

Instability and Patterning of Thin Polymer Films

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Lecture No. # 27

Intermolecular Forces between Particles and Surfaces – 1

Welcome back, today we are going to sort of shift gears a little bit and start taking up a new topic, which is related to the part of the course which we have not talked in greater detail and that is the instability. Now, in order to understand instability, we essentially would need a good concept about the intermolecular forces acting between surfaces, and particles.

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The image shows handwritten notes on a blue background. On the left, a box labeled "Intermolecular forces:-" contains the text: "Forces that act between neighbouring particles = molecules, atoms or ions." Below this, it says "Weaker than the INTRAMOLECULAR forces. (Forces that hold all the atoms together in a molecule)." and "Diff. Types of Interaction/ Intermolecular forces." followed by "Vander Waals Liquid" and a boxed equation $\gamma^+ = 0$, $\gamma^- = 0$, $\gamma_{AB} = 0$, and $\gamma = f(\gamma_{LH})$. On the right, a graph plots potential energy ϕ against distance r . It shows a curve with a minimum at $1/r^6$ and a repulsive region at $1/r^{12}$. Text next to the graph says "Between two interacting surfaces $\sim 1/r^2$ ". At the bottom right, it says "Interaction between the Tip and the Sample to be Scanned."

In many of the lectures before we have talk about the existence of Van Der Waals forces, we have also talk about the potential curve particularly to explain the approach sequence of an atomic force microscope, but we also understand a little bit about the one sixth attraction, and one twelveth repulsion. We also talked a little bit about the fact that between two fundamental particles this scaling is 1 by r to the power 6, and between two interacting surfaces it is of the order of 1 by r square. So, some of these things you

already know, and in the first few lectures we also had touched about a little bit about surface tension and other surface related critical phenomena.

Some example of which where we talk about rally instability in I think the sixth or the seventh class, we talk about the existence of Laplace pressure on the different sides of a non planer liquid surface, which essentially is a consequence of surface tension. We also defined what is an access symmetric surface, and tried to obtain an expression for Laplace pressure for an access symmetric surface, rather than the general expression of Laplace pressure in terms of the two orthogonal radii of carvacher - r_1 and r_2 .

Subsequent discussion, sort of we took up more in lines of patterning, and the topics we covered included; photo lithography, then soft lithography, nano imprint lithography, and then we are good that well we might be knowing all the techniques to make the structures, but it is centrally important to investigate how good or bad your structures are, because you are talking about sub micron, and an often in sub hundred nano meter literal length scales the patterns you are making.

And the patterns also are of different variety; they can be topography patterns, they can be chemical patterns. So, it is important that we learned some method to investigate them, and that is the reason we took up atomic force microscope a head of instability. But there are we had to use some of the concepts of intermolecular interaction, because as you understand the a f m operates based on the basic physics of atomic forces, so we needed to understand them.

But now it is time before we move on to instability, we understand the precise nature of intermolecular forces, we do sum bit of quantitative analysis in terms of these intermolecular interactions, try to quantify them, try to understand what are the intermolecular forces which might be present, and then we would sort of quantify in terms of the fact that we are talking about the polymer. So, some of the instead most of the polymer are polar, so polar components of the polar interactions might not be present. So, these are some of things that you can expect was to sort of discussing the next two or three lectures.

So, intermolecular forces; they are forces that act between neighboring particles molecules, particles which can be let us say molecules, atoms or ions. Now, these forces

are off course weaker than the intra molecular forces. Now, what are intra molecular forces? I think you should be able to understand, before I tell there is another name which immediately will understand what they are. So, intra molecular forces are forces that hold atoms together in a molecule and therefore, now no marks for guessing what it is, so these covers all chemical bonds.

So, first thing needs to understand that intermolecular forces are not bonds, **there are not bonds** they are distinct from the intra molecular forces or the chemical bonds, as well as the nuclear forces which sort of wholes and atoms, that the interaction forces that goes on between the nuclear particles.

The different type of intermolecular forces, we have already talked about some of them, primarily the Van Der Waals forces, but we will talk about a little bit detail. So, the other important thing is, these intermolecular forces can sort of act between or I would often be using another word interchangeably the interaction forces, and at times we will find this is more of a appropriate word, because of the fact that we write intermolecular forces, but then again we are talking about interaction between molecules, atoms or ions.

So, I would prefer that in many cases, that we talk about the so called interaction forces rather than intermolecular forces, and the other important reason why probably interaction forces is a better terminology, that soon we will talk about interaction between surfaces. You may be able to recall already, that **we talk about** when we talk about the interaction between and a f m tip. When we talked about an a f m, we essentially talked about the interaction between the tip and the sample to be scanned; and therefore, we are not talking about the interaction between two molecules or atoms or ions here, but what we are talking about where the interaction between two surfaces.

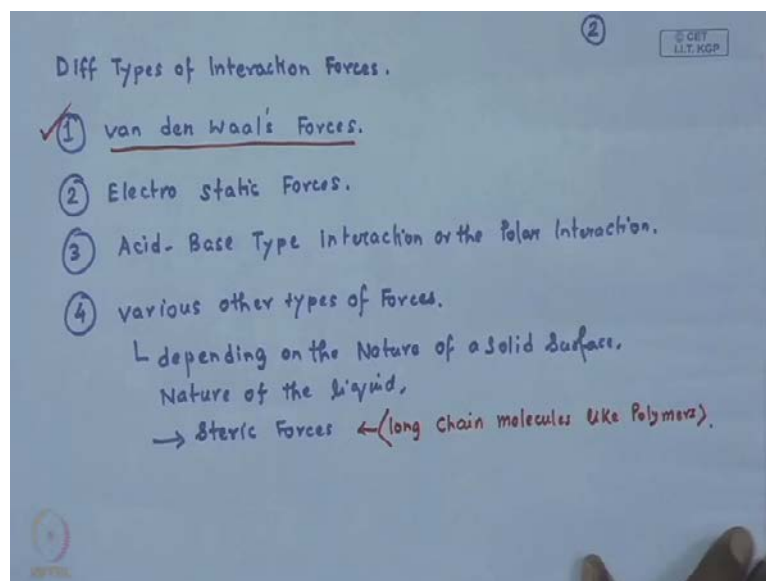
So, it is important that we understand, that though interchangeable we might be using the word intermolecular forces, more appropriate would be to use the word interaction forces. So, all these r to the power 6 scaling, and all these things and we have already talk about one specific form of intermolecular forces, and that is the induce dipole induce dipole type Van Der Waals forces, which is often are loosely refer to as the Van Der Waals forces, but more appropriately they are the London forces or the dispersion forces. Why they are dispersion forces we already understand, because we have argued that they

remain dispersed within the entire bulk of the matrix, so it is all instantaneous, it is temporary dipole temporary dipole type interaction.

But let us try to sort of figure out or identify, what can be the possible interaction or inter molecular forces, and then based on that try to find out that under what settings all these forces are cooperative or the operational. You might recall that we have identify that this induce dipole induce dipole type Van Der Waals forces is the most generic form, because this acts in all types of molecules irrespective of whether they are polar none polar irrespective of the medium that is surrounding them.

But there can be other types of forces which can be operational only in specific types of molecules for example, we have talk about the a b component of surface tension already in one of our initial lectures, which is the access base component of surface tension, but then one has to understand that this component is present only if you have a polar liquid. So, **we talk that we also** I think we talk about what is a Van Der Waals liquid, and we argued that a liquid which does not any polarities. So, γ_{+} if you may recall, so what we argued was that both the γ_{+} and γ_{-} , both the components are zero for this specific liquid and therefore, what happens is the γ_{AB} component is zero. So, the surface tension is a pure function of the LW or the Van Der Waals component of surface tension. So, we will identify these types of systems today.

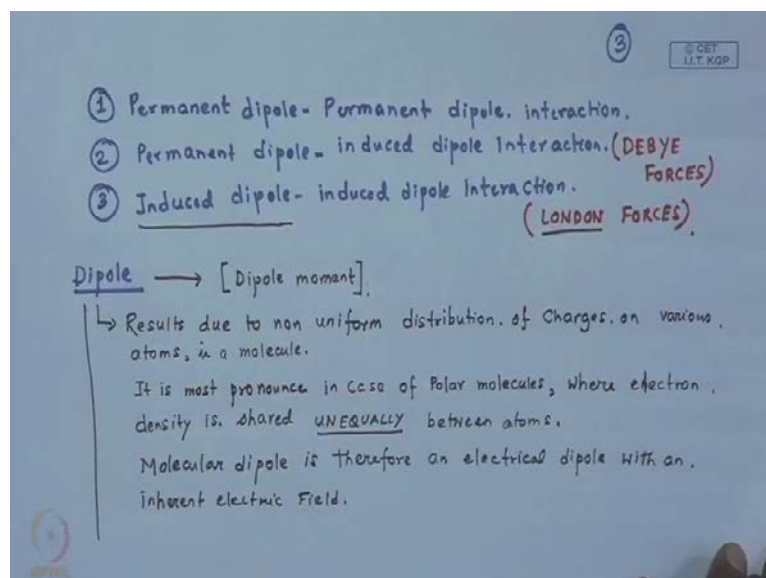
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So, the different type of intermolecular or the interaction forces would be are as follows. Firstly, we have the Van Der Waals forces, second is the Electro static forces interaction or the polar interaction, and there can be various other forces depending on the nature of the solid surface, nature of the liquid, nature of the force field etcetera. So, these forces can be related to steric forces, while specifically I point it out steric force has you can identify from the name, these are due to direct interaction between neighboring molecules, so sort of may be even the different parts of a molecule, and these are predominant in long chain molecules like polymers. There can be magnetic forces, if depending on the situation, if you have a magnetic field and if you have a ferro magnetic material or surface.

So, there can be various other types of forces, but for our condition what is most important is to talk about some of the aspects Van Der Waals forces, and we will also talk a little bit about the electro static and the acid base type of forces.

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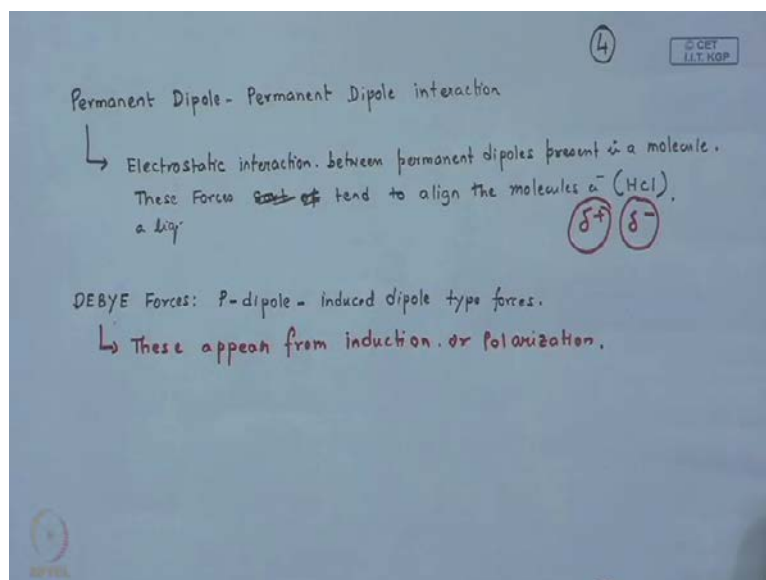
So, amongst the Van Der Waals forces there are three categories, I think we have briefly talk about it. So, there can be three categories of Van Der Waals forces; the first one being the Permanent dipole-permanent dipole interaction, the second one is Permanent dipole-induced dipole interaction, and the third one is off course the Induce dipole interaction. You may just want to note down that this permanent dipole, induce dipole

interaction is often refer to as the Debye forces, and these are refer to as the London forces; named after two scientist.

I guess all of you understand what is dipole? It is sort of results due to non uniform distribution of charges on various atoms in a molecule. It is most pronouns in case of polar molecules, where electron density is shared unequally between atoms. Molecular dipole, this is important to remember is therefore, and electrical dipole with an inherent electric field. The dipole is sort of quantified, as you have probably leant in your undergrad physics itself or may be in twelfth standard physics.

Dipole is quantified in terms of dipole moment, and in terms so we understand that this is we talk about the permanent dipole, which results due to unequally sharing of electron density across atoms. But in absolutely natural, as well as molecules, as well as atoms due to the localization of the electron cloud around the nuclear at any given instance of time, there is the origin of the so called induce dipole, which induces a mirror charge on the neighboring molecule, and there is this which is the origin of the London forces; which we have already talk about.

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So, in permanent dipole interaction... Of course, let me also just mentioned one particular thing, the strength of the interaction sort of is highest for a permanent dipole permanent dipole interaction is followed by the permanent dipole induce dipole

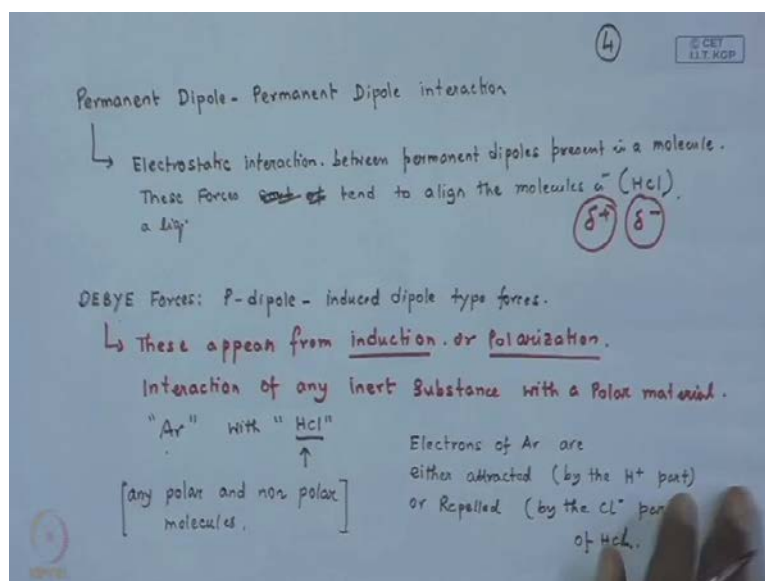
interaction, and is lowest in case of induce dipole induce dipole interaction. So, these are the strongest once, and these are the weakest once. Important thing to understand, that even the permanent dipole permanent dipole type interaction, the magnitude of the interaction forces are far lower than any chemical bond.

So, bonds are much stronger as compare to intermolecular interactions, and amongst the intermolecular interaction when we talk about the Van Der Waals forces there are three, so we talk about different type of interaction or intermolecular interaction forces, we talk about the Van Der Waals forces, and for once we are talking now in a little greater detail.

So, amongst the Van Der Waals forces has three types; it is it is possible to have three types of forces, or in other word may be I will put it straightly better as three different type of interactions are loosely clubbed or generically clubbed as Van Der Waals forces. There are the permanent dipole permanent dipole type interaction, permanent dipole induce dipole type interaction, and the most generic thing the induce dipole induce dipole type interaction. Now, if we look back about our course, you will find that we have mostly talk about the induce dipole induce dipole type interaction.

So, I will give you a few minutes think over, why in our contest this particular force is very important, while I talk a little bit about the permanent dipole permanent dipole type, and the permanent dipole induce dipole type interaction.

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So, this type of interaction is electrostatic interaction between permanent dipoles present in a molecule, these forces... So, some molecule an example, can be let us say molecule like HCL, these forces sort of tend to align the molecules to increase the attraction.

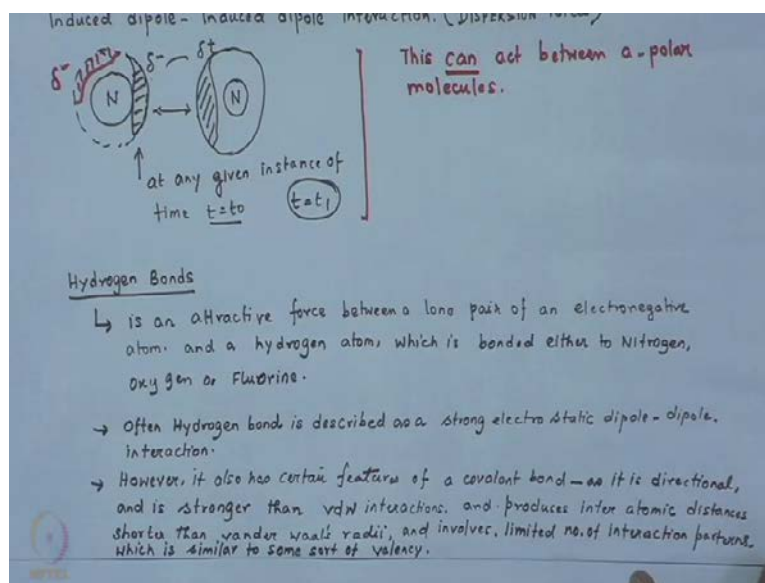
The Debye forces or the permanent dipole forces if we talk about, these appear from induction or polarization. So, here you have already a permanent positive dipole and a negative dipole present in a molecule, it is the origin or its existence is due to the unequally charge sharing. So, there is... So, one part of the molecules sort of is electron rich which has a negative charge localization, the other part is electron deficient which has a positive charge localization, and the dipole sort of interacts between these two zones.

So, this is important, so there is no question of any induction. But the moment you talk about the second and the third type of forces; that is the Debye forces and the London forces, there is the question of induction comes in. So, what is important that one part of the molecule might be reach due to electron deficiency or electron; I mean excess electrons, and that induces a negative a mirror charge on neighboring zone.

So, this appears from induction or polarization of molecules, so generic example can be interaction of any inert substance with a polar material or a liquid. So, if we consider one of the classic example is the interaction of argon with HCL. So, we have already talk that

HCL is a polar compound it has permanent dipole, and so the electrons over here of argon are either attracted by the H plus part or repelled by the CL minus part of HCL. So, this type of interaction is possible between any polar and non polar molecules

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The third type of interaction off course is the induce dipole- dipole interaction, and which we have already talk about; it is most generic form. So, it is due to the charged electron cloud localization at any given instance of time, so this induces a sort of results in a localized delta minus charge which sort of induces a mirror charge on the neighboring molecule, which is delta plus, and as a consequence of that there is a attraction that results insinuations attraction, but this attraction does not result in any sort of a permanent attraction or bonding, because of the fact that this you have to understand that this charge localization is valid at any given instance of time t equal to t zero.

And the next moment; sort of when the very next moment at t equal to t one, the position of the charge localization changes. So, this is the most generic form of fundamental force, because this now I will come to word can act between a polar molecules. In the previous two cases; that the permanent dipole permanent dipole type interaction and the Debye forces or the permanent dipole induce dipole type interaction, we saw that the interaction takes place between at least one of the molecule as to be polar.

But here the most important thing is that even in a polar molecule, where there is no polarity, where there is no permanent dipole present within the molecular structure these forces can act. What is important to realize, that even if you have polar molecules these forces are present there as well, but they might not be dominant as their magnitude is as we have pointed out is weaker than any interaction that includes or involves a permanent dipole.

Therefore, one thing we have always heard and so this is probably the time to realize it firmly, that this induce dipole induce dipole type interaction or the London forces as they are called, or often they are also called the dispersion forces they are the most fundamental form of interaction. The other question I post to you just couple of few minutes back is that; so far in our discussion you have only concentrated on these dispersion forces, and we did not consider in greater detail the other two types of Van Der Waals forces.

I just told you to think over what is the reason for that? The reason for that is that mostly you observe carefully we are talking about polymer thin films; that is the course objective. And polymer molecules; you know there organic molecules, so in most cases; I would not say in all cases, but most cases they do not have any polarity. So, the majority of the cases the interaction between them is a polar in nature and therefore, the Van Der Waals forces dominate to a large extent.

There can be certain other examples; I think it is an appropriate time to highlight few of them. You can have a situation, where they are ah permanent dipole centers within a molecule, but there is no affective permanent dipole of the molecule, and this happens in some symmetric molecules a like carbon tetrachloride or type of a thing, so where because of the presence of chlorine minus ions there is all the bonds are sort of; there is a localization of the electron towards the chlorine end of the molecules.

But what is important is that, since this molecule has tetragonal symmetric structure the polarization sort of cancels out within the molecules itself, and the effectively there is no net dipole present in this type of a molecule. The other important thing what you may think a little bit, another term that what you have heard from your school days is hydrogen bonding, not that hydrogen bonds are going to be that greatly important for

polymers, but there are several questions which you might have already encountered; several phenomena which are attributed to hydrogen bonding.

One of them is the boiling point of water is pretty high at 100 degree centigrade, the other thing is that water has the highest density at 4 degree centigrade and issues like that, and in most cases you know that they are attributed to the existence of hydrogen bond. So, question to ask is, is hydrogen bond a chemical bond or is hydrogen bond... so you also know that hydrogen atoms or ions cannot exist in water, so it is always in the form of an hydroxyl sodium ions H_3O^+ . The question to ask is hydrogen bond a chemical bond or it is a permanent dipole permanent dipole type of an interaction? And the answer is, so let us try to find out what is hydrogen bond? It is an attractive force between a lone pair of an electronegative atom and a hydrogen atom, which is bonded either to nitrogen, any chemistry book will give you this definition, oxygen or fluorine.

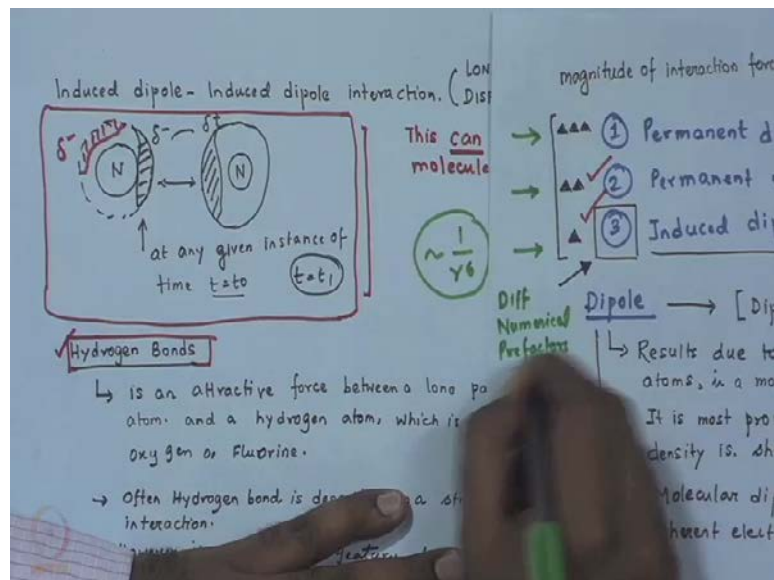
In often, an hydrogen bond is described as a strong electro static dipole-dipole interaction. However, it also has certain features of a covalent bond, as it is directional stronger than **and is stronger than** Van Der Waals interactions, and produces inter atomic distances shorter than Van Der Waals radii and also involves limited number of interaction partners, **which is sort of** which is similar to some sort of valency.

Therefore, you may; I mean without going in to any greater detail may realize, that hydrogen bond is somewhere in between a permanent dipole permanent dipole type Van Der Waals force, and an polar chemical bond. So, this is just for your information cum learning I would say, because hydrogen bonds are also very important in many settings, but what we need to understand that they strictly do not fall in to the category of Van Der Waals forces.

So, to a large extent we will be dealing with polymers, we will be focusing on the induced dipole induced dipole type Van Der Waals forces, but it is important to note that the attractive interaction. So, the other thing to understand is all the three types of interactions, at least at the molecular level they are attractive in nature, between surfaces we will show that there can be situations, of course in air or vacuum even between two surfaces the Van Der Waals interaction is always attractive.

But in a presence of a third medium; primarily a liquid medium, we will show that a Van Der Waals - pure Van Der Waals interaction between two surfaces, so two surfaces in a third liquid; each one is completely a polar, so the entire component of surfaces energy is **Van Der Waals** the liquid is Van Der Waals liquid the surfaces are polar, but you still can have a situation where you can have a an effective repulsion which origins from Van Der Waals forces. But what is important to understand, that are the molecular level as well as the interaction between two surfaces, in air or vacuum Van Der Waals interaction is always attractive.

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So, the other important thing to understand, that between at the molecular level; between molecules the scaling is $1/r^6$. And for all the three types of forces, there can be some numerical pre factors which sort of the once the relative strength of the three types of forces. So, the scaling is; the relation between the separation distance remains as $1/r^6$, but depending on the precise nature you can have different settings, or you can have different numerical pre factor which takes care of strength of each of these forces.

So, with this much of amount of understanding, so let us to a quick recap. Other important thing is that these electro static forces; for example, before I move on I must have a quick mention about it.

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Electrostatic forces:-

↳ At least one of the surfaces carry charge, in that case it will ~~induce~~ ^{accumulate} a mirror charge (opposite charge), on the other surface, because of the presence of free or mobile ions in a liquid medium.

These mobile charges screen the surface charge by accumulating near the surface, having opposite charge.

These forces are often referred to as the double layer forces.

[Zeta Potential] Stern Layer. @ Bulk Condition of charge neutrality

Electric Double Layer.

Solid Surface

Liquid medium.

Free Ions are free to move.

Screened the Surface.

So, these electrostatic forces; the second type of forces that we talked, these electrostatic forces are operative when at least one of the surfaces carry charge, in that case it will induce a mirror charge or opposite charge on the other surface, because of the presence of free mobile ions in a liquid medium. Sort of, I would probably remove the word induce; **it will sort of** in that case it will accumulate mirror charge I would say liquid medium. So, what it is; I am just coming to it an example, so these mobile charges screen the surface charge by accumulating near the surface with opposite charge having. These forces are often referred to as the double layer forces.

So, what happens is, let us say you have a surface which is in contact with a liquid medium which has free ions, so both positive and negative ions are there. Let us say the surface is sort of positively charged, so what happens is? So, these ions are sort of, so first important thing is this liquid medium, so this free is what these ions are free to move and therefore, as a consequence that the ions are free to move or free to sort of orienteer position themselves. So, what happens is the surface as positive charge, so what will happen this negatively charged ions will sort of migrate close to the surface, and they will form a layer close to the surface.

So, if you now see the individual word; it sort of makes sense, so at least one of the surface carry charge. So, here is a solid surface which carry charge, and that will accumulator attract the mirror charges; that the negative charges. A layer of ions will

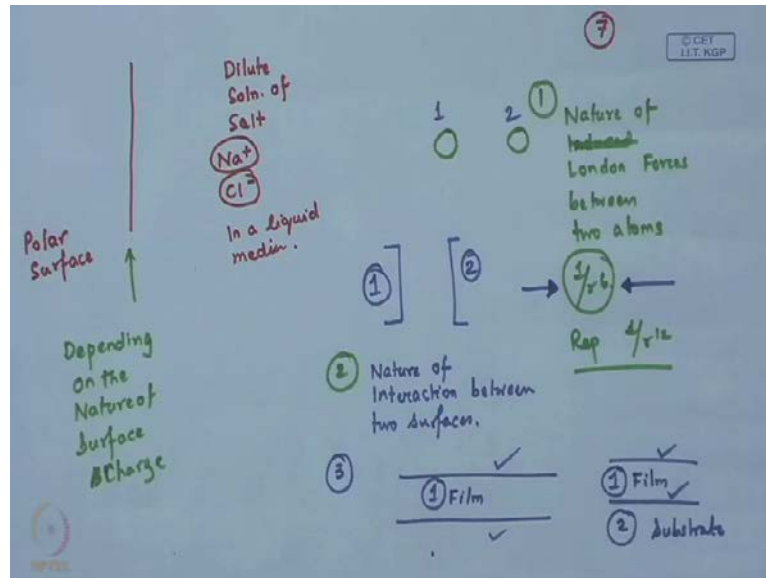
form along the in close proximity with the surface, which as the opposite charges on the other surface because of the presence. So, what is the source of these negatively recharged ions? The source of the negatively recharged ions is that there are free or mobile ions available in a in a liquid medium.

So, these mobile charges once they accumulate, they sort of screen the surface charge by accumulating near the surface, so what does screening in this context mean? It means, that now to the liquid the surface does not appear to be positively charge, but it appears as if the effectively the surface has a negative charge. So, what this layer of accumulated ions has done? It has sort of screened the actually surface charge, and what will further happen now? There will be a localized accumulation now of the positively charged ions closes to this, and then eventually at the bulk there will be a condition charge neutrality.

So, this whole structure close to the surface of the charge surface is known as or referred to as the electric double layer, there are certain critical concepts associated to an electric double layer, I think towards the later in end of the course we will talk about zeta potential stern layer and all these concepts. Most likely, towards the end of the course we will discuss, even otherwise you are welcome. Now, that you understand the basic structure of an electric double layer, you are encouraged to have a look at some of these things in the internet or any standard test book.

So, these type of forces also play a very important role, so let us say you have a layer of surface which is coated with sodium chloride; let us it is a solid coated surface which is in contact with water. So, sodium ions are sort of ions are dissolving, so it has an effective polarity or in any surface forget about this particular example. So, any surface which has a polarity, and is in contact with a polar liquid or which as ions, so let us say that a dilute solution of salt is in contact with a polar surface.

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So, you have a surface just withdraw that example, so you have a polar surface which is in contact with a dilute solution of let us say salt therefore, you have these ions which are feeling moving in the liquid medium. So, what is going to happen? Ideally, in this liquid medium these concentrations of the ions is uniformly distributed, but see close to the polar surface what is going to happen is depending on the nature of the surface charge. So, if it is a positive charge surface the chloride ions will accumulate close to the surface, if it is a negatively charge surface the sodium ions will accumulate towards the surface.

So, and it results to the formation of an electric double layer, so this results in some sort of an additional surface potential which is quantified in terms of the zeta potential, which can be physically measured in experiments using an instruments zeta meter. So, this gives you an idea about the strength of the electric double layer forces.

But, then coming back to our system which is the polymers, so now even if you have a scenario that you have a polymer thin film, over which let us say salt solution is flowing. Since, the polymer surface does not have any polarity, so there will be no electric double layer formation, and because of the fact that there is no driving force for either of the ions either positively charged or negatively charged to sort of migrate; preferentially migrate towards the surface.

Therefore, we understand that electro static forces can be very important in many settings, but for a polymer thin film particularly what we are talking about; polymer thin film in air or because most of the patterning's we have turn. We have talk about essentially a layer of polymer thin film, and then we have patterned it with a stamp, master or whatever, these forces are rather in significant.

Therefore, we need to focus most on the Van Der Waals forces or the London forces; the desperation forces, because in polymer they are charged neutral; there is no permanent dipole, but these forces interaction forces are always going to be present there. Off course, the additional thing that one should not neglect, and we have talked about it a little bit in terms when we are discussing about nano imprint lithography, if you remember we talk about the velocity profile and the stress accumulation in nano imprint lithography.

So, these are all attributed to the longer chain molecules, which are the polymer molecules are long chine molecules the, even the linear chine molecules or long chain. Of course, they can be additional complex it is a rising because of the fact, because of cross linking we have talked a great deal about Sylgard 184 or Elastomer which are cross linkable, so there are additional interaction that originate. So, now once a matrix is cross links, so it is now physically interconnected; the molecules are physically interconnected, and depending on the rhea logy of the system or the visco elasticity this cross link matrix can be flexible, can be rigid, so you can have room temperature elasticity and all these effects.

But the next thing that we are going to talk about is the spontaneous in stability in a liquid or visco elastic polymer thin film, the most important thing that is going to sort of come up; or the most important interaction force that is going to come up is the Van Der Waals forces or the dispersion forces. So therefore, we will be focusing in our subsequent class on this specific aspect, that is induce dipole induce dipole type interaction.

So, this is how we plane to sort of rigid the story, so we first talk about or identify about the nature of induce, or the nature of London forces between two atoms, which we know is $1/r^6$, the attractive part and also there is a repulsive part which is $1/r^{12}$, then so this is the first thing which we already understand.

Then the next thing that we take up in the next lecture itself is the nature of interaction between two surfaces, subsequently once we understand the nature of interaction between two surfaces, so first we talk about the interaction of two blocks let us say of one and two. So, let us say these are two molecules of one and two, then we talk about the interaction between two blocks of one and two, and then eventually we will talk about this type of interaction.

So, we have a film of material one which can be a self standing film, so here also we have two surface; the two film you are interfaces what is the nature of interaction between them, or a more generic case we have already talk about a spin coated or a dip coated thin film. So, you have a film of liquid layer one which is coated on a substrate.

So, how the interaction between this and this interface governs the evaluation dynamics or the stability of a system? These are some of the things, which we are going to look up in the subsequent couple of lectures, and the standing basics point; the fundamental concept which is based on the induce dipole induce dipole interaction between molecules. Thank you.