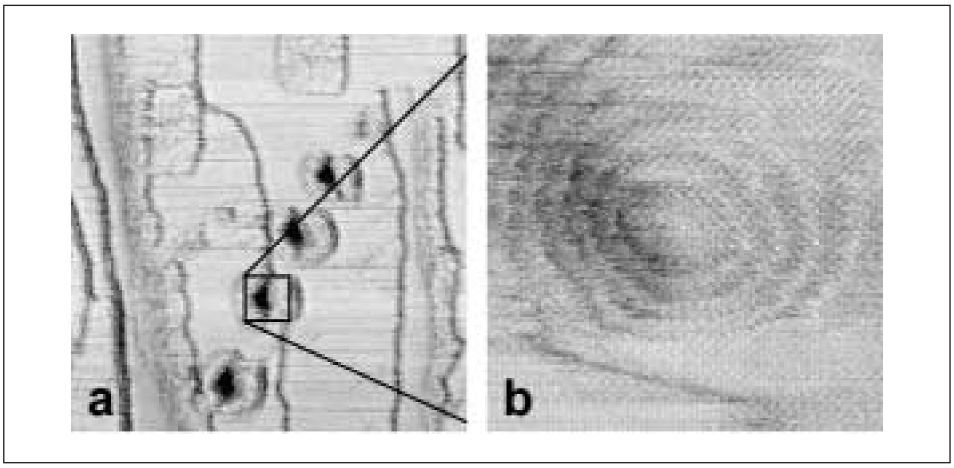

Fig. 5. Lateral force images of pits and mounds produced by 256 scratches on 5×5 nm^2 areas with different loads F_N = 5.7, 10.0, 14.3, 18.6, and 22.8 nN. Frame sizes: (a) 150 nm, (b) 17 nm.

CHIMIA **2002**, *56*, No. 10

are pressed together and reciprocally translated under pressure. The contact area is measured by optical or capacitive techniques. Despite the limited resolution of the instrument, the SFA was successfully applied to reveal the effects of a liquid layer between the two surfaces in contact. As an example, the layering of the liquid in discrete strata was studied as a function of the applied load [21]. The QCM, which is commonly used to measure thin film growth, was first applied to nanotribology by Krim and coworkers [22]. The QCM consists of a single crystal of quartz which oscillates in a shear mode with a high quality factor Q. Changes of Q can be related to the slippage of an adsorbed film. For example, the slip times for chemisorbed oxygen/silver surfaces were found to be longer than for silver, which suggests an important electronic contribution to friction in the case of conducting surfaces [23].

Strong support for nanotribology is also given by molecular dynamics (MD) simulations. Landman and coworkers first used MD to study adhesion, nanoindentation and fracture occurring when a nickel tip approaches a gold surface [24]. The MD technique deals with time scales which are orders of magnitude shorter than in the experiments, and it gives insight on details which are difficult to observe in other ways, like the displacement of the surfaces scanned by the AFM tip, and the transfer of material onto the tip at high loads [25][26].

Possible industrial applications of the new tools at our disposal are discussed in the handbook of tribology edited by Bhushan [27]. Among them, magnetic storage devices and microelectromechanical systems (MEMS) are domains where AFM is an ideal testing tool. The need for high recording densities in magnetic storage devices requires a reduction in the height of the read/write magnetic head with respect to the magnetic medium, which can lead to contact with serious consequences for the device. These problems are even more severe in MEMS, where objects a few micrometers in size are repeatedly brought into contact at high speed.

At the end of this overview we searched the term ‘tribology’ on the web, and obtained 42 500 results. The term ‘nanotribology’ gave 1800 results, which means a relative ratio of 42×10^{-3} in the number of occurrences. As the ratio of the linear dimensions of the objects considered in the two fields is 10^{-9}, the result gives an idea of the interest of people in this small but fascinating new branch of physics and technology.

Received: July 25, 2002

[1] ‘Handbook of Micro/Nanotribology’, Ed. B. Bhushan, CRC Press, Boca Raton, **1995**, p. 5.
[2] G. Binnig, C.F. Quate, C. Gerber, *Phys. Rev. Lett.* **1986**, *56*, 930.
[3] C.M. Mate, G.M. McClelland, R. Erlandsson, S. Chiang, *Phys. Rev. Lett.* **1987**, *59*, 1942.
[4] U.D. Schwarz, O. Zwörner, P. Köster, R. Wiesendanger, *Phys. Rev. B* **1997**, *56*, 6987.
[5] J.A. Greenwood, J.B.P. Williamson, *Proc. Roy. Soc. Lond. A* **1966**, *295*, 300.
[6] M. Enachescu, R.J.A. van der Oetelaar, R.W. Carpick, D.F. Ogletree, C.F.J. Flipse, M. Salmeron, *Phys. Rev. Lett.* **1998**, *81*, 1877.
[7] E. Meyer, R. Lüthi, L. Howald, M. Bammerlin, M. Guggisberg, H.-J. Güntherodt, *J. Vac. Sci. Techn. B*, **1996**, *14*, 1285.
[8] R.W. Carpick, N. Agraït, D.F. Ogletree, M. Salmeron, *J. Vac. Sci. Techn. B* **1996**, *14*, 1289.
[9] C. Polaczyk, T. Schneider, J. Schöfer, E. Santner, *Surf. Sci.* **1998**, *402*, 454.
[10] K.L. Johnson, K. Kendall, A.D. Roberts, *Proc. Roy. Soc. Lond. A* **1971**, *324*, 301.
[11] B.V. Derjaguin, V.M. Muller, Y.P. Toporov, *J. Colloid Interface Sci.* **1975**, *53*, 314.
[12] E. Gnecco, R. Bennewitz, T. Gyalog, Ch. Loppacher, M. Bammerlin, E. Meyer, H.-J. Güntherodt, *Phys. Rev. Lett.* **2000**, *84*, 1172.
[13] R. Bennewitz, T. Gyalog, M. Guggisberg, M. Bammerlin, E. Meyer, H.-J. Güntherodt, *Phys. Rev. B* **1999**, *60*, R11301.
[14] E. Riedo, F. Levy, H. Brune, *Phys. Rev. Lett.* **2002**, *88*, 185505.
[15] E. Meyer, R.M. Overney, L. Howald, R. Lüthi, J. Frommer, H.-J. Güntherodt, *Phys. Rev. Lett*. **1992**, *69*, 1777.
[16] G.A. Tomlinson, *Philosoph. Mag. Ser.* **1929**, *7*, 905.
[17] E. Gnecco, R. Bennewitz, T. Gyalog, E. Meyer, *J. Phys.: Condens. Matter* **2001**, *13*, R619.
[18] E. Gnecco, R. Bennewitz, E. Meyer, *Phys. Rev. Lett*. **2002**, *88*, 215501.
[19] C. Loppacher, R. Bennewitz, O. Pfeiffer, M. Guggisberg, M. Bammerlin, S. Schär, V. Barwich, A. Baratoff, E. Meyer, *Phys. Rev. B* **2000**, *62*, 13674.
[20] O. Pfeiffer, R. Bennewitz, A. Baratoff, E. Meyer, P. Grütter, *Phys. Rev. B* **2002**, *65*, 161403.
[21] P. Frantz, N. Agraït, M. Salmeron, *Langmuir* **1996**, *12*, 3289.
[22] J. Krim, D.H. Solina, R. Chiarello, *Phys. Rev. Lett*. **1991**, *66*, 181.
[23] C. Mak, C. Daly, J. Krim, *Phys. Rev. Lett.* **1994**, *253*, 190.
[24] U. Landman, W.D. Luedtke, N.A. Burnham, R.J. Colton, *Science* **1990**, *248*, 454.
[25] A.L. Shluger, A.L. Rohl, R.T. Williams, R.M. Wilson, *Phys. Rev. B* **1995**, *52*, 11398.
[26] M.R. Sørensen, K.W. Jacobsen, P. Stoltze, *Phys. Rev. B* **1996**, *53*, 2101.
[27] ‘Modern Tribology Handbook’, Ed. B. Bhushan, CRC Press, Boca Raton, **2001**.