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Entropic Barriers in Nanoscale Adhesion

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Entropic Barriers in Nanoscale Adhesion

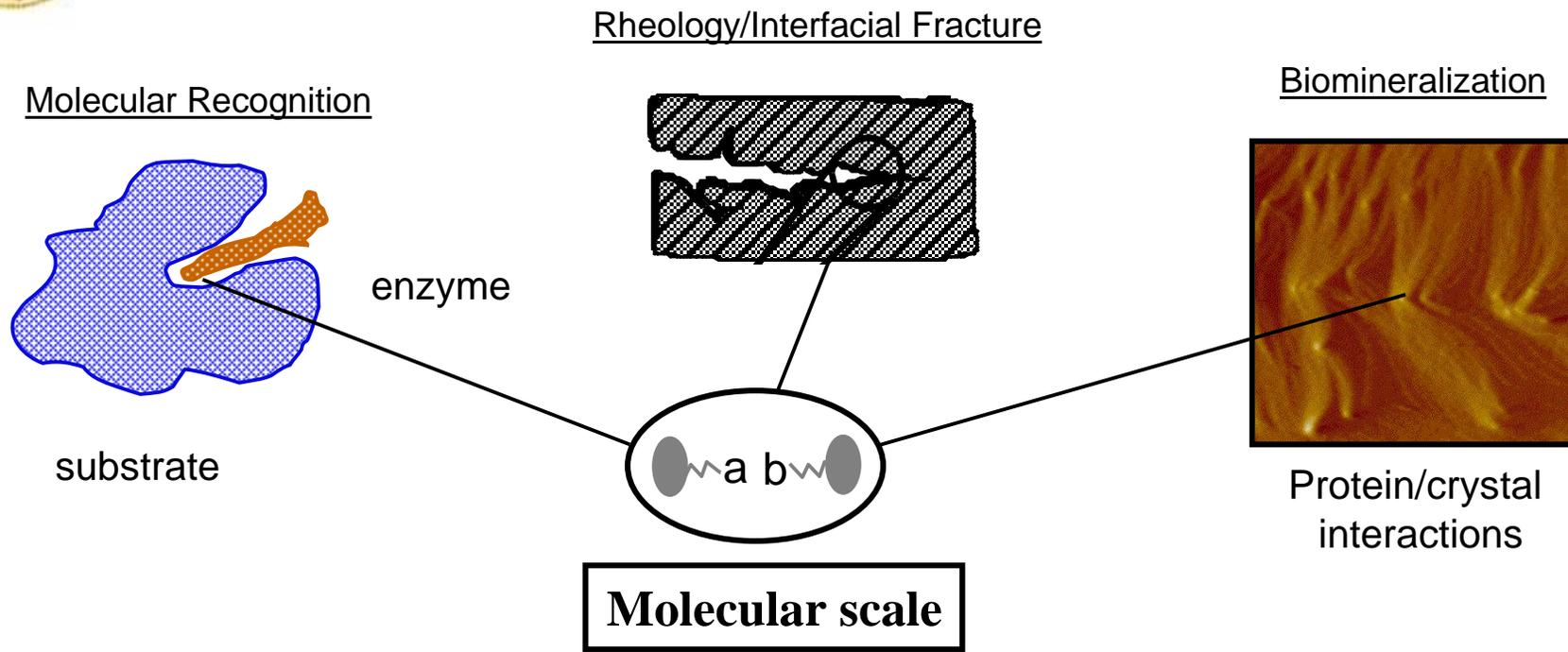
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Intermolecular interactions

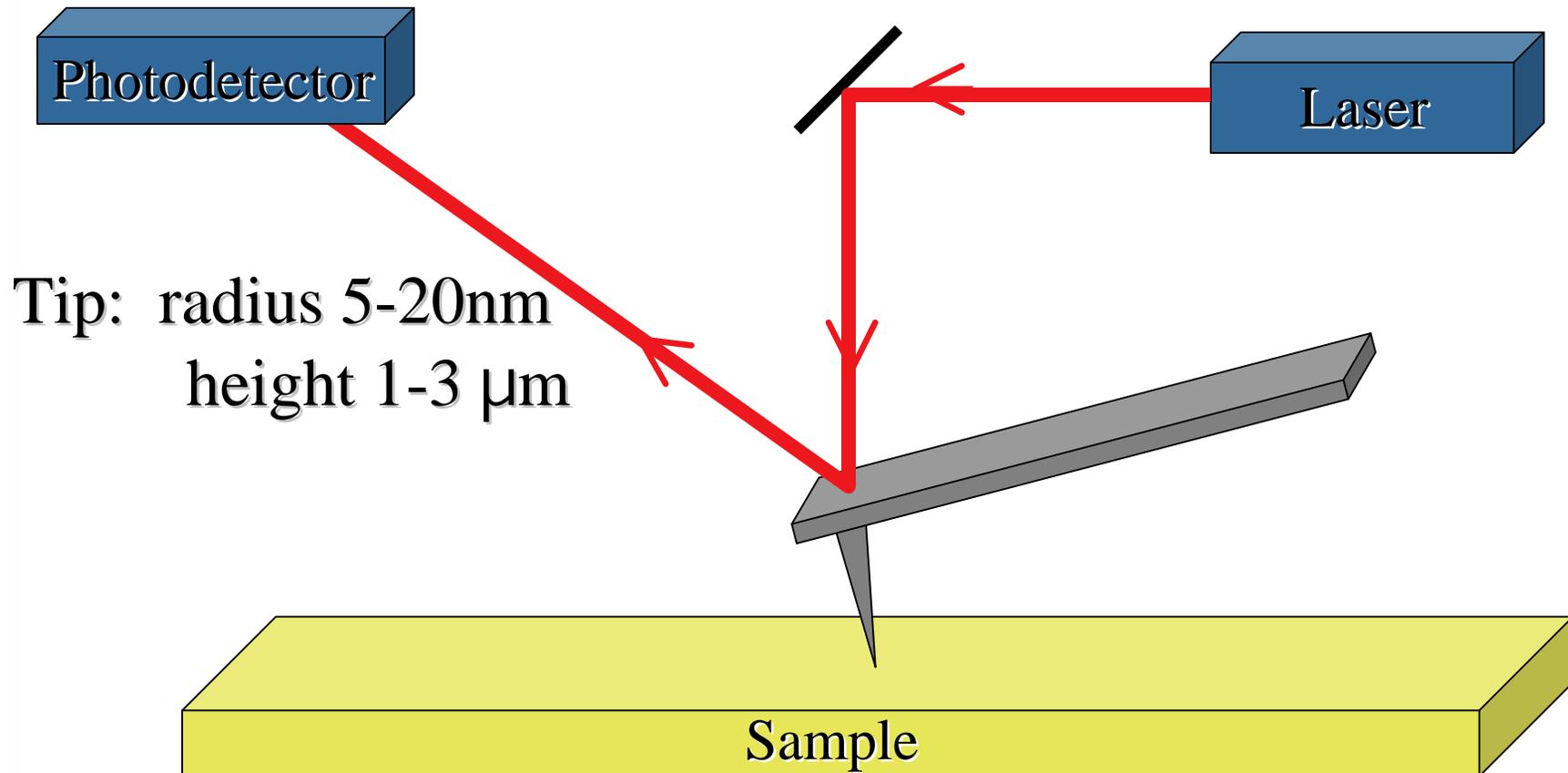


- Intermolecular interactions are at the center of many condensed phase phenomena
- Most processes involve specific functional groups at the nanometer scale

Study energy barriers for interactions between specific chemical functional groups at the molecular scale

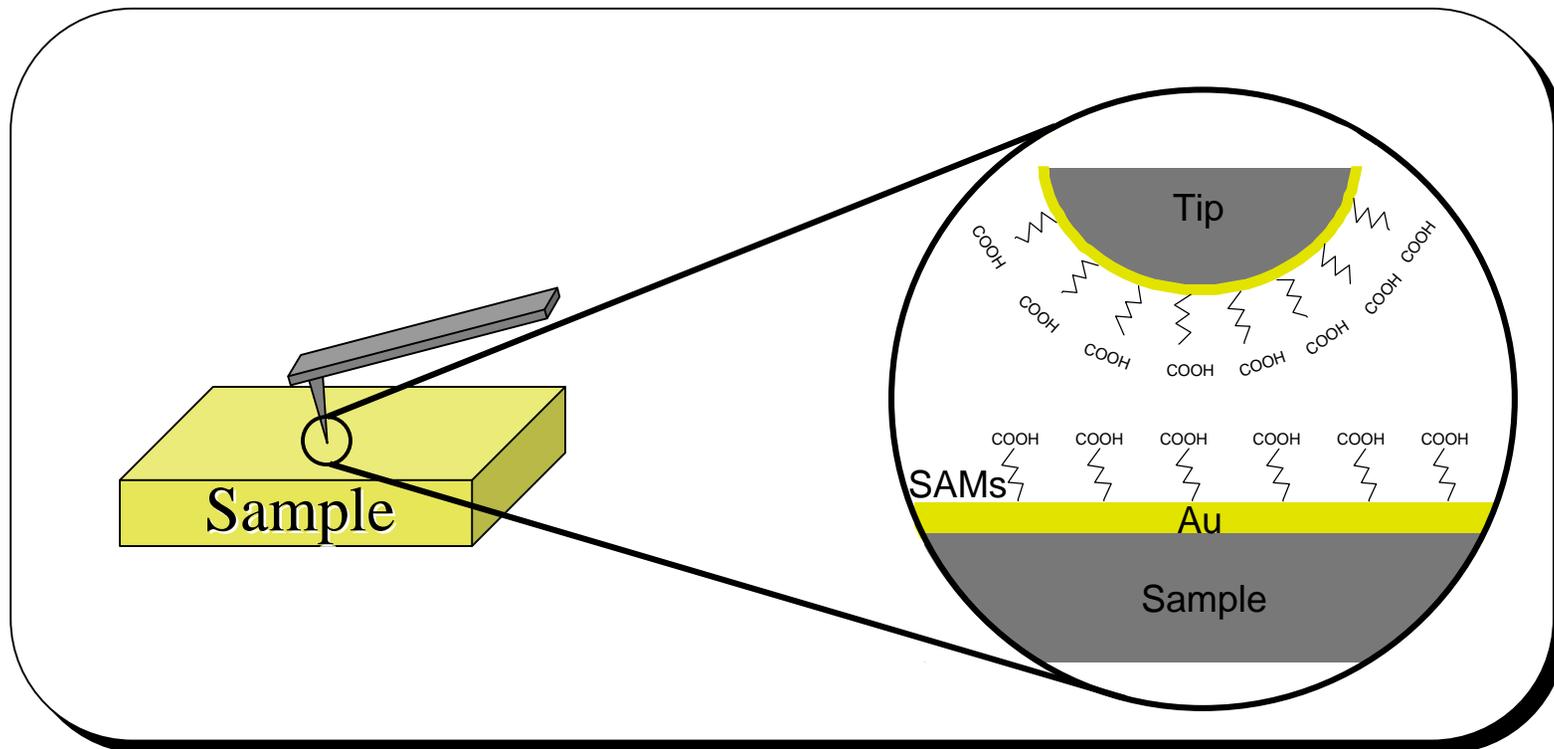


Atomic Force Microscopy





Measuring molecular scale forces: Chemical Force Microscopy

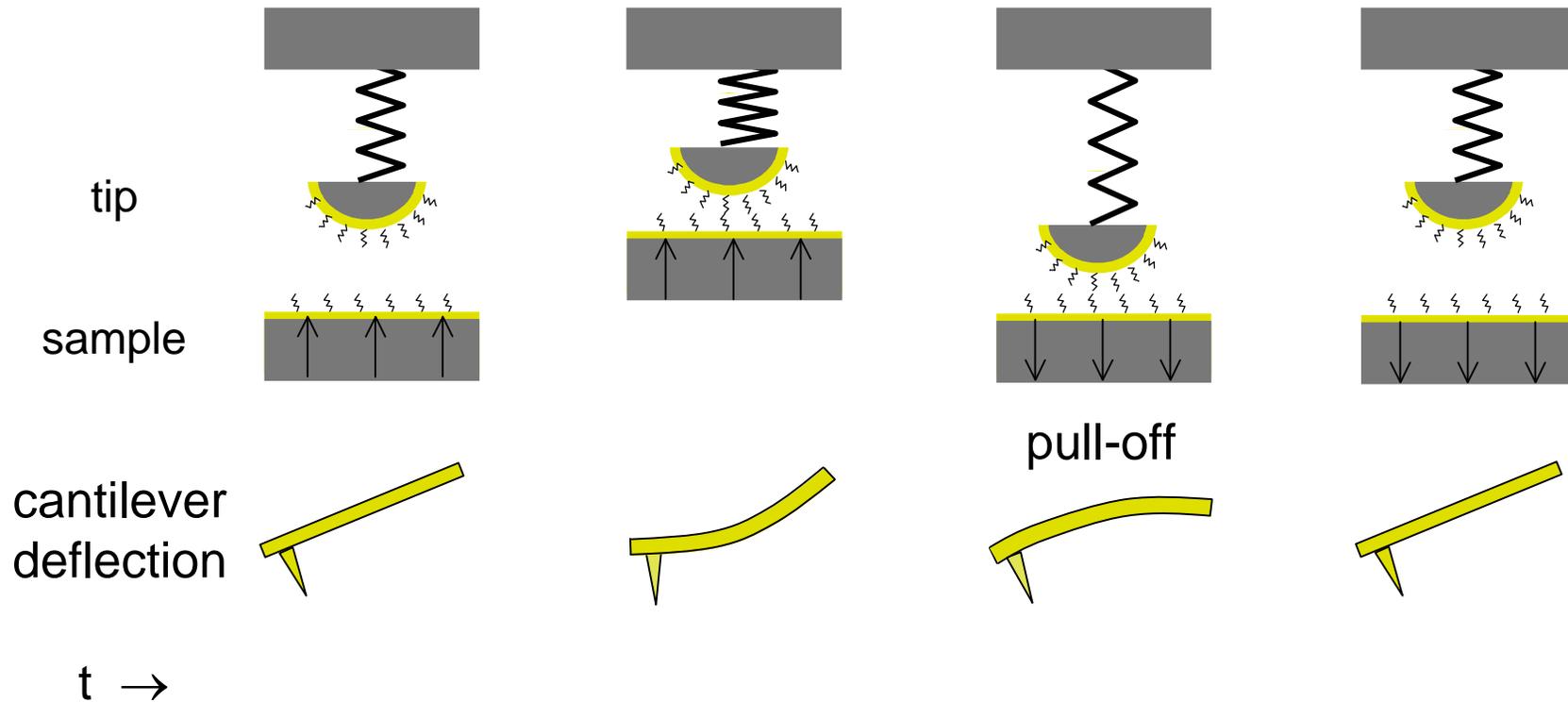


Key features

- Robust crystalline monolayers
- Chemistry of both surfaces in contact is well known
- Terminal functionality of both surfaces can readily be varied



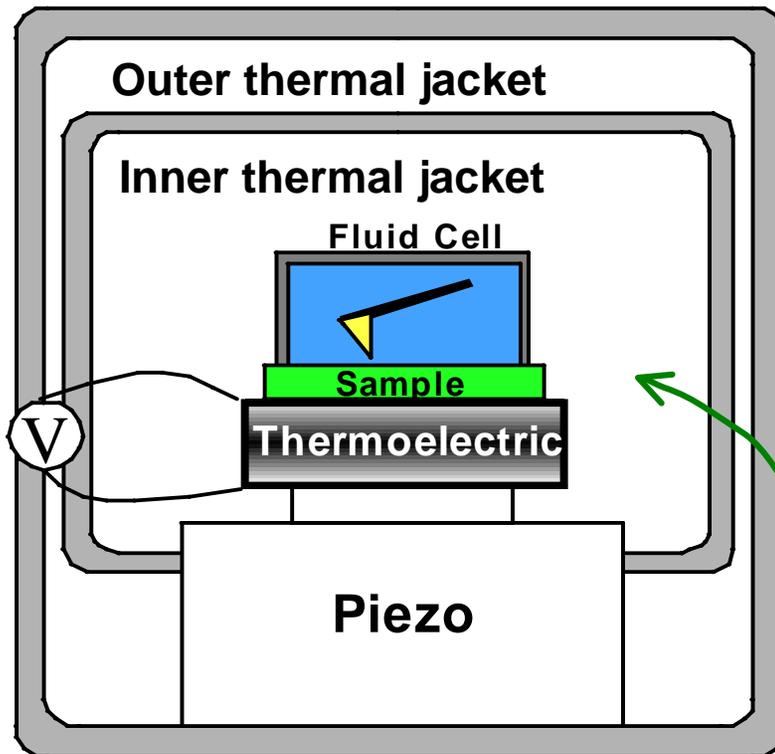
Force Calibration Mode



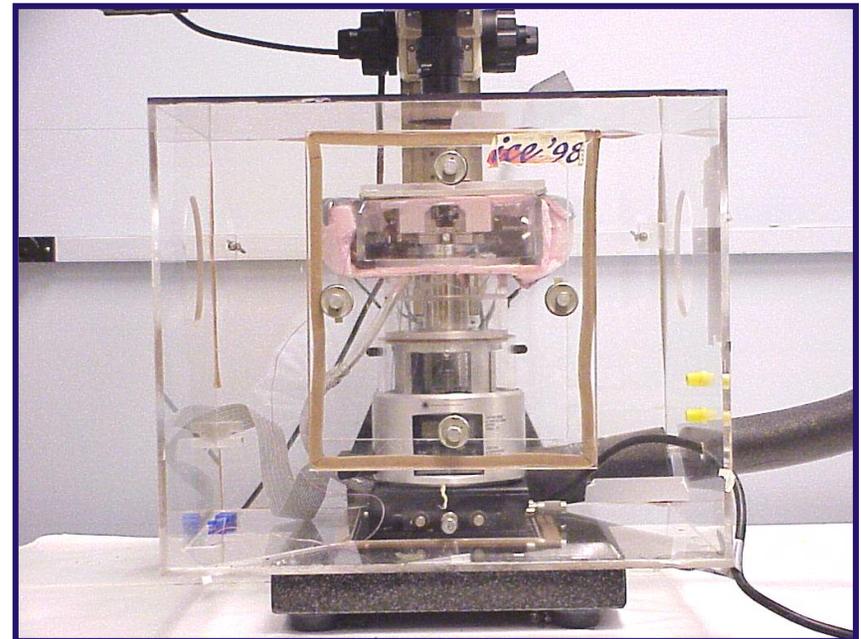
Deflection at pull-off gives the pull-off force
 $f_{pull-off} = k x$, k -spring constant, x -deflection



Looking at the energy barriers: Variable temperature CFM



(Zepeda, Yeh, Orme, RSI, **72**, 4159, 2001)



▪ **Chamber: cooled with N₂ from dewar, ± 2 °C**

- Energy barriers: Need to measure interaction as a function of temperature

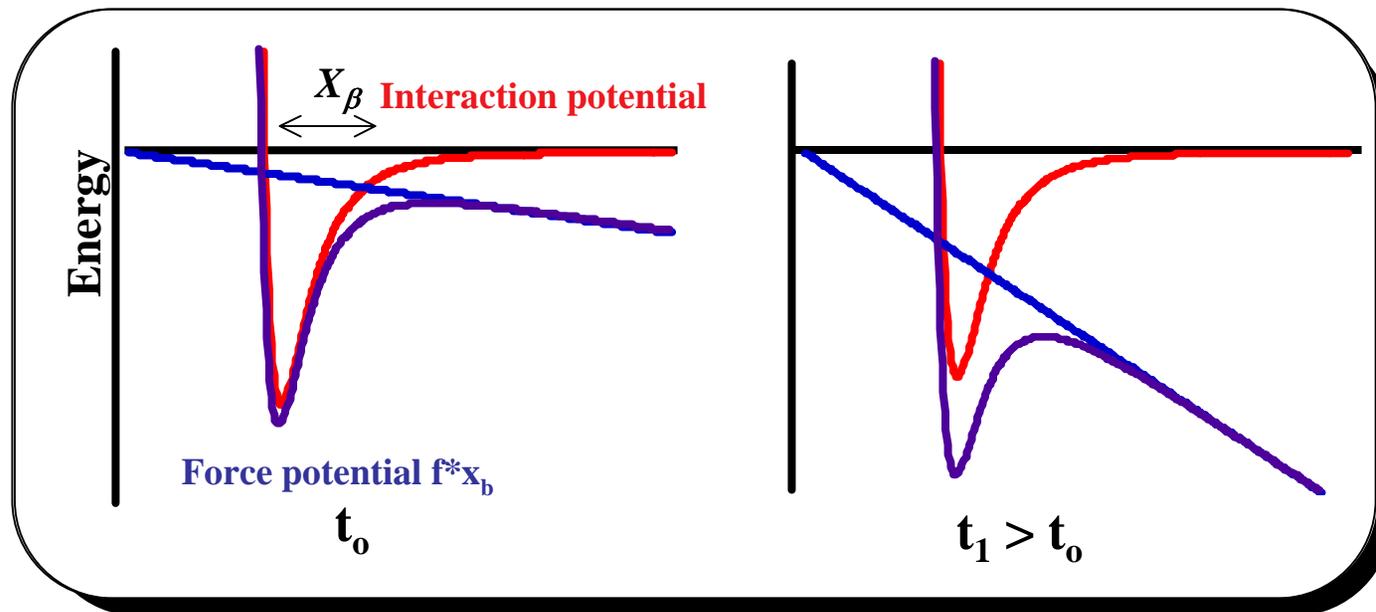


How does a bond behave under an external load?

Kinetic model: Force-assisted Escape From a Bound State

$$\frac{dP}{dt} = -k_{off} P \quad k_{off} = \frac{1}{t_D} e^{-\frac{(E_o - f(t) \cdot x_b)}{kT}}$$

t_D characteristic diffusion time
 x_b Extension in the transition state
 $f(t) = r_f \cdot t$ applied force
 r_f loading rate



▪ Applied force potential tilts the energy landscape facilitating escape.

(Evans, E, Ritchie, K., *Biophys J* 1997, 72, 1541-1555)



Model predicts the pull-off force depends on loading rate

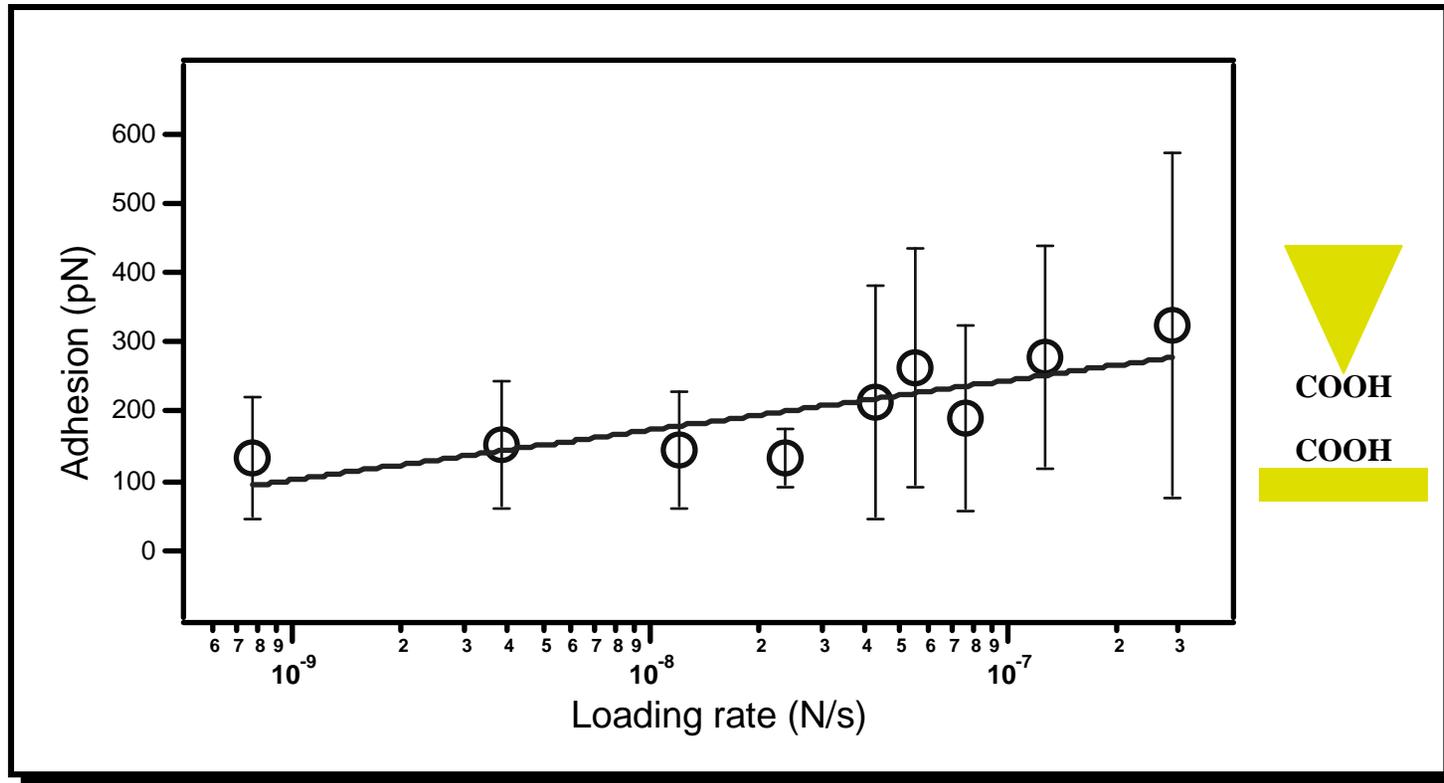
$$f_{pull-off} = \frac{k_B T}{x_b} \ln \left[\frac{\tau_D x_b \exp\left(\frac{E_0}{k_B T}\right)}{k_B T} \right] + \frac{k_B T}{x_b} \ln r_f$$

x_β - distance between bound and transition state
 r_f - force loading rate

$f_{pull-off}$ vs r_f will give x_β



COOH/COOH in Ethanol



COOH/COOH

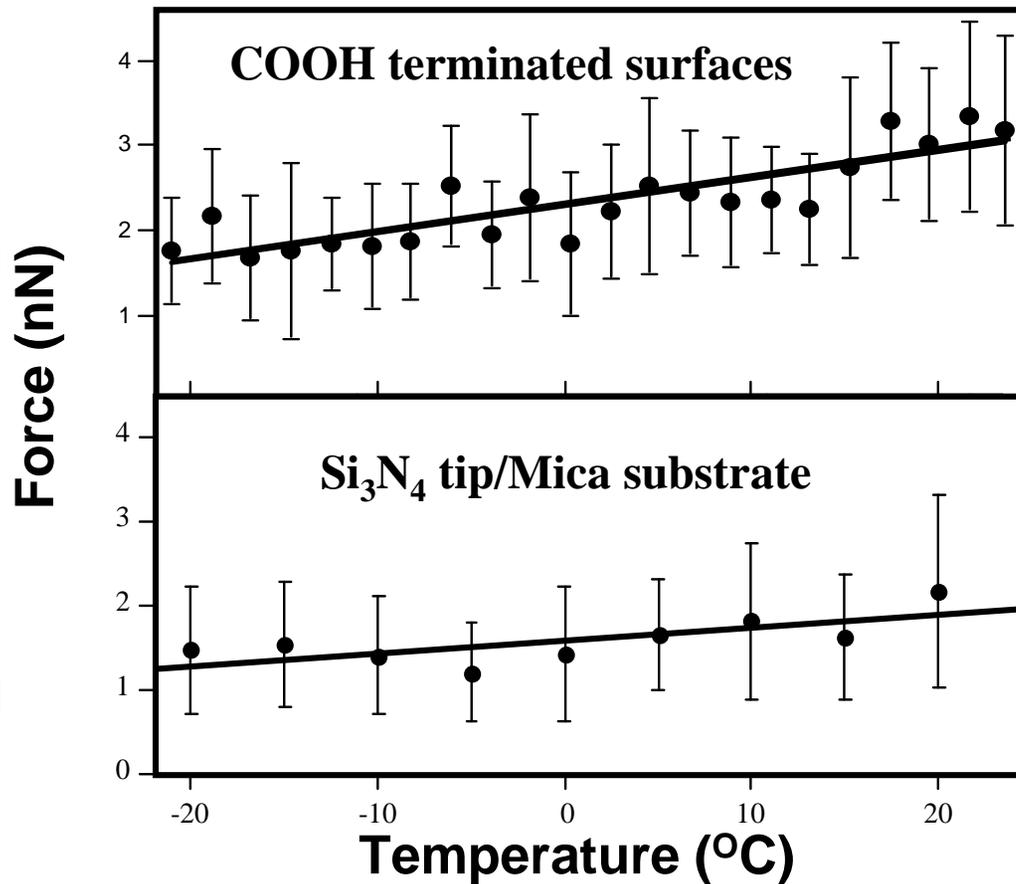
$$X_{\beta} = 1.34 \text{ \AA}$$

water H-bond

$$X_{\beta} = 1.85 \text{ \AA}$$



COOH/COOH interaction strength in EtOH increases with temperature!

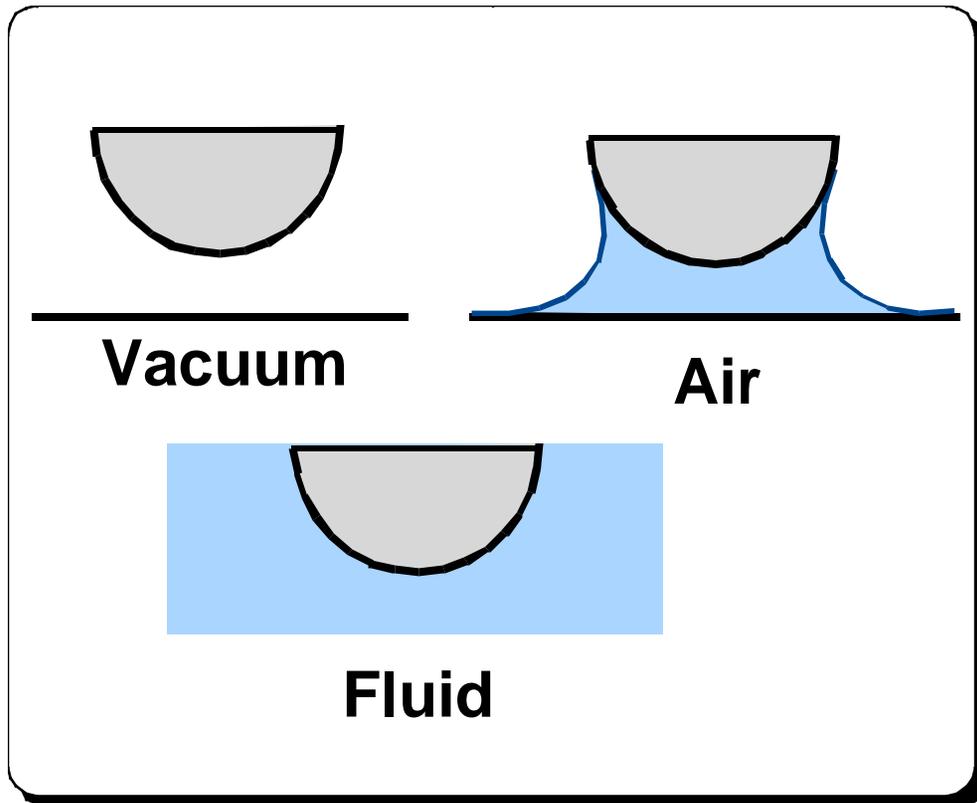


•Each point represents an average of 40 individual force measurements

•Si₃N₄ tip/Mica substrate control rules out thiol chain entanglement



What interaction is measured?



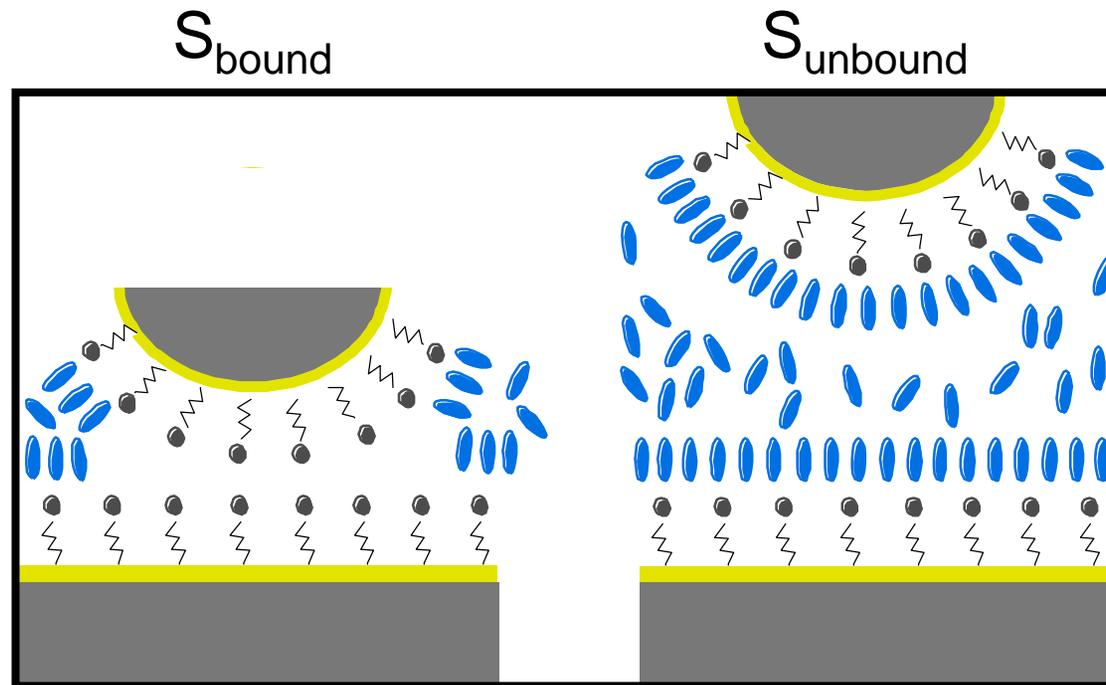
Vacuum
-bare surfaces

Ambient Air
-capillary layers
dominate the force

Fluid Environment
-interaction between
solvated surfaces



Surface Solvation



$$S_{\text{unbound}} < S_{\text{bound}} \rightarrow \Delta S < 0$$

Solvent orders on the surface upon detachment giving a lower entropic state.



Model predicts two unbinding regimes: Thermal vs. Entropic Kinetics

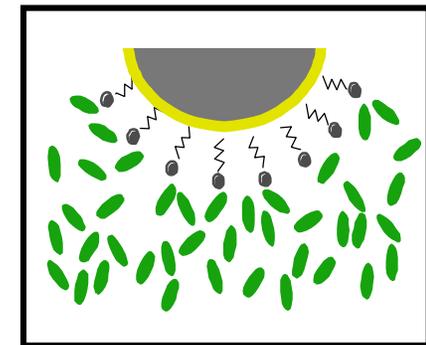
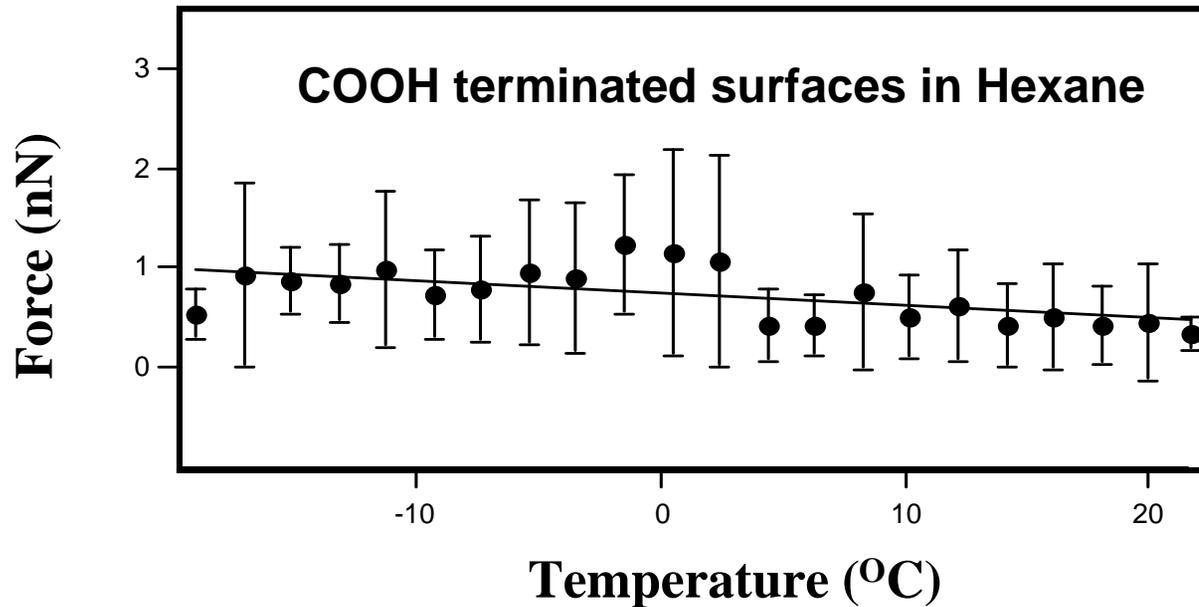


$$f_{pull-off} = \underbrace{\frac{\Delta H}{x_b}}_{\text{Enthalpic term}} - \underbrace{T \frac{\Delta S}{x_b}}_{\text{Entropic term}} - \underbrace{\frac{kT}{x_b} \ln \left[\frac{kT}{r_f t_D x_b} \right]}_{\text{Thermal Activation}}$$

- Thermally activated regime
- Entropically dominated regime
- Furthermore, large negative ΔS can change the f vs T trend



Experimental test: Changing solvent



- Entropy change upon dissociation minimal
- Observed behavior due to surface-surface interactions
- Kinetics dominated unbinding regime!



Comparison with the model



$$f_{\text{pull-off}} = \frac{\Delta H}{x_b} - T \frac{\Delta S}{x_b} - \frac{kT}{x_b} \ln \left[\frac{kT}{r_f t_D x_b} \right]$$

COOH tip

COOH substrate

Experiment

Model

In hexane

Slope = -2.7pN/k

$df/dT = -2.1\text{pN/k}$

*assume only thermal activation term contributes

In EtOH

$\Delta S/\text{functional group} \sim 1.75 \cdot 10^{-22} \text{ J/k}$

JKR model: ~ 20 groups interact

Consistency check

$k_B = 1.38 \cdot 10^{-23} \text{ J/k}$

In hexane, experimental value matches model quite well!

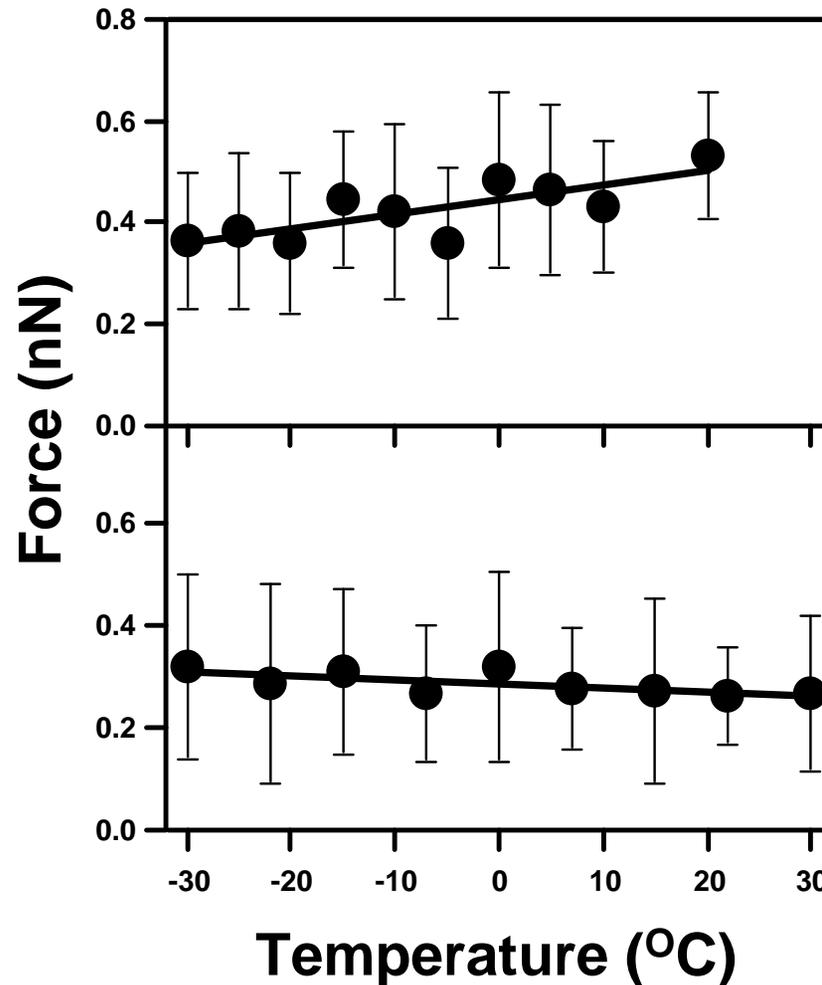
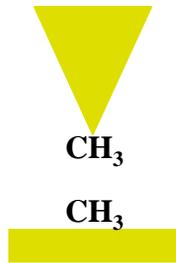
Thermally-activated Unbinding

In EtOH, observed entropic effect is far greater than the thermal energy.

Entropically-dominated unbinding



Me-Me: Weakly Interacting Surfaces



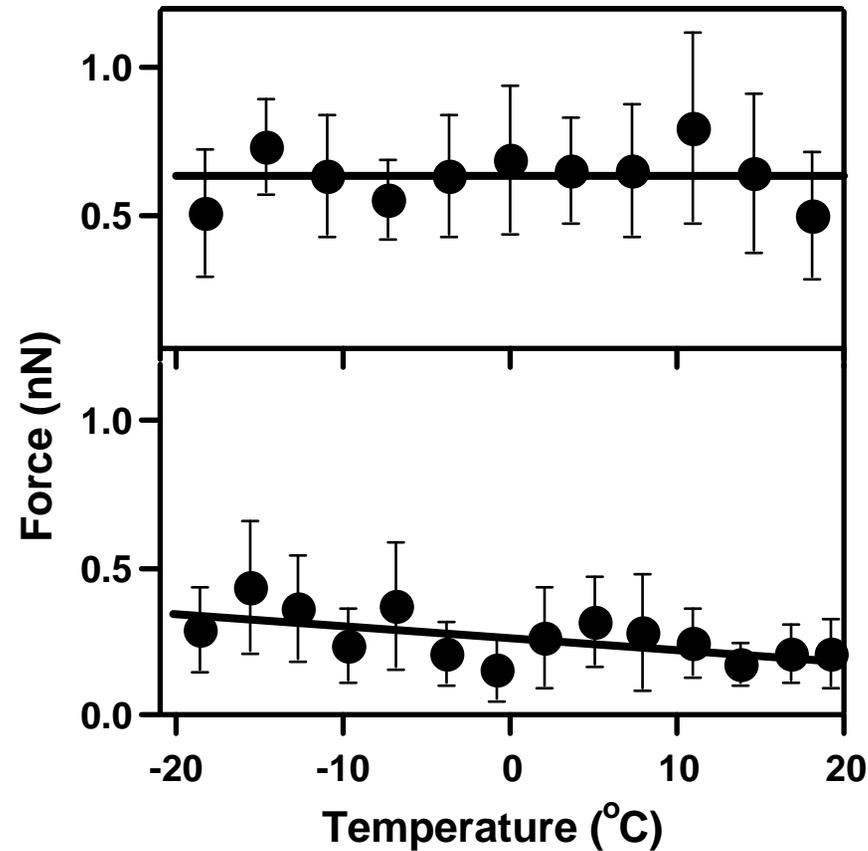
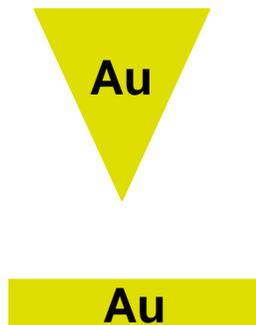
EtOH

Hexane

EtOH: Rate of Increase is an order of magnitude smaller than COOH
Hexane: thermally dominated unbinding regime



Au-Au: Non-specific interactions



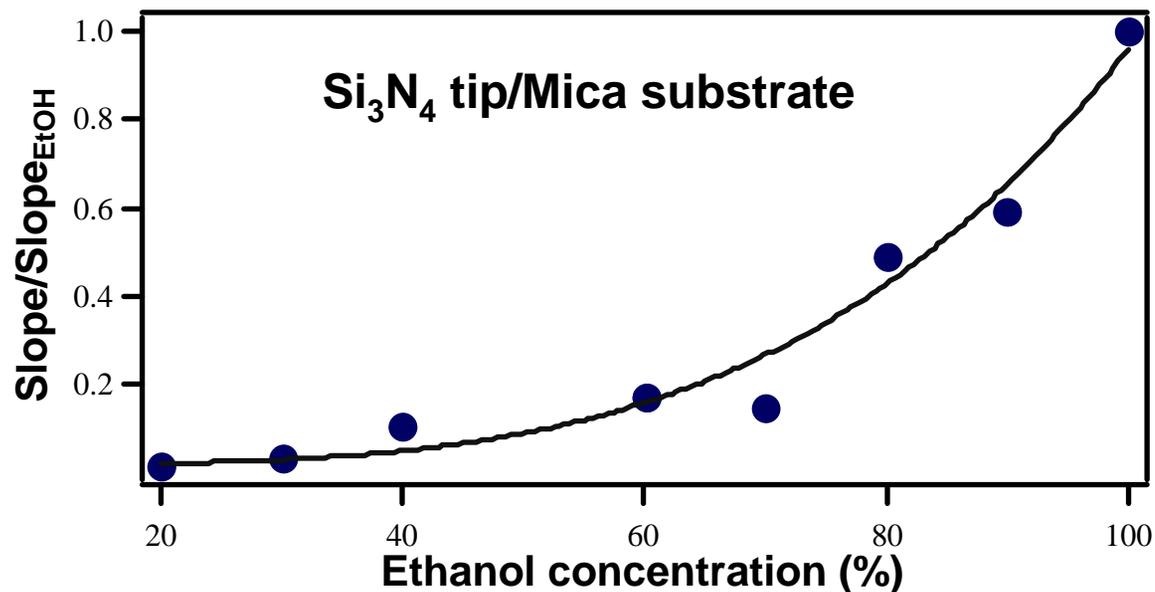
EtOH

Hexane

- Only van der Waals surface-surface interaction
- Weak surface-solvent interaction



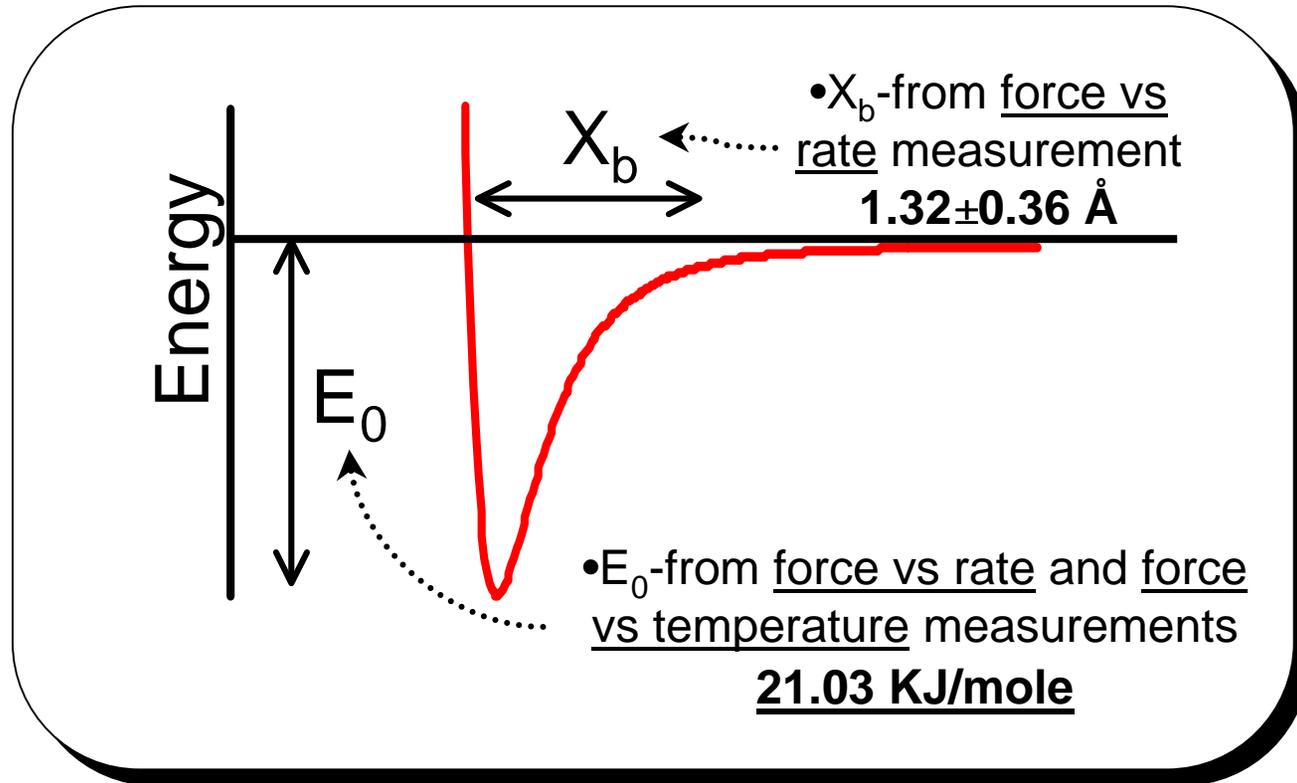
Varying Entropic Contribution Continuously in EtOH/Hexane mixtures



- Si₃N₄ tip-mica substrate
- Ethanol concentration varied by adding hexane
- Slope normalized to 100% EtOH experiment (Maximum entropic effect)
- Entropic contribution clearly diminishes with the addition of Hexane



Energy well parameters: Combining Both Experiments



- Comparing with water: $X_\beta = 1.85 \text{ \AA}$, $E_0 = 14.2 \text{ KJ/mole}^*$
- Results are comparable, but are not entirely attributable to H-bonding

* (Curtiss et al, j phys chem 71:2703-2711)

(Zepeda et al, Langmuir, 19, 145, 2003)



Conclusions

- Developed a method for probing the energy barriers of intermolecular interactions
- Entropic barriers can be a common feature of nanoscale adhesion!
- **Solvation effects can play a major role in measured binding forces. *SOLVENT MATTERS!***

S.Zepeda Acknowledges the UCD/LLNL Student Employee Graduate Research Fellowship(SEGRF).
This work was performed under the auspices of USDOE contract no. W-7405-ENG-48.



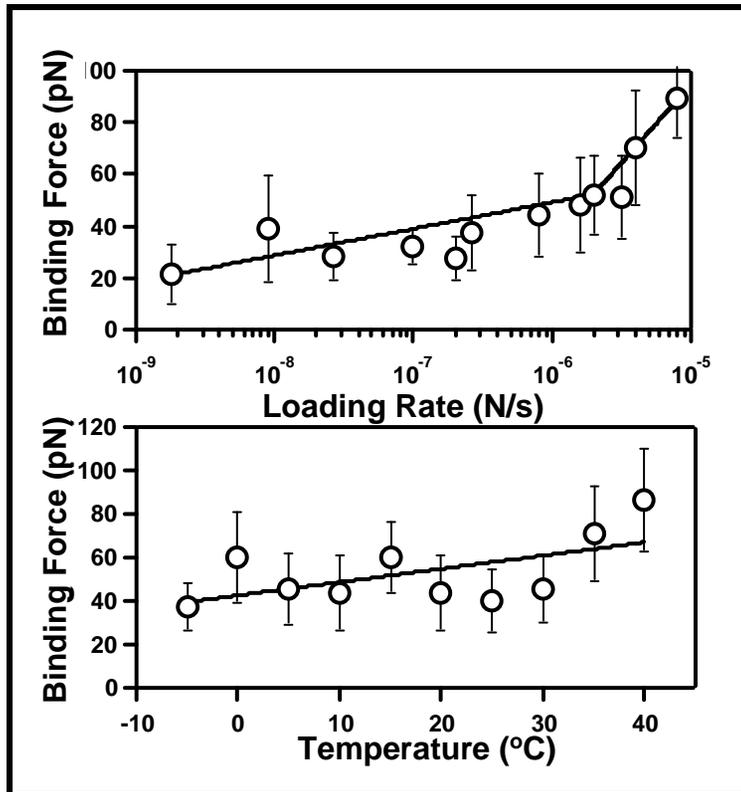
Table 1. Measured Slopes and Relative Fluctuations of the Adhesion Force vs temperature data shown in Figures 3, 4, 5, 6, and 7

probe	sample	solvent	slope, dF/dT , (pN/K)	average relative fluctuations, $\langle \Delta F/F \rangle$
Au/COOH	Au/COOH	hexane	-2.7 ± 1.4	0.8 ± 0.2
Au/COOH	Au/COOH	ethanol	30.5 ± 4.1	0.3 ± 0.1
Au/COOH	Au/COOH	ethanol/ hexane 1:1	4.8 ± 3.8	0.2 ± 0.05
Au/CH ₃	Au/CH ₃	hexane	-0.82 ± 0.32	0.5 ± 0.1
Au/CH ₃	Au/CH ₃	ethanol	2.9 ± 0.8	0.3 ± 0.1
Au	Au	ethanol	-0.09 ± 1.75	0.3 ± 0.07
Au	Au	hexane	-3.9 ± 1.55	0.5 ± 0.08
Si ₃ N ₄	mica	ethanol	3.3 ± 0.4	0.6 ± 0.2

JACS, Noy et al, 2003, 125, 1356-1362



Si₃N₄/Mica



f vs rate show two energy barriers

$$X_{\beta} = 11.65 \pm 3.54 , \\ 1.43 \pm 0.40$$

(Zepeda et al, Langmuir, 19, 145, 2003)

For the outer barrier: $E_0 = 40.70$ KJ/mole

- water/mica: x-ray reflectivity shows 1 well ordered solvation layer at 2.5\AA and a loosely bound layer extending to $\sim 10\text{\AA}$ (Cheng et al, Phys Rev Lett, 2001, 8715, 6103, U6186-U6188)