Lecture 8
Interaction forces II -

Tip-sample interaction forces

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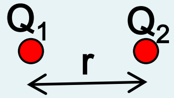
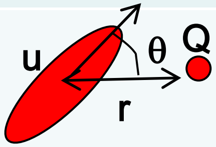
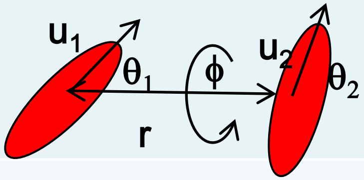
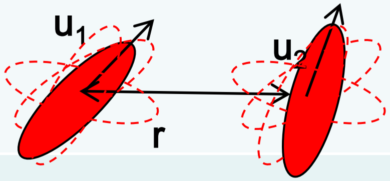
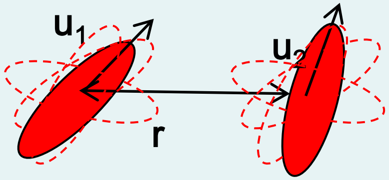
Summary of last lecture

	Type of interaction
	Ion-ion electrostatic $U(r)=\frac{Q_1Q_2}{4\pi\varepsilon\varepsilon_0 r}$
	Dipole-charge electrostatic $U(r)=-\frac{Qu\cos(\theta)}{4\pi\varepsilon\varepsilon_0 r^2}$
	Dipole-dipole electrostatic $U(r)=-\frac{u_1u_2\left[2\cos(\theta_1)\cos(\theta_2)-\sin(\theta_1)\sin(\theta_2)\cos(\phi)\right]}{4\pi\varepsilon\varepsilon_0 r^2}$
	Angle-averaged electrostatic (Keesom force) $U_{Keesom}(r)=-\frac{u_1^2u_2^2}{3(4\pi\varepsilon\varepsilon_0)^2k_BTr^6}$
	Angle-averaged induced polarization force (Debye force) $U_{Debye}(r)=-\frac{u_1^2\alpha_{02}+u_2^2\alpha_{01}}{(4\pi\varepsilon_0\varepsilon)^2r^6}$
	Dispersion forces act between any two molecules or atoms (London force) $U_{London}(r)=-\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0\varepsilon)^2r^6}\frac{(h\nu_1)(h\nu_2)}{h\nu_1+h\nu_2}$

Adapted from J. Israelachvilli, “Intermolecular and surface forces”.

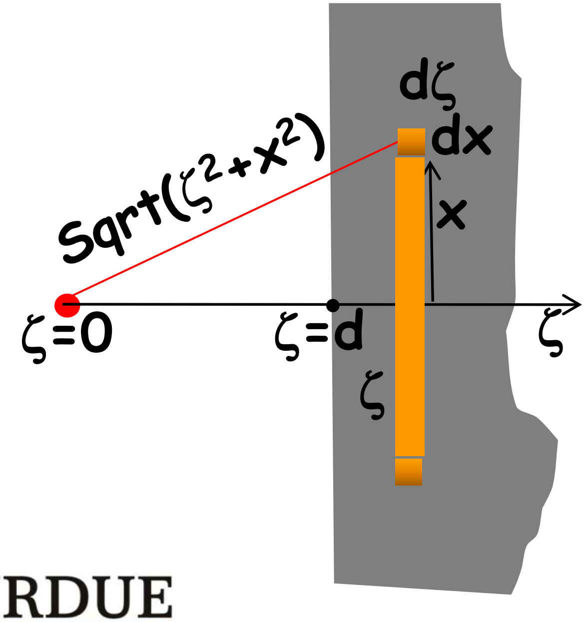
From interatomic to tip-sample interactions-simple theory

First consider the net interaction between an isolated atom/molecule and a flat surface.

Assume that the pair potential between the atom/molecule and an atom on the surface is given by $U(r)=-C/r^n$.

Assume additivity, that is the net interaction force will be the sum of its interactions with all molecules in the body.

No. of atoms/molecules in the infinitesimal ring are $2\pi\rho x dx dz$ where ρ is the number density of molecules/atoms in the surface



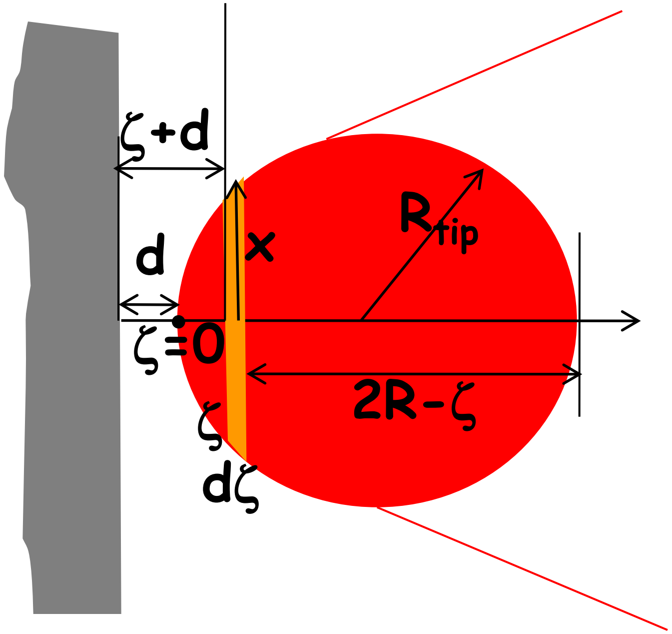
$$W(d) = -2\pi C\rho \int_{\zeta=d}^{\zeta=\infty} d\zeta \left(\int_{x=0}^{x=\infty} \frac{dx}{\left(\sqrt{\zeta^2+x^2}\right)^n} \right)$$

$$= \frac{-2\pi C\rho}{(n-2)(n-3)d^{n-3}}, \quad for\ n>3$$

$$W_{VdW} = \frac{-\pi C\rho}{6d^3}\ for\ n=6$$

From interatomic to tip-sample interactions-simple theory

Next integrate atom-plane interaction over the volume of all atoms in the AFM tip. Number of atoms/molecules contained within the slice shown below is $\pi\rho x^2 d\zeta = \pi\rho(2R_{tip}-\zeta)\zeta d\zeta$. Since all these are at the same equal distance d+ζ from the plane, the net interaction energy can be derived by using the result on the previous slide.



$$W(d) = \frac{-2\pi^2 C\rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=2R_{tip}} \frac{(2R_{tip}-\zeta)\zeta d\zeta}{(d+\zeta)^{n-3}}$$

$$\text{If } d \ll R_{tip},$$

$$W(d) \sim \frac{-2\pi^2 C\rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=\infty} \frac{R_{tip}\zeta d\zeta}{(d+\zeta)^{n-3}}$$

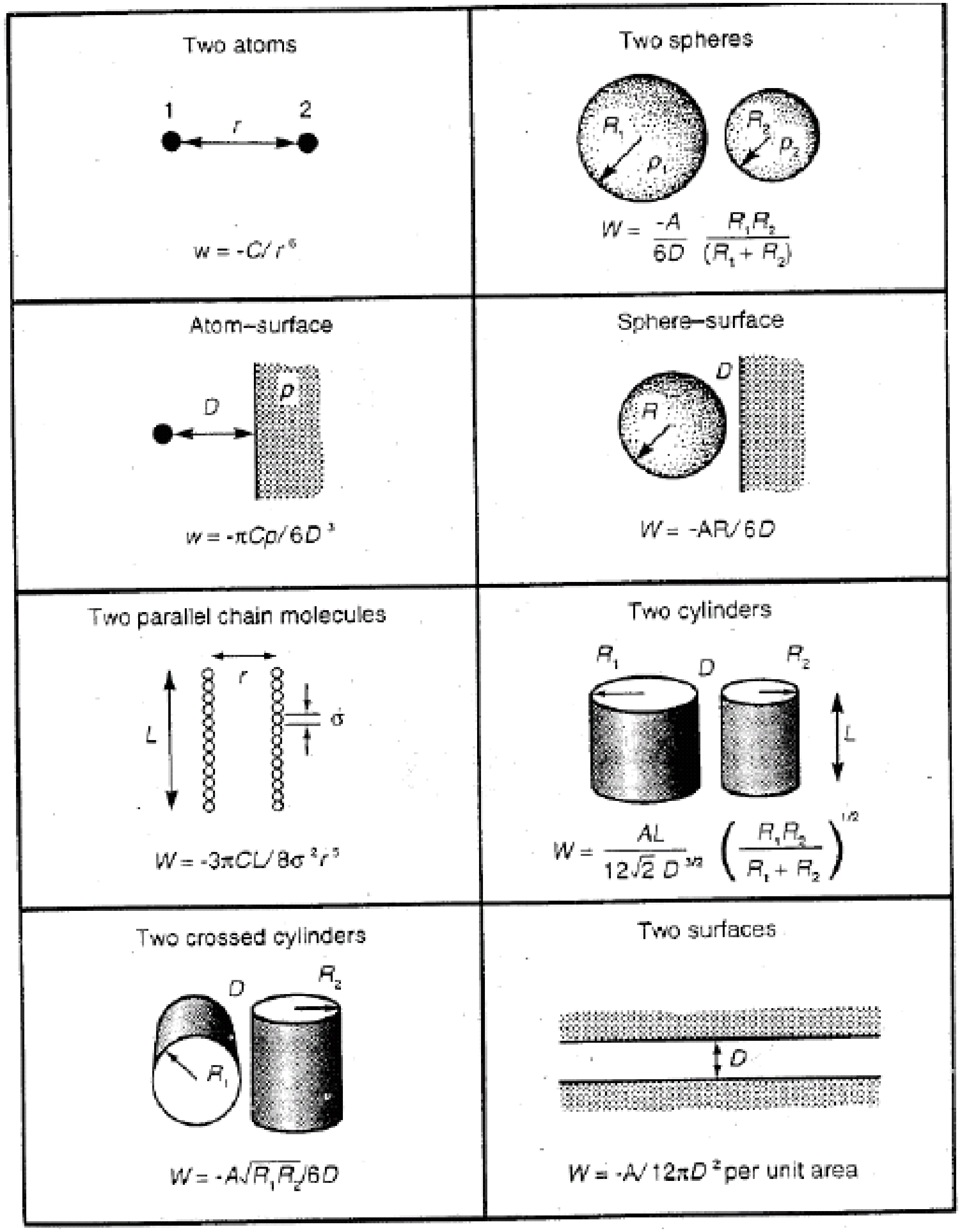
$$= -\frac{4\pi^2 C\rho^2 R_{tip}}{(n-2)(n-3)(n-4)(n-5)d^{n-5}}$$

$$\text{For } d \ll R_{tip},\ n = 6$$

$$W_{VdW}(d) \sim -\frac{\pi^2 C\rho^2 R_{tip}}{6d} = -\frac{HR_{tip}}{6d}$$

H : Hamaker's constant

VdW interactions between bodies



Two atoms $w = -C/r^6$	Two spheres $W = \frac{-A}{6D}\frac{R_1R_2}{(R_1+R_2)}$
Atom–surface $w = -\pi C\rho/6D^3$	Sphere–surface $W = -AR/6D$
Two parallel chain molecules $W = -3\pi CL/8\sigma^2r^5$	Two cylinders $W = \frac{AL}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Two crossed cylinders $W = -A\sqrt{R_1R_2}/6D$	Two surfaces $W = -A/12\pi D^2$ per unit area

Source J. Israelachvili, “Intermolecular and surface forces”.

Surface-surface interactions

Following the steps in previous slides it is possible calculate the interaction energy of two planar surfaces a distance of 'd' apart, specifically for the unit area of one surface interacting with an infinite area of the other.

$$W(d) = \frac{-2\pi C\rho^2}{(n-2)(n-3)} \int_{\zeta=d}^{\zeta=\infty} \frac{d\zeta}{(\zeta)^{n-3}}$$

$$= -\frac{2\pi C\rho^2}{(n-2)(n-3)(n-4)(n-5)d^{n-4}}$$

$$\mathit{For}\ n = 6$$

$$W_{VdW}(d) = -\frac{\pi C\rho^2}{12d^2}\ \mathit{per\ unit\ area}$$

The Derjaguin approximation

Plane-plane interaction energies are fundamental quantities and it is important to correlate tip-sample force to known values of surface interaction energies

For a sphere-plane interaction we saw that

$$W(d) = -\frac{4\pi^2 C\rho^2 R_{tip}}{(n-2)(n-3)(n-4)(n-5)d^{n-5}}$$

$$F(d) = -\frac{dW}{dd} = -\frac{4\pi^2 C\rho^2 R_{tip}}{(n-2)(n-3)(n-4)d^{n-4}}$$

Comparing with previous slide we see that

$$F(d)_{sphere-plane} = 2\pi R_{tip} W(d)_{planes}$$

It can be shown that for two interacting sphere of different radii

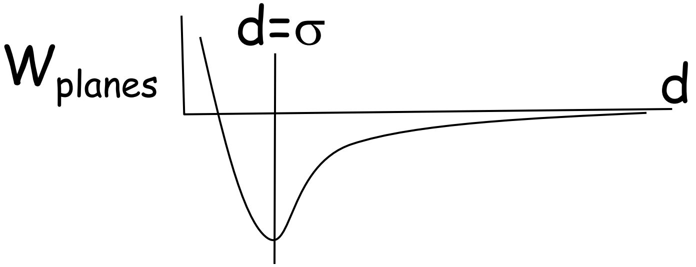
$$F(d)_{sphere-sphere} = 2\pi\left(\frac{R_1 R_2}{R_1 + R_2}\right) W(d)_{planes}$$

Implications of Derjaguin's approximation

- We showed this for $W(r)=-C/r^n$ however it is valid for any force law, attractive, or repulsive or oscillatory for two rigid spheres
- For two spheres in contact $d=\sigma$, the value of $W(\sigma)$ is basically $2\gamma_{12}$ the conventional surface energy per unit area of a solid surface. Thus:

$$F_{sphere-sphere}(\sigma) = F_{adhesion} = \frac{2\pi W_{plane-plane}(\sigma)}{(\frac{1}{R_1}+\frac{1}{R_2})}$$

This approximation is very useful while converting measured F_{ad} in AFM experiments to surface energy



Short range chemical forces

Giessibl (2003)

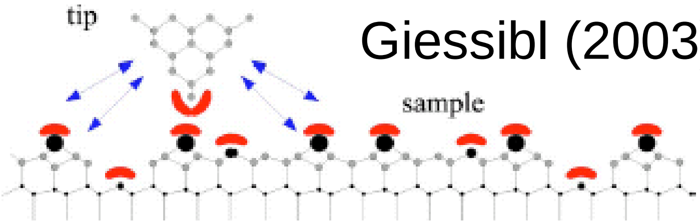


FIG. 6. (Color in online edition) Schematic view of an AFM tip close to a sample. Chemical short-range forces act when tip and sample orbitals (crescents) overlap. Long range forces (indicated with arrows) originate in the full volume and surface of the tip and are a critical function of the mesoscopic tip shape.

- A prototype of the covalent chemical bond can be arrived at from quantum mechanical calculations for a H_2^+ ion (Israelachvili 1991). The Morse potential describes a chemical bond with bonding energy E_{bond}, equilibrium distance σ and decay length κ. With a proper choice of the parameters the Morse potential is an excellent fit for the exact solution of the H_2^+ problem.

$$E_{Morse}(r) = -E_{bond}\left(2e^{-\kappa(r-\sigma)} - e^{-2\kappa(r-\sigma)}\right)$$

- The Lennard-Jones potential has an attractive term from van der Waals forces and a short range repulsive term

$$E_{Lennard-Jones}(r) = -E_{bond}\left(2\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right)$$

- The Stillinger-Weber and Tersoff potentials take into account the directionality of chemical bonds also, and have been used to explain subatomic features in Si images

Continuum description of contact

- If the contact area involves tens or hundreds of atoms the description of net repulsive force is best captured by continuum elasticity models

Capella & Dietler

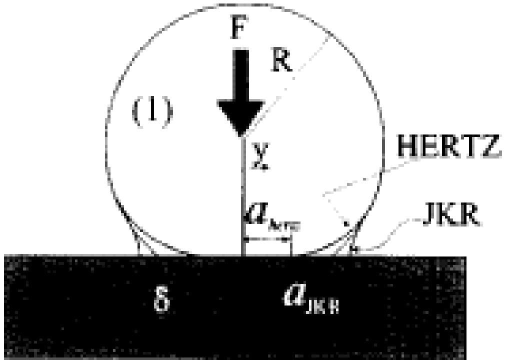


Fig. 8. Deformation of an elastic sphere on a flat surface following Hertz and JKR theory. The profile of the spherical tip in the DMT theory is the same as in the Hertz theory. F is the loading force, R the radius of the sphere, y the distance from the center of the contact area, δ the penetration depth, a_{Hertz} and a_{JKR} are the contact radius following the Hertz and the JKR theories.

- Hertz (1881) takes into account neither surface forces nor adhesion, and assumes a linearly elastic sphere indenting on a elastic surface
- Sneddon's analysis considers a rigid sphere or other rigid shapes on a linearly elastic half space. Neither theory however considers surface forces
- Bradley analysis considers two rigid spheres interacting with the Lennard-Jones potential; Derjaguin-Müller-Toporov (DMT) considers elastic sphere with rigid surface but includes van der Waals forces outside the contact region; Johnson-Kendall-Roberts (JKR) neglects long-range interactions outside contact area but includes short-range forces in the contact area;
- Maugis theory is even more accurate

Adhesion

- Work of adhesion and cohesion: work done to separate unit areas of two media 1 and 2 from contact to infinity in vacuum. If 1 and 2 are different then W_{12} is the work of adhesion; if 1 and 2 are the same then W_{11} is the work of cohesion.
- Surface energy: This is the free energy change γ when the surface area of a medium is increased by unit area. Thus

$$W_{11} = 2\gamma_1$$

- While separating dissimilar materials the free energy change in expanding the "interfacial" area by unit area is known as their interfacial energy γ_{12}

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$

- Work of adhesion in a third medium

$$W_{132} = \gamma_{13} + \gamma_{23} - \gamma_{12}$$

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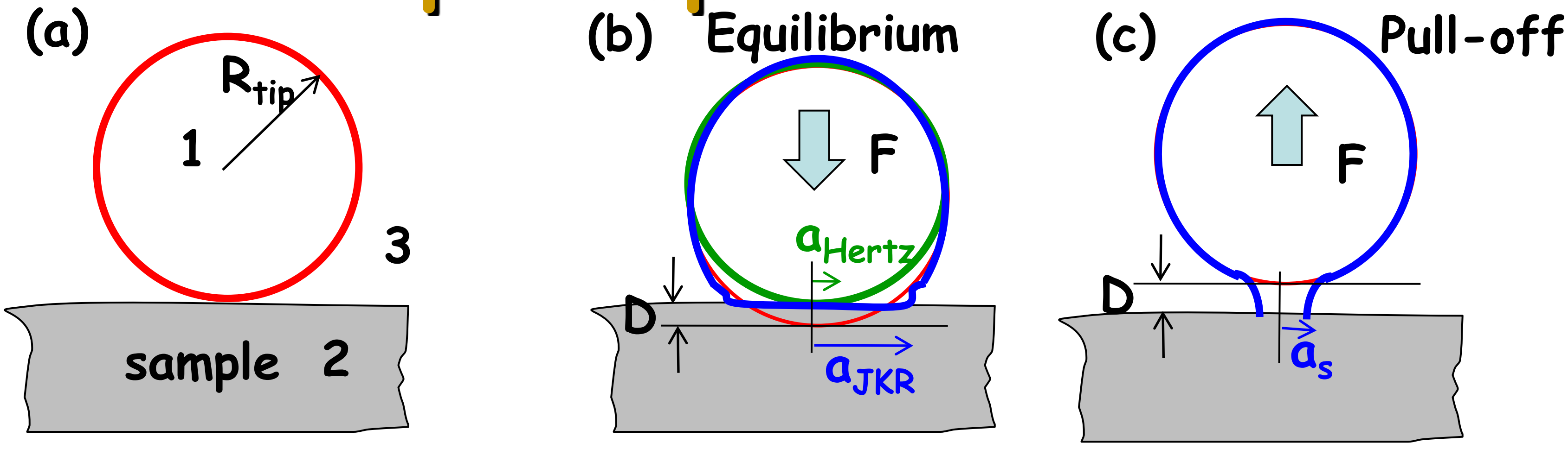
Tip-sample adhesion



Rigid tip-rigid sample

Deformable tip and rigid sample*

- From the Derjaguin approximation for rigid tip interacting with rigid sample we have

$$F_{tip-sample}(\sigma) = F_{adhesion} = 2\pi R_{tip} W(\sigma) \sim 2\pi R_{tip} W_{132} = 2\pi R_{tip}(\gamma_{13} + \gamma_{23} - \gamma_{12})$$

- Real tips and samples are not rigid. Several theories are used for this (Hertz, DMT, JKR)
- * These theories also apply to elastic samples, they are just shown on rigid sample to demonstrate key quantities clearly. For example D is the combined tip-sample deformation in (b)

Hertz vs. DMT vs. JKR

	Hertz	**DMT**	**JKR**
a	$\left(\frac{R_{tip}F}{E_{tot}}\right)^{1/3}$	$\left(\frac{R_{tip}(F+2\pi R_{tip}W_{132})}{E_{tot}}\right)^{1/3}$	$\left(\frac{R_{tip}(F+2\pi R_{tip}W_{132}+\sqrt{6\pi R_{tip}W_{132}F+(3\pi R_{tip}W_{132})^2})}{E_{tot}}\right)^{1/3}$
D	$\frac{a^2}{R_{tip}}=\left(\frac{F^2}{R_{tip}E_{tot}^{\;2}}\right)^{1/3}$	$\frac{a^2}{R_{tip}}=\left(\frac{(F+2\pi R_{tip}W_{132})^2}{R_{tip}E_{tot}^{\;2}}\right)^{1/3}$	$\frac{a^2}{R_{tip}}-\frac{2}{3}\sqrt{\frac{6\pi W_{132}a}{E_{tot}}}$
F_{ad}	0	$2\pi R_{tip}W_{132}$	$3\pi R_{tip}W_{132}/2$

$$\frac{1}{E_{tot}}=\frac{3}{4}\left(\frac{1-\nu_s^{\;2}}{E_s}+\frac{1-\nu_t^{\;2}}{E_t}\right)$$

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Contact forces

Ã: normalized contact area

d: normalized penetration

F: normalized force

Butt, Cappella and Kappl

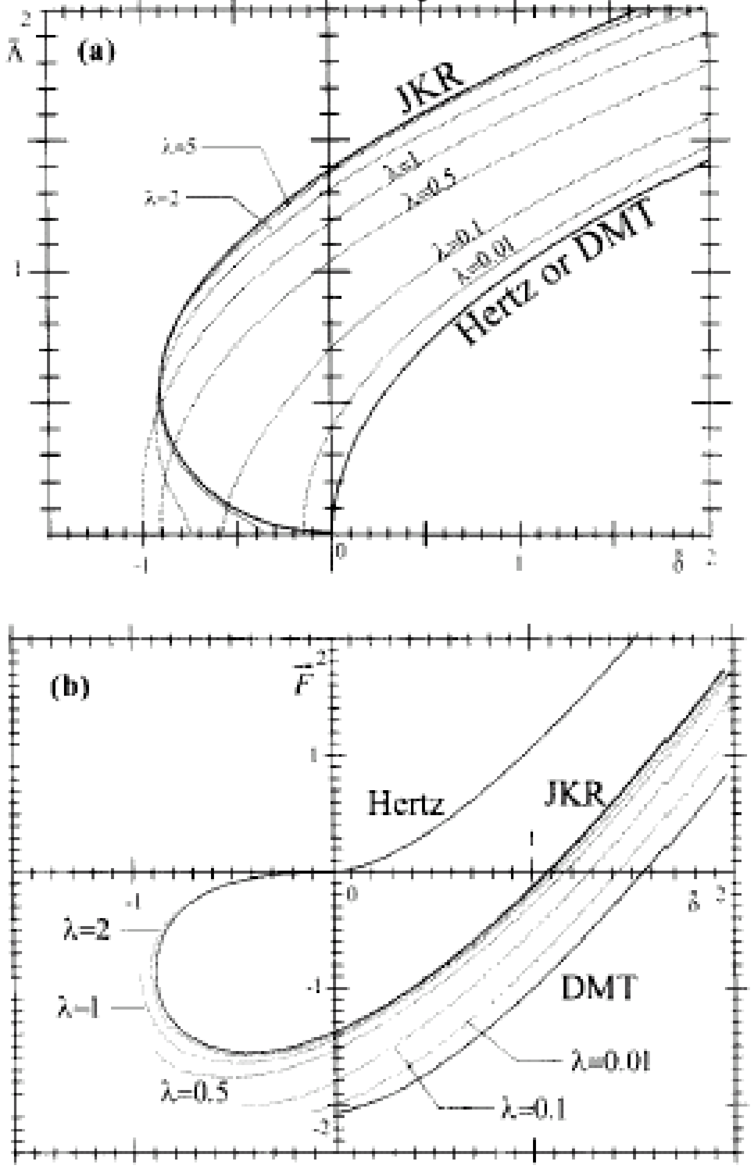
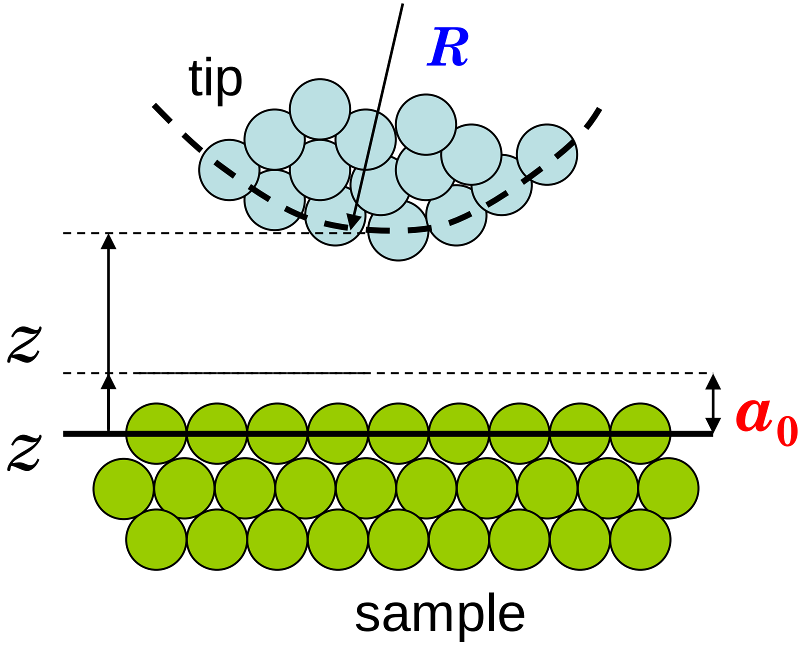


Fig. 9. The dependence of $\bar{A}$ on $\bar{\delta}$ (panel (a)) and the dependence of $\bar{F}$ on $\bar{\delta}$ (panel (b)) as functionals of λ calculated using Maugis theory. The JKR [30] and the DMT [29] limits are indicated. $\bar{A}$, $\bar{F}$, and $\bar{\delta}$ are the dimensionless contact radius, force and penetration depth given by Eqs. (2.11a)–(2.11c).

Simple tip-sample interaction models

- van der Waals force + DMT contact

$$F_i(z) = \begin{cases} -\frac{AR}{6z^2}, & (\text{for } z > a_0) \\ -\frac{AR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}\,(a_0 - z)^{3/2}, & (\text{for } z \le a_0) \end{cases}$$



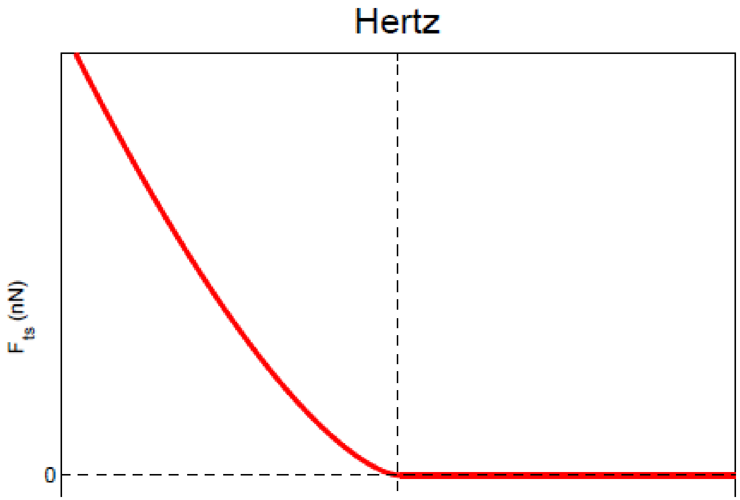
A : Hamaker constant (Si-HOPG)

R : Tip radius

E* : Effective elastic modulus

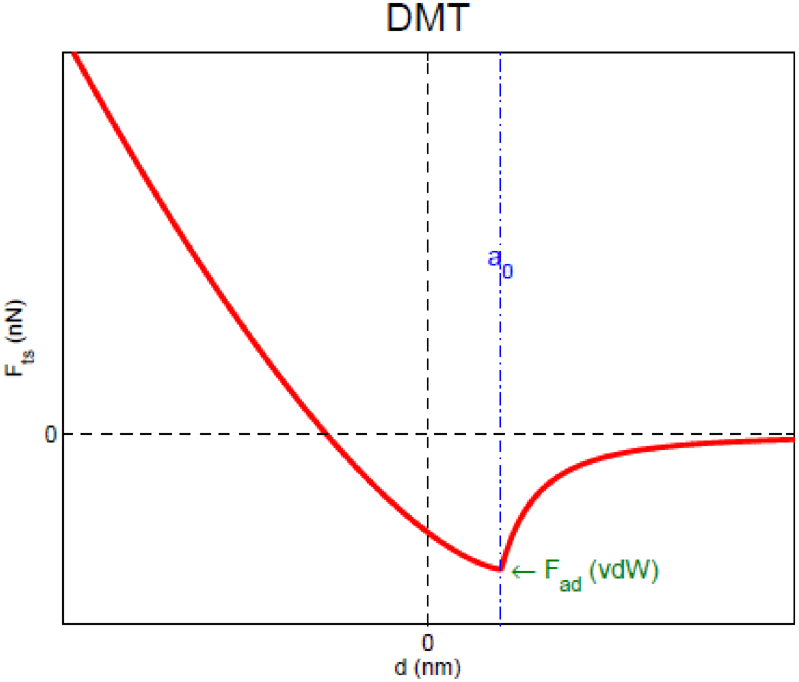
a_0 : Intermolecular distance

Raman et al, Phys Rev B (2002), Ultramicroscopy (2003)



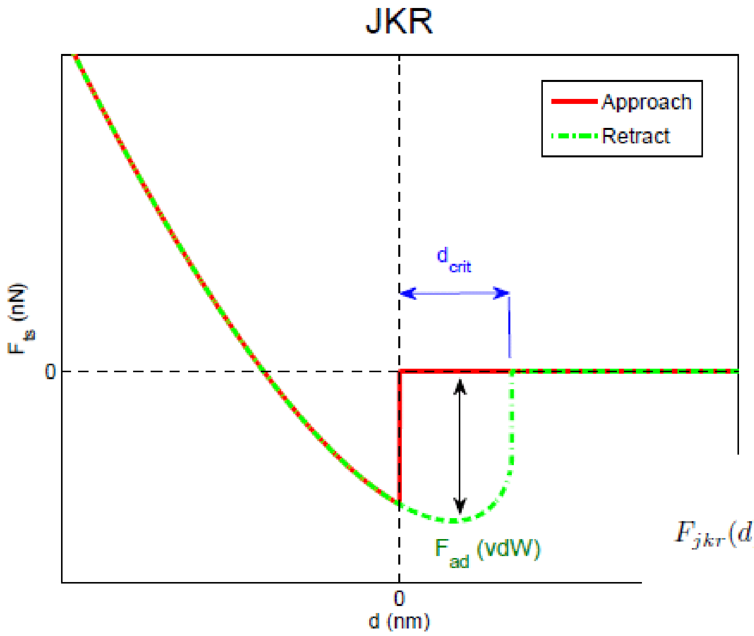
$$F_{ts}(\delta) = \begin{cases} 0, & d < 0 \\ \frac{4}{3}E^{*}\sqrt{R}(-d)^{3/2}, & d \geqslant 0 \end{cases}$$

$$E^{*} = \left[\frac{1-\nu_{tip}^{2}}{E_{tip}} + \frac{1-\nu_{sample}^{2}}{E_{sample}}\right]^{-1}.$$



$$F_{DMT}(d) = \begin{cases} -\frac{HR}{6d^{2}}, & d > a_{o} \\ -\frac{HR}{6a_{0}^{2}} + \frac{4}{3}E^{*}\sqrt{R}(a_{0}-d)^{3/2}, & d \leqslant a_{0} \end{cases}$$

$$E^{*} = \left[\frac{1-\nu_{tip}^{2}}{E_{tip}} + \frac{1-\nu_{sample}^{2}}{E_{sample}}\right]^{-1}.$$



$$F_{jkr}(d) = \begin{cases} 0, & Approaching, d > 0 \\ \frac{4E^{*}a^{3}}{3R} - \sqrt{8\pi W_{jkr}E^{*}a^{3}}, & (Approaching\ and\ d < 0)\ or\ (Retracting\ and\ d < d_{crit}) \\ 0, & Retracting, d > d_{crit} \end{cases}$$

Comments on these theories

- JKR predicts infinite stress at edge of contact circle.
- In the limit of small adhesion JKR -> DMT
- Most equations of JKR and Hertz and DMT have been tested experimentally on molecularly smooth surfaces and found to apply extremely well
- Most practical limitation for AFM is that no tip is a perfect smooth sphere, small asperities make a big difference.
- Hertz, DMT describe conservative interaction forces, but in JKR, the interaction itself is non-conservative (why?) …for a force to be considered conservative it has to be describable as a gradient of potential energy.

Next lecture

- Couple cantilever mechanics to tip sample interaction forces
- F-Z vs. F-d curves