

## Particle Characterization

Prof. Dr. R. Nagarajan

Department of Chemical Engineering

Indian Institute of Technology, Madras

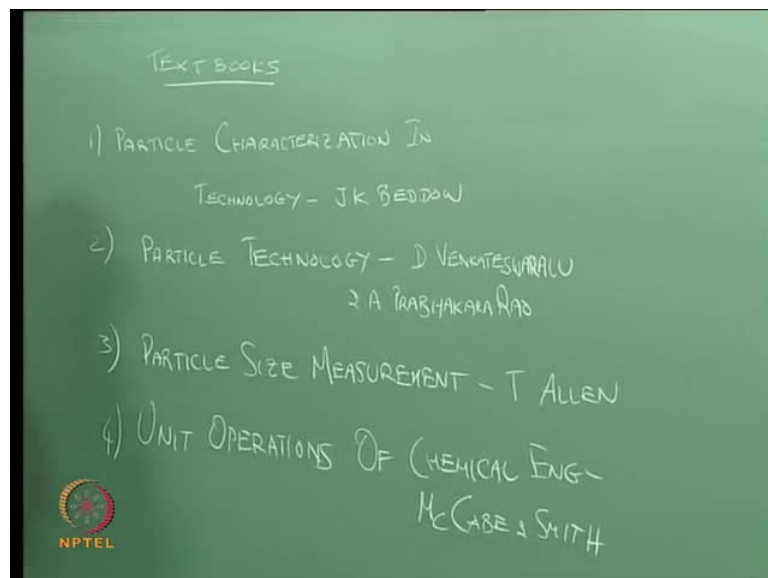
Module No. # 06

Lecture No. # 15

### Surface Adhesion: Forces

Welcome to this lecture in our particle characterization course. In the previous lecture, we had discussed particle structure characterization. Then, we started discussing aspects of surface interaction with its surroundings. Now, before we continue that discussion, I just want to take a minute, to list some text books that you will find useful, in order to learn more about the topics that we have been discussing. The first part of the course, particularly the shape characterization, and some of the earlier methods of size characterization, are taken from the book by Beddow, Particle Characterization in, in Technology.

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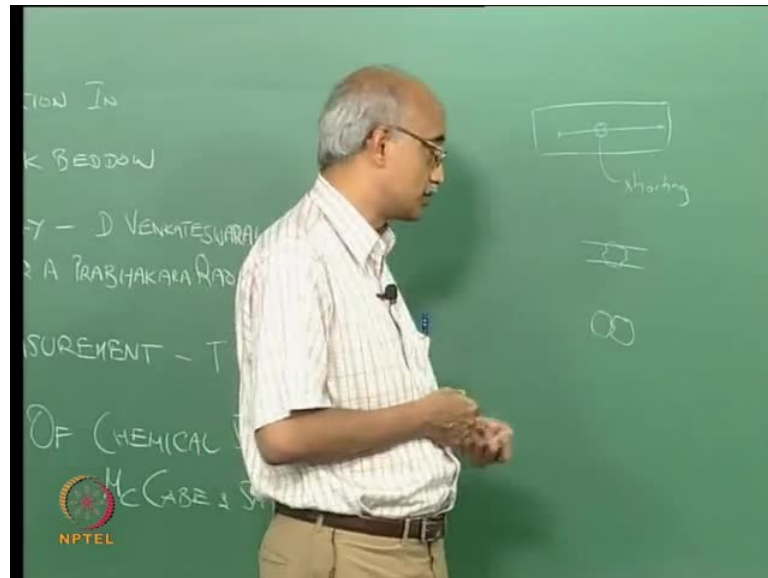
So, as far as a single text book is concerned, that would be the most useful for you to refer to. The book by Venkateswarlu and Prabhakar Rao on Particle Technology also contains much useful information. The book by Allen on Particle Size Measurement covers some of the more recent aspects of size measurement technologies, in particular, based on dynamic light scattering techniques and submicron particle size measurement as well. Finally, the McCabe and Smith book on Unit Operations of Chemical Engineering, I am sure, many of you have referred to it in the past, does contain many, many references to particle technology, particulate processes and particulate characterization. So, these are a good set of books to refer to. Now, in addition to this, there is much reading material that can be accessed, through recent journal publications.

Particle characterization is a field, that is evolving, virtually, daily, and so, it, it, it is important that, if you are really interested in staying on top of this technology, you have to refer to current publications; both conference papers as well as journal publications, in order to be fully up-to-date on, on what is going on in this field. So, easiest way to do that is, if you have access to a search engine that can look into literature, just type particle characteristics or particle characterization, and you will come up with lot of references. In one of the later lectures, I will also give you a list of more recent publications, which deal specifically with the aspects of particle characterization that we are now starting to cover, and which we will be covering in future; aspects, such as particle adhesion, cohesion, particle removal from surfaces, particle transport, particle deposition, as well as functional properties of particles. So, we will be referring to a, a, a different set of books, which cover those aspects in, in more detail.

So, coming back to the topic under discussion, the way that a particle interacts with its surface, is primarily characterized by the outer surface. Although, as we saw, certainly, in aspects such as adsorption and absorption, the subsurface can also play a key role by, either by enhancing, or by delaying, the rate at which transport is happening between the surrounding fluid and the suspended particle. In particular, adhesion of particles to surfaces, as well as to each other, is of grave importance in many manufacturing industries. In many, particle adhesion is to be avoided. For example, coming back to semiconductor manufacturing, if you are making a silicon wafer, or a circuit, it is very important that, the electrical parts that have been laid out on the wafer, remain intact. A wafer or any semiconductor is designed such that, there are specific conductive paths,

there are specific semiconducting paths, and there are specific insulating paths, and you want to keep them separate, in order for the device to function.

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Now, imagine that, you have a conducting area; let us say that, you are supposed to have electrical conduction occur between these two points; supposing a, an insulating particle drops into the middle of this conductive section. This could be, for example, a plastic particle, or even something as simple as, you know, clothing fiber, or human skin, or hair, which is essentially non-conducting, compared to the metal conductor that the, the device is based on. What that is going to do is, essentially, short the circuit. Or, alternatively, if you have two parallel paths, which are designed to be non-conducting, and you get a conducting particle deposit, so that, it bridges those paths, then, you get a conductive path, which is going to interfere again, with the functionality of the device. Now, if this phenomenon is instantaneous, in other words, the particle comes, sticks to the surface, and then, is removed, there is no long term consequence of the particle.

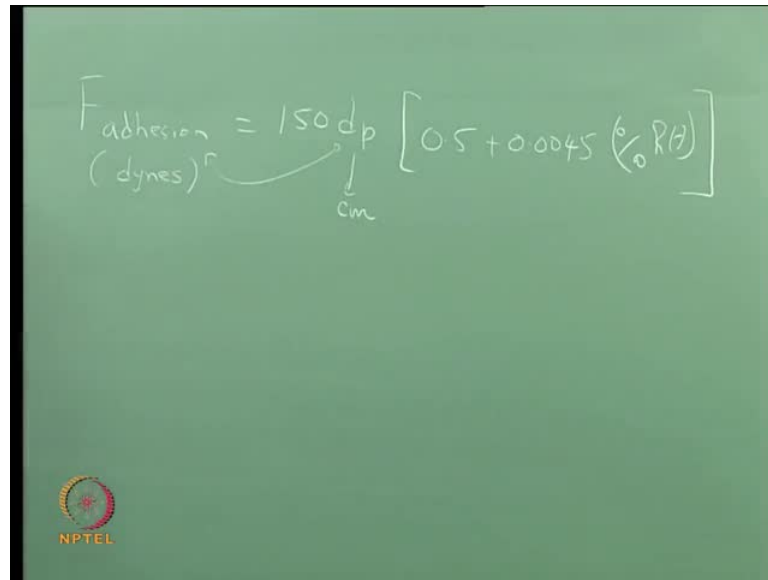
It may cause a yield loss in, in your manufacturing line, but may not cause a reliability hit, in the field. However, if this particle has a high adhesion force, it is going to stay there, virtually, forever. So, the device is never going to function in the field. So, it is not a short term problem; it becomes a long term problem. So, in this particular illustration, the adhesion forces of the particle that bind it to the surface, play a, play a huge role in determining whether it is a simple early life problem, or whether it is a long term

reliability problem. Now, when we talk about particle to particle cohesion, this again, for the most part, is something that you want to avoid in manufacturing process. I mean, the whole reason for preparing a particular slurry, or a suspension, is to keep the particle separate, and isolated as particles. So, it, it kind of defeats the purpose, if two adjacent particles simply come together, and stick to each other. So, in this case, the particle to particle adhesion, in a, in a medium, which is also known as cohesion, is something to be avoided. Now, there are many reasons for this. For example, again, in the pharma industry, the, the processibility of the powder is an important issue.

If you are taking, for example, a pharma powder, and you have to transport it from the vessel in which you are manufacturing it, into a container into which you want to fill it, or into a capsule form, you have to transport it across tubes, or some kind of plumbing, that you send this suspension through. When particles are discrete, the suspension acts like a Newtonian fluid. When the particles start coagulating, it starts to behave like a non-Newtonian fluid. So, there is a tremendous difference in the flowability characteristics of any suspension, depending on whether the particles stay isolated, or whether it start to conglomerate. So, clearly, adhesion of particles to surfaces, and to each other, is of huge practical significance, and it is worth studying it in more detail. People have actually done empirical experiments on particle adhesion to surfaces.

In fact, there is a class of experiments that have been done, on metal surfaces that are very clean, where, where the metal surfaces do not have any oils, or other types of contaminants on them; and particle adhesion force has been studied, as a function of particle size close to room temperature. And, when all the data were gathered, and this really consists of, virtually millions of data points, and the data were analyzed, and the data were fitted with a model.

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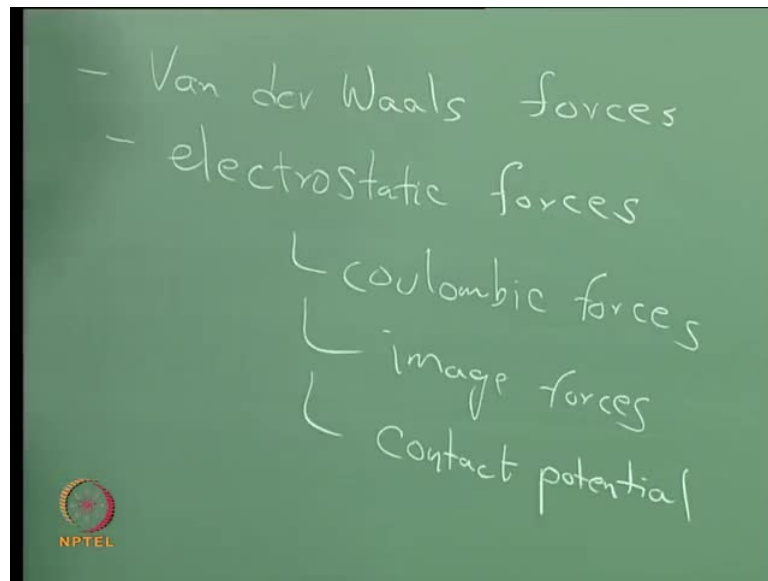

$$F_{\text{adhesion}} \text{ (dynes)} = 150 d_p \text{ (cm)} \left[ 0.5 + 0.0045 (\%RH) \right]$$

The model that came out, looked something like this;  $F_{\text{adhesion}}$  expressed in dynes equals 150 times  $d_p$ , where the particle diameter is expressed in centimeters, times 0.5, plus 0.0045 times percent relative humidity. Now, this is an interesting equation, because, it says that, adhesion forces, basically scale as particle size. In other words, the larger the size of the particle, the greater will be its force of adhesion to a surface, and it is basically a linear dependency. It also says that, the relative humidity plays a huge role in this. In fact, when you go to 100 percent relative humidity, this term becomes comparable to this term; you are essentially, doubling the adhesion force. And, the reason, of course, for that is, relative humidity is, basically moisture. And, when moisture gets between the particle and the surface, you form liquid bridging, as well as solid bridging, which can provide very high adhesion forces. It is basically a surface tension phenomenon. But even in the dry case, you can see that, there is a fairly clear, linear dependence of the force of adhesion on particle size.

Now, that is interesting, because, when you actually look at the forces that bind particles to surfaces, or to each other, there is a fairly large number of them. So, given that, this fairly simple and straight forward dependence that has been observed experimentally, is useful, and to some extent surprising, because, it is somewhat counter-intuitive. You know, what this equation says is, larger particles have higher adhesion force to the surface; but if that is true, you know, based on your practical experience, you would have seen that, if you have, you know, number of particles on the surface and let us say, you

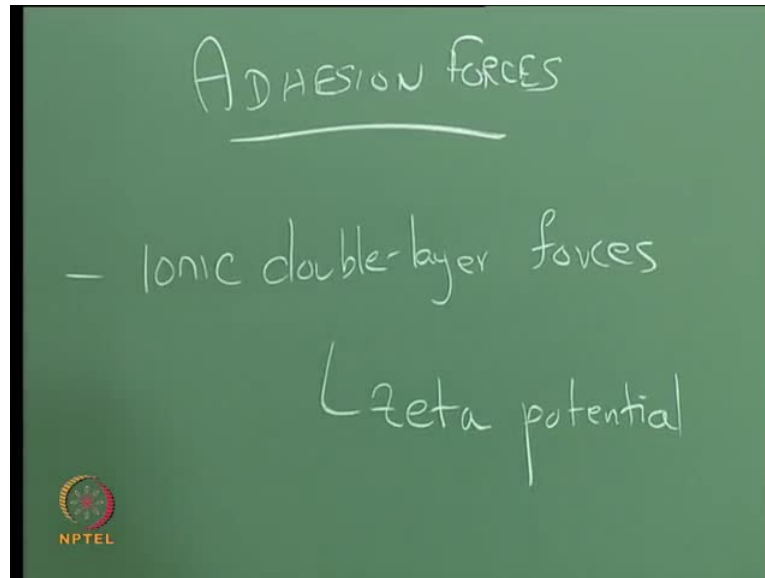
blow on them. Which particles will be removed first? The bigger particles, right. Now, how does, how is that consistent, with what you are saying here? If it is true that, larger particles have greater adhesion force, why is it that, when we employ a simple cleaning procedure like blowing on it, you always remove the larger particles, before the finer particles? Think about it. It is something we will get back to, during the course of the next few lectures.

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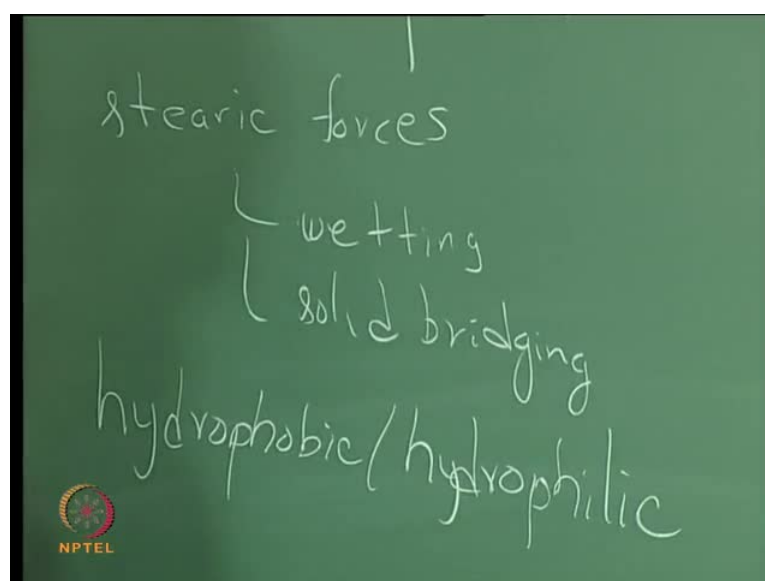
Now, I said that, there is a variety of adhesion forces that bind a particle to a surface. What are some of them? We already talked about Van der Waals' forces yesterday; these are the forces of inter-molecular adhesion, which would prevail, even when the particle is completely dry, and the surface is completely dry; or, the two particles are completely dry. The second are electrostatic forces. Again, electrostatic forces would apply, even in a completely dry environment. And, by the way, when we talk about electrostatic forces, they can be sub-classified into three types; you have your Coulombic forces, which you probably studied about in Electrical Engineering. Then, you have, what are known as image forces. The difference between these, these two is, Coulombic forces apply, when both the particle and the surface are charged; the image forces apply, when only the particle is charged, and the surface is not; and, we will look at the difference between these two. Then, you have, what are known as contact potential forces.

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So, the net magnitude of the electrostatic forces, is a combination of all of these. So, what are some of the other forces that prevail? There are also ionic double layer forces, which prevail, when the intervening fluid between the two particles, or the particle and the surface is a liquid; and because of the presence of ions in solution, which preferentially solvate, the particle and the surface, you build up a charge; and, that leads to forces of, either adhesion or repulsion, and these are represented by zeta potential.

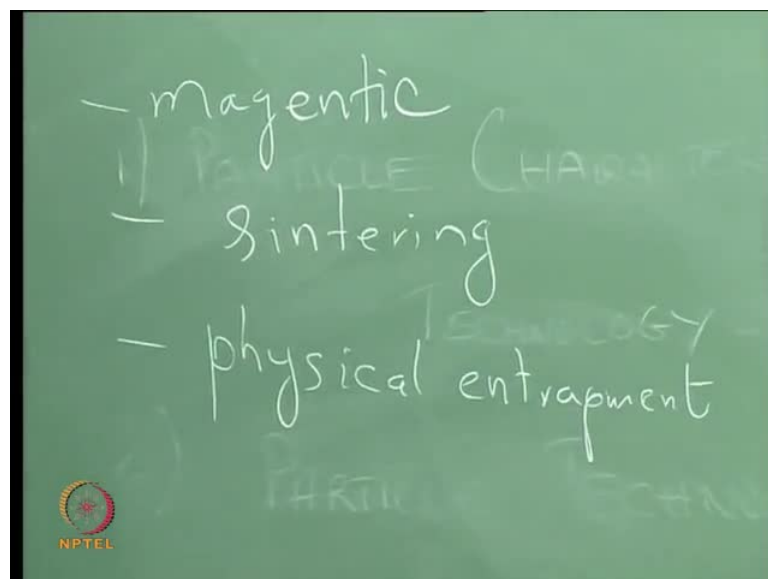
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Another type of force is, what are known as stearic forces, which is a name for surface tension based forces. So, the wetting or non-wetting of a surface, plays into this. When we talk about stearic forces, again, they can be sub-classified, as wetting and solid bridging forces. When a liquid first wets the interface between a particle and the surface, and provides an additional adhesion force, that is called the wetting action. Now, if you take that same interface, and you dry it, then, the adhesion force, actually increases by several orders of magnitude, because, the liquid that is trapped between the particle and the surface, now solidifies, and actually forms a solid bond between the two. So, that is called solid bridging. Then, you have hydrophobic, hydrophilic interactions, which essentially dictate, whether two surfaces are going to attract each other, or repel each other. And, it takes into account, the properties of the intervening medium. So, the way the two hydrophobic surfaces will react, will be very different, depending on whether the intervening fluid is also hydrophobic in nature, or hydrophilic in nature.

Similarly, the way the two hydrophilic surfaces will interact, will depend on whether the intervening fluid is hydrophilic or hydrophobic. So, we will discuss that also, in a little more detail, later on. Now, in addition to this, there are a variety of forces that apply in specific situations. These are forces that are universal; whatever the combination of particle and surface, you would expect these forces to apply.

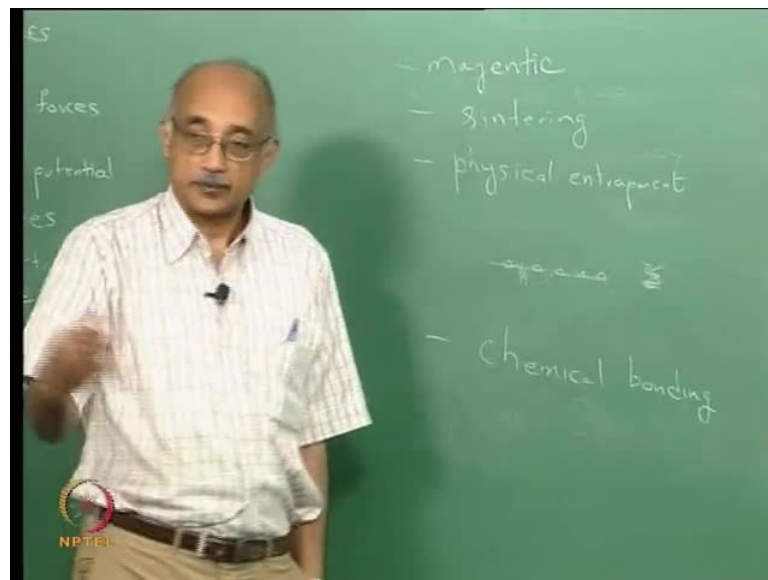
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But, there are other forces, such as magnetic forces; obviously, if you have two magnetisable surfaces, the adhesion force between them, or the repulsion force between them, will be dominated by the magnetic field that is setup between them. Another example is sintering. This is especially important in metallurgical casting processes, where you can provide an extremely high binding energy, between one material and the next, by sintering them together, by applying a, essentially, a high temperature process, to glue them to each other, virtually. So, sintering provides extremely high bonding forces.

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Another classification would be, physical entrapment, which can happen, when, for example, the surface has certain features that the particle can latch on to, or lock on to. So, for example, if, if the surface has cavities, and the particles essentially, settle into these cavities, that would be a, an example of a surface feature, that provides entrapment of the particle. Another example would be, porosities, that particles can diffuse into and get captured. Another example would be, matched roughness elements. If two surfaces are brought together in such a way, that their roughness asperities are used to interlock them together, that would be another physical entrapment. So, these, again, these are examples of forces that are somewhat unique to the application, but, which provide adhesion forces, that are far in excess of the forces, that would apply otherwise, in the lack, in the absence of these fields.

Now, compared to all these, the final force that we are going to talk about, chemical bonding, can be orders of magnitude higher. It is just like physisorption versus chemisorption; while physisorption can be an intense phenomenon, chemisorption, in theory, can be orders of magnitude larger, because, here, you are not only using physical bonding, you are also using chemical bonding. So, this is a situation, where the surface that is, that is being approached by a particle, is actually capable of chemically reacting with the particle; or, two particles that are approaching each other, can have, not only physical interactions, but also, chemical interactions. Now, in that situation, the interactive force between the, the two particles, or the particle and the surface, can be very large and also, it can be irreversible. You know, one of the things we should also mention is that, all these other forces we have been talking about, are in principle, reversible; if a particle is trapped on a surface, or attached to a surface, you can always do something to remove it.

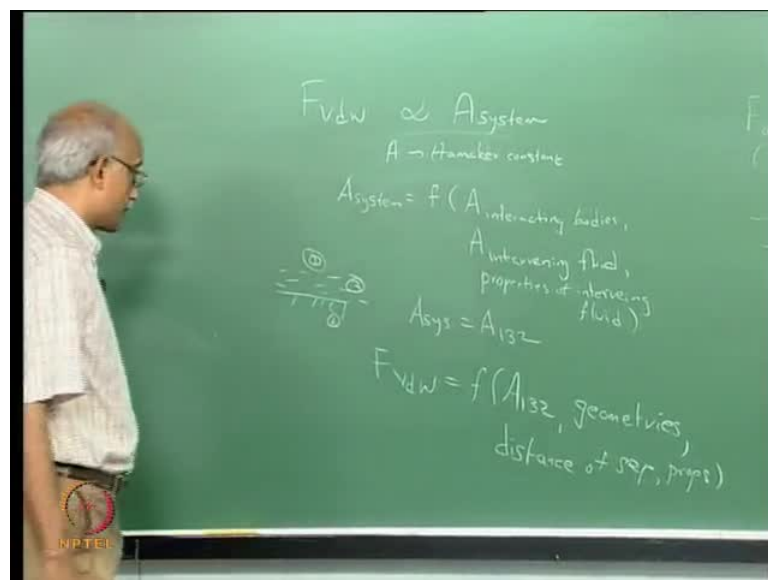
However, when the process of bonding is chemical in nature, it may never be possible; the process may be entirely irreversible. So, depending on whether we want the adhesion to happen or not, you might, either want to promote such chemical bonding, or preclude it from happening. Alright, so, you have so many possible forces that can, that can apply, when you have two surfaces in contact. And, we have not even covered, I mean, when you talk about field induced adhesion, there are so many varieties of forces that can, that can be applied. For example, you can even use a thermal gradient; just like a thermal gradient can induce a velocity, the thermal gradient can also induce adhesion of a particle to a surface. You can build up charge by various mechanisms; **tribo** electricity can be used to bond particles to a surface. But, even without considering all these, we have a large number of potential adhesive phenomena, that can bond two surfaces together.

So, we will, we will deal with some of these, in, in more detail, starting with Van der Waals' forces. Again, Van der Waals' forces are very fundamental, because, that is where it all begins. All you have to do is, bring any two atoms together, or molecules together, or particles together, and there will be an immediate atomic level force, that is setup between them. And, that is called the Van der Waals' force. Now, so, what Van der Waals' force is, it is basically, the sum of all the interactions that are set up, due to induced dipoles, between adjacent atoms. So, these are essentially, dispersive forces in nature, and they start, as soon as you bring two molecules together. All it requires, is the

presence of the molecules, or the particles near each other, for this force to be set up, and it is a summation.

So, if you have many, many atoms, many, many molecules, and many, many particles that are in contact with many neighbors, the net Van der Waals' force is much higher. Van der Waals' force, as we again discussed in the last class, is characterized by a parameter called the Hamaker constant. The Hamaker constant is the most fundamental representation of Van der Waals' forces binding two surfaces. The Hamaker constant, therefore, plays a huge role in determining the force of adhesion between two surfaces, particularly under dry conditions, where some of these other forces that we have been talking about, do not apply.

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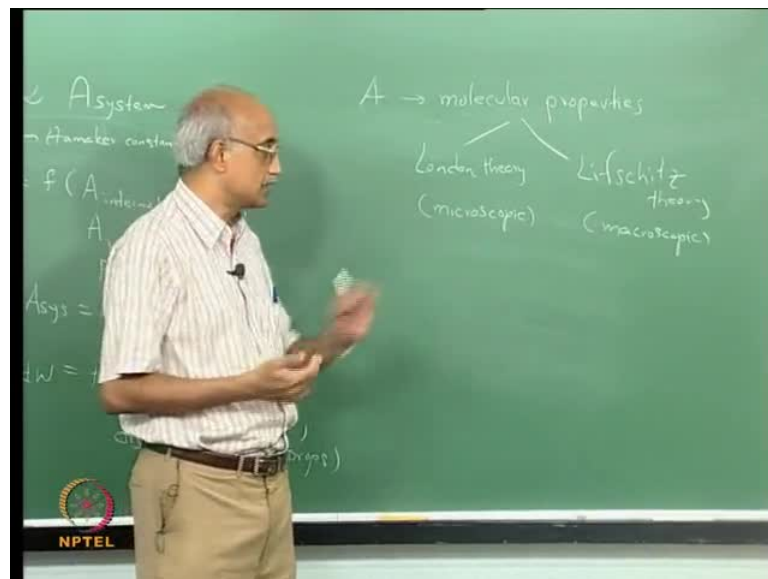


So, this  $F_{vdw}$  is a function of Hamaker constant of the system. The Hamaker constant is represented here, by  $A$ . And, this  $A$  itself, of the system, is a function of the Hamaker constant of the interacting bodies, Hamaker constant of the intervening fluid and the other properties of the intervening fluid. So, for a system, where you have, let us say, a particle and a surface, with some intervening fluid, let us call this, 1, 2, 3, then, a system equals  $A_{132}$ . The Hamaker constant for the entire system, reflects the Hamaker constants for 1, for 2, and for 3, as well as the various physical properties of the intervening fluid.

The Van der Waals' force itself,  $F_{vdw}$ , is a function of  $A^{-1/3}$ ; but, it is not only a function of the Hamaker constant; the Hamaker constant, is one of the key parameters and it is mostly a linear dependence. As the Hamaker constant increases, Van der Waals' force will also increase; but, there are other parameters, that also dictate the Van der Waals' forces. For example, the geometries of the bodies; for example, two spheres, will interact very differently, compared to a sphere to a surface, compared to a cylinder to a sphere, and so on. So, the geometry of the bodies, plays a significant role in determining adhesion forces. It also depends on the distance of separation.

As, as with virtually all forces of attraction, or repulsion, the distance of separation between the bodies, will play a significant role, and for the most part, it will be an inverse dependence, right; it will go as distance, linear, or the distance squared, or distance cubed; but, in any case, force will typically fall off with distance. And again, the properties of the intervening fluid, will also play a role in determining the Van der Waals' forces. The, the Hamaker constant, by the way, is itself, a function of the molecular properties of the fluid. Now, how do you calculate the Hamaker constant? There are really two theories, of calculating Hamaker constant of a fluid.

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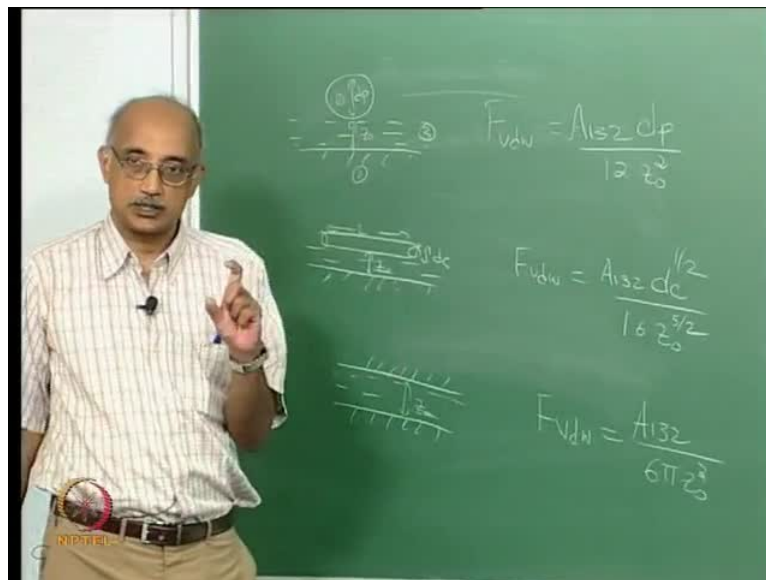


So, it depends on molecular properties and the two theories are London theory, and Lifschitz theory. The London theory is also known as the microscopic theory and the Lifschitz theory is known as the macroscopic theory. So, the, according to the London

theory, you can calculate the Hamaker constant, by characterizing piece-wise binary interactions, between adjacent particles and then, adding them up. So, that is why, it is called a microscopic approach, because, it looks at individual pairs of atoms or molecules or particles, estimates the forces of interaction between them, and then, kind of, does it sequentially and adds them all up. The Lifschitz theory, on the other hand, is based on quantum electro-dynamics. It looks at the entire system, and applies wave theory, to calculate the interaction forces between particles. It allows action at a distance.

The difference is, in the London theory, you are assuming that, only the adjacent particle can exert a force on the particle nearest to it; in the Lifschitz theory, a particle that is further removed from, from a particle, can exert an influence on it, essentially by propagation of waves of energy. And, that is a primary difference between the two. But, these two theories are used quite extensively, to calculate Hamaker constants for systems. So, let us look at some examples, of how the geometries of the bodies, as well as the properties of the intervening fluid, play a role in determining the Van der Waals' forces of adhesion.

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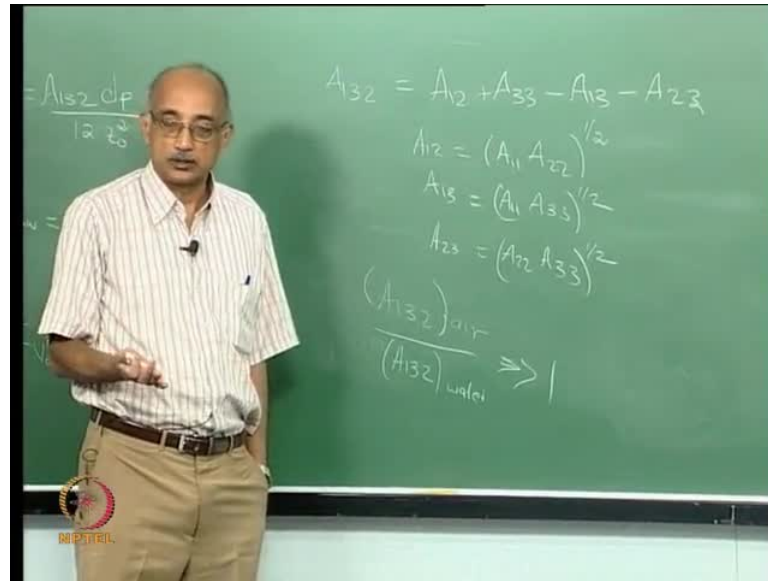
The first case we will look at, is a surface and a spherical particle, that is close to it. So, let us say that, the, this diameter of the particle, is some  $d_p$  and this distance from the end of the particle to the surface, is some  $z_0$ . And again, let us call this material 1; the surface is material 2 and the intervening fluid, let us call that material 3. For this

particular geometry of a spherical particle, that is in near contact with a surface, the corresponding Van der Waals' force, is given by, again  $A \frac{1}{3} \frac{2}{z^2}$ , certainly appears again, in this equation, as well, times  $d_p$  divided by  $12 z_0^2$ . So, in this case, in the case of a sphere interacting with the planar surface, the Van der Waals' force is proportional to the Hamaker constant; it is proportional to the diameter of the particle, and inversely proportional to the distance of separation between the particle and the surface.

Let us look at a case, where again, you have a planar surface, but now, you have a cylindrical particle of some length  $l$  and diameter  $d_c$ . And, let us say that, this again, is the distance of separation between them. In this case, the Van der Waals' force is given by, again  $A \frac{1}{3} \frac{2}{z^2}$ , but now, there is a square root dependence on the diameter of the cylinder, divided by  $16$  times  $z_0$  to the power  $5/2$ . So, just by changing the shape of the particle, from sphere to cylinder, you change not only the magnitude of the adhesion force, you actually change, the qualitative nature. For example, even the dependence on diameter is different, as is the distance dependence; the distance between the object and the surface.

The third case we look at is, two surfaces that are in contact. Here again, the distance of separation is some  $z_0$  and there is an, an intervening fluid, just like in the other two cases. So, here, what is Van der Waals' force? It is again  $A \frac{1}{3} \frac{2}{z^2}$ , because, there is no characteristic diameter now; it is just two planar surfaces. In the denominator, you have  $6 \pi z_0^3$ , where  $z_0$  is again, the separation distance between the two surfaces. So, if we compare these three equations, the only thing that is common to all of them is, the linear relationship between adhesion force and the Hamaker constant; all the other dependences change, based on the geometries of the objects. So, that is something that is very interesting, and something, that you can actually use to your benefit, when you are in a manufacturing environment.

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Now, how do we define this  $A_{132}$  parameter?  $A_{132}$  is the Hamaker constant for the entire system; but obviously, it will depend on, as we said, the Hamaker constants of the individual objects, as well as the intervening fluid. So,  $A_{132}$  is defined as  $A_{12}$  plus  $A_{33}$  minus  $A_{13}$  minus  $A_{23}$ . Now, what do we mean by that?  $A_{12}$  equals  $A_{11}$  times  $A_{22}$  to the power half; and similarly,  $A_{13}$  equals  $A_{11}$  times  $A_{33}$  to the power half and  $A_{23}$  equals  $A_{22}$  times  $A_{33}$ . What is  $A_{11}$ ? It is the Hamaker constant representing the interaction between two particles of the same material 1, without an intervening fluid. So, essentially, when you bring these two particles together in vacuum, this is the Hamaker constant, that characterizes the interaction. Similarly,  $A_{22}$  is for bringing two particles of material 2 together;  $A_{33}$  represents the Hamaker constant for bringing two molecules of the fluid together. And,  $A_{13}$  is then, the Hamaker constant associated with bringing molecule of 1 and molecule of 3 together, which is taken as the weighted, the square root of the individual Hamaker constants.

So, you can calculate the associated Hamaker constants using these rules, and then, you can proceed to estimate the Van der Waals' forces of adhesion. Now, where does the nature of the fluid come into play? Obviously, the  $A_{33}$  parameter is critical, and it turns out that,  $A_{132}$ , the Hamaker constant for the system, if you have air as your intervening fluid, versus, if you have again  $A_{132}$  with water; if you take the ratio of the system Hamaker constants, the only change being, 1 and 2 are the same; 3 has now been

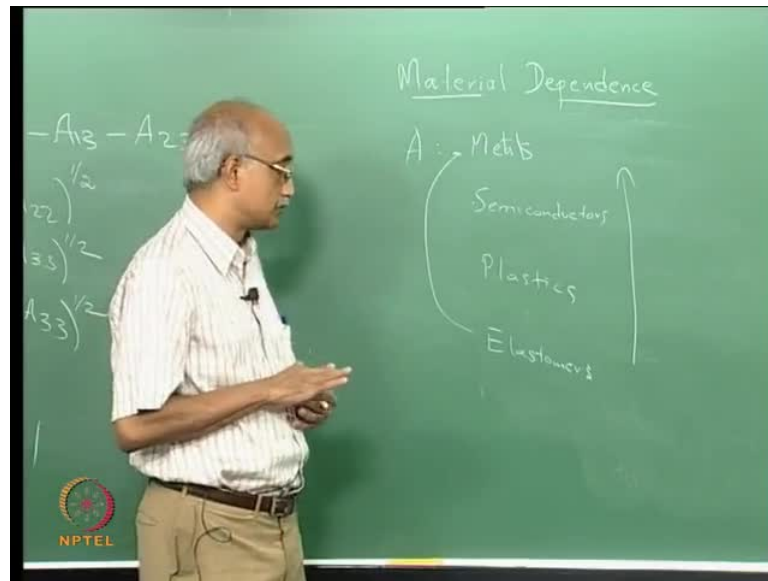
changed from air to water. What do you think will be this ratio? Will it be close to 1, less than 1, greater than 1?

Much, much greater than 1. In other words, the Hamaker constant is, is much lower, when the intervening fluid is a liquid, such as water. Now, does that have practical implications? I think, you all know from your, from your every day experience, that it is easier to wash dishes, for example, when you have soaked them in water, right. Why is that? One reason is that, as soon as you take this dry interface between whatever it is, food particles or dust particles, and a plate, or some other solid surface, the Hamaker constants are very high. So, the, the food material is strongly adhered to the, to the surface. As soon as you soak it in water, the Hamaker constant drops by, of an order of magnitude, by about 10 times. So, the effective  $A_{132}$  also drops, not by 10 times; maybe, by about 5 times and because of that, the Van der Waals' forces of adhesion also decrease significantly; and that is why, wet washing is always easier to accomplish, than dry cleaning.

That is one important implication here. The other thing that you should think about is, when, when we talk about Hamaker constants, it is not only a geometry dependence, it is also a material dependence; different materials, for example, why would  $A_{11}$  be different from  $A_{22}$ ? For example, if material 1, the particle, let us say, it is a metal and 2 is a semiconductor; what is going to be the difference in the Hamaker constants for the two?



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The material dependence of the Hamaker constant is again, something that we really need to fully appreciate, in order to make use of it, in a beneficial manner. So, if you take metals, then, you take semiconductors, take plastics, and you take elastomers, or rubber materials, what do you think will be the approximate range of  $A$  values? Which will have the highest and which will have the lowest?

The magnitude of the Hamaker constant goes this way; metals have the highest Hamaker constants; semiconductors have less of a Hamaker constant; plastics even less and rubbers even less. In a way, it is related to the hardness of the material; that is one way to visualize it. And, as we discussed earlier, when we were talking about surface energy, there is also a relationship of surface energy to Hamaker constant. Metals and semiconductors are high surface energy materials. Plastics and elastomers are low surface energy materials; and that is why, there is also this dependence on the material type. When you take a metal, and when we say it has a high Hamaker constant, what it means is, anything that it, that it comes in contact with, will accumulate on the surface and stay on the surface.

Now, that maybe again, beneficial, if you are using a metal surface, as a collector for something. But sometimes, it is harmful. For example, if again, the metal is something you are, you are making your hard drive disks with, you do not really want material to stick to it. So, what you can do is, apply coatings to it, right. Then, if you want, if you

want to take a high surface energy, or high Hamaker constant material, and change it into a low surface energy, or low Hamaker constant material, just coat it with a, with a low surface energy material. So, for example, polymer coatings on metals are typically employed, to reduce their surface energy; to reduce their Hamaker constant; to reduce their Van der Waals' forces. How do you increase the, how do you reduce the surface energy or Hamaker constant of a plastic? Well, the harder the plastic, the more energy that it has, or the, the higher the Hamaker constant, that it has.

So, if you mold the plastic so that, it is softer, essentially, you can actually make it less binding to the particle. So, the use of, for example, composite structures, is one way, that you can accomplish it, although, in many cases, the composite material will actually increase the rigidity of the structure. So, you have to design the system in such a way, that whatever material you add as a composite, actually, reduces the hardness or surface energy of the material. For example, carbon fillers are typically, while they are stronger, while they are harder, with respect to polymers, they are softer, with respect to hard plastics. So, that is one case, where you can actually mold some, some softer material into a plastic, to get, to reduce its rigidity, or Hamaker constant. Also, you know, that, the combinations are interesting, when you have a, for example, a silicon oxide particle, approaching, let us say, a silicon surface. The Hamaker constant for silicon, is greater than the Hamaker constant for silicon oxide.

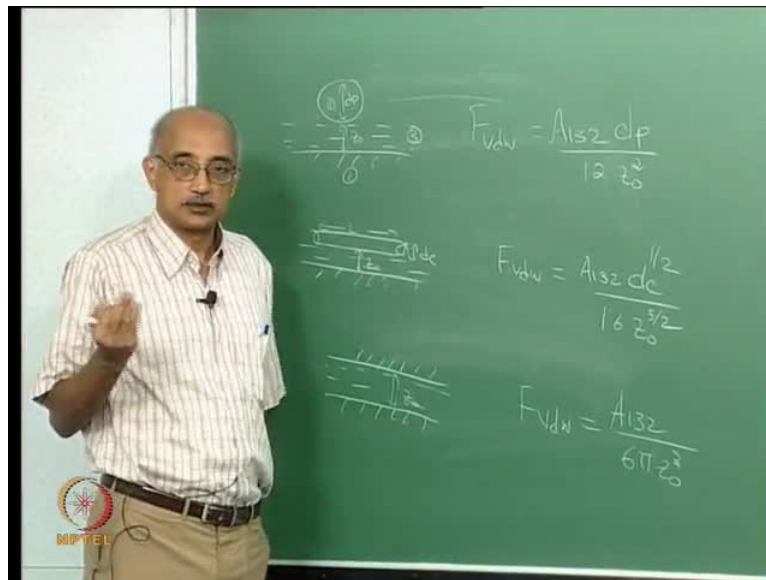
So, what does that imply? The affinity of silicon for the silicon oxide that is approaching, is greater than the affinity for the silicon oxide to the silicon. Now, again, that is mostly positive, because, that means that, if you are trying to make silicon, silicon oxide is not going to act as a contaminant; however, if you are taking a silicon surface and you want to polish it using a silicon oxide abrasive, that is not so good, because, there is going to be a repulsion. So, the silicon oxide particles may find it difficult to make contact and provide good polishing for the silicon surface.

So, you may need to use, again, additives to improve the contact between the polishing abrasive and the surface that you are trying to polish. So, there are a lot of interesting implications of, of this type of behavior, that we need to be aware of. And again, remember that, we are only talking about one type of adhesion force; the net adhesion force is a combination of all the ones that we talked about. So, you may choose a material, which minimizes one type of adhesion force, but at the same time, it might

actually, increase another type of adhesion force. For example, if you are trying to reduce Hamaker constants, you might want to use plastics instead of metals, right; that makes sense, but the problem is, from an electrical conductivity viewpoint, plastics are much worse; they are more likely to build up a static charge.

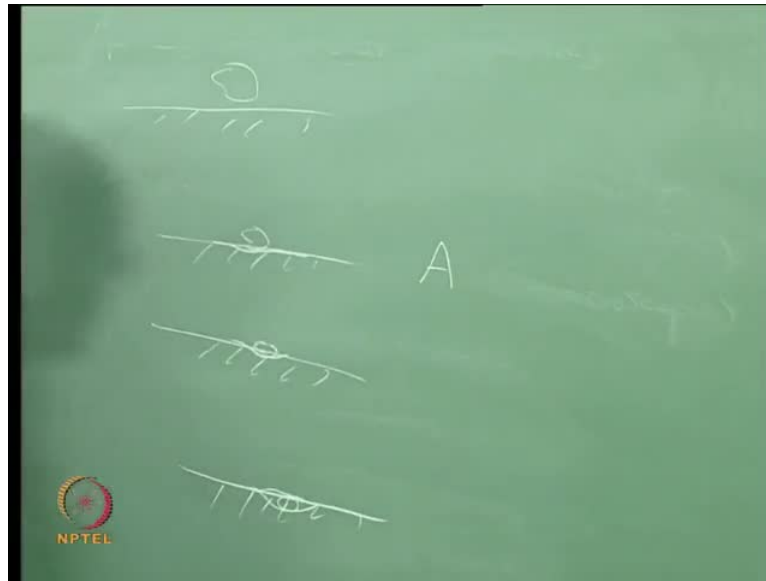
So, electrostatic attraction forces will be much greater, when you use plastics, compared to when you use metals. So, the net adhesion force may actually be increased, by using plastics instead of metals. So, you have to think about it, in a systems way; you have to think about all the implications of the material pair that you are using, on the associated adhesion forces and make the right choice for your application; whether it will maximize the, the adhesion, or minimize the adhesion. Now, the other thing we need to think about is, what role does the hardness of the material and the surface play.

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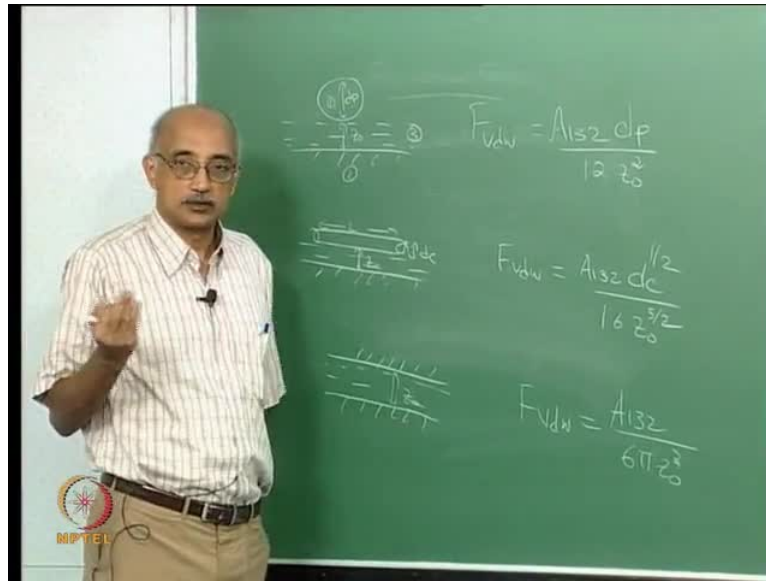
If you have, the simple theory that we have talked about here is really, only applicable, when you think about it for the case where, as the particle approaches the surface, there is no deformation of the surface; that the surface remains as a planar surface.

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Supposing the surface itself, is relatively soft, compared to the approaching particle, and, it actually deforms when the particle approaches, then, what happens. So, imagine a situation that, initially, you have a surface and you have a particle on top of it. Now, when the particle approaches the surface, the next instant, you may actually start to see, a slight deformation of the surface, as it tries to accommodate the approaching particle. And over time, it may actually form like a dimple on the surface, in which the particle starts to nestle and eventually, this may lead to a situation, where you have physical encapsulation of the particle. Now, in such a situation, how do you characterise a Hamaker constant? At  $t$  equal to 0, when the particle first approaches the surface, the Hamaker constant will be, what we have calculated earlier.

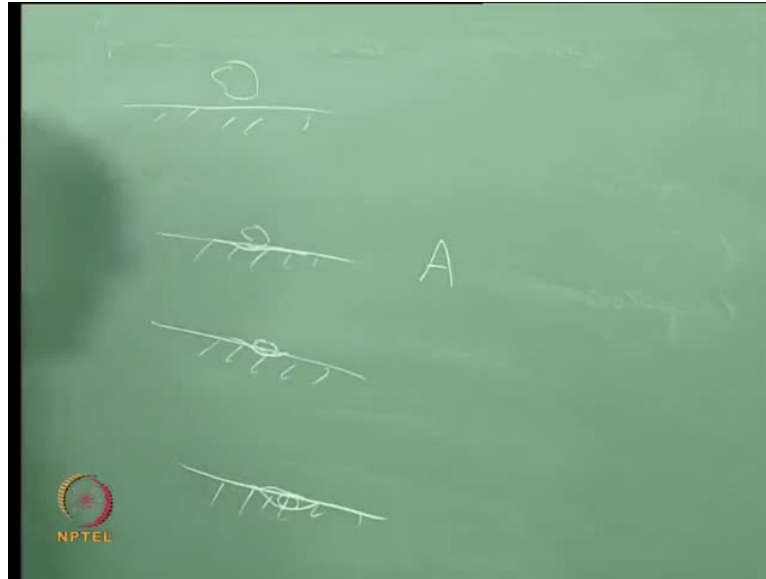
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But then, over time, the Hamaker constant itself, remains the same; however, what is changing; why you put the force of adhesion increase with time; if the Hamaker constant is remaining the same, why would the force increase? What is in the equation, that will allow that to happen? Well, one is this  $z_0$  in the denominator, right. As the material deforms, the particle can essentially, make much more intimate contact with the surface.

So, remember, we talked about the equilibrium distance of separation? That can drop to virtually zero, when you have a deformable material, surface or even a deformable plastic, I mean, deformable particle. In both cases, the intimacy of contact between the two approaching surfaces will be much more, which means that, the values of  $z_0$  will be much smaller. And the other reason is,  $d p$ . Now, what do we mean by particle diameter? It is the surface, in reality, it is the effective  $d p$  that makes contact with the surface, right. In the case of a hard particle approaching a hard surface, the contact area, it is going to be limited to a very small sector of the particle.

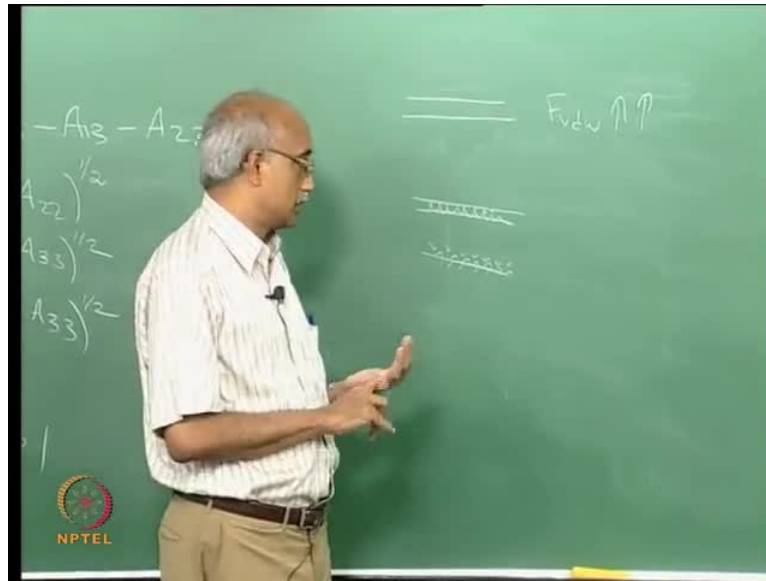
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Whereas, as we showed in this illustration, as the particle and, or the surface becomes more and more deformable, the effective area of contact increases with time; and force is, obviously, pressure times area; and therefore, as area increases, the adhesion force increases as well. So, basically, when we have two rigid particles in contact with each other, and you calculate the adhesion force, or estimate the adhesion force associated with that, and compare it to a case, where the two bodies are now considered to be deformable, the adhesion forces that develop in the latter case, can be orders of magnitude higher, compared to the adhesion forces that develop in the first case.

Here again, this is something, that you can use to your advantage, or it may work to your disadvantage, depending on your process. If you are concerned about adhesion and you want to minimize it, then, this would say that, you know, basically, make sure that, you use surfaces that are not deformable, which are hard, and in fact, some of the same arguments, apply for roughness also. When you have two smooth surfaces contacting each other, versus two rough surfaces, again, the adhesion forces are different, and the reason for that, again is, the differences in the area of contact, more than anything else.

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So, when you have two smooth surfaces, that come in contact, or a highly polished particle in, in, that is approaching a surface, the Van der Waals' force is very, very high. In fact, I am sure, you have heard of the experiment, where you bring two highly polished surfaces together, you can almost, never take them apart; the force of adhesion are virtually, infinite. But supposing, now, you roughen the bottom surface, so that, you introduce some asperity and now, the top surface comes down; the forces are going to be reduced, right; because, the effective area of contact, is now only the peaks of the asperities and so, it virtually, halves the area, that is available for contact.

Now, if the top surface is also rough, then, what happens? Well, that depends. Sometimes, it lead, it leads to reduced forces, but sometimes, it can lead to this interlocking mechanism, that we talked about; it can actually, result in an increase in the adhesion force. But clearly, the point is, properties of the, physical properties of the particles and the surfaces, including their hardness, deformability, as well as roughness, also play influential roles, in determining the forces of adhesion between these particles. Alright, so, in this lecture, we have just covered Van der Waals' force of adhesion. In the next lecture, we will start discussing the electrostatic forces. Any questions on what we have talked about today? See you at the next lecture, then.