Measuring Properties of Elastomers using AFM Force Curves

Key Words
Atomic Force Microscopy, Elastomers, Intermolecular interactions, Force curves, Contact mode, Non-contact mode, Cantilever

Object

It aims to learn basic concepts of measuring physicochemical properties of elastomers collecting force curves by using atomic force microscopy (AFM).

Introduction

In the past decade, chemical, physical, and biological applications of atomic force microscopy (AFM) have increased markedly, entering mainstream research either as supplements to other surface analysis techniques or as exclusive means of study. Chemistry research in particular has seen a dramatic rise in studies focusing on material properties and surface reaction chemistry, and AFM has been a key tool for such applications. It is now common for primarily undergraduate institutions to have one or more atomic force microscopes. In this lab, we use AFM to examine the surface properties of the common elastomer polydimethylsiloxane (PDMS). PDMS elastomers have extensive applications throughout industry and research, including use in soft lithography, biomedical devices, microelectromechanical (MEMS) devices, and a variety of insulation and protective applications.

Students performing the experiment described herein use AFM to collect force curves on PDMS samples prepared with different base-to-curing agent ratios. Because force curves allow for quantitative assessment of properties such as sample stiffness and sample–tip adhesion events, these are often more useful than conventional AFM imaging for chemistry applications throughout industry and research.

Background Information

Theory

Atomic Force Microscope (AFM)

The atomic force microscope (AFM) or scanning force microscope (SFM) was invented in 1986 by Binning, Quate and Gerber. The AFM raster scans a sharp probe over the surface of a sample and measures the changes in force between the probe tip and the sample.

1. Working concept

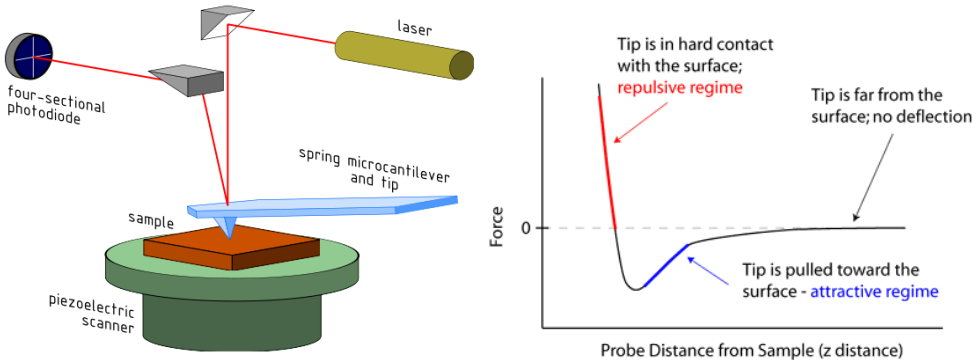


Figure 1. Scheme of an atomic force microscope and the force-distance curve characteristic of the interaction between the tip and sample.

- A cantilever with a sharp tip is positioned above a sample surface.
- Depending on this separation distance, long range or short range forces will dominate the interaction.
- The force is measured by the bending of the cantilever by an optical lever technique: a laser beam is focused on the back of a cantilever and reflected into a photodetector. Small forces between the rip and sample will cause less deflection than large forces.
- By raster-scanning the tip across the surface and recording the change in force as a function of position, a map of surface topography and other properties can be generated.

2. Basic set-up of an AFM

In principle the AFM resembles a record player and a stylus profilometer. The ability of an AFM to achieve near atomic scale resolution depends on the three essential components: (1) a cantilever with a sharp tip, (2) a scanner that controls the x-y-z position, and (3) the feedback control and loop.

- **Cantilever with a sharp tip.** The stiffness of the cantilever needs to be less the effective spring constant holding atoms together, which is on the order of 1-10 nN/nm. The tip should have a radius of curvature less than 20-50 nm (smaller is better) a cone angle between 10-20 degrees.
- **Scanner.** The movement of the tip or sample in the x, y, and z-directions is controlled by a piezo-electric tube scanner, similar to those used in STM. For typical AFM scanners, the maximum ranges for are 80μm x 80μm in the x-y plane and 5μm for the z-direction.
- **Feedback control.** The forces that are exerted between the tip and the sample are measured by the amount of bending (or deflection) of the cantilever. By calculating the difference signal in the photodiode quadrants as shown in Figure 2, the amount of

deflection [(A+B)-(C+D)] can be correlated with a height. Because the cantilever obeys Hooke's Law for small displacements, the interactions force between the tip and the sample can be determined.

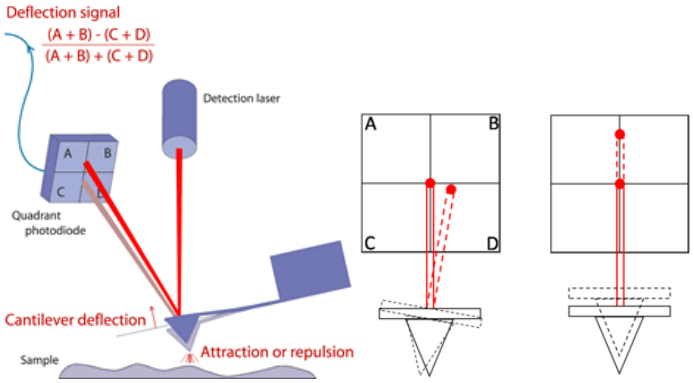


Figure 2. Diagrams showing the effect of cantilever movement with the photodetector represented by the square with quadrants labelled A, B, C and D. Torsional bending of the cantilever (left) leads to a change in lateral deflection and vertical displacement of the cantilever (right) leads to a change in vertical deflection.

The AFM can be operated with or without feedback control. **If the electronic feedback is on**, as the tip is raster-scanned across the surface, the piezo will adjust the tip-sample separation so that a constant deflection is maintained or so the force is the same as its setpoint value. This operation is known as *constant force mode*, and usually results in a fairly faithful topographical (hence the alternative name, *height mode*).

If the feedback electronics are switched off, then the microscope is said to be operating in *constant height* or *deflection mode*. This is particularly useful for imaging very flat samples at high resolution. Often it is best to have a small amount of feedback-loop gain to avoid problems with thermal drift or the possibility of a slightly rough sample damaging the tip and/or cantilever. Strictly, this mode should then be called *error signal*. The *error signal* may also be displayed while the feedback is on; this image displays slow variations in topography and highlights the edges of features.

3. Modes of operation for the AFM

The three general types of AFM imaging are (1) contact mode, (2) tapping mode and (3) non-contact mode.

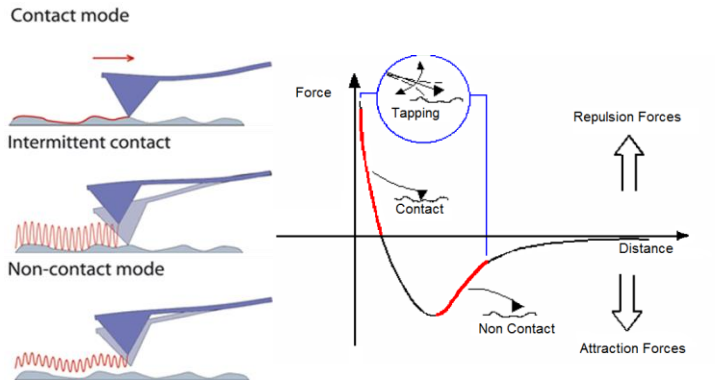


Figure 3. The modes of operation for AFM and diagram of Force (F) versus Distance (r).

- **Contact mode** is the most common method of operation of the AFM and is useful for obtaining 3D topographical information on nanostructures and surfaces. As the name suggests, the tip and sample remain in close contact as the scanning proceeds. "Contact" represents the repulsive regime of the intermolecular force curve (the part of the curve above the x-axis in Figure 3). Most cantilevers have spring constants < 1 N/m, which is less than effective spring constant holding atoms together. One of the drawbacks of the tip remaining in contact with the sample is that large lateral forces can be exerted on the sample as the tip is dragged over the specimen. These large forces can result in deformed images and damaged samples. However, small lateral forces can be used to provide information on the friction (drag resistance) between the tip and sample in a mode known as *lateral force microscopy* (LFM).

  LFM measures the torsional deformation of the cantilever while the tip scans over the surface. While topographic images are recorded by the difference between the top and bottom quadrants of the photodiode, the frictional images are recorded by the difference between the left and right portions of the photodiode. Simultaneous measurement of the topographic and frictional images can be recorded. LFM is useful for obtaining chemical contrast in samples whose features are all of the same height.

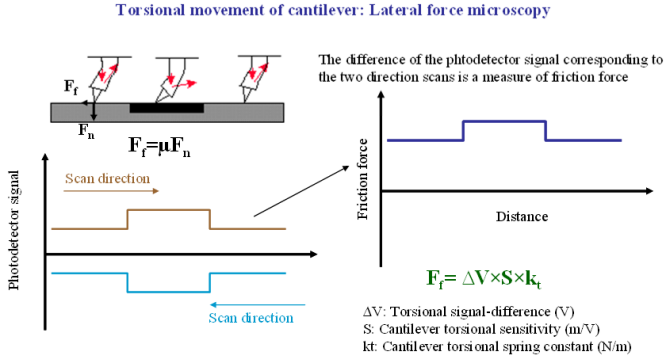


Figure 4. Scheme of lateral force imaging and an example showing higher friction force observed on the scratched area on a BOPP film, which is due to higher surface energy on the scratched area. Force-distance curves obtained on the normal and striped (scratched) areas are shown above, revealing that the friction force contrast seen is related to the adhesion force.

- **Tapping mode (intermittent mode)** is another mode of operation for AFM. Unlike the operation of contact mode, where the tip is in constant contact with the surface, in tapping mode the tip makes intermittent contact with the surface. As the tip is scanned over the surface, the cantilever is driven at its resonant frequency (hundreds of kHz). Because the contact time is a small fraction of its oscillation period, the lateral forces are reduced dramatically. Tapping mode is usually preferred to image samples with structures that are weakly bound to the surface or samples that are soft (polymers, thin films). There are also two other types of image contrast mechanisms in tapping mode:
  - *Amplitude imaging.* The feedback loop adjusts the z-piezo so that the amplitude of the cantilever oscillation remains (nearly) constant. The voltages needed to keep the amplitude constant can be compiled into an (error signal) image, and this imaging can often provide high contrast between features on the surface.
  - *Phase imaging.* The phase difference between the driven oscillations of the cantilever and the measured oscillations can be attributed to different material properties. For example, the relative amount of phase lag between the freely oscillating cantilever and the detected signal can provide qualitative information about the differences in chemical composition, adhesion, and friction properties.
- **Non-contact mode** is a method where the cantilever is oscillated above the surface of the sample at distance such that it is no longer in the repulsive regime but in the attractive regime of the inter-molecular force curve. The operation of non-contact imaging is quite difficult in ambient conditions because of the existing thin layer of water on the tip and the surface. As the tip is brought close to the surface, a small capillary bridge between the tip and the sample and cause the tip to “jump-to-contact”.

The choice for which AFM mode to use is based on the surface charateristics of interest and on the hardness/stickiness of the sample. Contact mode is most useful for hard surfaces; a tip in contact with a surface, however, is subject to contamination from removable material on the surface. Excessive force in contact mode can also damage the surface or blunt the probe tip. Tapping mode is well-suited for imaging soft biological specimen and for samples with poor surface adhesion (DNA and carbon nanotubes). Non-contact mode is another useful mode for imaging soft surfaces, but its sensitivity to external vibrations and the inherent water

layer on samples in ambient conditions often causes problems in the engagement and retraction of the tip. A summary of the different modes of operation is found in the table below.

Mode of Operation	Force of Interaction
Contact mode	Strong (repulsive) – constant force or constant distance
Non-contact mode	Weak (attractive) – vibrating probe
Tapping mode	Strong (repulsive) – vibrating probe
Lateral force mode	Frictional forces exert a torque on the scanning cantilever

4. Samples

The AFM is useful for obtaining three-dimensional topographic information of insulating and conducting structures with lateral resolution down to 1.5nm and vertical resolution down to 1.15nm. These samples include clusters of atoms and molecules, individual macromolecules, and biological species (cell, DNA, proteins). Unlike the preparation of samples for STM imaging, there is minimal sample preparation involved for AFM imaging. Similar to STM operation, the AFM can operate in gas, ambient, and fluid environments and can measure physical properties including elasticity, adhesion, hardness, friction and chemical functionality. A table of representative surfaces and structures is shown below.

Inorganic and synthetic materials	
Surfaces	**Nanostructures**
Surface topography	Carbon nanotubes
Surface Chemistry	Surfaces of polymers
Silicon wafers	Diffraction gratings
Data storage media	Integrated circuits
Ceramics	Nanowires
Biological Materials	
Polymers and Polymer Matrices	**Biological Structures**
Natural resins and gums	Bacterial flagellae
Muscle proteins	Amyloid-beta
DNA	Chromosomes
Plant cell walls	Cell and membrane surfaces

5. Effects of the tip

Ideally the AFM tip would act simply as a probe, where it interacts with the surface only to characterize its properties but not influence the measured properties. There are several negative influences, however, that a tip can have on an image.

- *Broadening of features.* Tip convolution occurs when the radius of curvature of the tip is comparable with, or greater than, the size of the feature that is imaged. Figure 5 illustrates this problem; as the tip scans over the specimen, the sides of the tip make contact before the apex, and the feedback mechanism begins responding to the feature.

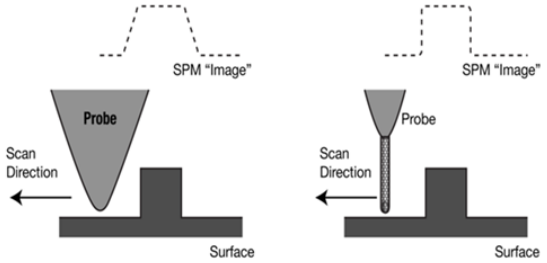


Figure 5. Tip convolution effects on sample features.

- *Compression of features.* Compression occurs when the tip is situated over the feature that is imaged. It is difficult to determine in many cases how important this affect is, but studies on some soft biological polymers (such as DNA) have shown the apparent DNA width to be a function of imaging force. Although the force between the tip and sample may only be nN, the *pressure* may be in the rage of MPa.
- *Strong interaction with sample.* Interaction forces between the tip and sample are the reason for image contrast with the AFM. Some changes that may be perceived because of topography, however, may be due to a change in the force of interaction. For example, forces due to the chemical nature of the tip are important, and chemical mapping using specially treated or modified tips is an imaging mode called *chemical force microscopy*.

Experimental Background

1. Elastomers and Cross-linking:

Elastomers, which are polymers with elastic properties, have a wide variety of commercial applications including insulation, anticorrosion coatings, and soft nanolithography. In this lab, you will be using a silicone elastomer comprised of polydimethylsiloxane (PDMS) polymers that have been cross-linked to form a colorless, rubbery solid. However, the relative ratios of polymer base and crosslinking agent have been varied to yield elastomers with potentially different properties. The base and curing agent used in PDMS are shown in Figure 6.

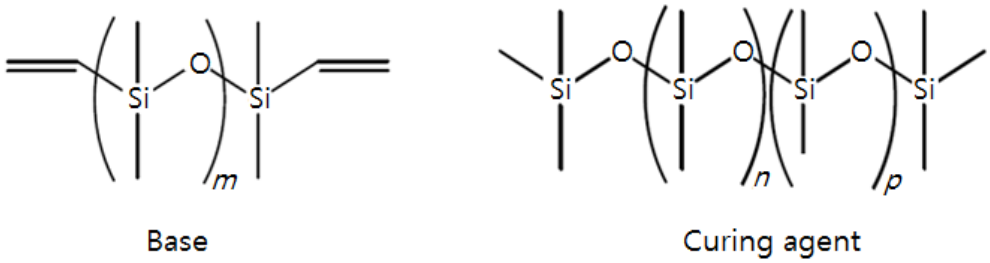


Figure 6. Structures of PDMS base and curing agent.

Crosslinking is the process of joining two or more molecules by the formation of a covalent bond. When preparing PDMS, both the polymer base and the crosslinking polymer (the curing agent) contain dimethylsiloxane functionalities. However, the curing agent also contains multiple Si-H bonds, and these can be added across the terminal double bonds in the base via hydrosilylation, as shown in Figure 7. This results in the different polymers becoming linked in a network.

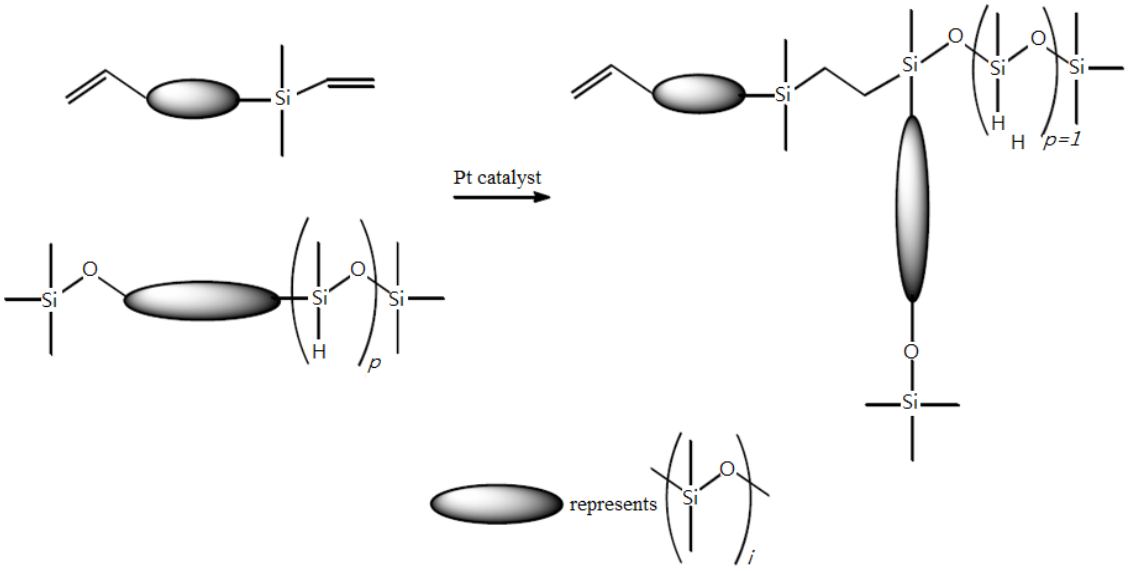


Figure 7. Crosslinking reaction between base and curing agent. Note that one vinyl group remains on the base and p–1 groups containing a Si–H bond remain in the curing agent. These groups are available for further crosslinking with other molecules, yielding a network of polymers bonded together.

2. AFM Contact and Force Modes

AFM can be operated in several capacities; the two modes referred to in this experiment are contact and force. In contact mode, the AFM tip remains in "contact" with the sample surface by applying a constant small pressure to that surface. This commonly yields topographic surface data in the form of an image. In contrast, force curves enable quantitative analysis of the attractions and repulsions between the tip and the sample.

The cantilever is positioned in one location and extended in the z direction toward the sample, then retracted back (Figure 8).

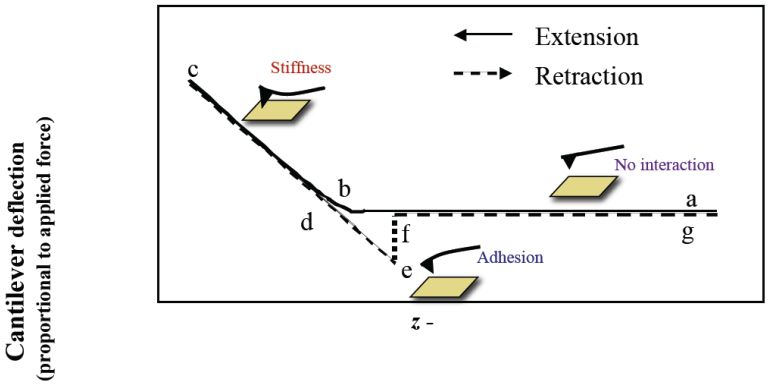


Figure 8. Schematics of a force curve. The cantilever starts far from the surface (a) and extends until it comes into contact with the sample (b). It is then deflected as it pushes farther into the surface to its most extended point (c). During retraction, sample-tip adhesion forces cause the cantilever to remain deflected past its initial point of contact (d) until abruptly breaking free (e to f) and completing the retraction (g).

The two most common types of sample information gained from AFM force curves are sample stiffness and sample-tip adhesion forces. The cantilever deflection as a function of z position (i.e., the slope) during extension reflects sample stiffness or elasticity. When retracting, adhesion forces between the sample and the tip (e.g., van der Waals forces, electrostatic interactions) cause the tip to remain deflected past its initial point of sample contact before breaking free of the surface and springing back to neutral position. Figure 9 shows idealized force curves of samples with different properties.

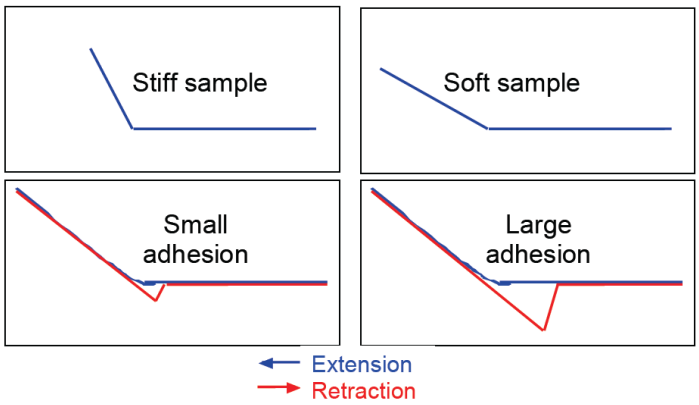


Figure 9. Representative force curves for samples with different stiffness ($k_{substrate}$, top two panels) and tip-sample adhesion (bottom two panels).

When force curves are collected on a sample in air (rather than a sample sitting under a fluid), the adhesion forces observed between the sample and the AFM tip as the tip is retracting are generally quite high. This is because all surfaces at normal relative humidities are covered with a thin layer of water, and the capillary forces of water cause the hydrophilic AFM tip to be highly attracted to the sample surface. Thus, any chemical attractions between the sample and the tip are typically overwhelmed when performing force curves in air. In this experiment, you will be primarily considering the slope of the extension curve, which is not dependent on whether the sample is measured dry or wet. However, the capillary forces of water and the natural stickiness of the elastomer yield such high adhesive forces that the tip may be unable to retract, which severely compromises the data. Thus, all your experiments will be conducted in water.

3. Making quantitative measurements with force curves

When planning experiments and interpreting data, it is important to consider the characteristics of the AFM cantilever being used. If you use a particularly floppy cantilever, the cantilever will deflect much more readily, yielding a steeper slope on the extension curve, whereas a stiffer cantilever would need to encounter more resistance from the surface before it deflected significantly. The stiffness of the cantilever is expressed as a spring constant k typically given in N/m (or pN / nm on atomic force microscopy scale). This is the same spring constant that described "real" springs in general physics. A larger value of k means the cantilever is more stiff – that is, it takes more pN of applied force to make the cantilever bend by 1 nm.

To quantitatively describe the stiffness of a sample, we use both the spring constant of the cantilever ($k_{cantilever}$) and the slope of the extension curve when the curve is plotted as force versus distance. Both values have units of N/m (or pN/nm or some other Force / Distance), and the slope of the extension curve is actually a combination of the stiffness of the substrate and the stiffness of the cantilever. This is analogous to putting two springs together and measuring the overall spring constant as shown in Figure 10. Thus, the effective spring constant of the substrate can be determined.

$1/k_{combined} = 1/k_1 + 1/k_2$

$1/k_{combined} = 1/\text{slope}$
$= 1/k_{cantilever} + 1/k_{substrate}$

Figure 10. The effective spring constant of two springs in series can be calculated as a function of the individual spring constants (left). This general physics model can be applied to AFM because both the cantilever and the substrate (sample surface) will be bent or depressed by a certain amount when a give force is applied to them. Since the cantilever position during a force curve is a function both of the stiffness of the cantilever and the stiffness of the sample, the slope of the force curve is equivalent to a combined spring constant.

4. Calibrating your cantilever

In order for the $k_{substrate}$ obtained from this two-spring approach to be valid, the spring constant of the cantilever must be accurately known. Commercial cantilevers are sold with reported nominal $k_{cantilever}$ values, but these can be off by 20% or more. Multiple cantilever calibration techniques have been developed, and the method that you will be using invokes the property that a cantilever's slight fluctuations in response to thermal noise are affected by the spring constant of the cantilever. Physics' equipartition theorem describes the average energy of a system at thermal equilibrium, and for an ideal one-dimensional spring, the equipartition theorem states that

$$\tfrac{1}{2}\ k_B T = \tfrac{1}{2}\ k\langle x^2\rangle$$

where k_B is Boltzman's constant, T is temperature in Kelvin, k is the spring constant, and $\langle x^2\rangle$ is the mean square displacement of the spring from its equilibrium position. In AFM, measuring the movement of an "at rest" cantilever, referred to as taking a thermal spectrum, i.e. fluctuation, allows us to calculate $\langle x^2\rangle$ and therefore $k_{cantilever}$. In practice, the above equation is modified to account for the differences between a cantilever and an ideal spring.

Since the detected signal in AFM comes from a laser reflecting off the top of the cantilever and being detected by a photodiode, we must determine the optical lever sensitivity (OLS; given as inverse OLS in the software you'll be using) of the cantilever in order to properly interpret $\langle x^2\rangle$ from the thermal spectrum. OLS describes how the laser signal relates to the actual movement of the cantilever. OLS is calibrated by pressing the cantilever a known distance into a hard surface – freshly cleaved mica in this case - then normalizing by the resulting change in photodiode signal. Since changing the medium through which the laser moves from air to water will change the path that the laser light takes, it is important to recalibrate OLS after you add water to your sample.

Pre-Laboratory Questions

1. Show a sample calculation demonstrating how you convert the slope value of common force curve into effective spring constants. Include your units.
2. Draw scheme for a force curve. And describe how you can interpret the scheme. (x-axis: distance, y-axis: force)
3. Why would AFM measurements be particularly sensitive to external noise?

Materials

Reagents

Sylgard 184 (Dow Corning); its principle ingredient (55-75%) is dimethyl, methylhydrogen siloxane (CAS 68037-59-2).
DI water

Apparatus

Nanosurf easyScan 2 AFM system
(CONTR-10 POINTPROBE-Silicon SPM-Sensor Contact Mode, $k_{cantilever}$ = 0.2 N/m)
(NCLR-10 POINTPROBE-Silicon SPM-Sensor non-Contact Mode, $k_{cantilever}$ = 48 N/m)
DI water bottle
10-100 μL micropipette and tips
47 mm diameter Plastic petri dishes
Vacuum desiccator
Oven
Glass slide
Disc of mica
Calculator

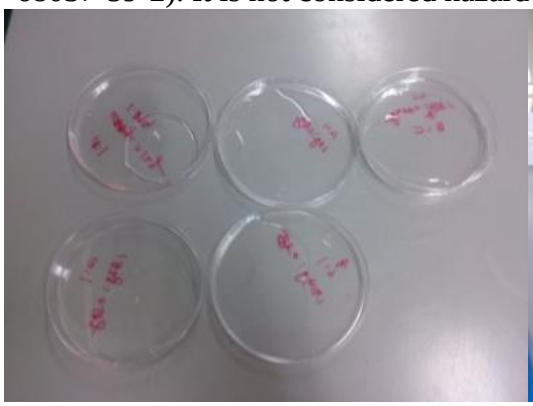
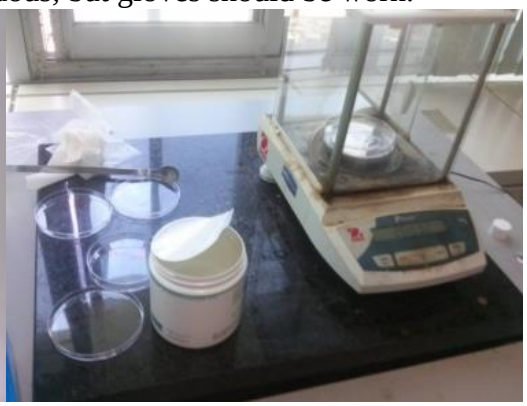
Safety and Hazards

There are no significant chemical hazards associated with the activities students participate in during this experiment. If the experiment is modified so that students prepare their own elastomers, students should wear gloves while handling the base and curing agent.

Experimental Procedure

1. Samples
    1) Prepare Sylgard 184 PDMS elastomers with different base:curing agent ratios (2:1, 4:1,

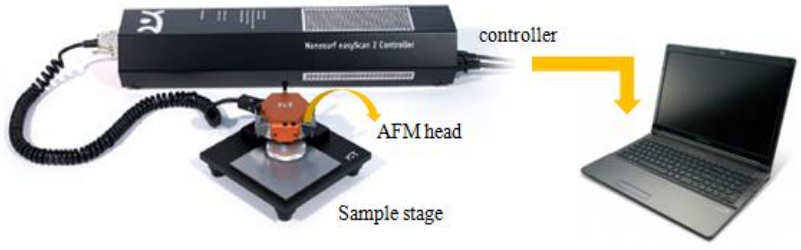
6:1, 10:1, 18:1) in plastic Petri dishes. Sylgard 184 is prepared by Dow Corning; its principle ingredient (55-75%) is dimethyl, methylhydrogen siloxane (CAS 68037-59-2). It is not considered hazardous, but gloves should be worn.

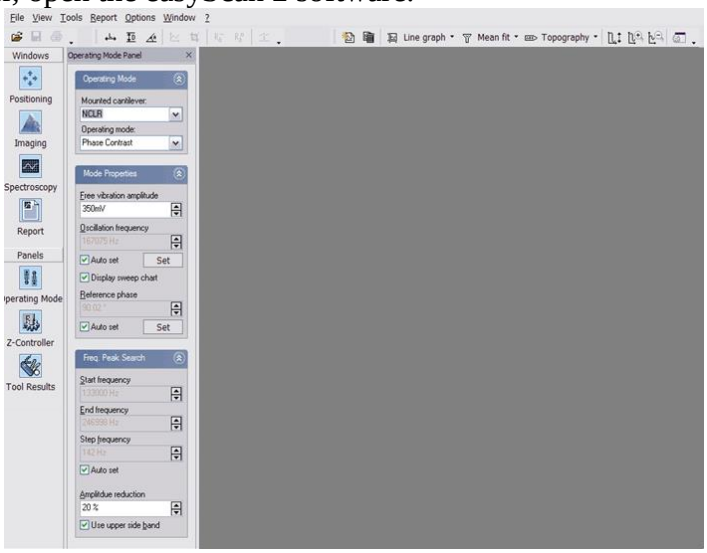
- For 47 mm diameter Petri dishes, 2.0 g total elastomer is adequate.
- Mix the base and curing agent together with a popsicle stick, micropipette tip or other disposable stirrer.
- Place the petri dishes in a vacuum desiccator for 15 minutes to remove air bubbles introduced by stirring.
- Cure the elastomers in a 60 ℃ oven for 4 hours. Curing time and temperature affect elastomer stiffness, so all samples should be prepared under equal conditions.

2) Glass slide with disc of mica mounted on it.
3) For AFM instruments that do not allow samples to be mounted in Petri dishes, prepare the elastomers in the same fashion and then slice a portion of the elastomer to mount on the AFM puck or slide.
4) Various silicone elastomers with base:curing agent ratios ranging from 2:1 to 18:1 have been prepared in Petri dishes. You will need to squirt a drop of DI water on top of each of the samples before analyzing by AFM.

5. Instrument: Inspection
   1) Identify the AFM head, sample stage, and controller. And observe the “table stable” that the instrument setup sits upon. Follow the cords to determine what parts are interacting with other parts of the instrument (connection). Next, note that the AFM head has 3 thumbwheels: raise and lower the three legs of the AFM head to control the z dimension.



2) On the computer, open the easyScan 2 software.

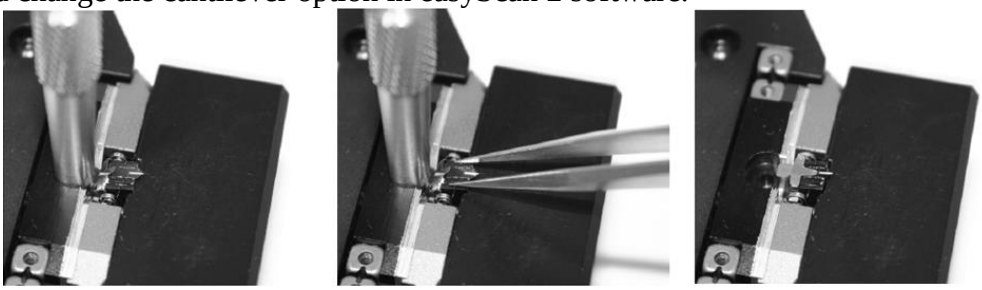


6. Measurements

1) Take the glass slide with a mounted disc of mica and place a piece of sample on the mica.
2) Place it on the AFM sample stage.
3) Carefully turn the AFM head down using two hands to approach the tip on the sample. When you approach the tip, you can observe the vertical location of tip by comparing the shadow with tip through the lens attached on the AFM head.

View of the cantilever after manual approach: left: top view, right: side view

4) Approaching the tip on the sample using two hands and your eyes, click the "Positioning" icon (on the left) and "approach" subtab for elaborate approach. The closer the tip is, the less time the automatic final approach takes.
5) After the "approach is done" pop-up massage, "Imaging" will be automatically started. The instrument was set to automatically start measuring after the automatic approach.
6) After "imaging" is over, click "spec" in the Imaging bar. When the Spectroscopy window is activated from the Imaging bar, the currently measured image is transferred to the Spectroscopy window.
7) Set the start value (-7.5μm) and end value (+7.5μm) in "Modulation" tab.
8) Click the "Point" to select XY measurement position using the mouse cursor.
9) Then, click the "start" to start a spectroscopy measurement.
10) Capture the graph after the measurement.
11) Repeat the steps 1)-10) for every samples.
12) After finishing the above steps, change the cantilever mode to the noncontact mode and change the cantilever option in easyScan 2 software.

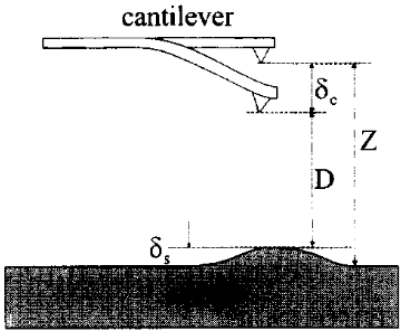


Mounting the cantilever: top left: Inserting the cantilever insertion tool; top right: Inserting/ Removing the cantilever; bottom right: Correctly inserted cantilever

13) Choose one sample for comparison of two images (contact mode vs noncontact mode) and start "imaging".

7. Calculations
   1. Convert deflection in nanometers (nm) into force in nanonewtons (nN).
      Note that the spring constant of cantilever ($k_{cantilever}$) is 0.2 N/m.

$$F = - k_c \delta_c$$



2. Calculate and compare each slope in deflection curves (force-distance curve). Remember that this slop indicates the combined spring constant ($k_{combined}$).

Sample	Slope (N/m), $k_{combined}$
2:1	
4:1	
6:1	
10:1	
18:1	

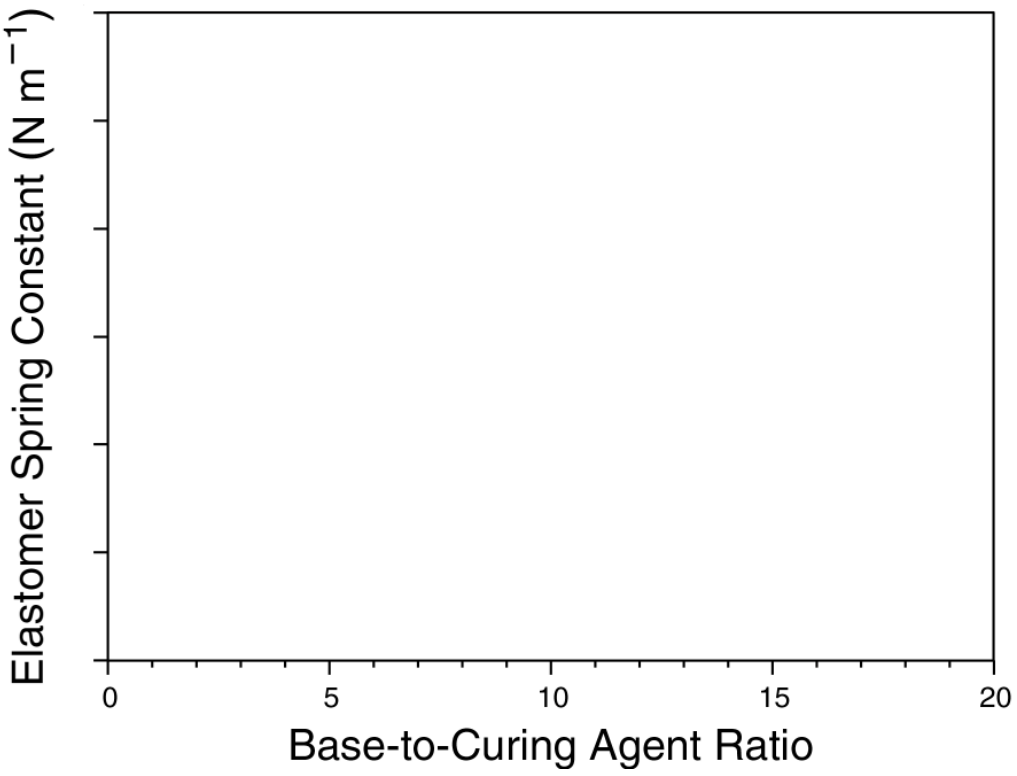
Post-Laboratory Data Evaluation

1. Using the following equation, calculate the spring constant of elastomer.

$$1/k_{combined}=1/slope=1/k_{cantilever}+1/k_{elastomer}$$

Sample	$k_{elastomer}$ (N/m)
2:1	
4:1	
6:1	
10:1	
18:1	

2. Find out the trend of spring constants of elastomer with varying B:C values and draw the graph (X-axis: B:C ratio, Y-axis: spring constant). (below)



3. Expect whether elastomer spring constants would change depending on the tip location on the elastomer.
4. Predict how B:C ratio will have an effect on elastomer spring constant and tip-sample adhesion, respectively.
5. Compare two images obtained by contact mode or noncontact mode, and explain the appropriate mode for imaging polymers.

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