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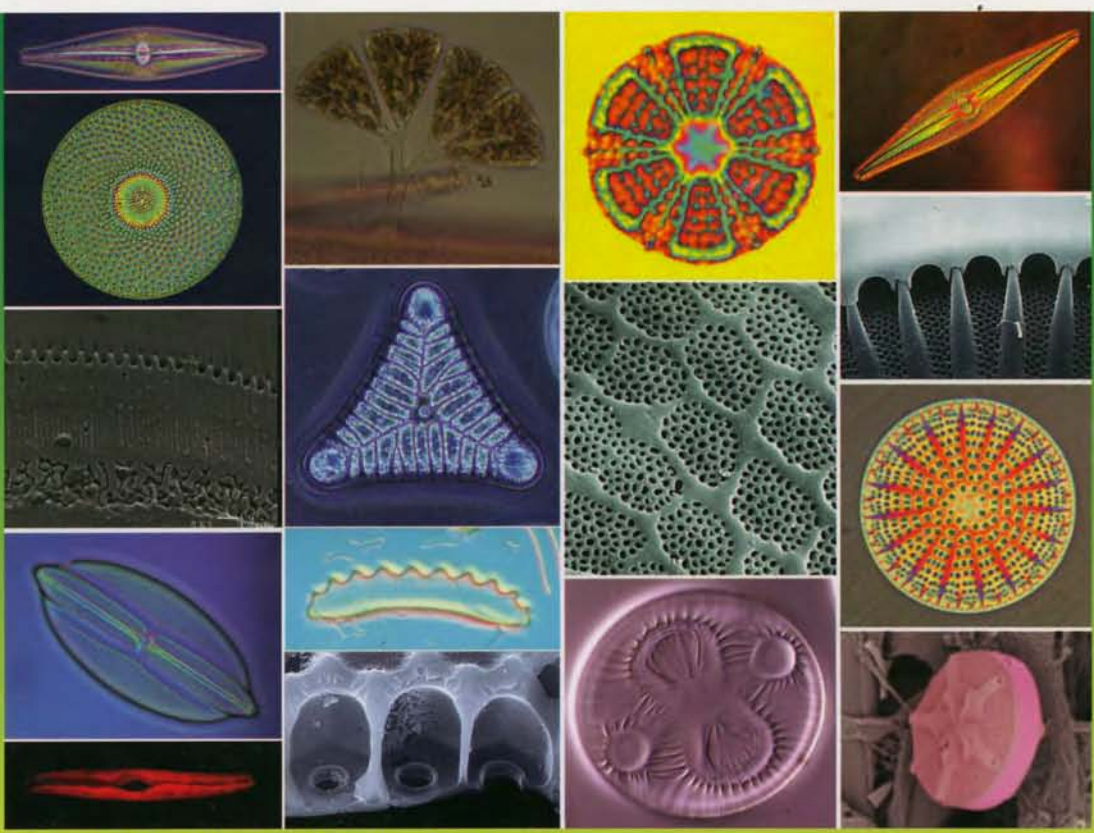

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A Special Issue on

Diatom Nanotechnology

GUEST EDITORS
Richard Gordon, Frithjof Sterrenburg, and Kenneth Sandhage

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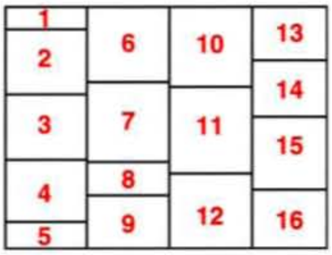


ON THE COVER: Diatoms have fascinated scientists and amateurs for well over 200 years. In celebration of their beauty, we present a montage of a few species and close-ups on the cover of this special issue on Diatom Nanotechnology: Journal of Nanoscience and Nanotechnology 5(1) (2005), taken with various microscopy techniques. These show the incredible variety of shapes, patterns, and details available to behold and perhaps use in diatom nanotechnology. Please contact the microscopists for further details. (Richard Gordon, GordonR@ms.Umanitoba.ca)

1 *Pinnularia* #1: A typical pennate diatom shell, light microscopy, Jamin Lebedeff interference light microscopy, length = 195 µm. Stephen Nagy, snagymd@pol.net.

2 *Craspedodiscus coscinodiscus*: Jamin-Lebedeff interference light microscopy, diameter = 150 µm, Stephen Nagy, snagymd@pol.net.

3 *Ellerbeckia arenaria*: scanning electron micrograph detail on a single shell (supplied by Annemarie Schmid), height of teeth-like structures 0.7 µm, Ille C. Gebeshuber and James C. Weaver, gebeshuber@iap.tuwien.ac.at.

4 *Navicula lyra*: differential interference contrast (DIC) light micrograph, length = 41 µm, Stephen Nagy, snagymd@pol.net.

5 *Gyrosigma*: confocal scanning laser micrograph, girdle view showing the chloroplast arrangement, chloroplast length = 68.5 µm, Maria Blasi and Mònica Roldán, monicaroldan@ub.edu.

6 *Licmophora*: light micrograph of live cells, girdle view (for individual cells, apical axis = 5–6 µm), Charles J. O'Kelly, cokelly@bigelow.org.

7 *Triceratium morlandii*: Phase light microscopy of a triangular diatom shell, width = 72 µm, Stephen Nagy, snagymd@pol.net.

8 *Eunotia serra*: differential interference contrast light microscopy, length about 100 µm, Patrick M. Eggleston, pegglest@keene.edu.

9 *Coscinodiscus wailesii*: loculate areolae, mean diameter of the chambers = 4 µm. Mario De Stefano, mario.destefano6@tin.it.

10 *Actinoptychus sp.*: a centric diatom, Jamin-Lebedeff interference light microscopy, diameter = 60 µm, Stephen Nagy, snagymd@pol.net.

11 *Campyloneis grevillei var. argus*: scanning electron micrograph detail of the external surface of the siliceous cribra, mean pore diameter 1.5 µm, Mario De Stefano, mario.destefano6@tin.it.

12 *Auliscus sculptus*: imaged with differential interference contrast light microscopy. Eduardo A. Morales, morales@acnatsci.org, diameter = 79 µm.

13 *Pinnularia* #2: Jamin-Lebedeff interference light microscopy, length = 185 µm. Stephen Nagy, snagymd@pol.net.

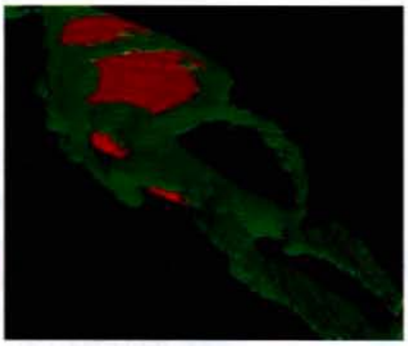
14 *Planothidium quarnerensis*: detail of the column-shaped internal costae linking the valvocopula, spacing between costae = 1.5 µm, Mario De Stefano, mario.destefano6@tin.it.

15 *Arachnoidiscus ehrenbergii*: desilicified, Jamin-Lebedeff interference light microscopy, diameter = 78 µm, Stephen Nagy, snagymd@pol.net.

16 *Asteriomphalus spp.*: scanning electron microscopy, diameter = 40 µm, Ivo Grigorov, ivo_grigorov@hotmail.com.

REVIEWS

A major goal of this research is to exploit diatom proficiency in biogenic silica formation to develop strategies for bio-inspired nanofabrication of silicon based materials. Development of high-throughput methods for the functional analysis of diatom genes is a key step toward this goal. In this article we review the different techniques available to investigate gene and protein function in diatoms. Choice of a diatom model organism should be made on the basis of several criteria, such as the ease of genetic manipulation, ecological relevance, or biomineralization capability. Phaeodactylum tricornutum *is one of the principal three species that are candidates for such a model. For this species we have accomplished the first large-scale analysis of 12,000 expressed sequence tags (ESTs) and have organized it in a queryable database,* Phaeodactylum tricornutum *database (PtDB). A summary of the functional analysis of this EST collection is presented, and genes of particular interest are highlighted.*



Ceramic Nanoparticle Assemblies with Tailored Shapes and Tailored Chemistries via Biosculpting and Shape-Preserving Inorganic Conversion

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M. B. Dickerson, R. R. Naik, P. M. Sarosi, G. Agarwal, M. O. Stone, and K. H. Sandhage
J. Nanosci. Nanotech. 2005, 5, 63–67

A novel biosynthetic paradigm is introduced for fabricating three-dimensional (3-D) ceramic nanoparticle assemblies with tailored shapes and tailored chemistries: biosculpting and shape-preserving inorganic conversion (BaSIC). Biosculpting refers to the use of biomolecules that direct the precipitation of ceramic nanoparticles to form a continuous 3-D structure with a tailored shape. Fluid(gas or liquid)/silica displacement reactions leading to a variety of other oxides have also been identified. This hybrid (biogenic/synthetic) approach opens the door to biosculpted ceramic microcomponents with multifarious tailored shapes and compositions for a wide range of environmental, aerospace, biomedical, chemical, telecommunications, automotive, manufacturing, and defense applications.

Controlled Silica Synthesis Inspired by Diatom Silicon Biomineralization

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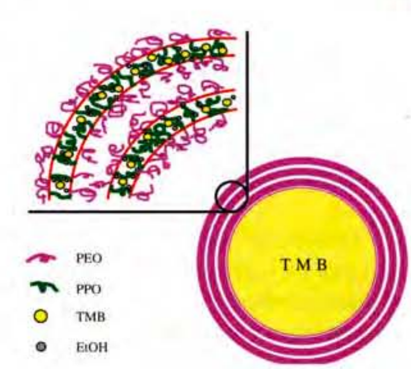
Engel G. Vrieling, Qianyao Sun, Theo P. M. Beelen, Sandra Hazelaar, Winfried W. C. Gieskes, Rutger A. van Santen, and Nico A. J. M. Sommerdijk
J. Nanosci. Nanotech. 2005, 5, 68–78



The production of highly structured silica from cheap starting materials and under ambient conditions, which is a target for many researchers, is already realized in the formation of diatom biosilica, producing highly hierarchical ordered meso- and macropores silica structures. Using bio-analogous reaction conditions and reagents, such as waterglass and (combinations of) poly(ethylene oxide) (PEO) based polymers, we demonstrate in this review the synthesis of tailor-made mesoporous silicas in which we can, as in biosilica synthesis, control the morphological features of the resulting materials on the nanometer level as well as on the micrometer level.

Diatom Bionanotribology—Biological Surfaces in Relative Motion: Their Design, Friction, Adhesion, Lubrication and Wear

79

Ille C. Gebeshuber, Herbert Stachelberger, and Manfred Drack
J. Nanosci. Nanotech. 2005, 5, 79–87

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

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Diatom Bionanotribology—Biological Surfaces in Relative Motion: Their Design, Friction, Adhesion, Lubrication and Wear

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Tribology is the branch of engineering that deals with the interaction of surfaces in relative motion (as in bearings or gears): their design, friction, adhesion, lubrication and wear. Continuous miniaturization of technological devices like hard disc drives and biosensors increases the necessity for the fundamental understanding of tribological phenomena at the micro- and nanoscale.

Biological systems show optimized performance also at this scale. Examples for biological friction systems at different length scales include bacterial flagella, joints, articular cartilage and muscle connective tissues.[1]

Scanning probe microscopy opened the nanocosmos to engineers: not only is microscopy now possible on the atomic scale, but even manipulation of single atoms and molecules can be performed with unprecedented precision. As opposed to this top-down approach, biological systems excel in bottom-up nanotechnology.

Our model system for bionanotribological investigations are diatoms, for they are small, highly reproductive, and since they 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.[2]

There are several diatom species that actively move (e.g. *Bacillaria paxillifer* forms colonies in which the single cells slide against each other) or which can, as cell colonies, be elongated by as much as a major fraction of their original length (e.g. *Ellerbeckia arenaria* colonies can be reversibly elongated by one third of their original length). Therefore, we assume that some sort of lubrication of interactive surfaces is present in these species.

Current studies in diatom bionanotribology comprise techniques like atomic force microscopy, histochemical analysis, infrared spectrometry, molecular spectroscopy and confocal infrared microscopy.

Keywords: Tribology, Lubrication, Friction, Wear, Biomimetics, Diatoms, Nanotribology, Bionanotribology, Natural Lubricants, Natural Adhesives, Environmentally Friendly Materials, Renewable Resources.

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1. INTRODUCTION

Diatoms are excellent. Their beauty is breathtaking and as organisms they are adapted to the many different aquatic environments in which they live. They offer invaluable hints about Nature's response to challenges. After all, Nature is an "engineering office" which has been "in business" for millions of years. We can learn a lot from these little gems. You are a tribologist and would like to understand lubrication in microsystems? Look at diatoms! You are an architect who wants to build lightweight, beautiful yet robust structures? Look at diatoms! You are a nanotechnologist who is looking for fast bottom-up rather than slow top-down approaches?[a] Look at diatoms!

Nanotechnology is the creation of functional materials, devices, and systems through control of matter on the nanometer (1 to 100+ nm) scale and the exploitation of novel properties and phenomena developed at that scale. Nanotechnology has just begun, whereas many natural systems have evolved complex nanostructures during millions of years (see e.g. Fig. 1). Even the most complex molecular machines of a biological cell are no bigger than 25–50 nm. For a captivating description of miniature machinery in nature and technology see the book "Travels to the nanoworld."[3]

On December 29th 1959, the Nobel prize laureate Feynman gave his classic after-dinner speech "There's plenty of room at the bottom-an invitation to enter a new field of physics" at the annual meeting of the American Physical Society at the California Institute of Technology[4] (for online version see http://www.zyvex.com/nanotech/feynman.html). In his speech, Feynman encouraged the scientific community to "think small" and predicted that many developments would accrue from our acquiring the ability to manipulate matter on very fine, even atomic, scales. He predicted the development of ultra-fast integrated circuits, electron beam lithography and even the ability to make objects by picking-and-placing single atoms. As a consequence, many consider him justifiably to be the father of the subject.

From Feynman's speculative beginnings, the field of nanotechnology has grown to the point of general public recognition of its philosophies and ideals. The total societal impact of nanotechnology is expected to be greater than the combined influences that the silicon integrated circuit, medical imaging, computer-aided engineering, and man-made polymers have had in the 20th century.

In 1999, Parkinson and Gordon pointed out the potential role of diatoms in nanotechnology via designing and producing specific frustule morphologies.[5] In the same year, at the 15th North American Diatom Symposium, Gebeshuber and co-authors introduced atomic force microscopy and spectroscopy to the diatom community as new techniques for *in vivo* investigations of diatoms.[6] These scanning probe techniques allow not only for the imaging of diatom topology, but also for the determination of physical properties like stiffness and adhesion.[2,7–11]

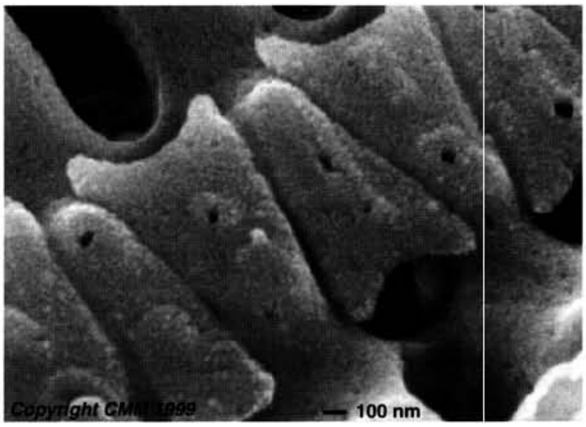

Fig. 1. Zipper-like structural detail on a diatom frustule (sample obtained from swimming pool filter material, probably *Aulacoseira granulata*). © Centre for Microscopy and Microanalysis, University of Queensland, Australia. Scalebar 100 nm.

2. SCANNING PROBE MICROSCOPY METHODS

In scanning probe microscopy (SPM), surface properties can be studied at or near the atomic level. A scanning probe microscope raster scans a sharp probe over a surface. The mechanical, electrical, magnetic, optical and chemical interaction between the sharp probe and the surface provides a 3D representation of surface parameters. The samples can be in air, vacuum, or immersed in some liquid.

The most versatile and prominent type of SPM for uses in physics, chemistry and biology is the atomic force microscope (AFM). There are many good overviews on AFM available, e.g. Refs [12, 13]. The AFM senses forces that occur between a probe tip and a substratum. The probe used in AFM is a flexible cantilever, i.e. a horizontal structural element supported at one end, with a sharp tip at its free end. AFM cantilevers are very soft, i.e. have small spring constants, which allow for measurement of very small forces.

The development of scanning probe microscopy (SPM) with its ability not only to image but also to systematically organize and manipulate matter on the nanometer scale down to single atoms and molecules largely contributed to the birth of nanotechnology.

A classic experiment in SPM-related nanotechnology took place in 1990 when researchers from IBM Almaden positioned 35 Xenon atoms on a Nickel surface to spell the letters "IBM".[14] In 1993, Eigler and co-workers positioned 48 iron atoms into a circular ring in order to

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[a] Top-down refers to the increasingly precise machining and finishing of materials from the macroscopic down to nanoscopic scales, bottom-up to synthesis from individual molecules or atoms.

"corral" some surface state electrons and force them into quantum states of the circular structure. The ripples in the ring of atoms reveal the density distribution of a particular set of quantum states of the "corral".[15]

As beautiful and interesting as these top-down nanotechnological experiments are, it takes many hours to manipulate and place the individual atoms and the experiments must be carried out at very low temperatures close to absolute zero. Another problem of top-down nanotechnology is that it faces problems building complex three dimensional structures.

Bottom-up nanotechnology, on the other hand, attempts to build up complex entities by using the self-assembling properties of molecular systems. This is more like a chemical or biological approach and it has some potential for making three dimensional structures cheaply, and in large quantities.

3. APPROPRIATE TECHNOLOGY IN TRIBOLOGY

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 specifically, the development of monolayer lubricants, of new adhesives and the construction of advanced artificial joints can result from such studies.[1] Especially in sensitive environments, the use of non toxic biodegradable lubricants is of paramount interest.[16]

The total amount of chain oils discharged into forest nature has been calculated at about two million litres per annum. The biodegradation 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.[17]

The release of lubricants into the water stream after passage through hydraulic turbines is also 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.[18] 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.

4. DIATOMS AS TRIBOLOGICAL MODEL SYSTEMS

We propose a new field in diatom nanotechnology: diatom bionanotribology.

Biological systems which endure friction have optimized their lubrication during evolution as far as necessary. The better the lubrication of a system which experiences friction is, the less is the wear. However, total elimination of wear is impossible in any system with moving parts.

Algae can serve as interesting model organisms for nanotribological investigations. For an overview on algae see van den Hoek and co-authors.[19] The class within the algae, which we favour for tribological studies, are diatoms (Fig. 2). For an overview on diatoms see Round et al.[20]

Ellerbeckia arenaria is a diatom which lives in waterfalls (Fig. 3). *E. arenaria* cells form string like colonies which can be several millimeters long. A. M. Schmid told us in 2001 about their interesting mechanical properties: not only can these colonies be elongated by about one third of their original length, when released, they even swing back like a spring. Therefore, we performed the following experiment: *E. arenaria* cell colonies in water were visualized with a Zeiss Axiovert inverted microscope. One end of the colony, which was several millimeters long, was tightly held in place with forceps mounted on a 3D micromanipulator. The other end of the colony was approached with a very sharp scanning

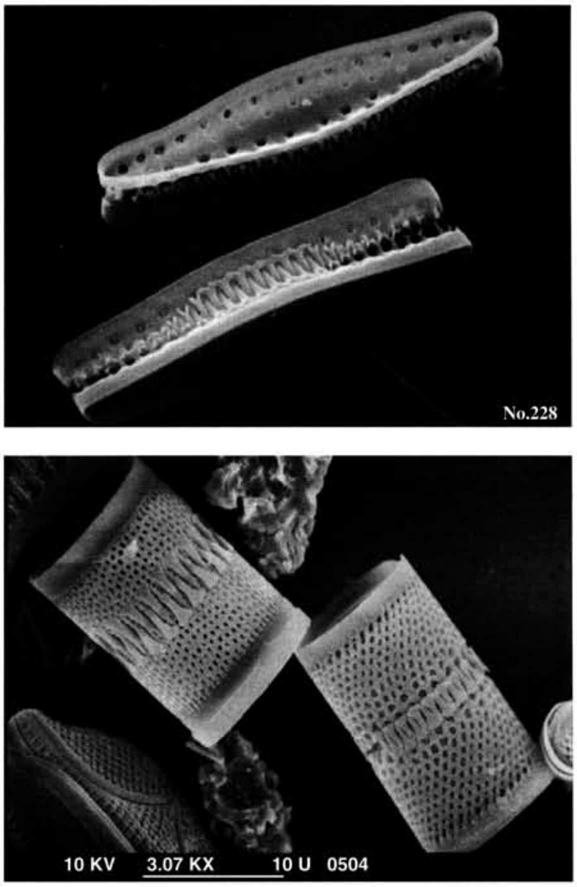

Fig. 2. The images show structural details of various diatom species which have interlocking fingerlike protuberances. These mechanical interlocks experience stress and strain, and therefore these species might be rewarding samples for bionanotribological investigations. Top: *Cymatoseira belgica* Grunow, bottom: *Aulacoseira italica* (Ehrenberg) Simonsen (left) and *Aulacoseira valida* (Grunow) Krammer (right). © RM Crawford, AWI Bremerhaven, Germany.

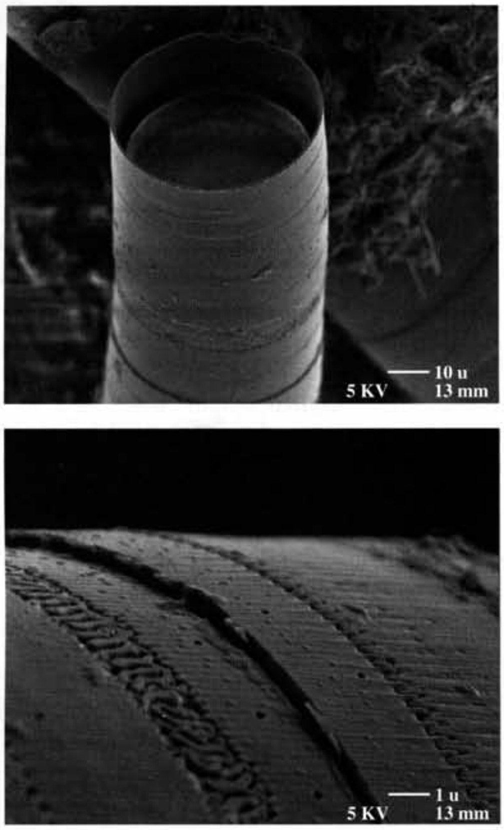

Fig. 3. *Ellerbeckia arenaria* is a colonial diatom which lives in waterfalls. The cell colonies can be reversibly elongated by about one third of their original length. These "biological rubber bands" might have solved any lubrication problems with techniques yet unknown to engineers.

tunneling microscope tip mounted on a second 3D micromanipulator. Under visual control, the tip was stuck into one diatom close to the end of the colony. Now, the STM tip was horizontally moved until the elongation of the attached diatom colony was about one third of its original length. The STM tip was then released from the cell colony (via vertical movement), resulting in a "swing back" of the colony. From inserting the tip until release, the experiment took about five seconds.

This elongation and "swing back" indicate that there are parts in relative motion in *E. arenaria* colonies. It is yet to be determined whether these moving parts face friction and wear because of sheer forces in the interface or whether expansion and contraction of organic material which links the parts takes place.

There might also be tribologically interesting processes in growing diatoms: Diatoms seem to show highly efficient self lubrication while girdle bands telescope, as the cells grow (for detailed discussion, see Ref. [2]). When we investigated an unknown benthic freshwater diatom species *in vivo* on the nanoscale with an atomic force microscope, we found bead-like features on the edges of certain 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 (Fig. 4).

Although diatoms are photosynthesising microalgae, there are several species within this group that actively move: *Pseudonitzschia sp.* and *Bacillaria paxillifer* (the former name of this diatom is *Bacillaria paradoxa,* because if its unusual behaviour, Fig. 5) are good examples. *B. paxillifer* shows a remarkable form of gliding motility: Entire colonies of five to 30 cells expand and contract rhythmically and in coordination.[21] Anomalously viscous mucilage excreted through a fissure that covers much of the cell length, may provide the means for the cell-to-cell attachment.[22] Consequently, *Pseudonitzschia sp.* and *Bacillaria paradoxa* join *Ellerbeckia arenaria* as our candidates for bionanotribological investigations.

5. Technical Tribology

Biological and technical microsystems have many things in common. First of all, the mechanical interaction occurs at identical size and force scales.[23] In both types of systems, surface properties, e.g. wettability, nanostructure or surface chemistry have a strong impact on the performance of the system.

Micro- and nanotribology–considered as the mechanical interaction of moving bodies—is the science of friction, adhesion, lubrication and wear on the scale of micrometers to nanometers and the force scale of millinewtons to nanonewtons.

Some of the publications about nanoscale force measurements in diatoms (e.g. Refs [2, 8, 10, 11]) are indeed more than "just" nanoscale measurements, they even reach the single molecule level: Higgins and coworkers[11] 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.*

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

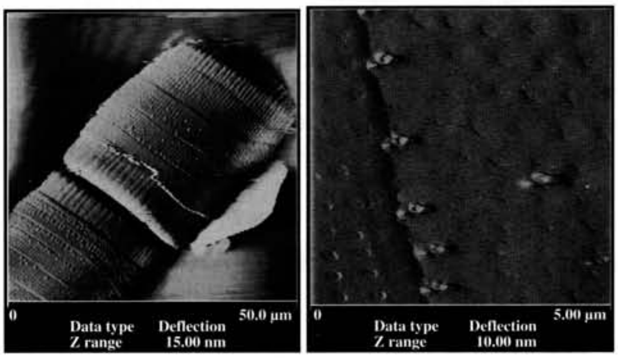

Fig. 4. Atomic force microscopy images (topography) of two interconnected diatom cells showing bead-like features, which might reduce friction. For detailed discussion see Gebeshuber et al. 2003. Left: Two cells of a yet unknown diatom species. Right: 5 μm zoom. © *J. Microsc.* Oxford.

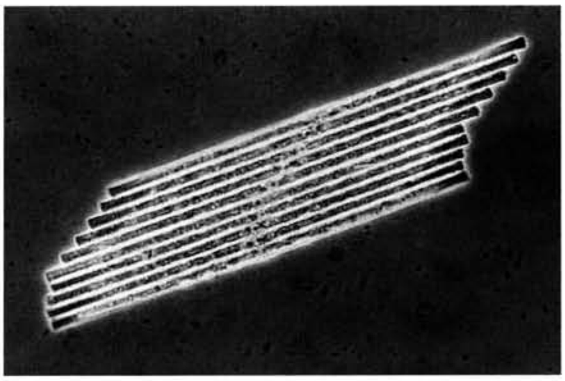

Fig. 5. A colony of ten *Bacillaria paxillifer* diatoms. The single cells are about 100 μm long. In motion, the cells glide along each other. We assume that biogenic lubricants protect the single cells from wear. © Wim van Egmond, Microscopy-UK.

5.1. Contact Mechanics

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. 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 Ref. [24].

5.2. Viscoelasticity

The behaviour of a material is called viscoelastic if it combines flexible deformation according to Hooke's law ($F = -k \cdot x$) with Newtonian viscous flow. Newtonian viscous flow was first described by Newton in Principia in 1687.[25] It describes the simplest relation between shear stress and shear strain rate, namely that in which the shear stress is linearly proportional to the shear strain rate: $\tau = \eta\dot{\gamma} \cdot \eta$ the parameter eta is called the viscosity coefficient and may vary with the shearing rate. Viscoelasticity is characterized by the following features: relaxation, creep and hysteresis. Most, if not all biological tissues possess viscoelastic behaviour.[26]

Subhash and co-workers performed a study of the indentation hardness and elastic properties of centric frustules of *Coscinodiscus concinnus* using nanoindentation.[27] These authors analysed more than one hundred indentations and found that the hardness varied between 0.001–0.189 GPa and the Young's modulus varied between 0.107–1.724 GPa. The Young's modulus values appear to be strongly dependent on the location of the indentation and the orientation of the frustule. In general, the frustule is stronger on the outer edge than inside.

5.3. Friction

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.

An important concept in macroscale friction theory is the coefficient of friction, μ. The friction coefficient is defined as the relationship between the tangential (friction) force and the normal force. Note that only on the macroscale, this coefficient can be assigned a general value. On the micro- and nanoscale, the subtle influences of single contact points (asperities) can no longer be averaged due to the small dimensions and small normal forces.

Macroscale friction can be 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 does a moving body experience 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 forms a third body.

Asperities on the surface of diatoms might serve to counteract friction, otherwise the cingula may not be pulled apart easily.

In 2500 BC the Egyptians discovered 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 size 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 micro-world, stick/slips appear in mechanical and in biological systems. Even on the atomic scale, stick/slip phenomena are revealed by atomic force microscopy. However, many different mechanisms may come into play to construct friction forces and it is not yet established what mechanism predominates at what size scale.

Macro- and microtribological systems show a dependence of the friction force on the sliding velocity for dry as well as for lubricated systems.

5.4. Adhesion

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 (two surfaces can be more effectively adhered the smoother they are), 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 physically accommodate the roughness profile of the counter surface, leading to intimate contact.

A large proportion of diatom species are usually found attached to a diverse variety of surfaces. The adhesives they use have been studied by several groups (e.g. Refs [8, 9, 11, 28–32]). Some of these studies even reached the single molecule level[11] and chemical characterisation of the diatom adhesives is highly desirable. On the one hand, the adhesive industry can profit from new ideas (which are in fact not new but millions of years old), and on the other hand, knowledge of the diatom adhesives might promote the development of adhesive solvents for removal of undesirable organisms (e.g. in technical devices like tanks and pipelines as well as in biofouling of ships and marine structures).

The investigation of diatom adhesives at the molecular scale may result in innovations regarding optimized (bio)nanotechnologically constructed man-made materials, like adhesives and lubricants.

5.4.1. Molecular Forces in Adhesion

The finest scale of interaction is governed by molecular forces. To induce strong attraction, the spacing between the solids must be reduced less than about 10 nm.

In 1999, Smith and co-workers attempted to explain the molecular mechanistic origin of the toughness of natural adhesives, fibres and composites.[33] 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 3000 times more fracture resistant than a single crystal of the pure mineral![34] Natural materials are renowned for their strength and toughness. As another example: spider dragline silk has a breakage energy per unit weight two orders of magnitude greater than high tensile steel.[35]

Adhesive force analyses of individual keratinous hairs of the Tokay gecko support the hypothesis that in this biological system adhesion operates by van der Waals forces. Van der Waals forces are extremely weak at greater than atomic distance gaps, and require intimate contact between the adhesive and the surface.[36]

5.4.2. Electrostatic Forces

Bulk excess charges present on the surface induce the classical Coulomb attraction. This force vanishes after proper grounding of the samples.

The second contribution besides these charges arises from the electrostatic contact potential, resulting in the electrical double layer force. Unlike Coulomb attraction, this double-layer force remains constant after grounding. Most biological macromolecules are charged when surrounded by water, since the molecules expose weak acidic and basic functional groups.

5.4.3. Capillary Forces

Capillarity is closely connected to adhesion, cohesion and surface tension. A wetting liquid is pulled upwards in a capillary due to surface tension. In sliding systems, two surfaces are brought in close contact. The resulting slits and pores act as capillaries.

Of all the attractive forces in the micro-range, capillarity has the strongest impact provided that electrical excess charges can be neglected due to grounding. The liquid monolayers that are in direct contact with the solid are subject to electrical double-layer enforced ordering. Molecular forces act in the nano-Newton range. They are responsible for the mutual attraction or repulsion of liquid molecules and their interaction with the confining solids. Furthermore, blunt, ball-shaped probes (like the SILICON model system[1]) detect capillary forces, while sharp, needle-like probes (like the tip of an atomic force microscope) penetrate the double layers and also experience molecular forces due to intimate contact with the solid.

5.5. Lubrication

Lubrication is one of the key aspects of micro- and nanotribology.[37] 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 (see e.g. Ref. [38]). The main effect in thin film lubrication is solidification.

Molecular forces are not only important for biological systems concerning adhesion (see Section 5.4.1.) but are also important in lubrication.

5.5.1. Water–Bulk Properties and Molecular Film Properties

All surfaces are covered by water, unless they are hydrophobic or dried. Water is of great importance for any known living being, since it influences the constitution of biological structures as the common solvent for all biological activities. Throughout the centuries, water has been the subject for intensive research.[39] Water is a small molecule with low viscosity. However, it is a dipole molecule which is able to form hydrogen bonds to neighbouring water molecules or to solid surfaces. Water shows even in the bulk state many special properties and anomalies and has a high degree of short range order. Nature solves its lubrication problems with water as a base stock and biomolecules as additives. Therefore, detailed knowledge of water properties is important if we were to mimic biological lubrication.

To absorb water, a surface has to be able to keep the liquid. This means that the surface must have hydrophilic surface properties in order to be wetted. A hydrophilic surface is a polar surface while a hydrophobic surface is non-polar. Polar surfaces tend to build an aqueous double layer with distinctively different properties to those of bulk water. An example of water confinement in biological systems is the lipid bilayer membrane.

Continuum mechanics cannot be applied any more at very small distances of the separated bodies. Sophisticated simulation techniques have to be applied. The short-range forces in liquids (pertaining at the scale of a few nanometres) comprise van der Waals forces, electrostatic and ion correlation forces, salvation and structural forces, hydration and hydrophobic forces, polymer-mediated forces and thermal fluctuation forces. Some of these forces even switch from being attractive to repulsive or vice versa at some finite distance: in such cases, the potential energy minimum which determines the adhesion force or energy, occurs not at true molecular contact between the surfaces, but at some small distance farther out.[40]

Short-range forces might be also relevant in the totally unexplored matter of exchange of materials through the diatom cell wall. The smallest pores in the diatom cell wall have diameters in the range of about 20 to 200 nm.

5.5.2. Solid Lubrication

Solid lubricants reduce friction because of particles which easily slide against each other. Examples are powders (dry graphite, Teflon®, Molybdenum disulfide, aluminium, copper, etc.) or ceramic particles. Solid lubricants are often used as additives for grease and they are utilised at thermally stressed locations.

A closed lubricant cycle is not possible in many cases, and therefore solid lubricants, which can be applied highly localised, have major advantages as opposed to fluid lubricants.

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.

5.6. Wear

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. For example, microscale wear analysis is performed for hip-replacement materials.[41] Wear on the atomic scale is accompanied by the formation of crystallographic defects like point defects or kinks.

Tribologists and diatomists are invited to combine their knowledge in bionanotribology, since fruitful technological innovations resulting from such synergistic endeavours are highly possible.

6. OUTLOOK

6.1. Diatom Bionanotribology

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 nanoscale. Furthermore, the chemical composition and properties of natural adhesives and lubricants are accessible to chemical analysis.

We suggest *Pseudonitzschia sp.*, *B. paxillifer* and *E. arenaria* for detailed bionanotribological investigations. Current experiments comprise determination of the composition of the bead-like features (cf. Fig. 4), 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, and knowledge of the diatom adhesives might also promote the development of adhesive solvents for removal of undesirable organisms.

Diatoms cannot only provide ideas in the field of lubrication and adhesion.

One of the beauties of the diatoms is that there is a fantastic variation on a simple theme—the "Bauplan" of two valves and a series of girdle bands. The way in which the diatom organised (in evolutionary terms) the cell-wall to facilitate cell division inside a rigid box of silica brought with it special problems and it is these problems and the ways in which the diatom overcame them that can be of great interest to the tribologist!

However, tribology is just one field where biomimetic approaches originating from diatom research can innovate technology. Biological systems are highly controlled from the nanometer to the macroscopic levels, resulting in complex, hierarchical architectures that provide multifunctional properties that usually surpass those of analogous synthetically manufactured materials with similar phase compositions.[42]

6.2. Bionanotechnology

Possible future applications of atomic force microscopy and spectroscopy techniques in biology, and especially in diatom research are manifold, interesting and challenging: e.g. watching cell division in real time at the nanoscale, finding out how diatoms produce their amorphous silica frustules, revealing what tricks they apply to generate strong adhesives or how their lubricants minimize friction in moving parts.

Biological materials are simultaneously "smart," dynamic, complex, self-healing, and multifunctional, characteristics difficult to achieve in purely synthetic systems. Biomimetics, the use of biological principles in materials synthesis and assembly, may be a path for realizing nanotechnology, such as molecular and nanoscale electronics.[42]

It is wonderful to dive deeper and deeper into the nanoworld, to watch biological processes at unprecedented resolution and to consider how their secrets might be applied in technological innovations. However, one should bear in mind that this focussed approach teaches us only about biomolecular interactions. Like all other organisms, diatoms are more than just an assemblage of simply interacting biomolecules. With their emerging complex properties, they can teach us about life itself. After all—to say it with A. N. Whitehead,[43] the English philosopher and mathematician—"physics has to be explained in terms of a generalized theory of the organism"!

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