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Module No. # 06 Lecture No. # 16 Surface Adhesion: Electrostatic and Surface-Tension Forces

Welcome to the sixteenth lecture in our particle characterization course. In the last lecture, we started discussing adhesive phenomena between particles and surfaces, and also between adjacent particles. In particular, we dealt with the case of Van der Waals forces of intermolecular or inter particulate adhesion, which are predominant in the case where the adhesion is happening in gaseous medium.

We noted that the Van der Waals forces are very much dependent on the Hamaker constant; and we establish the relationship between the Hamaker constant for a system, and the associated Van der Waals force of adhesion. And the key point there was that the geometry of the particle plays a significant role in determining not only the magnitude of the adhesion force, but also the qualitative dependence on properties such as the size of the object as well as the distance between the objects. And we also noted that the intervening medium plays a significant role in either enhancing or reducing the force of attraction. And finally, we discussed aspects such as the hardness of the surface and the roughness of the surface and their influence on the Van der Waals forces of adhesion.

Now, in today's lecture, we are going to take up the topic of electrostatic attraction between a particle and another particle or a surface. Electrostatic forces are quite strong, particularly again in air or gases or vacuum as the medium electrostatic forces are typically weakened, when you take the particle, particle, system or a particle surface system, and immerse it in a liquid such as water; there is an immediate order of magnitude reduction in the forces of electrostatics between the surfaces, but certainly again in dry environments, it plays a considerable role.

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Now, we are all familiar with some forces of electrostatic attraction; the Coulombic forces, I am sure you have all dealt with in your earlier courses. The Coulombic force is basically, reflected as follows; so if you have a particle and a surface, and this particle diameter is some d p, and this distance is again some z 0, and let us says that this particle is carrying a charge Q; so, it is a charged particle; and let us say that the surface is also charged either with the same charge or an opposite charge of Q. The associated Coulombic force can be written as Q squared over 4 phi epsilon 0 epsilon R times z 0 plus d p by 2 the whole squared, which is the distance between the center of the particle and the surface. Here epsilon 0 is the permittivity of free space, and epsilon r is the dielectric constant of the medium. So, we know how charged surfaces or charged particles interact, and the force are develops between them.

(Refer Slide Time: 04:33)



But if you have a charged particle, and let us say you have a neutral surface, is it still possible to develop a Coulombic force of either attraction or repulsion between them. So, in that case, you again have a particle of diameter d p, charge Q, and you have a surface with a distance of separation of z 0; but we let us say that the only difference is the surface itself is neutral. It turns out that even in such a case a Coulombic force thus develop between these surface; essentially this particle is reflected as an image - inside the surface, at a distance that is also exactly equal to z 0, it is like a an mirror or an image that it sets up.

And so in this case, the force associated with that is called the image force, and this is given by Q squared divided by 4 phi epsilon 0 epsilon R. The distance of separation now between the two bodies this roughly twice where it was in the previous case right. So, we write this as d p plus 2 z 0 the whole square. So, the image force is roughly equal to a quarter of the Coulombic force that prevails between two charged surfaces or two charged bodies; so, it is substantially weaker, but non-zero. So, even when you have a neutral surface, and you have a charged particle approaching it or when you have two particles, in which one is charged and the other is not, you can still setup a Coulombic force between them. So, that is an important consideration that we need to be aware of.

(Refer Slide Time: 06:43)



Now the other type of electrical force that can be setup between two surfaces that are again in air or a gaseous medium or in vacuum is called the electronic double-layer force; and this force is associated with the electrostatic contact potential between the two solid objects; in fact, the force is also known as the contact potential force. Now, how does the electrostatic contact potential happen? This potential is created, because of differences in the energy states as well as essentially, the electronic work functions of particles that are adjacent to each other.

Now, there is an immediate tendency then for the particles are the two objects to equilibrate; this equilibration proceeds until we reach what is known as a constant Fermi level. Electrons are transferred from one object to another till this constant Fermi level is reached across the pair of objects. Now as this process proceeds of exchange of electrons, you setup a potential between the two surfaces and that is known as the contact potential.

Now, this electrostatic contact potential is can be quite significant. So, this potential V c p can be of the order of half a volt. So, that is quite large; particularly, this this force is an especially important for finer particles. The force essentially increases somewhat linearly with respect to the inverse of the particle size. Although we will see that the potential itself is proportional to the particle size; however, as particles get larger, the tendency to equilibrate by exchanging electrons actually decreases. So, the linear dependence on

particle size of this potential is only applicable in finer size ranges not in the larger size ranges.

Now basically this potential is sets up an electronic double-layer between the two objects. Now, this double-layer can actually extend even into the object; for example, especially if you have a dielectric particle, semiconducting particle or an insulating particle, and you have two particles that are adjacent to each other; this field can actually extend into the particle up to one micron within the particle; this is for again insulators and semiconductors. However for an a conductor like a metal, the force stays only on the surface; in other words the potential or the or the electronic double-layer is restricted to the surface of the particle, it does not extend into the interior or bulk of the particle.

(Refer Slide Time: 10:47)



So, this electrostatic contact potential is again an important force that can either attract or repel particle pairs or particle to surface pairs, and the force in this case F contact potential is proportional to the square of the voltage or the potential that is setup times d p times there is also a pi and epsilon, and the distance plays a role. But the difference here is that here you have a z 0 squared dependence whereas, in that case you have a z 0 dependence. What that means is the contact potential force is an action at a distance; it can act over much longer distances compared to the Coulombic force.

So, another way to imagine this is we have two particles that are separated then the contact potential force is dominant, until they reach much shorter distance of separation,

at which time the Coulombic forces start to become dominant. And similarly, when we look at particle size, as the particle size increases, the Coulombic forces gain in magnitude; as a particle size decrease, the electrostatic contact potential forces become important.

Now this equation by the way is for a spherical particle, and a highly polished surface. The equations can be quite different and much more complex, when dealing with irregularly shaped objects as well as again parameters such as rough surfaces or asperities on a on a surface and so on. But in the simplest case, we can represent the force associated with contact potential in this fashion. Again the reason that this develops is because of an imbalance in the energy states of adjacent particles, and the associated tendency to exchange electrons till they are neutralized. Now, in the case where the particle is actually immersed in a liquid, something analogous happens, except that now instead of an electron distribution, it is an ionic distribution that happens.

(Refer Slide Time: 13:22)



So in the case where the particle is immersed in a liquid; the potential that develops it is called an ionic double-layer potential, also known as zeta potential. Now, this zeta potential happens particularly, in liquids of high ionic conductance; and that typically requires high concentration of electrolyte. So, when you prepare an electrolytic solution, in which you have a large concentration of ions that are dissolved in the solution, what happens is distribution of these ions.

(Refer Slide Time: 14:43)



So, let us say that you have a situation, where you have a surface; and on top of that, you have a liquid; and in the liquid, you have particles; and let us say that in this liquid, you have various ions positive and negative ions that are floating around; what are these ions going to want to do? They want to attach themselves either to the particle or to the surface or both. Now, if it happens that let us say that you get a bunch of negative ions attaching themselves to a particle, because they are attracted to it; and if the surface also has a negative ion buildup, then there is going to be a repulsive force between them. Similarly, if you have a tendency for adjacent particles to accumulate charges of the same sign, again they will repel; whereas, if they buildup charges of opposite signs they will attract.

So, every particle has what is known as an ion cloud around it, which happens, because particles have a natural ions have a natural tendency to separate themselves from the electrolytic solution, and attach themselves to the nearest solid that they see. And this essentially can be visualized as a layer of charges that are built up around the particle. So, if you have one particle with a certain charge built up, and you have an adjacent particle with let us say the opposite charge; this again sets up a potential between them, which is known as the zeta potential and that reflects in an attractive or repulsive force as the as the case may be.

The definition of the zeta potential is the the potential difference, which is setup at the interface between the object and the liquid, where the definition of the object includes the ion cloud that is surrounding that object. So, the shear boundary that exist at the exterior of the surface charges is considered the interface; and so the potential is actually setup if this is the liquid, the potential is setup between this boundary, and the liquid that surrounding the object.

Now zeta potential obviously, has huge implications in manufacturing industries, where you use slurries of particles in a solution; one of the examples is a polishing process that is used in semiconductor manufacturing called CMP Chemical Mechanical Planarization, which really makes use of abrasive particles that are in in suspension to provide a high surface finish to wafer surfaces by the combined action of mechanical polishing as well as preferential chemical reactions with the with the material on the surface.

Now when we do this chemical mechanical planarization process, the size of the particle plays a huge role in its effectiveness. Now, what can happen, again if you have high zeta potential in the system; depending on whether it is a it's an attractive potential or a repulsive potential between the particles; you can either get a well segregated suspension of particles in solution, which is what you desire really you require a high degree of dispersion of the particles or if the particles have carry opposite charges, you will start to see agglomeration effects.

Now, as the particles change size from their original size ranges to the agglomerated size ranges, there is a resulting change in their polishing characteristics as well, so that is one aspect. The other aspect is the zeta potential difference between the particle and the surface that you are trying to polish. So, here again if you have a repulsive interaction between them, the nature of the polishing process is going to be very different compared to if you have an attractive process between the particle and the surface.

So, in slurries, it is very important to characterize zeta potential; it has huge implications for the stability of the suspension; again if you can induce charges so that particles in suspension repel each other, they are likely to remain stable in suspensions much longer than if they carry no charge or if they carry an attractive charge. So, by essentially by controlling the zeta potential, which can be done for example, by controlling the pH of the solution, by controlling the composition of the electrolyte and the as well as the

concentration of the electrolyte, you can influence charge buildup on discrete particles and cause them to either try to come together or a move apart.

So, many of the for example, particle size analyzers that are used in manufacturing industries will also come with a zeta potential measuring device, because the simultaneous measurement of the size distribution and the zeta potential is important to characterize the long term stability of the suspension. So, if you if you measure a certain size distribution of particles at time 0, but your zeta potential measurement says that there is a high attractive force between the particles. Then you can expect that over time you will see significant clumping of the particles, and a significant size change; whereas if the zeta potential is zero or repulsive in nature, you can rest assure that even with the passage of time, the particle size distribution is not going to change significantly, because there is no agglomeration going on.

(Refer Slide Time: 21:20)



Let us say that you have setup this ion cloud and you have now setup a zeta potential, again there is a force associated with it, and that is called the ionic double-layer force. So, the ionic double-layer force is what prevails in in a liquid particularly, in a liquid of high conductivity; and this force F i d l is given by 2 phi epsilon 0 epsilon r d p zeta potential of the particle zeta potential of the surface times a parameter kappa times exponential of minus kappa time's z 0 over 1 plus exponential of minus kappa times z 0; where again epsilon 0 is a permittivity of free space, epsilon r is the dielectric constant of

the liquid, the zeta values are the zeta potentials that develop over the particle, and over the surface or it could be two adjacent particles, kappa is the inverse of the double-layer thickness.

So, this parameter is very much influenced by the ionic conductance of the liquid, and the electrolyte concentrate concentration in the liquids. So, kappa is very sensitive to how conductive the liquid is the basically they are concentration of ions in solution; and z 0 is again the distance of separation between the two objects, whether it is a particle under surface or two adjacent particles. Now, just like with the electronic double-layer force, the ionic double-layer force, which by the way this again is an expression for a sphere, in this case in contact with the smooth surface. You can see that again there is a linear dependence of this force on particle size; in fact, if you review most of the forces that we have talked about, adhesion forces have a linear dependence on size, which is why if you recall the equation that I wrote down first you know, the empirical equation based on experimental measurements; there is a linear dependence of measured adhesion force on particle size.

So in general, it is true that most attractive forces or most adhesive forces tend to scale linearly with particle size; larger the particle, the higher will be the force of adhesion. So, this ionic double-layer force can again be quite significant particularly when significant amounts of zeta potential or built up in solution. However, even in cases, where you essentially have a neutral solution; there are still two kinds of forces that are setup in liquids, which have a huge bearing on particle to surface adhesion forces as well as particle to particle adhesion forces. So, we will talk about those next.

(Refer Slide Time: 25:02)



The first type of force is a surface tension force; now surface tension forces are important whenever you have two particles in contact or a particle in a surface in contact, where there is an intervening liquid layer. Now, the liquid layer could be there, simply because of high humidity; and again if you recall their empirical equation, you will recall that there was dependence on on the relative humidity, which is also roughly linear. So, clearly humidity plays a huge role, primarily through the surface tension phenomenon.

Now the other situation where this can happen is if you have a surface on which you have particles, and is and you immerse this entire system inside the liquid, and then pull it out and let the liquid dry on the surface; or alternatively if you have a suspension of particles, let us say in a solvent, and you evaporate the solvent, so that you essentially turned a system that was initially wet into a system that is now dry; in in that situation also surface tension forces play a significant role.

And the reason for that is if you have a particle sitting on a surface, when there is no intervening liquid, the forces of adhesion are primarily the Van der Waals forces of adhesion and electrostatic forces of adhesion **right**. If you have a liquid that is present, then again if they are charged particles or if it is a conductive or if there are ions present in the liquid, then again you can get ionic double-layer forces. But let us say that you have a liquid which is neutral, there are no free ions, let us take water and you are just wetted this surface with water, what is going to happen to it? Water will essentially dip

between the particle and the surface and form a bridge. Now, this process is known as capillary condensation, also known as liquid bridging.

It is simply reflex fact that the liquid will try to get into the interface between the particles and the surface, it will try to wet the interface, and as it does, it will provide a surface tension force. Now, surface tension forces are always attractive; surface tension forces will try to draw the particle to the surface, and make it stick that. However in order for that to happen, the liquid has to be able to wet the interface between the particle and the surface; that requires that the liquid have low surface tension. If it has a high surface tension, it is really not going to able to penetrate into the interface between the particle and the surface; and so you need a wetting agent in order to get the liquid to fill the interface between the particle and the surface between the particle and the surface between the particle and the surface between the particle and the surface.

The reason you add a surfactants to water to improve its cleaning or a detergent to water to improve its cleaning. There is two reasons that could be a chemical reason for example, detergents can chemically dissolve organic materials for example; but the physical reason is when you add a surfactant to a liquid, it lowers its surface tension; and makes it possible for the liquid to now get in between the particle and the surface. See again the reason why it is easier to remove particles from a surface, when it is immersed in a liquid. As we saw yesterday, the first reason is Van der Waals forces are reduced; the second reason actually we did not talk about it earlier on, the contact potential forces that I talked about or even the Coulombic forces; they all have this dielectric constant as one of the terms right.

The dielectric constant of water relative to air is 80 times. So, if you look at the equation for the forces, the dielectric constant appears in the denominator. So, the Coulombic forces, the image forces, they are all significantly weaker in the case, where water or a liquid is the medium. There is an immediate reduction in the electrostatic contact potential forces also by a factor of about 80. So, when you take a particle surface combination in immerse it in a liquid, everything is reduced; I mean, the Van der Waals forces are reduced, electrostatic forces are reduced. However, the forces that could potentially increased or surface tension forces and ionic double-layer forces; but surface tension forces will really not set in, until you actually take the surface out of water. If you keep it immersed this will happen, but as long as you keep it wet, the particles are still loose on the surface.

Now if you take this and you dry it, either just allows it to dry over time or you actually provide active heating to convert this liquid bridge into a solid bridge, then the adhesion forces increase exponentially. Again from our everyday life the example is, if you, you know, if you take a plate, which you have not cleaned, and you just let it set, and you try to clean it afterwards it is going to be hard, because adhesion forces develop over time. Now, if you take that dirty plate and immerse it in water, but do not complete the cleaning, take it out and again let it set actually it is going to be even more difficult, because now the particles are going to be solidly bonded to the plate surface, because of this solid bridging phenomenon.

So, the key point is that when you when you are washing dishes or whether you are washing semiconductor wafers, never let particles dry on the surface after they have been soaked in a liquid, because of these phenomena. Initially you will form a liquid bridge between the particle and the surface, and eventually it will turn in to what is known as a solid bridge. A solid bridge actually acts like a physical entrapment; you have to physically break it off, in order to get the particle released from the surface. So, if you want to avoid particle adhesion to surfaces, it is very important to make sure that you never allow a particle to dry on a surface, after it has been immersed in a liquid.

(Refer Slide Time: 32:12)



Now, the force of attraction, the surface tension force is I am sure, you have familiar with the equations essentially 2 pi d p gamma, where d p is the particle diameter, and gamma is the surface tension of the liquid; of course, in this equation there is an implicit assumption that the contact angle is virtually zero. Surface tension forces really only come into play, when you have low contact angles; in other words the surface must be capable of being wetted. So, if you have a surface, and the liquid does this, then surface tension forces become possible, because now we have a particles sitting here, you develop this capillary layer between them.

On the other hand if you have a surface and you have a liquid on it, which has a high contact angle something that tends to bead up like this right. Now, the particle to surface adhesion force is definitely not going to be increased by the presence of the liquid; in fact, it could reduce the adhesion force. So, it is it is a very important consideration that surface tension forces only coming to play, when the combination of the surface, the particle, and the liquid is such that the liquid can wet the interface between the particle and the surface.

So, if you have for example, a hydrophobic surface, and you have water as the as the liquid, it is not going to do this, it is going to do this; and so surface tension forces are not going to come into play as something that increases adhesion forces. On the other hand if you have a hydrophilic surface and water on top of the hydrophilic surface, it will spread nicely on the surface, and then as the particle approaches the capillary condensation will happen, and you will get bridging between the particle and the surface. So, the general equation for the force of adhesion is cos of theta, where theta is the contact angle. So, as the contact angle approaches 90 versus a low contact angle in this case, this will approach 0. So, surface tension forces can play a huge role, but not always; you have to match the liquid to the particle and the surface.

(Refer Slide Time: 35:19)



Now, what role the surfactant play? The surfactant essentially will reduce gamma; if you plot if you plot the surface tension of a liquid against for example, volume percent of surfactant, what kind of behavior will you see? Be a rapid drop right, so as soon as it reaches the critical my cell concentration, you will see a steep drop in the surface tension. What is the practical implication of that? That means that actually this F value will decrease, when you add when you add a surfactant. Now it is kind of contradict whatever saying earlier right that adding a surfactant helps to remove particles. But the reason is you are essentially trading of two things; if you do not lower the surface tension, then this will happen. In other words, the surfactant that you add influences not only this, but this also; and its influence on this, typically overwhelms the reduction in the surface tension of the liquid itself.

It does not matter if this if the surface tension is very high, if if the liquid is not able to get in between the particle and the surface. So, adding a surfactant enables us to introduce the liquid in to the interface between particle and the surface. But you pay a slight penalty in the fact that now the surface tension itself is reduced, so the adhesion force is reduced, again if you are trying to remove the particle that again is goodness, because a lower surface tension means that the particle can be more easily dislodged from the surface; so, it kind of benefits in both ways, when you do that.

Surface tension can also is adjusted by changing the nature of the liquid for example, instead of using water, you can actually use other liquids, solvents, other chemical blends that have a lower surface tension than water. And in fact, many solvents actually work better in cleaning applications, because they have better surface tension characteristics than water. So, if you are ever trying to reduce adhesion between particles on a surface using a liquid, the first stable you should look at is one at least surface tension of various liquids, because that plays the first order role in terms of influencing particle to surface adhesion phenomena.

(Refer Slide Time: 37:57)



Now, kind of related to this, the other type of force that prevails in liquid solutions is the hydrophobic hydrophilic force. What we mean here is that when you have a suspension, and you have particles, let us say that the suspension is in water, which is of course, highly hydrophilic you know, hydrophilic basically means like water. So, water is the most hydrophilic substance that is known to mankind. And let us say that you have two particles, which are both hydrophobic that is water repelling; now, this could be because of the nature of the material itself or because they have some coating, an organic coating on them; for example, or an oil coating, which are which is repelling water.

Now, when you look at this combination; are these two particles - the two hydrophobic particles that are suspended in this hydrophilic medium? Are they going to want to attract each other or repel each other? They have a huge attractive force between them.

The reason is that this is a hydrophobic particle, and it is surrounded by essentially water molecules, which it does not like; so, it tries to push the water molecules out of the way. And similarly, this particle is also surrounded by water molecules, which it it does not like. So, they keep, they both keep repelling the hydrophilic molecules around them, and they keep doing it, until they actually find each other, and then they start attracting each other.

It is basically a free energy minimization situation; the lowest free energy state or equilibrium state for the system is where it is actually an entropic effect. The particles that are hydrophobic try to repel or expel the hydrophilic molecules out of their way, and they keep doing it, and they keep pushing towards the each other, till they find each other, which is why when you have hydrophobic particle suspended in water; they have a huge tendency to agglomerate; again going back to nano particle processing, the reason that it is very difficult to keep nano particles suspended as discrete particles in a water suspension is because of this tendency for hydro phobic particles to attract and find each other.

Now, suppose we look at the situation, where instead of being hydrophobic, let us say that these particles are hydrophilic. Now, what happens? Will they try to repel or will they try to attract? They are both hydrophilic particles; they would still right to repel each other, but why I mean, like particles I mean, the hydrophobic particles wanted to attract each other right, because they are both hydro phobic. Now here, you have two particles that are both hydrophilic. So, why would not they want to attract? The reason is water is the most hydrophilic substance, no one. So, even though these are hydrophilic, because the surrounding molecules are even more hydrophilic; the hydrophilic particles would prefer to stay in contact with the hydrophilic water molecules rather than try to find each other.

So, hydrophobic particles suspended in a hydrophilic medium - attract; hydrophilic particles suspended in a hydrophilic medium, do they always attract? I mean, do they always repel? No, it depends on the hydrophilicity of the medium versus the hydrophilicity of the particle. Since, water is the has the highest hydrophilicity hydrophilic particle particles that are suspended in water will always repel. However if the hydrophilic particles are suspended for example, in an alcohol, which is combination of hydro hydrophobic and hydrophilic material; the alcohol may still be hydrophilic in

nature, but the hydrophilcity of the alcohol may be lower than the hydrophilicity of the particles, in which case they will try to attract each other.

Now, let us reverse it again; suppose you have a hydro phobic liquid, let us say that you have an organic solvent, in which you have a hydrophobic particles suspended, then what happens? Here again, it is a relative hydrophobicity of the material; if the solvent is more hydrophobic compared to the suspended materials, then they will repel each other. On the other hand if it is less hydrophobic than the suspended materials, they will attract each other. Hydrophilic particles in a hydrophobic liquid that is an easy one; basically, the hydrophilic particles will have a tremendous attractive force towards each other.

So, again in terms of, if you are trying to estimate whether particles in a suspension will have an attractive behavior or a repulsive behavior, the parameter that you need to go after first, the table that you need to compile is hydrophobicity and hydrophilicity of the material that you are suspending, and of the various liquids that you are planning to suspend there the material in, that will tell you quickly what that tendency is for agglomeration? Does it tell you the rate?

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No, because that depends on many factors, most importantly the size of the particle. As you approach the finer particles sizes, the tendency to either attract or to repel will be greater, because they have greater kinetic energy in the sense that they will diffuse much faster as the size decreases.

So, again to summarize the forces of adhesion that we have discussed so far, we started by discussing the Van der Waals forces then the electrostatic contact or or electronic double-layer forces, then we discuss the ionic double-layer or zeta potential forces, then we discussed the surface tension or steric forces and finally, the hydrophobic hydrophilic interaction forces of course, earlier we also discussed others special types of forces such as sintering forces, physical entrapment, magnetic forces and so on, and again remember the key point I made that chemical bonding forces are very important also, and they can be orders of magnitude higher than any of these physical bonding forces that we have discussed so far. If the particle, if two particles are reactive, they are going to bond to each other with with much higher strengths than what we have described so far. Similarly, if you have a particle and a surface that are reactive then these factors may not be important, even if the surface tension is not favorable, even if hydrophobic, hydrophilic is not favorable. The tendency for chemical reactivity can overwhelm all that especially in higher temperature systems, higher pressure systems that promote chemical reactions. The chemical bonding forces can be orders of magnitude higher than physical bonding forces, just as chemisorptions forces can be or is a magnitude higher than physisorption forces in the case of interaction between a gas and a solid particle.

The next aspect that we should discuss is how do you measure adhesion forces, because in order to characterize particle adhesion to a surface, we need to be able to measure the force with which it adheres. We have given some expressions for the adhesion force, but these are theoretical expressions; you want to be able to measure the actual force of adhesion. In the next lecture, we will begin by describing how to measure adhesion forces of particles to surfaces. Any questions? See you at the next lecture then.