

Applications of AFM to tribology studies

**Tribology: the science of contact,
adhesion, friction, wear, ...**

The Continuum mechanics view

Hertz Contact (1882)

$$\delta = \left(\frac{3P}{4E^* R^{1/2}} \right)^{2/3}$$

Deformation

$$a = \left(\frac{3PR}{4E^*} \right)^{1/3}$$

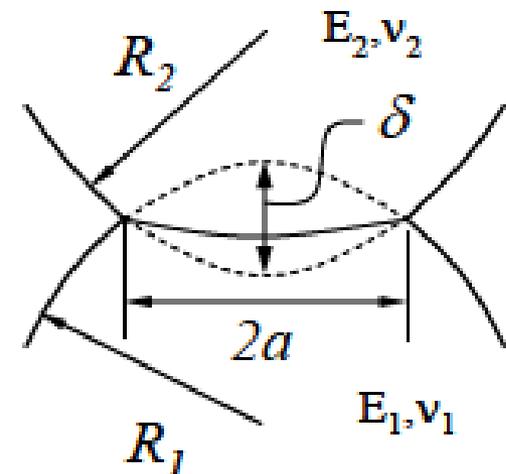
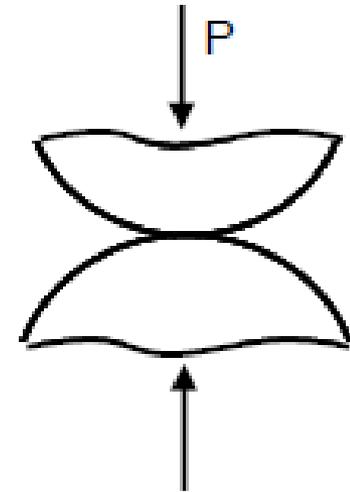
Contact Radius

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

Effective
Young's modulus

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

Effective Radius
of Curvature



Models including attraction between bodies: JKR and DMT

The Hertz model does not include adhesion forces and neglects also long range attractive forces (like the van der Waals forces discussed above).

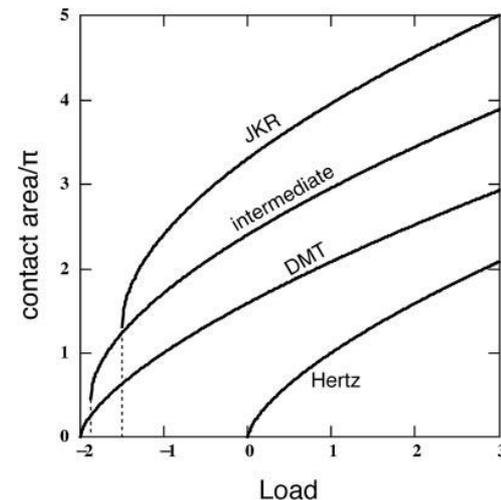
The Johnson-Kendall-Roberts (JKR) model explicitly includes the adhesion by way of the interface energy (gamma) of the contact:

$$\frac{a^3 K}{R} = P + 3\pi\Delta\gamma R + \sqrt{6\pi\Delta\gamma R P + (3\pi\Delta\gamma R)^2}, \quad K = \frac{4}{3} E^*$$

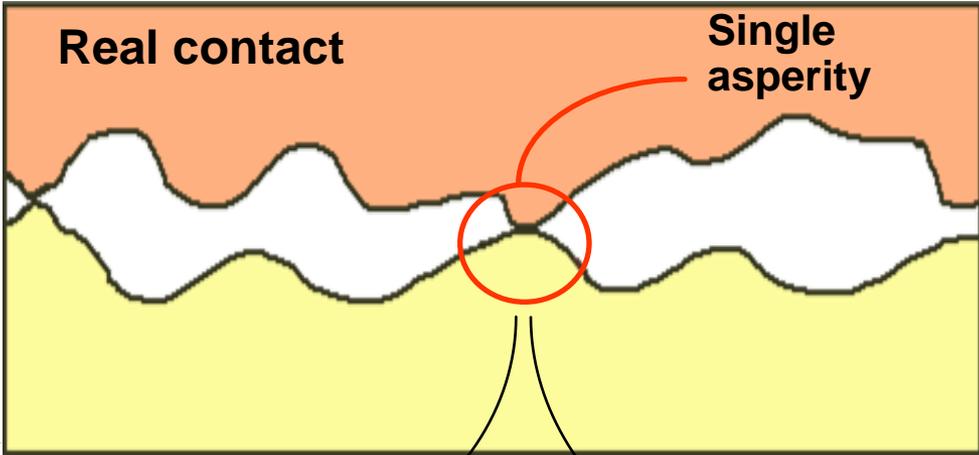
$$\delta = \frac{a^2}{R} - \sqrt{\frac{8\pi a \Delta\gamma}{3K}} \quad P_{\text{Pull-off}} = 1.5\pi\Delta\gamma R$$

The contact radius at zero applied load is:

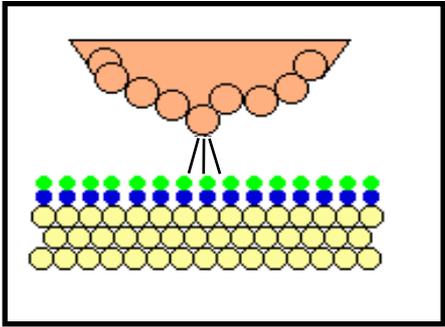
$$a_0 = \left(\frac{6\pi\Delta\gamma R^2}{K} \right)^{\frac{1}{3}}$$



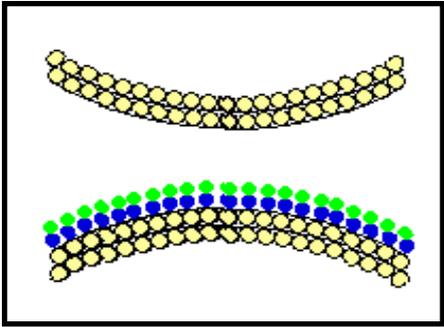
Single asperity: the basic unit of contact mechanics



STM & AFM

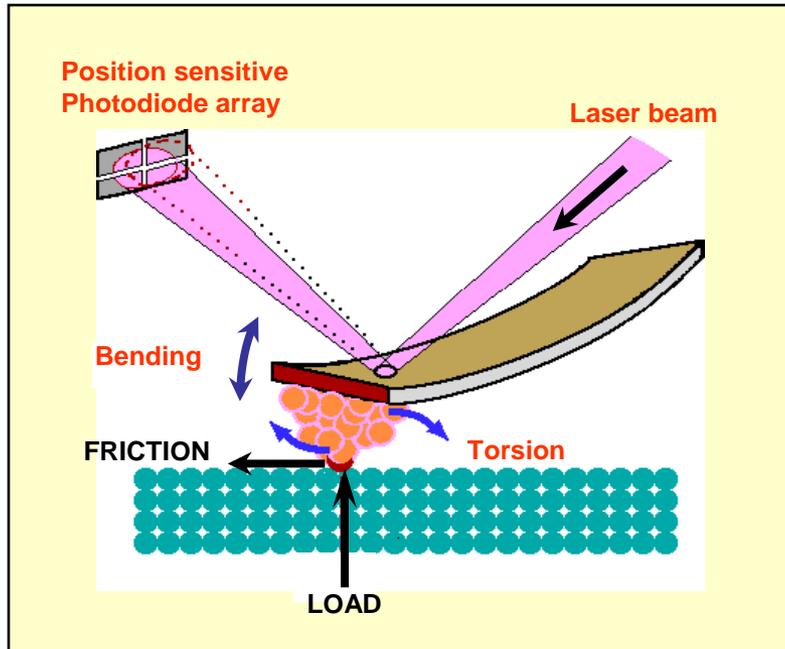


SFA

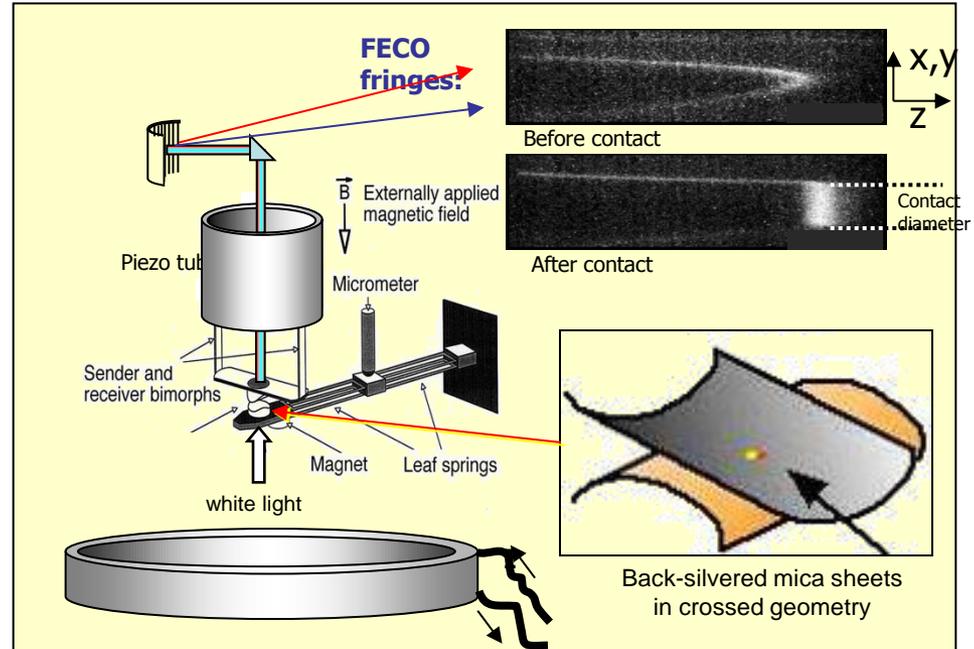


Our tools:

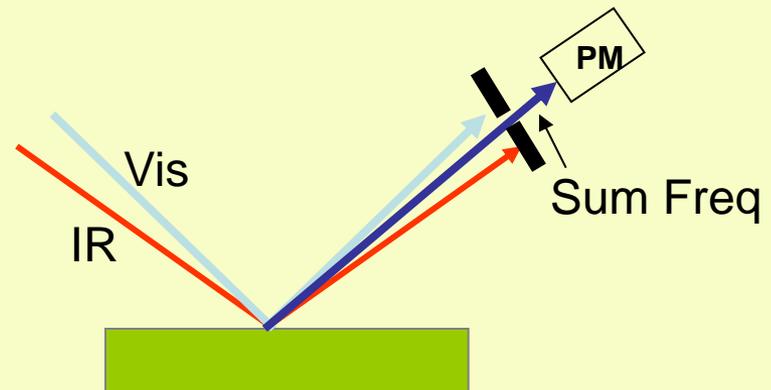
ATOMIC FORCE MICROSCOPE (AFM)



SURFACE FORCES APPARATUS (SFA)

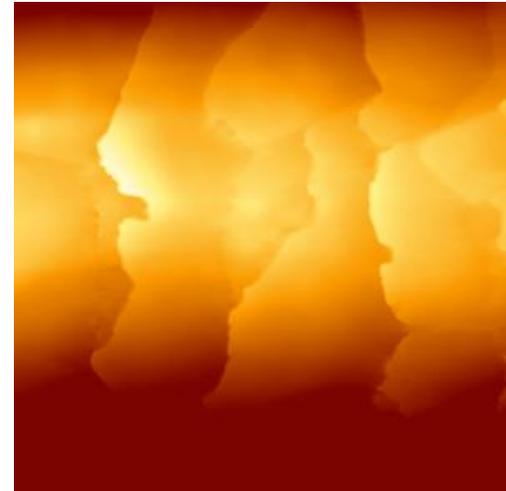
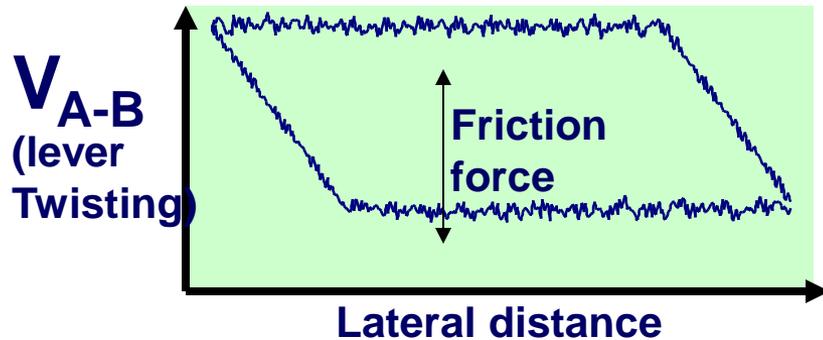
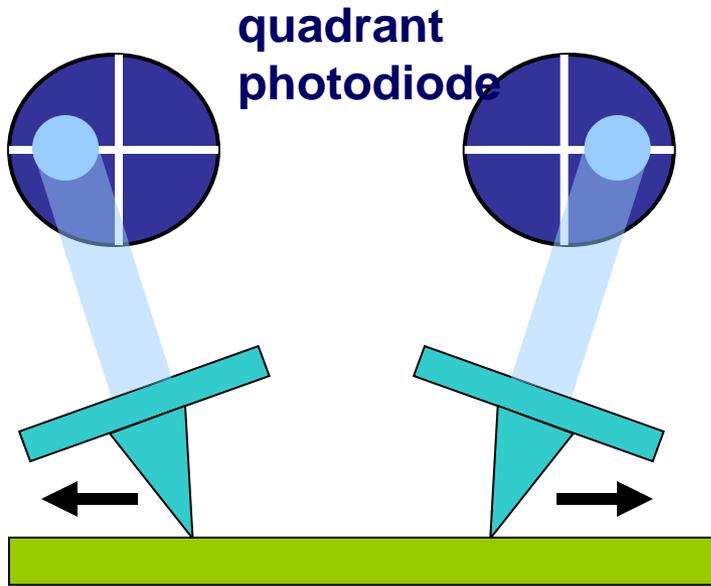


Non-linear optical spectroscopy: Sum Frequency Generation (SFG)

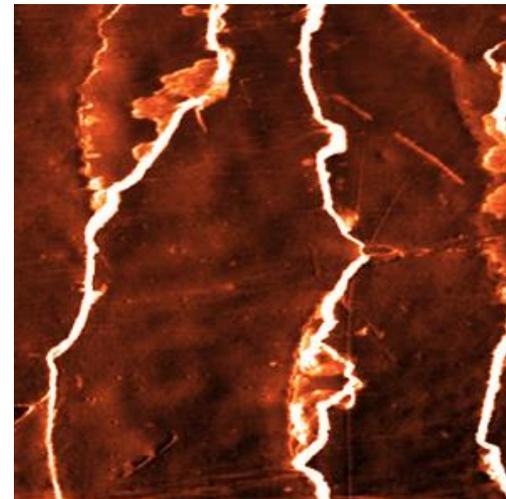


Friction force microscopy

Friction measurement



Hair (contact AFM image)



Hair (friction image)

Atomic scale stick-slip

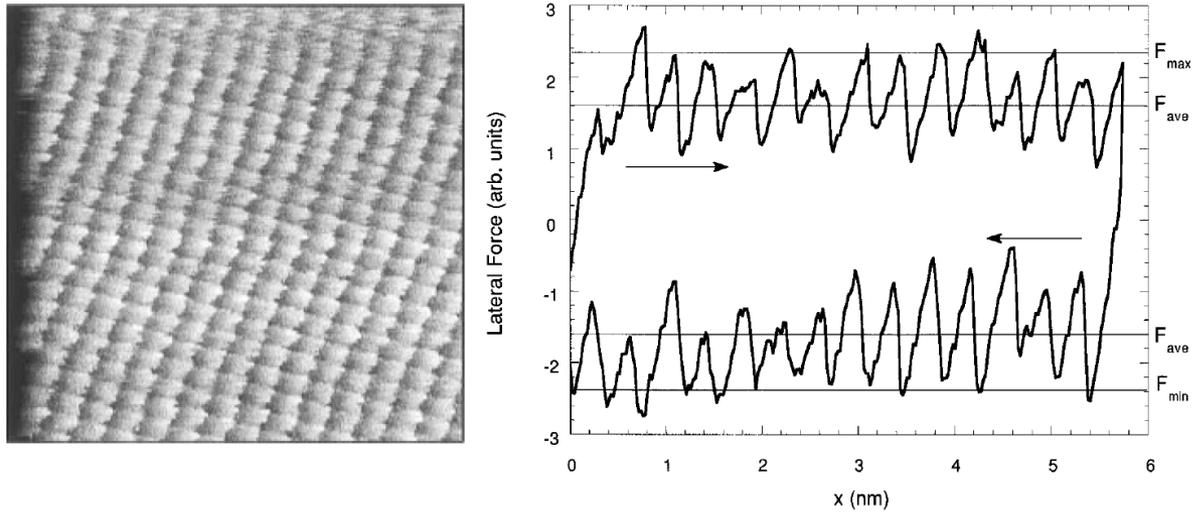
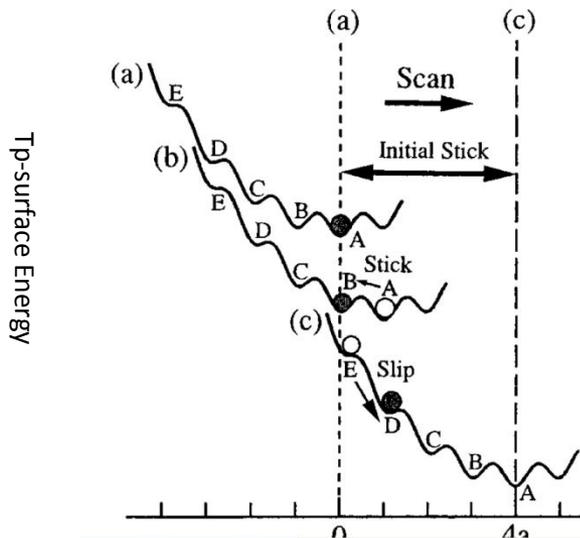
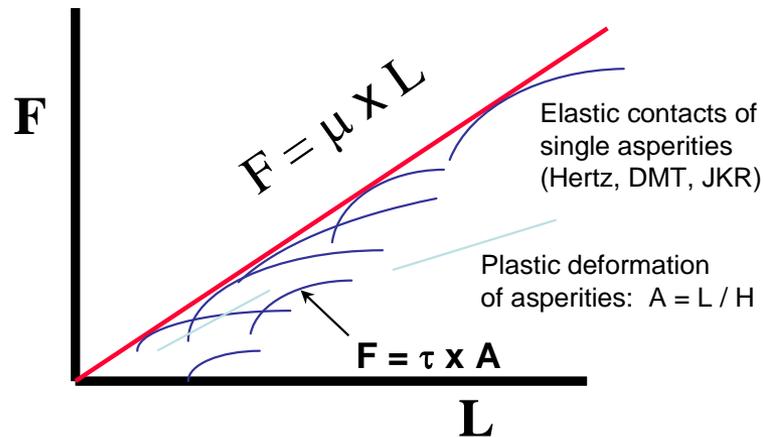


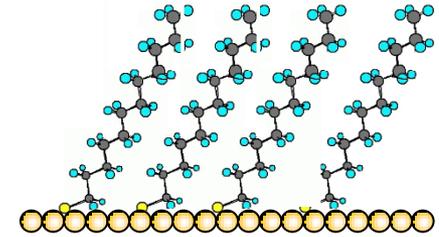
Figure 2. (a, left) A 6 by 6 nm² lateral force image of KF(001) cleaved and imaged in UHV with a silicon nitride tip. Stick-slip motion with the periodicity of the KF unit cell is observed. The scan direction is from left to right. (b, right) A “friction loop” from a single line of the image shown in a and the corresponding right to left lateral force image. The arrows indicate the scan direction for each half of the friction loop. The stick-slip motion is clearly evident. Hysteresis in the loop signifies that energy is dissipated. The average and maximum lateral forces for each scan direction are indicated.



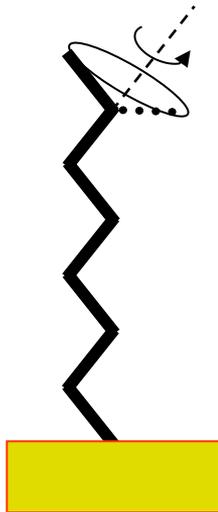
Amontons's Law



Bending and twisting long-chain molecules

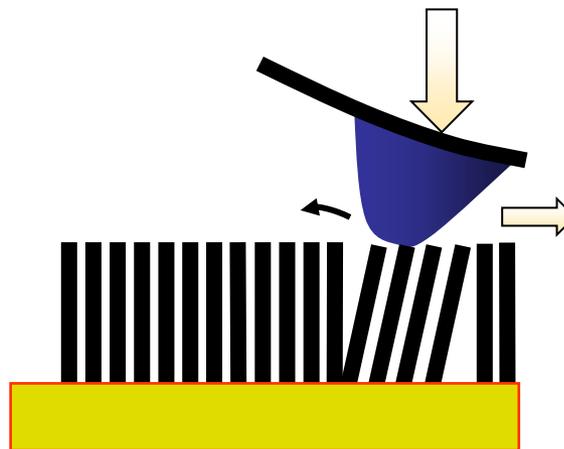


Terminal gauche deformations



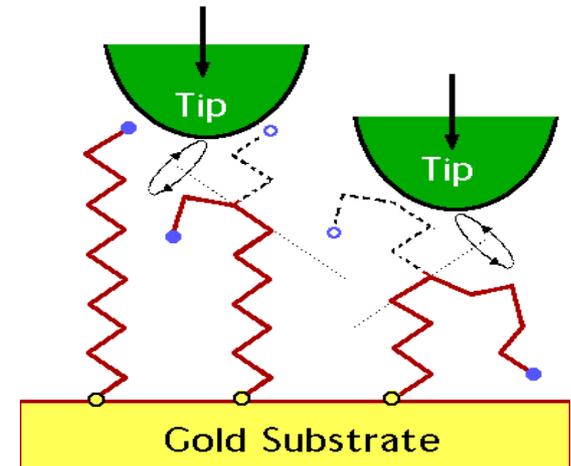
Easiest to produce because terminal groups have few steric constraints

Rigid chain tilts



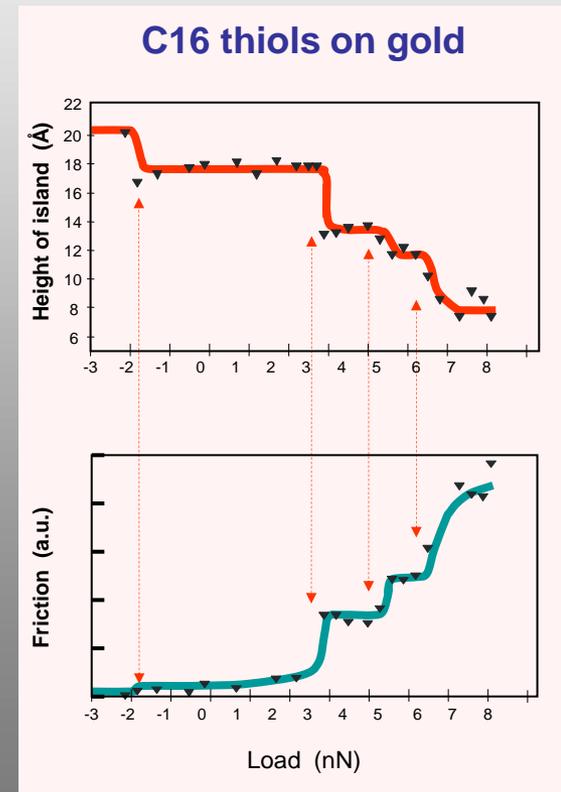
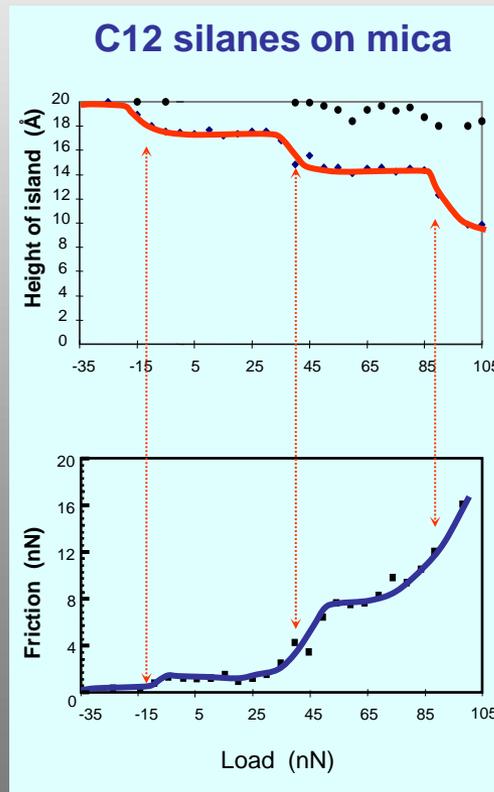
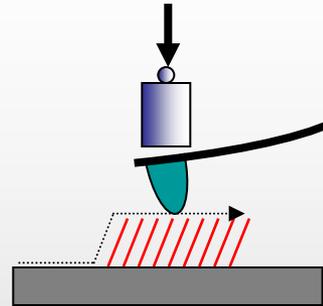
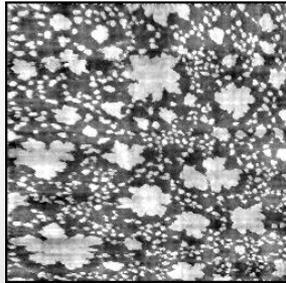
Most favorable deformation due to strong chain-chain attractive forces and steric constraints

Internal gauche deformations



Most difficult to produce in compact films due to steric constraints

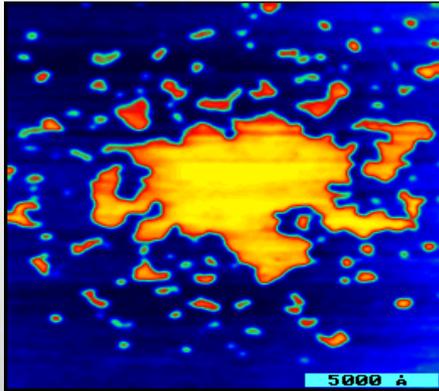
Friction and structure of alkane-chain SAMs under pressure



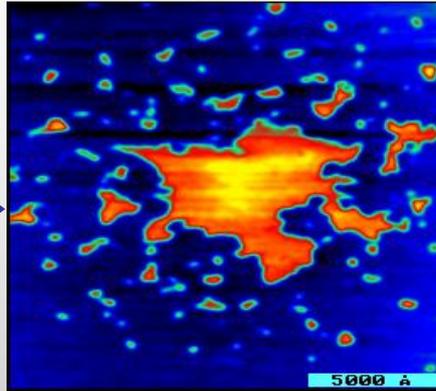
Molecular tilting starts at island periphery

Alkylsiloxanes on mica

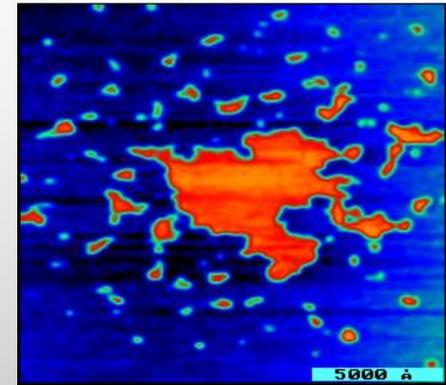
L = 10 nN



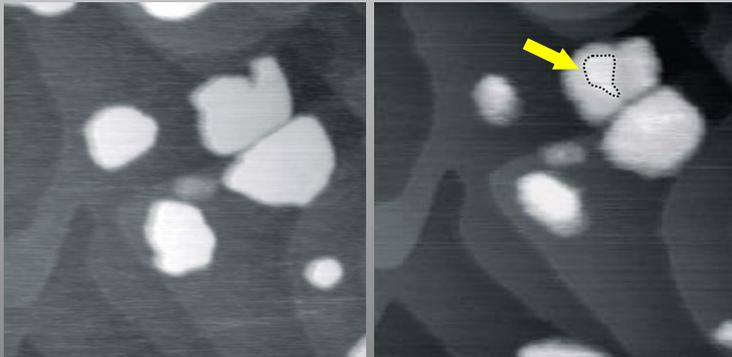
L = 25 nN



L = 35 nN

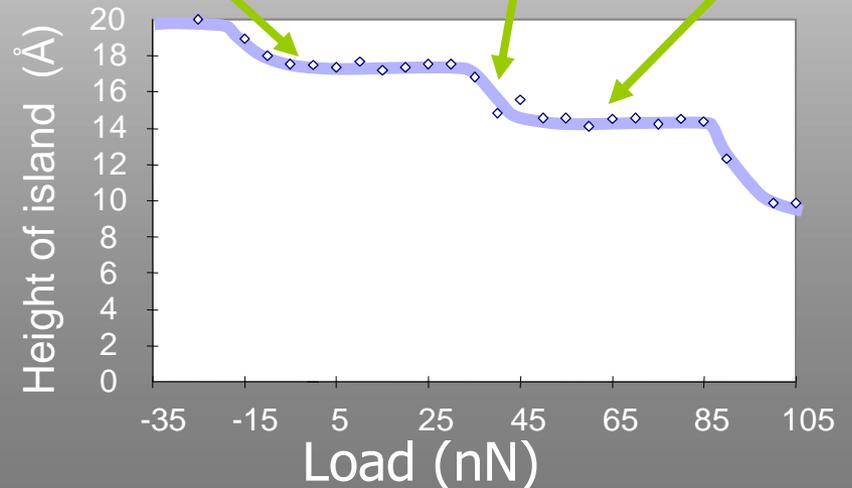


Alkylthiols on gold(111)

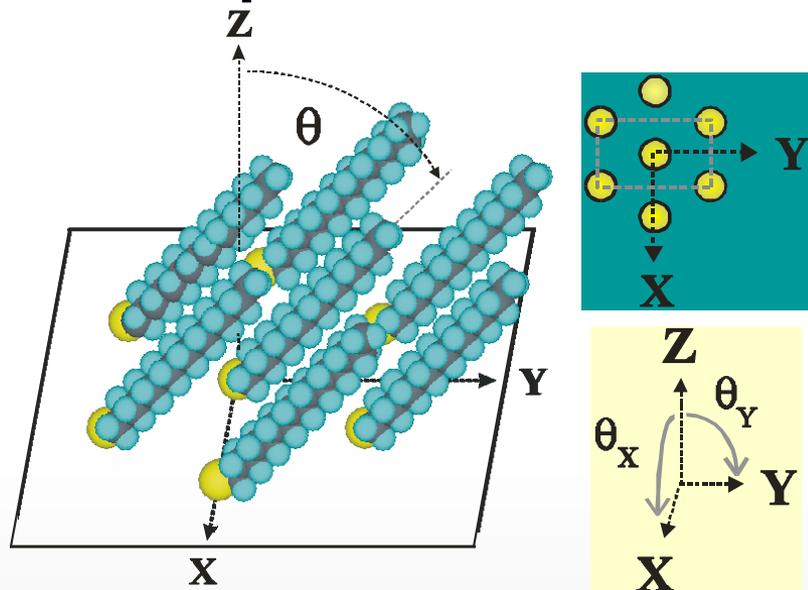


Molecular density increases from the edge to center due to slow diffusion and aggregation processes

n^{th} plateau Center = n^{th} plateau $n^{\text{th}}+1$ plateau
Periphery = $n^{\text{th}}+1$ plateau



The explanation: Concerted molecular tilting of alkane chains

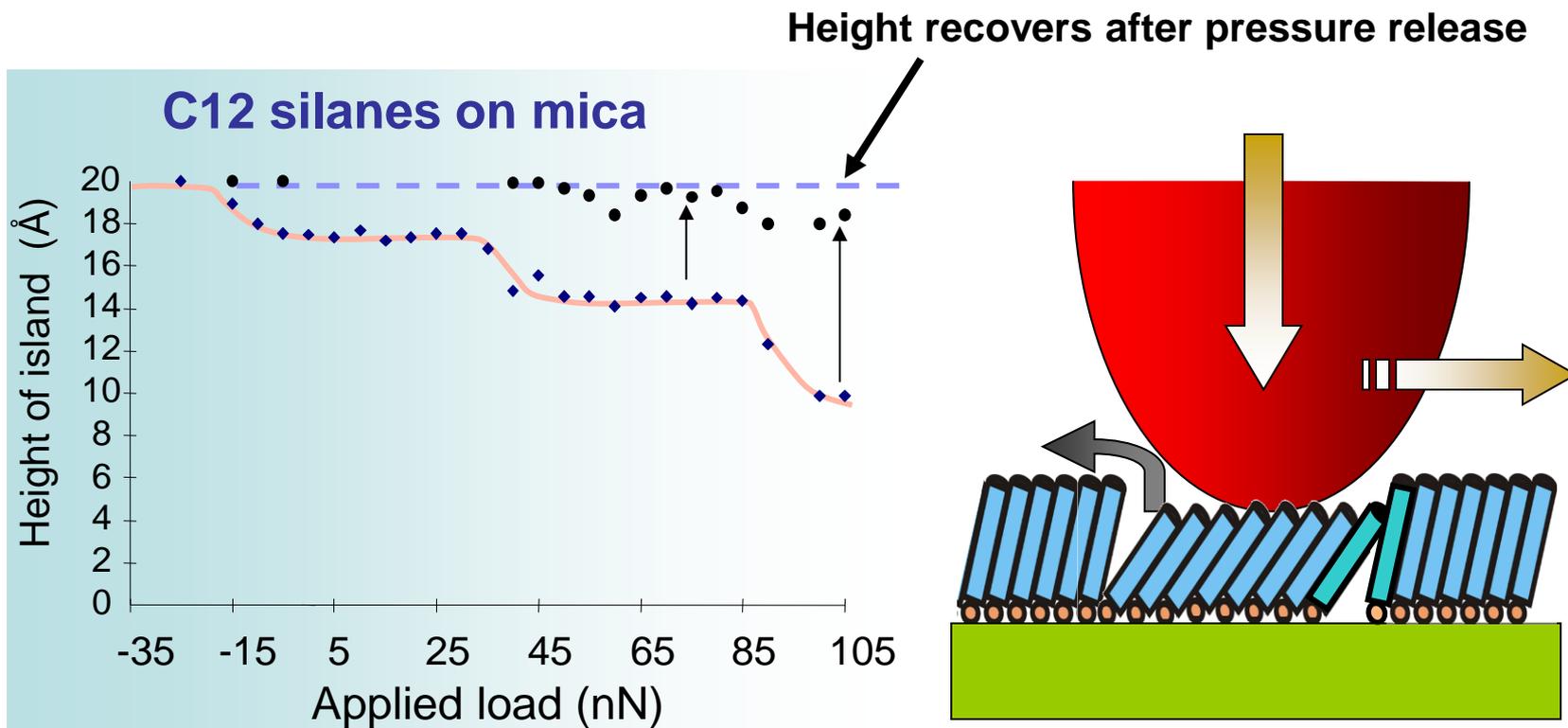


$$\tan \theta_X = \frac{n a}{d_X}, \quad n = 0, 0.5, 1, 1.5, 2 \dots$$

$$\tan \theta_Y = \frac{m a}{d_Y}, \quad \frac{m}{2} = 0, 0.5, 1, 1.5, 2 \dots$$

Experimental (C16)	2D model			
Height (Å)	n	m/2	α	Height (Å)
19.7 ± 0.4	0	1	35°	19.6
18 ± 1	1	1	43°	17.6
16 ± 1	1	1.5	50°	15.7
14.2 ± 0.5	2	1	55°	13.9
12 ± 1	2.5	1	59°	12.2

Stability of tilted phases

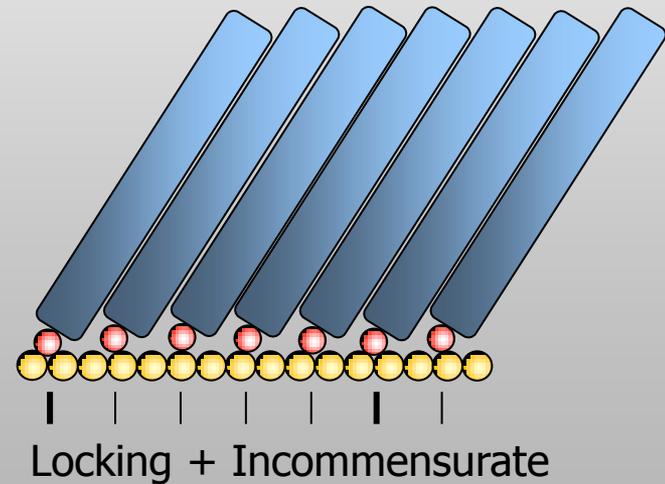
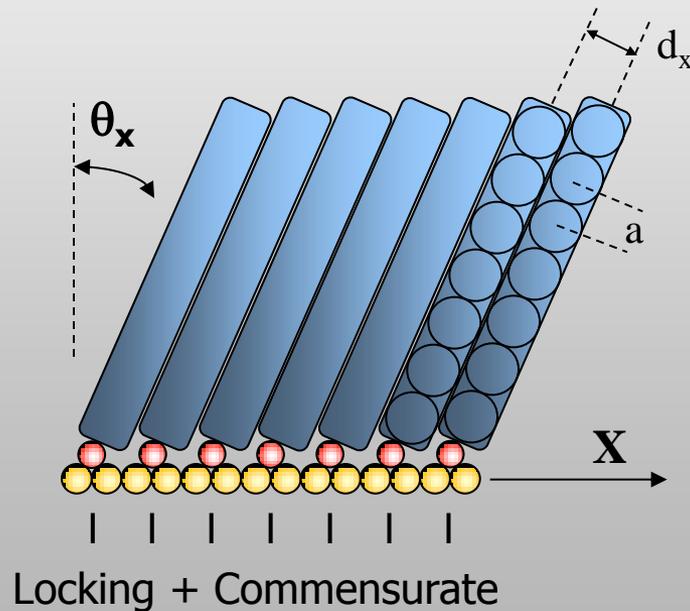


Are the tilted phases stable only under the load of the tip ?

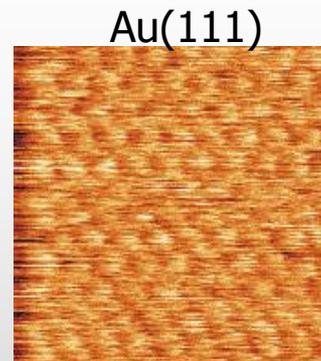
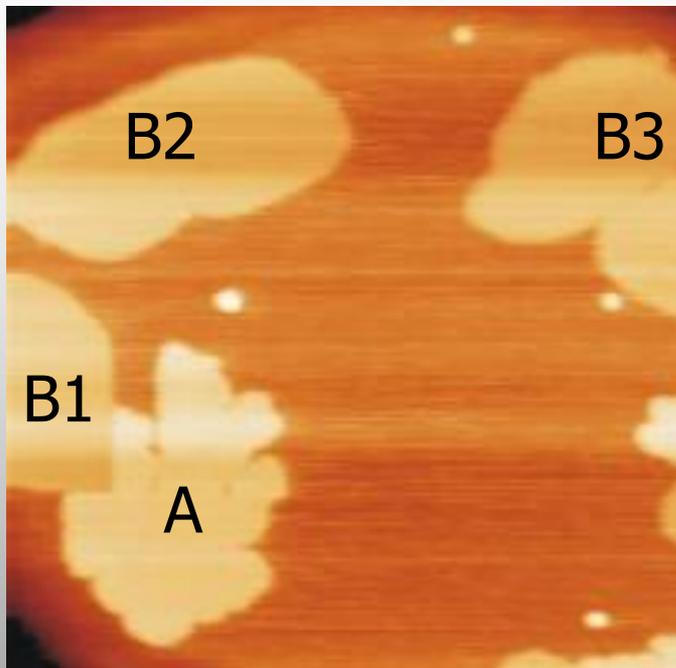
Geometrical constrains for tilted phases

Chain-locking conditions:
$$\begin{cases} \tan \theta_x = \frac{n a}{d_x}, & n = 0, 0.5, 1, 1.5, 2 \dots \\ \tan \theta_y = \frac{m a}{d_y}, & \frac{m}{2} = 0, 0.5, 1, 1.5, 2 \dots \end{cases}$$

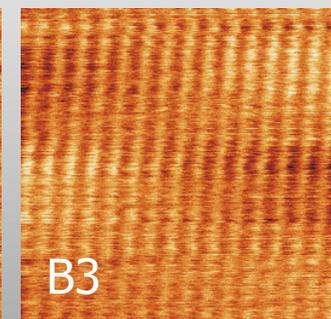
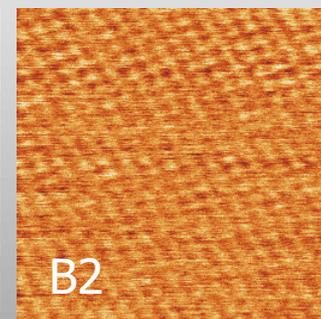
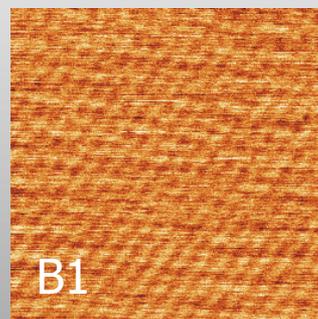
Commensurability conditions:
$$\begin{cases} \cos \theta_x = d_x / n' L_x \\ \cos \theta_y = d_y / m' L_y \end{cases}$$



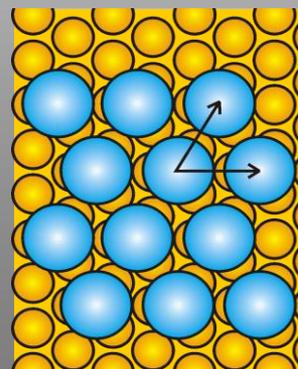
C18 thiols on gold



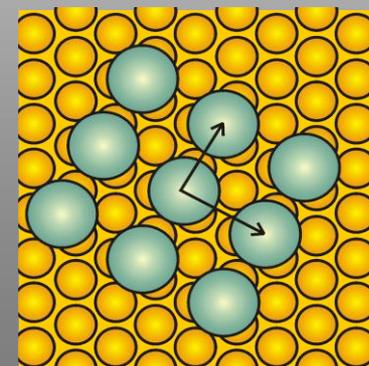
3 Domains



$n = 0$	$n = 1$	$\alpha = 30^\circ - 35^\circ$
$m/2 = 1$	$m/2 = 1.5$	$\alpha = 50^\circ$



A: $(\sqrt{3} \times \sqrt{3})R30^\circ$

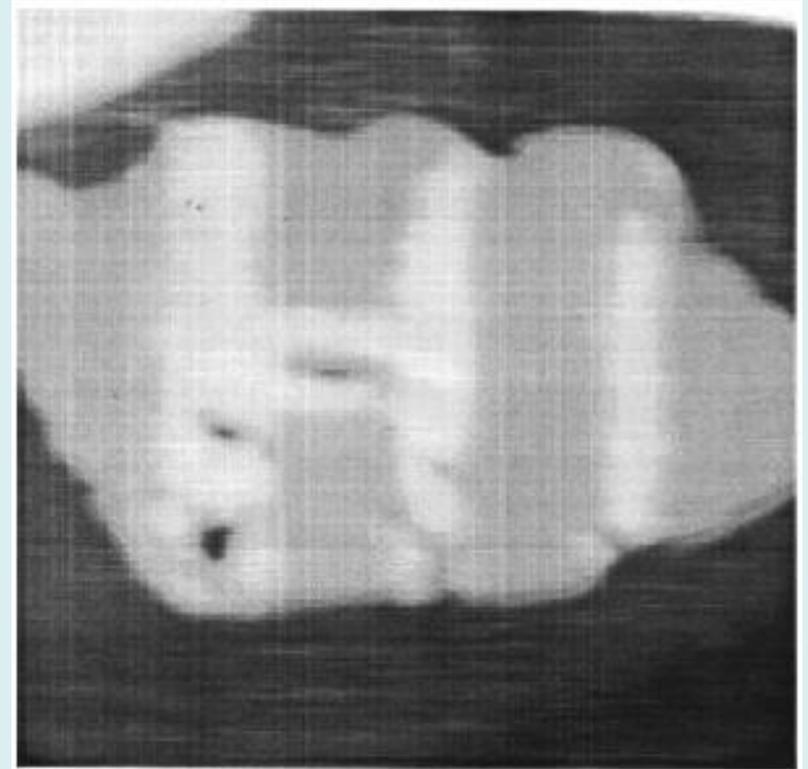
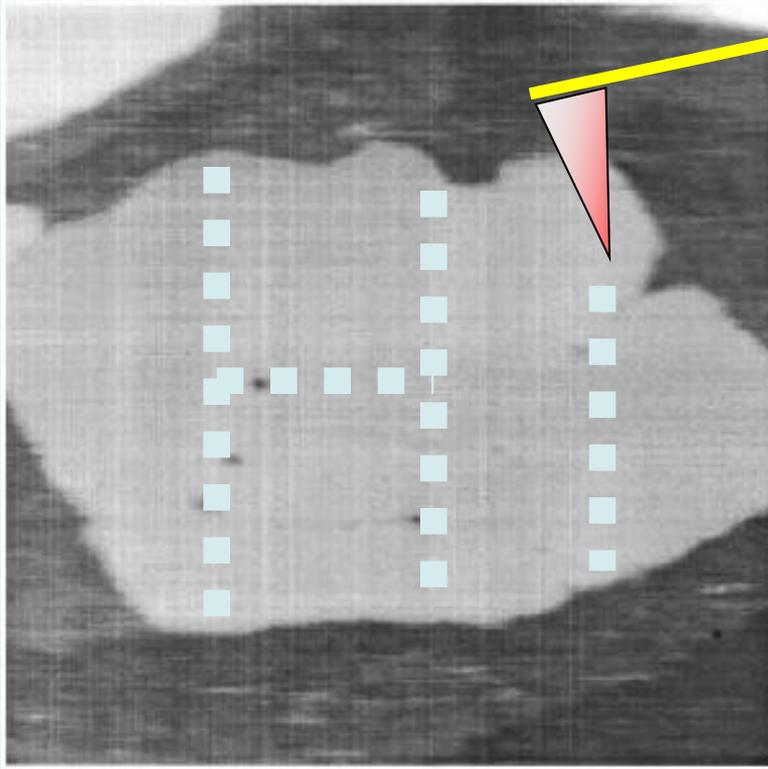


B: $(2 \times \sqrt{3})rect$

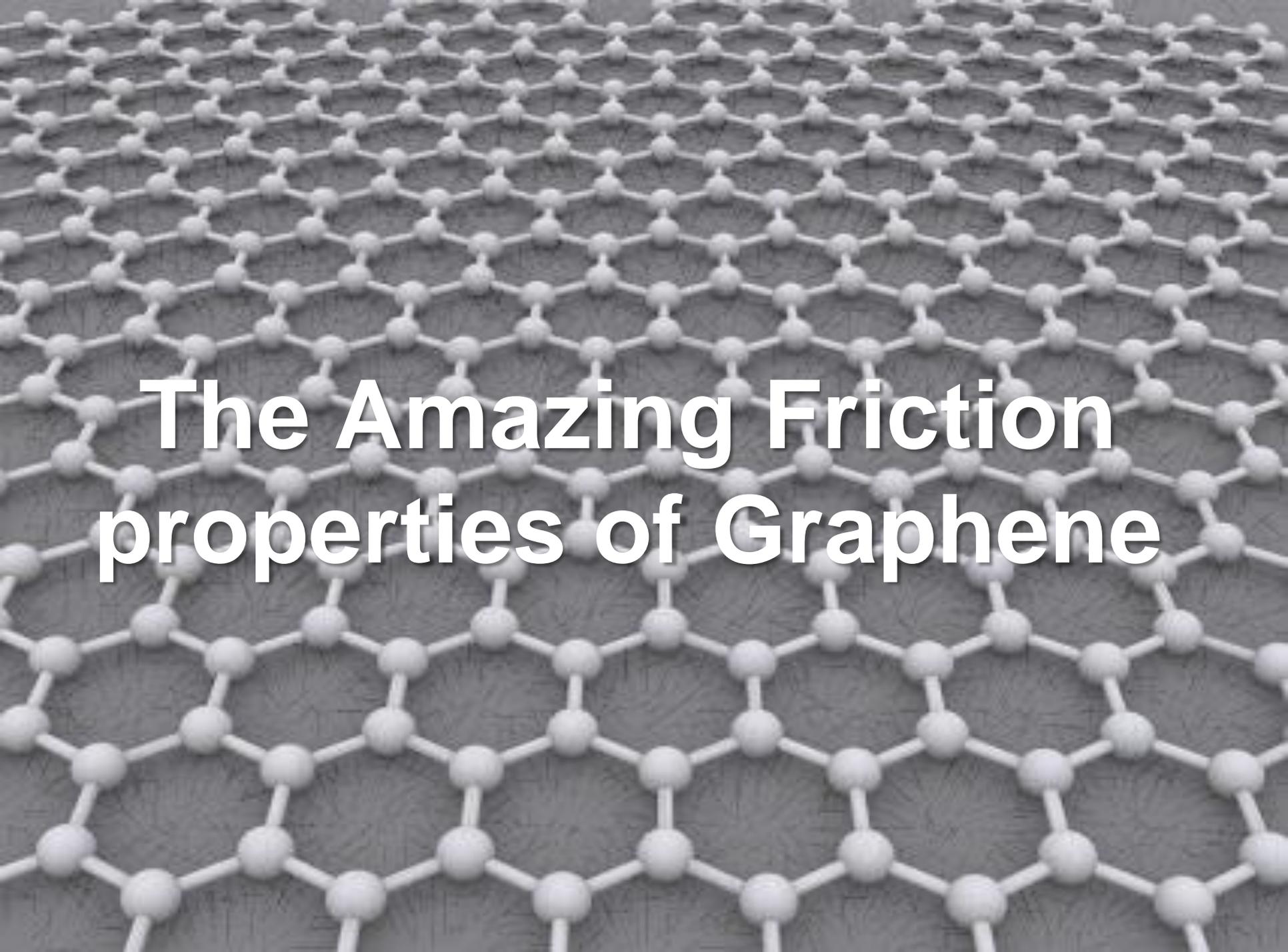
Mechanical stability: C18 thiols on gold

Imaging load = 0 nN

16 nN \sim 1 GPa

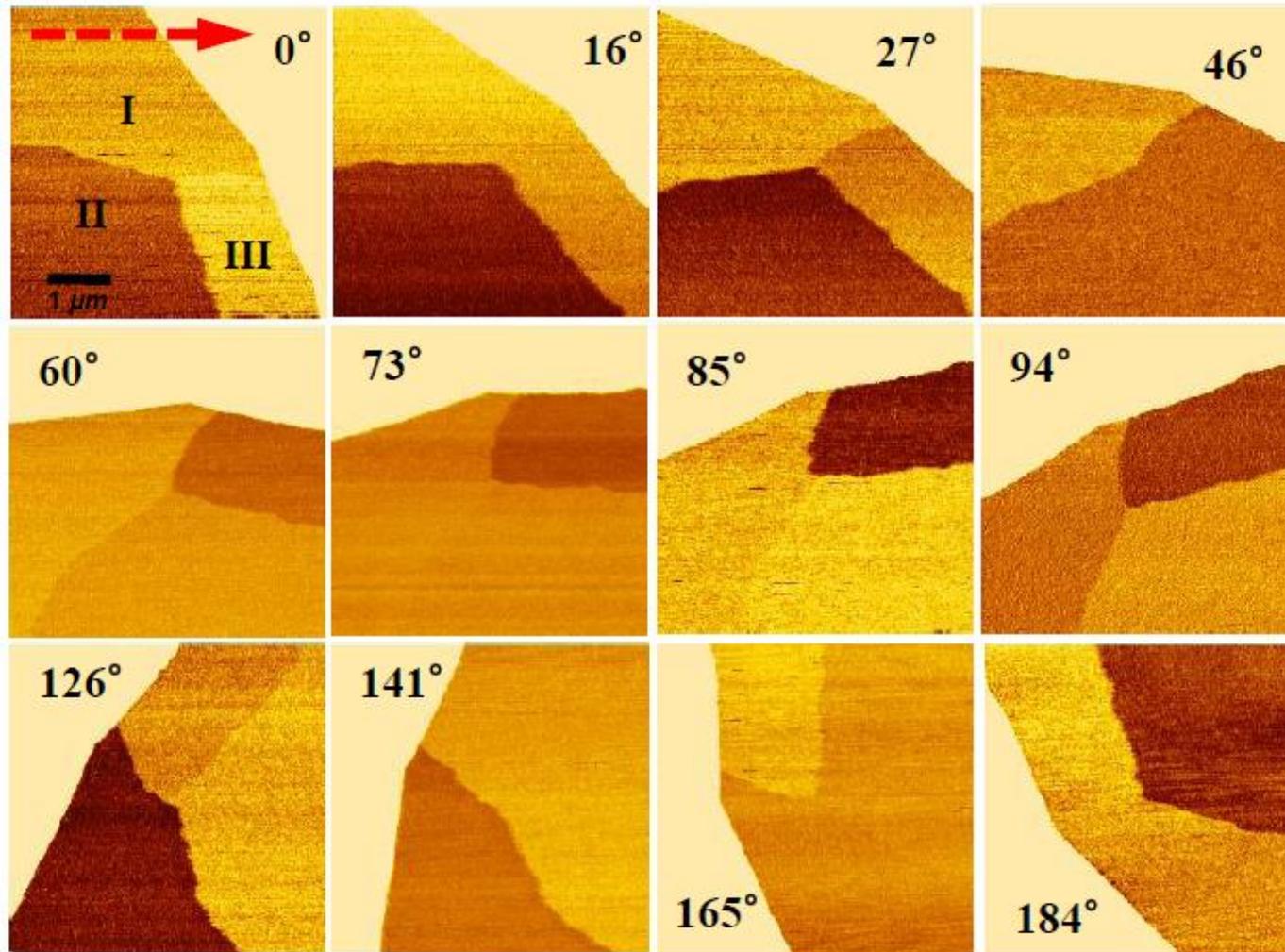


E. Barrena, C. Ocal and M. Salmeron. *J. Chem. Phys.* 114, 4210 (2001)

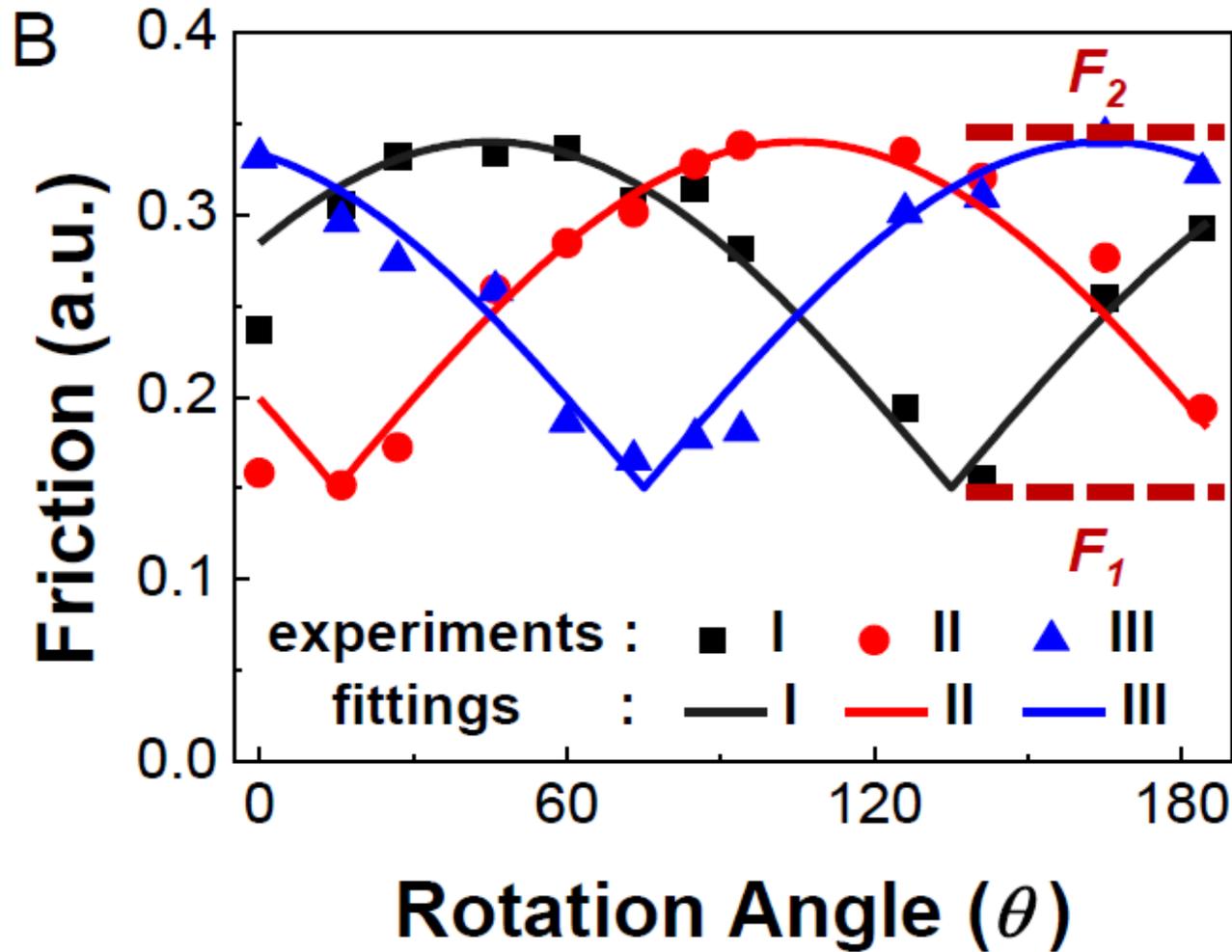


The Amazing Friction properties of Graphene

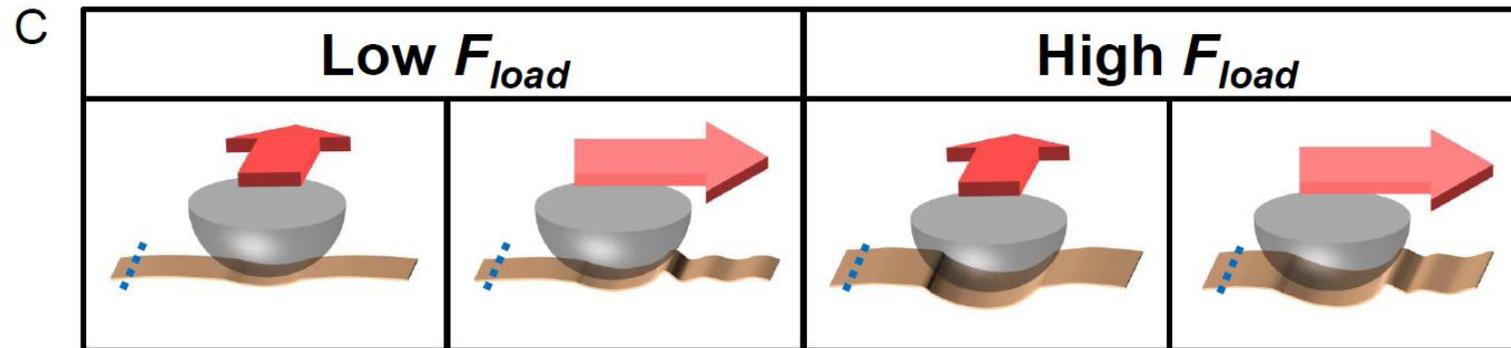
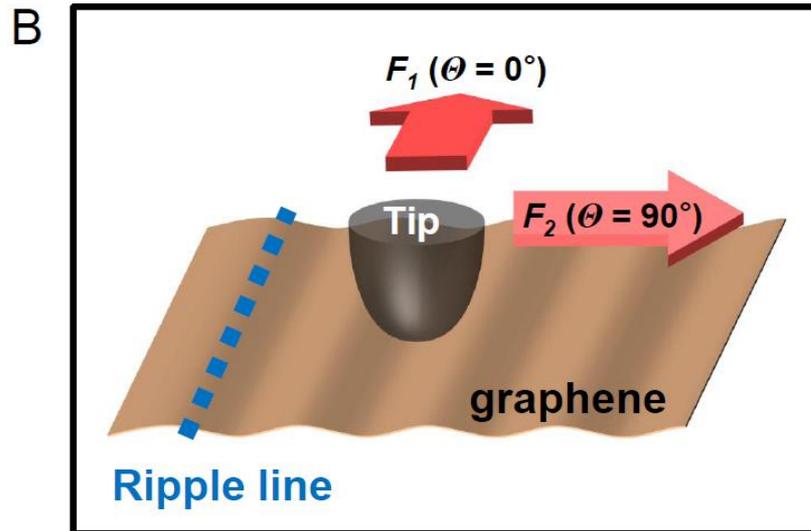
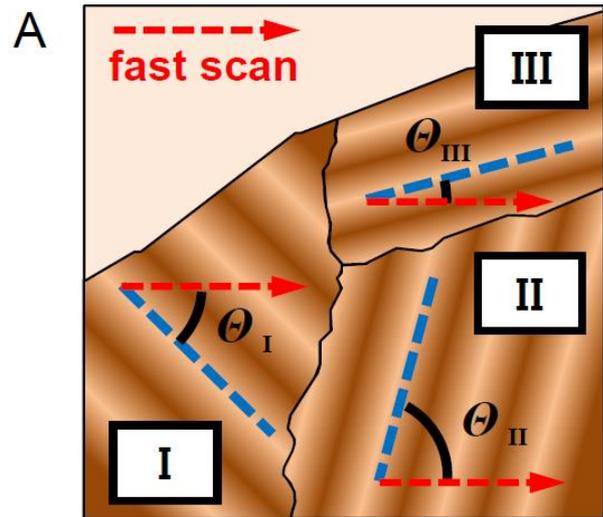
Friction changes with scanning direction in each c



Anisotropy Periodicity is 180° !



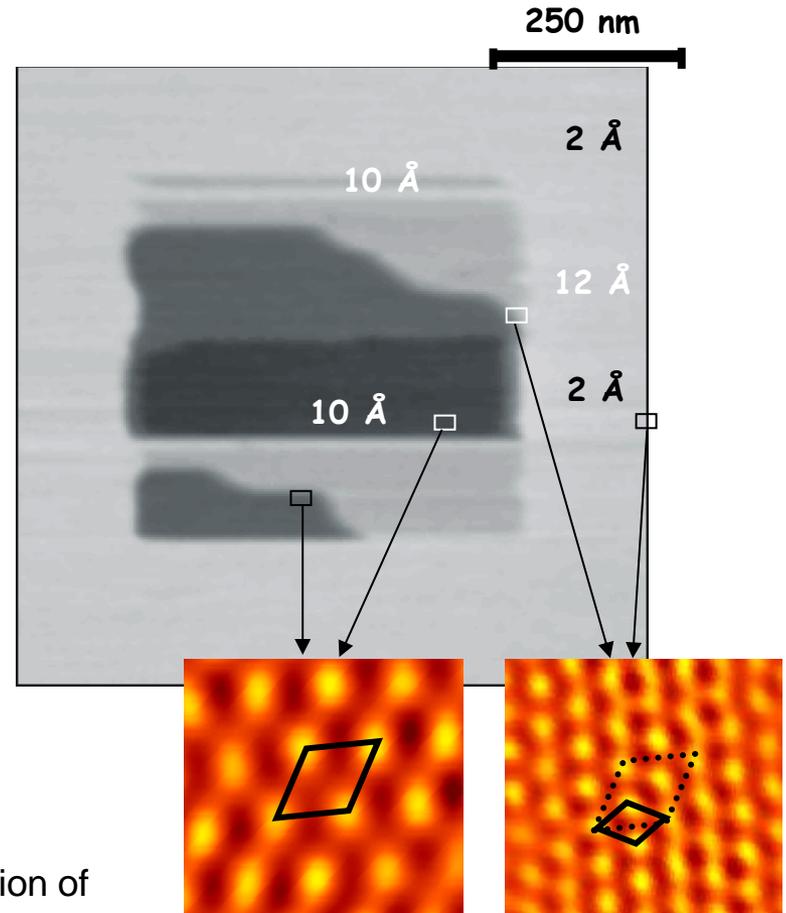
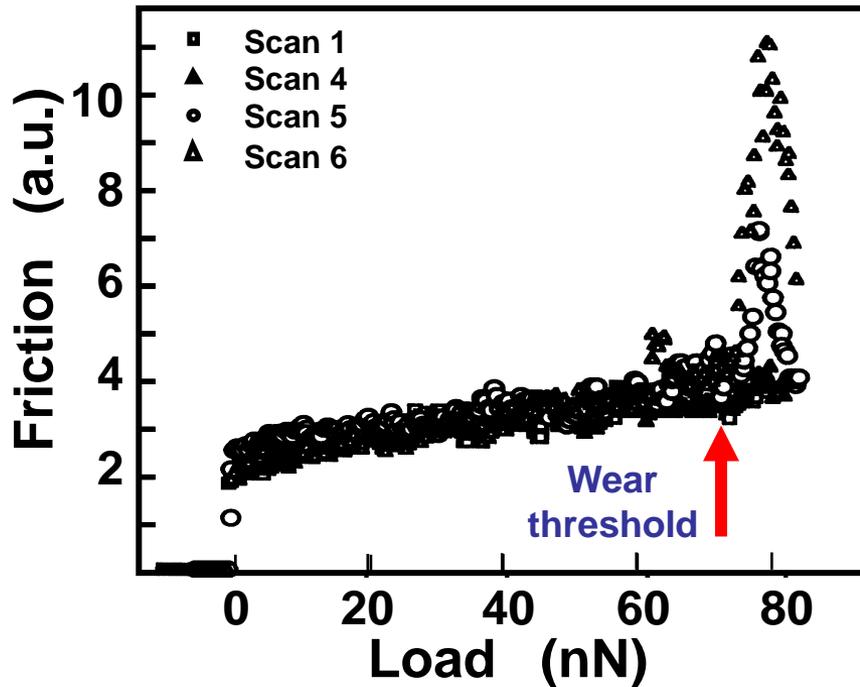
Formation of ripples due to local pinning on the Si wafer



→ The ripples on graphene form preferentially along crystallographic directions of easy bond bending: zig-zag, arm chair,

WEAR

Wear of mica at large loads



Mica wears layer-by-layer at low loads due to accumulation of point defects produced by the tip-surface interaction

The structure of mica

