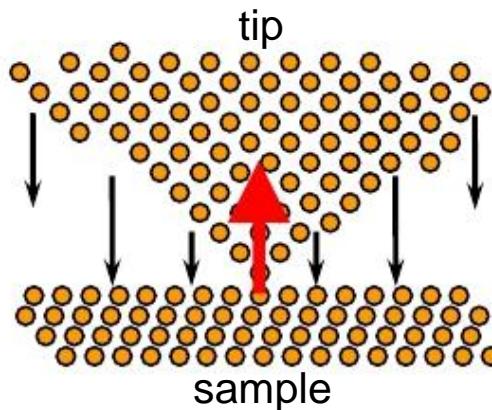
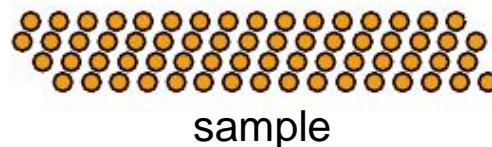
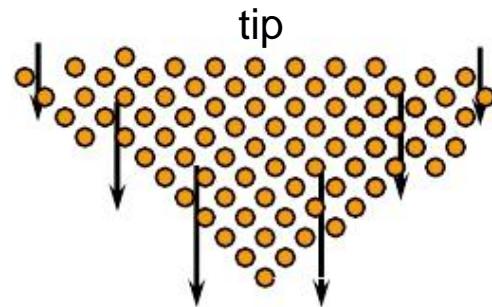


Relevant Forces

- typical long-range forces (> 1nm)
van der Waals
electrostatic, magnetic, ...
- forces in liquids
hydrophobic / hydrophilic forces
steric forces
solvation forces
- typical short-range forces
(contact/near contact)
short-range repulsive forces
(Pauli exclusion) or ionic repulsion forces
short-range chemical binding forces



Short Range Force

- due to overlap of electron wave functions and from the repulsion of the ion cores.
- can be both attractive:
 - attractive when the overlap of electron waves reduces the total energy. These situations are comparable to molecular binding.
 - around 0.5 - 1 nN per interacting atom at tip-sample distances typical for STM operation.
 - decay length of the order of atomic units, i.e. 0.05 nm for metallic adhesion, but around 0.2 nm for covalent bonding.
 - true atomic resolution AFM operates with these forces
- or repulsive:
 - repulsive when strong electron wave overlap (Pauli exclusion principle). These forces are directly connected to the total electron density. The ionic repulsion acts for small distances, where the screening of the ion cores by the electrons falls away.
 - usual contact AFM operates with these forces.
- Model potentials like the Lennard-Jones or the Morse potential are used to describe short range forces.
- However, their application is essentially limited to the pair wise interaction of atoms. For the tip-sample interaction, at least the interaction with the nearest neighbor atoms has to be included and, furthermore, the displacement of atoms by the action of the short-range force has to be taken into account.

van der Waal's Forces (vdW)

Dipole-dipole forces between non-permanent dipoles (dispersion forces). These act between dipoles that arise from fluctuations and dipoles induced in their electric field. They are always present and attract even chemically inert noble gas atoms. The range of dispersion forces is limited. When the distance between molecules is larger than the way light can travel during the characteristic lifetime of the fluctuations, the dispersion forces are weakened. This effect is called retardation. The vdW force at short distances decays like $F = 1/r^6$, beyond $r > 5$ nm this power law reduces to $F = 1/r^7$.

Because the range of vdW forces is limited, the tip-sample geometry of the force microscope can be well approximated as a sphere approaching a semi-infinite body. For this configuration, the vdW force is

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

where H denotes the Hamaker constant, R the tip radius, and D the distance between tip and sample surface.

The value of the Hamaker constant H is of the order of 10^{-19} J. For materials with high dielectric constant like metals it is about a factor of ten higher than for insulators. For a tip of radius $R = 30$ nm, the vdW force in vacuum at a distance of $D = 0.5$ nm is of the order of $F_{vdW} = 2$ nN. The vdW force can also be determined for more complex tip-sample geometries like a half-sphere at the end of a truncated cone.

Electrostatic Forces

- the strength and distance dependence of electrostatic forces obey Coulombs law.
- charges can easily be trapped at sample surfaces in the course of surface preparation, for example by sample cleavage or by UHV techniques like ion sputtering.
- contact electrification can charge tip and sample after their contact is broken. Even in air such charge can persist for hours particularly on polymers, in vacuum for days.
- charges on the surface attract conductive tips. The method to determine the force is to calculate the interaction between the charges and their mirror image in the tip.
- neutral but polar surfaces interact with a conductive tip via image forces. Likewise, a polar group at the tip apex causes an attractive force towards a conductive sample.

- electrostatic forces also act between conductive tips and conductive samples when they are on a different potential. If one considers the system tip-sample as a capacitor with the distance dependent capacitance C , the force is given by

$$F_{el} = \frac{\partial C}{\partial z} (U_{bias} - U_{cpd})^2$$

where U_{bias} is the bias voltage and U_{cpd} is the contact potential difference due to different work functions.

- zero bias voltage normally does not correspond to a minimal electrostatic force but that the contact potential difference has to be compensated
- the work function is very sensitive to perturbations at of the surface. The irregular shape of a the tip gives rise to patch charges, which can not be completely compensated by a bias voltage.

For tip radius $R = 20$ nm at a tip-sample distance of $z = 0.5$ nm and $U_{bias} - U_{cpd} = 1$ V the electrostatic force is about $F_{el} = 0.5$ nN.

$$F_{el} = \pi \varepsilon_0 \frac{R}{z} (U_{bias} - U_{cpd})^2$$

Magnetic Forces

The forces that act on magnetic dipoles located in a magnetic field are called magnetic forces. In force microscopy experiments the magnetic dipoles are usually contained in the ferromagnetic material on/of the tip of the cantilever and the magnetic sample.

A field is produced by a ferromagnetic sample or a current distribution located in close proximity of the tip. The current distribution may be the one of a current carrying device or be present in a superconductor.

$$E = \frac{\mu_0}{2} \left[\int \mathbf{M}_{Tip} \cdot \mathbf{H}_{Sample} dV + \int \mathbf{H}_{Tip} \cdot \mathbf{M}_{Sample} dV \right] = \mu_0 \int \mathbf{M}_{Tip} \cdot \mathbf{H}_{Sample} dV$$

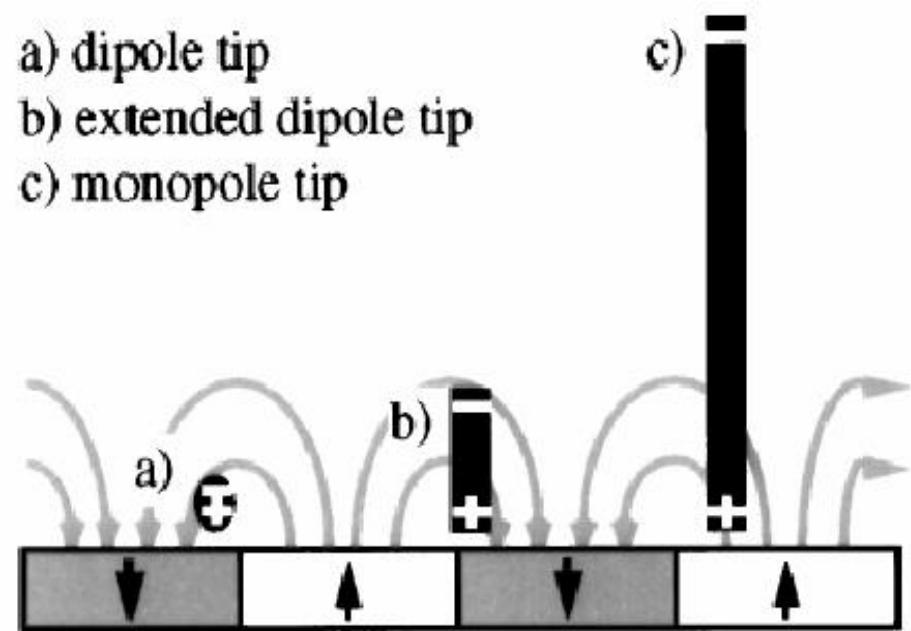
The force on the tip is then given by the derivative of the magnetostatic energy.

$$F_z(\mathbf{t}) = -\mu_0 \int \mathbf{M}_{Tip}(x', y', z') \cdot \frac{\partial}{\partial z'} \mathbf{H}_{Sample} [(x', y', z') + \mathbf{t}] dV'$$

Note that the z-derivative of the stray field is inside the integral expression. Thus when the integration is performed along a long slab like tip (see figure), the integration along the z-axis will lead to an expression for the force that is proportional to the stray field times the magnetic charge at the lower tip end (plus the stray field times the magnetic charge at the upper tip end – however for a long tip this part can be neglected).

Attention

The magnetic force is rather proportional to the stray field (and Not to the derivative of the stray field as documented in many manuals of SPMs and publications !!!)



Capillary Forces

- microcontacts act as nuclei of condensation.
- In air, water vapor plays the dominant role.
- If the radius of curvature of the microcontact is below a certain critical radius (approximately equal to the Kelvin radius) a meniscus will be formed.
- The Kelvin radius is given by

$$r_K = \frac{\gamma V}{RT \log(p/p_s)}$$

where γ is the surface tension, R the gas constant, T the temperature, V the molar volume and p_s the saturation vapor pressure.

- The surface tension of water is $\gamma = 0.074$ N/m at $T = 20$ C which gives the parameter $\gamma V / RT = 0.54$ nm. Therefore we obtain for $p/p_s = 0.9$ a Kelvin radius of 100 nm.
- In Scanning Force Microscopy, typical tips having radii of less than 100 nm are possible nuclei of condensation. If a meniscus is formed an additional capillary force acts on the tip.
- A simple estimation is given by:

$$F = \frac{4\pi R \gamma \cos \Theta}{1 + D/(R(1 - \cos \phi))}$$

where R is the radius of curvature, Θ the contact angle, D the distance between tip and sample and ϕ the angle of the meniscus. The maximum force is given by $F_{max} = 4\pi R \gamma \cos \Theta$. For a tip radius of 100 nm we obtain a force $F_{max} = 9.3 \times 10^{-8}$ N, which is significantly stronger than the corresponding van der Waals force.

- Typical force vs. distance curves in ambient conditions reveal forces of the order of 10-8-10-7N, which mainly originates from capillary forces.

These adhesion forces limit the minimum force which acts on the outermost tip region, and have to be equilibrated by the repulsive force in this small contact region. Consequently, capillary forces can determine the size of the contact and play an essential role in force microscopy measurements in air.

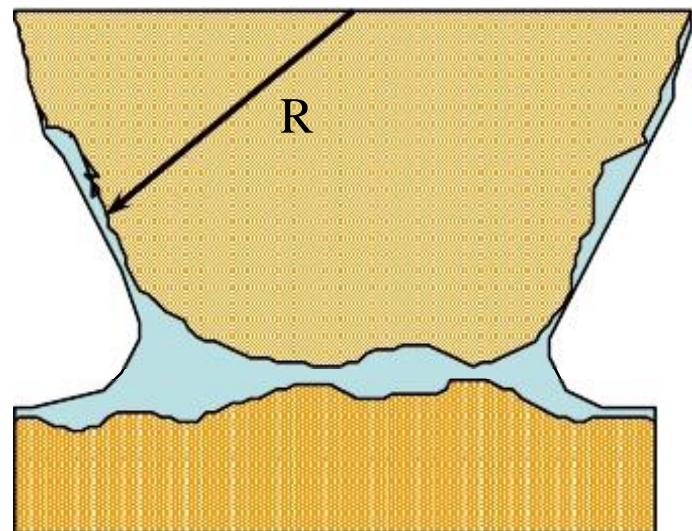
$$F_{\max} = 4\pi R \gamma \cos\Theta$$

$$\gamma (\text{H}_2\text{O}) = 0.074 \text{ N/m}$$

$$R = 100\text{nm}$$

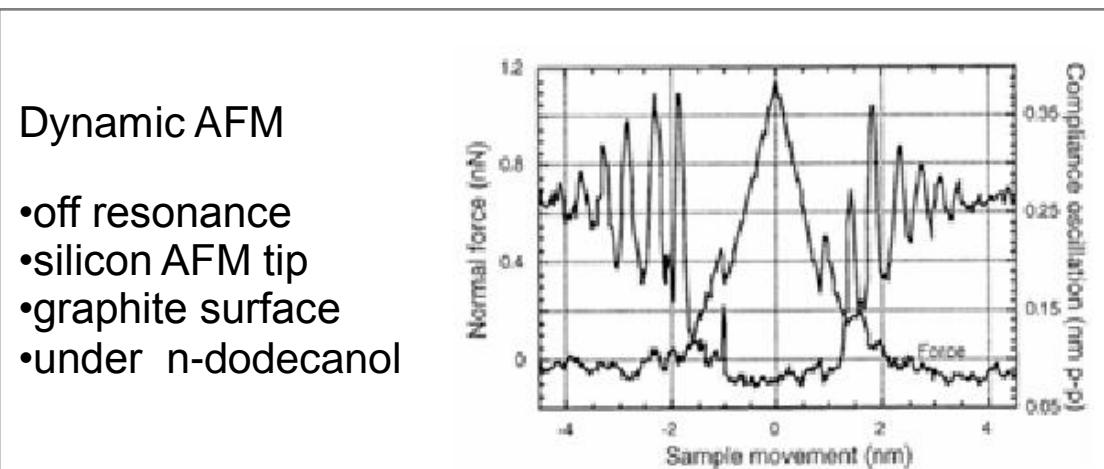
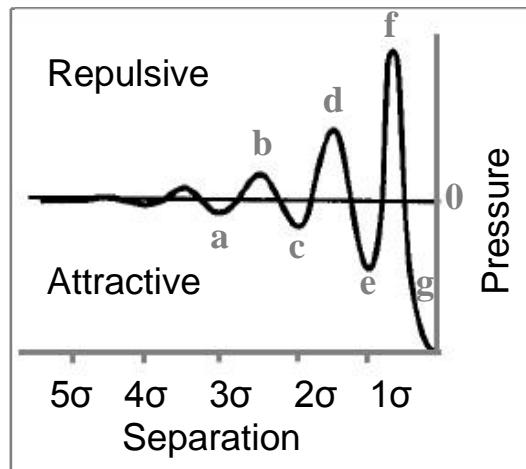
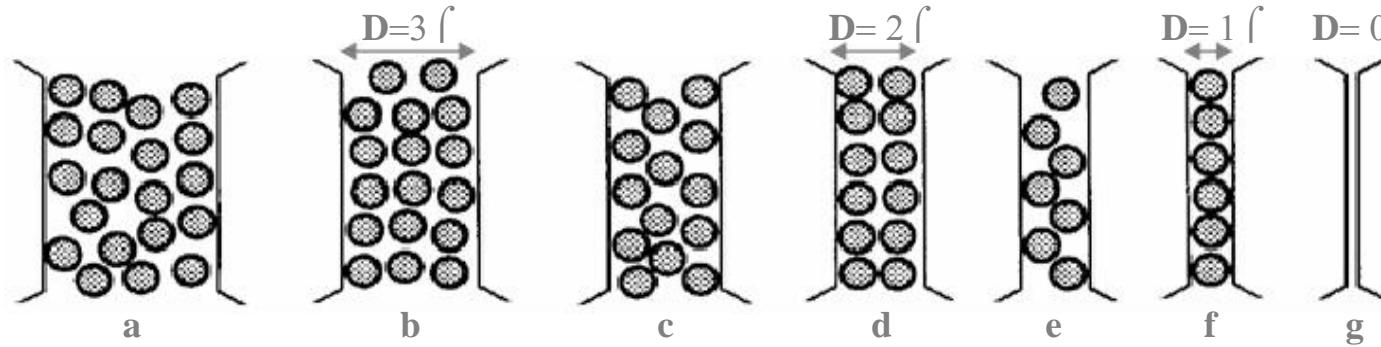
Contact angle for hydrophilic surfaces $\Theta \approx 0^\circ$

$$F_{\max} = 90 \text{ nN}$$



Solvation Forces

Due to the confinement of liquid between two surfaces force is more pronounced for larger tip radius and large molecules (e.g. OMCTS, hexane)



Operation Modes in Force Microscopy

Several modes of operation have been introduced in force microscopy, with a variety of names describing their characteristic features.

