

Chemistry and Physics of Surfaces and Interfaces
Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 36
Atomic Force Microscopy (AFM)-1

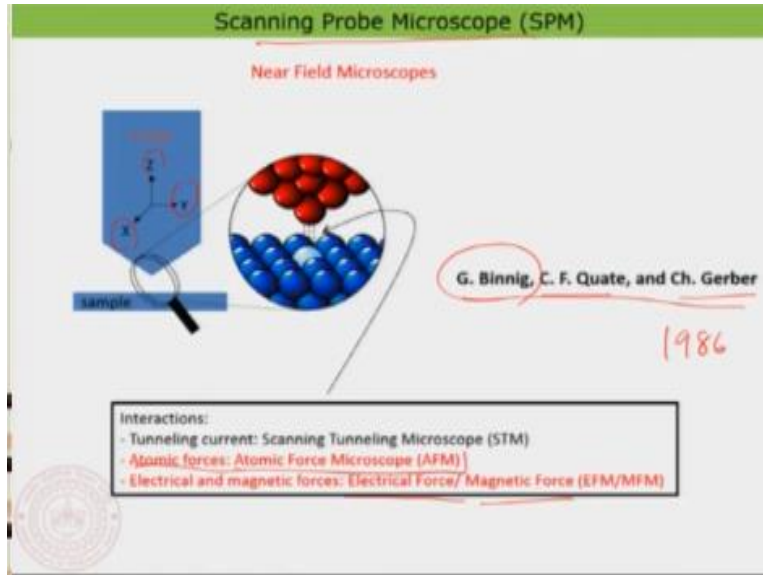
Hello everyone. Welcome back to lecture number 36. In this lecture onwards we will be familiarizing the atomic force microscope. Atomic force microscope is a similar class of microscope like the scanning probe microscope or the scanning tunneling microscope.

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So, in this lecture we will try to look into the technical aspect of this microscope and what we really measure in this in greater detail. And then through this couple of lectures I will also be showing a few examples that you can also study using atomic force microscope. So, I have already shown you an image in the previous class about atomic force microscope. But now are going to see it in greater detail.

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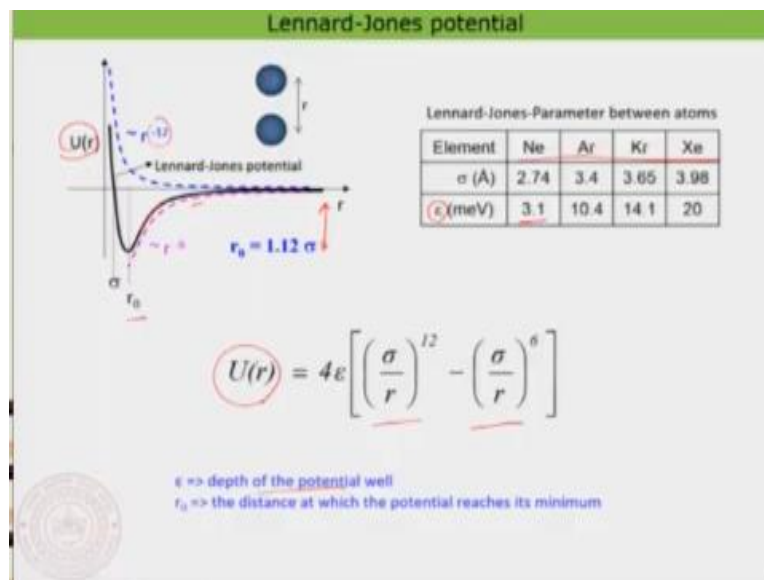
So, it again comes under the bigger family of scanning probe microscopy. So, that something we have already talked about and you were also seeing this. So, in this case also what we have here again here is a probe which is actually able to move along the x z and y direction. So, that is quite important. So, you can basically just move them like this and you can retract them, approach them. So, you can basically just do a three dimensional scanning using this tip.

What we are going to measure or what we particularly going to focus now is the atomic forces that is what you do it in the atomic force microscope. And also there are two more modes so special kinds of modes that you can use using atomic force microscopy that is the electrical force and magnetic force. You can also measure electrical force on a surface or even the magnetic force that is acting between the tip and the sample is also something that you can measure. We will not go into the greater detail, but I will show you how that works towards the end of this particular topic. So, well you can notice that these are the people who invented in 1986 they published this paper on atomic force microscope. And you can notice that this gentleman here Gerd Binnig was actually also the co-inventor of scanning tunneling microscope microscopes. But then he stayed back and researched for a longer time and actually worked with this two other people Quate and Gerber.

So, they have actually together invented scanning tunneling scoring the atomic force microscope. And this is also a very, very celebrated microscope in this field and it is also nowadays been

attracted towards biological application. Because this is actually a sample where you do not require a conducting sample that means its broadness in application is much wider than scanning tunneling microscopy. Because you remember that for the scanning tunneling microscopy, we need actually a conducting sample and a conducting tip. But that is not required in this case, because you are just looking at the atomic force. Therefore this is actually much more versatile than scanning tunneling microscope. So, you will actually just see that and I will show you a few examples in that direction so that you get an idea. But in general microscopy is important for us, because we want to investigate surfaces and interfaces using this.

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Let us go on. So, now before we start what I want to do is actually I want to give you an idea about the atomic forces itself. What are we talking about what is the contributions that we are talking about in terms of the atomic forces? So, for this I have a very simple scheme here. So, I have supposed to be like two atoms or atom like objects which are actually coming closer and closer and they are kind of interacting. So, when they are far away from each other so there are kind of long range interactions. So, that is what is indicated here in the magenta color, so there is called long range interactions which are more attractive in nature and that is why you see that in the so called interaction potential which is a function of distance is going negative that is actually indicating that you are basically just getting a more attractive force.

But when you come very very close vicinity of these two atoms or atom like objects then what happens is that there is this huge police repulsion. Because you are actually trying to put two nucleuses together, that is very tremendous a force which is actually a kind of a repulsive force .and that is going typically in the order of 10^{-12} order of magnitude with respect to distance. So, it is actually something meaning that you will only see that in the very very close vicinity you are going to feel it, but it actually is a very strong repulsive force. So, now you see it means that when you actually just bring these two objects together in the beginning there is kind of an attractive force and when it comes closer there is kind of a repulsive force. So, all together what you are going to feel is kind of an effective potential of both this repulsive and attractive forces and that is actually commonly known as a Lennard Jones potential which is actually having a shape like this the black curve. So, this is a typical curve that you would see when two objects are coming together. So, that is actually indicating that they are actually kind of attractive in the beginning then everything is kind of a repulsive in nature. Now the forms of the potential as you already see that it has two contributions. So, one is basically a kind of an r^{-12} contribution and another one is basically an r^{-6} , inverse contribution and that is basically deciding the potential where you have this epsilon indicating the depth of the well. So, I have already indicated here. So and then you have basically r_0 that is kind of a the distance at which the potential is becoming minimum. So, now that is also indicated here and then you can basically just understand that using this kind of a Lennard Jones potential between the two different atoms that are coming together, you can actually understand what is the strength of the interaction between these two atom like objects. So, you can also just see that using a couple of examples here. I have here a table of all the normal gas atoms that are interacting together and you clearly see that the amount of energy so that basically meaning that this depth of the potential well is actually in the order of a few milli electron volt that means this three milli electron volt is actually 10 times smaller than the energy that is present at room temperature which would mean that you will never be able to just let this two argon atoms or neon atoms interact because they are actually much smaller.

But when you actually just cool down you would actually just start to see that even these atoms can basically interact and they can even form a kind of dimer or trimer or whatsoever because their interaction is also becoming important when the temperature is lower. But none the less

what I want to just basically show you that you can take any different type of atoms or atom like objects.

When I say atom like object is basically that in this approximation you always assume that you have a spherical type of geometry, but it could also be like a larger molecule having a special shape. Then they also would do a similar way that always in the in the closer in the further vicinity you have kind of a stronger attractive or a weaker attractive interactions and as you go closer and closer they will start to be more repulsive. So, that is the typical Lennard Jones potential.

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Typical attractive forces

van der Waal's potential

$$U_{vdW} = U_{\text{polarization}} + U_{\text{induction}} + U_{\text{dispersion}}$$

dipole-dipole interaction $U_{dd}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\epsilon_0)^2(3k_B T)^2} \frac{1}{r^6}$

induced dipole $U_{\text{induced}}(r) = -\frac{\mu_1^2\alpha_2}{4\pi\epsilon_0} \frac{1}{r^6}$

London dispersion force $U_{\text{disp}}(r) = -\frac{3}{2} \alpha_1 \alpha_2 \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{1}{r^6}$

μ , dipole moment
 α , static polarizability
 I , ionization potential

Now in this itself there are typically several attractive forces. So, we just want to first discuss the most important one which is actually known as the Van Der Waals potential or the Van Der Waals interaction. The Van Der Waals interaction is actually majorly having three contributions like what I have shown here. This is when two dipoles interact or when one dipole interacts with the neutral atom or molecule or when there are two neutral atoms or molecules interact. So, I will just demonstrate it. So, when you have let us say like a dipole like this the two dipoles are interacting. So, I am just showing these arrows are indicating the two different dipoles. So, when the two dipoles are interacting so their interaction potential is strongly dependent on the dipole moment of the two dipoles. So, that is what is given by this U_{dd} . So, that is actually U potential which; is corresponding to the dipole-dipole interaction and if it is actually kind of a rotating or

kind of a moving dipole. So, typically their relation of the potential with the; distance between the two dipoles. So, this would be something like the distance which I am calling it as r is actually inversely six times with respect to the potential. So, that is that is why it is actually a $1/r^6$ dependence. Now this is actually the interaction between the two dipoles. But you can also have kind of a dipole interacting with let us say a neutral atom or a molecule. So, that let us say like you do not have a dipole for the second one. But what can happen is actually that this dipole can kind of induce a dipole on to this. And then you can basically just depending on the orientation you can create positive charge on one side and negative charge on another side and then you can actually just create kind of a dipole for the neutral molecule which came closer to the original dipole. So, that means the dipole moment of the molecule and also something called the polarizability so that is the polarizability of the second molecule would decide polarizability is actually the strength of a given molecule how much it actually can be polarized so that is what it means. So, that two quantities would basically decide the potential for the induced dipole. So, that also has a kind of $1/r^6$ dependence and you also see that the μ and the α is telling basically the dipole moment and the polarizability and that is one type.

And now you can also have like two neutral molecules or two neutral atoms that are interacting. So, I am just depicting them again with two spheres. Now the interesting thing about this is actually they are actually hauled by something called a London force. London is the name of the persons who actually just understood or first taken this interaction. So, we know that for any atom that you take so there is actually kind of an instantaneous fluctuation of the electron cloud in an atom or in a molecule. So, with that you can basically just depict an atom like this that you have always kind of a fluctuation giving rise to a positive and negative ends for a given molecule, but this is momentarily instantaneous. So, it can actually change from the next moment to a different one. Now when this kind of a thing we interact with another atom in the neighborhood so that actually can also just polarize the next one. And then it actually can have something like this.

Now you see that I again have two dipoles that I have created and they started to align with respect to each other. So, this would be the distance between them, this is again r that is the

distance between them and now you can see you can also just kind of generate a new type of interaction which is actually known as a London force. And that also has kind of a $1/r^6$ dependence to the energy. And the interesting thing here is that it is important for these atoms that are actually atoms or molecules that are involving in this what is the ionization potential and the polarizability. Ionization potential is actually nothing, but the energy required for you to remove an electron from the system that is the true one. If a system is actually having lower ionization potential you can basically just induce a stronger London force and so on. So, that is what is basically something you can understand using this. So, generally the Van der Waals potential itself for the Van Der Waals force itself is kind of having all these components together. But it depends on different type of molecules or different type of the nature of the molecules or atoms that you are taking whether it is a dipole whether is a dipole and a neutral molecule or two neutral atoms or two neutral molecules and so on. Depending on that you would basically just see the different contribution and this is actually one of the most important and ubiquitous force that is present everywhere. We do not need to have like you know any anything special for that you can even just bring them together they are interacting. So, that is something ubiquitous so that is why London Van Der Waals for potential of Van Der Waals interaction is something that you cannot just avoid, everything is interacting therefore.

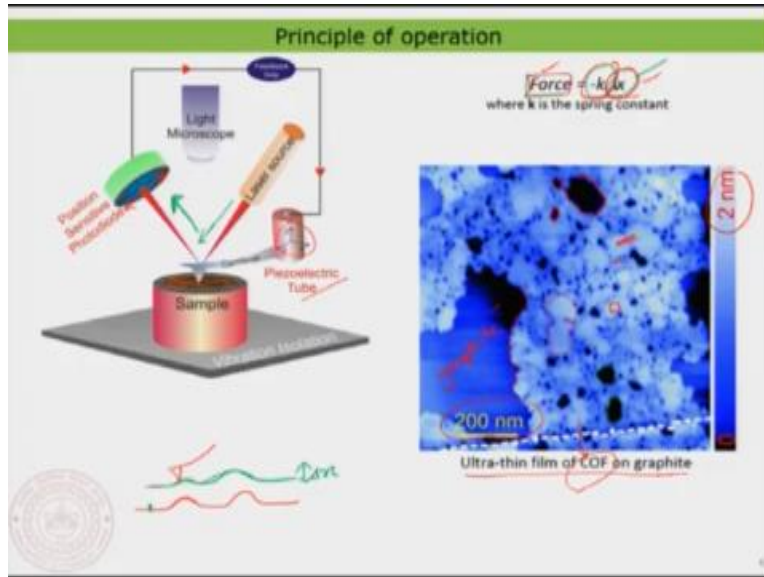
So, this is one of the major type of force that is actually present when you bring two atoms together.

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Then you also have other important attractive forces like π π interaction that is also kind of Van Der Waals interaction, but people call it with different name. Then you have stronger interactions like electrostatic interaction just between two poles, you can also have stronger electrostatic interaction, hydrogen bonding is also some kind of a dipole-dipole interaction but in a stronger level. Then these are actually like kind of forces that you would call it like let us say acting between two molecules or something at the molecular level. But when there are more molecules interacting together or repelling each other and so on then you would actually just call it something like hydrophobic and hydrophilic interaction. But these interactions are also originating basically by Van Der Waals or hydrogen bonding or electrostatic interaction. But they are much more collectively or bulk type of force or adhesive force for example. But these are all forces that are present and the repulsive forces are typically the so-called Pauli's repulsive force that because you are actually bringing two atoms together you always have something like a repulsion because you are trying to put two nucleuses together. There are many different type of attractive forces that are present, but the repulsive forces are generally the so called Pauli's repulsion due to the similar charges coming together. So, that is what typically that you would understand in atomic force microscope. So, you will have to deal with these forces. So, how do we basically just do this and before that let me also just show you the principle.

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So, we are going to basically use those forces later in understanding everything. But right now I am just calling it as a force. We do not know really what is that force, but we know that there is a force acting but this force could be any of those forces that we talked about. And force using Hooke's law you can generally relate it to the force constant and a distance change. And now I will come to that in the context of an atomic force microscope. I am bringing this equation in the context of an atomic force microscope do you will understand it in better detail. So, now imagine that this is kind of the system that you are looking at which has actually most important the sample that something that you want to investigate. Let me also just put a scheme here for you to kind of get along with the scheme. So, what I am having is a kind of topography that looks like this.

So, that is what the topography of that is just a line scan. Now I have the sample and now the cantilever is basically connected. So, that is the interesting thing about the atomic force microscope. So, it is not just a tip that we have, it is actually a tip that is going to be connected to a cantilever. So, that is the interesting thing about it. So, you clearly see and this cantilever tip assembly is now connected to a piezoelectric tube. So, that is nothing, but the scanner actually. You directly see that this scanner pho is capable of moving in the z x and y direction so that means we are able to basically just scan the tip and the cantilever assembly in the x y and z direction this is quite important. So, that is the thing. Now the interesting thing is when I am basically just trying to move, let us say like my cantilever along this path, you directly see that

whenever I get this kind of topography so this kind of topographic elevation I am going to basically get a larger force applied onto the cantilever under the tip. Therefore the cantilever is going to deflect, that means the tip would also follow some kind of a profile that is same as that of the surface. So, I am just going to have a profile that is looking similar like the topography. So, at some point so around this region you will see that the tip will be attracted therefore the cantilever will go down and whenever there is a higher topography the force between the tip and the sample is actually increasing.

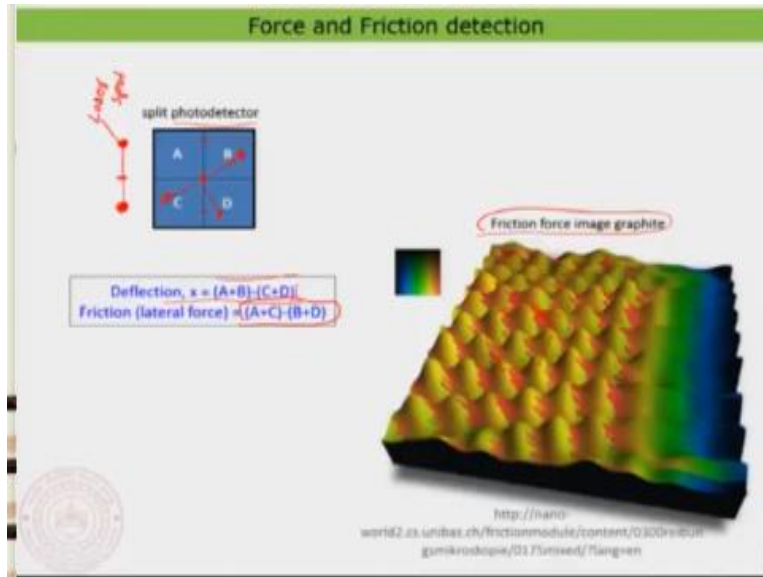
Therefore the cantilever will bend backward that means whenever the tip is actually moving across the surface depending on the topography you might have like a cantilever going down, up, down, up and so on depending on the change. So, that is nothing but our Δx , the change in the distance and you also know the force constant or the spring constant of the cantilever is something known to us. So, therefore I can basically calculate the force that is acting directly between them or this Δx is directly the topography for example. So, I know because there is a force that is acting between the tip and the sample I have basically a certain bending of the tip cantilever down or up. So, that bending down or up is a direct indicator of the topography of the surface. So, that is something you can directly see. The green line is clearly now a representation of the topography of the surface and this is nothing but the Δx and this is something that you are ideally measuring. So, that is good. Now the question is how do I basically measure this deflection? Because in STM; you were measuring the tunneling current. But now here I am basically measuring the force but due to the force I am actually just deflecting the tip up and down. So, how do we measure the deflection. So, that is the question. So, the deflection is measured by this combination of laser and a photo sensor, a position sensitive photodiode.

So, what you do is you shoot a laser onto the back side of your cantilever and then reflect that back onto a position sensitive photodiode. When there is no deflection in a so called neutral position, the position sensitive photodiode the laser will be focused at the center of the photodiode. And as soon as there is a deflection what happens is basically that the position of the beam will basically move in any of this direction. So, that means depending on how much is deflected how much cantilever is deflected, you can detect that kind of a change in the position sensitive photodiode. So, that is the interesting thing. So, ideally that means using this

combination of laser source and position sensitive photodiode, ideally you can measure the deflection of the cantilever. So, that is what I want. If I would measure the deflection so that is nothing but the Δx then I know the force constant k is something known because I prepare my cantilever. So, I know it, I will actually just show you a few examples a little later. So, once I know that then I can clearly have the force or even the topography that is nothing but the Δx . Now I can look at an image. So, this is again the ultra thin film of that COF, you remember the COF that we have discussed in the previous class on graphite. And all this bright region so you can see here the scale its about 2 nanometer height and 0 is actually indicating this part here. So, this is nothing but the graphite surface. This is the graphite surface and the bright is nothing but your COF. So, this is good. So, now I can clearly see the topography of a thin film island of a cough. So, this is actually like a very big island here and you can also see like in some part of the island there are defects. So, there are some small defects, there some parts are with looking very smooth in this region here, they are looking, more rough and all those things. So, you can now see the microscopic structure or the so called topography of this so called combination of COF on top of graphite is nicely depicted in this case. So, in in many cases people do first an atomic force microscopy because that will give you an idea about the global view. So, you see the scale here is like 200 nanometer, you can actually just make several tens of micrometers large images using AFM atomic force microscope. And therefore you can actually understand a large area view or means a global understanding about the surface. Because in scanning tunneling microscope you are typically limited to a few hundreds of nanometer. Because what you really do with STM is to go really within this small area and see what is inside. So, that is also something I have shown you in the previous class, I have actually just discussed the application of AFM and STM together.

For COF there you have seen that after looking at the COF, what I have done is basically zoomed into that small region using STM and I could basically see what is the real microscopic structure or the molecular level structure. So, but now I already see a lot about this in the AFM itself. So, that is the thing.

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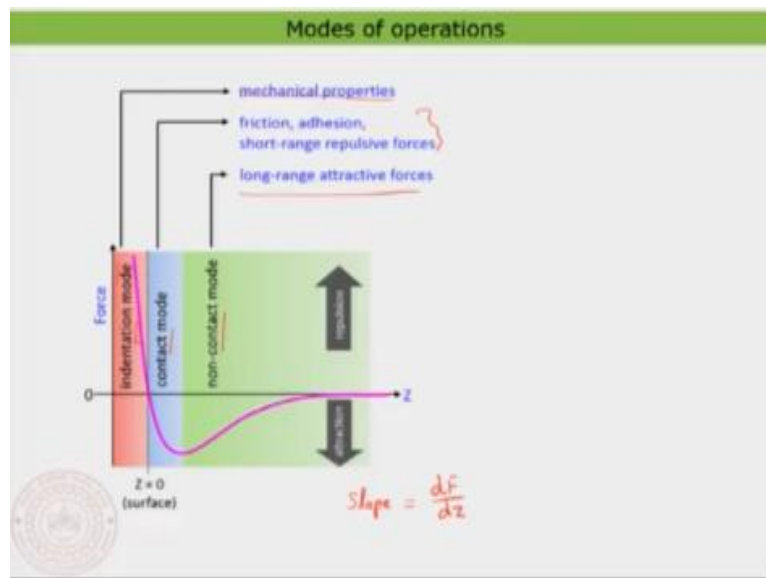


Now one more important thing, so, like now I am basically having that photo detector or the photodiode here and you basically I told you so this photo detector is a kind of position sensitive photo detector but it actually has four segments and these segments are labeled as A, B, C and D. That is because you want to basically just detect the deflection. Now normally when the cantilever is in a kind of neutral position so you have basically no deflection. That time the laser will be focused at this corner of A, B, C, D segments which is meaning that the photo current that you would generate will be 0 at that position. But now when there is a deflection that means a cantilever goes down or up you would be basically seeing that the spot corresponding to the laser would from the main position go down or up like this. So, this is the laser spot and this pod would either move up or down.

Now you clearly see that the new sport is somewhere here and somewhere here depending on whether it is going upward or downward. So, that actually means depending on the attractive force or repulsive force it would either go down or upward. Now I can basically just measure this distance using this equation I have to basically just see the deflection by just taking the photo current. Because as you go further away from the center the photo current basically increases that is indicating the kind of deflection that I have in typical nanometer. So, then I can actually calculate the deflection using this. But it is not necessary that all the time the cantilever go up and down, it may also have some kind of a shear force due to the fact that there are also like kind of lateral interaction called friction. Because when you are trying to move your tip on the surface

it is not necessary that the cantilever always go up and down, you can also just deflect like that. In that case the laser spot may actually just go to another place like here or it may go here or it may go here. So, there are actually combinations possible depending on the shear in this. That case you would basically calculate the photocurrent using this equation. But lateral forces are quite interesting you can basically just measure the lateral force. And using the lateral force or friction force you can even get atomic resolution. So, this is actually again graphite surface you remember, the hexagonal graphite surface. So, this spots are actually indicating the different carbon atoms and that actually gives rise to a hexagonal pattern on the surface and that is actually nothing but the atomic resolution of graphite. So, that is a possibility. But the problem with the friction microscope is that it actually will scratch your surface. So, you do not want to scratch your surface because you will see in later example we do not want to basically scratch your surface, because that is also going to damage your tip. So, the lifetime of the measurement or the tip is actually not very good if you start to do the scratching or the so called friction microscope. So, therefore it is not a very commonly used microscope. But it is been used to understand the friction force at the interface.

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Now therefore we would basically be just looking at the typical mode. So, that is the typical modes of operation that you are going to do. So, now depending on the position; so this is something that you have already seen. So, now I have converted it into force. So, you see the typical force curve has this kind of a shape that means in the beginning it is more attractive and

then when you come closer to the surface it is going to be repulsive. So, depending on where you position the tip and the sample, you can call it as either a non-contact mode. where the tip is not in contact with the surface, or you have a contact mode where the tip is basically just in contact with the surface, or you have another mode which is basically kind of an indentation where you really push the tip into the sample and measure the mechanical property. So, depending on the different type of forces that you are of a regime of the forces that you are looking at you can actually just measure the long range attractive forces. If you are looking in the contact regime you can basically look at the short range forces. If you are actually just doing the indentation mode where you are really pushing the tip into the sample then you can basically measure something known as the mechanical property. Because the slope of this curve in the indentation mode is nothing but df/dz and that is nothing but the hardness of a material because how much you can deform a material as a function of the pushing. So, this is something will give you an idea about the mechanical property of the material. So, this is what the typical modes are and in the next class we are going to start and understand a bit more about these force modes itself. And then we will try to see other possible modes that are also available for the atomic force microscopy. I thank you very much and I see you in the next class.