

# 原子力显微镜及其应用 (1)

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中科院物理所

# 内容提要

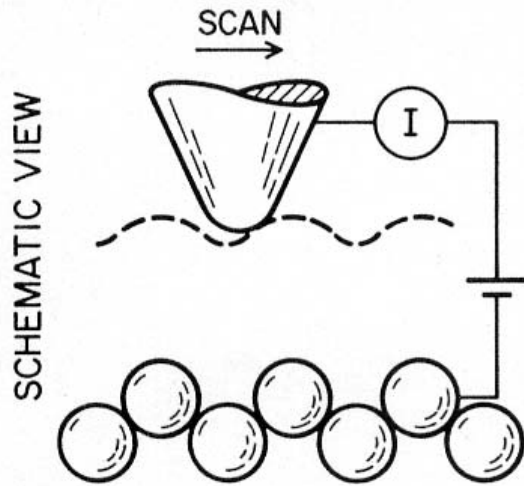
- 原子力显微镜的原理
- 接触**&**非接触**AFM**
- **AFM**应用实例

# STM & AFM

STM

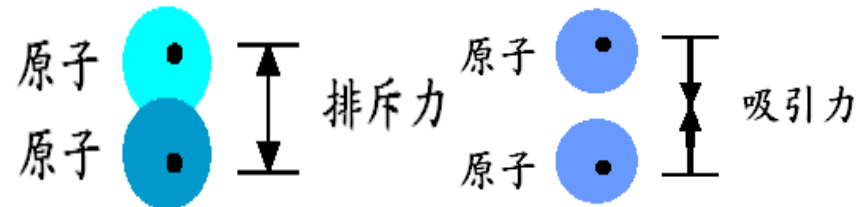
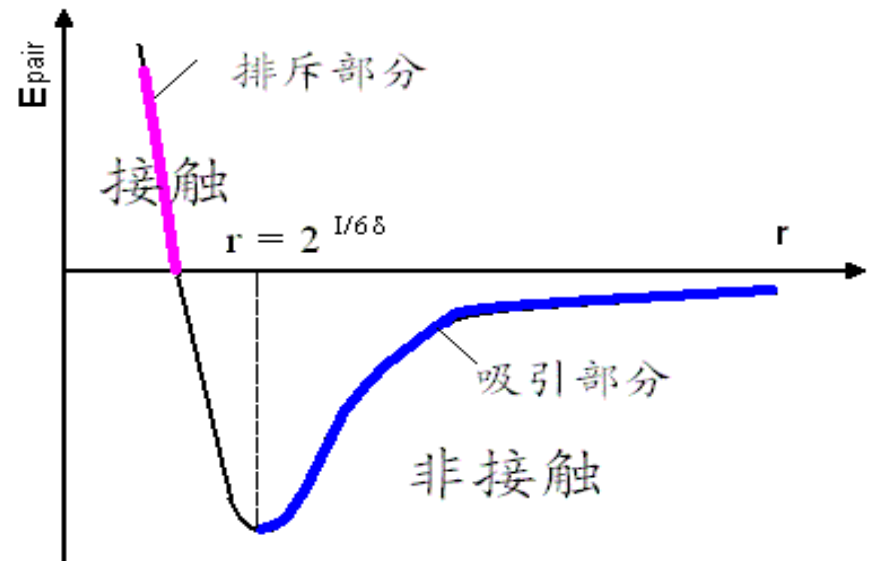
**I = constant**

F = constant (AFM)



STM 只能扫描导体表面  
特殊情况：超薄绝缘体

原子间范德华力

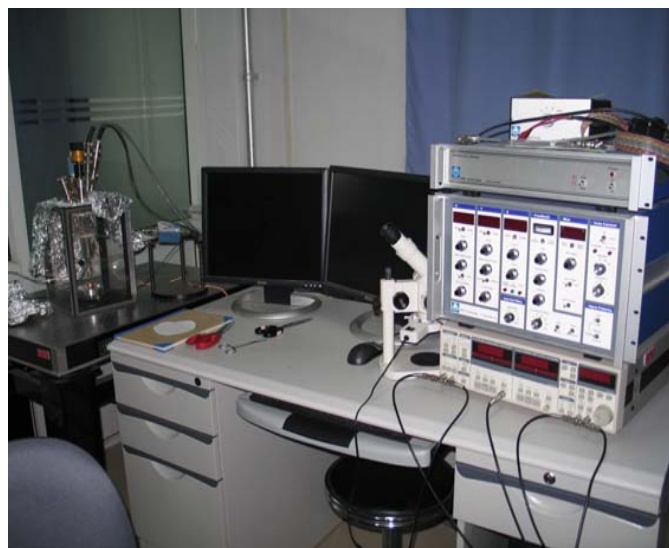
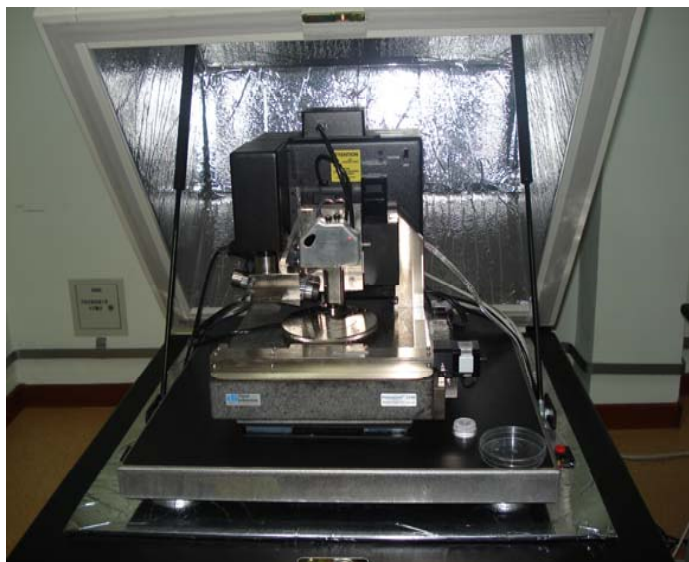
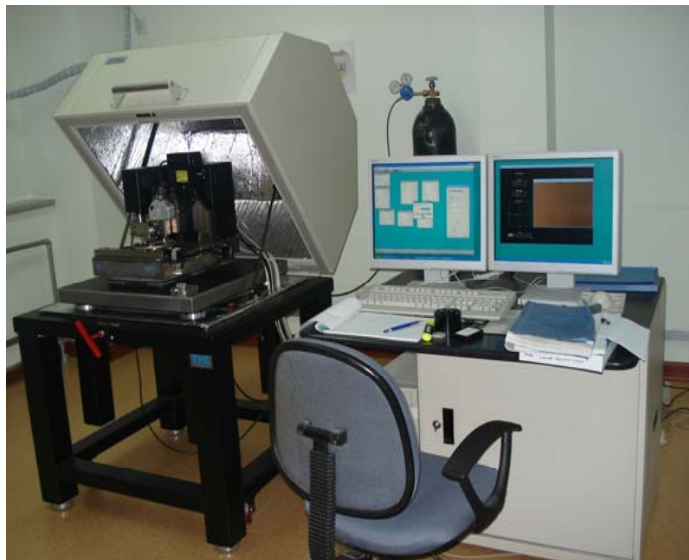


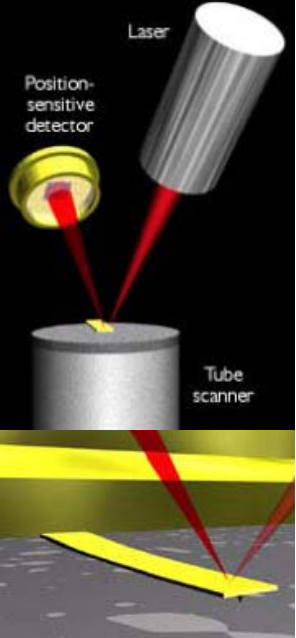
# The first AFM



G. Binnig, Ch. Gerber and C.F. Quate,  
Phys. Rev. Lett. **56**, 930 (1986)

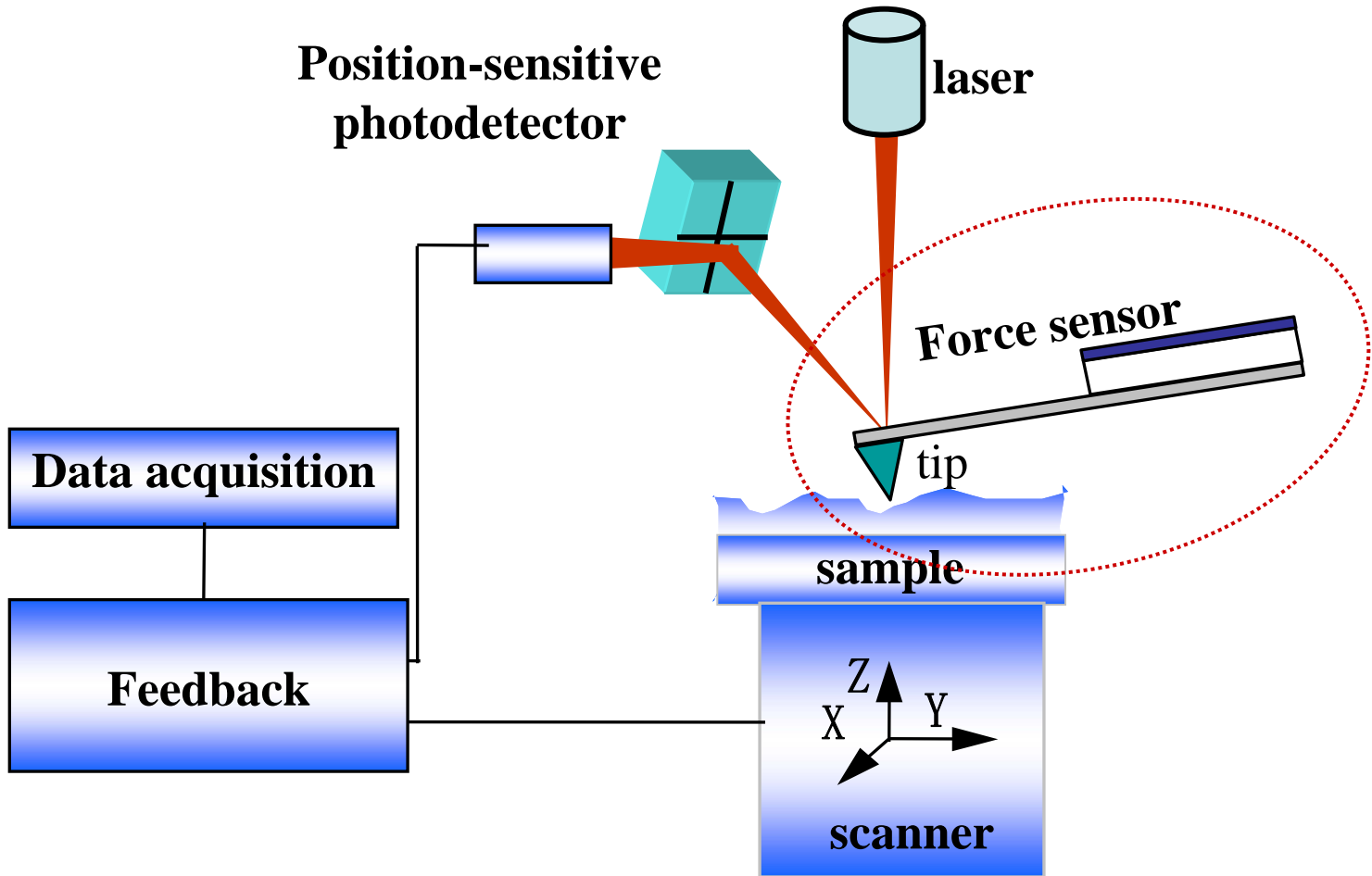
# AFM Systems





# Principle of AFM

Atomic resolution & Multifunction



In static AFM the force  $F_{ts}$  interacting between tip and sample translates into a deflection of the cantilever, and the image is a map  $z(x, y, F_{ts})$  with  $F_{ts} = \text{constant}$

# Forces between atoms

## ‘Back of the envelope’:

- Atomic energy scale:

$$E_{bond} \sim 1-4 \text{ eV} \sim 2-6 \cdot 10^{-19} \text{ J}$$

- Typical bonding length:

$$a \sim 0.2 \text{ nm}$$

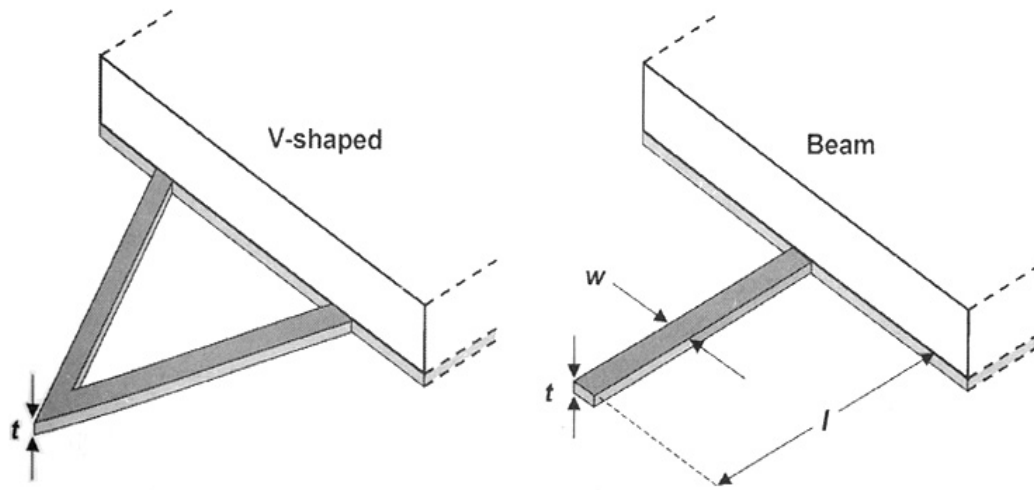
- Typical forces:

$$F = E/a \sim 1-3 \text{ nN}$$

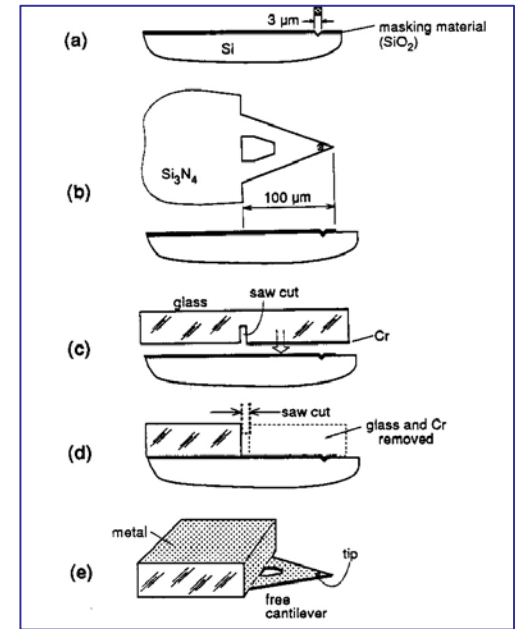
## Bonding energies:

- Quantum mechanical (covalent, metallic bonds): 1-3 nN
  - Coulomb (dipole, ionic): 0.1-5 nN
  - Polarization (induced dipoles): 0.02-0.1 nN
- J. Israelachvili ‘Intermolecular and Surface Forces’ Academic Press

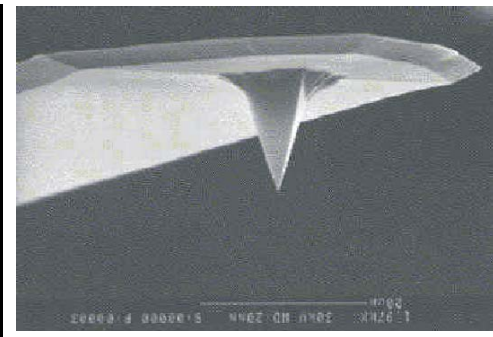
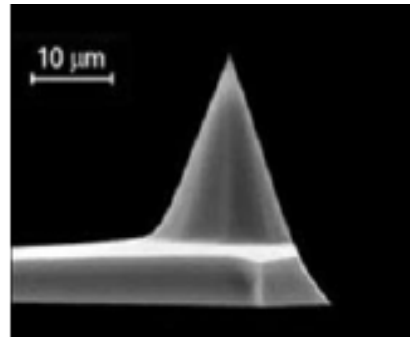
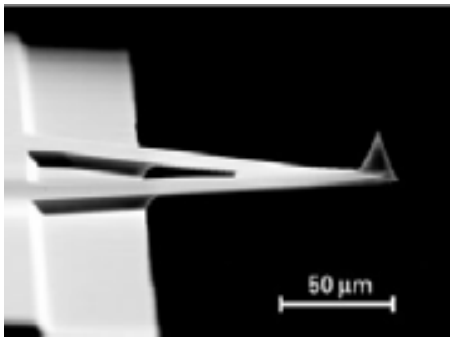
# AFM cantilever



V-shaped and beam SFM cantilevers.



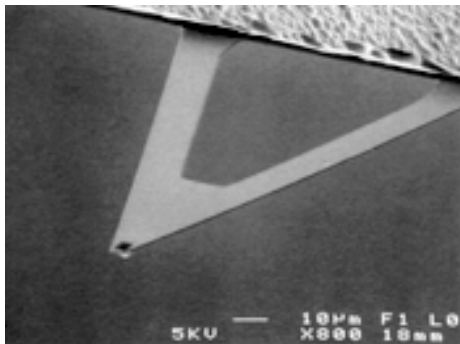
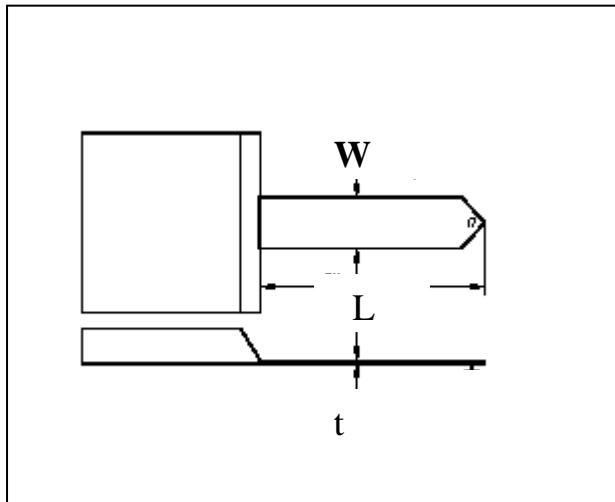
microfabrication



# Design of AFM cantilever

- 很小的**力常数**一般为**0.01~100 N/m**  
微悬臂变形量的检测灵敏度可以达到**nm**量级，这样针尖与样品之间零点几个纳牛顿（**nN**）作用力的变化就可以被检测到
- **共振频率**必须足够高，减小振动和声波的干扰（**>10kHz**）
- 微悬臂要有较高的**横向刚性**
- 非固定端带有一个纵横比较高的尖锐针尖
- 光学偏转法检测微悬臂位移的仪器，要求微悬臂的背面有平滑的**光学反射面**

# Spring constants $k$ and resonant frequency $f$ of cantilevers



Spring constant  $k$  :

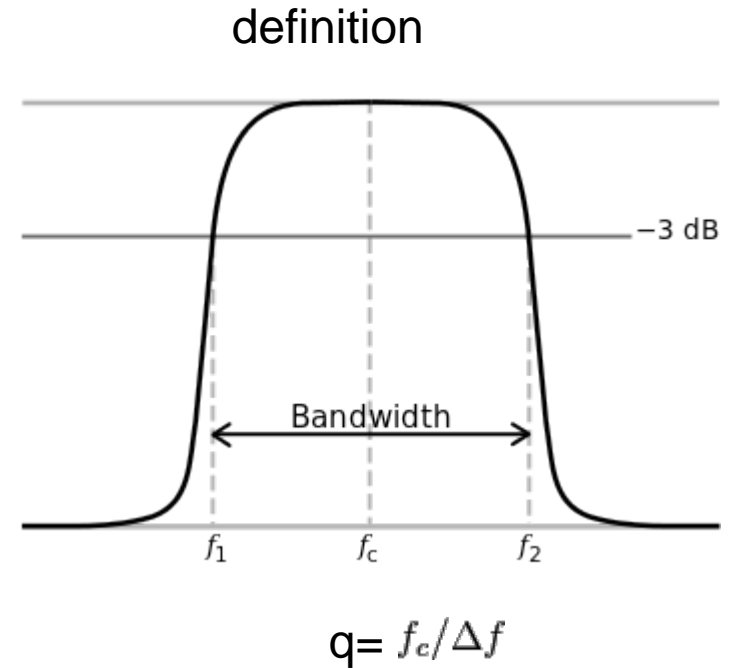
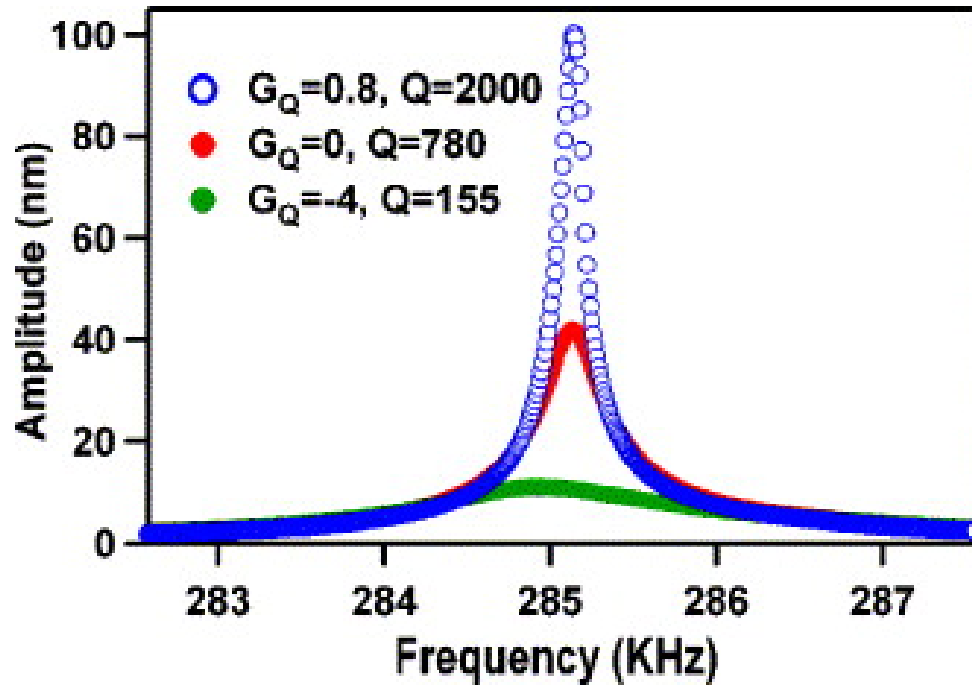
typical values: 0.01 - 100 N/m

Young's modulus  $E_Y \sim 10^{12}$   
N/m<sup>2</sup>

Resonant frequency  $f_o$ :

typical values: 7 - 500 kHz

# Q-factor



the **quality factor** or **Q factor** is a [dimensionless](#) parameter that describes how [under-damped](#) an [oscillator](#) or [resonator](#) is,[\[1\]](#) or equivalently, characterizes a resonator's [bandwidth](#) relative to its center frequency.[\[2\]](#) Higher  $Q$  indicates a lower rate of energy loss relative to the stored energy of the resonator; the oscillations die out more slowly. A pendulum suspended from a high-quality bearing, oscillating in air, has a high  $Q$ , while a pendulum immersed in oil has a low one. Resonators with high quality factors have low [damping](#) so that they ring longer.

# Measuring forces



Harmonic oscillator:

$$f^2 = k/m$$

$F'$  acts like a spring in series:

$$(f + \Delta f)^2 = (k + F')/m$$

Force:

$$F = k \Delta z$$

Force gradient  $F'$  :

$$F' = 2k \Delta f/f$$

approximation good if

$$d^2 V / dz^2 = \text{constant for } \Delta z$$

otherwise: Giessibl, APL **78**, 123  
(2001)

# Calibration of cantilever spring constant $k$

## Methods:

- **Thermal**

Hutter and Bechoefer, RSI **64**, 1068 (1993)

- **Sader method** (measure geometry)

Sader RSI **66**, 9 (1995)

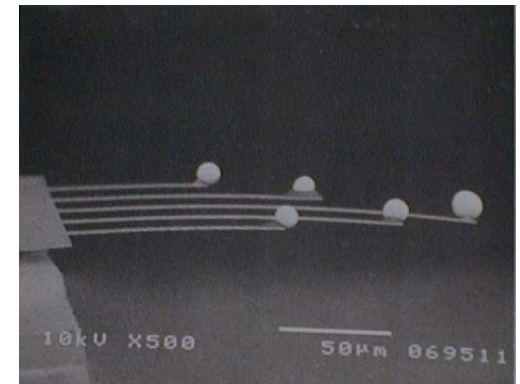
- **Reference spring method**

M. Tortonese, Park Scientific

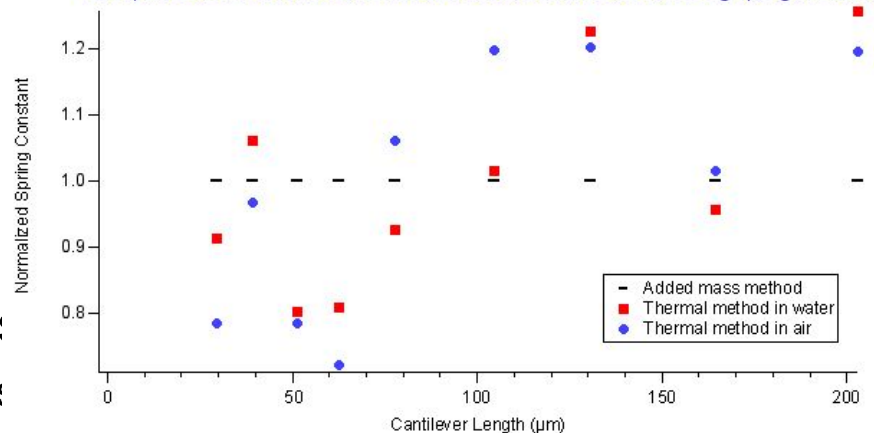
- **Added mass**

Walters, RSI **67**, 3583 (1996)

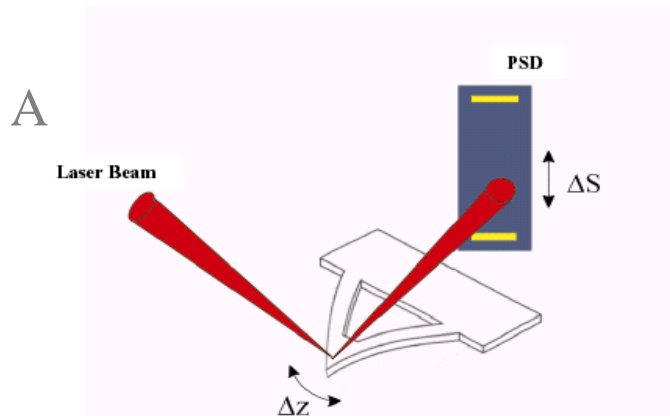
Excellent discussion and reference:  
[www.asylumresearch.com/springconstant.a](http://www.asylumresearch.com/springconstant.a)



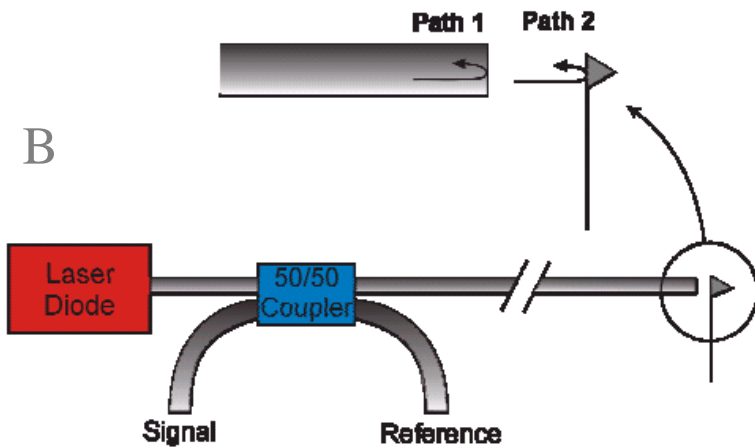
Comparison between thermal and added-mass methods for determining spring constant



# Deflection sensors



Meyer and Amer, APL **53**, 1045 (1988)

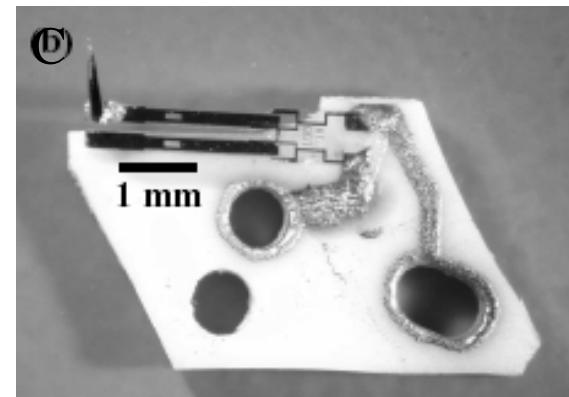


Rugar et al., APL **55**, 2588 (1989)

A) Beam deflection

B) Interferometry

C) Piezoelectric



Giessibl, APL **73**, 3956 (1998)

# AFM常用工作模式

(1) **Contact mode**: 利用原子斥力的变化而产生表面轮廓为接触式原子力显微镜), 探针与试片的距离约数个Å。

由于表面摩擦和粘滞可能会有假象。  
可能会使表面破坏, 针尖磨损钝化。

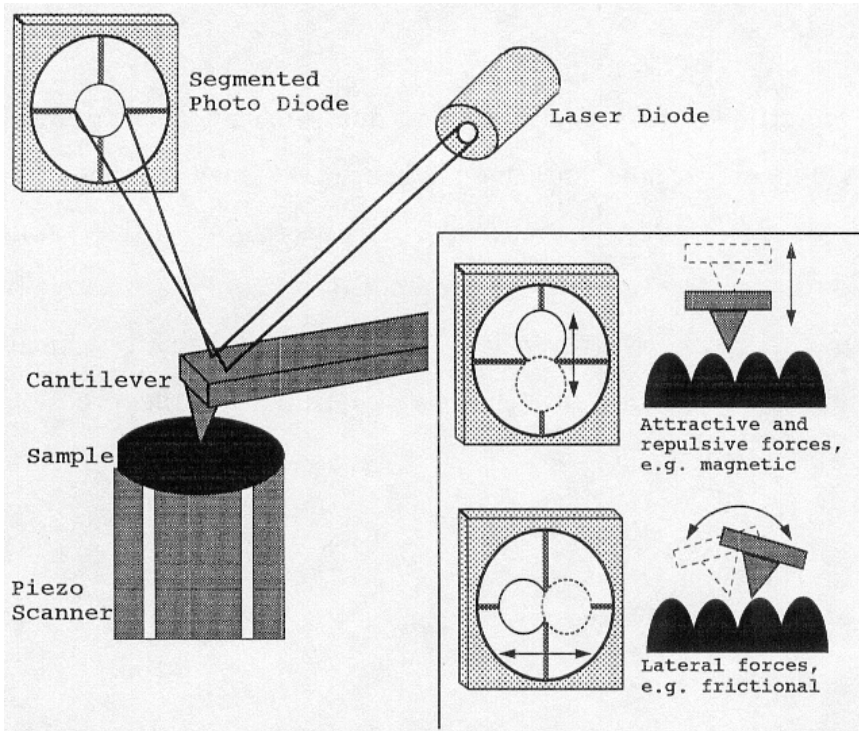
(2) **Tapping mode**: 探针悬臂以一定的频率振动。当针尖刚接触样品时, 悬臂振幅会减少到某一数值。在扫描过程中, 反馈回路维持悬臂振幅在这一数值恒定。

可对软样品成像, 消除由剪切力引起的分辨率的降低和对样品的破坏几乎消失。  
克服了室温大气环境下大多数样品表面上薄液层的粘滞

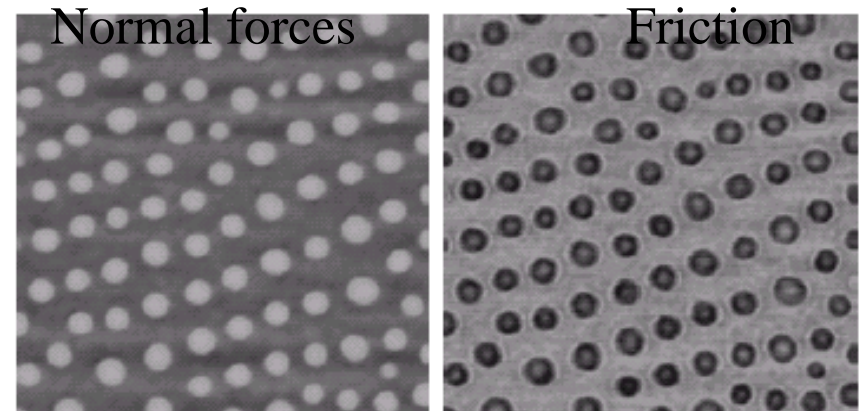
(3) 利用原子吸引力的变化而产生表面轮廓为非接触式原子力显微镜 (**non-contact AFM**), 探针与试片的距离约数十到数百Å

一般是频率调制或者是相位调制, 分辨率更高。  
操作复杂, 环境噪声干扰大, 一般在真空中能够实现。  
最新**non-contact AFM**的发展能够工作在各种力的范围, 实现极高分辨率。

# lateral force Imaging



## Diblock co-polymer:



Meli, Badia, Grutter, Lennox,  
Nano Letters **2**, 131 (2002)

# Van derWaals forces

$$F_{vdW} = AR/6z^2$$

A...Hamaker const.

R...Tip radius

z...Tip - sample separation

A depends on type of materials (polarizability). For most materials and vacuum  $A \sim 1\text{eV}$

Krupp, Advances Colloidal Interface Sci. 1, 113 (1967)

$R \sim 100\text{nm}$  typical effective radius

**->  $F_{vdW} \sim 10\text{ nN}$  at  $z \sim 0.5\text{ nm}$**

# Electrostatic forces

$$F_{\text{electrostatic}} = \pi \epsilon_0 R U^2 / z$$

$U$ ...Potential difference

$R$ ...Tip radius

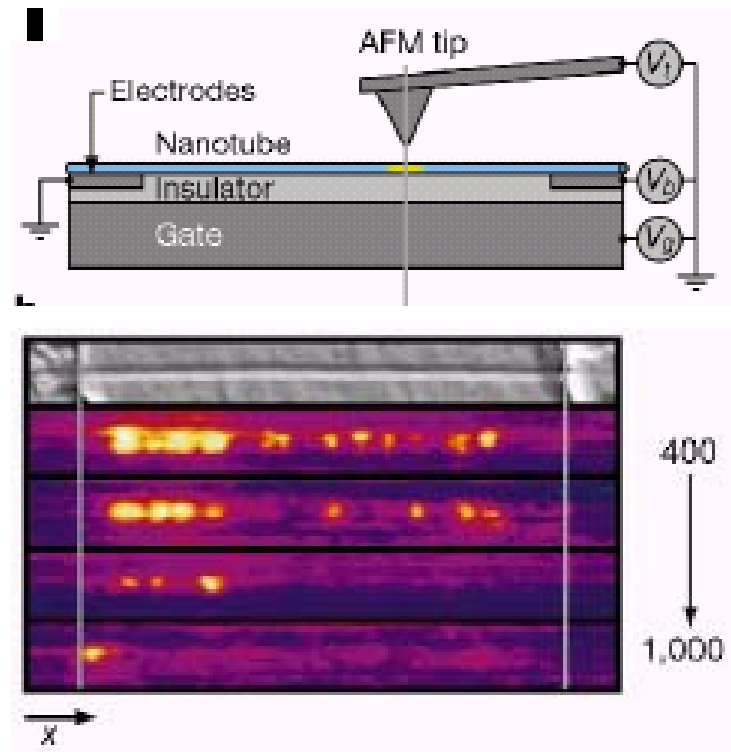
$z$ ...Tip - sample separation

$R \sim 100\text{nm}$  typical effective radius

$U = 1\text{V}$

->  $F_{\text{electrostatic}} \sim 5\text{ nN}$  at  $z \sim 0.5$

**nm**



Tans & Dekker, Nature **404**, 834 (2000)

# Chemical forces

$$F_{Morse} = E_{bond}/z \cdot (2e^{-\kappa(z-\sigma)} - e^{-2\kappa(z-\sigma)})$$

$E_{bond}$  ...Bond energy

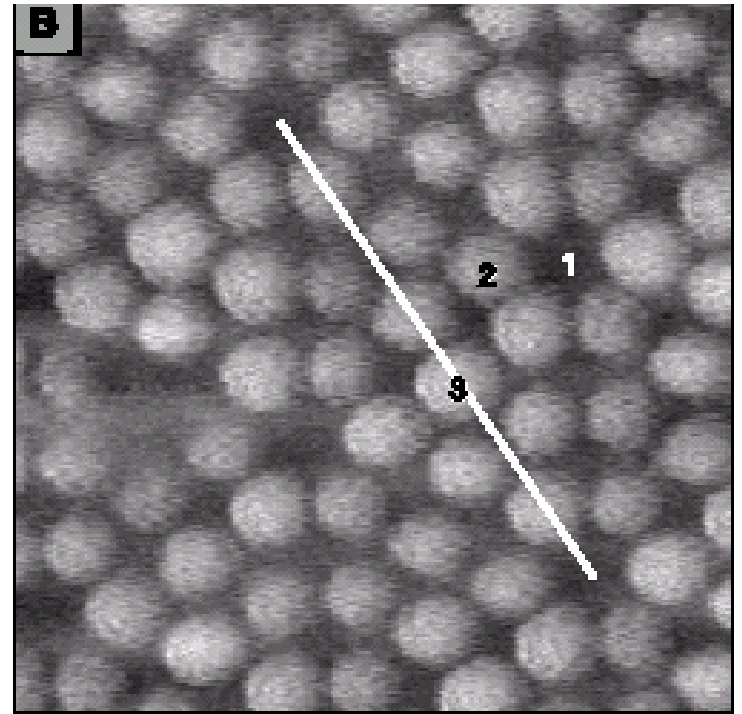
$\kappa$  ...decay length radius

$\sigma$ ...equilibrium distance

Other popular choice:

12-6 Lennard Jones potential

Si(111) 7x7



Lantz et al, Science **291**, 2580 (2001)

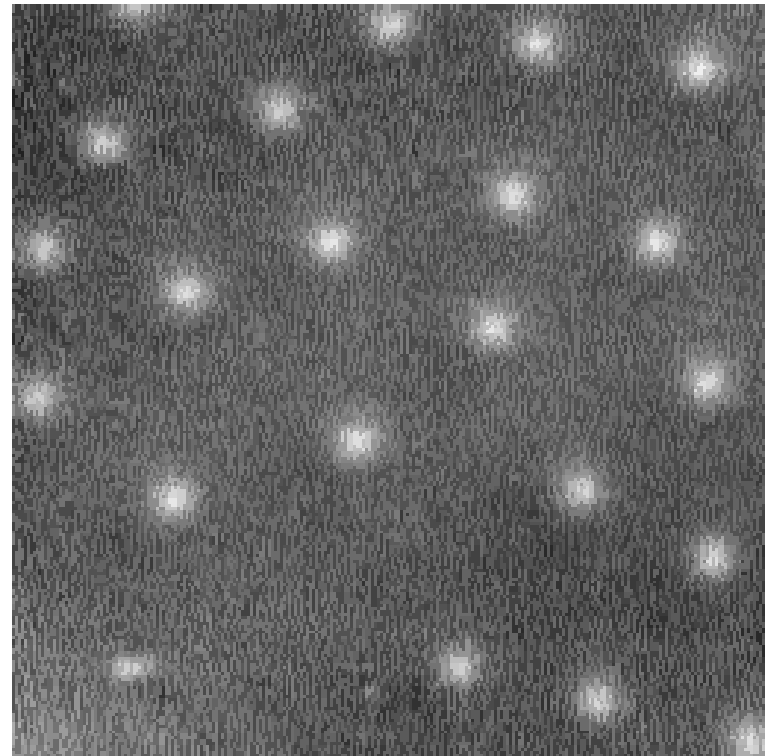
# Magnetic Forces

$$\mathbf{F}_{magnetic} = \mathbf{m}_{tip} \cdot \nabla \mathbf{H}_{sample}$$

Images stray field and thus very useful  
in the magnetic recording industry, but  
also in science.

Comprehensive review:  
Grutter, Mamin and Rugar, in  
'Scanning Tunneling Microscopy II'  
Springer, 1991

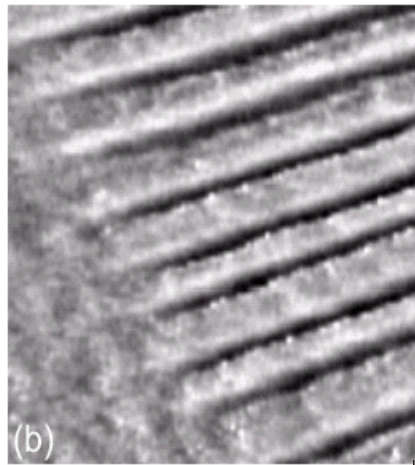
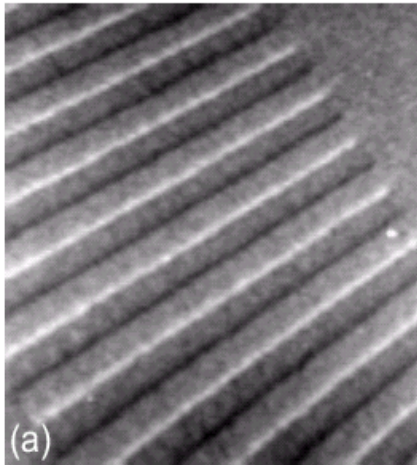
## Melting of flux lattice in Nb



Roseman & Grutter, unpublished

# Magnetic Force Microscopy

Tracks on



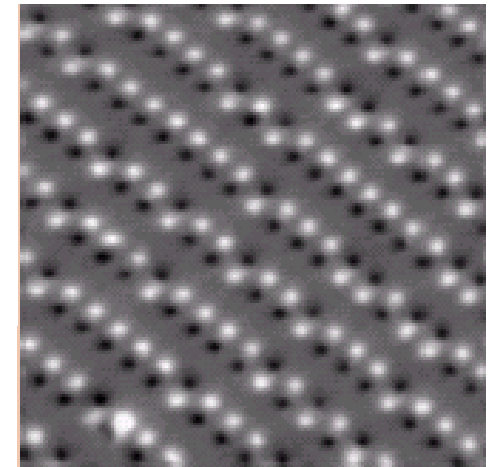
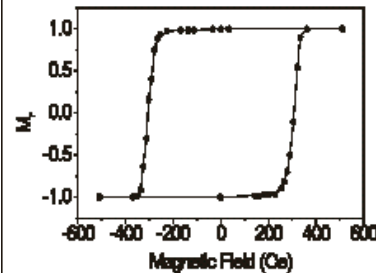
hard disk

floppy disk

image size 10 and 30 micrometers.

M. Roseman (McGill)

Magnetic reversal studies by MFM  
particles size 90 x 240 x 10 nm  
X. Zhu (McGill)



# Capillary forces (water layer)

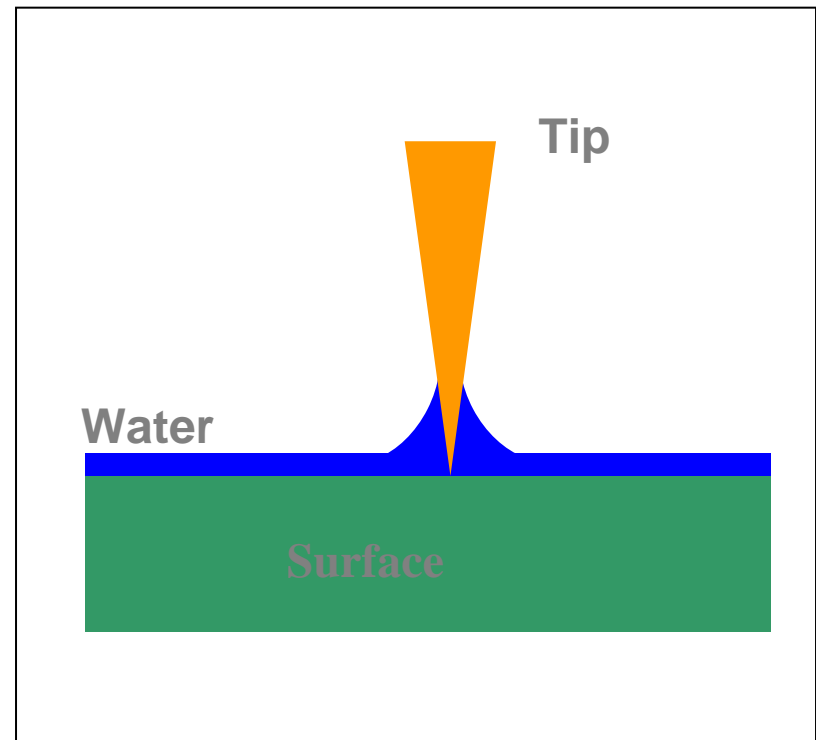
**Total force on cantilever**  
=  
**sum of ALL forces**

There is always a water layer on a surface in air!

$$F_{capillary} = 4\pi R \gamma \cos\theta$$

$\gamma$  ... surface tension, ~10-50 mJ/m<sup>2</sup>

$\theta$  ... contact angle

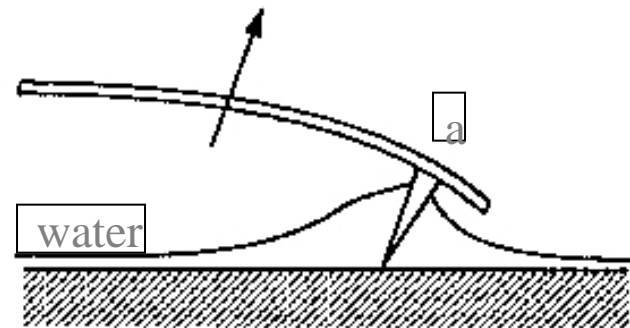
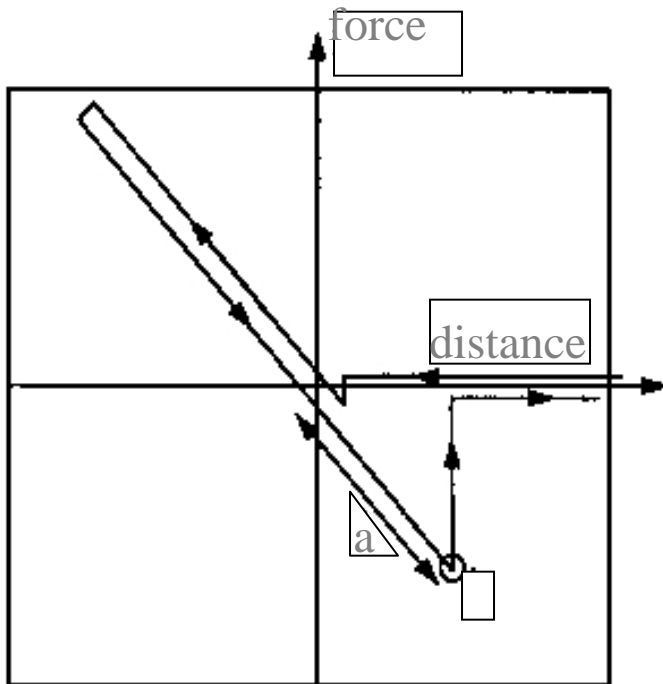


Can be **LARGE** (several 1-10 nN)

# Force Spectroscopy

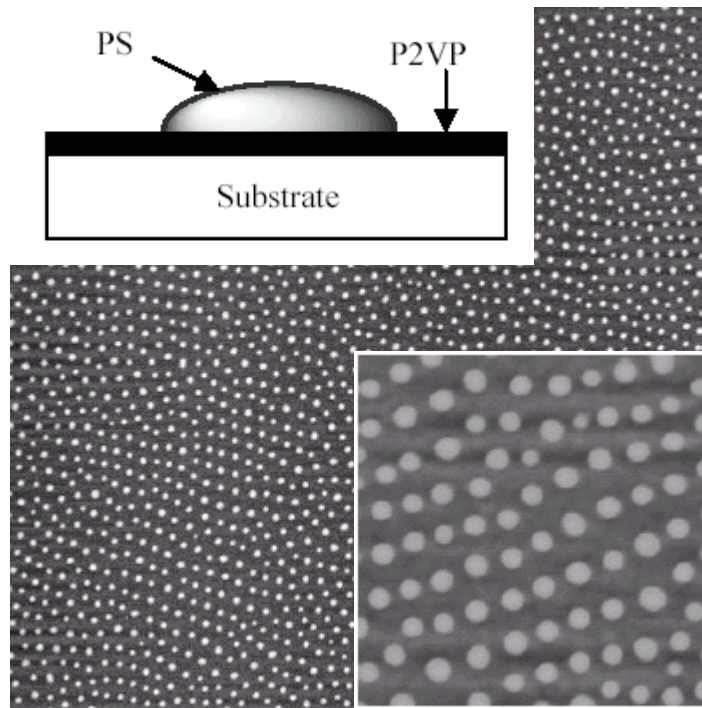
Snap in condition:  $k < F'$

For meaningful quantitative analysis,  $k >$  stiffness of molecule



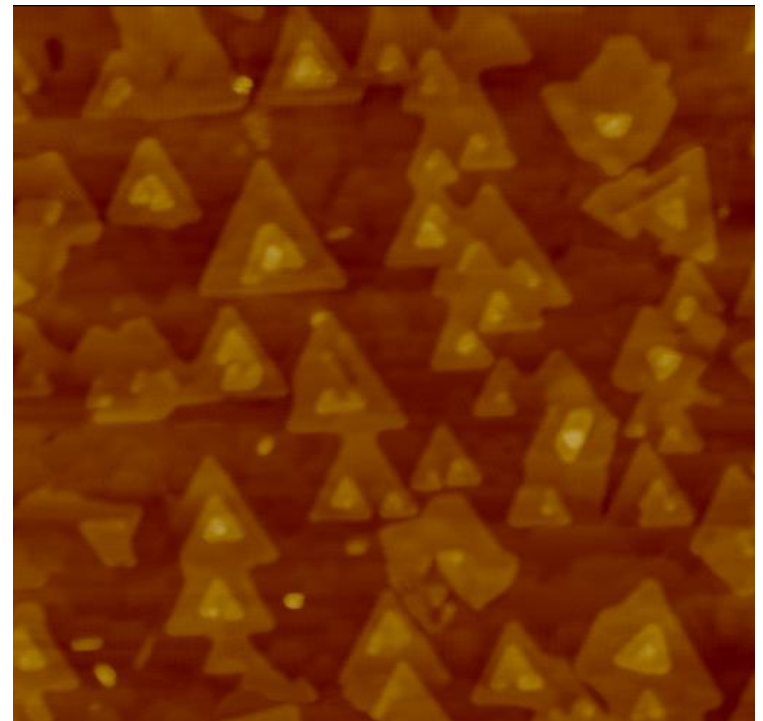
# Repulsive Contact Forces

**Diblock co-polymers used as self assembled etch mask**



Meli, Badia, Grutter, Lennox,  
Nano Letters **2**, 131 (2002)

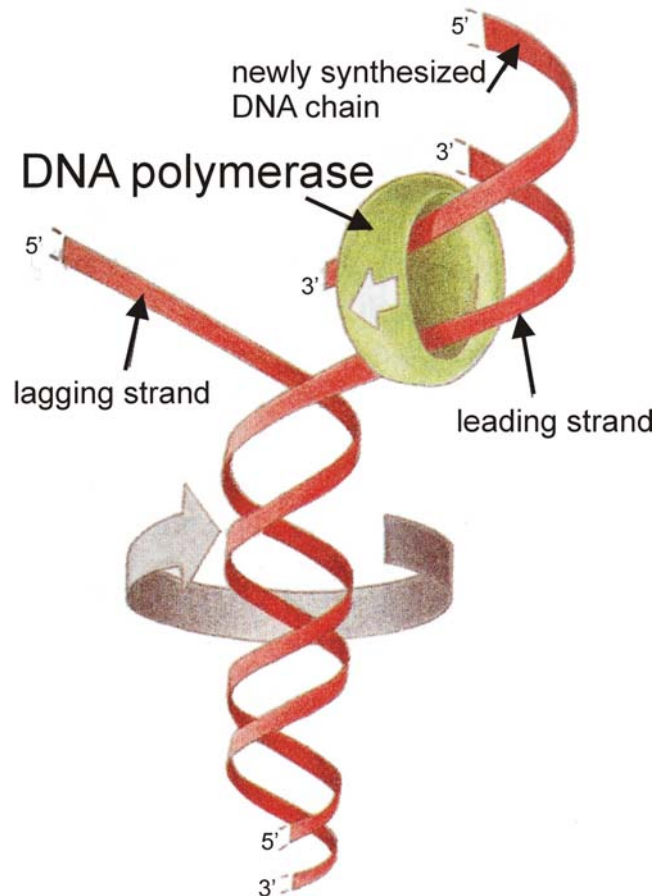
**Topological insulator Bi<sub>2</sub>Se<sub>3</sub> film**  
**Tapping mode**



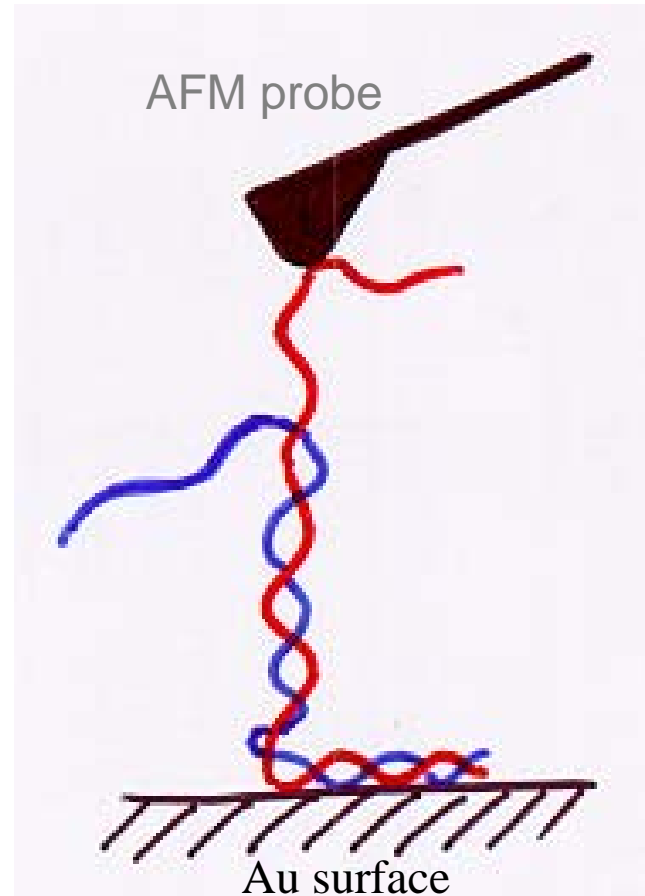
S. Yang et al. unpublished

# DNA “Unwinding”

Anselmetti, Smith *et. al.* **Single Mol.** 1 (2000) 1, 53-58



Nature - DNA replication,  
polymerization

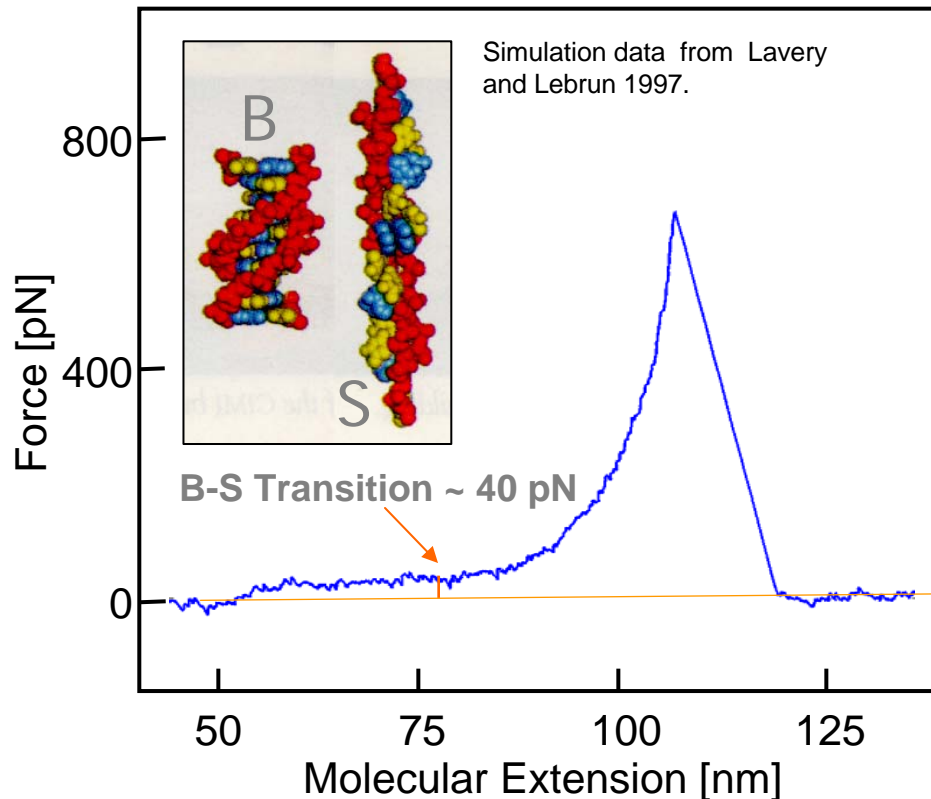


Experiment - AFM force  
spectroscopy

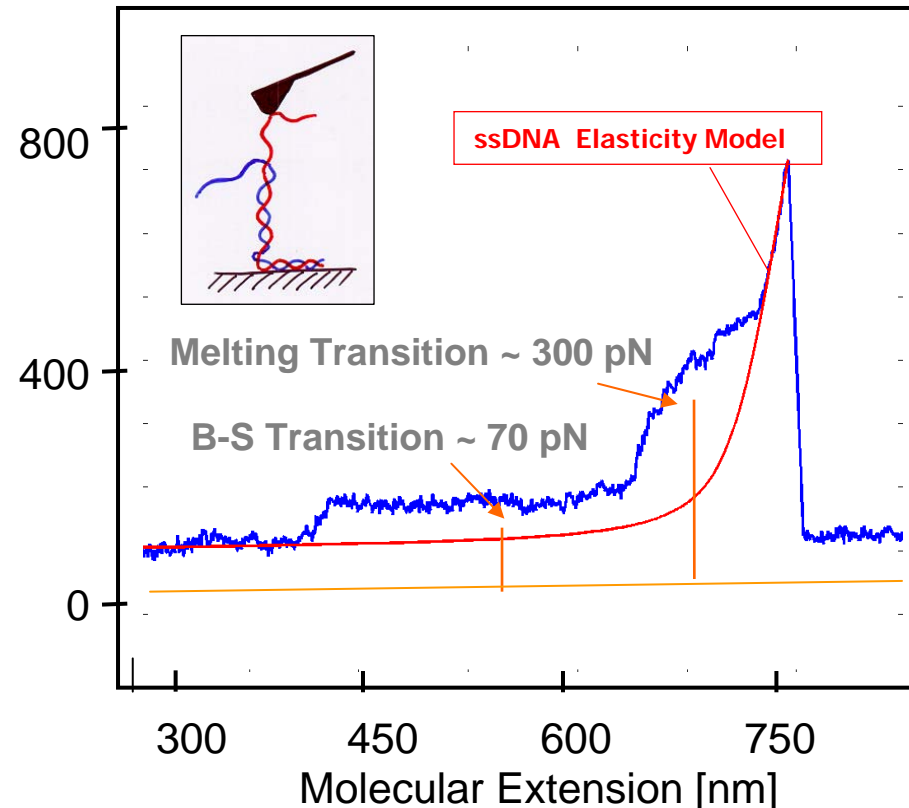
# DNA Structural Transitions

## AFM Force Spectroscopy in TRIS Buffer

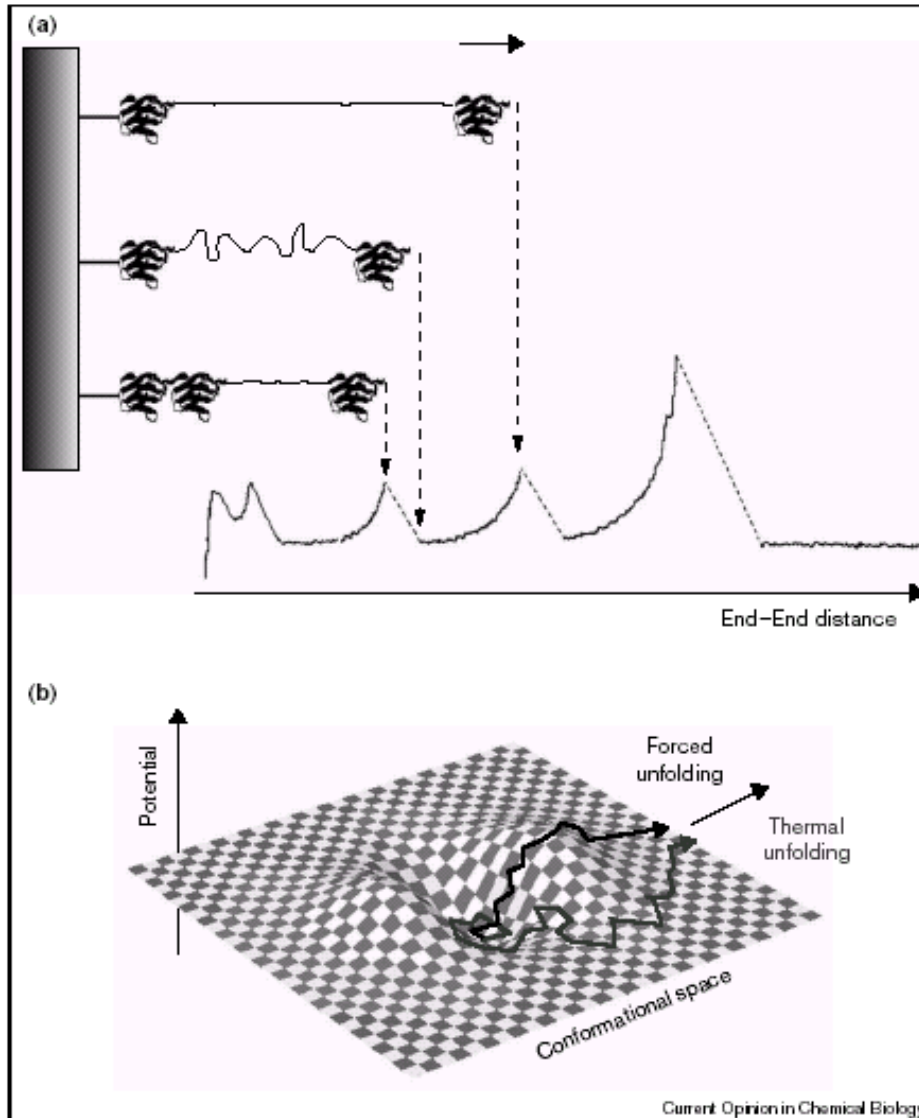
### Duplex poly(dA-dT)



### Duplex poly(dG-dC)



# $F(z)$ as a function of pulling speed



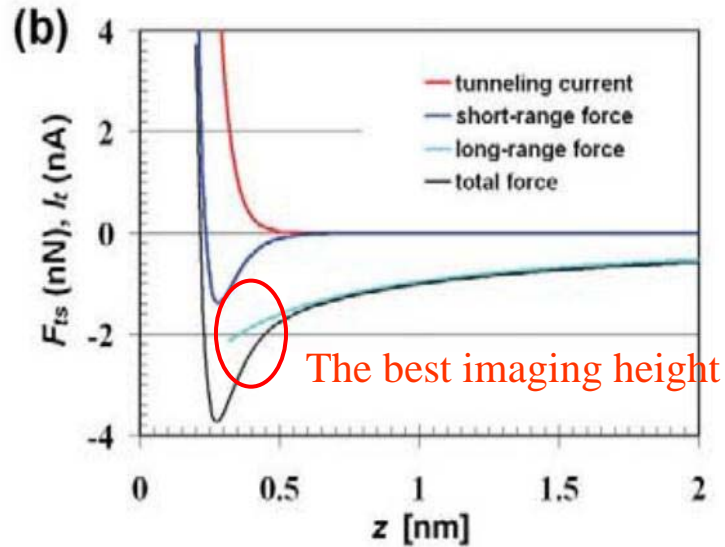
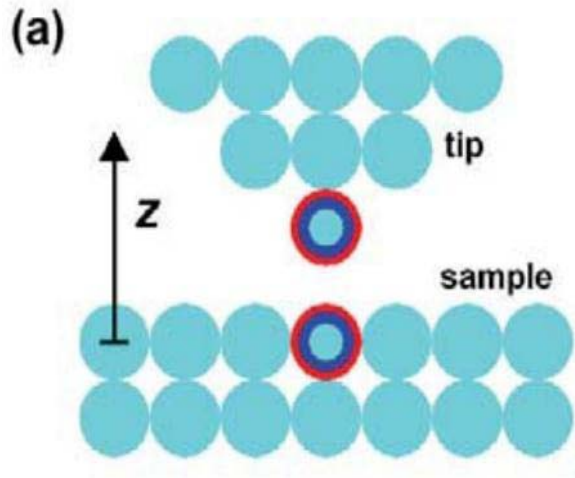
Allows the determination of energy barriers and thus is a direct measure of the energy landscape in conformational space.

Clausen-Schaumann et al., *Current Opinions in Chem. Biol.* **4**, 524 (2000)

Merkel et al., *Nature* **397**, (1999)

Evans, *Annu. Rev. Biophys. Biomol. Struct.*, **30**, 105 (2001)

# 接触式AFM的困难



$$K_{\text{cantilever}} = 1 \text{ N/m}$$
$$K_{\text{ts}} = 10 \text{ N/m}$$

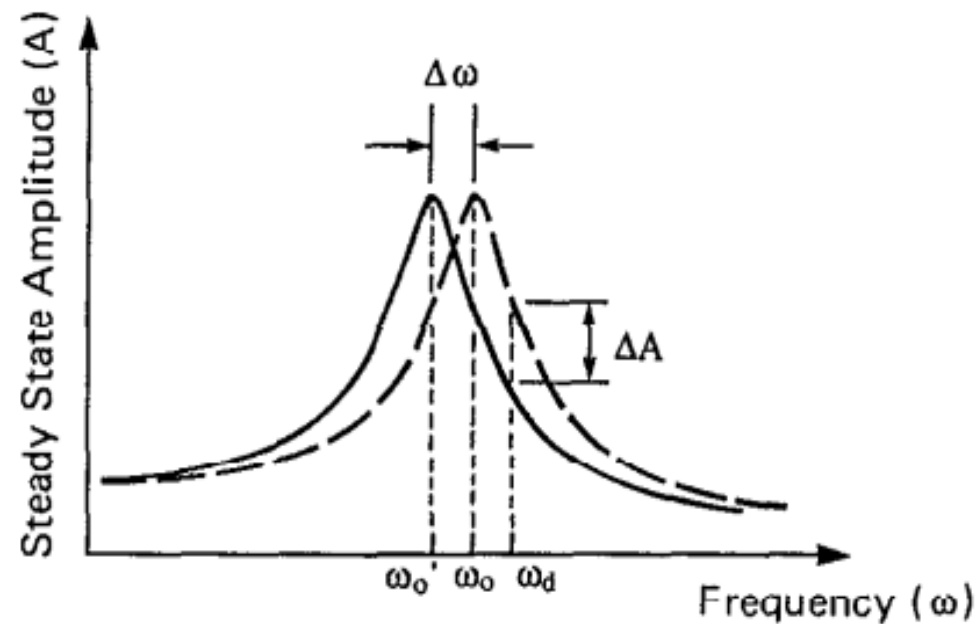
斥力区：针尖与多个原子作用，横向分辨率降低。

引力区：当针尖逐渐靠近样品到一定临界高度，由于悬梁臂的回复力不能抵抗原子的吸引力，针尖会突然向下发生不可控的高度跳变（jump to contact），使得悬梁臂很难在引力区稳定工作。

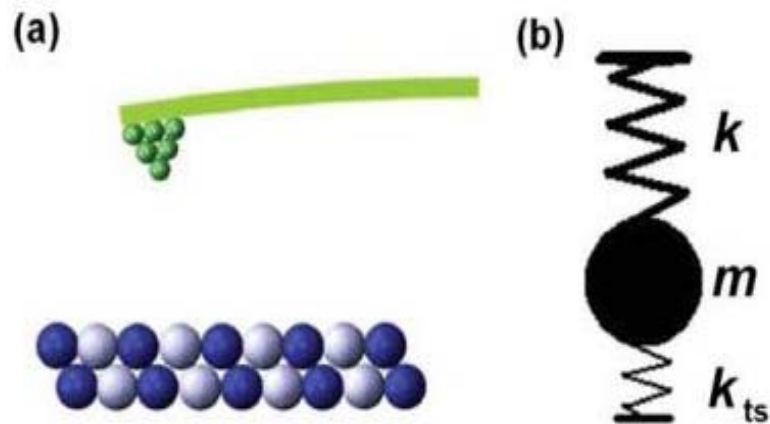
High force resolution → small stiffness → jump to contact

# Noncontact AFM

AM模式下悬梁臂受力后  
振幅改变和频率改变的关系



## Simple model for NC-AFM



$$f = \sqrt{\frac{k + k_{ts}}{m}}$$

$$\Delta f = \frac{f_0}{2k} k_{ts}$$

# Non-contact AFM

## Dynamic mode

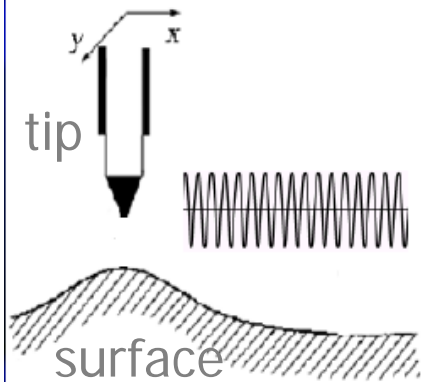
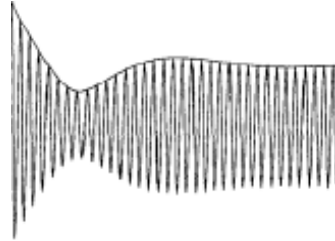
### AM-AFM

#### Tapping mode

Image signal: amplitude

Bandwidth:  $f_0/2Q$

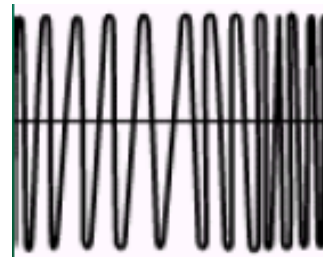
高信噪比, 高Q, 慢响应, 热漂移



### FM-AFM

Image signal: frequency shift

Bandwidth: independent of Q → Fast scan



FM & AM

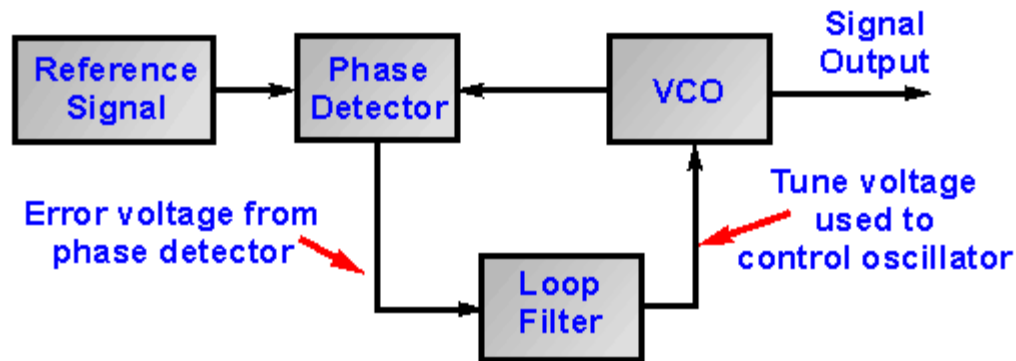
*The role of Q-factor:*

*proportional to the sensitivity of image signal,  
inversely proportional to thermal noise.*

# FM-AFM 工作原理

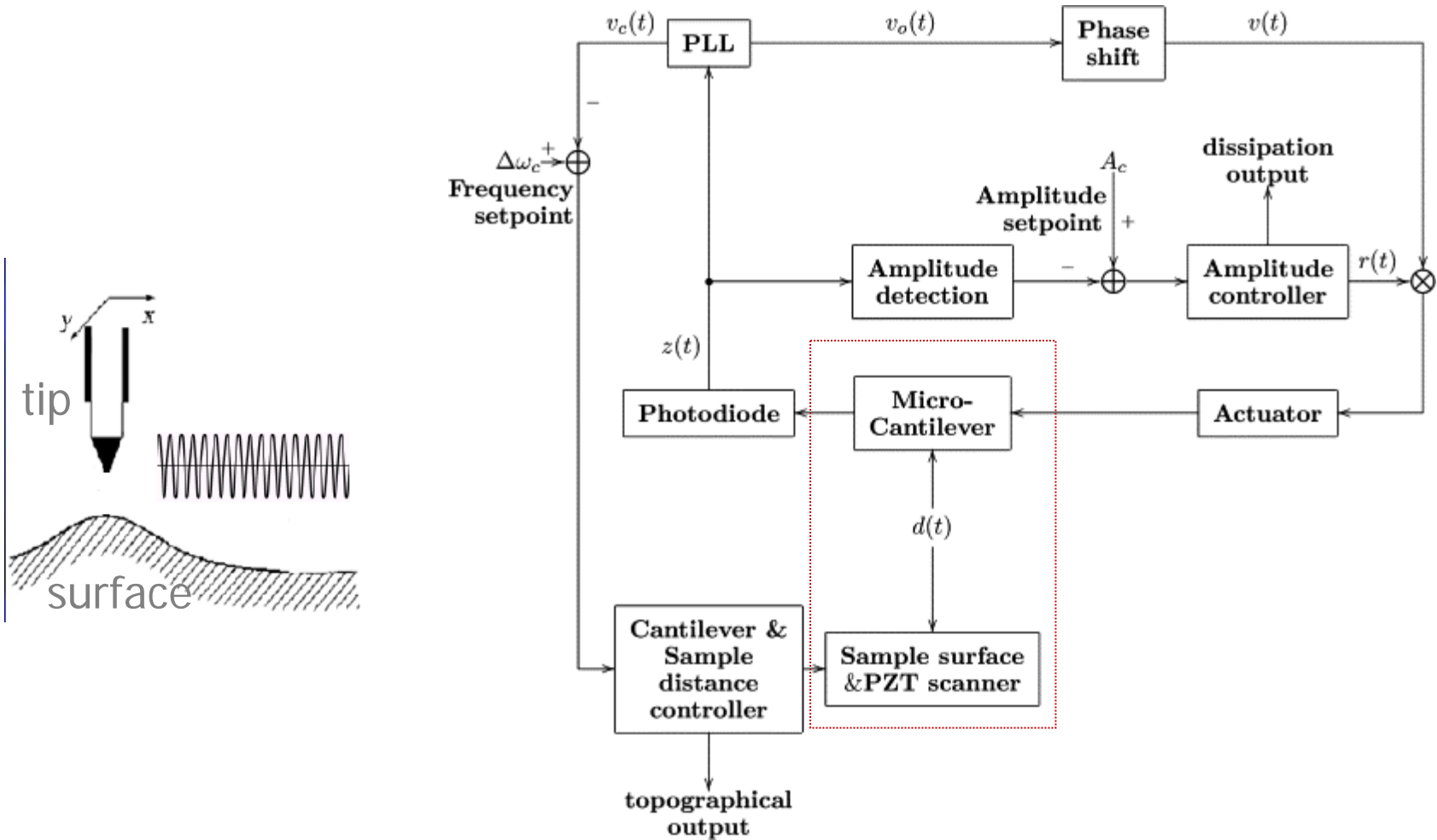
1. 使用一定频率的电压信号 $u(t)$ 激励AFM探针以一定振幅和频率振荡。
2. 测量探针振荡的振幅和频率（压电效应）
3. 使用Automatic Gain Control loop (AGC) 控制探针振幅恒定
4. 使用Automatic Distance Control loop (ADC), 控制针尖高度，使得针尖的振荡频率维持恒定。

# Phase lock loop

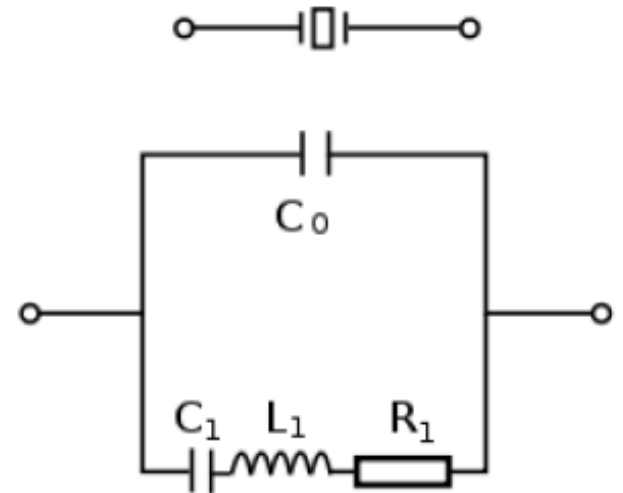
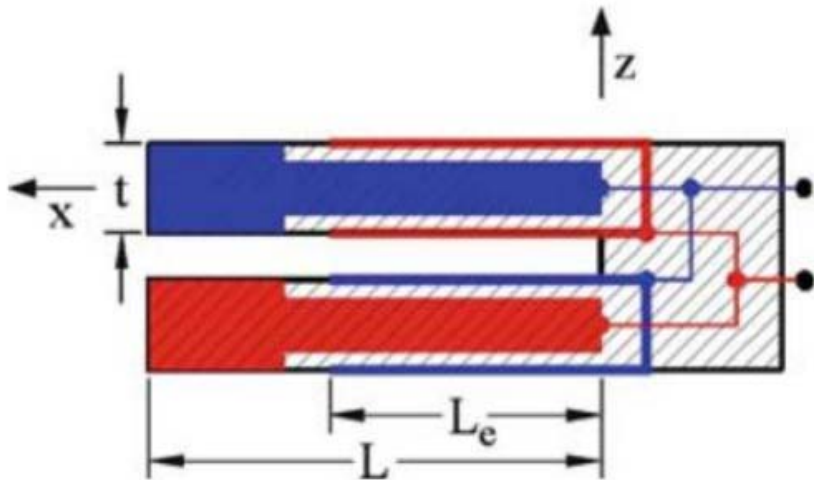
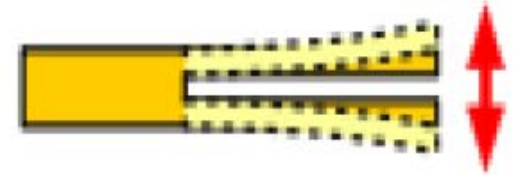
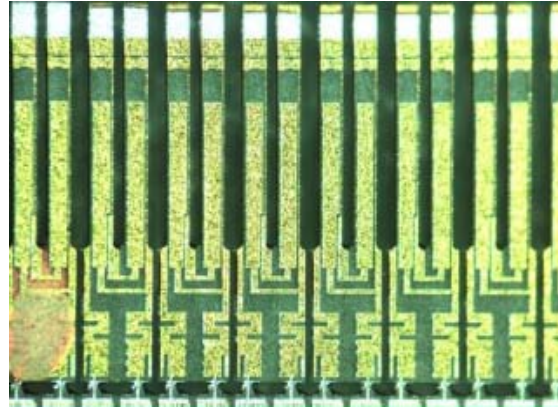
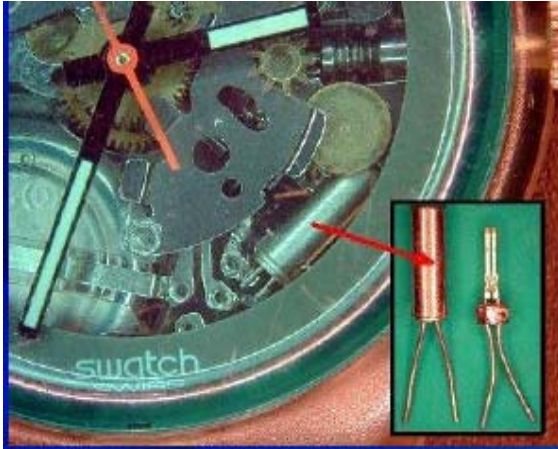


The PLL is a closed loop control system composed of a phase detector (**PD**), a low-pass filter (**LF**) and a voltage controlled oscillator (**VCO**), that synchronizes the local VCO output to the incoming signal  $z(t)$

## Block diagram of FM-AFM control system.

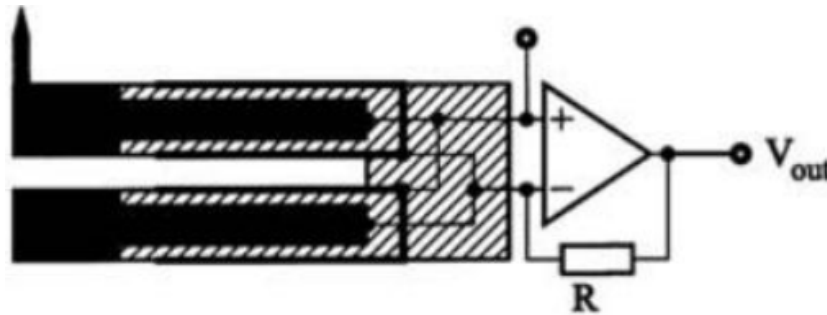


# Tuning fork



Advantages: large stiffness  $10^3 \sim 10^4$   
much smaller thermal drift  
high Q value  $10^5$

# Q plus



**Symmetry broken** → **Dramatic decrease of Q value**

**Q plus: fix the prong without tip onto a rigid substrate firmly**

**Advantages:**

**High Q value**

**Very small thermal drift of  $f_0$**

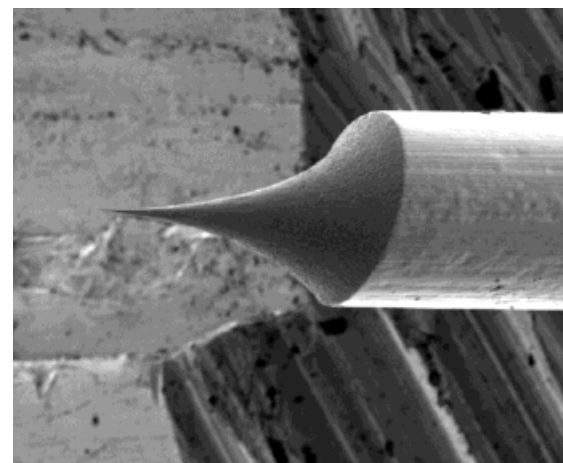
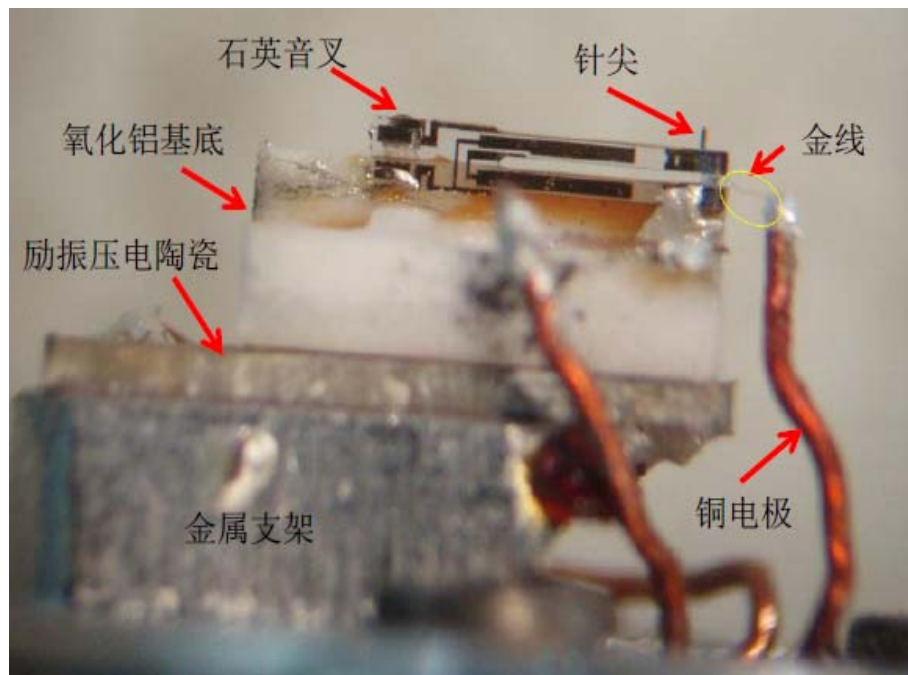
**Compact configuration**

**Low temperature compatible**



**$K=1800\text{N/m}$ , contribution from short range force is detected by small A**

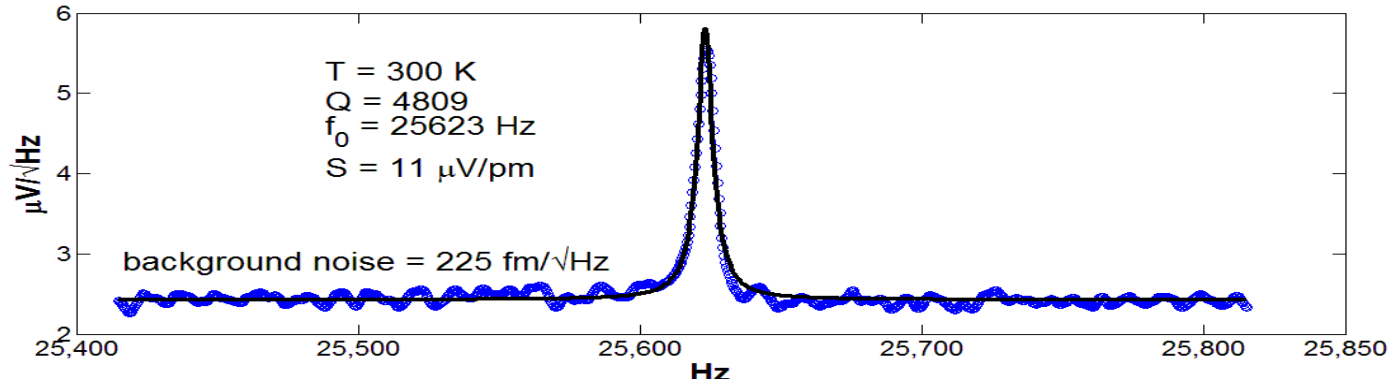
# Q-plus sensor



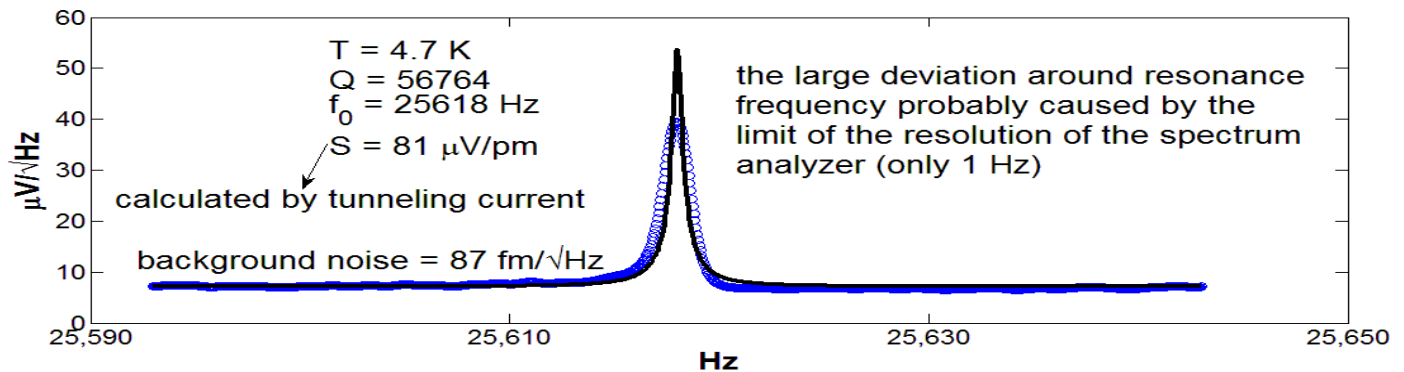
温度条件\与文献比较	自制 Q-plus sensor	文献报道 <sup>[20, 50]</sup>
室温	2000~6000	“a few thousand”
液氮	8000~20000	
液氦	10000~140000	50000

# Noise level

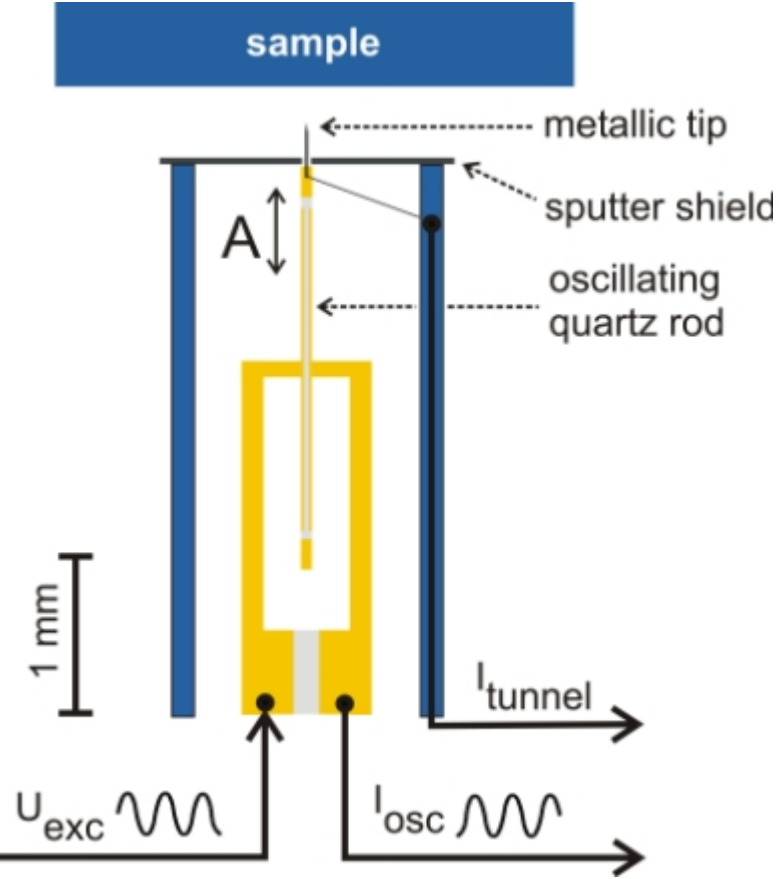
RT



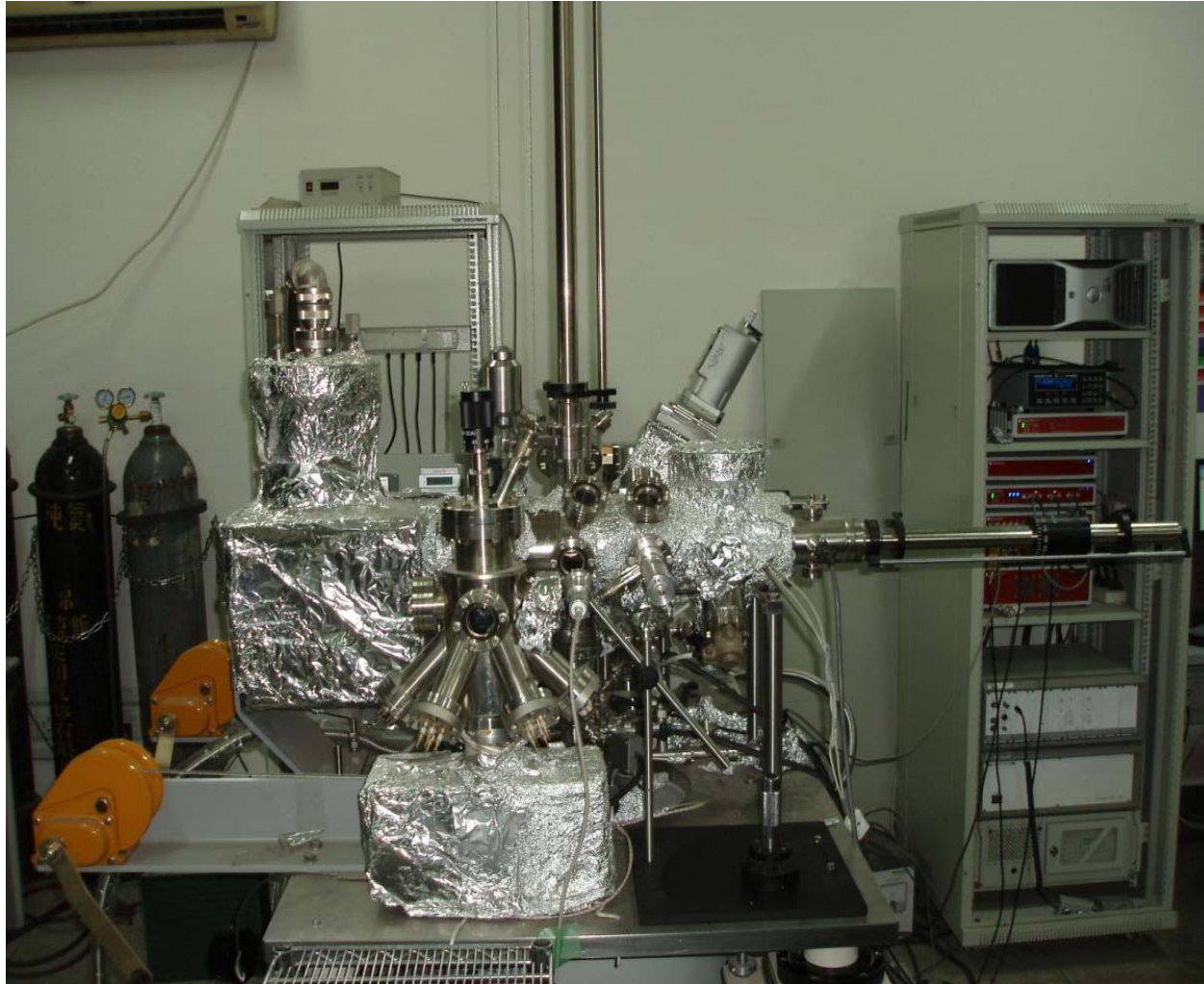
4.7 K



# Kolibri Sensor



# Instrument



*USM1500 STM/AFM*

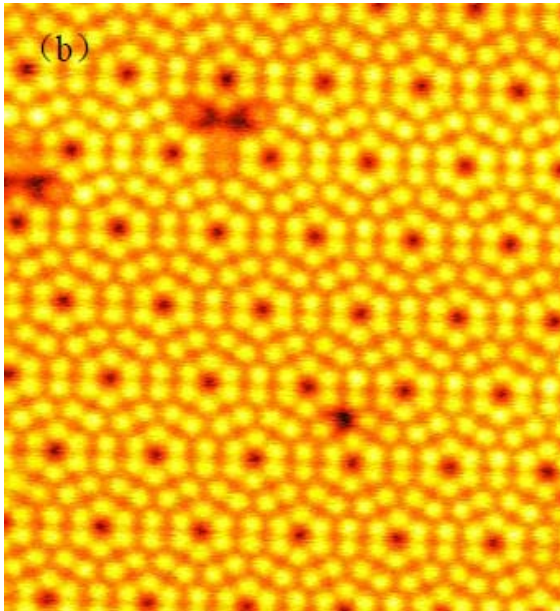
*Nanonis (SPECS) controller*

*Magnetic field: 8T*

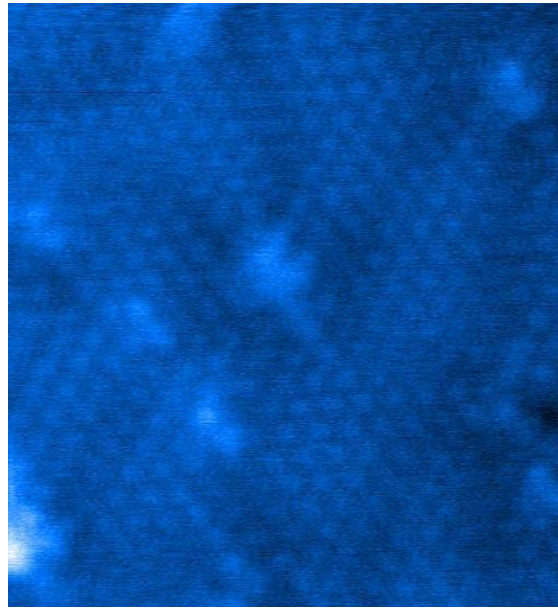
*Base temperature: 2K*

*Vacuum:  $5 \times 10^{-11}$  Torr*

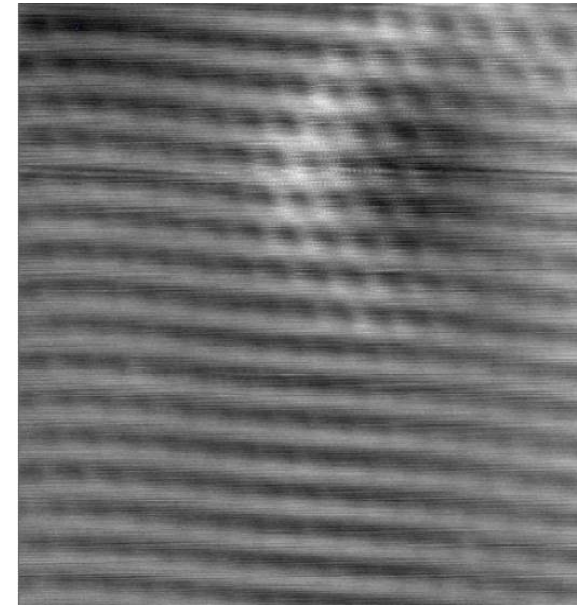
# AFM gallery



*Si(111)-7 × 7,  
10 nm × 10 nm,  
df = -3Hz,  
Amp = 90 pm,  
Bias = 1.2 V,  
77 K*



*Pb SIC phase,  
8 nm × 8 nm,  
df = -4.1 Hz,  
Amp = 350  
pm,  
Bias = 470  
mV,  
77 K*



*Pb(111),  
5 nm × 5 nm,  
df = -13.7Hz,  
Amp = 350 pm,  
Bias = 34 mV,  
4.3 K*

# Figure 3: Pentacene imaged with STM and NC-AFM.

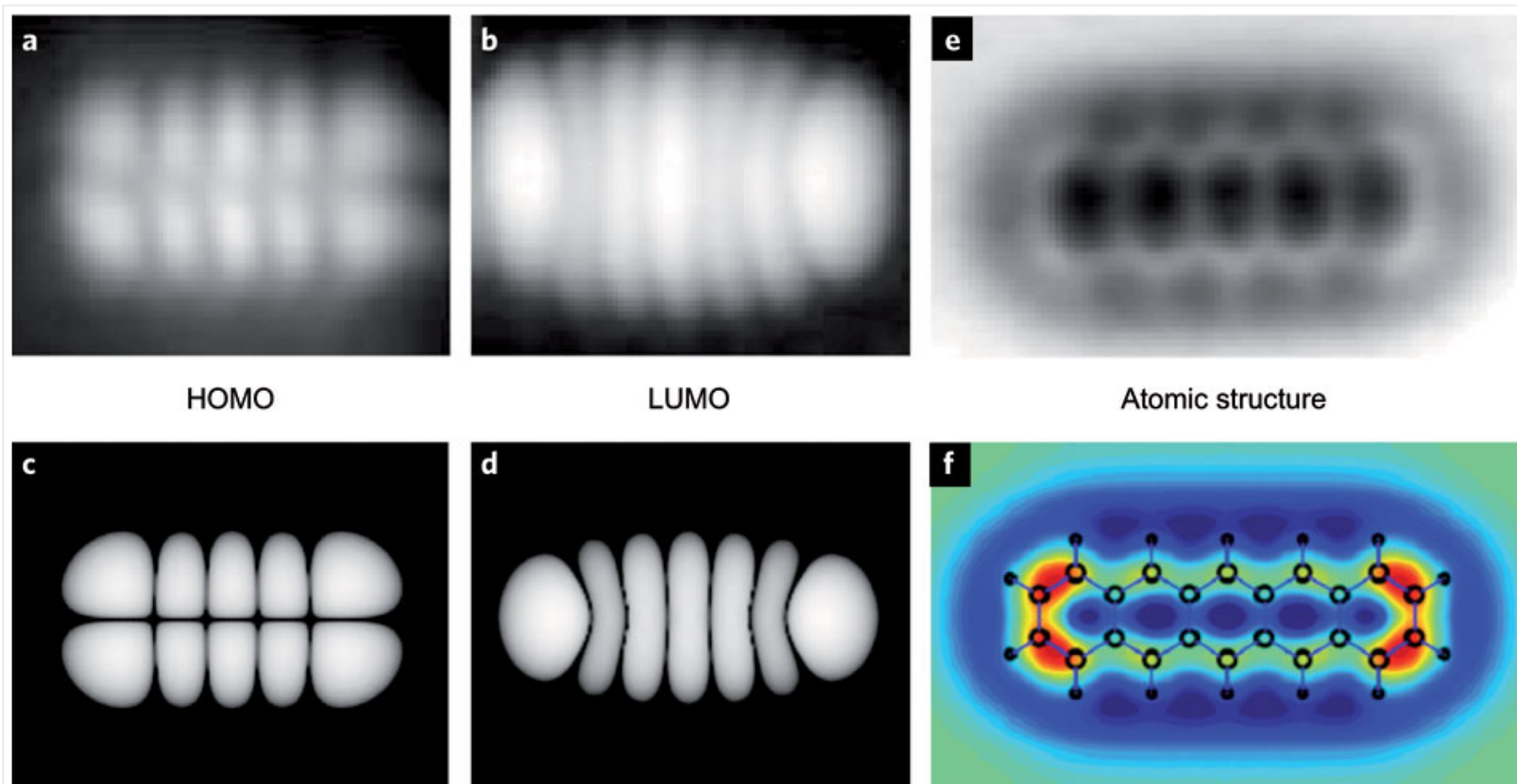
From

[Recent advances in submolecular resolution with scanning probe microscopy](#)

Leo Gross

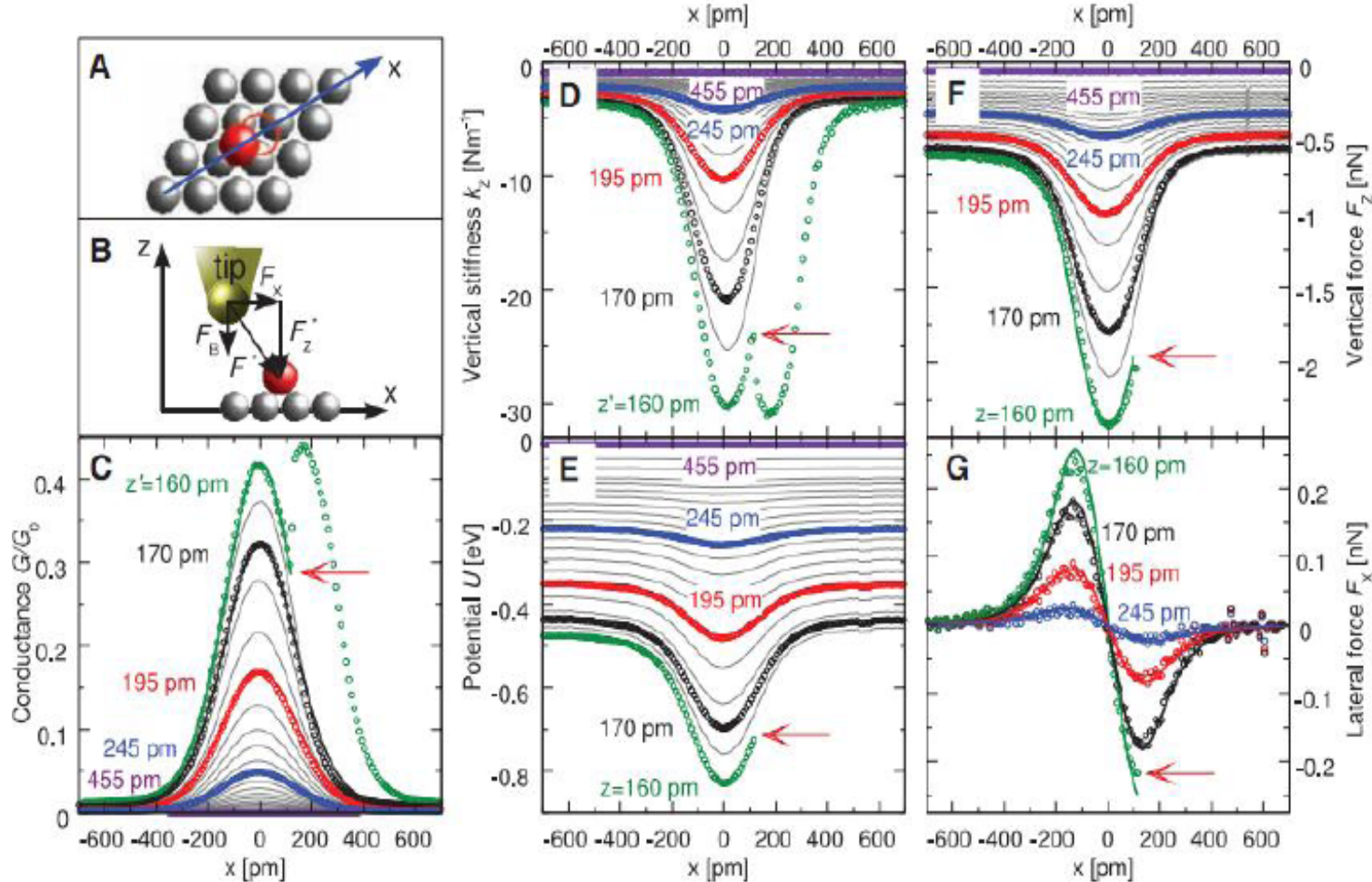
*Nature Chemistry* **3**, 273–278 (2011) | doi:10.1038/nchem.1008

Published online 24 March 2011 | Corrected online 08 April 2011



**a,b**, Molecular orbital images of pentacene on two monolayer NaCl on Cu(111) obtained by STM using a pentacene-terminated tip. Image size 2.5 nm × 2.0 nm; constant current. The HOMO (**a**) was imaged by setting the sample voltage to the first resonance at negative bias at  $V = -2.5$  V, thus tunnelling out of the molecular orbital. The LUMO (**b**) is imaged by electrons tunnelling from the tip into the orbital at positive bias  $V = +1.7$  V. **c,d**, Contours of constant orbital probability distribution of the HOMO (**c**) and LUMO (**d**) of the free pentacene molecule obtained by DFT. **e**, NC-AFM image of pentacene on two monolayer NaCl on Cu(111) obtained using a CO-functionalized tip. Image size 2.2 nm × 1.4 nm; oscillation amplitude  $A = 0.07$  nm. **f**, Computed frequency shift for an intermolecular distance  $d = 0.475$  nm between CO and pentacene. Reprinted with permission from: **a-d**, ref. 9, © 2005 APS; **e**, ref. 1, © 2009 AAAS; **f**, ref. 34, © 2010 IOP.

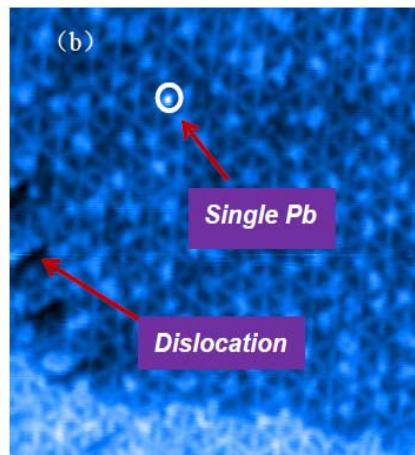
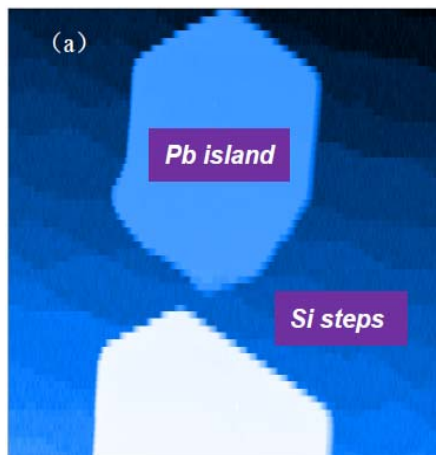
# 单个Pb原子扩散势的测量



不同高度扫描，垂直方向力在不同高度分布  
积分，不同高度势能分布  
水平方向微分，水平力  
跳跃点对应水平力临界值

*Science 319, 1066(2008)*

# 单个铅原子扩散势的测量



Pb island + Pb atom

$$\Delta = E_{fcc} - E_{hcp}$$

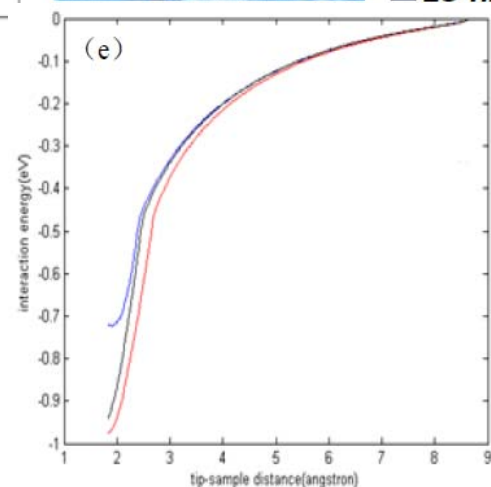
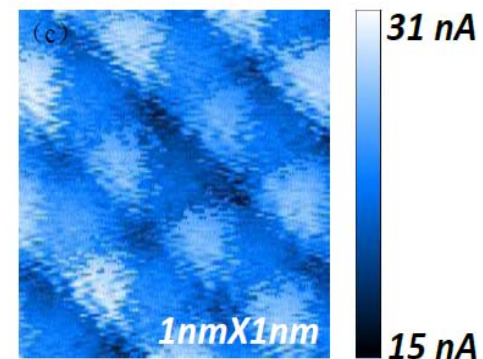
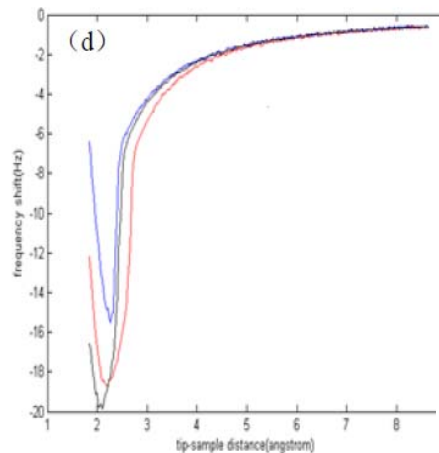
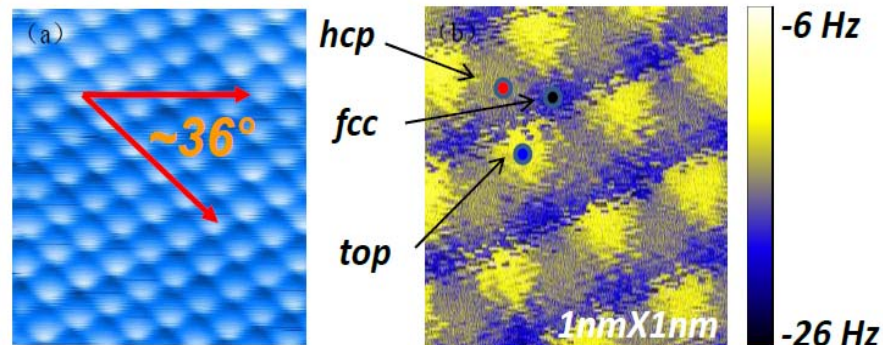
STM, 确定晶格取向

AFM, 拖动增原子, 针尖在临界高度之下

df-Z curve

根据能量与df关系, 计算出各点势能

$$\Delta = 38 \text{ meV}$$



鉴相器:通常由模拟乘法器组成也可以由数字电路组成

$$\begin{aligned}U_d &= A_d U_i(t) U_o(t) \\ &= A_d \sqrt{2} \cos[\omega_o(t)t + \phi_o(t)] \sqrt{2} \sin[\omega_i(t)t + \phi_i(t)] \\ &= A_d \sin\{[\omega_o(t)t + \phi_o(t)] + [\omega_i(t)t + \phi_i(t)]\} \\ &\quad + A_d \sin\{[\omega_o(t)t + \phi_o(t)] - [\omega_i(t)t + \phi_i(t)]\}\end{aligned}$$

低通滤波器:

$$U_c = A_d \sin\{[\omega_o(t)t + \phi_o(t)] - [\omega_i(t)t + \phi_i(t)]\}$$

压控振荡器: 压控特性为线性

$$\omega_o(t) = \omega_r + A_o U_c$$

初始的  $\omega_0 = \omega_r$ ,  $\omega_r$ 指环路无输入信号、环路对VCO无控制作用时VCO的振荡频率, 称为电路的固有振荡频率或自由振荡频率。

# 锁相环如何实现锁相

瞬时相位差  $\phi_d = [\omega_o(t)t + \phi_o(t)] - [\omega_i(t)t + \phi_i(t)]$

$$d\phi_d/dt = d[\omega_o(t)t - \omega_i(t)t]/dt + d[\phi_o(t) - \phi_i(t)]/dt$$

(a) 如果上式等于零,

$$\omega_o(t) - \omega_i(t) = 0 \quad \phi_o(t) - \phi_i(t) = c$$

锁相环进入相位锁定的状态, 此时输出和输入信号的频率相等、相位差保持恒定不变的状态,  $u_c$  的直流分量为恒定值。

(b) 当不等于零时,  $\omega_o(t) - \omega_i(t) \neq 0$ ,

$$|\Delta\omega_i| = \omega_i(t) - \omega_o(t) \quad \text{称为捕捉带}$$

若  $\Delta\omega_i$  很大, LPF 无  $u_c$  输出,  $\omega_o(t) = \omega_r$ 。——失锁。

若  $\Delta\omega$  很小, LPF 产生  $u_c$  输出,  $\omega_o(t) = \omega_r + A_o u_c$ ,  $\omega_r$  上下按正弦规律摆动。一旦能够摆动到  $\omega_i(t)$  并符合正确的相位关系时, 环路锁定, PD 的输出  $u_d$  经 LPF 后的直流分量保持不变