



Nanotechnology

10th lecture



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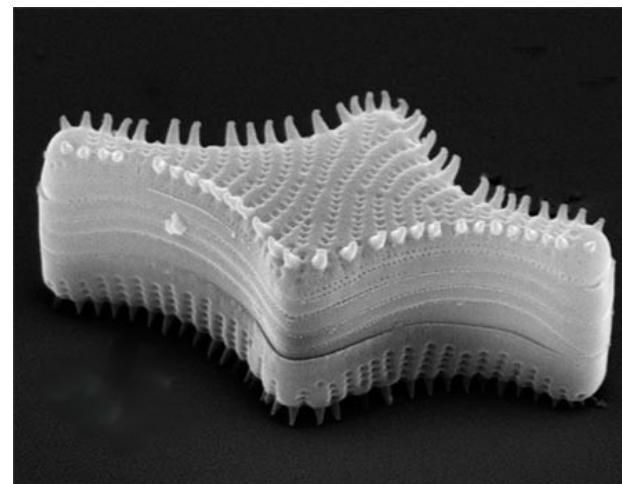
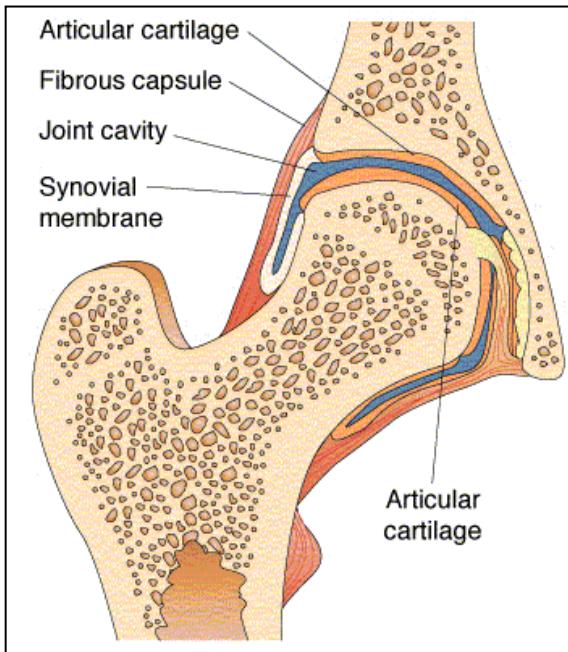
Tribology in Biology

Ille C. Gebeshuber¹, Manfred Drack² and Matthias Scherge³

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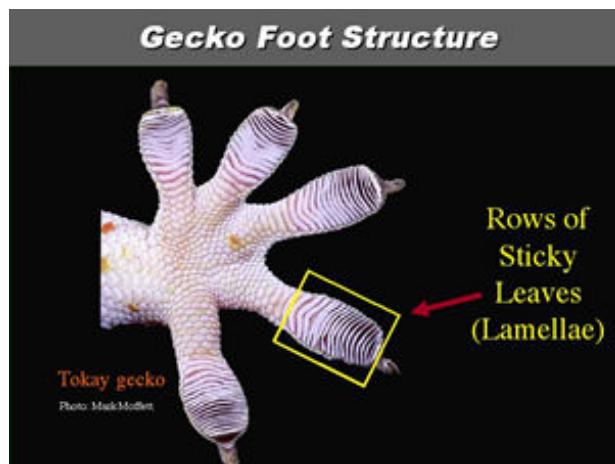
Outline

- Introduction
- Synovial joints - articular cartilage
- Switchable adhesives - adaptive adhesion
- Diatoms - glass making microorganisms

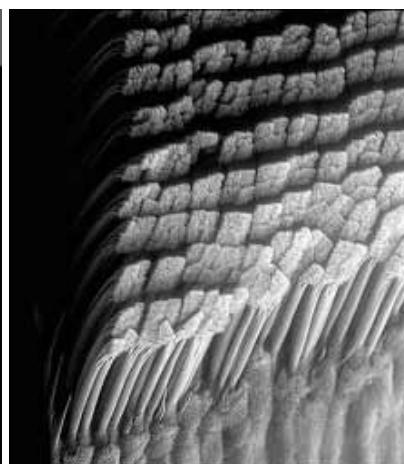
Biotribology

The aim of biotribology is to gather information about friction, adhesion, lubrication and wear of **biological systems** and to apply this knowledge to technological innovation as well as to development of environmentally sound products.

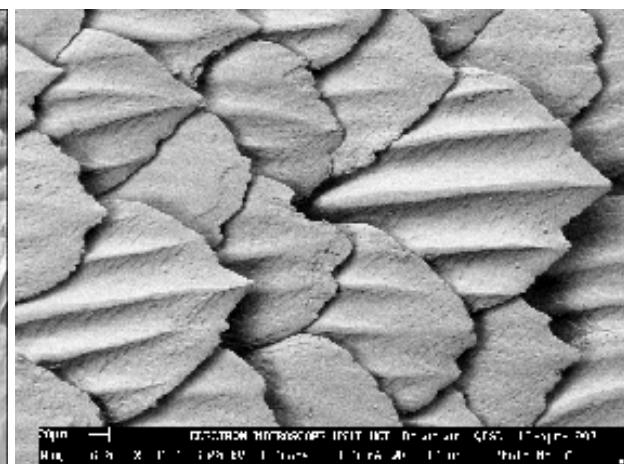
This new interdisciplinary field of research combines methods and knowledge of physics, chemistry, mechanics and biology.



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Why **biomicro** and **-nanotribology** ?

Continuous **miniaturization** of technological devices like hard disk drives and biosensors increases the necessity for the fundamental **understanding** of tribological **phenomena** at the **micro- and nanoscale**.

Biological systems excel also at this scale and therefore their strategies can serve as templates for new engineering devices.

- Tough materials
- Smart materials
- Adaptive materials
- Functional materials
- Materials with molecular precision
- Hierarchical materials
- Multiuse materials

Examples for tribology in biology

- Tribology is omnipresent in biology.
- Surfaces in relative motion occur e.g. in joints, in the blinking with the eye, in the foetus moving in the mothers womb.
- **Systems with reduced friction**
 - joints and articular cartilage
- **Systems with increased friction**
 - bird feather interlocking devices
 - friction in fish spines

Examples for tribology in biology

- **Systems with increased adhesion**
 - sticking in tree frogs
 - adhesion pads in insect
 - stable, strong and self-healing underwater adhesives

Material Properties

- Sophistication, miniaturization, hierarchical organizations, hybridation, resistance and adaptability.
- The hydrodynamic, aerodynamic, wetting and adhesive properties of natural materials are remarkable.
- Elucidating the basic components and building principles selected by evolution allows for the development of **more reliable, efficient and environment-respecting materials**.

- The results of evolution often converge on **limited constituents or principles**.
- For example, the **same material** component will be found just **slightly but effectively varied** to obey different functions in the same organism (e.g. collagen occurs in bones, skin, tendons and the cornea)
- One smart feature of natural materials concerns their beautiful organization in which **structure and function are optimized at different length scales**.

- Another recurring feature in natural systems is the **high level of integration**: miniaturization whose object is to accommodate a maximum of elementary functions in a small volume, hybridization between inorganic and organic components optimizing complementary possibilities and functions and hierarchy.
- **Hierarchical constructions** on a scale ranging from nanometers, micrometers, to millimetres are characteristic of biological structures introducing the capacity to answer the physical or chemical demands occurring at these different level.

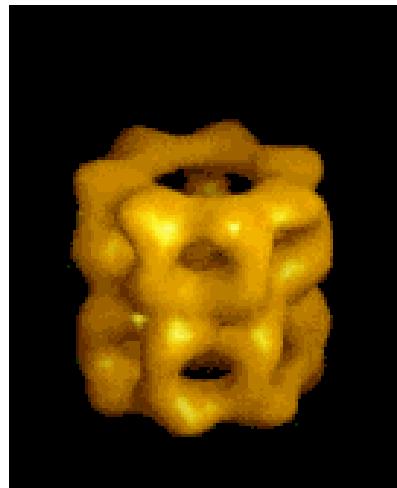
- Biomolecules like proteins and amino acids are defined in their structure down to the atomar level. They are materials built with **molecular precision**. Even small changes in their three dimensional structure would render them not working correctly anymore.
- In principle, each and every cell, plant, animal and person can be called a nanotechnological wonder.
- Nowadays, materials scientists can only dream about man made materials of such precision.

- Living systems constantly **sense the environment** with sets of diversified sensors **and react to it**.
- We have just started to develop smart materials, **functionally gradient materials** (e.g. a functional surface with a gradient of hydrophobicity that makes water run uphill) and multipurpose materials.
- **Smart materials** respond to external stimuli such as solvent, pH, light, electric field, or temperature. For example, water-swollen cross-linked polymer gels can respond to electric fields by contracting in a way that is similar to muscle.

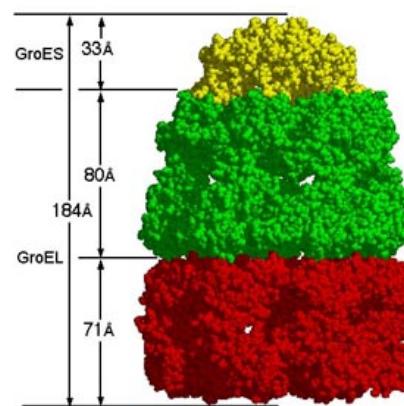
- However, the **thermal and hydrolytic sensitivities** of biological material **limit** their **applicability** in many important synthetic materials applications.
- A **real breakthrough requires** an **understanding of the basic building principles of living organisms** and a study of the chemical and physical properties at the interfaces, to control the form, size and compaction of objects.

- Magnetic bacteria
- Nanostructured glass
- Micro- to millimeter small organisms with strontiumsulfate exoskeleton
- Life itself is still a miracle. Complex, open system far away from thermal equilibrium.

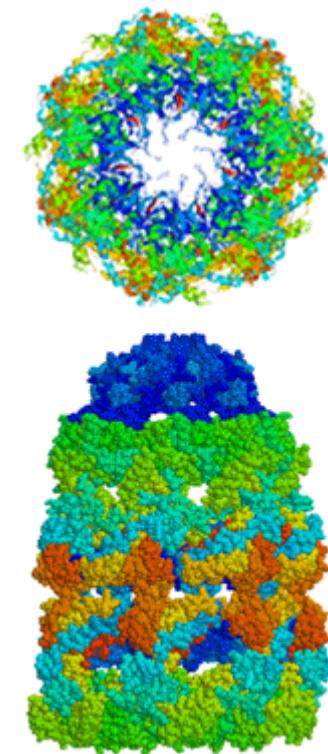
Chaperonins GroEL-GroES



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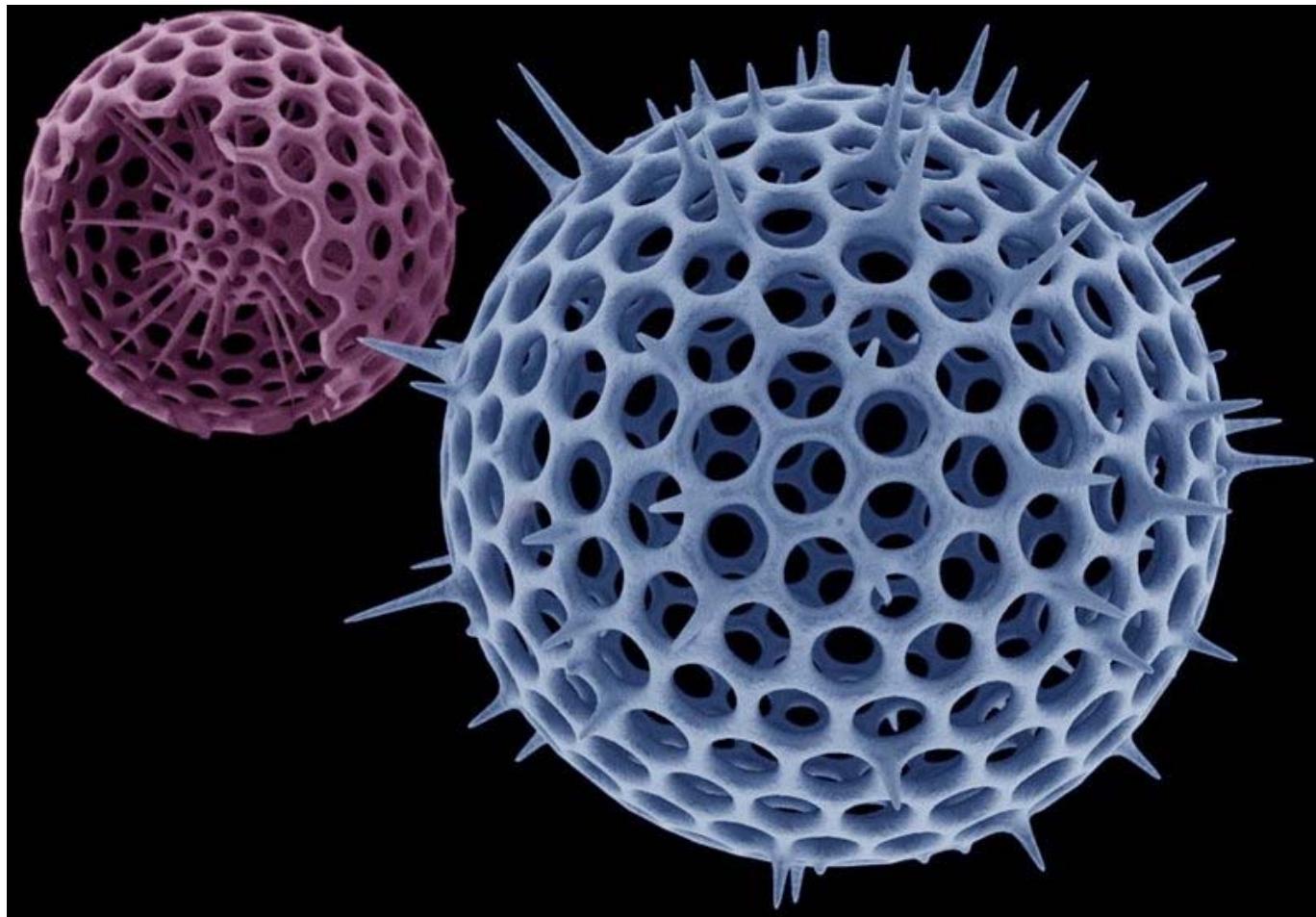
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htaguchi/chaperonin/cpn_structure.html](http://www.res.titech.ac.jp/~seibutu/htaguchi/chaperonin/cpn_structure.html)



Chaperonins are proteins involved in making certain other proteins form properly.

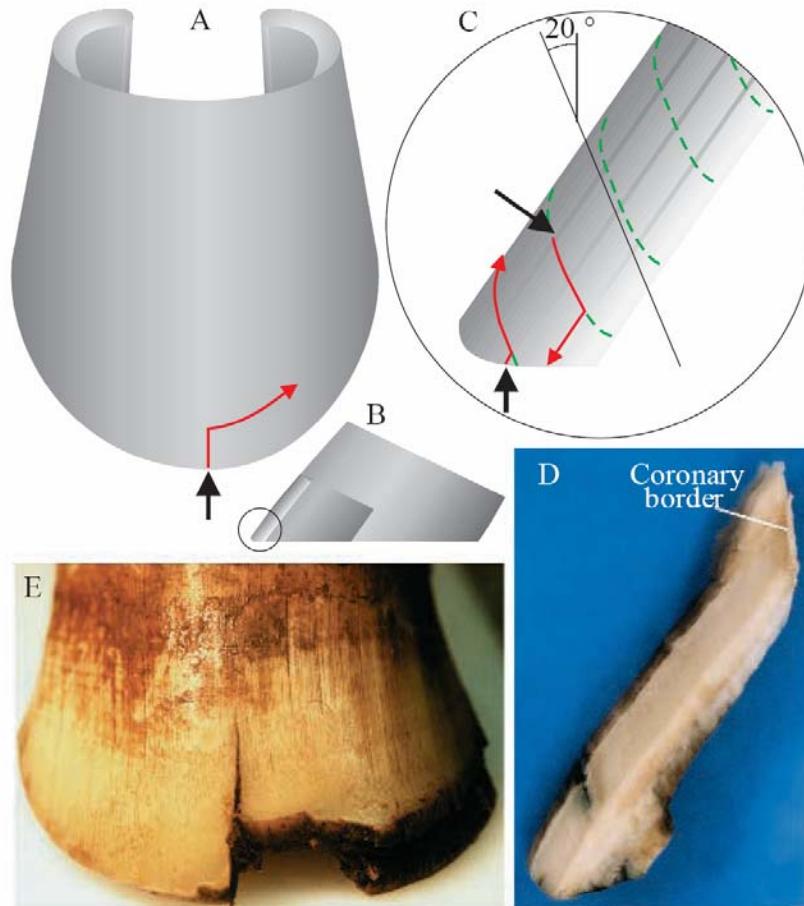
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Radiolaria



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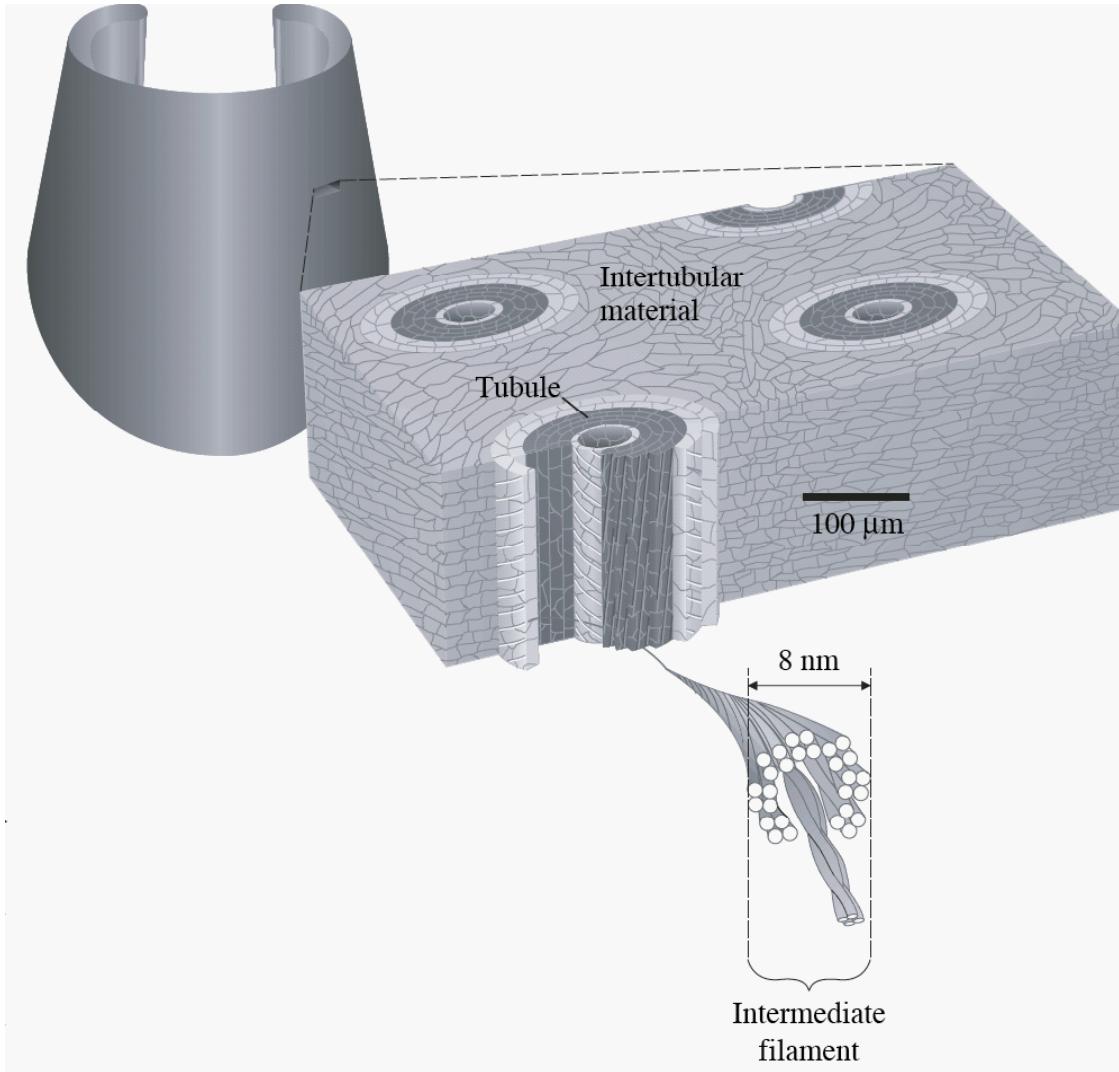
Equine hoof



The equine hoof is a nanoscale composite with the ability of crack-redirection.

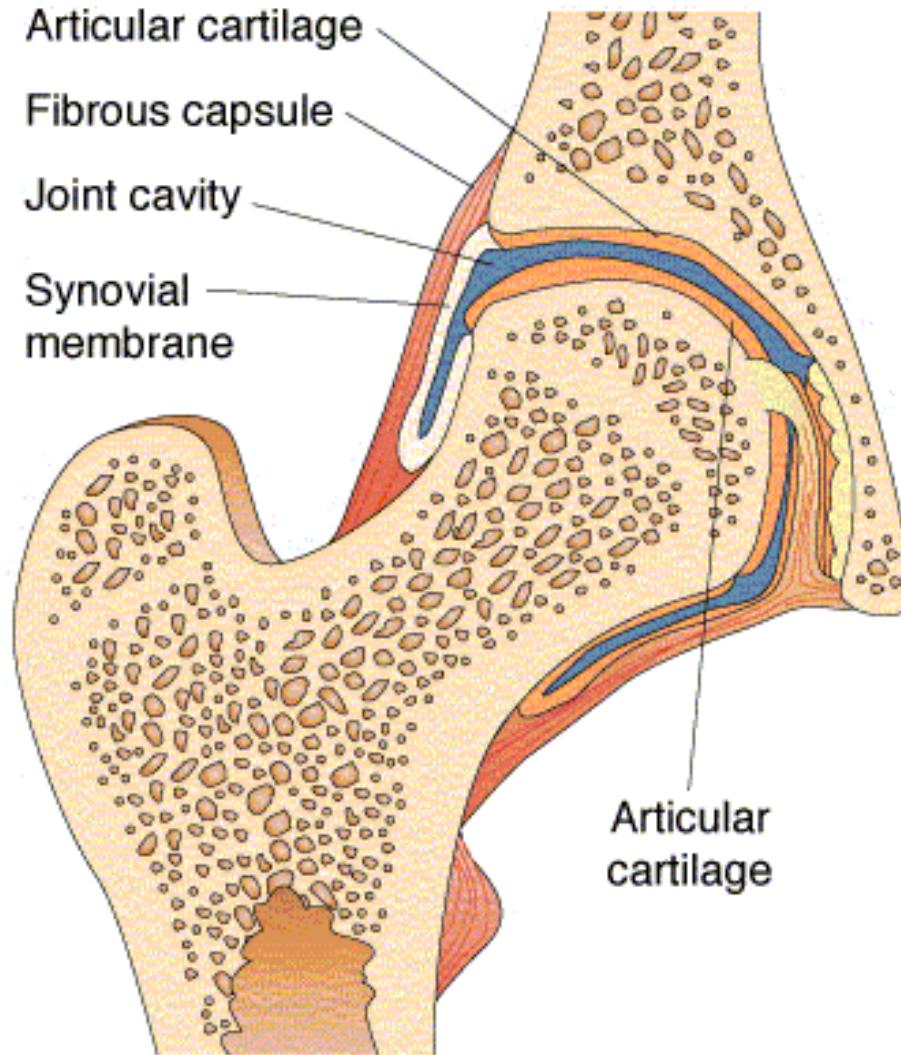
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Equine hoof

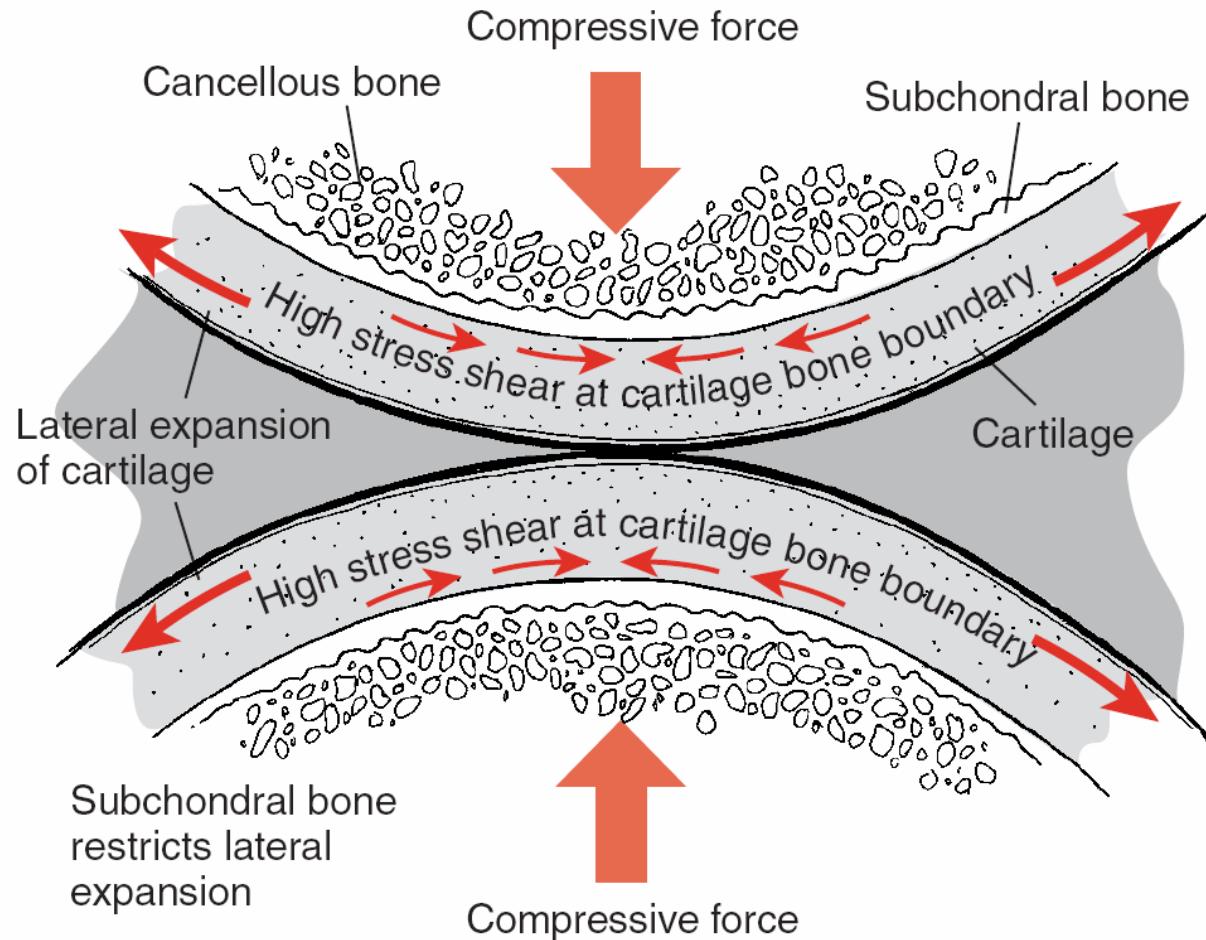


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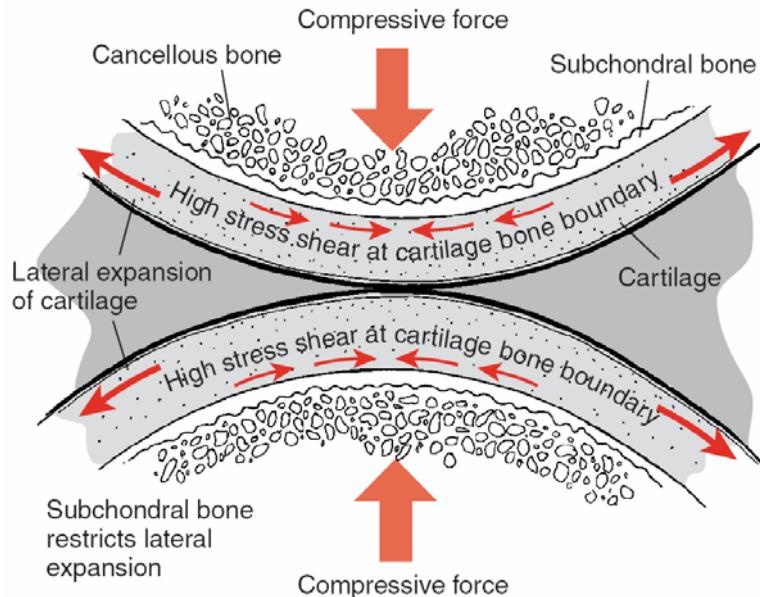
Synovial Joints



Synovial Joints

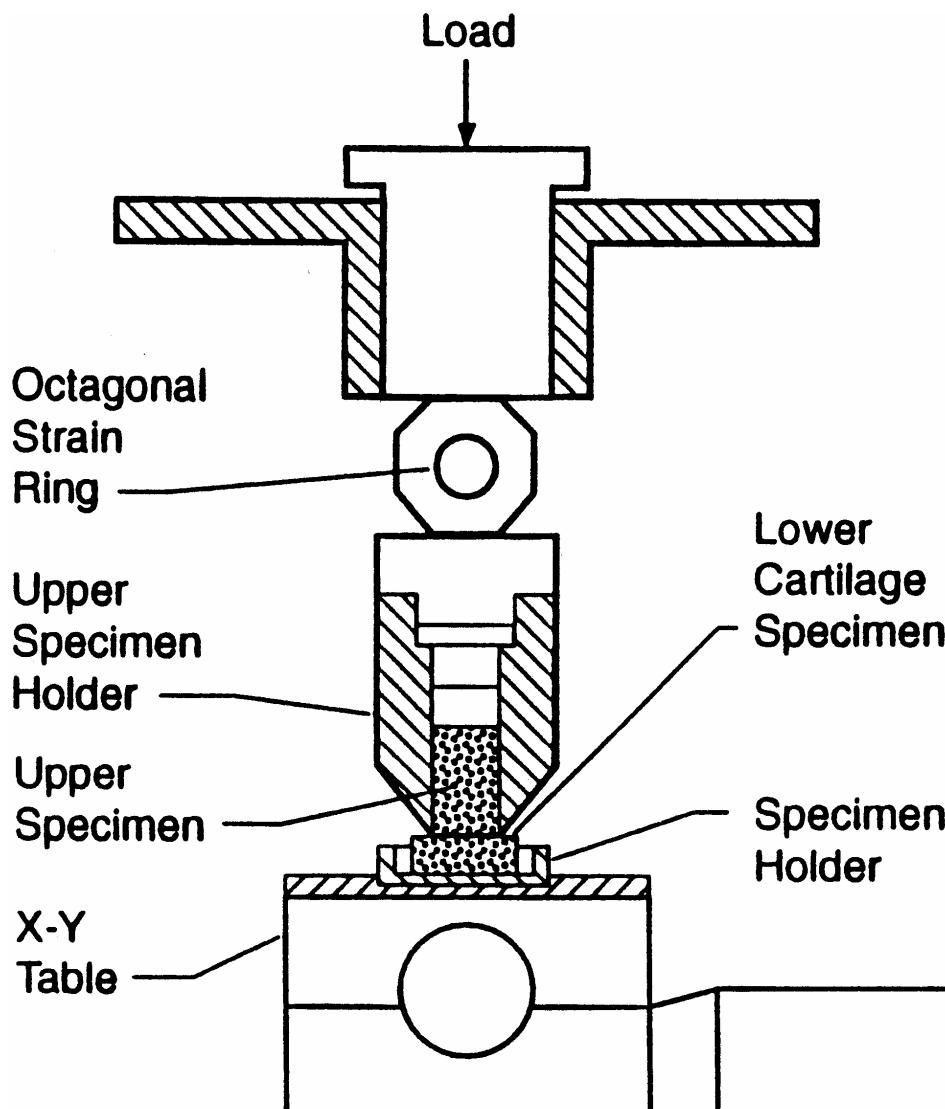


Synovial Joints



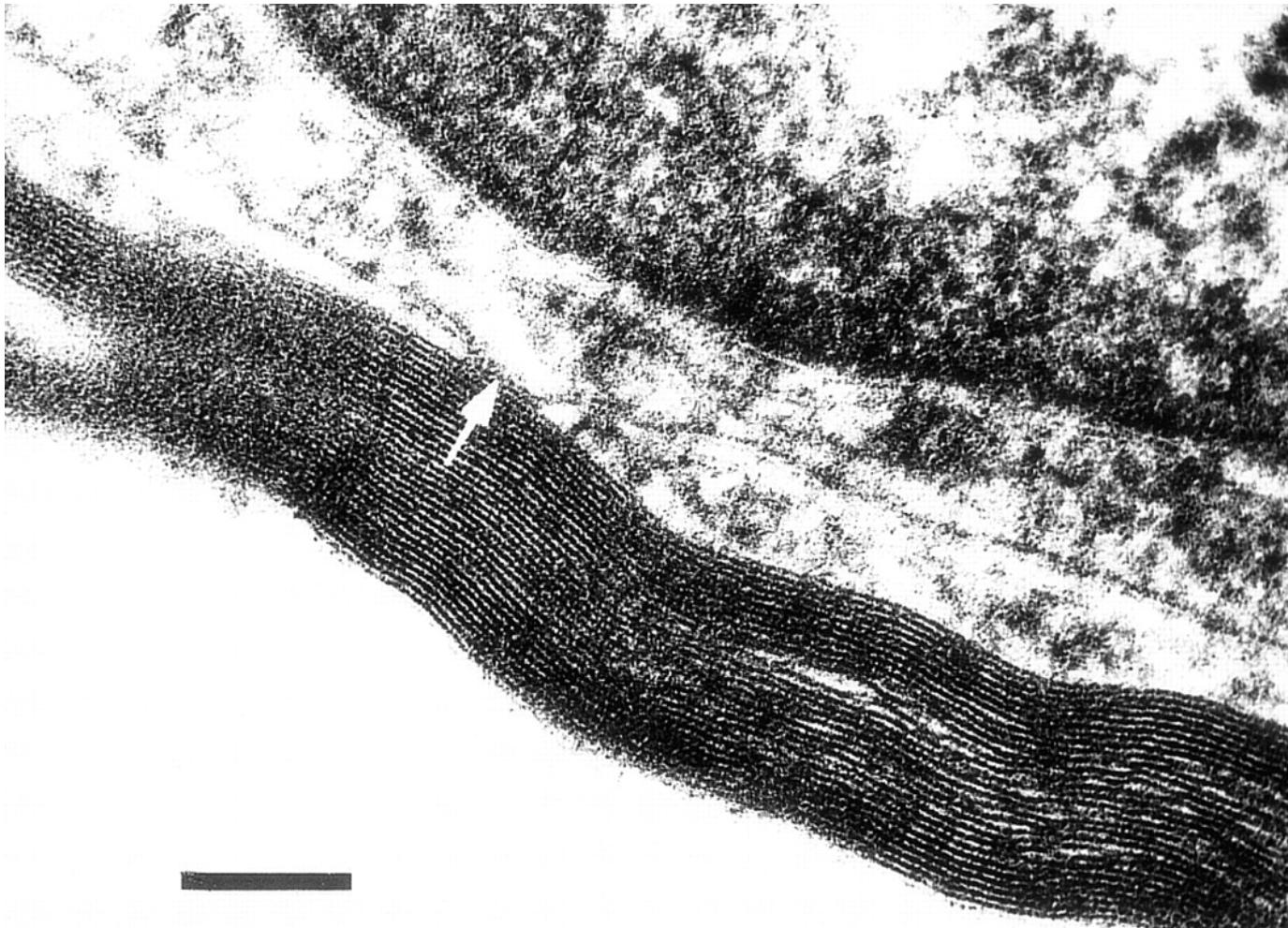
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Under impulsive compressive loads, the cartilage experiences a relatively large lateral displacement due to its high Poisson's ratio. This expansion is restrained by the much stiffer subchondral bone, causing a high shear stress at the cartilage bone interface.



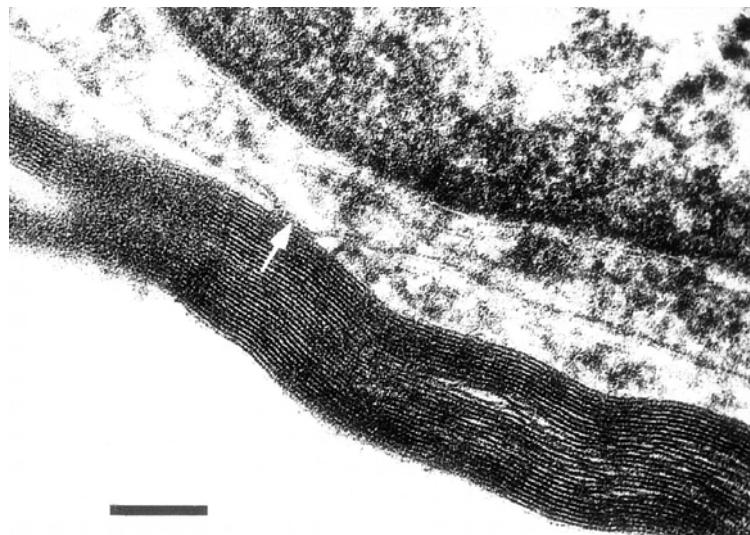
Dr. Furey, device for *in vitro* cartilage wear studies

Fig. 12. An electron micrograph of human lung produced by using lipid fixatives following the method of Ueda et al



Hills, B. A. J Appl Physiol 87: 1567-1583 1999

Fig. 12. An electron micrograph of human lung produced by using lipid fixatives following the method of Ueda et al



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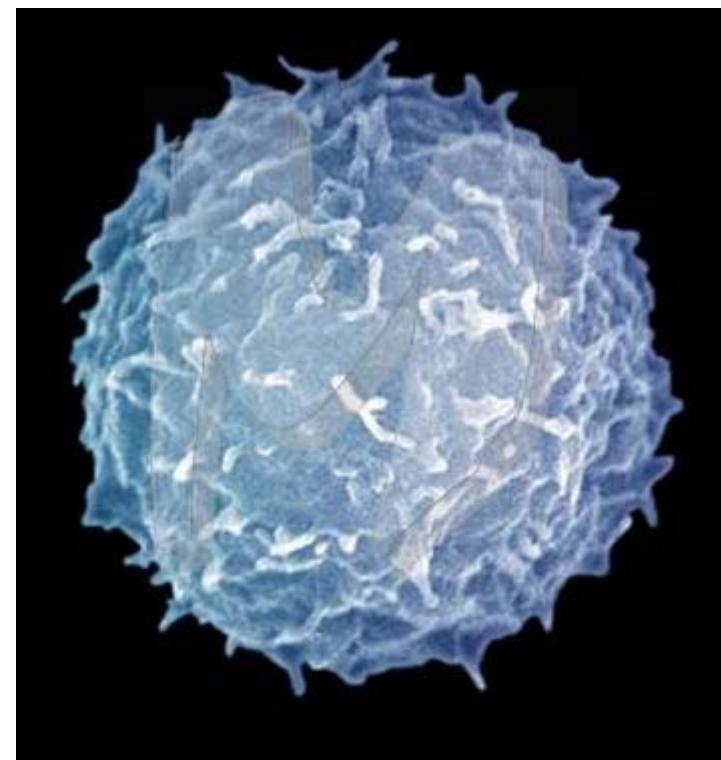
Electron micrograph of human lung showing layers of **surface-active phospholipid (SAPL)** directly adsorbed to alveolar epithelium which is also typical for other sliding surfaces *in vivo*. The interlamellar spacing is about 4.5 nm. Scale bar 100 nm. [Hills and Masters 1999]. © 1999 American Physiological Society.

Switchable adhesives

Leukocyte rolling on the endothelium



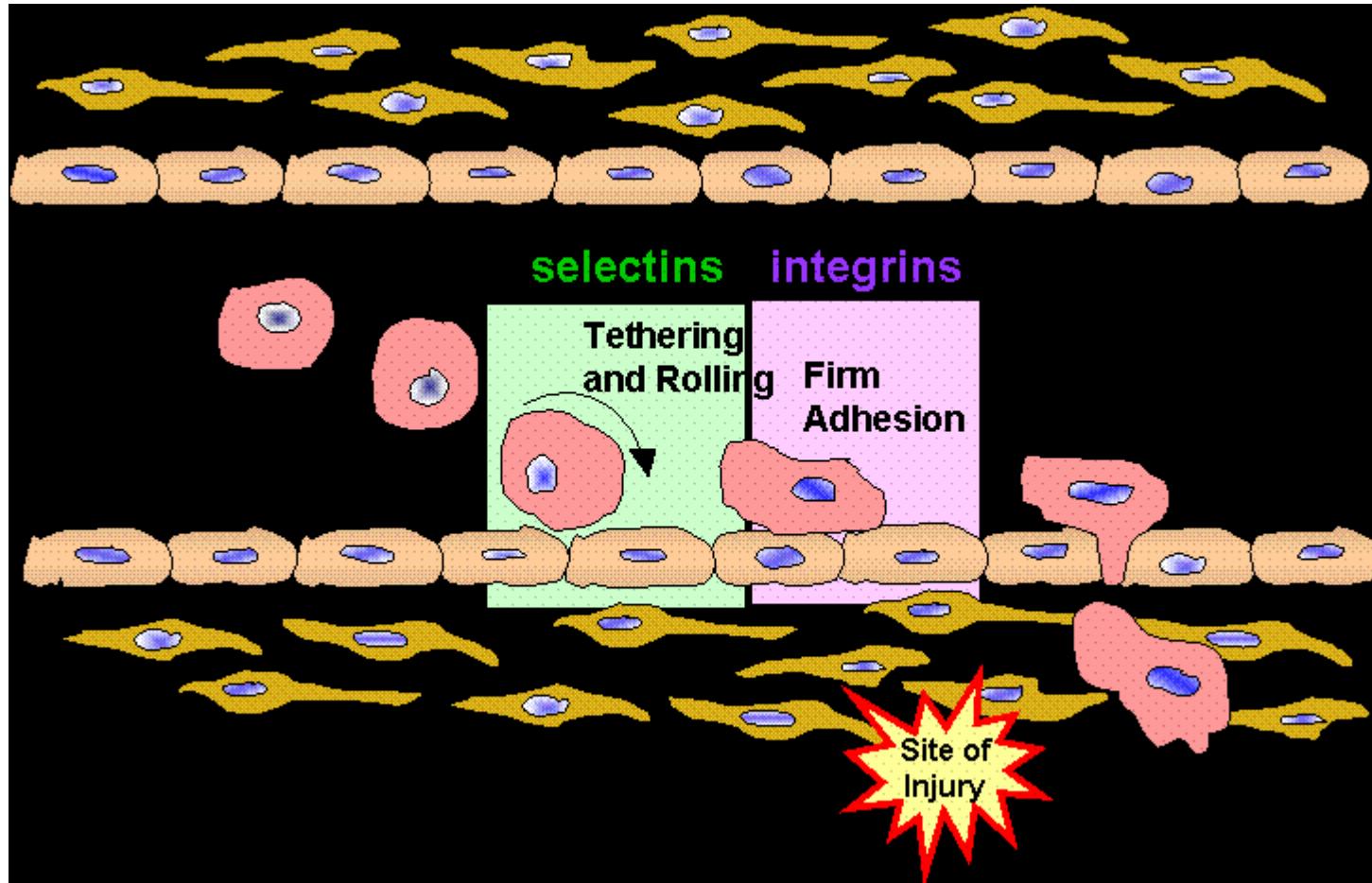
lymphocyte, SEM x15,500



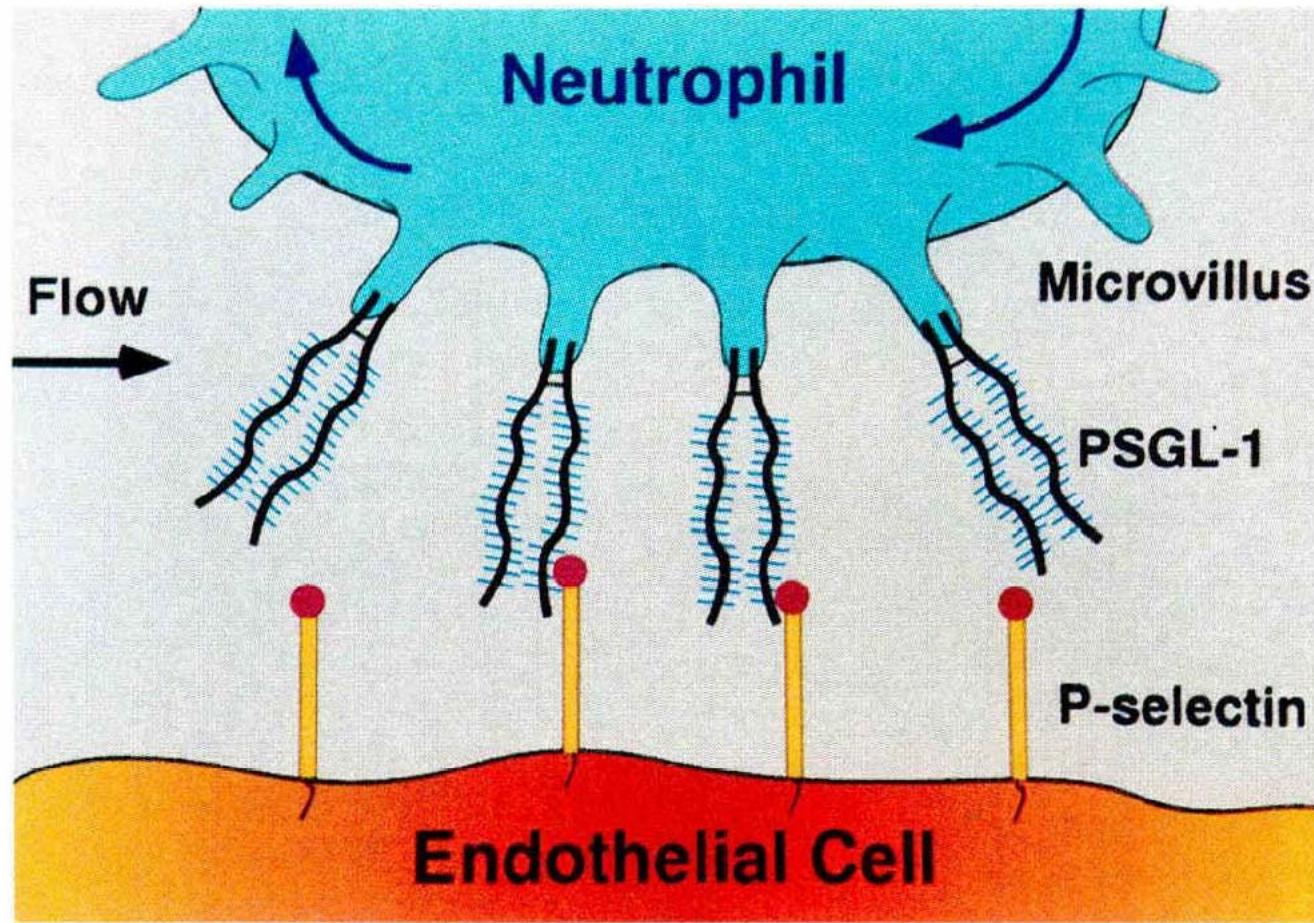
leukocyte x10,000

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Switchable adhesives



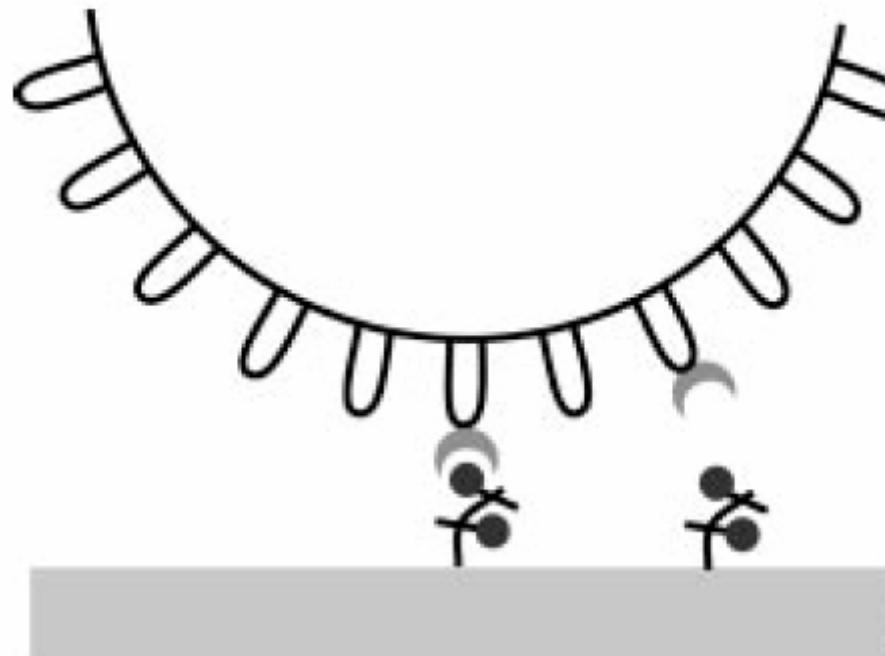
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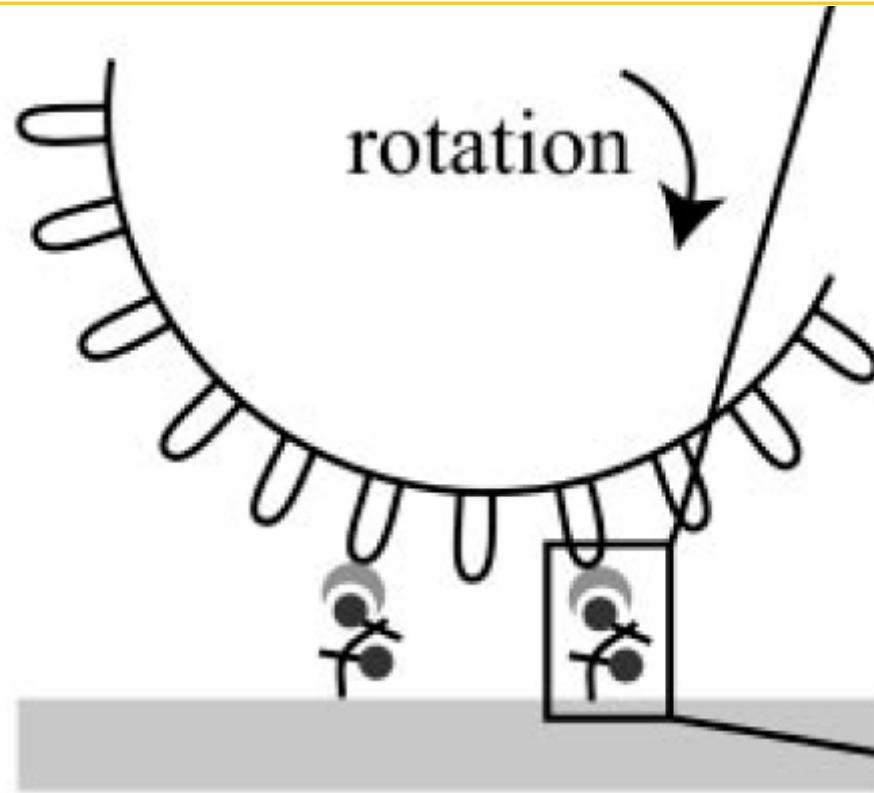
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Selectin mediated Leukozyte tethering

A schematic representation of the mechanisms involved in L-selectin mediated leukocyte tethering to diluted carbohydrate ligands.

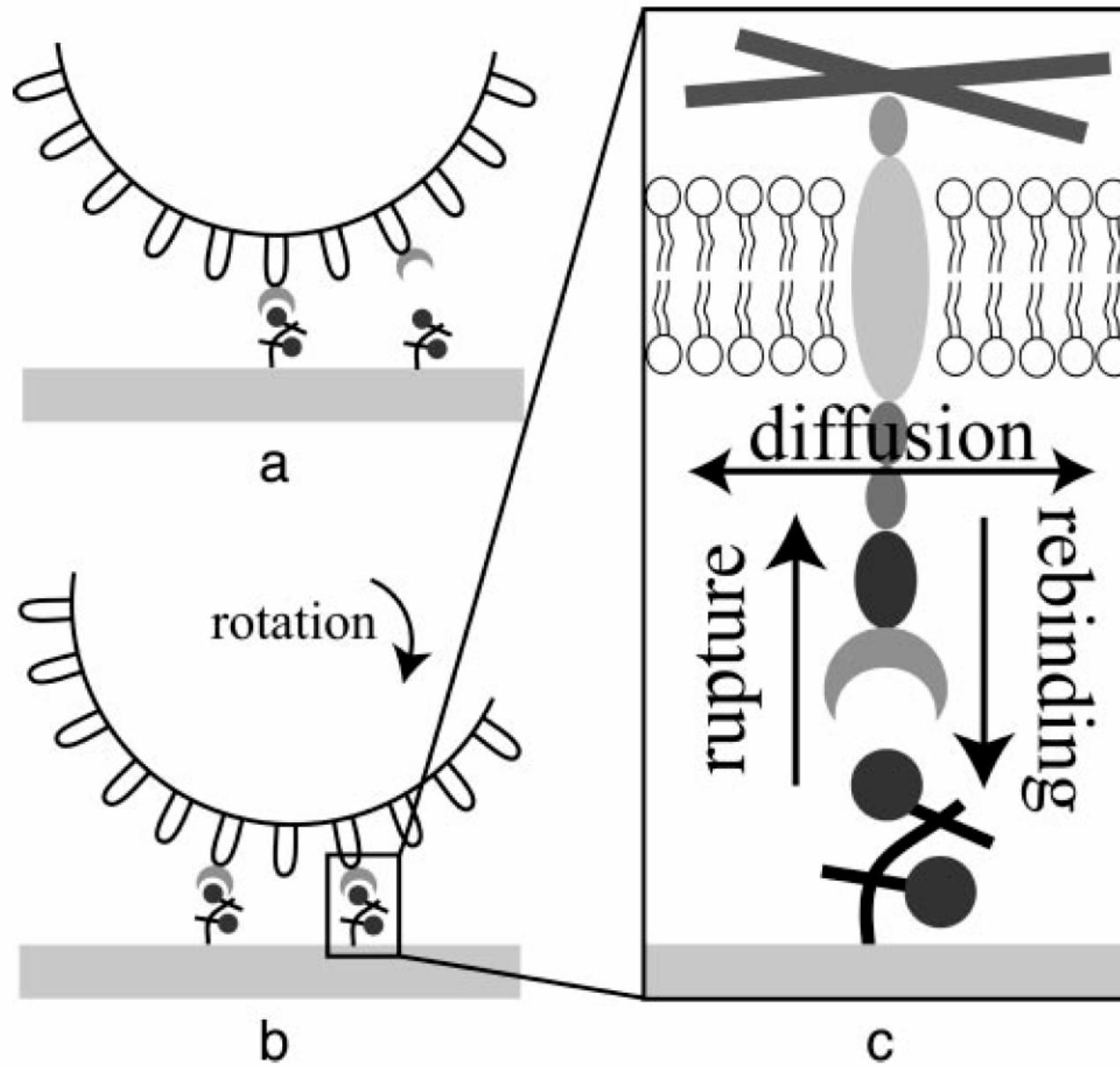


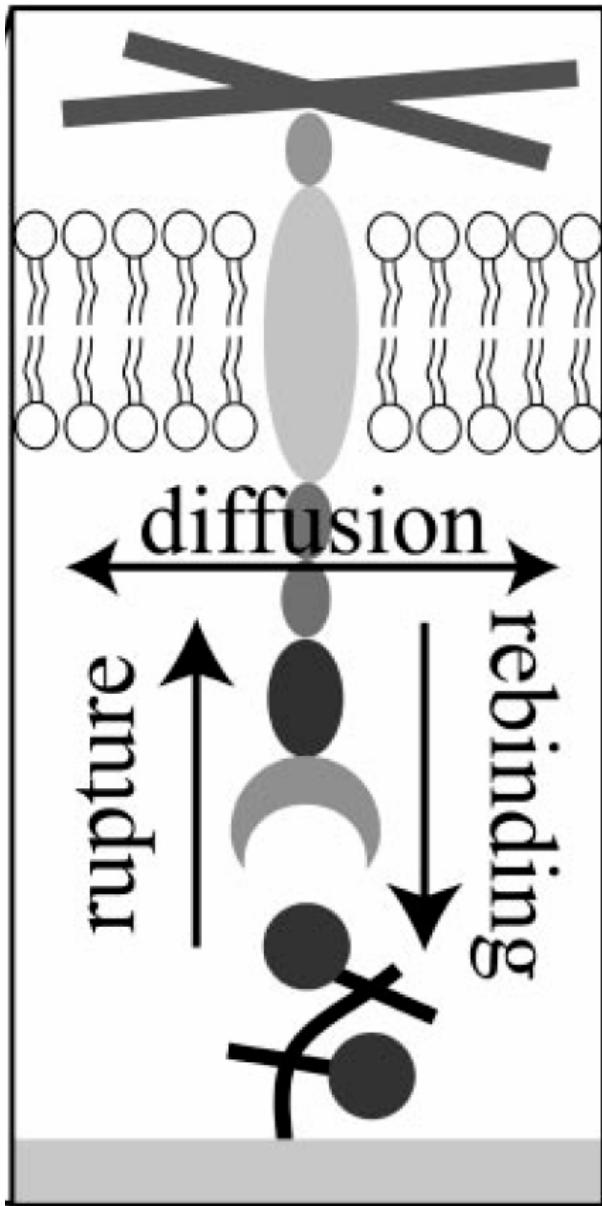
Initial binding most likely corresponds to one L-selectin receptor localized to the tip of one microvillus binding to ligand presented on a glycoprotein scaffold on the substrate. At low shear, stabilization through additional bonds is unlikely, because the distance between scaffolds is larger than the microvilli's tips, and the probability of two microvilli simultaneously hitting two ligands is very low.



At sufficiently high shear, shear-mediated rotation of the cell over the substrate leads to the establishment of an additional bond on another microvillus.

In contrast to this 2D cartoon, in practice, the two microvilli are expected to coexist with similar latitude, so they can share force in a cooperative way.





Close-up of the cell-substrate interface. The L-selectin receptor can move laterally in the membrane, with an effective diffusion constant that depends on cytoskeletal anchorage. If a receptor has bound to ligand on the substrate, it will rupture in a stochastic manner, depending on shear-induced loading. If an additional bond (most likely on the second microvillus) holds the cell during times of rupture, rebinding can occur at the first microvillus, thus increasing tether stabilization.

Rolling adhesion and firm adhesion of hamster leukocytes investigated by *in vivo* optical microscopy (real time)

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Leukozyte rolling in post-capillary venules *in vivo*

ROLLVIVMOVEMENTAND
QuickTime™ and a
Sorenson Video decompressor
are needed to see this picture.

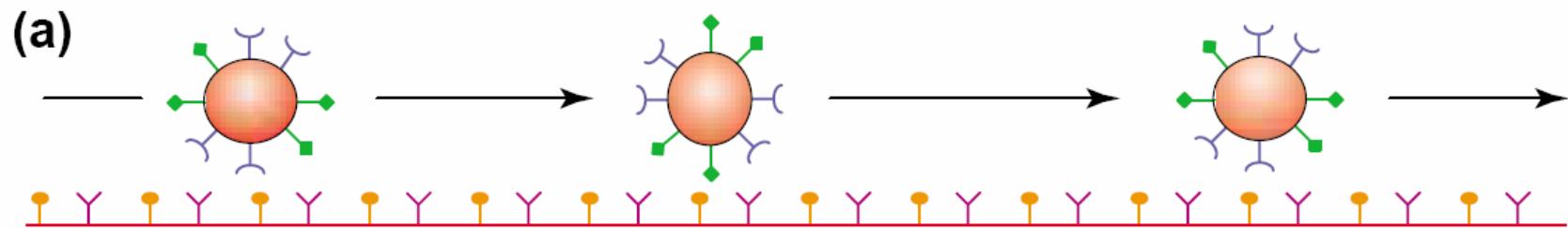
Leukozyte firm adhesion

QuickTime™ and a
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Leukozyte emigration *in vivo*

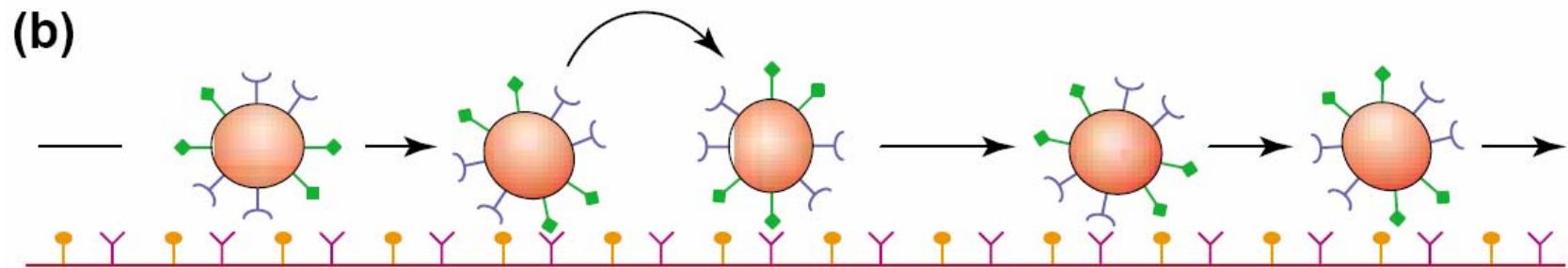
EMIGRATI.MOV

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are needed to see this picture.



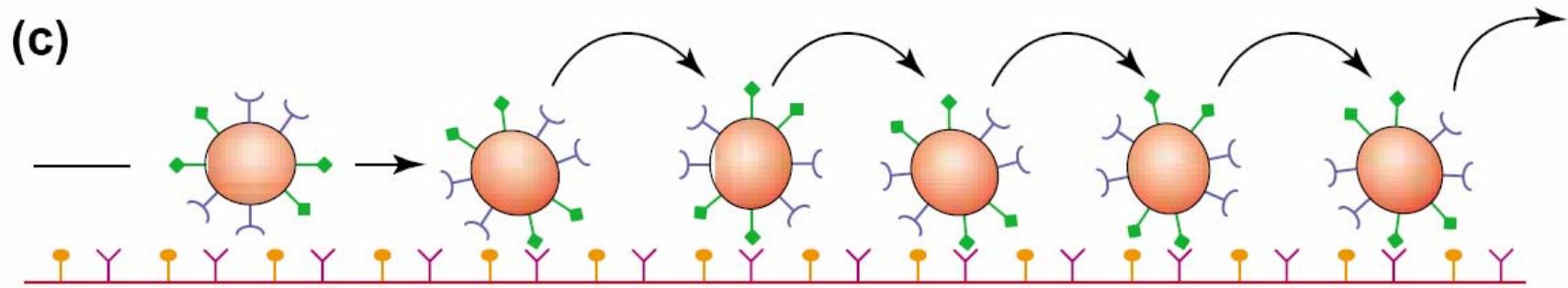
No adhesion; cells contact the surface but do not bind. Cells always move at or near the bulk fluid velocity.

Green, selectin;
red, selectin ligand;
blue, integrin receptor;
orange, integrin ligand.



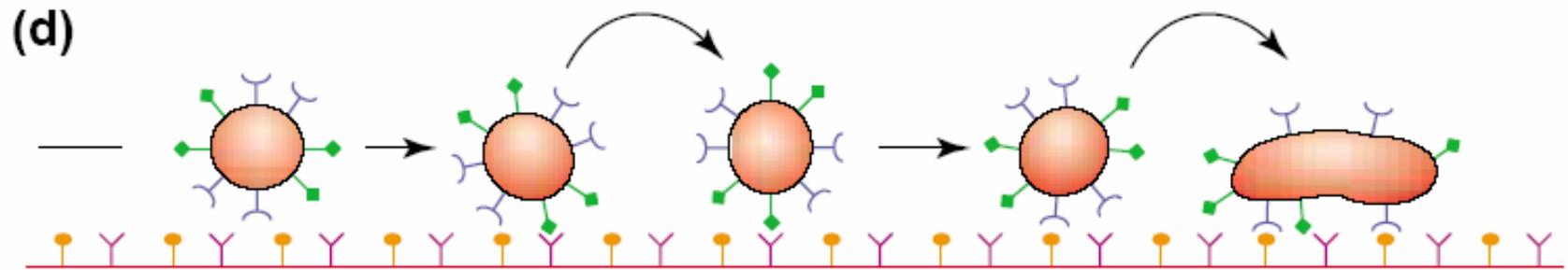
Transient adhesion mediated by selectins. Cells bind very briefly and slow below the bulk fluid velocity. Cells rapidly lose contact with the surface and achieve bulk fluid velocity.

Green, selectin;
red, selectin ligand;
blue, integrin receptor;
orange, integrin ligand.



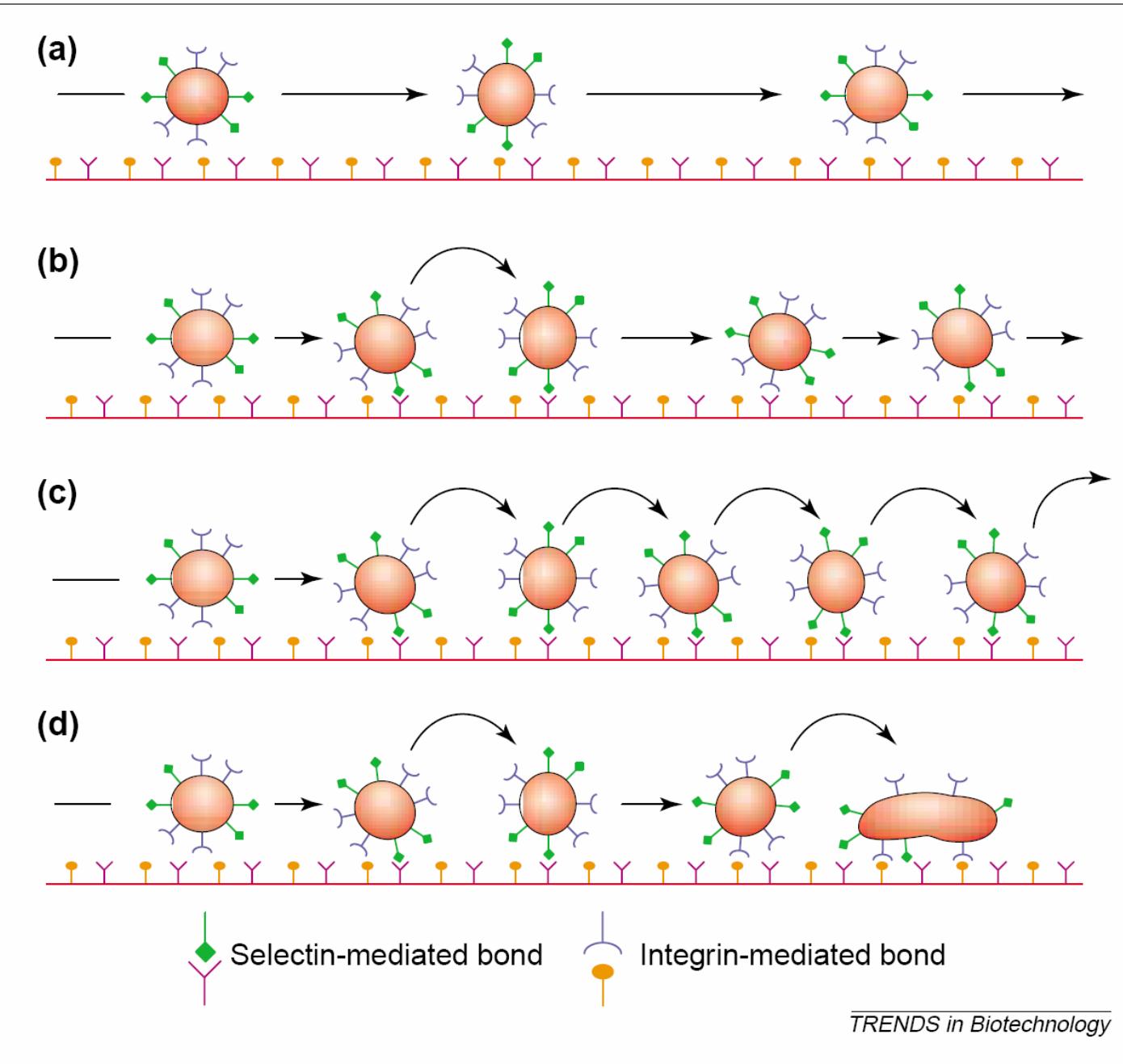
Rolling adhesions mediated by selectins; cells bind and translate along the surface at a reduced velocity.

Green, selectin;
red, selectin ligand;
blue, integrin receptor;
orange, integrin ligand.

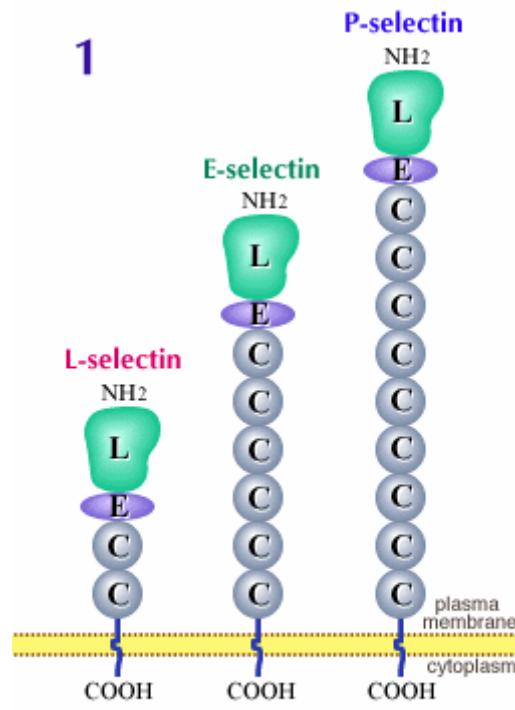


Firm adhesions mediated by integrins; cells bind strongly to the surface and move at a very slow rate.

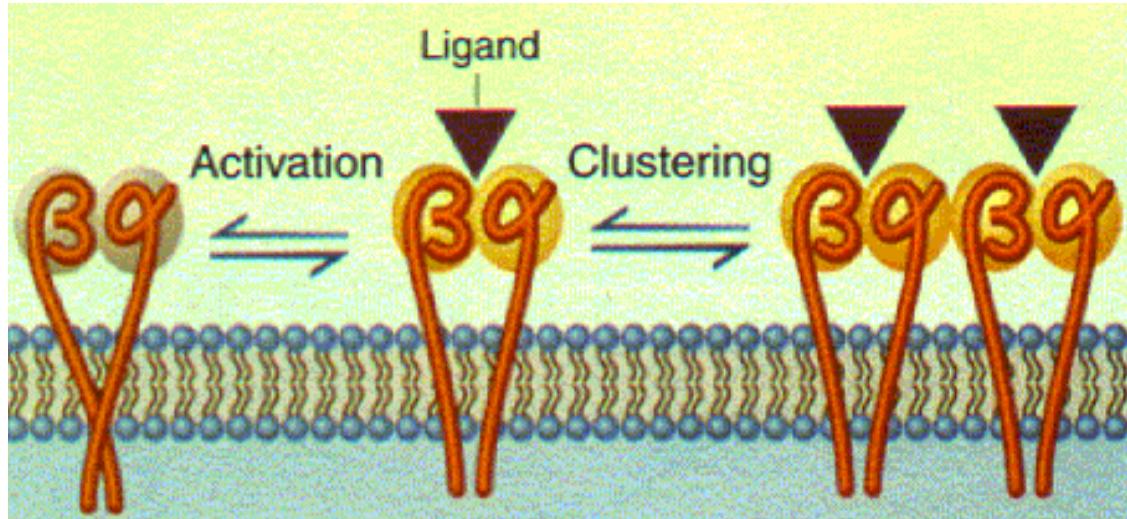
Green, selectin;
red, selectin ligand;
blue, integrin receptor;
orange, integrin ligand.



Selectins



Integrins

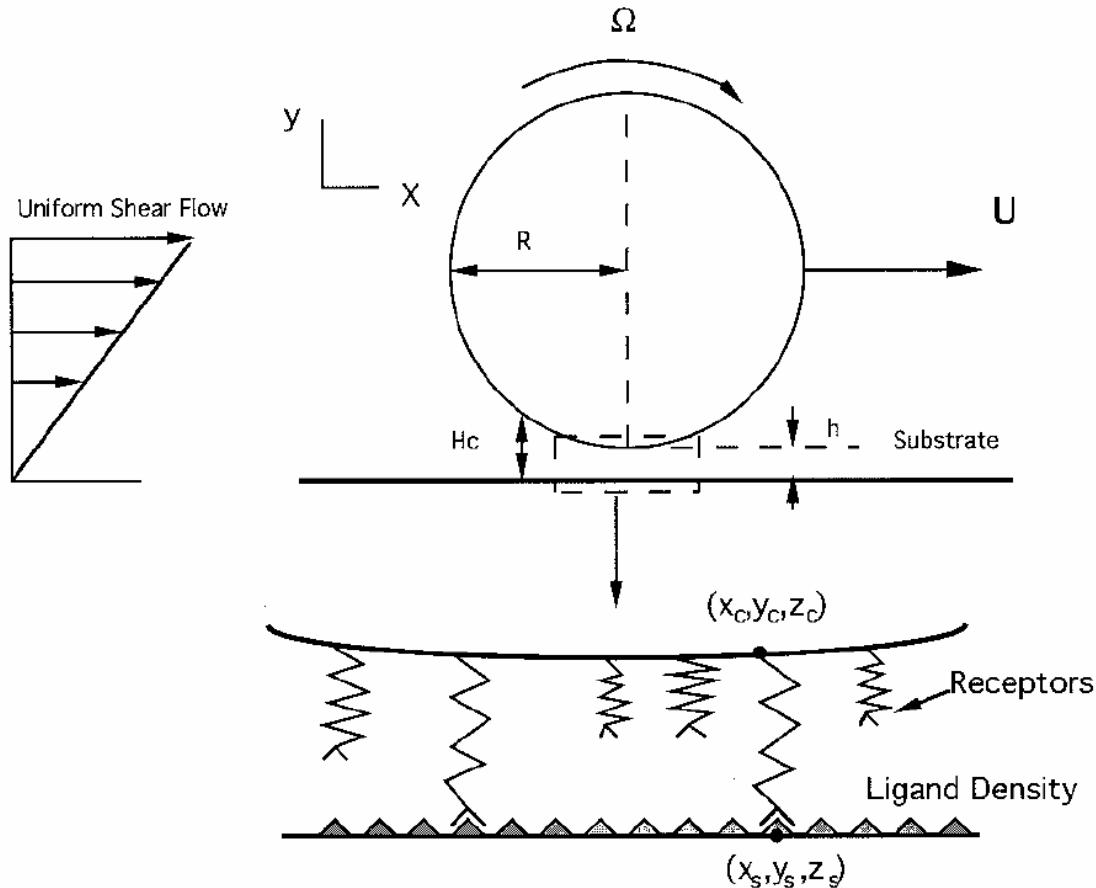


© [http://student.biology.arizona.edu/honors2001/
group08/intro/integrin-ab.GIF](http://student.biology.arizona.edu/honors2001/group08/intro/integrin-ab.GIF)

Integrins can be thought of as velcro on the surface of the cell.

When the cell is at rest, most of the integrins are inactive, that is to say they are present, but do not bind the ligands present in the extracellular matrix.

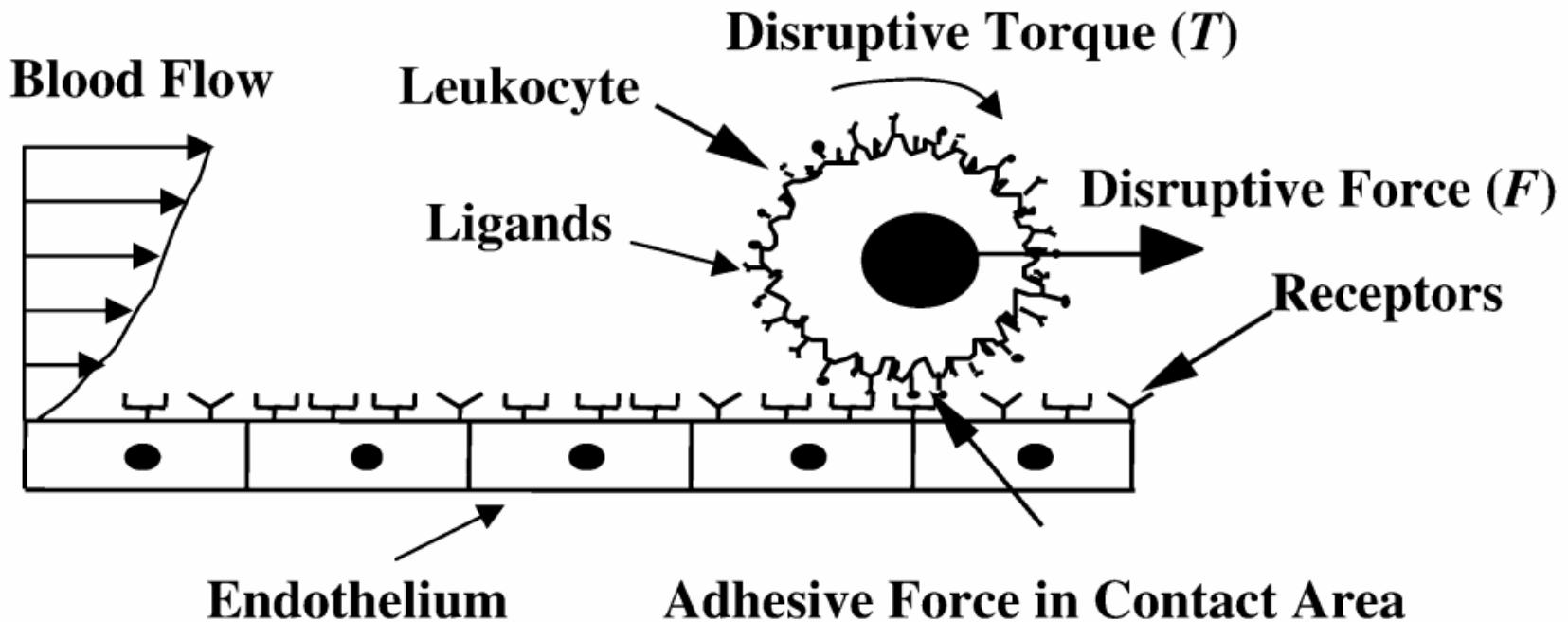
Leukocyte rolling and firm adhesion



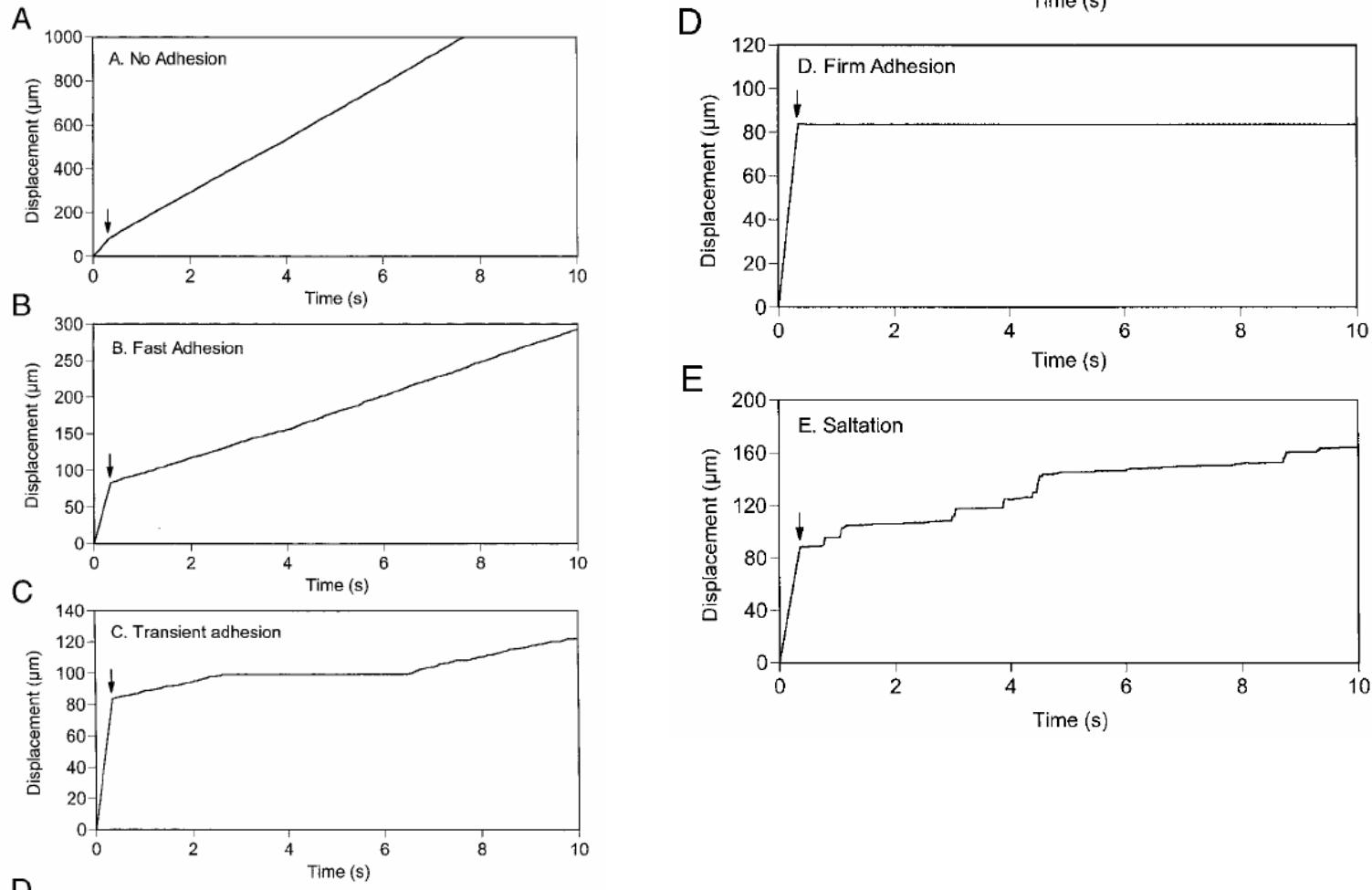
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From: K.C. Chang, D.F. Tees, D.A. Hammer, The state diagram for cell adhesion under flow:
Leukocyte rolling and firm adhesion, Proc. Natl. Acad. Sci. U S A. 97 (2000) 11262-11267.

Leukocyte rolling and firm adhesion

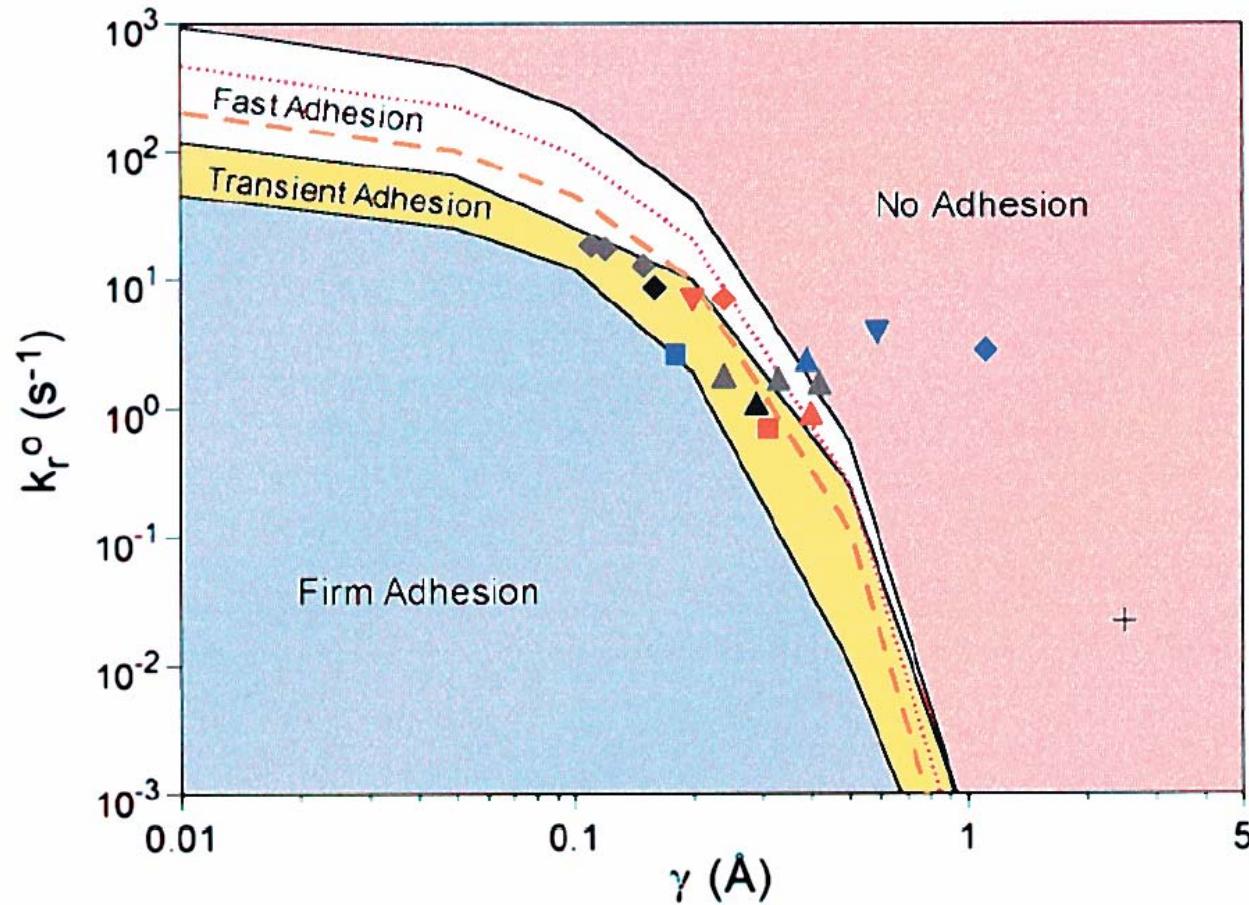


Leukocyte rolling and firm adhesion

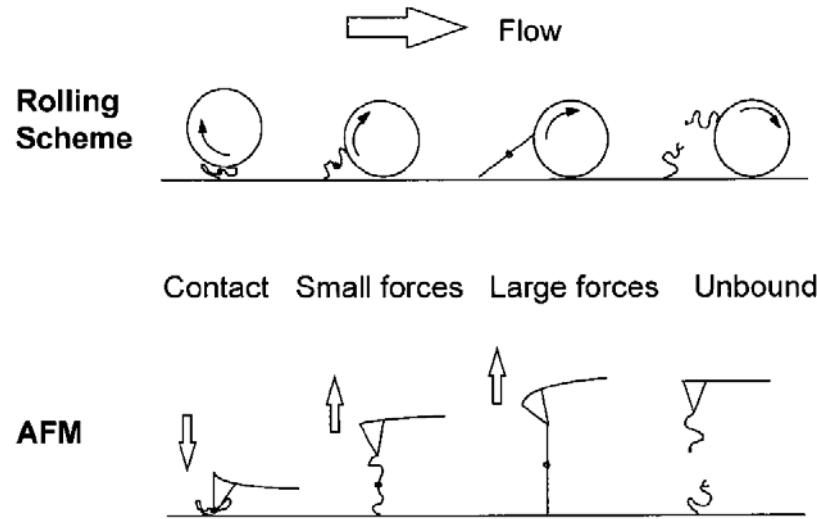


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Leukocyte rolling and firm adhesion

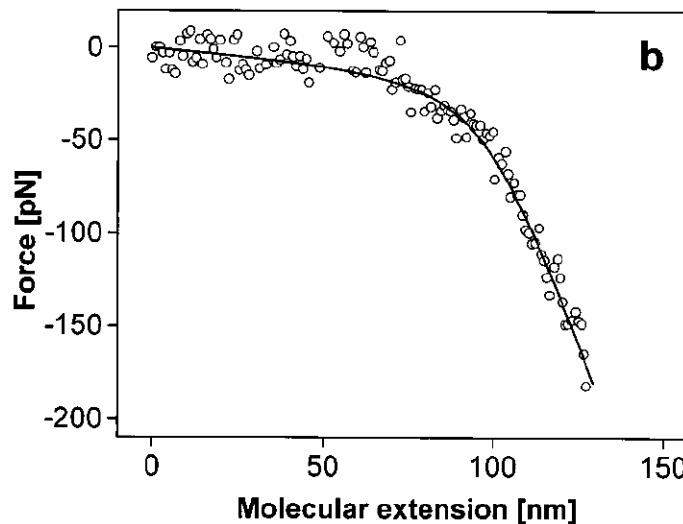
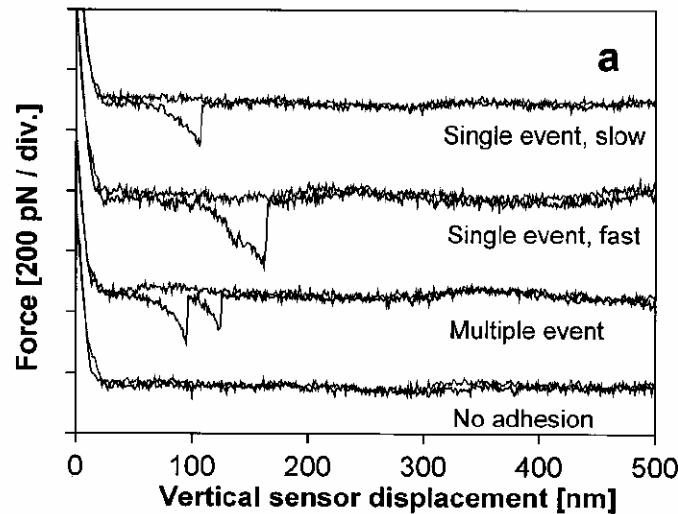


AFM experiments

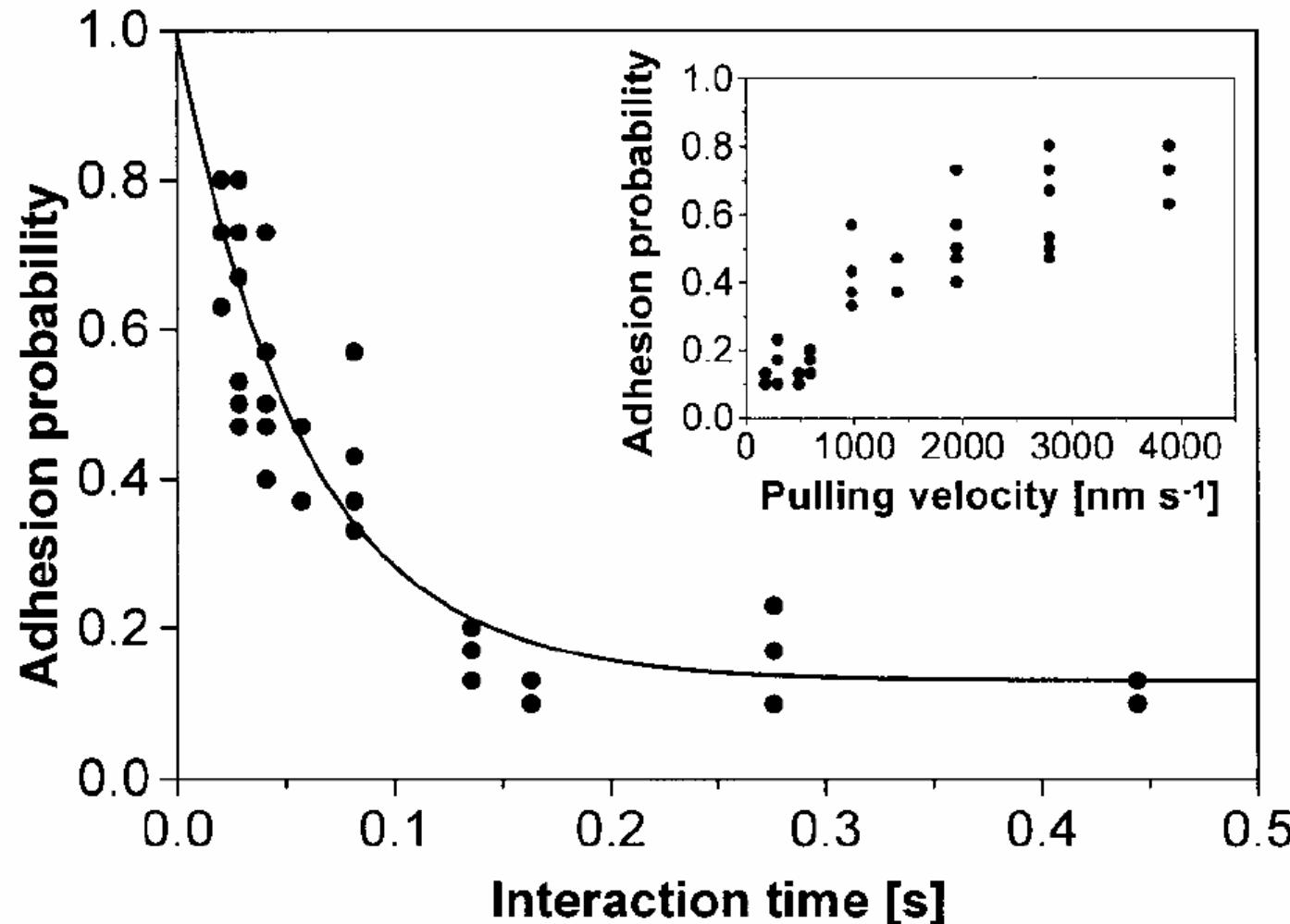


From: J. Fritz et al. © (1998) PNAS 95: 12283-8

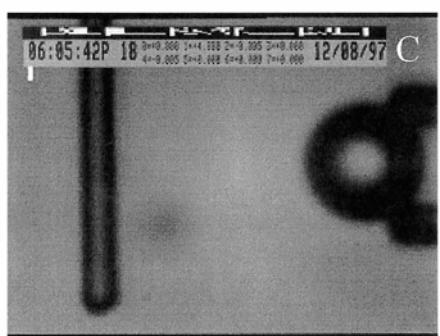
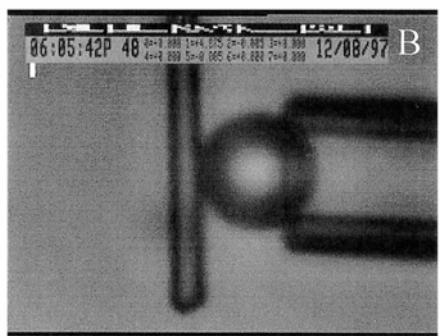
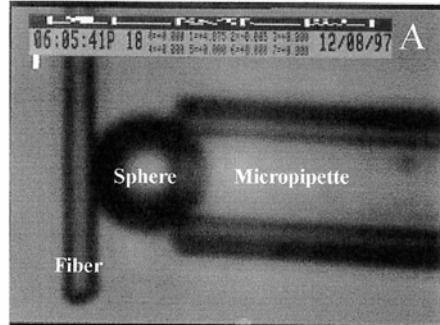
AFM experiments



AFM experiments

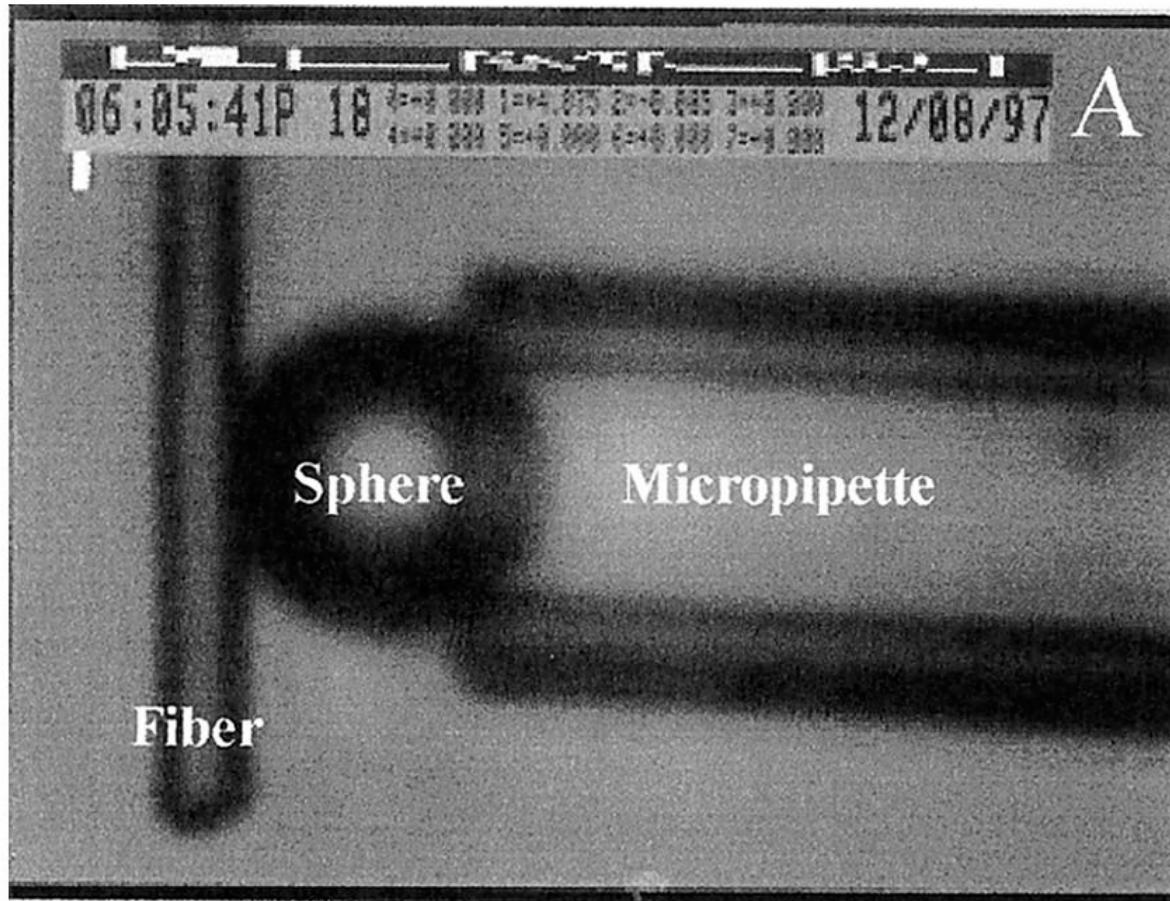


Microcantilever device



A sequence of video frames from an adhesive event. In frame *A*, the bead and fiber are apposed, with the fiber given a small negative displacement with respect to its rest position (frame *C*). In frame *B*, the micropipette is retracted and a bond between bead and fiber leads to positive deflection of the fiber. Immediately after this frame, the bond dissociated. Frame *C* shows the bead and fiber in their final rest positions.

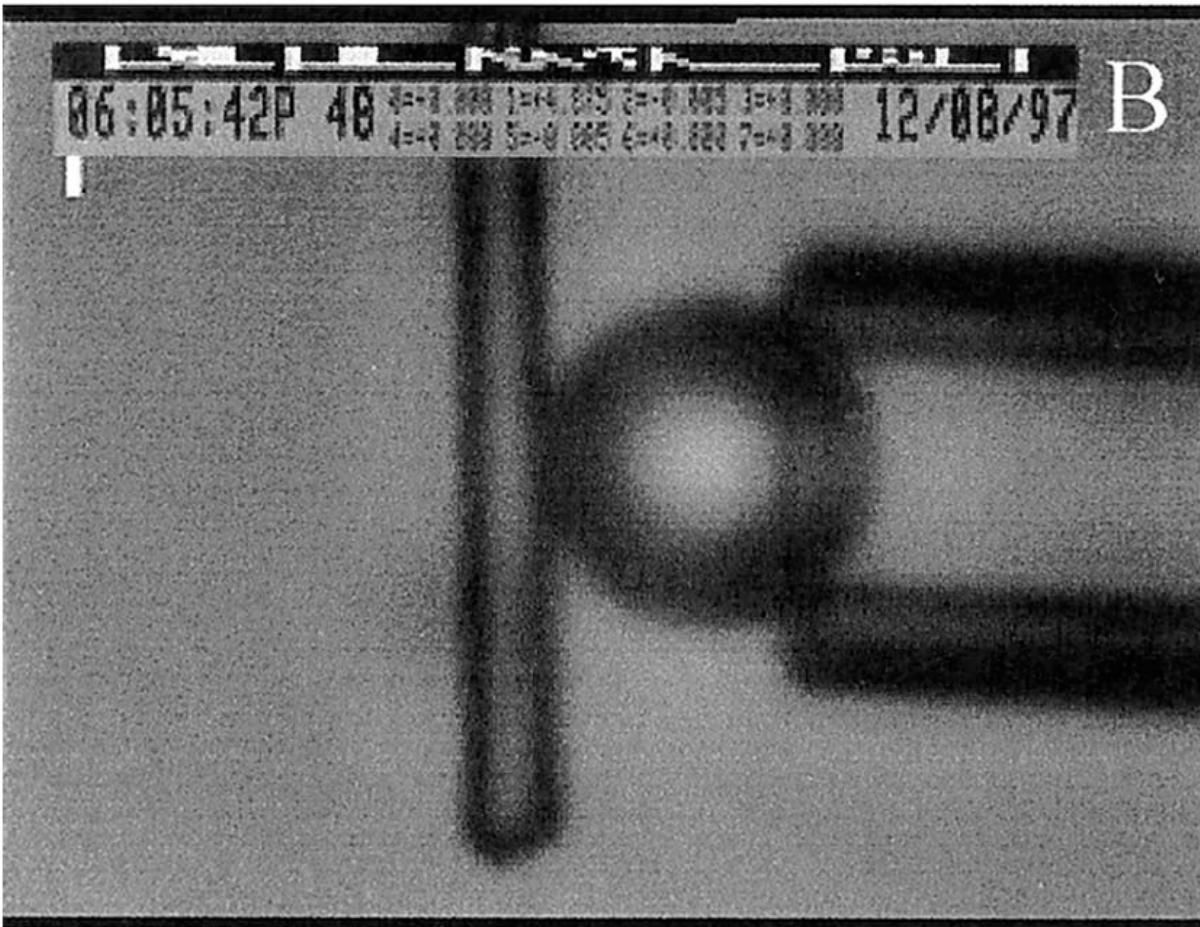
Microcantilever device



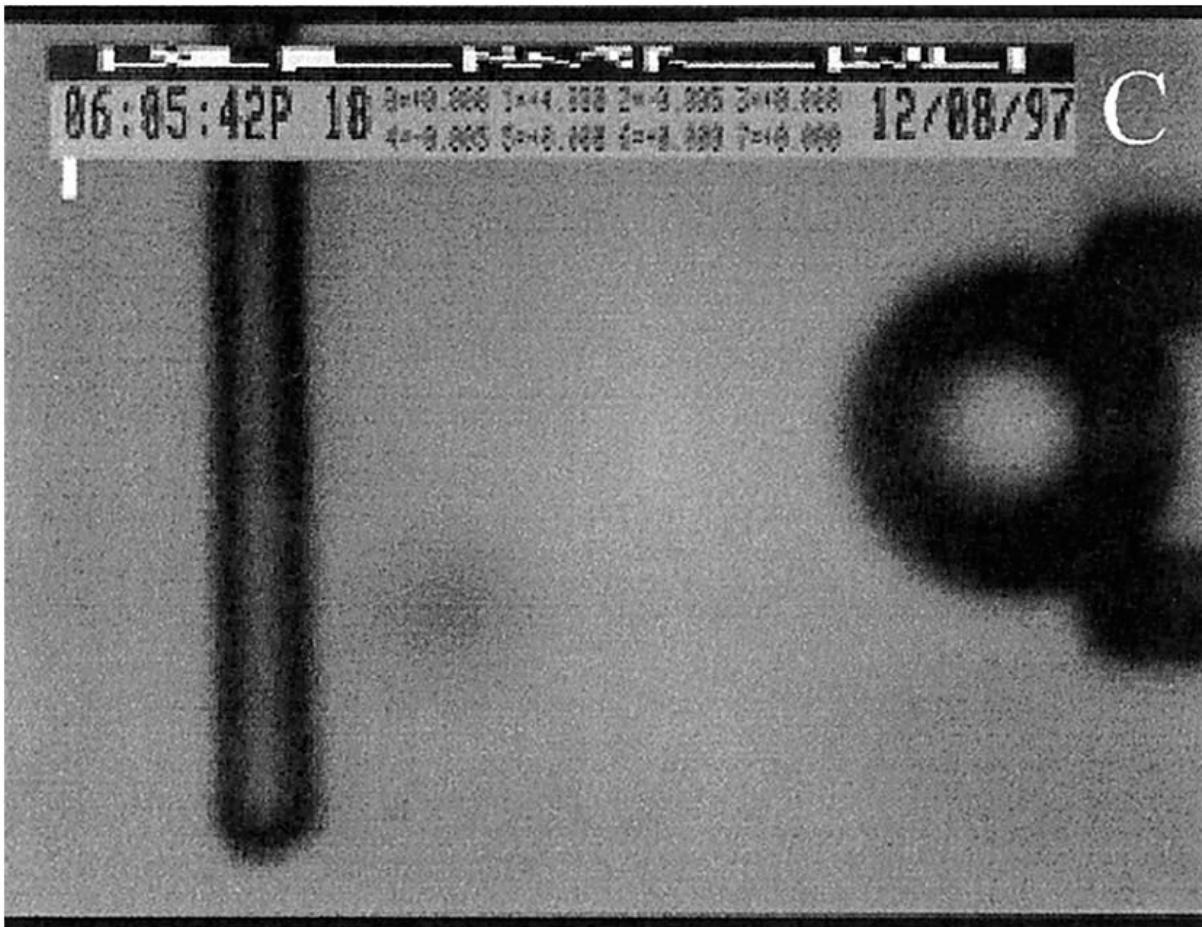
Microcantilever device

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Microcantilever device





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K*plus*
Kompetenzzentren-Programm

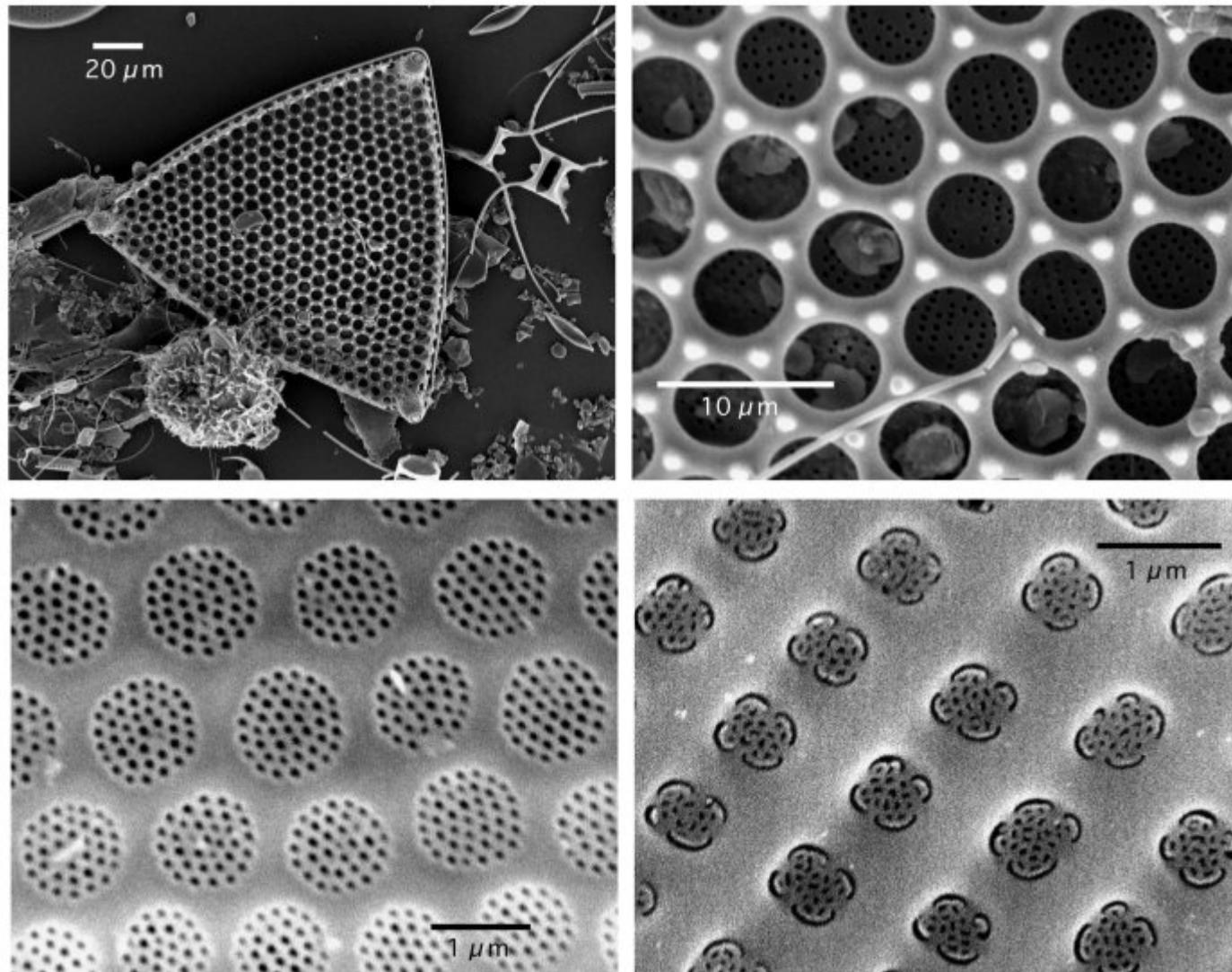
Diatoms

Diatoms

- single cellular organisms
- size some micrometers
- 10 000s different species
- reproduce via cell division
- under ideal conditions, within ten days the offspring of one single cell number one billion cells (*Fließband*, i.e. assembly line production of nanostructures !)
- nanostructured surfaces made from amorphous silicates



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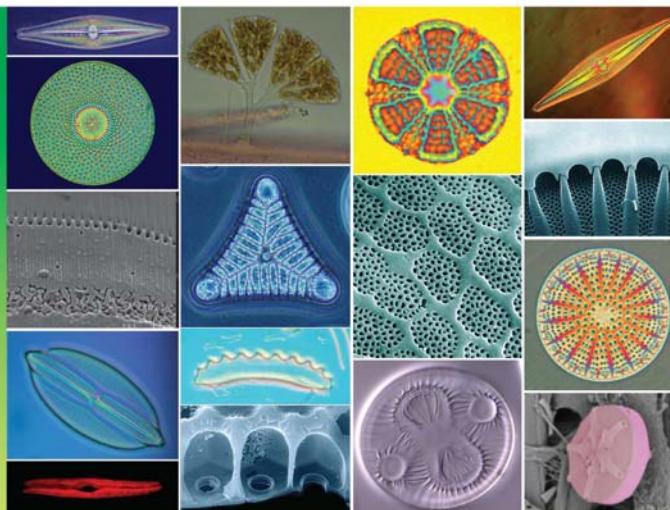
Top: *Tricaeratium favus*, bottom left: *Roperia tessellata*,
bottom right: *Achnathes brevipes* © Gebeshuber *et al.*, J. Mat. Sci. 2002

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Journal of

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A Special Issue on **Diatom Nanotechnology**

GUEST EDITORS
Richard Gordon, Frithjof Sterrenburg, and Kenneth Sandhage

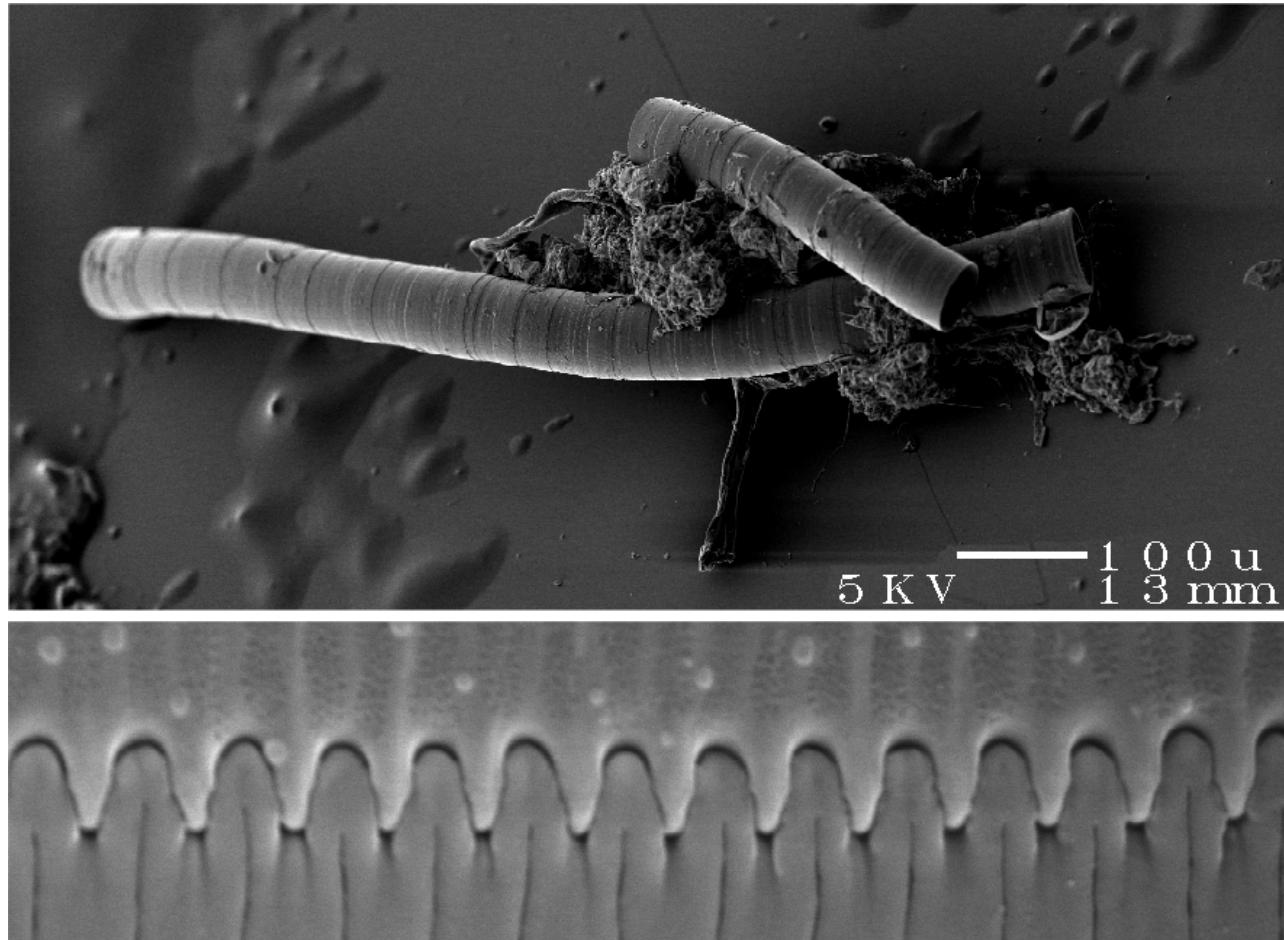


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- Diatoms: Toward Diatom Functional **Genomics**
- Nanostructures in Diatom Frustules: Functional Morphology of Valvocopulae in Coccconeidacean Monoraphid Taxa
- Nature's Batik: A Computer **Evolution** Model of Diatom Valve Morphogenesis
- Potential Roles for Diatomists in Nanotechnology
- Biosynthesis of Silicon-Germanium Oxide Nanocomposites by the Marine Diatom *Nitzschia frustulum*
- Investigation of Mechanical Properties of Diatom Frustules Using **Nanoindentation**
- Comments on Recent Progress Toward Reconstructing the Diatom Phylogeny
- Ceramic Nanoparticle Assemblies with **Tailored Shapes** and **Tailored Chemistries** via Biosculpting and Shape-Preserving Inorganic Conversion
- Controlled Silica Synthesis Inspired by Diatom Silicon **Biomineralization**
- Diatom Bionanotribology-Biological Surfaces in Relative Motion: Their Design, Friction, Adhesion, Lubrication and Wear
- Engineering and Medical Applications of Diatoms
- Zeolitisation of Diatoms
- Frustules to Fragments, Diatoms to Dust: How Degradation of Microfossil Shape and Microstructures Can Teach Us How Ice Sheets Work
- Crystal Palaces - Diatoms for Engineers
- The Evolution of **Advanced Mechanical Defenses** and Potential **Technological Applications** of Diatom Shells
- Geometry and Topology of Diatom Shape and Surface Morphogenesis for Use in Applications of Nanotechnology
- Diatom Auxospore Scales and Early Stages in Diatom Frustule Morphogenesis: Their Potential for Use in Nanotechnology
- Valve Morphogenesis in the Diatom Genus *Pleurosigma* W. Smith (Bacillariophyceae): Nature's Alternative Sandwich
- Prospects of Manipulating Diatom Silica Nanostructure
- Approaches for Functional Characterization of Diatom Silicic Acid Transporters
- Comparison of Diatoms, Exfoliated Graphite, Single-Wall Nanotubes, Multiwall Nanotubes, and Silica for the Synthesis of the **Nanomagnet Mn12**
- A Guide to the Diatom Literature for Diatom Nanotechnologists

Diatom biotribology

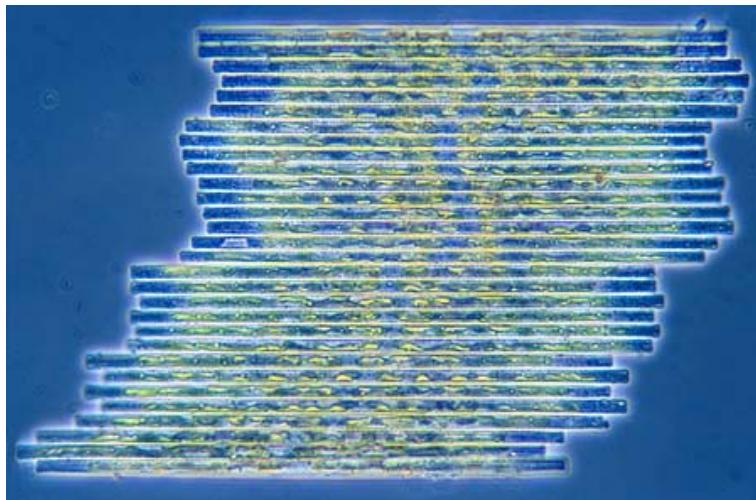
Ellerbeckia arenaria – the „rubberband“ diatoms:



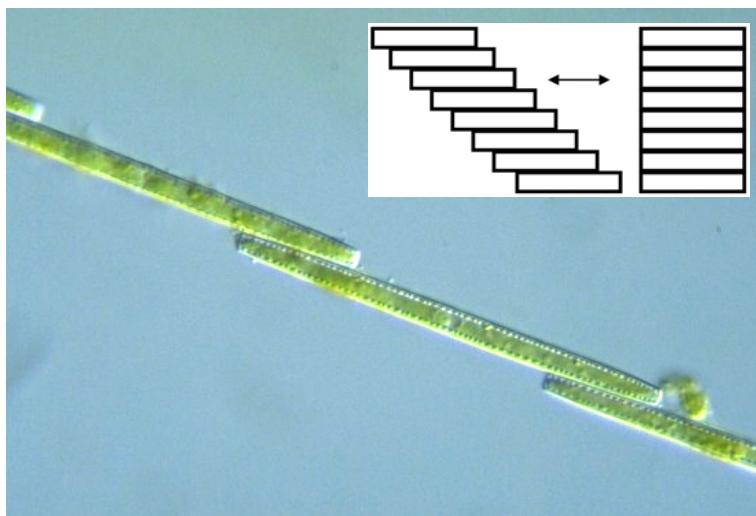
www.ac2t.at

Diatom biotribology

Bacillaria paxillifer – the moving diatoms:



©Wim van Egmond
www.micropolitan.org



© Protist information server
<http://protist.i.hosei.ac.jp/>

Diatom biotribology

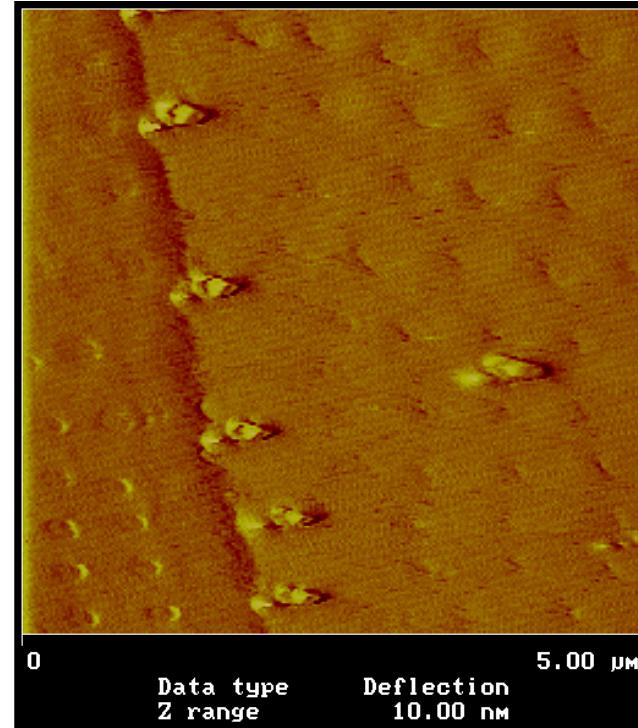
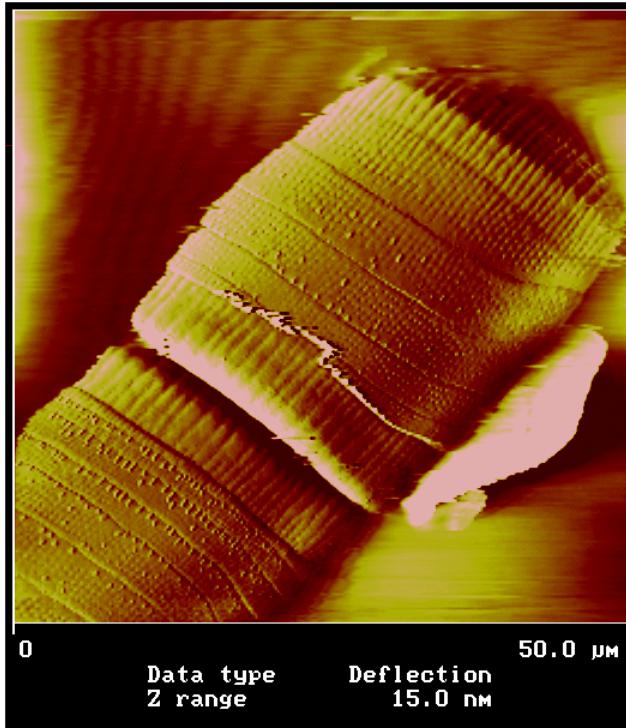
Bacillaria paxillifer – the moving diatoms:

movie

QuickTime™ and a
Sorenson Video 3 decompressor
are needed to see this picture.

Diatom biotribology

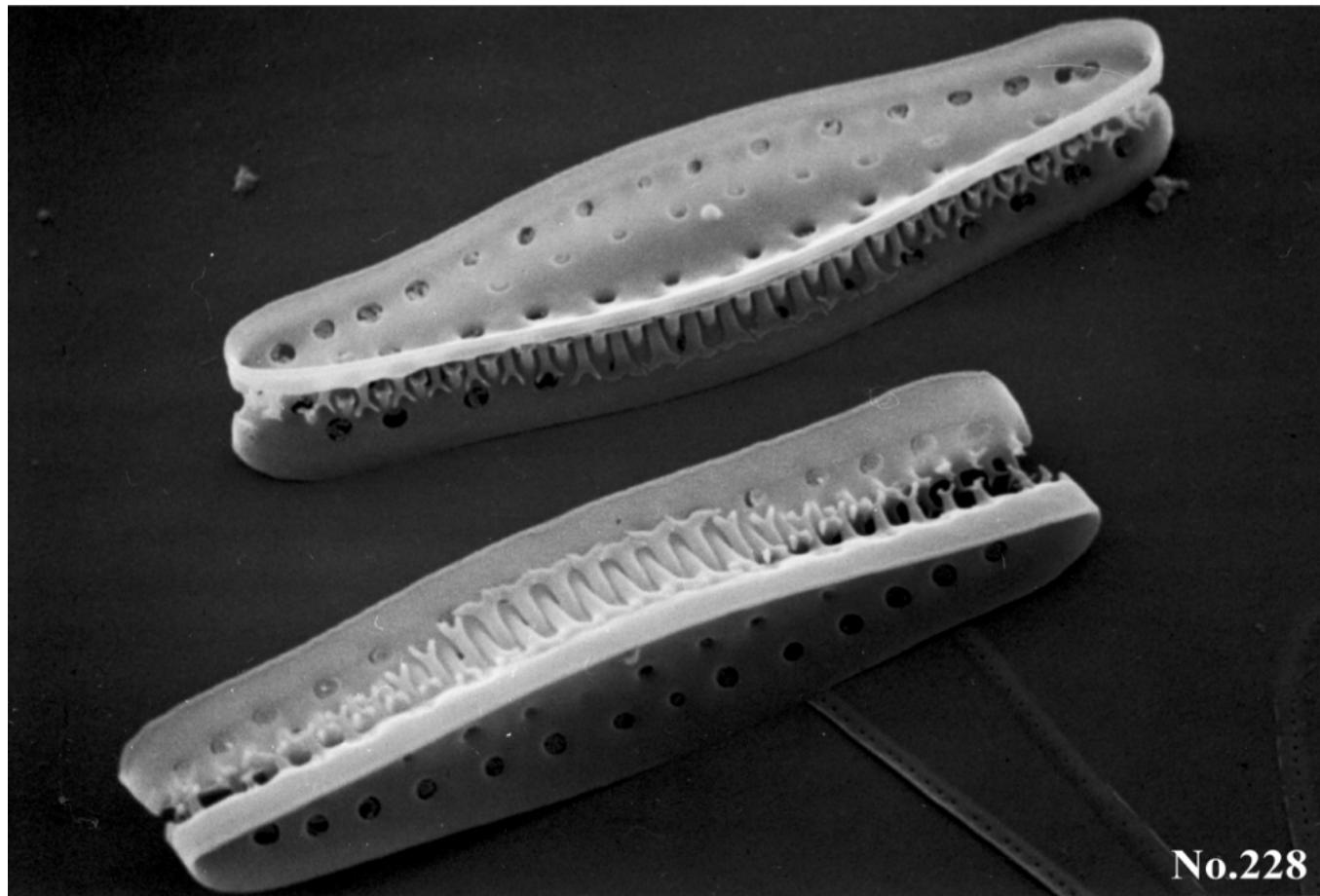
Ballbearings? Solid lubricants? In a protist ?!
An unidentified diatom visualised *in vivo* with an atomic force microscope:



© Gebeshuber *et al.*, J. Microsc.-Oxf. 2003

Diatom biotribology

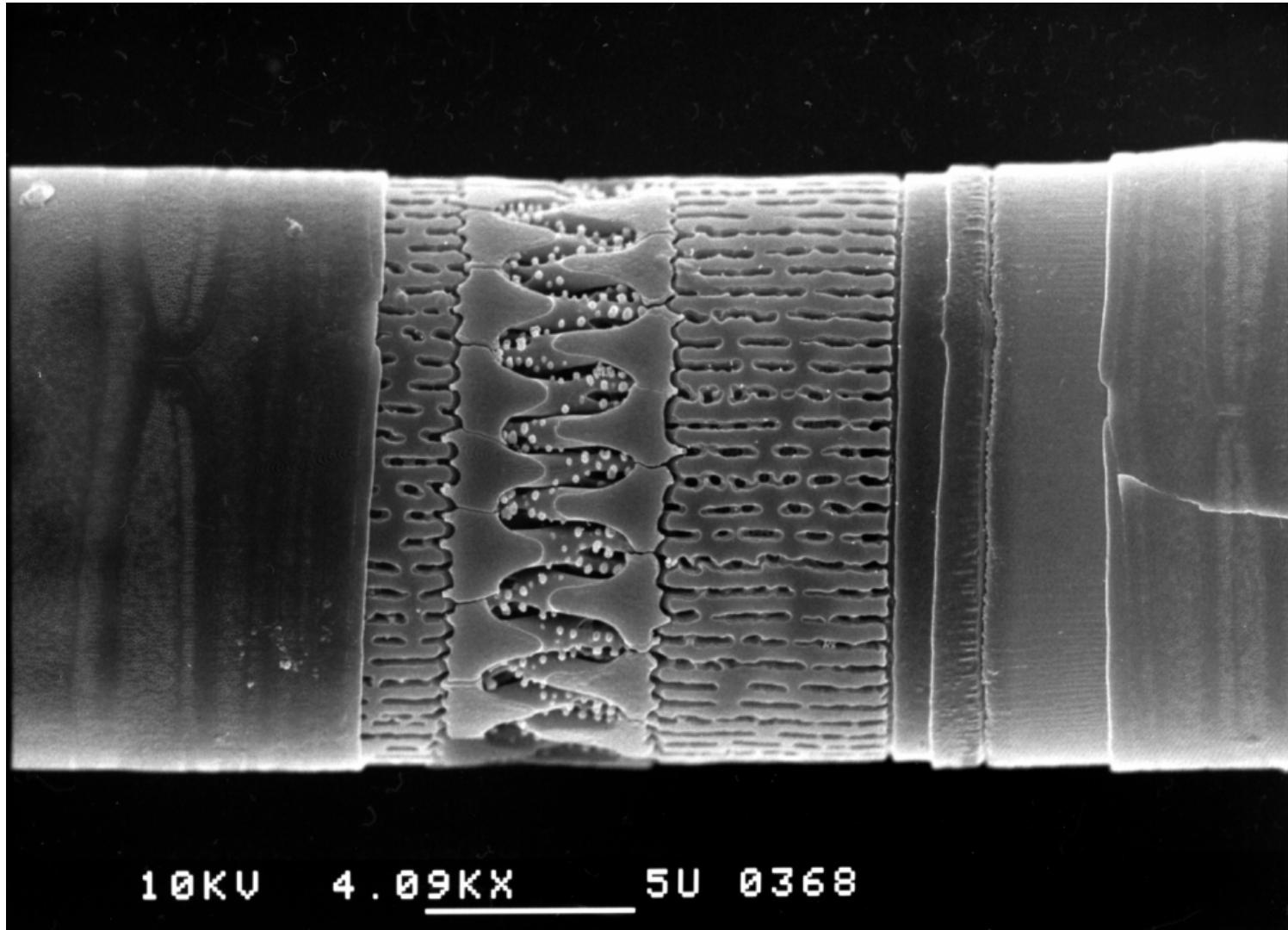
A melange of other interesting diatom species interesting for bionanotribological investigations:



No.228

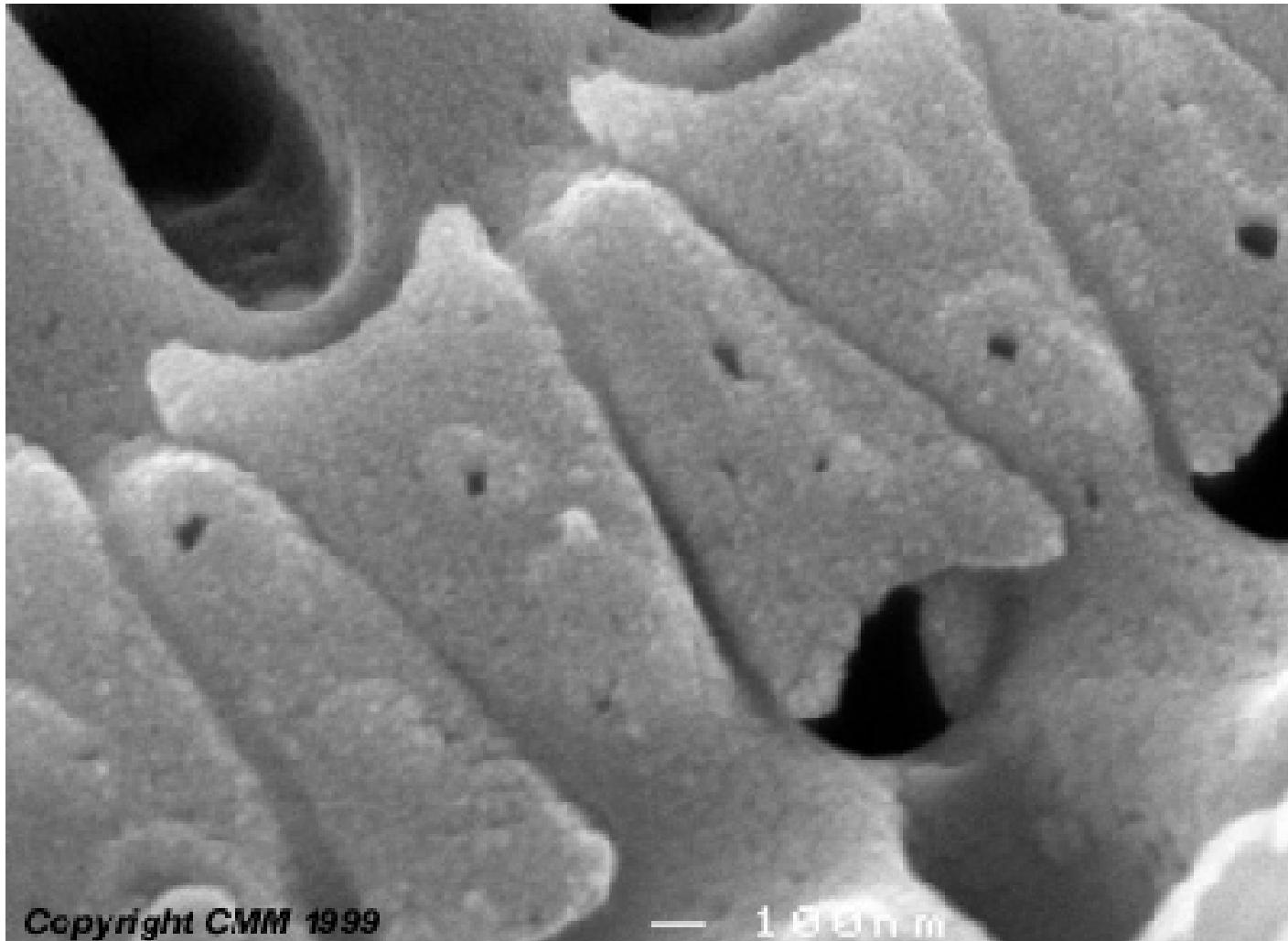
Cymatoseira belgica Grunow, © Richard M. Crawford, AWI Bremerhaven

Diatom biotribology



Aulacoseria italica. © RM Crawford, AWI Bremerhaven

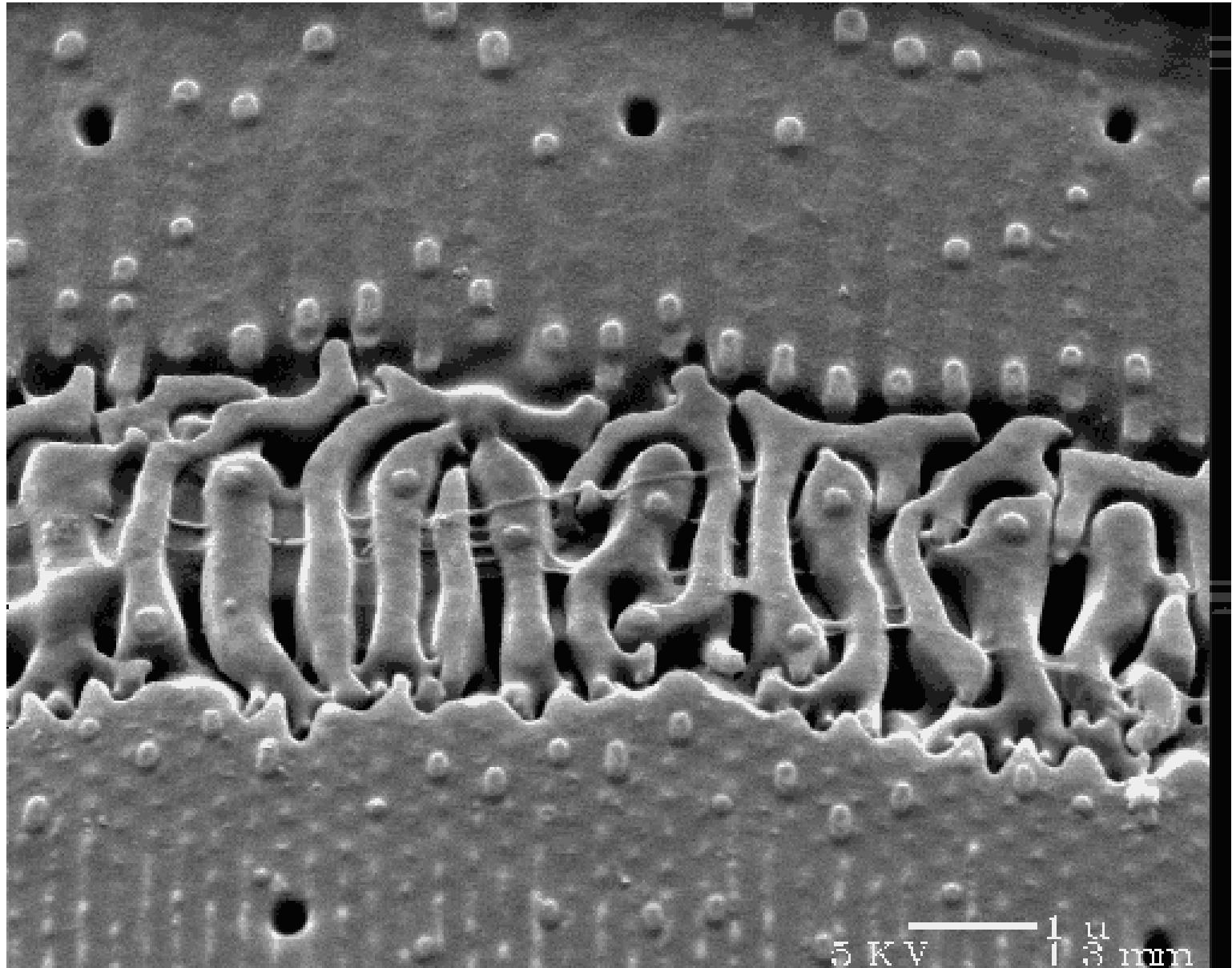
Diatom biotribology



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— 1.0 μm

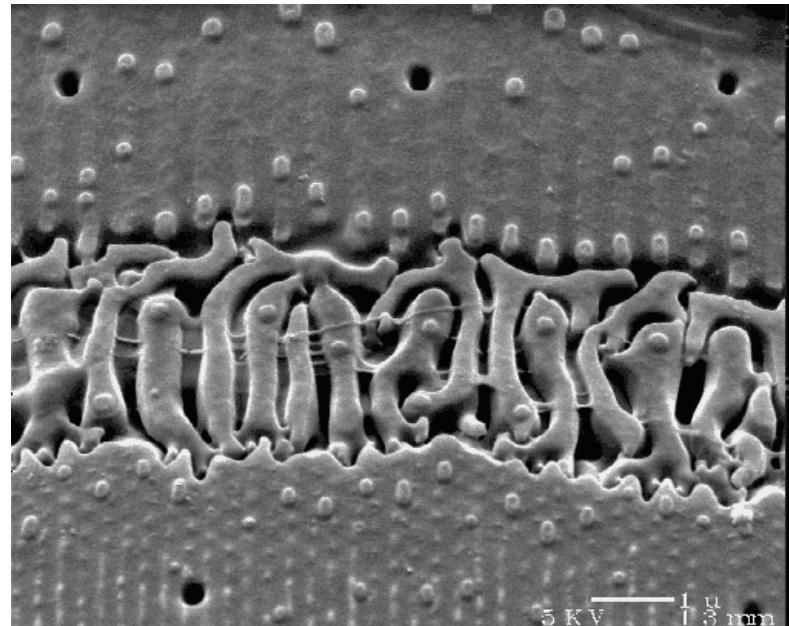
Aulacoseira granulata (?), Scalebar 100 nm



5 KV 1 μ m

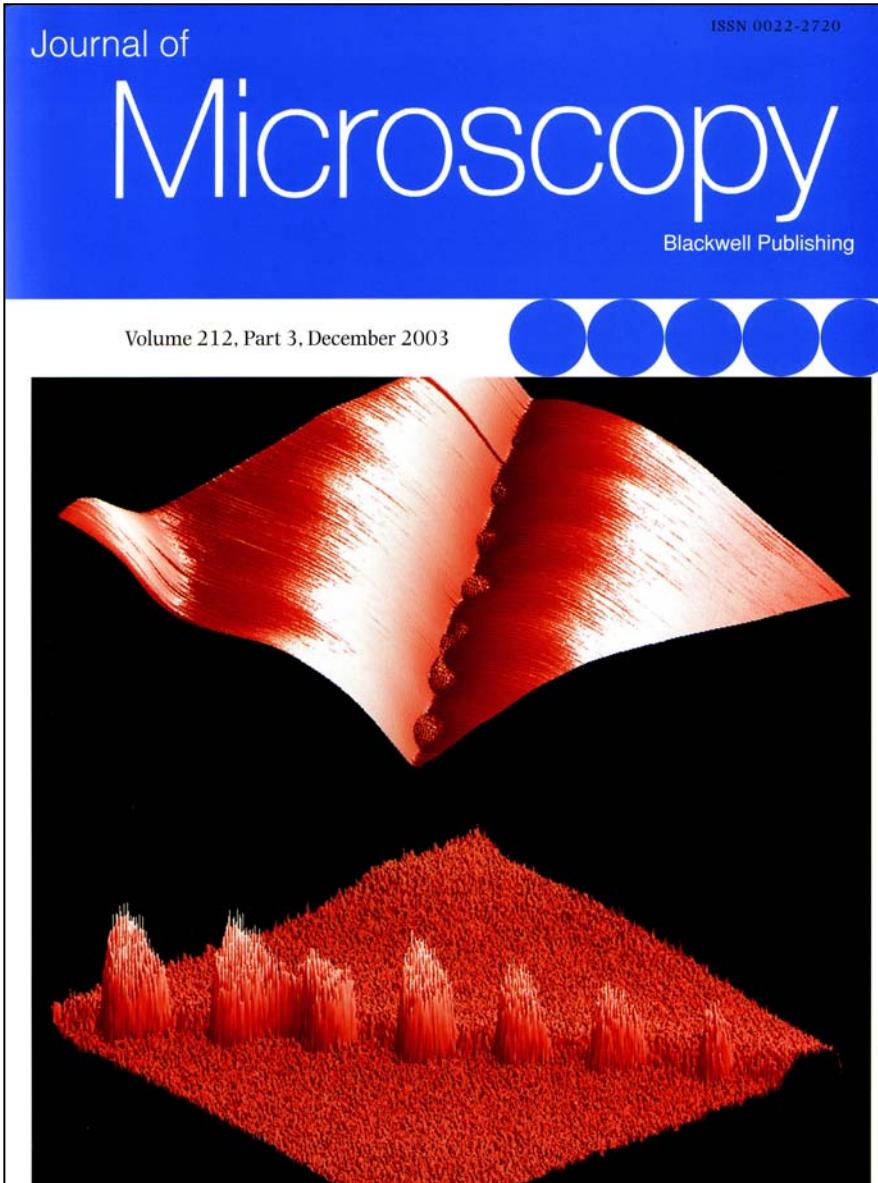
ॐ भूर्भुवः स्वः
तत्सत्त्विर्वरेण्यं ।
भर्गो देवस्य धीमहि
धियो यो नः प्रचोदयात् ॥

Gayatri mantra,
written in Sanskrit



Ellerbeckia arenaria,
the rubberband diatom

Biogenic adhesives



Gebeshuber I.C. et al. (2002) "In vivo nanoscale atomic force microscopy investigation of diatom adhesion properties", Mat. Sci. Technol. **18**, pp. 763-766.

Gebeshuber I.C. et al. (2003) "Atomic force microscopy study of living diatoms in ambient conditions", J. Microsc. Oxf. **212**, pp. 292-299.

Conclusions and Outlook

- Current **man-made** adhesives and lubricants are **not perfect**.
- Man has only done research in this field for some hundreds of years. **Nature** has been producing lubricants and adhesives for **millions of years**.
- Biomicro- and -nanotribology, the investigation of micro- and nanoscale tribological principles in biological systems, may be a path for realizing simultaneously "**smart**", **dynamic**, **complex**, **environmentally friendly**, **self-healing**, and **multifunctional** lubricants and adhesives.