Scanning Probe Microscopy – the Science of Localized Probes

原子力探针显微术基础及其进展

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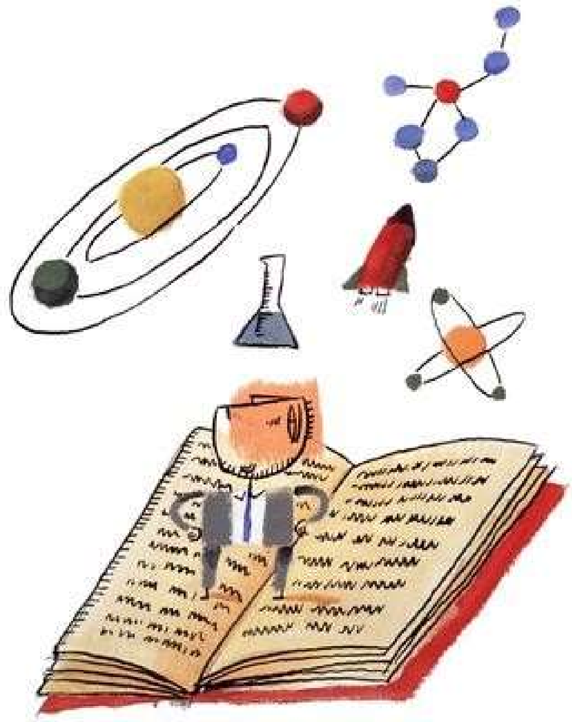
纳米，纳米科学与技术

Nano-science & Nano-technology

研究在纳米尺度上物质呈现出的与宏观块体材料不同的物理、化学、力学、生物效应等。

- 微电子技术的进步
- 显微分析技术的发展
- 纳米材料与纳米结构



纳米科技的诞生

- 显微分析技术的发展

透射电子显微镜（1986年）

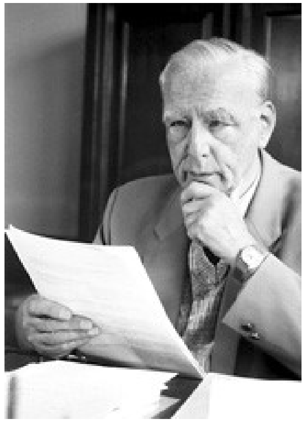
扫描隧道显微镜（1986年）

超高分辨光学显微镜（2014年）

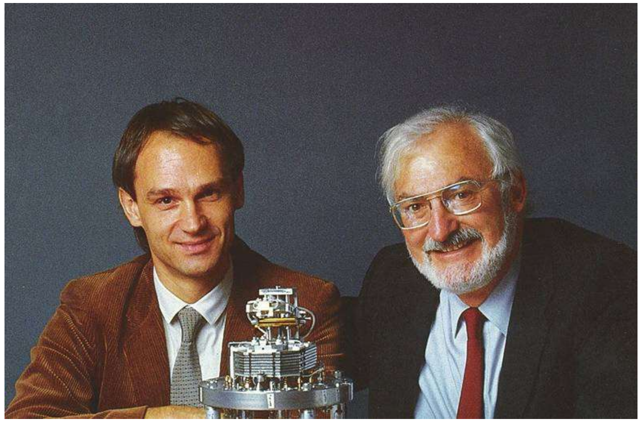
生物冷冻电子显微镜（2017年）

Major events in the history of science are called scientific revolution. There are two kinds of scientific revolutions, those driven by new concepts and those driven by new tools.

------- Freeman Dyson



Ernst Ruska



Gerd Binnig Heinrich Rohrer

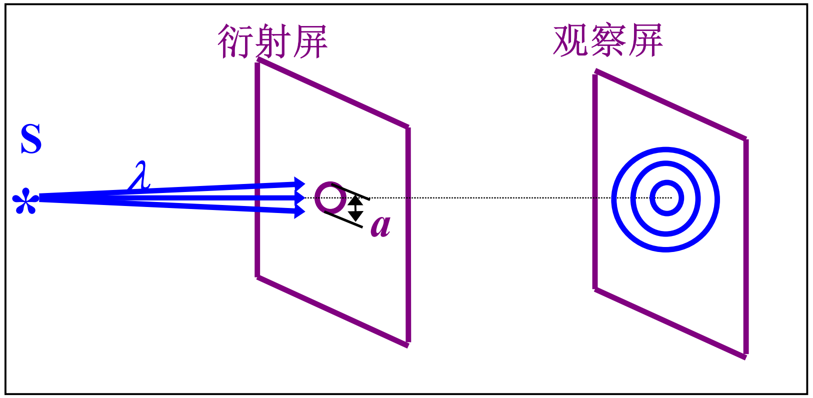
Eric Betzig

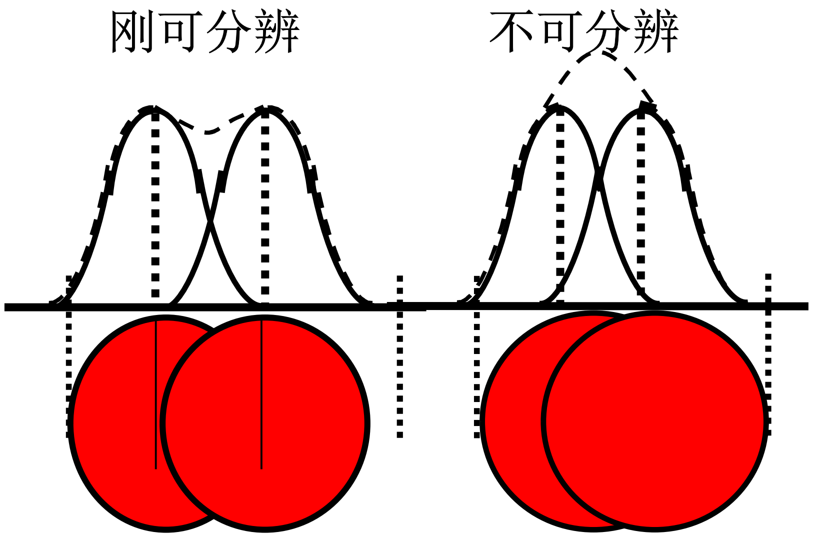
Stefan W. Hell

William E. Moerner

光学显微镜：远场探测

衍射效应





最小分辨距离：阿贝公式

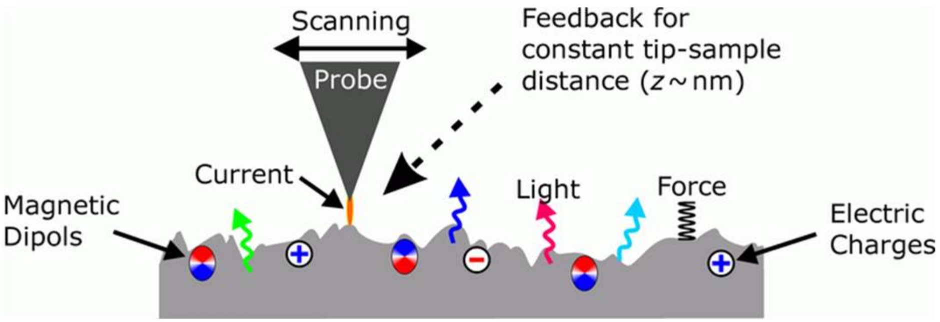
$$r \geq \frac{1.22\lambda}{2n \cdot \sin\theta}$$

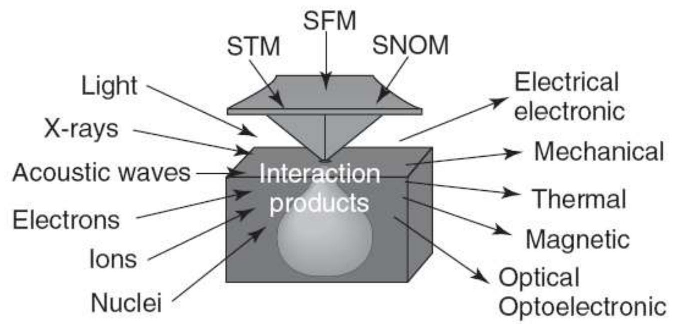
r~0.2um （3000倍）

扫描探针显微术：核心概念

SPM：通过建立扫描探针与样品之间的不同相互作用类型，来研究样品的不同特性。

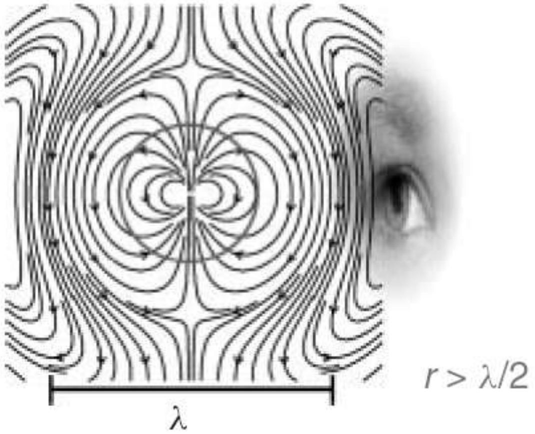
核心：扫描整个样品表面以建立某种图像的探针。



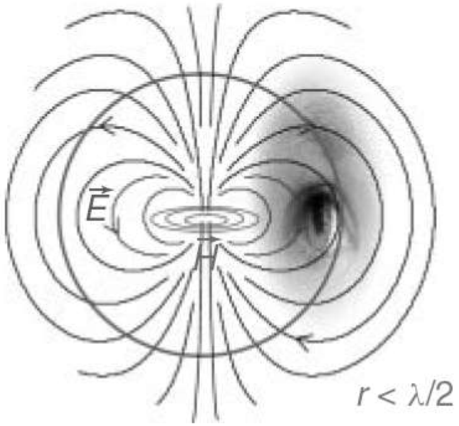


扫描+探针+距离+样品+相互作用+外部激励/环境等

近场相互作用



振荡偶极：远场

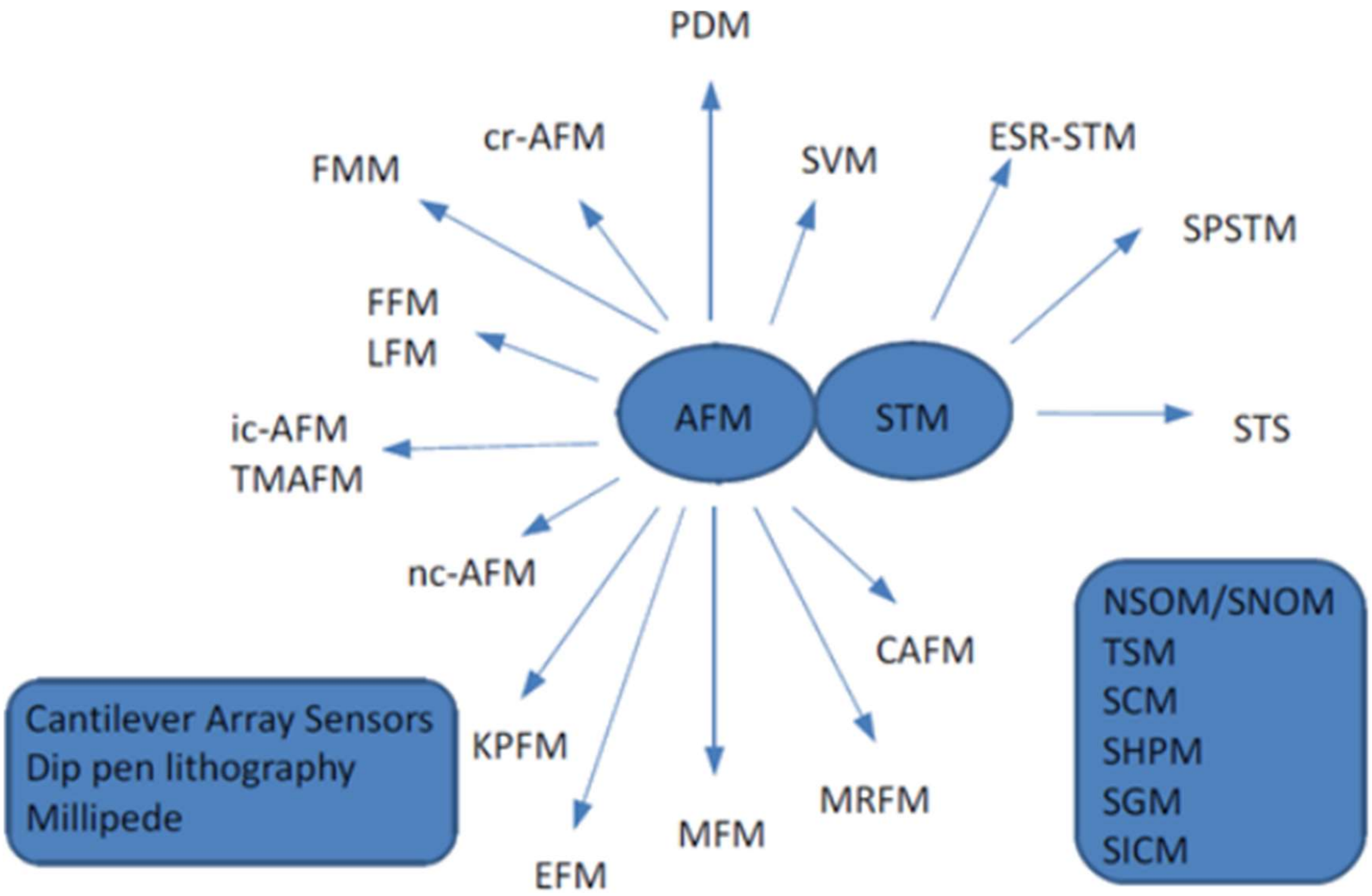


振荡偶极：近场

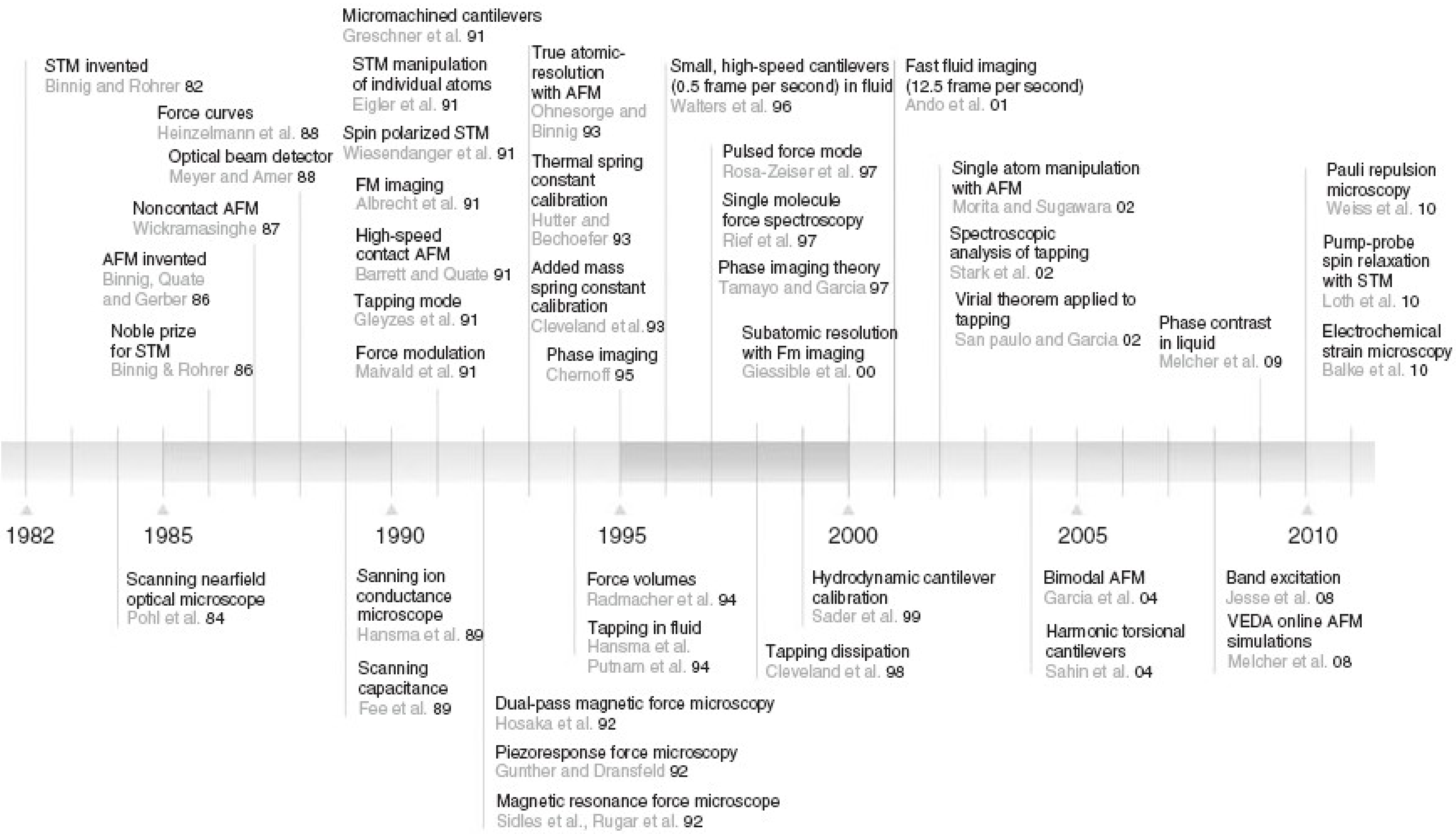
	Near-field			
	Electrostatic fields (ionic crystals)	Optical surface evanescent waves	Mean square fluctuating near-fields	Electronic wavefunction (metal)
Decay law	exponential $\exp(-R\eta)$	exponential $\exp(-R\eta)$	R^{-n} $(n = 3, 4, \ldots)$	exponential $\exp(-R\eta)$
Typical decay length η^{-1} (Å)	≃0.6	≃2000	≃1000	≃0.45

	Surface near-field			
	Electrostatic near-field $\boldsymbol{E}$	Optical surface evanescent field $\{\boldsymbol{E}; \boldsymbol{B}\}$	Mean square fluctuating near-fields $\mathcal{E}$	Electronic wave function at metal $\psi(\boldsymbol{r})$
Physical detected quantity	Force	Photon energy flow	Force	Electric current
Magnitude order	nN	$\sim 10^9$ Ph s^{-1}	nN	nA
Experimental device	AFM	SNOM PSTM/STOM	Noncontact AFM	STM

扫描探针显微术家族

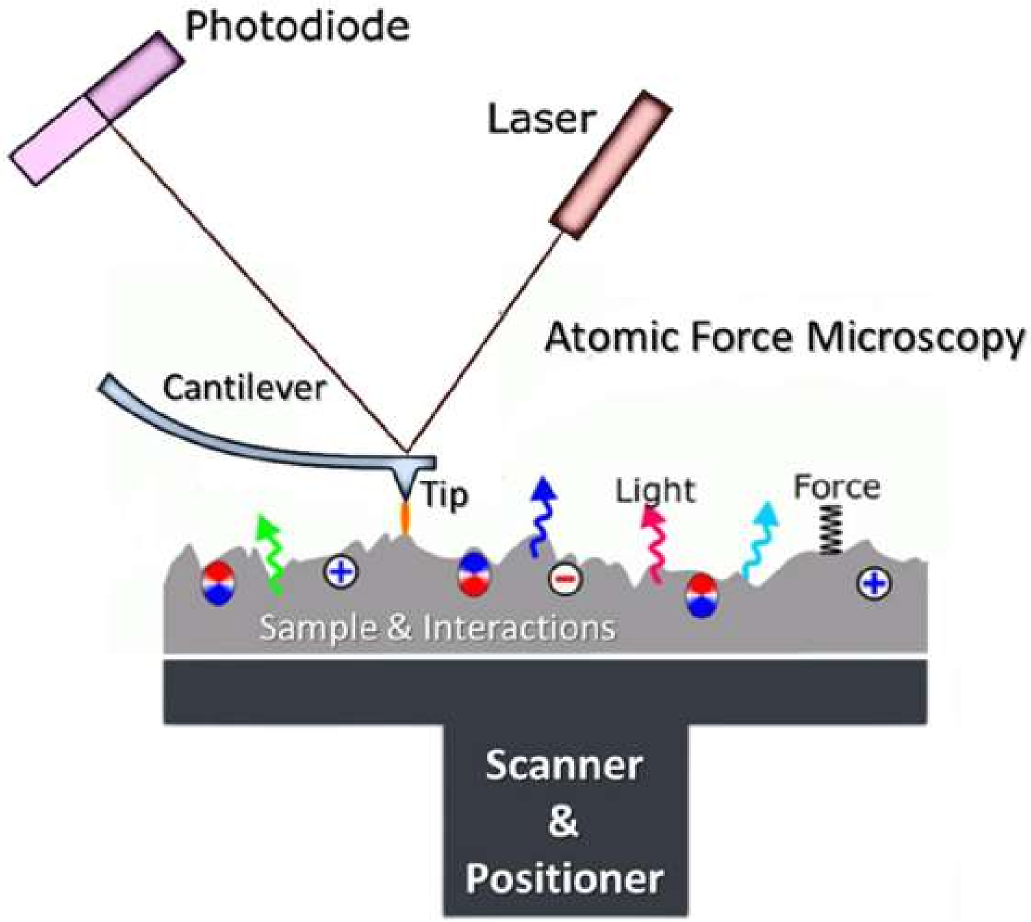

PDM
cr-AFM
FMM
SVM
ESR-STM
SPSTM
FFM
LFM
AFM
STM
STS
ic-AFM
TMAFM
nc-AFM
CAFM
KPFM
MRFM
MFM
EFM
Cantilever Array Sensors
Dip pen lithography
Millipede
NSOM/SNOM
TSM
SCM
SHPM
SGM
SICM

扫描探针显微术：不断发展



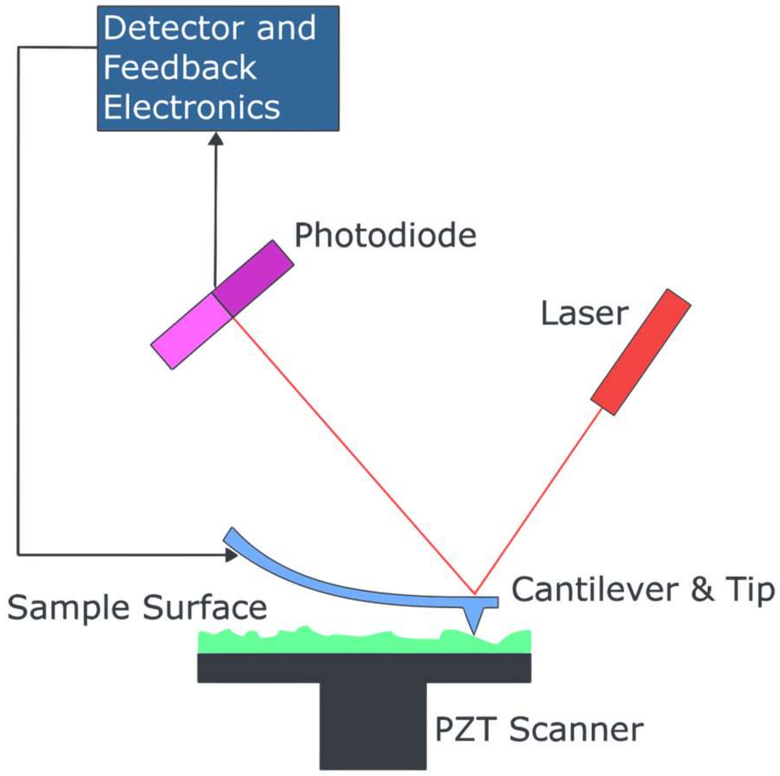
SPM timeline

原子力探针显微学

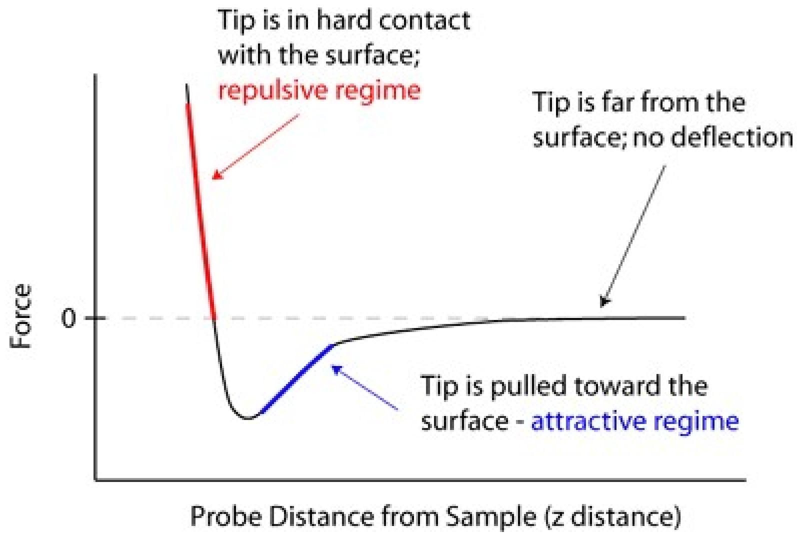


- 1 基本理论基础、仪器及相互作用
- 2 核心基础工作模式及其进展
- 3 功能化原子力探针显微术

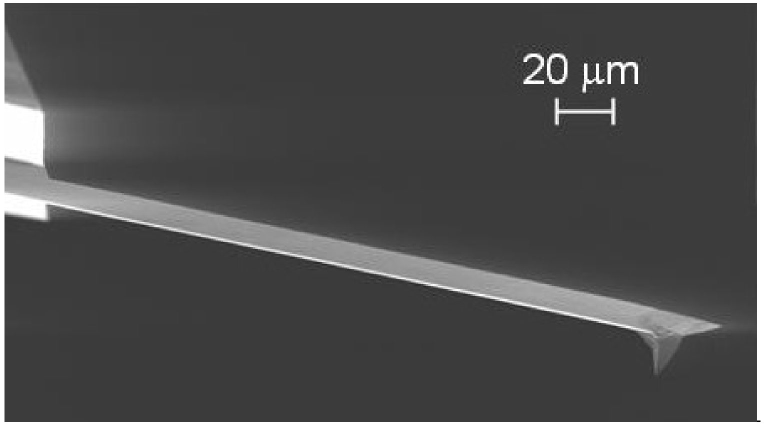
原子力探针显微术：AFM



基本仪器原理

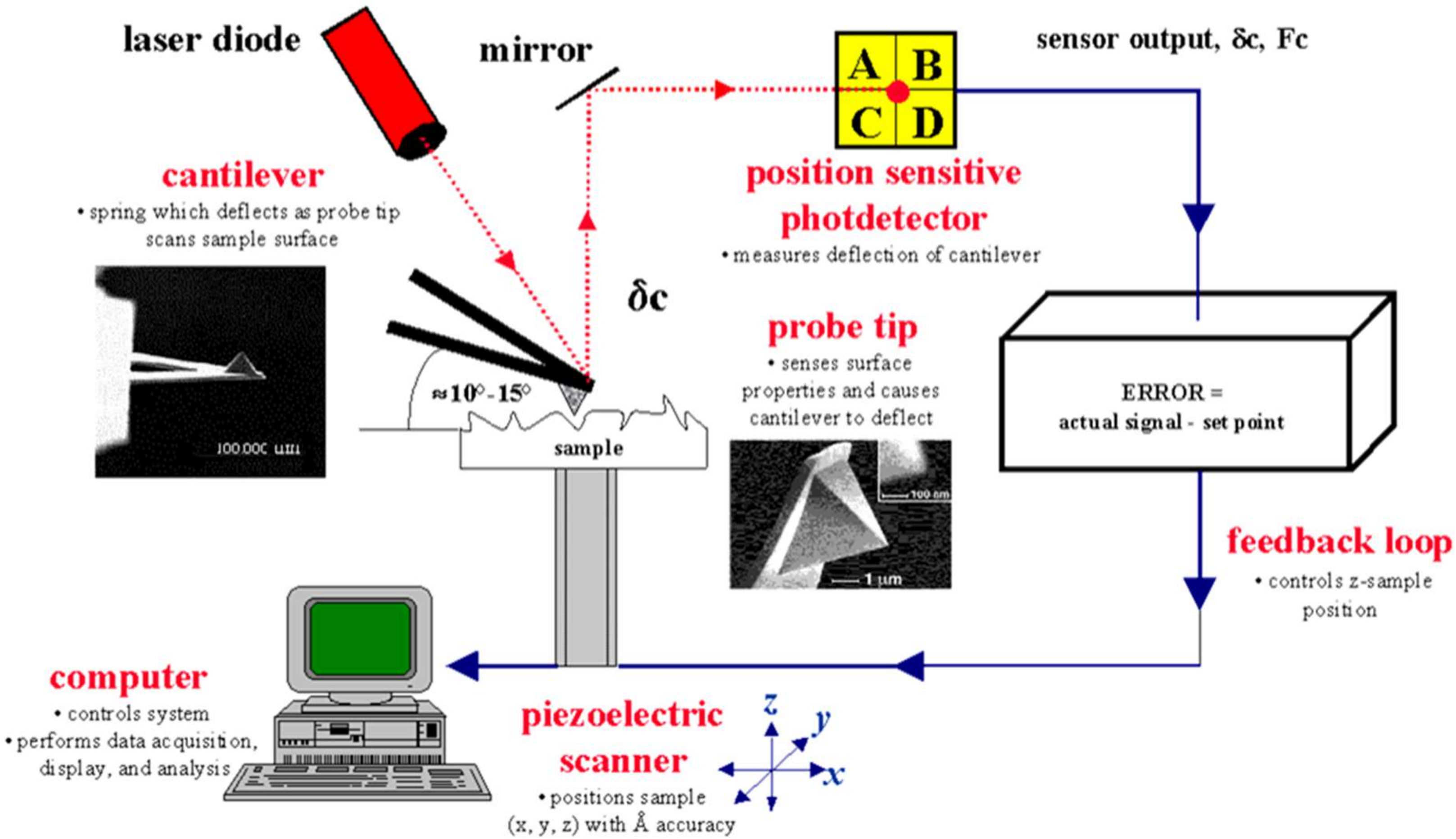


基本相互作用力



核心探测部件

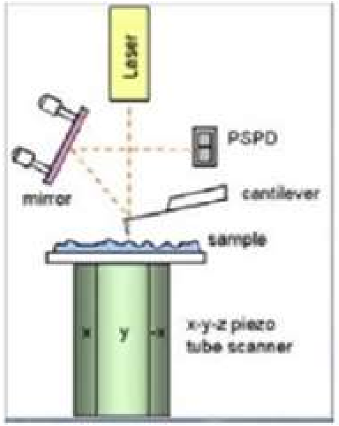
基本仪器组成：原理

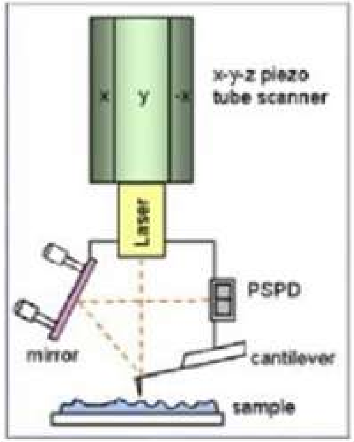


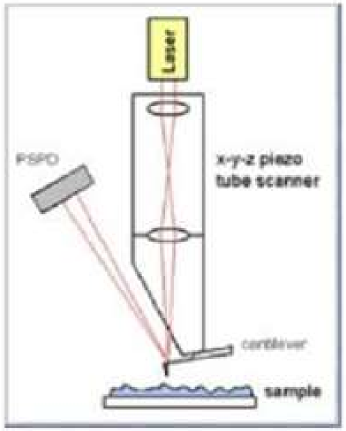
laser diode
mirror
A
B
C
D
sensor output, δc, Fc
cantilever
• spring which deflects as probe tip scans sample surface
100.00C um
position sensitive photdetector
• measures deflection of cantilever
δc
≈10°-15°
sample
probe tip
• senses surface properties and causes cantilever to deflect
100 nm
1 μm
ERROR = actual signal - set point
feedback loop
• controls z-sample position
computer
• controls system
• performs data acquisition, display, and analysis
piezoelectric scanner
• positions sample (x, y, z) with Å accuracy
z
y
x

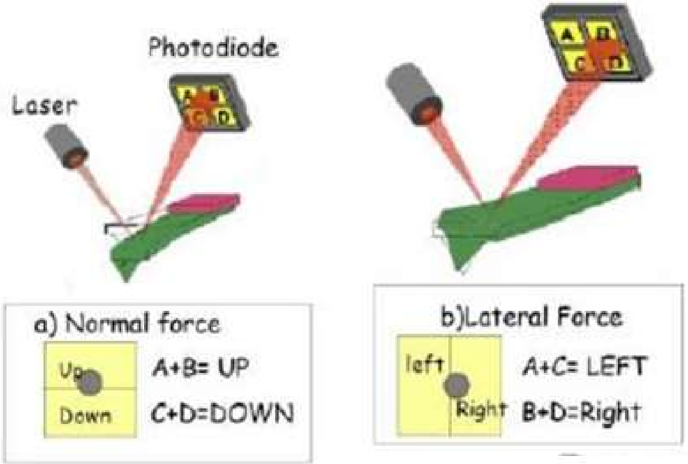
微悬臂的形变检测：PSD

The Beam Deflection method





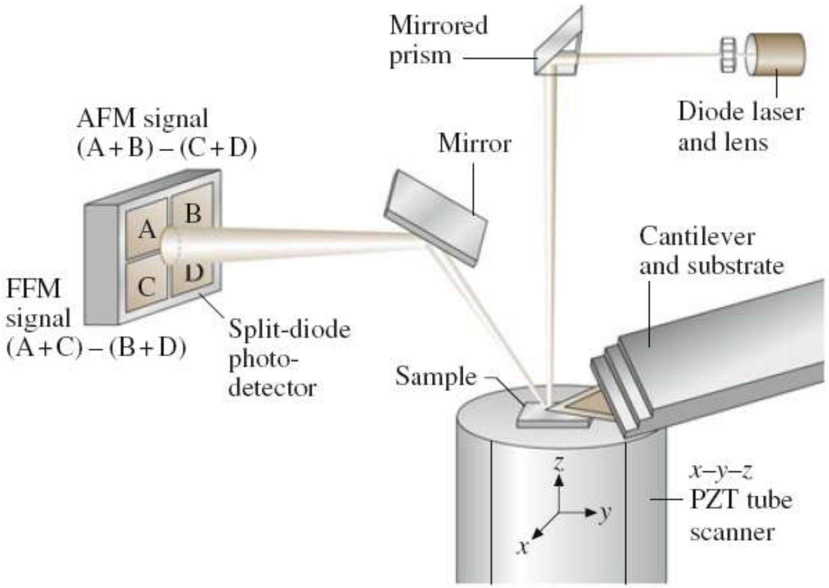




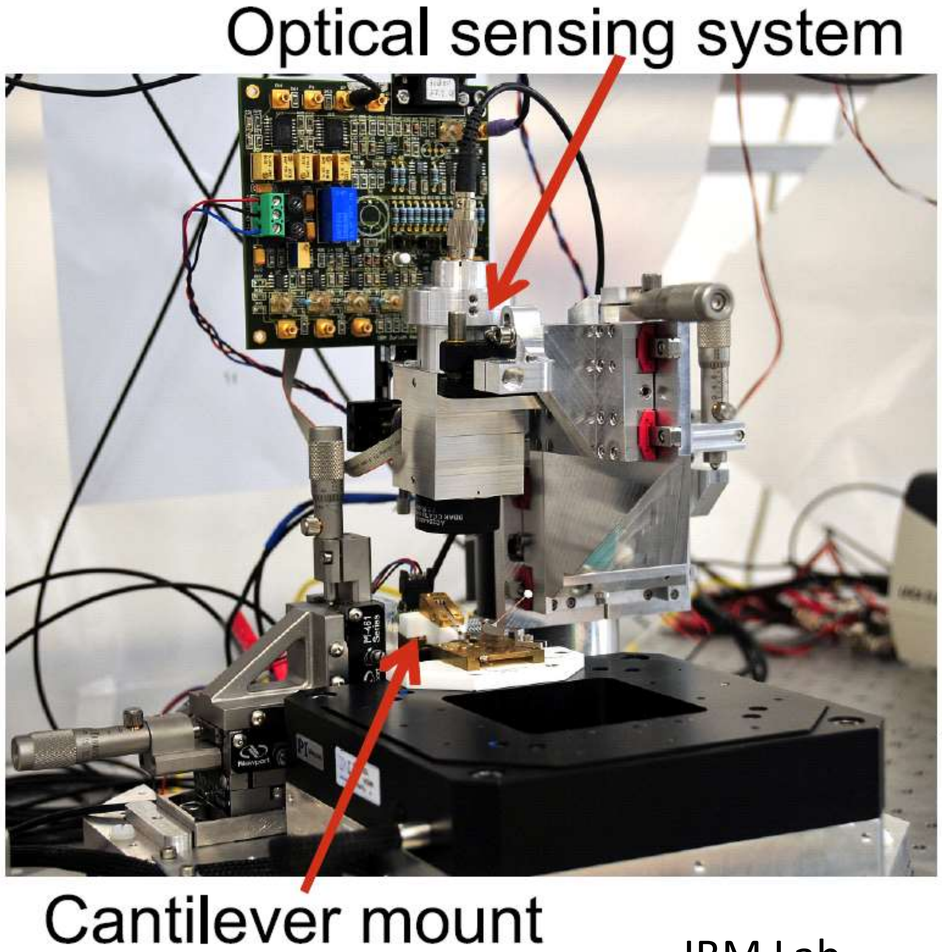
微悬臂的deflection和torsion：

垂直方向与水平方向的力

基本仪器组成：部件



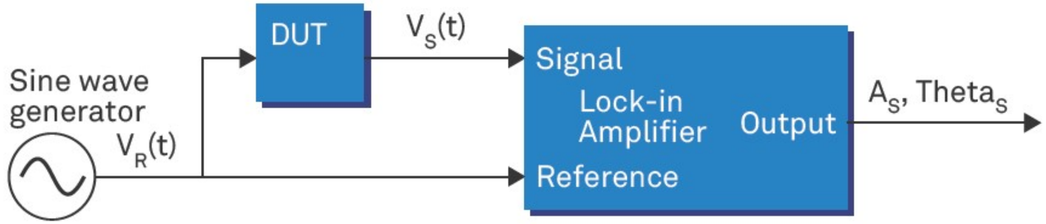
1 cantilevers and probes
2 optical detection system
3 x-y-z positioner and scanner
4 electronics and software
5 others

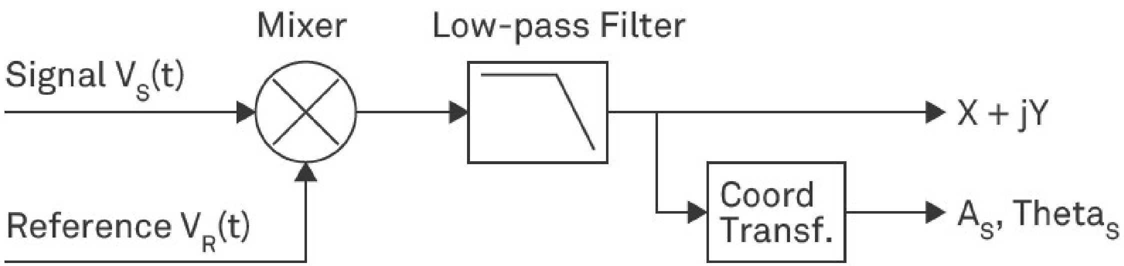


IBM Lab

锁相技术：Lock-in

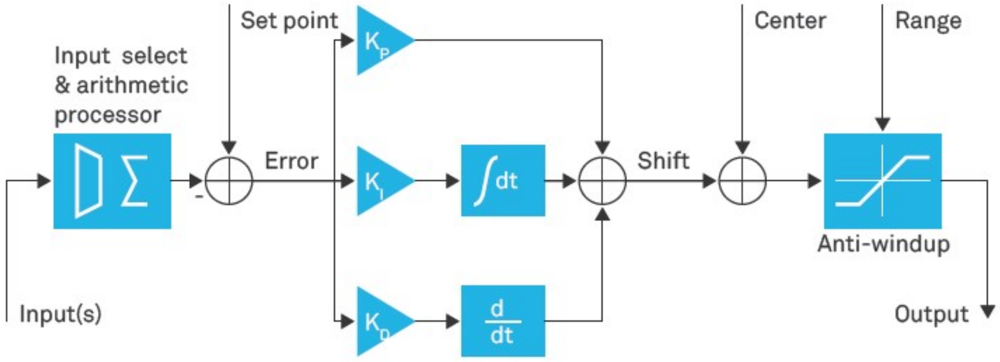
周期性测量
周期性信号





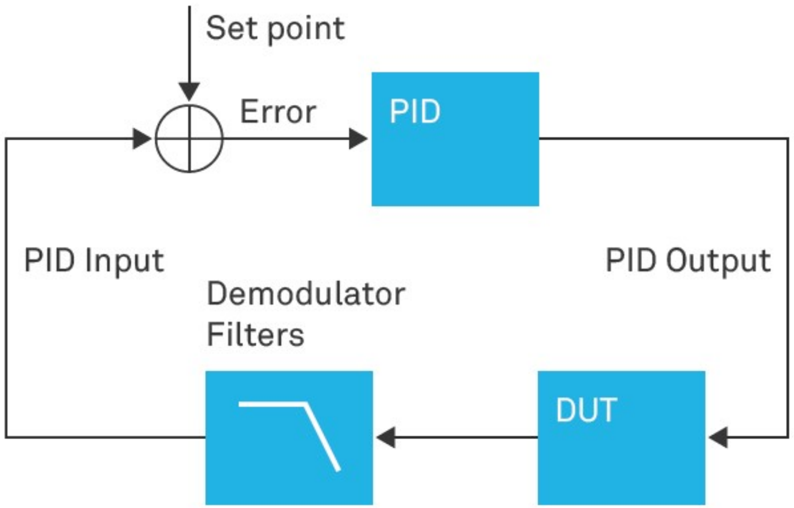
$$V_S(t)*V_R(t)=V_S(t)*\sqrt{2}\,e^{-j\omega_R t}=\frac{A_S}{\sqrt{2}}e^{+j[(\omega_S-\omega_R)t+\Theta_S]}+\frac{A_S}{\sqrt{2}}e^{-j[(\omega_S+\omega_R)t+\Theta_S]}$$

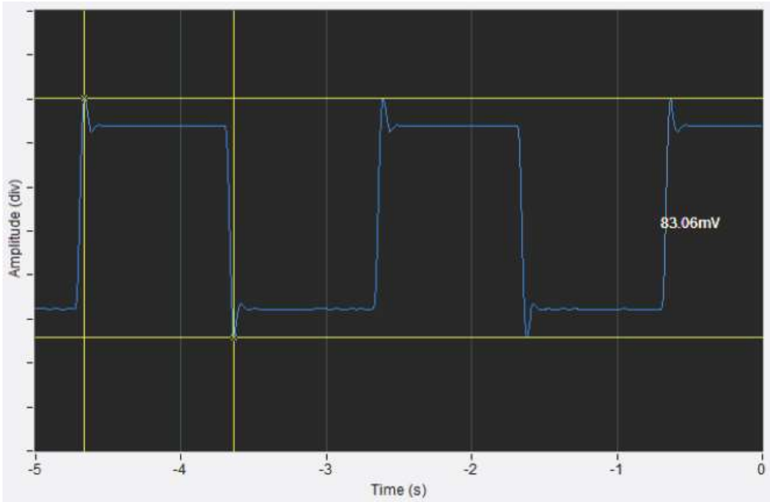
反馈技术：PID



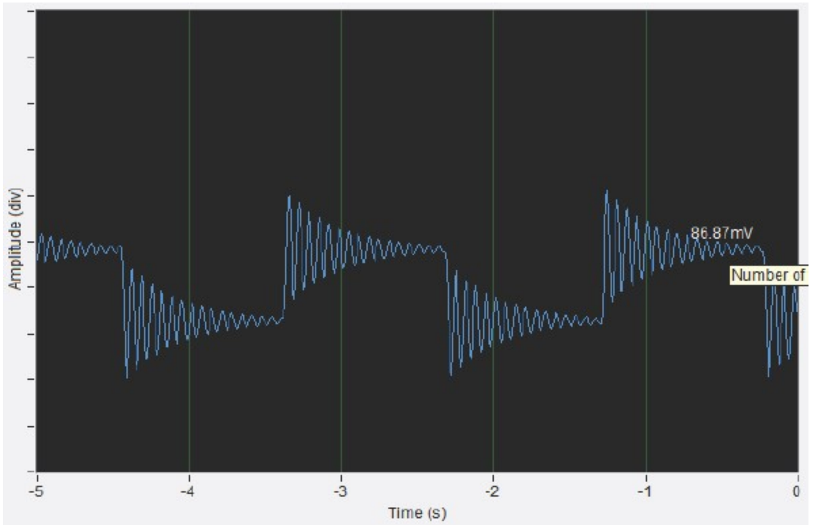
测量值 – 设定值 = 误差值

$$\text{Shift} = K_P*\text{Error} + K_I*\int \text{Error}dt + K_D*\frac{d}{dt}\text{Error}$$





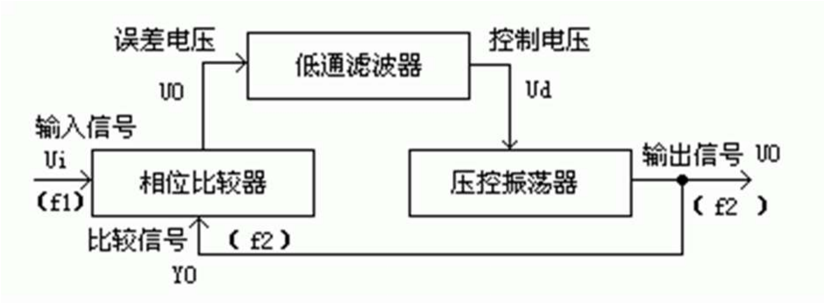
正常反馈



过反馈

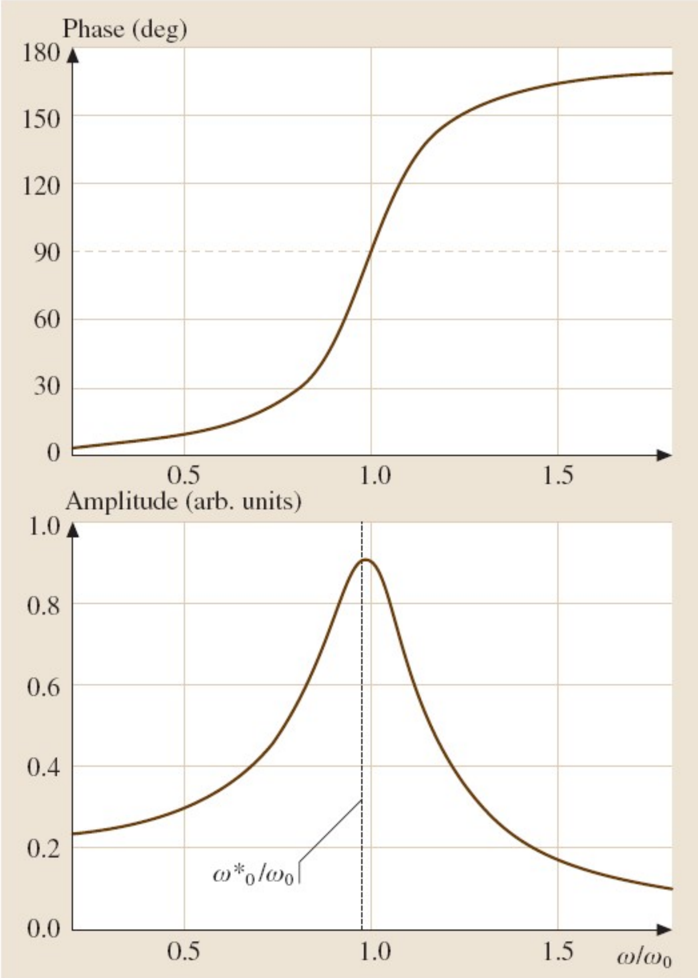
Proportional **I**ntegral **D**erivative (PID)

锁相环技术：Phase Lock Loop(PLL)



用途：始终跟踪共振频率的实时变化
原理：通过锁定相位来追踪共振频率
模式：一般用于频率调制AFM模式

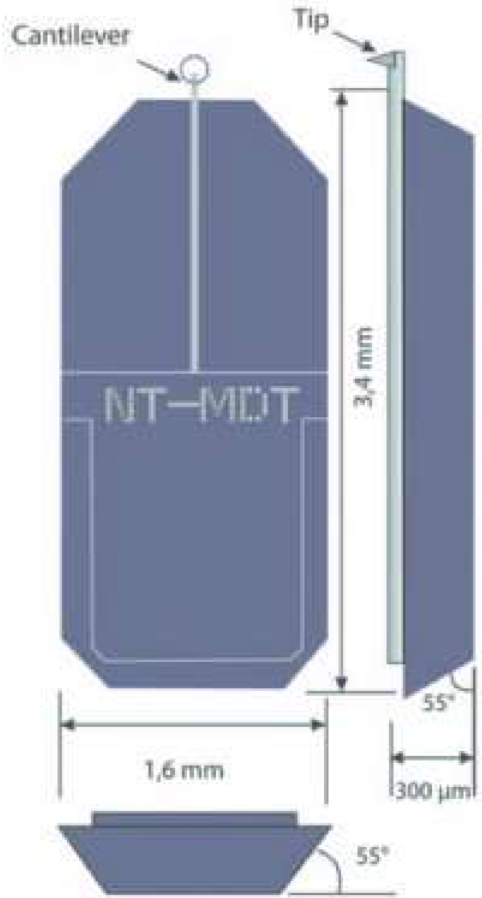
$$\begin{cases} A_0 = \dfrac{A_\mathrm{d} \cdot Q \cdot \omega_0^2}{\sqrt{\omega^2\omega_0^2 + Q^2(\omega_0^2 - \omega^2)^2}} \\ \varphi = \arctan\left(\dfrac{\omega \cdot \omega_0}{Q \cdot (\omega_0^2 - \omega^2)}\right). \\ \omega_0^* = \omega_0\sqrt{1 - \dfrac{1}{2Q^2}} \end{cases}$$



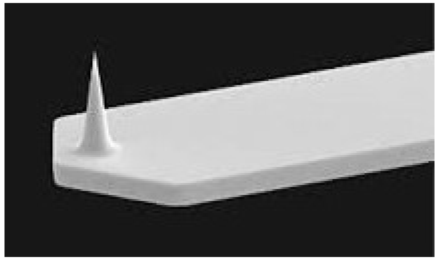
共振峰的描述：简谐振子模型

微悬臂探针：微悬臂+探针+其他

AFM 探针基本结构：基片(substrate or base)；微悬臂梁(Cantilever)； 针尖(tip)



1. 基片/芯片：固定微悬臂、方便夹持、方便电路制作。
2. 微悬臂：sense 部分，力信号检测。
3. 针尖：力探测，尖端大小影响分辨率。



微悬臂探针(自身)参数：
- 弹性常数
- 基础共振频率
- 品质因子
- 共振频率稳定性：温度等
- 传递函数

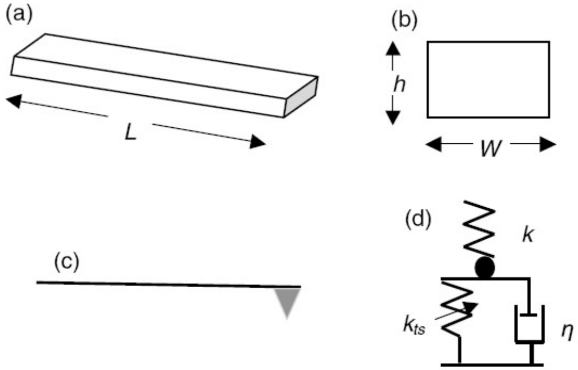
传感器参数：
- 温度灵敏度
- 电阻率
- 磁镀层
- 等等

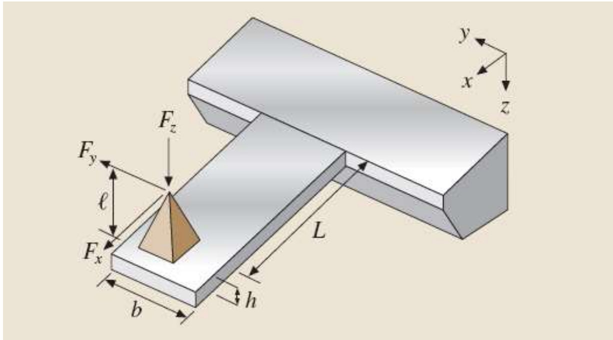
针尖高度、尖端半径、硬度 … …

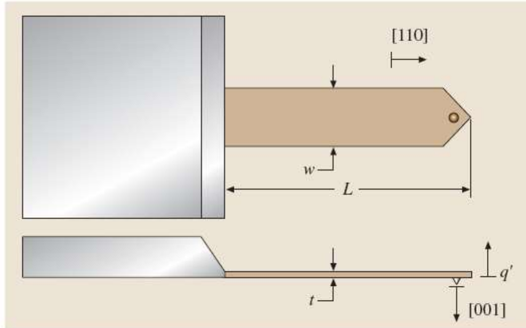
实验(外部)参数：振动频率、振动振幅等

如何设计、选择和确定这些参数：举例，固体中原子间力常数：一般小于10N/m，…

矩形微悬臂







静态力常数：$k_s = k = \frac{EWh^3}{4L^3}$

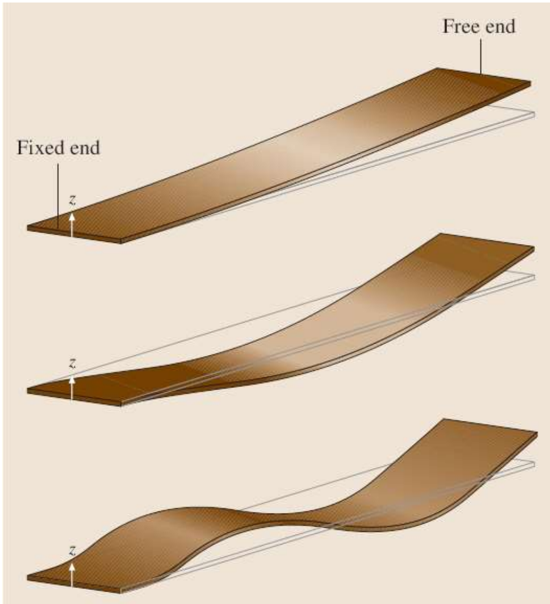
共振频率：

$$\kappa_n \cong \pi\left(n - \frac{1}{2}\right) \quad for \;\; n \geq 3$$

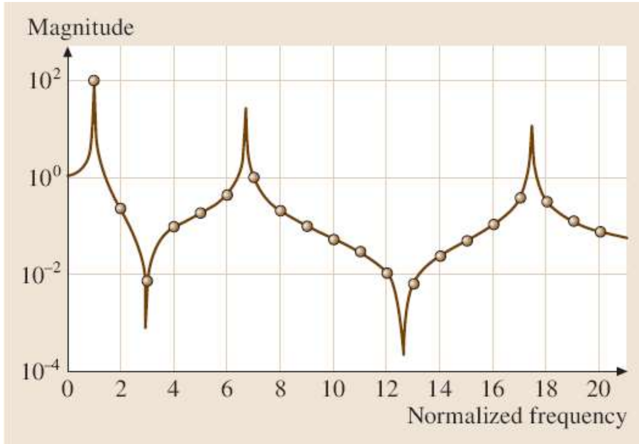
$$\kappa_1 \cong 1.875 \qquad \kappa_2 \cong 4.964$$

$$f_n = \frac{1}{2\pi}\frac{\kappa_n^2}{\sqrt{12}}\sqrt{\frac{E}{\rho}}\frac{h}{L^2}$$

***E* 杨氏模量，ρ质量密度**

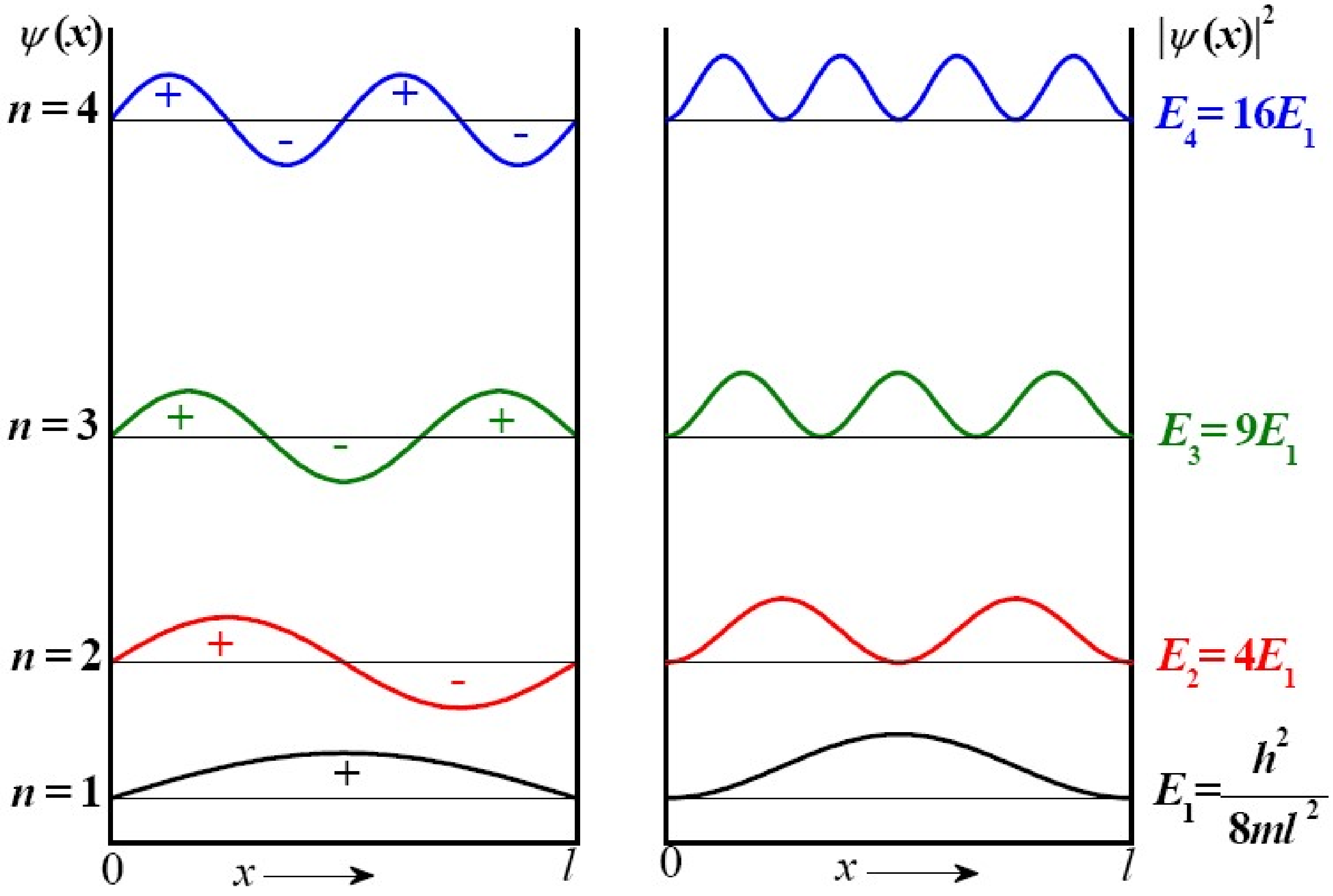


模态分析



传递函数分析：同样激励大小，不同激励频率下的微悬臂振动振幅

振动的基态与激发态



量子力学势阱：基态与激发态

微悬臂探针：定量化，校准

为了定量获取表面力和/或材料性质等，还需要确定微悬臂的力常数，悬臂梁偏转探测法的光学灵敏度，针尖尖端形状尺寸（电镜等）以及其他微悬臂探针参数。

微悬臂力常数的校准：

1 热噪音法：能量均分定理　　Room Temperature: ~24meV

$$\frac{1}{2}k\langle z^2\rangle = \frac{1}{2}k_{\mathrm{B}}T$$

其中，$\langle z^2\rangle$ 是热振动引起的微悬臂偏折的均方值。

利用微悬臂振动的振动分解展开，可以推导出微悬臂静态力常数与一阶本征模式力常数的关系表达式

$$k = \frac{k_{\mathrm{B}}T}{\langle z^2\rangle} = \frac{12k_{\mathrm{B}}T}{1.875^4\langle z_1^2\rangle} = 0.9707k_1$$

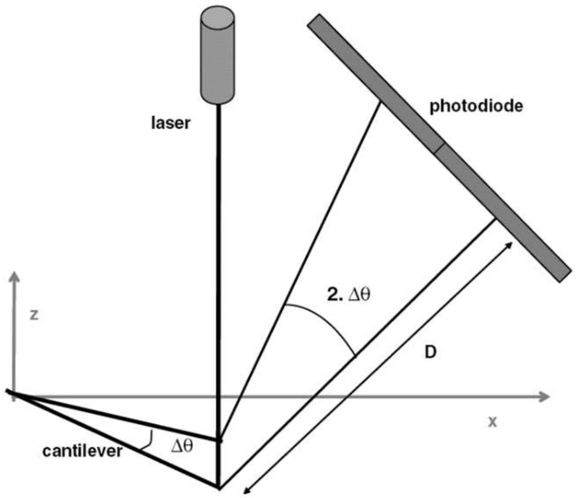
2 Sader法：流体耗散效应对微悬臂动力学行为的影响

$$k = 7.524\rho_f W^2 L Q_1 \Gamma_i(f_1) f_1^2$$

适用于确定矩形微悬臂的力常数。

其中，f_1是流体（大气、真空或液体）中测到的基础共振频率，Q_1 是基础共振频率的品质因子，ρ_f是流体密度，$\Gamma_i(\omega)$是流体动力函数的虚部，微悬臂的俯视图形状（长度L、宽度W）。

微悬臂偏折的光学探测



微悬臂偏折探测：光束反射式

力F施加在微悬臂的自由末端产生的微悬臂偏折：

$$z(x)=\frac{F}{2k}\left[3\left(\frac{x}{L}\right)^2-\left(\frac{x}{L}\right)^3\right]$$

自由末端处的偏折为：

$$z(L)=\frac{2L}{3}\frac{dz(L)}{dx}$$

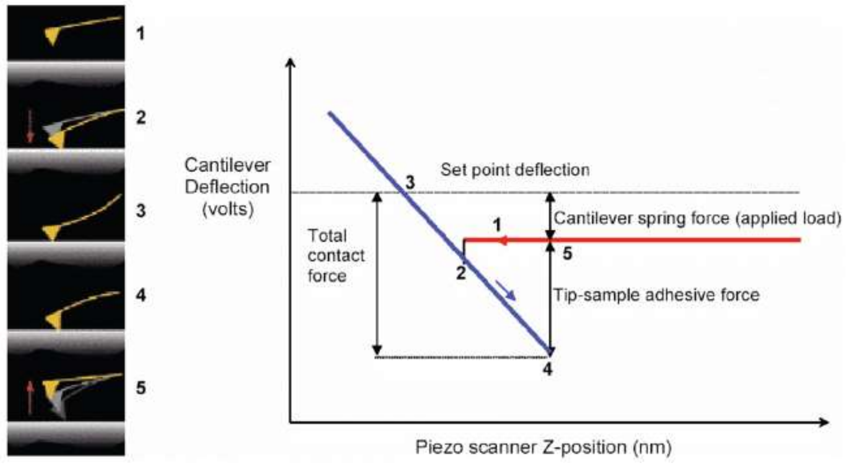
微悬臂偏折的放大倍数为：$\Delta A\approx 2\frac{D}{L}\Delta z$

光电探测二极管输出的光电流信号最终会转换成电压信号输出，为了精确测量长度单位下的微悬臂偏折信号，需要确定上述电压信号（伏）与真实偏折大小（纳米）的转换关系，即光学灵敏度。

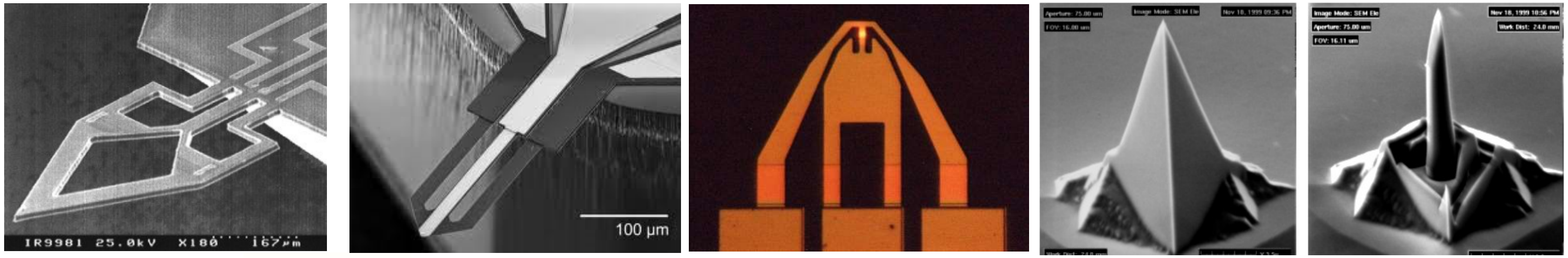
静态光学灵敏度 $\sigma_s=\frac{\Delta V}{\Delta z}$

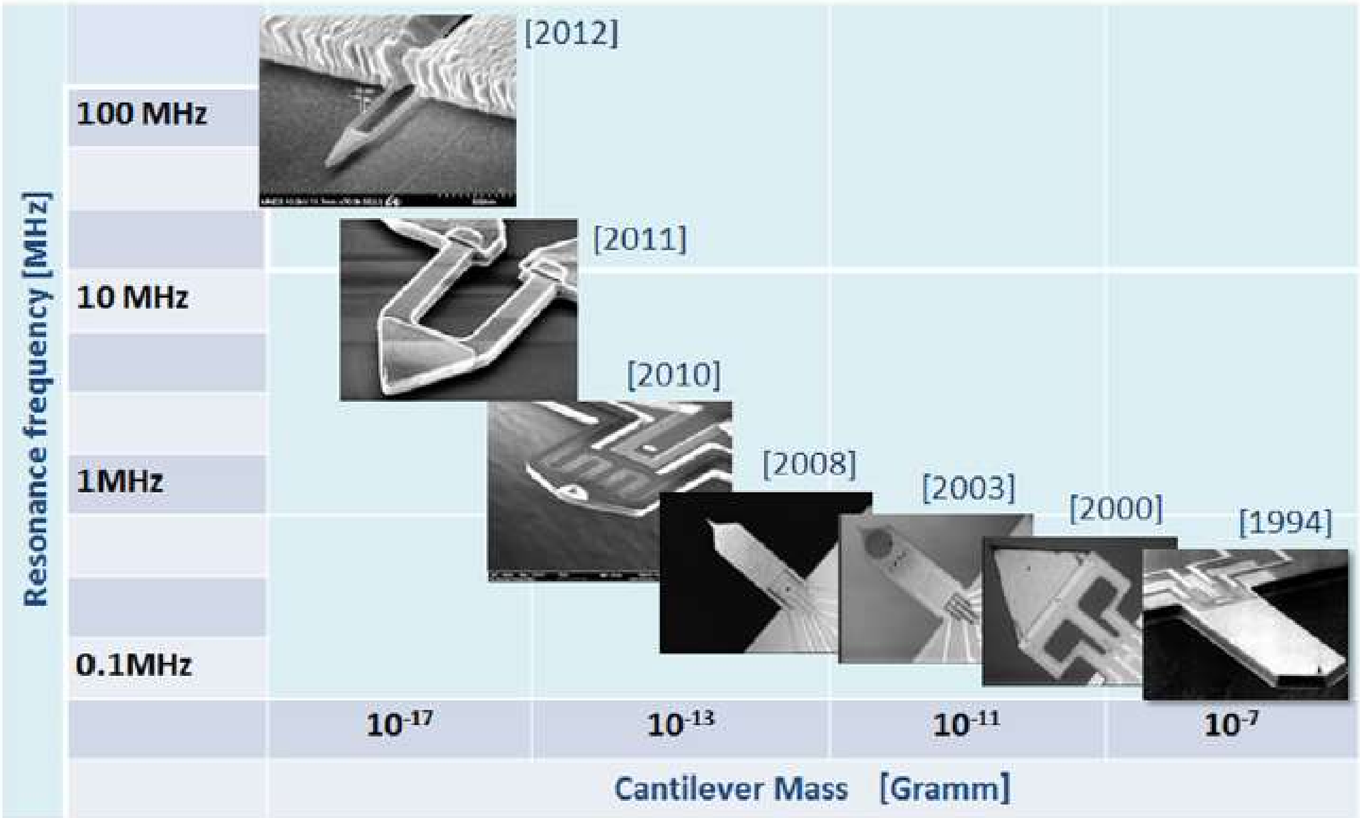
静态灵敏度可以通过偏折与针尖-样品间距离的依赖关系给出，这需要比较硬的针尖-样品界面。

微悬臂的形状决定了其本征激发模式及其对应的灵敏度。本征模式n的灵敏度（σ_n）可以从静态灵敏度（σ_s）推导出来，其相对比值正比于微悬壁的斜率。



多种多样的微悬臂探针



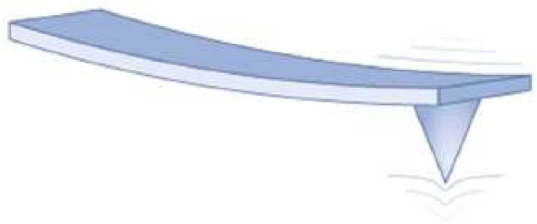


Development of scanning probes in terms of resonance frequency and effective mass with respect to time scale.

原子力微悬臂探针：形貌成像

中国人民大学 RENMIN UNIVERSITY OF CHINA

NC / AC / Tapping Mode AFM Probes



https://www.nanosensors.com/

PPP-NCHR
Non-Contact High frequency
Backside Reflex coating
C = 42 N/m; fo = 330 kHz

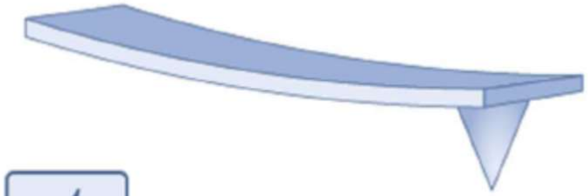
The probe offers unique features:
guaranteed tip radius of curvature < 10nm
tip height 10 - 15 µm
highly doped silicon to dissipate static charge
Al coating on detector side of cantilever
high mechanical Q-factor for high sensitivity

Cantilever data:

Property	Nominal Value	Specified Range
Resonance Frequency / kHz	330	204 - 497
Force Constant /(N/m)	42	10 - 130
Length /µm	125	115 - 135
Mean Width /µm	30	22.5 - 37.5
Thickness /µm	4	3 - 5

原子力微悬臂探针：电学测量

Electrostatic Force Microscopy /
Electrical Measurement AFM Probes



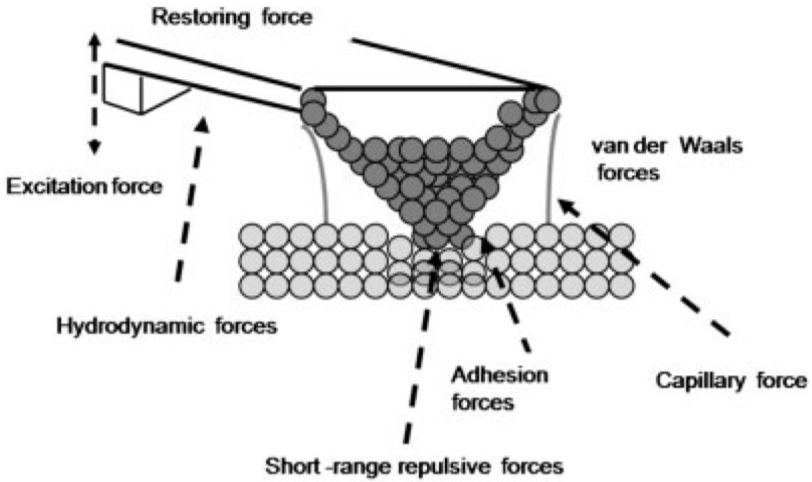
https://www.nanosensors.com/

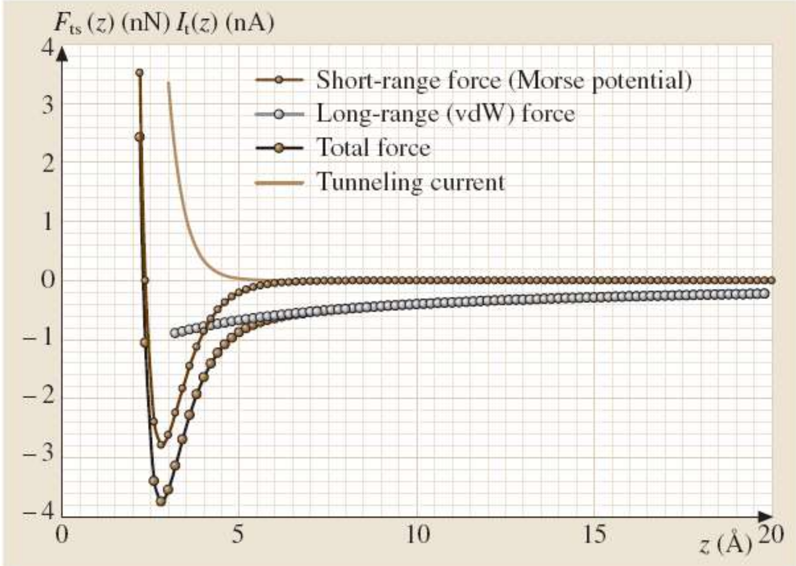
PPP-EFM PtIr5 coated probe C = 2.8 N/m; fo = 75 kHz
The probe offers unique features: metallic conductivity of the tip radius of curvature better than 25 nm tip height 10 - 15 µm high mechanical Q-factor for high sensitivity alignment grooves on backside of silicon holder chip precise alignment of the cantilever position (within +/- 2 µm)

Cantilever data:

Property	Nominal Value	Specified Range
Resonance Frequency / kHz	75	45 - 115
Force Constant /(N/m)	2.8	0.5 - 9.5
Length /µm	225	215 - 235
Mean Width /µm	28	20 - 35
Thickness /µm	3	2 - 4

针尖-样品间相互作用力：





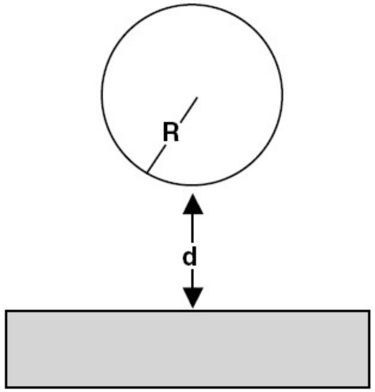
Excitation force：激励力
Restore force：恢复力
van der Waals forces：范德华力
Hydrodynamic forces: 水合力
Adhesion forces: 黏附力
Capillary force: 毛细力
Short-range forces: 短程力
Electrostatic forces: 静电力
and more, …

多种相互作用力：不同大小、范围、特性、衰减尺度等等

微纳米尺度描述：
大气、液体等环境

多组成、非线性、非单调、大小、方向、耗散、环境等

范德华相互作用力



球-平面模型（常用）

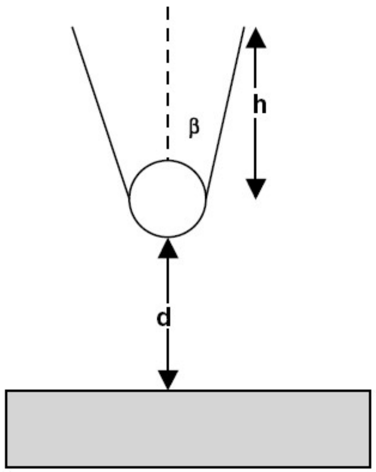
$$F_{vdW} = -\frac{HR}{6d^2}$$

H 为Hamaker常数，依赖于材料和中间介质，典型值在10^{-2} J量级；

R 为针尖尖端半径，从几纳米到上百纳米，可设计制备，可用电镜表征测量等；

d 是瞬时针尖-表面间距。

注意：分子间距a_0标准参考值0.165nm。当间距d小于分子间距a_0时，应考虑为接触力学模型中的黏附力。



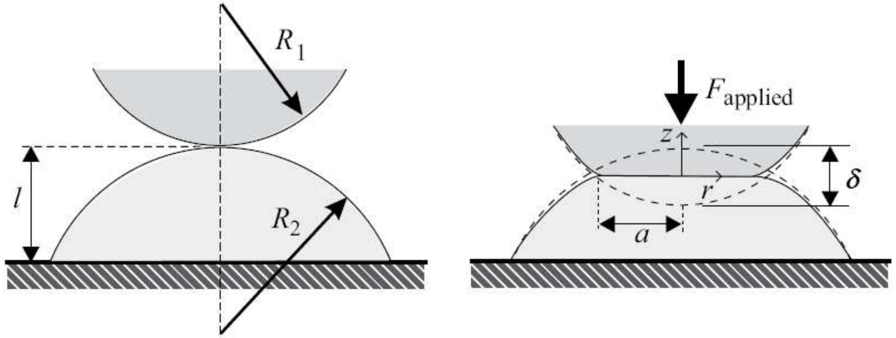
锥球-平面模型

$$F_{vdW} = -\frac{H}{6}\left(\frac{R}{d^2} + \frac{tan^2\beta}{d + R_\beta} - \frac{R_\beta}{d\left(d + R_\beta\right)}\right)$$

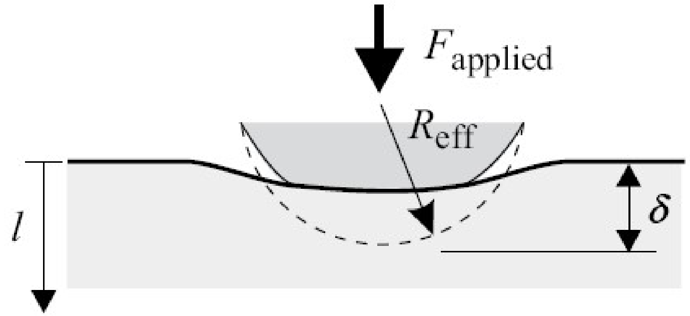
其中，β为圆锥半角，而$R_\beta = R(1 - \sin\beta)$。注意到当$d < R$时，范德华力主要由半球形盖决定，可近似简化为球-平面模型。

接触力学模型（Hertz 模型）

中国人民大學
RENMIN UNIVERSITY OF CHINA



Hertz接触模型：球-球接触



球-平面模型

接触半径 $$a = \left(\frac{3F_{applied}R_{eff}}{4E^*}\right)^{1/3}$$

有效半径 $$R_{eff} = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1}$$

压入深度 $$\delta = \frac{a^2}{R_{eff}} = \left(\frac{9F_{applied}^2}{16R_{eff}E^{*2}}\right)^{1/3}$$

有效杨氏模量 $$\frac{1}{E_{eff}} = \frac{1-\upsilon_t^2}{E_t} + \frac{1-\upsilon_s^2}{E_s}$$

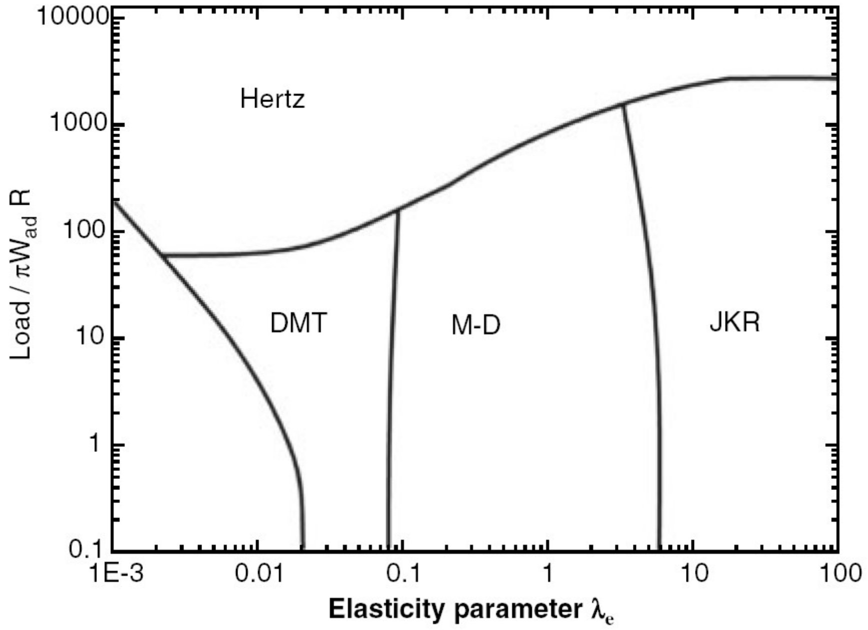
接触力 $$F_{Hertz} = \frac{4}{3}E_{eff}\sqrt{R}\delta^{3/2}$$

适用于描述相对较硬物质的力学接触

接触强度 $$k_{normal} = \frac{\partial F_{applied}}{\partial \delta} = 2E^*\sqrt{R_{eff}\delta} = 2aE^*$$

针尖/样品杨氏模量，
针尖/样品泊松系数等等

接触力学模型：黏附力



模型基本理念：Hertz模型 + 黏附力

$$F_{total} = F_{adhesive} + F_{applied}$$

适用于描述相对较软物质间的力学接触

Derjaguin-Muller-Toporov（DMT）模型：弱粘附力和小针尖半径下的硬接触

$$F_{\text{adhesive, DMT}} = 2\pi R_{\text{eff}} W_{\text{adh}}$$

$$F_{\text{DMT}} = \frac{4}{3} E_{\text{eff}} \sqrt{R}\delta^{3/2} - 4\pi R\gamma$$

$$W_{ad} = 2\gamma$$ 其中，γ为表面能

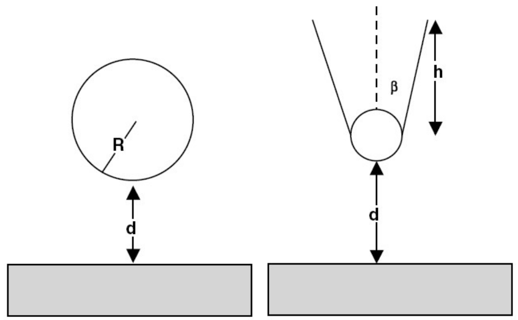
Johnson-Kendall-Roberts（JKR）模型：硬度相对较低、粘附力和针尖半径较大的接触情形

$$F_{\text{adhesive, JKR}} = \frac{3}{2}\pi R_{\text{eff}} W_{\text{adh}}$$

压入深度：$$\delta_{\text{JKR}} = \frac{a_{\text{JKR}}^2}{R_{\text{eff}}} - \left(\frac{2\pi W_{\text{adh}} a_{\text{JKR}}}{E^*}\right)^{1/2}$$

接触半径：$$a_{\text{JKR}} = \left\{\frac{3R_{\text{eff}}}{4E^*}\left[F_{\text{applied}} + 3W_{\text{adh}}\pi R_{\text{eff}} + \sqrt{6W_{\text{adh}}\pi R_{\text{eff}} F_{\text{applied}} + (3W_{\text{adh}}\pi R_{\text{eff}})^2}\right]\right\}^{1/3}$$

静电相互作用力



静电力一般是长程的，这意味着作用在样品表面的静电力不仅来自于探针尖端的原子，也可来自于探针锥型本体甚至整个微悬臂。

$$U = \mathrm{C}(\mathrm{V}-\mathrm{V_c})^2/2$$

$$F_\mathrm{e} = -\frac{1}{2}\frac{dC}{dz}(V-V_\mathrm{c})^2$$

一般模型 $F_\mathrm{e} = -\pi\varepsilon_0(V-V_\mathrm{c})^2\mathrm{g}(d)$

其中，ε_0为真空介电常数，$\mathrm{g}(d)$是包含探针尖端、探针锥体和微悬臂贡献的几何因子。

锥球-平面模型 $F_\mathrm{e} = -\pi\varepsilon_0(V-V_\mathrm{c})^2\left[\frac{R^2}{d(d+R)} + p^2\left(\log\frac{d+R}{h} - 1 + \frac{R}{\sin\beta\,(d+R)}\right)\right]$ $p = \frac{1}{\log\tan(\beta/2)}$

当针尖-表面距离$d < 100$ nm时，微悬臂贡献可以忽略不计。

球-平面模型 $F_\mathrm{apex} = -\pi\varepsilon_0\frac{R(V-V_\mathrm{c})^2}{d}$

AFM中计算估计静电力比较常用的表达式。

当顶端半球半径远大于针尖-表面间距，即$R \gg d$时。

毛细力

开尔文方程 $$R_g T \log\frac{P}{P_0} = \frac{\gamma_L V_m}{r_k}$$

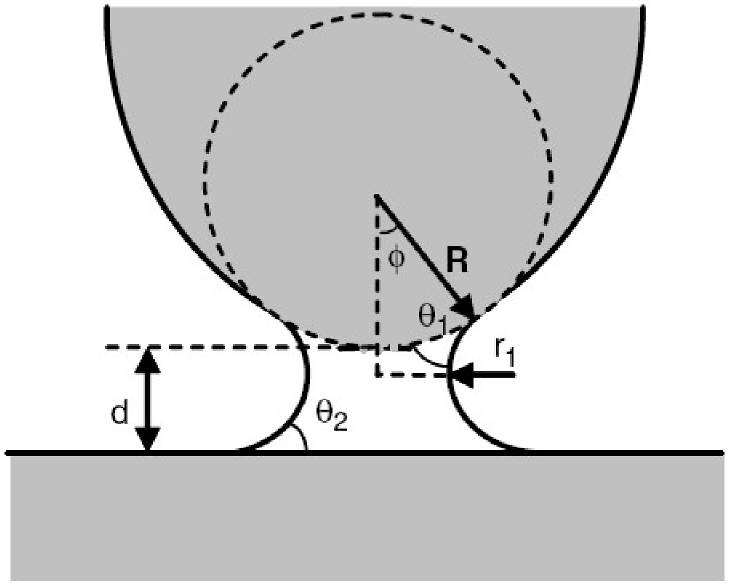
其中，R_g为气体常数，γ_L为液体的表面张力，P为实际蒸汽压，P_0饱和蒸汽压，V_m液体的摩尔体积，r_1和r_2是弯月形的主半径。对于水汽凝结，P/P_0为相对湿度。

$$\frac{1}{r_k} = \frac{1}{r_1} + \frac{1}{r_2}$$

开尔文半径（Kelvin radius，r_k）给出了弯月形液膜尺寸的信息。

$$\Delta P = \gamma_L\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

弯月形水凝结体的内部压强大于外部，杨-拉普拉斯方程（Young-Laplace equation）进一步给出了弯月形界面两侧的压强差。

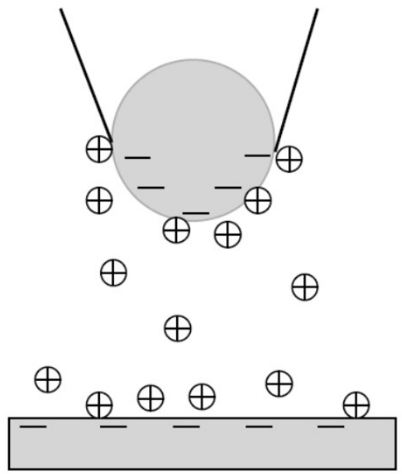


$$F_{cap} = \frac{4\pi R\gamma_L \cos\theta}{1 + d/d_0}$$

最大的毛细吸引力发生在球形针尖与平坦表面刚接触（$d = 0$）时，

$$F_{cap} = 4\pi R\gamma_L \cos\theta$$

液体中的力



静电双层力

双电荷层分为两个区域：一个是靠近表面的一薄层抗衡离子区域，称之为亥姆霍兹层（Helmholtz layer），另一个是由于热运动延伸到远离表面的抗衡离子区域，称之为扩散双层（diffuse double layer）。

溶剂化力

来源于物质由分立的原子/分子组成，溶剂化力引起靠近固体表面处液体密度相对其体密度的振荡，这一振荡的延伸范围为几个分子尺寸，而周期为分子大小。

水合力

可分为排斥的憎水力和吸引的亲水力。

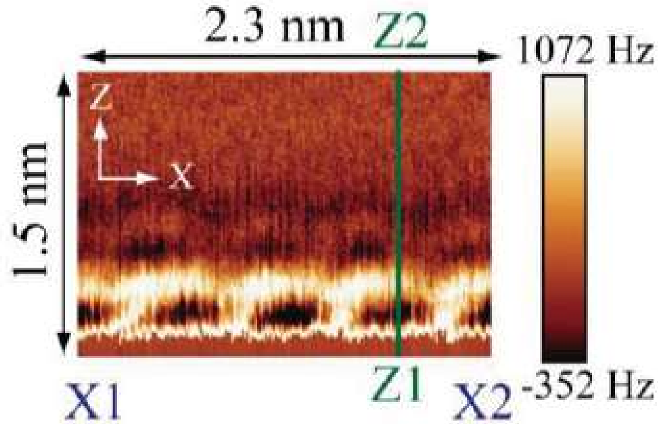
Derjaguin-Landau-Verwey-Overbeek模型：

其中，λ_{D}、ε和ε_0分别为德拜长度、介质介电常数和真空介电常数；σ_{t}和σ_{s}分别为针尖和样品的表面电荷密度。

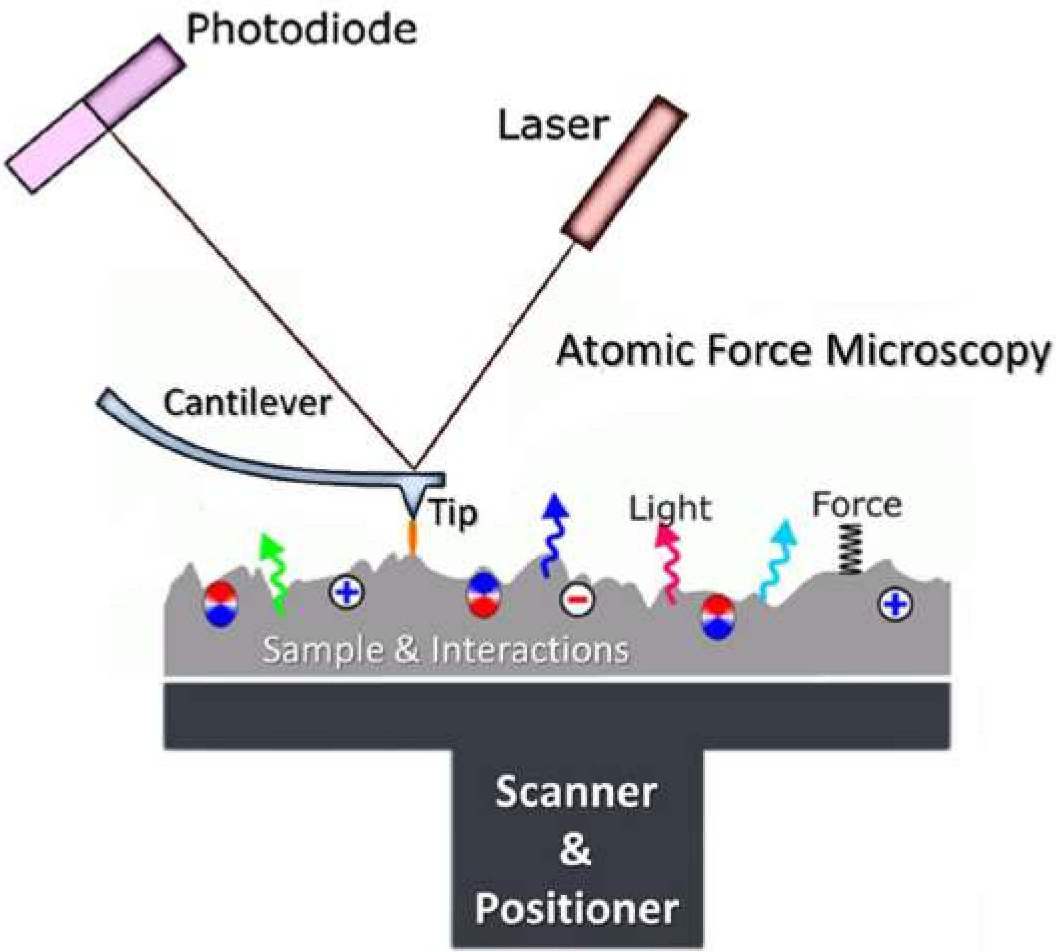
$$F_{\mathrm{DLVO}} = \frac{4\pi R}{\varepsilon\varepsilon_0}\sigma_{\mathrm{t}}\sigma_{\mathrm{s}}\lambda_{\mathrm{D}}\exp(-d/\lambda_{\mathrm{D}}) - \frac{HR}{6d^2}$$

溶剂化力： 其中，a_{m}为分子尺寸，$\tan\varphi = \lambda_{\mathrm{sv}}/a_{\mathrm{m}}$。

$$F_{\mathrm{sv}} = F_0\cos\left(\frac{2\pi d}{a_{\mathrm{m}}} + \varphi\right) exp(-d/\lambda_{\mathrm{sv}})$$



主要核心内容：第一部分



- 1 基本理论基础、仪器及相互作用

近场相互作用

基本仪器组成

微悬臂探针

探针-样品间的力

等等

基本工作模式：形貌成像

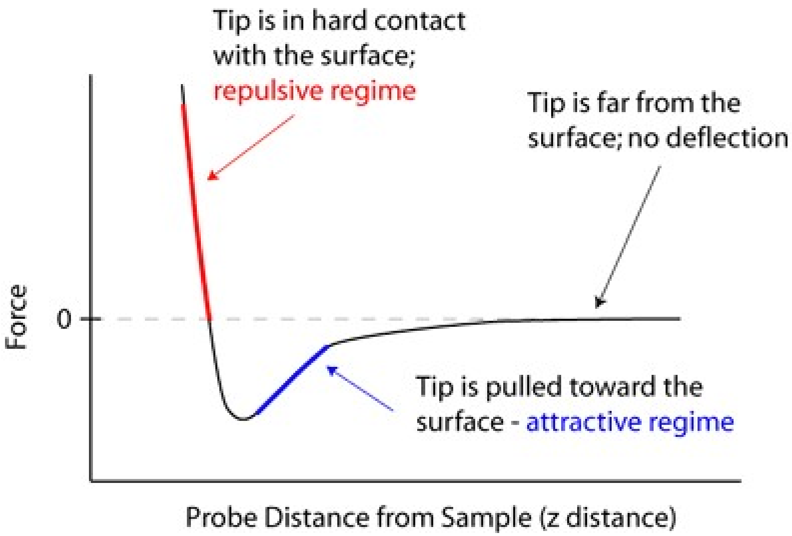
1 静态接触模式：直接接触力，微悬臂偏转

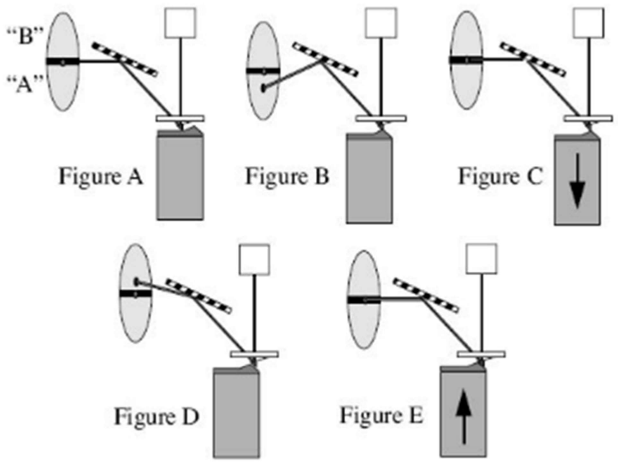
2 动态非接触模式：非接触力，微悬臂振动

轻敲模式（振幅调制模式）；非接触模式（频率调制模式）等

3 动态接触模式：接触力，微悬臂偏转/振动

基本工作模式：静态接触模式





多种功能模式的基础：

摩擦力显微术 （FFM）

扫描电容显微术（SCM）

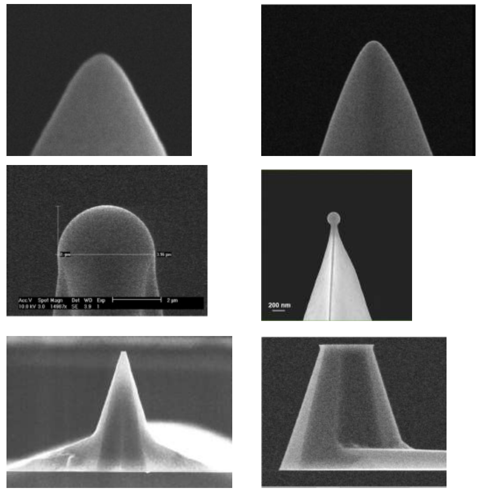
扫描热学显微术（SThM）

扫描阻抗显微术（SIM）

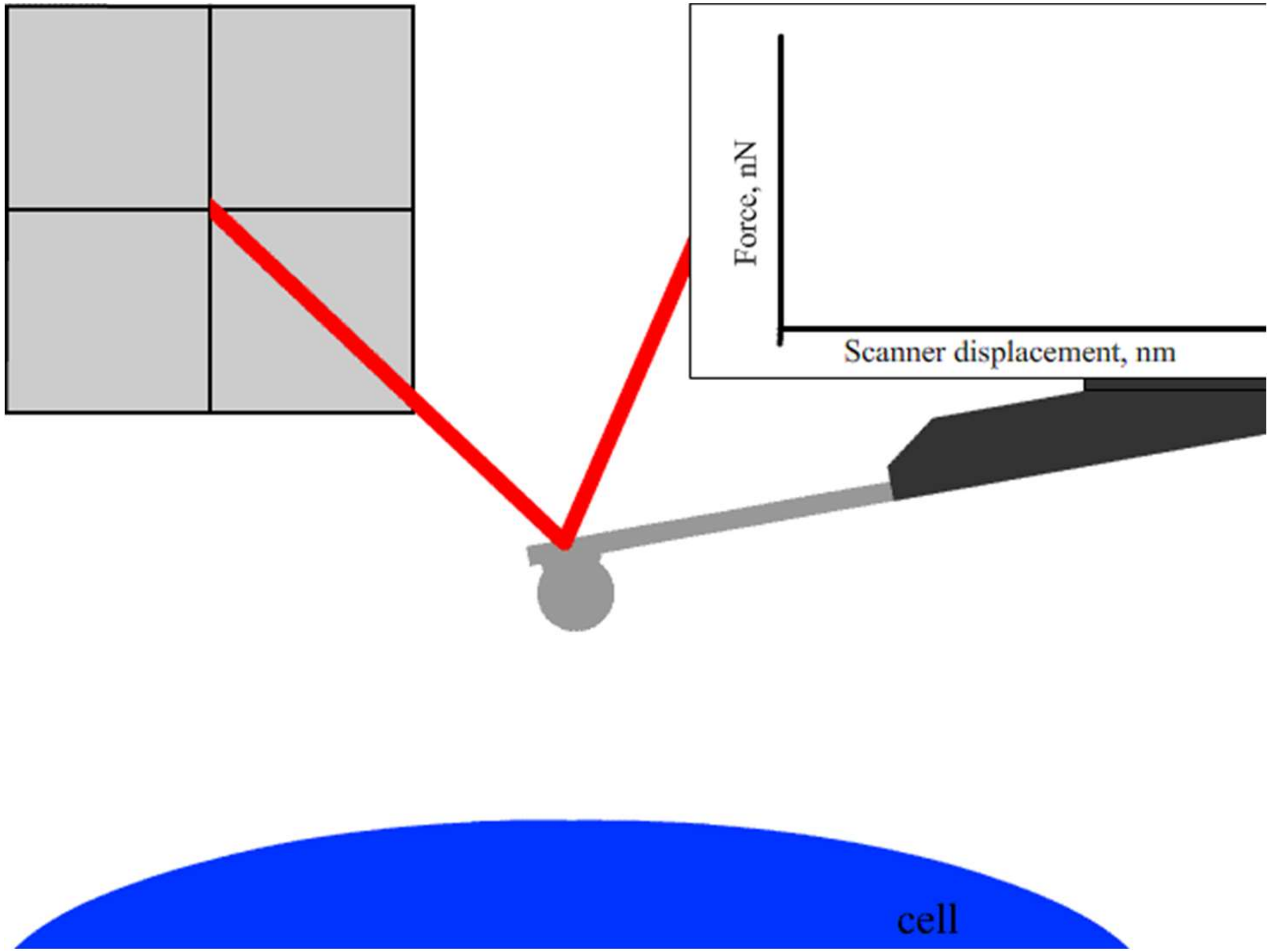
。。。

Jump-to-contact/snap-in
Drift/Noise,
Stiff or soft cantilever
Load ……

金刚石探针等
可控尖端形状
有限元方法 ……



基本工作模式：力谱模式



接触力谱+接触力学模型

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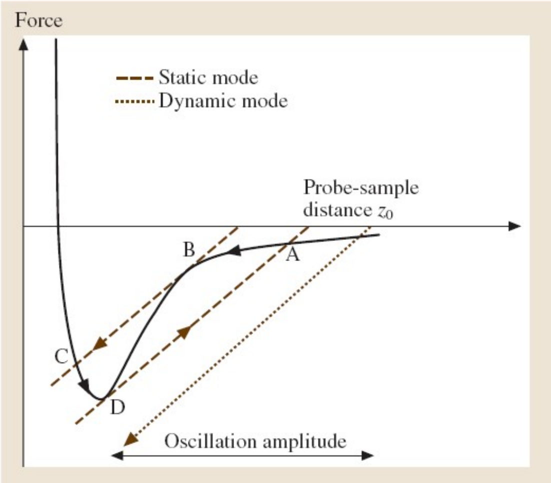
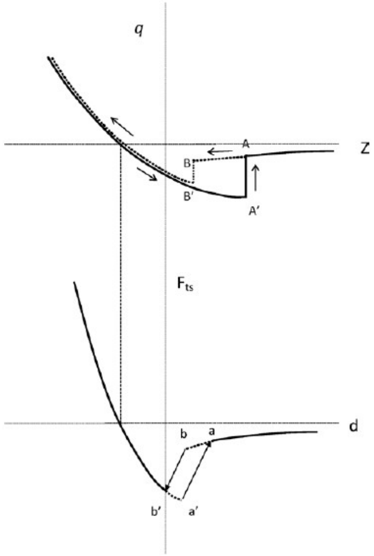


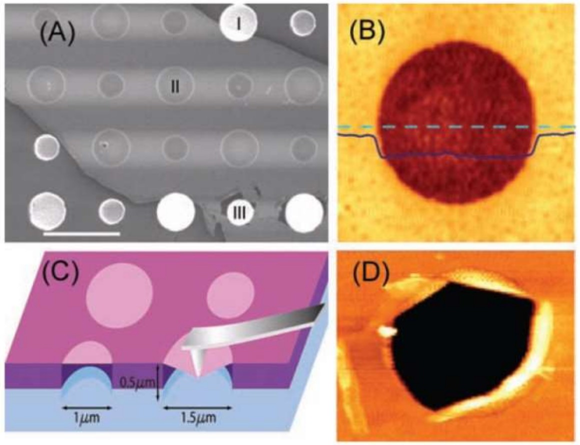


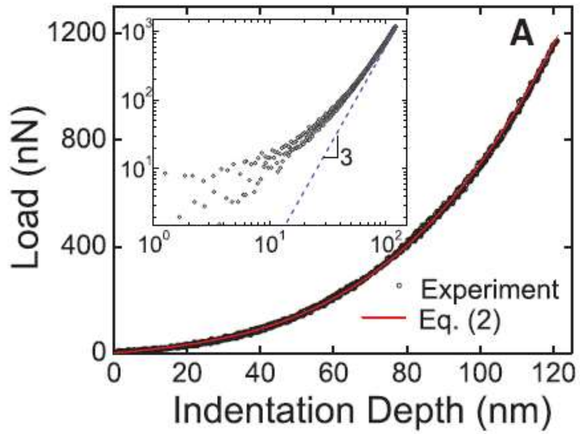
针尖-样品间距离
压电陶瓷管位置

Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene

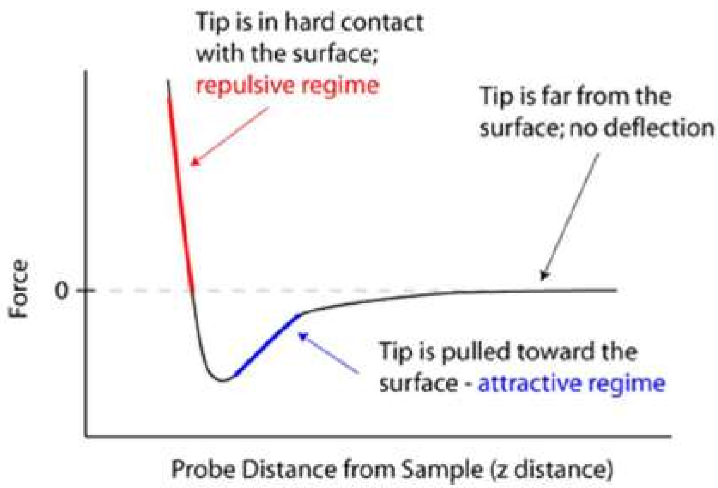
Changgu Lee,[1,2] Xiaoding Wei,[1] Jeffrey W. Kysar,[1,3] James Hone[1,2,4]*

We measured the elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes by nanoindentation in an atomic force microscope. The force-displacement behavior is interpreted within a framework of nonlinear elastic stress-strain response, and yields second- and third-order elastic stiffnesses of 340 newtons per meter (N m^{-1}) and −690 N m^{-1}, respectively. The breaking strength is 42 N m^{-1} and represents the intrinsic strength of a defect-free sheet. These quantities correspond to a Young's modulus of E = 1.0 terapascals, third-order elastic stiffness of D = −2.0 terapascals, and intrinsic strength of σ_{int} = 130 gigapascals for bulk graphite. These experiments establish graphene as the strongest material ever measured, and show that atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime.

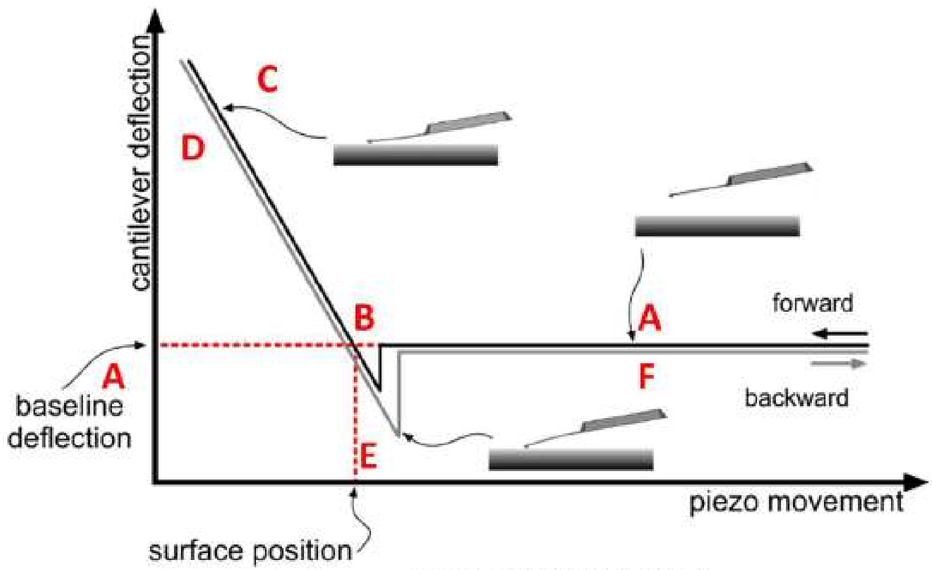




力谱 与 针尖-样品间相互作用



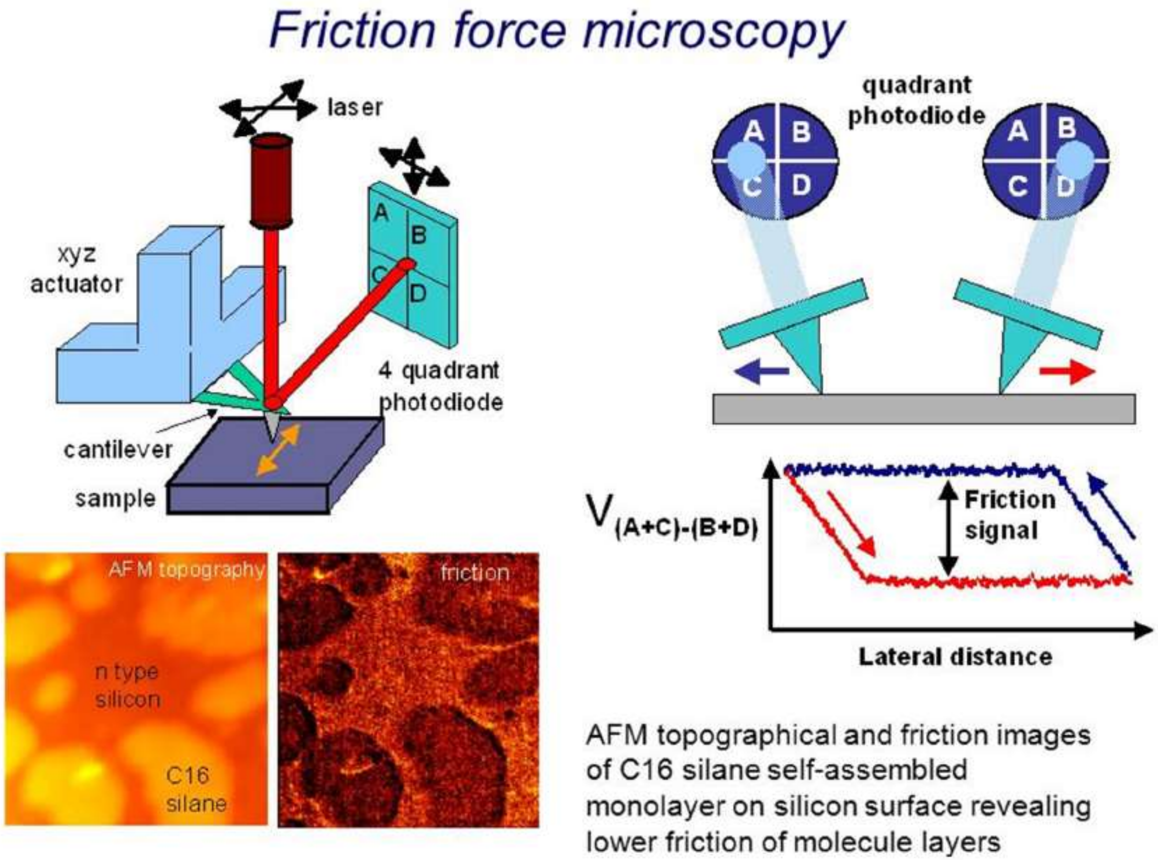
针尖-样品间距离

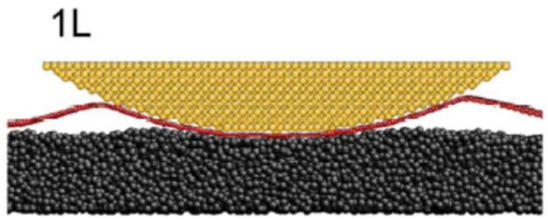


压电陶瓷管位置

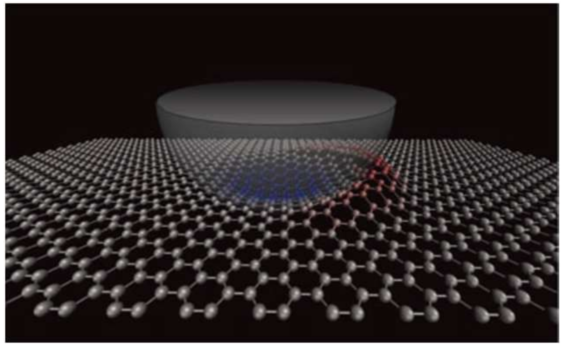
大家可以思考一下，上面两幅图之间的联系！

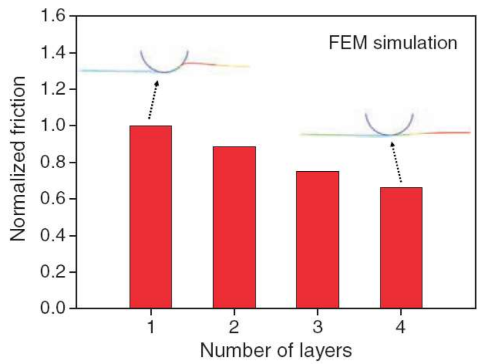
摩擦力显微术：常规扭转模式





Nature, 539, 541-545 (2016)

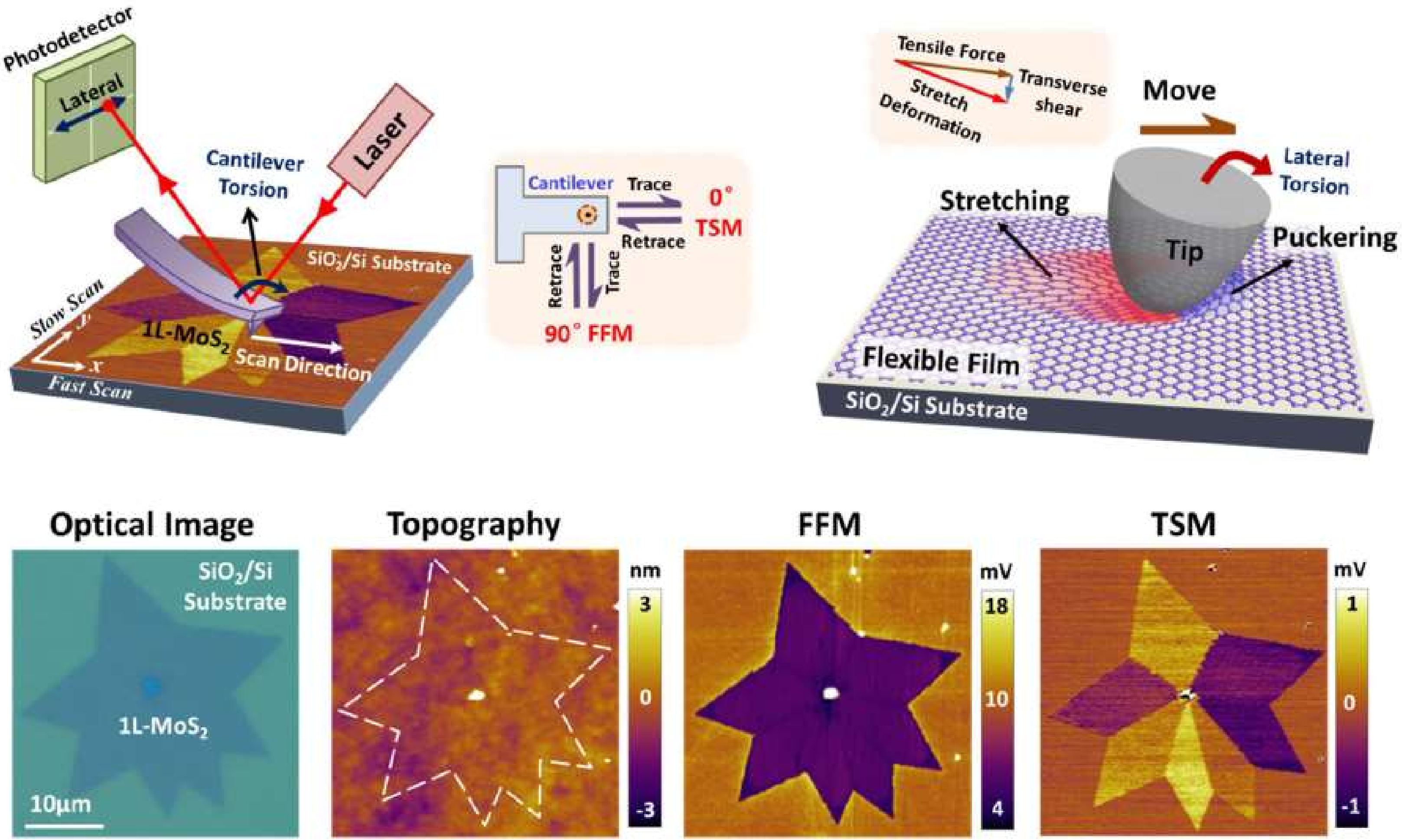




SCIENCE, 328, 76-80 (2010)

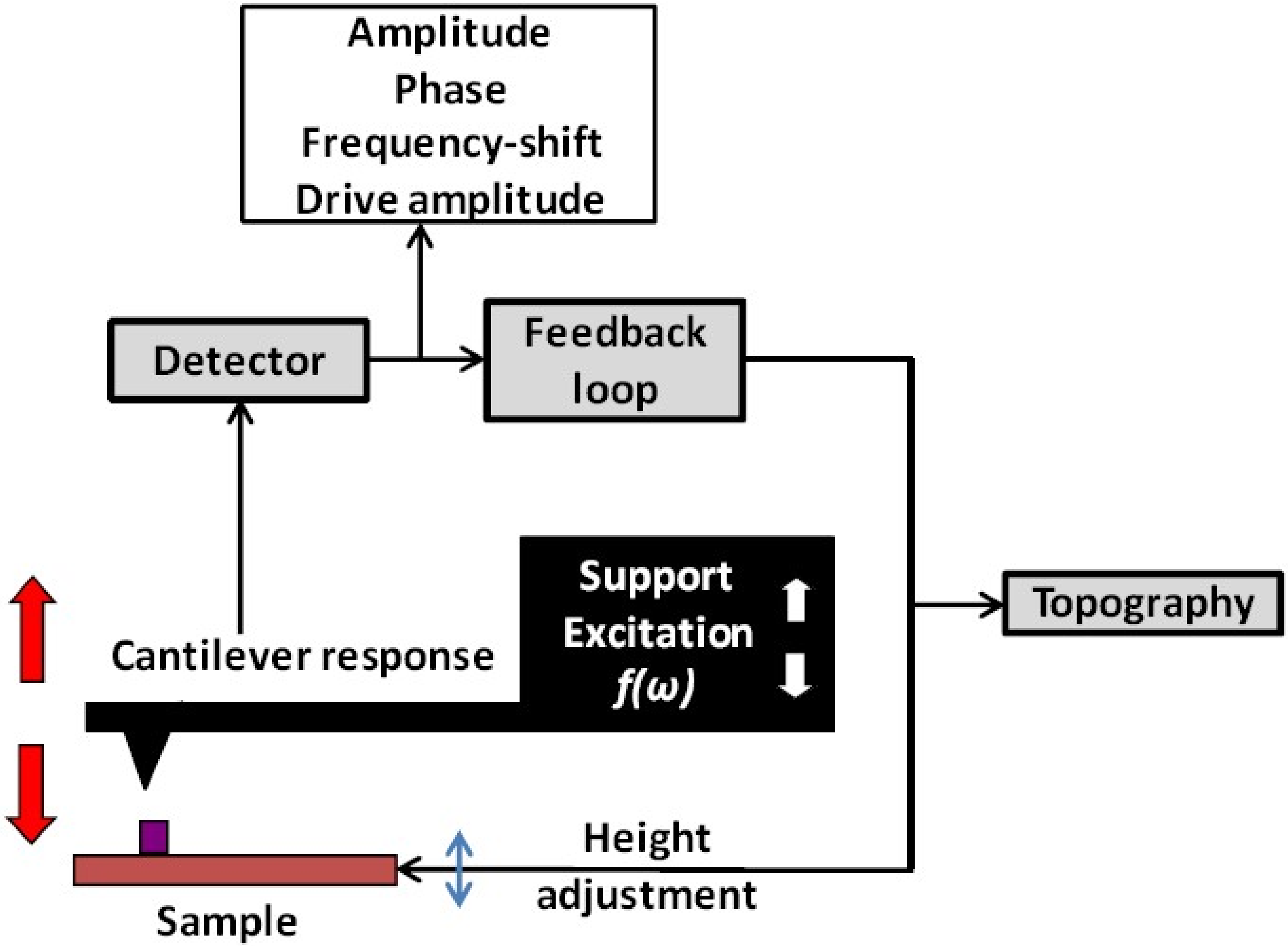
摩擦力显微术：剪切扭转模式

中国人民大学 RENMIN UNIVERSITY OF CHINA

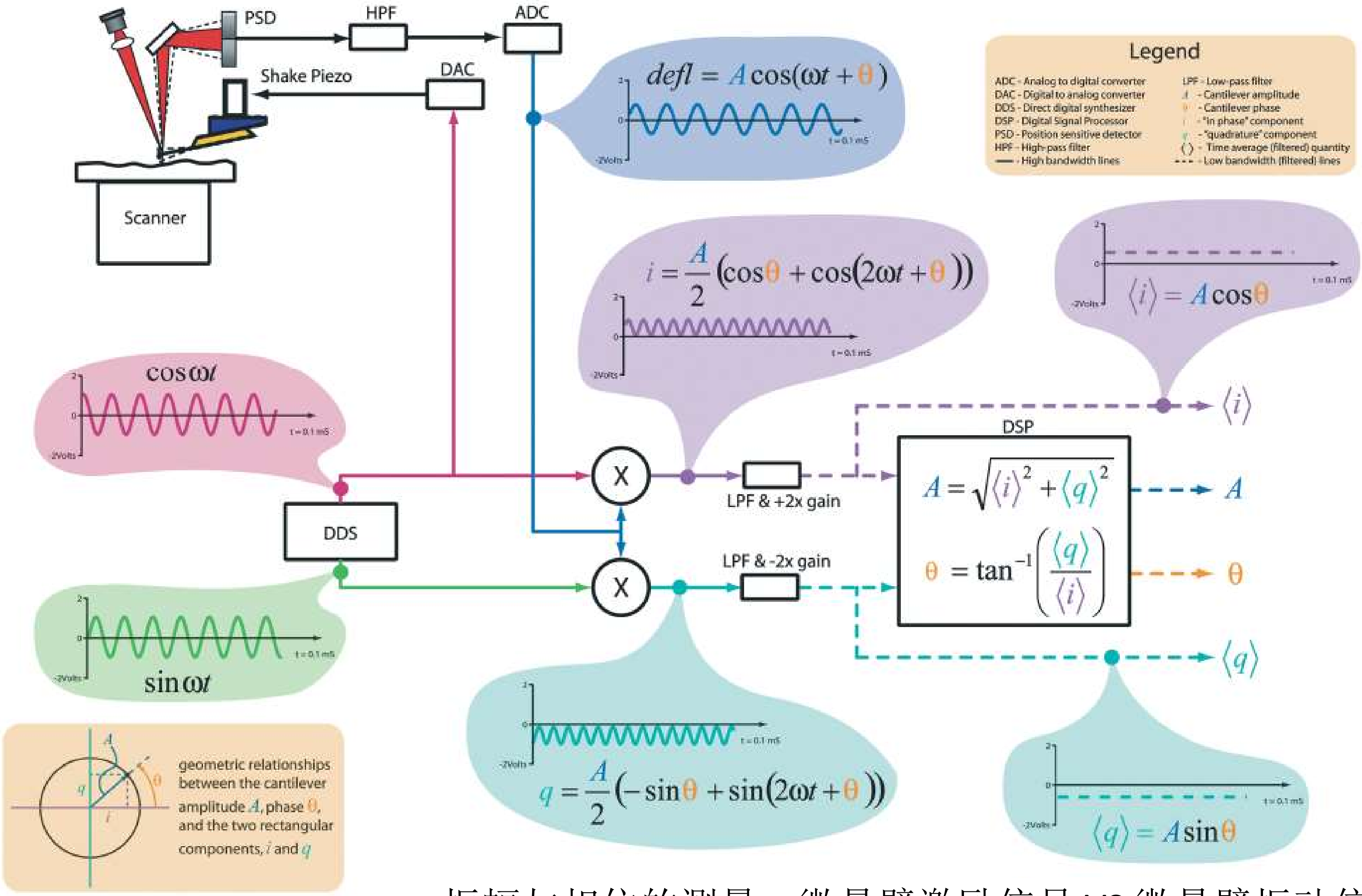


Appl. Phys. Lett. **115**, 063101 (2019)

基本工作模式：动态模式


Amplitude
Phase
Frequency-shift
Drive amplitude
Detector
Feedback loop
Support Excitation f(ω)
Topography
Cantilever response
Height adjustment
Sample

基本工作模式：动态模式



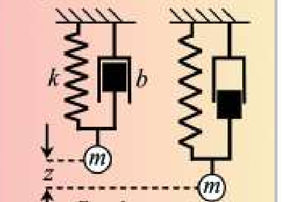
振幅与相位的测量：微悬臂激励信号 VS 微悬臂振动信号

振动 与 共振

基本工作模式：动态模式

The Physics of Atomic Force Microscopy

Simple Harmonic Oscillator



$F = -kz \quad T = \frac{2\pi}{\omega_0}$

$\omega_0 = 2\pi f_0 = \sqrt{\frac{k}{m}} \quad A \propto \exp(-t/\tau)$

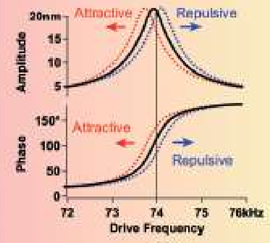
$Q = \frac{k}{\omega_0 b} = \frac{\pi\tau}{T} = \frac{A_{max}}{A_{drive}} \cong \frac{\omega_0}{\Delta\omega}$

$m\frac{d^2z}{dt^2} = F_{drive} - b\frac{dz}{dt} - kz + F_{ext}$

$F_{drive} = kA_{drive}\cos\omega t$

$A = \frac{A_{drive}\omega_0^2}{\sqrt{(\omega_0^2-\omega^2)^2 + (\omega\omega_0/Q)^2}}$

$\tan\theta = \frac{\omega\omega_0/Q}{\omega_0^2-\omega^2}$



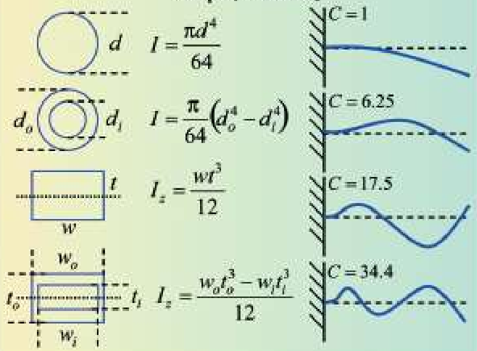
$\delta A_{(\max slope)} = \frac{2QA_0}{3\sqrt{3}(k-F')}F'$

$\delta\omega_0 \approx -\frac{\omega_0 F'}{2k} \quad \delta\theta_{(res)} = \frac{Q}{k}F'$

$\bar{P}_{tip} = \frac{1}{2}\frac{kA^2\omega}{Q}\left[\frac{QA_{drive}\sin\theta}{A} - \frac{\omega}{\omega_0}\right]$

Cantilever Beam Theory

$k = 3\frac{EI}{l^3} \quad f_0 = \frac{C}{2\pi}\sqrt{\frac{k}{m_t + 0.24m_c}} \quad m_c = \rho Al$



$I = \frac{\pi d^4}{64}$

$I = \frac{\pi}{64}(d_o^4 - d_i^4)$

$I_z = \frac{wt^3}{12}$

$I_z = \frac{w_o t_o^3 - w_i t_i^3}{12}$

Energies

k_BT = 4 pNnm

ATP hydrolysis
12-21 k_BT
Hydrogen Bond
4-18 k_BT
Covalent Bond
100-200 k_BT
Protein Stability
6-20 k_BT

	Young's Modulus E (GPa)	Density ρ (kg/m³)	Speed of Sound (m/s)	Thermal Expansion (um/mK)	Thermal Conductivity λ (W/mK)	Heat Capacity c_p (J/gK)
Stainless	200	7760	5100	10-13	12-25	.5
Steel	210	7850	5200	11	35	.46
Ti	116	4500	5100	8.9	17	.528
Al	70	2700	5100	24	190	.88
Invar	148	8050	4300	1.3	10.15	.515
SiN	260-320	3100	~9800	3	30	.71
Si	179	2330	8800	2.6	150	.7
Cu	117	8900	3600	17	383-391	.385
W	400	19300	4500	4.4	163	.134
Granite	20-60	2500-2700	~5000	3.7-11	1.4-4.2	.21-.35
Pyrex	61	2250	5500	4.4	163	.134

Cantilever Shapes

$h_{end}(x) = \frac{3Lx^2 - x^3}{2L^3}$

$h_{dist}(x) = G(\cosh\kappa x - \cos\kappa x) + H(\sinh\kappa x - \sin\kappa x)$

Shot Noise

$\delta V_{rms} = R\sqrt{2e\eta P_0 B}$

Johnson Noise

$\delta V_{rms} = \sqrt{4k_BTRB}$

Thermal Noise

on resonance

$\delta z_{rms} = \sqrt{\frac{4k_BTBQ}{k\omega_0}}$

off resonance

$\delta z_{rms} = \sqrt{\frac{4k_BTB}{Qk\omega_0}}$

Forces

Covalent Bonds
2-5 nN
Unzipping DNA
20 pN (GC)/10 pN (AT)
1 mW of light reflecting off of a surface
7 pN

Distances

Covalent Bonds
0.1nm
Hydrogen Bond
0.25 nm
Tip Radius of Curvature
2-50 nm
DNA diameter
2nm

Stiffness

Covalent Bond
10N/m
Cantilevers
0.01 -100N/m

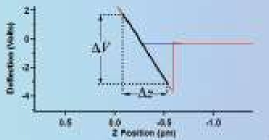
Added Mass Correction

$m_t = m_m\left(\frac{L-\Delta L}{L}\right)^3$

Reference Spring

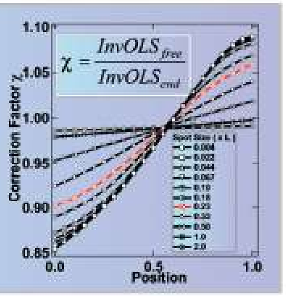
$k = k_{ref}\left(\frac{\Delta z_{ref}}{\Delta z} - 1\right)$

Thermal Method



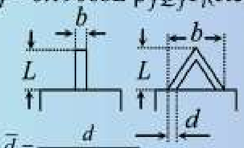
$InvOLS_{end} = \Delta z / \Delta V \ (nm/volt)$

$k = \frac{k_BT}{\langle\delta V^2\rangle\chi^2 InvOLS^2}$



Sader Method

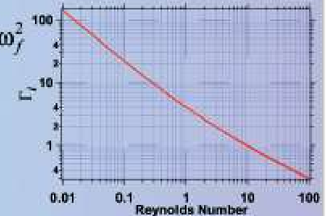
$k_{rect} = 0.1906 bL^2 \rho_f Q_f \Gamma_i(\mathrm{Re})\omega_f^2$



$\bar{d} = \frac{d}{\sqrt{1 + b^2/4L^2}}$

$D_0 = k_{rect}\frac{4L^3}{b} \quad \mathrm{Re} = \frac{\rho\omega b^2}{4\eta}$

$k_{tri} = \frac{D_0\bar{d}}{2L^3}\left(1 + \frac{4\bar{d}^3}{b^3}\right)^{-1}$



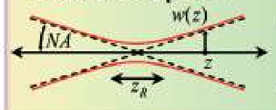
$\rho_{water} = 1x10^3 kg/m^3$

$\eta_{water} = 8.9x10^{-4} kg/m \cdot s$

$\rho_{air} = 1.18 kg/m^3$

$\eta_{air} = 1.86x10^{-5} kg/m \cdot s$

Gaussian Optics



$w(z) = w_0\sqrt{1 + \left(\frac{\lambda z}{\pi w_0^2}\right)^2}$

$z_R = \frac{\pi w_0^2}{\lambda} \quad N.A. = \frac{\lambda}{\pi w_0}$

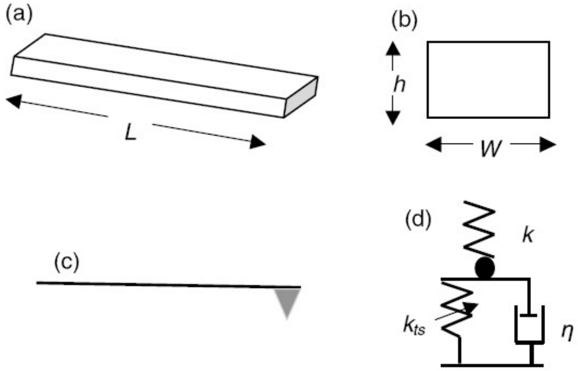
Coherence Length

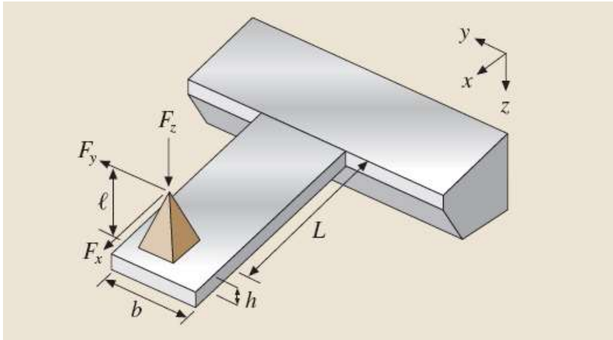
$\Delta l = c\Delta t \cong \frac{\lambda_0^2}{\Delta\lambda_0}$

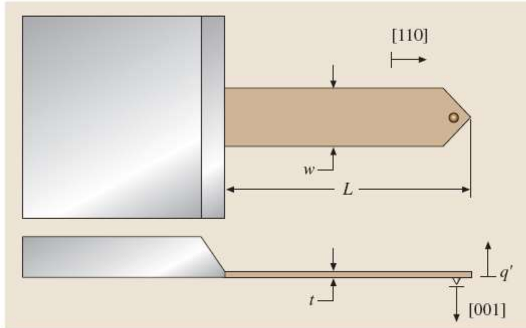
Thin Lens

$\frac{1}{s} + \frac{1}{s'} = \frac{1}{f}$

矩形微悬臂







静态力常数： $k_s = k = \dfrac{EWh^3}{4L^3}$

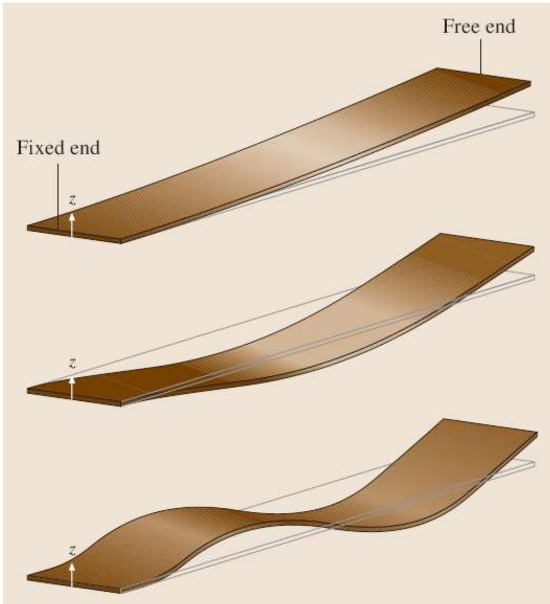
共振频率：

$$\kappa_n \cong \pi\left(n - \frac{1}{2}\right) \quad for \;\; n \geq 3$$

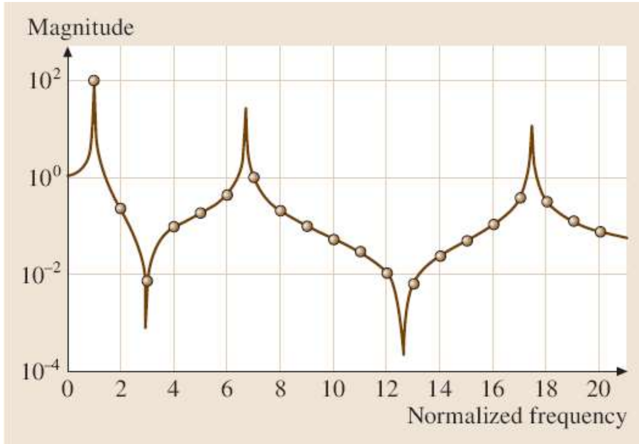
$$\kappa_1 \cong 1.875 \qquad \kappa_2 \cong 4.964$$

$$f_n = \frac{1}{2\pi}\frac{\kappa_n^2}{\sqrt{12}}\sqrt{\frac{E}{\rho}}\frac{h}{L^2}$$

***E* 杨氏模量，ρ质量密度**

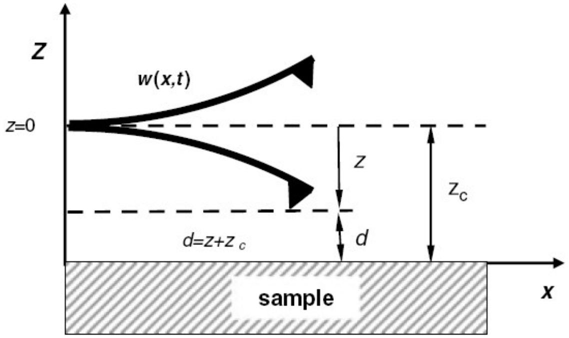


模态分析



传递函数分析：同样激励大小，不同激励频率下的微悬臂振动振幅

微悬臂运动：主方程

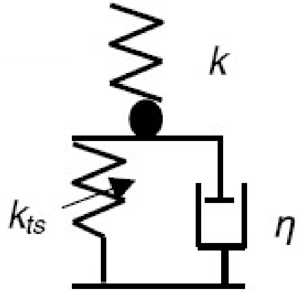


欧拉-伯努利（Euler-Bernoulli）方程

$$EI\frac{\partial^4}{\partial x^4}\left[w(x,t)+a_1\frac{\partial w(x,t)}{\partial t}\right]+\rho Wh\frac{\partial^2 w(x,t)}{\partial t^2}=-a_0\frac{\partial w}{\partial t}+\delta(x-L)[F_{\mathrm{exc}}(x,t)+F_{ts}(d)]$$

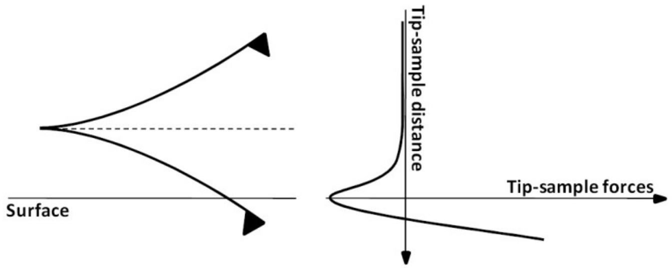
点质量弹簧谐振子模型

$$m^*\ddot{z}=-kz-\frac{m^*\omega_0}{Q}\dot{z}+F_0\cos\omega t+F_{\mathrm{ts}}(d)$$



$$\omega_0=\sqrt{\frac{k}{m^*}}$$

F_0和ω是分别是激励力的大小和角频率；
m^*，Q，ω_0和k分别是自由微悬臂的有效质量，品质因数，自然角频率（无阻尼的）和力常数。
悬臂有效质量 m^*与微悬臂真实总质量m_c的关系为$m^*\approx 0.25m_c$。



针尖–样品间相互作用力：多组成、非线性、非单调、大小、方向、耗散、路径依赖、环境依赖等

微悬臂运动：自由简谐振子

针尖远离样品（无相互作用力）

一般情形：

$$z = B\exp\left(-\frac{\alpha}{2}t\right)\cos(\omega_r t - \beta) + A\cos(\omega t - \Phi)$$

$(\alpha = \omega_0/Q)$

$$\begin{cases} A(\omega) = \dfrac{F_0/m}{[(\omega_0^2 - \omega^2)^2 + (\omega\omega_0/Q)^2]^{1/2}} \\ \tan\Phi = \dfrac{\omega_0\omega/Q}{\omega_0^2 - \omega^2} \end{cases}$$

$$\begin{cases} \omega_m = \omega_0\left(1 - \dfrac{1}{2Q^2}\right)^{1/2} \\ A_m = \dfrac{QF_0}{k}\dfrac{1}{\left(1-(1/4Q^2)\right)^{1/2}} \end{cases}$$

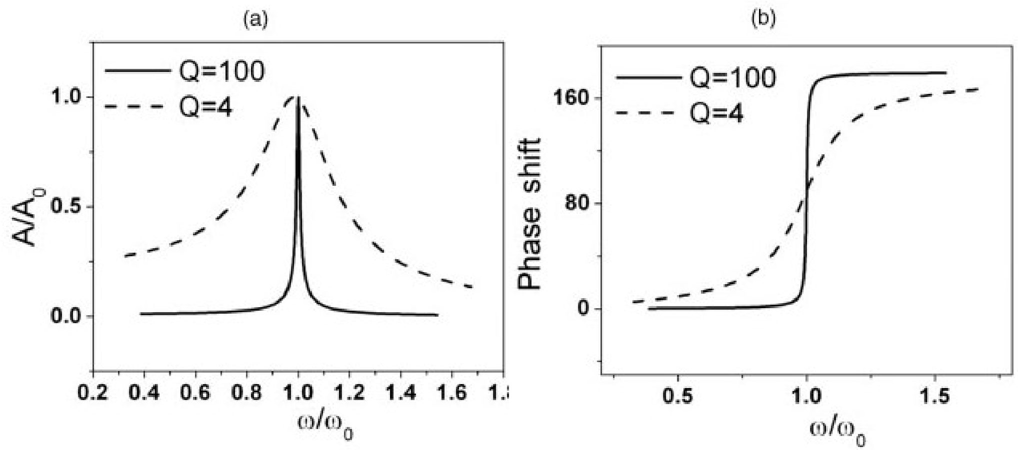
$\omega \approx \omega_0$时，$A_0 = \dfrac{QF_0}{k} = QA_d$

$$m^*\ddot{z} = -kz - \frac{m^*\omega_0}{Q}\dot{z} + F_0\cos\omega t$$

两种极限情形：

1 在激励频率远低于自由共振频率时，谐振子的运动响应由其倔强系数决定，谐振子与激励力协调一致运动，振幅约为F_0/k（准静态）。

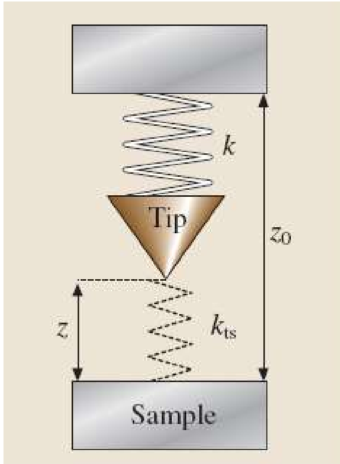
2 在当激励频率远大于ω_0时，回复力项kz相对$\frac{d^2z}{dt^2}$较小，此时，由于谐振子的加速度与其位移的相位差为180°，谐振子振幅较小且相位偏移为180°，谐振子运动响应由其惯性质量决定。



当有阻尼存在时，振幅最大时的激励频率和谐振子能量吸收最大的激励频率并不一致。最大的能量吸收（或功率）发生在激励频率ω等于自然共振频率ω_0时，即$\omega \approx \omega_0$，此时的相位偏移精确等于90°，且不依赖与品质因子Q的大小。这些结果表明了自然共振频率的特殊重要性。

弱扰动下的简谐振子

针尖靠近样品（存在相互作用力）： $m^{*}\ddot{z}=-kz-\frac{m^{*}\omega_0}{Q}\dot{z}+F_0\cos\omega t+F_{\mathrm{ts}}(d)$



针尖-表面间作用力可近似表示为： $F_{ts}(z)=F_{ts}(0)+(dF_{ts}/dz)_0 z$

$$k_{ts}=-(dF_{ts}/dz)_0$$

受迫阻尼谐振子的运动方程：

$$m\ddot{z}=-(k-k_{ts})z-\frac{m\omega}{Q}\dot{z}+F_o\cos\omega t+F_{\mathrm{ts}}(0)$$

因此，有效弹性力常数k_{eff}：

$$k_{\mathrm{eff}}=k-(\mathrm{d}F_{ts}/\mathrm{d}z)_0$$

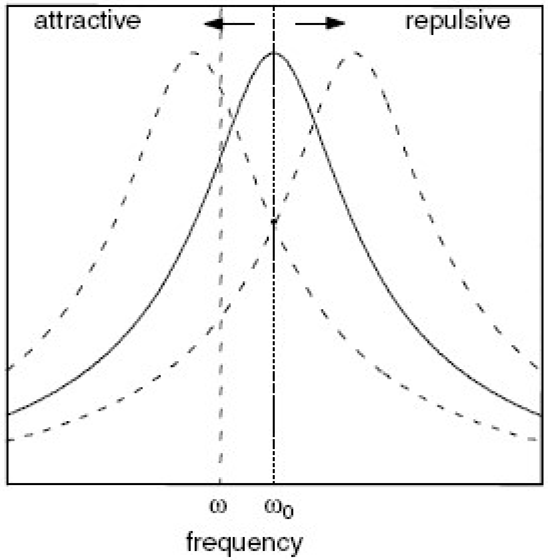
新的有效共振频率ω_{eff}可以由下式给出：

$$\omega_{\mathrm{eff}}=(k_{\mathrm{eff}}/m)^{1/2}$$

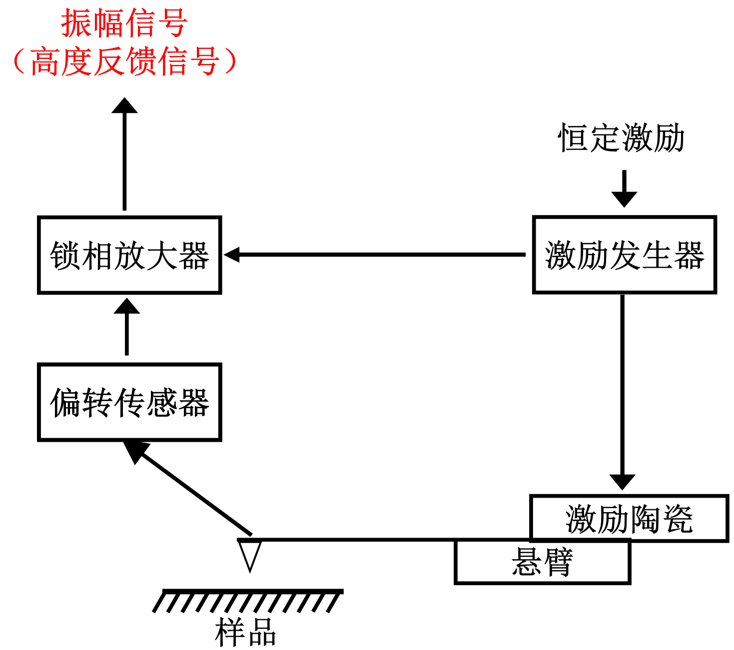
且频率差$\Delta\omega=\omega_{\mathrm{eff}}-\omega_0$可以近似为：

$$\Delta\omega\approx-(\omega_0 k_{ts}/2k)$$

上述方程表明，当相互作用力作线性近似时，振幅调制AFM的行为将如同一个线性谐振子，其共振频率依赖于相互作用力的力梯度。



振幅调制/轻敲模式

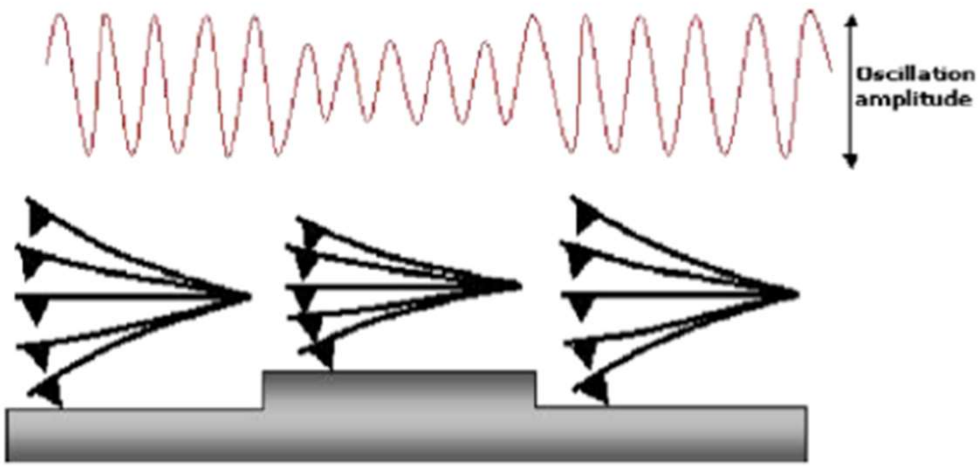


AM-AFM原理图
(恒定激励频率和振动振幅测量)

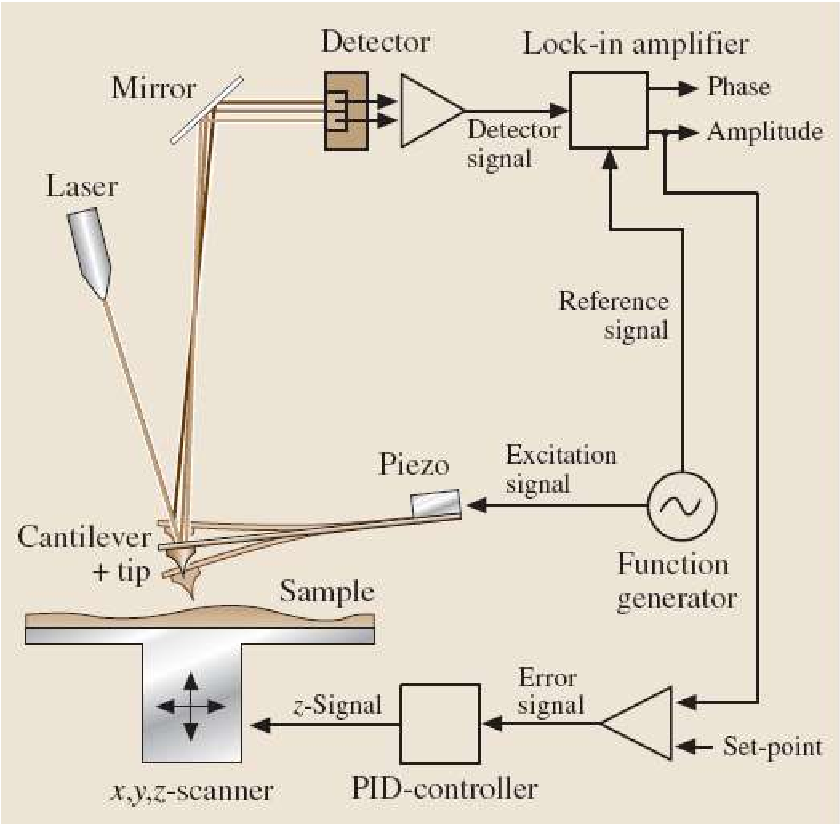
微悬臂探针的运动方程：

$$m^*\frac{d^2x}{dt^2}+\frac{m^*\omega_0}{Q}\frac{dx}{dt}+k_0x=F_{ts}+\boxed{F_0\cos(\omega t)}$$

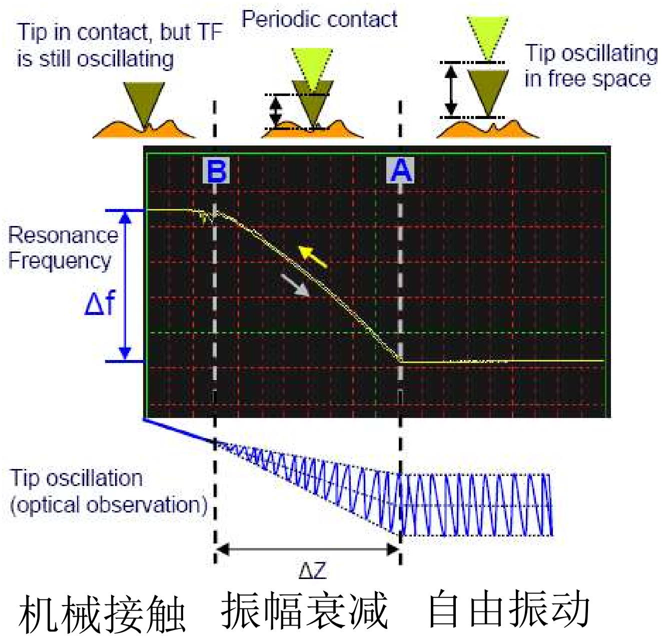
悬臂在固定的激励频率和激励振幅下振动，检测微悬臂探针振幅变化，作为反馈信号，可同时得到相位偏移信号。

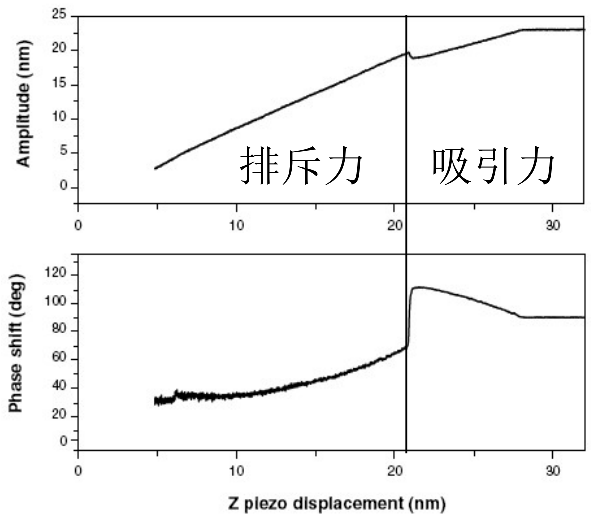


振幅调制/轻敲模式



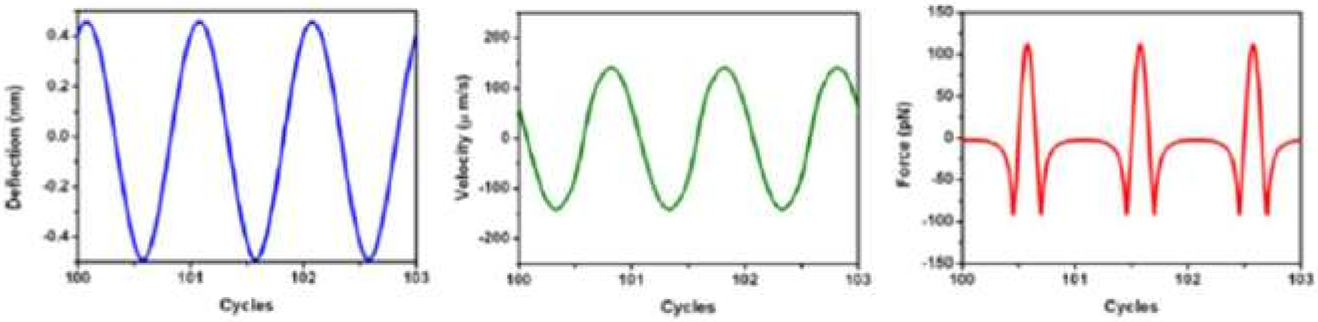
AM-AFM原理图
(恒定激励频率和振动振幅测量)

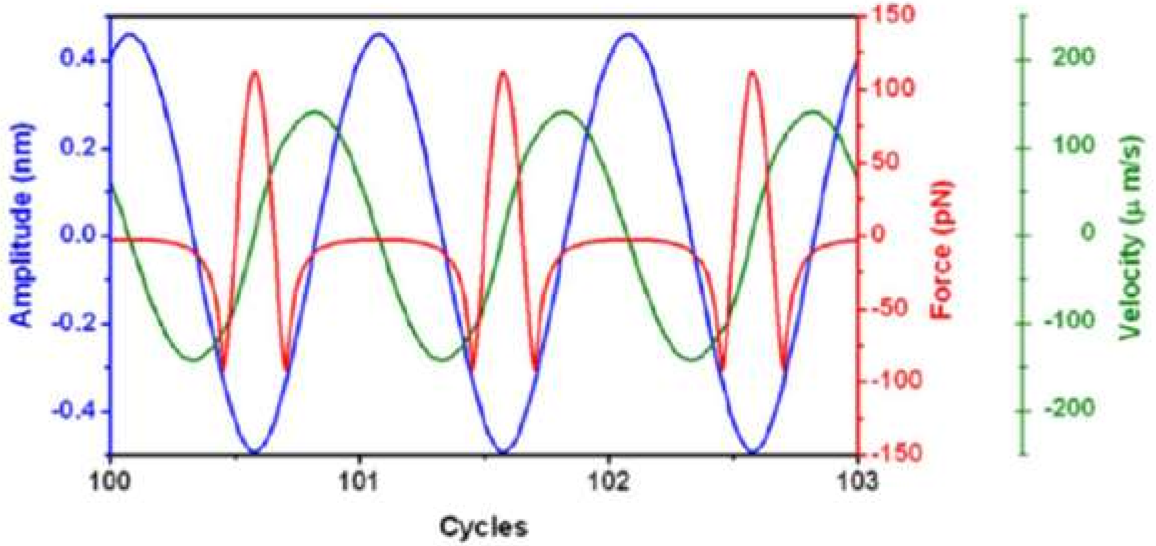




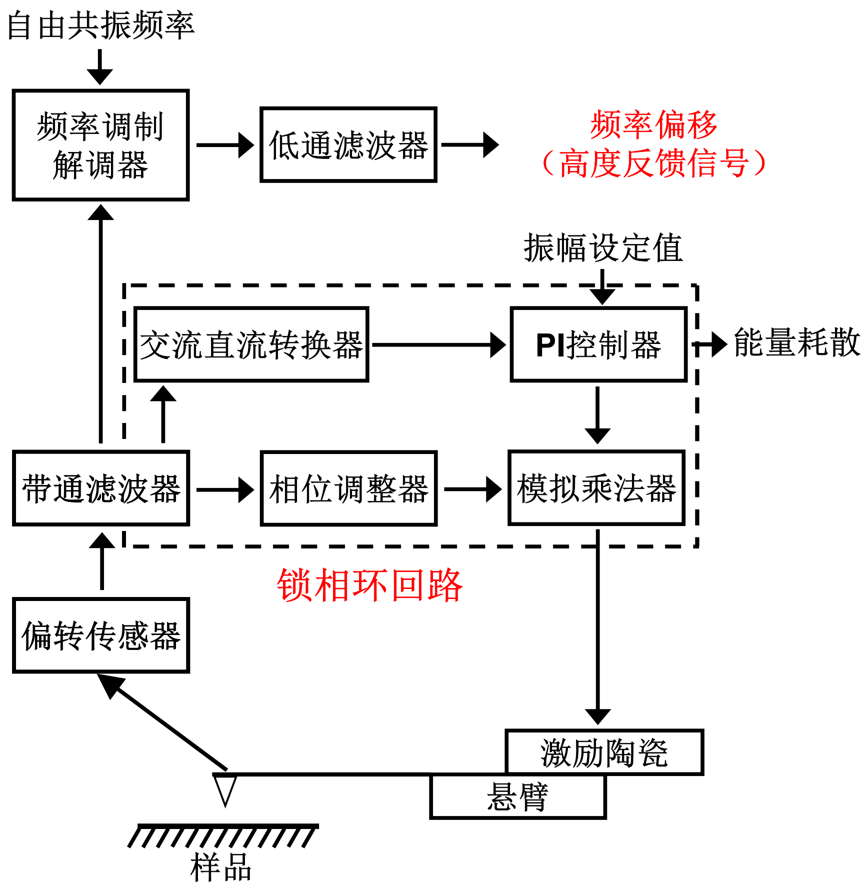
轻敲过程中的物理量

悬臂偏折 针尖速度 针尖-样品相互作用力





频率调制/非接触模式



FM-AFM电路原理图
(恒定振幅控制和频率偏移测量)

悬臂的运动方程：

$$m^*\frac{d^2x}{dt^2}+\frac{m^*\omega_0}{Q}\frac{dx}{dt}+k_0x=F_{ts}+F_0\cos(\omega t)$$

⇓

$$m^*\frac{d^2x}{dt^2}+k_0x=F_{ts}(x)$$

⇓

悬臂在当前共振频率 f 下，以恒定振幅简谐振动。

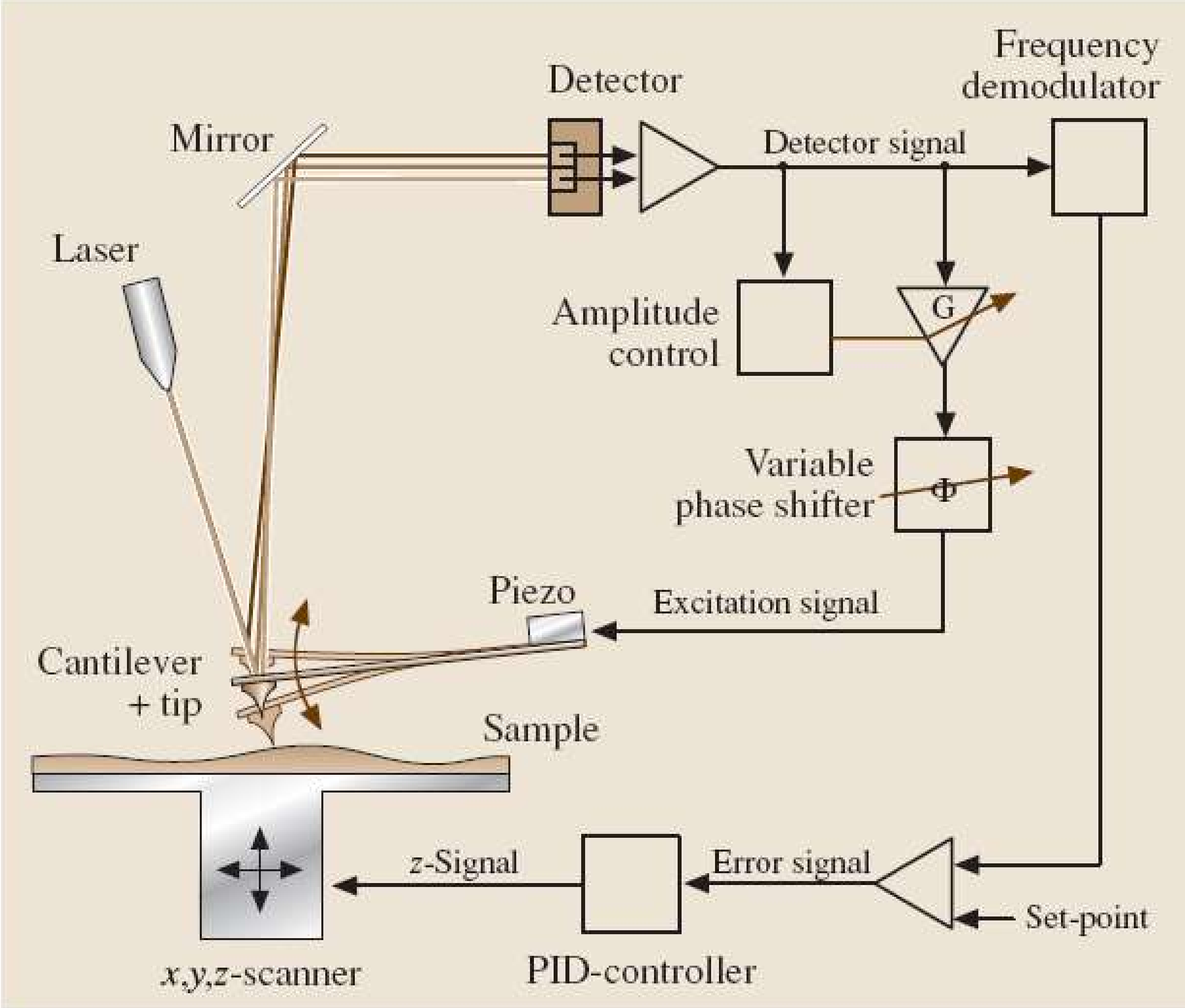
频率偏移的物理意义

$$\Delta f=-\frac{f_0}{2\pi k_0A^2}\langle F_{ts}x\rangle$$

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

小振幅近似

频率调制/非接触模式



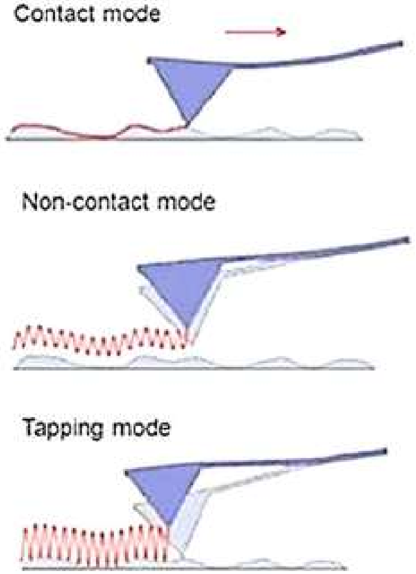
FM-AFM电路原理图
(恒定振幅控制和频率偏移测量)

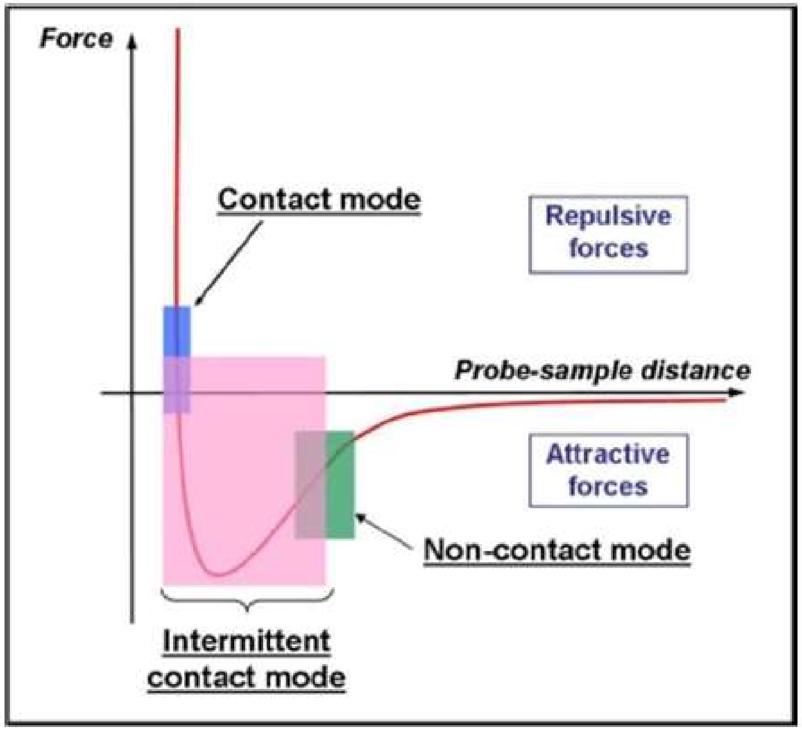
三种基本模式：对比与作用范围

接触模式 VS 非接触模式 VS 间歇接触模式

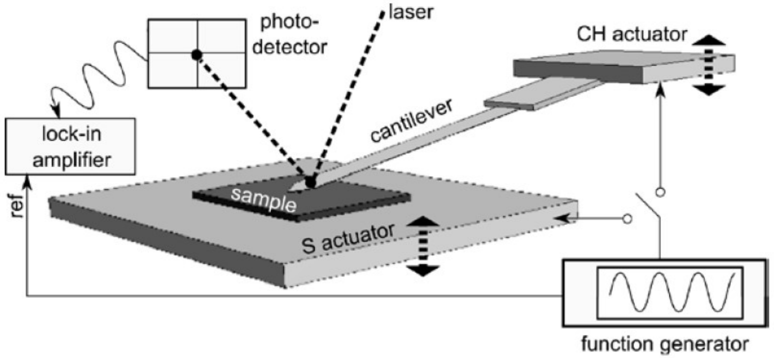
Modes of operation. There are 3 modes of AFM operation

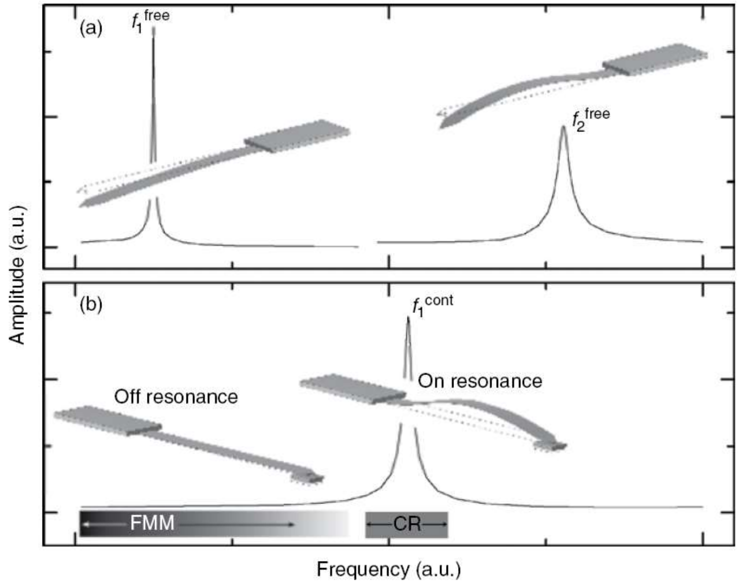
1. Contact mode
2. Non-contact mode
3. Tapping mode

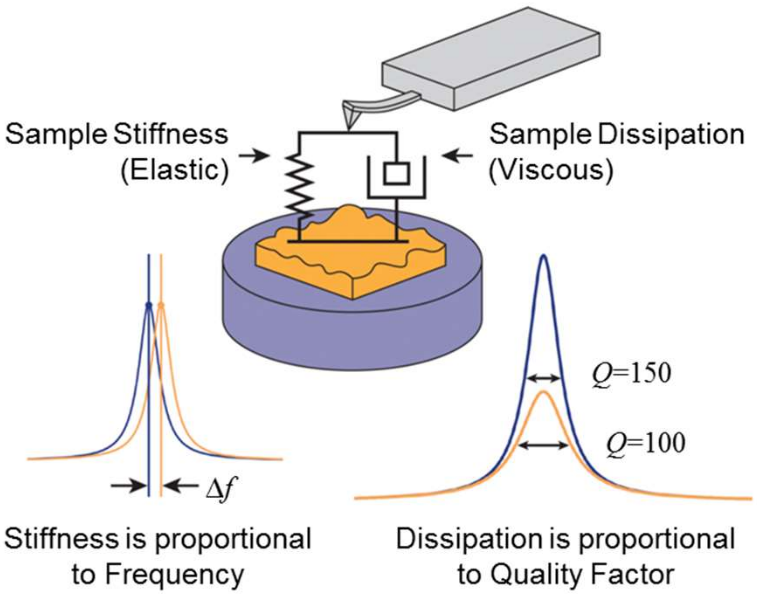




动态接触模式：力调制与接触共振







Kelvin-Voigt Mechanical Model

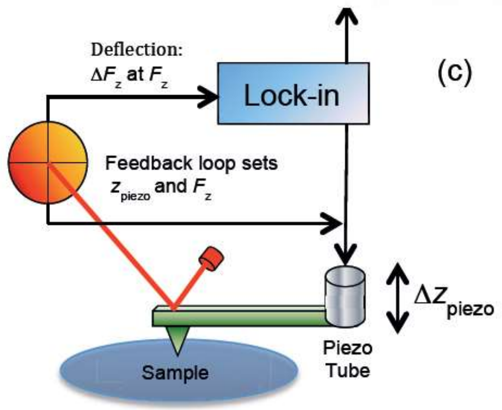
力调制模式：接触模式下，施加一个频率远低于接触共振频率的振动激励信号，测量微悬臂的振动响应（振幅，相位等）。

接触共振模式：接触模式下，通过锁相环技术始终锁定在当前共振频率下，施加一个振动激励信号，测量微悬臂的振动响应（共振频率、品质因子等）

CR-AFM Frequency: Stiffness (Elastic)

CR-AFM Q Factor: Energy Dissipation (Viscous)

力谱+力调制模式+接触力学模型



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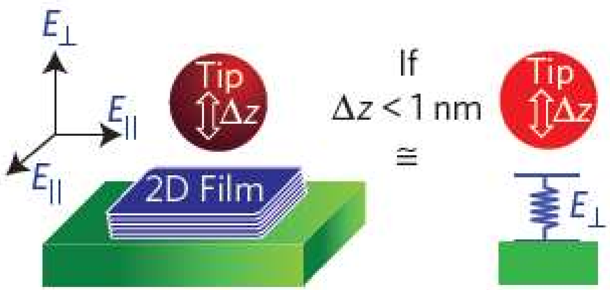
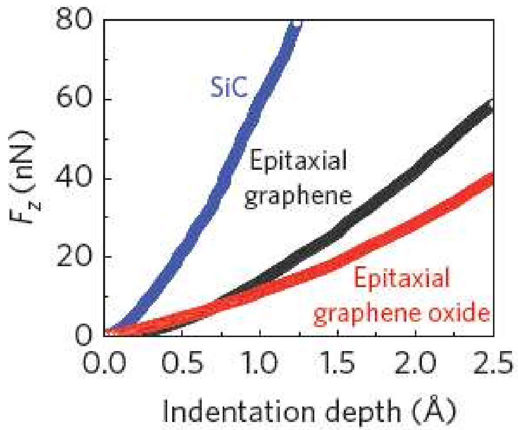
Elastic coupling between layers in two-dimensional materials

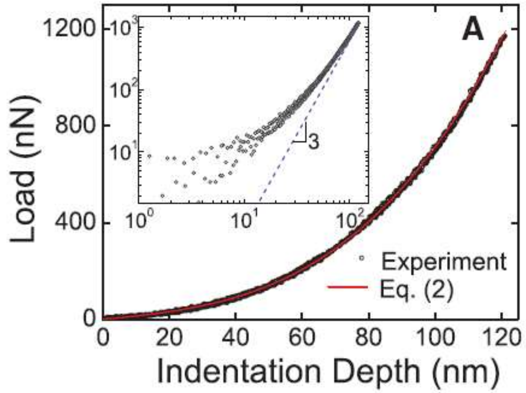
Yang Gao[1,2†], Suenne Kim[3†], Si Zhou[1], Hsiang-Chih Chiu[4], Daniel Nélias[5], Claire Berger[1,6], Walt de Heer[1,7], Laura Polloni[8], Roman Sordan[8], Angelo Bongiorno[1,9★] and Elisa Riedo[1,2★]

力谱模式
+
力调制模式

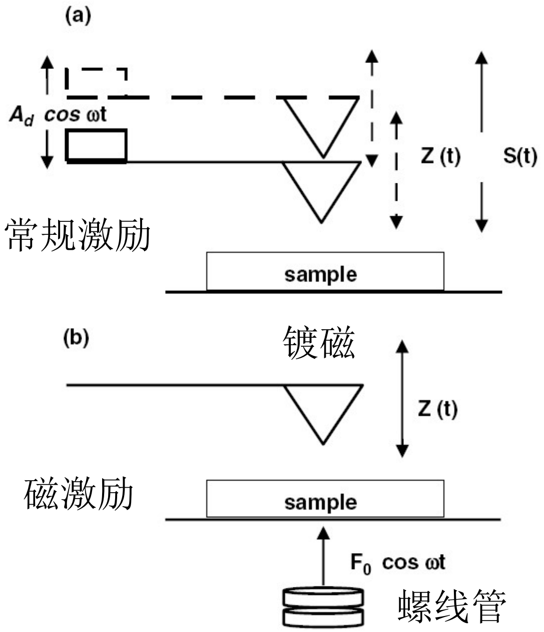
$$z_{\mathrm{indent}}(F_z) = \int_0^{F_z} \frac{\mathrm{d}F_z}{k_{\mathrm{cont}}(F_z)} \quad \Rightarrow \quad F_z = \frac{4}{3} E^*(R)^{1/2} z_{\mathrm{indent}}^{3/2}$$

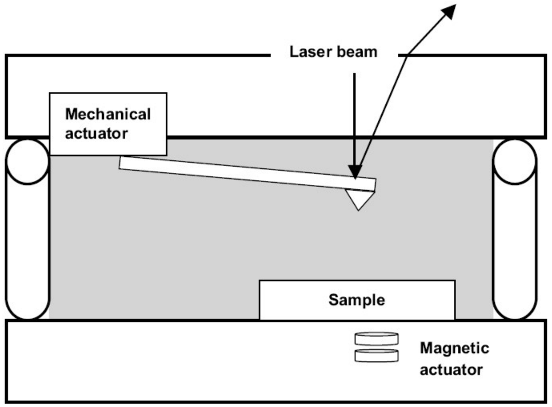




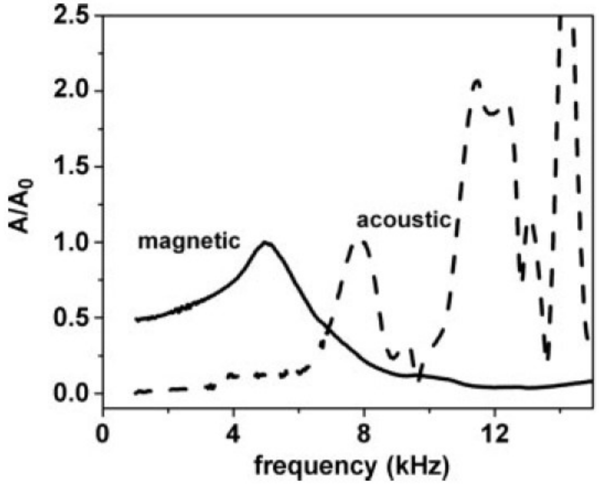


特殊激励模式：磁激励

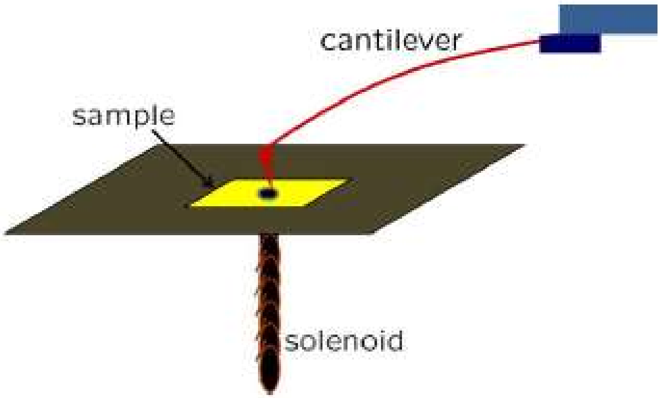


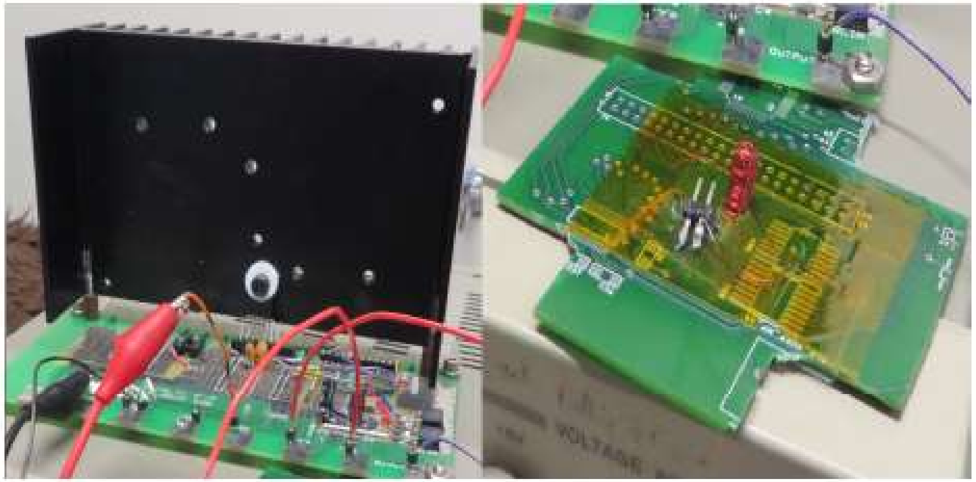


液体池

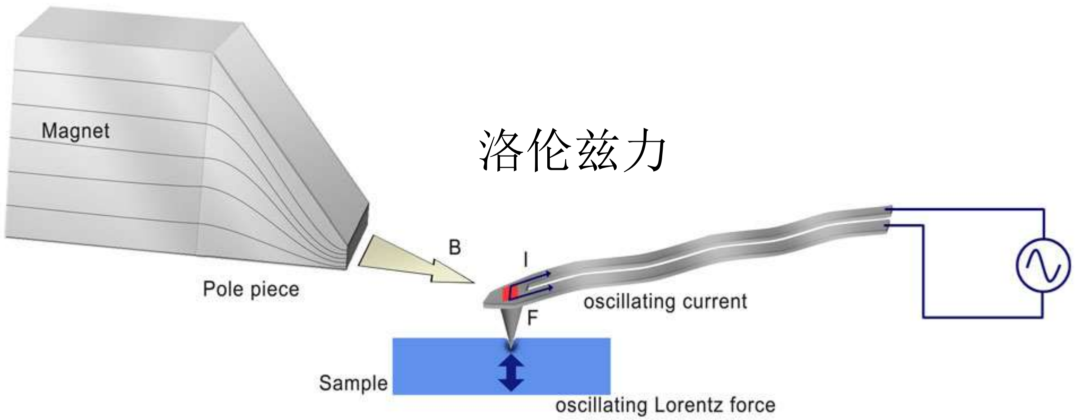


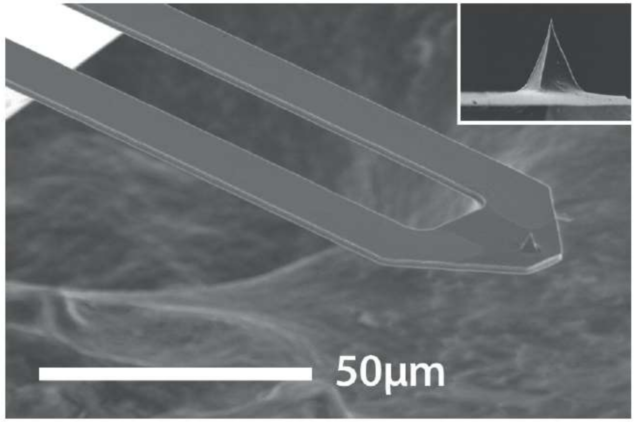
扫频曲线

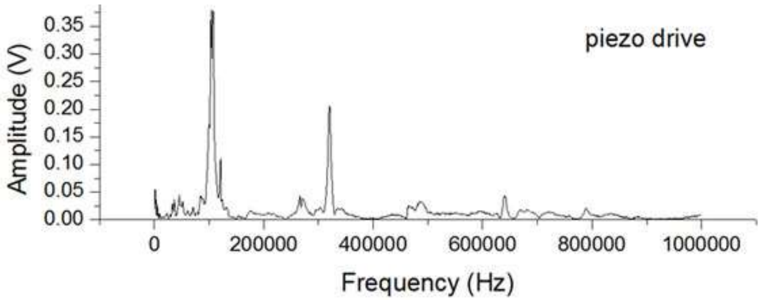


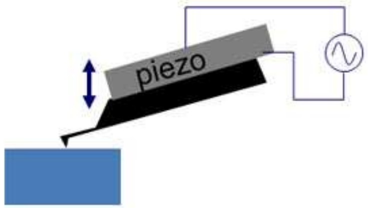


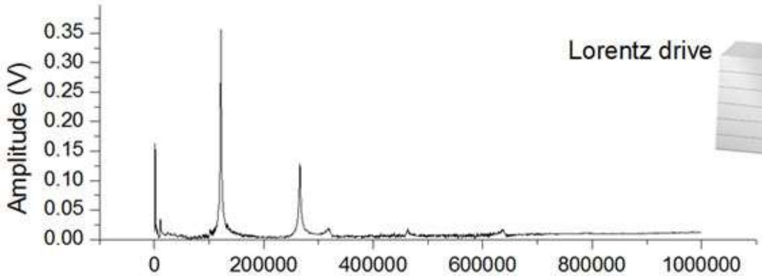
特殊激励模式：洛伦兹激励

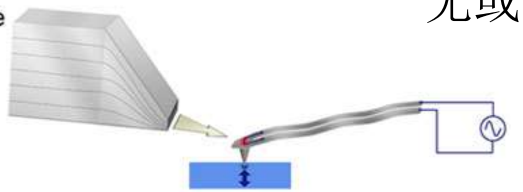












压电陶瓷激励 vs. 洛伦兹电激励

无或较少的寄生杂峰

特殊激励模式：静电型激励

中国人民大學 RENMIN UNIVERSITY OF CHINA

REVIEW OF SCIENTIFIC INSTRUMENTS 86, 073703 (2015)

Modular apparatus for electrostatic actuation of common atomic force microscope cantilevers

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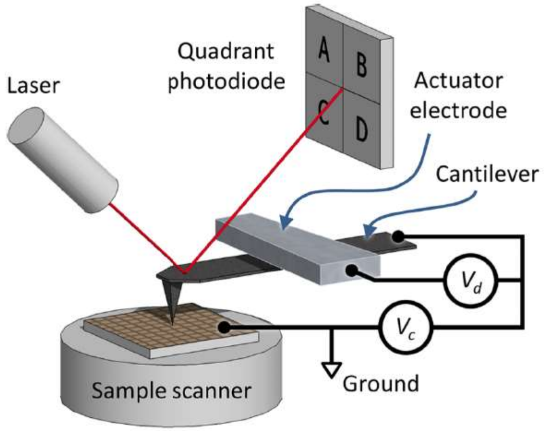
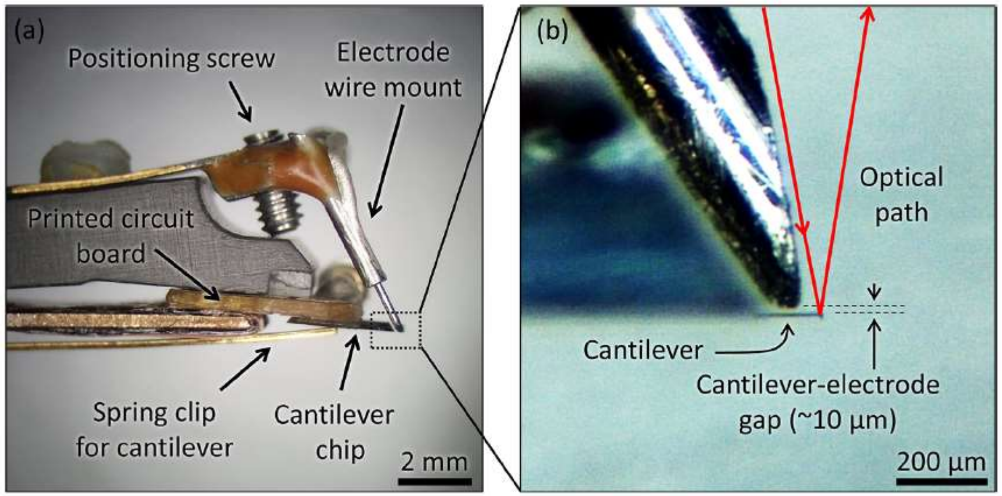


FIG. 2. Schematic of electrical connections to the sample, cantilever, and actuator electrode. V_c is a common bias to both the cantilever and electrode, while V_d is a differential bias between the actuation electrode and the cantilever. The connection of the sample to ground is optional, though it is useful for conducting samples in order to establish a well-defined surface potential.



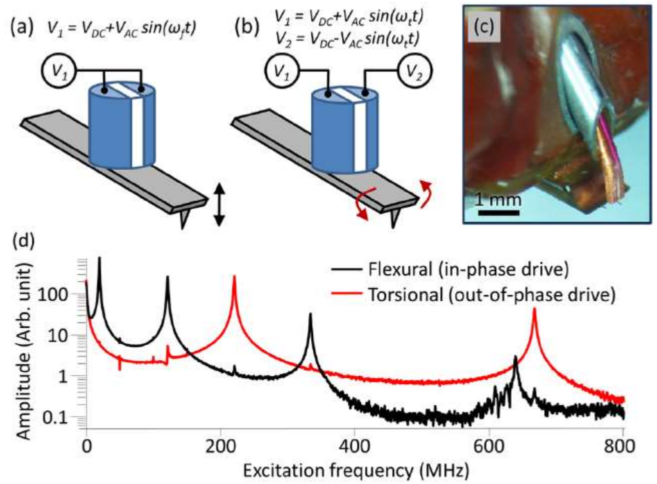
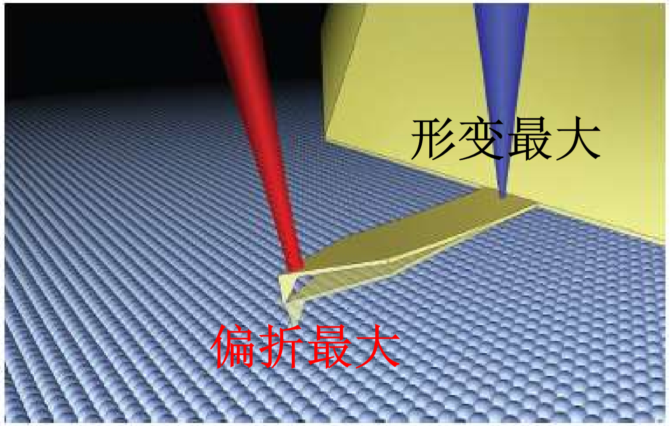


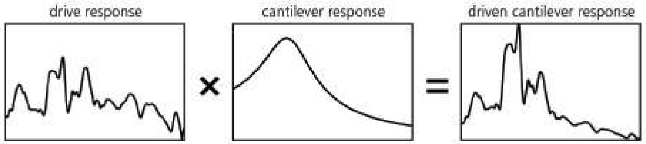
FIG. 6. Excitation of flexural and torsional cantilever modes using multiple electrodes. (a) shows a schematic in which both actuation electrodes are driven in-phase to excite the flexural modes of the cantilever. In (b), the actuation electrodes are driven with a common DC bias but with an out-of-phase AC bias to excite torsional modes of the cantilever. (c) shows an optical microscope image of a dual-electrode electrostatic actuator with a cantilever aligned to the electrodes. (d) The flexural and torsional actuation spectra are shown for the setup in (c). The cantilever is a model RC800PSA (Olympus, Tokyo, Japan). For both flexural and torsional excitations, a DC bias of 4 V and an AC bias of 4 V were applied to the electrodes.

特殊激励模式：光热激励



Photothermal excitation for improved cantilever drive performance in tapping mode atomic force microscopy

Aleksander Labuda, Jason Cleveland, Nicholas A. Geisse, Marta Kocun, Ben Ohler, Roger Proksch, Mario B. Viani and Deron Walters
Asylum Research, an Oxford Instruments company, Santa Barbara, CA, USA



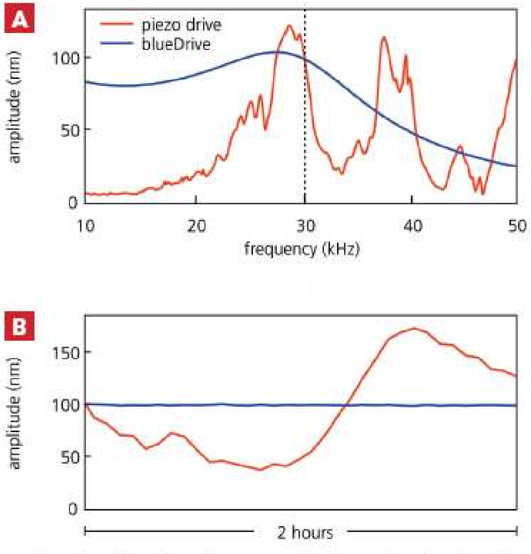
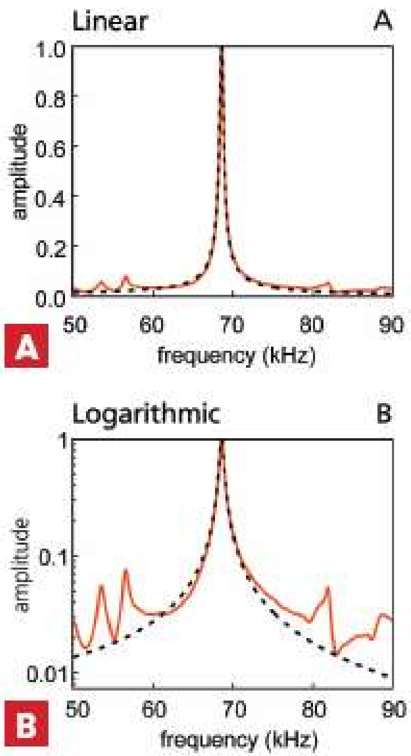
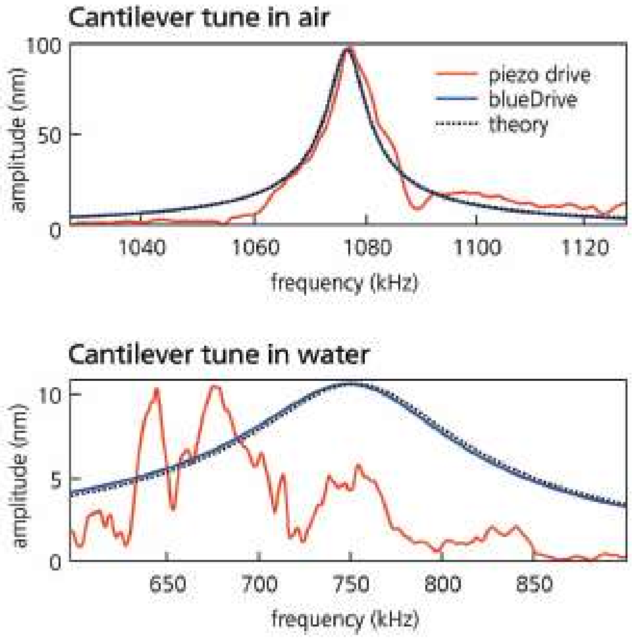


FIGURE 1,above, The driven cantilever response is the product of the drive response of the excitation source, here piezoacoustic, and the intrinsic resonance response of the cantilever

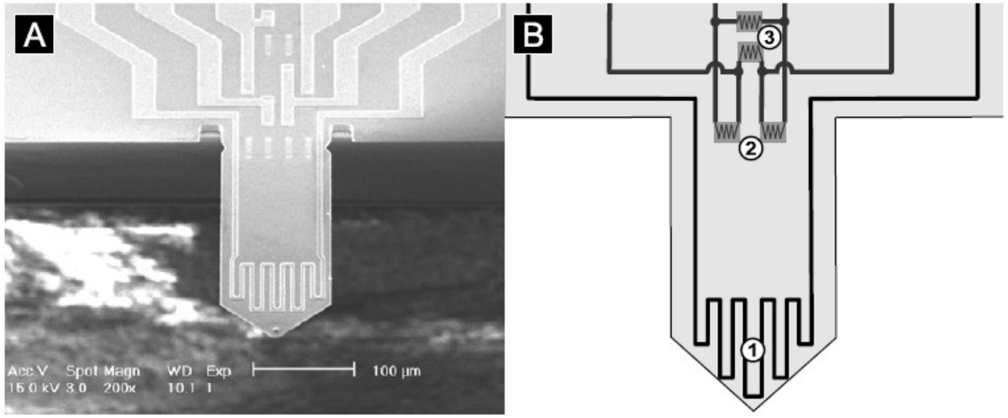
FIGURE 2
A. Representative cantilever tunes measured in water using piezoacoustic excitation and blueDrive photothermal excitation on an Asylum Research Cypher S AFM using an Olympus BL-AC40TS cantilever.
B. Amplitude stability measured over two hours for the same conditions



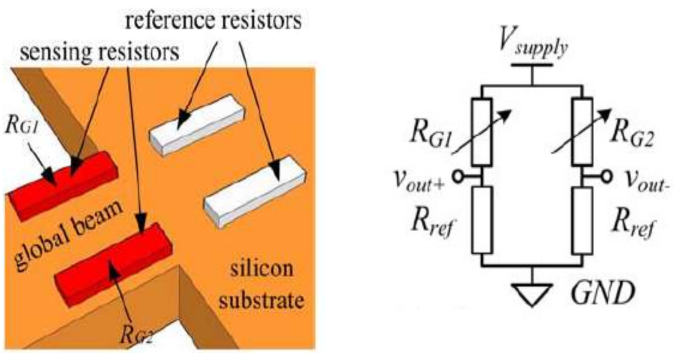


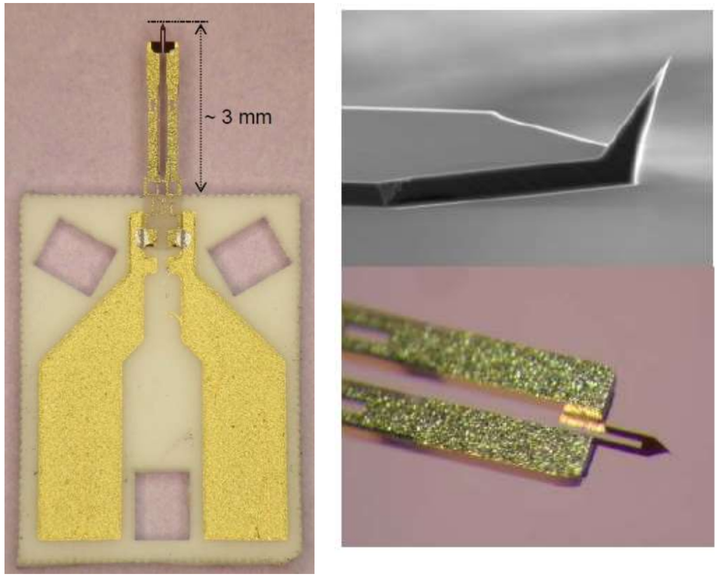
特殊微悬臂探针：自激励/自检测型

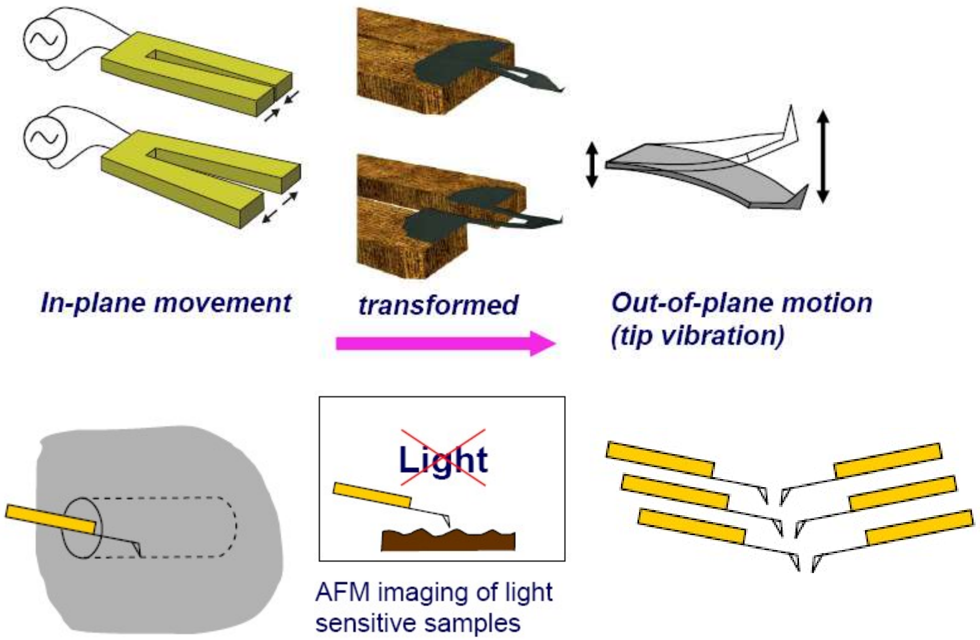
焦耳热激励，压阻检测



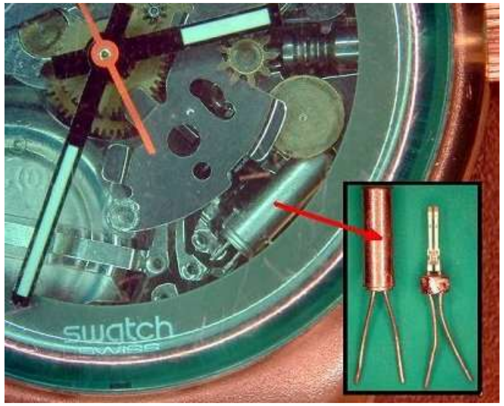
惠斯通电桥接法







qPlus力传感器



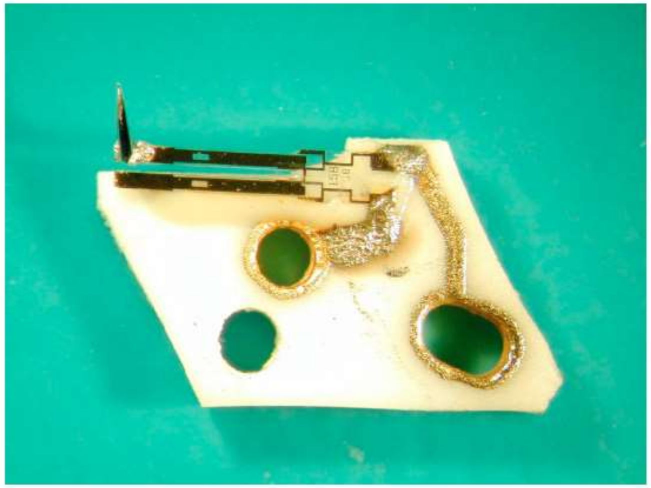
石英表的石英音叉

主要技术优势:

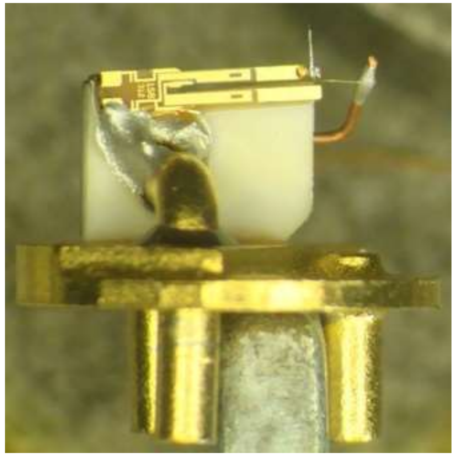
1、自感应，无需激光检测;
2、共振频率的温漂很小;
3、同时测量电流和力信号;
4、易于制作不同材料的探针，具有良好的拓展性。

基本技术指标:

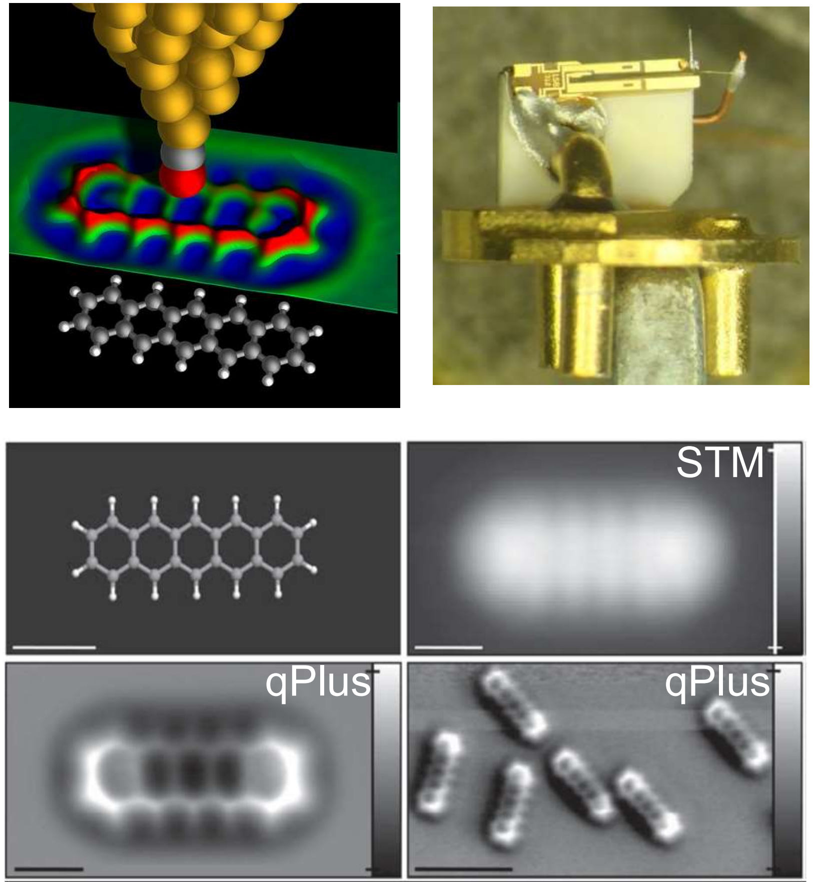
共振频率: 2^{15}=32768 Hz
弹性常数: 1800 N/m
品质因子: >50000
稳定工作振幅: ~ 0.5 Å,
(C-C 键长: ~ 1.54 Å)



qPlus-STM/AFM

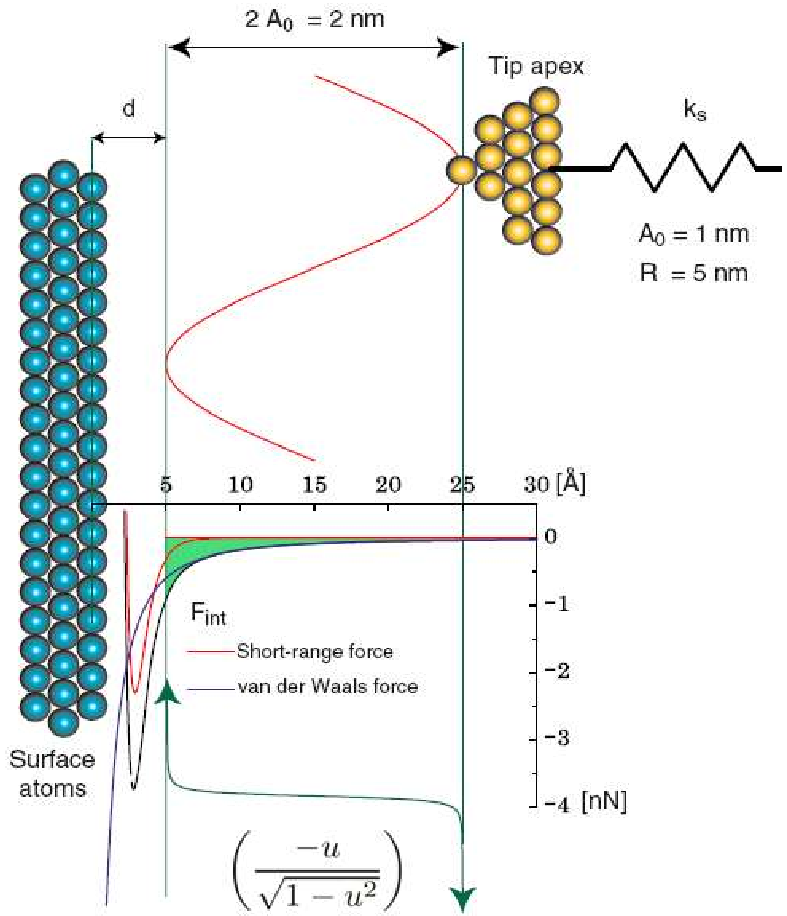


分子化学结构成像



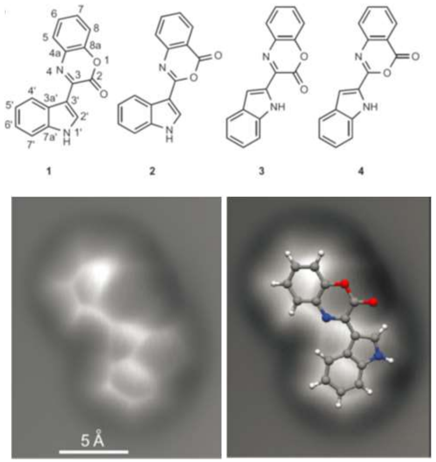
Pentacen on Cu(111): STM and qPlus-AFM image

L. Gross et al., Science 325, 1110 (2009)

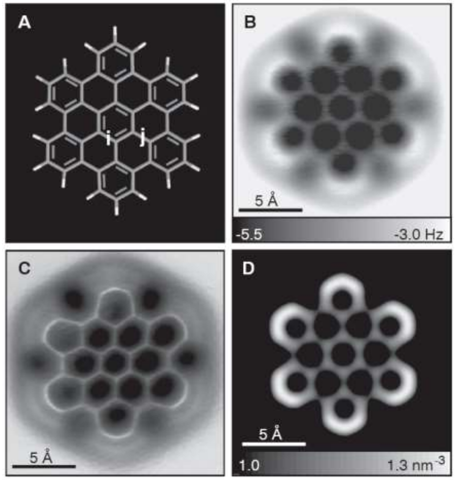


- Sub Å vibration amplitude
- Short-range chemical force and Pauli repulsion (quantum)
- Total electron densities

分子化学结构成像



L. Gross et al., Nature Chem. 224, 821 (2010)

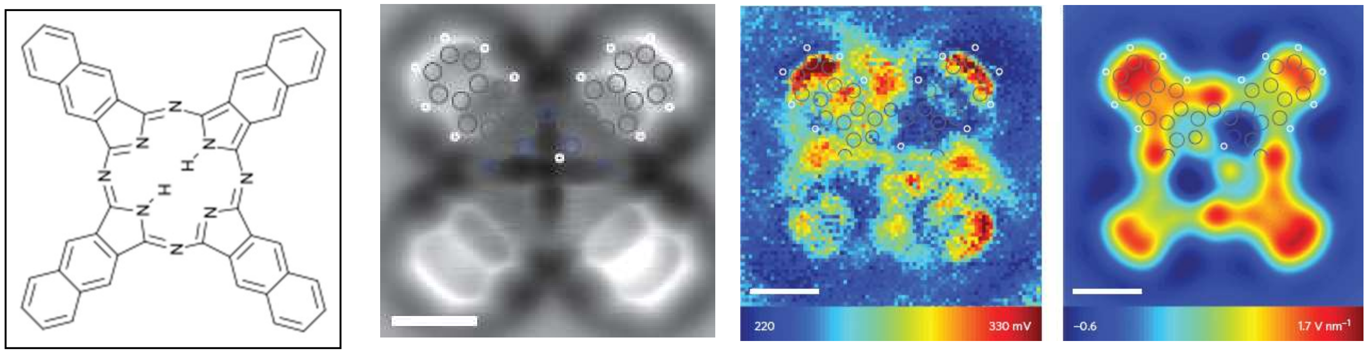


Leo Gross et al, Science 337, 2012 (2012)

AFM

KPFM

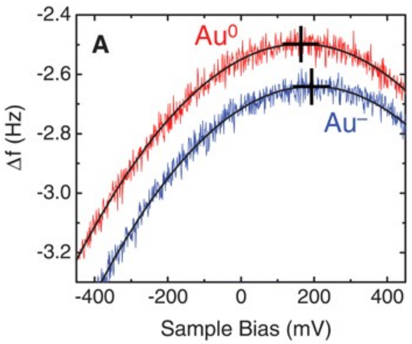
Charge Distribution

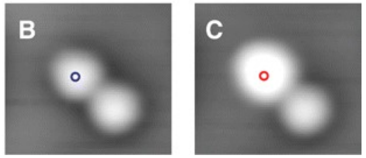


Nature Nanotech. **227**, 231 (2012)

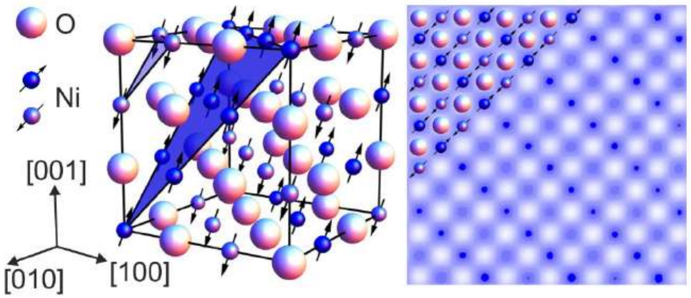
单原子尺度物理探测

静电力显微术：单电荷态





Science 324, 1428 (2009)

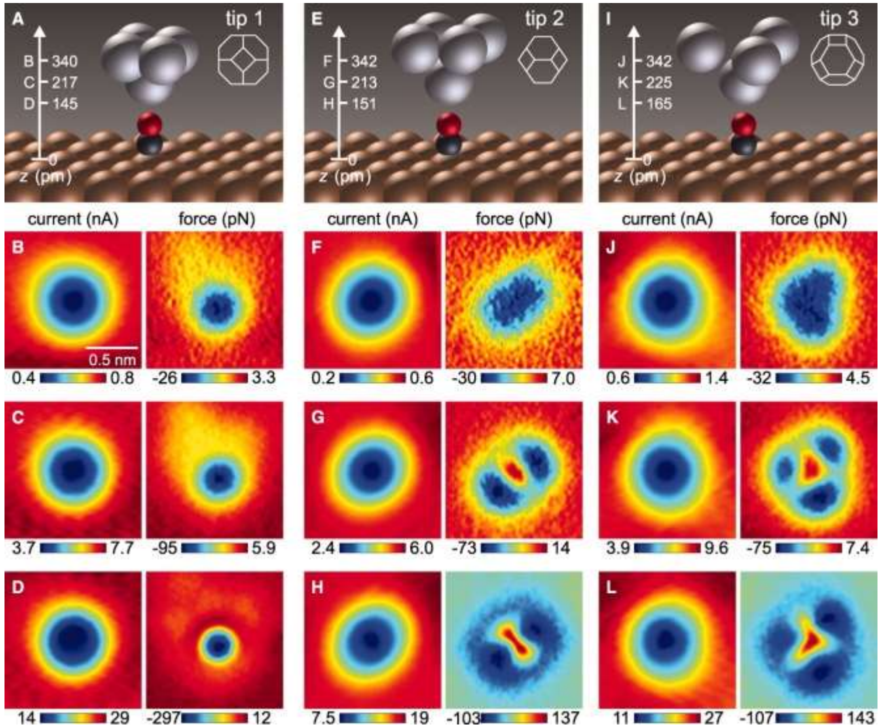


Phys. Rev. Lett. **110**, 266101 (2013)

磁交换力显微术：MExFM　量子自旋液体

电荷，自旋，轨道

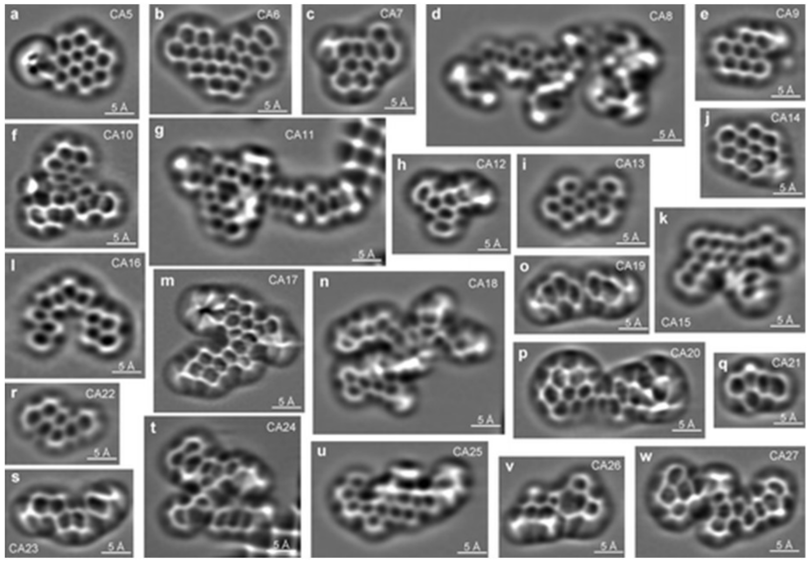
原子外层电子轨道成像？

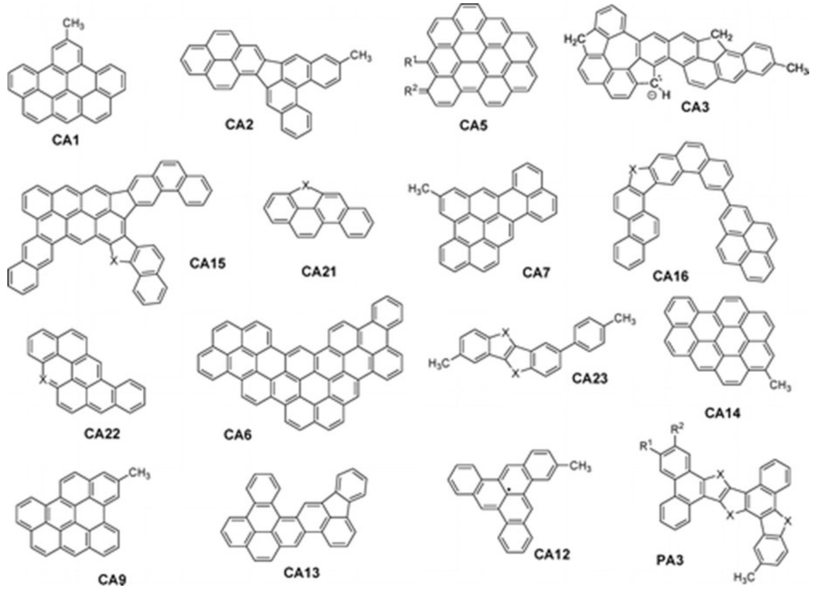


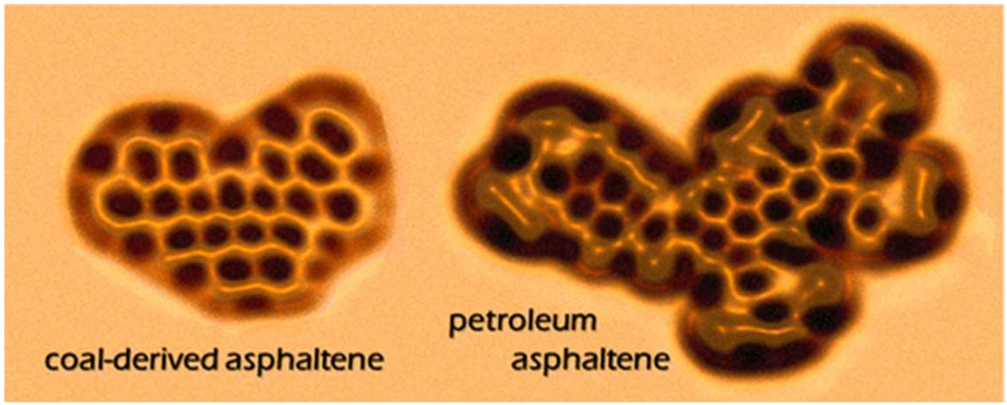
Science 336, 444 (2012)

Asphaltenes: from coal and petroleum

中国人民大學
RENMIN UNIVERSITY OF CHINA







煤炭焦油　　　　石油焦油

Structure Analysis

J. Am. Chem. Soc., **2015**, *137* (31)

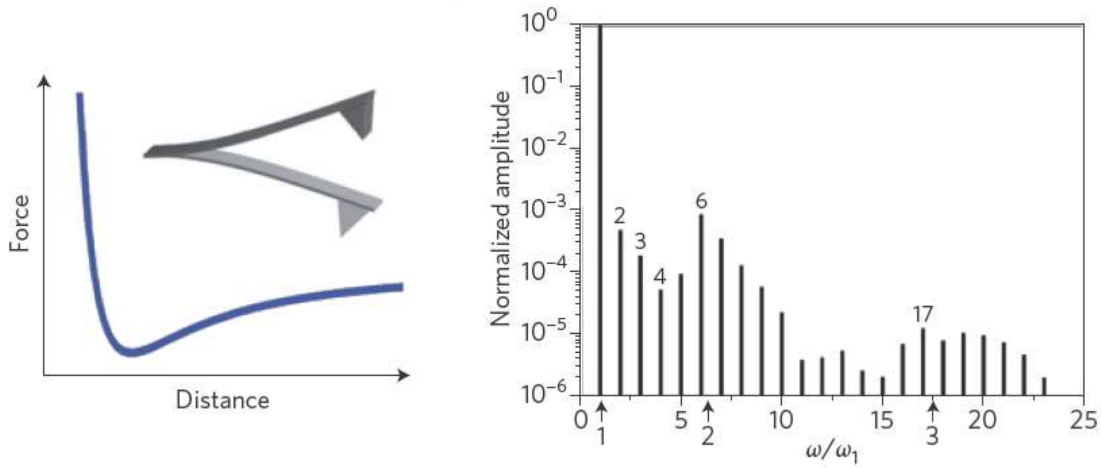
nature nanotechnology

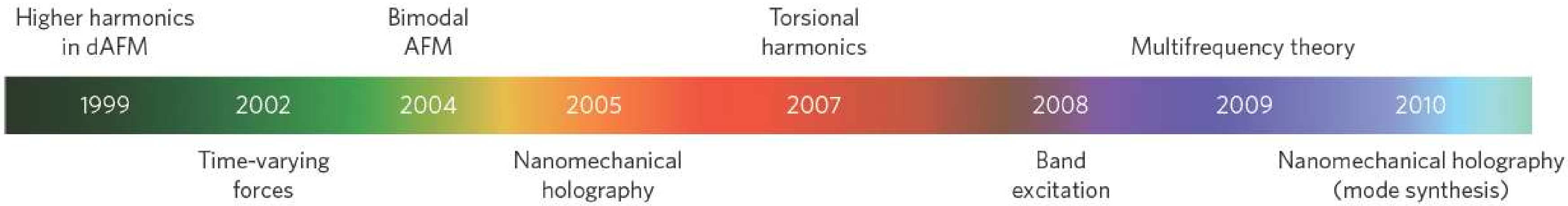
REVIEW ARTICLE

PUBLISHED ONLINE: 1 APRIL 2012 | DOI: 10.1038/NNANO.2012.38

The emergence of multifrequency force microscopy

Ricardo Garcia* and Elena T. Herruzo



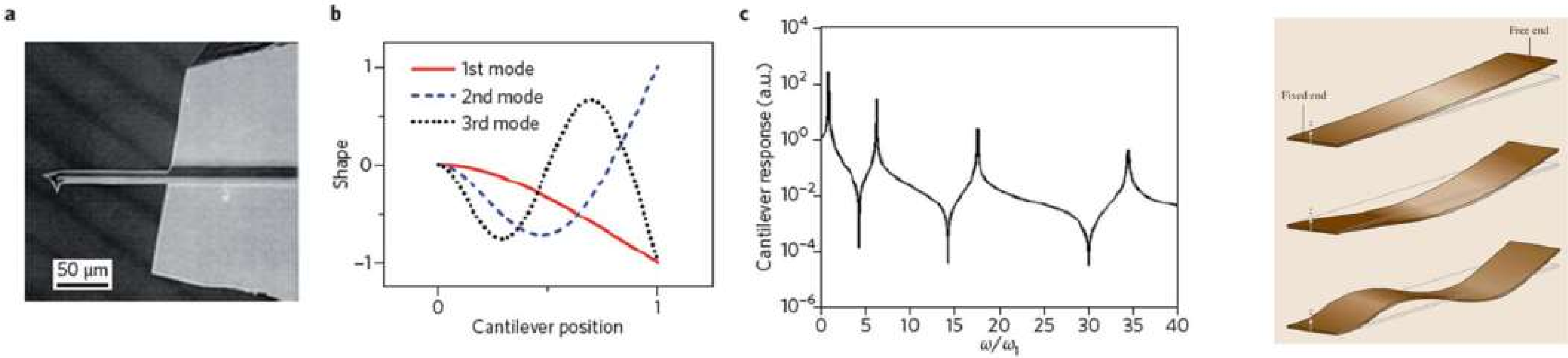


多频原子力探针显微术：基础原理

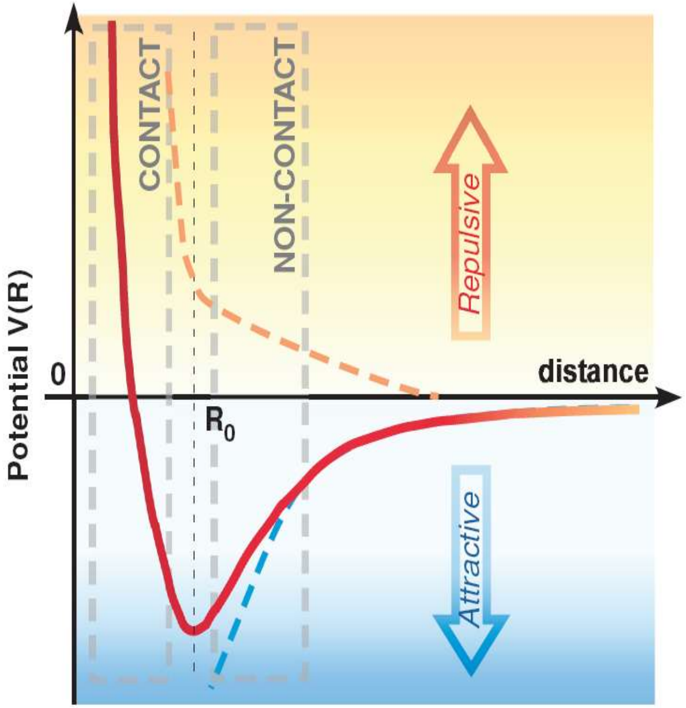
Table 1 | Cantilever properties.

Eigenmode (flexural)	κ_j	Frequency	Force constant	Quality factor (no internal damping)	Optical sensitivity
j		$\omega_j = \left(\frac{\kappa_j}{\kappa_1}\right)^2 \omega_1$	$k_j = \left(\frac{\omega_j}{\omega_1}\right)^2 k_1$	$Q_j = \frac{\omega_j}{\omega_1} Q_1$	$\sigma_j = \frac{\varphi'_j}{\varphi'_1} \sigma_1$
1	1.875	$\omega_1 = \omega_0$	k_1	Q_1	σ_1
2	4.694	$6.27\ \omega_0$	$39.31\ k_1$	$6.27\ Q_1$	$3.473\ \sigma_1$
3	7.855	$17.55\ \omega_0$	$308\ k_1$	$17.55\ Q_1$	$5.706\ \sigma_1$
4	10.996	$34.39\ \omega_0$	$1183\ k_1$	$34.39\ Q_1$	$7.985\ \sigma_1$

Adapted from refs 26, 32 and 45. The eigenmodes of the AFM cantilever are characterized by four parameters: the effective stiffness k_j (force constant), the resonant frequency $\omega_j = 2\pi f_j$, the quality factor Q_j and the optical sensitivity σ_j. For a rectangular cantilever without a tip there are several relationships among these parameters, which are approximations to describe real AFM cantilevers. κ_j are the real roots of a characteristic equation of the cantilever ($1 + \cos\kappa_j \cosh\kappa_j = 0$)[26]. φ_j is the shape of the jth eigenmode at the free end of the cantilever.



高次谐振：Multiharmonic

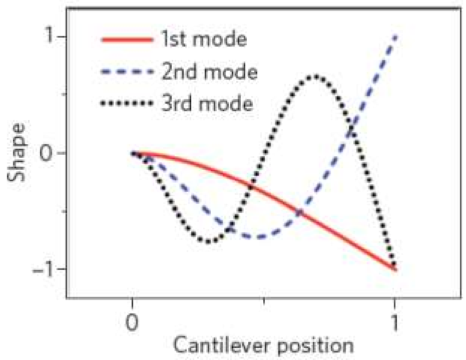


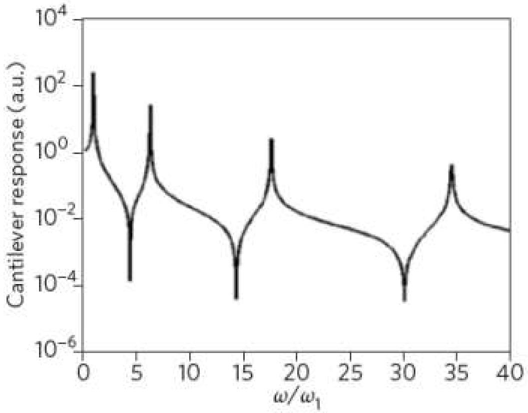
原子轨道间的力是非线性的！

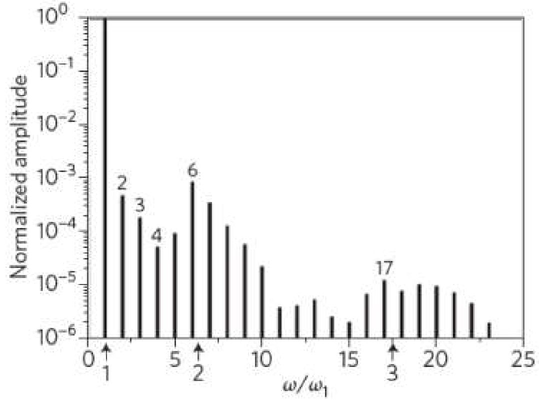
$$V_{Morse} = -E_{bond}(2e^{-\kappa(z-\sigma)} - e^{-2\kappa(z-\sigma)})$$

$$V_{Lennard\text{-}Jones} = -E_{bond}(2\frac{z^6}{\sigma^6} - \frac{z^{12}}{\sigma^{12}})$$

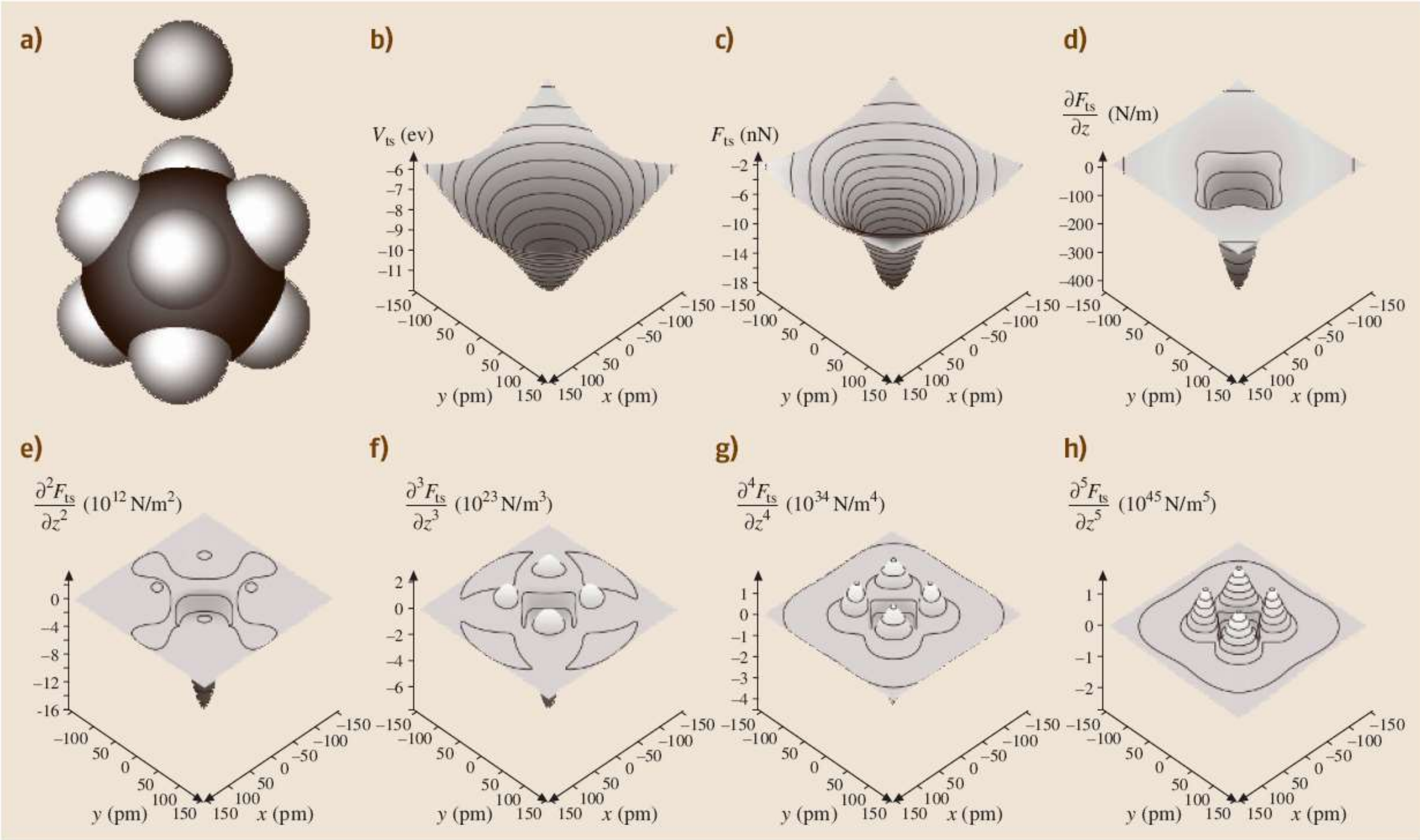
$$a_n = \frac{2}{\pi k}\frac{1}{(1-n^2)}\frac{1}{(2n+1)\ \ldots\ 3\cdot 1}A^n \times \int_{-1}^{1}\frac{\mathrm{d}F_{ts}^n(z+Au)}{\mathrm{d}z^n}(1-u^2)^{n-1/2}\,\mathrm{d}u$$







高次谐振应用：更高空间分辨



原子不是圆的，而是有形状的！

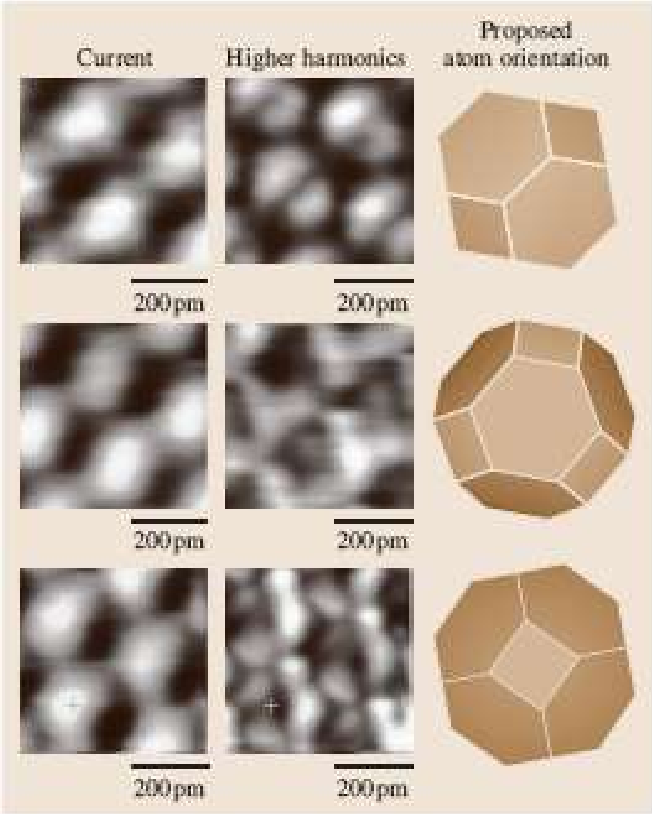
高次谐振应用：更高空间分辨

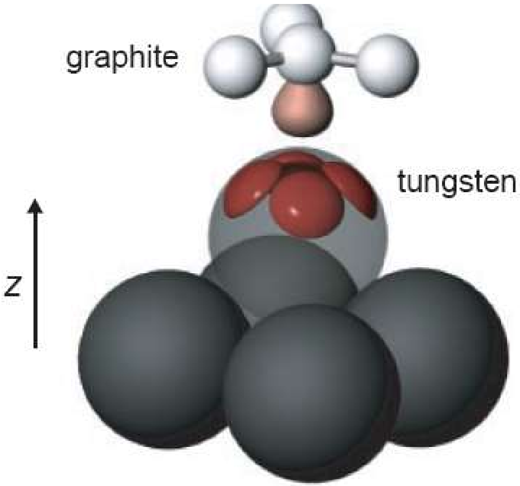
REPORTS

Force Microscopy with Light-Atom Probes

Stefan Hembacher, Franz J. Giessibl,* Jochen Mannhart

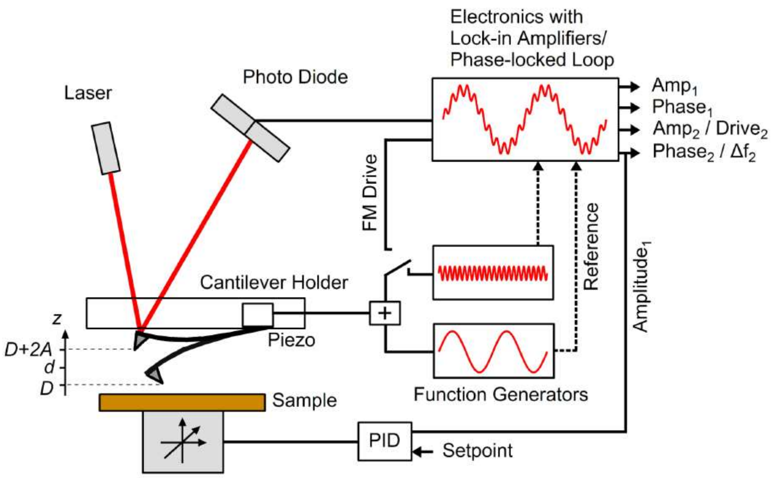
The charge distribution in atoms with closed electron shells is spherically symmetric, whereas atoms with partially filled shells can form covalent bonds with pointed lobes of increased charge density. Covalent bonding in the bulk can also affect surface atoms, leading to four tiny humps spaced by less than 100 picometers in the charge density of adatoms on a (001) tungsten surface. We imaged these charge distributions by means of atomic force microscopy with the use of a light-atom probe (a graphite atom), which directly measured high-order force derivatives of its interaction with a tungsten tip. This process revealed features with a lateral distance of only 77 picometers.



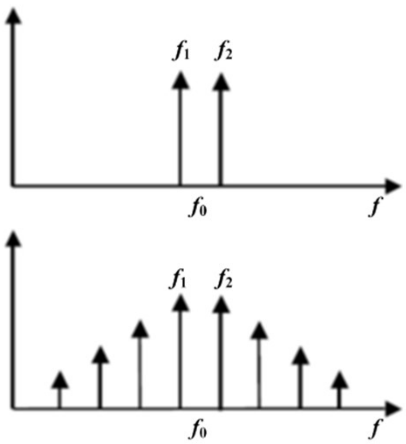


$$a_n = \frac{2}{\pi k}\frac{1}{1-n^2}\frac{A^n}{1\cdot 3\cdot \ldots \cdot (2n-1)}\int_{-1}^{1}\frac{d^n F_{ts}(z+Au)}{dz^n}(1-u^2)^{n-1/2}du \qquad (1)$$

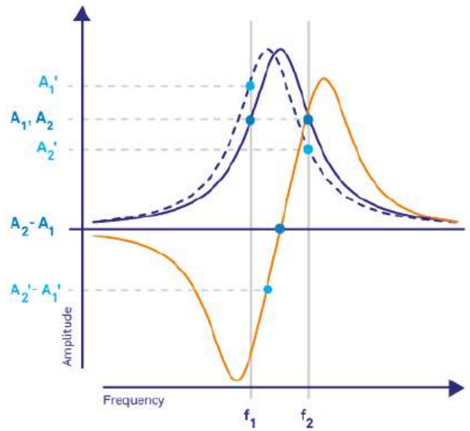
Multifrequency-AFM



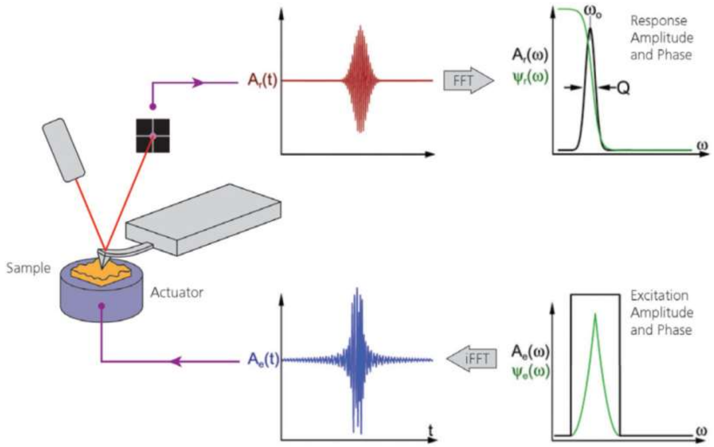
Bimodal



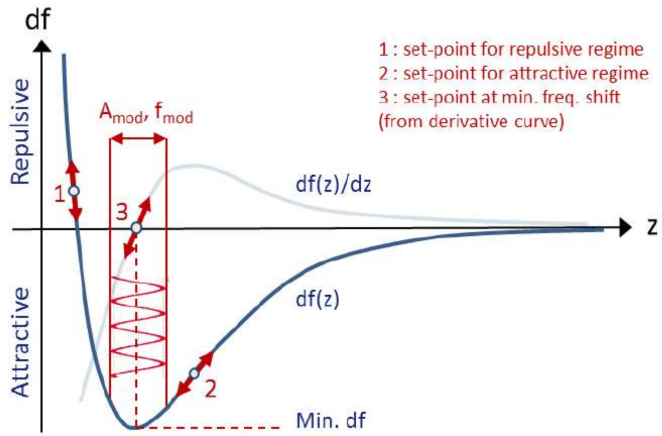
Intermodulation



Dual-Frequency
Resonance-Tracking

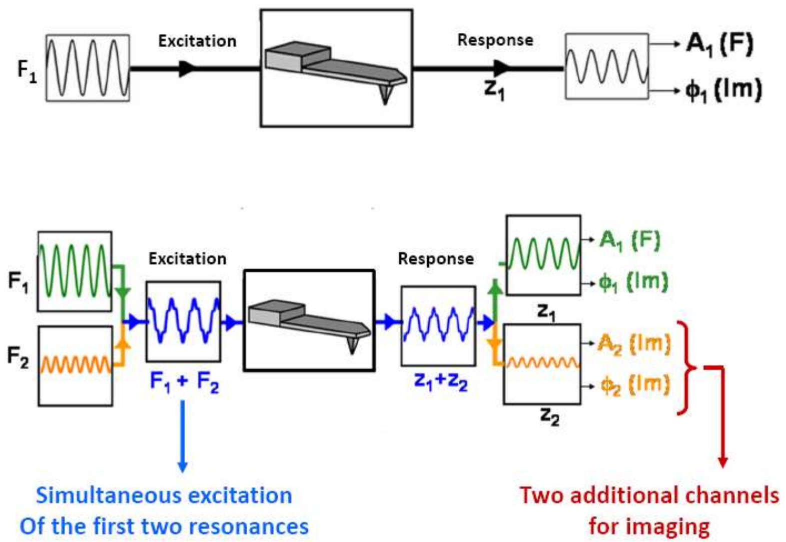


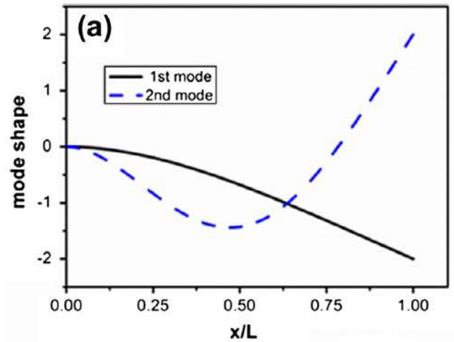
Band Excitation

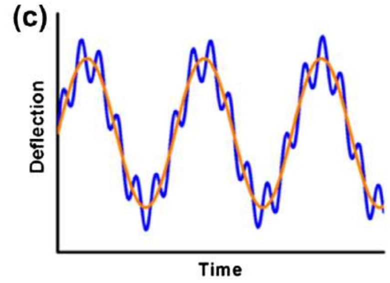


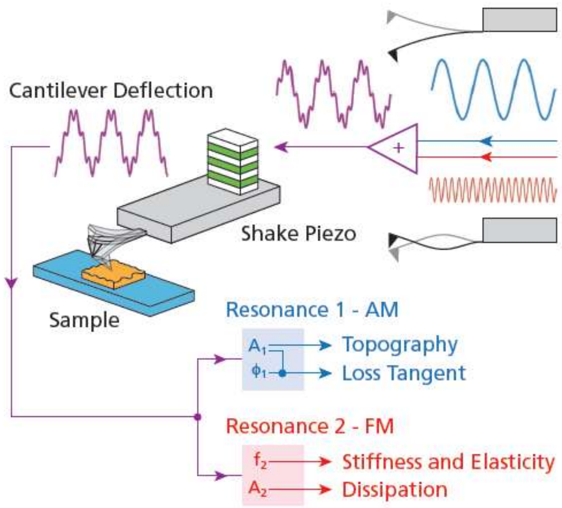
dip-Δf method

双模式：Bimodal









一般来说，一阶基础模式仍为普通AM-AFM模式，

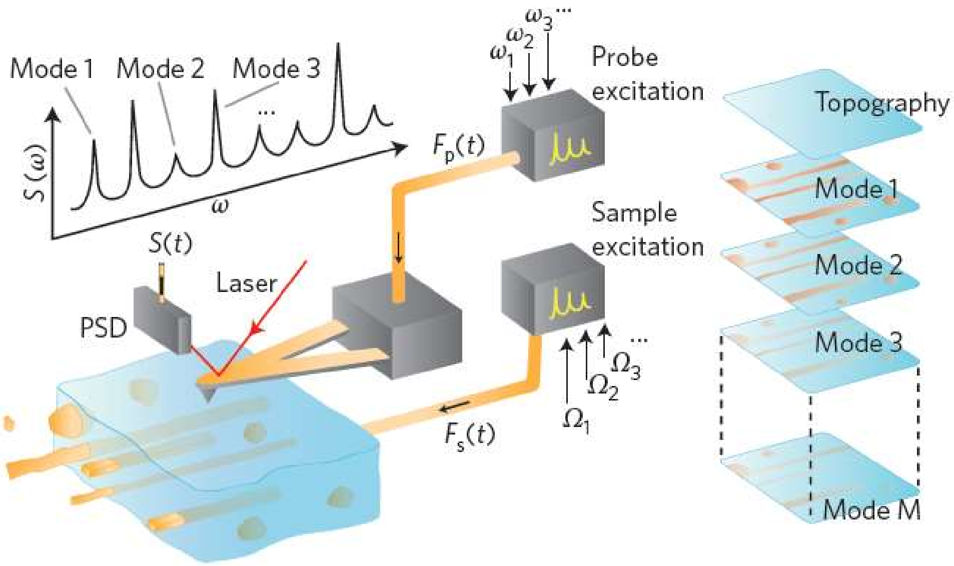
二阶模式为开环激励，一般振幅小很多。

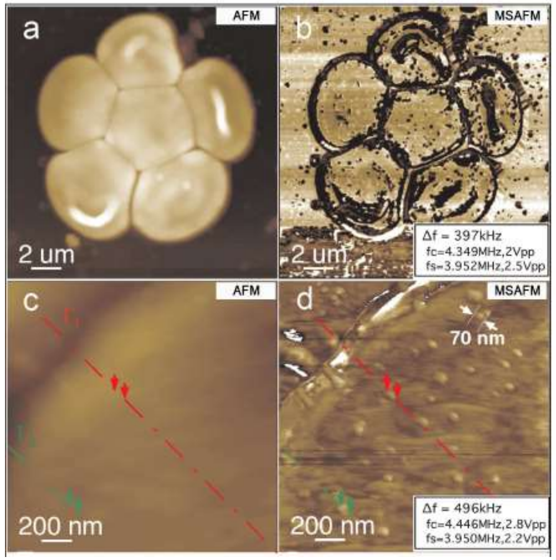
Table 1
Bimodal AFM configurations.

Mode name	Feedback mode 1	Feedback mode 2	Observables	Quantitative observables[a]	Material property
Bimodal AM	AM	Open	A_1, A_2, ϕ_1, ϕ_2	ϕ_1	Dissipation
Bimodal AM–FM	AM	FM	$A_1, A_2, \phi_1, \phi_2, \Delta f_2$	Δf_2	Dissipation, stiffness, Young modulus,
Bimodal FM	FM	Open	$A_1, A_2, \phi_1, \phi_2, \Delta f_2$	ϕ_1, A_2, ϕ_2	Dissipation, stiffness, Young modulus

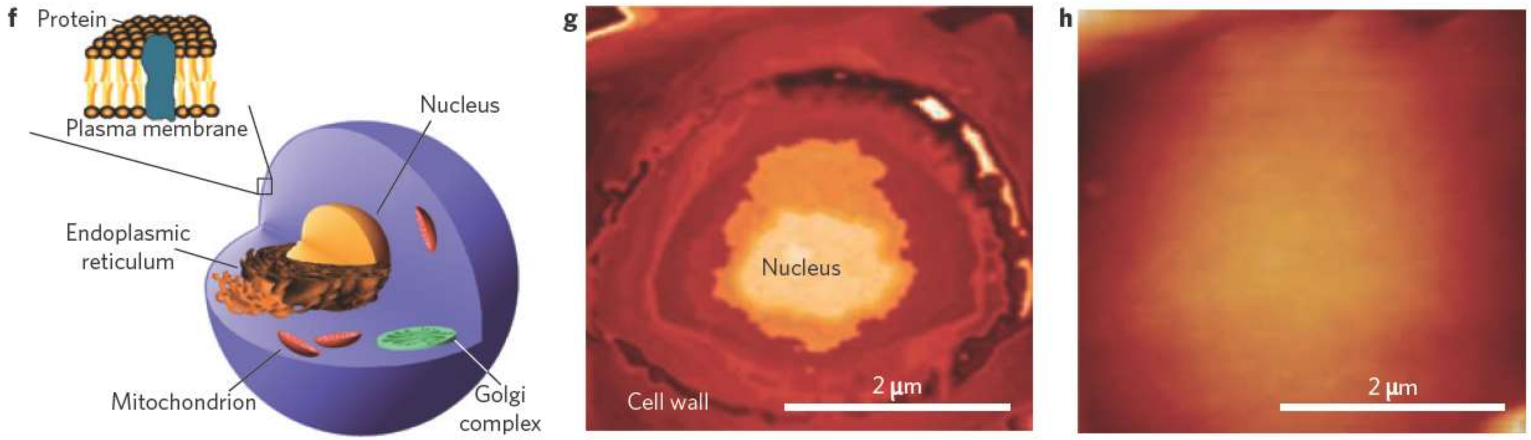
[a] Observables that have an analytical relationship with a nanoscale property.

模式合成：mode synthesizing





红血球细胞内的纳米颗粒



频带激励：Band Excitation

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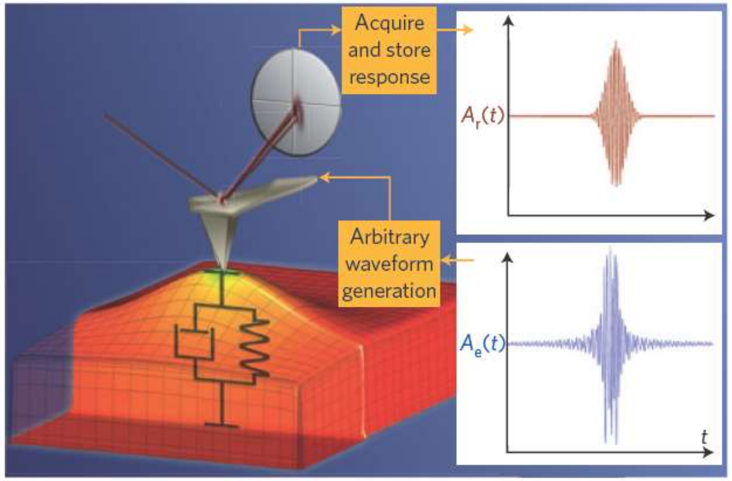
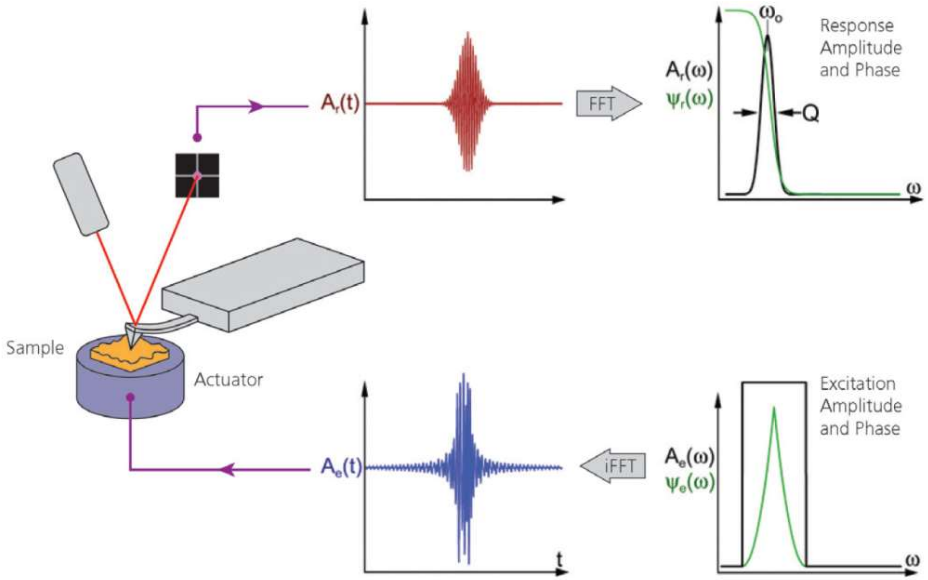
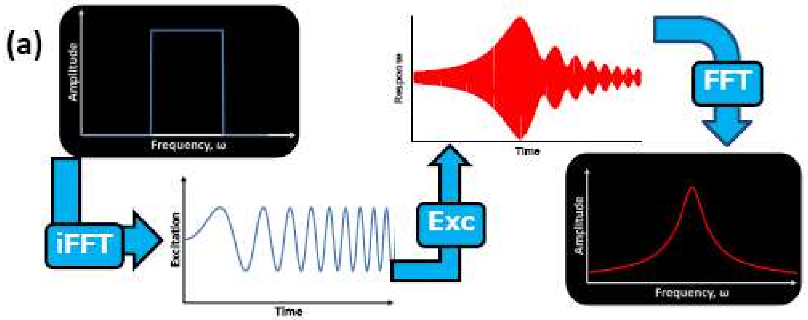
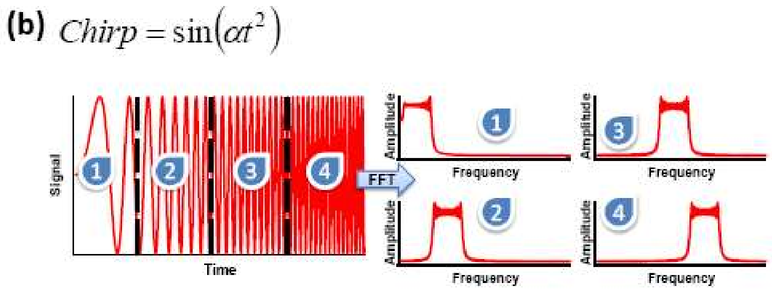








波包型频带激励，可以实现针尖-样品间耗散力测量（甚至可以达到单个声子精度）

总结：深刻理解

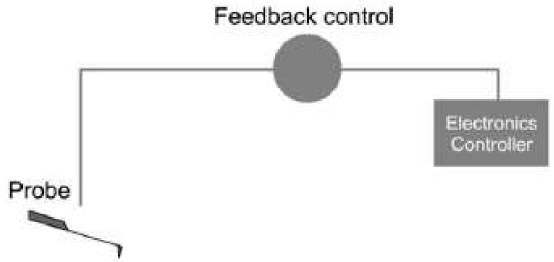
1 探针—样品 间的相互作用及其性质

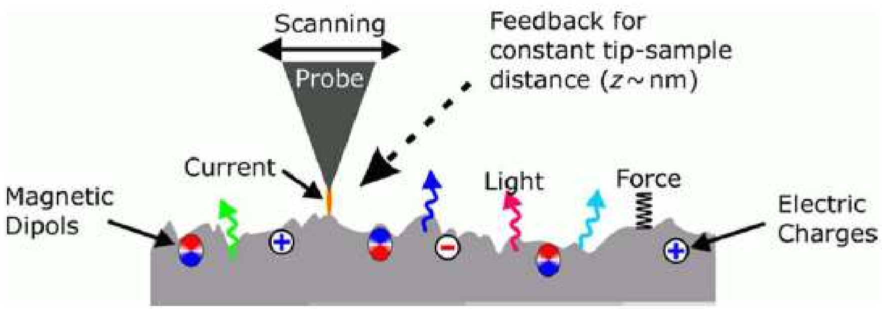
2 微悬臂探针的基本性质与参数

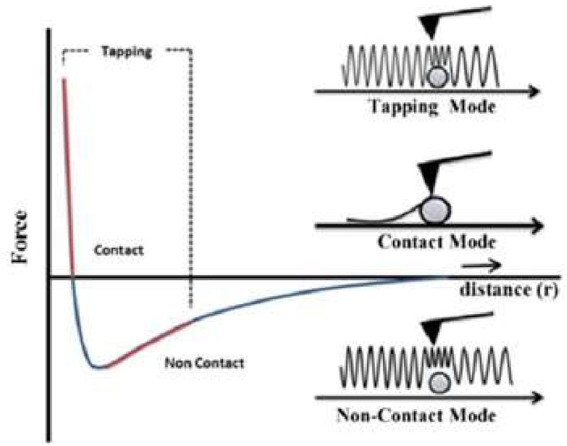
3 微悬臂探针与样品间的相对运动

4 成像探测过程中，那些是主动控制的；
那些是探测得到的信号；
那些是用于反馈的探测量；
反馈后的控制信号具体是什么；

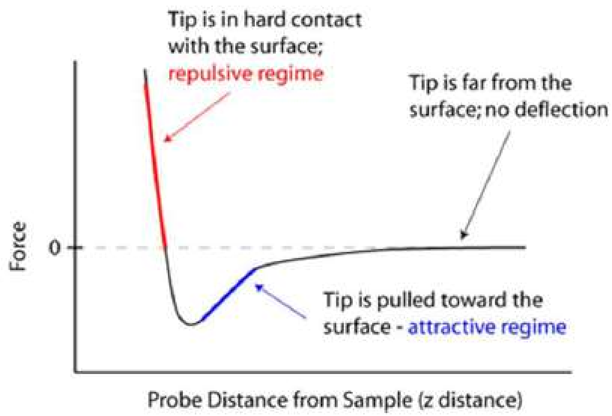
以及在成像探测过程中，具体发生了什么物理过程与现象等。这些物理过程与现象，又是如何依赖于样品（和探针）的性质、状态等的。

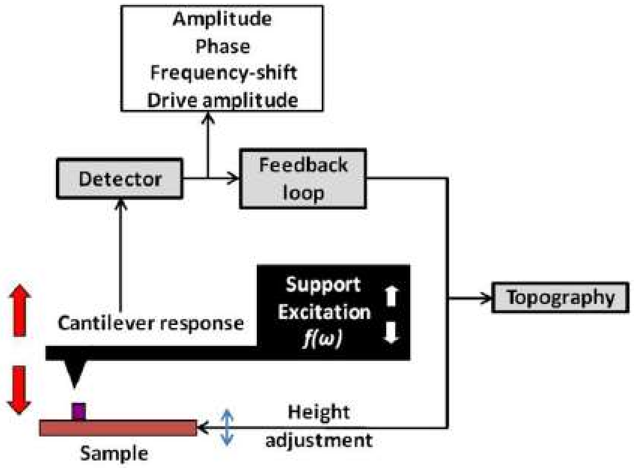






主要核心内容：第二部分





- 2 核心基础工作模式及其进展

基础接触模式

静态模式与动态模式

振幅调制与频率调制

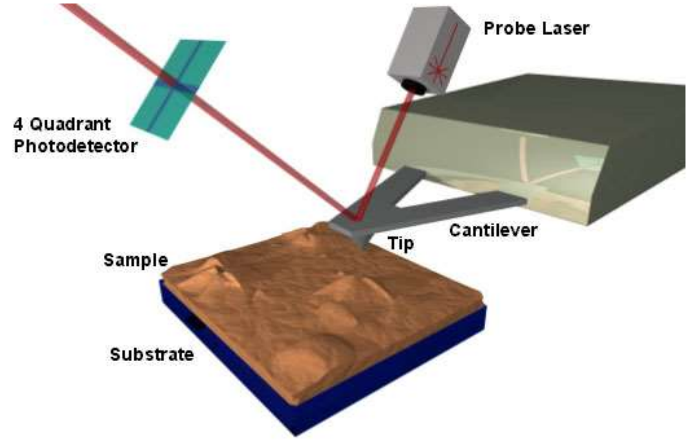
样品形貌与力学性质

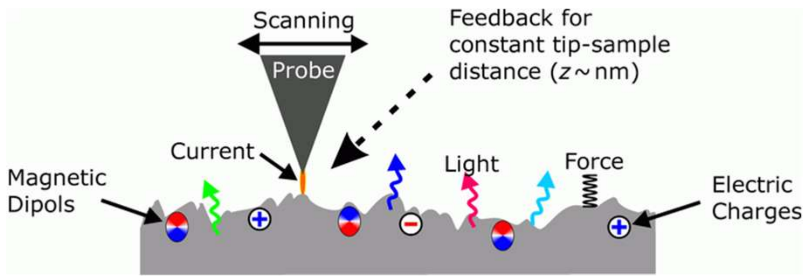
多频原子力显微术

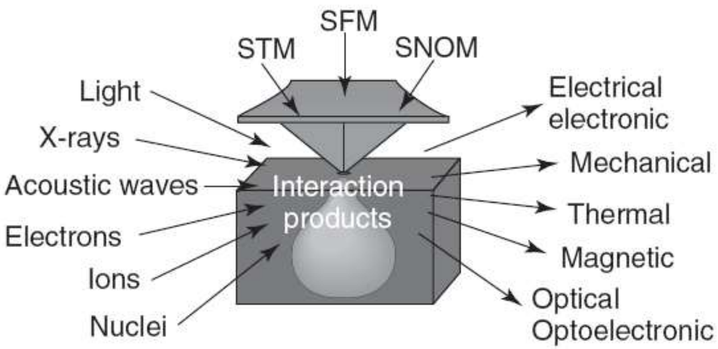
等等

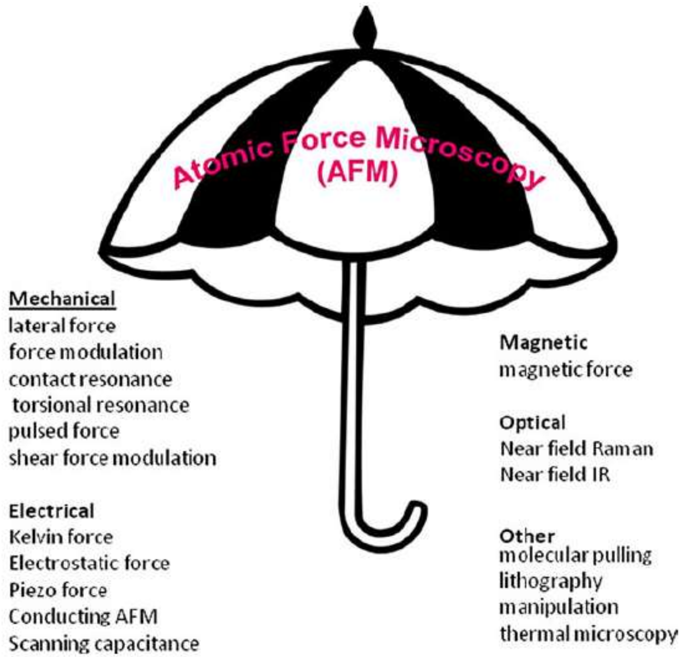
形貌、分辨率以及力学性质

Functional AFM：AFM+





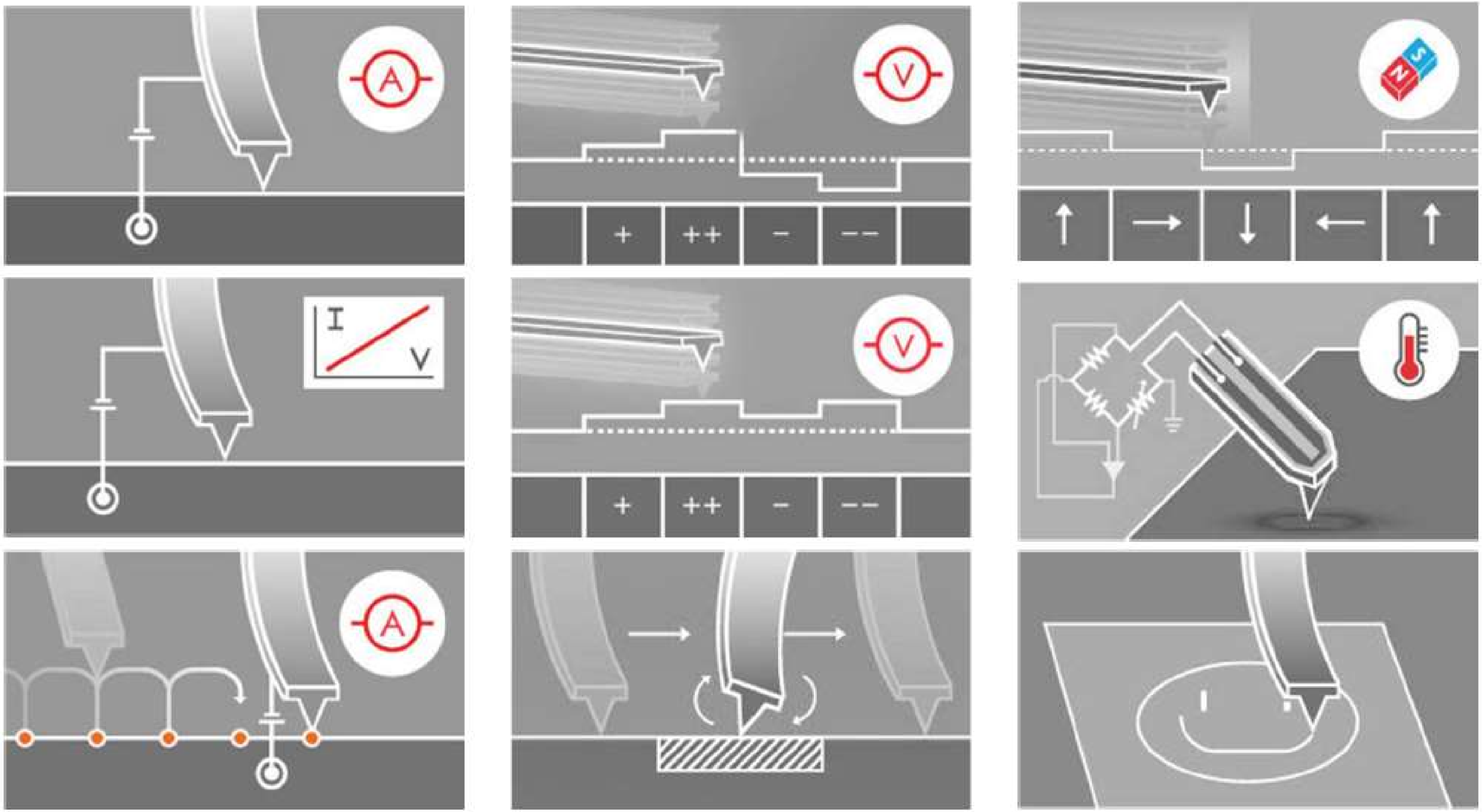




（整体） + （局域） = 局域性质

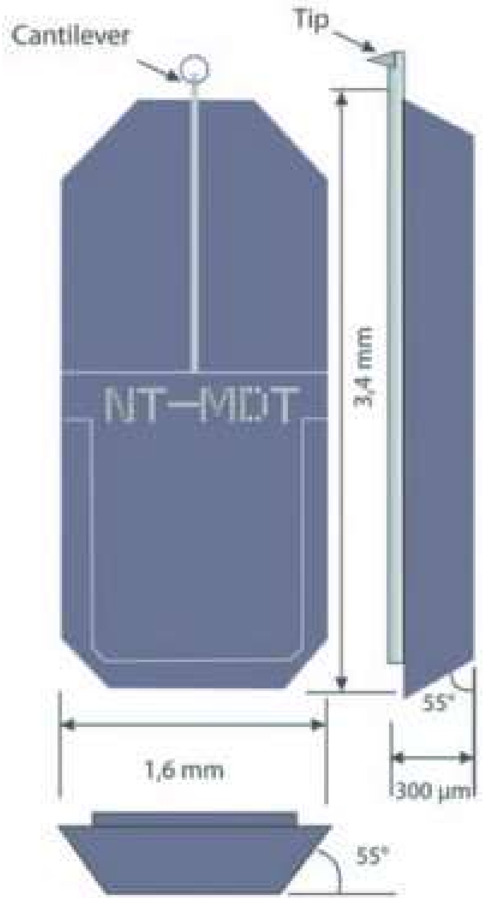
力学、电学、磁学、热学、光学、多场耦合、微纳加工等等！

功能化原子力探针显微模式

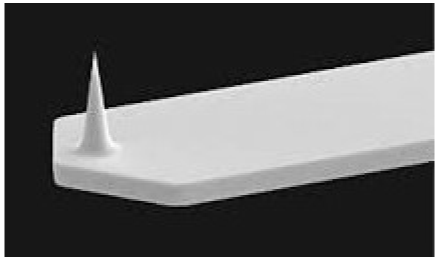


微悬臂探针：微悬臂+探针+其他

AFM 探针基本结构：基片(substrate or base)；微悬臂梁(Cantilever)；针尖(tip)



1. 基片/芯片：固定微悬臂、方便夹持、方便电路制作。
2. 微悬臂：sense 部分，信号检测。
3. 针尖：力探测，尖端大小影响分辨率。



微悬臂探针(自身)参数：
- 弹性常数
- 基础共振频率
- 品质因子
- 共振频率稳定性：温度等
- 传递函数

针尖高度、尖端半径、硬度……

传感器参数：
- 温度灵敏度
- 电阻率
- 磁镀层
- 等等

实验(外部)参数：振动频率、振动振幅等

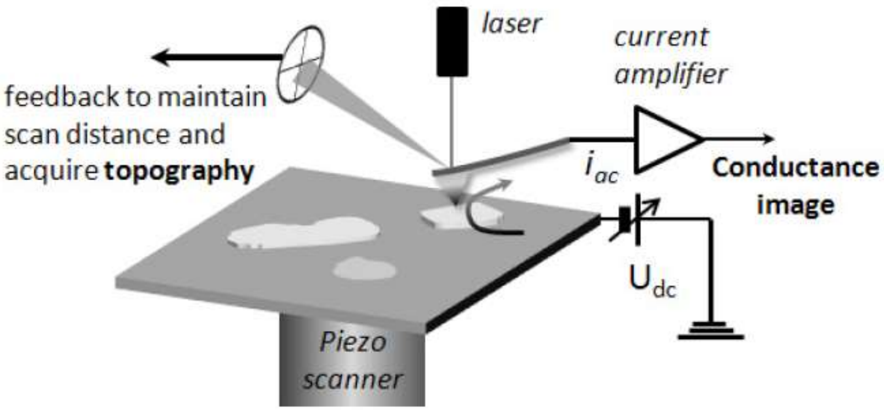
电学测量模式：

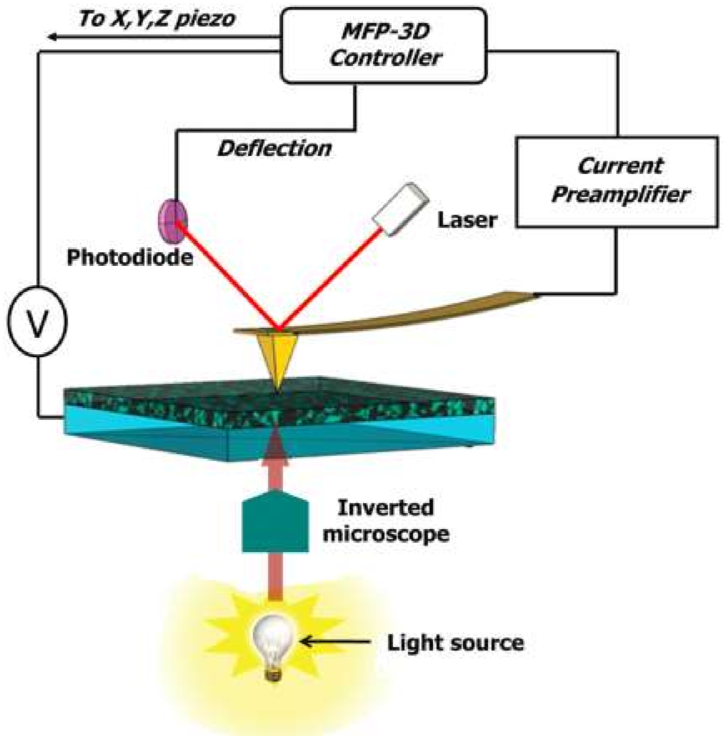
Mode	What is sensed	Information
导电原子力显微术	电流	Conductivity, film uniformity and defects, dielectric breakdown, dopant distribution
静电力显微术	静电力	Electrostatic gradients, capacitance variations, embedded conductors
扫描开尔文探针显微术	电势	Surface potential, work function, film uniformity and coverage
扫描微波显微术	射频/微波的复阻抗	Film thickness, dielectric constant, permittivity and conductivity variations, buried charge
压电力显微术	材料的力-电耦合/响应	Piezoelectric domains, polarization vector and switching, ferroelectric coercive field
磁力显微术	静磁力	Magnetic domains, magnetization hysteresis, magnetic coercive field
扫描电容显微术	电容	Film thickness, dielectric constant, permittivity and conductivity variations, buried charge
扫描栅极显微术	器件的电学响应	Local gate effects

导电原子力显微术：Conductive-AFM

核心：接触模式，以纯金属（如Pt）或外层镀有金属电极等的微悬臂探针为电极，研究样品的电学性质等

Conductive AFM, C-AFM



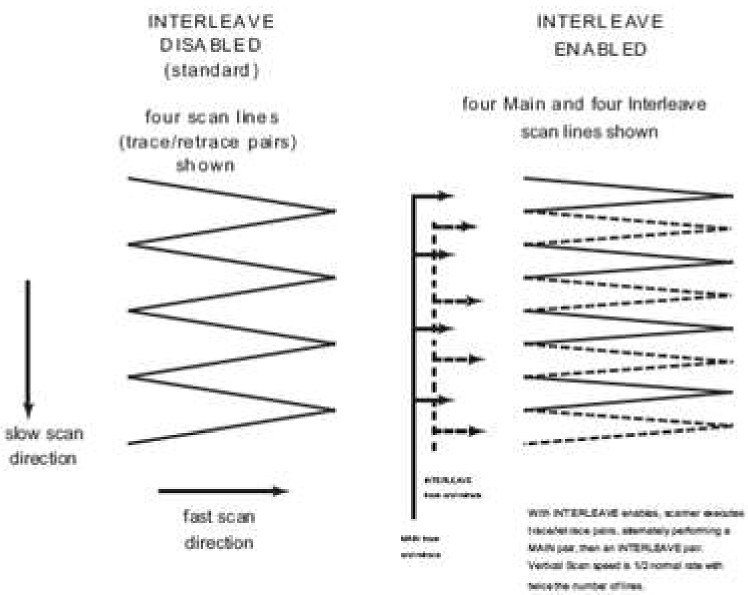


- 测试pA-uA的电流
- 施加的电压，直流/交流，频率
- 同时对样品进行电流、电阻、电容等成像
- SCM, SSRM,

扩展：
光电响应下的导电原子力显微术；
利用导电原子力探针实现局域注电；
测试特定激励下的电压信号(扫描热电显微术等）；
………

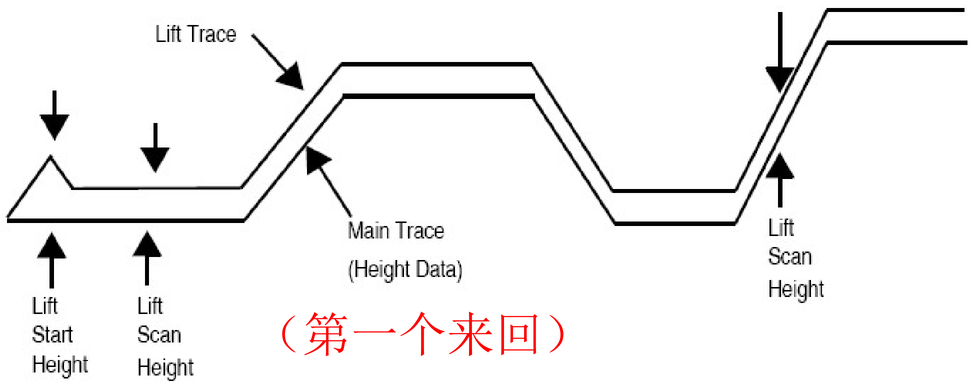
Interleave and Lift Mode

X-Y Scan Pattern



（第二个来回）

LiftMode Profiles



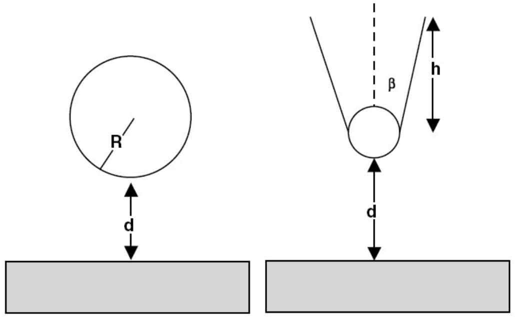
1 每条扫描线，扫描两个来回
（第一个来回：形貌测量）
（第二个来回：性质测量）

2 第二个来回，针尖-样品间的相对距离，可在第一次形貌扫描的基础上，可进行人为控制。例如，相对提高100nm，以排除形貌等的影响，而只探测长程力（静电力、磁力等）

3 第二个来回，针尖的振动状态可以通过不同方式进行激励和探测。如，可以通过机械激励或交变静电力激励，激励可以位于悬臂共振频率（或不位于共振频率）。探测可以通过振幅或相位（灵敏）等。

4 EFM，SKPM，MFM等的基础

静电相互作用力



静电力一般是长程的，这意味着作用在样品表面的静电力不仅来自于探针尖端的原子或分子也可来自于探针锥型本体甚至整个微悬臂。

$$U = \mathrm{C}(\mathrm{V}-\mathrm{V_c})^2/2$$

$$F_\mathrm{e} = -\frac{1}{2}\frac{dC}{dz}(V-V_\mathrm{c})^2$$

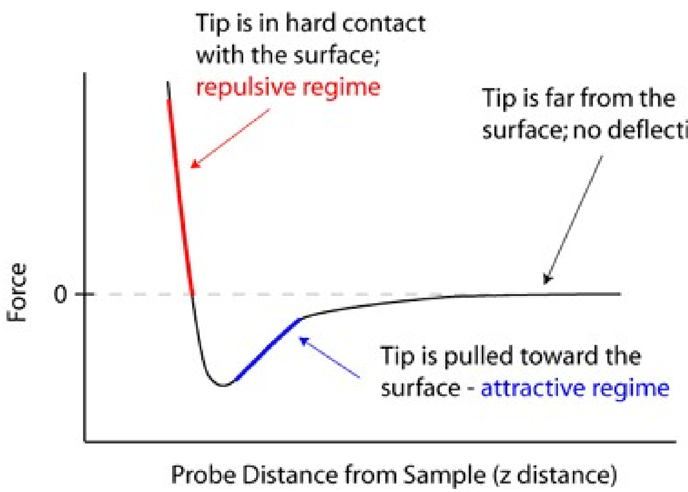
一般模型 $$F_\mathrm{e} = -\pi\varepsilon_0(V-V_\mathrm{c})^2\mathrm{g}(d)$$

其中，ε_0为真空介电常数，$\mathrm{g}(d)$是包含探针尖端、探针锥体和微悬臂贡献的几何因子。

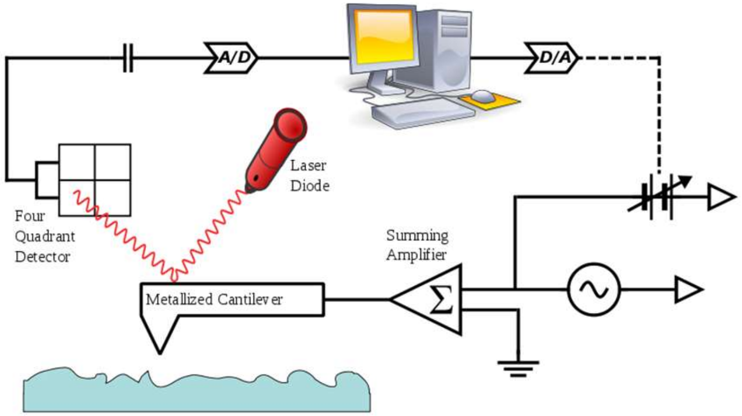
球-平面模型 $$F_\mathrm{apex} = -\pi\varepsilon_0\frac{R(V-V_\mathrm{c})^2}{d}$$

AFM中计算估计静电力比较常用的表达式。

当顶端半球半径远大于针尖-表面间距，即$R \gg d$时。



针尖-样品间静电力：



施加

$$
\begin{cases}
V = (V_{DC} - V_{CPD}) + V_{AC} \cdot \sin(\omega t) \\
E = \frac{1}{2}C[V_{DC} + V_{AC}\sin(\omega_0 t)]^2 \\
\quad = \frac{1}{2}C[2V_{DC}V_{AC}\sin(\omega_0 t) - \frac{1}{2}V_{AC}^2\cos(2\omega_0 t)] \\
F = \frac{1}{2}\frac{dC}{dz}V^2
\end{cases}
$$

$$F = F_{DC} + F_{\omega} + F_{2\omega}$$

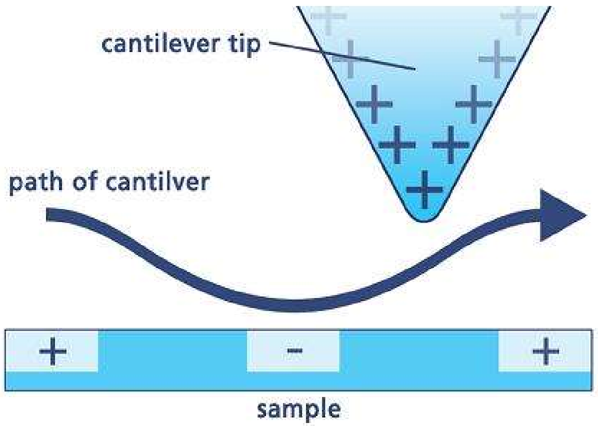
探测

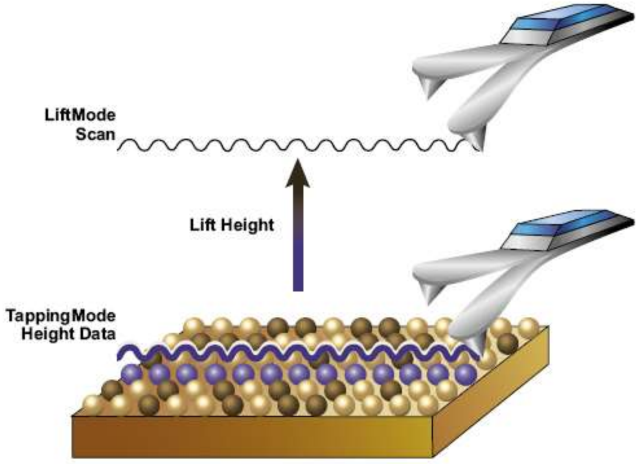
$$
\begin{cases}
F_{DC} = \frac{dC}{dz}[\frac{1}{2}(V_{DC} - V_{CPD})^2 + \frac{1}{4}V_{AC}^2] \\
F_{\omega} = \frac{dC}{dz}[V_{DC} - V_{CPD}]V_{AC}\sin(\omega t) \\
F_{2\omega} = -\frac{1}{4}\frac{dC}{dz}V_{AC}^2\cos(2\omega t)
\end{cases}
$$

施加在微悬臂上的交流电压，引起探针与样品间变化的静电力，从而引起微悬臂的振动，通过探测微悬壁振动的信息，如振幅，相位等，来探测针尖-样品间的静电力，从而实现样品电学性质的表征。

核心：此时的微悬臂探针振动来源于施加的交流电压引起的交变的静电力相互作用，而不是激励压电陶瓷。

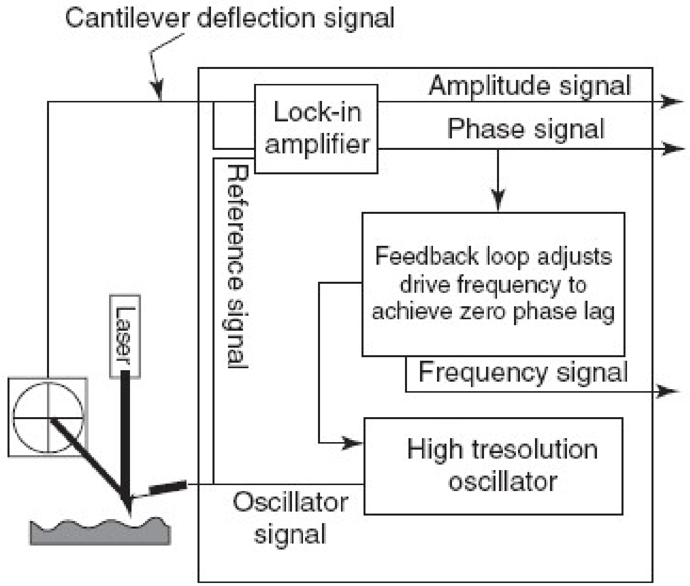
静电力显微术：EFM





Double pass mode/lift mode

Electrostatic Force Microscopy (EFM)



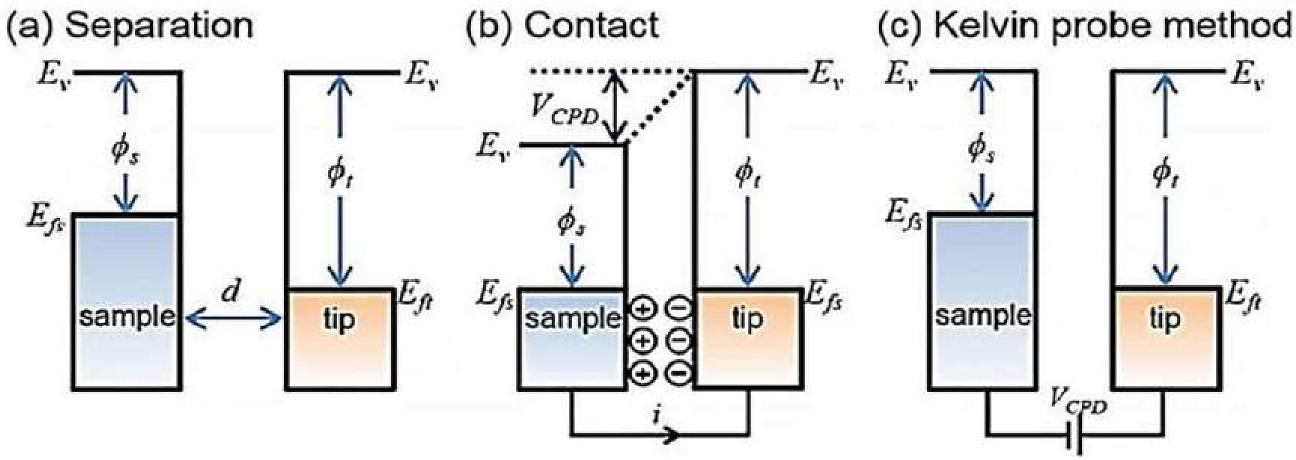
(a) EFM

只施加交流偏压，可远低于共振频率，也可选为微悬臂的一阶共振频率。

通常采用lift mode，从而排除样品表面形貌的影响。

定性，很难定量，较为简单

扫描电势显微术：SKPM



$$V_{CPD} = \frac{\phi_{sample} - \phi_{tip}}{|e|}$$

Kelvin Probe Force Microscopy (KPFM)

KPFM高空间分辨率

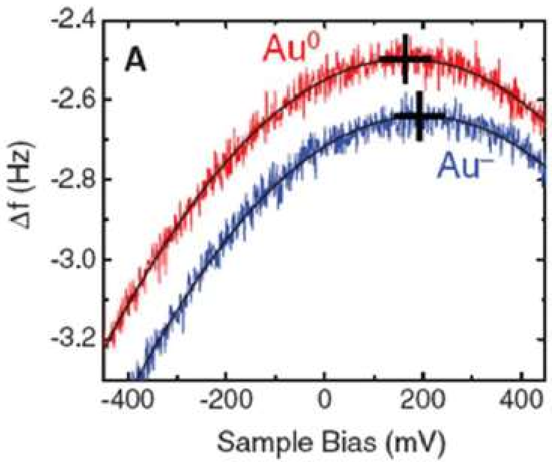
(局域接触势差，LCPD)

1.交流电压调制

2. $\Delta f(V)$曲线

$$\Delta f_{el} = -\frac{1}{2}\frac{d^2C_{t\text{-}s}}{dz^2}(V_{DC} - V_{LCPD})^2$$

单电荷敏感



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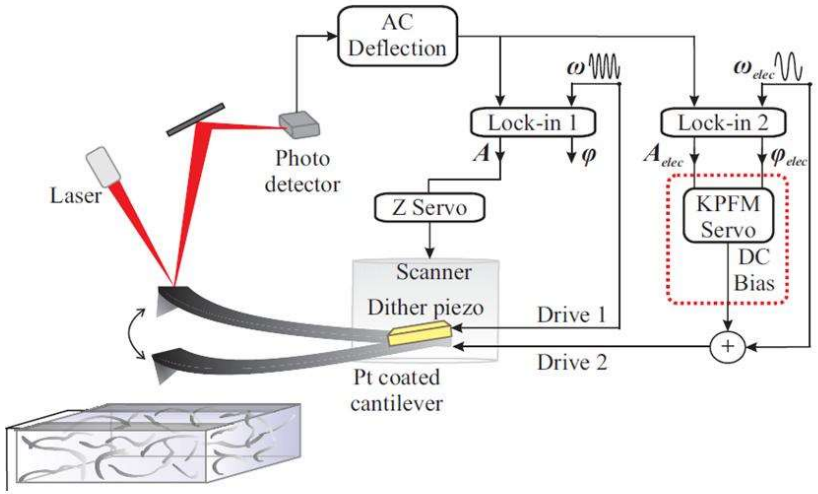
扫描电势显微术：KPFM

Schematic KPFM technique



- This is for the single-pass implementation (single-pass and two-pass is discussed later)
- Lock in amplifier 1 tracks the tip oscillation amplitude at the cantilever resonance
- Lock in amplifier 2 tracks the tip oscillation amplitude at the electrical excitation frequency ω_{elec}
- The KPFM servo applies a DC bias to null the tip oscillation at ω_{elec}
- Sometimes a 3rd lock-in amplifier is used to track the signal at 2 ω_{elec}

$$F = F_{DC} + F_{\omega} + F_{2\omega}$$

$$F_{DC} = \frac{dC}{dz}[\frac{1}{2}(V_{DC} - V_{CPD})^2 + \frac{1}{4}V_{AC}^2]$$

$$F_{\omega} = \frac{dC}{dz}[V_{DC} - V_{CPD}]V_{AC}\sin(\omega t)$$

核心：通过调节所施加的DC偏压，使得所施加的交流电压引起的微悬臂振动最小。

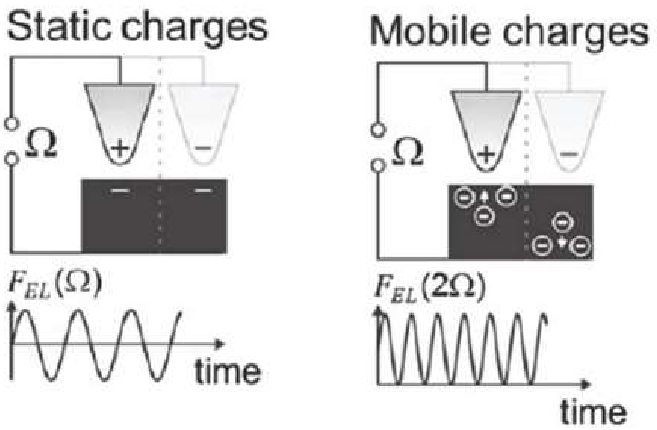
有多种实现形式，定量化等

1：可以采用和EFM类似的lift mode，只需增加DC偏压和反馈回路；
2：也可以采用单次扫描模式，在普通形貌扫描（一阶模式下的tapping mode）的同时，施加一个交流偏压（频率为二阶模式的共振频率）引起微悬臂的振动，调节DC偏压使得微悬臂的二阶振动模式的振动最小。
3：其他方式：FM-KPFM AM-KPFM

Kelvin Probe Force Microscopy (KPFM)

Multiharmonic-Electrostatic Force Microscopy

中国人民大學
RENMIN UNIVERSITY OF CHINA



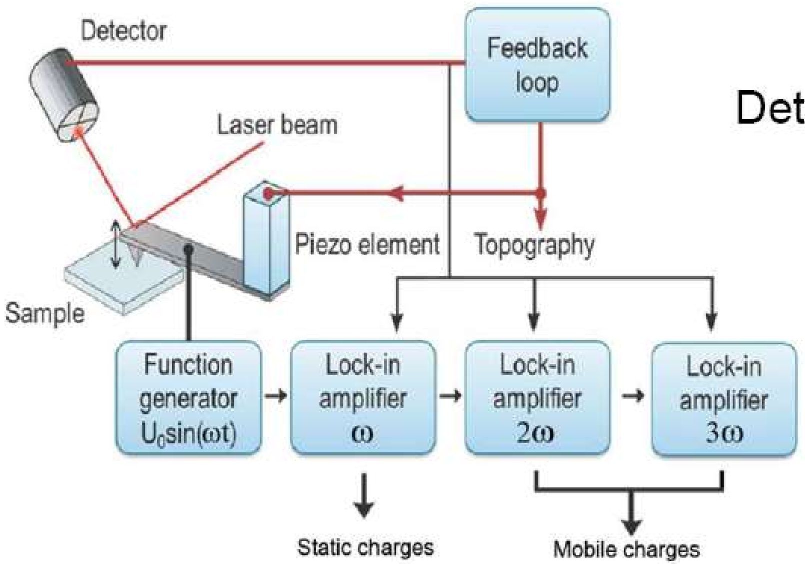
Applied

$$
\begin{cases}
V = (V_{DC} - V_{CPD}) + V_{AC}\cdot\sin(\omega t) \\
E = \frac{1}{2}C[V_{DC} + V_{AC}\sin(\omega_0 t)]^2 \\
\quad = \frac{1}{2}C[2V_{DC}V_{AC}\sin(\omega_0 t) - \frac{1}{2}V_{AC}^2\cos(2\omega_0 t)] \\
F = \frac{1}{2}\frac{dC}{dz}V^2
\end{cases}
$$

$$F = F_{DC} + F_{\omega} + F_{2\omega} + F_{3\omega}$$

Detected

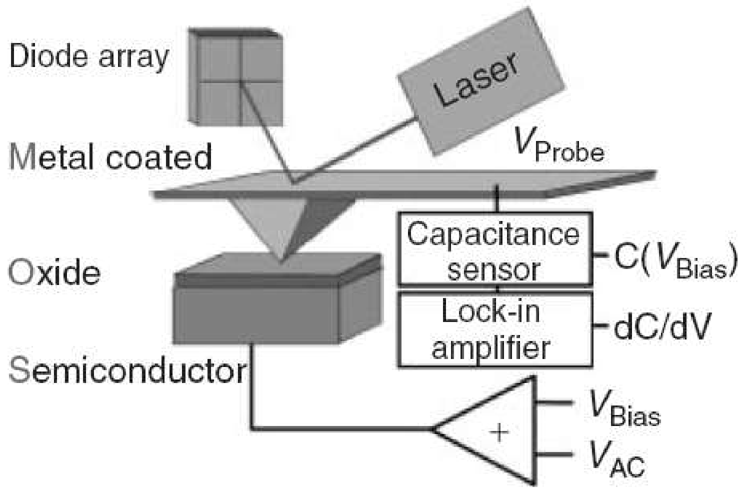
$$
\begin{cases}
F_{DC} = \frac{dC}{dz}[\frac{1}{2}(V_{DC} - V_{CPD})^2 + \frac{1}{4}V_{AC}^2] \\
F_{\omega} = \frac{dC}{dz}[V_{DC} - V_{CPD}]V_{AC}\sin(\omega t) \\
F_{2\omega} = -\frac{1}{4}\frac{dC}{dz}V_{AC}^2\cos(2\omega t) \\
F_{3\omega} = -\frac{1}{8}\left(\frac{\partial^2 C(V_{DC},z)}{\partial V\partial z}(V_{AC})^3\cos 3\omega t\right)
\end{cases}
$$



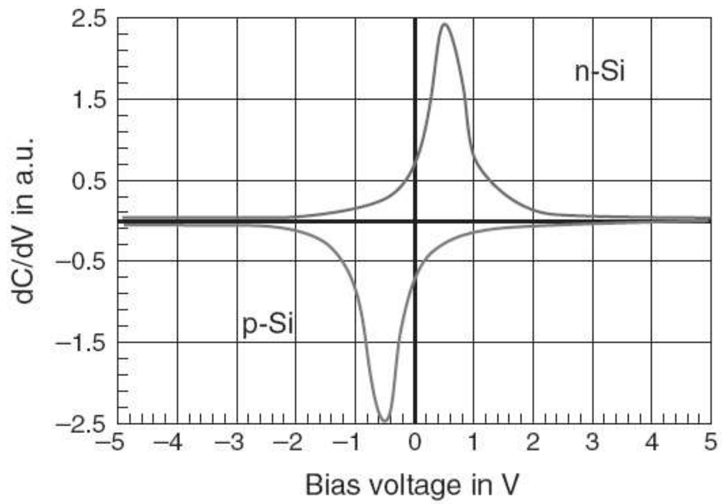
Local electrostatic properties:

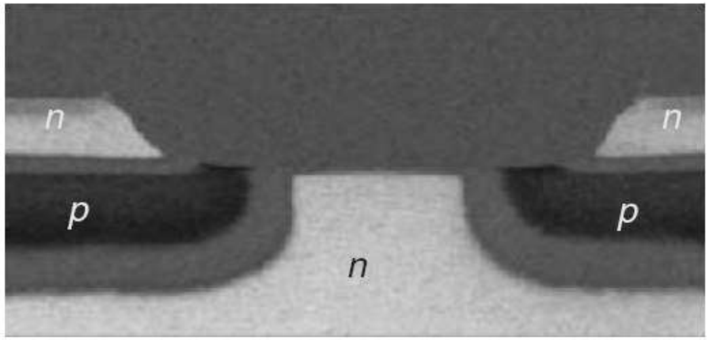
- Surface potential, work function, static charge
- Capacitive effects, mobile charge carrier
- Local gate effects, carrier's type and concentration

扫描电容显微术：SCM



Experimental setup of SCM





dC/dV image of depleted and doped regions.

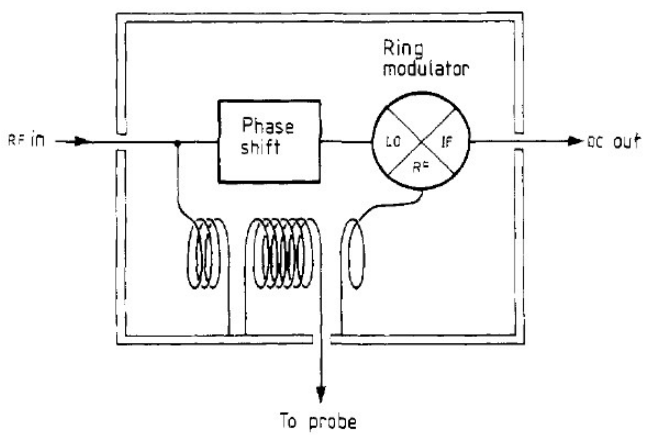


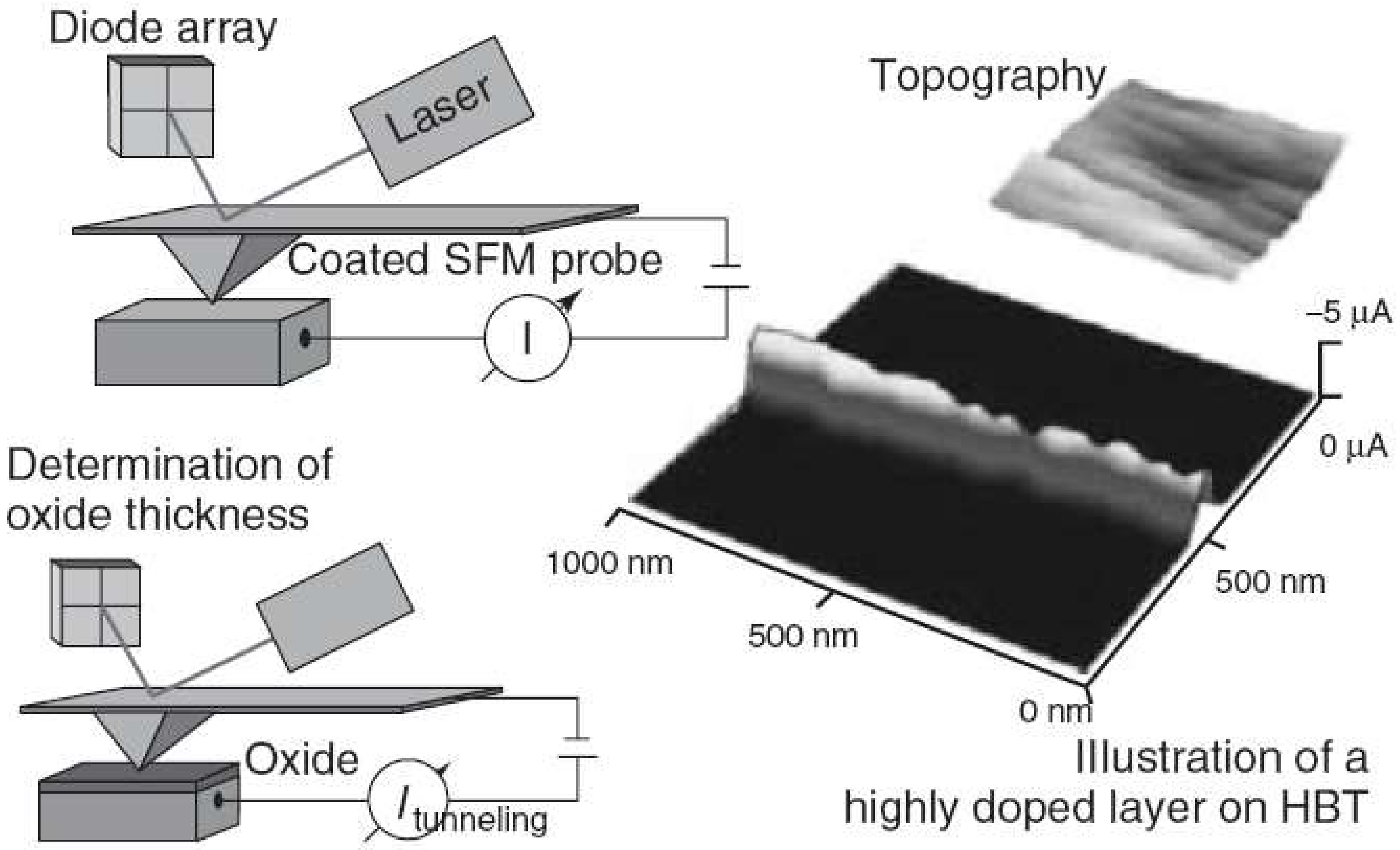
Figure 3. Layout of the capacitance sensor showing *LCR* circuit, the ring modulator and the phase shifter.

核心：研究样品的局域交流电容性质。

Scanning Capacitance Microscopy (SCM)

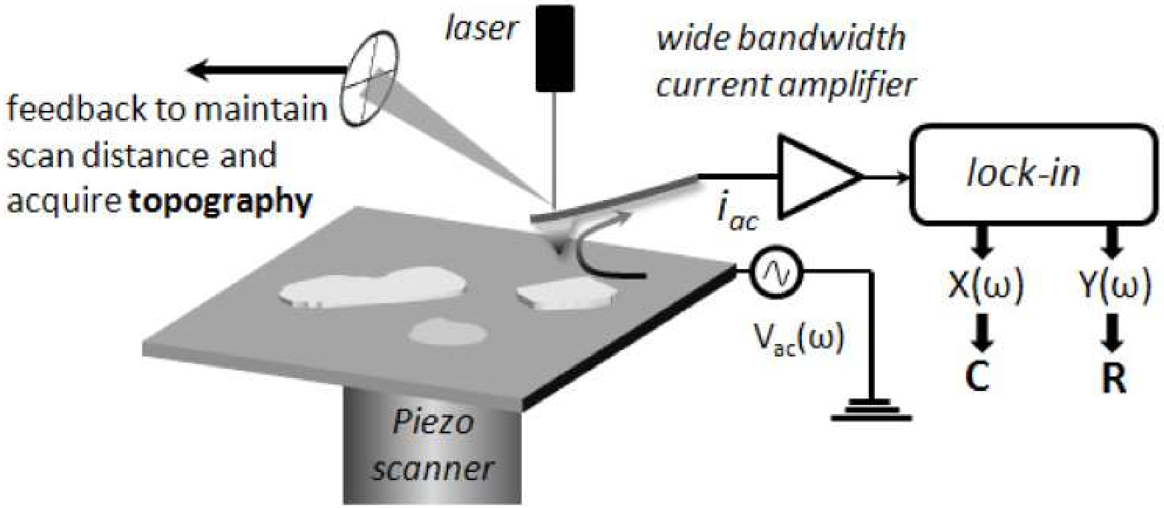
扫描扩散电阻显微术：SSRM

Scanning Spreading Resistance Microscopy (SSRM)



核心：研究样品的局域直流阻抗性质。

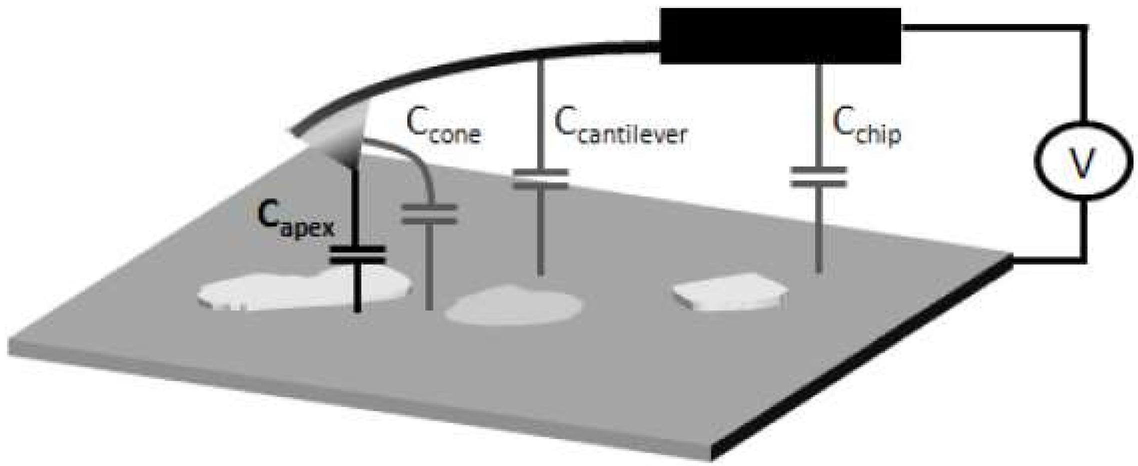
扫描阻抗显微术：SIM



核心：研究宽频范围内，样品的局域交流阻抗性质。

可以看作是局域的阻抗分析仪

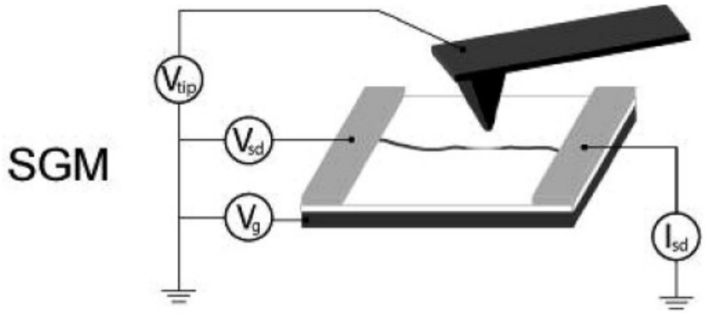
$$C_{meas} = C_{apex} + C_{cone} + C_{cantilever} + C_{chip} = C_{apex} + C_{stray} = 0.01\ fF + 30\ fF$$

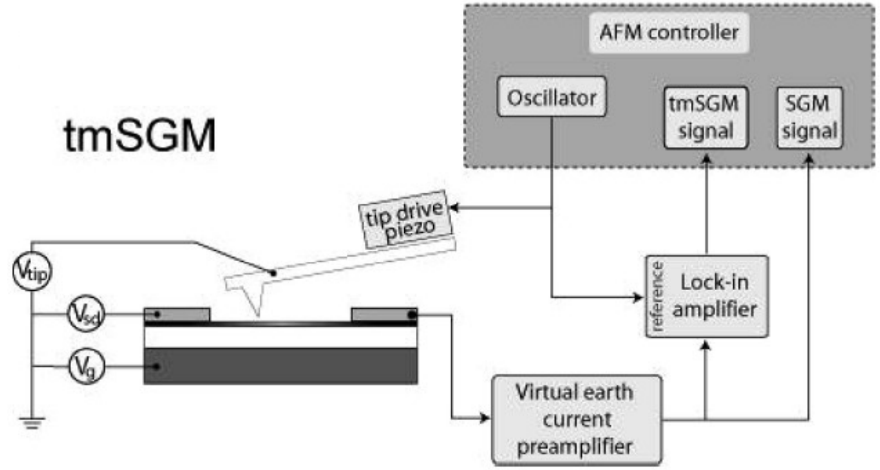


Scanning Impedance Microscopy (SIM)

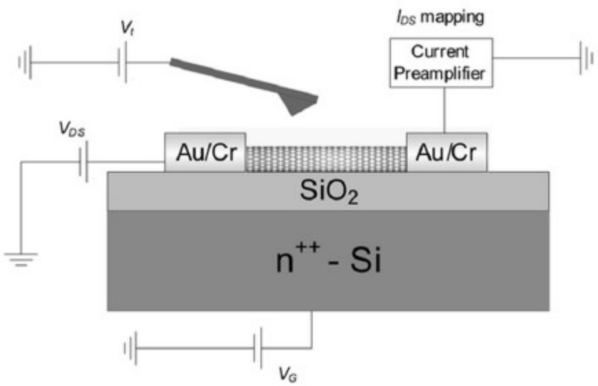
扫描栅极显微术：SGM

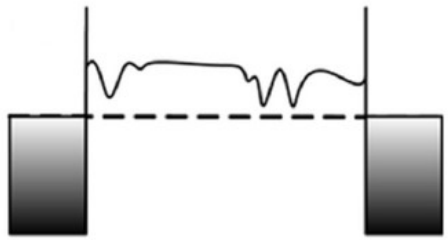
Scanning Gate Microscopy

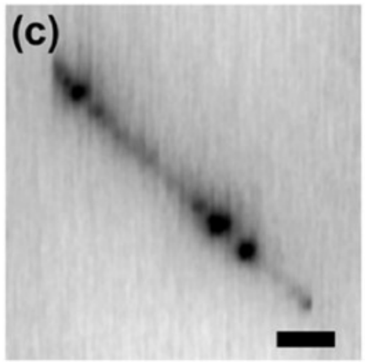




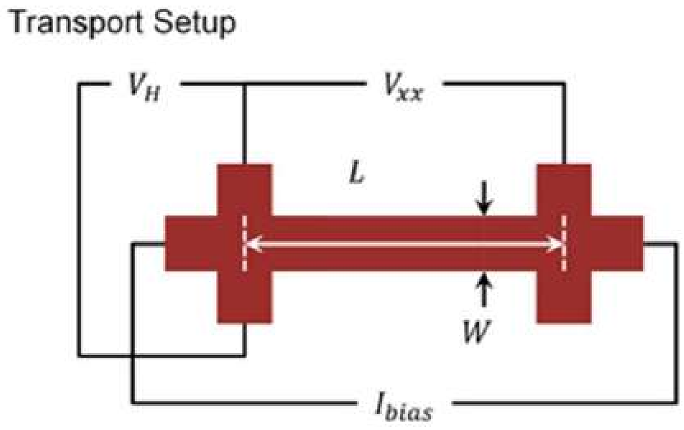
核心：利用施加DC+AC偏压的金属微悬臂探针作为局域栅极，研究局域栅压对器件输运性质的影响。

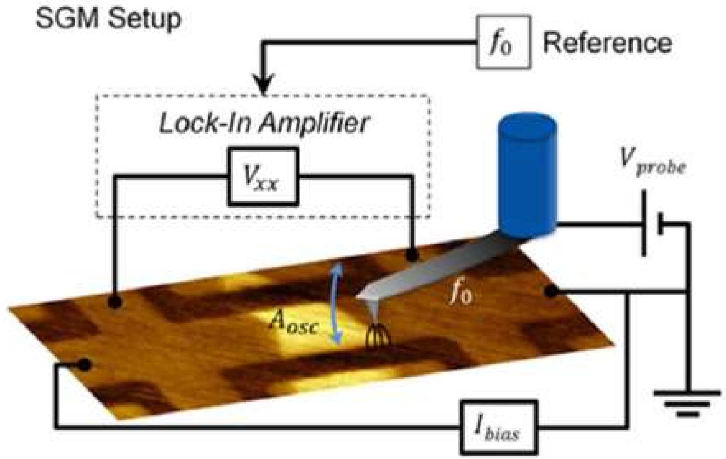






AFM + 器件输运测量





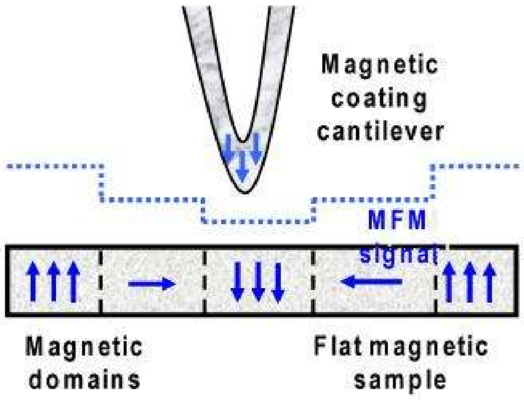
器件输运性质
（宏观整体）

+

AFM针尖场效应
（微观局域）

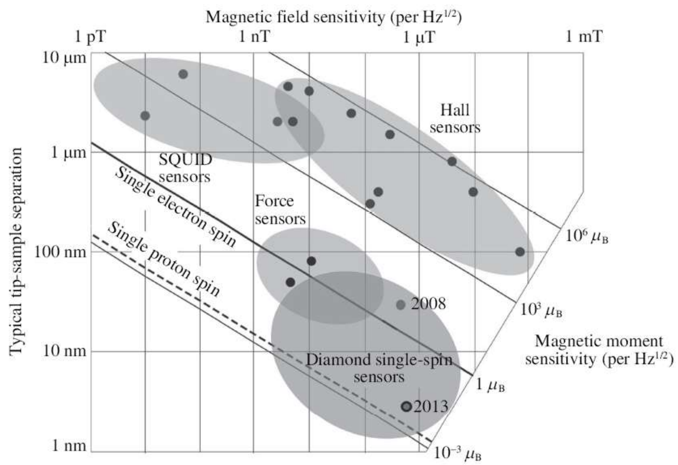
磁力显微术：MFM

Magnetic Force Microscopy

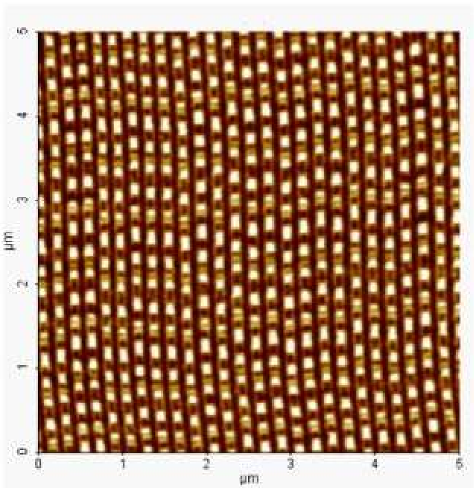


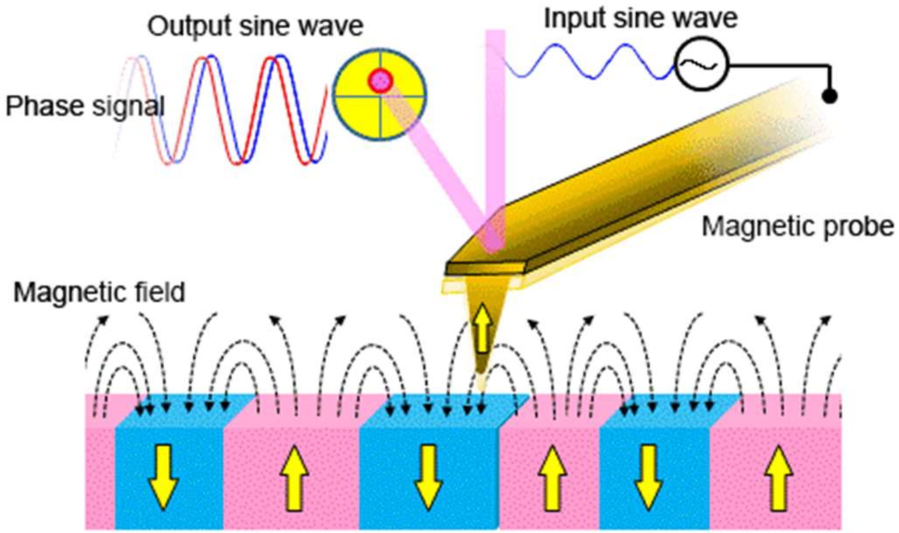
12GB Small Form FactorHD - 25bit/μm²
(scan size : 5 x 5μm)

$$\vec{F} = \mu_0 (\vec{m} \cdot \nabla) \vec{H}$$

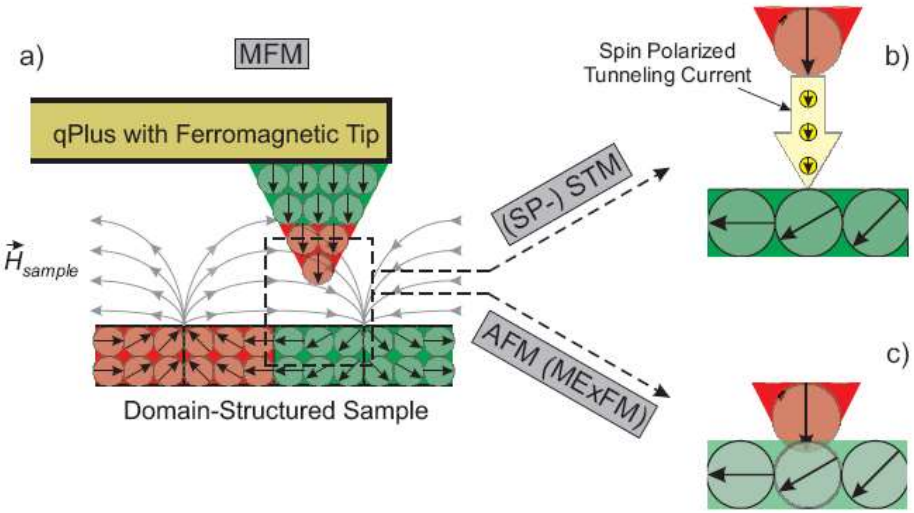


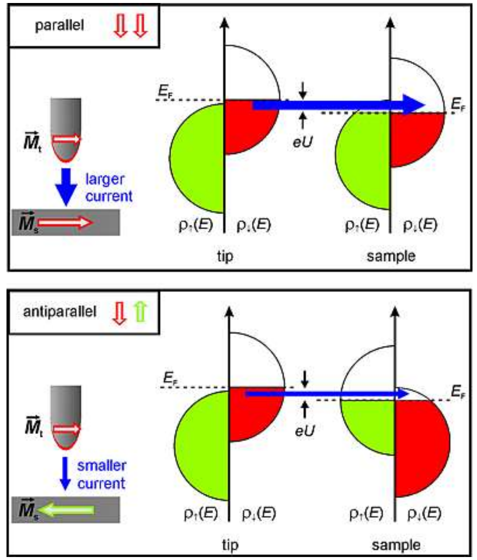
MFM Image of Hard Disk Drive

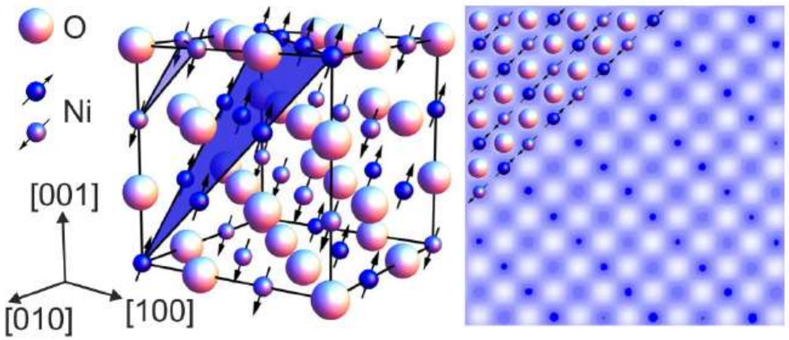


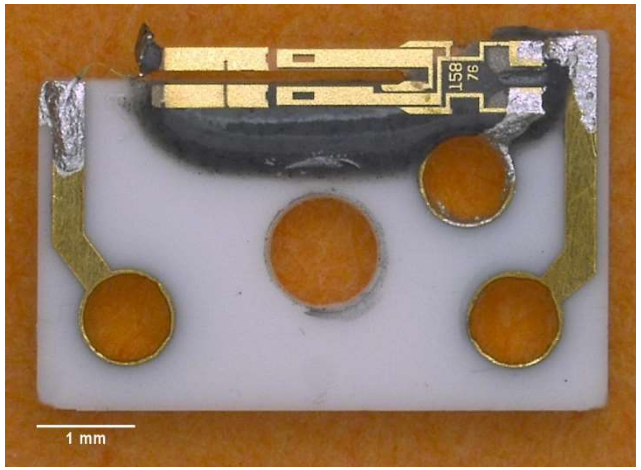


磁交换力显微术：MExFM





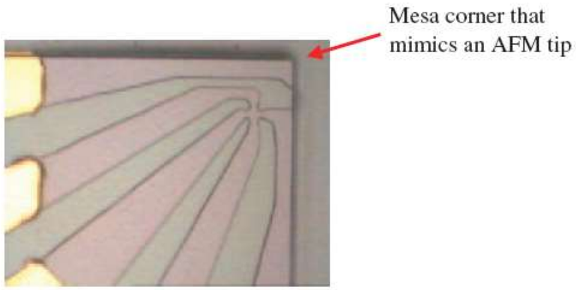




$$H = -J_{12}\vec{S}_1 \cdot \vec{S}_2$$

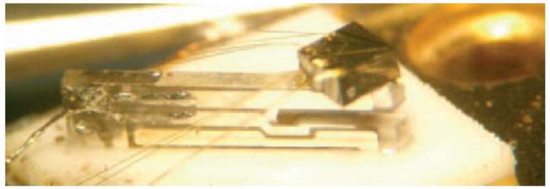
Phys. Rev. Lett. **110**, 266101 (2013)

扫描霍尔显微术与扫描SQUID显微术

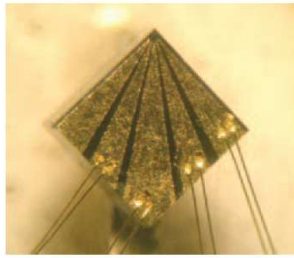


(c)

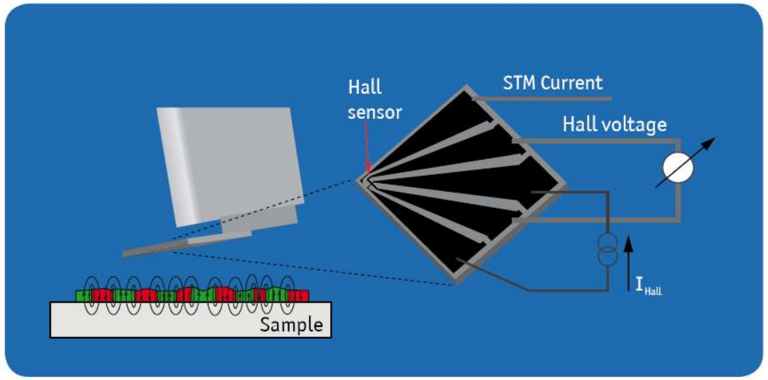
Fig. 1. A micro fabricated 1 × 1 × 0.5 mm Hall probe mounted on a 100 kHz quartz crystal fork. (a) Side view, (b) top view, and (c) sensor detail.

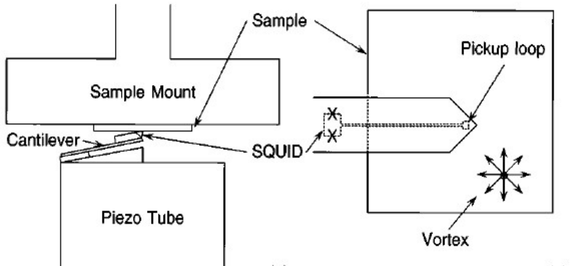


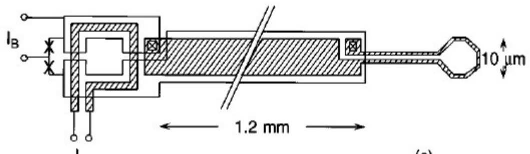
(a)



(b)







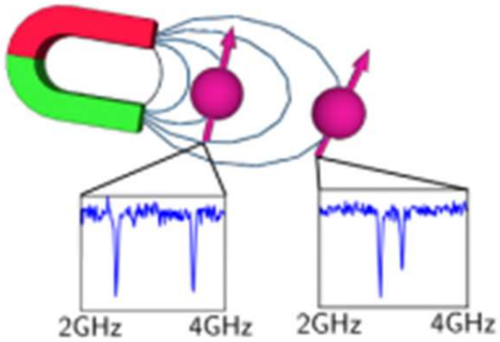
扫描NV-Center显微术：量子探测

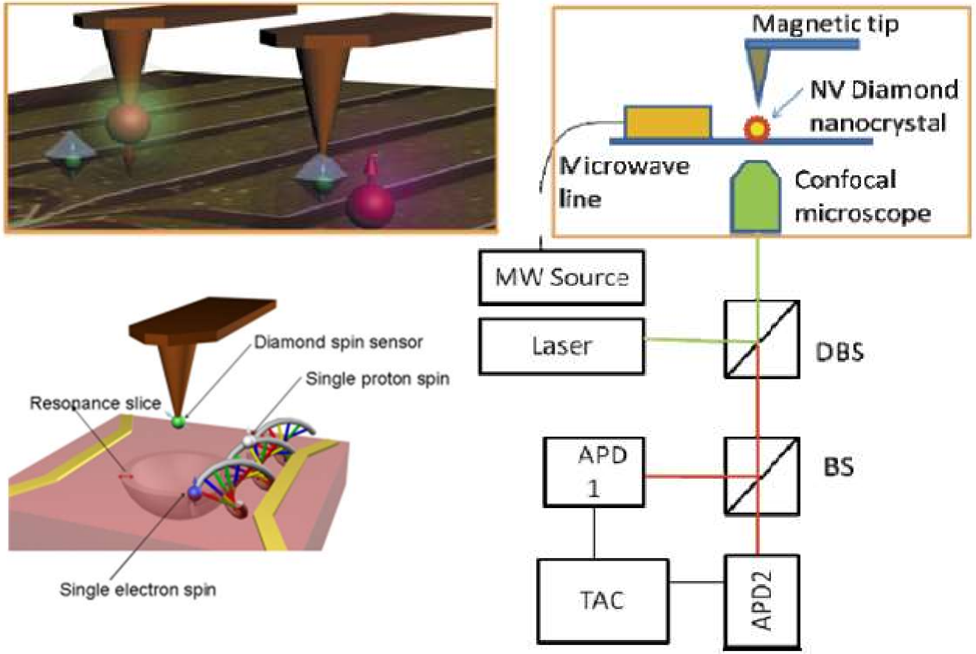
nature Vol 455|2 October 2008|doi:10.1038/nature07278

LETTERS

Nanoscale imaging magnetometry with diamond spins under ambient conditions

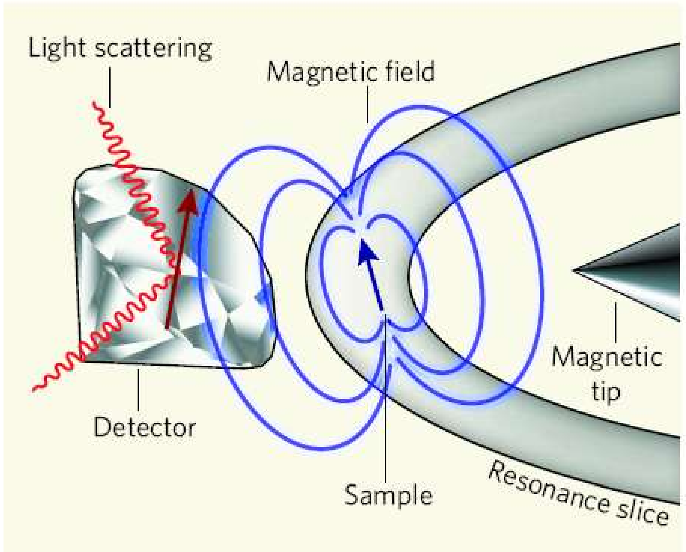
Gopalakrishnan Balasubramanian[1], I. Y. Chan[2]†, Roman Kolesov[1], Mohannad Al-Hmoud[1], Julia Tisler[1], Chang Shin[3], Changdong Kim[3], Aleksander Wojcik[3], Philip R. Hemmer[3], Anke Krueger[4], Tobias Hanke[5], Alfred Leitenstorfer[5], Rudolf Bratschitsch[5], Fedor Jelezko[1] & Jörg Wrachtrup[1]



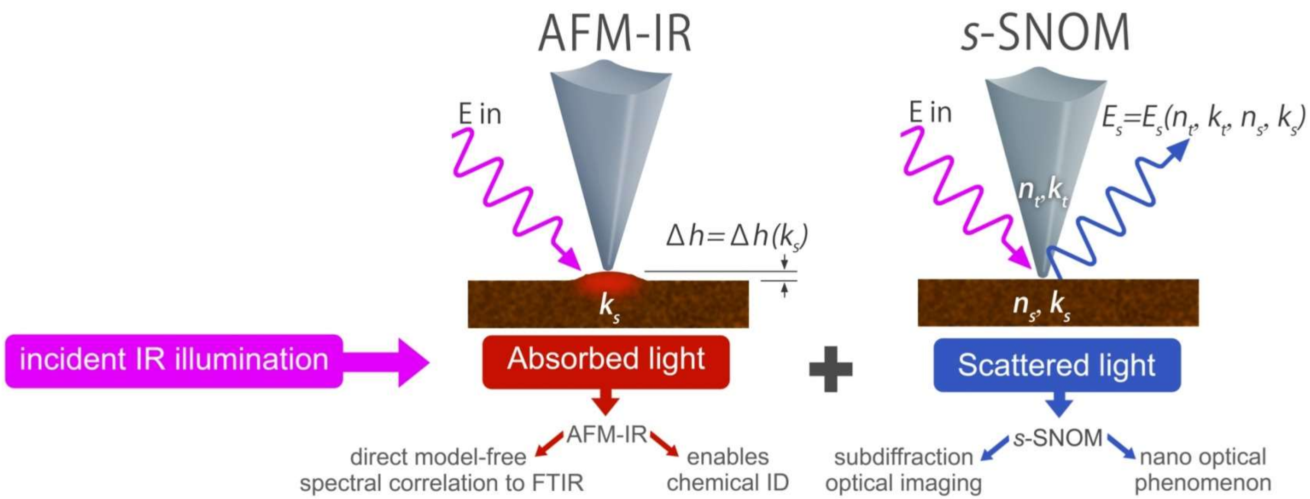


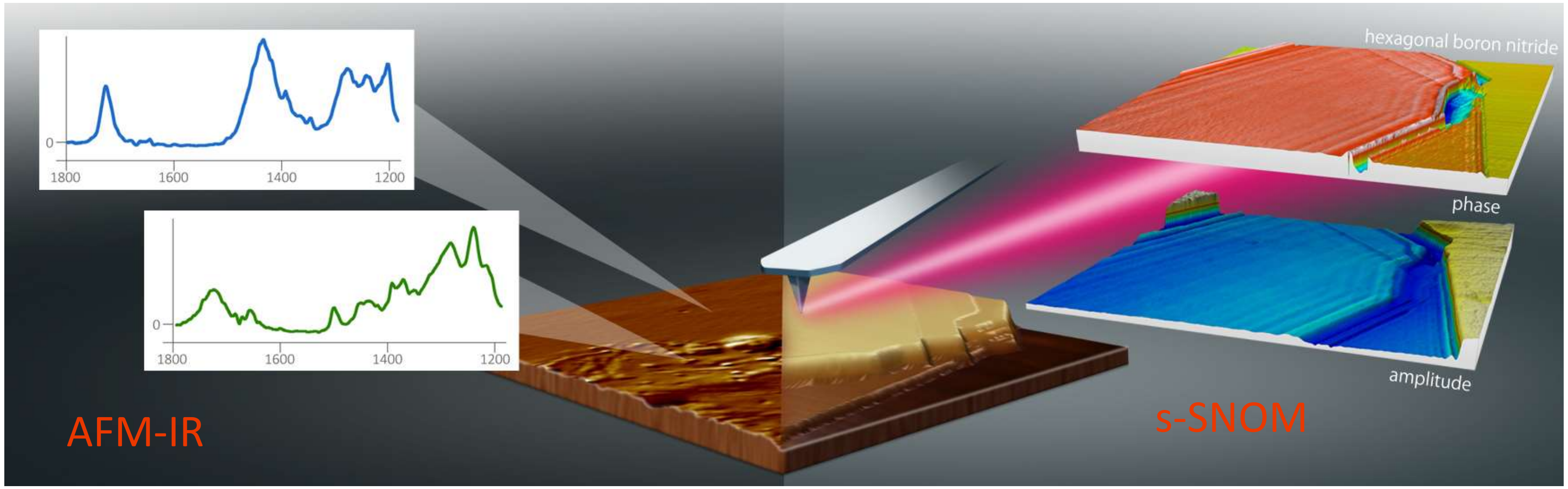
A home-built scanning confocal microscope combined with an AFM (MFP-3D Asylum Research).

The world's smallest magnetic field sensor - the Nitrogen-Vacancy center



扫描光学显微术：AFM-IR & s-SNOM



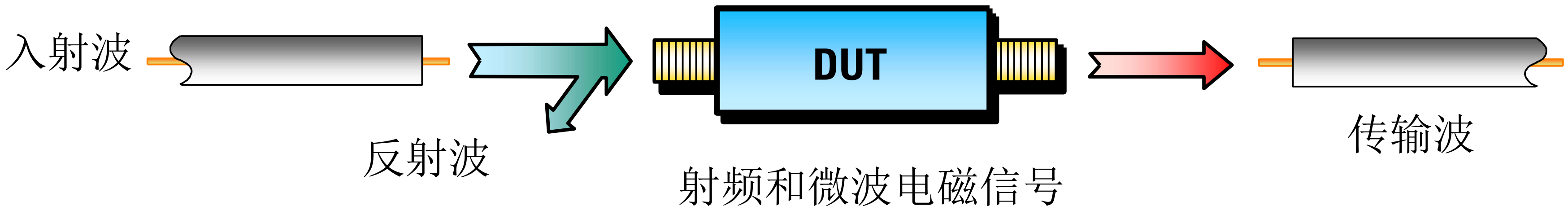


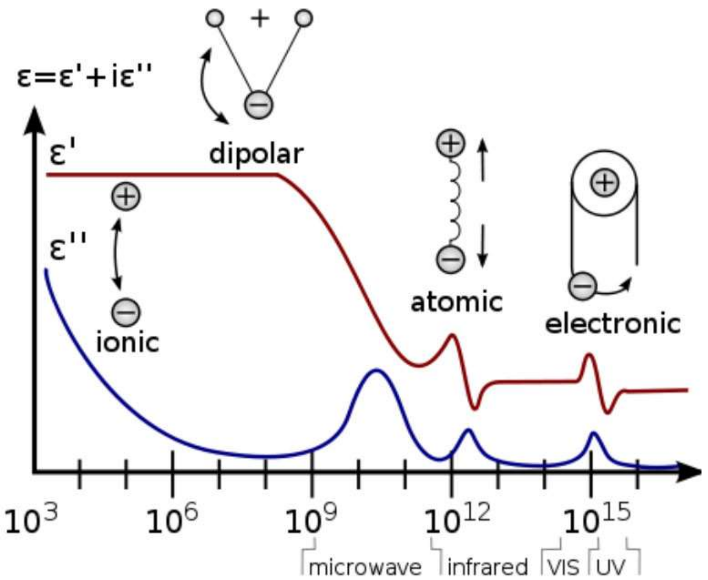
Life sciences • Polymers • Organics

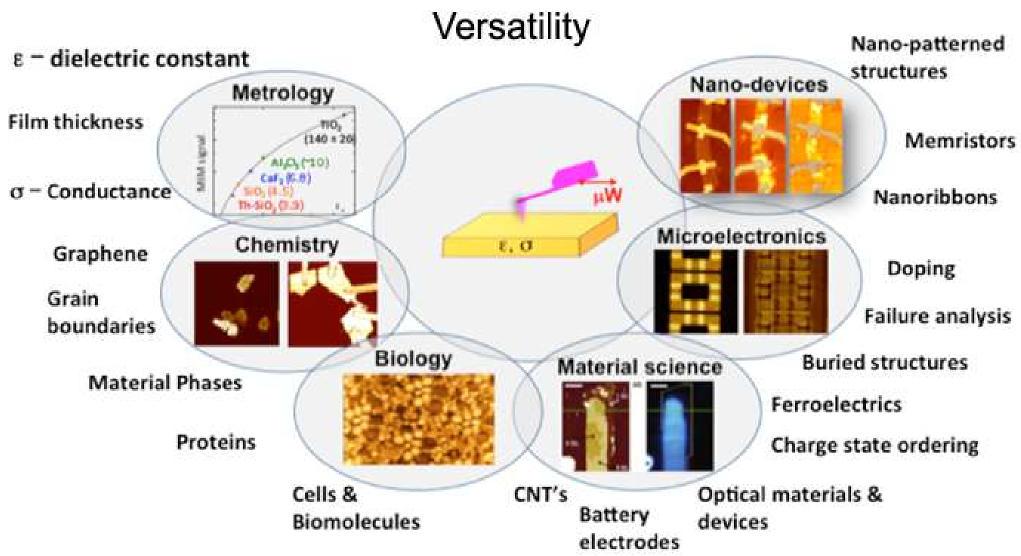
Graphene • 2D materials • Photonics • Inorganics

扫描微波显微术：SMM

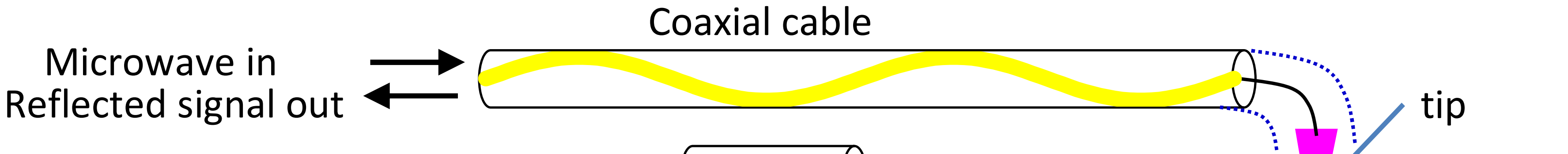
Scanning Microwave Microscopy







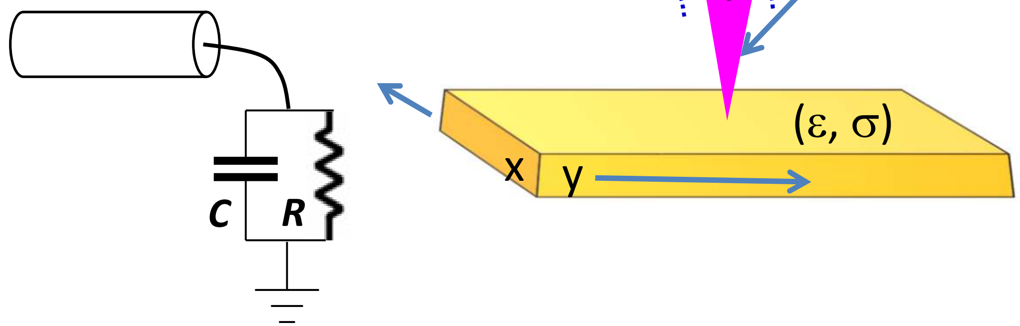
扫描微波显微术：SMM

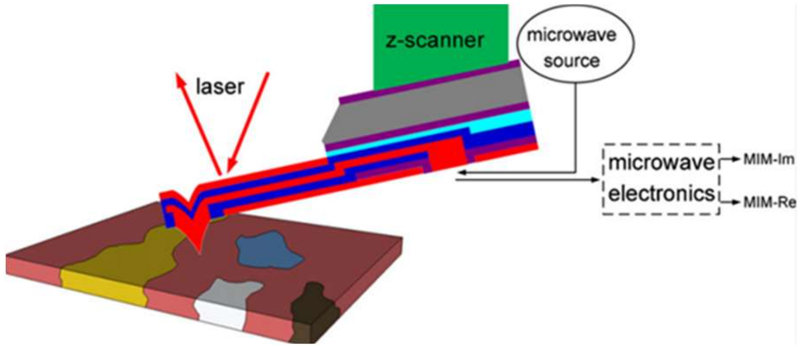


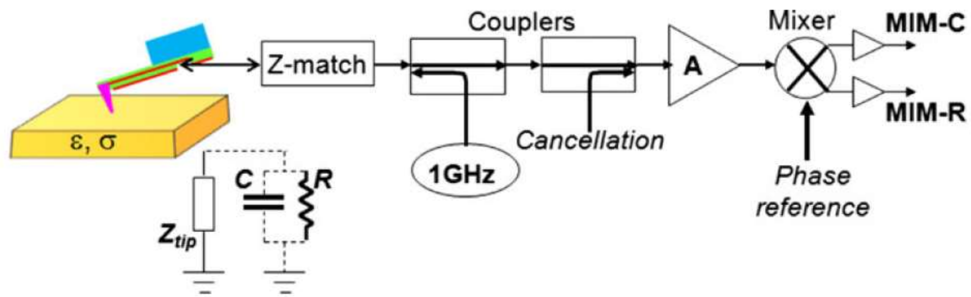
$$Reflection = \frac{Z_{tip} - 50\Omega}{Z_{tip} + 50\Omega}$$

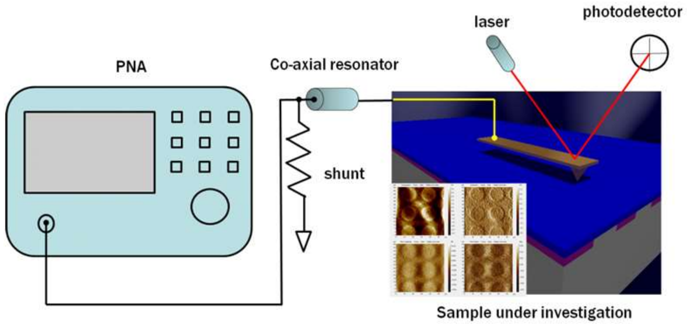
C = ε*(A/d)

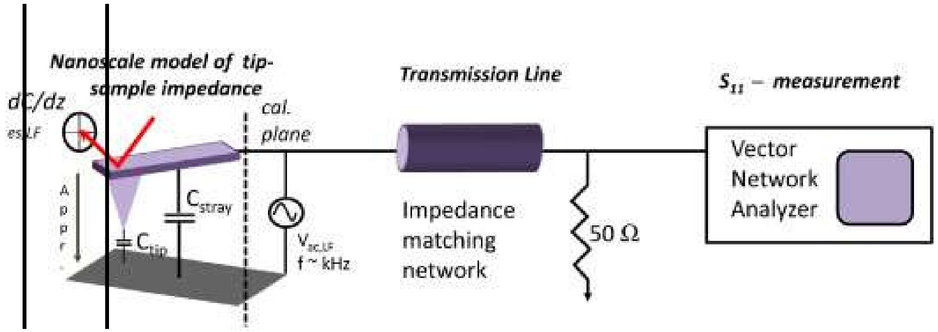
R = (1/σ)*(d/A)







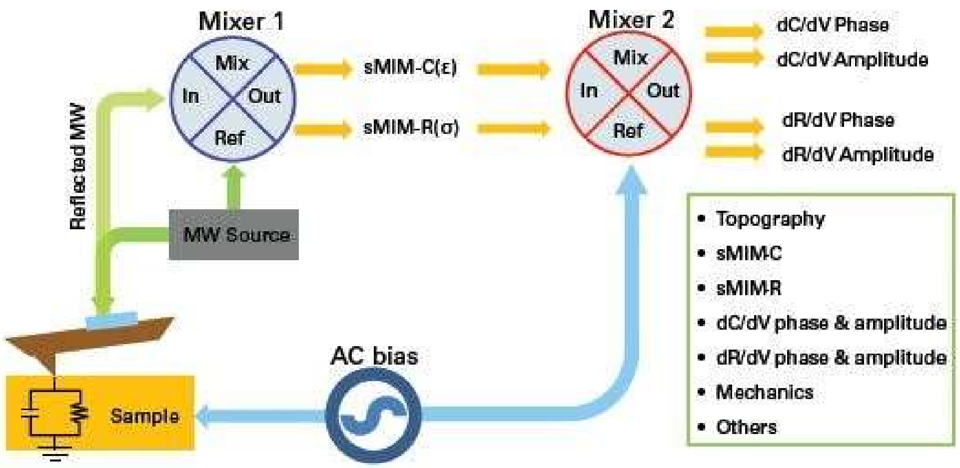




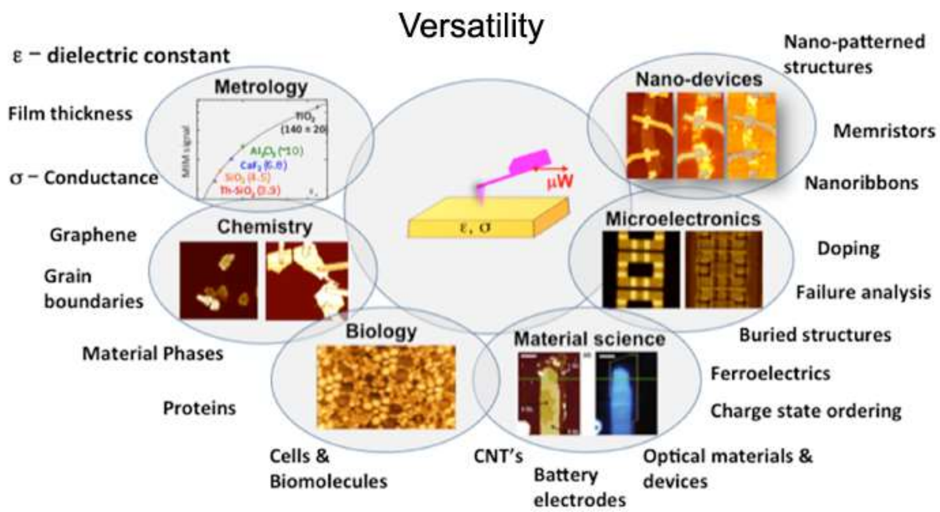
扫描微波显微术：SMM

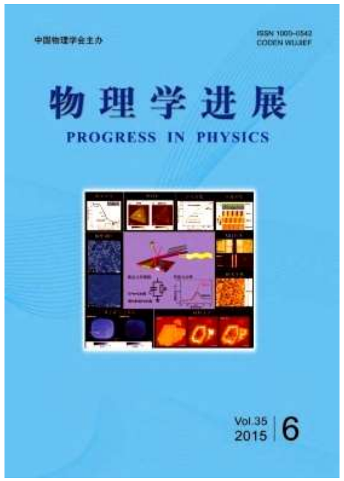
中国人民大學
RENMIN UNIVERSITY OF CHINA

Scanning Microwave Microscopy



- 直接探测电学性质
  - 介电常数和电导的直接测量
  - 载流子类型、载流子浓度的直接测量
- 可探测各种材料
  - 金属、半导体、导体
  - 工作于各种模式接触、轻敲模式、非接触模式
  - 可工作于各种环境，例如大气、真空、强磁场和液体等。
- 亚表面探测
  - 约~100nm的探测深度

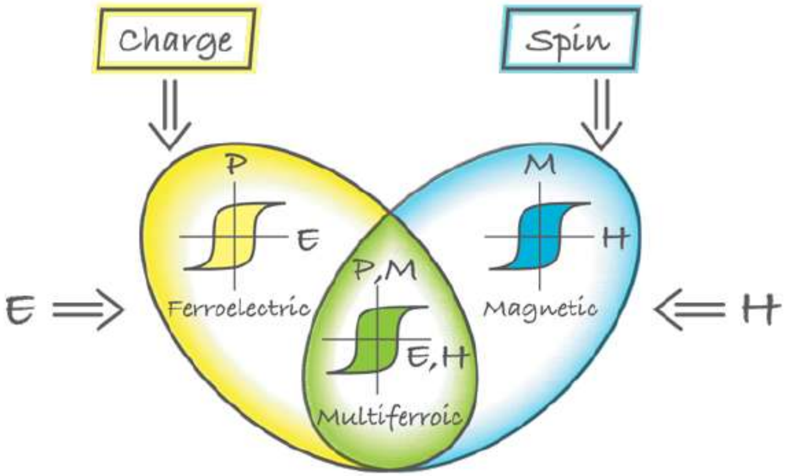


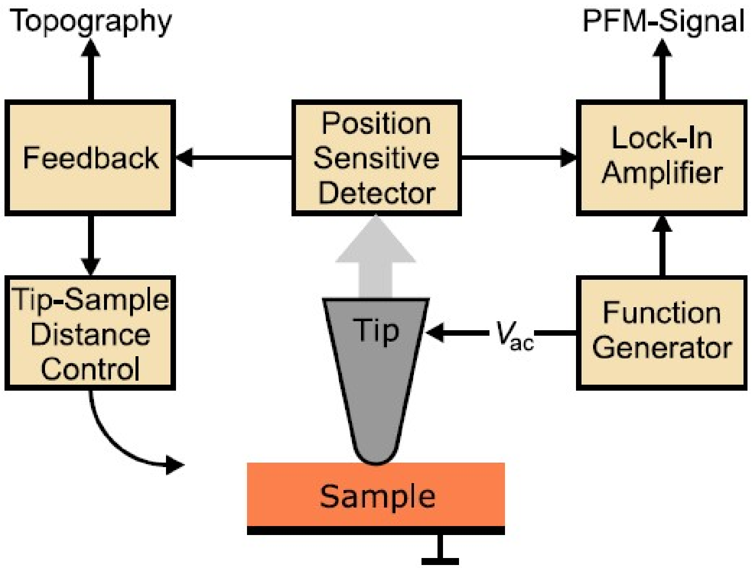


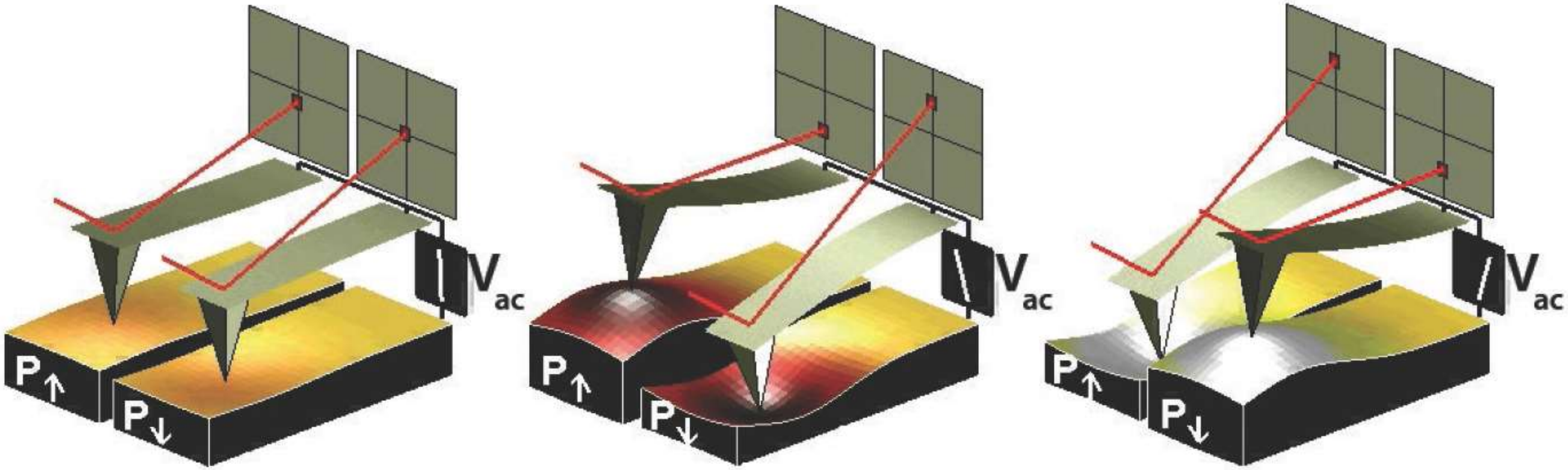
许瑞，郑志月，季威，程志海，《新型扫描微波显微术》，物理学进展，第35卷第6期，241-256，2015年12月。

压电力显微术：PFM

Piezoresponse Force Microscopy (PFM)

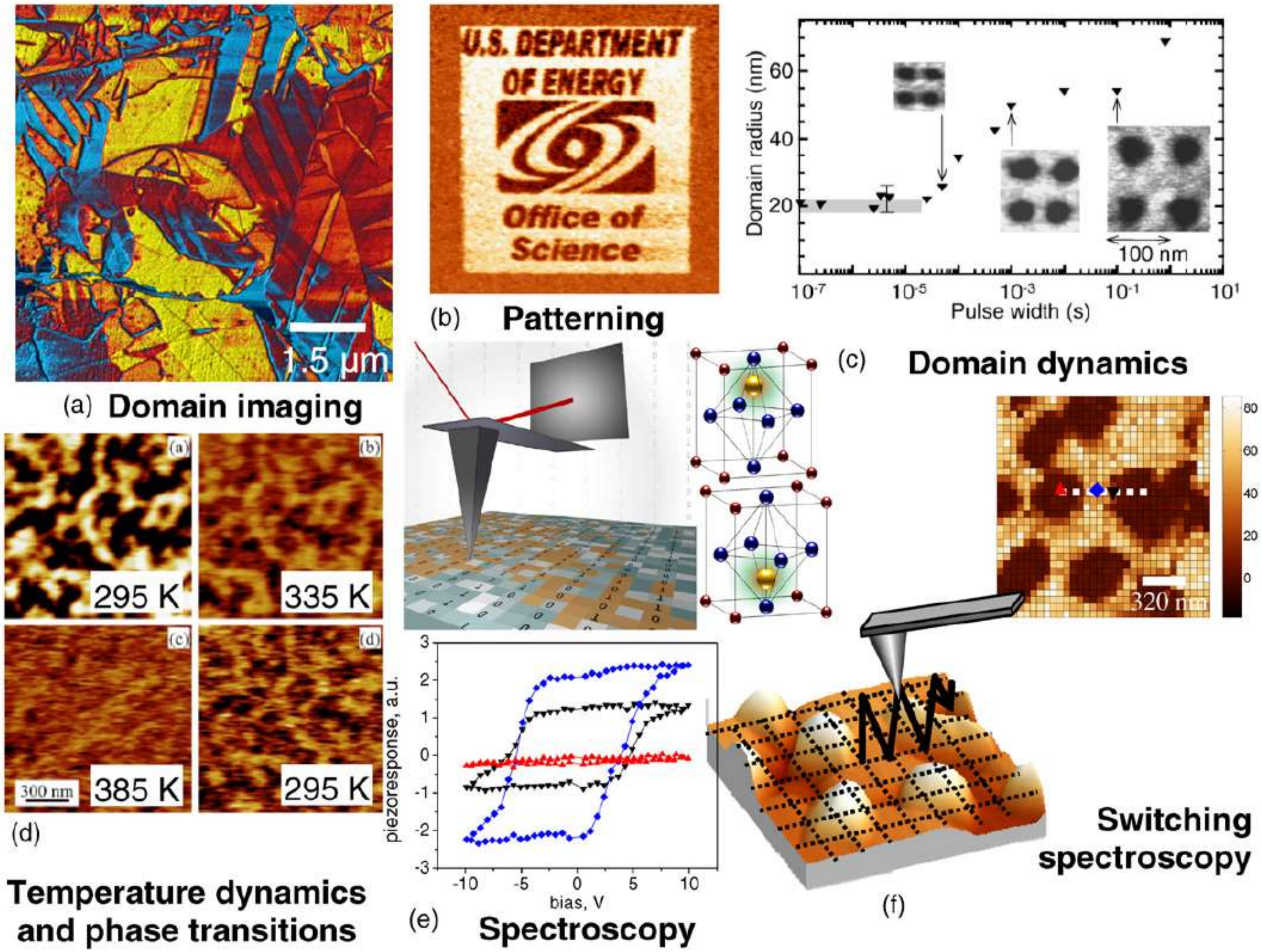






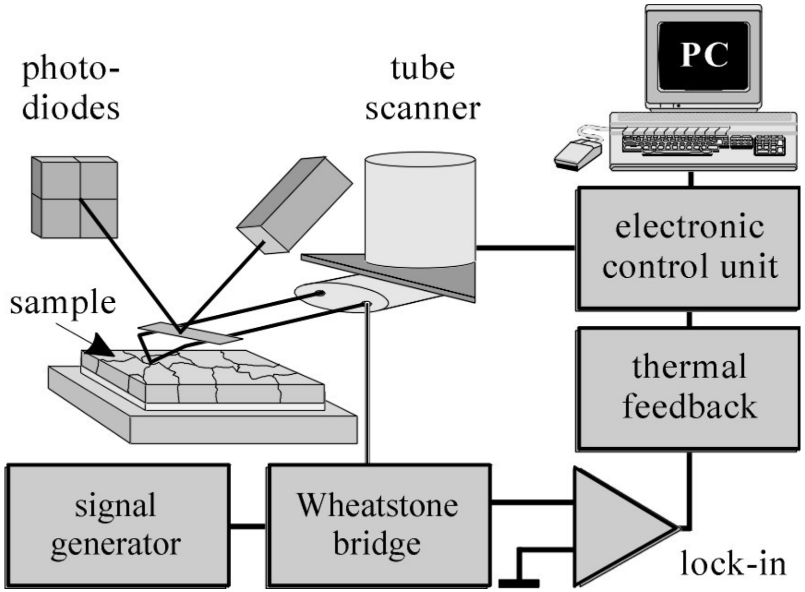
压电力显微术：PFM

Piezoresponse Force Microscopy (PFM)

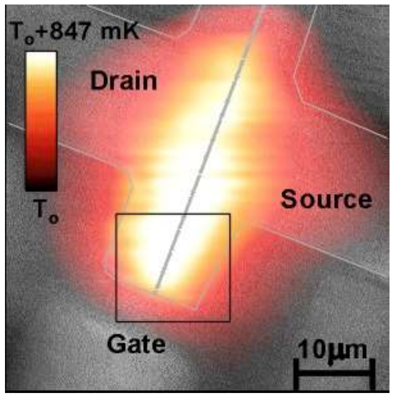


扫描热学显微术：SThM

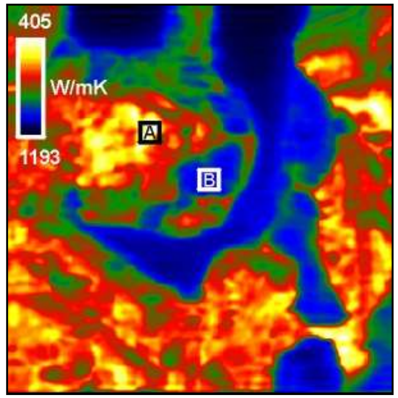
测温型探针：热电阻型(如Pt)，热电偶型（如Au/Cr)等，测温为主，有一定的加热控温能力



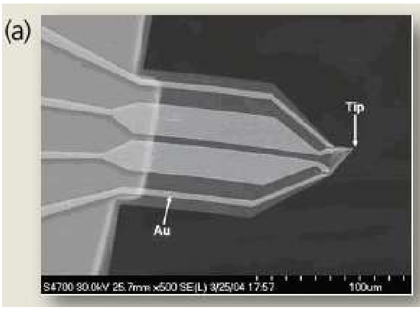
Scanning Thermal Microscopy



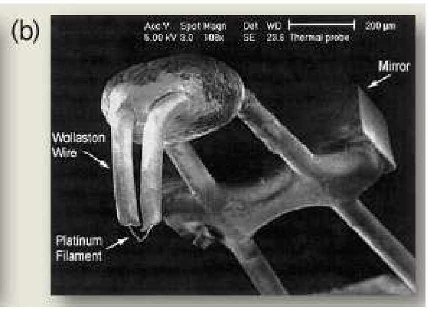
温度测量



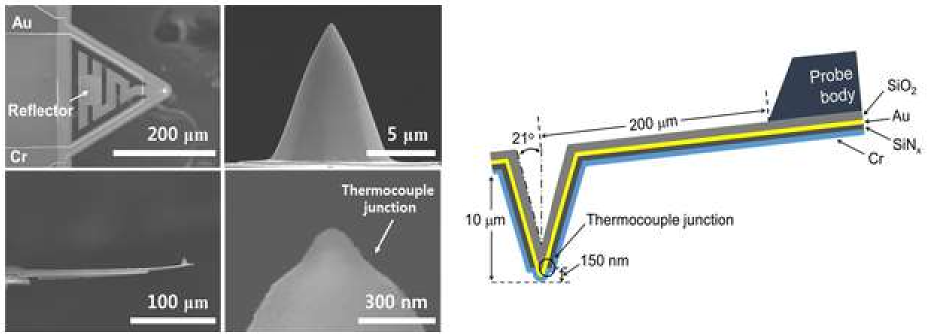
热导测量



电阻型（微加工）

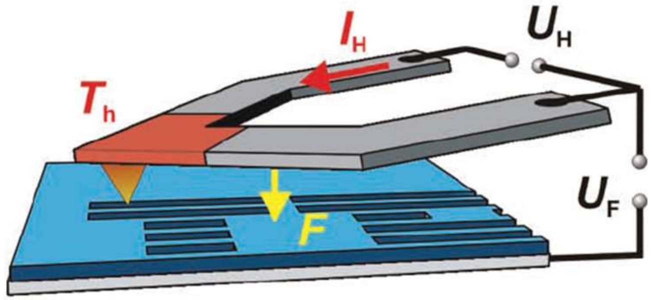


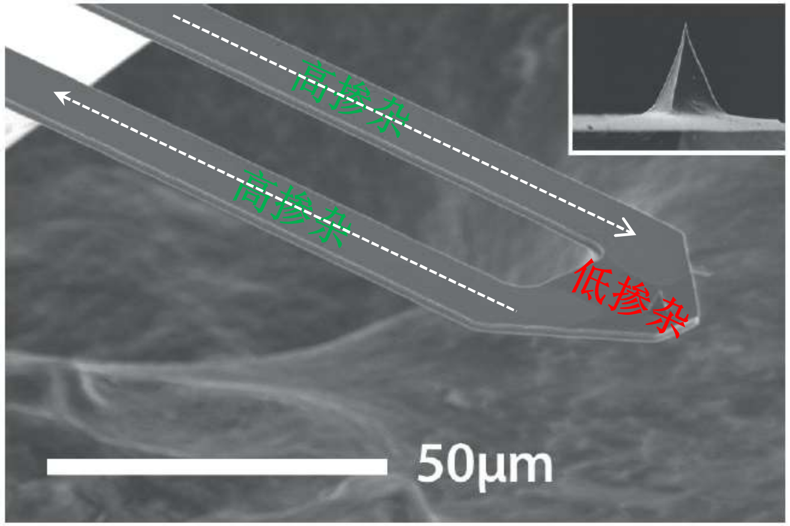
电阻型（铂丝）



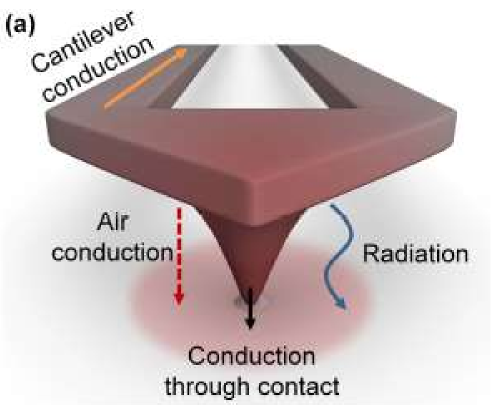
热电偶型（微加工，Au/Cr）

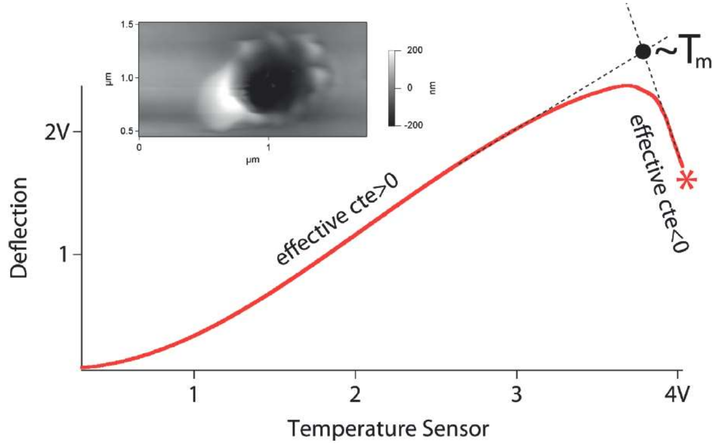
Scanning Probe Thermometry

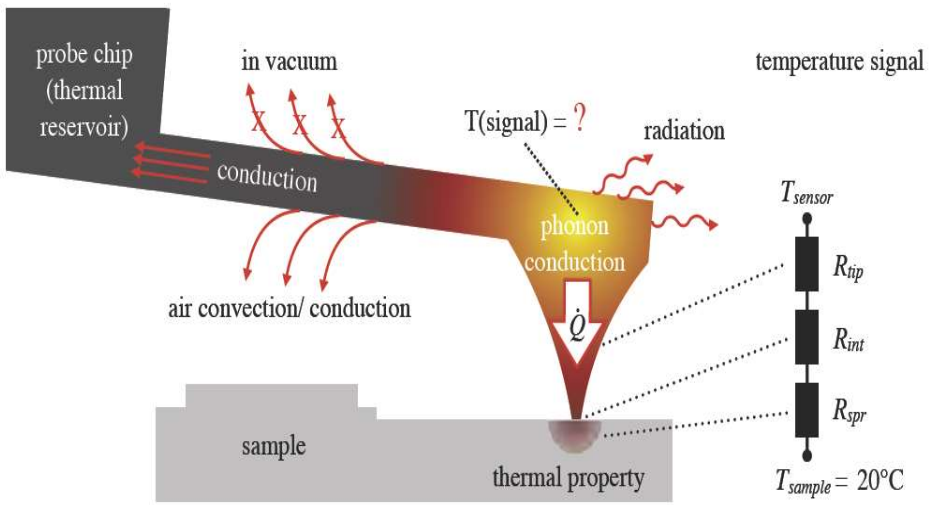




加热/测温元件在悬臂梁末端







纳米质谱：扫描热学探针+质谱

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analytical chemistry

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Atomic Force Microscope Controlled Topographical Imaging and Proximal Probe Thermal Desorption/Ionization Mass Spectrometry Imaging

Olga S. Ovchinnikova,[†] Kevin Kjoller,[‡] Gregory B. Hurst,[†] Dale A. Pelletier,[§] and Gary J. Van Berkel[†,*]

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[‡]Anasys Instruments, Santa Barbara, California 93101

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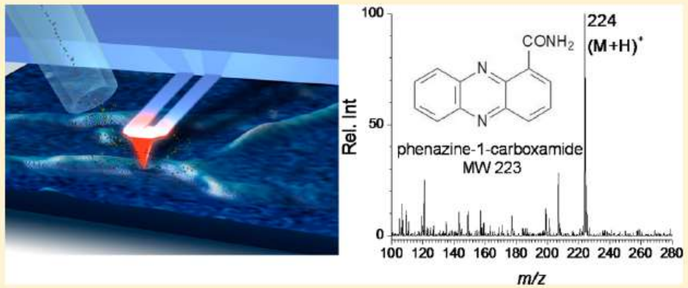
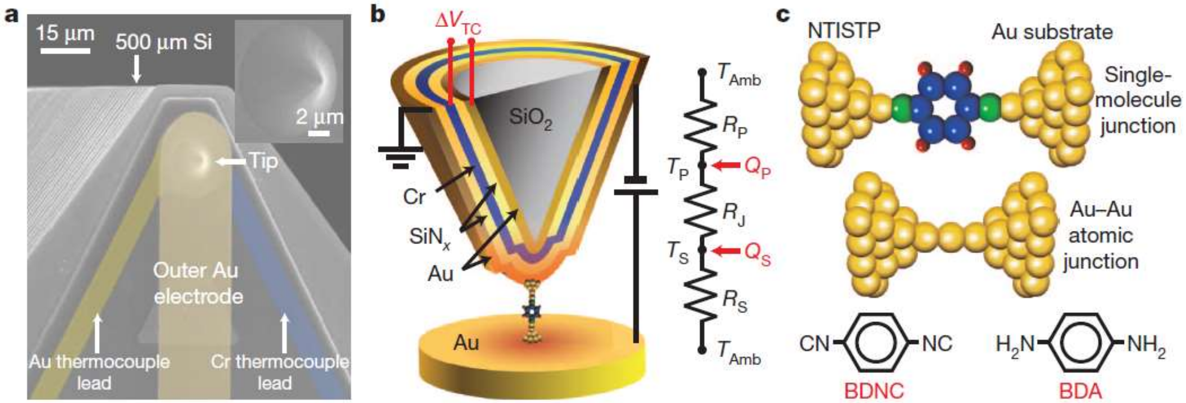
Supporting Information



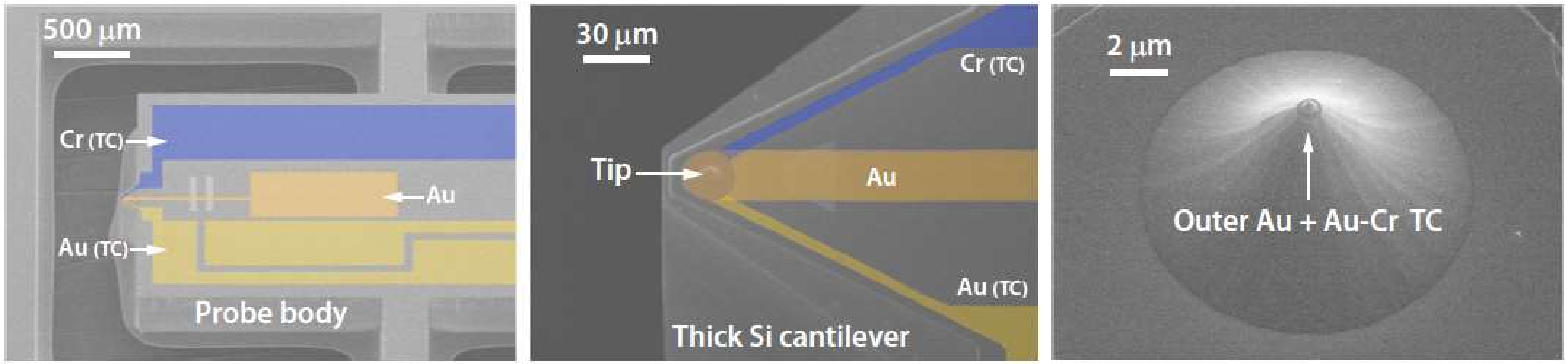
ABSTRACT: This paper reports on the development of a hybrid atmospheric pressure atomic force microscopy/mass spectrometry imaging system utilizing nanothermal analysis probes for thermal desorption surface sampling with subsequent atmospheric pressure chemical ionization and mass analysis. The basic instrumental setup and the general operation of the system were discussed, and optimized performance metrics were presented. The ability to correlate topographic images of a surface with atomic force microscopy and a mass spectral chemical image of the same surface, utilizing the same probe without moving the sample from the system, was demonstrated. Co-registered mass spectral chemical images and atomic force microscopy topographical images were obtained from inked patterns on paper as well as from a living bacterial colony on an agar gel. Spatial resolution of the topography images based on pixel size (0.2 μm × 0.8 μm) was better than the resolution of the mass spectral images (2.5 μm × 2.0 μm), which were limited by current mass spectral data acquisition rate and system detection levels.

扫描热学探针+电学性质测量

电极+测温 型AFM 探针 Nature 498, 209(2013).



研究原子尺度单分子隧道结的热传递和热耗散特性，进而研究电子的传输性质。



Scanning Probe Lithography

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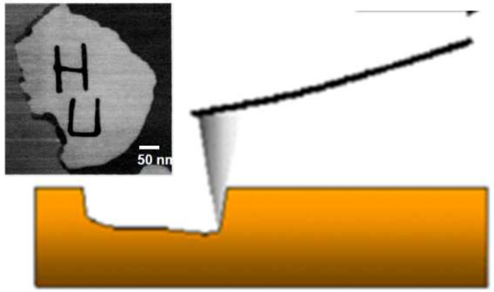
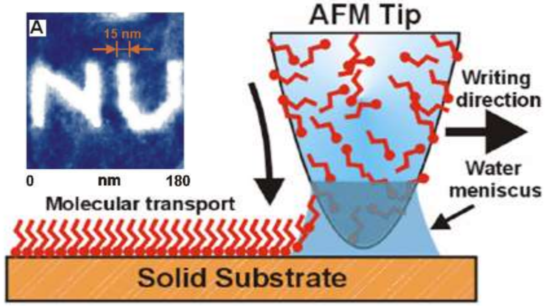
Nano-patterning by SPL: Forced-induce, Heat-induced, Electric-field-induced

Mechanical patterning



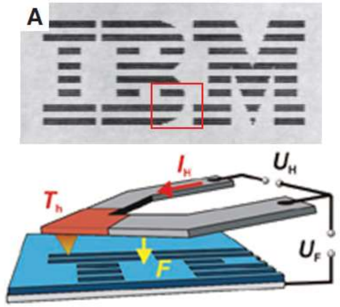
Science 257, 375(1992).

Chemical and molecular patterning



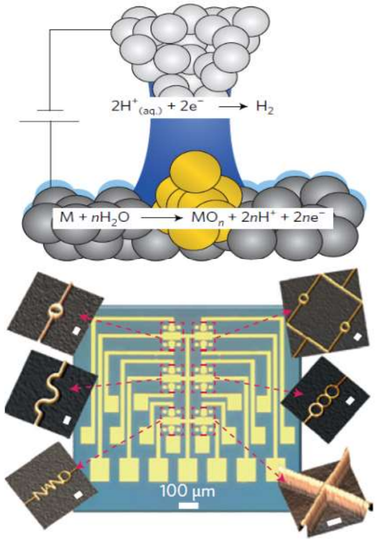
Science 286, 523-525(1999).

Local heating



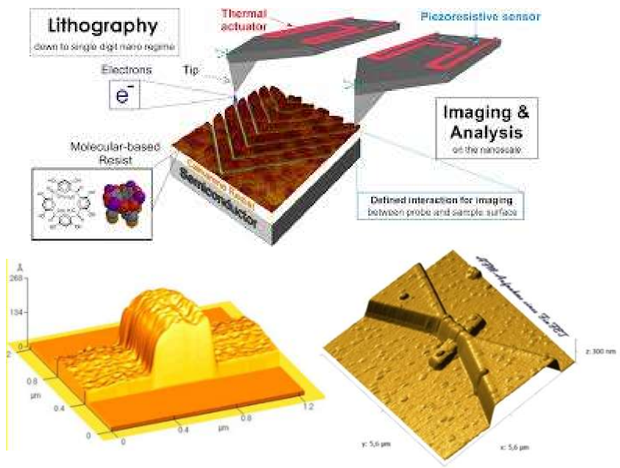
Science 238, 732-735(2010).

Field-induced oxidation



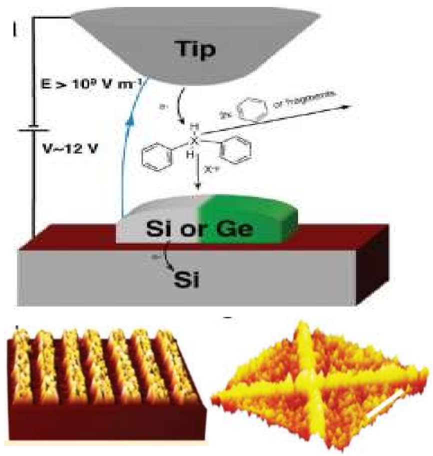
Nat. Nanotechnol. 9, 577(2014).

Field-induced exposure



Quate's group (Stanford)
Rangelow's group (Ilumeau)

Field-induced deposition



Nano Lett. 11, 2386(2011).
Rolandi's group

Scanning Probe Lithography

nature nanotechnology
REVIEW ARTICLE
PUBLISHED ONLINE: 5 AUGUST 2014 | DOI: 10.1038/NNANO.2014.157

Advanced scanning probe lithography

Ricardo Garcia[1], Armin W. Knoll[2] and Elisa Riedo[3]*

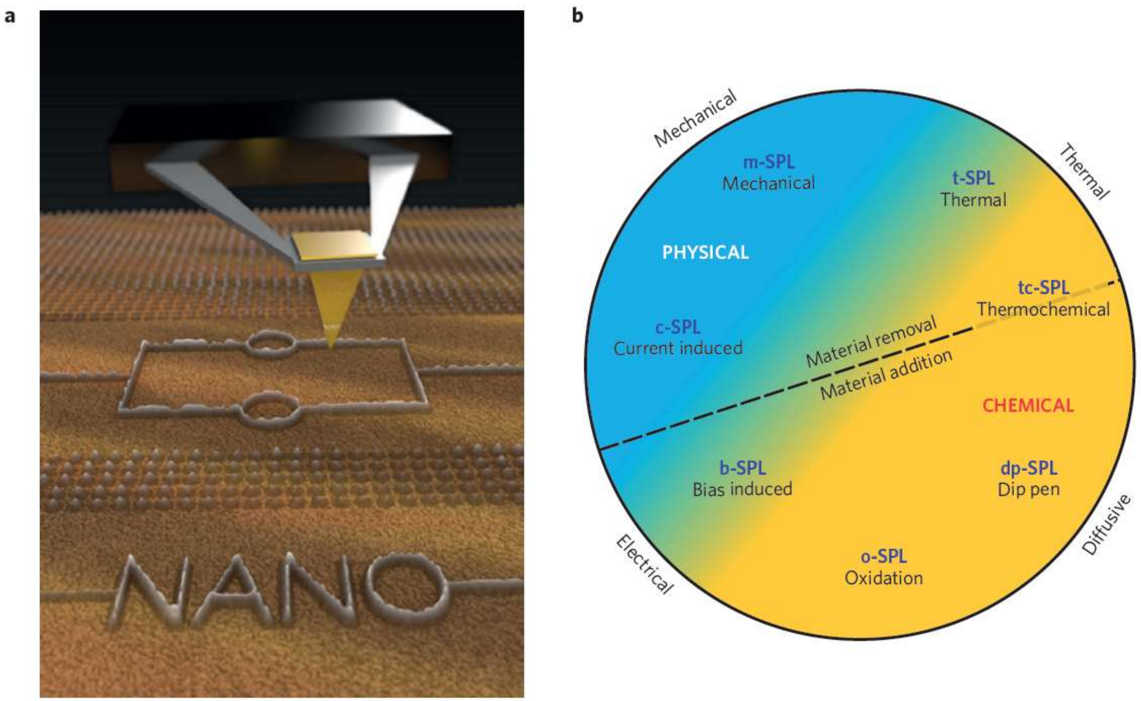


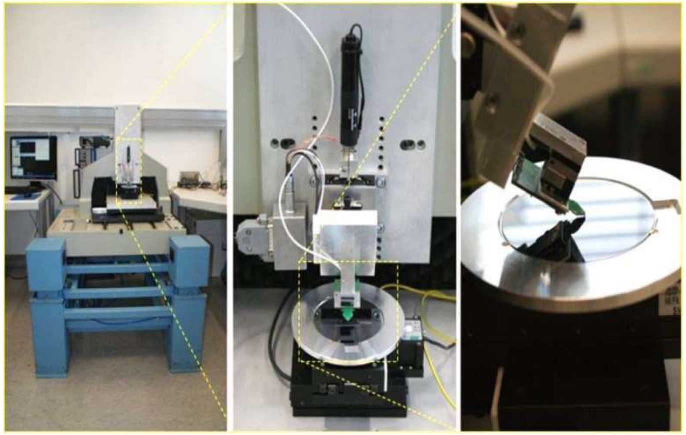
Figure 1 | Scanning probe lithography. a, Schematic of scanning probe lithography (SPL) where imaging and patterning applications are orthogonal. **b**, Classification of SPL methods according to the dominant tip–surface interaction used for patterning, namely electrical, thermal, mechanical and diffusive processes.

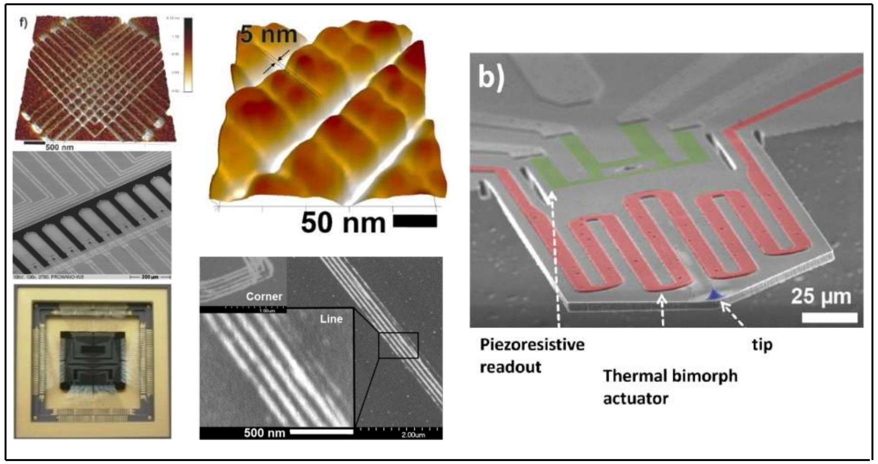
Scanning Probe Lithography

Nano Analytik

-- Low energy field emission exposure SPL

(Rangelow's group, Ilumeau)



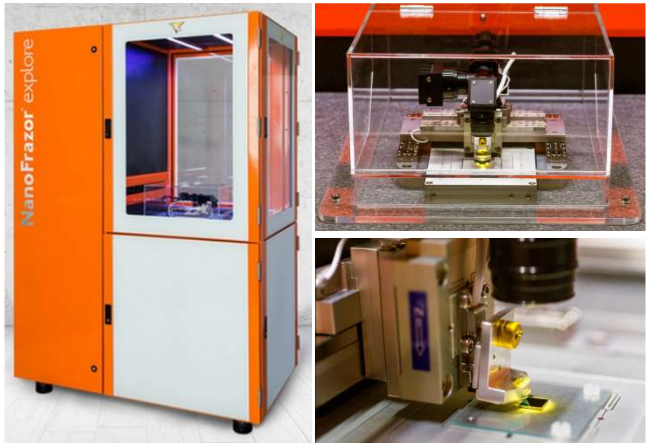


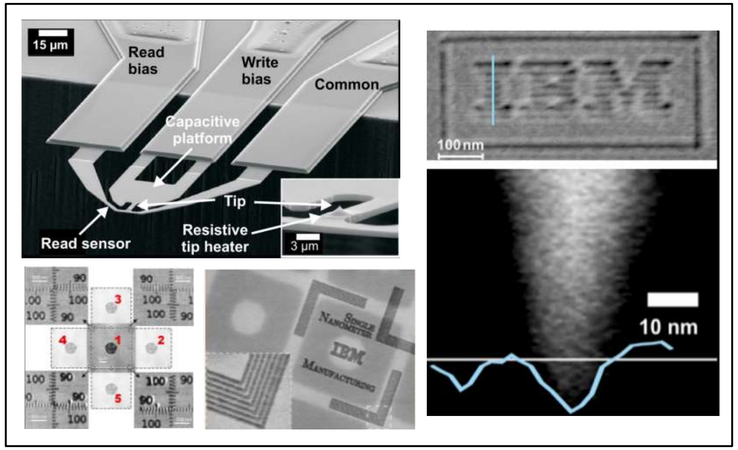
http://www.nanoanalytik.net/

NanoFrazor

-- Local thermal evaporation SPL

(IBM Reseach - Zurich)





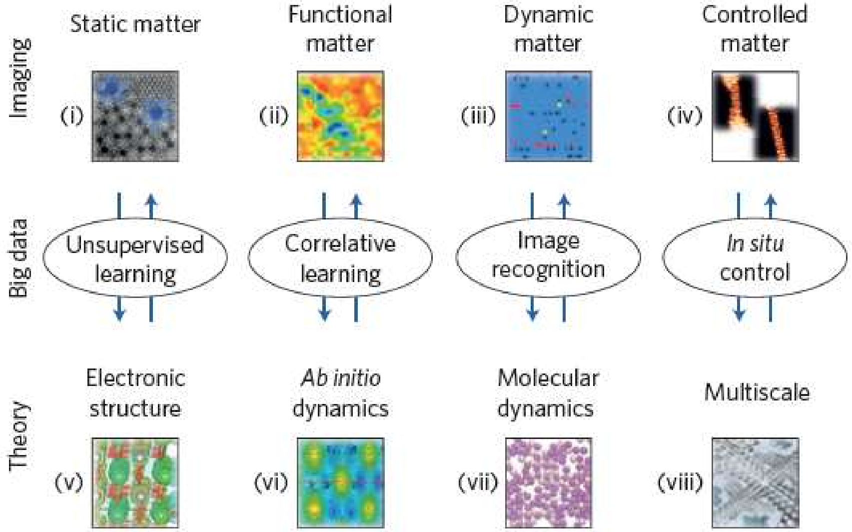
http://www.nanofrazor.com/

nature materials
PROGRESS ARTICLE
PUBLISHED ONLINE: 23 SEPTEMBER 2015 | DOI: 10.1038/NMAT4395

Big-deep-smart data in imaging for guiding materials design

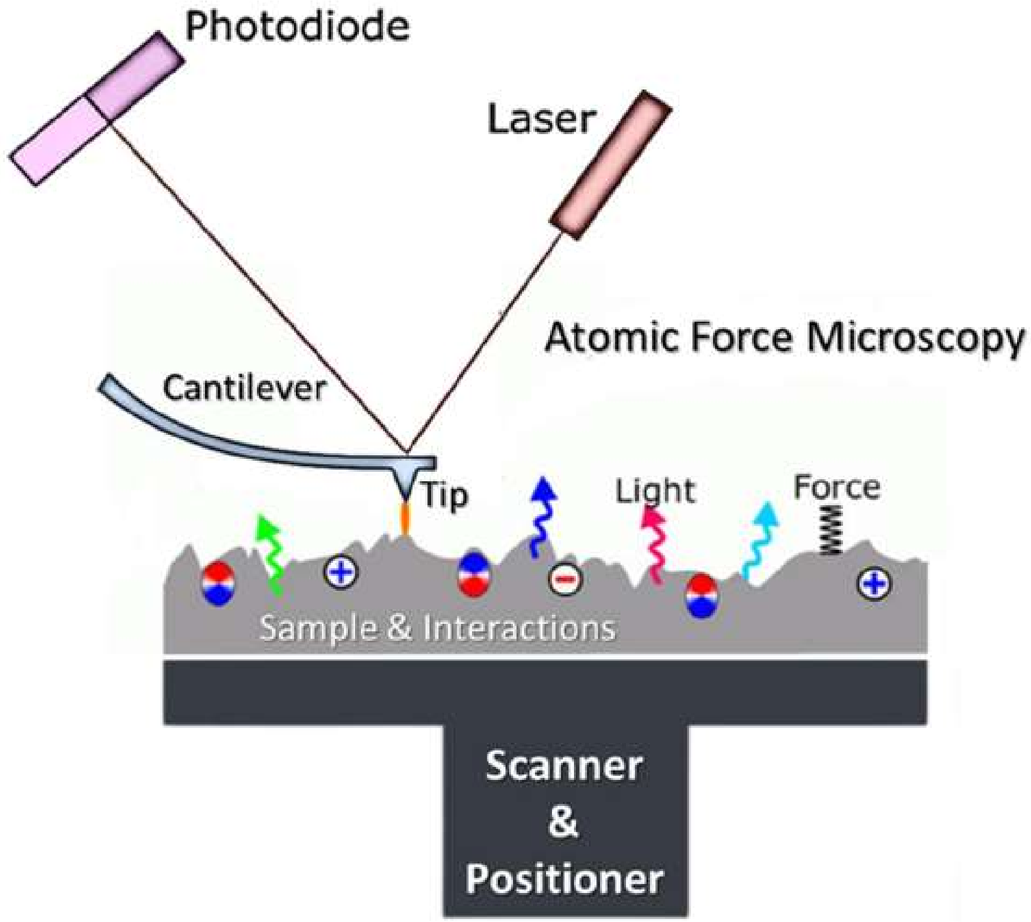
Sergei V. Kalinin[1,2*], Bobby G. Sumpter[1,2,3] and Richard K. Archibald[1,3]

Harnessing big data, deep data, and smart data from state-of-the-art imaging might accelerate the design and realization of advanced functional materials. Here we discuss new opportunities in materials design enabled by the availability of big data in imaging and data analytics approaches, including their limitations, in material systems of practical interest. We specifically focus on how these tools might help realize new discoveries in a timely manner. Such methodologies are particularly appropriate to explore in light of continued improvements in atomistic imaging, modelling and data analytics methods.



原子力探针显微学

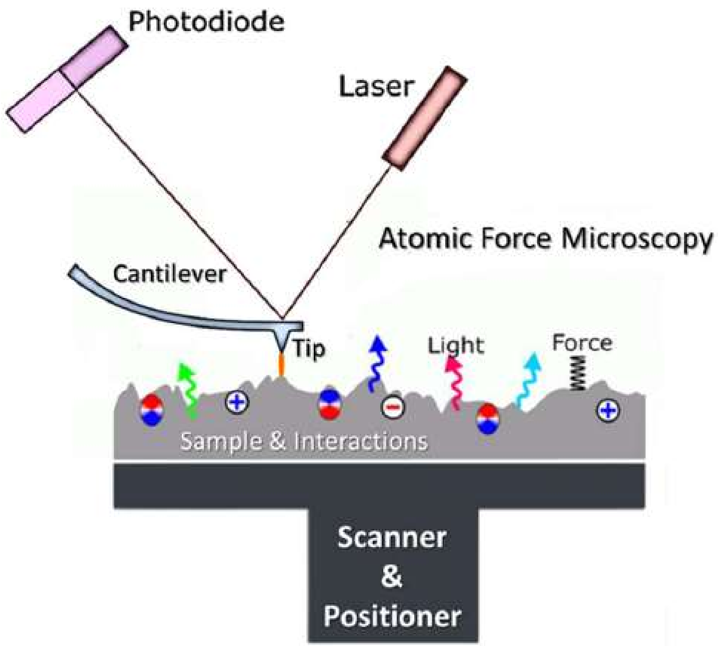
中国人民大學 RENMIN UNIVERSITY OF CHINA

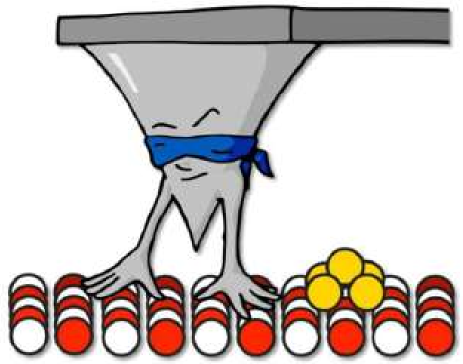


- 1 基本理论基础、仪器及相互作用
- 2 核心基础工作模式及其进展
- 3 功能化原子力探针显微术

总结与展望

See, Measure and Control the Small World with AFM !





致谢

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Thanks for your attention!

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