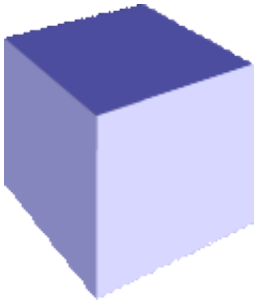
Probing the nano-scale

31 January 2012
09:02

(aka a probe for every occasion)
Firstly, what is the nanoscale?
Nanos is the Greek word for dwarf
1 grain of sand ⌀~1 mm $(10^{-3}m)$
Human hair ~50μm $(50 * 10^{-6}m)$
Smoke particle ~4μm $(4 * 10^{-6}m)$
Transistors ~$2 - 20\mu m$ $(wide)$
DNA ~2 $nm\ wide$ (2×10^{-9})
1 nanometer= $\frac{1}{10^6} of\ \ a\ mm$
1 atom ~ $\frac{1}{10} nm = \sim 10^{-10} = 1\mathring{A}$
We can now build quantum structures <20nm wide
Surface science aside:



Bulk surface
Atoms in bulk behave differently to surface atoms
As object shrinks, surface area overtakes bulk
3 main areas:
(not comprehensive list)

1. Electronics:
   - Faster electronics
     - Computers/memory etc
2. Materials:
   - Optoelectronics
   - Catalysts
   - High performance materials (eg auto industry)
   - Sensor development
3. Medicine:
   - DNA chips
   - Drug delivery
   - Toxic properties
   - Bio-compatible

Need to characterise materials on the smallest scale possible

- Quantum physics

Nanoscale resolution is not easily obtained

- Need a new breed of microscopes (pre-1980)

  Why? Conventional optical microscopy has a fundamental limit
  - Diffraction limit

Optical Microscopy

03 February 2012
09:09

Numerical aperture (NA)

Brightness of image depends on amount of light gathered by objective

Depends on NA of objective

$NA = n \sin \mu$

Resolution in optical microscopes

Two governing approaches

Raylegh criterion &the Abbe limit

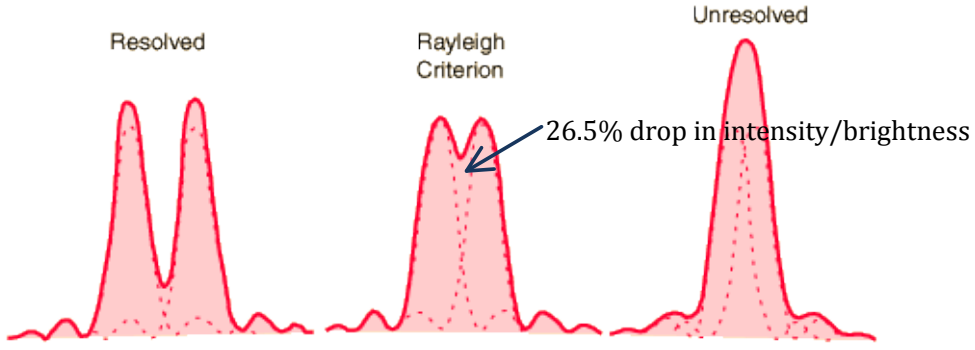
Diffraction exists in two general traditional forms

Fresnel & Fraunhoffer

- Wavelike properties of light

Huygens's principle states that each point on a propagating wavefront is an emitter of secondary wavelets

Wavelets form propagating waves which can interfere and produce fringe pattern -Diffraction



Rayleigh criterion

$$d = \frac{1.22\lambda}{2n \sin \mu} = \frac{0.61\lambda}{NA}$$

Abbe limit=

$$\frac{\lambda}{2n \sin \mu} = \frac{\lambda}{2NA}$$

Concerned with what happens in the immediate vicinity of a diffracting object or aperture

⇒ light / observation plane is at finite distance (pin-hole camera)

<u>Fraunhoffer diffraction</u>

Plane waves (collimated → infinite) illumination lens in focusing at finite plane

<u>Scanning probe microscopy (SPM)</u>

Used to overcome the limit of optical microscopy based upon the interactions of a probe with the aim of generating resolutions $< \mu m$

$\sim < 100nm$

Range of instruments available -$10^{-10} \rightarrow \mu m$

1st development of any instrument for these types of measurements was the scanning tunnelling microscope (STM)

This is NOT scanning electron microscope, SEM or transmission electron microscopy (TEM) or (STEM)

An STM, scanning tunnelling microscope uses quantum mechanical tunnelling

Electron tunnelling was just demonstrated by Giaever (Sp?) in earlier 60's (shared Nobel prize in '73)

Escki also demonstrated tunnelling in diodes

(tunnel diodes) → very fast

Young & co-workers produced vacuum tunnelling & electron field emission scanning (topographer) in '70s

Decade later ('81/'82) Binning & Kohrer (IBM) produced the STM → clear atomic imaging

~ How does it work?

~What equipment does it require?

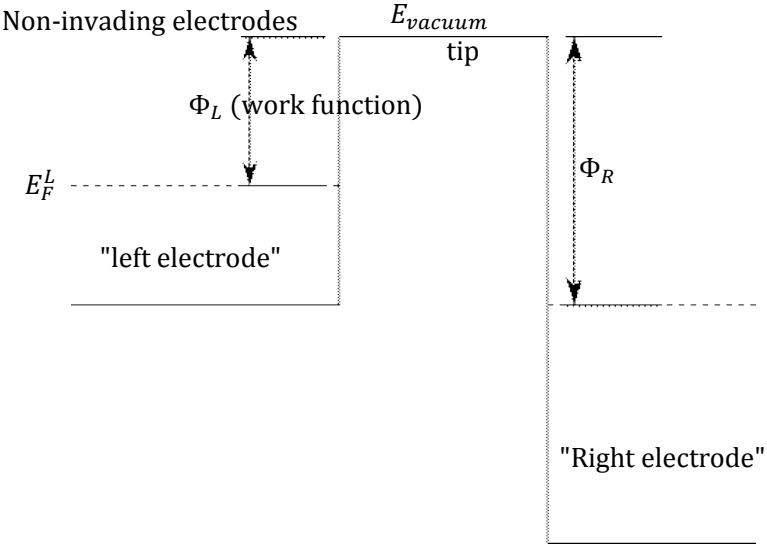
~What is it that you measure?

Latter developments in SPM such as atomic force microscope.

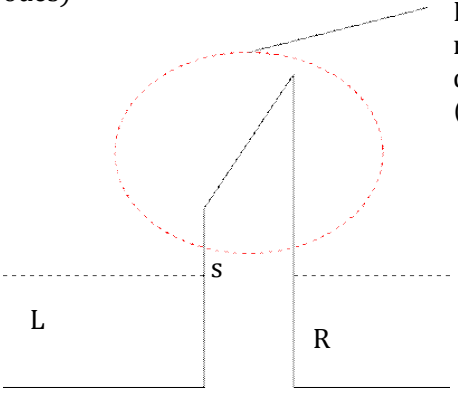
STM- How does it work?

In vacuum tunnelling, the potential in the vacuum region acts as a barrier to electrons & if the metal electrodes are placed close together, the vacuum region- in STM: One of the electrodes is a sharp metal tip & the other is a "metal" surface

i) Non-invading electrodes

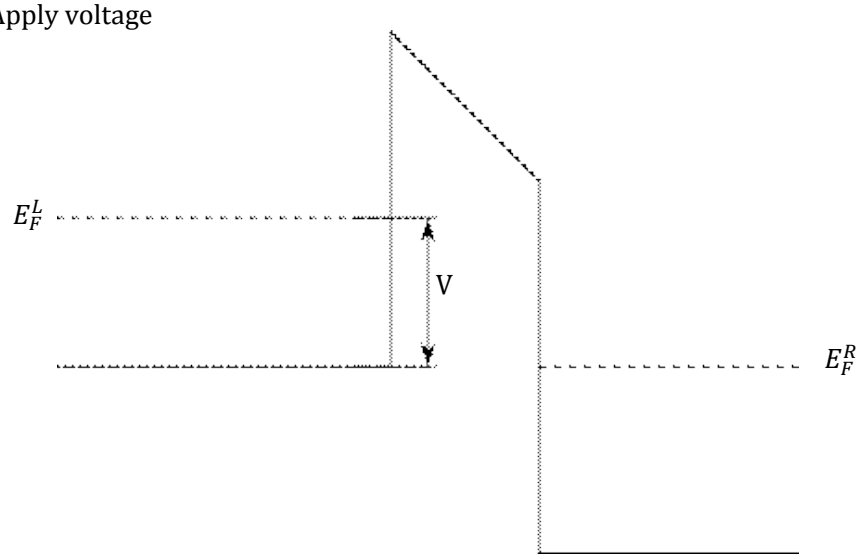


ii) Electrical equilibrium gives a unique common fermi level across both electrodes (eg grounding both electrodes)



Electric field in the vacuum region makes up for the original difference in the work functions (Φ)

iii) Apply voltage



Field in vacuum barrier region is now both a combination of $\Delta\Phi$ and the applied V

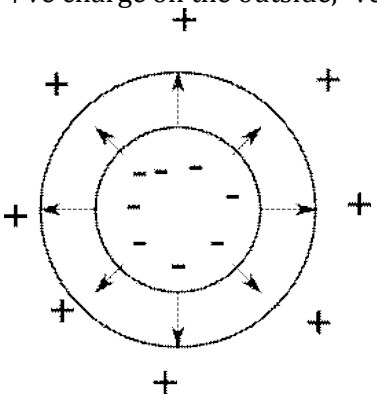
In a classical sense the electrons need to overcome the barrier (field emission) but in STM, Q.M. tunnelling through the barrier is made possible

Tubes are polarised at elevated temperatures,

Typically apply a high +ve voltage to the outer electrode on the tube (inner at ground)
Dipoles align ⇒ radial polarisation
Ceramic is cooled ⇒ permanently polarized

Can be ruined with high temp and also high voltages

+ve charge on the outside, -ve charge on the inside

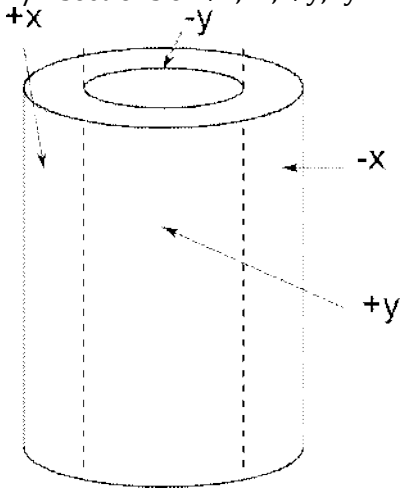


When the same sign voltage is applied (as was used to generate the polarisation) i.e. +ve on the outside

You get expansion in the primary direction
Radius expands with expansion in polarity direction

Contraction in positive direction ie z
Opposite occurs if negative voltage on the outside of the tube

1/4 sections of +x, -x, +y, -y



Same voltage but opposite polarity on the x- directions (+x, -x)
Gives orthogonal x-movement (i.e. z does not change)

To change z-displacement, apply a voltage $\hbar$ at outer electrodes (the same), get displacement in Z
Three main types of scanner:

Orthogonal tripod

Bar+rod
Simplest system
Polarisation in three orthogonal directions

Tube Scanner (binnie & smith, 1986)

Most popular, low noise
Binnorph: stacked layers of piezo ceramic discs
Benefits of tube scanner: Compact
Simple

High sensitivity
High resonant frequency (less interference -mechanical)

Rem:

Z- lateral mode displacement

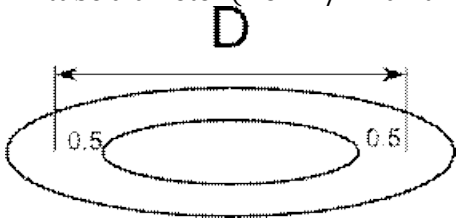
$$\Delta l = d_{31} * \frac{V}{t} * l$$

d_{31}=piezo-electric coefficient
V=applied voltage
t=thickness of wall
l=original length
(normally -ve, when +ve voltage applied

x,y lateral tip displacement

$$\Delta x = d_{31} \frac{l^2}{Dt} V_x \frac{2^{\frac{3}{2}}}{\pi}$$

D=tube diameter (from 1/2 wall thickness)



Note, if D is small & t is small, we get more displacement
As l increases, voltage increases with the square

Typical tube values,

$$d_{31} \approx -2 \times 10^{-10} \frac{m}{V}$$

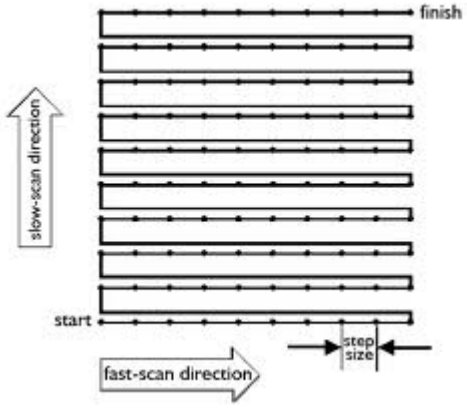
Contracts when voltage applied

$D = 6.3mm$
$t = 0.56mm$
$l = 12.7mm$

- Beware Temperature effects, thermal expansion/contraction

Non-linearities in the scan tube

Hysteresis: return path differs to the extension path



Going over each point in both directions in fast scan direction eliminates this problem: get a forward image and a reverse image

Non-linear deflection at high deflections

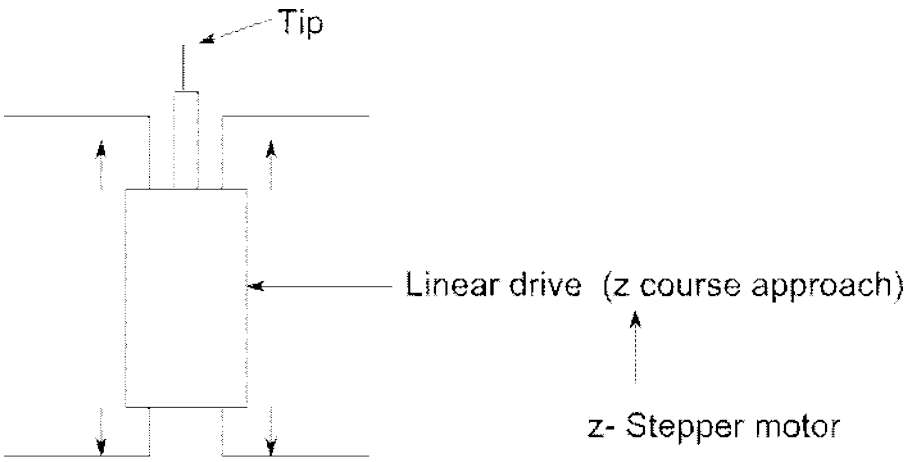
We need more voltage to create anticipated deflection

Creep

Driving voltage on the ceramic causes movement quickly but find 5% slow!
∴ creeps the extension or deflection
We modified driving voltages to overcome this effect

Tunnelling → how do you achieve it?

Tube houses the tip
We need to approach sample
Dual mechanism of coarse and fine approach



So tunnelling is achieved by a combination of piezoceramic extension/retraction followed by a course step - course step is still small <full extension of piezo

1. Extend pizo fully → I_T detected?
   $I_T = tunnel\ constant$
2. If no, retract piezo fully
3. Make one small step (coarse)
4. Extend piezo I_T detected?
   No= go to 2
   If I_T detected → how do we maintain?

Devices for course approach

- Stepper motor- fine pitched, siren thread 1/8 turn<fully extended piezo (~0.1 μm)
- Inch worm → walks with two feed, body is a piezo, can extend and retract with clamped feet
- Stick-slip, uses frictional forces & inertia

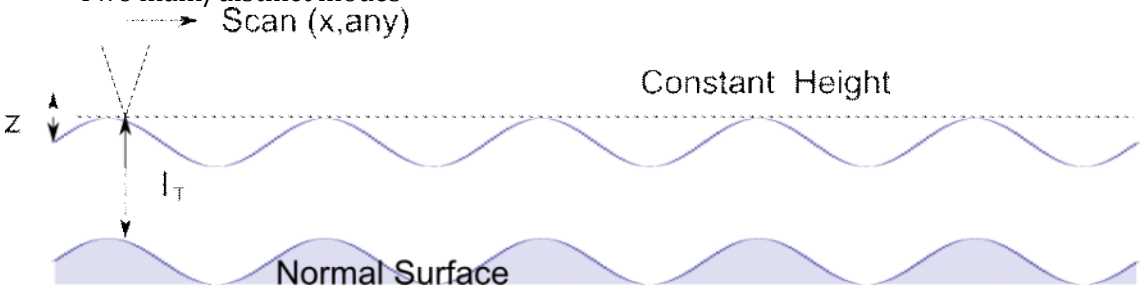
Sample holder/ thus the sample itself can also be moved by similar methods - so tip can be positioned on area of interest

Control electronics:

- To produce a scan, control x,y,z
- To maintain a tunnel current, I_T AND
- To <u>not</u> crash the tip - control z-gap

Modes of operation

Two main/distinct modes



Modes

- Constant current, I_T, must follow the topography of the sample
- Constant height mode, I_T varies as a function of d_z

Remember: STM measures the variation in the local density of states and is not just a atomic surface profiler

Requires good feedback controls!!

Unless pure constant height is used once I_T established → need feedback always to establish I_T

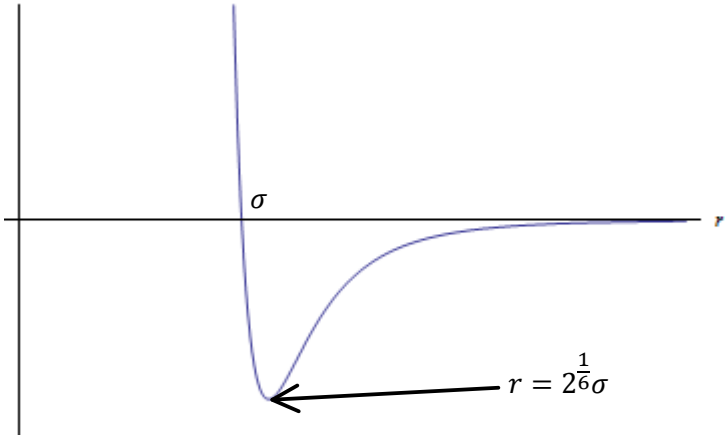
Z- control

x,y control

Voltage current requirements

Atomic Force Microscopy

24 February 2012
09:24



σ = diameter of the atoms involved i.e. separation between atoms [hard sphere radius = $\frac{\sigma}{2}$]
Variations in the pair-potential energy [E_{pair}] with separation r between two atoms (identical) is described by the Lennard-Jones potential (or 12:6 potential)
AFM seeks to exploit the force of attraction & repulsion between atoms & molecules
Forces of attraction & repulsion due to charge & in balance of charge (dipoles) is often termed generally as Van der Waals forces

$$E_{pair}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

σ& ϵ are constants → material dependent
σ= hard sphere diameter of atoms involved

When r is small, $(\sigma/r)^{12}$ dominates.
E_{pair} → Repulsive regime
Pauli-Exclusion principle (electron clouds overlapping)
When r is large, $(\sigma/r)^{6}$ dominates, E_{pair} is -ve cohesion forces, attraction between atoms
Van der Walls forces are also known as displacive force(?), dipole interaction can be long range
AFM takes a probe and looks at the forces of interaction between the sample and the probe apex- exploiting the L,J potential
Other forces:

Electromagnetic interaction forces can be detected
Ionic bonds (+ve and -ve ions, strong attraction)

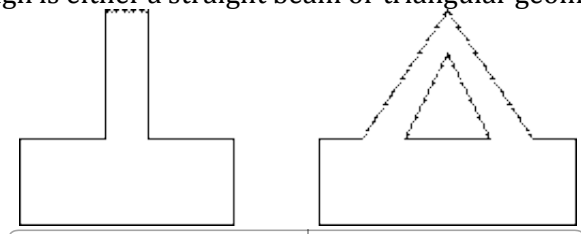
$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

Covalent bonding- forces: electron exchange. Charge density between atoms
Metallic adhesion forces: Free valence electrons interacting between ionic cores
Repulsive forces: nuclear charge, repulsion, electrons su (?)
Pauli exclusion principle, 2 electrons can't have same state (space)
Van der Walls:

Dipole-dipole interactions (permanent dipoles)
Dipole-undfined dipole (
Dispersion forces → instantaneous dipoles forced (non-polar molecules)

The AFM uses a pulse at the end of a cantilever to sense the force interaction with the sample.
The cantilever is "like" a record stylus, it can move up and down.
Cantilever has a low spring constant. Can control force between tip & sample to great

precision.
Cantilevers can be made to many different designs.
Two main types fabricated using Si-based technologies
Cantilevers are usually made from Si and silicon nitrate
Design is either a straight beam or triangular geometry



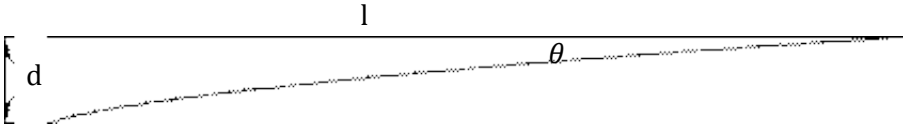
Beam (top view)	Triangular
Measure effects of friction via twisting modes (shear forces) +normal forces	Resistant to twisting Normal forces only

Hooke's law defines the action,

$F = -kd$

F=force
k=spring constant
d=displacement (deflection)

Minus sign indicates force acts in opposite direction



$\sin\theta = \frac{d}{l}$

For small angles, $\sin\theta \sim \theta$

$\therefore \theta \approx \frac{d}{l}$

$\therefore \theta$ is greater if l is small -i.e. Short cantilevers give larger change in θ

How can θ be measured? (see handouts)

1. Optical lever

Laser beam focused on the back of the cantilever
Reflections are directed onto a photon sensitive detector
Deflection allows detection by an "optical lens" → amplifying the motion

Alternative methodse (not so comonly found) include

2. Inferometer; light path changes, interference occurs, changes in pattern reflect displacement
3. tunnelling detector; metal coatide cantilever forms part of a STM system to register motion of the cantilever

I heard you like microscopes, so I put a STM on your AFM so you can scan while you scan

Optical lever method is the one found in commercial instruments- 4 segmented photodiode detection

By measurement of displacement for a cantilever, the force can be mapped.

A force-distance curve can be generated to study the forces between the tip & the sample as a function of their separation

Diagram (handout) sequences 1-6

Cantilever deflection ($\Rightarrow F$) vs distance between tip & sample

1. Large separation (>100nm)
   ⇒ spring like nature of cantilever, no deflection
2. Decrease separation ⇒ attractive regime, cantilever starts to bend (measured deflection)
3. The tip is now very close to contact and can snap into contact with the sample (rapid change)

Due to forces → tip is now in contact (large deflection)

4. As sample is pushed closer, cantilever deflection straightens (less deflection, can vary somewhat if sample is soft)
5. Cantilever deflection is zero, balancing the attractive forces & repulsive forces when in contact ⇒ low force (minimum) is good for "contact" imaging
6. Repulsive forces take over, deflection upwards, forces can damage sample.
   Easier to image areas where force gradient is larger, region of non contact is harder to measure

AFM modes of operation → main types!

1. Contact mode: the tip tracks the surface like a record stylus, i.e. the tip is in contact mode imaging- also referred to as d.c. mode.
   Can be implemented in a number of ways.
   1. Constant - force mode: Piezo scanner drives the sample into the tip to a pre-defined deflection, i.e. set up an imaging force ($F = -kd$)
      ⇒ maintains ths force when scanning by z-motion in the piezo tube
      ⇒ we have to have feedback
   2. Variable deflection mode, deflection signal used to show displacement
      ⇒No feedback forces can be quite variable & ∴ high (e.g. can be used to "cut up" (soft) material with high forces)
2. Non-contact mode (a.c. mode) uses the long range attractive forces which are weaker, more gradual & thus harder to exploit
   Two main types: tapping & true non-contact
   1. Tapping: Excite beam type, cantilever resonates: Amplitudes of ~100nm
      So it can start to tab the surface
      How?
      Stick a cantilever tip to a piezo electronic material and apply an a.c. voltage
      ⇒ tip vibrates with a frequency of the a.c. voltage.
      ⇒ tune to resonance of the cantilever - maximum deflection response
   2. True non-contact: oscillation amplitude is damped by the long range forces. ∴ monitor A as a function of distance - measure the van der Waals forces directly
      Signal can vary too much and system looses feedback
      Frequency or phase is more sensitive- use this in feedback

We have considered the forces that exist between atoms & molecules

Forces in relation to scanning force microscopy

Need to consider environment
(Forces change depending on whether measured in air, vacuum or liquid)
Scanning is dynamic- lateral/shear forces e.g. frictional forces
Deformation of the sample ⇒ even destruction
Bonding between tip-sample ⇒ re-arrangements on surface
Many bodied problem, rather than sample two-bodied Lennard Jones Potential

Van der Waals (non-bonded (generalisation, can be found in crystal bonds))

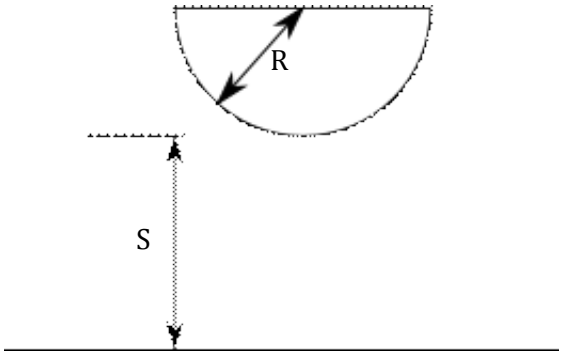
Dipole-dipole, dipole-truncated dipole or transitory (instantaneous) dipoles (London forces)
Range of a few Å's to a few 100 Å's
-significant force
They can be modelled- simple power law with Hamaker constant for the materials
Force between tip (sphere) and a plane(surface)

$$F(s) = -\frac{AR}{6S^2}$$

s=separation
A=hamaker constant
R=radius of curvature of tip (sphere)

Van der Waals

06 March 2012
09:06

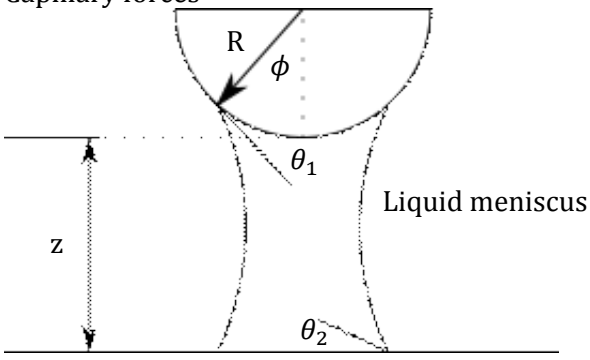


Sphere-plane interaction

$$\boxed{F(S) = -\frac{AR}{6S^2}}$$

A= hamaker constant
R=radius of tip (sphere)
S=Separation

Capillary forces



A meniscus can form between the tip & sample. This produces pressure→ force
Capillary force can be estimated from the following equation,

$$F = \frac{4\pi R\gamma \cos\theta}{1 + \frac{z}{[R(1-\cos\phi)]}}$$

This assumes $\theta_1 = \theta_2$
And

γ = surface tension of water
R= radius of curvature of the tip
θ = contact angle
ϕ = angle of the meniscus
z=tip-sample distance

Maximum attractive force $F_{max} \approx 4\pi R\gamma \cos\theta$

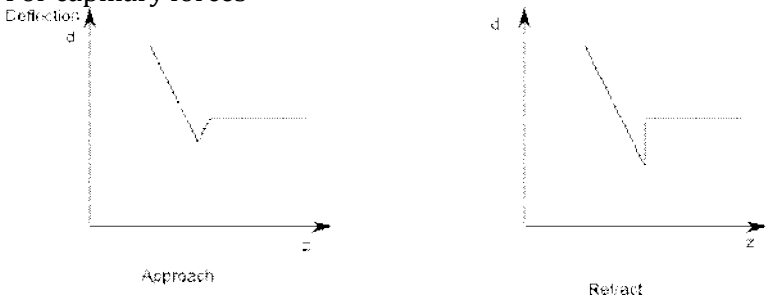
$F_{max} \approx 9 \times 10^{-8} N$

Which is <u>quite high</u>
Compared to other forces acting in SFM

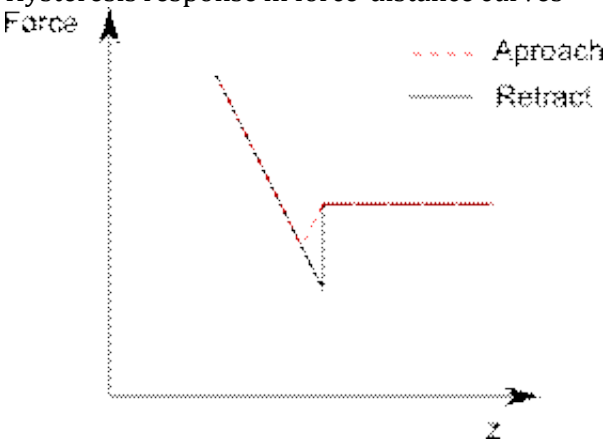
This attractive force can limit the repulsive force in humid conditions- tip wear evident!

Force-distance curves can tell us a lot about forces & reactions (e.g. you could functionalise your tip with special

coatings)
For capillary forces



Hysteresis response in force-distance curves



The blunter the tip, stronger the force
Interestingly, some polymers can act like liquids and show strong capillary/adhesion forces
Can functionalise tips to look at other types of forces

e.g.1 magnetic forces; magnetic force microscopy (MFM)

Use a ferromagnetic tip to probe samples' magnetic properties

e.g.2 Potentials, use a charged tip to map attractive/repulsive forces-

Forms microprobes like Kelvin Probe & Summary capacitance microscopy

<u>Cantilevers</u>

- Vibrating cantilevers are affected by forces
- Using optical detection and lock-in techniques the modulation frequency is chosen to be close to the resonant frequency of the cantilever
- Regulating to a constant amplitude or phase keeps frequency f constant

Remember

$$\boxed{f - \frac{1}{2\pi}\sqrt{\frac{k}{m}}}$$

$$\boxed{F = -kx}$$

$$f \propto \sqrt{k - F'}$$

Where F' is the force gradient

$$\left(F' = \frac{\delta F}{\delta z}\right)$$

This can be viewed as a modified or connected spring constant

The probe tip will now measure or "trace" lines of constant force-gradient
Sensitivity; minimum detectable force is determined by the sensitivity of the detector/deflector system.

Typically better that 0.01nm with a 1N/m

cantilever (k=1N/m)

This corresponds to a detectable force of

$F_{min} = 10^{-11}N$

Force gradient detection by interaction with long range Van der Waals forces can be considered in ac mode where the resonant frequency changes are "monitored"

Spatially varying force, ex force gradient

$$\frac{\delta F_z}{\delta z} = f'$$

Gives

$$k_{eff} = k - F'$$

Change in effective spring constant changes the resonant frequency of the cantilever

$$\omega_0' = \left(\frac{k_{eff}}{m}\right)^{\frac{1}{2}} = \left(\frac{k - F'}{m}\right)^{\frac{1}{2}}$$

For small F' compared to k, we get by expansion

$$\omega_0' \approx \omega_0\left(1 - \frac{F'}{2k}\right)$$

Where ω_0 is the response with no forces or force gradient acting on cantilever

For attractive force, $F' > 0$ (i.e. +ve)

$$\omega_0' < \omega_0$$

Shift in the resonance curve ⇒when driven at a forced frequency ω_0, this results in the change of the oscillation amplitude A, by ΔA

Deflection sender can measure both change in A, or phase, $\Delta\omega$

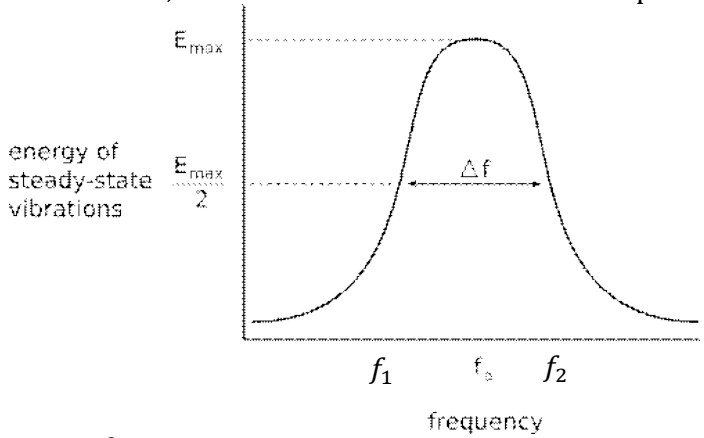
The amplitude of the cantilever vibration depends on the resonance angular frequency ω_0' according to the normal behaviour of a decoupled harmonic oscillator (Lorenzian lineshape)

$$A(\omega_0') = \frac{A_0\left(\frac{\omega_0'}{\omega_0}\right)}{\left[1 + Q^2\left(\frac{\omega_0}{\omega_0'} - \frac{\omega_0'}{\omega_0}\right)^2\right]^{\frac{1}{2}}}$$

Where A_0 is the amplitude when $\omega_0' = \omega_0$ and Q is the quality factor fo the cantilever resonance

$Q =$ quality factor

$$= \frac{\text{resonance frequency}}{\text{Full width, half maximum value of the resonant peak}}$$



$$Q = \frac{f_0}{f_2 - f_1}$$

For maximum sensitivity to changes in ω_0' the drive frequency is chosen so that $A(\omega_0')$ has the steepest slope, this occurs at

$$\omega_D \approx \omega_0' \left(1 \pm \frac{1}{\sqrt{8}Q}\right)$$

Scanning near field optical microscopy (SNOM (EU)) (NSOM(US))

09 March 2012
09:29

- This technique utilises optical effects taking place in the near-field
- Near field optics,

    Near field optics is the branch of optics that considers configurations that depend on the passage of light to, from, through or near an element with a subwavelength feature, and the coupling of that light to a second element located a sub-distance from the first

(1928) Edward H Synge proposed a sub-wavelength hole/aperture in a screen as a mechanism for imaging as sub-wavelength limits

- His letters to Einstein bore a remarkable similarity to modern SNOM instruments

(1972) Ash & Nicals used microwaves (λ =3cm) to image metal gratings (0.5mm)
(1984) Pohl's group in Zurich (IBM) and Lenis (Israel) published SNOM instrumental details- visible light

B.E.E.M.

16 March 2012
09:06

Ballistic Electron Emission Microscopy

Used to characterise sub-surface/buried interfaces

- Electron transport in structures very important
- Electronic materials/interfaces are normally characterised by tools such as

I/V (current-voltage), C/V (capacitance-voltage), photo-response, & photoelectron spectroscopy etc (X-rays or UV)

All large scale measurements → no (or little) spatial resolution

BEEM produces ballistic electrons produced from an STM tip (localised pulse)

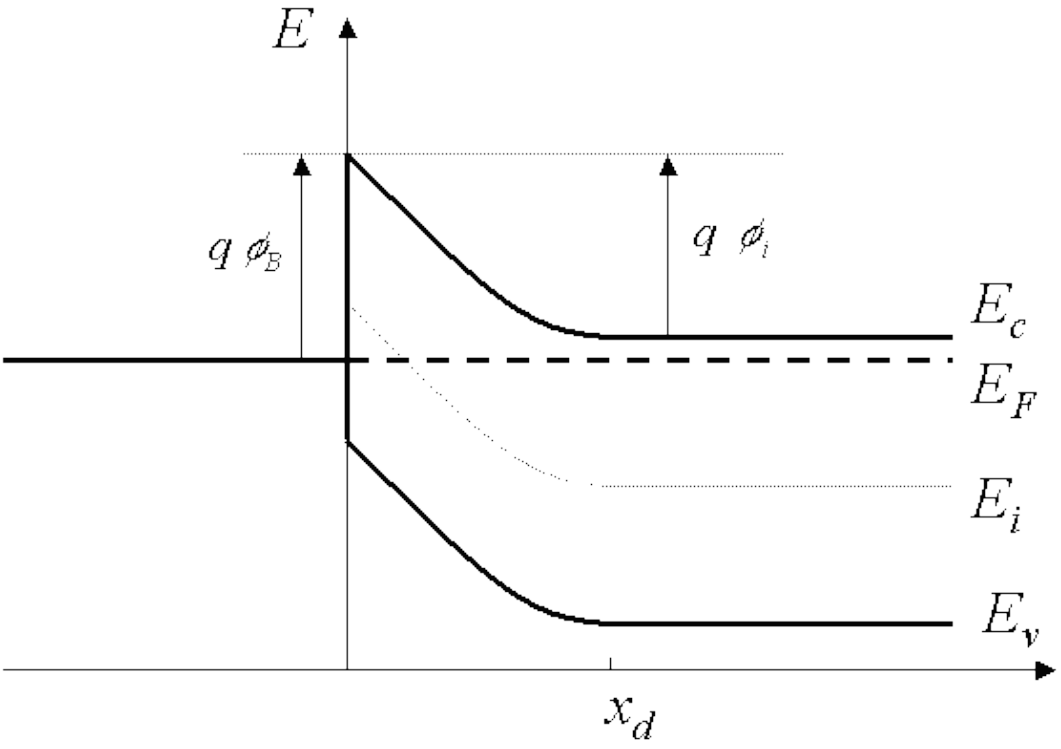
When applied to a layered structure it can give very important information on the "quality" of interface i.e. it's electronic properties

We need an example of a device interface & need to understand how interfaces are important for device physics

A metal contact to a semiconductor can form a diode

A Schottky diode

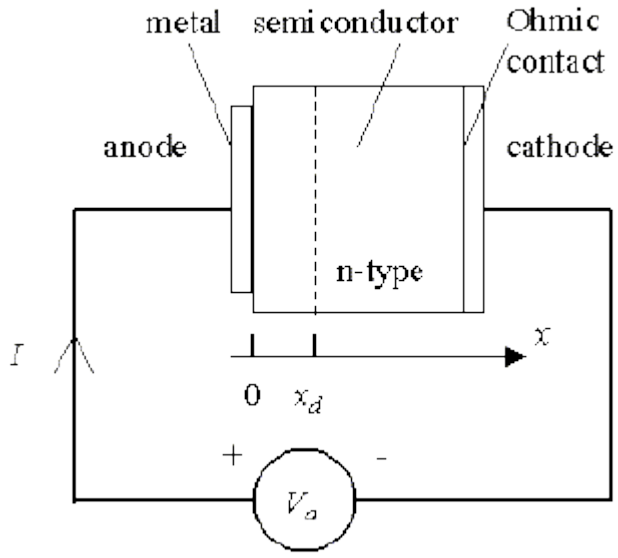
(http://www.pfk.ff.vu.lt/lectures/funkc_dariniai/diod/schottky.htm)



n-type contact to a metal and a barrier forms ϕ_E and it inhibits electron flow from semiconductor to metal (forward bias).

Inhibits electrons with energy less than $e\phi_E$

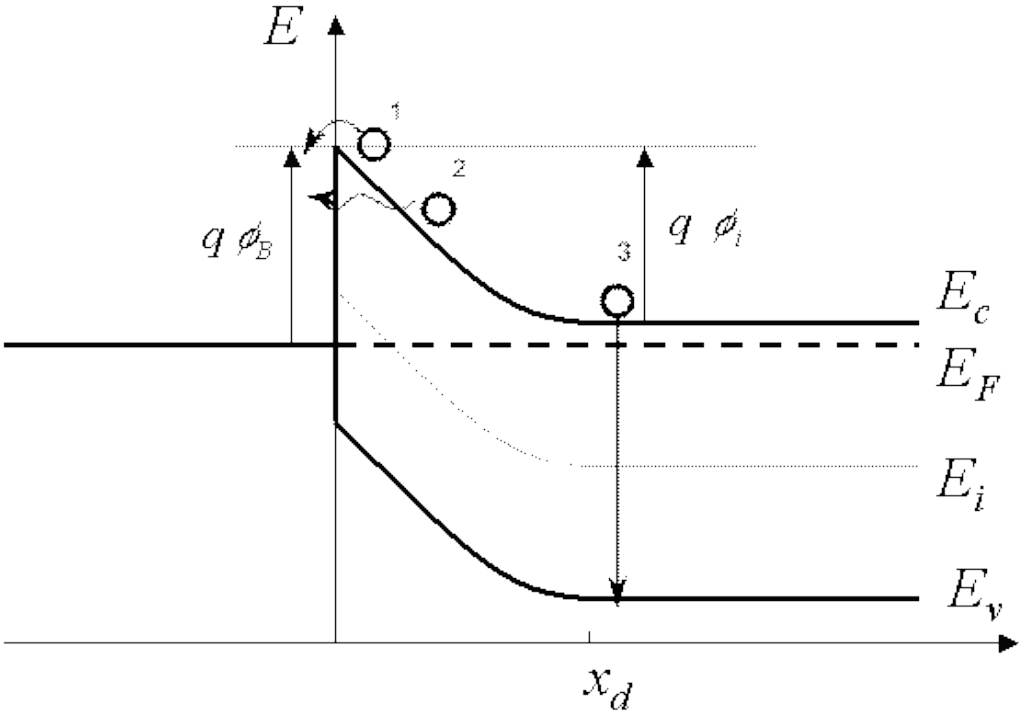
As brought into contact, the Fermi level of both align.



Can tailor ϕ_E properties by understanding the interface physics
e.g. a different crystalline face of a s/c may give different ϕ_E

But can we measure localised changes in ϕ_E?

Transport over Schottky barriers



1. Thermionic emission or diffusion
2. Q.M. tunnelling- depends on W, depletion width of S/C (narrower the better)
3. Recombination

We are going to consider 1- Thermionic emission-diffusion

For high mobility s/c thermionic emission dominates

The diode equation ⇒

$$I = I_0\left(e^{\frac{eV}{nkT}} - 1\right)$$

I=current
V=applied voltage
k=Boltzmann's constant
t=temp(k)
n=ideality factor
I_0= saturation const

Moderate forward bias

$$e^{\frac{eV}{nkT}} \gg 1$$

$\therefore I = I_0 e^{\frac{eV}{nkT}}$

(1)

$I_0 = A^* T^2 e^{-\frac{e\phi_E}{kT}}$

A^*=Richardson constant

$= \frac{4\pi e m_e^* k^2}{h^3}$

By taking $\log_e$ □ of (1) & plotting, we get ln I *vs* V and ϕ_E can be determined

The ideality factor, n, should=1 if it is a perfect diode, deviation from 1 indicates a problem with diode

If we form a 3- contact measurement using an STM tip & tunnelling, we can observe current flow across buried interfaces

e.g.