Nanotribology, Nanomechanics and Materials Characterization Studies and Applications to Bio/nanotechnology and Biomimetics

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Micro/nanoscale studies

Bio/nanotribology  Bio/nanomechanics  Biomimetics

Materials sci., biomedical eng., physics & physical chem.

Techniques

AFM/STM  Microtriboapparatus  Nanoindentor

Numerical modeling and simulation

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
- Aging Mech. of Li-Ion Batt.

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Outline

• Introduction
  - Nanotribology
  - Examples of a magnetic storage device, MEMS/NEMS and BioMEMS/BioNEMS

• Measurement Techniques

• Results and Conclusions
  - Surface Imaging, Adhesion, Friction and Wear
  - Adhesion, Friction and Wear of CNTs
  - Bioadhesion Studies
  - Hierarchical Nanostructures for Superhydrophobicity, Self Cleaning and Low Adhesion
  - Conclusions
**Introduction**

**Nanotribology**

- 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, e.g., in magnetic storage and MEMS/NEMS components

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Example of a Magnetic Storage Device

Magnetic rigid–disk drive (Bhushan, 1996)

MR type picoslider

Thin–film disk

Examples of MEMS/NEMS and BioMEMS/NEMS

Microengine driven by electrostatically-actuated comb drive
Sandia Summit Technologies (www.mems.sandia.gov)

Microgear unit can be driven at speeds up to 250,000 RPM. Various sliding comp. are shown after wear test for 600k cycles at 1.8% RH (Tanner et al., 2000)

Stuck comb drive
Microfabricated commercial MEMS components

The generating points of friction and wear due to interaction of a biomolecular layer on a synthetic microdevice with tissue (Bhushan et al., 2006)
Mechanical properties of nanotube ribbons, such as the elastic modulus and tensile strength, critically rely on the adhesion and friction between nanotubes.

(Chen et al., 2004)

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.

(Chen et al., 2004)

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.

(Roman et al., 2005)
Measurement Techniques

Surface Force Apparatus (SFA), 1968

Scanning Tunneling Microscope (STM), 1981

Atomic Force Microscope (AFM) and Friction force Microscope (FFM), 1985

Schematic of a small sample
AFM/FFM

Schematic of a large sample
AFM/FFM
Results – Surface Imaging and Friction

STM images of a solvent-deposited C₆₀ film on gold coated mica

CNN Headlines News, 3/18-3/19/93, etc.
Topography and friction force maps for HOPG

$\mu = 0.006$


National Public Radio, 4/12/95; Business Week, 5/1/95 etc.
Friction force map and line plots of friction force profiles for HOPG. Friction force changes discontinuously with sudden jumps. This leads to saw tooth pattern and it occurs due to atomic-scale stick-slip. Can use mechanical model proposed by Tomlinson in 1929.

The tip needs to overcome the energy barrier in order to jump from a stable equilibrium on the surface into a neighboring position. The tip remains stuck until energy stored in the spring is high enough to overcome the energy barrier.
## Scale effect on friction

| Sample         | RMS* (nm) | Coefficient of Friction |  |  |
|----------------|-----------|-------------------------|  |  |
|                |           | Nanoscale* with Si₃N₄ tip | Microscale with Si₃N₄ ball |  |
| Si(100)        | 0.14      | 0.06                    | 0.47                     |  |
| HOPG           | 0.09      | 0.006                   | 0.1                      |  |
| Natural Diamond | 2.3      | 0.05                    | 0.2                      |  |
| DLC film       | 0.14      | 0.03                    | 0.19                     |  |

*Scan area = 1 μm x 1 μm

Roughness, nano- and macroscale friction data of various samples

Comparing the conditions of nanoscale and macroscale tests, there are at least four differences

• Contact size in FFM is small—particles are ejected readily

• Mechanical properties have size effect—properties on nanoscale are superior to the bulk properties

• Applied loads in FFM are low—elastic contact regime (little plowing)

• Small radius of tip results in lower friction
Custom piezo stages for high velocity sliding

Ultrahigh velocity stage (upto 200 mm/s)
High velocity stage (upto 10 mm/s)

Schematic of experimental setup

Friction mechanisms vary with surfaces
At different velocity regime, different mechanisms dominate friction

Nanofriction maps

Friction force contour map for DLC
(contour lines are constant friction force lines)

Contour map showing friction force dependence on normal load and sliding velocity.

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Nanowear map for DLC illustrating effect of sliding velocity and normal load.

Adhesion and Friction between Individual Nanotubes

Experimental Schematic

(1) Scan of MWNT tip in lateral direction across suspended SWNT bridge

(2) Ramp of MWNT tip in vertical direction against suspended SWNT bridge

Average diameter of suspended SWNT bridge is 1.43 nm
The diameter of the MWNT tip is about 100 nm.
Method (1) works for flexible MWNT tip while method (2) is suitable for stiff MWNT tip


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(A) Nanotubes came into contact and formed a movable junction. By analyzing the dissipated power of the vibrating cantilever, the kinetic friction between nanotube is proportional to the attenuation of the cantilever amplitude during the initial contact of nanotube: 
\[ F_F = 4 \pm 1 \text{ pN} \]

(B) The junction slipped to the end of the MWNT tip with the deformation of the tip.

(C) The adhesive force between nanotubes forced the nanotubes to deform more until they detached from each other.

Multiplying cantilever deflection at the point of detachment with cantilever spring constant gives:
\[ F_A = 0.7 \pm 0.3 \text{ nN} \]

The coefficient of kinetic friction is calculated from \( F_F / F_A \):
\[ \mu = 0.006 \pm 0.003 \]

Comparable to values reported on graphite on nanoscale.
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

Streptavidin has four biotin-binding pockets. Two or one may be attached to the biotin on the surface, with the remaining 2 or 3 available to bind the biotin analyte.
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.
Biomimetics

• Nature has gone through evolution over 3.8 billion years. It has evolved objects with high performance using commonly found materials.

• Biological inspired design or adaptation or derivation from nature is referred to as biomimetics. It means mimicking biology or nature. Biomimetics is derived from a Greek word “biomimesis.” Other words used include bionics, biomimicry and biognosis.

• Biomimetics involves taking ideas from nature and implementing them in an application.

• Biological materials have hierarchical structure, made of commonly found materials.

• It is estimated that the 100 largest biomimetic products had generated $1.5 billion over 2005-08. The annual sales are expected to continue to increase dramatically.

Montage of some examples from nature.

(a) Lotus effect (Bhushan et al., 2009), (b) Glands of carnivorous plant secrete adhesive to trap insects (Koch et al., 2009), (c) Water strider walking on water (Gao and Jiang, 2004), (d) Gecko foot exhibits reversible adhesion (Gao et al., 2005), (e) Scale structure of shark reduces drag (Reif, 1985), (f) Wings of a bird in landing approach, (g) Spider web made of silk material (Bar-Cohen, 2006), (h) Moth’s eye are antireflective (Genzer and Efimenko, 2006)

One of the crucial properties 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 surfaces 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).


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

Wenzel’s equation:

\[ \cos \theta = R_f \cos \theta_o \]

Droplet of liquid in contact with a smooth and rough surface

Effect of roughness on contact angle

Effect of roughness

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

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


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

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.

$\theta_{adv} - \theta_{rec} = \frac{R_f \sqrt{1 - f_{LA} (\cos \theta_{rec} - \cos \theta_{adv})}}{\sqrt{2 (R_f \cos \theta_0 + 1)}}$ for high contact angle ($\theta \to 180^\circ$)

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

$\alpha$: Tilt angle

$\theta_{adv}$: Advancing contact angle

$\theta_{rec}$: Receding contact angle

Fabrication and characterization of nanopatterned polymers
Study the effect of nano- and microstructure on superhydrophobicity

Nanopatterns

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

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

Micropatterns

Lotus patterned

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


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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>R_f</th>
<th>LAR</th>
<th>HAR</th>
<th>Lotus</th>
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<tr>
<td></td>
<td>2.1</td>
<td>5.6</td>
<td>3.2</td>
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</table>
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, -tetrahydroperfluorodecylltrichlorosilane (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.to pitch (P) would be in Cassie-Baxter regime.

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

Droplet size = 1 mm in radius

- 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 and characterization of hierarchical surface

Fabrication of microstructure

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

Fabrication of nanostructure and hierarchical structure

- Nanostructure
  - Self assembly of the Lotus wax deposited by thermal evaporation
    - Expose to a solvent in vapor phase for the mobility of wax molecules
- Hierarchical structure
  - Lotus and micropatterned epoxy replicas and covered with the tubules of Lotus wax

Lotus wax (0.8 μg/mm²) after seven days with ethanol vapor (50° C)

Hierarchical structure using micropatterned Si replica

Static contact angle, contact angle hysteresis, tilt angle and adhesive force on various structures

Lotus wax (0.8 \( \mu \text{g/mm}^2 \)) after seven days with ethanol vapor (50° C)

- Nano- and hierarchical structures with tubular wax led to high static contact angle of 167° and 173° and low hysteresis angle on the order of 6° and 1°.
- Compared to a Lotus leaf, hierarchical structure showed higher static contact angle and lower contact angle hysteresis.

Self-cleaning efficiency of various surfaces

Self-cleaning experiments using 1-10 μm SiC particles

Lotus wax

- As the impact pressure of the droplet is zero or low, most of particles on nanostructure were removed by water droplets, resulting from geometrical scale effects.
- As the impact pressure of the droplet is high, all particles which are sitting at the bottom of the cavities between the pillars on hierarchical structure were removed by the water droplets.
Conclusions

• AFM/FFM has been developed as a versatile tool for fundamental studies in nanotribology, nanomechanics and material characterization.

• It has been successfully used for studies of surface imaging, adhesion, friction, scratching/wear, lubrication, measurement of mechanical and electrical properties, and in-situ localized deformation studies.

• Examples of nano/biotechnology and biomimetics research are presented.
Acknowledgements

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References


http://mecheng.osu.edu/nlbb
Questions & Answers

• Question 1
Questions & Answers

• Question 2
• Question 3
Questions & Answers

- Question 4
Questions & Answers

- Question 5
• Question 6
Questions & Answers

• Question 7
• Question 8