Surfaces in relative motion: bionanotribological investigations

Ille C. Gebeshuber[1], Herbert Stachelberger[2] and Manfred Drack[3]

md@grat.at

[1] Austrian Center of Competence for Tribology AC²T research GmbH, Viktor Kaplan-Strasse 2, A-2700 Wiener Neustadt, Austria & Institut für Allgemeine Physik, Technische Universität Wien, Wiedner Hauptstr. 8-10/E134, A-1040 Vienna, Austria

[2] Institute of Chemical Engineering, Technische Universität Wien, Getreidemarkt 9/E1667, A-1060 Vienna, Austria

[3] Center for Appropriate Technology, Technische Universität Wien, Wiedner Hauptstr. 8-10/E0965, A-1040 Vienna, Austria

Abstract

Tribology is the science of friction, adhesion, lubrication and wear. Continuous miniaturisation of technological devices like hard disc drives and biosensors increase the necessity for the fundamental understanding of tribological phenomena at the micro- and nanoscale.

Biological systems show optimised performance also at this scale. After all, Nature is an “engineering office” which has been “in business” for millions of years. Examples for biological friction systems at different length scales are bacterial flagellae, joints and articular cartilage and muscle connective tissues[1].

Our model system for bionanotribological investigations are diatoms[2], for they are small, highly reproductive, and since many of them are transparent, they are accessible with different kinds of optical microscopy methods. Furthermore, certain diatoms have proved to be rewarding samples for mechanical and topological *in vivo* investigations on the nanoscale[3].

There are several diatom species which actively move (e.g. *Bacillaria paxillifer* forms colonies in which the single cells move along each other) or which can – as cell colonies – be elongated a major fraction of their original length (e.g. *Ellerbeckia arenaria* colonies can reversibly be elongated by one third of their original length[4,5]). Therefore, we assume that some sort of lubrication is present in these species. Pending endeavours in diatom bionanotribology comprise techniques like atomic force microscopy, histochemical analysis, infrared spectrometry, molecular spectroscopy and confocal infrared microscopy.

1. Introduction

The aim of biotribology is to gather information about friction, adhesion, lubrication and wear of biological systems and to apply this knowledge to innovate technology as well as to develop environmentally sound products. More specific, the development of monolayer lubricants, of new adhesives and the construction of better artificial joints can result from such studies[1]. Especially in sensitive environments, the use of non toxic biodegradable lubricants is of paramount interest[6].

The total amount of chain oils discharged into forest nature was calculated to be about two million litres per annum. The biodegradability of tall oil and rape seed oil (green oils) is clearly faster than that of mineral oils both in the laboratory and on the field[7].

Some parameters related to environmental issues, like biodegradable performance, energy balance, eco-toxicity and technical performances (wearing and cleanliness) have been studied in detail by JAHAN[8]. The definition of future standards should take into account all the environmental characteristics of the lubricant.

The release of lubricants into the water stream after passage through hydraulic turbines is an environmental issue of concern. It was found that the use of self-lubricating bearing materials is the predominant technology available to satisfy environmental concerns for hydraulic equipment[9]. As an alternative to the currently widely used metallic and polymer materials, hydraulic equipment can be lubricated with an environmentally sound lubricant. However, further research is necessary to optimize these lubricants concerning biodegradability and non-toxicity.

2. Diatoms as tribological model systems

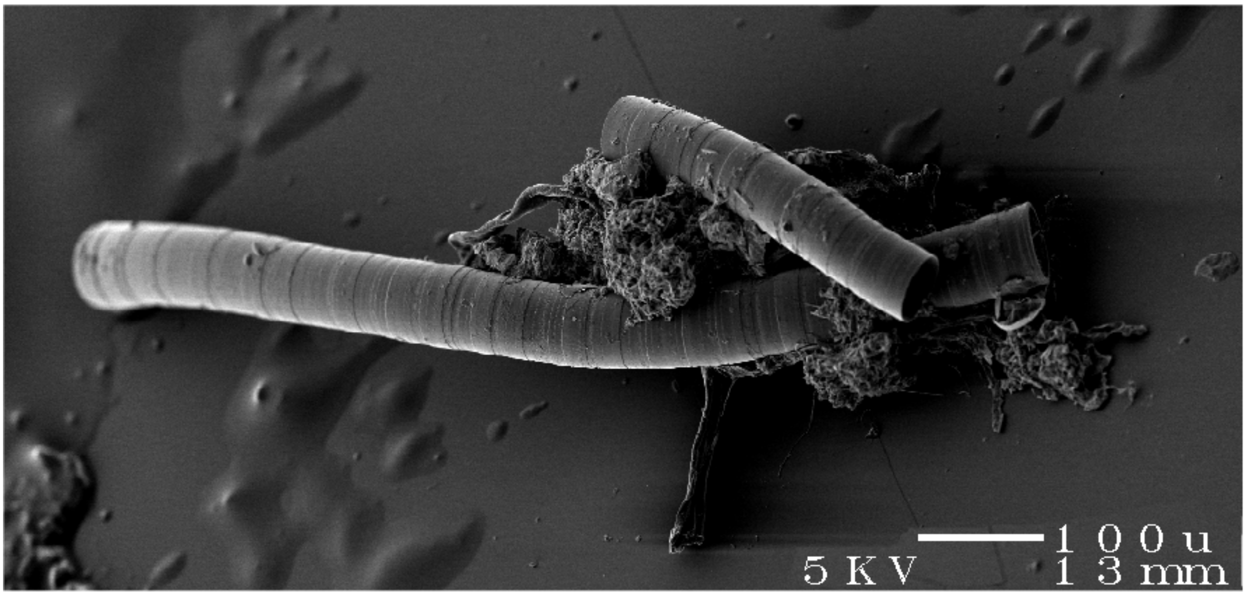
Biological systems with moving parts have optimised their lubrication during evolution. Algae can serve as interesting model organisms for nanotribological investigations: they are small, mostly easy to cultivate, highly reproductive, and since many of them are transparent, they are accessible to different kinds of optical microscopy methods. For an overview on algae see VAN DEN HOEK and coauthors[10]. The class within the algae, which we favour for tribological studies, are diatoms. For an overview on diatoms see ROUND and coauthors[2].

Diatoms are unicellular microalgae with a cell wall consisting of a siliceous skeleton enveloped by an organic case essentially composed of polysaccharides and proteins[11]. The cell walls form a pillbox-like shell (called the frustule) consisting of two valves that fit within each other with the help of a set of girdle bands. Frustules vary greatly in shape, ranging from box-shaped to cylindrical, they can be symmetrical as well as asymmetrical and exhibit an amazing diversity of nanostructured frameworks.

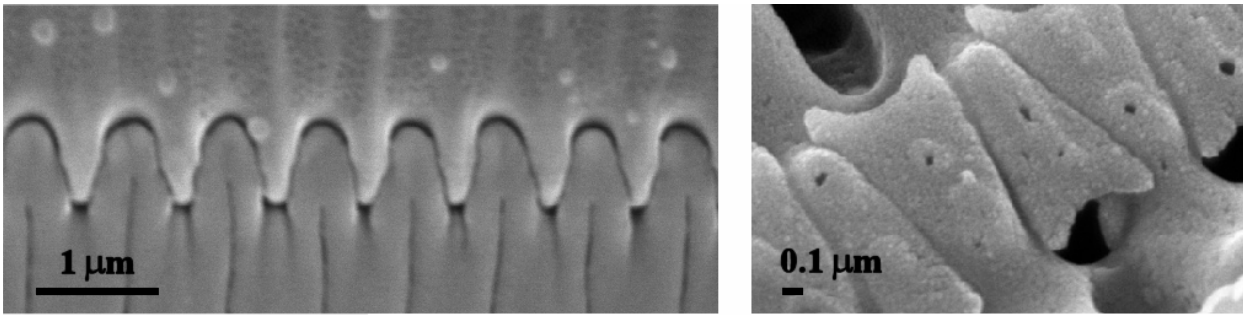
Diatoms are found in both freshwater and marine environments, as well as in moist soils, and on moist surfaces. They are either freely floating (planktonic forms) or attached to a substrate (benthic forms), and some species may form chains of cells of varying length. Individual diatoms range from 2 micrometers up to several millimeters in size, although only few species are larger than 200 micrometers. Diatoms as a group are very diverse with 12 000 to 60 000 species reported[12,13].

Ellerbeckia arenaria is a diatom which lives in waterfalls. *E. arenaria* cells form stringlike colonies which can be several millimeters long. Not only that these colonies can be elongated about on third of their original length, when released, they even swings back like a spring[4,5]! This interesting feature makes us suggest that there are parts in relative motion in this species, facing friction and wear.

Scanning Electron Micrograph (SEM) of two strings of two* Ellerbeckia arenaria *colonies

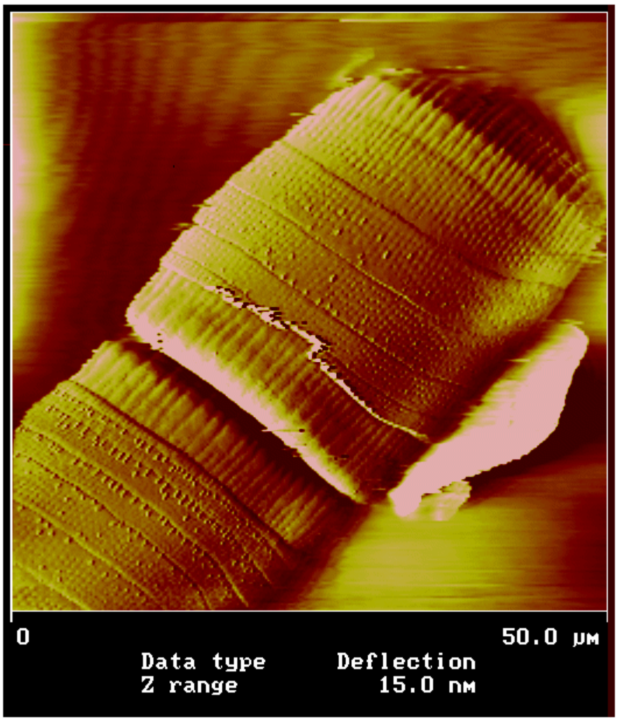


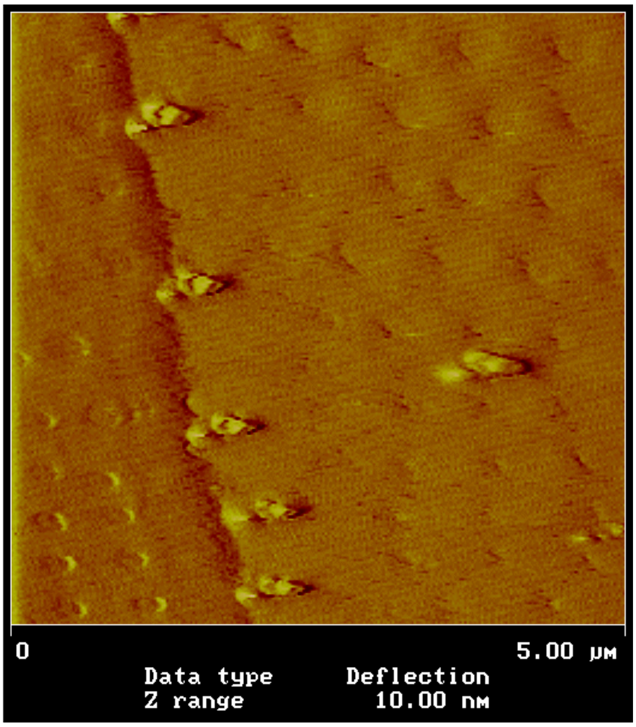
***Structural details of* E. arenaria *(left) and another diatom species, possibly* Melosira sp.**
(right, © Centre for Microscopy & Microanalysis, University of Queensland, AU)



Diatoms seem to show highly efficient self lubrication while girdle bands telescope, as the cells elongate and grow[3]. When we investigated diatoms *in vivo* on the nanoscale with an atomic force microscope, we found bead-like features on the edges of girdle bands which might well act as lubricant, either by means of ball bearings or as solid lubricant – or following a lubrication strategy which still is completely unknown to engineers.

Atomic force microscopy of two interconnected diatom cells showing bead-like features, which might act as biogenic lubricants[3] © J. Microsc. Oxford





Although diatoms are plants, there are several species within this group which actively move: *Pseu-donitzschia sp*. and *Bacillaria paxillifer* (former name because if its unusual behaviour: *Bacillaria paradoxa*) are good examples. *B. paxillifer* shows a remarkable form of gliding motility: Entire colonies of 5 to 30 cells expand and contract rhythmically and coordinated[14]. Anomalously viscous mucilage excreted by a fissure, which covers 99% of the cell length, may provide the means for the cell-to-cell attachment[15].

3. Friction, Adhesion, Lubrication and Wear

Biological and technical microsystems have many things in common. First of all, the mechanical interaction occurs at identical length and force scales[16]. In both types of systems, surface properties, e.g. wettability, nanostructure or surface chemistry have a strong impact on the performance of the system. The main difference between biological and technical microsystems is their performance. Biological systems perform reliably, whereas technological systems continuously encounter technical problems due to the lack of reliable concepts.

Micro- and nanotribology – considered as the mechanical interaction of moving bodies – is the science of friction, adhesion, lubrication and wear on the length scale of micrometers to nanometers and the force scale of millinewtons to nanonewtons. Biomicro- and -nanotribology is a new interdisciplinary field of research combining methods and knowledge of physics, chemistry, mechanics and biology.

Some of the publications about nanoscale force measurements in diatoms[e.g.3,17,18,19] are indeed more than “just” nanoscale measurements, they are on the single molecule level: HIGGINS and coworkers report binding forces in the range of a few hundred piconewtons (1 pN = 1^{-12} N) for single adhesive strands protruding from the raphe of *C. australis*[19].

If two bodies contact each other in a point or a line, then the action of the compressive forces results in deformation. This has a strong impact on adhesion and friction. **Contact mechanics** represents a sophisticated synthesis of elasticity theory, fracture mechanics and surface science. Most of the contact models in tribology are based on the assumption of the contact of ideally smooth spheres. However, biological surfaces are not completely smooth. Recent models also incorporate the effects of roughness as well as the action of attractive forces inside the contact and in the vicinity of the contact radius. Since biological surfaces can be extremely flexible and soft, an intimate contact can be established. For a good overview on contact mechanics in tribology, see GORYACHEVA[20].

Friction is an everyday experience. On one hand, friction is a desired property, and in fact necessary, for example for an insect to initiate motion. On the other hand, friction means loss of energy, and when friction is accompanied by wear, it also means damage and destruction.

Macroscale friction can be considerably caused by mechanical interlock due to the roughness of the contacting surfaces. To maintain the motion of a body against the friction force, it is necessary to perform work. Not only a moving body experiences a friction force – force is also necessary to overcome inertia and static friction. It is necessary to differentiate between static, sliding and rolling friction. In sliding and rolling friction, wear is involved, and debris form a third body.

In 2500 before Christ the Egyptians found out that their carriages slid better on damp sand and therefore poured water (or possibly an emulsion of olive oil) on their pathway!

The history of microfriction is much shorter. Friction measured on different length and force scales very often shows instabilities expressed in periodic stick/slip cycles. Squeaking doors or violin playing are examples of stick/slip on the macroscale. In the microworld, stick/slips appear in mechanical and in biological systems. Even on the atomic scale, stick/slip phenomena are revealed by atomic force microscopy. Many different mechanisms may come into play to construct friction forces and that it is not yet established what mechanism is predominant at what length scale.

Adhesion can be regarded as a state of minimum energy that is attained when two solids are brought into intimate contact. This means that a certain force is needed to separate the solids. Adhesion increases with decreasing roughness, showing that adhesion has a distinct range of action. In addition to small roughness, soft and flexible materials can also show strong adhesion, since these materials replicate the roughness profile of the counter surface, leading to intimate contact.

The shortest range of interaction is governed by molecular forces. To induce strong attraction, the spacing between the solids must be reduced to a distance lower than about 10 nm. In 1999, SMITH and coworkers attempted to explain the molecular mechanistic origin of the toughness of natural adhesives, fibres and composites[21]. These authors mainly concentrated on the abalone shell, which is a composite of calcium carbonate plates sandwiched between organic material. This biomaterial, where the organic component comprises just a few per cent of the composite by weight, is 3 000 times more fracture resistant than a single crystal of the pure mineral[22]! Natural materials are renowned for their strength and toughness. Another example: spider dragline silk has a breakage energy per unit weight two orders of magnitude greater than high tensile steel[23].

Lubrication is one of the key aspects of micro- and nanotribology[24]. A lubricant is mainly used to keep two solids at a distance where the asperities are prevented from getting in direct mechanical contact with each other. This requires that the lubricant has to be sufficiently viscous in order for it not to be squeezed out of the contact. To describe lubrication effects at the macroscale, a Newtonian fluid model normally suffices. As the dimensions and forces decrease, nonlinear effects have to be included. Friction and adhesion forces with magnitudes lower than about 1 mN acting on contact areas in the micrometer range are strongly affected by the action of adsorbed liquids.

As the thickness of the lubricant decreases below about 10 nm, molecular influences become notable. Significantly altered physical properties are found in the range of a few monolayers[25]. The main effect in thin film lubrication is solidification. Continuum mechanics looses its ability at very small separations of the bodies. Sophisticated simulation techniques have to be applied.

Graphite and MoS_2 are the most widely used materials for **solid lubrication**. These materials have a layered crystalline structure and show strong anisotropy in their response to shear, leading to the sliding of individual layers. A possible way to obtain new solid-like lubricants involves careful selection of molecular properties leading to a robust lubrication film. Valuable clues about desirable molecular properties might very well arise from studies on natural lubricants.

Like adhesion and friction, **wear** can also be divided into macro-, micro- and nano-events. On the macroscale, repeated plastic deformation and the generation of surface and subsurface failures and heat during friction lead to degradation of the material that is called wear. Microscale wear analysis is for example performed for hip-replacement materials[26]. Wear on the atomic scale is accompanied with the formation of crystallographic defects like point defects or kinks.

4. Outlook

Nature solves its lubrication problems with water as a base stock and biomolecules as additives. The precise mechanisms differ, depending on the specific application, and thus e.g. the hip, the mouth, the eye, and the lungs all involve different, but related biomolecules.

Today, advances in physics and chemistry enable us to measure the adhesion, friction, stress and wear of biological structures on the micro- and nanonewton scale. Furthermore, the chemical composition and properties of natural adhesives and lubricants are accessible to chemical analysis.

We suggest *Pseudonitzschia sp.*, *B. paradoxa* and *E. arenaria* for detailed bionanotribological investigations. Pending experiments comprise determination of the hardness of the bead-like features in *E. arenaria* (to determine whether a solid lubricant is present), confocal microscopy combined with histochemical analysis of diatom mucilage, and techniques like mass and infrared spectrometry for organic compound identification on gliding surfaces. Furthermore, systematic analysis of diatom adhesives and lubricants to determine their strength and durability is highly desirable.

The adhesive and lubricant industry can profit from new ideas (which are in fact millions of years old), and knowledge of the diatom adhesives might promote the development of adhesive solvents for removal of undesirable organisms (e.g. in tanks or pipelines).

Acknowledgements

ICG thanks PK Hansma from UCSB, who introduced her to AFM and provided the perfect environment to start her work with diatoms. What he can teach about doing science has no parallel. The authors thank AM Schmid for revealing the interesting mechanical properties and providing first samples of *E. arenaria* and R Krisai for introducing us to their natural habitat. JC Weaver from UCSB helped in using the SEM. Furthermore, the authors express gratitude for stimulating discussions with RM Crawford, F Kinnen and J Kreuzer. A special thank you goes to M Scherge and S Gorb, who with their book “Biological Micro- and Nanotribology – Nature´s solutions” reinforced our decision to work on diatom bionanotribology.

Bibliography

[1] Scherge, M and Gorb, S: Biological Micro- and Nanotribology. Nature's Solutions (NanoScience and Technology), Springer-Verlag, Berlin Heidelberg (2001).

[2] Round, FE, Crawford, RM and Mann, DG: Diatoms: Biology and morphology of the genera. Cambridge University Press (1990).

[3] Gebeshuber, IC, Kindt, JH, Thompson, JB, Del Amo, Y, Stachelberger, H, Brzezinski, M, Stucky, GD, Morse, DE and Hansma, PK: Atomic force microscopy study of living diatoms in ambient conditions. J. Microsc.-Oxf. (2003) vol. 212(3), pp. 292-301.

[4] Schmid, AM: personal communication (2001).

[5] Gebeshuber, IC and Kindt, JH: unpublished data (2001).

[6] Landwehr, J and Goetz, D: Nachwachsende Rohstoffe für die Chemie. Edited by Fachagentur Nachwachsende Rohstoffe e.V. Landwirtschaftsverlag, Münster (2003) p.343.

[7] Lauhanen, R, Kolppanen, R, Kuokkanen, T, Sarpola, S and Lehtinen, M: The environmental effects of oils used in forest operations. Teho Helsinki (1998) vol. 48(4), pp. 32-34.

[8] Jahan, A: Lubrifiants biodegradables - "la solution du futur?" Pétrole et Techniques (1997) vol. 407, pp. 42-45.

[9] Brown, KJ and Matson, K and Taylor, D: New lubricating material for hydraulic turbine equipment. Proceedings Canadian Electrical Association engineering and operating conference. Montreal (1993) pp. 1-20.

[10] van den Hoek, C, Mann, D and Jahns, HM: Algae: An introduction to phycology. Cambridge University Press (1995).

[11] Hecky, RE, Mopper, K, Kilham, P and Degens ET: The amino acid and sugar composition of diatom cell walls. Marine Biol. (1973) Vol. 19, pp. 323-331.

[12] Werner, D: The biology of diatoms, University of California Press (1977).

[13] Gordon, R and Drum, RW: The chemical basis for diatom morphogenesis. Int. Rev. Cytol. (1994) vol. 150, pp. 243-372.

[14] Kapinga, MRM and Gordon, R: Cell motility rhythms in *B. paxillifer*. Diatom Res. (1992) vol. 7(2) pp. 221-225.

[15] Kapinga, MRM and Gordon, R: Cell attachment in the motile colonial diatom *Bacillaria paxillifer*. Diatom Res. (1992) vol. 7(2) pp. 215-220.

[16] Fujimasa, I: Micromachines: A New Era in Mechanical Engineering. (1997) Oxford University Press.

[17] Gebeshuber, IC, Thompson, JB, Del Amo, Y, Stachelberger, H and Kindt JH: *In vivo* nanoscale atomic force microscopy investigation of diatom adhesion properties. Mat. Sci. Technol. (2002) vol. 18, pp. 763-766.

[18] Higgins, MJ, Sader, JE, Mulvaney, P and Wetherbee, R: Probing the surface of living diatoms with atomic force microscopy: the nanostructure and nanomechanical properties of the mucilage layer. J. Phycol. (2003) vol. 39, pp. 722-734.

[19] Higgins, MJ, Molino, P, Mulvaney, P and Wetherbee R: The structure and nanomechanical properties of the adhesive mucilage that mediates diatom-substratum adhesion and motility. J. Phycol. (2003) vol. 39, pp. 1181-1193.

[20] Goryacheva, IG: Contact mechanics in tribology (Solid mechanics and its applications), Kluwer Academic Publishers, The Netherlands (1998).

[21] Smith, BL, Schäffer, TE, Viani, M, Thompson, JB, Frederick, NA, Kindt, J, Belcher, A, Stucky, GD, Morse, DE and Hansma, PK: Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites. Nature (1999) vol. 399, pp. 761 – 763.

[22] Watable, N and Wilbur, KM (eds.): The mechanisms of biomineralization in invertebrates and plants. University of South Carolina Press, Columbia, SC (1976).

[23] Hinman, M, Dong, Z, Xu, M and Lewis, RV: Biomolecular Materials. Edited by Viney, C, Case, ST and Waite, JH, Materials Research Soc., Pittsburgh (1993) pp. 25-34.

[24] Hsu, SM and Zhang, K: Lubrication: Traditional to Nano-scale Films, in Micro/Nanotribology and its Applications. Edited by Bhushan, B, Kluwer Academic Publishers, The Netherlands (1997) pp. 399-414.

[25] Kolm, R, Jogl, C, Kleiner, R, Gebeshuber, IC, Werner, WSM and Störi H: Characterisation of monomolecular lubricant films, Proceedings 14th International Colloqium Tribology, Technische Akademie Esslingen (2004).

[26] Scholes, SC, Unsworth, A, Hall, RM and Scott, R: The effects of material combination and lubricant on the friction of total hip prostheses. Wear (2000) vol. 241(2), pp. 209-213.