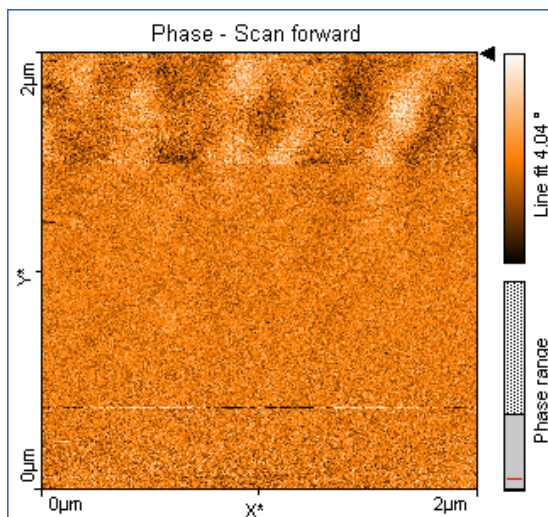


## LAB UNIT 2: Electrostatic Force Microscopy (EFM)

### Specific Assignment: Electrical Properties of Conjugated Polymer Films

<b>Objective</b>	This lab unit introduces Electrostatic Force Microscopy to characterize the electrical properties of a blended conjugated polymer film by studying the changes in tip oscillation due to electrostatic force gradients between the tip and the sample.
<b>Outcome</b>	Learn the basics of electrostatic force microscopy, applying concepts including Coulomb force, capacitance, force gradients and damped driven simple harmonic motion.
<b>Synopsis</b>	We learn the basics of electrostatic force microscopy by characterizing a thin film composed of a blend of electron-donating and electron-accepting organic semiconductors.
<b>Materials</b>	Thin film of 4:1 PCBM:MDMO-PPV on gold Gold film Indium tin oxide-coated glass  Tweezers Alligator clip mounted on a glass slide Alligator clip-terminated wire (both ends) Voltmeter Pair of small magnets  Easy Scan 2 AFM system Pt-coated non-contact mode EFM tip with 1–5 N/m spring constant (probe model: ANSCM-PT from AppNano)
<b>Technique</b>	Intermittent-contact mode AFM imaging, electrostatic force microscopy (EFM)



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## 1. Assignment

The assignment is to learn about the basic concepts of electrostatic force microscopy, apply them to measure surface potentials and to characterize a phase-separated blend of conjugated polymers as might be done in studying organic solar cells.

1. Familiarize yourself with the background information provided in Section 4.
2. Test your background knowledge with the provided Quiz in Section 2.
3. Prepare a grounded sample of a conductive polymer blend, evaporated Au and ITO for EFM as instructed in Section 3.
4. Perform topographical, electrostatic measurements and study the phase shift as a function of applied bias as instructed in Section 3.
5. Fit a function to collected data to determine the work function difference between indium tin oxide (ITO) and Au.
6. Finally, provide a written report discussing the following results:
  - (i) What is the Q factor of the tip you used? Include a graph of the frequency sweep and corresponding phase shift.
  - (ii) Using the phase shift versus voltage plots for ITO and Au, fit the data to the following function (just like PreLab Question 2):

$$f(x) = -\arcsin(A(x - V_0)^2)$$

What value of  $V_0$  do you get for each metal? Calculate the difference in work function between ITO and Au.

- (iii) Include the topography image and the EFM images of the surface: arrange them by increasing distance from the surface.
- (iv) What is the maximum variation in height (look at your topography scan)? How does this value compare to the changes in the phase contrast at different heights?
- (v) What causes the contrast in the EFM scans (ie, what physical property are you measuring?) How does the contrast change as you increase the tip-surface distance?
- (vi) How does the EFM image compare to the topographical image? What might this say about the polymers?
- (vii) What are the limitations of this method of EFM? How might you improve the experiment?

## 2. Quiz – Preparation for the Experiment

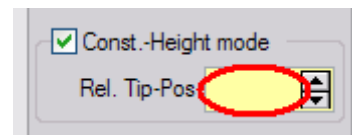
### Theoretical Questions

- (1) Derive the expression for the amplitude and resonance frequency of a damped, driven simple harmonic oscillator with damping constant  $b$  and natural frequency  $\omega_0$ . (See Section 4.) The following steps will guide you:
  - a. Give the differential equation describing the motion of a damped, driven simple harmonic oscillator. What do each of the variables represent?
  - b. In the text, we give the form of the solution for  $z(t)$ . Plug this into (a). Group the terms into a  $\cos \omega t$  and a  $\sin \omega t$  term. For this equation to be true at all  $t$ , both terms must be 0, i.e. the prefactors of these two terms must go to zero independently.
  - c. Using the prefactor for the  $\sin \omega t$ , solve for the phase shift,  $\delta$ .
  - d. Using the prefactor for  $\cos \omega t$ , solve for  $A$ , the amplitude of oscillation as a function of frequency. (Hint: To get the expression into the form given in the text, remember that if  $\tan x = a/b$ , then  $\sin x = a/\sqrt{a^2+b^2}$ .)
  - e. For what driving frequency  $\omega$  is the amplitude of oscillation the greatest? (Hint: Find  $\omega$  for which  $A$  has a local maximum.) This is the resonance frequency  $\omega_R$ .
  - f. Assume that the damping factor is very small, so  $\omega_R \approx \omega_0$ . What is the phase shift between the driving force and the oscillator response at this frequency? (Your answer should be an actual number.)
  
- (2) Write down the functional forms for the distance dependence of van der Waals (vdW) and Coulomb forces. Do these forms explain why electrostatic forces can still affect the tip motion at ranges where vdW forces cannot? Explain.
  
- (3) Consider a simple parallel plate capacitor consisting of two circular plates 200 nm in diameter, spaced 50 nm apart.
  - a. What is the capacitance of this structure?
  - b. If this capacitor is charged to 5 V, what is the charge on each plate?
  - c. How much energy is stored in the capacitor?
  - d. What is the force acting between the capacitor plates when they are charged to 5 V?
  
- (4) Write a description in words explaining what is meant by the quality factor, or "Q" of an oscillator. Write down at least three different formulas for determining the Q of an oscillator.
  
- (5) In an ideal instrument the minimum detectable force is limited by the thermal noise in the cantilever motion. In this case the minimum detectable force gradient is  $F' = \sqrt{\frac{4k_B T B k}{Q \omega_0 A^2}}$  (where  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature

(Kelvin),  $B$  is the measurement band,  $k$  is the spring constant of the cantilever,  $\omega_0$  is the natural frequency of the spring,  $Q$  is the quality factor of the resonance and  $A$  is the amplitude of oscillation). What is the minimum theoretically detectable  $F'$  for a typical cantilever operating at room temperature at  $B=1000$  Hz? (Use  $k=1$  N/m,  $\omega_0=30$  kHz,  $A=1$  nm,  $Q=100$ ). At what distance is the force gradient between two point charges comparable to this value?

**Prelab Quiz**

- (1) Suppose you want to position the cantilever 75 nm above the surface in constant height mode. What value should you type in the highlighted box?



- (2) Use the following data points into Excel (in the provided worksheet). Fit the points with the following function:

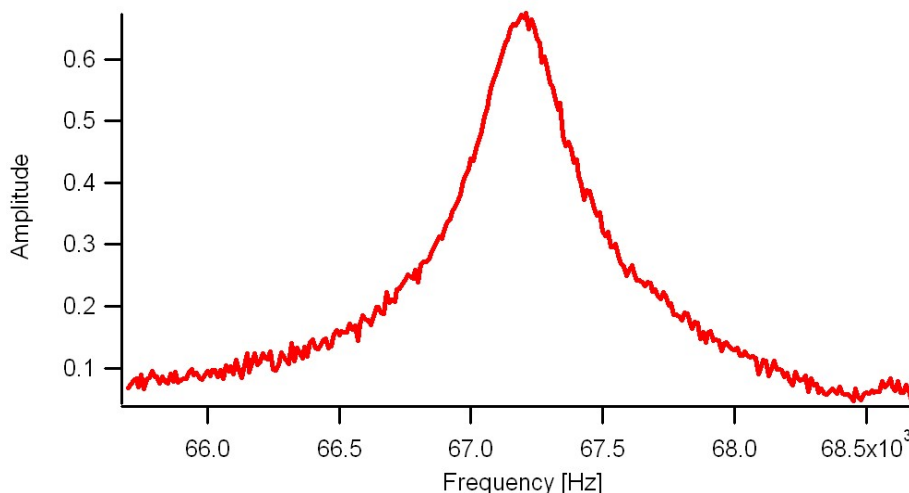
$$f(x) = -\arcsin(A(x - V_0)^2) + B$$

Hint: Solve the equation for  $A(x - V_0)^2$ , then use Excel to fit the parabola. The best fit to  $B$  is reasonably approximated by the maximum value of the phase shift.

What value do you get for  $A$ ?  $V_0$ ?

What physical quantity does  $V_0$  represent?

- (3) Given the following plot (see exact points in spreadsheet), find  $Q$ .



### 3. Experimental Assignment

#### Goal

Perform intermittent contact mode imaging and electrostatic force microscopy on a polymer blend sample. Examine domains of PCBM and MDMO-PPV with both intermittent-contact SFM and EFM. Find the difference in work function between ITO and gold.

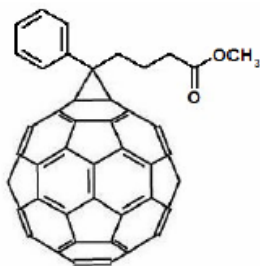
#### Materials

##### *Instrumental Setup*

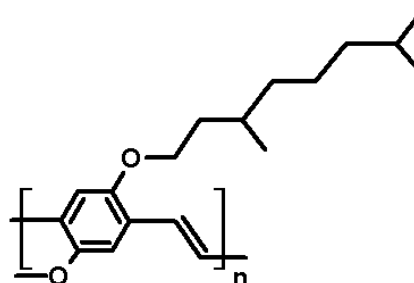
- Easy Scan 2 AFM system with Pt-coated non-contact mode EFM tip with 1–5 N/m spring constant (probe model: ANSCM-PT from AppNano)
- Alligator clip-slide holder
- Alligator clip-terminated wire (both ends)
- Pair of small magnets
- tweezers (one for the EFM tip, one for the sample)
- Samples: Au film, polymer film on Au film, ITO (see sample prep below)

##### *Sample Preparation*

- spin coater
- sonicator (with acetone and isopropanol)
- voltmeter with probes
- thermal evaporator with gold (for the silicon/silicon oxide gold-coated substrate)
- silicon/silicon oxide substrate with a thermally evaporated 15 nm gold layer
- indium tin oxide (ITO) coated glass
- poly[2-methoxy-5-(3',7'-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV)
- methanofullerene [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM)
- toluene
- acetone
- isopropanol



PCBM



MDMO-PPV

#### Safety

- Wear protective gloves and safety glasses when working with solvents and the spin-coater
- Review the Chemical Hazards below

- Refer to the General rules of the AFM lab

*Chemical Hazards:* This is only a summary of the Material Safety Data Sheets for the chemical reagents we will be using.

**Toluene:** Flammable liquid and vapor. Causes eye, skin, and respiratory tract irritation. Breathing vapors may cause drowsiness and dizziness. May be absorbed through intact skin. Aspiration hazard if swallowed. Can enter lungs and cause damage. Possible risk of harm to the unborn child. May cause central nervous system depression. Target Organs: Central nervous system, respiratory system, eyes, skin.

**Isopropanol:** Flammable liquid and vapor. Irritant to eyes and skin. Vapors can cause drowsiness or dizziness. Target Organs: nerves and kidneys

**Acetone:** Irritant, especially to eyes. Repeated exposure may cause skin dryness or cracking. Vapors may cause drowsiness and dizziness. Target organ(s): liver and kidneys

**MDMO-PPV** poly(2,5-bis(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene)  
**PCBM** ([6,6]-Phenyl C61 butyric acid methyl ester)

These polymers have not been fully characterized for toxicity.

## Experimental Procedure

### Reagent preparation

- (1) Prepare a ~10 mg/mL stock solution of MDMO in toluene. This may take a few days and/or mild heating/stirring to completely dissolve.
- (2) Prepare a ~20 mg/mL stock solution of PCBM in toluene.
- (3) Mix a volume of 1 part MDMO and 2 parts PCBM. The final weight ratio should be 4:1 PCBM:MDMO.

### Substrate preparation

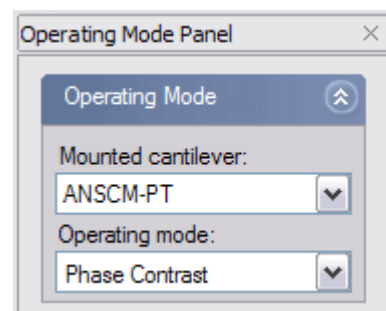
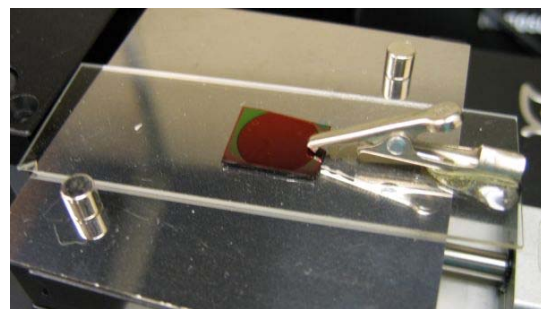
Substrates should be cut to a size that is small (to conserve materials), yet large enough to be handled easily. A 1 cm x 1 cm square is a good size.

- (4) After cutting the substrate to size, sonicate both ITO slides and silicon/silicon oxide in an acetone bath, then an isopropanol bath for 20 minutes each
- (5) Blow the substrates dry with a nitrogen stream.
- (6) (Optionally, plasma clean the ITO for about 5 minutes.) Store the cleaned ITO in a covered container (petri dish) to keep it clean.
- (7) Evaporate about 15 nm of gold onto the silicon/silicon oxide substrates.
- (8) Set the spin-coater to spin at 2000 rpm for 30 seconds. Gently deposit about 50  $\mu$ L of 4:1 PCBM/MDMO-PPV (in toluene) onto the gold-coated substrate and start the spin-coater. Reserve a gold-coated substrate for later use.

### Initial Set-Up of the Instrument

See start up procedure in Easy Scan 2 AFM System SOP (Standard Operational Procedure) for more details.

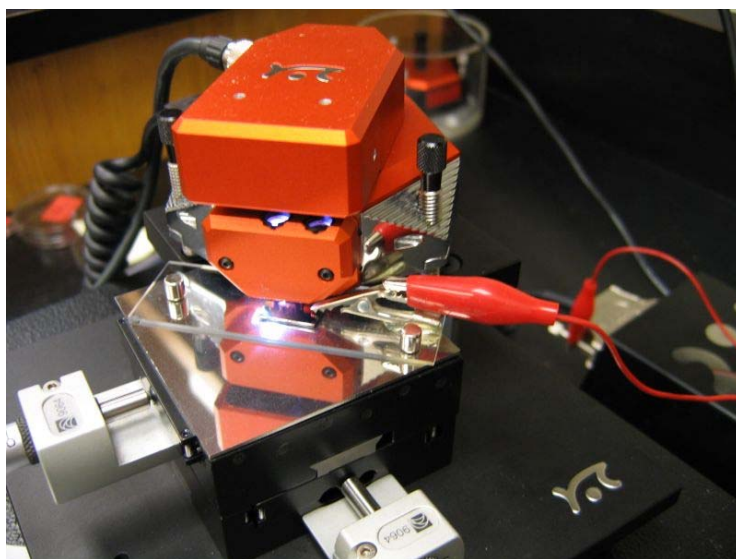
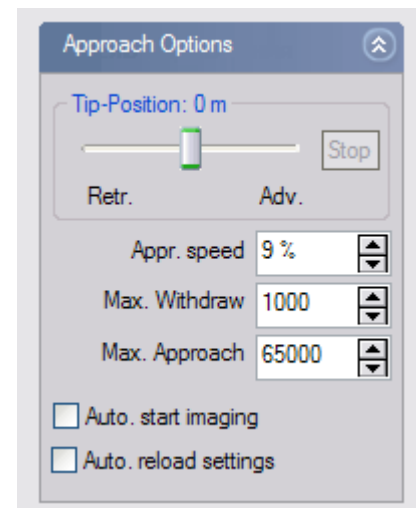
- (1) Clip the polymer-film substrate into the substrate holder. Set the voltmeter to measure resistance. Touch one probe to the conductive part of the substrate and the other probe to the alligator clip holding down the substrate. A resistance of ~10-15  $\Omega$  indicates a satisfactory contact has been made. If not, gently push the clip down on the substrate, and wiggle the clip to “clean the contact” if necessary.
- (2) Load an EFM cantilever ( $k=1-5$  N/m) into the AFM head. (ANSCM-PT tips)
- (3) Select the Operating Mode Panel: Select *ANSCM-PT* for the cantilever, and the *Phase Contrast* operating mode. (If the cantilever option is not there, go to *Options > Cantilever*





*Options*, create a new cantilever profile with the tip name, and enter in the properties for the ANSCM-PT cantilever. Save, then select the tip in *Operating Mode*.)

- (4) *Uncheck* the auto start imaging under *Approach Options* in the Positioning Window
- (5) Make sure the AFM tip has enough clearance (>1 mm) for the substrate and glass slide before carefully sliding under the tip.
- (6) Anchor the glass slide to the translation stage with the small magnets.
- (7) Ground the sample by connecting the clip to the Nanosurf controller by the alligator-clip terminated wire.



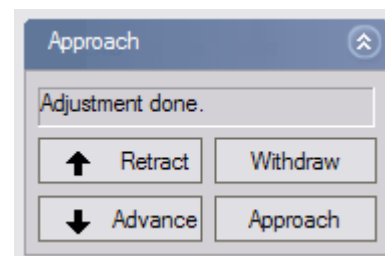
### Non-Contact/Intermittent-Contact Imaging

- (8) In the Operating Mode Panel: Mode Properties, make sure the checkboxes for *Auto set* and *Display sweep chart* are checked. Tune the cantilever tip manually by clicking *Set*. Note the shape of the response curve (cantilever amplitude versus driving frequency).

Click on the graph, then save the data from the resonance curve (File > Export > Current Chart... and save as a Comma Separated z-Values (\*.CSV) file). You will need this later to determine the Q-factor for your cantilever.

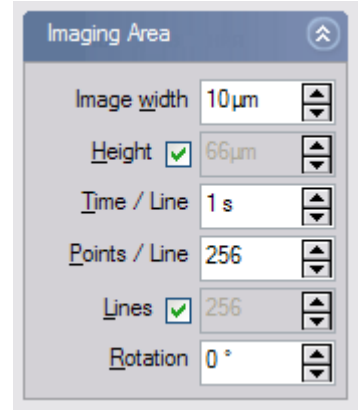
Examine the oscillation amplitude as a function of drive frequency and record the resonant frequency of your cantilever (shown grayed out in *Mode Properties: Vibration frequency*).

- (9) Quickly advance the tip closer to the surface by clicking and holding down on the *Advance* button in the Approach panel. Approach the tip to the surface by clicking on 'Approach' in the Approach panel.

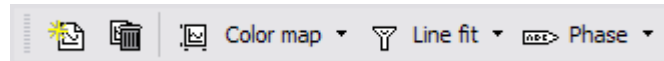




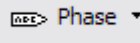
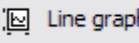
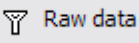
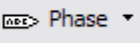
## LAB UNIT 2

- (10) In the Imaging Panel, adjust the image width to image a  $10\ \mu\text{m}$  wide square on the sample, and check that the other parameters are set to the same as the image on the right. Click *Start* to start the scan. As you scan, make sure you have a relatively “flat” region of the sample. If the line trace appears crooked, use the menu option: *Script > Imaging – Adjust Slope* to straighten it out. Repeat for *Rotation:  $90^\circ$* . Large pieces of dirt will adversely affect the EFM imaging in the next step.
- (11) Once you have scanned a region that is mostly free of dirt, click *photo* to save the image when the scan is done. Allow the scan to finish. When the window pops up with the completed image, click on the image, then *File > Export*, and save it as a Windows Bitmap Image (\*.BMP).
- (12) We will choose a smooth subsection of this region to perform EFM. Click on *Zoom* in the toolbar above, and draw a box (try for about  $2\ \mu\text{m}$ ) around the cleanest region. The *Tool Results Panel* will pop up on the left as you do. Click *Zoom* to confirm your selection.
- (13) Obtain a topography image of this narrowed region. Check that you have a good saved image and area. If the height variation is bigger than  $50\ \text{nm}$ , image a new area. Once you have a good image you can stop imaging, by clicking *Stop*.



### Electrostatic force microscopy

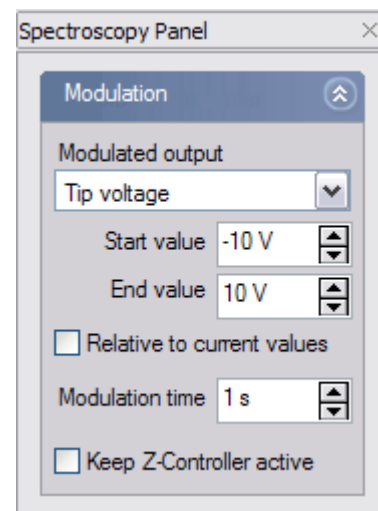


- (1) We need to rearrange the chart window to show EFM data. From the toolbar (shown above), click  to create a new display graph. Choose  to show a 2D graph, and select  as the data to be shown. Add yet another display, except choose:    to make a line graph of the phase data.
- (2) In the Imaging Panel: Imaging Modes, set *Rel. Tip\_Pos* to  $-150\ \text{nm}$ . This is the distance that the EFM will withdraw from the surface during the measurement, i.e. the tip will retract  $150\ \text{nm}$  above the surface from the initial “contact” point. You should know if the current spot is “clean” from the topography scan you just did. If there are features taller than  $50\ \text{nm}$  (most likely dirt), NanoSurf will not remember they are there, and try to run the tip through them when we scan at lower heights.
- (3) Set the tip bias to  $5\ \text{V}$ , in *Z-Controller Panel: Tip Properties*.
- (4) Check the *Const.-Height mode* to start EFM measurements.
- (5) Click *Start* in the Imaging Panel and watch the phase map. Let the AFM scan for a few lines up (at least  $1/5$  of the total image area). Do you see any contrast? Move the tip closer to the surface by  $25\ \text{nm}$ . Keep decreasing the tip-to-substrate distance (be careful not to go below  $-50\ \text{nm}$ ). How does the contrast change? Save this scan when it completes.

- (6) Once you find a good distance for contrast, scan the entire area at the same height. Make sure to select *photo* to save the image when it is done scanning.
- (7) Recall the height variation you observed in the AC mode topography scan. Increase the tip-sample distance by half this value, and reimage the area. Save the image. Increase the distance again by the same amount, and obtain another scan of the area.
- (8) When you are done, reset the tip voltage to 0 V.

### “Calibrating” the EFM scan

- (9) Withdraw, retract the tip, and then carefully raise the AFM head from the sample. Switch samples to the gold substrate.
- (10) Approach the surface. As before, make sure *Autostart Imaging* is **not** checked.
- (11) Click on *Spectroscopy* in the left panel. Change the *Modulated Output* to *Tip voltage*.
- (12) Configure the display panel to show *Phase*, as before. Use only the line graph, and display *Raw Data*.
- (13) Select *Const-Height* mode, in the Imaging Panel, and set the distance to  $-70$  nm.
- (14) In the *Spectroscopy: Measurement* panel, change the number of averages to 20.
- (15) Click on Start. If the shape that emerges is not a downward-facing parabola, first check that the substrate is firmly grounded. Alternately, withdraw the tip, move to a new location and repeat. You may also want to approach the tip to the surface to dissipate any charges collected on the tip. You will have to reselect *Constant Height Mode* after doing so.
- (16) Save the trace, and repeat 4 times.
- (17) Repeat with the ITO substrate, or try other conductive surfaces.



## 4. Background: Intermittent-Contact Mode Force Microscopy & Electrostatic Force Microscopy (EFM)

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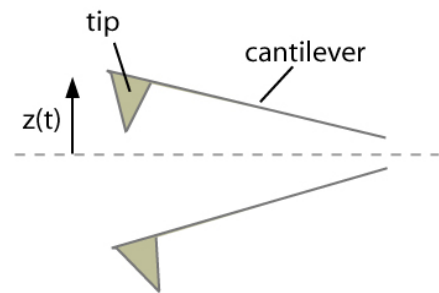
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### Motivation

Contact mode, non-contact mode, and intermittent-contact mode scanning probe microscopy (SPM) all use short range van der Waals forces to probe the topographic features of a sample. However, if we move the scanning probe further away from the surface (~20-60 nm), we can examine longer range forces, such as electrostatic and magnetic forces. In doing so, we can learn about the electrical properties of a material with high spatial resolution. Electrostatic force microscopy (EFM) and its variants are used to study topics as diverse as dopant profiles in silicon transistors, charge injection in organic diodes, and changes in photosensitive reaction complexes in biological membranes. Both intermittent-contact mode and EFM make use of the changes of the motion of an oscillating tip to produce images. In order to understand these imaging modes we first need to review the motion of an oscillating tip. If you have studied simple harmonic motion in your physics or math classes, the next section may be familiar to you.

### Simple Harmonic Motion

The SPM tip sits at the end of a long, flexible cantilever. This cantilever is flexible and behaves like a spring: if the tip is pushed in one direction the cantilever exerts a force in the opposite direction in an attempt to restore the tip to its original position. Since we are going to be examining the motion of the tip in more detail, we first define some parameters:



- $z(t)$  position of the tip as a function of time
- $F$  force exerted on the tip
- $m$  mass of the tip
- $k$  effective spring constant of the cantilever

Remember that the velocity  $v(t)$  and acceleration  $a(t)$  of the tip are related to its position  $z(t)$  through the following derivatives:

$$v(t) = \frac{dz}{dt} \qquad a(t) = \frac{dv}{dt} = \frac{d^2z}{dt^2}$$

Newton's third law ( $F = ma$ ) relates the forces on the tip to its motion. We already mentioned that the cantilever behaves much like a spring, and will we approximate the restoring force using Hooke's law relating spring constants and restoring forces ( $F = -kz$ ). Combining these two equations gives us the following equation of motion:

$$F = ma = -kz$$

$$m \frac{d^2z}{dt^2} = -kz$$

The tip and cantilever are real materials moving through air, so the motion is also damped by both air friction and by losses in the spring. These losses are both approximately proportional to the velocity and so we modify our equation of motion with a "drag force" or damping term  $-bv$ :

$$F = ma = -kz - bv$$

$$m \frac{d^2z}{dt^2} = -kz - b \frac{dz}{dt}$$

Rearranging a bit, we can write this as a differential equation describing basic motion of the tip far away from any substrate (and still without any driving force yet either)

$$m \frac{d^2z}{dt^2} + b \frac{dz}{dt} + kz = 0$$

$$\frac{d^2z}{dt^2} + \beta \frac{dz}{dt} + \omega_0^2 z = 0$$

where  $\omega_0^2 \equiv k/m$  and  $\beta \equiv b/m$ .  $\omega_0$  is the natural frequency of the cantilever.

Most non-contact/intermittent contact SPM is performed while applying a sinusoidally oscillating drive force on the tip, so we must also add the driving force to our equation of motion:

$$\frac{d^2z}{dt^2} + \beta \frac{dz}{dt} + \omega_0^2 z = D \cos \omega t$$

This equation may look familiar. It is the classic equation for the damped and driven simple harmonic oscillator. The solution to this equation is a steady-state motion of the system should oscillate with the driving force, plus a potential phase shift  $\delta$ . You can check that the solution has the form:

$$z(t) = A \cos(\omega t - \delta)$$

## LAB UNIT 2

where:

$$\delta = \tan^{-1}\left(\frac{\omega\beta}{\omega_0^2 - \omega^2}\right)$$

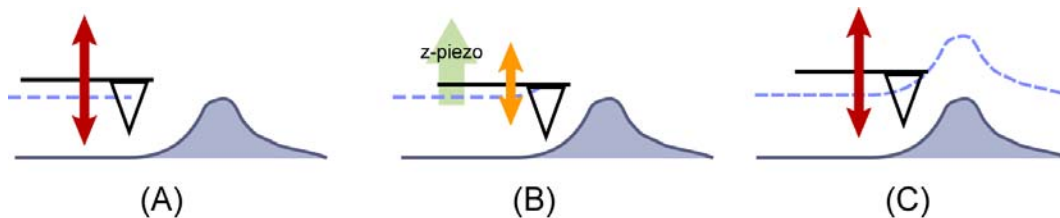
The amplitude,  $A$ , of oscillation is:

$$A = \frac{D}{\sqrt{(\omega_0^2 - \omega^2)^2 + \omega^2\beta^2}}$$

The “resonance frequency” of the oscillator is defined as the driving frequency at which  $A$  is maximized. If the damping is small, the amplitude is at a maximum when the driving frequency equals the natural frequency  $\omega_0$ . The amount of damping in a simple harmonic oscillator is commonly characterized by the quality factor,  $Q$ .  $Q$  is defined as the resonance frequency divided by  $\beta$ , and is a measure of the total energy stored in the oscillator divided by the energy lost per period of oscillation. For systems that are only weakly damped (like an AFM tip vibrating in air), a practical method of determining  $Q$  is to divide the resonance frequency by the width of the resonance peak (where the width is taken at the points where the amplitude is equal to  $1/\sqrt{2} \approx 0.707$  of the maximum).

### AC-Mode Imaging

In a common form of topography imaging, called intermittent-contact mode (or a variation called “Tapping Mode™” by some manufacturers), the AFM is driven at a frequency close to the resonant frequency of the tip. When the tip comes close to the surface, it interacts with the surface through short range forces such as van der Waals forces. These additional interactions change the resonance frequency of the tip, thereby changing the amplitude of oscillation and its phase lag. Typically, an image is formed by using a feedback loop to keep the oscillation amplitude constant by varying the tip sample distance with the z-piezo (see figure below). By plotting the z-piezo signal as a function of position it is then possible to generate an image of the height of features on the surface. It is possible to image in both the attractive, and the repulsive regions of the van der Waals potential, and strictly speaking this divides the classification of AC-Mode imaging techniques into “non-contact” and “intermittent contact” AFM respectively). However, intermittent contact AC-mode imaging is more common for routine imaging.



**Schematic for intermittent-contact mode AFM.** (A) The AFM tip is driven near its natural resonance frequency to obtain a target amplitude of oscillation. (B) As the tip approaches changes in topography, the increasing van der Waals forces shift the resonance frequency, which causes the tip’s oscillation amplitude to decrease. In response, the Z-piezo lifts the tip away from the surface so (C) the original oscillation amplitude is reestablished. By tracking the Z-motion of the tip, we obtain the measured topography of the surface (dashed line).

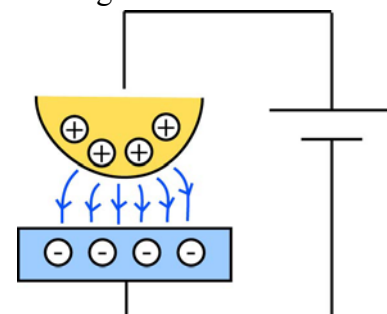
Of course, the material properties of the sample affect tip-surface interactions, so the topography image obtained by AC-mode imaging isn't perfectly free of artifacts (some imaging modes even exploit differences in elastic properties of the surface to differentiate materials). Nevertheless, AC-mode imaging is much gentler and can be used to image a wider variety of soft samples than contact mode imaging.

### Electrostatic Force Microscopy

The goal of an EFM experiment is not to image the surface topography, but rather to image the electrical properties of the surface. This is accomplished by vibrating a metal-coated tip some distance away from the surface — beyond the range of short range van der Waals interactions, so that only long-range forces (such as electrostatic forces) remain.

As the tip scans over a surface, its motion is affected by the forces between it and the surface below. To understand EFM, it is useful to think of the tip and sample as forming two plates in a very small capacitor. The potential energy,  $U$ , of a capacitor with capacitance  $C$  charged to a voltage  $V$  is given by:

$$U = \frac{1}{2} CV^2$$



The force  $F$ , is always given by the first derivative of the potential  $U$ , as a function of position  $z$ . The force between the tip and the cantilever is then:

$$F = -\frac{dU}{dz} = -\frac{d}{dz} \left( \frac{1}{2} CV^2 \right) = -\frac{1}{2} \frac{dC}{dz} V^2$$

This force depends on both the applied voltage (independent of distance) and the capacitance (depends on distance). This is really an electrostatic force (Coulomb's Law) in a different form. The potential difference causes opposite charges to build up on the tip and the substrate (as seen in the cartoon), which pulls the tip towards the substrate.

How does this force affect the tip motion? Well, to first order it doesn't! (You may remember from your physics coursework that the resonant frequency of a spring-mass oscillator doesn't depend on the value of the local gravitational acceleration). It is not the electrostatic force, but rather the *force gradient* that determines the oscillation of the tip. For example, the force gradient using the restoring force from the cantilever (Hooke's Law) is

$$F = -kz$$

$$\frac{dF}{dz} = -k$$

This is the spring constant, which shows up in the natural frequency  $\omega_0$  of the oscillator. Any other forces on the cantilever that have a significant force gradient will affect the tip's motion. In this case, we are interested in measuring the electrostatic force by how

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it affects our oscillating tip. It is easier to see the effect of this additional force on the tip's motion by writing its contribution to the total force gradient:

$$F = -kz - \frac{1}{2} \frac{dC}{dz} V^2$$
$$\frac{dF}{dz} = -k - \frac{1}{2} \frac{d^2C}{dz^2} V^2$$

Assuming  $\frac{d^2C}{dz^2}$  is relatively constant for the range of motion, we can consider this new factor as a change in the spring constant,  $k' = k + \Delta k$ . **In other words, the electrostatic force gradient works like a change in the effective spring constant of the cantilever.** This will change the natural oscillation frequency, now  $\omega_0'$ , and the phase shift  $\delta'$  between the cantilever and drive signal for some constant driving frequency  $\omega$ .

$$\omega_0' = \sqrt{\frac{k'}{m}}$$
$$\delta' = \arctan\left(\frac{\omega\beta}{\omega_0'^2 - \omega^2}\right)$$

For small damping factors and a driving frequency at the resonance frequency ( $\omega_0 = \omega$ ), we can approximate the change in phase shift as [3]:

$$\Delta\delta = -\arcsin\left(\frac{Q}{2k} \frac{d^2C}{dz^2} V^2\right)$$

In real experiments, the phase shift versus voltage curve has a non-zero offset,  $V_0$ :

$$\Delta\delta = -\arcsin\left(\frac{Q}{2k} \frac{d^2C}{dz^2} (V - V_0)^2\right)$$

This offset is attributed to the difference in work function between the tip and the sample.

## Applications

Electrostatic force microscopy and variations of EFM (such as scanning Kelvin probe microscopy (SKPM), measuring differences in surface potential; magnetic force microscopy (MFM), measuring magnetic moments) can be used to characterize many different samples, such as dopant profiles in silicon-based transistors, polarization in piezoelectric materials, and charge distributions in organic semiconductors. In this lab, you apply EFM to characterize metal films as well as semiconducting polymer blends.

## References

1. *Scanning Probe Microscopy and Spectroscopy: Techniques, and Applications*. Edited by Dawn Bonnell, Wiley-Interscience Publication, 2nd Ed., New York, 2001.
2. *Classical Dynamics of Particles and Systems*. Jerry B. Marion and Stephen T. Thornton, Harcourt Brace & Company, 4th Edition, 1995.
3. C H Lei, A Das, M Elliot, J E Macdonald, "Quantitative electrostatic force microscopy-phase measurements." *Nanotechnology*. **15** (2004) 627-634.