Gebeshuber I.C., Stachelberger H., Drack M. and Franek F. (2005) *"Biotribology at the micro- and nanoscale as exemplified by diatoms"*, Proceedings 1st Vienna International Conference Micro-and Nano-Technology, March 9-11, 2005, Vienna, Austria, pp. 135-140.

BIOTRIBOLOGY AT THE MICRO- AND NANOSCALE AS EXEMPLIFIED BY DIATOMS

I.C. Gebeshuber[a,b], H. Stachelberger[c], M. Drack[d] and F. Franek[a]

[a] Austrian Center of Competence for Tribology AC^{2}T Research GmbH, Viktor Kaplan-Straße 2, A-2700 Wiener Neustadt, Austria
[b] Institut für Allgemeine Physik, Technische Universität Wien, Wiedner Hauptstraße 8-10/E134, A-1040 Vienna, Austria
[c] Institute of Chemical Engineering, Technische Universität Wien, Getreidemarkt 9/E1667, A-1060 Vienna, Austria
[d] Center for Appropriate Technology, Technische Universität Wien, Wiedner Hauptstraße 8-10/E0965, A-1040 Vienna, Austria

SUMMARY

Systems with parts in relative motion experience friction and wear. The need to understand tribology on the micro- and nanoscale increases in importance with decreasing technological device sizes. Micro- and nanoelectromechanical systems often experience failure due to stiction (static friction).

During millions of years of evolution, natural systems have optimized their tribological and other performances. The aim of biotribology is to gather information about friction, adhesion, lubrication and wear of biological friction systems and to apply this knowledge to innovate technology, with the additional benefit of environmental soundness. Examples for biological friction systems at different length scales are bacterial flagellae, joints and articular cartilage as well as muscle connective tissues.

Our model system for biotribological investigations at the micro- and nanoscale are diatoms. Diatoms are single celled microalgae with a cell wall consisting of amorphous glass enveloped by an organic layer. Diatoms are small, highly reproductive, and accessible with different kinds of microscopy methods. There are several diatom species which actively move (e.g. *Bacillaria paxillifer* forms colonies of 5 to 30 cells which rhythmically expand and contract) or which can – as cell colonies – reversibly be elongated by a major fraction of their original length (e.g. *Ellerbeckia arenaria*). Diatoms also seem to show highly efficient self lubrication while cells divide and grow.

These algae might provide lubrication strategies which are still unknown to engineers!

Keywords: biotribology, nanotechnology, biomimetics, adhesives, microtribology, nanotribology

1 INTRODUCTION

Continuous miniaturization of technological devices asks for understanding of tribology at the micro- and nanoscale, since simple downscaling cannot be applied [1]. The old, empirical laws of friction do not always hold in such systems. This is due to their high surface-to-volume ratio, and the greater importance of surface chemistry, adhesion and surface structure or roughness. Conventional tribological and lubrication techniques used for large objects can be ineffective at the nanometer scale, which requires new methods for control [2].

There is an increasing need for a multidisciplinary, system-oriented approach to manufacturing micro- and nanoelectromechanical systems (MEMS/NEMS) that function reliably. Comprehensive understanding of tribology at the micro- and nanoscale can only be achieved through the cross-fertilization of ideas from different disciplines and the systematic flow of information and people among research groups.

Common potential failure mechanisms for MEMS/NEMS that need to be addressed in order to increase reliability are: adhesion, friction, wear, fracture, fatigue, and contamination. Due to the large surface area to volume ratio in MEMS/NEMS, they are particularly prone to stiction (high static friction) as part of normal operation.

A common case of stiction in everyday life is the condition in which a hard disk drive read/write heads become stuck to the disks platters with enough strength to keep the platters from spinning, resulting in harddrive failure. When a computer is turned off, its harddrives read/write heads park on the platter's landing zones. Under normal circumstances, the heads will lift off the platter when the computer's harddrive is activated and the platters rotate. Stiction typically occurs when a computer has been turned off for long periods of time.

The stiction that occurs during the operating lifetime of the device (so called in-use stiction) is due to the condensation of moisture on the surfaces, electrostatic charge accumulation, or direct chemical bonding. Surface passivation using self-assembled monolayers or organic thin films can be used to reduce the surface energy and reduce or eliminate the capillary forces and direct chemical bonding. A recent development are computer disk surfaces which are using 2-4 nm thick perfluoroether polymer layers chemically attached to the carbon surfaces (mimicking cartilage surfaces of joints, where the lubricant is chemically attached to the surface).

The materials properties of thin films are often not known, making fatigue predictions prone to error. Many MEMS/NEMS devices operate near their thermal dissipation limit. They may encounter hot spots that can cause failures, particularly in weak structures such as diaphragms or cantilevers. Thermal stressing and relaxation caused by thermal variations can create material delamination and fatigue in cantilevers.

Packaging has been a big problem. The contamination, which probably happens in packaging and during storage, can also strongly influence the reliability of MEMS/NEMS. For example, a particulate dust landed on one of the electrodes of a comb drive can cause catastrophic failure.

Mechanical properties are known to exhibit a dependence on specimen size. Hence mechanical property evaluation of nanometer-scaled structures is carried out to help design reliable systems, since good mechanical properties are of critical importance in such applications. Some of the properties of interest are: Young's modulus of elasticity, hardness, bending strength, fracture toughness, and fatigue life. Finite element modelling is carried out to study the effects of surface roughness and scratches on stresses in nanostructures. When nanostructures are smaller than a fundamental physical length scale, conventional theory may no longer apply, and new phenomena may emerge.

Biotribology aims to promote a better conception of the basic principles of tribology, focusing on lubrication in biological systems.

The development of new environmentally sound approaches to lubrication and wear-reduction and the application thereof to the solution of tribological problems is highly desirable.

2 TRIBOLOGY AT THE MICRO- AND NANOSCALE

Micro- and nanotribology 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.

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, hardly anything at the micro- and nanoscale is 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. For a good overview on contact mechanics in tribology, see Goryacheva [3].

Friction is an everyday experience. On the one hand, friction is a desired property, and in fact necessary, for example for an insect to initiate motion [4]. 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.

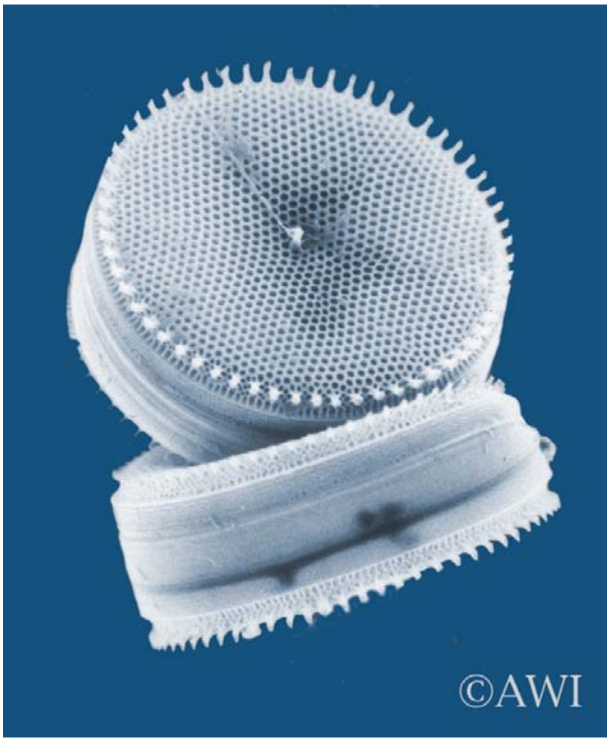

Figure 1.: *Two disc shaped diatom cells (*Thalassiosira sp.*) © Friedel Hinz, AWI Bemerhaven. Diatom species vary greatly in shape and size, from box-shaped to cylindrical, from about two micrometers up to several millimeters in size.*

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 [2]. Even on the atomic scale, stick/slip phenomena are revealed by atomic force microscopy [5, 6]. Many different mechanisms may come into play to construct friction forces and 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.

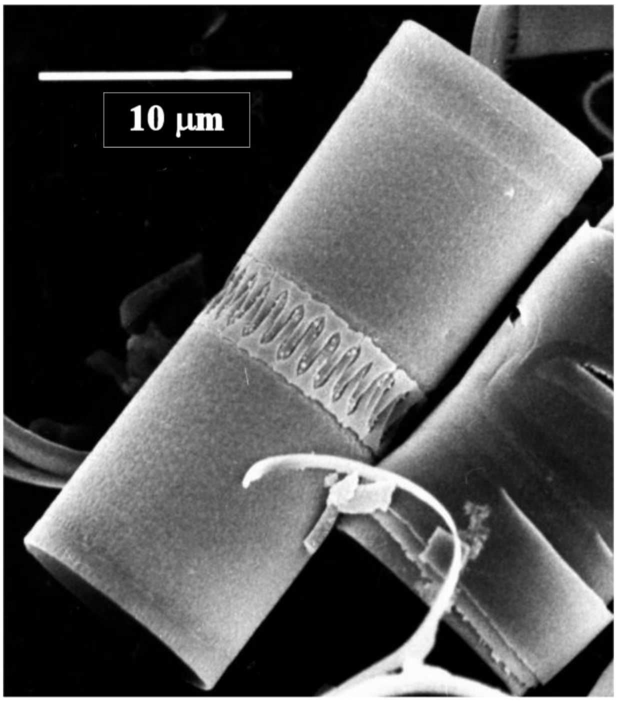

Figure 2.: The amorphous glass housing of the diatom Aulacoseira *has interlocking fingerlike protuberances. These mechanical interlocks experience stress and strain. © R.C. Crawford, AWI Bremerhaven.*

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.

Lubrication is one of the key aspects of micro- and nanotribology [7]. 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 the lubricant 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 [8].

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 [9]. Wear on the atomic scale is accompanied with the formation of crystallographic defects like point defects or kinks.

3 BIOTRIBOLOGY

Biomicro- and -nanotribology is a new interdisciplinary field of research combining methods and knowledge of physics, chemistry, mechanics and biology.

Biological and technical micro- and nanosystems have many things in common. First of all, the mechanical interaction occurs at identical length and force scales [10]. In both types of systems, surface properties, e.g. wettability, nanostructure or surface chemistry have a strong impact on the system. The main difference between biological and technical microsystems is their performance. Biological systems perform reliably, whereas technological systems continuously encounter technical problems (e.g. stiction) due to the lack of reliable concepts.

4 EXAMPLES FOR HIGH PERFORMANCE BIOLOGICAL MATERIALS

Natural materials are renowned for their strength and toughness. An intriguing example of a high performance biological material is the abalone shell. The abalone, which is a composite of calcium carbonate plates sandwiched between organic material 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 calcium carbonate crystal [11]! In 1999, Smith and coworkers succeeded in explaining the molecular mechanistic origin of the toughness of this biocomposite [12].

Another example for a high performance biological material is spider dragline silk, which has a breakage energy per unit weight two orders of magnitude greater than high tensile steel [13].

5 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 [14]. The class within the algae, which we favour for tribological studies, are diatoms (Figs. 1, 2). For an overview on diatoms see Round and coauthors [15].

Diatoms are unicellular microalgae with a cell wall consisting of a siliceous skeleton enveloped by an organic case essentially composed of polysaccharides and proteins [16]. 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.

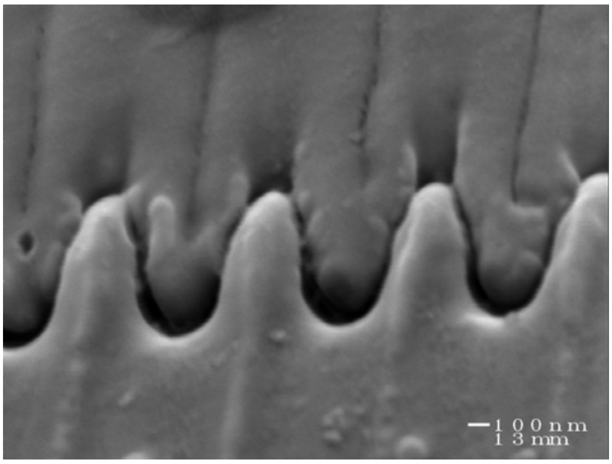

Figure 3.: Teethlike structures on Ellerbeckia arenaria *shells. © I.C. Gebeshuber and J.C. Weaver.*

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 [17, 18].

Some of the publications about nanoscale force measurements in diatoms [e.g. 19-22] are indeed more than “just” nanoscale measurements, they were carried out 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* [22].

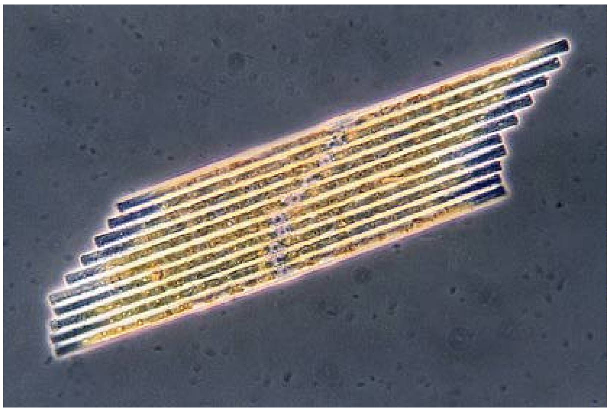

Figure 4.: Bacillaria paxillifer *is a colonial diatom. This colony consists of ten single cells, which are each about 100 µm long. In motion, the cells glide along each other, which is the reason why effective biogenic lubricants may have evolved to protect the single cells from wear. ©* http://www.microscopy-uk.org.uk/pond/*, Wim van Egmond.*

Ellerbeckia arenaria (Fig. 3) 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 swing back like a spring [23,24]! This interesting feature makes us suggest that there are parts in relative motion in this species, coping with friction and wear.

Diatoms seem to show highly efficient self lubrication while girdle bands telescope, as the cells elongate and grow [19]. 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 friction reducers, either by means of ball bearings or as solid lubricant, or following a strategy which still is completely unknown to engineers.

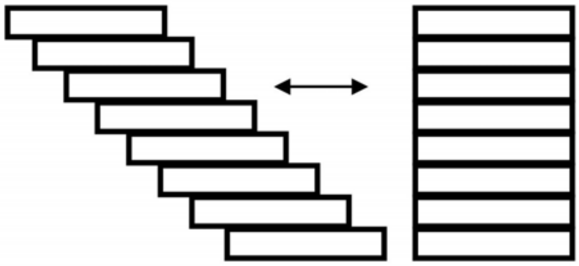

Figure 5.: Model of a moving Bacillaria paxillifer *colony. The single cells glide against each other, simultaneously to the left or to the right, resulting in elongated and stacked positions of the colony. Figure from [24], © Elsevier Publishing.*

Although diatoms are photosynthesizing, there are several species within this group which actively move: *Pseudonitzschia sp*. and *Bacillaria paxillifer* (former name because of its unusual behaviour: *Bacillaria* *paradoxa*) are good examples. *B. paxillifer* (Figs. 4, 5) shows a remarkable form of gliding motility: Entire colonies of 5 to 30 cells expand and contract rhythmically and in a coordinated manner [25]. Anomalously viscous mucilage excreted by a fissure, which covers 99% of the cell length, may provide the means for the cell-to-cell attachment [26].

6 OUTLOOK

Through the process of natural selection, Nature has produced lubricant systems with water as a base stock and biomolecules as additives. The precise mechanisms of the natural lubricants 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 (for further information, see homepage of the department of materials, ETH Zürich).

The natural lubricants by far outclass the best oil-based lubricants of most man-made devices [4]; to emulate these systems is one of today´s great challenges.

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

I.C.G. thanks P.K. Hansma from the physics department at the University of Califonia in Santa Barbara, who introduced her to research in experimental physics and provided the perfect environment to start her work with diatoms. What he can teach about doing science has no parallel.

The authors thank A.M. Schmid for revealing the interesting mechanical properties and providing first samples of *E. arenaria* and R. Krisai for introducing us to their natural habitat.

Furthermore, the authors express gratitude for stimulating discussions with R.M. Crawford, F. Kinnen and J. Kreuzer.

A special thank you goes to B. Bhushan, who with his book “Springer Handbook of Nanotechnology” made clear many of the current problems in man-made nanotechnology and enforced our drive to do research in the biotribological field.

Partly, this work was funded from the "Austrian Kplus-Program" and has been carried out at the "Austrian Center of Competence for Tribology".

REFERENCES

[1] Bhushan, B.: Springer Handbook of Nano-technology, Springer Verlag, Berlin Heidelberg, 2004.

[2] Urbakh, M., Klafter, J., Gourdon, D. and Israelachvili, J. The nonlinear nature of friction. Nature 430 (2004), 525 - 528

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

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

[5] Stark, R.W., Schitter, G and Stemmer, A.: Velocity dependent friction laws in contact mode atomic force microscopy. Ultramicroscopy 100(3-4) (2004), 309-317.

[6] Zhang-Xiangjun, Meng-Yonggang and Wen-Shizhu: Nano/microtribology stick-slip number under an atomic force microscope and its characteristics. Tribology-Letters 15(4) (2003), 407-414.

[7] 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, 399-414.

[8] Störi H., Kleiner R., Werner W.S.M., Kolm R., Gebeshuber I.C. and Jogl C.: Characterisation of monomolecular lubricant films, Proceedings 14th International Colloqium Tribology, Technische Akademie Esslingen, Volume III, 2004, 1663-1666.

[9] Scholes, S.C., Unsworth, A., Hall, R.M. and Scott, R.: The effects of material combination and lubricant on the friction of total hip prostheses. Wear 241(2) (2000), 209-213.

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

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

[12] Smith, B.L., Schäffer, T.E., Viani, M., Thompson, J.B., Frederick, N.A., Kindt, J., Belcher, A., Stucky, G.D., Morse, D.E. and Hansma, P.K.: Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites. Nature 399 (1999), 761 – 763.

[13] Hinman, M., Dong, Z., Xu, M. and Lewis, R.V.: Biomolecular Materials. Edited by Viney, C., Case, S.T. and Waite, J.H., Materials Research Soc., Pittsburgh (1993), 25-34.

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

[15] Round, F.E., Crawford, R.M. and Mann, D.G.: Diatoms: Biology and morphology of the genera. Cambridge University Press (1990).

[16] Hecky, R.E., Mopper, K., Kilham, P. and Degens E.T.: The amino acid and sugar composition of diatom cell walls. Marine Biol. 19 (1973), 323-331.

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

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

[19] Gebeshuber, I.C., Kindt, J.H., Thompson, J.B., Del Amo, Y., Stachelberger, H., Brzezinski, M., Stucky, G.D., Morse, D.E. and Hansma, P.K.: Atomic force microscopy study of living diatoms in ambient conditions. J. Microsc.-Oxf. 212(3) (2003), 292-301.

[20] Gebeshuber, I.C., Thompson, J.B., Del Amo, Y., Stachelberger, H. and Kindt J.H.: In vivo nanoscale atomic force microscopy investigation of diatom adhesion properties. Mat. Sci. Technol. 18 (2002), 763-766.

[21] Higgins, M.J., Sader, J.E., 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. 39 (2003), 722-734.

[22] Higgins, M.J., 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. 39 (2003), 1181-1193.

[23] Gebeshuber, I.C., Stachelberger, H. and Drack, M.: Diatom bionanotribology - Biological surfaces in relative motion: their design, friction, adhesion, lubrication and wear. J. Nanosci. Nanotechnol., in press

[24] Gebeshuber, I.C., Stachelberger, H. and Drack, M.: Diatom Bionanotribology. Tribology and Interface Engineering Series, Elsevier, in press.

[25] Kapinga, M.R.M. and Gordon, R.: Cell motility rhythms in B. paxillifer. Diatom Res. 7(2) (1992), 221-225.

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