

## Part One

### Microscopy Fundamentals



## 1

## Introduction

The invention of the STM microscopic technique in the early 1980s by Rohrer, Binnig, and coworkers soon established a new class of proximity probe microscopies, SPM, in the 1980s, followed by an explosion of SPM studies on various mostly conductive materials in the early 1990s [1,2]. The invention of STM was soon followed by the introduction of atomic force microscopy (AFM), a milestone in the field of nanoscience and nanotechnology, especially in the case of soft materials. Fast spreading AFM applications involved all-important soft materials ranging from synthetic to biological ones. AFM utilizes intermolecular forces between the tip and the surface to obtain the topographic information on the surface and other physical properties.

In the past two decades of active SPM (both STM and AFM) studies, a number of excellent reviews have been published in this field, which discussed different aspects of SPM studies, but are naturally limited to a particular class of molecules or materials, or a particular scanning mode(s) by the limited space of articles in professional journals [3–13]. Readers might study these excellent reviews if specific aspects of SPM imaging of a particular class of materials are of interest.

The common fundamental feature among the wide range of scanning probe techniques introduced, which include a variety of specific scanning modes and probing regimes, is a sharp hard probe (usually of nanoscale dimensions) integrated with long and flexible microcantilever. The sharp probe with a radius of curvature around 10 nm interacts with a selected substrate in a gentle (imaging), modest (probing), or even damaging (lithography) manner. Monitoring of one or more physical or chemical interactions (such as van der Waals forces, electrostatic interactions, elastic and plastic resistance, electrical current, capacitance, or conductivity) is then employed to unveil the surface morphology, surface and subsurface organization, and/or physical and chemical properties of the materials under investigation with unprecedented nanoscale lateral and vertical spatial resolution.

It is worth noting that initially the traditional AFM contact mode was widely used to image soft materials in the late 1980s through the early 1990s, but excessive surface damage, frequent and prominent artifacts, and difficulties with the stable imaging of compliant materials limited its applicability and overall impact on various soft matter-related research fields. However, this instrumentation problem

was quickly realized and “fixed.” A new instrumentation development led to the introduction of “noncontact” mode AFM and its practical and robust version, the so-called tapping mode version, is widely accepted [14]. The introduction of this reliable and low-damaging scanning mode that became popular very quickly was critical for the expansion of robust and near-nondamaging AFM imaging to a range of synthetic and biological soft materials and to numerous research groups besides professional AFM developers. Rapid expansion of various scanning and probing modes observed in the 1990s “converted” the SPM technique into a universal and highly versatile tool of the twenty-first century, which can be found in virtually every science and engineering department in the world. The appearance of this family of close-proximity probe microscopies dramatically affected research landscapes in many science and technology fields – an effect similar to that observed with the rapid expansion of transmission and scanning electron microscopies in the 1970s and 1980s.

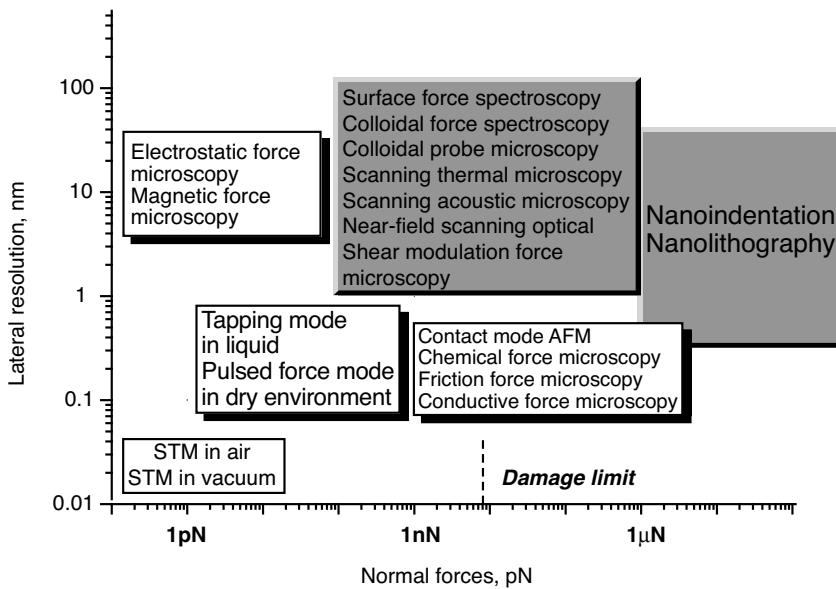
The relative affordability of AFM instruments, their high (near-molecular) resolution, robust scanning procedures, fast learning curve for beginners, ambient and easily controllable (gas, liquid, or temperature) conditions for scanning, and the versatility in measuring not only surface morphology but also a wide range of important surface physical and chemical properties with a nanoscale resolution, all resulted in a fast expansion of the application of this new microscopic method toward virtually all types of soft materials and across all science disciplines in the 1990s and early 2000s.

However, this rapid spreading, especially in the very beginning of the SPM era, frequently resulted in overhyped promises and a number of high-profile artifacts in imaging of prominent molecular features published in journals across different disciplines. Many of those were later withdrawn or overturned or just forgotten. It took nearly a decade to settle the dust, sort out results and artifacts, regain trust of the non-SPM science community, and finally establish robust experimental routines in SPM operations that are accepted by the majority of the research community in science and engineering. At present, major experimental procedures and instrumentation basics are well established, and only a few imaging artifacts and overhyped scans are still published from time to time in major archival journals.

The next important round of experimental developments came with the realization that various interfacial forces and interactions such as electrical, thermal, and magnetic, apart from basic atomic interactions (short-range repulsive and van der Waals type of interactions exploited in early modes), can be readily utilized to image and probe a wide range of material properties. Corresponding developments, mostly in the end of 1980s and in the beginning of 1990s, gave rise to an extended family of new SPM techniques including scanning thermal microscopy, conductive force microscopy, electrostatic force microscopy, magnetic force microscopy, chemical force microscopy, shear force microscopy, pulse force microscopy, near-field scanning optical microscopy, and various probing methods of force spectroscopies such as surface force spectroscopy, colloidal force spectroscopy, nanoindentation, or various versions of nanolithography including dip-pin lithography and mechanical, oxidative, electrostatic, and thermomechanical nanolithography (see some related original papers [15–23]). These modes (and some other more recent modes such

peak-force mode), which will be reviewed in this book, have been designed to probe surface interactions and properties as a function of the AFM tip proximity to and location on the probing surface.

Two primary physical quantities could be used to characterize the minute interactions between the AFM tip and the surface and present a broad picture of the applicability of various SPM modes to different soft materials. These physical parameters are the normal force applied to the surface by the sharp AFM tip in different modes of operation (usually expressed in pN or nN) and the characteristic lateral resolution attained using these modes (usually expressed in nanometers) (Figure 1.1). These two parameters are critical for the evaluation of SPM applicabilities because they determine if a particular soft material can be imaged or probed without ultimate physical damage and if a particular property/feature can be probed with the spatial resolution required for a given application.



**Figure 1.1** Resolution-force “diagram” of SPM modes for soft materials with common scanning parameters.

As is well known, a normal load applied to the AFM tip can vary over a wide range for a particular SPM mode of operation and can be precisely (pN) controlled by a preset microcantilever deflection, microcantilever stiffness, the tip radius of curvature, and scanning operation conditions. On the other hand, local deformation of the substrate or the gap between the SPM tip and the surface defines the achievable lateral resolution during imaging or lithographical modes as presented in Figure 1.1 for different SPM modes. Apparently, the level of surface damage (which is an especially sensitive issue for soft matter) is ultimately determined by the local mechanical deformation and shear/normal stresses and can be set to be around

10 nN assuming a regular AFM tip shape with a radius of curvature of around 10 nm. In a practical scanning regime, the actual threshold depends upon the yield strength of the soft materials and surface stiffness, and thus can be as low as less than 1 nN for delicate biological materials and hydrogels and as high as 100 nN for high-performance composites and fibers.

As can be concluded from this simplified force-resolution representation, under practical imaging conditions, a number of SPM modes are capable of resolving surface features with a spatial resolution well below 1 nm in a nondamaging regime. True (rare) and near-molecular (difficult) resolutions (below 0.5 nm) can be achieved usually only in the contact AFM mode and under special imaging conditions (e.g., scanning in liquid with very low loads). It is worth noting that in terms of the ultimate spatial resolution, STM still remains a superior mode that, however, cannot be a primary choice for soft material studies due to the mostly nonconductive nature of the polymeric materials considered here.

On the other hand, some scanning modes, if applied with high and controlled forces, are capable of inducing excessive but controlled surface deformation that might result in severe and highly localized permanent surface damage (plastic deformation, indentation), thus limiting the probing and imaging abilities of various SPM modes (Figure 1.1). However, the same ability of the AFM tip to leave permanent localized marks on soft material surface with nanoscale lateral and vertical dimensions can be used in a highly controlled manner in nanolithographical approaches (the right side of the mechanical threshold in Figure 1.1). This mode of SPM operation is widely exploited for high-resolution SPM nanolithography, as will also be discussed in this book. In Part One, we will briefly introduce the basics of SPM techniques and the fundamental principles behind SPM applications.

## References

- 1 Binnig, G., Rohrer, H., Gerber, C., and Weibel, E. (1982) Surface studies by scanning tunneling microscopy. *Phys. Rev. Lett.*, **49** (1), 57–61.
- 2 Binnig, G. and Rohrer, H. (1987) Scanning tunneling microscopy: from birth to adolescence. *Rev. Mod. Phys.*, **59** (3), 615–625.
- 3 Giessibl, F. (2003) Advances in atomic force microscopy. *Rev. Mod. Phys.*, **75** (3), 949–983.
- 4 Cappella, B. and Dietler, G. (1999) Force–distance curves by atomic force microscopy. *Surf. Sci. Rep.*, **34** (1), 1–104.
- 5 García, R. and Pérez, R. (2002) Dynamic atomic force microscopy methods. *Surf. Sci. Rep.*, **47** (6–8), 197–301.
- 6 Sheiko, S.S. (1999) Imaging of polymers using scanning force microscopy: from superstructures to individual molecules. *Adv. Polymer Sci.*, **151**, 61–174.
- 7 Magonov, S. and Reneker, D. (1997) Characterization of polymer surfaces with atomic force microscopy. *Annu. Rev. Mater. Sci.*, **27**, 175–222.
- 8 Tsukruk, V.V. and Reneker, D.H. (1995) Scanning probe microscopy of polymeric and organic molecular films: from self-assembled monolayers to composite multilayers. *Polymer*, **36** (9), 1791–1808.
- 9 Tsukruk, V.V. (1997) Scanning probe microscopy of polymer surfaces. *Rubber Chem. Techn.*, **70** (3), 430–467.
- 10 Sheiko, S.S. and Möller, M. (2001) Visualization of macromolecules: a first step to manipulation and controlled

- response. *Chem. Rev.*, **101** (12), 4099–4124.
- 11 McConney, M.E., Singamaneni, S., and Tsukruk, V.V. (2010) Probing soft matter with the atomic force microscope: force-spectroscopy and beyond. *Polym. Rev.*, **50**, 235–286.
  - 12 Hansma, P.K., Elings, V.B., Marti, O., and Bracker, C.E. (1988) Scanning tunneling microscopy and atomic force microscopy: application to biology and technology. *Science*, **242** (4876), 209–216.
  - 13 Dürig, U. (2000) Interaction sensing in dynamic force microscopy. *New J. Phys.*, **2**, 5.1–5.12.
  - 14 Zhong, Q., Inniss, D., Kjoller, K., and Elings, V.B. (1993) Fractured polymer/silica fiber surface studied by tapping mode atomic force microscopy. *Surf. Sci. Lett.*, **290** (1–2), 688–690.
  - 15 Williams, C.C. and Wickramasinghe, H.K. (1986) Scanning thermal profiler. *Appl. Phys. Lett.*, **49** (23), 1587–1589.
  - 16 Martin, Y. and Wickramasinghe, H.K. (1987) Magnetic imaging by “force microscopy” with 1000 Å resolution. *Appl. Phys. Lett.*, **50** (20), 1455–1457.
  - 17 Burnham, N.A. and Colton, R.J. (1989) Measuring the nanomechanical properties and surface forces of materials using an atomic force microscope. *J. Vac. Sci. Technol. A*, **7** (4), 2906–2913.
  - 18 Terris, B.D., Stern, J.E., Rugar, D., and Mamin, H.J. (1989) Contact electrification using force microscopy. *Phys. Rev. Lett.*, **63** (24), 2669–2672.
  - 19 Hesjedal, T., Chilla, E., and Fröhlich, H.-J. (1995) Scanning acoustic force microscope measurements on grating-like electrodes. *Appl. Phys. A*, **61** (3), 237–242.
  - 20 Frisbie, C.D., Rozsnay, L.F., Noy, A., Wrighton, M.S., and Lieber, C.M. (1994) Functional group imaging by chemical force microscopy. *Science*, **265** (5181), 2071–2074.
  - 21 Salmeron, M., Neubauer, G., Folch, A., Tomitori, M., Ogletree, D.F., and Sautet, P. (1993) Viscoelastic and electrical properties of self-assembled monolayers on Au(111) films. *Langmuir*, **9** (12), 3600–3611.
  - 22 Rosa-Zeiser, A., Weilandt, E., Hild, S., and Marti, O. (1997) The simultaneous measurement of elastic, electrostatic and adhesive properties by scanning force microscopy: pulsed-force mode operation. *Meas. Sci. Technol.*, **8** (11), 1333–1338.
  - 23 Ge, S., Pu, W., Zhang, W., Rafailovich, M., Sokolov, J., Buenviaje, C., Buckmaster, R., and Overney, R.M. (2000) Shear modulation force microscopy study of near surface glass transition temperatures. *Phys. Rev. Lett.*, **85** (11), 2340–2343.

