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International Centre for Theoretical Physics

United Nations
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International Atomic
Energy Agency

SMR.1759 - 9

**Fourth Stig Lundqvist Conference on
Advancing Frontiers of Condensed Matter Physics**

3 - 7 July 2006

Dynamics of molecules at confined interfaces

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Dynamics of molecules at confined interfaces

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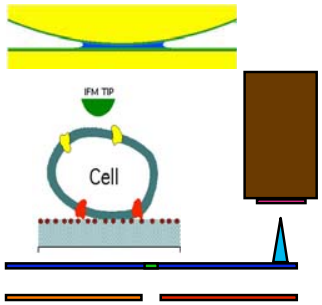
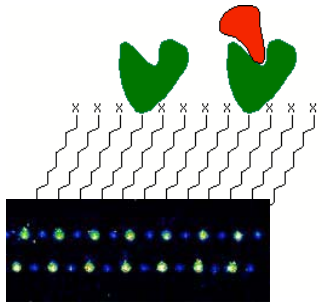
Minneapolis, MN 55455, USA

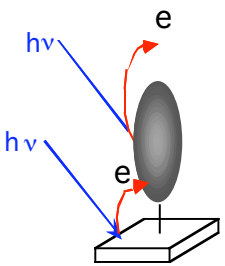
http://www.chem.umn.edu/groups/zhu



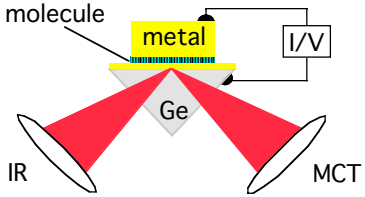
Nanomechanics, biophysics



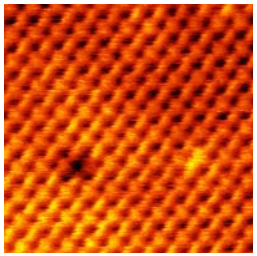
Proteomics, biotech



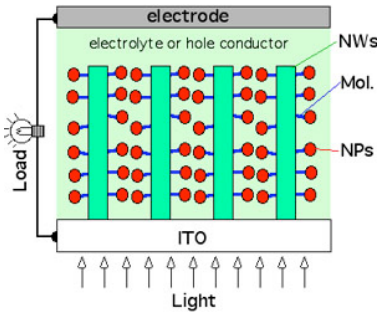
Electron transfer/transport



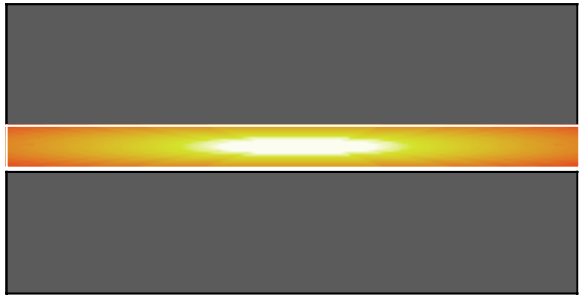
Molecular junctions



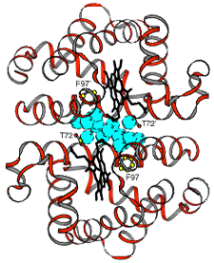
Organic semiconductor

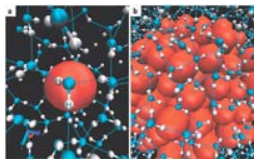


Photovoltaic

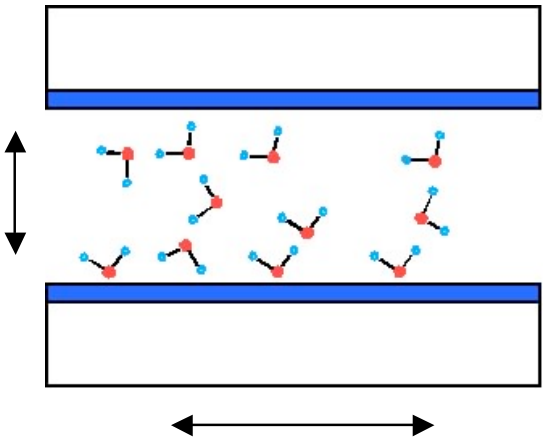


What is the consequence of confinement on molecular motion?





Nature, *437*, 640 (**2005**).

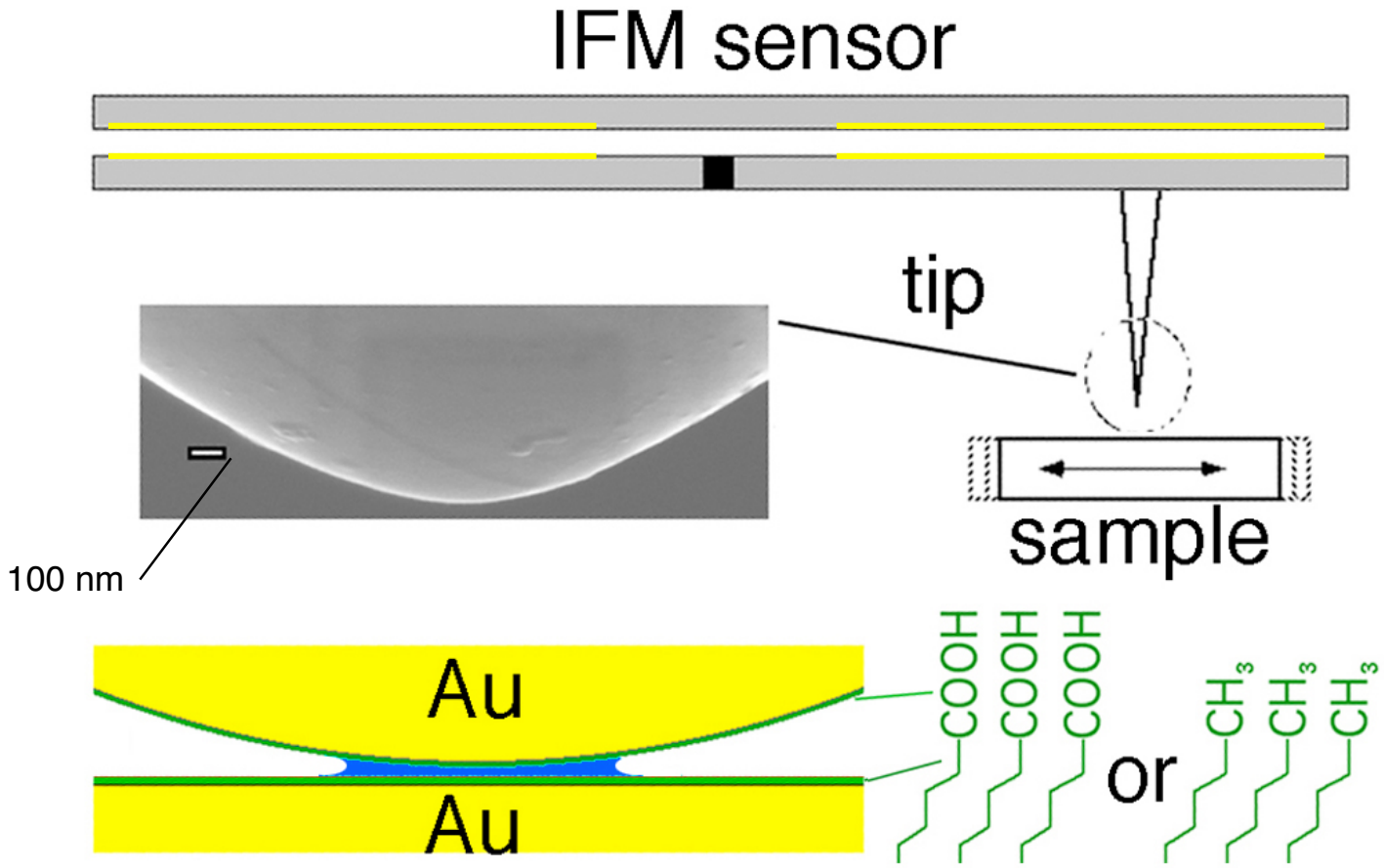


Ryan Major

Matt Goertz

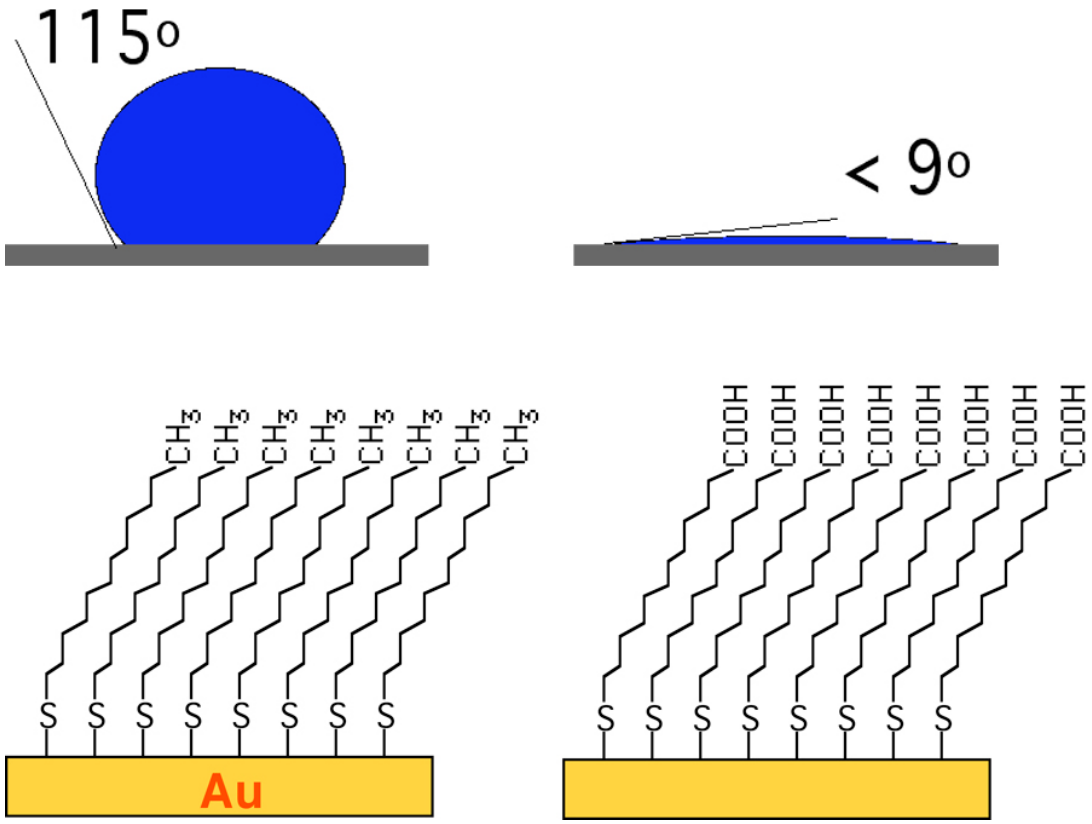
$

Sandia National Laboratories

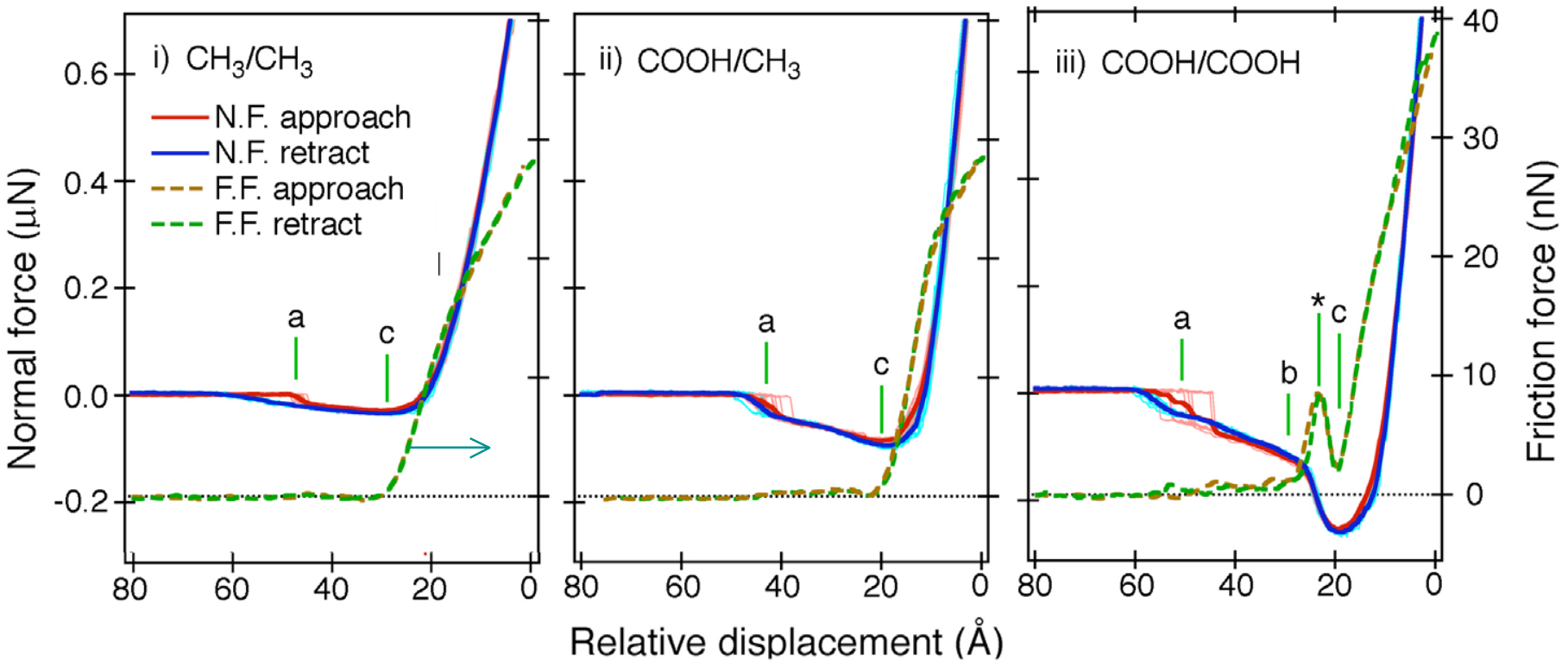

IFM sensor
tip
sample
100 nm
Au
Au
COOH
COOH
COOH
or
CH3
CH3
CH3

Hydrophobic

Hydrophilic



SAM


i) CH3/CH3
N.F. approach
N.F. retract
F.F. approach
F.F. retract
ii) COOH/CH3
iii) COOH/COOH
a
b
c
*
Normal force (μN)
Friction force (nN)
Relative displacement (Å)
0.6
0.4
0.2
0.0
-0.2
40
30
20
10
0
80
60
40
20
0

$$\eta_{eff} = \frac{\text{shear stress}}{\text{shear rate}} \approx 1.2 \times 10^{4}\ \text{Pa} \cdot \text{s}$$

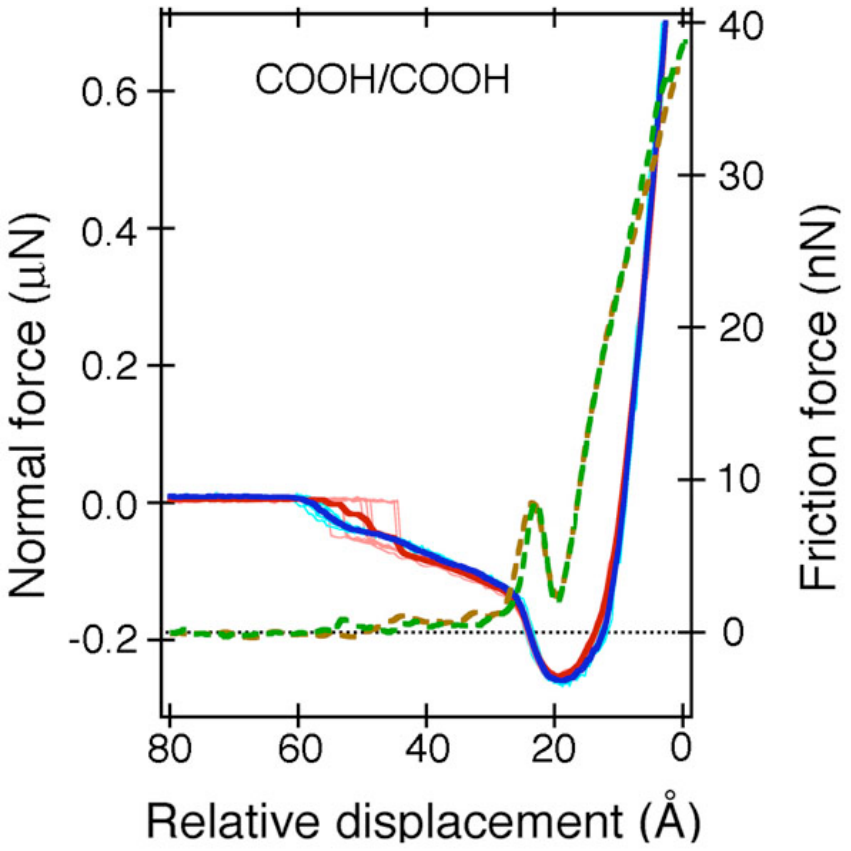
or $\approx 3 \times 10^{4}\ \text{Pa} \cdot \text{s}$ (sphear/plate)

$d^* = 0.6$ nm (interfacial separation)

$v_s = 500$ nm/s (shear velocity)

$F_\mu{}^* = 8.6$ nN (peak friction force)

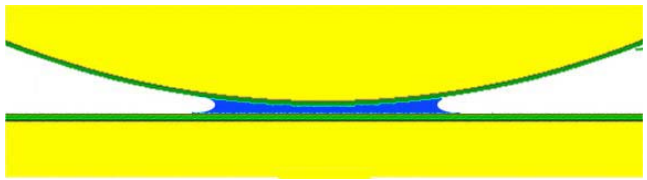
$A_m = 2600$ nm^2 (meniscus size)

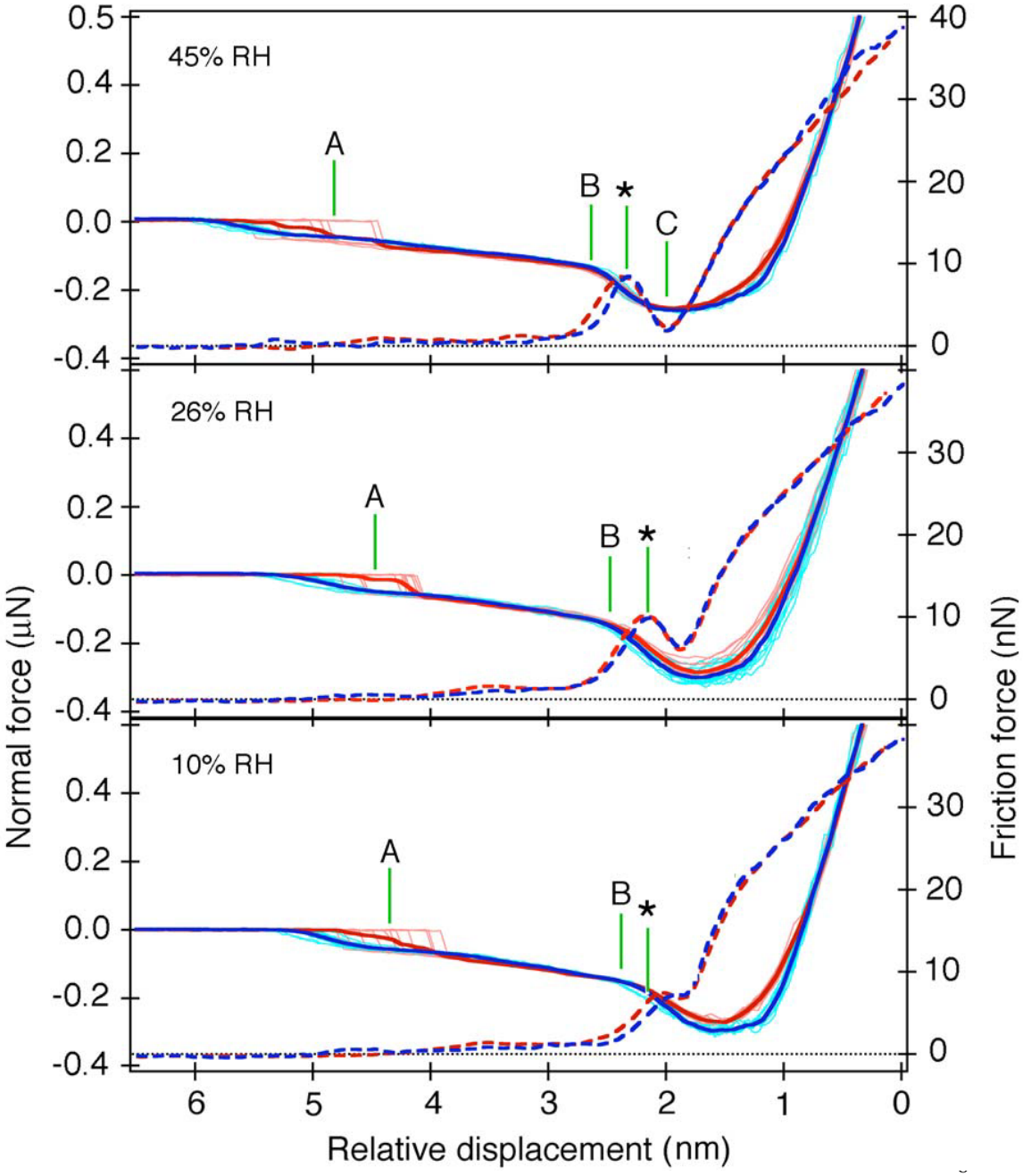


$\eta_{bulk\ water} = 8.6 \times 10^{-4}$ Pa·s

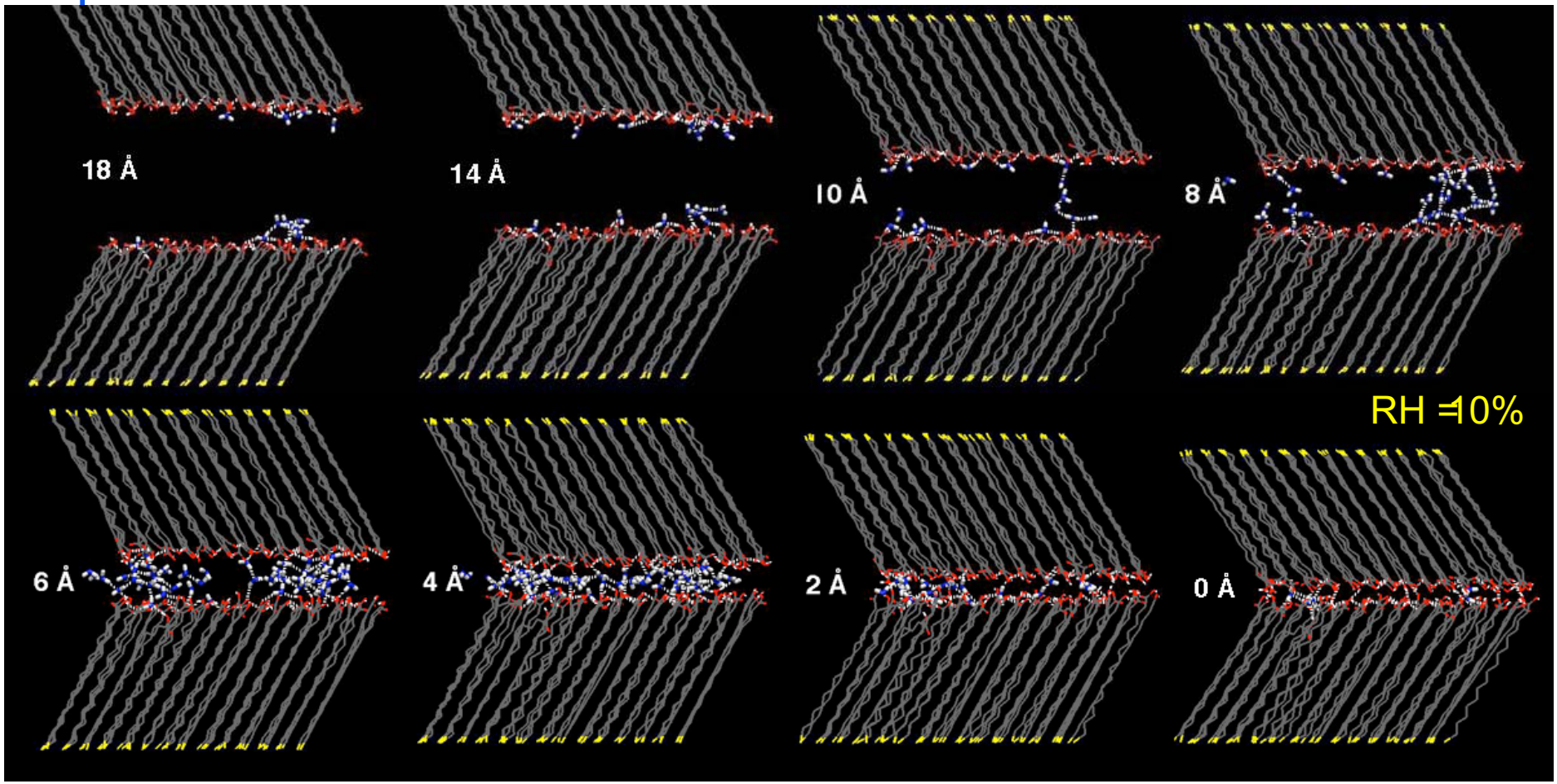
$_2O$

Relative humidity	Radius of meniscus
45%	29 nm
26%	23 nm
10%	18 nm





Grand Canonical Monte Carlo simulation



The formation of H-bonded bridges!

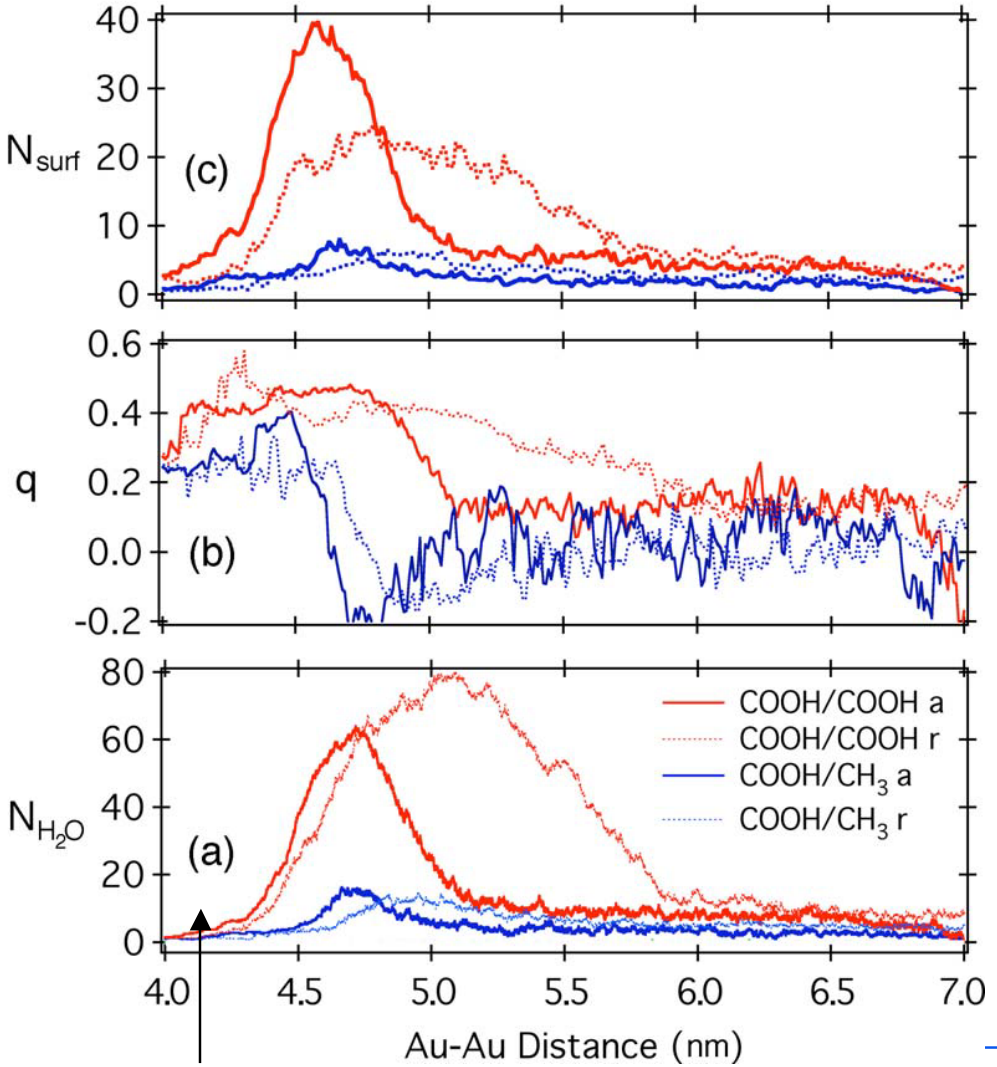
Structure

Number of H-bonds to -COOH surface

Tetrahedral order parameter

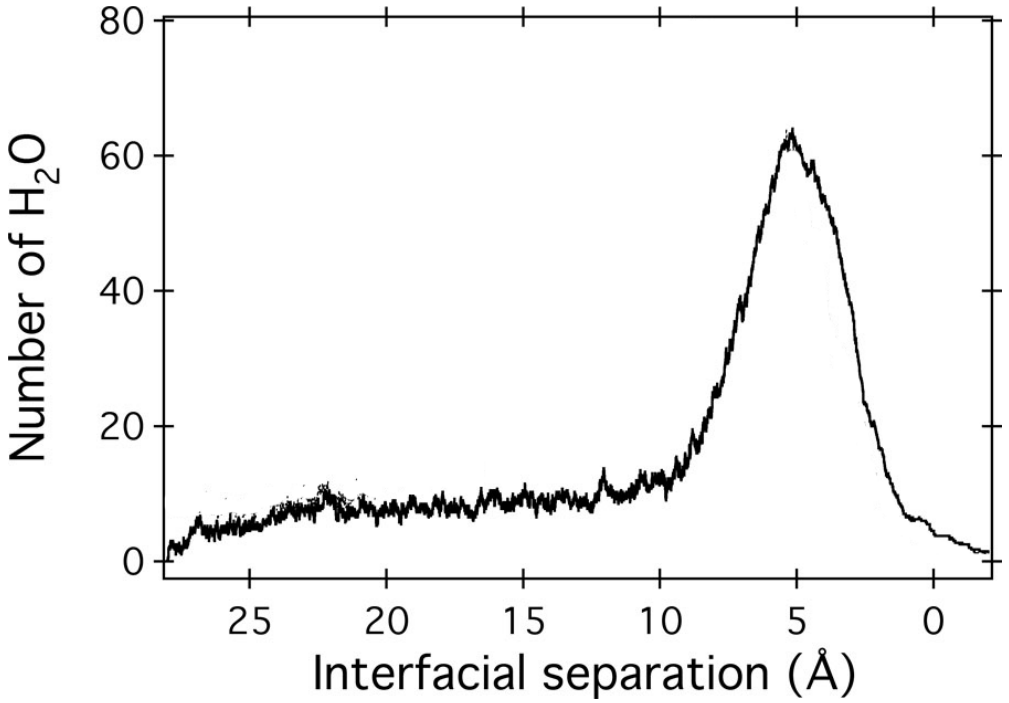
Nature 409, 318 (2001)

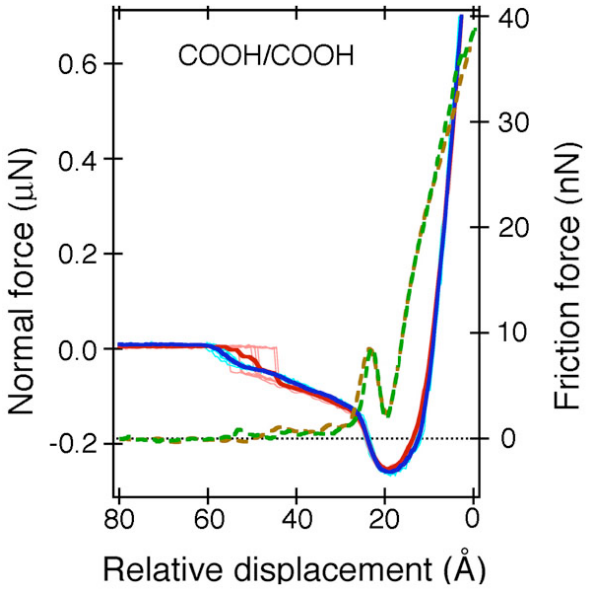
Population of H_2O within the nanogap

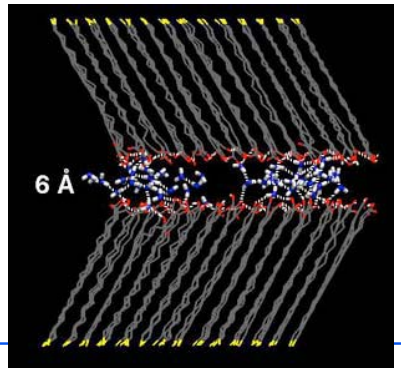


Interface

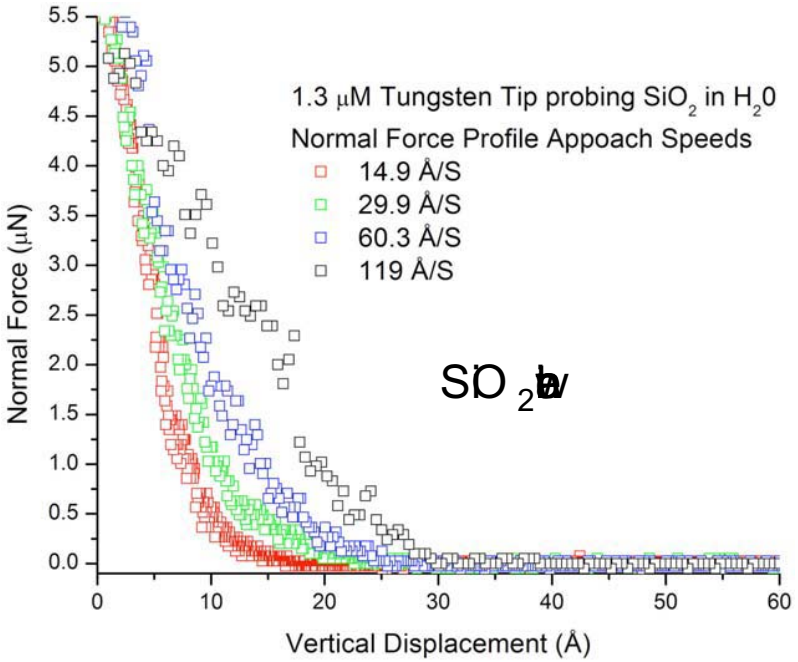
Simulation results for COOH/COOH

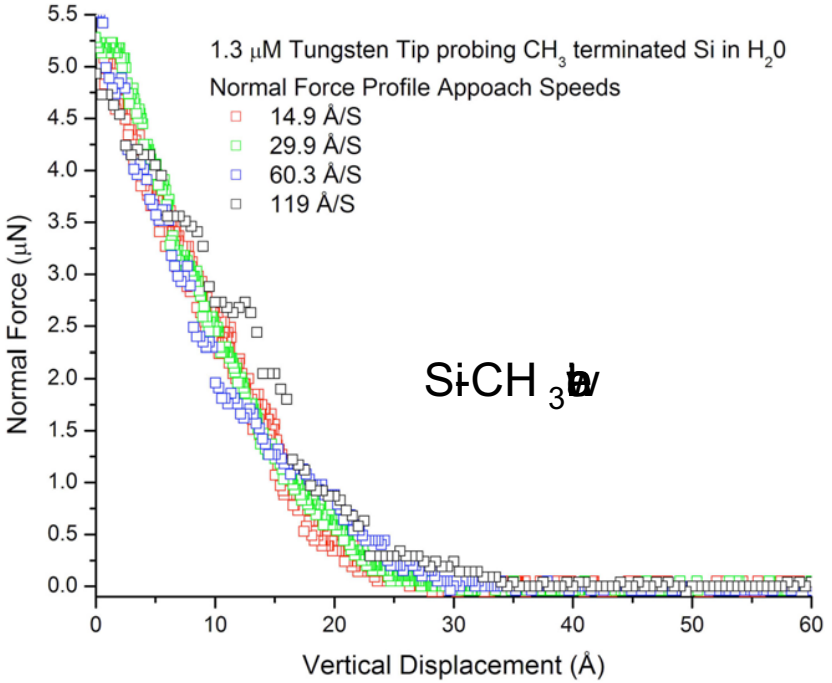


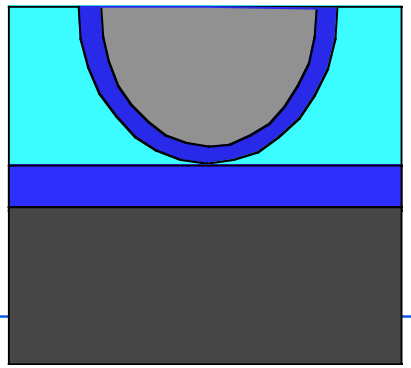




70Å x 80 Å, periodic



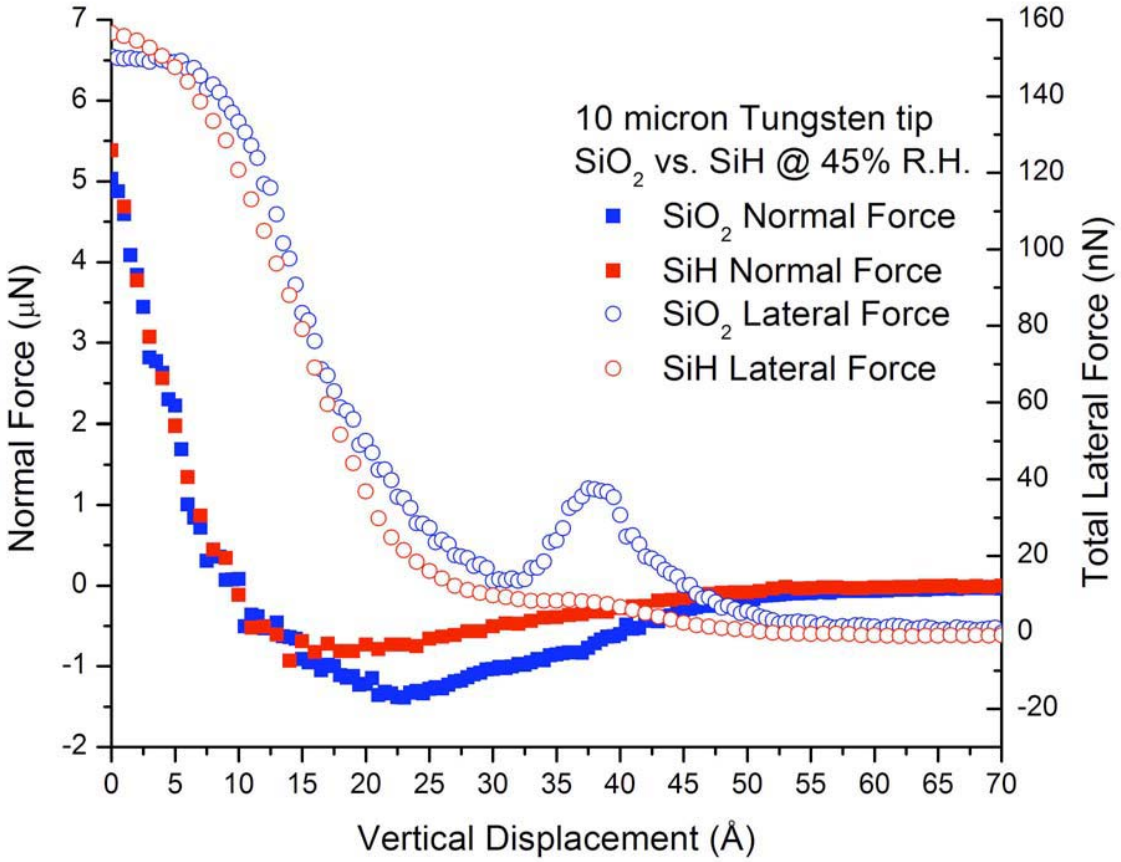




$$_{eff} \approx 7 \quad 10^{3}\ \mathrm{Pa \cdot s}$$

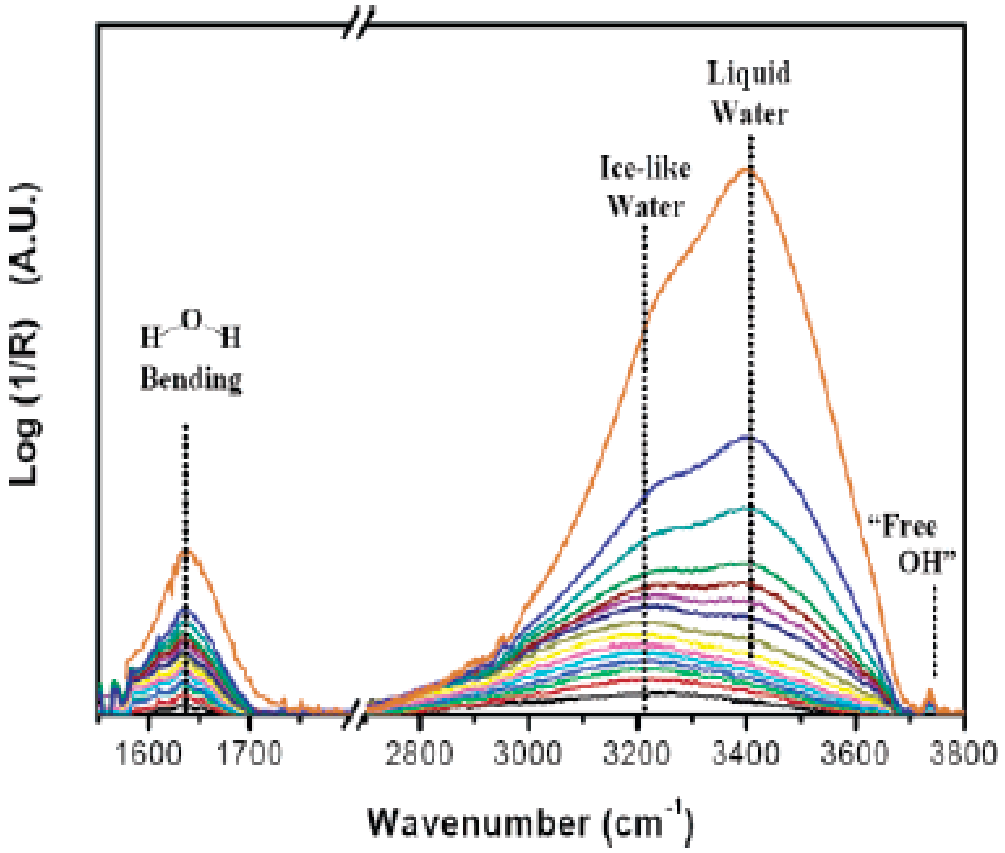
Feibelman, P. J.*Langmuir;* **2006**; *22*(5); 2136

H_2O/SiO_2 - measurement in air



$$\eta_{eff} \approx 2 \quad 10^3 \ \mathrm{Pa \cdot s}$$

Spectroscopic evidence of “ice-like” water on hydrophilic surfacs



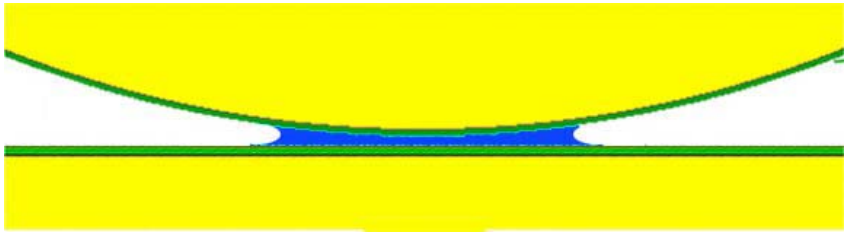
D. B. Asay & S. H. Kim, *J. Phys. Chem. B* **2005,** *109,* 16760-16763

Other studies: SFG

Q. Du, E. Freysz, and Y. R. Shen, Phys. Rev. Lett. **72**, 238 (1994).

V. Ostroverkhov, G. A. Waychunas, and Y. R. Shen, Phys. Rev. Lett. **94**, 046102 (2005).

The interfacial H_2O is like… peanut butter

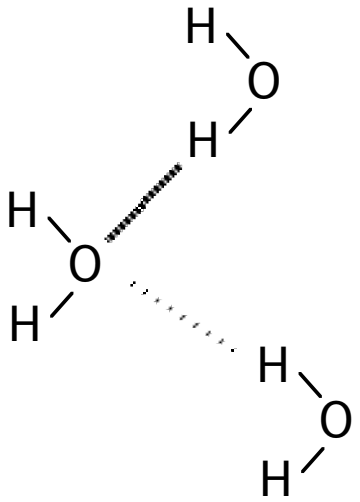


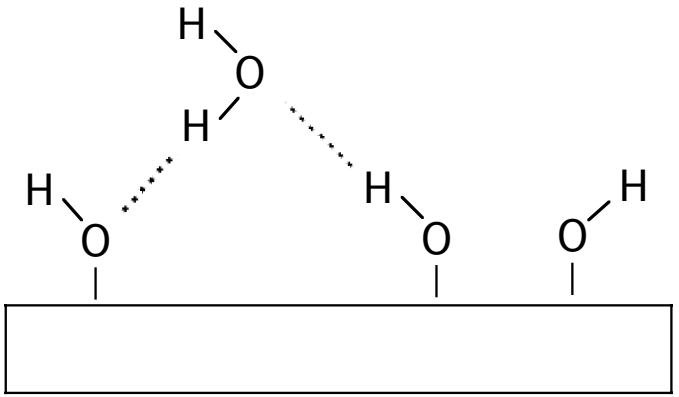
$10^{6\text{-}7}$ times η_{water}

6×10^4 η_{water}

1.2×10^6 η_{water}

WHY is interfacial water so different???





- An H-bond to the surface is not much stronger than that in H_2O, but
- Breaking an H-bond in water is assisted by the forming of a new one. Energy cost minimal
- Breaking an H-bond at the surface or confined interface is not assisted. Energy cost significant

It's confinement!

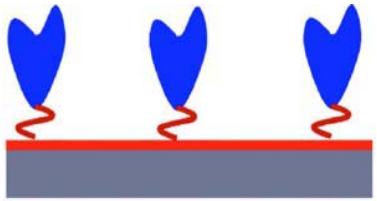
Acknowledgement: Steve Scheiner

S#

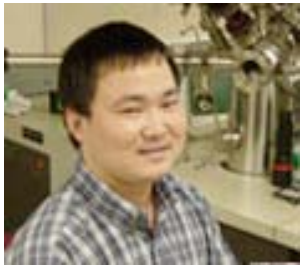
C

$_2$O.

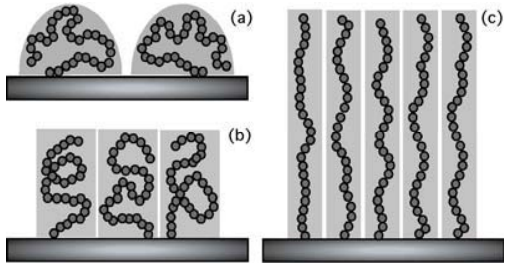
- *Confinement is the sole reason*?

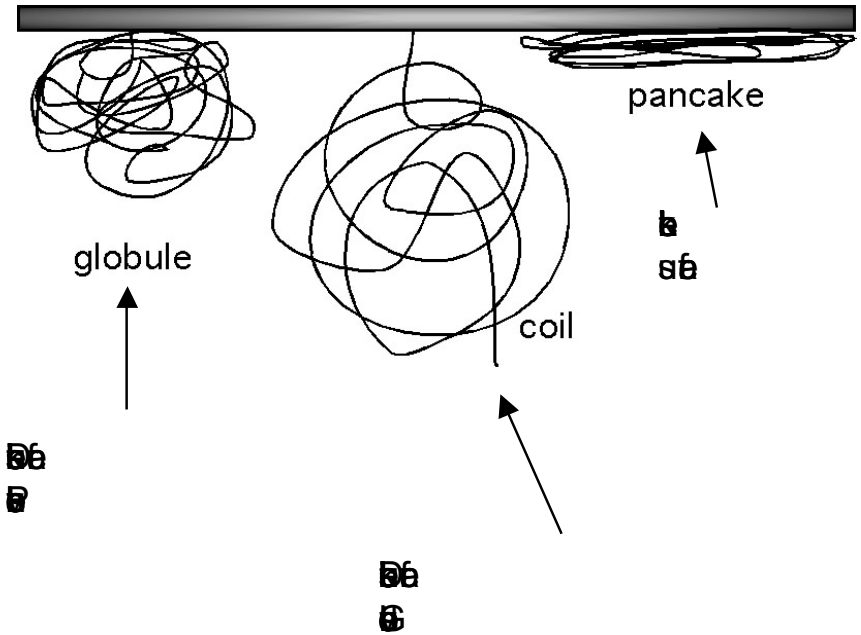


Breaking a covalent bond from non-covalent interactions



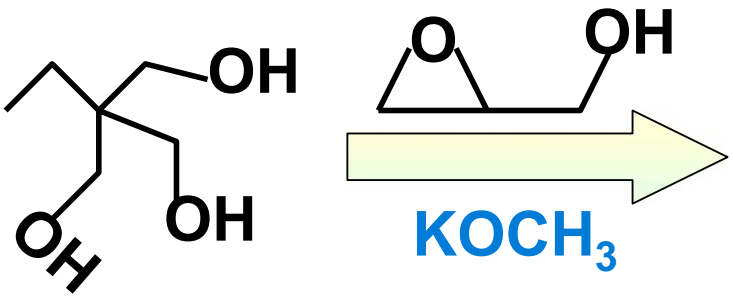
H



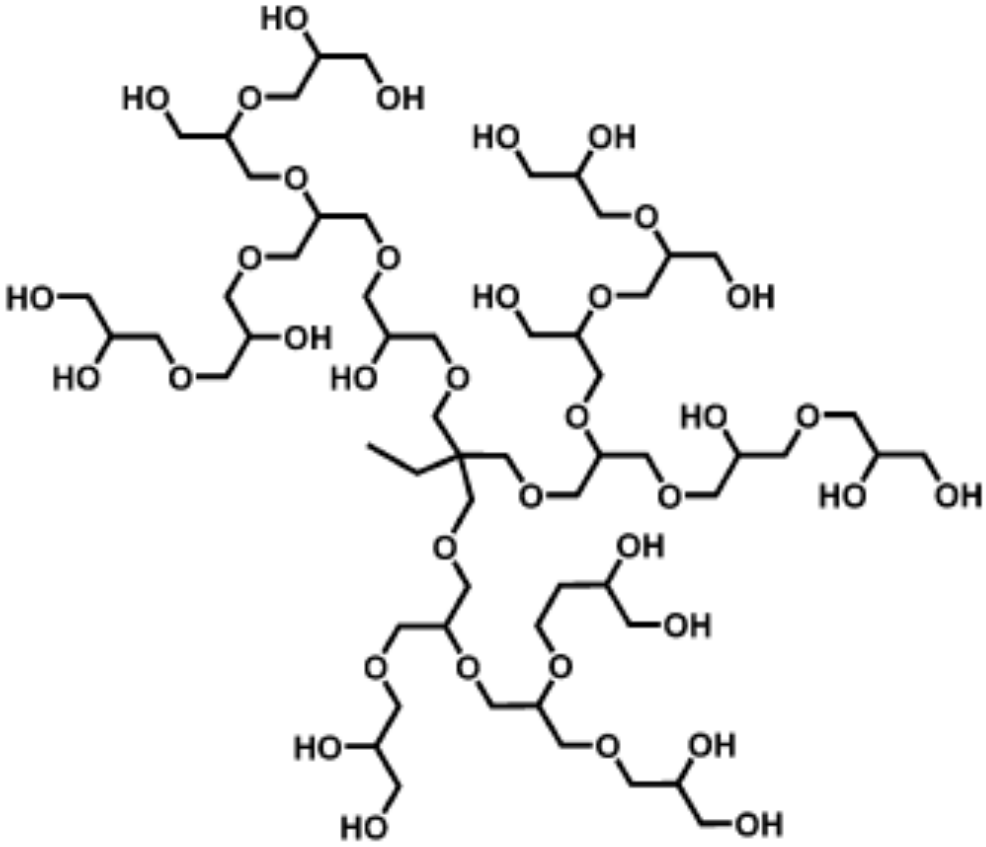


What happens to the thread or anchor?

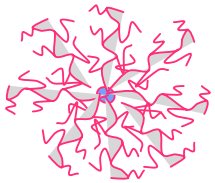
Hyperbranched Polyglycidol (HPG)



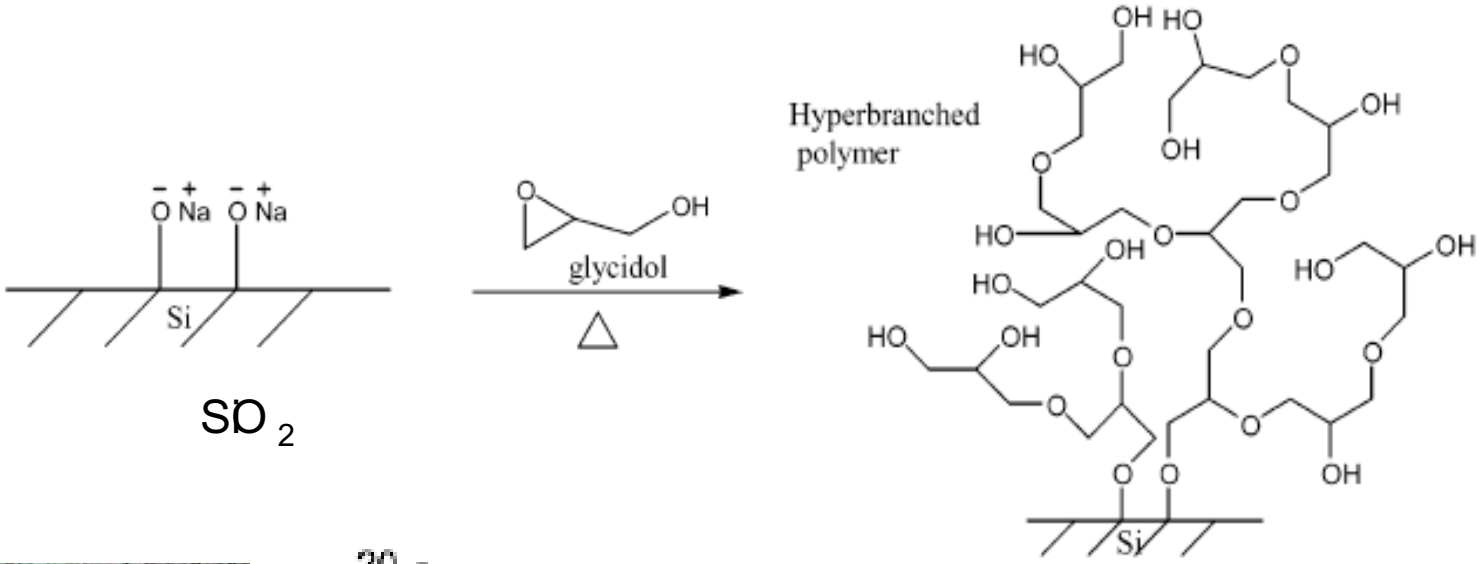
1999,3

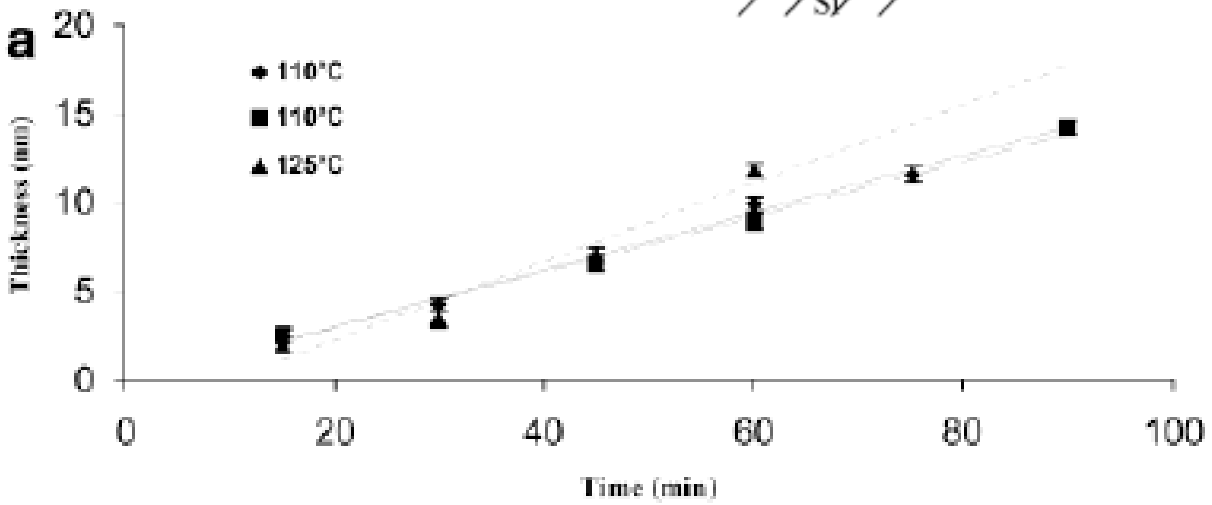


COOH instead of



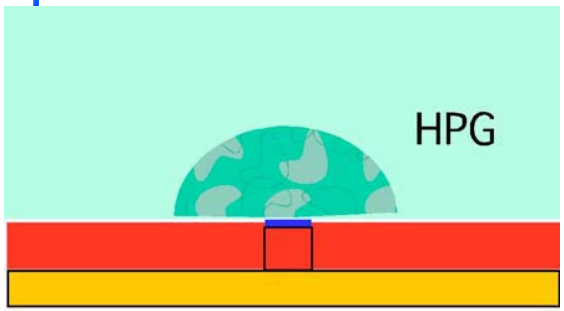
Surface-Initiated Polymerization of Hyperbranched Polyglycidol (HPG)





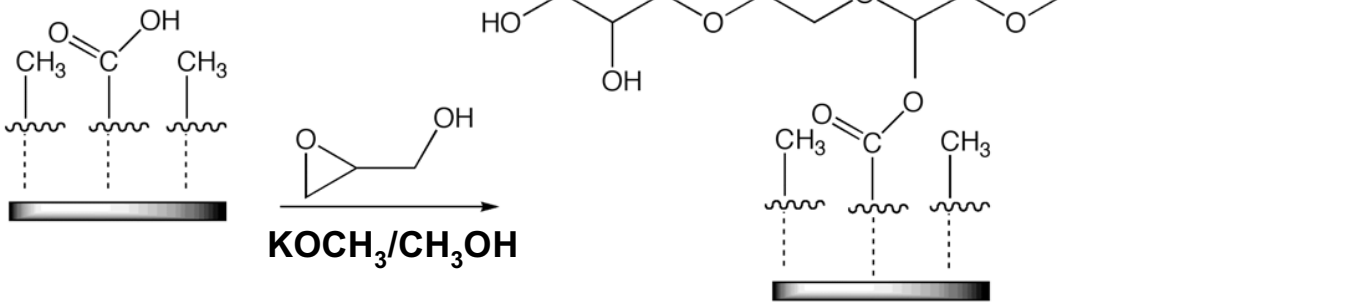
Majad Khan and Wilhelm T. S. Huck Macromolecules 2003, 36, 5088-5093

Surface

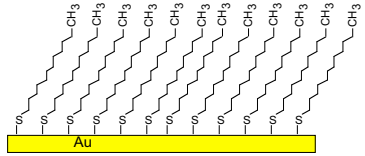


Hydrophilic
-COOH

Hydrophobic
$-CH_2-$, $-CH_3$



$HS(CH_2)_{10}COOH$ = C10A; $HS(CH_2)_9CH_3$ = C10



C10

5 μm

C10A

5 μm

5 μm

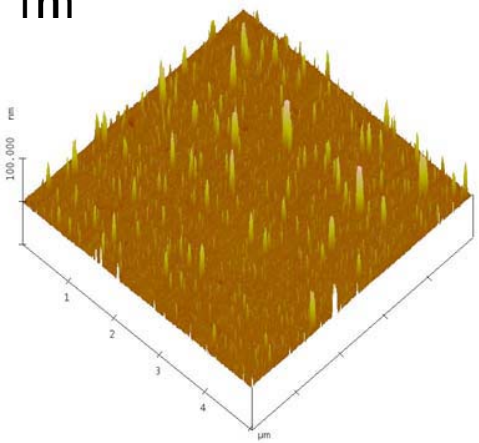
1 μm

°C

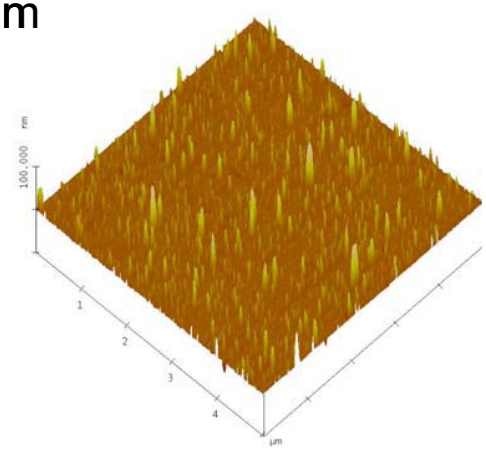
HS

$HS(CH_2)_{10}COOH : HS(CH_2)_9CH_3 = 1:20,\ 40^oC$

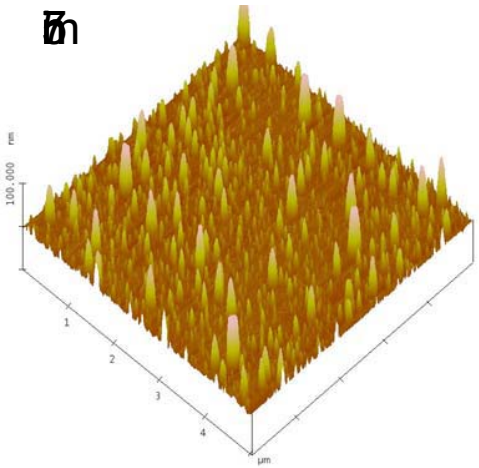
1m



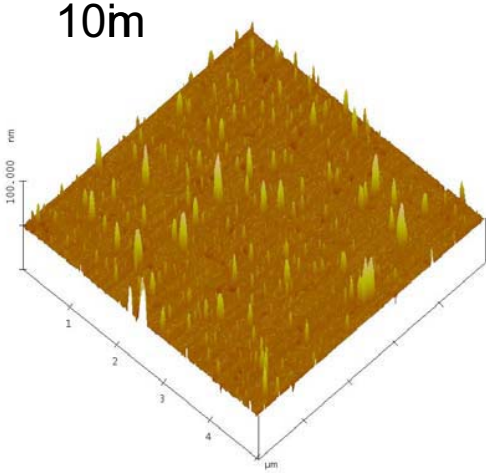
3m



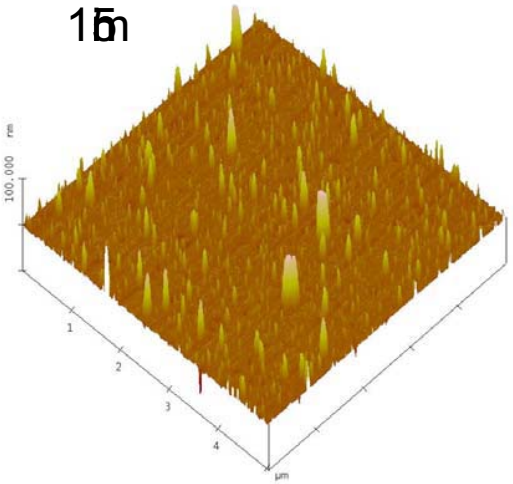
7m



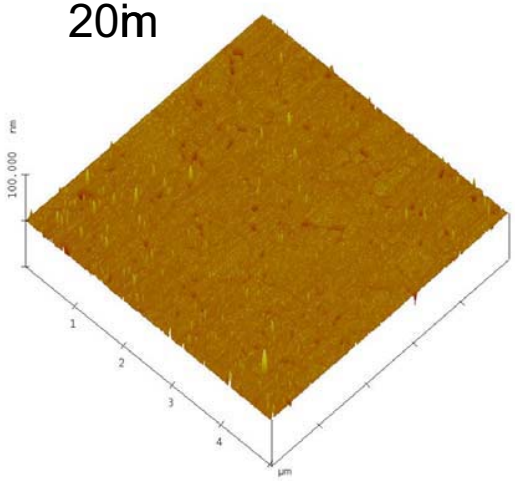
10m



15m

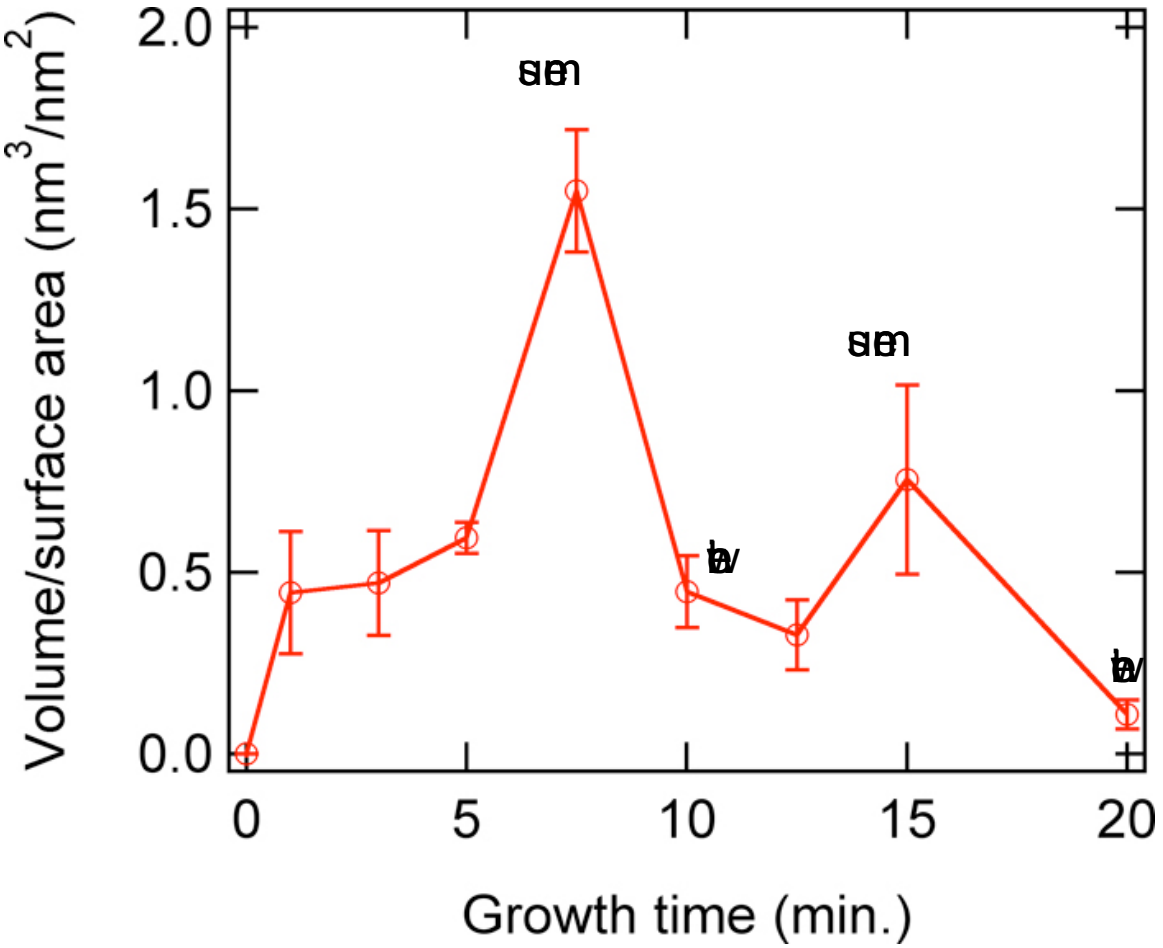


20m



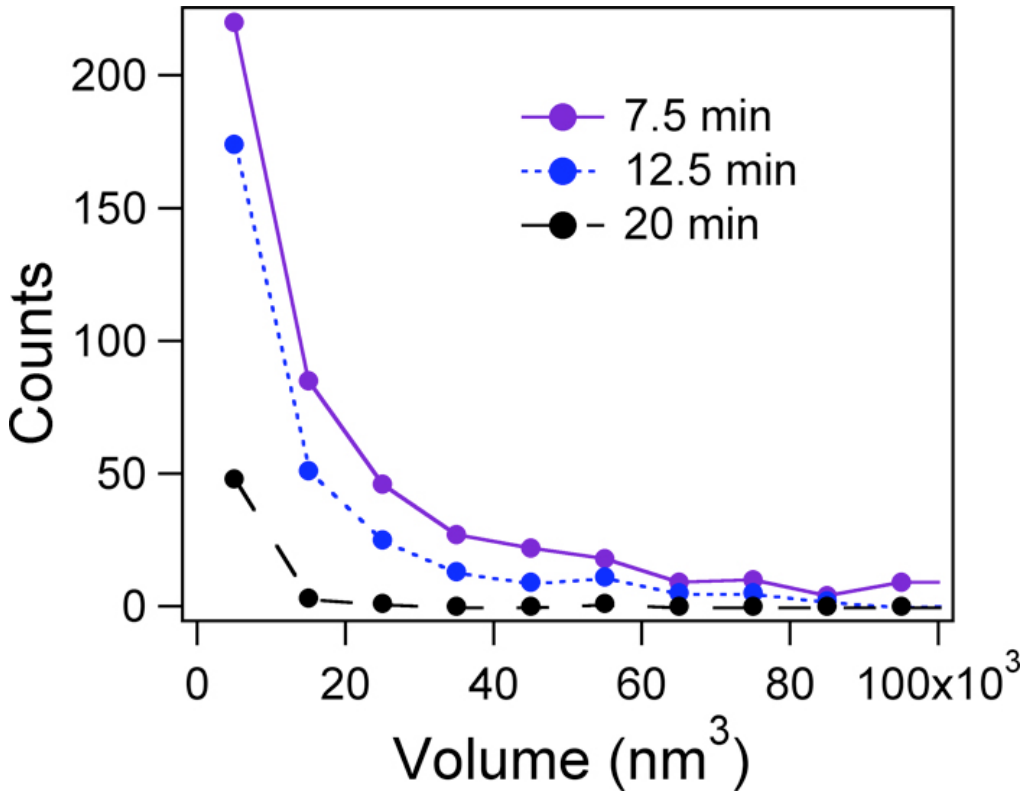
μm μm)

Surface coverage vs. growth time

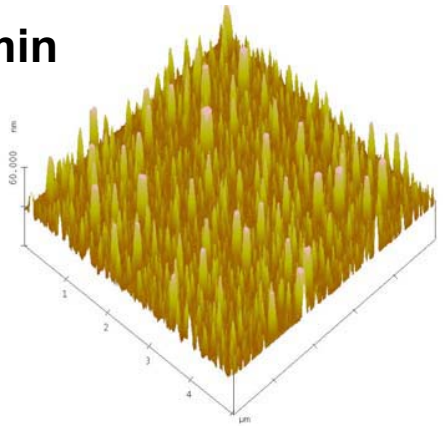


$HS(CH_2)_{10}COOH : HS(CH_2)_9CH_3 = 1:20,\ 40^oC$

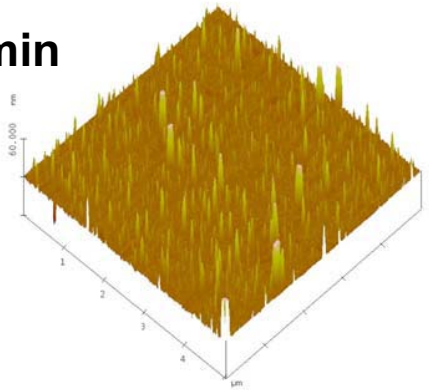
Volume Distribution of HPG molecules



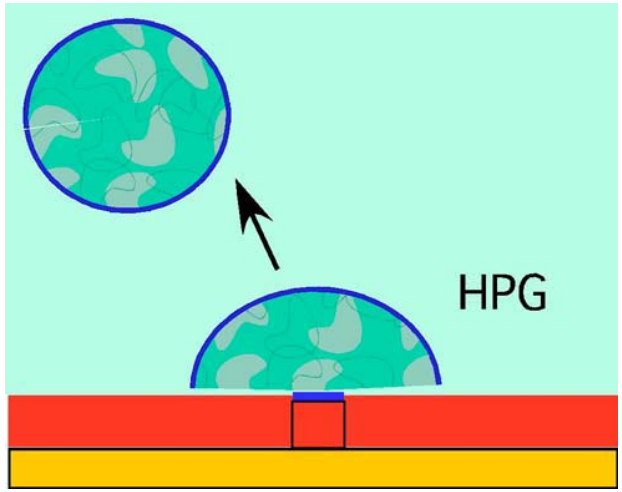
7.5min



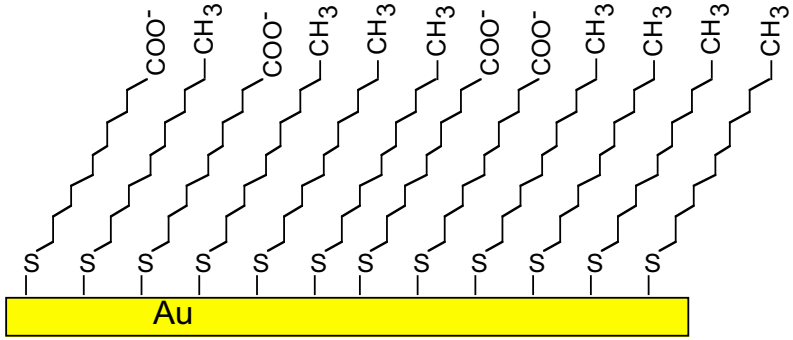
12.5min



$HS(CH_2)_{10}COOH : HS(CH_2)_9CH_3 = 1:20$

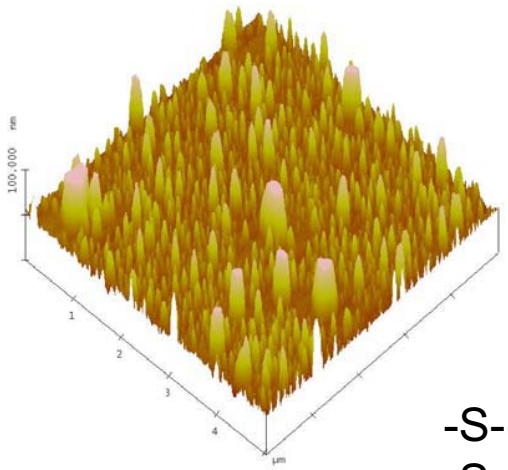


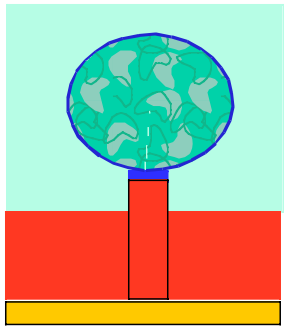
Hydrogen Bond Energy
2-10kcal/mol
Au-S Bond Energy
40kcal/mol
VdW energy in the SAM
~30 kcal/mol



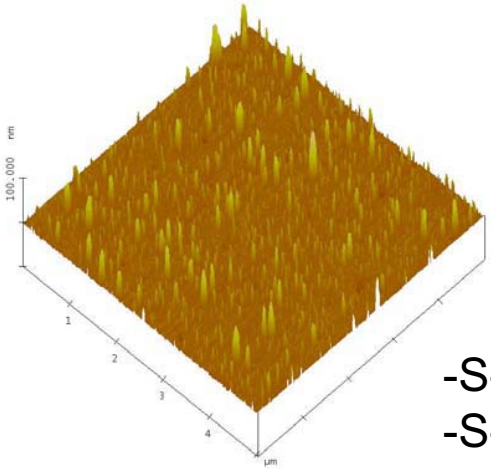
Controlling the local environment

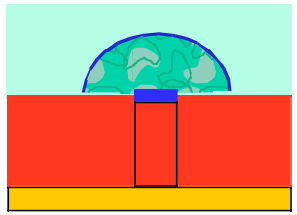
-COOH :-CH_3=1:20



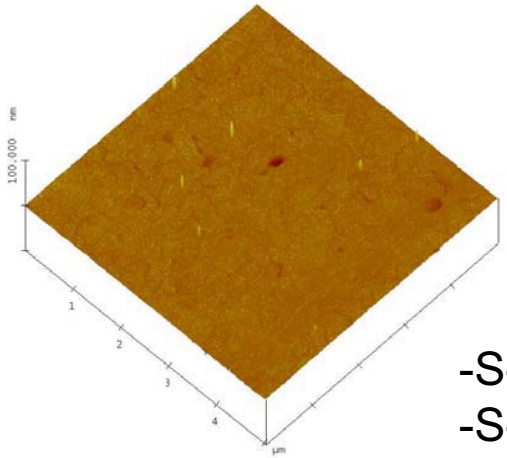


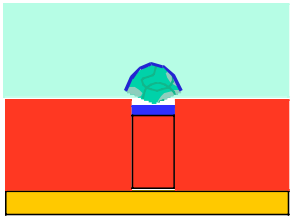
-S-$(CH_2)_{15}$-COOH
-S-$(CH_2)_9$-CH_3



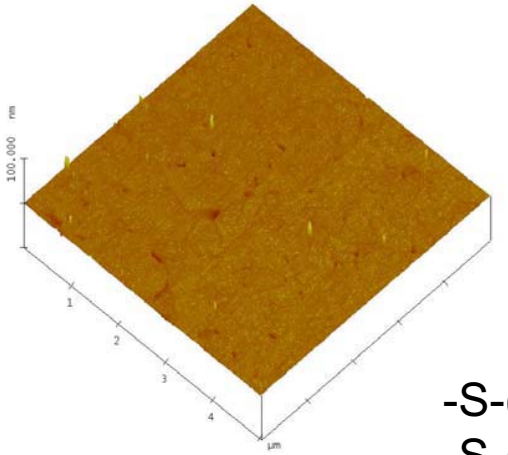


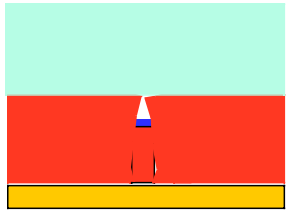
-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_9$-CH_3





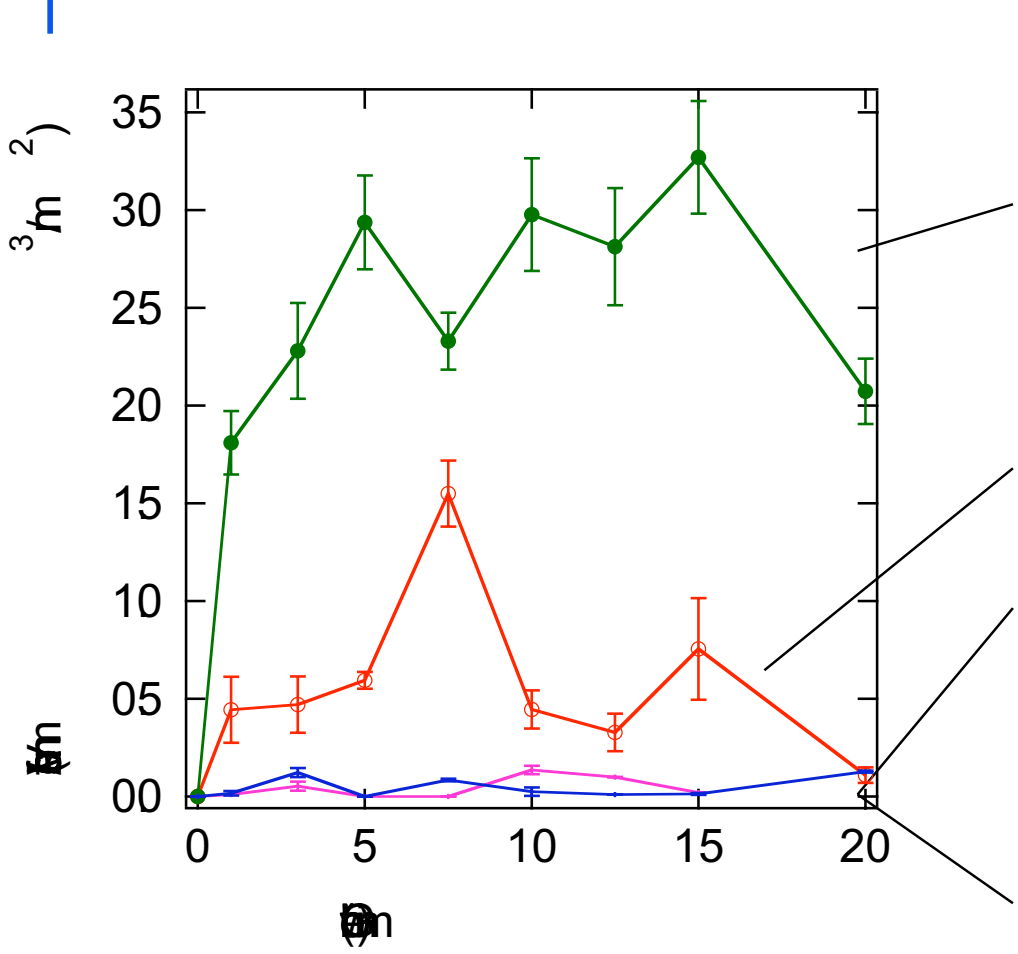
-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_{11}$-CH_3

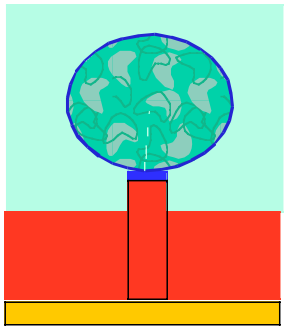




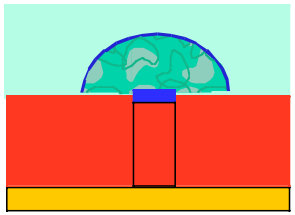
-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_{15}$-CH_3

Controlling the local environment

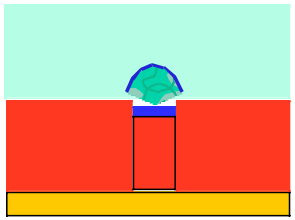




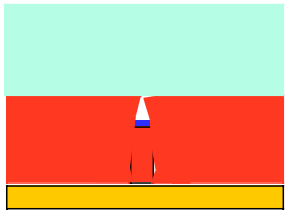
-S-$(CH_2)_{15}$-COOH
-S-$(CH_2)_9$-CH_3



-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_9$-CH_3



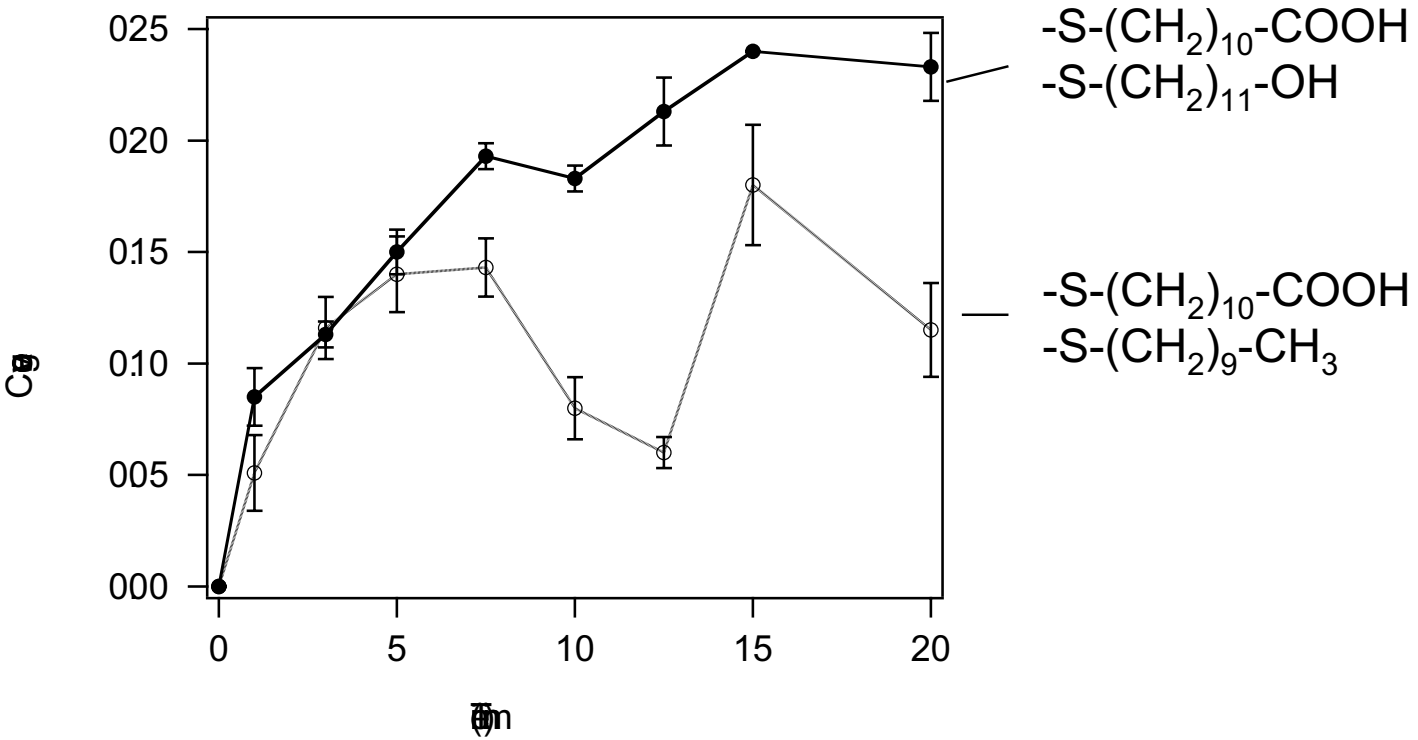
-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_{11}$-CH_3



-S-$(CH_2)_{10}$-COOH
-S-$(CH_2)_{15}$-CH_3

-COOH :-CH_3=1:20

When the matrix is also hydrophilic…

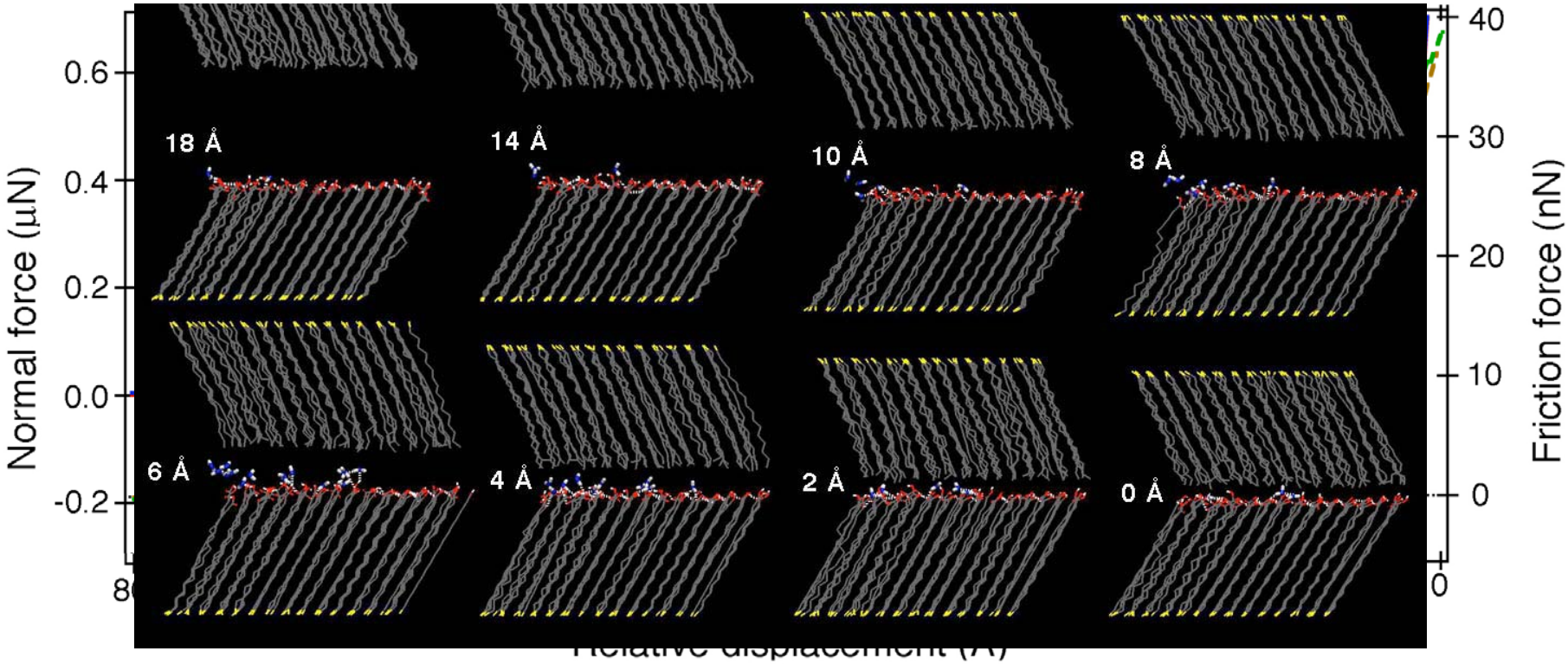


Story #2

Conclusion

- Nocovalent interaction with the local environment can lead to the breaking of covalent bond for a surface tethered macromolecule.

Capillary condensation and meniscus formation between hydrophobic and hydrophilic surfaces



CH_3/COOH

But no friction peak due to the slip plane at the -CH_3 surface