

Instability & Patterning of Thin Polymer Films

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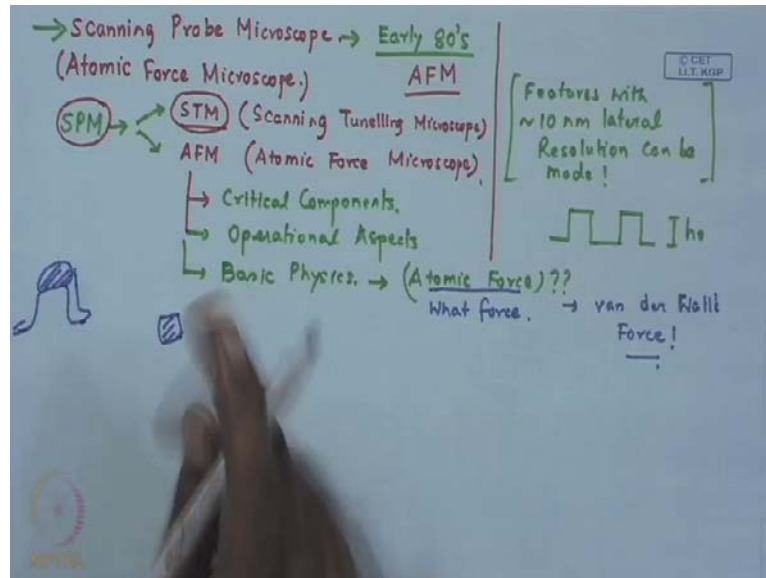
Lecture No # 22

Atomic Force Microscope - 1

Welcome back. We now change give us a little bit and start talking of something likely different. As you can see from the title of the lecture itself, we are now going to talk about atomic force microscope. I do not know how many of you are aware with this name of atomic force microscope or the AFM as it is commonly known; it is very unique a special type of a micro scope and is very widely use these days. Now, you might wonder in a course of instability and patterning, we have so far primarily focused on the patterning aspect. And we have not talked about in much of instability as of now, but which we will do in the subsequent lectures.

You might wonder why all of a sudden you pick up a special type of a micro scope. There are many courses available both on line as well as class room courses, which talk about materials characterization, where you learn a whole lot of techniques; and whenever you talk of seen something small, you tend to sort of relay on the fact that we go for a micro scope.

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But if you remember the last couple of slides about soft lithography, we talk that features with 10 nanometer lateral resolution can be made by soft lithography. So, critical question to ask is, how does one see these structures? I mean you might have made something, but how really does one see this, because a normal microscope even the highest and optical microscope with a hundred x objective, which magnifies your image by thousand times. You won't be able to see anything below 400-500 nanometer or maybe a micron and that pretty faintly.

The other thing is you have been routinely talking about topographic patterns like this, and we talked about all sorts of things high these, that. Question to ask again is how do you measure the feature height? Because a normal microscope what you see. Normal microscope I also include a scanning electron microscope in this regard, where the only difference with an optical microscope, it is very advanced equipment. But the major difference with an optical microscope lies in terms of the optical source. In an optical microscope, you essentially use white light to illuminate your sample. In scanning electron microscope you use a stream of electrons. So, that your wavelengths are small and therefore, you can resolve to much higher extent.

But do not forget I mean this course does not permit me to go into the details of microscope. But do not forget that in an optical microscope or in scanning electron microscope, ultimately what you see is more like a projection, that is like a picture you take in

your camera. It is a 2 D projection of a 3 D system. So, with your digital camera or cell phone camera if you take a picture, you are taking a picture of the 3 D world, but you are seeing it on a 2 D plane. So, looking at a picture you really cannot say suppose, two people are standing at some distance one is closer to you, one is far away.

So, if you take a picture all you can see is the person who was standing closer to you is appearing larger in the picture. And the person who was standing further away from you is appearing smaller in the picture. But, you cannot looking at the picture say, how what was the separation distance between them, how far the second person was standing from the first person. So, what happens is that since you are looking at a 2D projection, the information about the depth sort of is lost. Exactly the same thing happens in optical micro scope or scanning electron micro scope. You cannot get a clear idea about the feature height, which is very, very important when you are talking about nano and meso scale patterns.

So, this atomic force micro scope which is a special and the I would say the most popular instrument in the class of set of instruments which again is relatively new early 80's. The developments started what is known now as the scanning probe micro scope group of techniques. So, this goes by the name SPM why the name comes, how it works we will eventually discuss everything in very, very simplistic fashion. So, you do not have to be earlier big time physicist to understand this. We will have all the understanding considering that you are an engineering student of an undergraduate college or post graduate student in with a predominantly background in chemical engineering. So, do not worry about that.

So, SPM it is known as the scanning probe micro scope. Typically, it has two major micro scopes; one is the STM which is known as the scanning tunneling microscope, what is tunneling effect? I will discuss very shortly, but you can just do a quick Wikipedia search what is tunneling and the atomic force micro scope. Why I talked about STM is STM was actually the predecessor of AMF and based on the developments of STM only the AMF came up, but STM works only for a conducting surface. So, since you are talking mostly about a polymer surface STM does not work an AMF works perfectly well over there.

So, you will talk about and AMF in much greater detail, but, just to give you an introduction. So, that you do not feel like left out I did not know, I do not know S T M, but I talk about AMF you do not realize that day falling to the same group of methods. I just spend a few minutes talking to about STM. So, remember that AMF is a special class of scanning probe microscope probably the most popular class of these methods. And let us see what have an AMF works. So, what we are going to do we are going to talk about the critical components and some operational aspect.

As well as we talk about the basic physics, which is extremely fascinating and we talk about here what is this atomic force? What force exactly are we talking about? And it is actually a nice breeze between the two parts of the course that is the pattering part on the instability part because the forces we introduce here or talk about here. Or significantly, responsible for the instability in the first or the second lecture of the course we talked about instability spontaneous instability. So, those instability as we will see or cross by the same forces which are used to generate an image in an atomic force microscope.

You can guess it primarily we will be talking about the Vander walls force (No audio from 08:26 to 08:30). And we will see how this is used for imaging, as well as in subsequent lectures may be after five six lectures we will start realizing how these forces are responsible for spontaneous instability or different types of instability in thin films.

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In the early 1980's scanning probe microscopes (SPMs) produced the first real-space images of a surface.

Now, SPMs are used in a wide variety of disciplines, including fundamental surface science, routine surface roughness analysis, and spectacular three-dimensional imaging—from atoms of silicon to micron-sized protrusions on the surface of a living cell.

The scanning probe microscope is an imaging tool with a vast dynamic range, spanning the realms of optical and electron microscopes. It's also a profiler with unprecedented 3-D resolution. In some cases, scanning probe microscopes can measure physical properties such as surface conductivity, static charge distribution, localized friction, magnetic fields, and elastic moduli. As a result, applications of SPMs are very diverse.

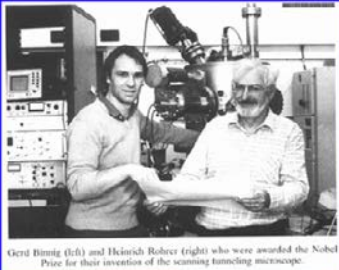
So in early 80's scanning probe microscopes were first introduced and they are able to produced first real space images of a surface. What is real space image? It is a essentially the three dimensionally images of a surface. So, that you do not only see the lateral structures, you do not see only the lateral dimension or only could measure the lateral dimension of the structures But you also get at two information about the height of the feature height. So, in normal microscope so, if you have a let us say feature like this, in a normal microscopy we will see something like this. An AMF you will not only see like this, but you will also get an idea about height. So, this is in very not shell, this is one of the major advantages what an atomic force microscope or an SPM group of method gives.

So, now, SPMs are used to an wide variety of disciplines including fundamental surface science, routine surface roughness analysis, spectacular three dimensional imaging from atoms, two micron sized protrusions of surface living cells. Also, the scanning probe microscope is an imaging tool with a vast dynamic range spanning the realms of optical and electronic microscopes. It is also a profiler with unprecedented 3 D resolution. In some cases, scanning probe microscopes can measure physical properties such as surface conductivity, static charge distribution, localize friction, magnetic fields and etcetera.

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AFM was discovered in 1986.
Gerhard Binnig and Co - workers IBM Corporation
Physical Review Letters, 56,930 (1986).
(An extension cum derivative of the STM)

Gerd Binnig and Heinrich Rohrer were awarded Nobel Prize in 1986 for their Discovery of STM in 1982.




Gerd Binnig (left) and Heinrich Rohrer (right) who were awarded the Nobel Prize for their invention of the scanning tunneling microscope.

SCANNING TUNNELING MICROSCOPY - FROM BIRTH TO ADOLESCENCE

Nobel lecture, December 8, 1986

by
GERD BINNIG AND HEINRICH ROHRER
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

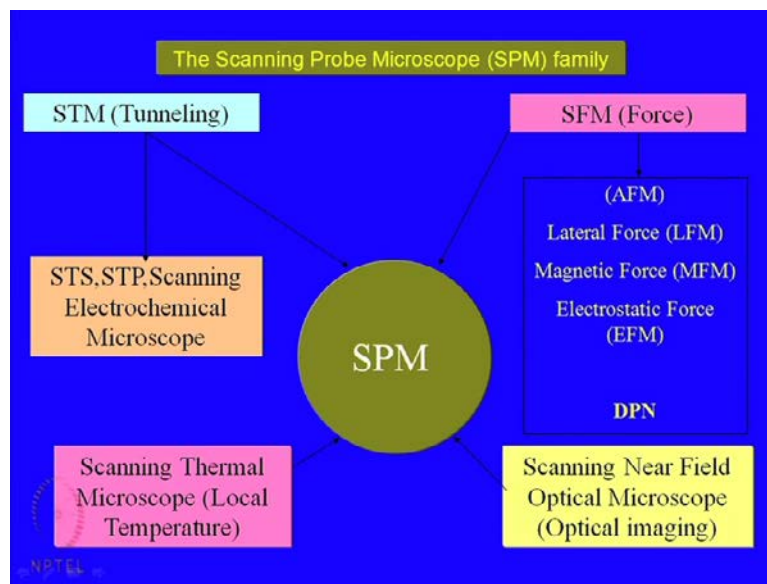


Short History of AFM
<http://hansmalab.physics.ucsb.edu/afmback.html>

Which is another you need think I will do not be apply I mean really possible do with all what, where is written here you will understand all these things. So, AMF was

discovered does I already pointed out it was early 80's. So, AMF was discovered in 1986 by Gerd binning and co workers at IBM Corporation, this particular paper if you have the access to P R L physical review letters, this 1986 paper contain the details about A F M. So, it is essentially an extension cum derivation of the STM. And binning and Rohrer were awarded Nobel Prize. The discovered was so unique that within four years of discovery of STM the got the Nobel prize in 1986. If you are interested about the short history of A F M, here is link you can sort of look into and you can get very nice idea.

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So, this is the scanning probe microscope or SPM group of family of techniques. And one side we have the scan scanning tunneling microscope there are so, STS, STP scanning electro thermal microscope. Scanning thermal microscope which gives a you an idea about the local temperature etcetera. For our purpose please do not be over burdened with these parts. So, here we will just talk in a little bit about the scanning tunneling micro scope. Because this side the left side of this view graph whatever you have do not forget they require a conducting surface. (No audio from 11:56 to 12:03).

So, we will since, we are talking primarily about polymer so, we will not worry about that. Next comes the SFM a again a generic names scanning force microscope of which the of course, the most significant member the major platform is the atomic force micro scope. It has several additional features lateral force microscopy, phase contrast microscopy, magnetic force microscopy, electrostatic force microscope. And also an

AMF platform can be used itself as one of the direct write patterning techniques which is known by the name DPN or dipen nano lithography.

We have talked about some of the direct write methods, in while talking about patterning. So, here is another method and I will talk about it in some details. There can be so, AMF platform can also be augmented with an optical microscope platform and you can have something like scanning near field optical microscope. Or, which is known as the s normal n some which actually produced an optical image and since you are imaging at the near field so, this sort of over comes the diffraction limitation. But we will not go into the details of that, we will talk only a little bit about the same very little, very fundamental basics of a STM we will talk about and then you will move on to an AFM.

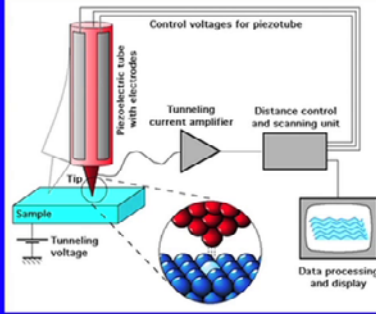
So, I will as I have already pointed out I will try to give you a sort of a prospective so that you understand the operational aspects of an AMF along with the physics and the key components. Now, AMF sort of started to with the market or commercially they started to get available in early 90's. And now very many companies in the world make their own atomic force microscopes. Various institutes in India now have AFMs all the major IITs and many other research institutes. So, AMF is pretty routine now, but still the physics is extremely fascinating and if you understand how the images are generated. I am sure you will really like it and also it is important from the standpoint of using an AMF that you understand the basic physics. Because that will really help you to enhance the resolution or quality of your image to a large extent.

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Scanning Tunneling Microscope (STM)

The STM is based on the concept of quantum tunneling.

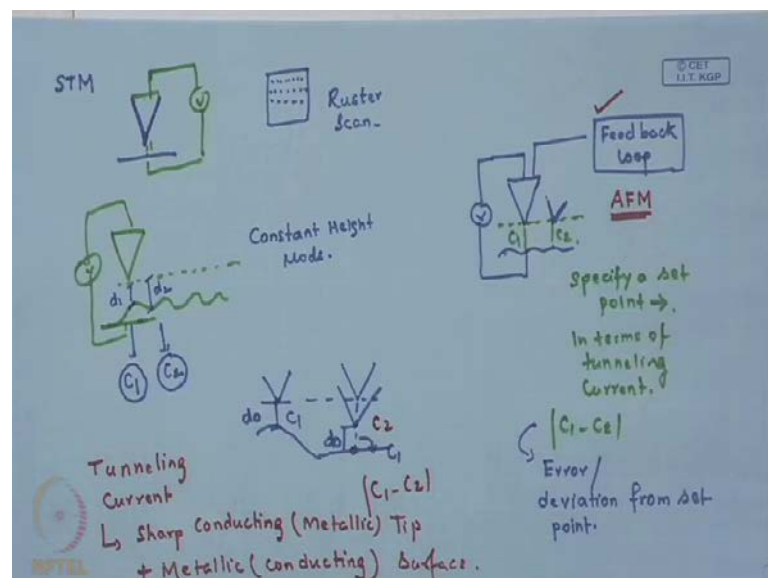
When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them.



The diagram illustrates the components of an STM. A piezoelectric tube with electrodes is used to precisely position a sharp tip above a sample. A tunneling voltage is applied between the tip and the sample, causing electrons to tunnel through the vacuum gap. The resulting tunneling current is amplified and fed into a distance control and scanning unit, which maintains a constant tip-sample distance. The data is then processed and displayed on a monitor.

So, this is how we will proceed. So, this is what is a scanning tunneling microscope is all about. It uses of very sharp metallic tip to scan a metallic surface sorry conducting surface. Now, this is based on the concept of quantum tunneling, which very simply put when a conducting surface is brought or conducting sharp tip is.

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The handwritten notes describe the operation of an STM and its relationship to AFM. It shows a circuit diagram for a tunneling junction with a voltage source and a current meter. A diagram of a tip and sample shows the tunneling current I and the distance d . The notes mention "Constant Height Mode" and "Feedback loop" for "AFM". A note specifies a set point in terms of tunneling current, and another note indicates the error/deviation from the set point is $|C_1 - C_2|$. The notes also mention "Tunneling Current" and "Sharp conducting (Metallic) Tip + Metallic (conducting) Surface".

So, you have a sharp metallic tip let us say very sharp metallic tip is brought in contact proximity in very close proximity to another metallic surface. And you apply a voltage or bias between the two, what happens is the do their might not be direct contact between

the two, you still can have a flow of electrons between these two surfaces like this. So, this is what is known as the tunneling current. And the tunneling current once you start having so, once you apply a specific voltage and you have a tunneling current. The magnitude of this current is a function of the separation distance between the tip and the sample or between the tip and the surface.

So, in other words, if you decide to move your tip along with the voltage over the surface at a constant height and the surface is something like this. So, as the tip moves there is now a variation in the separation distance between the tip and the surface. So, as a consequence of this variation in the heights so, let us say it is d_1 over here and d_2 over here what is going to happen as the tip moves? So, the location one the tunneling current the magnitude tunneling current will be different from the magnitude of the current tunneling current at the second location.

So, this the principle based on which an STM works. So, idea is that you take a surface so, this is we are seeing from the top, you have the tip like this and the tip sort of Rusters so, what is Ruster scan? It is more like a do loops. So, the tip starts from the one edge goes all the way up to here comes back, starts from here goes all the way up to here, comes back goes to the next line again goes comes back again goes comes back like this. So, what are the essential features? You have sharp metallic tip. you have a conducting surface, you apply a bias or a voltage and then the tip scans Rusters. Now, since the magnitude of the tunneling current is a function of the separation distance. So, the unduly sense of the on the surface.

During the unduly sense on the surface, the tip encounters during undergoing this Ruster scan gets reflected in a change get reflected as change in the magnitude of tunneling current. And then you can map this there are two different modes I am going to talk about it very quickly and very shortly. But this can itself the variation in the tunneling current itself can sort of act as a major of the surface topography. So, here it is, when a conducting tip is brought very near to the surface to be examined which has to be a conducting surface also. And bias which is a voltage difference is apply between the two then electrons tunnel through the vacuum or air between them. Of course, this typically works in vacuum so that the electrons the tunneling electrons do not collide with the molecules of air and sort of ionize get the stacked.

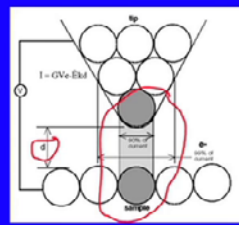
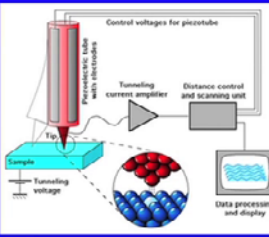
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Scanning Tunneling Microscope (STM)

The resulting *tunneling current* is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample.

Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form.

STM can be a challenging technique, as it can require extremely clean and stable surfaces, sharp tips, excellent vibration control, and sophisticated electronics.



The resulting tunneling current is a function of the tip position applied voltage. So, tip position essentially here means the distance between the tips from the surface. And the applied voltage and the local density of state of the sample you can ignore this, if you are interested you can look into. Now, what local density of state means, but forget about that for specific sample at a given condition, what is more important is that the tip position and the applied voltage they sort of determine the magnitude of the tunneling current. So, information is acquired by a monitoring the current as the tips position scans across the surface. So, this particular sentence if you paragraph, if you now look at we have already talked that the tip sort of under takes a Ruster scan and one can acquired the, one can monitor the information is acquired by monitoring the current how it is done we will see.


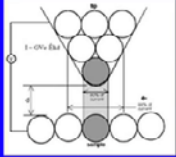
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Scanning Tunneling Microscope (STM)

STMs can be designed to scan a sample in either of two modes: *constant-height* or *constant-current* mode.

In constant-height mode, the tip travels in a horizontal plane above the sample and the tunneling current varies depending on topography and the local surface electronic properties of the sample.

The tunneling current measured at each location on the sample surface constitute the data set, the topographic image.



The diagram shows a tungsten (W) tip with a sharp apex positioned above a sample surface. The tip is connected to a circuit with a current source $I = 0.01 \text{ nA}$ and a voltage source $V = 100 \text{ mV}$. The sample surface is represented by a grid of atoms, with a shaded region indicating the area of interest. The tip is shown in contact with the surface, and the tunneling current is indicated by an arrow pointing from the tip to the sample.

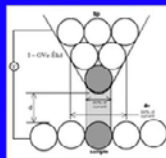
Practically STM can be a challenging technique as it requires extremely clean and flat surfaces, sharp tips, excellent vibration control and sophisticated electronics, but let us not talk about that. STM can be designed to scan a sample in two possible modes. So, this is important if you can have two different modes; one is the constant height mode and the other one is the constant current mode. The one we briefly described to you here is actually the constant height mode. So, you maintain a constant height and go on scanning the surface or raster the surface. And this is done by the tip at a fixed height encounters the undulations you keep track of the change in the magnitude of the tunneling current and from that you try to reconstruct the surface.

Understanding the fact that if your tunneling current, if the magnitude of the tunneling current is higher, then the surface was closer to the tip. If it is lower than the surface was further away from the tip and so you can reconstruct the surface. So, this is the constant height mode the tip travels in a horizontal plane above the sample. And the tunneling current varies depending on topography and the local surface electronic properties of the sample. The tunneling currents measured at each location on the sample surface constitute the data set which is the topography image. So, essentially the variation in the tunneling current itself is a measure of the topography of the surface.

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Scanning Tunneling Microscope (STM)

STMs can be designed to scan a sample in either of two modes: *constant-height* or *constant-current* mode.



In constant-current mode, STMs use feedback to keep the tunneling current constant by adjusting the height of the scanner at each measurement point.

For example, when the system detects an increase in tunneling current, it adjusts the voltage applied to the piezoelectric scanner to increase the distance between the tip and the sample.

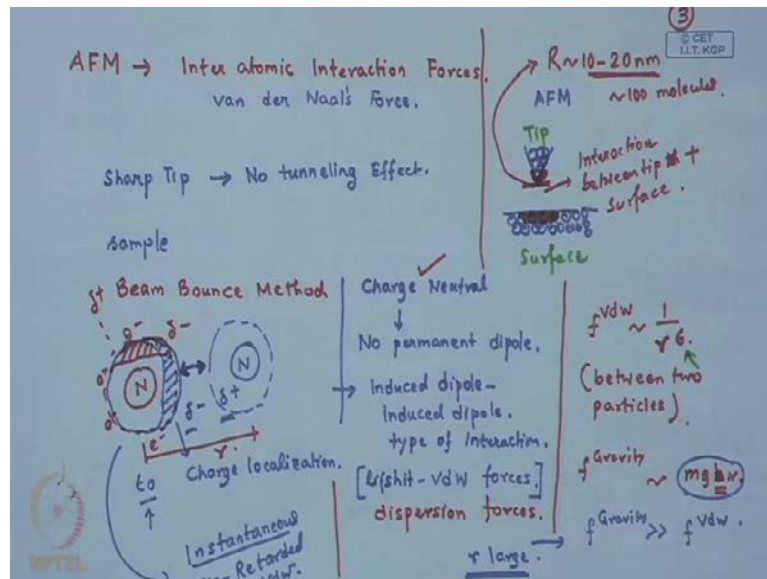


The other mode, in the constant current mode the STM now uses a feedback loop. So, in addition to the hardware we have already talked about. So, you have a tip you have a conducting surface. You apply a bias and you also have a feedback loop, this is important you are all chemical engineering students you are all understand what is the feedback. So, what it does that you have a set point specify a set point in terms of the tunneling current. (No audio from 21:52 to 22:01). Now, the tip starts to Ruster, starts to scan so, let us say this was the set point the c_1 it goes to the second location where the current is now c_2 because of the surface topography. This c_1 minus c_2 is know the deviation from the set point or the error. (No audio from 22:22 to 22:34). This error is now fed to the feedback loop which then allows the tip to move up at down.

How it is moved? We will discuss when we talk about an atomic force microscope. But this error is now fed to the feedback loop so that it adjusts the position of the tip. So, let us say the tip was here it was corresponding to a. (No audio from 23:00 to 23:06). So, this is let us say the set point configuration, the current was c_1 it has now gone to the second point, the distance has increased. So, the current reduce actually so, this c_1 minus c_2 is now the error and based on this the error is fed to the feedback loop. So, that it allows the tip again to comeback so that this distance matches this distance here and the current again becomes c_1 . So, in this case, the location of that tip it is self reflex the contour of the surface and you can generate the image like this.

Now, it is important to understand the existence of the feedback, we will going to we are going to talk about it in greater detail because all the commercial of the current AFMs what with this feedback loop mechanism. So, this is in a very brief nut shell the operation of an STM. Important thing to need is that the principle of a STM requires tunneling current. And which is possible only with a very sharp (No audio from 24:16 to 24:23) metallic tip and a metallic again a conducting surface. And therefore, though it is extremely useful, scientifically extremely fascinating. It has unfortunately limited application in terms of polymer structures, imaging in polymer structures. I was still I think this much amount of fundamental knowledge in STM will help you, both to understand how the AMF evolve. And also STM has a technique itself is extremely power full and there are many application areas where the STM finds rather significant application.

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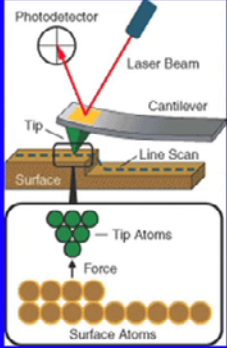
With that we now move on to atomic force microscope, which as I have already pointed out is to large extent based on the developments related to STM or in every two sense the STM was the predecessor of the A F M. So, let us see what are the advantages? Firstly, the first thing without going into any details you need to understand, that AMF does not suffer from the one major limitation which is their in an STM. AMF does not require a conducting sample or conducting surface and can work for any type of sample. Therefore, since it does not require a conducting surface, it cannot work on the principle of tunneling, but it works on the principle of something that is more fundamental. And

that is the interaction forces between molecules or particles or surfaces. So, AMF realize between the inter atomic interaction forces. Now, one of our previous lectures we have actually talked about these interaction forces and I am I think I have already introduced you to the concept of Vander Waal's force, we will leave is it today.

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Atomic Force Microscope

- In an Atomic Force Microscope the imaging (or more accurately, the information about the topography) of a surface is done based on the modulation of interaction forces between two atoms (or molecules).
- In reality, the instrument operates based on the interaction between two surfaces, the sample and a sharp tip.
- The probing tip is attached to a cantilever and the force acting on the tip causes a small deflection of the cantilever.
- This deflection is detected and mapped as the tip scans the surface to obtain the image of the surface.



The diagram illustrates the AFM setup. A cantilever with a sharp tip is positioned above a surface. A laser beam reflects off the cantilever to a photodetector. A line scan is shown on the surface. An inset shows the interaction between tip atoms and surface atoms, with an upward force arrow.

ITKgp

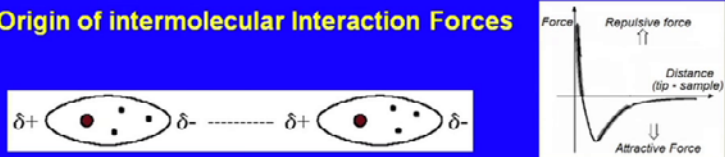
So, this is what we can be an atomic microscope, do not going to the details of the definitions and all these things, these are things that everything we will understand what, how it works and all that. In an atomic force microscope, the imaging or more accurately the information about the topography of a surface is done based on the modulation of interaction forces between two atoms. So, interaction forces this is important, we talk about the interaction forces between atoms or molecules. In reality we cannot go down to the atomic level and we work based on the interaction forces between two surfaces. The in reality the instrument operates based on the interaction between two surfaces the sample and a sharp tip. So, here also you have a sharp tip and you have a sample, but unlike STM, there is no tunneling effect arising out of the tip, but we will see how exactly it differs.

So, this is in nut shell the hot of an AMF operating hot. So, here you have a tip so, here you have molecules and here you have the surface molecules. So, the instrument essentially works based on interaction nut (No audio from 28:07 to 28:14) between the tip and the surface. This is a picture which you will see again and again and again. This

is this particular technique which is known as the standard industry standard of a cantilever mounted tip and a laser and a photo detector this is known as the beam bounce method. We will understand so, get you use this figure, but I can assure you that after two more lectures when you completed atomic force microscope, you will understand every single component of how it works and what it means.

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Origin of intermolecular Interaction Forces



- For a charge neutral sample scanned in air, the interaction force between the sample and the tip originates due to attractive van der Waal's interaction.
- Between two molecules (or atoms), the nature of van der Waal's force is always attractive and scales as $1/r^6$.
- The signature of non retarded van der Waal's interaction can be felt over ~ 10 nm separation distance.
- Between two surfaces, the scaling or decay shows a functionality of $1/r^2$.

So, with the open mind let us start understanding an AMF, what how it works? So, first thing we need to understand, what is this intermolecular interaction forces we are talking about. Now, these forces are the so called Vander Waal's forces and I am sure that you understand that will large extend what they are? They are the most fundamental form of force, somebody who has slide confusion. So, this is a nucleus and then you have the electrons which are in a atom for example, you have the electrons which are circling the nucleus. This is picture I am sure you have got use to from your school days, let us school days may be seventh or eighth standard.

In this picture we use to draw, but really it is that it is not so simple the it is either electrons or not like this isolate discrete entities rotating like the planets. I am sure in your school days you also learnt at some point of the other what is the similarity and the difference between the electronic structure and the solar system. In reality, it is very high frequency oscillation of the electrons around the nucleus. And at any given instance t g role let us say what happens is there is a charge localization. (No audio from 30:25 to

30:32). The moment there is charge localization this leads to a delta minus charge which is localized over this area. Now, this delta minus charge what it does? It sort of induces a delta plus positive charge on the neighboring atom.

And therefore, since this is this has opposite polarity the nature of interaction is sort of always attractive. But what happens is this delta minus is a temporary localization. So, we are talking about molecules which are charge neutral and there is no permanent dipole. So, even in charge neutral, non dipolar molecule you have this phenomena occurring at all instances of time so, this is the type of interaction which is known as the induced dipole (No audio from the 31:31 to 31:36) induced dipole type of interaction. This is what is known as the Lifshitz Vander Waal's forces and this the most fundamental form of force.

Now, what happens is the subsequent instants what happens is this localization the position of this localization now changes. So, this is now let us say localize here and it induces a charge over here. So, this force or this attraction though the overall nature of the interaction is attractive. There is no physical attraction present or any bond formation text place because of the fact that the charge localization sort of the position of the charge localization changes with every instance of time. And therefore, this attraction sort of is disperse over the entire material or entire bulk of the material. So, this is also often refer to as the dispersion forces.

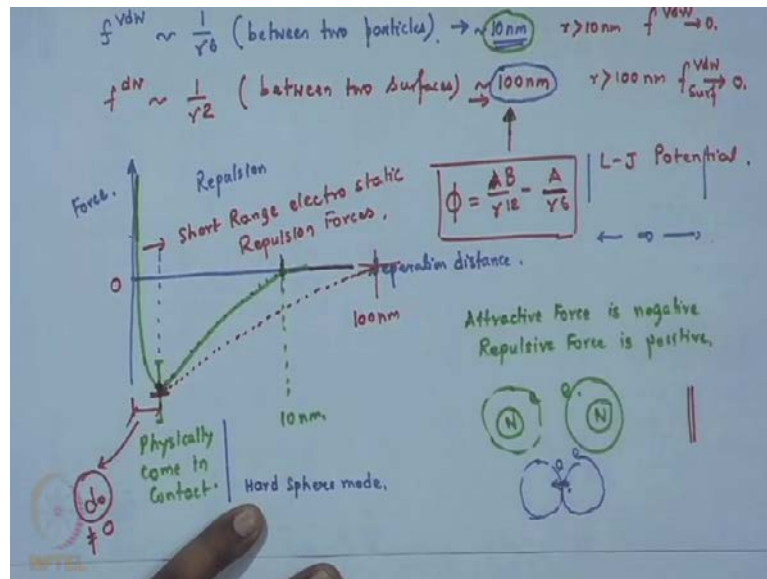
So, this is available or these results in all materials and some of you might be knowing the this is the most fundamental form of any force. What is important to realize the though this is the most fundamental form of force, in reality or in our microscope equal we hardly see the signature of Vander Waal's force. And everything we see is sort of a function or dominated by gravity. The reason for this is the, this interaction sort of scales with so, $v d w$ the Vander Waal's the interaction scales with one by r to power of 6 between two particles, next they let us say atoms or molecules. So, r is the separation distance between the two.

In contrast, your gravitational force scales with $m g h$, h is the separation distance. So, you can understand immediately that in the microscopic world where a $h r$ whatever so this can be r there equivalent here. If r is large, this term will be much much larger then Vander Waal's force. And therefore, in our macroscopic world we do not see any

signature of Vander Waal's interaction. However, you can now imagine if r is small, what happens? What happens is that since r is in the denominator therefore, with progressive reduction of r this term becomes dominating or becomes much much larger. And for very small r at the molecular level or at the meso scale, the Vander Waal's force sort of dominates much at much higher rate as compare to the gravitational force.

Now, one of the things that is interesting to note is that we talk so much about nanotechnology. So, everything everyone is talking about nanotechnology. Now, there are quite a few factors which make nanotechnology at this particular length scales. So, unique and even in the interaction of this particular course we did talk about some of these methods or some of these reasons. But one of the reasons of course, is the fact that at these length scales very small length scales. Length scales corresponding to few molecular diameter or let us say up to 10 or 100 nanometer what happens is you also have a very strong signature of these Vander Waal's forces and gravity is almost absent.

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So, many of the spectacular phenomena so call spectacular phenomena, once is at these length scale is attributed to the fact that the interaction forces or the intermolecular interaction forces have or have a significant role in some of those phenomena. So, for all understanding what is important to note that Vander Waal's force between two particles have a scaling of one by r to the power of 6. And for the timing you believe me that this sort of stretchers, this interaction stretchers to roughly around ten nanometer definitely

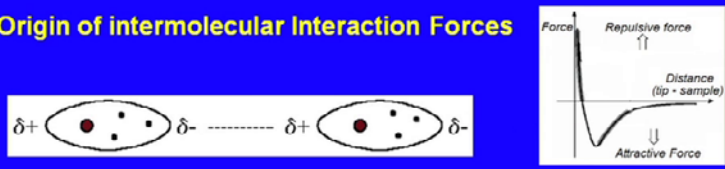
not beyond ten nanometer where this becomes large and eventually so for r greater than ten nanometer the tens to zero.

The other thing you need to understand at the this moment and it will I will we will take of the derivation in after couple of classes is that this same force scales as one by r square between two surfaces. How it comes? r square from r to the power minus six we will show. So, what happens is the $d k$, the nature of the $d k$ of the force becomes much weaker now. So, that it tapers of at much slower face and consequently the interaction sort of structures up to 100 nanometer beyond or greater than 100 nanometer. So, v w surface I would say again tend to 0.

Now, in one of the slides we have already mentioned that atomic force micro scope primarily operates based on the interaction between two surfaces. So, this is more of an important number for us and we will see how this becomes important. So, the signature of nano retarded Vander Waal's force, the type of Vander Waal's force we talked about is an induce dipole type interaction the what has been assumed implicitly is that this induction of the charge is instantaneous. (No audio from 38:08 to 38:15). And this is what is known as the non retarded Vander Waal's force, but you in you also have something called retarded Vander Waal's force to which about I suggest that you look into the internet and get an idea what it is, it is not essentially very important for this particular course to have a wait your idea about it.

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Origin of intermolecular Interaction Forces



- The signature of the interaction extends to ~ 80 nm to 100 nm.
- This force is in the range of inter-atomic forces $\sim 10^{-13} - 10^{-06}$ N.
- There can be host of other type of interaction forces acting between the tip and the sample like mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces Casimir forces, solvation forces etc.

So, between two fundamental particles the scaling is one by r to the power of 6 and stretches roughly up to 10 nanometer. Between two surfaces the scaling changes to one by r square and stretches are around 80 to 100 nanometer. The forces in the range of inter atomic forces is in the range of 10 to power of minus 13 to 10 to the power of minus 6 neutron. There can be host of other types of interaction forces between the tip and the sample like mechanical contact, Vander Waal's, capillary force, chemical bonding, electrostatic forces, magnetic forces, cassimere forces, solvent salvation forces etcetera.

Some of which we will take up in little be detail, but the most important thing to realize that an AMF sort of works for mostly based on the Vander Waal's forces. And like to sort of draw your attention at this point towards this particular potential curve. This some of you might be very well conversation to with this. This is a typically potential curve, it can be the famous leaner zones potential, it can be any other type of potential. So, what it gives you is an idea of how the force between let us say two particles or two surfaces change as function of separation distance. So, let us say you have two surfaces which are at infinite separation distance. So, then there is no interaction between them. So, the force is 0. Now, think of the fact that you are progressively bringing in one of the surface in close proximity to the other.

If you are talking about the Vander Waal's potential are the forces arising because of van Vander Waal's interaction. We already understand that this stretches maximum up to 100 nanometer. The other thing we understand that the nature of this interaction is attractive. So, here we follow a conversation that an attractive force is negative and repulsive force positive. So, this potential curve can be generated for two atoms, or two particles, or two surfaces whatever you want it is roughly the generic nature will be the same. Only thing is the curvatures and the distance is will change.

So, if you are talking about let us say between two particles which is easier to understand infinite separation distance apart there is no interaction. You bring the particles closer to each other and then you understand that once you cross this number 10 nanometer so, let us say it is over here, then the interaction starts or the interaction is no longer zero, the interaction starts and the interaction is attractive. So, the force is somewhere over here, you also have a scaling of one by r to the power of six and so, r progressively reducing

the interaction force sort of increases so, you get a curve like this. Till you with this point where if you look at the potentially curve you see a short increase.

So, all the way down to the repulsive regime so, I and I hope you have understood this part of curve. So, this is the point up to which this particular interaction sort of stretchers. Now, what is this point? This point is the point where the two atoms of the molecules sort of physically come in contact. So, you have this nuclear you have this electron and then the physically come in contact. What is assumed here or it is easy to understand actually we assume this the validity of the hard sphere mode, but even other ways if these two know or in contact and then you still try to force them closer to each other. What is going to happen? There is going to be an overlap of the electron clouds and there is going to be an electrostatic repulsion so that is what is captured here.

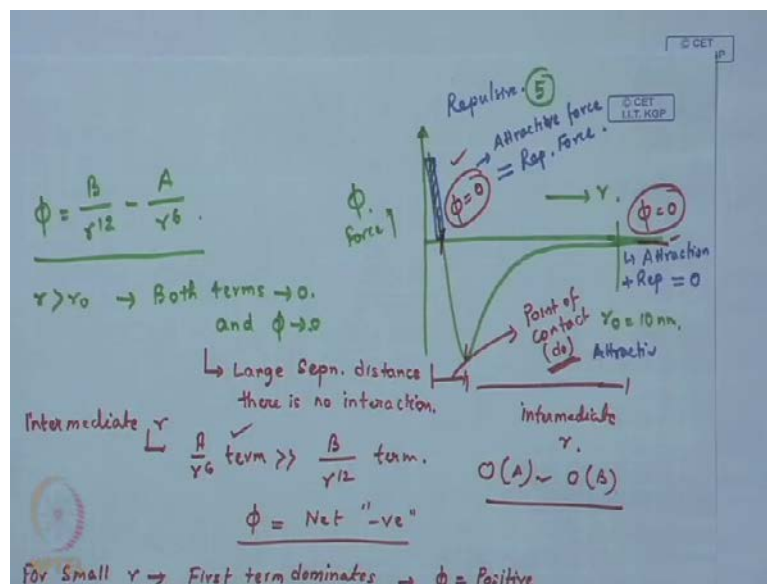
So, you force them even closer once they have coming direct contact with each other and you try to bring them even closer so there is going to be a strong sharp electrostatic repulsion. So, this is the repulsive regime, this is the attractive regime and beyond this point there is no interaction so, this is we have drawn it for let us say two particles. If you now consider this for two surfaces (No audio from 44:09 to 44:20) if you consider it for two surfaces for example, the nature of the curve will be roughly the same, only difference is this interaction will now stretch longer the d_k will be slower we understand that it is stretchers up to 100 nanometer.

So, the d_k will be little sluggish and rest of the rest the remaining part of the curves remains pretty much the same. So, here it is sort of which is a maxima in terms of the attraction beyond which repulsion starts so, which means that at this point the two surfaces coming direct contact. And so, this distance if you can measure, this is the minimum separation distance between two surfaces or two molecules. That is present that will be so; we will discuss this in one of our subsequent lectures. When they are in contact, they cannot be this is not equal to d_0 , d_0 is not equal to 0 because of the fact that if you try to bring them in absolute contact our make d_0 equal to 0, you have to overcome the physical repulsion of the electrons. So, which is not possible and beyond d_0 .

This Vander Waal's force is dominated by the electrostatic repulsion are which is known as the short range electro static repulsion forces. So, many times we follow a potential

curve like (No audio from 46:07 to 46:14) this is the rather famous Lennard-Jones potential. This I guess this a by r to the power of 6 to minus sign now you understand this part of the potential curve represents the attractive interaction due to the Vander Waal's forces. A is constant forget about this number, we do not worry about it. And then you have this B divided by r to power of 12 which is the sort range electrostatic repulsion force, here also you can see that if r is very large let us say it is beyond 10 nanometer then both the terms into 0. So, I will probably rewrite it.

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So, here is the potential curve. This is that let us say it is the limit 10 nanometer or whatever. So, this is the phi of the potential, this is r the separation distance. And if you have a potential like this there can be three situations; where r is greater than r zero both terms tend to zero and phi tend to 0. So, for a large separation distance there is no interaction. For an intermediate r, that is in this zone the second term dominates over the all we assume that order of A order of B order of B the same. So, what happens is you have the this terms the second terms of the dominates of the first term so, your phi it is sort of net negative and you have an attraction.

For very small r, again since r is the denominated so, smaller is the value of r, r to the power of 12 will start dominating the first term dominates (No audio from 48:55 to 49:02) and you have phi equal to positive. Two important points are this point, this is the point of contact whether separation distance is d 0 between two surfaces let us say and

this point is also important here again ϕ is equal to 0. But there is a difference between the ϕ equal to 0 over here and ϕ equal to 0 over here. Here, ϕ is equal to 0 because in this particular area attraction and repulsion both equal to 0, over here it is different and the attractive forces and the repulsive forces match each other.

So, (No audio from the 49:55 to 50:04) and beyond this so, this is the repulsive regime, this is the attractive regime. So, beyond this you have a ϕ only repulsive regime. So, this potential curve is going to very very important in understanding the operation of an AMF that is way I decide to spend some time into it. For the contacts of an AMF so, that is why we understood it is the interaction between two particles or two surfaces this also represents for an AMF interaction between (No audio from the 50:45 to 50:55) the tip and the surface to be scanned.

Because of the fact that you if you know look carefully, this is the configuration of an AMF so, this is the tip; this is the surface to be scanned. One additional information I am giving you right know the tip is sharp, radius of curvature where is between 10 to 20 nanometer. Assume in organic molecular as size roughly of the order of Angstrom. So, we are not talking about roughly hundreds of molecules of the order of that. So, this is also a surface the tip is not single molecule at the n like a STM tip. But so, essentially you are talking about the interaction between two surfaces and the two surfaces here of the surface of the AMF of tip and the surface of the sample you want to scan. So, the interaction between these two at close contact proximity is governed by this potential curve.

So, that is way this curve is very very important for the atomic force microscope. So, I guess we do a quick recap on this potential curve, we just introduce the concept of induce dipole induce dipole type interaction which is known as the Vander Waal's forces which is also known as the inter molecular interaction. And we understand that this type of interaction is the most fundamental form and is available or is present even in molecules which do not have any permanent dipole including in charge neutral molecules. So, we understand that this interaction has it is origin in quantum mechanical as quantum mechanical origin.

It is attributed in simple words to the localization of the electron cloud at any given instance of time, which induces a charge of opposite polarity on the neighboring

molecule. Since, the polarities are opposite therefore, the interaction is always attractive, but no physical movement of molecules takes place because of the attraction. Because the localization changes the position at every instance of time and it goes on changing, that is one of the reason void it also known as the dispersion forces. Now, this type of induce dipole induce dipole interaction is known as the Lifshitz Vander Waal's force.

Or the Vander Waal's force there can be other types of interaction as well which can be the permanent dipole permanent dipole type interaction or, the permanent dipole induce dipole type interaction, we are not going into the details. What we agree that this attraction between two fundamental particles scales as one by r to the power 6 and in comparison to gravity which is $m g h$ and therefore, at the nano scale these forces dominated, dominate a lot. Between two surfaces so, one by r to the power of 6 and it is sort of stretches up to roughly 10 nanometer between two surfaces the scaling changes to one by r square which we will see how it is change.

And therefore, the $d k$ becomes a little sluggish and the interaction sort of stretching up to roughly 100 nanometer. We then try to understand how these potential curves looks like, we also found out that in addition to the Vander Waal's force. Where is very short range electrostatic repulsion which are originate because of the overlap of the electron charge cloud. And then we introduce the concept of the Lennard-Jones potential a typically potential which is also call the six twelve potential sometimes. This part of the this particular term represents the representing the attraction, this term representing the repulsion and we understand that depending on the value of r , there can three distinct regimes for very large or both the terms are 0 and that is no interaction.

For intermediate or the second term may dominate over the first term and you might haven overall you haven overall attraction. And for very small r , the first term again dominates over the second time and we can have an effective repulsion. We also understand that this is the point at the two surfaces of the particles coming contact and there are electron clouds sort of start overlapping and therefore, the repulsion starts. We have already we also discussed that this interaction between the two surfaces is going to be very important in understanding the interaction between the tip and the sample in an atomic force microscope. We start discussing the operation and other critical issues about an AMF from this point. Thank you.