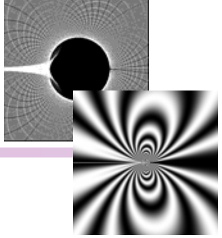
Experimental and Computational Issues Related to Adhesion and Friction of Surfaces Modified by Self-Assembled Monolayers



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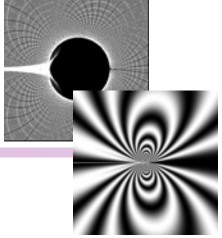
Acknowledgements



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  Chemistry and Biochemistry, UT Austin
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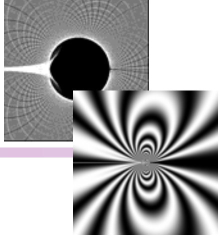
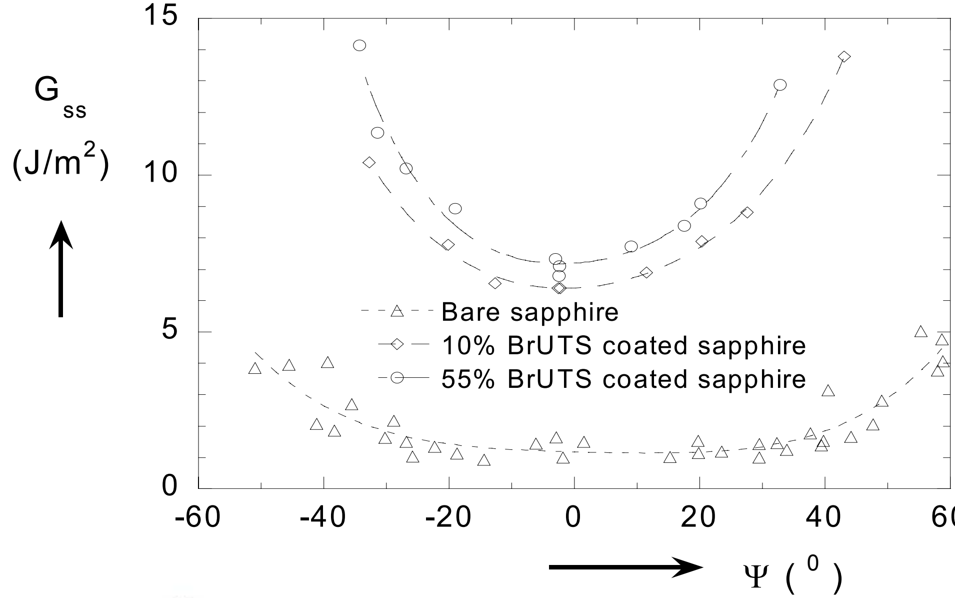
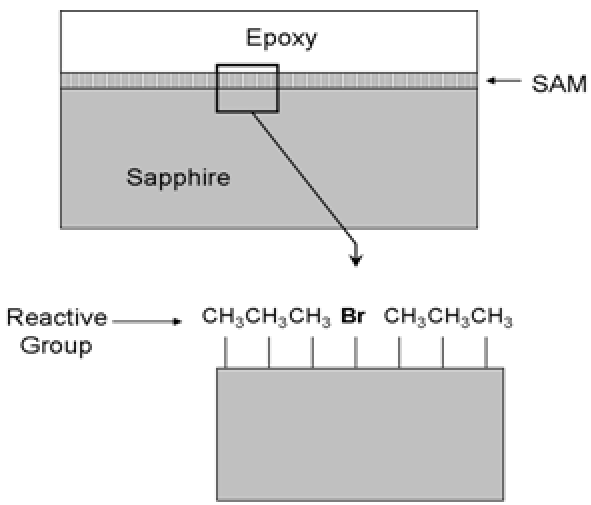
- Alberto Mello, Brazilian Air Force
- Financial
  - National Science Foundation
  - Department of Energy



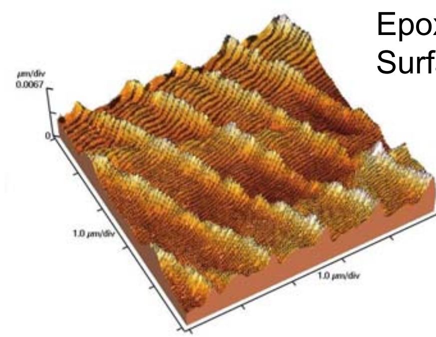
Effect of Self-Assembled Monolayers on Interfacial Toughness

*Zhuk, Evans, Hutchinson, and Whitesides, 1998, J. of Mat. Res., **13**, 3555-3564*
*Kent, Reedy et al., 2004, Journal of Materials Research, **19**, 1682-1695.*

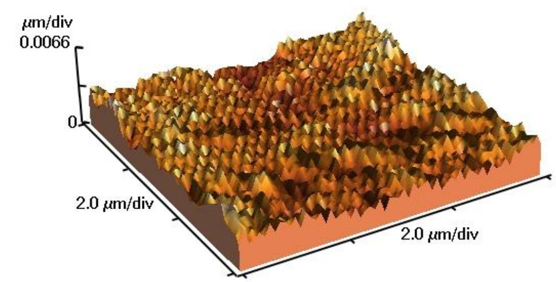




Epoxy Fracture Surfaces



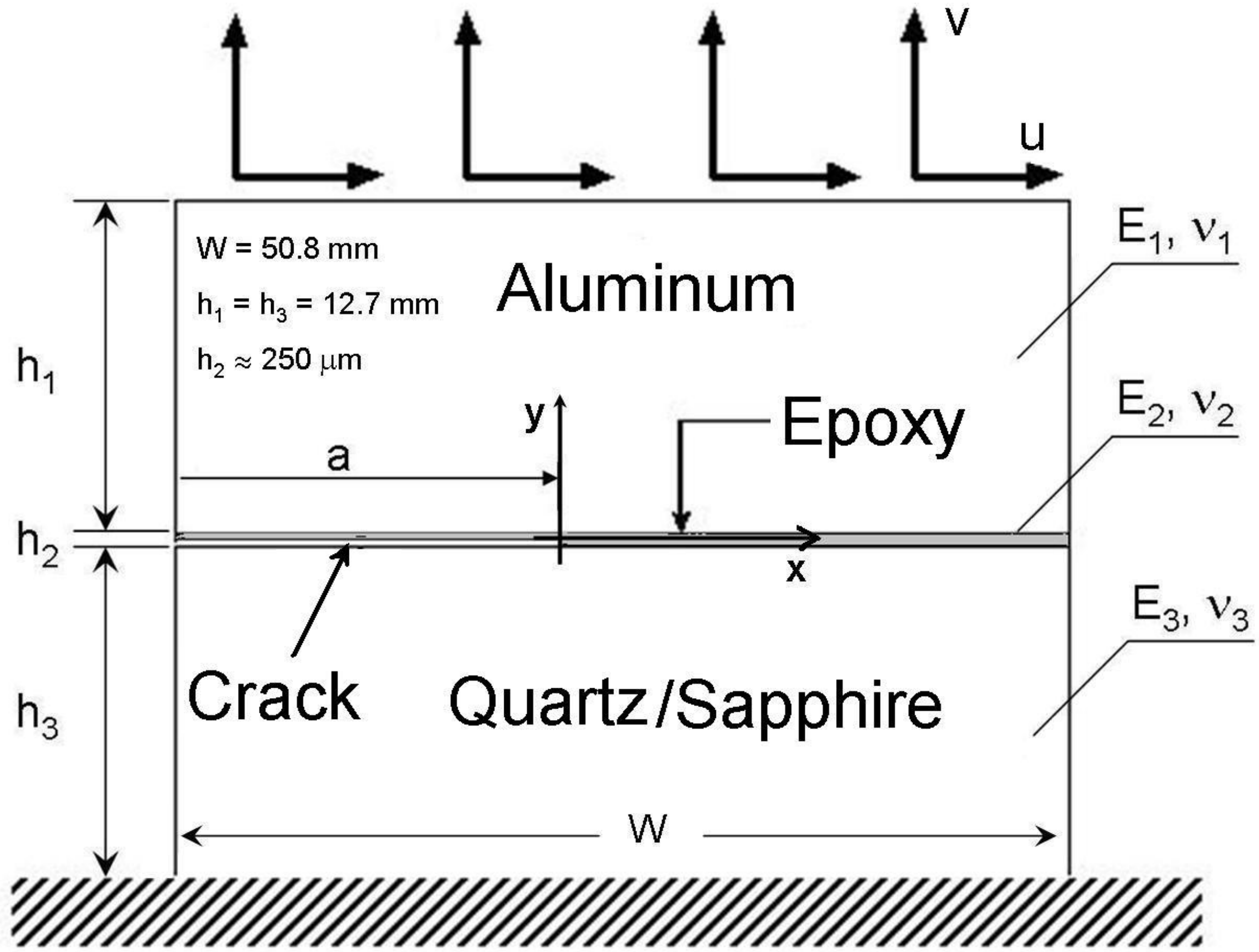
Bare Sapphire



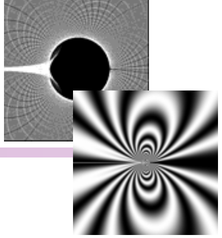
10% BrUTS on Sapphire

*Mello & Liechti, 2006, J. Appl. Mech., **73**, 860-870.*

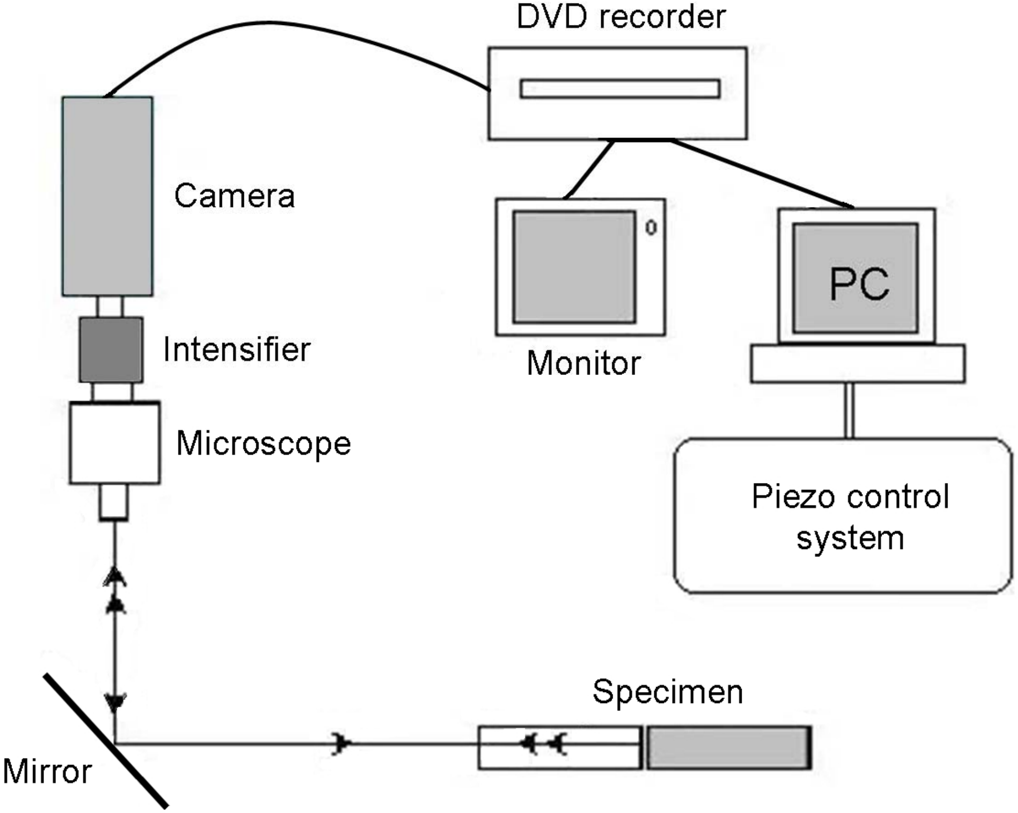
Specimen & Loading



Crack Opening Interferometry

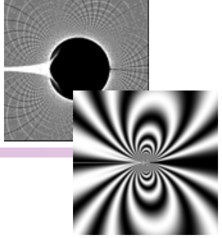


- NCOD measured with 30 nm resolution
- 800 nm from crack front



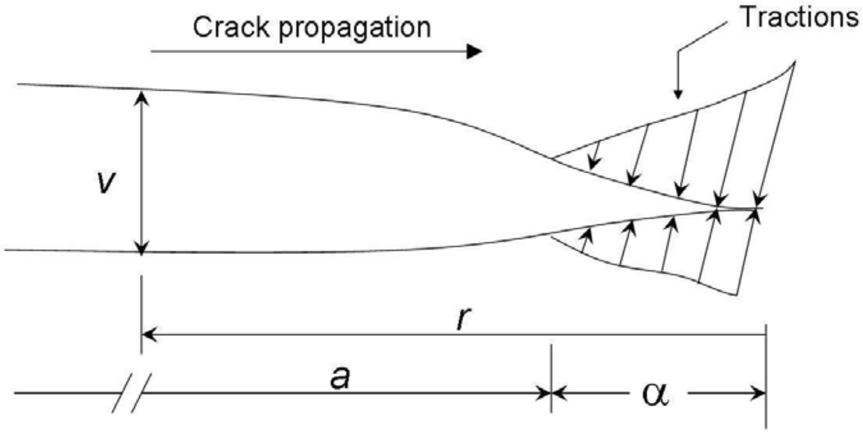
Mello & Liechti, 2004 *Experimental Mechanics*, **44**, 495-501.

Finite Element Analysis

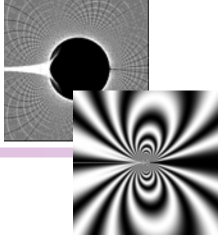


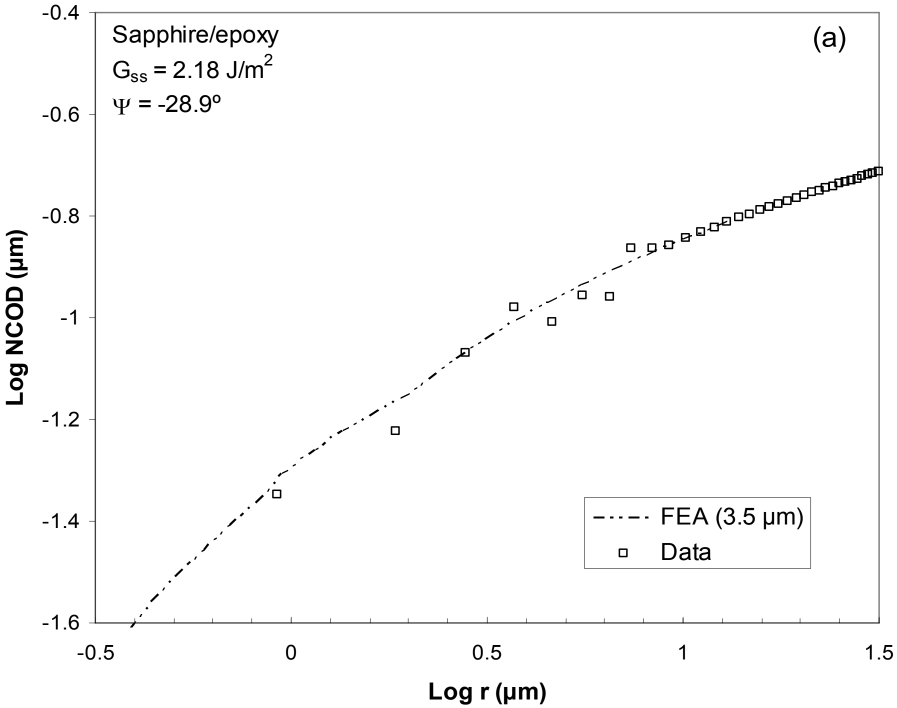
- ABAQUS® 6.2
- 15,750 plain strain elements with quadratic interpolation
- Highly refined mesh near crack tip
- Traction-separation laws were used to represent different interphases
  - Specify crack speed and traction decay
  - Select cohesive zone size (CZS)
  - Displacements from solution
  - Compare with measured NCOD
  - Iterate on CZS
  - Traction-separation law

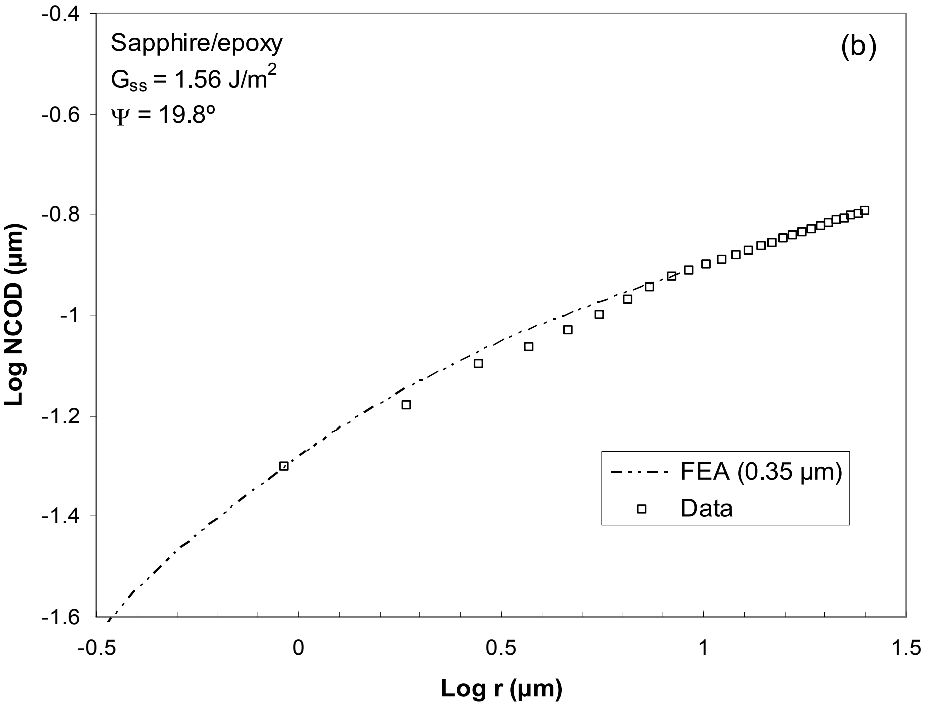
    from matched solution



Cohesive Zone Size……..Bare Sapphire

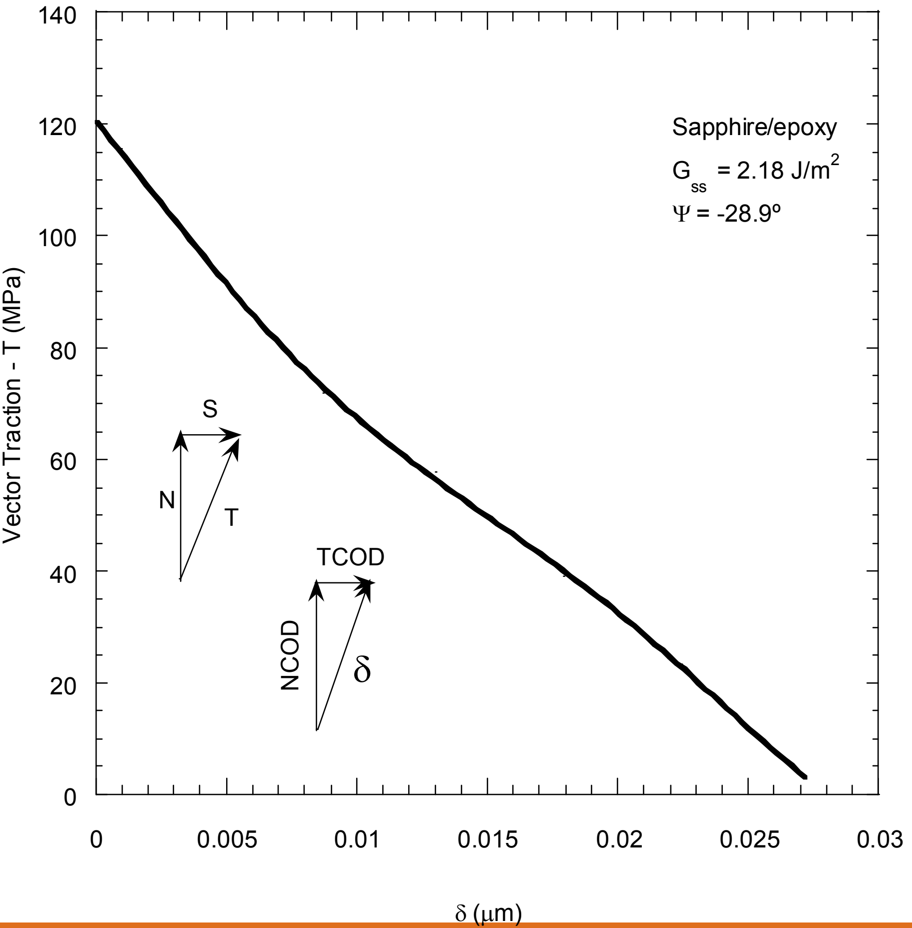


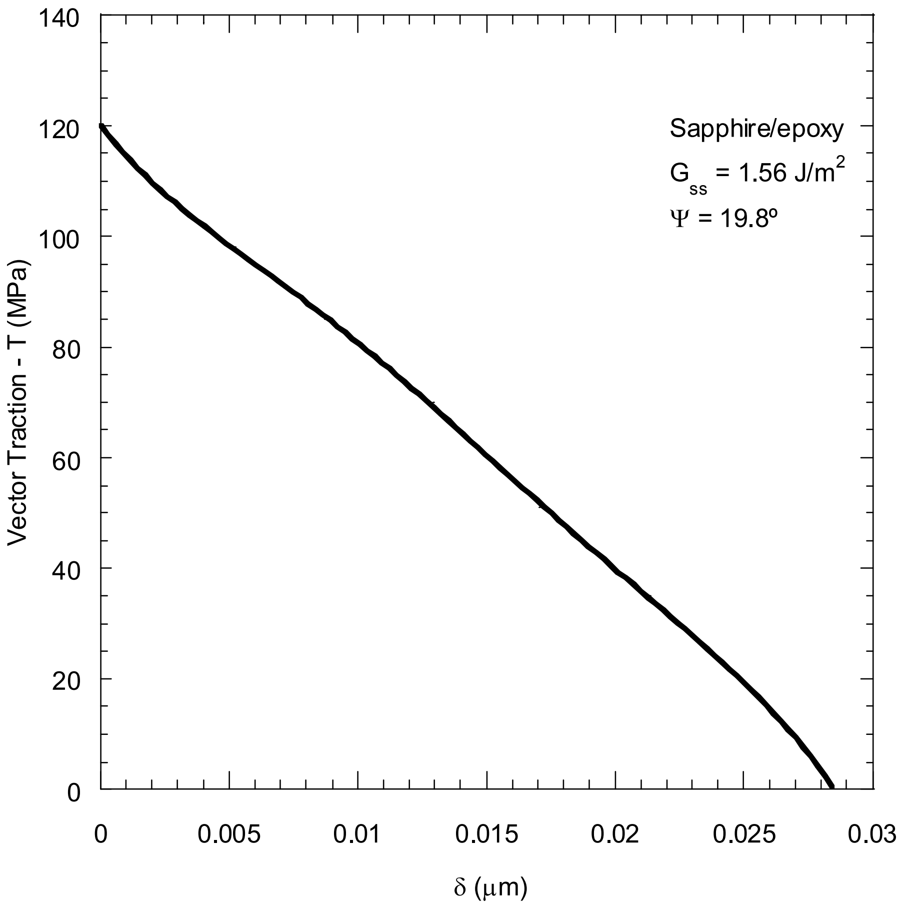




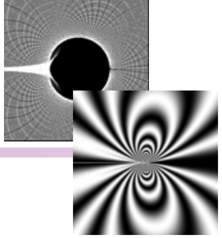
Traction-Separation Law…..Bare Sapphire

- Independent of mode-mix

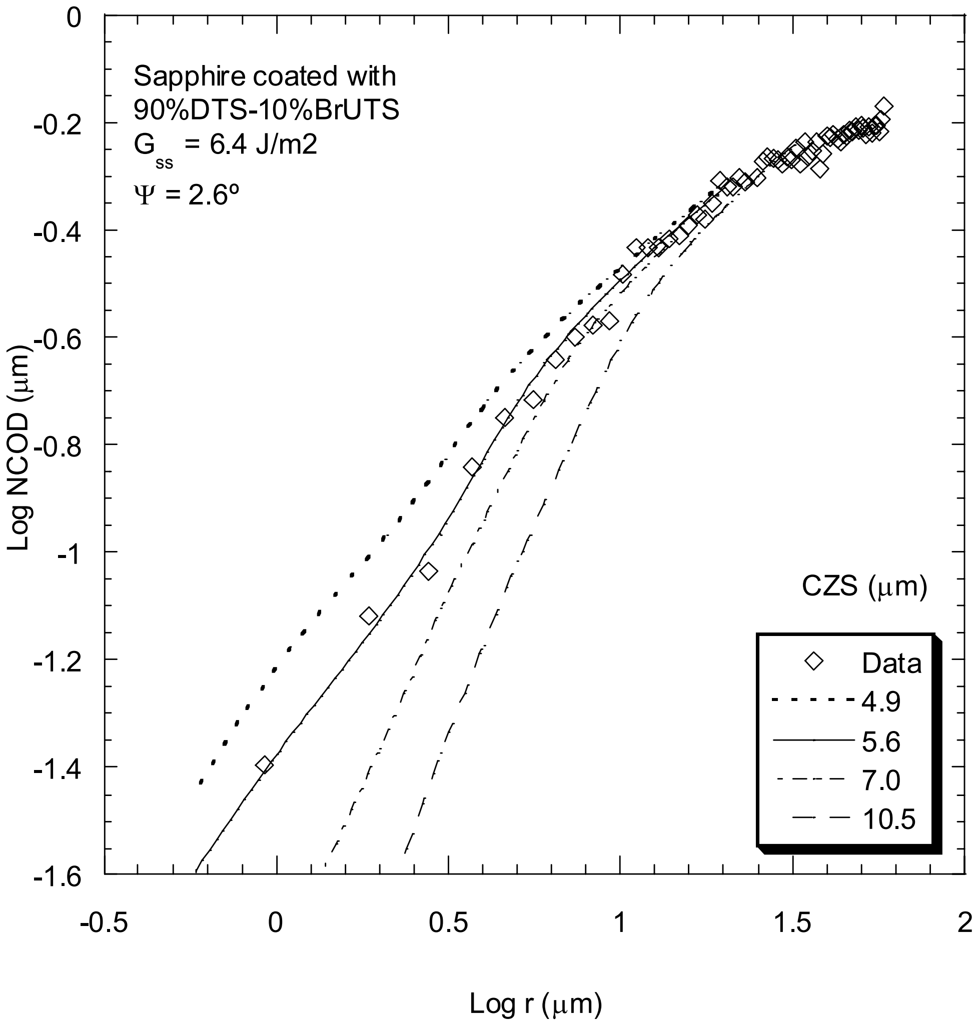




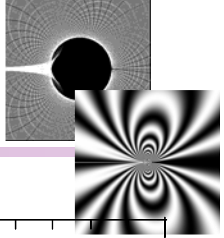
Coated Sapphire



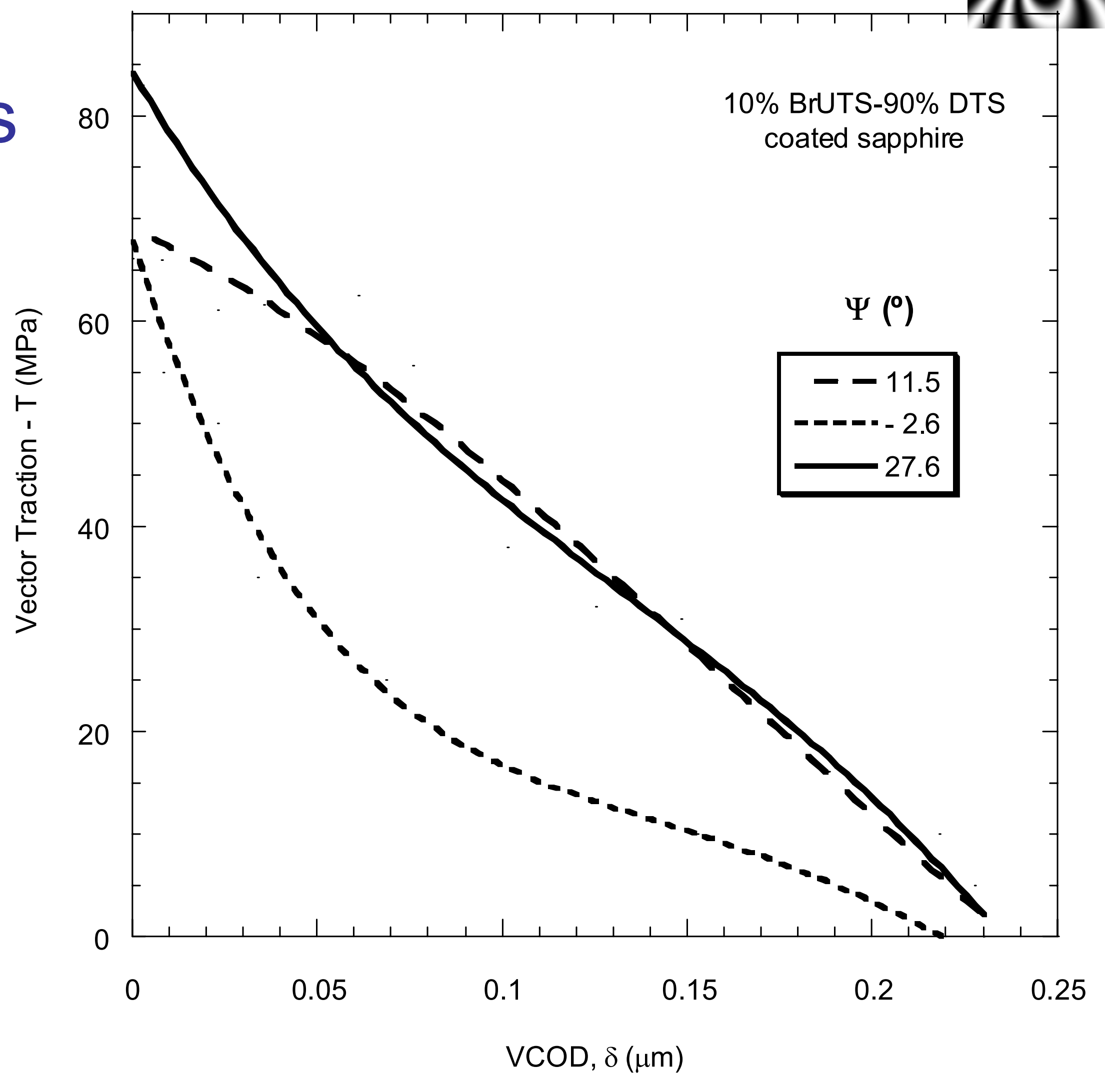
- 10%BrUTS
- Cohesive zone size selection



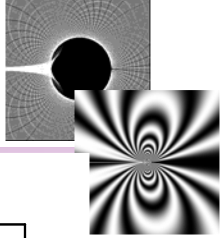
Traction-Separation Law..Coated Sapphire

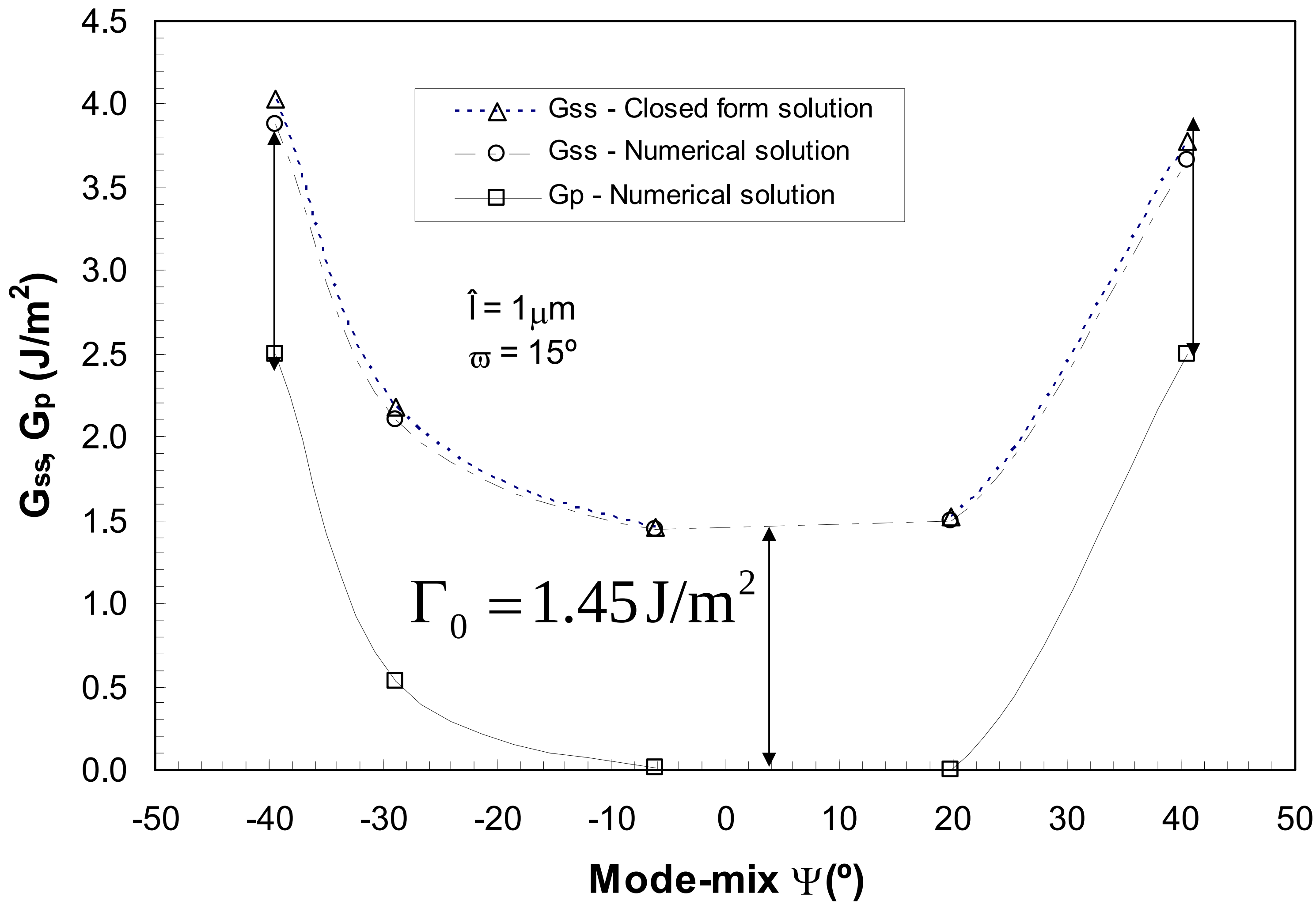


- T-δ law depends on mode-mix
- T_{max} is below the epoxy yield strength
- Large δ_c
- Larger Γ_0



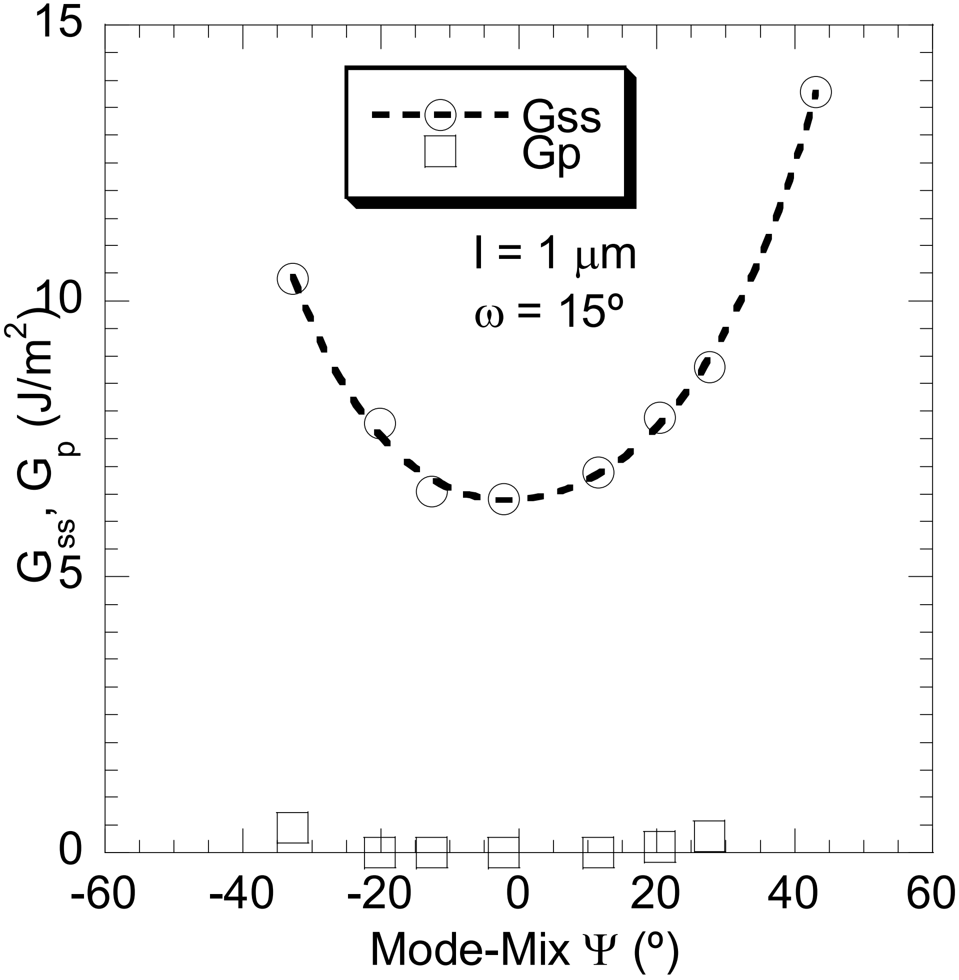
Viscoplastic Dissipation…..Bare Sapphire





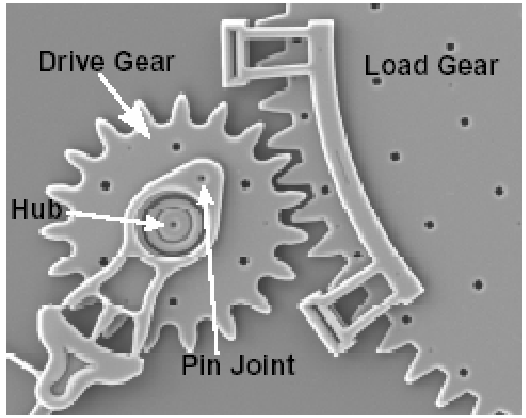
Viscoplastic Dissipation..Coated Sapphire

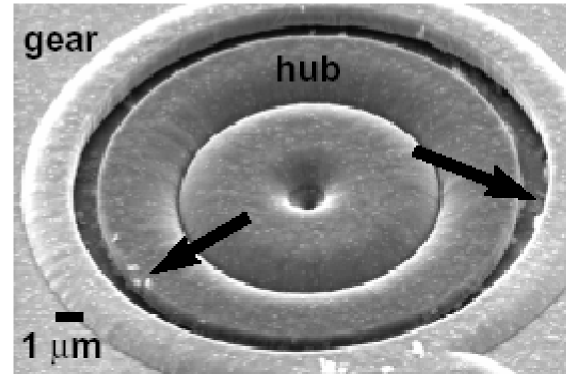
- Dissipation is negligible over mode-mixes that were considered
- Convergence problems at large mode-mix

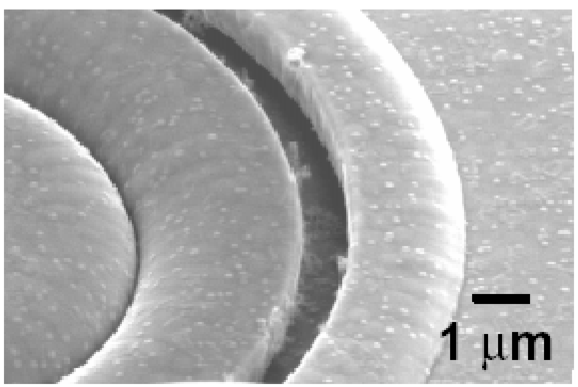


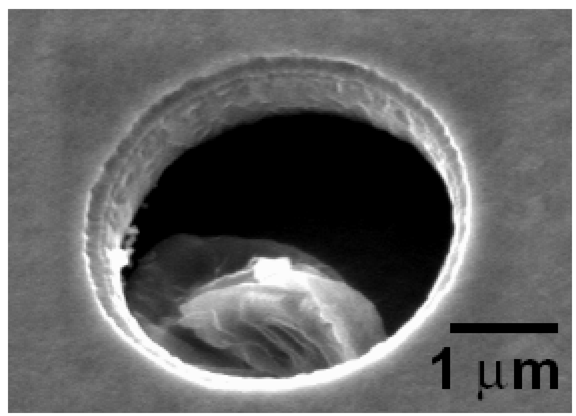
Wear in MEMS Devices

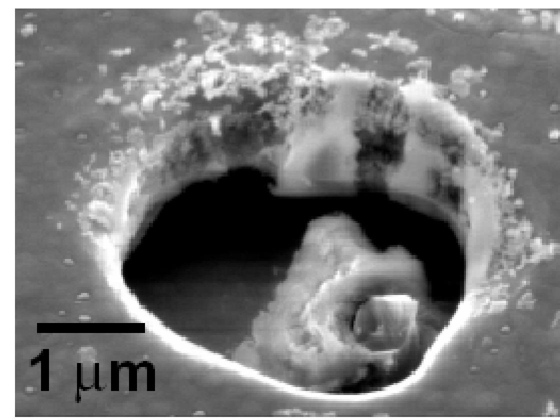
Tanner et al., 2000, *SAND2000-0091*









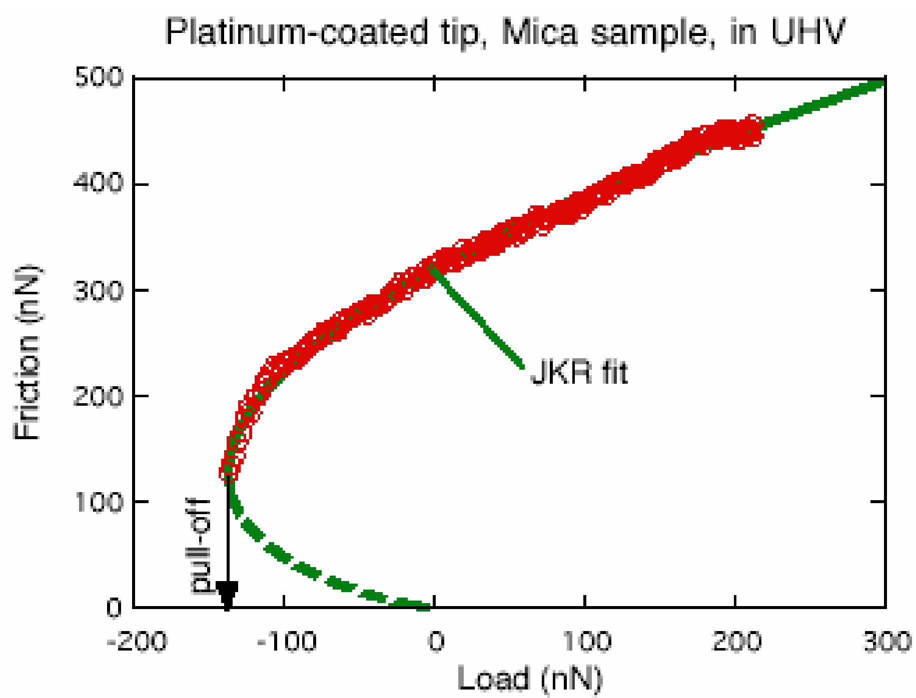


Analysis of SAM vs. SAM Friction

Single Asperity Contact

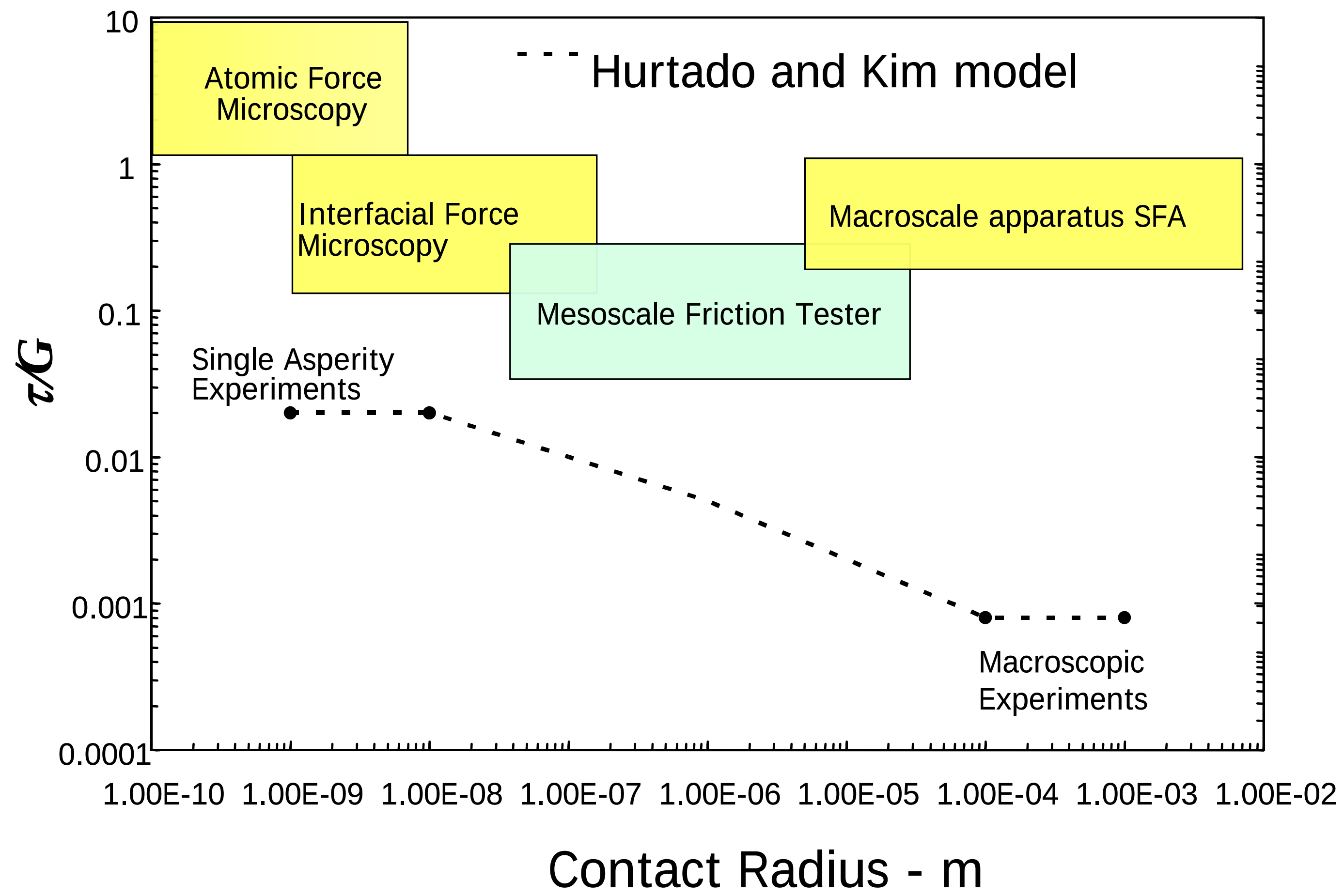
$$F = \tau A$$

- Contact mechanics yields
  - Work of adhesion
  - Contact Radius
- Extension to coated substrates?

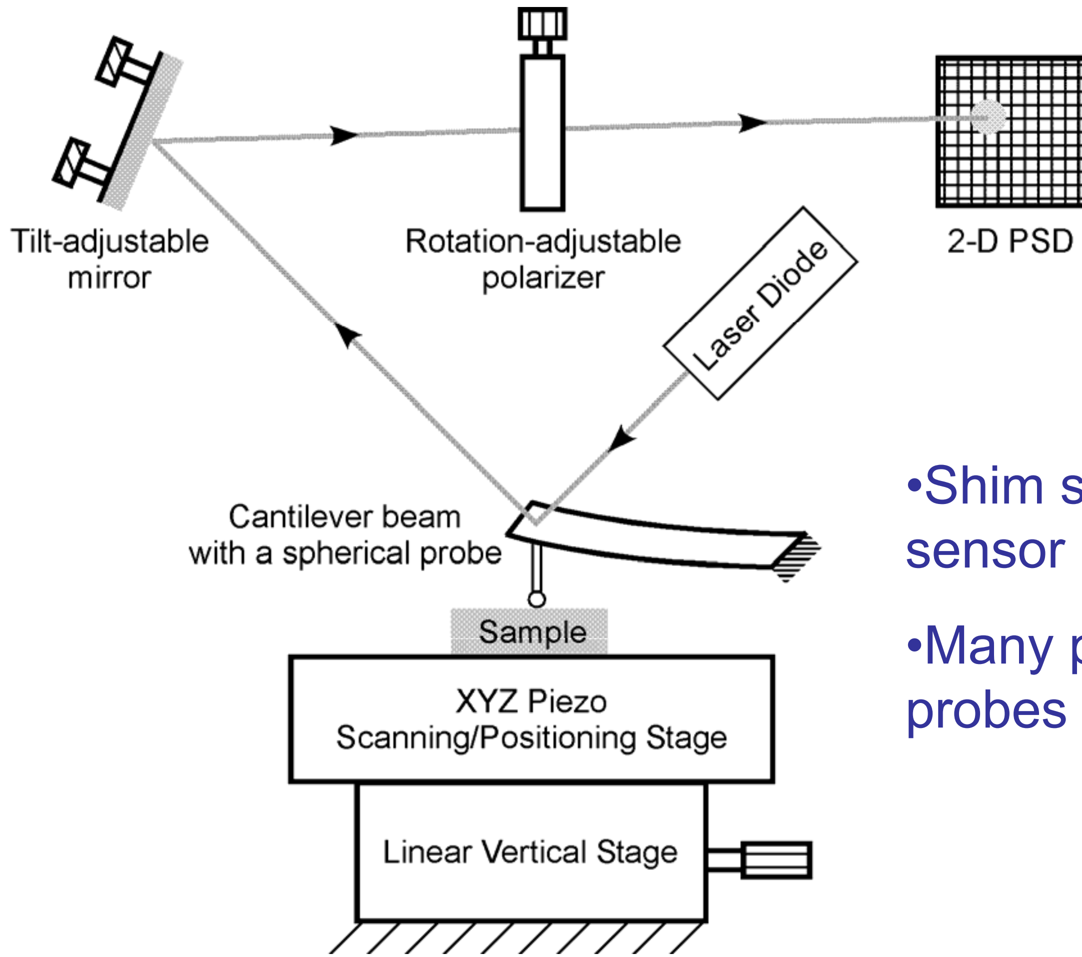


Carpick et al., 1996, *J. Vac. Sci. Technol. B* **14,** 1289-1295

Scale dependence in friction



Mesoscale Friction Test Apparatus



- Shim stock sensor beam
- Many potential probes

Effect of Relative Humidity

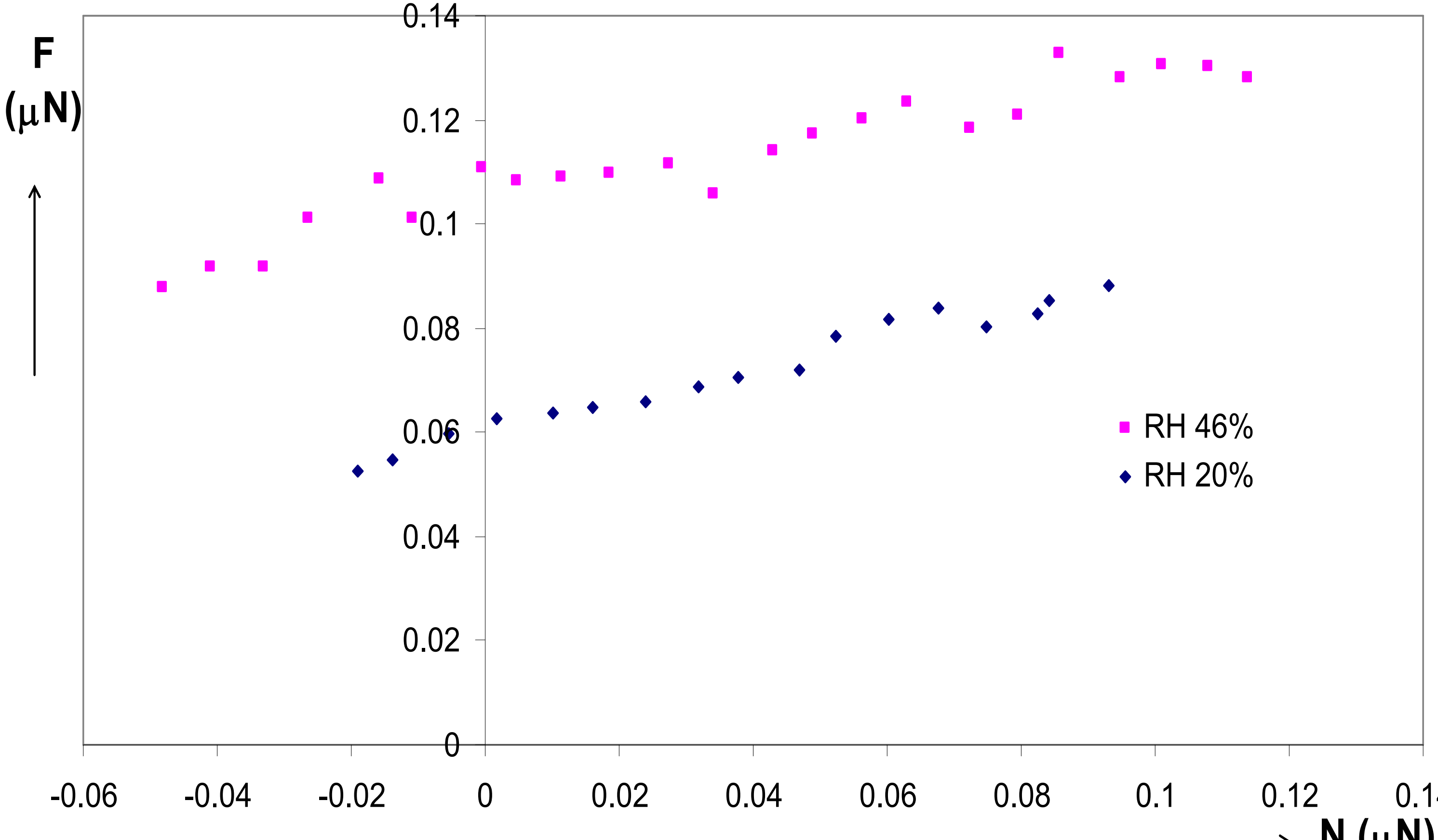
Tungsten on Mica

R=21 μm

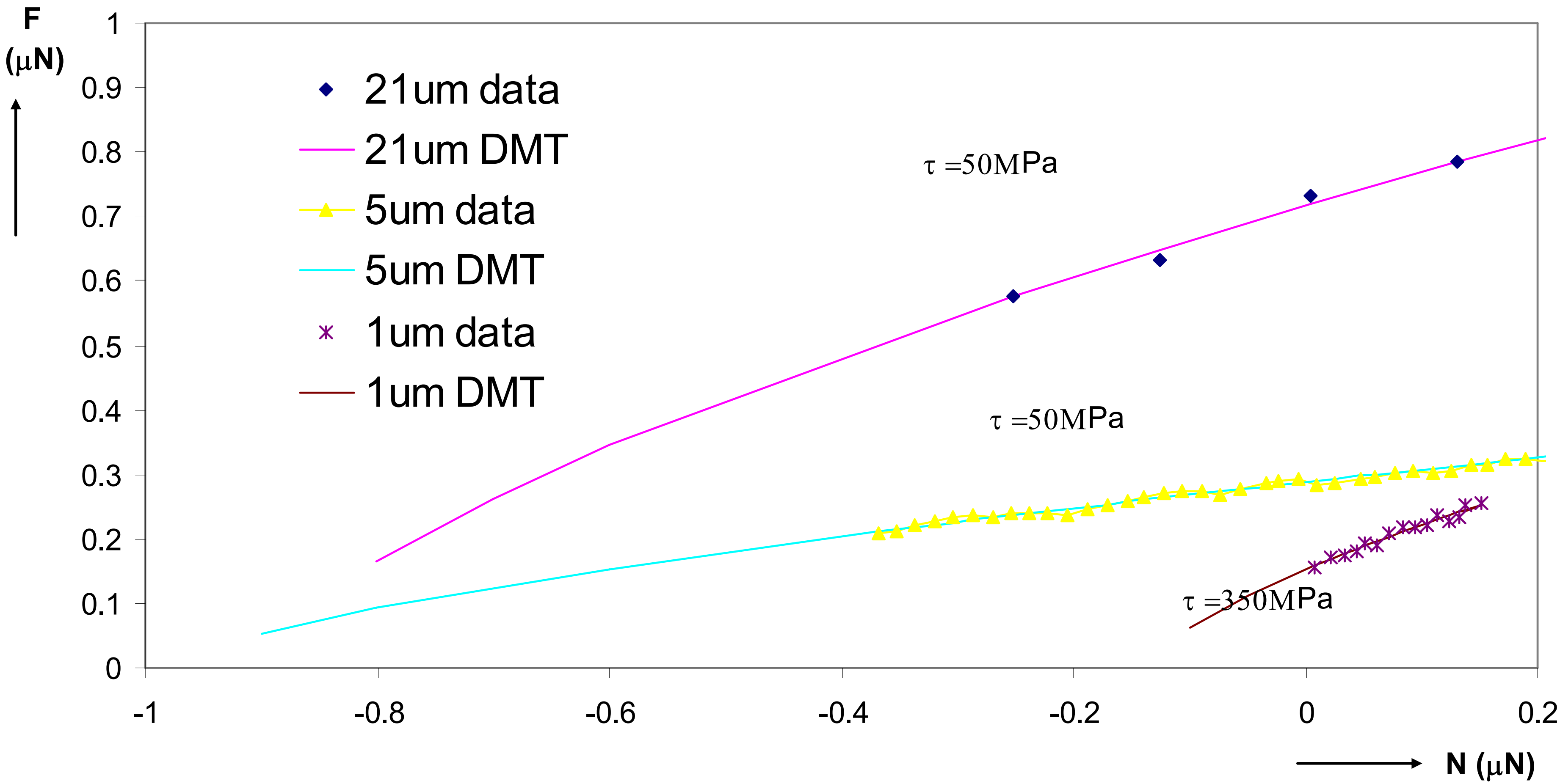
$$\mu = \left(\frac{Rw^2}{E^{*2} r_m^3}\right)^{1/3}$$

$$\mu = 0.01 \Rightarrow \text{DMT}$$

$$a = \left(\frac{R}{K}\left(P + F_c\right)\right)^{1/3}$$

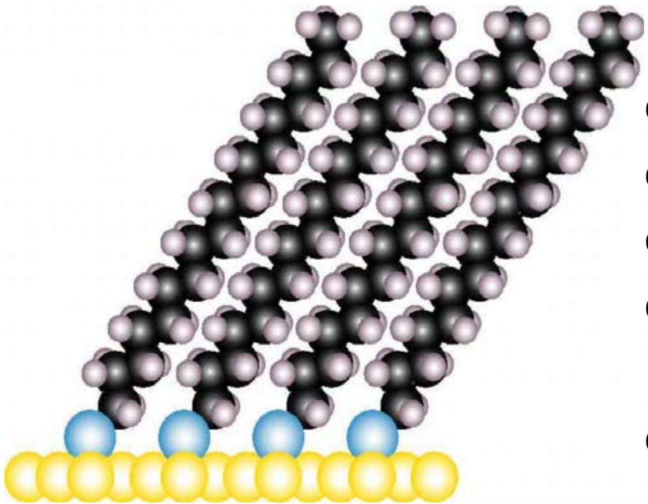


Effect of Tip Radius



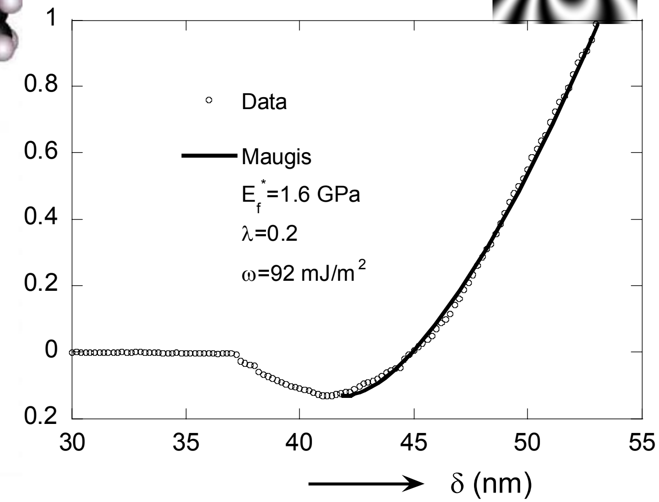
Critical Issues

- SAM Deposition
  - Processing
  - Diagnostics
  - Modeling
- SAM Probing
  - Indentation
  - Biaxial
- Analysis
  - Mechanical behavior
  - Adhesive interactions
  - Scale bridging

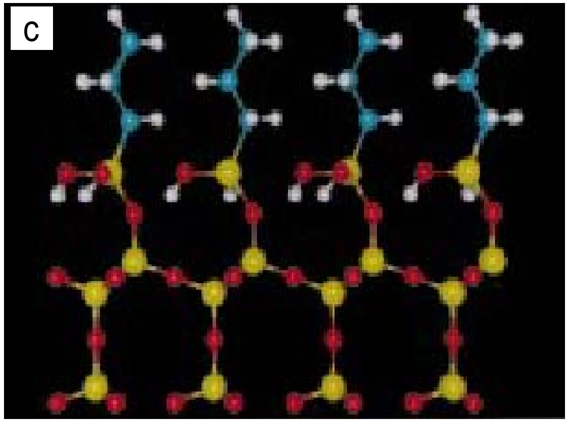


Weiss Group, Penn State

http://stm1.chem.psu.edu/



Wang et al. 2005, *Langmuir*, **18**, 1848-1857

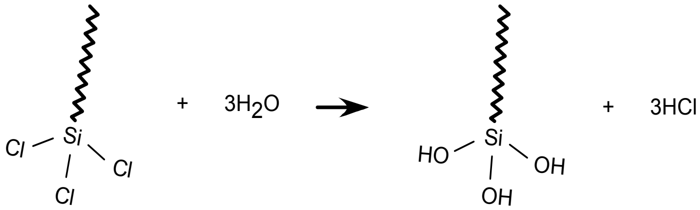


Stevens, 1999 *Langmuir*, **15**, 2773-2778

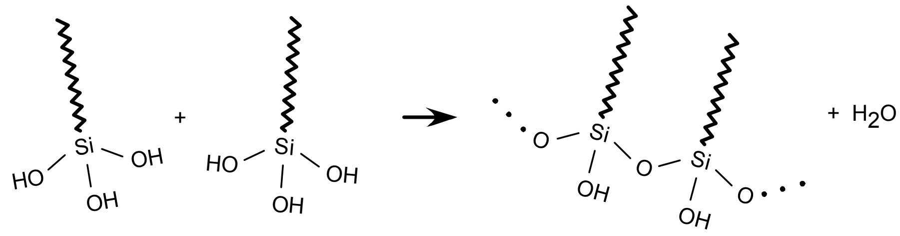
Self-assembly of OTS

Hydrous Processing

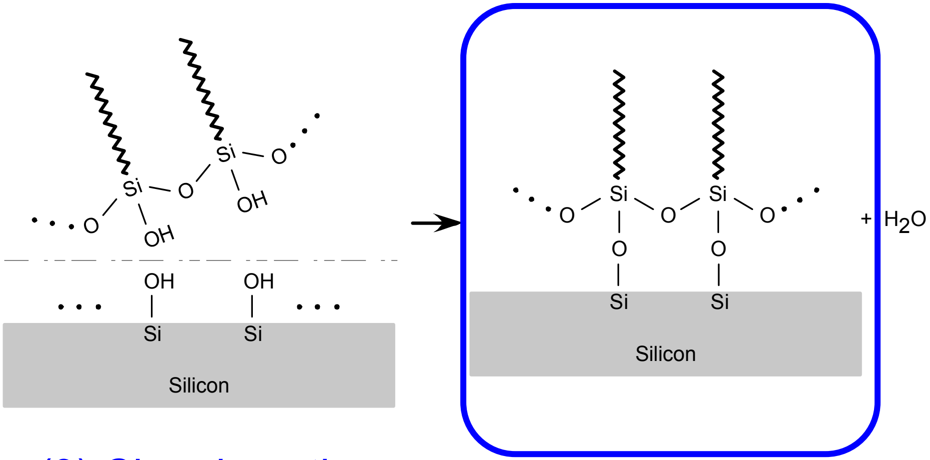
Octodecyltrichlorosilane (OTS): $CH_3(CH_2)_{17}SiCl_3$



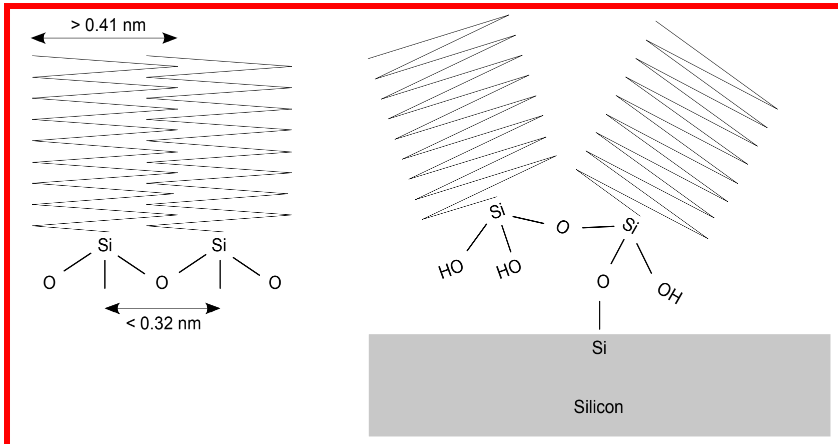
(1) Hydrolysis of silane group.



(2) Cross-polymerization.



(3) Chemisorption.



Overlap!

Tilt → Cluster

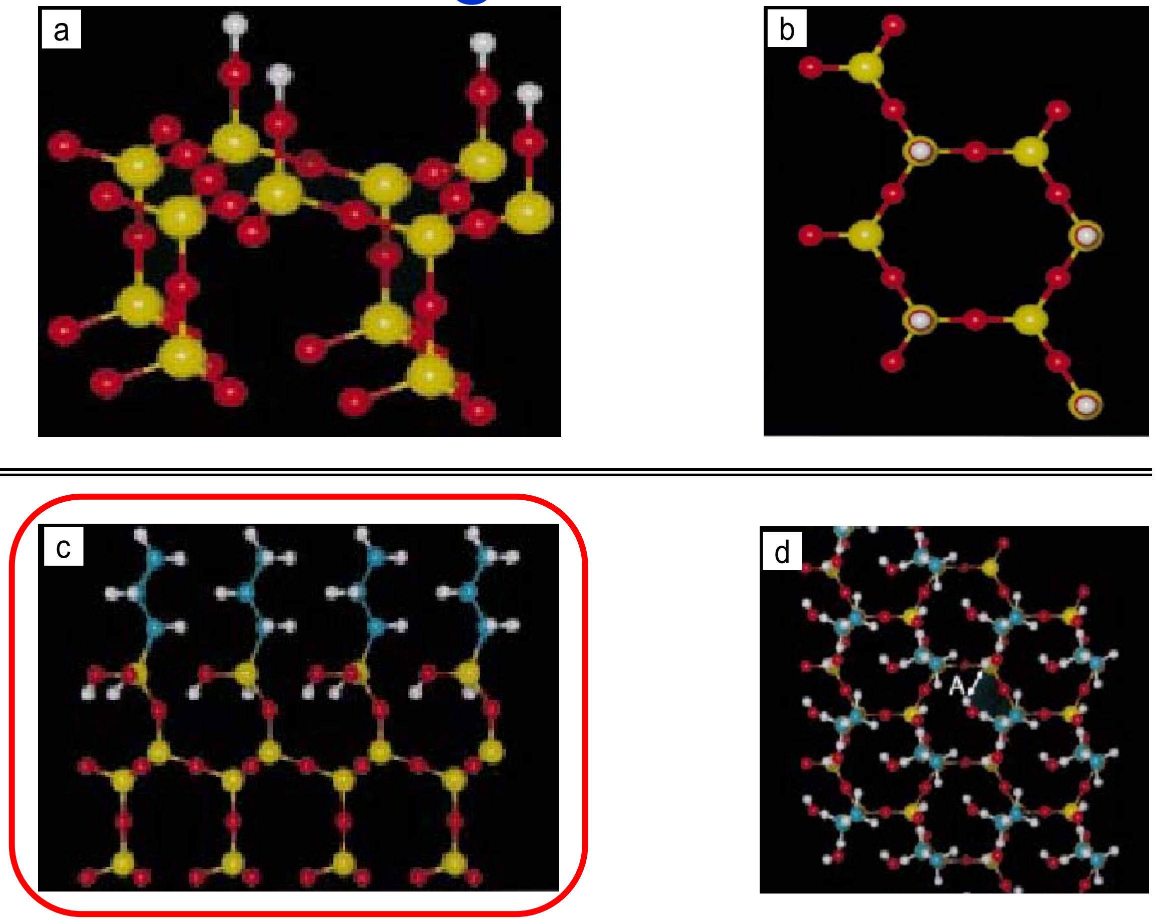
Self-assembly of OTS

Anhydrous Processing

SiO_2 model

1 OH/22 Å^2

OTS on SiO_2



M. J. Stevens, 1999 *Langmuir* **15**, 2773-78

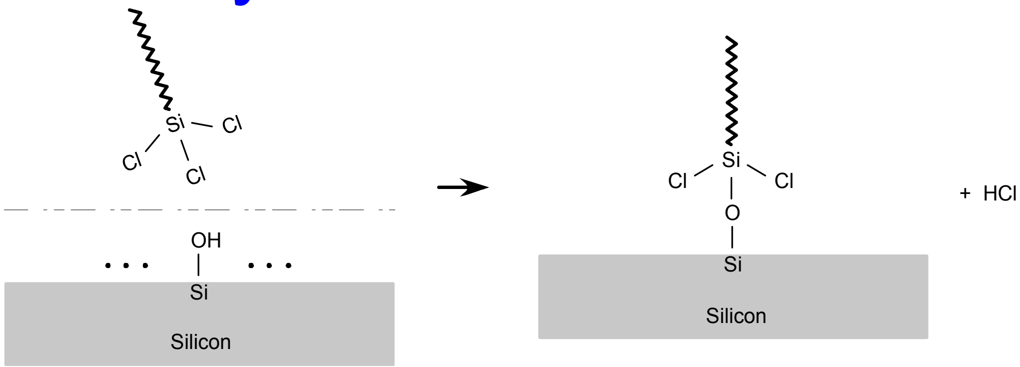
A Dry Cocktail

- **Surface Preparation: hydroxylate the silicon**
  1. Clean silicon surface: Acetone, IPA, DI water
  2. Sacrificial layer etch of native oxide layer in HF (1:36)
  3. Re-oxidation in piranha solution (H_2O_2:H_2SO_4=1:2) at 90°C
  4. Rinse with DI water and dry with N_2
- **Anhydrous OTS deposition (Ar dry-box: O_2 & H_2O < 1 ppm)**
  1. Prepare 10 ml 1 mM anhydrous solution of OTS in dicyclohexyl
  2. Place silicon chip in the solution for 24 hours
  3. Transfer the coated silicon to CCl_4 inside dry-box
- **Post Processing: remove physisorbed OTS**
  1. Sonicate in CCl_4, toluene, ethyl alcohol, DI water
  2. Rinse with DI water and dry with pure N_2

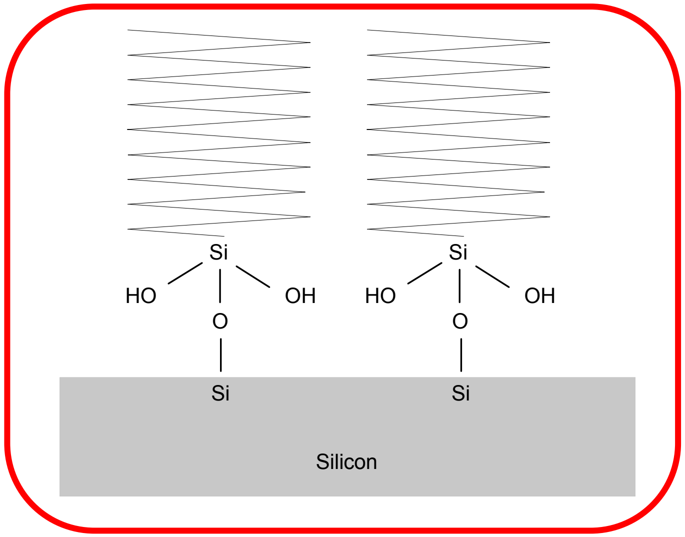
Wang et al. 2005, *Langmuir*, **18**, 1848-1857

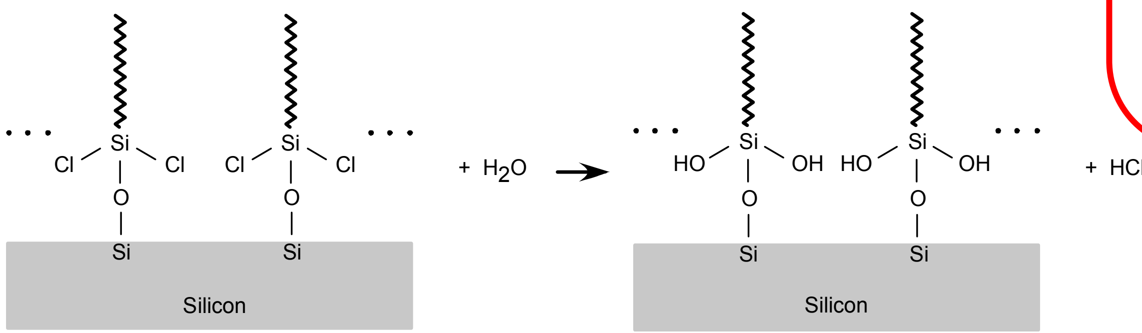
Self-assembly of OTS

Anhydrous conditions



(1) Anchoring the OTS molecules under anhydrous conditions

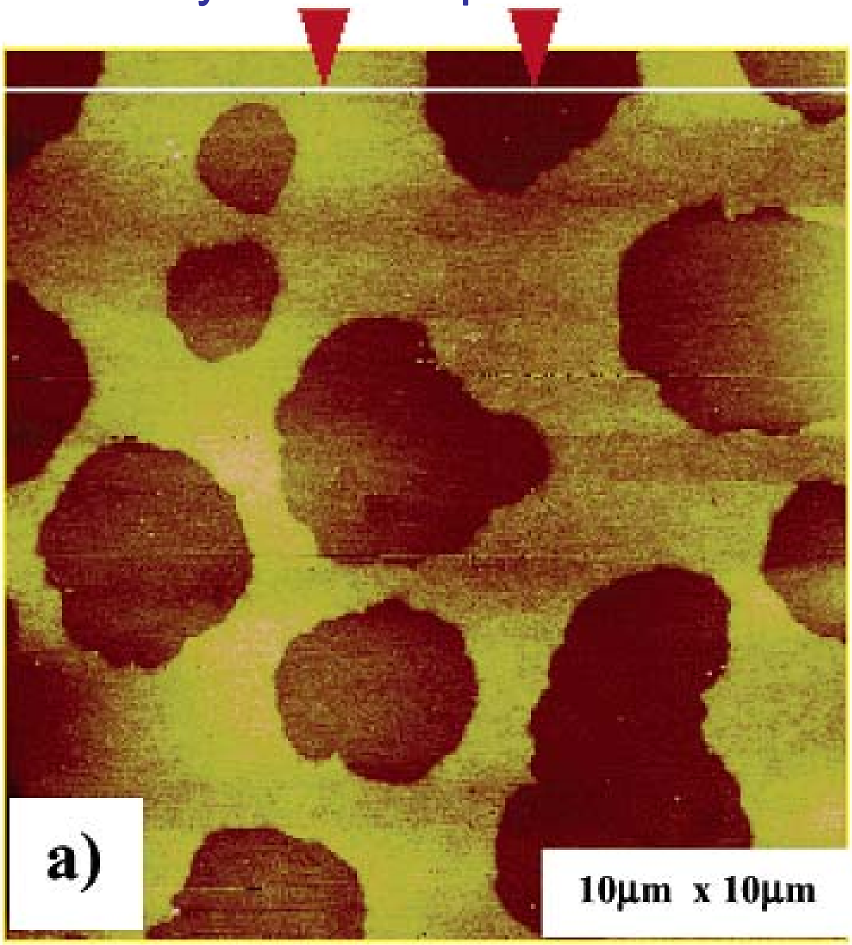




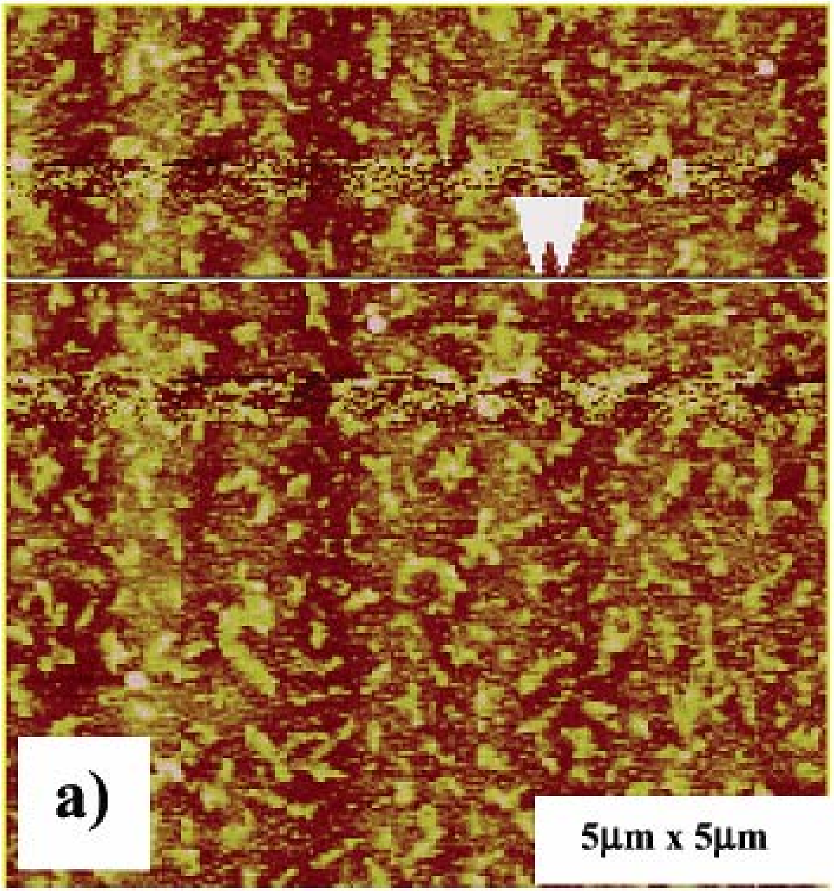
(2) Subsequent hydrolysis under environmental conditions

Dry Solution Process

Dry OTS in Isopar G

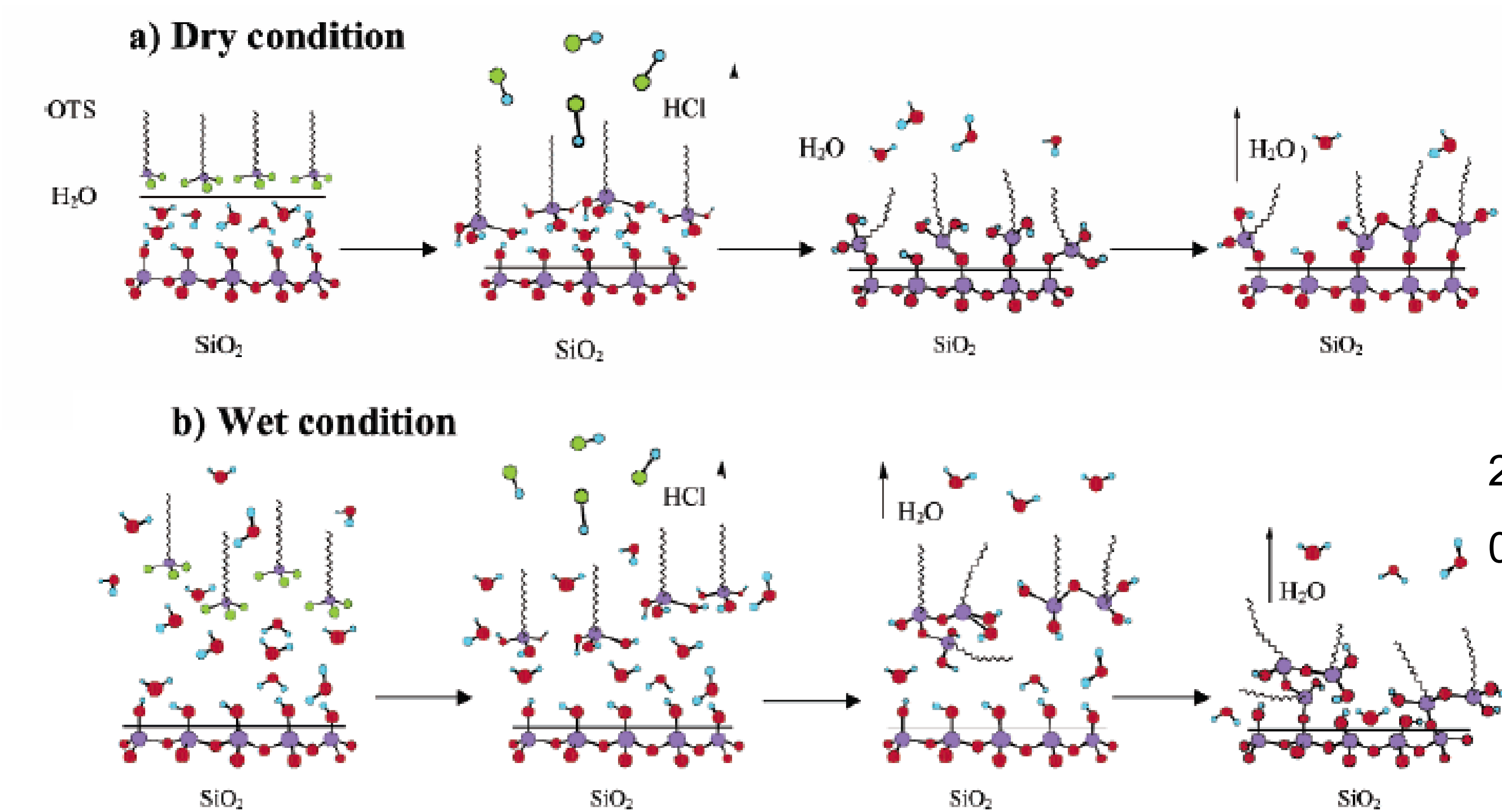


Wet



Wang, Y., and Lieberman, M., 2003 *Langmuir*, 19, 1159-1167.

Mechanism



48 hrs

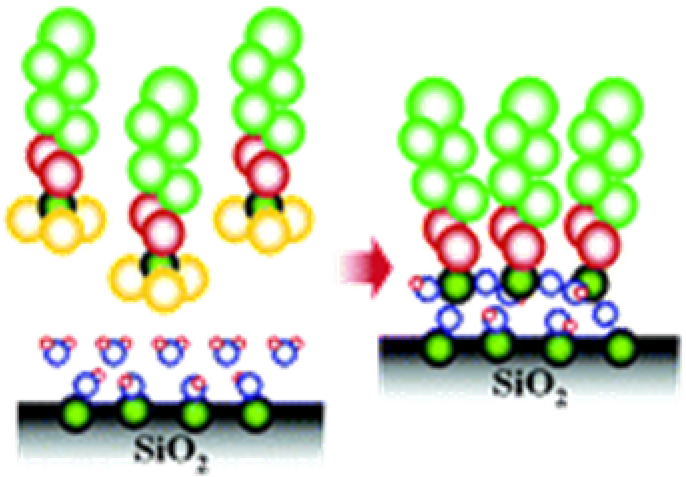
0.1 nm

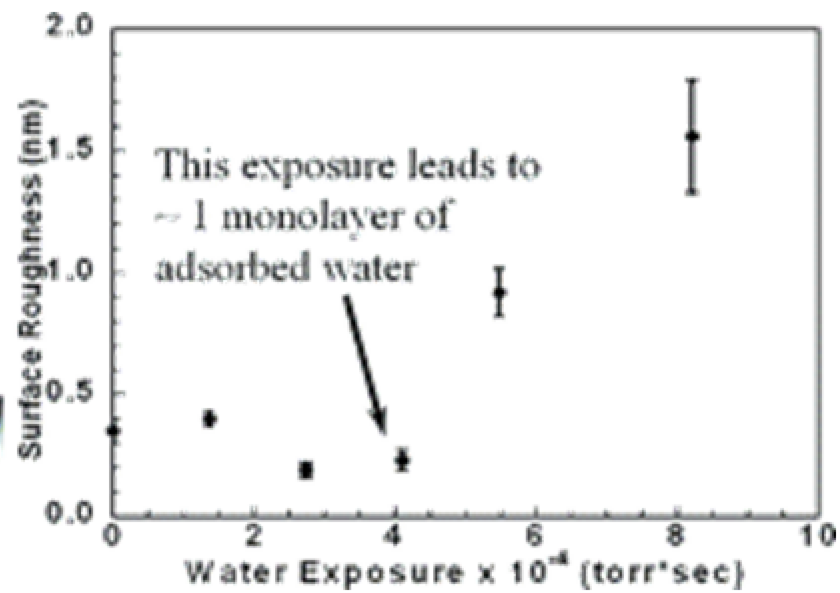
2 hrs

0.3 nm

Vapor Deposited Fluorinated SAMs

Tridecafluoro-1,1,2,2,-tetrahydrooctyltrichlorosilane (FOTS)





SAM monolayer indicated by 0.2 nm RMS roughness

Wu, K., Bailey, T. C., Willson, C. G. Ekerdt, J. G., 2005 *Langmuir*, **21**, 11795-11801.

Other SAMs

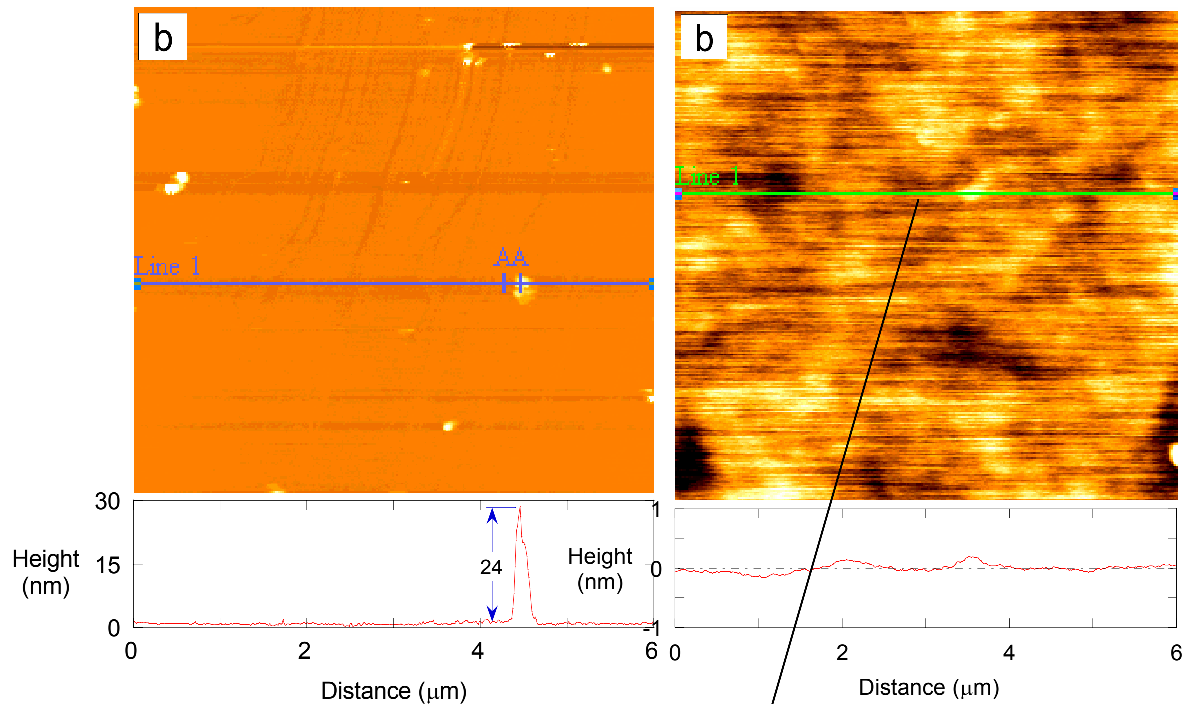
- Thiols on gold
  - Kumar, A., Biebuyck, H. A. and Whitesides, G. M. 1994, *Langmuir,* **10**, 1498-1511
- Silanes on silicon
  - Ashurst, W.R., Yau, C., Carraro, C. and Maboudian, R., 2001 *J. MEMS*, **10**, 41-49.
- Alkenes on silicon
  - Linford, M.R., Fenter, P., Eisenberger, P. M., and Chidsey, C. E. D., 1995 *J. Am. Chem. Soc*. , **117**, 3145.
- Phosphonic acid on metal oxides
  - Pellerite, M.J., Dunbar, T.D., Boardman, L.D., and Wood, E.J. 2003 *J. Phys. Chem. B*, **107**, 11726-36.

SAM Diagnostics

- Contact angle
- XPS
  - Species ID
  - Layer thickness
- Ellipsometry
  - Layer thickness
- AFM
  - Layer thickness
  - Surface roughness
- IFM
  - Lateral force
  - Mixed SAM
- STM
  - SAM formation kinetics
  - Mixed SAM

Tapping mode AFM

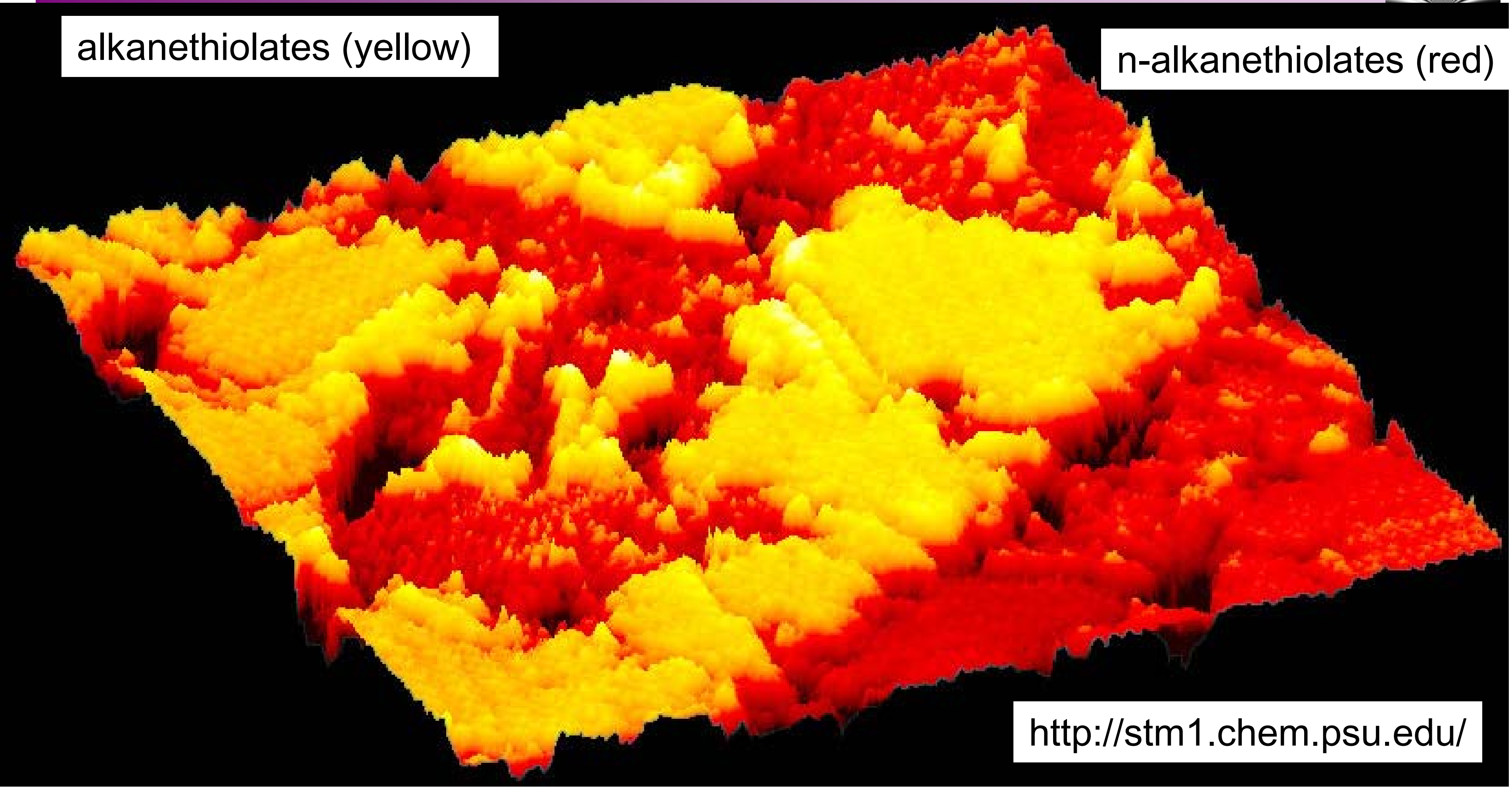
Hydrous OTS on Si | Anhydrous OTS on Si



RMS roughness < 0.07 nm

Wang et al. 2005, *Langmuir*, **18**, 1848-1857

Mixed SAMs



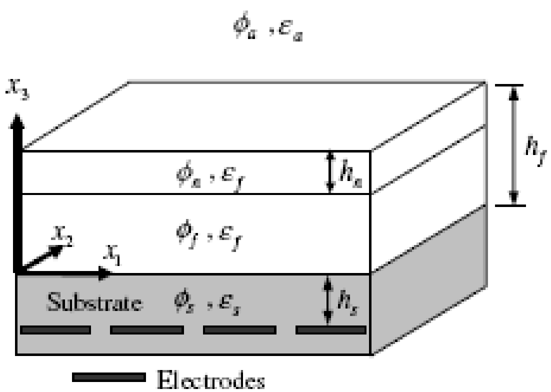
Spontaneous phase separation via buried H bonding

Smith *et al.* 2001 *J. Phys. Chem B,* **105**, 1119.
Lewis et al. 2001 *J. Phys. Chem B,* **105**, 10630.

Pattern Modeling

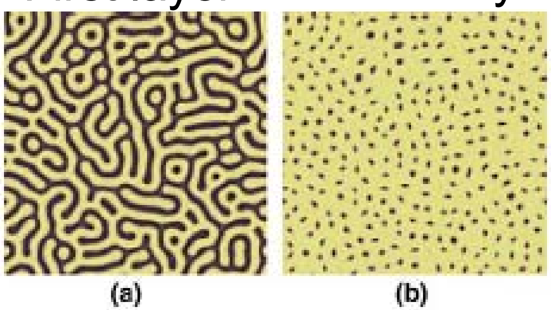
- Molecules are dipoles
- Phase field approach
- Diffusion of molecules in each layer is controlled by the one below
- Patterning

Lu and Salac, 2005 *Acta Materialia* **53**, 3253–3260

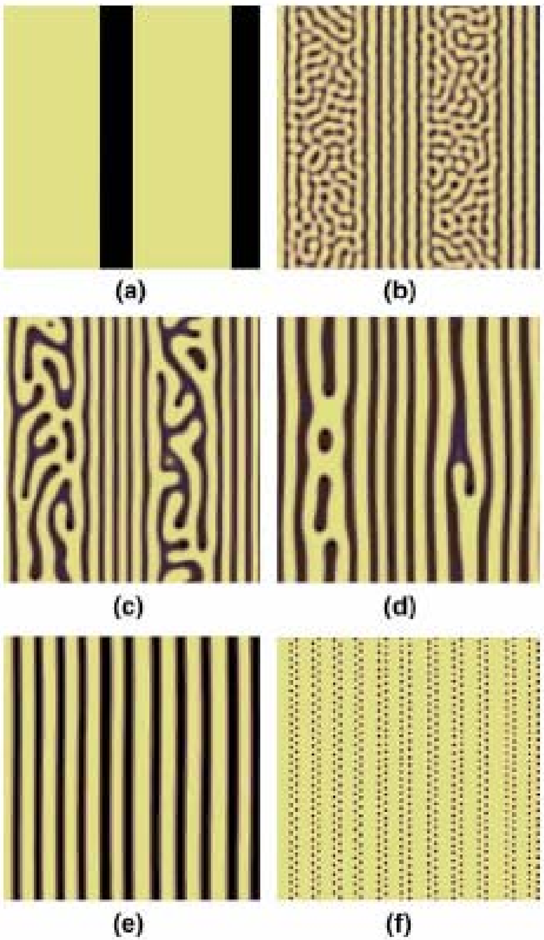


Structure

First layer Second layer



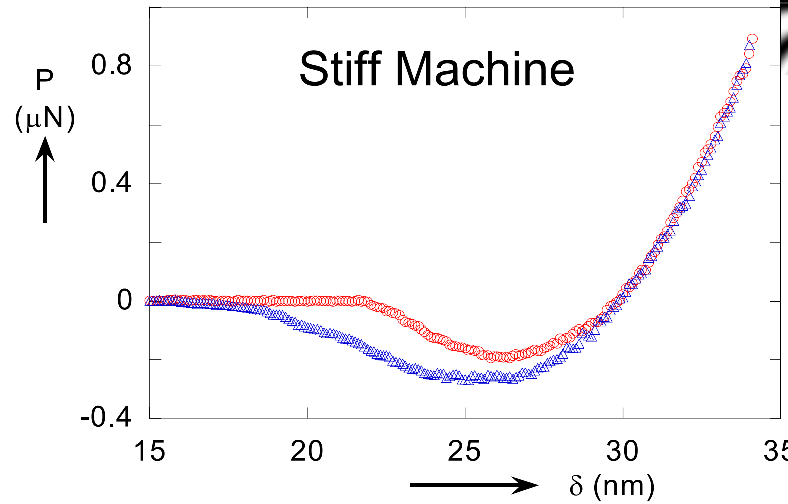
Zero potential



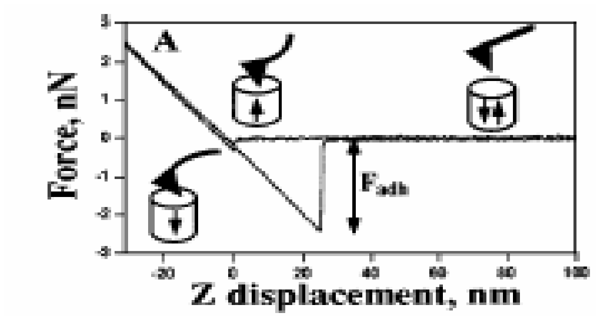
Striped potential

SAM Probing

- Normal loading
  - Adhesive interactions
  - Compressive behavior
- Shear loading
  - Pre slip
  - Post slip
- Combined loading

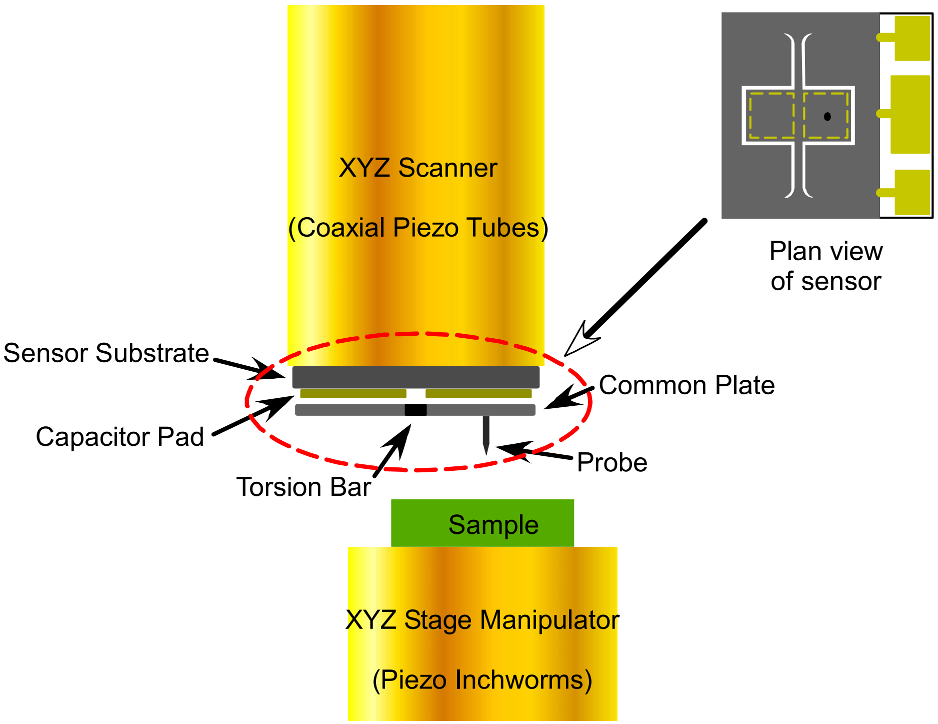


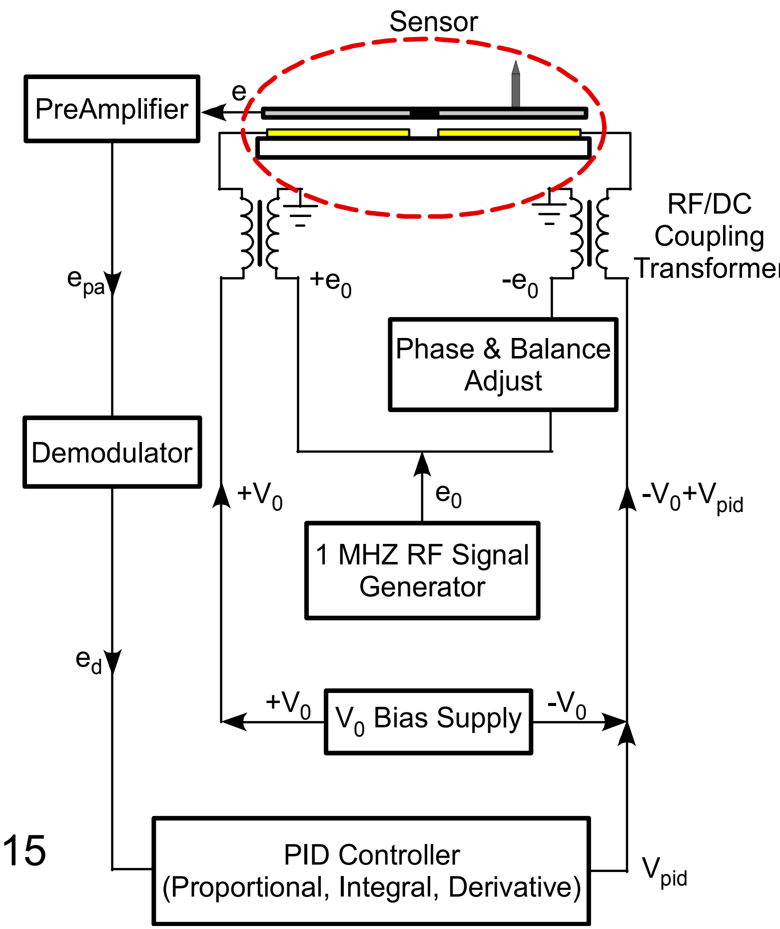
Soft Machine



Noy et al, 1997

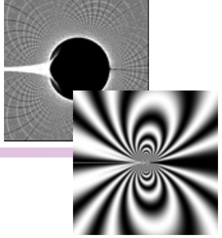
Interfacial Force Microscope

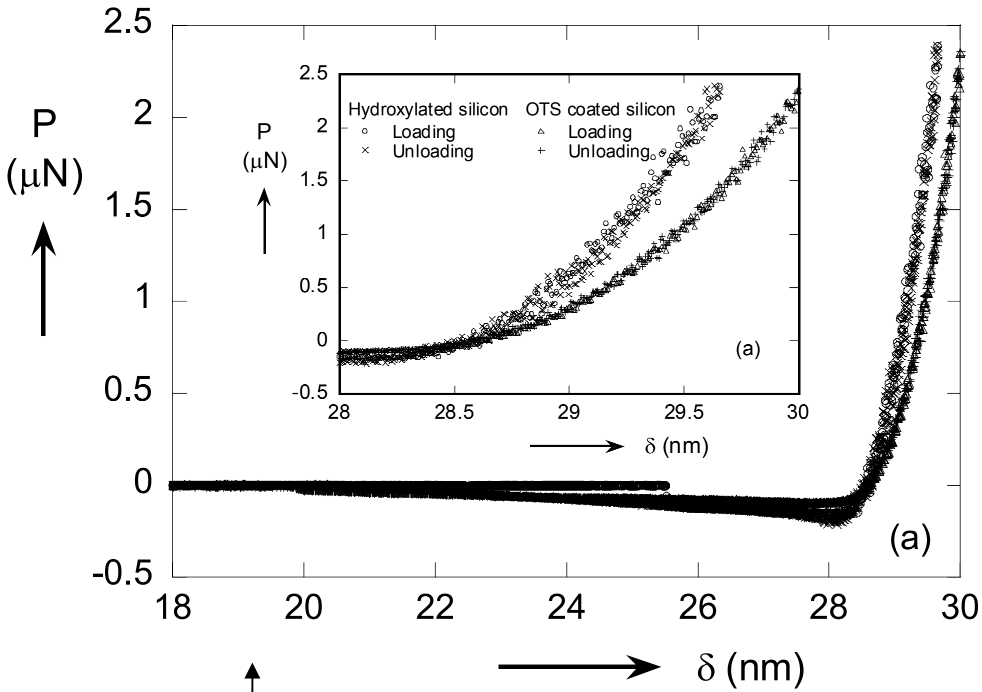




Joyce and Houston, *1991 Rev Sci Instru* ***62*** **,** 710-715
Houston and Michalske, *1992 Nature* ***356***, 266-67

SAM Probing…….Normal Load

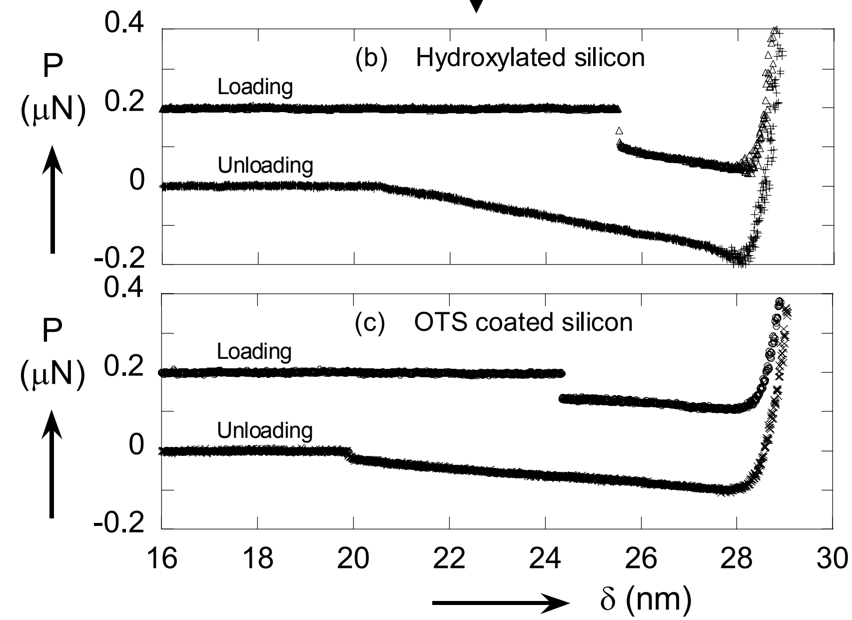




Interfacial force microscope (IFM)

Tungsten on OTS

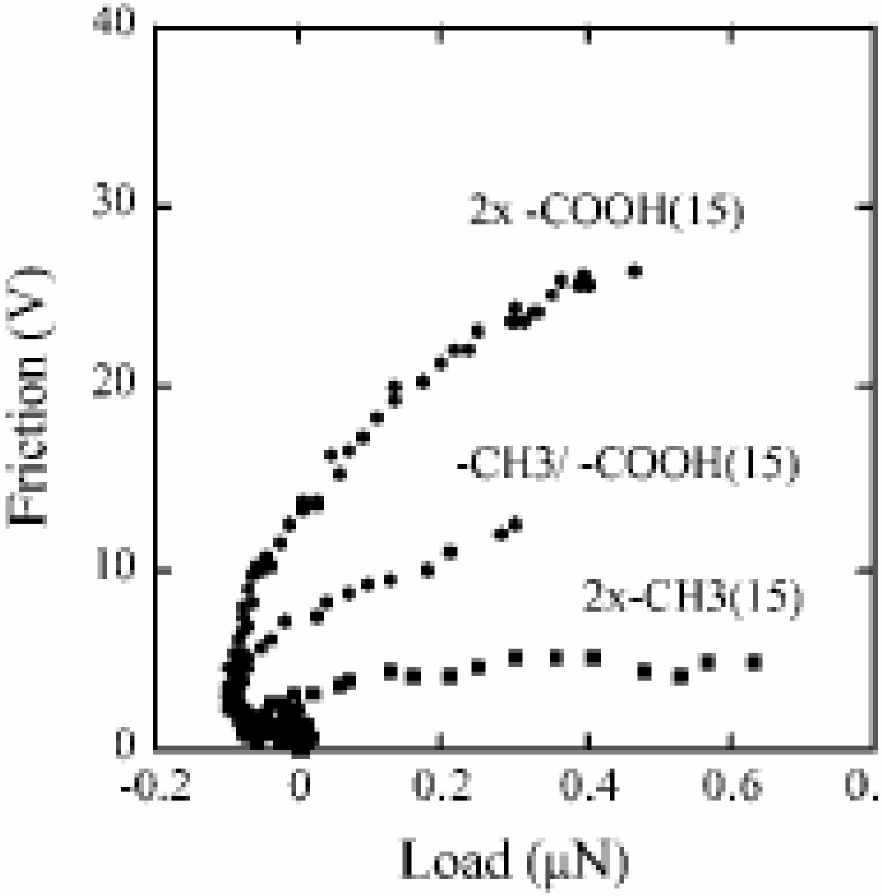
Adhesive Interactions



Compressive behavior

Wang et al. 2006 *J. Appl. Mech.* **73**, 769-777

SAM *vs.* SAM…..Normal and Shear load

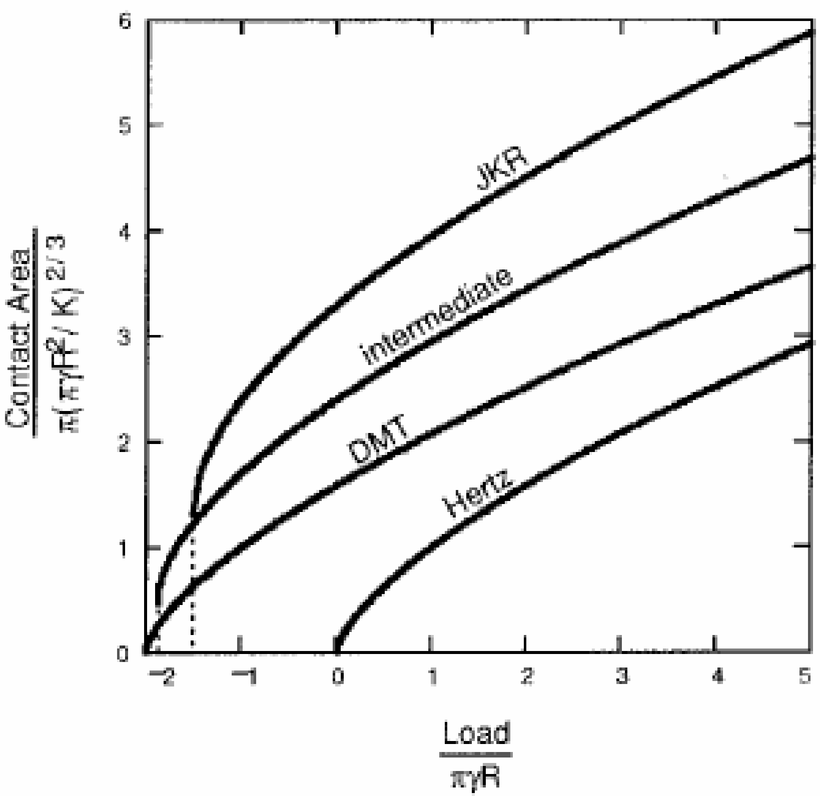


Houston & Kim, 2000 J. Am. Chem. Soc., ***122****,12045-12046*

IFM

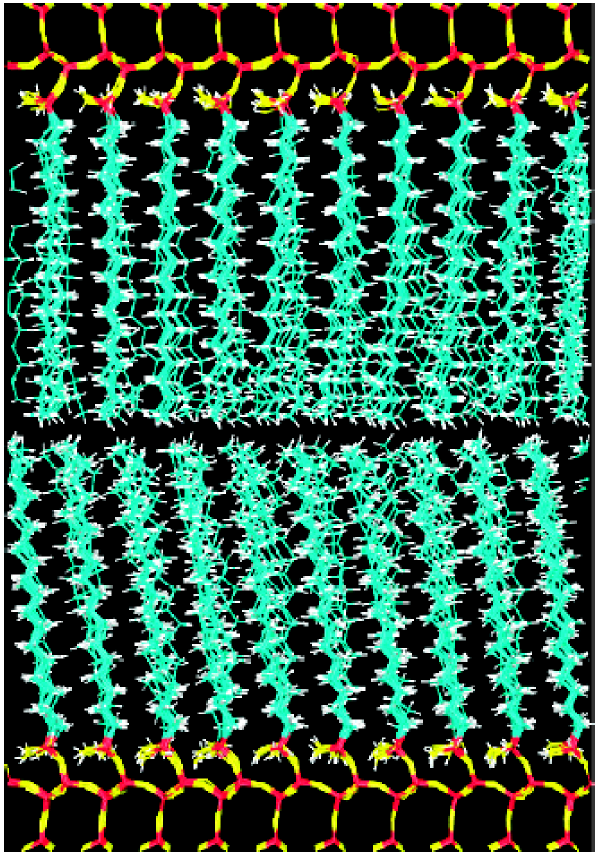
SAM-coated tip

SAM-coated substrate

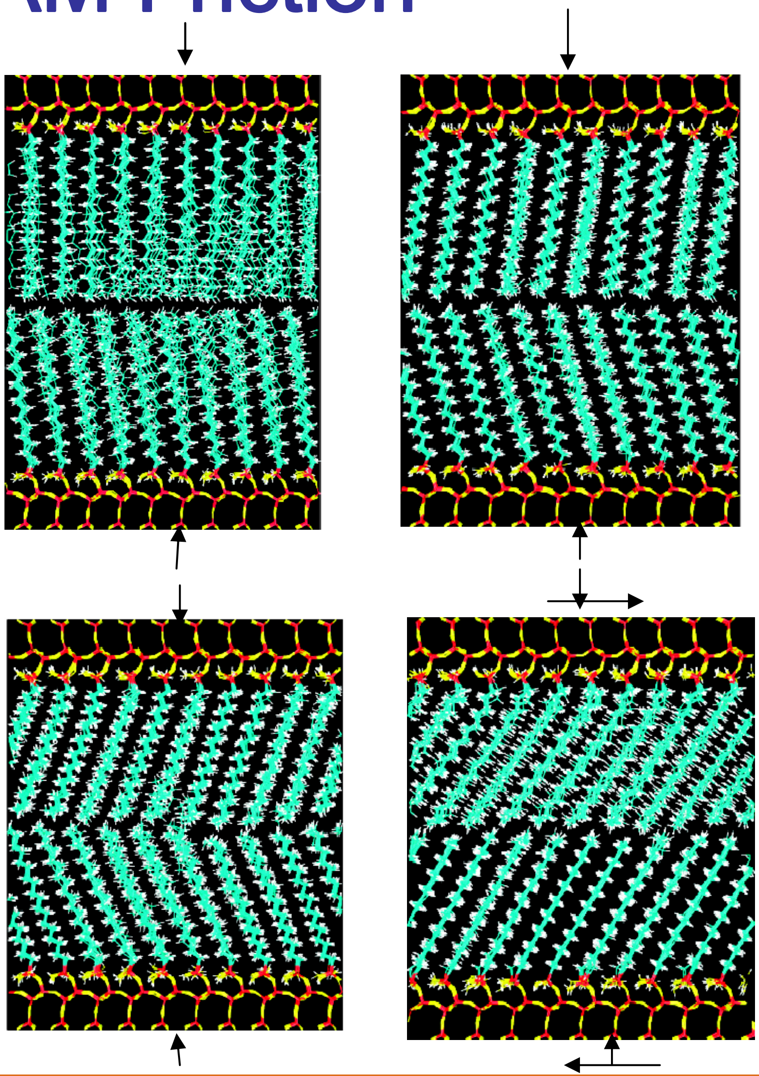


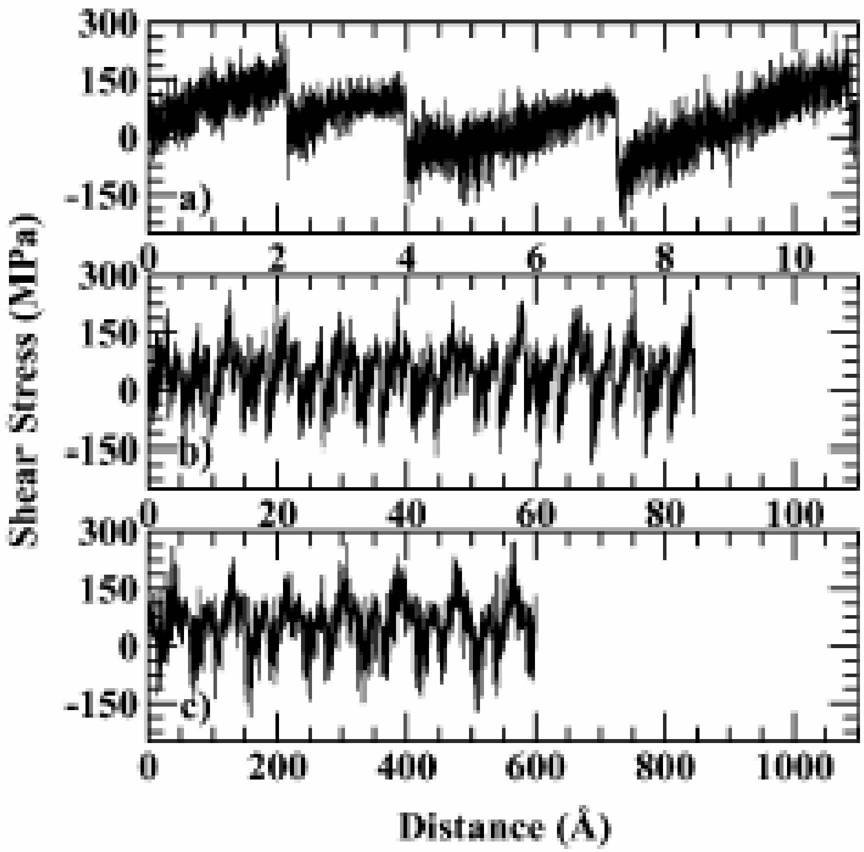
Analysis of Adhesion, Contact and Slip

- Atomistic
  - Simple geometries
  - Constitutive behavior from "first principles"
- Continuum
  - Complex geometries
  - Constitutive behavior based on phenomenological approach
- Hybrid



Molecular Dynamics Analysis of SAM *vs.* SAM Friction

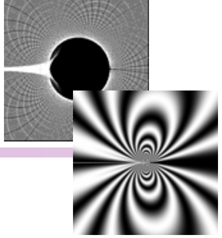




Chandros, Grest & Stevens, Langmuir, 2002;18, 8392.

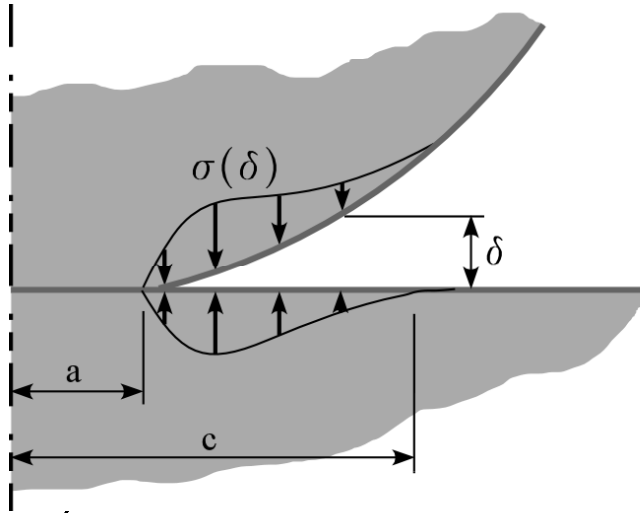
Tutien, Stuart & Harrison, Langmuir 2000;16, 291.

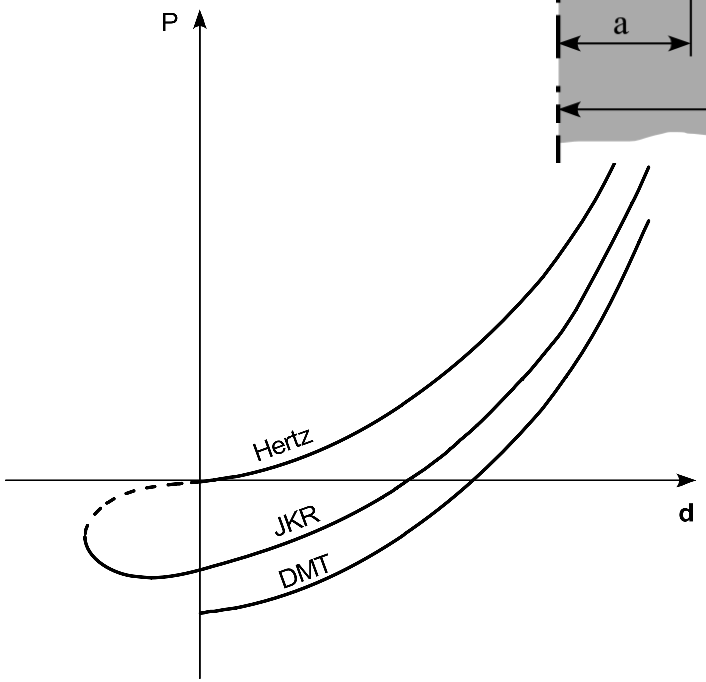
Contact Mechanics Theories



- Monolithic materials:
  - Hertz theory
  - JKR & DMT
  - Maugis: JKR-DMT transition
    - $\lambda \to 0$ DMT
    - $\lambda \to \infty$ JKR

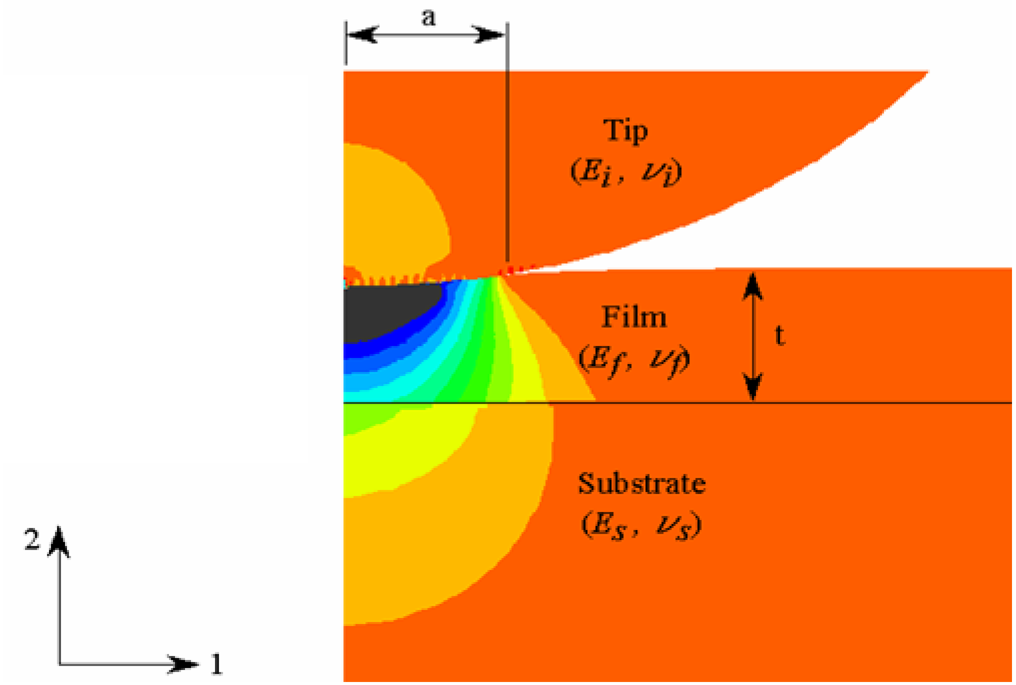
$$E^{*} = \frac{E}{1-\nu^{2}}$$





- Layered materials
  - Substrate effect
  - Poisson effect

Layer and Substrate Interaction



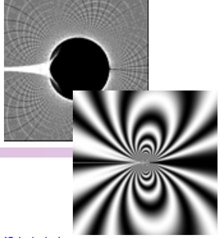
ε_{22}

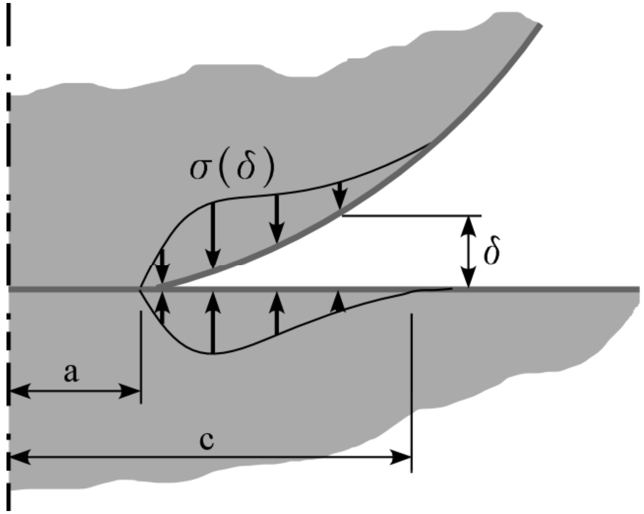
Guidelines

- Severe substrate effect
- E and ν need to be determined separately
- $\delta/t < 10\%$ rule does not hold
- Suggested rule: $a/t < 10\%$

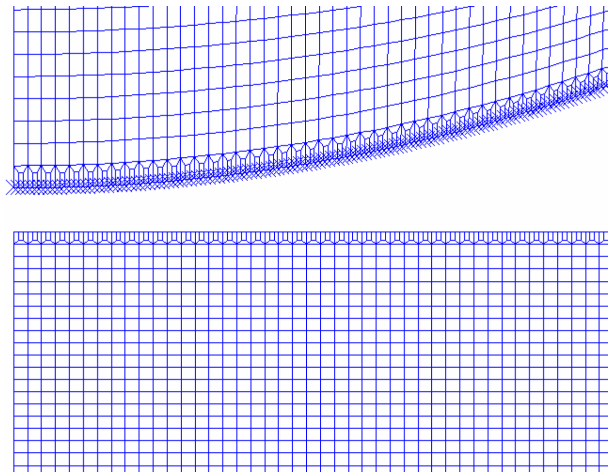
Wang, Liechti, White & Winter. 2004 *J. Mech. Phys. Solids*, **52**, 2329-2354.

Surface Interactions

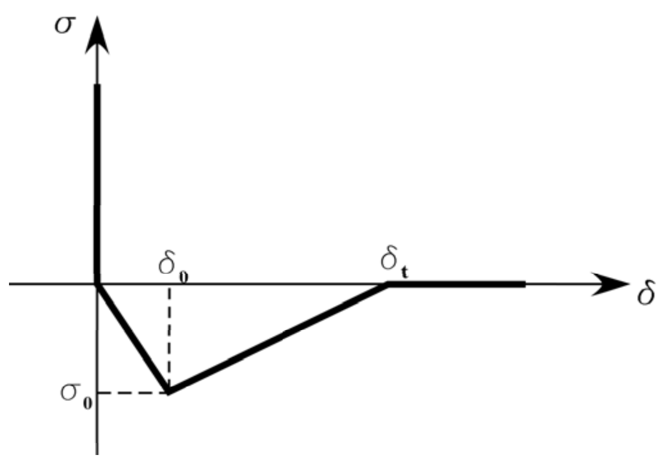




$\Rightarrow$

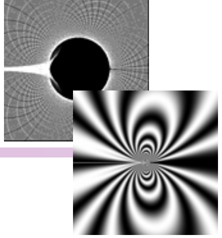


Triangular normal interactions



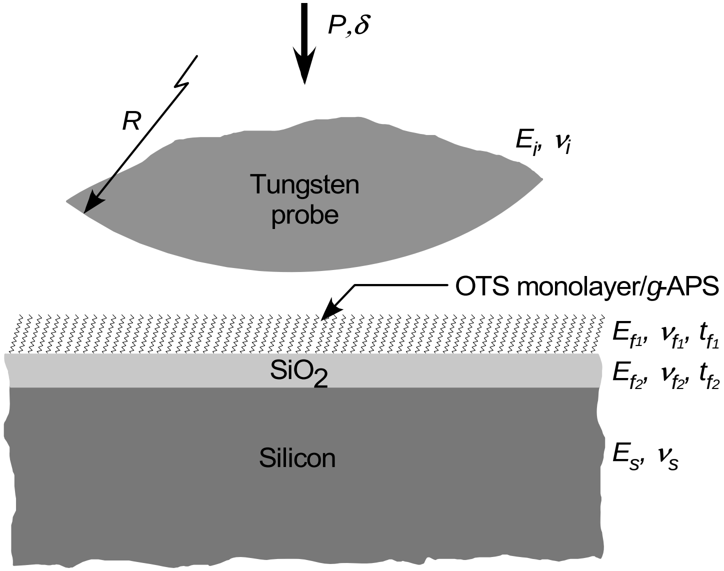
$$\omega = \frac{\sigma_0 \delta_t}{2}$$

Linear Elastic Analysis of IFM Force Profiles



- Linearly elastic

Material	E (GPA)	ν
Tungsten	392	0.28
SiO_2	73.6	0.17
Silicon	168	0.22



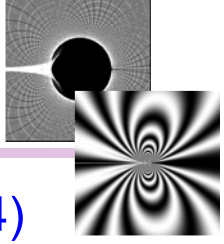
- Film thickness:

  SiO_2: 2.0 nm
  OTS SAM: 2.5 nm

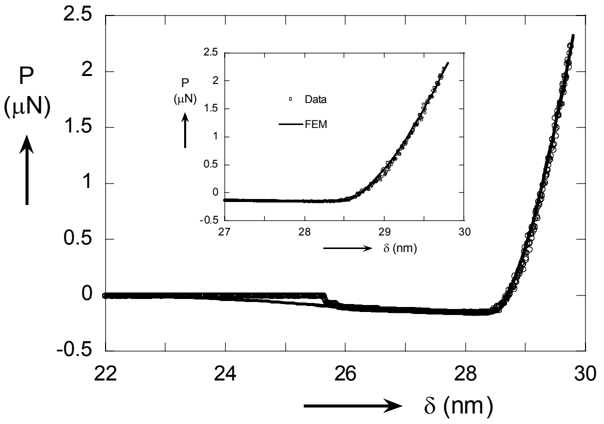
- Model

  Mechanical properties of OTS layer varied

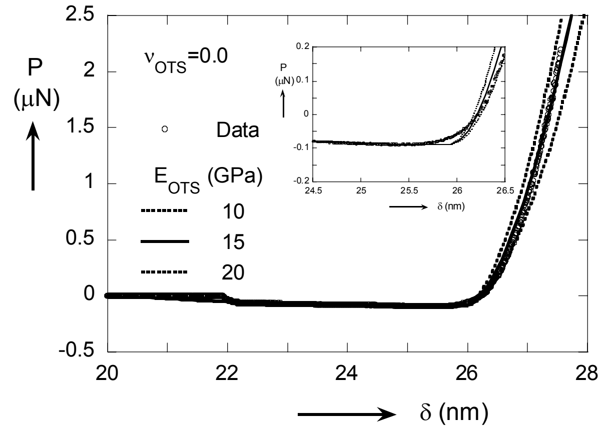
Linearly Elastic Analysis



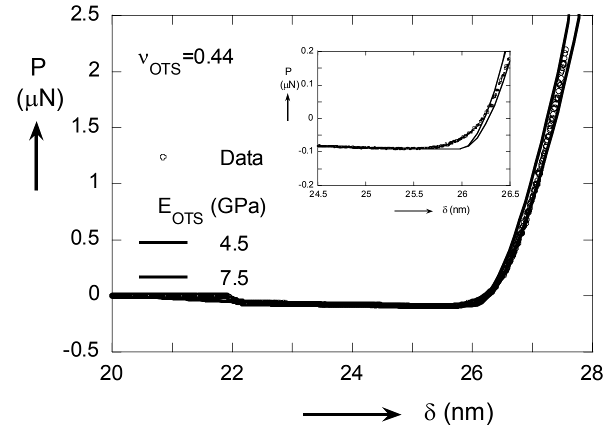
Bare silicon



OTS (ν=0.0)



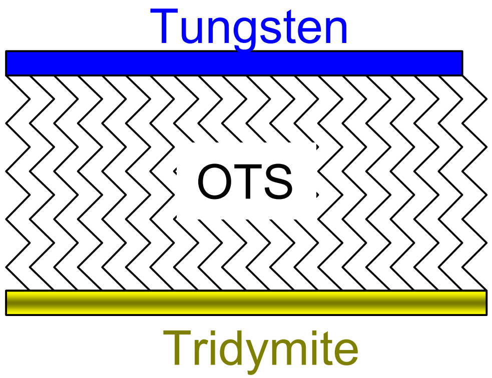
OTS (ν=0.44)



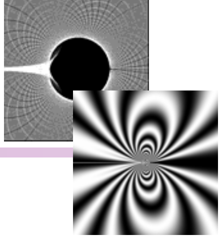
Reduced E* (GPa)		σ_0 (MPa)	δ_t (nm)	δ_0 (nm)	$\omega=\sigma_0 \times \delta_t /2$ (mJ/m²)
ν=0.0	ν=0.44				
15±5	6±1.5	35	7	5	122.5

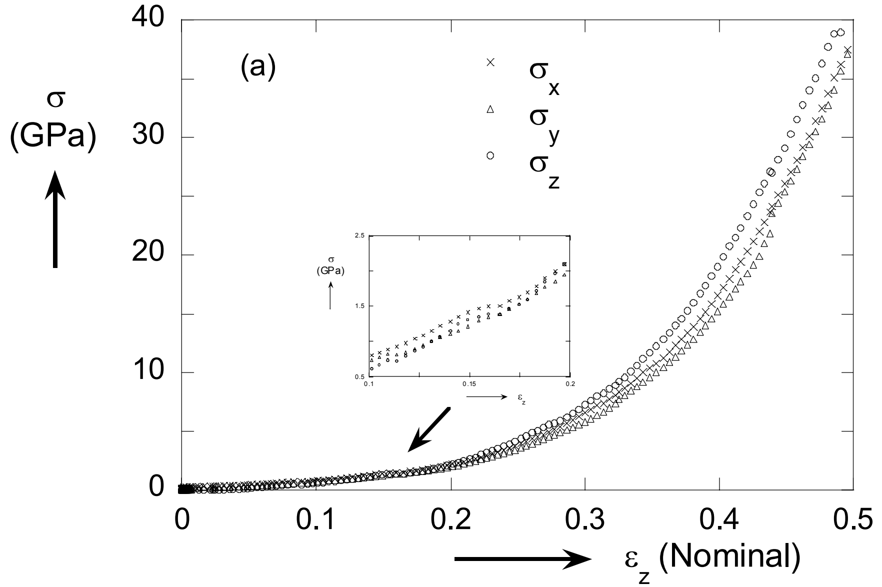
Molecular Dynamics Model for OTS

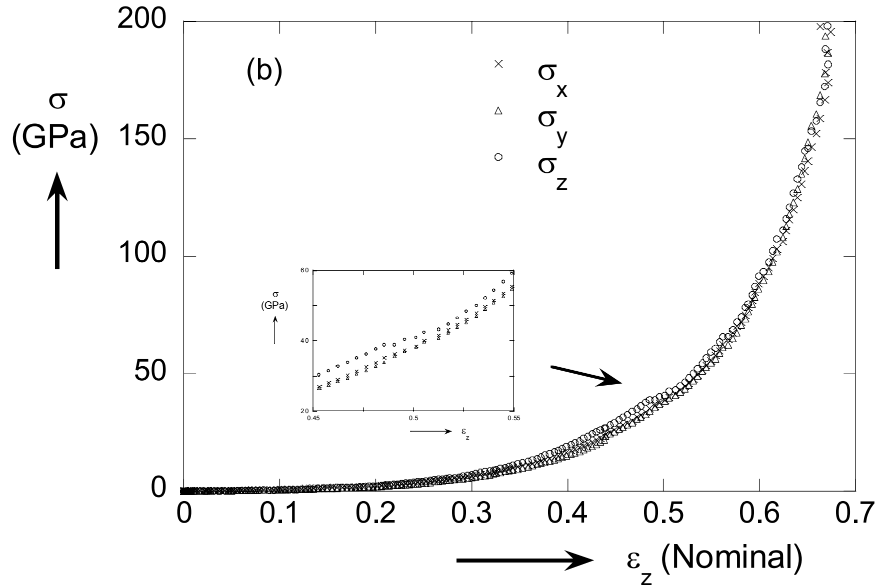
- MD software package: DL_POLY 2.0
- OTS on tridymite (SiO_2)
- Rigid planes: SiO_2 and tungsten
- CH_3, CH_2, and OH groups were treated as united atoms.
- Periodic boundary conditions: in-plane
- The simulation cell had dimensions of 2.6×2.7 nm^2 containing 30 OTS molecules.
- Intra-molecular interactions: harmonic bond, harmonic valence angle and cosine dihedral angle potentials. CFF93, OPLS-UA
- Inter-molecular interactions: Lennard-Jones van der Waals potentials.
- Room temperature, loading rate rate 10^7-10^8 nm/sec



Stress-Strain by MD Simulation

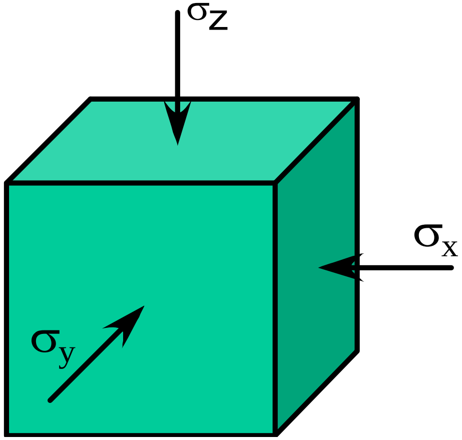






Hypo-elastic Material

- Assume: uniaxial strain state



$$\varepsilon_x = \varepsilon_y = 0$$

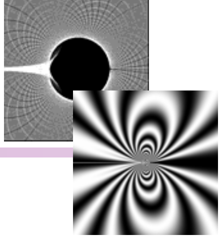
$$\sigma_x = \sigma_y = \sigma$$

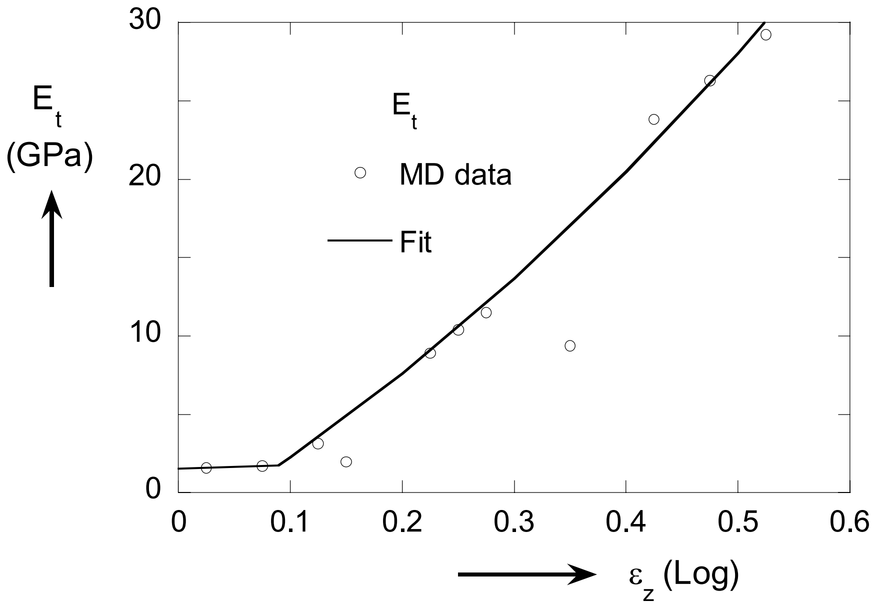
- Hypo-elastic: $d\varepsilon_i = \frac{1}{E_t}\left[d\sigma_i - \nu_t\left(d\sigma_i + d\sigma_k\right)\right]$ $\quad i, j, k = x, y, z$

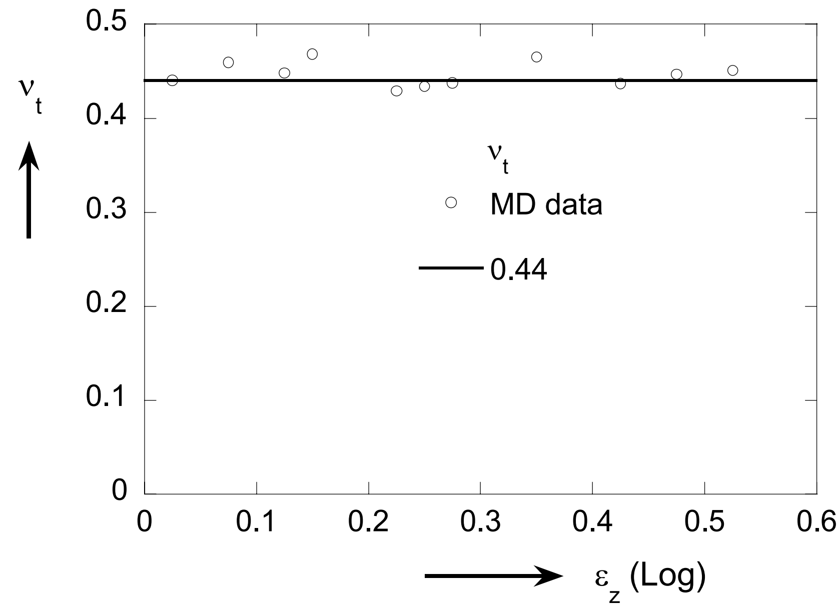
- $\Rightarrow$

$$\nu_t = \frac{\frac{d\sigma}{d\varepsilon_z}}{\frac{d\sigma}{d\varepsilon_z} + \frac{d\sigma_z}{d\varepsilon_z}} \qquad E_t = \frac{d\sigma_z}{d\varepsilon_z} - \nu_t\left(\frac{d\sigma_x}{d\varepsilon_z} + \frac{d\sigma_y}{d\varepsilon_z}\right)$$

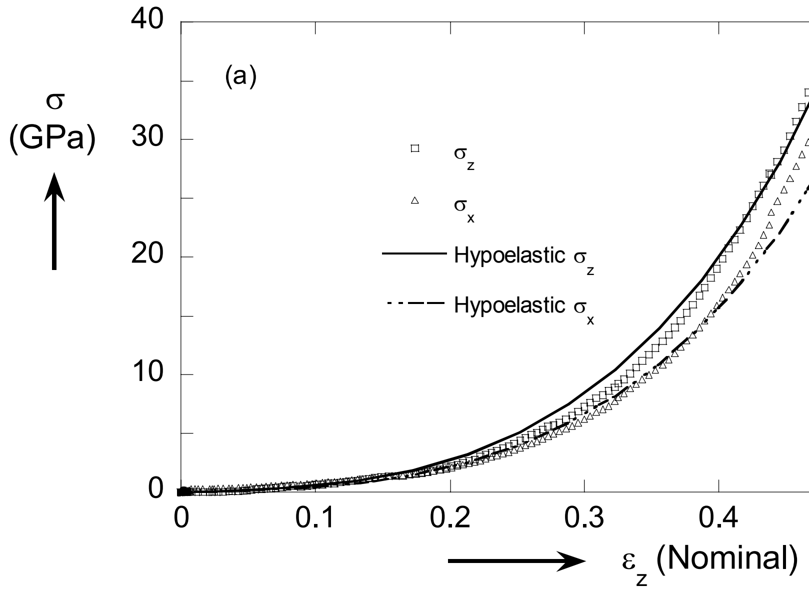
Hypo-elastic Model Parameters

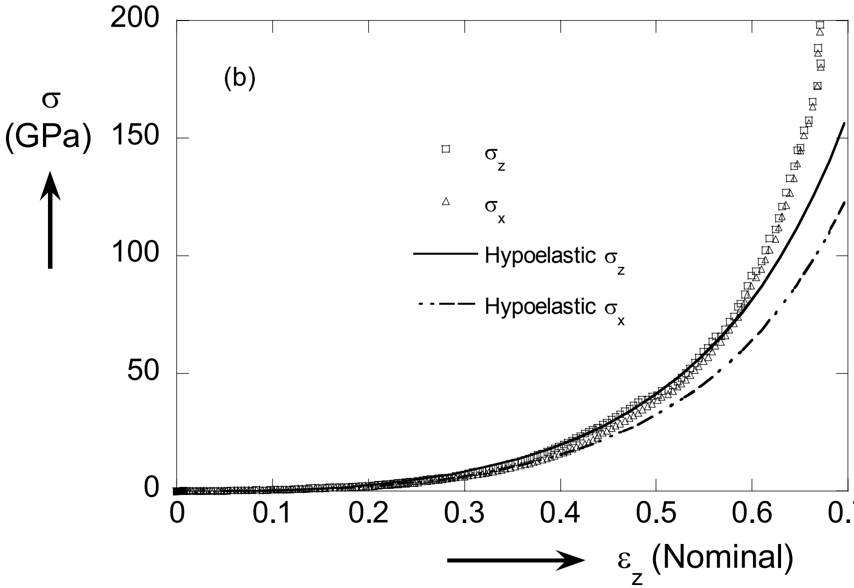




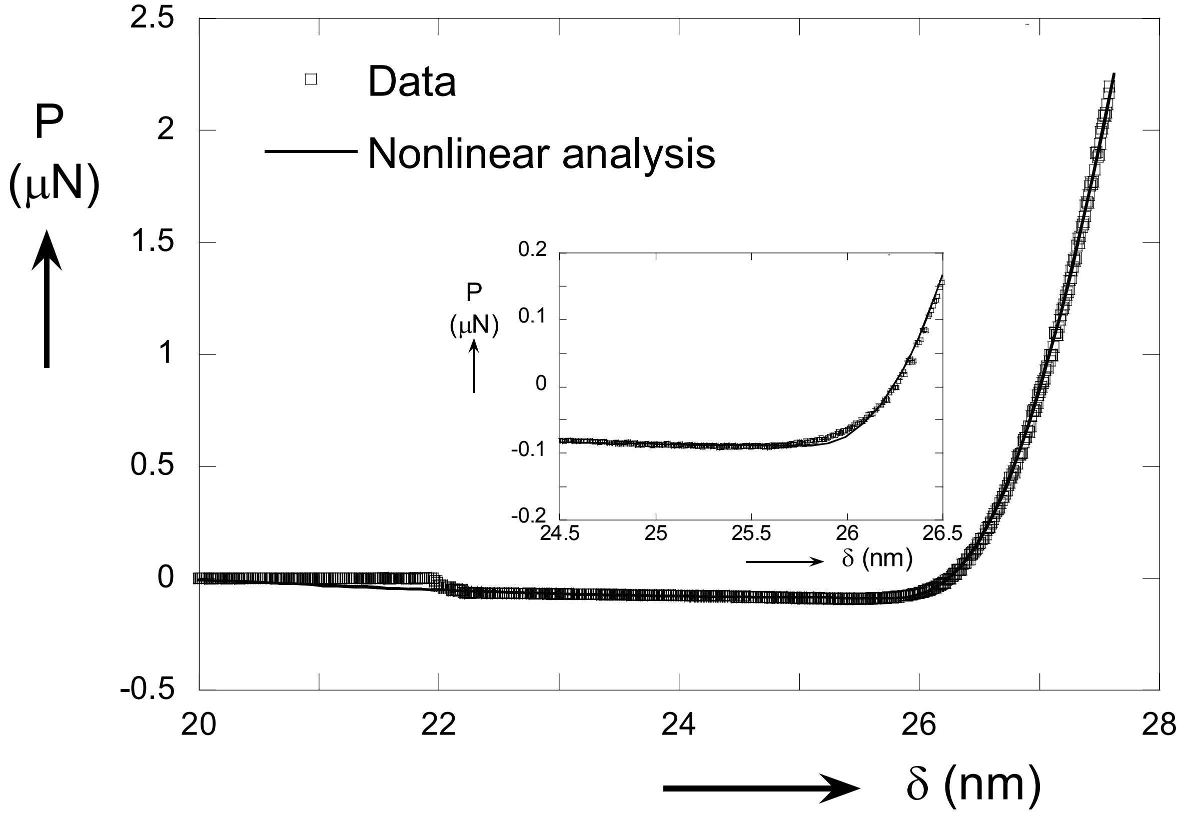


Comparison Between Hypo-elastic Model and MD Result





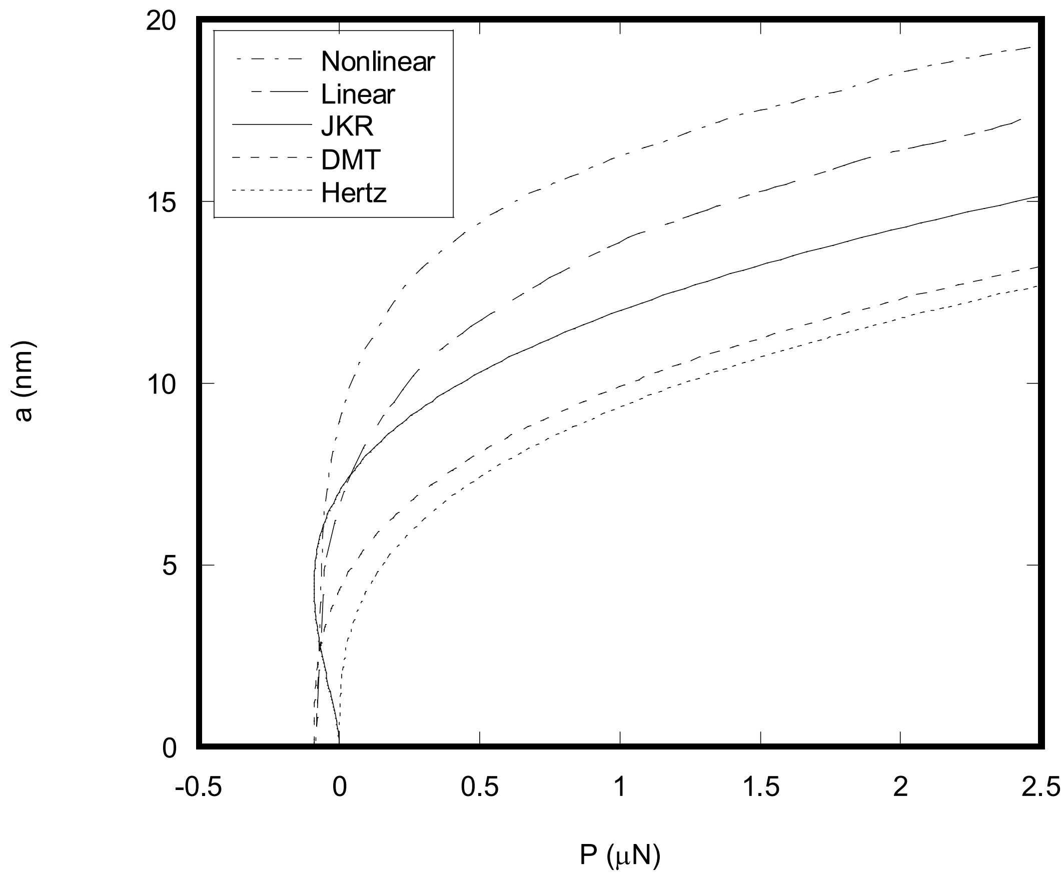
Nonlinear Analysis of the IFM Experiment



Wang, et al.. 2006 *J. Appl. Mech.*, **73**, 769-777

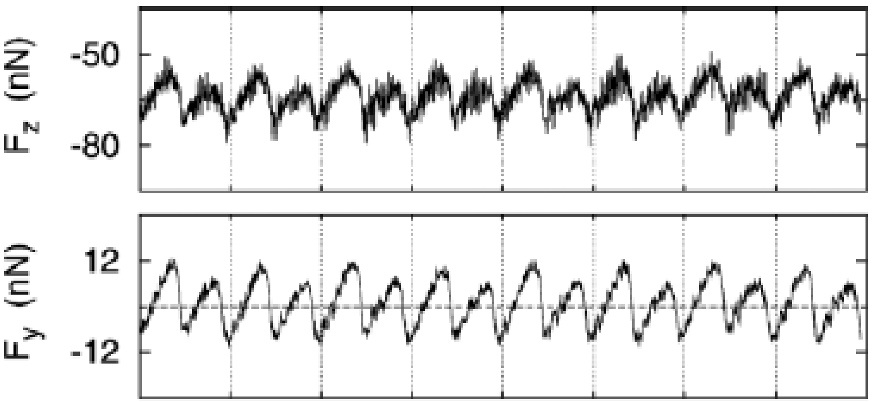
Contact Radius Comparison

- OTS on silicon
- Classical contact analyses severely underestimate the contact radius



Time Scales in Sliding

- Hydrogen terminated diamond substrates
- C_{13} n-alkane monolayer
- Sliding speed 50 m/s
  - 10^{-8} to 10^{-1} in AFM
- Periodicities in system response
- Smaller number of unit cells
- Longer time scales



Mikulski and Harrison 2001
Tribology Letters **10,** 29-35

Park, Chandross, Stevens, and Grest 2003 *Langmuir*, *19,* 9239-9245

Outstanding Issues

- SAM Processing
  - Patterning binary SAMs
  - Defects
- SAM Probing
  - Mach 2 IFM
- Modeling
  - Phase separation
  - Water
  - Time scales in sliding
- Wear