Nanotribology and Nanomechanics of MEMS/NEMS and BioMEMS/BioNEMS Materials and Devices and Biomimetics

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Micro/nanoscale studies
- Bio/nanotribology
- Bio/nanomechanics
- Biomimetics

Techniques
- AFM/STM
- Microtriboapparatus
- Nanoindentor

Materials/Device Studies
- Materials/coatings
- SAM/PFPE/Ionic liquids
- Biomolecular films
  - CNTs
- Micro/nanofabrication

Collaborations

Applications
- MEMS/NEMS
- BioMEMS/NEMS
- Superhydrophobic surfaces
- Reversible adhesion
- Beauty care products
- Probe-based data storage

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Outline

• Background
  - Definition of MEMS/NEMS and characteristic dimensions
  - Examples of MEMS/NEMS and BioMEMS/bioNEMS with tribology and mechanics issues

• Experimental
  - Atomic force/Friction force microscope (AFM/FFM)

• Tribological Studies of Lubricants
  - Perfluoropolyether lubricants and self-assembled monolayers

• Bioadhesion Studies
  - Surface modification approaches to improve bioadhesion

• Hierarchical Nanostructures for Superhydrophobicity and self cleaning (Lotus Effect)
  - Roughness optimization for superhydrophobic and self cleaning surfaces
  - Experimental studies

• Hierarchical Nanostructures for Reversible Adhesion (Gecko Feet)
  - Hierarchical structure for adhesion enhancement
  - Roughness optimization for reversible dry adhesives (*not included*)
Background

Definition of MEMS/NEMS and characteristic dimensions

MEMS - characteristic length less than 1 mm, larger than 100 nm
NEMS - less than 100 nm

Characteristic dimensions in perspective

Stiction – High static friction force required to initiate sliding. Primary source is liquid mediated adhesion

\[ F_m = 2\pi R \gamma (\cos \theta_1 + \cos \theta_2) \]

Formation of meniscus and contribution to the attractive force

Examples of MEMS with tribology and mechanics issues

- **Electrostatic micromotor (Tai et al., 1989)**
- **Microturbine bladed rotor and nozzle guide vanes on the stator (Spearing and Chen, 2001)**
- **Six-gear chain (www.sandia.gov)**
- **Ni-Fe wolfram-type gear system by LIGA (Lehr et al., 1996)**
Microgear unit can be driven at speeds up to 250,000 RPM. Various sliding components are shown after wear test for 600k cycles at 1.8% RH (Tanner et al., 2000)

Microengine driven by electrostatically-actuated comb drive

Sandia Summit Technologies (www.mems.sandia.gov)

Stuck comb drive
Examples of commercial MEMS devices

Capacitive type silicon accelerometer for automotive sensory applications (Sulouf, 1998)

Piezoresistive type pressure sensor (Parsons, 2001)

Thermal inkjet printhead (Baydo and Grosup, 2001)
Tilt mirror arrays for switching optical signal in input and output fiber arrays in optical crossconnect for telecom.
(Aksyuk et al., 2003)

Digital micromirror device for displays (Hornbeck, 1999)

RF microswitch
(Courtesy IMEC, Belgium)
Examples of NEMS

32 x 32 tip array
(http://www.ibm.com)

Probe-based NEMS data storage based on thermomechanical recording

- Intergrated tip heaters consist of tips of nanoscale dimension.
- Thermomechanical recording is performed on an about 40-nm thick polymer medium on Si substrate.
- Heated tip to about 400 °C contacts with the medium for recording.
- Wear of the heated tip is an issue.

Probe-based NEMS data storage based on ferroelectric recording

- Ferroelectric material, typically lead zirconate titanate (PZT)
- Electrical current switches between two different polarization states by applying short voltage pulses (~10 V, ~100 ms), resulting in recording. Temperature rise on the order of 80°C is expected.
- Piezoresponse force can be read out by applying an AC voltage of 1 V.
- Wear of the tip and medium at 80°C is an issue.
- Furthermore, the tip does not need to be in contact with medium during readback.
Mechanical properties of nanotube ribbons, such as the elastic modulus and tensile strength, critically rely on the adhesion and friction between nanotubes.

The electrical resistance of the system is sensitive to the adsorption of molecules to the nanotube/electrode. Adhesion should be strong between adsorbents and SWNT.

Force applied at the free end of nanotube cantilever is detected as the imbalance of current flowing through the nanotube bearing supporting the nanotube cantilever. The deflection of nanotube cantilever involves inter-tube friction.
Examples of BioMEMS/BioNEMS

BioMEMS-lab-on-a-chip
(Tang and Lee, 2001)
The generating points of friction and wear due to interaction of a biomolecular layer on a synthetic microdevice with tissue (Bhushan et al., 2006)
Two examples of polymer MEMS designed to measure cellular forces (Wei, Bhushan, Hansford and Ferrell, 2005)

Implantable immunoisolation biocapsule (Hansford et al., 2001)

1. Binding (0-8 hours after injection)
2. Plug rupture, drug release (12-48 hrs.)
3. Pore formation - cell lysis and death (12-48 hrs)

Intravascular nanoparticles for search and destroy diseased blood cells (Martin and Grove, 2001)
Tribology and mechanics issues during device operation

- Capacitive type accelerometer
- Digital micromirror device
- RF Microswitch
- BioFET sensor

Impact/Wear
Stationary plates
Stiction (meniscus effects)
Stiction and Wear

Field insulator (SiO₂)
Source metal (Al)
Receptor biological molecules
Drain metal (Al)
p⁻ Si
n⁺ source
Gate insulator (SiO₂)
n⁺ drain

Highly resistive substrate
Off-state
Need to address tribology and mechanics issues

The tribology and mechanics problems can drastically compromise device performance and reliability. To solve these problems, there is a need to develop a fundamental understanding of adhesion, friction/stiction, wear and the role of surface contamination and environment in MEMS/NEMS and BioMEMS/NEMS. This can be done by studying

- Tribology and mechanics of MEMS/NEMS materials
- Lubricant methods for MEMS/NEMS
- Bioadhesion Studies
- Development of superhydrophobic surfaces
- Device level studies

Approach

- Use an AFM/FFM for imaging and to study adhesion, friction, scratch and wear properties of materials and lubricants, which better simulates MEMS/NEMS and BioMEMS/BioNEMS contacts
- Develop and employ techniques to measure tribological phenomena in devices

Experimental

Atomic force/Friction force microscope (AFM/FFM)

• At most interfaces of technological relevance, contact occurs at numerous asperities. It is of importance to investigate a single asperity contact in the fundamental tribological studies.

• Nanotribological studies are needed
  - To develop fundamental understanding of interfacial phenomena on a small scale
  - To study interfacial phenomena in micro- or nanostructures and performance of ultra-thin films used in MEMS/NEMS components
Large sample AFM/FFM
Square pyramidal silicon nitride tip

Square pyramidal Single-crystal silicon tip

Three-sided pyramidal (natural) diamond tip

Carbon nanotube tip

Various AFM tips
Chemically bonded liquid and solid lubricants with monolayer thicknesses are desired for low friction and wear.

Lubricants must be hydrophobic to minimize effect of environment.

- Perfluoropolyether (PFPE) lubricants
- Self-assembled monolayers (SAMs)
Perfluoropolyether lubricants

Z-15: $CF_3-O-(CF_2-CF_2-O)_m-(CF_2-O)_n-CF_3$

Z-DOL: $OH-CH_2-CF_2-O-(CF_2-CF_2-O)_m-(CF_2-O)_n-CF_2-CH_2-OH$

- During cycling tests, the friction Z-DOL (BW) exhibits the lowest friction and Z-15 shows negative effect.

- During cycling tests, the friction of Si(100) and Z-DOL (BW) does not change. The friction of Z-15 film initially increases and reaches to a higher and stable value. The initial rise occurs because of the molecular interaction between the attached Z-15 molecules to the tip and the Z-15 molecules on the film surface.

Durability data

Self-assembled monolayers (SAMs)

Perfluoroalkylsilane and alkylsilane SAMs were deposited on Si(111) with natural oxide and perfluoroalkylphosphonate and alkylphosphonate on Al.

PFTS showed lower adhesive force than and comparable coefficient of friction to ODMS and ODDMS.
Chain length has little effect.
DP and ODP showed higher coefficient of friction and comparable adhesive force to ODMS and ODDMS.
A critical normal load was observed for SAMs, higher than that for substrates. Critical loads are lowest for ODMS and DP, moderate for PFTS, PFTP and ODP, and highest for ODDMS.
Bioadhesion Studies

- Study surface modification approaches - nanopatterning and chemical linker method to improve adhesion of biomolecules on silicon based surfaces.

Sample preparation

STA: Streptavidin
APTES: Aminopropyltriethoxysilane
NHS: N-hydroxysuccinimido
BSA: Bovine serum albumin
Schematic representation of deposition of streptavidin (STA) by chemical linker method.
Adhesion measurements in PBS with functionalized tips

**Patterned silica surface exhibits higher adhesion compared to unpatterned silica surface. Biotin coated surface exhibits even higher adhesion.**
Hierarchical Nanostructures for Superhydrophobicity & self cleaning

One of the crucial property in wet environments is non-wetting or superhydrophobicity and self cleaning. These surfaces are of interest in various applications, e.g., self cleaning windows, windshields, exterior paints for buildings, navigation-ships and utensils, roof tiles, textiles and reduction of drag in fluid flow, e.g. in micro/nanochannels. Also, superhydrophobic surface can be used for energy conservation and energy conversion such as in the development of a microscale capillary engine.

Reduction of wetting is also important in reducing meniscus formation, consequently reducing stiction.

Various natural surfaces, including various leaves, e.g. Lotus, are known to be superhydrophobic, due to high roughness and the presence of a wax coating (Neinhuis and Barthlott, 1997)

Rolling off liquid droplet over superhydrophobic Lotus leaf with self cleaning ability
Roughness optimization model for superhydrophobic and self cleaning surfaces

Wenzel’s equation:

\[ \cos \theta = R_f \cos \theta_0 \]

Droplet of liquid in contact with a smooth and rough surface

Effect of roughness on contact angle

Formation of the composite interface

Cassie-Baxter equation:

\[ \cos \theta = R_f f_{SL} \cos \theta_0 - f_{LA} \]
\[ = R_f \cos \theta_0 - f_{LA} (R_f \cos \theta_0 + 1) \]

\( f_{LA} \) requirement for a hydrophilic surface to be hydrophobic

\[ f_{LA} \geq \frac{R_f \cos \theta_0}{R_f \cos \theta_0 + 1} \text{ for } \theta_0 < 90^\circ \]

In fluid flow, another property of interest is contact angle hysteresis ($\theta_H$)

- Increased droplet volume $\rightarrow$ $\theta_{adv}$: Advancing contact angle
- Decreased droplet volume $\rightarrow$ $\theta_{rec}$: Receding contact angle

$\theta_H = \theta_{adv} - \theta_{rec}$

If $\theta_H$ is low, energy spent during movement of a droplet is small and a droplet can move easily at a small tilt angle $\alpha$

$\theta_{adv} - \theta_{rec} \approx \frac{R_f \sqrt{1 - f_{LA}} (\cos \theta_{rec} - \cos \theta_{adv})}{\sqrt{2(R_f \cos \theta_0 + 1)}}$

for high contact angle ($\theta \rightarrow 180^\circ$)

Increase in $f_{LA}$ and reduction in $R_f$ decrease $\theta_{adv} - \theta_{rec}$

Fabrication and characterization of nanopatterned polymers

Study the effect of nano- and microstructure on superhydrophobicity

Nanopatterns

Micropatterns

Low aspect ratio (LAR) – 1:1 height to diameter

High aspect ratio (HAR) – 3:1 height to diameter

Lotus patterned

- Materials
  - Sample
    - Poly(methyl methacrylate) (PMMA) (hydrophilic) for nanopatterns and micropatterns
    - Hydrophobic coating for PMMA
    - Perfluorodecyltriethoxyxilane (PFDTES) (SAM)

Contact angle on micro-/nanopatterned polymers

- Different surface structures: film, Lotus, LAR, HAR
- Hydrophobic film, PFDTES, on PMMA and PS surface structures

- In hydrophilic surfaces, contact angle decreases with roughness and in hydrophobic surfaces, it increases.
- The measured contact angles of both nanopatterned samples are higher than the calculated values using Wenzel equation. It suggests that nanopatterns benefit from air pocket formation. Furthermore, pining at top of nanopatterns stabilizes the droplet.

<table>
<thead>
<tr>
<th></th>
<th>LAR</th>
<th>HAR</th>
<th>Lotus</th>
</tr>
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<tbody>
<tr>
<td>$R_f$</td>
<td>2.1</td>
<td>5.6</td>
<td>3.2</td>
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Fabrication and characterization of micropatterned silicon

Transition for Cassie-Baxter to Wenzel regime depends upon the roughness spacing and radius of droplet. It is of interest to understand the role of roughness and radius of the droplet.

Optical profiler surface height maps of patterned Si with PF$_3$

- Different surface structures with flat-top cylindrical pillars:
  - Diameter (5 µm) and height (10 µm) pillars with different pitch values (7, 7.5, 10, 12.5, 25, 37.5, 45, 60, and 75 µm)

- Materials
  - Sample – Single-crystal silicon (Si)
  - Hydrophobic coating – 1, 1, -2, 2, -tetrahydroperfluorodecyltrichlorosilane (PF$_3$) (SAM)

Transition criteria for patterned surfaces

- The curvature of a droplet is governed by Laplace eq. which relates pressure inside the droplet to its curvature. The maximum droop of the droplet

\[ \delta \approx \frac{(\sqrt{2}P - D)^2}{R} \]

If \( \delta \geq H \) \( \implies \) Transition from Cassie-Baxter regime to Wenzel regime

- Geometry (P and H) and radius R govern transition. A droplet with a large radius (R) w.r.t. pitch (P) would be in Cassie-Baxter regime.

Contact angle, hysteresis, and tilt angle on patterned Si surfaces with PF$_3$

• For the selected droplet, the transition occurs from Cassie-Baxter regime to Wenzel regime at higher pitch values for a given pillar height.

The critical radius of droplet for the transition increases with the pitch based on both the transition criterion and the experimental data.
Structure of ideal hierarchical surface

• Based on the modeling and observations made on leaf surfaces, hierarchical surface is needed to develop composite interface with high stability.

• Proposed transition criteria can be used to calculate geometrical parameters for a given droplet radius. For example, for a droplet on the order of 1 mm or larger, a value of $H$ on the order of $30 \mu m$, $D$ on the order of $15 \mu m$ and $P$ on the order of $130 \mu m$ is optimum.

• Nanoasperities should have a small pitch to handle nanodroplets, less than 1 mm down to few nm radius. The values of $h$ on the order of 10 nm, $d$ on the order of 100 nm can be easily fabricated.
Fabrication of microstructure

- Microstructure
  - Replication of micropatterned silicon surface using an epoxy resin and then cover with the wax material

B. Bhushan et al., *Soft matter* 4, 1799 (2008); *Appl. Phys. Lett.* 93, 093101 (in press); ibid, (submitted)
Fabrication of nanostructure and hierarchical structure

- Nanostructure
  - Self assembly of the *T. majus* wax deposited by thermal evaporation
    - Expose to a solvent in vapor phase for the mobility of wax molecules
- Hierarchical structure
  - Micropatterned epoxy replica and covered with the tubules of *T. majus* wax

* T. majus wax with ethanol vapor (50°C)

Nanostructure (0.8 μg/mm²)  
Hierarchical structure (0.8 μg/mm²)

B. Bhushan, Y. C. Jung, A. Niemietz, and K. Koch (submitted)
Static contact angle, contact angle hysteresis, tilt angle and adhesive force on various structures

*T. majus* wax (0.8 μg/mm²) with ethanol vapor (50º C)

- Nanostructures and hierarchical with tubular wax led to high static contact angle of 160º and 171º and low hysteresis angle on the order of 5º and 2º.
- Hierarchical structure has low adhesive force due to decrease of the solid-liquid contact area in both levels of structuring.

B. Bhushan, Y. C. Jung, A. Niemietz, and K. Koch (submitted)
Hierarchical Nanostructures for Reversible Adhesion (Gecko Feet)

Several creatures, including insects, spiders and lizards (e.g., Gecko) have unique ability to cling to ceilings and walls utilizing dry adhesion. They can also detach at will by peeling.

- Gecko is capable of producing 20 N of adhesive force.
- This ability is due to the intricate micro/nanostructures that compose the skin of the gecko.
  - Lamellae, Setae, Branches, Spatulae

Potential Uses
- Everyday objects
  - Adhesive tape, fasteners, and toys
    - MEMS/NEMS
  - Wall climbing robots
  - Space (microgravity) applications
    - MEMS assembly

Courtesy MPI Stuttgart
Hierarchical structure for adhesion enhancement

Upper level of seta
- Length: 30-130 µm
- Diameter: 5-10 µm
- \( \rho \approx 14000 \text{ mm}^2 \)

Branches
- Length: 20-30 µm
- Diameter: 1-2 µm

Spatulae
- Length: 2-5 µm
- Diameter: 0.1-0.2 µm
- \( \rho/\text{seta} \approx 100-1000 \)

Tokay Gecko Surface Construction
(Autumn et al., 2000; Gao et al., 2005; Autumn, 2006)

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Simulation model

Schematic of three layer hierarchical morphology of gecko seta with three levels of branches: seta level, middle level, and spatula level.

One-, two- and three-level spring models for simulation effect hierarchical morphology on interaction seta with rough surface.

For one-level model, elastic force, \( F_{el} \) in the springs \( (k_I) \) due to compression of \( \Delta l \):

\[
F_{el} = -k_I \sum_{i=1}^{p} \Delta l_i u_i
\]

\( u_i = \begin{cases} 
1 & \text{if contact} \\
0 & \text{if no contact}
\end{cases} \)

For two-level model,

\[
F_{el} = -\sum_{j=1}^{q} \sum_{i=1}^{p} k_{ji} (\Delta l_{ji} - \Delta l_j) u_{ji}
\]

\( u_{ji} = \begin{cases} 
1 & \text{if contact} \\
0 & \text{if no contact}
\end{cases} \)

For three-level model,

\[
F_{el} = -\sum_{k=1}^{r} \sum_{j=1}^{q} \sum_{i=1}^{p} k_{kji} (\Delta l_{kji} - \Delta l_{kj} - \Delta l_j) u_{kji}
\]

\( u_{kji} = \begin{cases} 
1 & \text{if contact} \\
0 & \text{if no contact}
\end{cases} \)

where \( p, q \) and \( r \) are number of springs in level \( I, II \) and \( III \) of the model, respectively.

Adhesive force between hemispherical tip of a single spatula of radii \( R_c \) with work of adhesion of two surfaces \( E_{ad} \) (DMT theory)

\[
F_{ad} = 2\pi R_c E_{ad}
\]

Springs are pulled away from the surface when the net force (pull off force – attractive adhesive force) at the interface is equal to zero.
The effect of multi-level hierarchical structures on adhesion enhancement

The rate of relative increase for adhesive force \( a \) between one- and multi-level models.

Force-distance curves of one-, two- and three-level models in contact with rough surfaces with two different \( s \) values.
Summary of tribology of lubricants, bioadhesion, nanopatterned surfaces and reversible adhesion and device level studies

• **Lubricants for MEMS/NEMS**
  - Bonded PFPE lubricants and SAMs appear to be the best suited for lubrication of MEMS/NEMS

• **Bioadhesion studies**
  - Adhesion between silica surfaces and biomolecules using chemical linker method is stronger than by direct adsorption

• **Nanopatterned surfaces**
  - Optimum roughness distribution can be used to generate superhydrophobic surfaces.
  - Formation of air pockets is desirable. A transition criterion has been proposed.

• **Reversible adhesion (Gecko feet)**
  - Hierarchical structure results in adhesion enhancement.
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• The BioMEMS/BioNEMS studies were carried out in collaboration with Prof. S. C. Lee of OSU Medical School and Prof. D. Hansford of Biomedical Eng.

• DMD chips were supplied by Dr. S. Joshua Jacobs of Texas Instruments
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http://mecheng.osu.edu/nlbb
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