Nanoscale probing surface forces by AFM

- Introduction to surface forces
  - in vacuum
  - in air with the presence of water
  - in liquid
- Adhesion force model
- Force curve obtained by AFM
- Pull-off measurement—adhesion
- Pressing force measurement—indentation for nanohardness

Interfacial Adhesion

Use a ceramic/metal interface as a model system

\[ W_{ad} = \gamma_c + \gamma_m \]

Where, \( W_{ad} \) is the work of adhesion, which represents the energy consumed for separating the ceramic and the metal;
\( \gamma_c \) is the surface energy of ceramic;
\( \gamma_m \) is the surface energy of metal;

(a) van der Waals interaction (dipole–induced; dipole-dipole interaction),
(b) charge exchange between ions (ionic interaction; Coulomb interaction)
(c) sintering between two surfaces (atomic bonding)
Surface forces -- Van der Waals forces

- Interaction between permanent dipoles
- Induced dipoles
- London dispersion interactions, arising from the instantaneous polarization of nonpolar or polar molecules due to fluctuations in the charge distribution of neighboring molecules

The total interaction is a combination of a short-range repulsion and a relatively long-range attraction.

Long-range Van der Waals forces for different geometries

<table>
<thead>
<tr>
<th>Two atoms or small molecules</th>
<th>Surface charge</th>
<th>Energy</th>
<th>Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere or macroscopic of radius $R$ near a flat surface</td>
<td>$\gamma$</td>
<td>$-\frac{4\pi R}{6}$</td>
<td>$\frac{3\pi R}{2}$</td>
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<tr>
<td>Two spheres or macroscopic of radii $R_1$ and $R_2$</td>
<td>$\gamma$</td>
<td>$-\frac{4\pi R_1 R_2}{6}$</td>
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Surface force in the presence of moisture

When considering the adhesion of two solid surfaces or particles in air with the presence of moisture, it is easy to overlook or underestimate the important role of capillary forces, i.e., forces arising from the Laplace pressure of curved menisci formed by condensation of a liquid between and around two adhering surfaces.

The adhesion force between a non-deformable spherical particle of radius $R$ and a flat surface in an inert atmosphere according to DMT model

$$F_r = 4\pi R \gamma_w$$

But in an atmosphere containing a condensable vapor, the expression above is replaced by

$$F_r = 4\pi R \left( \gamma_w \cos \theta + \gamma_s \right)$$

where the first term is due to the Laplace pressure of the meniscus and the second is due to the direct adhesion of the two contacting solids within the liquid.

Adhesion force model

Johnson–Kendall–Roberts (JKR) theory [K. L. Johnson, K. Kendall, A. D. Roberts: Surface energy and the contact of elastic solids, Proc. R. Soc. London A 324 (1971) 301–313]. The JKR theory is applicable to easily deformable (soft balls), large bodies with high surface energy

$$F_s = 3\pi R \gamma$$

Where $\gamma$ is surface energy, the work of adhesion $W_{ad}=2 \gamma$

$$F_s = 3\pi R W_{ad}/2$$


$$F_s = 4\pi R \gamma$$

Surface force in the presence of moisture

Water readily adsorbs at many surfaces. At a crack or sharp corner it can condense to form a meniscus if its contact angle is small enough. The small gap between an AFM tip and a surface is, therefore, an ideal occasion for such condensation.

The classic theory of capillary condensation starts by considering the thermodynamics of capillary formation. If the capillary formation is isothermal, then one can derive the Kelvin equation:

$$RT \ln \frac{P}{P_0} = \gamma V \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

where $P_0$ is the saturation pressure of the liquid, $V$ is the molar volume of the liquid, $T$ is the temperature, and $R$ the molar gas constant. The ratio $P/P_0$ simply corresponds to the relative vapor pressure of the liquid, which in the case of water is just the relative humidity (RH). This is often rewritten in terms of the Kelvin radius $r_k$:

$$r_k = \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = \frac{R T}{\gamma V} \ln \frac{P}{P_0}$$
Surface forces in the presence of moisture

The Kelvin radius of water at 20 °C plotted as a function of the relative humidity

**Conclusion:** the size of meniscus is dependent on the relative humidity

Surface forces in liquid

Van der Waals Forces in Liquids—The dispersion interaction in a medium will be significantly lower than in vacuum, since the attractive interaction between two solute molecules in a medium (solvent) involves displacement and reorientation of the nearest-neighbor solvent molecules.

Electrostatic and Ion Correlation Forces—Most surfaces in contact with a highly polar liquid (such as water) acquire a surface charge, either by dissociation of ions from the surface into the solution or by preferential adsorption of certain ions from the solution. The surface charge is balanced by a layer of oppositely charged ions (counterions) in the solution at some small distance from the surface. In dilute solution, this distance is the Debye length, \( \kappa^{-1} \), which is purely a property of the electrolyte solution.

Repulsive double-layer force

The long-range electrostatic interaction energy at large separations (weak overlap) between two similarly charged molecules or surfaces is typically repulsive and is roughly an exponentially decaying function of distance \( D \)

<table>
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<tr>
<th>Geometry of bodies with surfaces</th>
<th>Electric “double-layer” interaction</th>
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<tr>
<td></td>
<td>Energy, ( E )</td>
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<td>( \frac{2e^2}{4\pi\varepsilon_0 r} )</td>
</tr>
<tr>
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<td>( \frac{4e^2}{4\pi\varepsilon_0 r} )</td>
</tr>
<tr>
<td>Two flat surfaces (infinite area)</td>
<td>( \frac{e^2}{4\pi\varepsilon_0 \kappa^{-1}} )</td>
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Surface forces in the liquid


Schematic plots of the DLVO interaction potential energy \( E \) between two flat, charged surfaces as a function of the surface separation normalized by the Debye length, \( \kappa^{-1} \).

The van der Waals attraction (inverse power-law dependence on \( D \)) together with the repulsive electrostatic “double-layer” force (roughly exponential) at different surface charge \( \sigma \) determine the net interaction potential in aqueous electrolyte solution.
Adhesion force model in liquid

In vacuum, the adhesion force is express by Johnson–Kendall–Roberts (JKR) model

\[ F_s = \frac{3\pi \rho_{Wad}}{2} \]

In the liquid, the general form for the JKR adhesion force may be modified to include the following additional forces:

\[ F_{adh} = \frac{3\pi \rho_{Wad}}{2} - \frac{4\pi}{6D} + 6\pi \rho_{Wad} \]

where the second term now includes the attractive van der Waals component and the third term is the repulsive double layer.

Force curve obtained by AFM

A: The cantilever starts not touching the surface.
B: As the probe tip is brought very close to the surface, it may jump into contact if it feels sufficient attractive force from the sample.
C: Once the tip is in contact with the surface, cantilever deflection will increase. If the cantilever is sufficiently stiff, the probe tip may indent into the surface at this point. In this case, the slope or shape of the contact part of the force curve can provide information about the elasticity of the sample surface.
D: After loading the cantilever to a desired force value, the cantilever is withdrawn, adhesion or bonds formed during contact with the surface may cause the cantilever to adhere to the sample some distance past the initial contact point on the approach curve (B).
E: A key measurement of the AFM force curve is the point at which the adhesion is broken and the cantilever comes free from the surface. This can be used to measure the rupture force required to break the bond or adhesion.

\[ f_{ad} = \frac{2\pi \rho_{Wad}}{2\pi} \]

\[ W_{ad} = f_{ad}/2R \]

K is the spring constant of the cantilever;
\( d \) is the deflection of the cantilever;
R is the tip radius
\( W_{ad} \) is the work of adhesion
The V-shaped cantilevers are far less easy to model mathematically than the alternative beam-shaped (diving board) cantilevers. The most commonly used treatment is the so-called two-beam approximation, in which the cantilever is described by two rectangular beams in parallel [J. E. Sader. Rev. Sci. Instrum. 66, 4583 (1995)]. This leads to the following expression for the spring constant $k$:

$$k = \left( \frac{l^3}{W} \right) \frac{E}{4}$$

Where $E$ is the elastic modulus of the bulk material, and $t$, $w$, and $l$ are the thickness, width, and length of the cantilever beams, respectively. The geometry parameters of the cantilever beams can be determined quite accurately from scanning electron microscopy (SEM) image.

The resonant frequency $\nu_0$ of the unloaded cantilever is given by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

The cantilever is approximated as a spring with a spring constant $k$ and an effective mass $m$. When a mass $M$ is added to the end of the cantilever, the resonance frequency becomes

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m + M}}$$

Rearranging this equation gives

$$M = \frac{k}{(2\pi\nu)^2} - m$$

Thus, measuring the resonant frequencies of the cantilever for various attached masses and plotting $M$ as a function of $(2\pi\nu)^2$ should give a line with a gradient equal to the spring constant.

Unfortunately, the cantilever cannot be treated as an ideal spring. A series of improvements lead to the correct calibration formula

$$k = 0.8174 \frac{k_B T}{s P} \left[ 1 - \frac{3D}{2L} \tan \phi \frac{\cos \phi}{\sin \phi} \right]$$

Where the numerical factor 0.8174 is a result of the geometry of the cantilever spring
$s$ is again the sensitivity calibration factor (in units of m/V)
$P$ is the positional noise power (in units of V$^2$) isolated in the fundamental resonant mode only
$D$ is the height of the tip
$L$ is the cantilever length (more correctly, the distance from the base of the cantilever to the tip)

AFM is equipped stand kit for thermal noise method.
Nanoscale probing the adhesion between metal and ceramic using AFM

The force-displacement curves for the different tip/sample pairs, which were measured in water,
(a) Au-coated tip/Al₂O₃(001) sample, \( W_{ad} = 59 \, \text{mJ/m}^2 \)
(b) Pd-coated tip/Al₂O₃(001) sample, \( W_{ad} = 59 \, \text{mJ/m}^2 \)
(c) Si₃N₄ tip/Al₂O₃(001) sample, \( W_{ad} = 27 \, \text{mJ/m}^2 \)

Chemical force measurement on single proteins or single molecule level

(A) Force measurements between avidin-functionalized AFM tip and biotin-derivated agarose bead in PBS buffer, and (B) after addition of soluble avidin (50 \( \mu \text{g/ml} \)). The tip of a scanned stylus AFM aligned directly over the center of the bead. Vincent T. Moy, University of Miami School of Medicine.

Force array map

A force volume data set – an array of regularly spaced force curves yields three-dimensional force information. In a force volume data set, the force curves will vary with x-y position.

Adhesion map of the platinum/glass interface. Lighter pixels represent greater adhesion. The map was constructed by plotting the minimum value of each retracting curve at its x-y position. Note the variation of adhesion across the interface.


Nano-indentation under AFM

- Local hardness on the nanoscale
- Applied to ultrathin thin films (MEMS, NEMS)
- Applied to ultra-soft sample like biological tissue and cells
Nanoindentation by AFM

Hardness, $H$, (eqn. 1) was calculated from the peak load, $P_{\text{max}}$, over the contact area, $A_c$.

$$ H = \frac{P_{\text{max}}}{A_c} $$

The plot of displacement and the area term was fit to a standard area function, where $C_i$ are the constants:

$$ A_c = C_0 h_c^2 + C_1 h_c^1 + C_2 h_c^0.5 + C_3 h_c^0.25 + C_4 h_c^0.125 + C_5 h_c^{0.025} $$

$$ h_c = h_m - 0.75 \cdot \frac{P_{\text{min}}}{(dP/db)} $$

Tapping mode AFM

Nanoindentation on the steel surface
Nano-indentation in biology

Biological Applications - Ant Mandible, Michelle Dickinson, Hysitron

References:
Scanning Tunneling microscope

STM-basic principle

1. If the STM tip is close enough to the surface then an applied voltage between the tip and sample will cause electrons to tunnel through the junction.

2. The tunneling current is exponentially dependent on the junction width and increases by a decade per Angstrom as the tip is brought closer to the surface.

3. In typical systems a tip-sample separation of 0.5 nm will produce currents of 1 pA ~ 10 nA for bias of 0.2 ~ 1.8 V.

STM - is the tunneling current between a metallic tip and a conducting substrate which are in very close proximity but not actually in physical contact.

AFM - is the van der Waals force between the tip and the surface; this may be either the short range repulsive force (in contact-mode) or the longer range attractive force (in non-contact mode).
STM-basic principle

The STM is approached to the surface of a sample within a short gap. This forms a tunnel-transparent barrier, which size is determined mainly by the values of work of electron emission from the material of a tip $\phi_p$ and a sample $\phi_s$. Upon qualitative examination the barrier can be considered rectangular with the effective height equal to the average material emission work:

$$\phi^* = \frac{1}{2}(\phi_p + \phi_s)$$

STM-basic principle

As it is known from quantum mechanics, the probability of electron tunneling (transmission coefficient) through one-dimensional barrier of rectangular form is equal to

$$W = \frac{|A_1|^2}{|A_0|^2} = e^{-k\Delta Z}$$

$A_0$: amplitude of electron wave function, moving to a barrier;  
$A_1$: amplitude of electron wave function, which passed the barrier;  
$k$: potential barrier;  
$\Delta Z$: width of a barrier (the gap between the tip and sample)

For the tunnel contact of two metals, the potential barrier (or attenuation constant) can be presented as

$$k = \frac{4\pi \sqrt{2m\phi^*}}{\hbar}$$

$m$: electron mass, $\phi^*$: average electron emission work,  
$h$: Planck constant.

STM-basic principle

The tip in the STM is approached to the surface of a sample within a short gap. This forms a tunnel-transparent barrier, which size is determined mainly by the values of work of electron emission from the material of a tip $\phi_p$ and a sample $\phi_s$. Upon qualitative examination the barrier can be considered rectangular with the effective height equal to the average material emission work:

$$\phi^* = \frac{1}{2}(\phi_p + \phi_s)$$

STM-basic principle

If the difference of potentials is applied to the tunnel contact, the tunnel current appears between a tip and a sample, electrons with energy near the Fermi level participate in the tunneling process. The tunnel current density (in one-dimensional approximation) is expressed by:

$$j = j_0(V) e^{-\frac{4\pi \sqrt{2m\phi^*}}{\hbar} \Delta Z}$$

The current density is exponentially dependent upon $\Delta Z$, the distance between the tip and the sample. Hence the current density is very sensitive to the variation of the distance.
**STM-set up**

The STM represents an electromechanical system with a feedback. The feedback system keeps the tunnel current value between a tip and a sample at the set level, which is selected by the operator. The control of the tunnel current value and consequently, the tip-sample distances is performed by means of moving the tip with a piezoelectric scanner.

**STM- operation mode**

- **Constant current mode**: The tunneling current is monitored as the tip is scanned parallel to the surface. This is achieved by adjusting the tip's distance above the surface so that the tunneling current does not vary with the lateral tip position. In this mode the tip will move slightly upwards as it passes over a surface atom, and conversely, slightly in towards the surface as it passes over a hollow.
- **Constant height mode**: The tunneling current is monitored as the tip is scanned parallel to the surface.

**STM- tip fabrication**

- STM tips are typically made of W wires or PtIr alloy wires
- STM tips are fabricated with electrochemical etching or mechanical cutting

The W wire acts as the anode and the stainless steel can be used as the counter-electrode (or cathode). The electrode reactions are given below:

- **Anode**: \( W(s) + 8(OH)^- \rightarrow (WO_4)^{2-} + 4H_2O + 6e^- \)
- **Cathode**: \( 6H_2O + 6e^- \rightarrow 3 H_2(g) + 6(OH)^- \)

**Condition for atomic-resolution image**

Requirement for obtaining atomic-resolution images

- STM tip
- Sample surface
- Vacuum
- Vibration/interference
- Temperature
How to obtain atomic resolution STM images

- To place a Si (111) sample into a holder
- Anneal the Si sample at 570 °C for 12 hours
- Direct heat the sample to 1200 °C and cool down to room temperature (thermal cycling) for 10 times to remove surface oxide
- Clean up and sharpen the STM tip

STM images of Si(111)

+2V, 105pA, frame size 152nm
+2V, 72pA, frame size 31.3 nm

STM image - HOPG (highly orientated pyrolytic graphite)

HOPG, single step
frame size 316 nm
frame size 97nm,
STM image - HOPG (highly orientated pyrolytic graphite)

frame size 5.05nm, 0.143V, 2.358nA

STM image, self assembled monolayer on Au surface

1.008V, 0.215nA, scan size 400nm

STM study on adsorption and reaction of single molecules on surface

Scan size: 47 Å, Vs = -2.2 V, I= 0.5 Na,

1.008V, 0.215nA, scanning size: 60nm wide, 80nm long,
Scanning tunneling spectroscopy

The dependence of current on voltage gives information about its electronic structure.

\[ I = e^{-\frac{e^2}{2}} \int dE \cdot \text{LDOS}_{\text{sample}}(E_f + E) \]

Thus, the first derivative of the tunneling current with respect to voltage \((dI/dV)\) is thus proportional to the local density of electronic states below the tip, at the given tunneling voltage.

By measuring \((dI/dV)\) as a function of voltage, one can probe the electronic states at that particular point on the surface.

Manipulation of individual atoms by STM

Another powerful STM capability is the ability to move atoms and molecules. This is achieved by placing the tip close enough to the surface adsorbate so that the tip-adsorbate attraction is comparable to the surface corrugation barrier. In this regime, the molecule will follow the tip wherever it is moved along the surface. One can then retract the tip, without causing the molecule to desorb from the surface.

http://www.physics.berkeley.edu/research/crommie/research_stm.html

"Atomic stadium"—STM images of quantum corral nanostructure (diameter 31.2 nm) composed of 36 Ag atoms, By S. W. Hla et al.

Iron atoms on Copper (111), Lutz & Eigler, IBM

STM image of a single Co atom on Cu(111) shown in a light shaded view. Trent 1 nA, sample bias -10 mV, T=2.3 K, J. A. Stroscio, R. J. Celotta, NIST

What is Nanotechnology

Atomic force microscope (AFM) lithography by Nick Wu

- Nanotechnology is the understanding and control of matter at dimensions of 1 to 100 nanometers;
- At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from bulk matter;
- Nanotechnology is an unique phenomena enable novel applications, toward understanding and creating improved materials, devices, and systems that exploit these new properties.

Acknowledgement

References
- V. L. Mironov, Fundamentals of scanning probe microscope,