# Force-distance curves by atomic force microscopy

B. Cappella, G. Dietler

Institut de Physique de la Matière Condersée, Université de Lausanne, CH-1015 Lausanne, Switzerland



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#### Abstract

Atomic force microscopy (AFM) force-distance curves have become a fundamental tool in several fields of research, such as surface science, materials engineering, biochemistry and biology. Furthermore, they have great importance for the study of surface interactions from a theoretical point of view.

Force-distance curves have been employed for the study of numerous materials properties and for the characterization of all the known kinds of surface forces. Since 1989, several techniques of acquisition and analysis have arisen. An increasing number of systems, presenting new kinds of forces, have been analyzed. AFM force-distance curves are routinely used in several kinds of measurement, for the determination of elasticity, Hamaker constants, surface charge densities, and degrees of hydrophobicity.

The present review is designed to indicate the theoretical background of AFM force-distance curves as well as to present the great variety of measurements that can be performed with this tool.

Section 1 is a general introduction to AFM force-distance curves. In Sections 2-4 the fundamentals of the theories concerning the three regions of force-distance curves are summarized. In particular, Section 2 contains a review of the techniques employed for the characterization of the elastic properties of materials. After an overview of calibration problems (Section 5), the different forces that can be measured with AFM force-distance curves are discussed. Capillary, Coulomb, Van der Waals, double-layer, solvation, hydration, hydrophobic, specific and steric forces are considered. For each force the available theoretical aspects necessary for the comprehension of the experiments are provided. The main experiments concerning the measurements of such forces are listed, pointing out the experimental problems, the artifacts that are likely to affect the measurement, and the main established results. Experiments up to June 1998 are reviewed. Finally, in Section 7, techniques to acquire force-distance curves sequentially and to draw bidimensional maps of different parameters are listed. © 1999 Elsevier Science B.V. All rights reserved

# 1. Introduction

#### 1.1. General overview: AFM and force-distance curves

Since 1989, the atomic force microscope (AFM) [1] has emerged as a useful tool for studying surface interactions by means of force-distance curves. A great deal of work has been performed on both its theoretical and experimental aspects. The heart of the AFM is a cantilever with a microfabricated tip that deflects when interacting with the sample surface. Provided the sample can be scanned by means of a piezoactuator, the cantilever deflection may be measured in different ways in order to reproduce the sample topography. A controller regulates, collects, and processes the data, and drives the piezo

scanner. The controller consists of a variable number of A/D converters that receive data from the detection system of cantilever deflections, some D/A converters that give signals to the piezo, and an interface with a computer that stores data.

AFM cantilevers are usually made out of silicon or silicon nitride. They have two shapes: rectangular and "V"-shaped. The cantilever back face (the face that is not in contact with the sample) is usually coated with a metallic thin layer (often gold) in order to enhance reflectivity. This is necessary in liquids, where the reflectivity of silicon nitride is much reduced.

The most common methods to detect cantilever deflections are the optical lever method, the interferometric method, and the electronic tunneling method. The optical lever method is the most used one, since it is the most simple to implement. It consists in focusing a laser beam on the back side of the cantilever and in detecting the reflected beam by means of a position sensor, that is usually a quartered photodiode. Both cantilever deflection and torsion signals may be collected. In the interferometric method, a laser beam focused on the cantilever interferes with a reference beam and the deflections are revealed by the variation of the interfering beam intensity. Finally, in the electronic tunneling method, the tunneling current between a metallic tip and the side of the cantilever that does not face the sample is revealed. Hence, the cantilever has to be conductive or coated with a conductive material. This method, employed in the early AFM, has several problems. First, the interactions with the metallic tip next to the cantilever are comparable to those with the sample. Furthermore this method does not work in liquids, and when used in air, contaminants accumulate between the cantilever and the tip, rendering the tunneling unstable.

The sample is scanned by means of a piezoactuator, that is able to perform minimal displacements of the order of 1 Å with high precision up to displacements of the order of  $100 \,\mu\text{m}$ . The piezoelectric actuators employed for atomic force microscopy are cylindrical tubes of different dimensions with an inside electrode, usually grounded, and an outside electrode, usually segmented in four quadrants. Unfortunately, the dependence of the displacement of piezo on the applied voltage is hysteretic and affected by creep, that is a delay effect depending on temperature. Because of creep, almost the entire displacement is performed at the beginning, but a little fraction is done later with a logarithmic time dependence. Efforts to eliminate these non-linearities follow four different approaches:

- 1. A posteriori calculation of non-linear deformations due to hysteresis and creep [2].
- 2. Independent measurement of piezo displacements with two different techniques, e.g., *capacitive technique* (the two plates of a capacitor are mounted one on the piezo and the other fixed on the support and the displacements can be calculated on the basis of capacitance variations) [3,4] and *interferometric technique* (the displacement of the interference fringes between a laser beam reflected by the piezo and a reference beam is measured) [5,6].
- 3. Use of electrostrictive transducers [7].
- 4. *Charge-drive technique*, which consists in driving the piezo by controlling the charge instead of the potential [8]. This may be achieved by inserting a capacitor between the amplifier and the piezo [9, 10].

AFM is able to acquire force-distance curves on every kind of surface and in every kind of environment, with high lateral (25 nm) [11], vertical (0.1 Å) and force (1 pN) [12] resolution. The entire force-distance curve can be collected. Moreover, force measurements can be correlated with topography measurements. Interacting surfaces can be reduced to  $10 \times 10$  nm. The AFM is the only

tool able to measure the interactions between nanometer sized surfaces, allowing local forces and sample properties to be compared.

When acquiring force-distance curves, the piezo must be ramped along the Z axis, i.e., the axis perpendicular to the surface. There are two principal modes of acquisition of force-distance curves. In the first mode, called the static mode, the sample is displaced along the Z axis in discrete steps and the variations in cantilever deflection are collected, as indicated in Section 1.2. In the second mode, called the non-contact mode, the cantilever is vibrated by an extra piezoelectric transducer while the sample is approached and withdrawn, and the amplitude or the resonance frequency of the cantilever oscillations are collected as a function of tip-sample distance. The principles of this mode of acquisition are introduced in Section 1.5.

The study of surface interactions can be performed with several other tools [13, 14]. Between all these tools the surface force apparatus (SFA), invented by Israelachvili [15] in 1978, is the leading instrument in surface force measurements. It contains two curved molecularly smooth surfaces of mica whose separation can be measured by use of interferometric techniques. The distance between the two surfaces is controlled by means of a piezoelectric tube and the force is measured by expanding or contracting the piezotube by a known amount while measuring optically the movement of the surfaces. Any difference between the two values, when multiplied by the stiffness of the spring separating the surfaces, gives the force difference between the initial and final position. Measurements may be carried out in liquid. The SFA has a vertical resolution of 0.1 nm and a force resolution of 10 nN [15]. The SFA employs only surfaces of known geometry, thus leading to precise measurements of surface forces and energies. Although there is a considerable overlap in the force measuring capabilities of the AFM and the SFA, we would like to point out several differences.

- 1. Interacting surfaces in AFM are  $10^4 10^6$  times smaller than those employed in SFA, but in AFM the shape of the surfaces is unknown.
- 2. When the substrates to be employed are not transparent, the interferometric technique cannot be used to measure forces (see Ref. [16]).
- 3. The SFA needs molecularly smooth samples, and therefore it can deal only with mica surfaces or thin layers of materials adsorbed on mica.
- 4. The SFA cannot characterize indentation or topography.
- 5. The viscous force on a spherical particle scales with the square of the particle radius. Therefore with an AFM, measurements can be performed at speeds  $10^4$  times greater while maintaining the same viscous force to surface force ratio [17].
- 6. Since the interacting surfaces are smaller, and the probability of trapping a contaminant particle is proportional to the square root of the interacting surfaces, the AFM is less subject to contamination [17].

The first study on force-distance curves acquired with an AFM, concerning the characterization of surface forces on LiF and graphite, dates back to 1988 [18]. The first works trying to interpret force-distance curves and related information appeared in 1989–1990. Since the first experiments, it has become clear that, when force-distance curves are acquired in air, meniscus forces exerted by thin layers of water vapor dominate any other interactions. Such forces can be eliminated by working in a controlled atmosphere or in a liquid environment.

In 1991 several studies of force-distance curves in liquids were performed, both theoretically and experimentally. Moreover, Mizes et al. [19] performed the first direct measurement of the spatial variation of adhesion.

Since then, two different research lines have characterized the research on force-distance curves: on one hand, the study of different interactions in several environments, on the other, the "mapping" of such interactions, drawn from force-distance curves, in order to distinguish materials with different physico-chemical properties (a kind of "surface spectroscopy").

In 1994, a further technique was introduced [20]. This technique employs functionalized tips, i.e., tips covered with particular molecules that selectively adhere to other, in order to study specific forces by means of force-distance curves.

# 1.2. Relation between AFM force-distance curves and tip-sample interaction force

An AFM force-distance curve is a plot of tip-sample interaction forces vs. tip-sample distance. In order to obtain such a plot, the sample (or the tip) is ramped along the vertical axis (Z axis) and the cantilever deflection  $\delta_c$  is acquired. The tip-sample force is given by Hooke's law:

$$F = -k_{\rm c}\delta_{\rm c}.\tag{1.1}$$

The distance controlled during the measurement is not the actual tip-sample distance D (Fig. 1), but the distance Z between sample surface and the rest position of the cantilever. These two distances differ because of cantilever deflection  $\delta_c$  and because of the sample deformation  $\delta_s$ . These four quantities are related as follows:

$$D = Z - (\delta_{c} + \delta_{s}). \tag{1.2}$$

Since one does not know in advance the cantilever deflections and the sample deformations, the only distance that one can control is the Z distance, i.e., the displacement of the piezo. Therefore, the raw curve obtained by AFM should be called "force-displacement curve" rather than "force-distance curve". This latter term should be employed only for curves in which the force is plotted versus the true tip-sample distance, that has been previously calculated from raw data. Such a distinction is used in this review. When not referring to the specific type of plot employed, the term "force-distance curve" is used.

An AFM force-displacement curve does not reproduce tip-sample interactions, but is the result of two contributions: the tip-sample interaction F(D) and the elastic force of the cantilever, Eq. (1.1). Such a result can be intuitively understood by means of the graphical construction shown in Fig. 2.



Fig. 1. The tip-sample system. D is the actual tip-sample distance, whereas Z is the distance between the sample and the cantilever rest position. These two distances differ because of the cantilever deflection  $\delta_c$  and because of the sample deformation  $\delta_s$ .



Fig. 2. Graphical construction of an AFM force-displacement curve. In panel (a) the curve F(D) represents the tip-sample interaction and the lines 1, 2, and 3 represent the elastic force of the cantilever. At each distance the cantilever deflects until the elastic force equals the tip-sample force and the system is in equilibrium. The force values  $f_a$ ,  $f_b$ , and  $f_c$  at equilibrium are given by the intersections a, b, and c between lines 1, 2, and 3 and the curve F(D). These force values must be assigned to the distances Z between the sample and the cantilever rest positions, i.e., the distances  $\alpha$ ,  $\beta$ , and  $\gamma$  given by the intersections between lines 1, 2, and 3 and the horizontal axis. This graphical construction has to be made going both from right to left and from left to right. The result is shown in panel (b). The points A, B, B', C, and C' correspond to the points a, b, b', c, and c'respectively. BB' and CC' are two discontinuities. The origin O of axis in panel (b) is usually put at the intersection between the prolongation of the zero line and the contact line of the approach curve. The force  $f_{c'}$  eventually coincides with the zero force.

In Fig. 2(a) the curve F(D) represents the tip-sample interaction force. For the present, since no surface force has been introduced yet and for the sake of simplicity, F(D) was chosen to be the interatomic Lennard-Jones force, i.e.,  $F(D) = -\mathbf{A}/D^7 + \mathbf{B}/D^{13}$ . By expressing tip-sample forces by means of an interatomic Lennard-Jones force, only a simple qualitative description of the mechanisms involved in force-displacement curves acquisition can be provided. In particular, the attractive force between surfaces actually follows a force law  $-D^{-n}$  with  $n \leq 3$  (and not n = 7) and the repulsive part of the force is much more complex than the one modeled by the Lennard–Jones force. In Section 2 we treat this in detail. The lines 1-3 represent the elastic force of the cantilever, Eq. (1.1). In panel (b) of Fig. 2 the resulting AFM force-displacement curve is shown. At each distance the cantilever deflects until the elastic force of the cantilever equals the tip-sample interaction force, so that the system is in equilibrium. The force values at equilibrium  $f_a$ ,  $f_b$ ,  $f_c$  are given by the intersections a, b and c between lines 1-3 and the curve F(D), respectively. These force values must not be assigned to the distances D at which the lines intersect the curve F(D), but to the distances Z between the sample and the cantilever rest positions, that are the distances  $\alpha$ ,  $\beta$ , and  $\gamma$  given by the intersections between lines 1–3 and the horizontal axis (zero force axis). Going from right to left, i.e., approaching to the sample, the approach curve is obtained. Making the same graphical construction from left to right, i.e., withdrawing from the sample, gives the withdrawal curve. The result is shown in panel (b) of Fig. 2. The points A, B, B', C, and C' correspond to the points a, b, b', c, and c', respectively.

Let us now give an analytical expression for the force-displacement curves, following the derivation of Hao et al. [21]. The cantilever-sample system can be described by means of a potential  $U_{tot}$  that is

the sum of three potentials:  $U_{cs}(D)$ ,  $U_c(\delta_c)$ , and  $U_s(\delta_s)$ .  $U_{cs}(D)$  is the interaction potential between the tip and the sample, e.g., the Lennard-Jones potential.  $U_c(\delta_c)$  is Hooke's elastic potential of the cantilever.  $U_s(\delta_s)$  is the potential that describes the sample deformation. Sample deformations are discussed in detail in Section 2. For the present derivation, the sample deformation is described by the Hooke's law:

$$U_{c}(\delta_{c}) = \frac{1}{2}k_{c}(\delta_{c})^{2},$$

$$U_{s}(\delta_{s}) = \frac{1}{2}k_{s}(\delta_{s})^{2},$$
(1.3)

in which  $k_c$  and  $k_s$  are the cantilever and sample elastic constants. Usually the interaction force can be written as

$$F = -\frac{\partial U_{\rm cs}}{\partial D} = -\frac{C}{D^n},\tag{1.4}$$

in which C and n depend on the type of forces acting between the tip and sample. The force expressed in Eq. (1.4) takes into account only the attractive part of the interaction, i.e., only the interaction prior to contact.

The relation between Z and  $\delta_c$  can be obtained by forcing the system to be stationary:

$$\frac{\partial U_{\text{tot}}}{\partial (\delta_{\text{s}})} = \frac{\partial U_{\text{tot}}}{\partial (\delta_{\text{c}})} = 0.$$
(1.5)

Since  $\partial U_{cs}/\partial(\delta_s) = -\partial U_{cs}/\partial(D)$  (see Eq. (1.2)), we obtain

$$\delta_{\rm s} = \frac{k_{\rm c}}{k_{\rm s}} \delta_{\rm c},$$

$$k_{\rm c} \delta_{\rm c} = \frac{C}{\left(Z - \delta_{\rm c} - \delta_{\rm s}\right)^n}.$$
(1.6)

Hence

$$k_{\rm c}\delta_{\rm c} = \frac{C}{\left(Z - \beta\delta_{\rm c}\right)^n},\tag{1.7}$$

in which  $\beta = (1 + k_c/k_s)$ . From Eqs. (1.6) and (1.7) both  $\delta_s$  and Z can be determined from the measured value of  $\delta_c$  as functions of the elastic constants  $k_c$  and  $k_s$ . Hence the measured force-displacement curve (panel (b), Fig. 2) can be converted into the force-distance curve (panel (a), Fig. 2), subject to the assumptions embodied in Eqs. (1.3) and (1.4).

#### 1.3. Differences between approach and withdrawal curve

In panel (b) of Fig. 2 two characteristic features of force-displacement curves can be noted: the discontinuities BB' and CC' and the hysteresis between approach and withdrawal curve. These features are due to the fact that in the region between b' and c' (panel (a), Fig. 2) each line has three intersections and hence three equilibrium positions. Two of these positions (between c' and b and between b' and c) are stable, while the third position (between c and b) is unstable. During the approach phase, the tip follows the trajectory from c' to b and then "jumps" from b to b' (i.e., from the force value  $f_b$  to  $f_{b'}$ ).

During retraction, the tip follows the trajectory from b' to c and then jumps from c to c' (i.e., from  $f_c$  to  $f_{c'}$ ). These jumps correspond to the discontinuities BB' and CC' in panel (b) of Fig. 2, respectively. Thus, the region between b and c is not sampled. The difference in path between approach and withdrawal curves is usually called "force-displacement curve hysteresis". The two discontinuities in force values are called "jump-to-contact" in the approach curve (BB' in panel (b) of Fig. 2) and "jump-off-contact" in the withdrawal curve (CC' in panel (b) of Fig. 2).

Let us return to Eq. (1.5), that is the condition for  $U_{\text{tot}}$  to be stationary. For the system to be in stable equilibrium, we must have  $\partial^2 U_{\text{tot}}/\partial (\delta_c)^2 > 0$ , i.e.,

$$\frac{k_{\rm c}}{\beta} > nC \frac{1}{\left(Z - \beta \delta_{\rm c}\right)^{n-1}},\tag{1.8}$$

in which  $k_c/\beta$  is referred to as the effective elastic constant.

If the force gradient is larger than the effective elastic constant, the cantilever becomes unstable and "jumps" onto the surface. This is the jump-to-contact discontinuity. From Eqs. (1.7) and (1.8) the cantilever deflection  $(\delta_c)_{jtc}$  and the tip-sample distance  $D_{jtc}$  at which the jump-to-contact occurs can be determined:

$$(\delta_{\rm c})_{\rm jtc} = \sqrt[n+1]{\frac{C}{(n\beta)^n k_{\rm c}}},$$

$$D_{\rm jtc} = \beta n (\delta_{\rm c})_{\rm jtc}.$$
(1.9)

These are the deflection and the distance of the point b in panel (a) of Fig. 2 and depend only on the attractive part of the interaction, Eq. (1.4). Since the repulsive part of the interaction has not been modeled yet, it is not possible to give the deflection and the distance of the point b' in the same figure. From Eq. (1.9) it is possible to calculate C and  $\beta$  once  $(\delta_c)_{jtc}$  and  $D_{jtc}$  are known. These equations are valid for any kind of attractive force and are adapted to the two main attractive forces, i.e., Van der Waals and hydrophobic (see Sections 6.2 and 6.6). No similar expression can be found for the jump-off-contact, since, in this case, sample deformations and contact elastic theories reviewed in Section 2 actually determine both the distance and the force.

The slope of the lines 1-3 in panel (a) of Fig. 2 is the elastic constant of the cantilever  $k_c$ . Therefore, using cantilevers with high  $k_c$ , the unsampled stretch *b*-*c* becomes smaller, the jump-to-contact first increases with  $k_c$  and then, for high  $k_c$ , disappears. The jump-off-contact always decreases, so that the total hysteresis diminishes with  $k_c$ . When  $k_c$  is greater than the greatest value of the tip-sample force gradient, hysteresis and jumps disappear and the entire curve is sampled. Fig. 3 shows the force-displacement curves that would be obtained with three different cantilevers of  $k_{c1} = 0.105$  N/m,  $k_{c2} = 0.06$  N/m, and  $k_{c3} = 0.04$  N/m and with an interatomic Lennard-Jones force (A =  $10^{-77}$  Jm<sup>6</sup>, B =  $10^{-134}$  Jm<sup>12</sup>). Once again, since a Lennard-Jones interaction is used, the presented dependence has only a qualitative meaning. The hysteresis is large for  $k_{c3}$ , decreases for  $k_{c2}$ , and finally the jumps overlap in the curve acquired with  $k_{c1}$ .

Fig. 4 shows the dependence of jump-to-contact distance and jump-off-contact distance on the elastic constant of the cantilever, and Fig. 5 shows the same dependence for the jump-to-contact and the jump-off-contact forces. Both graphs have been obtained using a Lennard-Jones interaction with  $\mathbf{A} = 10^{-77} \text{ Jm}^6$ ,  $\mathbf{B} = 10^{-134} \text{ Jm}^{12}$ .

In order to obtain complete force-displacement curves one should employ stiff cantilevers which, on the other hand, have a reduced force resolution. Therefore it is necessary to reach a compromise. In



Fig. 3. Force–displacement curves (broken lines) obtained with three cantilevers of different elastic constant for  $k_c \gg k_s$ . The continuous line is the tip–sample interaction, modeled with a Lennard-Jones interaction with  $\mathbf{A} = 10^{-77} \text{ Jm}^6$ ,  $\mathbf{B} = 10^{-134} \text{ Jm}^{12}$ .



Fig. 4. Dependence of jump-to-contact and jump-off-contact distances on the elastic constant of the cantilever. The tipsample interaction has been modeled with a Lennard-Jones interaction with  $\mathbf{A} = 10^{-77}$  Jm<sup>6</sup>,  $\mathbf{B} = 10^{-134}$  Jm<sup>12</sup>.

early AFMs, the cantilevers used for force-displacement curves measurements were tungsten wires, curved at one end, with high elastic constants (> 1 N/m) and with large radii of curvature (> 100 nm). The achieved force resolution was usually of the order of hundreds of pN so that the details of the tip-sample interaction could hardly be seen. Later, less stiff cantilevers with smaller radii of curvature have been employed, increasing the resolution up to nearly 10 pN.

Recently Aoki et al. [12] proved that the force resolution of the AFM can be increased to 0.1 pN. They employed home-made cantilevers with a spring constant of the order of  $10^{-4}$  N/m. Such flexible cantilevers undergo large brownian motions and hence need to be stabilized by feedback forces. In this case, the feedback force is exerted by means of laser radiation pressure. Besides a first laser beam aimed to the deflections detection, a second laser beam is focused on the cantilever. The intensity of this



Fig. 5. Dependence of jump-to-contact and jump-off-contact forces on the elastic constant of the cantilever. The tip-sample interaction has been modeled with a Lennard-Jones interaction with  $\mathbf{A} = 10^{-77}$  Jm<sup>6</sup>,  $\mathbf{B} = 10^{-134}$  Jm<sup>12</sup>.

second laser beam is varied with a fast feedback loop, in order to keep constant the deflection of the cantilever.

#### 1.4. The three regions of the force-displacement curve

Both approach and withdrawal force-displacement curves can be roughly divided in three regions: the contact line, the non-contact region and the zero line.

Zero lines are obtained when the tip is far apart from the sample and the cantilever deflection is nearly zero (on the right side of the point C' for both curves in Fig. 2). When working in liquid, these lines give information on the viscosity of the liquid.

When the sample is pressed against the cantilever the tip is in contact with the sample and D = 0. Therefore, from Eqs. (1.2) and (1.6), the relation between Z and  $\delta_c$  can be obtained:

$$k_{\rm c}\delta_{\rm c} = \frac{k_{\rm c}k_{\rm s}}{k_{\rm c} + k_{\rm s}}Z.$$
(1.10)

The corresponding lines obtained in the force-displacement curve are called "contact lines". In panel (b) of Fig. 2 they are represented by the lines B'A and CA. If the sample is much stiffer than the cantilever, the cantilever deflection  $\delta_c$  equals sample movement Z, whereas if  $k_s \ll k_c$ ,  $\delta_c \simeq (k_s/k_c)Z$ . Thus, the contact lines provide information on sample stiffness.

The origin of force-displacement curves O is usually put at the intersection between the prolongation of the zero line and the contact line of the approach curve. Referring to panel (b) of Fig. 2, the distances  $O\beta$  and  $O\gamma$  are called "jump-to-contact distance" and "jump-off-contact distance". The adhesion work equals the area between the negative part of the withdrawal curve and the Z axis. The hysteresis of the curve is the difference between the adhesion work and the area between the negative part of the approach curve and the Z axis.

The most interesting regions of force-displacement curves are the two non-contact regions, containing the jump-to-contact and the jump-off-contact. The non-contact region in the approach

curves gives information about attractive or repulsive forces before contact. In particular, the maximum value of the attractive force sampled prior to contact equals the pull-on force, i.e., the product of jump-to-contact cantilever deflection and  $k_c$ .

The non-contact region in withdrawal curves contains the jump-off-contact. The pull-off force, i.e., the product of jump-off-contact cantilever deflection and  $k_c$ , equals the adhesion force,  $F_{ad}$ . In order to relate the tip and sample surface energies ( $\gamma_t$  and  $\gamma_s$ ) and the adhesion force it is necessary to evaluate the deformations and the contact area of the sample. This can be done by means of different theories, reviewed in Section 2.

# 1.5. Non-contact mode

The non-contact mode was introduced by Martin et al. [22]. It consists of exciting the cantilever at a frequency  $v = \omega/2\pi$  while the sample is ramped along the Z axis. The cantilever may be modeled as a harmonic oscillator with effective mass  $m^*$  and spring constant  $k_c$ . The effective mass  $m^*$  is given by  $m^* = m_c + 0.24m_t$ , where  $m_c$  is the mass of the cantilever and  $m_t$  is the mass of the tip. Hence, when the tip is far away from the surface, the equation of motion of the cantilever is

$$m^* \frac{\mathrm{d}^2 \delta_{\mathrm{c}}(t)}{\mathrm{d}t^2} + \gamma \frac{\mathrm{d}\delta_{\mathrm{c}}(t)}{\mathrm{d}t} + k_{\mathrm{c}} \delta_{\mathrm{c}}(t) = F_0 \exp\left(\mathrm{i}\omega t\right),\tag{1.11}$$

in which  $\gamma$  is the damping coefficient and  $F_0 \exp(i\omega t)$  is the exciting force exerted by the driving piezo on the cantilever. Solving (1.11), the "free" amplitude of vibration as a function of frequency is obtained:

$$A(\omega) = \delta_{\rm c}(t) \exp[-\mathrm{i}(\omega t + \phi)] = \frac{F_0}{\gamma \omega_0} \frac{\omega_0/\omega}{\sqrt{1 + Q_0^2 [(\omega/\omega_0) - (\omega_0/\omega)]^2}},\tag{1.12}$$

in which  $\omega_0 = \sqrt{k_c/m^*}$  is the resonance frequency and  $Q_0 = m^* \omega_0/\gamma$  is the quality factor. When the cantilever is near the sample surface, surface forces modify the cantilever vibration and the force  $F[D + \delta_c(t)]$ , where D is the distance between the sample and the mean position of the cantilever, is to be added in the second term of Eq. (1.11). The general solution of such an equation cannot be obtained analytically, even when the force law is known. A convenient approximation is the small amplitude approximation, in which the surface force can be written in the form (we follow the derivation by Fontaine et al. [23]):

$$F[D + \delta_{\rm c}(t)] = F(D) + \frac{\mathrm{d}F}{\mathrm{d}D}\delta_{\rm c}(t).$$
(1.13)

Using such an approximation, Eq. (1.12) becomes

$$A(\omega, D) = \frac{F_0}{\gamma \omega_0} \frac{\omega'_0(D)/\omega}{\sqrt{1 + Q(D)^2 [(\omega/\omega'_0(D)) - (\omega'_0(D)/\omega)]^2}},$$
(1.14)

with

$$\omega_0'(D) = \omega_0 \sqrt{1 - \frac{1}{k_c} \frac{\mathrm{d}F}{\mathrm{d}D}(D)} \quad \text{and} \quad \mathcal{Q}(D) = \mathcal{Q}_0 \frac{\omega_0'(D)}{\omega_0}.$$
(1.15)



Fig. 6. Approach curves in the dynamic mode (operating frequency 328 kHz). Circles correspond to a Teflon surface and triangles to a gold surface. The squares correspond to mica and the vibration amplitude has been multiplied by 10 for the sake of comparison (reprinted with permission from [23]).

Dynamic force-distance curves are characterized by a horizontal line at the free amplitude, and a contact line at zero amplitude (when the cantilever is in contact with the sample it is no more longer to vibrate), with a region of decreasing amplitude in between, as shown in Fig. 6.

Non-contact force-distance curves are much less used than static force-distance curves. It is difficult to obtain a good quality factor in liquids. Furthermore, measurements are affected by a lot of artifacts (see Ref. [23]). Hence, in the following, only few experiments performed in this mode are presented.

#### 2. Theories of contact region

From the contact lines of force-displacement curves it is possible to draw information about the elasto-plastic behavior of materials.

Let us first consider an ideally elastic material. As shown in panel (a) of Fig. 7, during the approach curve, i.e., from O to A, the tip goes into the sample of a depth  $\delta$ , causing a deformation. During the withdrawal the tip goes back from A to O, and since the sample is elastic, it regains step by step its own shape, exerting on the tip the same force. Hence loading and unloading curves, i.e., the approach and withdrawal contact lines, overlap.

If the sample is ideally plastic (panel (b) of Fig. 7), it undergoes a deformation during the loading curve, and when the tip is withdrawn, it does not regain its own shape and the load decreases, whereas the penetration depth stays the same.

Most samples have a mixed behavior. Hence loading and unloading curves seldom overlap. In particular, at a given penetration depth, the force of the unloading curve is lesser than the force of the loading curve (see panel (c) of Fig. 7, where a force-displacement curve is shown, whereas the curves in panels (a) and (b) of Fig. 7 are deformation vs. load curves). The difference between the approach and the withdrawal contact lines is called "loading-unloading hysteresis".



Fig. 7. Load vs. penetration depth curves for an ideally elastic material (panel (a)) and an ideally plastic material (panel (b)). The force-displacement curve for an elasto-plastic material is shown in panel (c). H' is the "zero load plastic indentation", i.e., the penetration depth at which the force of the unloading curve equals zero. H is the "zero load elastic deformation", i.e., the distance the sample regains.

The penetration depth H' at which the force of the unloading curve equals zero is called "zero load plastic indentation". The distance H the sample regains is the "zero load elastic deformation". Both distances are determined by use of the tangent to the curve in A, in order to neglect the influence of the variations of contact area during the unloading process.

In the following we neglect the plastic deformations and review the theories dealing with elastic continuum contact mechanics, in which the tip and sample are assumed to be continuous elastic media. The geometry of a spherical tip in contact with a flat surface is indicated schematically in Fig. 8. Eq. (1.10) reveals that, along the contact lines, Z and  $\delta_c$  are proportional and that once the elastic constant of the cantilever is known, the elastic constant of the sample  $k_s$  can be determined from their proportionality ratio. The elastic constant of the sample  $k_s$  depends on contact area, Young modulus E and Poisson ratio  $\nu$  via

$$k_{\rm s} = 2a \frac{{\rm E}}{1-\nu^2},\tag{2.1}$$

in which *a* is the contact radius [24].



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,  $\delta$  the penetration depth,  $a_{\text{Hertz}}$  and  $a_{\text{JKR}}$  are the contact radius following the Hertz and the JKR theories.

In order to know the dependence of the contact radius and the force on the penetration depth it is necessary to make some assumptions. The different theories of such phenomena are summarized below.

## 2.1. Hertz and Sneddon

Hertz theory [25] dates back to 1881. It takes into account neither surface forces nor adhesion. The tip is considered as a smooth elastic sphere, while the sample is a rigid flat surface. For a sphere of radius R pressed onto a flat surface with a force F, the adhesion or pull-off force  $F_{ad}$ , the contact radius a, the contact radius at zero load  $a_0$ , the deformation  $\delta$  of the spherical tip, and the pressure P are given by

$$F_{\rm ad} = 0, \tag{2.2a}$$

$$a = \sqrt[3]{\frac{RF}{K}},\tag{2.2b}$$

$$a_0 = 0, \tag{2.2c}$$

$$\delta = \frac{a^2}{R} = \frac{F}{Ka},\tag{2.2d}$$

and

$$P(x) = \frac{3Ka\sqrt{1-x^2}}{2\pi R} = \frac{3F\sqrt{1-x^2}}{2\pi a^2},$$
(2.2e)

in which x = y/a, y is the distance from the center of the contact circle, and the reduced Young modulus K is given by

$$\frac{1}{K} = \frac{3}{4} \left( \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \right)$$
(2.3)

In Eq. (2.3) E,  $E_i$ ,  $\nu$  and  $\nu_i$  are the Young modulus and the Poisson ratios of the flat surface, i.e., the sample, and of the indenter, i.e., the tip. The geometry of the deformed sphere-substrate contact is indicated in Fig. 8.

In the limit of high loads or low surface forces, an AFM experiment can follow the Hertz theory. In most cases, however, the AFM tip is stiffer than the sample, and one has to consider the deformations of the flat sample, or in other cases, those of both the tip and the sample. Hertz theory cannot be used to calculate sample deformations by assuming a rigid tip. When a rigid spherical punch on an elastic surface is considered, Sneddon analysis has to be employed [26]. In Sneddon analysis [27] the elastic deformation is given by a transcendental equation that can be computed numerically. The force F exerted by the punch on the surface and the surface deformation  $\delta$  are given by

$$F = \frac{3}{8}K\left[\left(a^2 + R^2\right)\ln\left(\frac{R+a}{R-a}\right) - 2aR\right],\tag{2.4a}$$

and

$$\delta = \frac{1}{2}a \ln\left(\frac{R+a}{R-a}\right). \tag{2.4b}$$

Deformation and force can be computed for a generic axisymmetric punch:

$$\delta = \int_{0}^{1} \frac{f'(x)}{\sqrt{1 - x^2}} dx,$$
(2.5a)

and

$$F = \frac{3}{2} Ka \int_{0}^{1} \frac{x^2 f'(x)}{\sqrt{1 - x^2}} \, \mathrm{d}x, \tag{2.5b}$$

in which f(x) is the function describing the profile of the punch. Solutions for common geometries can be found in [27].

Simply summing Hertz and Sneddon deformations, i.e., tip and sample deformations, whenever surface forces are negligible, one can obtain the total deformation in an AFM measurement. When surface forces must be considered, one of the four theories described in Sections 2.2 and 2.3 has to be employed.

# 2.2. Bradley, Derjaguin-Müller-Toporov and Johnson-Kendall-Roberts

We present here three theories that take into account the effect of surface energy on the contact deformation. The Bradley analysis [28] considers two rigid spheres interacting via a Lennard-Jones potential. The total force between the spheres is

$$F(z) = \frac{8\pi WR}{3} \left[ \frac{1}{4} \left( \frac{z}{z_0} \right)^{-8} - \left( \frac{z}{z_0} \right)^{-3} \right],$$
(2.6)

in which  $z_0$  is the equilibrium separation, R the reduced radius of the spheres, i.e.,  $R = (1/R_1 + 1/R_2)^{-1}$ , and W is the adhesion work at contact.

In Derjaguin–Müller–Toporov (DMT) theory [29] the elastic sphere is deformed according to Hertz theory, but in addition to the external load F, also the forces acting between the two bodies outside the contact region are taken into account. These forces alone produce a finite area of contact. If an external load is applied, the area of contact is increased. If a negative load is applied, the contact area diminishes until it reaches zero. At this point the pull-off force reaches its maximum value. The corresponding expressions for the quantities of Eqs. (2.2a)-(2.2e) are found by minimizing the sum of the elastic and of the surface energy:

$$F_{\rm ad} = 2\pi R W, \tag{2.7a}$$

$$a = \sqrt[3]{(F + 2\pi R W)} \frac{R}{K},$$
(2.7b)

$$a_0 = \sqrt[3]{\frac{2\pi W}{K}}R^2, \qquad (2.7c)$$

$$\delta = \frac{a^2}{R},\tag{2.7d}$$

1

and

$$P(x) = \frac{3Ka\sqrt{1-x^2}}{2\pi R} = \frac{3F\sqrt{1-x^2}}{2\pi a^2}.$$
(2.7e)

DMT theory is applicable for systems with low adhesion and small tip radii.

Johnson-Kendall-Roberts (JKR) theory [30] neglects long range forces outside the contact area and considers only short range forces inside the contact region. With JKR assumptions, the corresponding equations of Eqs. (2.2a)-(2.2e) are:

$$F_{\rm ad} = \frac{3}{2} \pi R \mathbf{W}, \tag{2.8a}$$

$$a = \sqrt[3]{\frac{R}{K} \left[ F + 3\pi R \mathbf{W} + \sqrt{6\pi R \mathbf{W} F + (3\pi R \mathbf{W})^2} \right]},$$
(2.8b)

$$a_0 = \sqrt[3]{\frac{6\pi R^2 \mathbf{W}}{K}},\tag{2.8c}$$

$$\delta = \frac{a^2}{R} - \frac{2}{3}\sqrt{\frac{6\pi Wa}{K}},\tag{2.8d}$$

and

$$P(x) = \frac{3Ka}{2\pi R} \sqrt{1 - x^2} - \sqrt{\frac{3KW}{2\pi a}} \frac{1}{\sqrt{1 - x^2}}.$$
(2.8e)

The JKR theory behaves hysteretically. During unloading, a neck links the tip and sample (see Fig. 8), and contact is abruptly ruptured at negative loads. When separation occurs, the contact radius has fallen to  $a_s = 0.63a_0$ .

The JKR theory is suitable for highly adhesive systems with low stiffness and large tip radii. One difficulty with the JKR theory is that it predicts an infinite stress for x = 1, i.e., at the edge of the contact area. This unphysical situation arises because JKR theory considers only the forces inside the contact area and implicitly assumes that the attractive forces act over an infinitesimally small range. These infinities disappear as soon as a finite range force law, e.g., Lennard-Jones potential, is assumed.

DMT and JKR theories have raised a number of controversial experimental as well as theoretical issues after their publication. This controversy persisted from 1971 to 1984, when it was slowly realized that the two theories apply to two very different situations. Without citing the numerous publications on the controversy, we indicate here the most important works.

Attard and Parker [31] self-consistently calculated the elastic deformation and adhesion of two convex bodies interacting via finite range surface forces, namely an exponential law for repulsive force at small separations and a 9–3 Lennard-Jones law for the attractive forces. Hertz theory is confirmed to be suitable for short ranged repulsive forces and large loads, and thus agrees well with the results of Attard and Parker for both exponential repulsive forces and Lennard-Jones repulsion. Nevertheless, in general, Hertz theory overestimates the deformation caused by a given load. When the adhesive part of the Lennard-Jones potential is considered, JKR theory turns out to predict the force–deformation

relation very well and also the stress infinities at x = 1 disappear. Comparing the pull-off force with the value predicted by JKR theory, when a certain parameter  $\sigma_A$ , which is a function of surface energies, radii of curvature and materials stiffness, is much lesser than one, i.e., for stiff bodies with small surface energies and small radii of curvature, DMT value is more accurate than JKR value.

Müller et al. [32] presented a self-consistent numerical calculation abandoning the hypothesis that adhesion forces do not alter the hertzian geometry. The result is a continuous transition from the DMT to the JKR theory when a single  $\mu_M$  parameter is varied.

Pashley et al. [33] had already introduced a parameter  $\varphi_P$ , which is proportional to the ratio of *h*, i.e., the height of the neck formed when the sphere is under a negative load before detachment, and  $z_0$ , i.e., a typical atomic dimension:

$$\varphi_{\rm P} = \frac{h}{z_0} \simeq \sqrt[3]{\frac{RW^2}{K^2 z_0^3}}.$$
(2.9)

When  $\varphi_P < 1$ , i.e.,  $h < z_0$ , surface forces outside the contact area become important and the behavior approaches that of the DMT theory. Following the more complete analysis of Müller et al. [32] the DMT model holds when  $\varphi_P < 0.3$  (hard solids of small radius and low surface energies) and the JKR model holds when  $\varphi_P > 3$  (soft bodies with large radius and surface energies).

# 2.3. Maugis

Maugis theory [34] is the most complete and accurate theory in that it applies to all materials, from large rigid spheres with high surface energies to small compliant bodies with low surface energies. The full range of material properties is described by a dimensionless parameter  $\lambda$  given by

$$\lambda = \frac{2.06}{z_0} \sqrt[3]{\frac{RW^2}{\pi K^2}},$$
(2.10)

in which  $z_0$  is again a typical atomic dimension. This parameter  $\lambda$  is proportional to the parameter  $\mu_M$  introduced by Müller et al. [32] ( $\lambda = 0.4 \,\mu_M$ ), to the parameter  $\varphi_P$  introduced by Pashley, and to the parameter  $\sigma_A$  introduced by Attard and Parker [31] ( $\lambda \cong 0.4 \sqrt[3]{\sigma_A^2}$ ). A complete conversion table is given by Greenwood [35]. A large  $\lambda$  occurs for more compliant, large, and adhesive bodies, whereas a small  $\lambda$  occurs for small rigid materials with low surface energies.

In the Maugis theory following the Dugdale model [36], adhesion is considered as a constant additional stress over an annular region around the contact area. The ratio of the width of the annular region c to the contact radius a is denoted by m. By introducing the dimensionless parameters

$$\bar{A} = \frac{a}{\sqrt[3]{\pi W R^2/K}},\tag{2.11a}$$

$$\bar{F} = \frac{F}{\pi WR},\tag{2.11b}$$

and

$$\bar{\delta} = \frac{\delta}{\sqrt[3]{\pi^2 \mathbf{W}^2 R/K^2}},\tag{2.11c}$$

a set of parametric equations is obtained. In particular, the corresponding equations to Eqs. (2.2a) and (2.2d) are:

$$\bar{\delta} = \bar{A}^2 - \frac{4}{3}\bar{A}\lambda\sqrt{m^2 - 1},\tag{2.12}$$

$$\frac{\lambda\bar{A}^2}{2} \left[ \sqrt{m^2 - 1} + (m^2 - 2)\operatorname{arctg}\sqrt{m^2 - 1} \right] + \frac{4\lambda^2\bar{A}}{3} \left[ -m + 1 + \sqrt{m^2 - 1}\operatorname{arctg}\sqrt{m^2 - 1} \right] = 1,$$
(2.13)

and

$$\bar{F} = \bar{A}^3 - \lambda \bar{A}^2 (\sqrt{m^2 - 1} + m^2 \operatorname{arctg} \sqrt{m^2 - 1}).$$
(2.14)

Eqs. (2.12)–(2.14) form an equation system which enables the calculation of m, F and  $\overline{\delta}(\overline{A})$  if  $\overline{A}(\overline{\delta})$  is given. Eq. (2.12) reduces to Eq. (2.7d) for  $\lambda \to 0$  (DMT) and to Eq. (2.8d) for  $\lambda \to \infty$  (JKR).

The adhesion force  $F_{ad}$  given by Eq. (2.14) is  $2\pi RW$  for  $\lambda \to 0$  (DMT) and  $1.5\pi RW$  for  $\lambda \to \infty$  (JKR).

The results presented above are displayed in Fig. 9, showing the dependence of  $\overline{A}$  on  $\delta$  and the dependence of  $\overline{F}$  on  $\overline{\delta}$ . In panel (a) it is evident that the radius of contact at zero penetration is zero only



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

in the DMT limit. For  $\lambda > 1$  and  $\delta < 0$ , there are two values of  $\overline{A}$  (panel (a)) and of  $\overline{F}$  (panel (b)) for each  $\delta$  and the behavior is hysteretic.

Following Maugis theory, there is a continuous transition from the DMT deformation vs. load curve to the JKR deformation vs. load curve. This means that, at a certain applied load F, the deformation of the sample and the contact area, and hence the relation between  $k_s$  and E (see Eq. (2.1)) can be exactly known only if the surface energy, the tip shape and the stiffness of the sample are exactly known. In other words, provided the exact value of the elastic constant of the cantilever, for each value of load, one can calculate  $k_s$  from load/unloading curves, but in order to relate  $k_s$  to Young modulus E, one needs to know the contact radius a and hence the deformations  $\delta$  of the sample. This is not possible as the deformation depends also on surface energies, and when deducing surface energies from pull-off forces, one has also to know the Young modulus E, i.e., the quantity one wants to draw from the experiments. Quite exact values of E can be obtained only when the materials or the experimental conditions approach the Hertz-Sneddon limit, and hence the measure of the Young modulus is usually obtained from the high load part of the load curve in order to exclude the influence of surface energies. Furthermore, in AFM measurements, E, R, and W are the *local* values of the Young modulus, the radius of curvature and the surface energy, and not the bulk macroscopic values. In 1997, Johnson and Greenwood [37] constructed a map of the elastic behavior of bodies, shown in Fig. 10, permitting to find the theory to be applied depending on the material properties. The authors observe that AFM experiments usually fall in the Maugis region.

At our knowledge, the only experimental verification of the Maugis theory is that of Lantz et al. [38]. In this work, the contact area between a Pt/Ir coated Si tip and graphite is deduced from current, friction, and normal force measurements. The experimental data are shown to follow a Maugis model rather than an hertzian law. Measurements are repeated for a Si tip on NbSe<sub>2</sub>.

Finally, all the theories reviewed in this section are continuum elastic theories and hence assume smooth surfaces with no plastic deformation and no viscoelastic phenomena.



Fig. 10. Map of the elastic behavior of bodies.  $P_a/P$  is the ratio between the adhesive part of the load and the total load. When the adhesion is negligible, bodies fall in the Hertz limit (approximately  $F > 10^3 \pi WR$ ).  $\delta_1$  is the elastic compression, and  $h_0$  is an equilibrium distance. When  $\delta_1 \ll h_0$ , the bodies are rigid and follow Bradley theory ( $\lambda < 10^{-3}$ ).  $\delta_a$  is the deformation due to adhesion. When the adhesion is small the behavior of materials is described by the DMT theory (approximately  $10^{-2} < \lambda < 10^{-1}$ ), whilst JKR theory predicts the behavior of highly adhesive bodies (approximately  $\lambda > 10^1$ ). The Maugis theory suits to the intermediate region (approximately  $10^{-1} < \lambda < 10^1$ ) (adapted from [37]).

# 2.4. Artifacts

One of the most striking artifacts concerning contact lines is due to the piezoelectric actuators hysteresis and creep [7]. As a matter of fact, in order to acquire force-displacement curves sequentially, the piezo actuator has to be ramped repeatedly along Z. Hysteresis and creep affect the zero line of the approach curve and the contact line of the withdrawal curve, i.e., the regions near the inversion of motion.

Hysteresis and creep lead to an incorrect determination of displacements. In particular, because of creep, the loads in the unloading curve for a given displacement may appear bigger and finally overcome those of the loading curve. This unphysical phenomenon is called "reverse path effect".

Several methods have been proposed in order to compensate for hysteresis and creep effects. To our knowledge, the only method applied to force-distance curves is the one that uses lead magnesium niobate (PMN) actuators [7] which have less non-linearities when used in a cyclic application. However, PMN ceramics are electrostrictive materials for which the strain is proportional to the square of the applied field and the displacement is thus independent of the sign of the applied voltage yielding only one half the displacement range of a corresponding lead zirconate titanate (PZT) actuator. Furthermore, PMN response is much more temperature dependent.

Aimé et al. [24] have studied the elastic behavior of viscoelastic materials. For such materials, the work of adhesion is a function of the Z scan rate v, i.e.,

$$\mathbf{W}_{\nu} = \mathbf{W}(1 + \zeta(T)\nu^{n}), \tag{2.15}$$

in which  $\zeta(T)$  is a function characterizing the material, T is the temperature and n is found to be equal to 0.6. This dependence of the adhesion force, when inserted in the equations describing the elastic behavior of materials, leads to a dependence of the loading/unloading curves on velocity. Furthermore, since the hysteresis changes with the scanning frequency, the slope of the contact lines decreases with frequency, even in the case of hard, inorganic, non-viscoelastic surfaces.

Besides viscoelastic properties, another source of artifacts not accounted for in the elastic continuum media equations is surface roughness. Both AFM tips produced by electrochemical etching and tips produced through microfabrication techniques have on the surface some small asperities which can reach few nanometers in size. In the contact region of the force–displacement curve the effect of asperities is twofold. On the one hand, for a given load, the deformation depth is enhanced since the actual contact radius is much smaller than the macroscopic tip. On the other hand, the surface deformation is smaller than that expected for a single asperity contact since there are multiple contacts and the load will be distributed over many points. Cohen [39] has compared the deformations in the case of a smooth tip (radius 1  $\mu$ m) and of a rough tip on a flat gold surface. The roughness is described as a distribution of hemispherical minitips (radius 2 nm), and the contact is modeled with an hertzian law. Deformations due to the rough tip turn out to be larger than the one in the case of a smooth tip. Anyway, for forces above 1  $\mu$ N, the slope of the deformation vs. load curve is the same in the two cases, since above a certain load, the microasperities are buried and the entire tip surface comes in contact.

Hoh and Engel [40] have shown that the loading/unloading hysteresis is scan-rate dependent. At high scan rates the separation between the two contact lines is large. As the scan rate is decreased, this separation reaches a minimum after which it increases again. Such a scan-rate dependence is typical of stick slip friction and is not consistent with effects arising from electromagnetic forces. The authors propose that the friction between the tip and sample makes the cantilever bow forward after the tip

comes in contact, resulting in an offset of the contact line. As the tip is retracted, the cantilever bends upward, causing an opposite effect in the line. At the turn-around point, the deflection signal jumps nearly vertically, as it would be expected when the cantilever turns up from a forward bow. Unfortunately, no experiment has been carried out to separate the effects of friction and of scan rate dependent hysteresis.

Haugstad and Glaedfelter [41] have studied the effect of photodiode non-linearities on the contact lines of force-displacement curves. The withdrawal contact line is the portion of the forcedisplacement curves with the highest repulsive and/or attractive loads, and hence with high cantilever deflections. In turn, this means high displacements of the laser spot on the photodiode. The authors prove, experimentally and theoretically, that the difference between the measured contact line and the line  $\delta_c = Z$  is a cubic curve whose maximum contribution is about 8% of the total signal. This nonlinear contribution is related to the features of the photodiode. The measurements are done on a rigid material, namely polycrystalline Si<sub>3</sub>N<sub>4</sub>, so that sample deformations can be neglected.

# 2.5. Experimental results

The first pioneering work dealing with the determination of materials elasto-plastic properties by means of an AFM is that of Burnham and Colton [42]. Using a hertzian analysis, the modulus of elasticity has been drawn from the experiments for an elastometer, HOPG graphite, and gold, in rather good agreement with literature values.

Acquiring force-displacement curves on gold, Cohen et al. [43] have shown the effect of microasperities on an iridium tip, as indicated in Section 2.4. The same effect has been discussed by Blackman et al. [44] pointing out the inadequacy of continuum elastic theories and the need of models for atomic-scale contacts.

Hao et al. [21] have measured the slope of loading/unloading curves for graphite, mica, and stainless steel, finding inexplicable results for graphite. The authors account neither for elasticity theory nor for microasperities effects. Consequently, they are unable to explain the discrepancy between expected and measured values.

Aimé et al. [24] have characterized force-displacement curves on rigid and soft polymer films in controlled atmosphere. The authors point out several causes of misinterpretation of force-displacement curves: the lack of an accurate knowledge of the cantilever stiffness and of the tip size and the difficulty in separating viscoelastic, elastic, and plastic effects. Even with these numerous restrictions, AFM measurements can lead to a characterization of the film properties. Following the JKR theory and taking into account viscoelastic effects (see Section 2.4), a good agreement between theoretical and experimental values is obtained.

Thomas et al. [45] have acquired force-displacement curves between a W tip and a gold sample covered with a monolayer of docasanethiol. They show that the deformation follows an hertzian model for forces smaller than 15  $\mu$ N, but a considerable loading/unloading hysteresis appears for loads of about 25  $\mu$ N.

Weisenhorn et al. [46] have compared load vs. indentation curves on glass, polyurethane, and rubber, showing that it is possible to distinguish between two polyurethane layers of different Young's modulus (namely 14 and 30 MPa).

The measurement of elastic properties of biological materials has been pioneered by Tao et al. [47], who have measured elastic properties of bones, comparing them with stainless steel and rubber.

Radmacher et al. [48] have measured the indentation of an  $Si_3N_4$  tip on lysozyme adsorbed on mica. A good agreement between Hertz equation for a sphere on a flat surface and experimental data is reached (although the formula reported in the text is affected by an error, and it is not clear if the same error affects also the fit of the data). What is most important, the authors show the different behavior of lysozyme and mica in indentation measurements, thus leading to the possibility of distinguishing the two materials throughout the acquisition of force–displacement curves. Later on, Radmacher et al. [49], acquiring force–displacement curves on gelatin, have shown that the agreement with Hertz equation improves when the tip is modeled as a cone for higher loads and as a sphere for small loads. They proved the capability of AFM force–displacement curves to measure the change of gelatin elastic properties under various conditions. The gelatin was immersed in pure water, propanol, or mixtures of the two, and the measurement of the Young modulus reached a resolution of 0.5 MPa.

Domke and Radmacher [50] have determined the Young modulus of gelatin layers of different thickness. They have verified that the calculated Young modulus depends both on the thickness of the medium and on the portion of the contact line used for the calculation. In particular, the Young modulus of a thick film  $(1.1 \,\mu\text{m})$  depends very little on the range of analysis (it goes from 15.9 kPa for cantilever deflections in the range 10–30 nm up to 18.5 kPa in the range 170–200 nm). The load–deformation curve is well fitted with the hertzian model. In the case of the thin film (<300 nm), the Young modulus is 27 kPa in the range 10–30 nm and it is bigger than 1 GPa in the range 170–200 nm. The load–deformation curve cannot be fitted with the hertzian model. As a matter of fact, when the tip indents a thin film, at high loads the deformation–load curve is influenced by the presence of the rigid substrate, that in turn cannot be probed with a thick film.

Several load-indentation studies have been performed on cells. Ricci and Grattarola [51] have explored the possibility of measuring cell height by means of indentation-load curves. No calculation is presented for cells elastic modulus.

Finally, several works have exploited dynamic force-distance curves in order to characterize sample elasticity [52, 53].

Experiments dealing with the study of elastic properties of materials by means of the AFM have shown that the absolute measurement of Young modulus or other elastic properties is not a simple and straightforward issue, whereas the comparison of elastic properties of different materials gives quite satisfactory results. However, the AFM turns out to be the only instrument able to characterize the local elastic properties of materials with high lateral resolution (25 nm) [11].

## 3. Theories of non-contact region

# 3.1. Approach curve: jump-to-contact and attractive forces

The jump-to-contact is one of the important quantities one can measure in a force-displacement curve. As discussed in Section 1.3, this discontinuity occurs when the gradient of the tip-sample force is larger than the elastic constant of the cantilever. The general expressions of the cantilever deflection and the tip-sample distance at which the tip jumps onto the surface are given by Eqs. (1.9).

The jump-to-contact may be preceded by a region of attractive (Van der Waals or Coulomb force) or repulsive (Van der Waals force in certain liquids, double-layer, hydration, and steric) force. The jump-to-contact gives information on attractive forces between the tip and sample. The maximum

sampled value of the attractive force equals the jump-to-contact cantilever deflection  $(\delta_c)_{jtc}$  times the cantilever elastic constant. In order to evaluate such attractive forces it is necessary to know the force law and the tip shape. In Section 6 we consider in detail the different forces and the influence of the tip shape.

The onset of a jump-to-contact is predicted by any theory that takes attractive forces into account (JKR or Maugis) and is also predicted by numerical calculations [31, 35].

In AFM measurements the jump-to-contact instability is governed by the stiffness of the cantilever relative to the long-range tip-sample forces. As indicated in Section 1.3, if the cantilever elastic constant is bigger than the maximum value of the tip-sample force gradient, then the discontinuities virtually disappear. However, jump-to-contact is always present at an atomic scale, even if the cantilever can be modeled as an infinitely rigid body. In this case, the jump-to-contact instability is governed by the inherent stiffness of the tip and sample materials, related to their cohesive strengths. This phenomenon has been demonstrated by Pethica and Sutton [54] by means of calculations employing Lennard-Jones potentials and by Landman et al. [55] by use of molecular dynamics (MD) simulations.

Pethica and Sutton [54] have shown that in general it exists a minimum separation ( $\cong 1-2$  Å) below which the surfaces jump in contact irrespective of the rigidity of the holder. This instability is due to the fact that, at some small enough separation, the gradient of the surface forces exceeds the gradient of the elastic restoring force of the bodies. The instability is irreversible because surface forces have stronger separation dependence than does the elastic restoring force. The Lennard-Jones pair potential used by Pethica and Sutton is inapplicable to free surface structures. *N*-body potentials of the embedded-atom variety are much more reliable. They do not, however, account for long-range attractive forces, because they do not incorporate a Van der Waals term.

Landman et al. [55] verified the onset of jump-to-contact instability by means of MD simulations and compared their results to AFM measurements for a nickel tip interacting with a gold substrate. In MD simulations the tip is modeled as a pyramid with an effective radius of curvature of  $\cong 30$  Å and the sample is made up of 11 layers of 450 atoms per layer. The interatomic interactions governing the energetics and dynamics of the system are modeled by means of the embedded-atom method (EAM). In the EAM [56], the dominant contribution to the cohesive energy of the material is viewed as the energy to embed an atom into the local electron density provided by other atoms of the system. The AFM measurements were carried out with a nickel tip with a radius of curvature of  $\cong 200$  nm and the cantilever spring constant is  $\cong 5$  kN/m. The measurements were done under dry nitrogen.

MD simulation shows the onset of an instability when the tip is at a distance of 4.2 Å from the sample. This jump-to-contact is associated with a tip-induced sample deformation and the process involves large atomic displacements ( $\cong 2$ Å) occurring in a time span of  $\cong 1$  ps. When the tip jumps onto the surface, the distance decreases from 4.2 to 2.1 Å. Just after the jump-to-contact, in addition to the adhesive contact between the two surfaces, a partial wetting of the tip bottom by Au atoms induced by adhesion is observed (panel (a), Fig. 11). Pressure contours reveal that atoms at the periphery of the contact area are under extreme tensile stress ( $\cong 10$  GPa), in accord with the JKR theory (panel (b), Fig. 11). In the AFM experiment the magnitude of the force and the distance from the sample at which the tip begins to deviate from zero are much larger than those predicted by the MD simulation. The authors list several causes of these differences: tip dimensions, cantilever elastic constant, neglect of long range attractive forces in MD calculations, tip and sample roughness, and the exposure to air of the tip and sample.





Fig. 11. Atomic configuration generated by the MD simulation (panel (a)) and calculated pressure contours just after the jump-to-contact (panel (b)) (reprinted with permission from [55]; copyright 1990 American Association for the Advancement of Science).

# 3.2. Withdrawal curve: jump-off-contact and adhesion forces

The second discontinuity of force-displacement curves, the jump-off-contact, occurs when, during the withdrawal of the sample, the cantilever elastic constant is larger than the gradient of tip-sample adhesive forces.

As we have already seen in Sections 2.2 and 2.3, the jump-off-contact is related to tip and sample surface energies via equations that depend on materials dimensions, stiffness, and adhesion. The jump-off-contact force can be deduced from Fig. 9. For an infinitely stiff tip-holder, the pull-off load is given

by the horizontal tangent to the deformation-load curves in panel (b) of Fig. 9. When the apparatus has a finite stiffness, the tangent to the curve in panel (b) of Fig. 9 with a slope corresponding to the elastic constant of the support has to be drawn. It is evident that Maugis theory shows that the pull-off force gradually passes from  $(F_{ad})_{JKR} = -3/2\pi RW$  to  $(F_{ad})_{DMT} = -2\pi RW$  as the parameter  $\lambda$ , that describes tip and sample dimensions, stiffness, and adhesion, decreases. Similar results were obtained by Müller et al. [32] and have been confirmed by Greenwood [35]. Hence, measuring the pull-off force is not an accurate method to estimate surface energies. Nevertheless, the jump-off-contact shows a wide range of adhesive material properties.

The jump-off-contact deflection and the jump-off-contact distance are always greater than jump-tocontact deflection and jump-to-contact distance, respectively. This occurs for several reasons.

- 1. During the contact some chemical bonds or adhesive bonds may engender non-conservative forces.
- 2. During the contact, the sample deforms, buckles and "wraps" around the tip, increasing the contact area, because of the elastic behavior described in Section 2, but also under the influence of particular tip-sample forces (e.g., hydrophobic force and viscoelastic forces). Thus, soft materials with low cohesive energies containing hydrophobic groups, as some biological materials, have a large pull-off force in water, and the jump-off-contact occurs as a gradual detachment rather than a sharp discontinuity.



Fig. 12. Neck formation in the case of a separation without indentation (panel (a)) and a cut through the system at the point of maximum indentation, i.e., the point M in panel (c) (panel (b)). The calculated force-displacement curve corresponding to the situation in panel (b) is shown in panel (c). The capital letters from D to X indicate the stages of the non-monotonic detachment (reprinted with permission from [55]; copyright 1990 American Association for the Advancement of Science).



Fig. 12. (contd.)

- 3. Meniscus force exerted by layers of liquid contaminants (chiefly water) acts against the pull-off [57].
- 4. In the absence of chemical bonds, non-elastic deformations or meniscus forces, the interaction force could be described by a Lennard-Jones like force and the mechanisms involved in force-displacement curves acquisition would be well described by Fig. 2. It is evident that, also in this case, the discontinuity CC' is greater than BB'. This is the most important reason of force-displacement curves hysteresis, because it is almost always present.

As for the jump-to-contact, it is not possible to eliminate the jump-off-contact and the approachwithdrawal hysteresis, even in the absence of chemical bonds, non-elastic deformations or meniscus forces and even if the tip-holder is infinitely rigid. This phenomenon is illustrated by the MD calculations of Landman et al. [55] already discussed in Section 3.2.

In their work, both MD simulations and AFM experiments have been performed with and without indentation. When the tip is immediately withdrawn after jump-to-contact, i.e., it is not allowed to

indent the sample, the separation is associated with inelastic processes in which the surface atoms of the gold sample adhere to the tip. While the tip is further lifted, the contact area decreases and a thin "adhesive neck" forms, as shown in panel (a) of Fig. 12. This neck breaks at a distance of 9–10 Å. The pull-off force is of the order of 40 nN.

When the tip is allowed to indent the sample, the connective neck is wider and elongates for a larger distance during withdrawal, as shown in panel (b) of Fig. 12. The elongation process occurs in several stages in which the atoms of a layer disorder and then rearrange to build up another layer, i.e., to extend the neck. The number of atoms in the neck is roughly constant throughout the elongation process. These stages result in a series of monotonous decrease of attractive forces (just after the creation of a new Au layer in the neck) followed by increase (before the formation of a further layer), as indicated in panel (c) of Fig. 12. The pull-off force is about 60 nN and the neck breaks at a distance of about 13 Å.

The same behavior (a series of discontinuities) has been predicted for the case of the fracture between two identical materials by Lynden-Bell [58]. Pethica and Sutton [54] and Attard and Parker [31] obtained similar results by use of Lennard-Jones potentials.

The associated AFM experiments of Landman et al. exhibit approach-withdrawal hysteresis both with and without indentation. The jump-off-contact force is  $\cong 4 \,\mu N$  without indentation and  $\cong 5 \,\mu N$  with indentation. Pull-off distances are of the order of 16 nm. However, the non-monotonic features predicted by MD calculations are not discernible in the withdrawal curve after indentation. The experiment is apparently not sensitive to such individual atomic-scale events when averaged over the whole contact area.

In 1995, Agraït et al. [59] have succeeded in detecting such discontinuities during jump-to-contact and jump-off-contact. They have measured forces between a gold tip and a gold substrate in vacuum at liquid helium temperature (the substrate is mounted on the cantilever and also the tunneling current can be measured). They showed that necks are formed during jump-to-contact and jump-off-contact, and that such necks elongate (compress) during the unloading (loading) process. As the neck is elongated, the current decreases stepwise, while the force decreases with an oscillatory sawtooth-like behavior. Abrupt relaxations of current correlate to abrupt relaxations of force and they occur at 0.1–0.2 nm intervals in displacement. During a complete loading–unloading cycle, structural transformations are reversible. The neck radius varies about 1 nm in an elongation of 1 nm. The effective elastic constant of the necks varies linearly with the contact radius (see also Ref. [60]).

The increase of force–displacement curves hysteresis with indentation has also been observed by Weisenhorn et al. [61]. For indenting distances smaller than 10, 70 and 150 nm, the pull-off force is smaller than 0.35, 0.35 and 0.70 nN. Toikka et al. [62] have measured the dependence of pull-off force and adhesion energy on the loading force in air and in water. In air the adhesion energy goes from 3 mJ/ $m^2$  for zero load up to 5 mJ/ $m^2$  for a loading force of 120 nN. In water it goes from 0.3 mJ/ $m^2$  for zero load up to 1.2 mJ/ $m^2$  for 120 nN. These authors also verified an hysteretical behavior in the dependence of pull-off force along a complete cycle, i.e., first increasing and then decreasing the loading force.

We have already said that both the jump-to-contact and the jump-off-contact due to inherent stiffness of the tip cannot be eliminated, but in AFM force-displacement curves, jumps are also due to the stiffness of the cantilever, and so they could be eliminated using a stiffer cantilever to the detriment of force sensibility. Alternative approaches, making use of magnetic or electric force feedback loops, have succeeded in eliminating force-displacement curves discontinuities. In 1992, Gauthier-Manuel [63] devised a feedback loop, using an inhomogeneous magnetic field produced by a coil, in order to keep constant the force on a tip and prevent it from jumping onto the sample surface. By means of such an apparatus, the author could sample the entire tip-sample force law. The feedback loop was not applied to an usual AFM tip mounted on a cantilever, but the author himself noted that this would be possible. Jarvis et al. [64] and Yamamoto et al. [65] have developed a feedback loop (similar to the one of Gauthier-Manuel) to be applied to the AFM tip. The force on the cantilever, and hence the cantilever deflection, is kept constant and the tip-sample force is deduced from the feedback correction signal. In both works force-distance curves without hysteresis are shown. In order to make the tip sensitive to the applied magnetic field, a small piece of magnetic material is mounted directly behind the tip. Quite different approaches are that of Joyce and Houston [66], in which the force is counterbalanced by a differential capacitance sensor acting also as displacement detector, and that of Bryant et al. [67], in which the deflection of the cantilever is measured by means of

By using these feedback techniques, the stiffness of the cantilever is in practice infinitely increased (no displacement of the tip occurs, whichever is the amplitude of the force) without decreasing the force resolution. The distance dependence of the force can be entirely sampled without losing the details.

## 4. The zero line

The zero lines are the parts of force-displacement curves in which the tip exerts no force on the sample, e.g., when the tip and sample are far apart, and the tip does not deflect.

Despite that almost no force can be detected in this portion of the curve, zero lines have a great importance in that, as discussed in Section 1, all distances are referred to the cantilever rest position. Thus, the forces can be calculated only when the deflection of the cantilever, i.e., the difference between the current deflection and the rest position, is known. The latter is given by the zero line.

Zero lines seldom happen to be lines. They always have a superimposed oscillation due to optical interference between the beam reflected by the upper face of the cantilever and that scattered by sample surface, as shown in Fig. 13. The laser beam (*i* in Fig. 13) reaches the sample because the laser spot is not completely inside the lever surface and because of the fact that part of the light passes through the cantilever. The beam that reaches the sample is scattered, resulting in a second beam pointing towards the photodiode  $(r_2)$ .  $r_2$  interferes with the beam reflected by the upper face of the cantilever  $(r_1)$ . The resulting oscillation has a fixed spatial period determined by the laser light wavelength and by the microscope geometry.

The optical path difference s is given by [61]:

$$s = n \frac{(1 + \cos 2\Theta)}{\cos \Theta} D, \tag{4.1}$$

in which D is the cantilever-sample distance,  $\Theta$  the incidence angle and n is the refractive index of the medium. If  $\Lambda$  is the wavelength of the laser, the spatial period of the oscillation is given by

$$\bar{D} = \frac{\Lambda}{n((1 + \cos 2\Theta) / \cos \Theta)}.$$
(4.2)



Fig. 13. Schematic representation of the interference between the laser beam reflected by the upper face of the cantilever and the beam scattered by the sample surface, resulting in an oscillation on the zero lines of the force–displacement curves.

Also the zero lines exhibit a kind of hysteresis that results in a separation of approach and withdrawal traces. The hysteresis of zero lines is due to the viscosity of the medium. The viscous force pulls the cantilever upward when approaching the sample and makes it bend downward when the sample is withdrawn. Hoh and Engel [40] have measured this hysteresis by altering the viscosity of the medium and the scan rate. Force-displacement curves obtained in water and glycerol are shown in Fig. 14. In water, there is a notable effect for velocities bigger than 30 µm/s. The separation between approach and withdrawal zero lines is about 5 nm for a cantilever 200 µm long, a scan range of 500 nm and a scan rate of 40 µm/s. In a high viscosity medium such as glycerol (15 P instead of  $10^{-2}$  P for water) the separation becomes very large even at low scan rates ( $\cong 10$  nm for 0.6 µm/s and  $\cong 50$  nm for 4.8 µm/s). In a low viscosity medium such as air ( $2 \times 10^{-4}$  P) zero lines hysteresis is hardly detectable (see also Ref. [68]).



Fig. 14. Zero-lines hysteresis in water and in glycerol. On the x-axis, the sample position in nm. On the y-axis, the cantilever deflection in nm. (reprinted with permission from [40]; copyright 1993 American Chemical Society).

# 5. Calibration

### 5.1. Methods for the calculation of forces

All AFM, whether home made or not, provide the cantilever deflection as a function of the distance between the sample and the rest position of the cantilever. In order to know the tip-sample force, several transformations of the data have to be performed. Eq. (1.10) reveals that, if the sample is much more rigid than the cantilever and no deformation of the sample occurs, along the contact line the deflection of the cantilever equals the displacement of the piezoactuator, i.e.,  $\Delta \delta_c = \Delta Z$ .

Usually, if the optical lever method is employed, the deflection of the cantilever is given by the voltage output of the photodiode. This voltage, however, depends also on laser spot shape and dimensions. Along the contact line, the relation between the voltage output  $\Delta V$  and the displacement of the piezo is given by

$$\Delta\delta_{\rm c} = \Delta Z = \Delta V / \Omega, \tag{5.1}$$

where  $\Omega$  is a proportionality factor. In order to know  $\delta_c$  the zero deflection value  $V_0$  of the voltage is needed, and can be determined from the zero line.

A first problem with this procedure is associated with the hysteresis and the creep of the piezo, affecting the measurement of Z. As a general rule, the response of the piezo should be checked previous to any force-distance curves acquisition and Eq. (5.1) should be applied to approach curves. Furthermore, depending on the sample, the relation  $\Delta \delta_c = \Delta Z$  might not be correct at low loads. Hence, as a rule of thumb, it is always better to consider in the above procedure the tangent to the loading curve at high loads. The origin of the Z axis is placed at the beginning of the contact line. Because of tip asperities, the contact line may begin prior to intimate true contact. Thus, the asperities on the tip affect the determination of tip-sample distances. Taking into account all these effects, tip-sample distances can be determined by means of the equation:

$$\Delta Z = -\frac{L_{\rm p}}{w_{\rm p}} \, d_{31} \Delta V, \tag{5.2}$$

in which  $L_p$  and  $w_p$  are the length and the wall thickness of the piezotube,  $d_{31}$  is a proportionality factor characteristic of materials, and V is the voltage applied to the piezo.

The factor  $\Omega$  in Eq. (5.1) depends on the dimensions and on the shape of the laser spot on the photodiode, and hence depends on the refractive index of the medium in which the measurements are performed [69]. Furthermore, this factor may change in time due to the thermal drift of the components of the microscope, and should be checked previous to any measurement.

Once the deflection of the cantilever in nanometers is known, the product  $k_c \Delta \delta_c$  gives the force in newtons:

$$\Delta F = k_c \Delta \delta_c = k_c \Delta V / \Omega. \tag{5.3}$$

Once the true tip-sample distance is known, and the force has been deduced from cantilever deflections, the curve can be rearranged in order to give a "normalized" representation, i.e., a plot of the force vs. the true tip-sample distance D. This representation is referred to as the "force-distance curve" (see Section 1.2). This procedure corresponds to the reversal of the geometric construction presented in Section 1.2.

The main problem in the calculation of forces is given by the knowledge of the cantilever elastic constant.

# 5.2. The cantilever elastic constant and the tip radius

The nominal elastic constant of rectangular and "V"-shaped [70] cantilevers is given by

$$k_{\rm c} = \frac{E t_{\rm c}^3 w}{4L^3}$$
 (rectangular cantilever), (5.4)

and

$$k_{\rm c} = \frac{{\rm E}t_{\rm c}^3 Wb}{2b(L_1^3 - L_2^3) + 6WL_2^3} \quad (``V`'-shaped cantilever),$$
(5.5)

in which  $t_c$  is the thickness, E is the Young modulus and the other quantities are defined in Fig. 15. Eq. (5.5) is not an exact formula. The elastic constant of "V"-shaped cantilevers was calculated by use of the "parallel beam" approximation [71, 72], in which the "V"-shaped cantilever is modeled as a couple of rectangular cantilevers. Sader and White [73] have demonstrated the inaccuracy of such an approximation by means of a finite element calculation.

A more accurate formula has been given by Neumeister and Ducker [74]:

$$k_{c} = \left[\Delta_{I} + \Delta_{II} + \Psi\left(\frac{W}{\sin\alpha} - d\right)\right]^{-1},$$
  

$$\Delta_{I} = \frac{3}{Et_{c}^{3} \operatorname{tg}\alpha} \left[ \left(\frac{W}{\sin\alpha} - 2d\right)^{2} - d^{2} \left(2\log\frac{W}{d\sin\alpha} + 1\right) \right],$$
  

$$\Delta_{II} = \frac{L^{2}}{EWt_{c}^{3} \cos^{2}\alpha} \left[ \frac{2L}{\cos\alpha} + 3(W\cot\alpha - d\cos\alpha - \vartheta\sin\alpha) \right],$$
(5.6)



Fig. 15. Schematic representation of a rectangular and a "V"-shaped cantilever. L and w are the length and the width of the rectangular cantilever, W is the width of the arms of the "V-shaped" cantilever,  $\alpha$  is the angle between the arms, b and  $L_2$  are the base and the height of the triangle at the end of the "V-shaped" cantilever,  $L_1$  is the total height of the "V-shaped" cantilever, and d is the distance between the center of the tip and the end of the cantilever.

and

$$\Psi = \frac{3L(1+\nu)}{\mathrm{E}Wt_{\mathrm{c}}^3\cos\alpha} \left(\frac{W}{\sin\alpha} - d + \vartheta\cot\alpha\right),$$

in which  $\nu$  is the Poisson ratio and  $\vartheta$  is given by

$$\vartheta = \frac{L \operatorname{tg} \alpha + (W - d \sin \alpha)(1 - \nu) \cos \alpha}{2 - (1 - \nu) \cos^2 \alpha}.$$
(5.7)

All the above formulas depend on the knowledge of E and  $\nu$  (E = 304 GPa and  $\nu$  = 0.24 for the silicon nitride) that can be measured by different techniques (see Ref. [75] and references therein). Anyway, each cantilever has its own elastic constant that can vary between cantilevers on the same wafer, and hence, rather than calculate them, it would be better to measure them. Several methods have been proposed for doing this as indicated below.

The most effective method is that proposed by Cleveland et al. [76]. Consider a rectangular cantilever with elastic constant  $k_c$  and mass  $m_c$ . The resonance frequency of this cantilever is

$$\omega_0 = \sqrt{\frac{k_c}{m^*}}.$$
(5.8)

The effective mass  $m^*$  is given by  $m^* = m_c + 0.24 m_t$ , where  $m_t$  is the mass of the tip. When an extra mass M is added, the resonance frequency becomes

$$\omega_1 = \sqrt{\frac{k_c}{M + m^*}}.$$
(5.9)

By measuring  $\omega_1$  and  $\omega_0, k_c$  is given by

$$k_{\rm c} = \frac{M}{1/\omega_1^2 - 1/\omega_0^2}.$$
(5.10)

The added extra mass is usually a sphere placed near the end of the cantilever. Since the sphere is secured onto the cantilever by adhesive forces (e.g., capillary force), the method turns out to be non-destructive.

Senden and Ducker [77] have proposed a similar method in which a tungsten sphere (10–50  $\mu$ m in diameter) is glued at the end of the cantilever and the static deflection due to gravity is measured. Subsequently, the cantilever is turned upside down and the deflection is measured again. The difference  $\Delta \delta$  between the two measurements is twice the deflection due to the gravity. The deflections can be calibrated as shown in Section 5.1 and the spring constant is given by

$$k_{\rm c} = \frac{8\pi R^3 \rho g}{3\Delta\delta_{\rm c}},\tag{5.11}$$

in which R is the radius,  $\rho$  the density of the sphere and g is the gravitational acceleration. Hutter and Bechhoefer [78] have measured the spring constant of the cantilever from the power spectral density of cantilever fluctuations due to thermal noise. If the cantilever is modeled as a harmonic oscillator, then

$$\left\langle \frac{1}{2}m\omega_0^2\delta_c^2 \right\rangle = \frac{1}{2}k_{\rm B}T; \quad \omega_0^2 = k_{\rm c}/m \quad \text{and} \quad k_{\rm c} = k_{\rm B}T/\langle\delta_c^2\rangle.$$
 (5.12)

Rabinovich and Yoon [79] have calibrated the spring constant of a cantilever by comparing it with the spring constant of a glass fiber. The glass fiber spring constant is measured by detecting its deflection under a known weight. After mounting the glass fiber on a piezoactuator, it is brought into contact with the cantilever of unknown elastic constant. The cantilever spring constant is given by

$$k_{\rm c} = k_{\rm f} \left( \frac{\Delta Z}{\Delta \delta_{\rm c}} - 1 \right), \tag{5.13}$$

in which  $k_f$  is the spring constant of the glass fiber and  $\Delta Z$  is the displacement of the piezo. The same authors have tested their technique together with that of Ducker and Senden, and have compared the values obtained with those calculated by means of Eq. (5.4) [80]. All three methods give  $k_c$  values within  $\pm 7\%$  of each other.

Finally, Sader et al. [81] have developed a technique to calculate the cantilever spring constant once the mass or the density of the cantilever is known. These quantities are not provided by the manufacturers, so the method is rather useless.

Another major problem encountered when a quantitative treatment of force-distance curves is undertaken is the characterization of the size and shape of tips. Forces depend on the dimensions of the tip both on a mesoscopic (overall shape of the tip) and a microscopic range (shape of the apex and presence of asperities). Although several approaches to characterize AFM tips exist, none of them provides a reliable and general technique easily applicable to all cases.

A first approach is the examination of tips with the transmission electron microscope (TEM) [82]. If  $Si_3N_4$  tips are to be imaged by TEM, then a coating with Pt/Pd is needed in order to prevent charging, while silicon tips can be imaged without coating. Resolutions of the order of 1 nm can be attained.

Alternatively, once the process of image formation is known, given a surface of known profile employed as characterizer, the shape of the tip can be deduced from the artifacts in the image of the characterizer [83–89]. Such methods are affected by the uncertainty of characterizers profiles and by the poor reliability of mathematical reconstructions of imaging processes.

Two other methods of calibrating tip size and shape exploit the measurement by means of forcedistance curves of some forces, namely the Coulomb force [21] and the double-layer force [69]. These are treated in Sections 6.1.2 and 6.3.2.

In order to eliminate the problem of the unknown shape of the tip, Ducker et al. [17] have used modified cantilevers with tips of known geometry. Such a technique, generally known as "colloidal probe technique", has been widely employed in force–distance curves acquisition. It is implemented by gluing at the end of a cantilever a sphere of radius between 2 and 10  $\mu$ m by means of an epoxy resin. The radius of the sphere can be determined by electron microscopy and the mean roughness by AFM measurements. Fig. 16 shows a colloidal tip glued on a cantilever. A wide variety of materials has been employed: silica [17], TiO<sub>2</sub> [91], ZnS [62,92], gold [93], polystyrene [94] and others. When a colloidal probe is used, curves are often presented as a logarithmic plot of the ratio  $F/R_{\text{eff}}$  vs. the tip–sample separation. The advantage of this technique lies in the exact knowledge of the tip geometry, but it turns out to be disadvantageous when a high lateral resolution is needed. Thus, it cannot be effectively used in force–distance curves mapping.

#### 5.3. Noise and systematic errors

Some general considerations on noise and systematic errors in force-distance curves acquisition are discussed here. Other specific artifacts are listed in Sections 2.4, 6.2.3, and 6.3.3.



Fig. 16. A silica colloidal probe attached on a silicon nitride cantilever (reprinted with permission from [90]; copyright 1993 American Chemical Society).

The noise level of a force-distance curve, due to thermal agitation, mechanical vibrations of the apparatus and/or turbulence of the liquid environment, depends on the cantilever stiffness, and is usually  $\leq 30$  pN. Sources of the noise vary widely. Along the zero lines the noise is dominated by the thermal agitation, whereas along the contact lines, the thermal agitation is damped but mechanical vibrations are enhanced. In order to minimize the effects due to thermal drift, force-distance curves should be acquired with high scan rates but, over a certain threshold speed, dynamic effects begin to affect the measurement. This threshold value depends on the environment and can be roughly put at 1  $\mu$ m/s in air [95]. Another obvious approach to minimize thermal noise consists in averaging several force-distance curves acquired on the same point and in the same conditions. This approach implies a careful superposition of curves.

The calculation of forces is affected by systematic errors in the estimation of the cantilever spring constant and tip radius. Since deflections are obtained from the contact line through Eq. (5.1), errors due to the sample compliance are possible, and are specific for each material and sample.

The estimation of distances is affected by systematic errors in piezo response and by piezo hysteresis and creep, which depend on the history of the piezo and on the scan rate.

Finally, digitalization errors must be considered. Siedle and Butt [68] have demonstrated that the cantilever oscillates due to its coupling to the discrete steps of the piezo via the liquid. This oscillation affects both the zero deflection and the determination of the jump-to-contact.