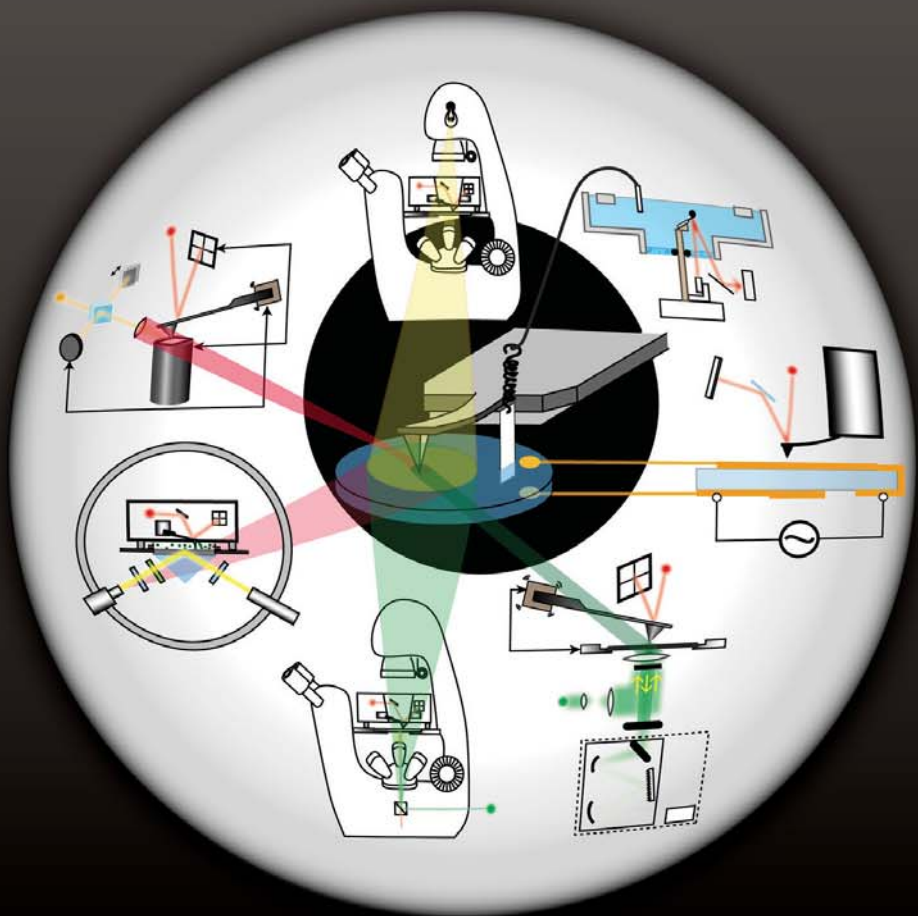


HYBRIDIZING SURFACE PROBE MICROSCOPIES

Toward a Full Description
of the Meso- and Nanoworlds



SUSANA MORENO-FLORES
JOSE L. TOCA-HERRERA

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Preface

Many are the books and reviews about scanning probe microscopies that cover the basics of their performance, novel developments, and state-of-the-art applications. This book may appear to be another of this kind. But it is not.

Indeed, this is not another book about scanning probe microscopy (SPM). As authors, we do not aim to focus on what SPM *can* do, but rather on what SPM *cannot* do and, most specifically, on presenting the experimental approaches that circumvent these limitations.

The approaches are based on the combination of SPM with two or more techniques that are complementary, in the sense that they can do something that the former cannot. This serves a double purpose; on the one hand, the resulting hybrid instrument outperforms the constituent techniques, since it combines their individual capabilities and cancels out their individual limitations. On the other hand, such an instrument allows performing experiments of dissimilar nature in a simultaneous manner.

But to understand the limitations of any technique also means to understand how this technique works. We do not skip this essential point; on the contrary, we have devoted a considerable amount of book space in explaining the basics of each technique as they are introduced. In the case of SPM, we have endeavored to present its fundamentals from a different, rather intuitive, perspective that, in our opinion, makes it distinctive from previous literature on the topic, and it ultimately serves a pedagogical purpose. At the same time, we have tried to avoid explaining the particularities of each SPM-based technique and opted for a rather generalized approach that may *suit everyone*. In this context, each member of the SPM family is presented as a particular case.

Though the contents of the book are organized in eight chapters, they follow a rather subtle scheme that revolves around the two main capabilities of SPM: that of imaging and that of measuring interactions. The fundamentals of SPM imaging are explained in Chapter 2 and followed by suitable combinations of SPM imaging with far-field and near-field optical microscopy, spectroscopy, and surface-sensitive techniques. These combinations are described in Chapters 3, 4, 5, and 6, respectively. Likewise, the fundamentals of SPM to measure interactions are explained in Chapter 7, followed by corresponding combinations with microinterferometry and film balance, which are both described in Chapter 8.

Each chapter that deals with one or more combinations of the type *technique A–technique B* starts with a historical account of the technique that is being introduced (*B*), followed by some background information that may be required to fully understand the contents of the chapter. The chapter then continues with the fundamentals of the *technique B* and the description of the combined *technique A–technique B* setup. The chapters end with some case examples where the combination has been applied in research. Research topics range from materials science to biosciences.

Because *this is not another book about scanning probe microscopy*, the content is addressed to a wide spectrum of readers, from researchers to teachers, without

forgetting the student community. We hope that the text will fulfill their expectations. This would make us happy.

Last but not least, we would like to greatly thank Dr. Rafael Benitez, Uwe Rietzler, and Dr. Enrico Gnecco as well as the respective libraries of the University of Extremadura, the Max Planck Society, and the Spanish CSIC for providing useful literature references. Likewise, we are greatly thankful to Jacqueline Friedmann, Dr. Roberto Raiteri, and Professors Helmut Möhwald, Andreas Fery, and Georg Papastavrou for their valuable comments and proofreading.

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1 Introduction

Experimental science is the framework we use to observe and understand nature. It comprises a series of instrumental techniques through which we constantly put nature to the test; mathematical tools to quantitatively describe the instrumental output; and our capacity of reasoning, background knowledge, and common sense to find a rational explanation out of it. The first two steps, namely measurement and analysis, are repeated a number of times to ensure that the observed result is reproducible before thinking of a possible explanation.

Nature is rather complex, so we humans have compartmentalized it in a series of objects, processes, and diverse phenomena that we can tackle separately. The division of nature has led to the division of knowledge in a series of scientific disciplines, each with its own battery of technical and theoretical tools and even with its own terminology and concepts. This parallel and, in some aspects, unequal run in understanding nature has ruled the way of doing science since its origins.

This remained the case until disciplines stopped and stared at what others were doing, and they realized that our understanding of nature could be largely benefited from the exchange of information between the different disciplines. Nowadays, interdisciplinarity dictates the tempo of science. The various fields of knowledge borrow concepts, theories, and even techniques from one another with the goal of fusing the diverse knowledge about nature.

The next step toward this goal may involve exactly this word, *fusing*—fusing concepts, fusing theories, fusing techniques. This book is about the latter. The integration of techniques, either from one discipline (intradisciplinary techniques) or from different ones (interdisciplinary techniques) may evolve our way of doing science and significantly improve our knowledge of nature.

But there is no need to wait that long. Indeed, combining techniques may have an immediate impact in the way we do experiments, and that is through what may be called simultaneous measuring.

OBSERVING NATURE: SEQUENTIALITY AND SIMULTANEITY

Obvious as it may appear, the study of processes or phenomena occurring in nature should be as complete as possible, and this mainly requires investigating them from different points of view. Each so-called point of view may focus on one characteristic property, usually obtained through experiment with an instrumental technique. Though convenient and informative in most cases, a single property may not suffice a comprehensive description of phenomena. Rather, it is preferred to gather as many characteristic properties as possible—therefore the need to employ more than one technique.

Observing nature with several techniques can be done either sequentially or simultaneously. The sequential approach may as well follow the “one for one” maxim: one sample for one technique at a time. The strategy is depicted in the upper-left part of Figure 1.1. The object of study (the sample) is measured with a first technique; after completion, the very same one, or another, which should be a duplicate of the first one, is measured with a second technique, and so on until the sample, or another identical, is measured with the i th-technique. We have already commented on the importance of obtaining reproducible results. In sequential measurements, the reproducibility follows the “all for one” maxim: all samples for one technique at a time. Each technique demands to repeat the experiment with several identical samples (upper-right part of Figure 1.1). If N is the number of samples per technique, a total of $N \cdot i$ measurements is required. The procedure can thus be demanding, lengthy, and prone to experimental mistakes, for example if errors occurred in the duplication of samples (as many as $N \cdot i$ in total). On the other hand, the method proves robust, since it thoroughly tests the reproducibility of the sample and the instruments.

However focusing on one single property at a time may make us not see the wood for the trees. A naturally occurring event of scientific interest may be efficiently described if it is simultaneously *covered* by a set of techniques—just as a program or event is broadcast on television, where a few cameras and microphones simultaneously track the images and sounds of the whole event from different angles and positions. Regardless of the preference of the stage manager or the likely bias of the broadcast channel, the wider the employment of technical means, the more accurate and faithful the coverage will be. The high-quality information that results from that is received by either the journalist or the audience, who will, in principle, be capable of making a good analysis.

The analogy serves us to introduce the simultaneous approach in observing data. Parallel measurements may thus obey the “one for all” motto: one sample for all techniques. The set of techniques is employed simultaneously to investigate the different aspects of the sample, as shown in the lower-left part of Figure 1.1. Reproducibility of results is accounted for by repeating the parallel measurements with several samples (see lower-right part of Figure 1.1). The total number of results will be still $N \cdot i$, but they will be attained in much shorter time with fewer samples (N).

If the *sample* is rather a dynamic process where various properties may change in parallel at differing time scales, the concept of reproducibility gains a new dimension. Processes are tested as a whole; results are not considered individually but rather in relation to others; and therefore reproducibility may as well be referred to whole processes rather than to single results.

The aim of this book is to describe a series of combined techniques that make parallel measurements possible. All combinations referred to in this book share one common partner: a scanning probe microscope (SPM). This technique is young, although it has quickly become essential in the study of the morphology of most materials with a resolution that allows the detection of molecules and even atoms. The technique is not restricted to that, though. It can also be used to track processes occurring at the boundary of two materials—interfaces—as well as to measure surface interactions. The technique is thus versatile, but it is not exempted from limitations. The combination with other techniques can greatly reduce these limitations as well as increase the

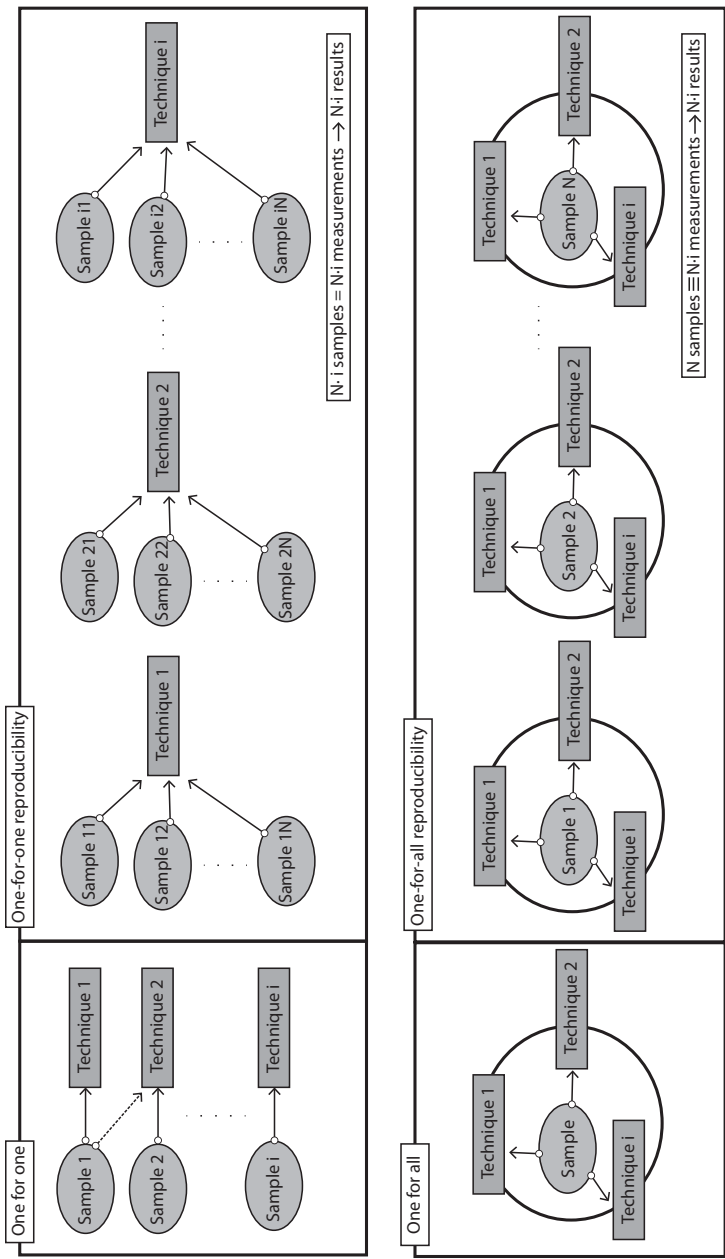


FIGURE 1.1 Measuring strategies. The upper half of the figure illustrates the “all for one” approach for sequential measurements. The same sample or several samples are used in turn with a particular technique to obtain a definite result one after the other. Repeating the same experiment with several samples (N) for each technique will prove the reproducibility of the results. The lower half of the figure illustrates the “one for all” approach for parallel measurements. In this case, a single sample is used by several techniques that simultaneously provide information about it. Reproducibility is checked by repeating the simultaneous measurement with several samples (N).

range of applicability of all techniques involved. In the following discussion, we will briefly comment on the possible synergic consequences of such combinations.

COMBINATION MACROSCOPIC/MICROSCOPIC: EXTENDING MEASURABLE RANGE TO BETTER UNDERSTAND THE CONNECTION BETWEEN ULTRASTRUCTURE AND FUNCTION

“The whole is more than the sum of its parts”...or not? Can we say more than “more”? We might dare answer the question by combining global and local techniques in order to investigate processes or characterize materials at the macroscopic, microscopic, or nanoscopic scales simultaneously.

Macroscopic techniques provide magnitudes that are actually average values over large sample regions. They include “classical” methodologies such as optical reflectometry, ellipsometry, or surface plasmon resonance. They all produce optical constants, such as thickness and/or refractive index, that is, single values to characterize samples as a whole. The combination of macro and micro techniques can shed light on how those magnitudes are affected by the microscopic and even nanoscopic nature of matter, a question of fundamental character in materials science.

An archetypical microscopic technique is optical microscopy, which is able to display images of specimens with a resolution of a few hundred nanometers. Although the technique is clearly outperformed by SPM or scanning near-field optical microscopy (SNOM) in terms of lateral resolution, its relevance is not at all undermined. Far from being mutually exclusive, optical microscopy and SPM are rather complementary. The latter significantly extends the measurable range of spatial dimensions down to very small objects, but the former ensures that we can still see the wood for the trees.

COMBINATION MODEL-BASED/DIRECT OBSERVATION

There are techniques that provide results as long as a mathematical model is applied. The model normally assumes that the sample fulfills a series of morphological characteristics, among other properties, that on the whole can be formulated mathematically. The assumptions oversimplify in the sense that they overlook to a certain extent the complexity of the real-life scenario. Consequently, models are intrinsically inaccurate.

Making the Right Choice

The key issue here is the right choice of a model. If the latter is based on assumptions of questionable validity or if it lacks in rigor, the results may be either false or inaccurate. The results are then affected by a certain uncertainty of analytical source, in addition to the usual instrumental uncertainty.

However, this inaccuracy may not stop us from using such techniques and obtaining reasonable results. Usually a model's complexity scales with accuracy, but sometimes this is not the case, and we can still use relatively simple models as long as the assumptions are “reasonable.”

How to Judge the Applicability of a Model

No doubt, a previous knowledge of our sample is a must to tackle such a question. A direct, assumption-free observation of our sample's morphology may dissipate most of the reasonable doubts, if not all. Then an imaging technique such as SPM steps in. Now we can observe the sample's morphology, and this helps us to decide whether the chosen model is wrong or not, or if it rather oversimplifies the problem and needs some refinement. The refinement may come in the shape of an SPM result: the numerical determination of sample's roughness, topological profile, spatial heterogeneity, or stiffness, which can be introduced as additional parameters in the model. The latter in turn produces a result that may be the sample's thickness, its refractive index, or its viscoelastic parameters. By using particular results and applying the refined model, we may lose generality in the short term. Yet, we immediately gain in accuracy and knowledge, which in the long run may pave the way for the generation of models of wider applicability.

COMBINATION PREPARATIVE/MEASURING TECHNIQUE

Usually sample preparation precedes the experiment, and this procedure is considered to be critically important. The procedure is essential, no doubt; without a sample there is no experiment to perform. But it is also critical in the sense that it often determines whether an experiment is a complete success or a complete failure. The protocol of sample preparation as well as the sample's transfer and mounting onto the measuring device are key steps that can simply go wrong. Sometimes we are lucky enough to detect the source(s) of error and find a solution; at other times, however, we cannot. Or, rather, we cannot find a solution.

One typical example may be the preparation of immobilized proteins onto solid supports. A simple method consists of casting one or more drops of protein-containing solution onto a clean surface, waiting a specific amount of time to allow the molecules to adsorb on the support, and rinsing the excess with water or buffer solution afterwards. The sample must be kept always in a liquid state, since the proteins may just degrade (denature) otherwise. Even if the proteins and solvents used are of the highest purity, there are many factors that may influence the sample's quality. The environmental conditions of the laboratory may bring contaminants to the exposed surface; even the sample handling by a not-too-careful experimentalist may be a source of contamination. Keeping the sample clean and wet at the same time as it is being transferred and mounted onto the instrument can be most challenging, and the process may be quite unsystematic. Given these difficulties, sample preparation can have a serious impact on the reproducibility of the results.

Combining a preparative measuring technique with SPM makes it possible to prepare the sample and perform the experiment in one pot. Using a film balance* in combination with the SPM allows to simultaneously produce monomolecular layers and study them in situ, skipping the most disturbing transfer step that may bring about

* For a detailed description of a film balance, the reader is referred to Chapter 8.

utter sample modification or even sample damage. Sensoring techniques such as quartz crystal microbalance (QCM) or surface plasmon resonance (SPR) used in combination with perfusion methods can also be integrated to track surface changes as the sample is being prepared. The number of unsystematic errors derived from the preparation of more than one sample or from mishandling will be significantly reduced.

COMBINATION OF LOCAL TECHNIQUES TO TRACK THE DYNAMICS OF PROCESSES

If one combines various local techniques that are sensitive to distinctive interfacial properties and have relatively high time resolution, it is possible to track the dynamics of processes at interfaces in a comprehensive way. For example, measuring surface interactions or the morphology of monomolecular layers as they are being formed, expanded, or contracted is possible with a combination of an SPM and a film balance; on the other hand, tracking in real time the kinetics of molecular physisorption or electrochemical deposition of matter is at hand with a combination of an SPM and an electrochemical technique and/or QCM or SPR.

COMBINATION OF LOCAL TECHNIQUES OF DIFFERENT CONTRAST

Being able to thoroughly characterize matter by measuring different properties at the same time is a goal easily achieved by combining SPM with chemical spectroscopic techniques. Mechanical contrast is the source of the first technique to detect sample features, but it undoubtedly lacks the specificity needed to be used as an identifying tool of sample constituents. Chemical spectroscopy provides the chemical contrast required in those cases, but it lacks lateral resolution. The combination of SPM and chemical spectroscopy as one type of scanning optical near-field microscopy (SNOM) makes it possible to perform local spectroscopy at a resolution of a few nanometers.

This addresses the techniques and their interrelations. But what about the objects of study? We should not forget that the ultimate goal is to attain a comprehensive view of nature. We give now two examples of systems worth studying with integrated techniques.

SYSTEMS THAT CAN PROFIT FROM COMBINED TECHNIQUES

LIVING CELLS

Cells are the building blocks of living organisms. Just as the atom is the smallest constituent of matter with chemical identity, a single cell may be considered the smallest living constituent of *living* matter. And yet it is one of the most complex single entities encountered in nature.

In a living cell, myriad processes occur simultaneously at diverse scales. Molecules and ions are constantly moving in and out of the cell through pores in the cell membrane; inside, chemicals are transported from one side of the cell to another wherever they are needed; vesicles are formed either at the cell membrane as a result of intake of nutrients (endocytosis) or inside the cell to serve as vehicles for biomolecules; the

cell can move, spread, or contract as a whole in its interaction with the environment; or it may grow, duplicate, and eventually die according to its living cycle. Each process is in itself a collection of events that involve molecular signaling, trafficking of self-organized structures, and orchestrated movements or deformations of large parts of the cell.

Single cells are certainly systems from which much can be learned if studied with combined techniques. Figure 1.2 illustrates a single cell in action while being simultaneously measured by different techniques. These techniques give complementary information, such as that provided by different cameras broadcasting a huge event. As an example, the process of cell adhesion on a solid support can be tracked in all its stages—from the anchoring step where the cell, initially suspended in solution, lands onto the support, until the spreading and growing steps where the cell significantly changes its morphology and, as well, its interaction with the solid support. Local changes at the basal membrane in close proximity with the support can be detected by techniques such as total internal reflection fluorescence (TIRF), reflection interference contrast microscopy (RICM), or QCM. If a microelectrode array is used as support, it is possible to measure the cell's extracellular potential or to locally electrostimulate the cell (Shenai et al. 2004; Saenz Cogollo et al. 2011). On the other hand, the apical membrane exposed to the surrounding fluid can be scanned by the probe of an SPM. Likewise, the probe can exert a local compression at a certain region of the cell membrane, and the transmission of this local pressure on other parts of the cell down to the basal membrane can be studied with confocal optical microscopy as well as with the other techniques mentioned previously.

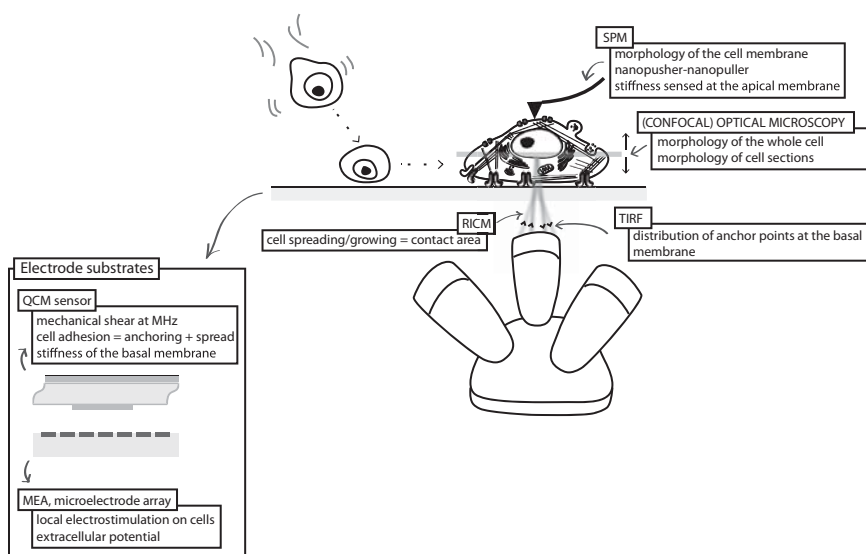


FIGURE 1.2 Samples for simultaneous measurements: living cells. Living cells are not only morphological entities, but the scenario of a plethora of interrelating processes that can simultaneously be studied by an appropriate set of combined techniques.

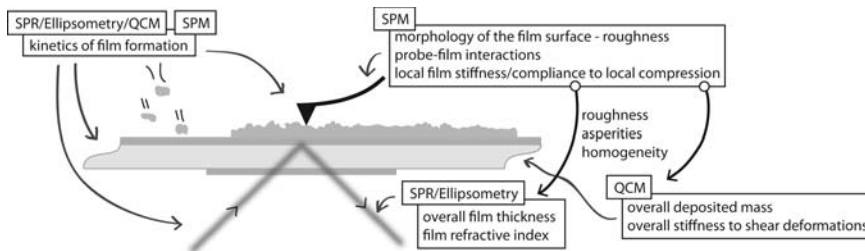


FIGURE 1.3 Samples for simultaneous measurements: films. Films can be fully characterized in terms of surface topology, surface roughness, thickness, reflectivity, and stiffness in a simultaneous manner by employing an appropriate set of combined techniques. The instruments can also be used as time-resolved techniques to track the process of film formation.

FILMS

Films made of either organic or inorganic materials can be fully characterized in a single combined experiment, as hinted in Figure 1.3. This may include the very process of film formation on a solid support, which can be tracked by techniques such as QCM, ellipsometry, or SPR. They all can record changes that occur at the boundary between the solid support and the surrounding medium. On the other hand, time-resolved SPM can be employed to observe the morphological changes of the interface as the film forms, which can greatly help to interpret the changes observed by the other techniques. Once the film is prepared, the morphology of the film surface can be scanned by SPM, whereas SPR or ellipsometry can provide optical constants of the film, such as thickness and refractive index. As we will see in Chapter 6, these magnitudes are calculated from models that assume a definite film morphology. However, if the techniques are combined with SPM and applied to single-layer films, film morphology is a direct result that can be used to validate the chosen model. An example of that is the ever-challenging issue of understanding the effect of roughness of surfaces. In this regard, topography images of the surface obtained with an SPM can be used as reference in the simulation of contact and in the determination of real contact areas between two rough surfaces that exhibit multiple asperities.

FINAL REMARKS

The book is divided into two main sections that refer to the two main capabilities of SPM: imaging and measuring interactions. Each section opens with a chapter where the fundamentals of SPM in each of its performance modes are described. The sections are completed with chapters devoted to a particular technique with which SPM has been combined. Each of those chapters starts with an account of the fundamentals of the technique, followed by a description of the combined setup(s), and ends with a few examples of scientific works where such combination has been employed.

Though we explain the basic working principles, the book is not intended to be a reference for each of the techniques mentioned here. For a deeper insight, the

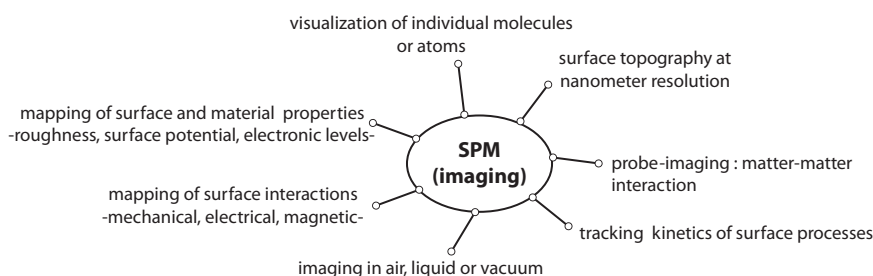
interested reader is referred to more comprehensive and specialized books and reviews listed in the reference section at the end of each chapter. The figures serve a didactic purpose and are not meant to be faithful representations of real life, inasmuch as they clarify ideas or concepts referenced in the text.

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2 Scanning Probe Microscopy as an Imaging Tool

The Blind Microscope



PROBE IMAGING

Just as an optical microscope produces a two-dimensional image through the interaction of light and matter, the scanning probe microscopies (SPMs) produce three-dimensional images through the interaction of matter and matter, the first “matter” being the sample and the second “matter” being a small, usually sharp probe.

The interaction between sample and probe can be of various types: mechanical, electrostatic, electronic, or magnetic, to mention a few. Those interactions are in most cases the source of image contrast in SPM. The information that one can extract from the sample is consequently as different as the interactions: morphology, topography, stiffness, compliance, electrical conductivity, magnetization. The results come in the shape of three-dimensional images, where each property is plotted as a function of the sample position and the lateral resolution is dependent on the probe size. To put it in numbers, ultimate lateral and vertical resolutions (in the case of topography images) amount to 5–10 nm and 1 nm, respectively. The SPM-generated imagery is routinely used in the most varied research fields, and their applicability is enormous. From micro-objects to nano-objects down to atoms—in air, in liquid, or in ultra-high vacuum—practically everything small can be *superficially yet utterly* imaged.

The history of SPM starts in 1982 with the invention of the first member of the family, the scanning tunneling microscope (STM) by Gerd Binnig and Heinrich Rohrer in the research laboratories of IBM. The revolutionary microscope was

capable of displaying the topography of surfaces down to atomic resolution. The invention constituted a major breakthrough in the field of physics, for which both scientists received the Nobel Prize just a few years later, in 1986. In that very same year, the same group published the invention of the atomic force microscope. Since then and mainly until the end of the past century, there has been a continuous flow of instrumental inventions that, in one way or another, derive from either an STM or an AFM (atomic force microscope) setup. (A detailed account of these inventions is shown in the timeline of Figure 2.1.) On the whole, the techniques constitute what has become known as the ever-expanding family of scanning probe microscopies. The twenty-first century starts off with the development of high-speed atomic force microscopy by the group of Toshio Ando. The work of these scientists has considerably improved the time resolution of the technique that now can operate at speeds comparable to video rates.

The discussion in the following background section will help the reader to understand the basics of scanning probe microscopy.

Background Information

PIEZOELECTRICITY AND PIEZO ACTUATORS

Piezoelectricity is an effect encountered in a few materials that develop an electric potential when mechanical pressure is applied to them.* Conversely, such materials can experience a mechanical deformation if an electric potential is applied instead. The deformation can be very precise and minute, on the order of nanometers, which makes them most suitable to be employed as actuators in nanopositioning and motion-control devices. This capability is of primordial importance in the field of scanning probe microscopies.

Naturally occurring piezoelectric materials such as quartz, tourmaline, or Rochelle salt exhibit very weak piezo effects, which motivated the development of synthetic polycrystalline ferroelectric ceramic materials such as barium titanate or lead (plumbum) zirconate titanate (PZT) with enhanced piezoelectric properties.

We will concentrate on PZT, since it is the material mostly employed in the SPM instrumentation. The crystalline structure of PZT is characterized by a cubic unit cell shown in Figure 2.2a that becomes deformed and asymmetric below a certain temperature, called the *Curie temperature*. Under these conditions, each individual crystallite has an associated electric dipole and is piezoelectric. Macroscopically, however, the material does not exhibit piezoelectricity as long as its microscopic electric dipoles are randomly orientated. To make it piezoelectric, it is required to induce a permanent polarization in the material by a process called *poling*, depicted in Figure 2.2b. During poling, the material is

* Unless otherwise stated, this information has been extracted from the Web page of the company Physik Instrumente (PI GmbH & Co., Karlsruhe, Germany): http://www.physikinstrumente.com/en/products/piezo_tutorial.php#DetTOC.

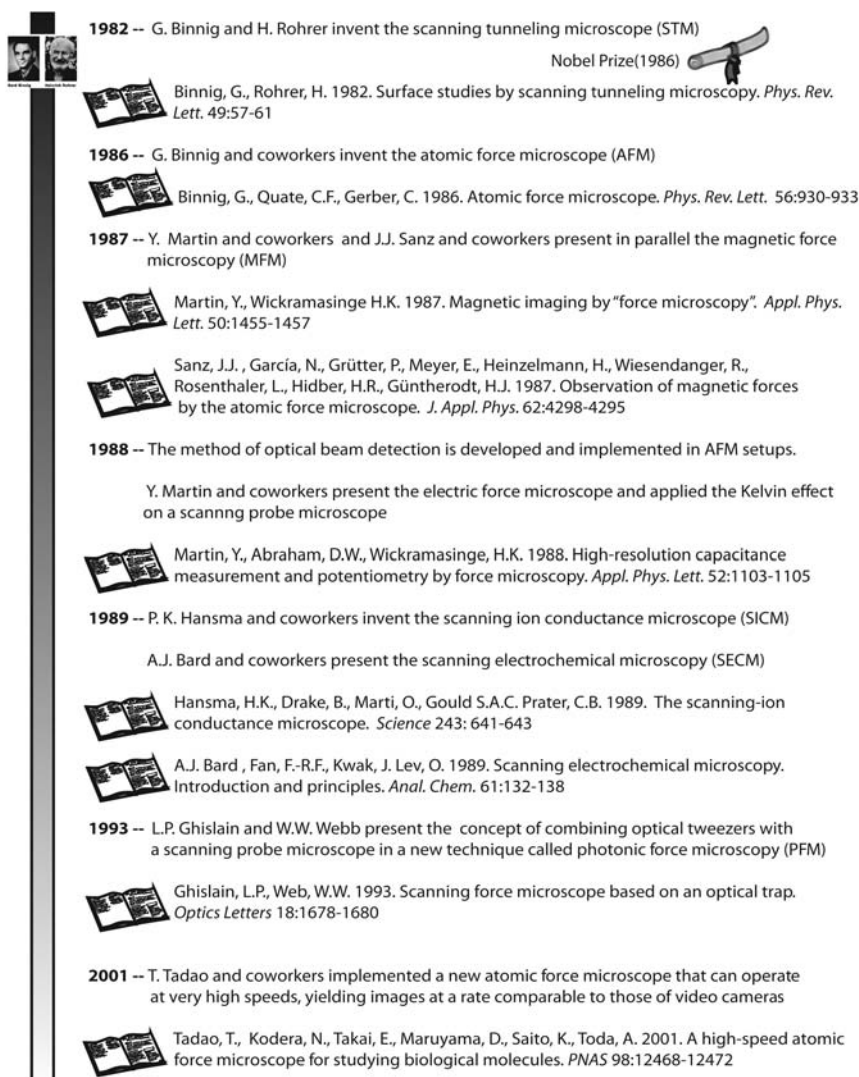


FIGURE 2.1 History of SPM. The SPMs are a collection of very young techniques with a great impact in the field of nanoscience.

subjected to a strong electric field that induces the alignment of the electric dipoles along a specific direction—that of the electric field—and hence produces an intense polarization. After poling, the PZT has a diminished though remnant polarization, which confers the material piezoelectric properties.

A piezo actuator is a piece of piezoelectric material with defined geometry. Most common geometries include the cylindrical in the case of tube piezo actuators and the rectangular in the case of laminar piezo actuators, among others. The piezo actuator has electrodes attached at specific places to generate deformations

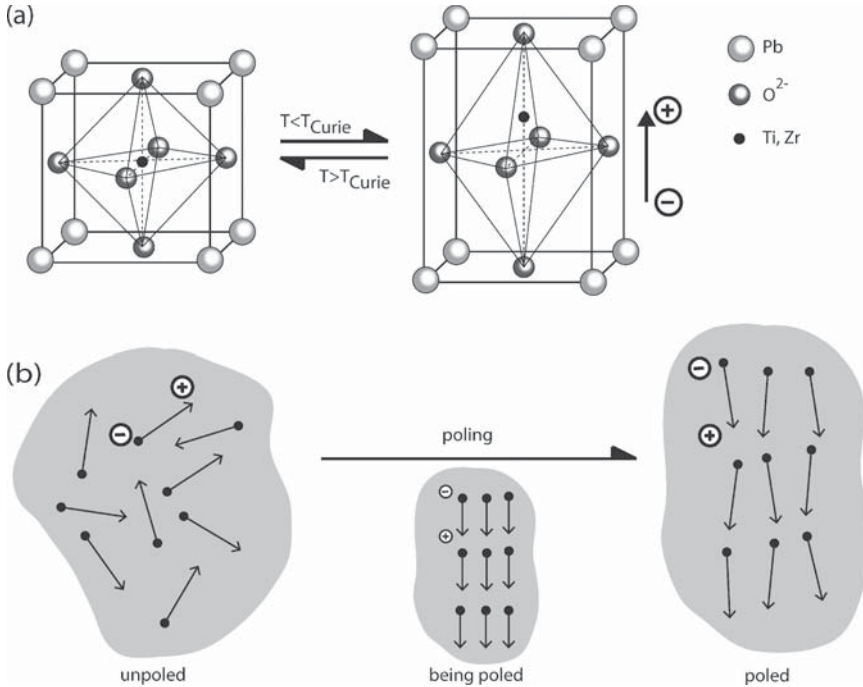


FIGURE 2.2 (a) Unit cell of a piezoelectric ceramic (PZT). Above the Curie temperature, T_{Curie} , the unit cell is cubic and has no associated dipole moment. Below T_{Curie} the unit cell deforms and so does the spatial distribution of the atoms. This results in the generation of a dipole moment, which is oriented as depicted in the figure. (b) Process of poling a piezoelectric ceramic. The dipole moments in the unpoled material are randomly oriented. During poling, the dipoles align along the applied electric field. After poling, the dipoles relax to a certain extent but remain aligned, creating a macroscopic polarization that makes the material piezoelectric.

along either one, two, or three main axes, x , y , z , denoted here as 1, 2, and 3, respectively, as shown in Figure 2.3a.

TUBE PIEZO SCANNERS

Tube piezo scanners consist of a thin-walled tube of ceramic material, silvered in and out to hold the electrodes. Two electrode pairs as long as the tube are attached at the outer wall of the cylinder, each pair oppositely placed and 90° from one another, as Figure 2.3b shows. An additional electrode is at the inner wall of the tube. An electric potential applied at each electrode pair of the outer wall results in a lateral displacement, either along the x -axis or the y -axis. To generate a tensile deformation along the z -axis (either elongation or contraction), an electric potential is applied between the outer and the inner walls of the tube. This is the *transverse piezo effect*.

The deformation along the z -axis, or in other words, the change of length of the tube, can be estimated by the following expression:

$$\Delta L \approx d_{31} L \frac{U}{d} \quad (2.1)$$

where d_{31} is the strain coefficient along the 3-axis when the potential is applied along the 1-axis (perpendicular), also called *piezo gain*. L is the original length of the tube; U is the applied potential; and d is the wall thickness. Values for d_{31} are negative and typically lie in the range of -180 to -262 pm/V (E. Meyer, Hug, and Bennewitz 2007).

Lateral displacements are achieved through tube bending. This is accomplished by applying electrical potential on the opposing electrodes at the outer walls, as Figure 2.3b shows. When the voltage is applied along one pair of electrodes, the tube flexes along one direction (e.g., along the x -axis); if the voltage is instead applied along the pair of opposed electrodes at 90° relative to the former pair, the tube will bend along the perpendicular direction, e.g., along the y -axis. The bending range ΔB , either along the x - or y -axis, can be approximated by

$$\Delta B \approx \frac{2\sqrt{2} \cdot d_{31} \cdot L^2 \cdot U}{\pi \cdot D_{\text{inner}} \cdot d} \quad (2.2)$$

where D_{inner} is the inner diameter of the tube.

Most SPMs rely on the lateral and vertical displacements of tube piezo actuators to move along the three spatial directions. Due to the tube geometry, lateral displacements are always accompanied by a displacement along the z -axis (see Figure 2.3b). This results in a vertical offset that is usually negligible for small lateral displacements compared to the tube length, i.e., $\Delta B/L \approx 10^{-7}$ (E. Meyer, Hug, and Bennewitz 2007).

STACK PIEZO SCANNER

A stack piezo scanner consists of a pile of ceramic disks separated by thin metallic electrodes (Figure 2.3b). The disks form a cylinder-like structure that elongates along its axis. This elongation of a stack piezo scanner can be estimated by the following expression:

$$\Delta L \approx d_{33} \cdot n \cdot U \quad (2.3)$$

where d_{33} is the strain coefficient (the displacement occurs alongside the field direction), n is the number of ceramic disks, and U is the applied voltage. These are the stiffest of all piezo actuator designs.

LAMINAR PIEZO ACTUATOR

Laminar piezo actuators are thin, laminated pieces of ceramics where the electrodes are placed at both sides of the slab in a sandwich-like configuration. An electric potential applied between the electrodes generates an elongation of the piezoelectric material parallel to the electrode plane (see Figure 2.3b).

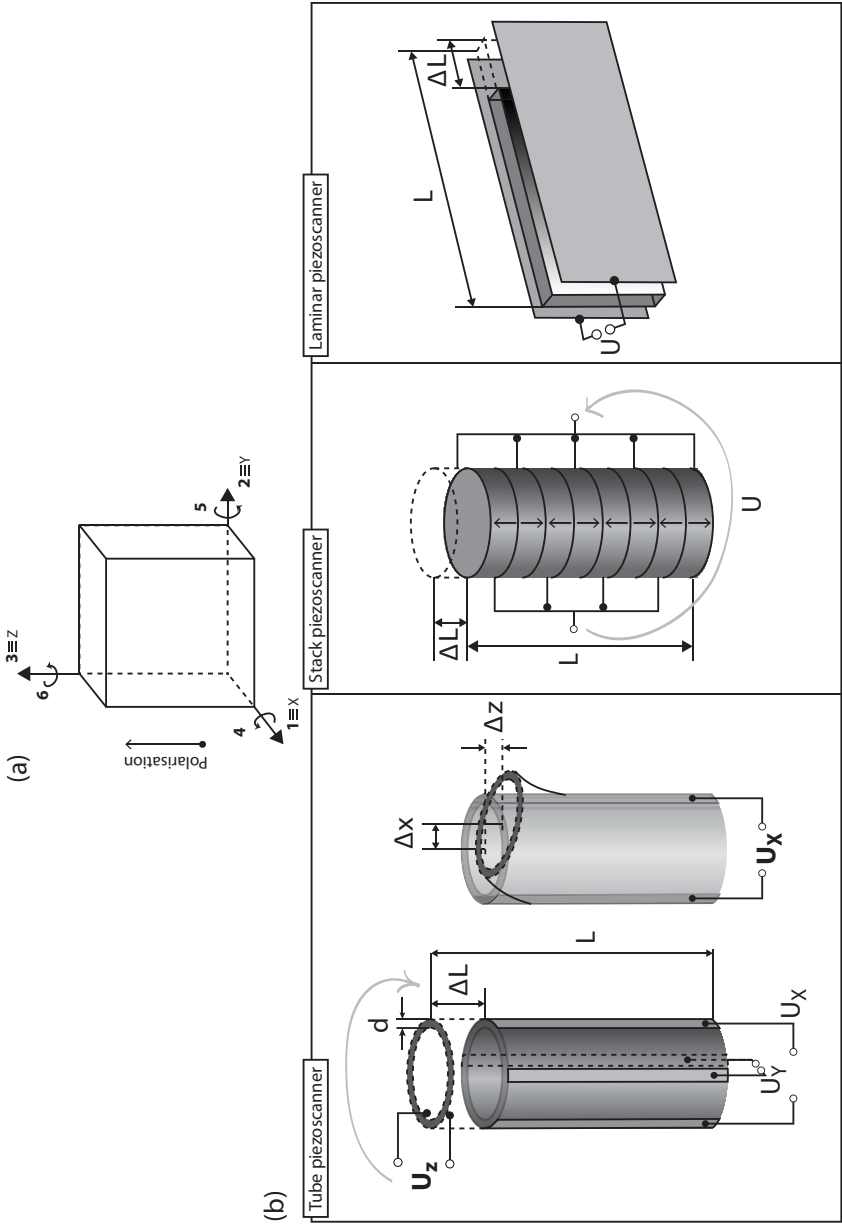


FIGURE 2.3 (See facing page.)

The displacement along the major axis of the laminar piezo actuator can be estimated by Equation (2.1); in this case, L is the major side of the slab and d its thickness.

LIMITATIONS

Piezo actuators are affected by several problems that limit their performance. These are mainly nonlinearity, hysteresis, and creep or drift.

Nonlinearity

Piezo scanners do not linearly deform with the applied voltage but exhibit certain deviation. The upper left graph of Figure 2.4 shows the elongation of a piezoelectric material when it is subjected to a gradually increasing voltage; the curve is not a straight line but, rather, it has an S shape. The ratio of the maximum deviation Δy to the ideal linear extension y , $\Delta y/y$, is called *intrinsic nonlinearity*, and it is expressed as a percentage. It typically ranges from 2% to 25% (Howland and Benatar 2000).

Hysteresis

Hysteresis is a feature that piezoelectric materials share with magnetic materials when they are subjected to a voltage cycle. As the voltage increases linearly from zero to a certain value and returns to zero in the same fashion, the actuator first elongates and then contracts. However, the position of the actuator during elongation does not coincide with that experienced during contraction.

The upper right graph in Figure 2.4 shows the change of length of the piezo actuator as a function of increasing and decreasing voltage: It follows two different paths. The hysteresis is defined as the ratio of the maximum deviation between the two curves to the maximum extension, $\Delta y/y_{\max}$. It increases with voltage, and it can be as high as 15%–20% (Howland and Benatar 2000; E. Meyer, Hug, and Bennewitz 2007), which greatly impairs the position repeatability.

Creep or Drift

Creep or drift is the time change in the piezo actuator deformation with no accompanying change in the voltage. This is especially evident after a sudden change of voltage, where the piezo actuator continues to move or deform well

FIGURE 2.3 (See facing page.) (a) Notation of axis and rotations. Axes x , y , and z are denoted 1, 2, and 3, respectively. Rotations around x , y , and z are referred as 4, 5, and 6, respectively. (b) Types of piezoscanners. (Left): The tube piezo scanner elongates its length when a potential (U_z) is applied between an outer and inner electrode by the *traverse piezo effect*. Lateral displacements are achieved by applying a potential between the oppositely oriented lateral electrodes attached at the outer side of the tube, either along the x -axis (U_x) or the y -axis (U_y). In the second case the pair of electrodes affected is that positioned at 90° with respect to the x -pair. (Middle): The stack piezo scanner is a pile of disk-like piezoceramics where the polarization is alternated, between upwards and downwards. The potential is established between the set of down-oriented and the set of up-oriented disks to produce an elongation along the axis of the stack. (Right): The laminar piezoscanner is sandwiched between two electrodes and it elongates along the direction parallel to the electrodes.

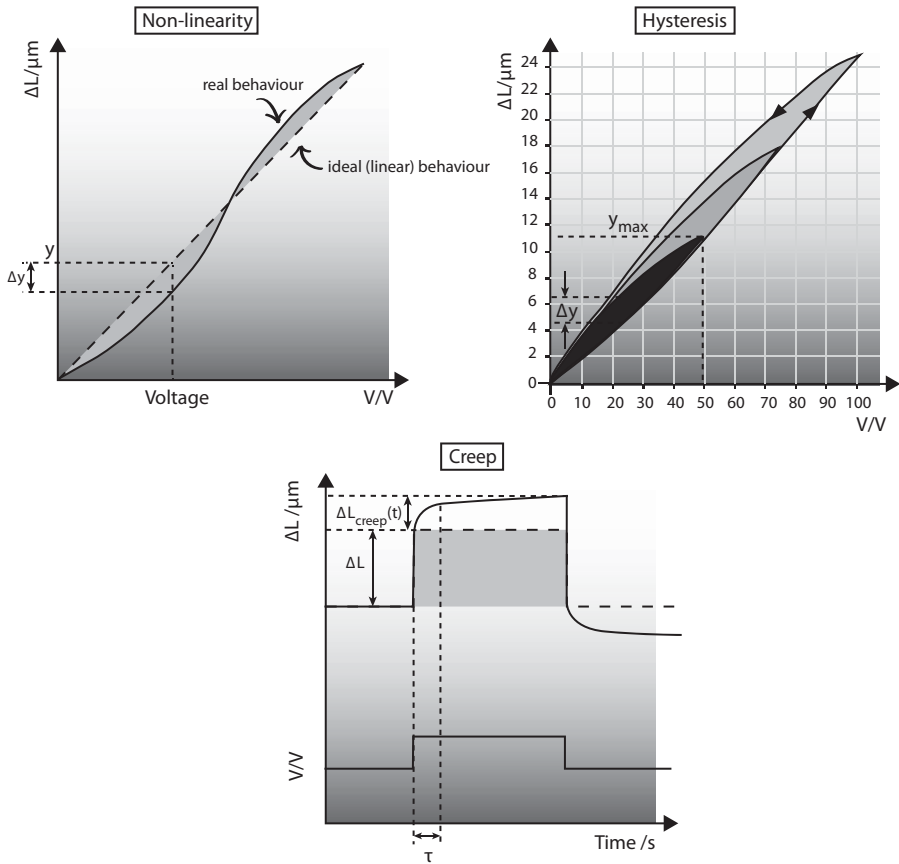


FIGURE 2.4 Limitations of the piezo scanners. (*Upper left*): Nonlinearity is described as a deviation from the ideal behavior, represented as a dashed line in the figure. The actual behavior of the piezoelectric follows an S shape. Quantitatively, it is expressed as the ratio $\Delta y/y$, Δy and y being the magnitudes depicted in the figure. (*Upper right*): Hysteresis loops where elongation is registered as the voltage increases and decreases back again to its original value. The piezoceramic does not exactly follow the same path. Hysteresis is quantitatively defined as a ratio between the greatest position difference between the two paths, Δy , divided by the maximum voltage applied, y_{max} . (*Lower graph*): Creep is the change of length experienced by the piezoceramic when no changes of voltage occur. Creep is mostly evident short after the application of a step voltage. The length of the piezoceramic continues to change even though the voltage is constant. The change of length, ΔL_{creep} , depends on time in a logarithmic manner, with a characteristic time constant, t .

after the voltage has been applied (i.e., time zero), as shown in the lower graph of Figure 2.4. Creep is enhanced at high temperatures and decreases logarithmically with time according to the expression,

$$\Delta L(t) \approx \Delta L_{t=0.1} \left[1 + \gamma \cdot \lg\left(\frac{t}{0.1}\right) \right] \quad (2.4)$$

where ΔL is the change of position as a function of time, and $\Delta L_{t=0.1}$ is the change of position 0.1 s after the voltage has been applied; γ is the creep factor that depends on the actuator properties, and it is usually 0.01–0.02.

AGING

Far from being constant, the strain coefficient d_{31} of piezoelectric materials changes exponentially with time and use. The aging effect is linked to the polycrystalline nature of the material and the fact that each crystallite has an associated dipole moment. With use and repeated application of a voltage in the same direction, more and more dipoles are aligned. The response of the piezoelectric material increases with the number of aligned dipoles, and therefore the former will deform more with time. Contrarily, if the scanner is not often used, more and more dipoles will lose their orientation, and the piezoelectric response will diminish with time.

CLOSED-LOOP ACTUATORS

Nonlinearity, hysteresis, and creep hamper accuracy of piezo actuators, but they can be virtually eliminated by employing a *servo-control* on the performance of the piezo actuator. Figure 2.5 shows the principle of closed-loop actuators. A sensor attached to the moving stage registers the position of the stage, y , after the application of a certain voltage V to the piezo actuator. A controller receives the sensor signal and compares it with the set value (called reference value), y_{ref} , which results in a position difference, $\Delta y = y - y_{\text{ref}}$. If Δy is not zero, the controller converts the magnitude into a voltage difference $\Delta V(\Delta y)$. The amplifier applies the new voltage signal $V + \Delta V(\Delta y)$, thus compensating for any deviations to the expected value. Closed-loop actuators rely on either strain gauge sensors or capacitor sensors to monitor the position of the piezo actuator. Capacitive sensors provide the best accuracy.

TUNNELING EFFECT

It is evident that a solid body cannot traverse walls. This is what we observe in everyday life. The physics of macroscopic objects such as those we can observe or feel is ruled by classical mechanics. However the world of very small objects, such as molecules or atoms, is ruled by quantum mechanics. And in this world, traversing walls is a likely event.

Tunneling is a quantum mechanical phenomenon in which a particle may penetrate a potential barrier even if it has not enough energy to surmount it. If the potential barrier has a height V and a thickness L and the energy of the

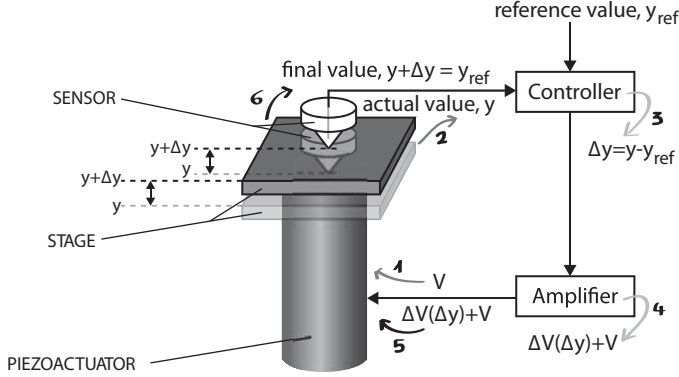


FIGURE 2.5 Closed-loop actuators. Any hysteretic effect, creep or nonlinearity can be compensated if the actuator is equipped with a servo-control. To an applied voltage, V the piezo actuator responds by changing its length (step 1). A sensor attached to a stage on top of the piezo actuator registers the position, y (step 2). The controller receives the sensor signal and compares it with the reference value y_{ref} . If the difference $\Delta y = y - y_{ref}$ is not zero, the controller sends a signal proportional to the difference to the amplifier (step 3), which in turn applies to the piezoactuator a compensating voltage $V + \Delta V(\Delta y)$ (step 5). The new position, $y + \Delta y$ now coincides with the expected value, y_{ref} (step 6).

particle is E , such as $E < V$, the probability of the particle traversing the barrier can be expressed as (Atkins and de Paula 2006)

$$T = \left[1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16 \cdot \frac{E}{V} \cdot \left(1 - \frac{E}{V}\right)} \right]^{-1} \quad (2.5)$$

where $\kappa \hbar = [2m(V - E)]^{1/2}$ and m is the mass of the particle. If the barrier is high and/or thick so that $\kappa L \gg 1$, the expression in Equation (2.5) simplifies to

$$T = 16 \cdot \frac{E}{V} \cdot \left(1 - \frac{E}{V}\right) \cdot e^{-2\kappa L} \quad (2.6)$$

As Equation (2.6) shows, the transmission probability exponentially decreases with the thickness of the barrier as well as with $m^{1/2}$. This means that tunneling is likelier to occur through thin barriers than through thick ones and that light particles are more able to tunnel than heavy ones. Tunneling is thus more important for electrons than for protons or neutrons, which are considerably heavier.

Electron tunneling is behind one modality of scanning probe microscopy called *scanning tunneling microscopy* (STM). In STM, an electric potential is applied between a sharply pointed metal wire and a conducting solid, i.e., the sample. The tip of the wire is positioned very close to the sample's surface so that

electrons may tunnel across the barrier, which is the small space gap between the wire tip and the sample's surface.

As we will see later in this chapter, the amount of electrons that may flow from the wire tip to the sample or vice versa is a complex function of the applied potential, the tip-sample separation, and the density of quantum energy states at the *Fermi level* of the sample.

ENERGY STATES IN METALS

The structure of metals can be viewed as a network of N atoms of the same kind surrounded by a “cloud” of electrons. The electrons are distributed in certain space regions called *molecular orbitals*, each of them characterized by an energy level. The number of molecular orbitals is N , as many as atoms. Each molecular orbital can be in turn occupied by one or two electrons at most or remain unoccupied. In metals, the energies of these orbitals are so close together that they form bands. Different bands result from the overlapping of different types of orbitals, and they may be separated by energy gaps of diverse magnitude.

In metal conductors, electrons partly occupy a band of closely spaced energy levels, so that the band contains unoccupied levels as well as occupied levels, as Figure 2.6a shows. The electrons can *easily* move to the unoccupied levels if these are close enough to one another—high density of states—and if the electrons have enough thermal energy; this movement confers the material its electrical conductivity. Consequently, the highest occupied molecular orbital (HOMO) depends on temperature. At $T = 0$, all electrons occupy the lowest energy levels, and the HOMO is the Fermi level.

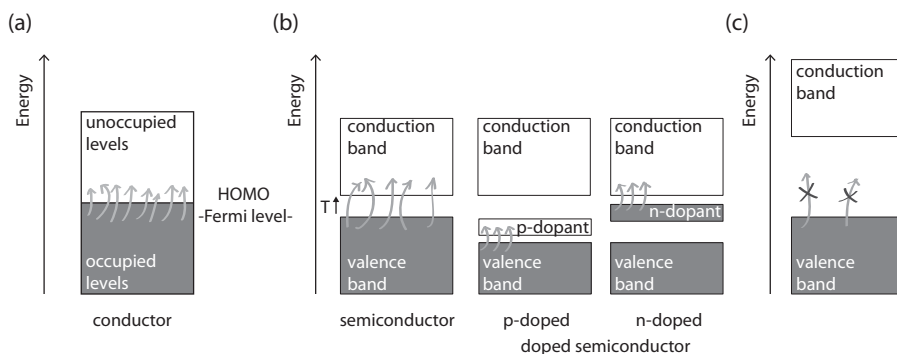


FIGURE 2.6 Band diagrams and electron distributions in metals. (a) In a conductor. The band is partially occupied with electrons that can easily promote to the unoccupied levels. The Fermi level is the highest occupied molecular orbital (HOMO) at $T = 0$. In semiconductors (b) and insulators (c), the Fermi level lies at the top of the band. The valence bands are fully occupied. To enhance material's conductivity, electrons should be promoted to the conduction band, i.e., by increasing the temperature. Alternatively, the energy gap between the bands can be reduced by introducing impurities or dopants, either electron donors (n-doping) or electron acceptors (p-doping). In insulators, only a few electrons, if any, can surmount the big energy gap.

In semiconductors and insulators, all the molecular orbitals that conform the lowest energy band are already occupied at $T = 0$. In these cases, the Fermi level lies on the top of this band, which is called the *valence band*. The electrons could only leave the valence band and reach the next unoccupied band, the *conduction band*, if they can overcome the energy gap between them. In semiconductors, the electrons can gain sufficient energy to reach the conduction band if the temperature is moderately increased (see Figure 2.6b). If the band gap is large so that at moderate temperatures there are very few electrons that promote to the conduction band, the material is an insulator (see Figure 2.6c) (Tipler and Mosca 2003).

HARMONIC OSCILLATOR

Let us assume we have a mass connected to the end of a spring, whose other end is attached to a solid wall. If we displace the mass a bit, the spring will oscillate around the equilibrium position. If the mass-spring system were undamped, it would move endlessly, and its motion would be described as a sinusoidal oscillation, with constant amplitude and a constant, *natural frequency* ω_0 or f_0 .* That is the motion of a *harmonic oscillator*.

Real-life oscillators, such as the mass-spring system or a pendulum, do not move endlessly, but stop after a certain time. The motion is said to be damped, usually by frictional forces proportional to the velocity, and therefore they are called *damped oscillators*. To maintain the harmonic motion of an oscillator, it is necessary to apply an external force that varies sinusoidally with time. The purpose of such a force is to supply the oscillator with energy that otherwise would be lost during motion due to friction. In this case, the oscillator is said to be a *driven oscillator*.

Driven oscillators may be used as probes in SPM, as we will see later. In this case, the driving force comes from a piezo actuator that is attached to the oscillator, a bending spring. The piezo actuator is fed with a sinusoidal voltage and thus deforms in a sinusoidal manner. If the frequency at which the piezo actuator operates, ω , coincides with that of the oscillator, ω_0 , the transfer of energy will be maximal and the amplitude of the oscillator will reach a highest value. This phenomenon is called *resonance*.

If the driving force depends on time according to the following expression,

$$F_{\text{driving}} = F_0 \cos \omega t \quad (2.7)$$

the motion of a driven oscillator at the stationary state can be described as

$$x(t) = A \cdot \cos(\omega t - \varphi) \quad (2.8)$$

* The variable f is the linear frequency and ω is the angular frequency, related through the expression $\omega = 2\pi f$. Both linear and angular frequencies are indistinctively used throughout this chapter.