Introduction to Soft Matter
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Lecture 16
Introduction to Soft Matter

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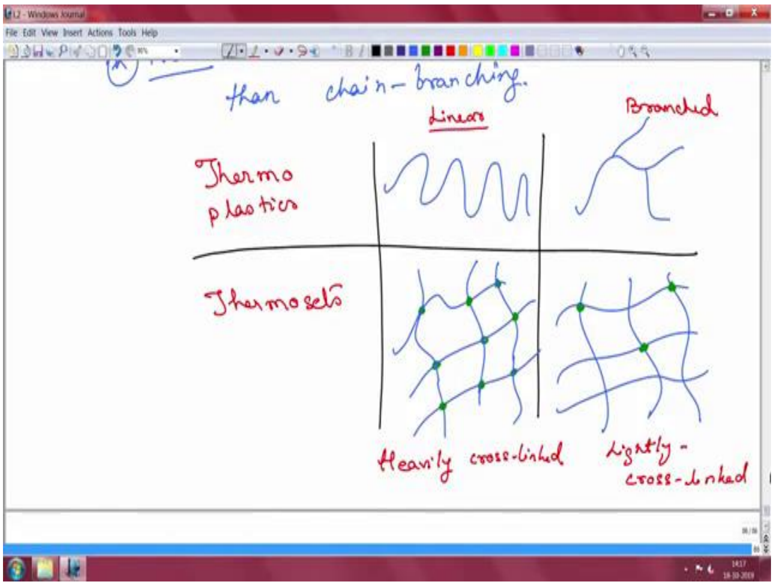

So, welcome back to another lecture on Introduction to soft matter. And what we are doing last time is we were looking at polymers and we had started taking a look at the molecular perspective for these materials. So, let us continue with this that perspective. Let us look at a couple of more important issues. Now polymers as we discussed yesterday, they are made of macromolecule so, it is made up of a large segment of many atoms which are being put together, let us say in a linear fashion. If that is the case, then you would expect, if you have taken a very simple knife geometrical approach to it, you would think that the entire polymer molecule would be the number of monomers multiplied by the size of the individual monomer but that does not occur.

And we also discuss partly why that does not occur. That is because at the molecular scale, you have atoms exhibiting thermal Brownian motion, thermal motion, and that would make them rotate in different ways. And that is why the actual molecule looks like a convoluted, it looks like a spaghetti, or a ball of wool that you use that you might have seen at home maybe. So, let us just continue with that discussion and let us try to be a little bit more quantitative in that respect. So we had a very qualitative discussion of that. So, let us keep on with the molecular viewpoint and we said that the polymers are these flexible molecules.

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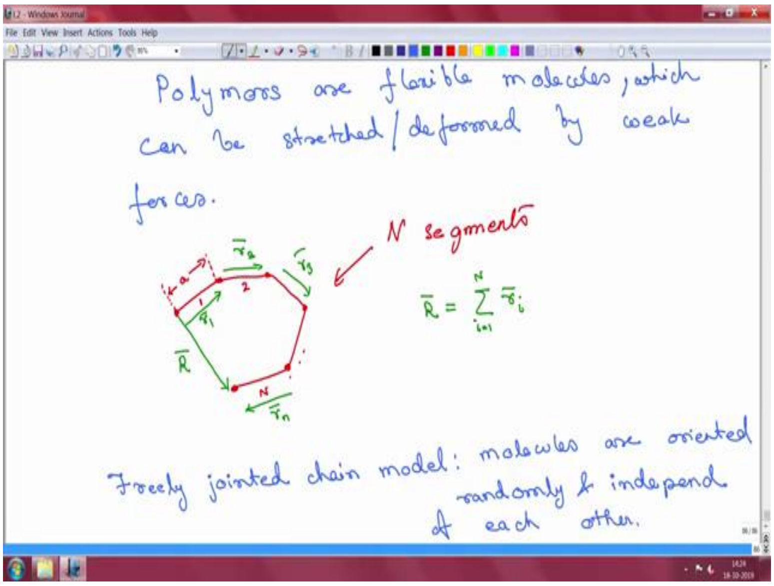

Polymers are flexible molecules, which can be stretched / deformed by weak forces.

N segments

$$\bar{R} = \sum_{i=1}^{N} \bar{r}_i$$

Freely jointed chain model: molecules are oriented randomly & independ of each other.

So, polymers are flexible molecules which can be stretched or even deformed by weak forces. When we say weak it is obviously in a relative perspective. And what do you mean is, a force which is of the order of kt. So, thermal motion is very, requires a very small amount of force something of that sort. So, let us consider a situation where you have a polymer molecule and let us say it (compete) consists of n segments. So let us say this is some atom join to another one, join to another one, join to another one. And so there are equal segments so let us draw it a little bit carefully, approximate equally.

So let us say there are these n segments, so we have n segments of this Polymer. So this polymer molecule that I am drawing is made up of n segments. And each of this segment, let us say is of length a. So, this is your segment 1, this is your segment 2 and so on, till you reach the nth segment. And the question is, you might, so what we want to understand is what is the size of this molecule? So let us associate a vector with each of these, so let us say this first chain length segment is given by a vector r 1. Similarly, the second one is given by a vector r 2 and third one is given r 3, and certainly the last one r n. And then this final closure, so this was the beginning position, this is the last. So the distance between the two will indicate by let us say capital R.

So from vector algebra, you can say that R bar, this vector R here is the sum of all the small we are summing over n. Now we will assume particular type of model, so now we have to figure out what this R bar is, but how do we do that? So we will take a case or a particular approach to this which is a particular model which is also known as the freely jointed. So this is a freely jointed chain model, so this is a freely jointed chain model. And how are these different bounce rotating. So, let us say in the case of polyethylene, you have the carbon-carbon single bonds and they are rotating because you have the thermal energy which is allowing these molecules to rotate. And how it rotates keeping that 109 degree in that case, is it can rotate in any of the degrees any of the way, except for it cannot just collapse back on itself.

So, there is one small area which is not allowed for it to visit but anywhere else, it can just keep on rotating. So here what we will do is this static part we will forget about that. I will assume that this Theta angle around which these individual ones are oriented, that is a random number independent of each other, so we will say that molecules are oriented randomly, and independent of each other, add one more page here.

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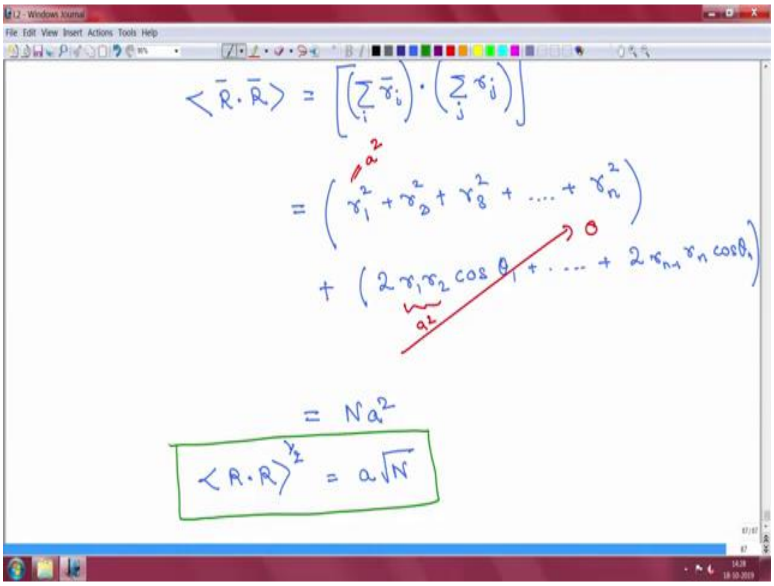


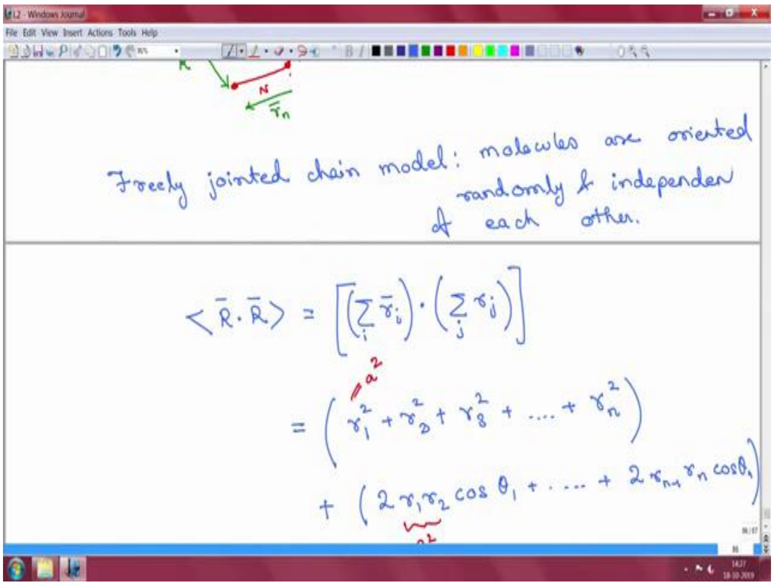
$$\langle \bar{R}\cdot\bar{R}\rangle = \left[\left(\sum_i \bar{r}_i\right)\cdot\left(\sum_j \bar{r}_j\right)\right]$$

$$= \left(\overset{a^2}{r_1^2} + r_2^2 + r_3^2 + \dots + r_n^2\right)$$

$$+ \left(2\underbrace{r_1 r_2}_{a^2}\cos\theta_1 + \dots + 2 r_{n-1} r_n \cos\theta_1\right) \rightarrow 0$$

$$= N a^2$$

$$\boxed{\langle R\cdot R\rangle^{1/2} = a\sqrt{N}}$$



Freely jointed chain model: molecules are oriented randomly & independent of each other.

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$$= \left(\overset{a^2}{r_1^2} + r_2^2 + r_3^2 + \dots + r_n^2\right)$$

$$+ \left(2\underbrace{r_1 r_2}_{a^2}\cos\theta_1 + \dots + 2 r_{n-1} r_n \cos\theta_1\right)$$

So, let us try to calculate what this would be. So, let us evaluate this particular vector what will this vector be? Now, this vector is basically to write it is summation of RI vectors dot producted with, I am trying to calculate the magnitude of r. So, how do we calculate the magnitude of any vector? You take a dot product with itself, take a square root so we are just doing that. So, here it goes from I, this is it j. So this if you open this up, what you will end up with r 1 square plus r 2 square, where these are the magnitudes of the individual vectors and so on. Then you have to sum up the nth vectors plus the other terms.

Maybe we will just do one quick thing, which is, we had said here that the size of each of these is a. So since we are talking about the magnitude of these vectors, we will just go ahead and replace them, so each of them is we will just write it here and then we will do the sum. So each of them is basically a square. So these different numbers are actually the same and they are all equal to a square. And then you have a set of other numbers which will, so this is a dot product, so you have the Theta term. So you will have this 2 r 1 r 2, then you have the Theta terms, Cos Theta 1 and then this will keep on going, and you will have all the various you have to sum up about the various Theta terms, all the various possible combinations of the Theta.

Now again, this quantity is a squared, so all Thetas are basically you have the same coefficient. So you are basically summing over all the cos Thetas possible. Now, we have already assumed that there the molecules are oriented randomly and independent of each other. Or this is the spelling is wrong, this is independent of each other. So all these different terms, this entire thing is sum over to yeild 0, because these thetas are all random numbers and they are distributed equally between 0 and 2 Pi.

So finally, you are just left with N times a squared. So your length, which is going to be half of this is basically a times root over of N. So, this is a very very important formula because it gives you the approximate length of a polymer. Obviously, this is subject to the model that we have taken the simple jointed, there are other models and they will again yield something very similar. So, this number will change a little bit, but we have the order of root over n.

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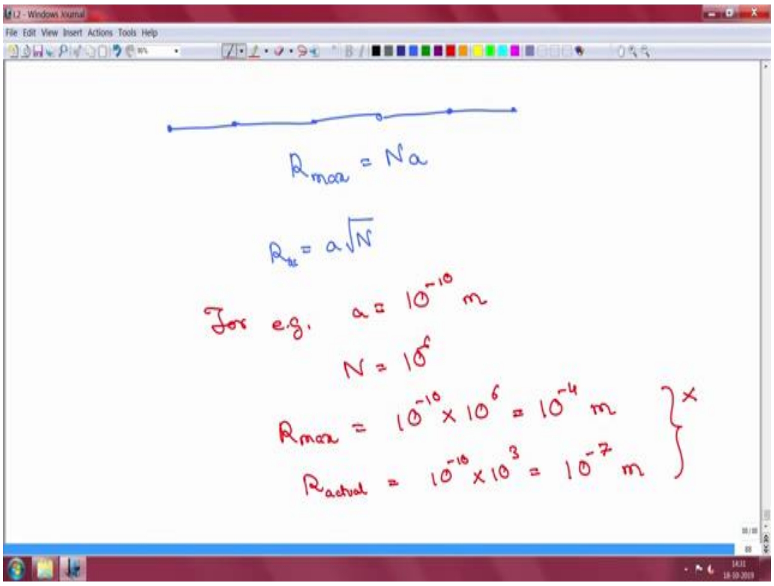

$R_{max} = Na$

$R_{ac} = a\sqrt{N}$

For e.g. $a = 10^{-10}$ m

$N = 10^{6}$

$R_{max} = 10^{-10} \times 10^{6} = 10^{-4}$ m

$R_{actual} = 10^{-10} \times 10^{3} = 10^{-7}$ m $\Big\} \times$

So I just draw a linear polymer like this, if you had all the polymer molecules laid out next to each other, and I am just drawing a simple schematic, then this R max in this case, the maximum R, R Max in this case would have been N times of a. In our case, what we just saw that the R is actually a times root over n actual a c. So you can see that this is actually going to lead to a lot of difference.

So if you had, if you take for example, an a value of let us say Armstrong 10 to the power minus 10 meters, and n equal to let us say 10 to the power 6, then your R max here is 10 to the minus 10 power 6 is equal to 10 to the minus 4 meters whereas your R actual is actually 10 to the minus 7. So, there is a big difference right here, and this you almost never find and this is what is happens in reality. So, this number as I said, you can use different models, but you will get approximately the same number in all these different cases.

So, we had quite a bit of discussion on polymers, I said in the beginning itself, we were discussing soft materials. So, we are trying to enumerate different types of soft materials because we want to understand how the soft materials behave or what are the different types how they differ from your normal liquids and crystalline solids so, that is why we took this example of polymers. So, let us look at a couple of more examples before we gather a good molecular level understanding of these materials.

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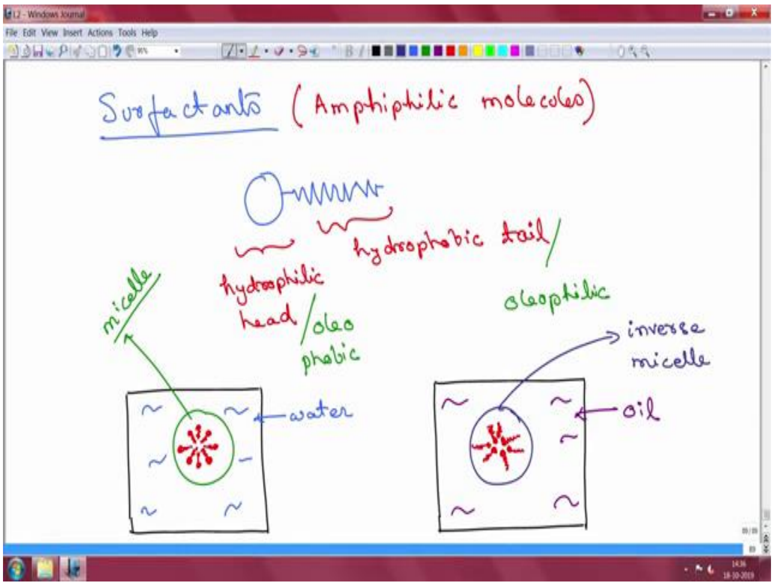

So maybe we will also take a look at something called surfactants. So, surfactants are also what are called amphiphilic molecules, because they have a very interesting structure. So, they have hydrophilic head and then this compound is such that so this is usually represented in this kind of a manner where these are amphiphilic molecules and they can dissolve both in oil and water. And what they have is they will have hydrophilic head and hydrophobic tail.

And interestingly, the part of that is hydrophilic is actually also oleophobic and vice versa. So the hydrophobic tail becomes an oleophilic and oleo here means oil. So, basically this part the hydrophobic head. So, why do we call it hydrophobic? Because it loves water. So, when you put it in water this part will have a tendency to dissolve whereas the hydrophobic tail would not have a tendency to do that. So, the hydrophilic head is also oleophobic. So if you put it in oil, this attitude of the molecule towards the solvent flips.

So how does this kind of a molecule actually end up dissolving in water? So the way it happens is so let us maybe make a box, let us say we have this. Here we have water, this draw cartoon, so this is water and the way these molecules will dissolve is the hydrophobic head has no problems with water, but the hydrophilic head does not have a problem with water, but the hydrophobic tail does.

So, the tail must not see water molecule. So, the way it happens is because these end up forming what are called mycelia where the hydrophobic heads are all directed outwards. And these mycelia form only when you reach a certain critical concentration of the surfactants. And what will happen is once you have that critical concentration, the hydrophobic heads philic heads will all arrange themselves outward and the end all the hydro, the tails will be inwards.

So this configuration is also called mycelia, and this is how these surfactant molecules, which amphiphilic in nature, they can actually end up dissolving in water, even though they have a hydrophobic tail. If you had oil, what would happen? So let us take this, so this is oil, so for oil, the hydro phobic tail becomes oleophilic. So, this arrangement just reverses, so you have and this is also called an inverse mycelia so this is how they can dissolve in oil phase. Now, let us say so by the way these molecules, so these are what I have tried to draw here, they are spherical mycelia, but mycelia can occur in other forms as well.

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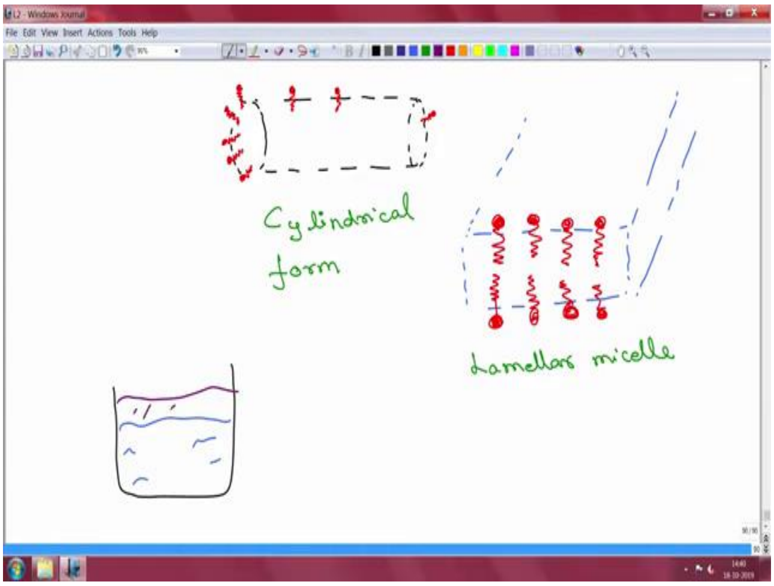

They do not need to be these small spherical balls. They can also be, you can have a mycelia arrangement where it is in the form of a cylinder so you have, so I am not going to draw all the possible locations. I am just drawing it for your illustration here so this is a cylindrical mycelia. But perhaps the one you might be acquainted with even more is what is called a lipid bilayer, where they can actually form for very, very long distances so they can extend.

So you can actually have in a lamellar mycelia, this structure extends in the form of a 2D film. And this film, it can just become extremely large. So you have so obviously I am not drawing the other positions, but this entire thing can become a very very large lamellar so these are also called. So, surfactants are also, they do fall under the category of colloids and as we had, discussed remember maybe I just quickly try to find it in the definition of colloids.

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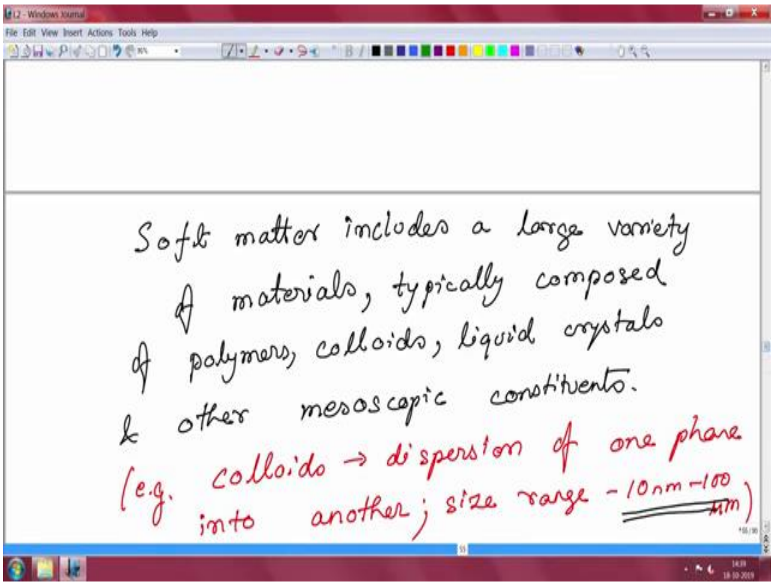
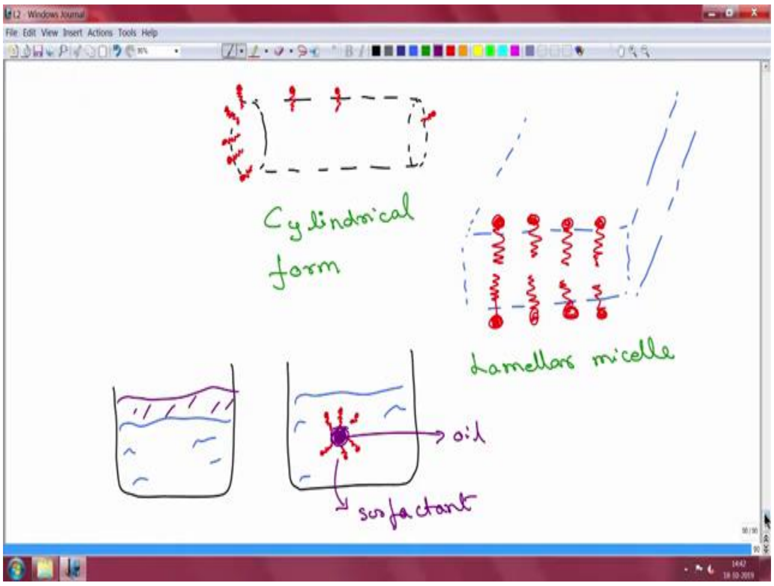


Soft matter includes a large variety of materials, typically composed of polymers, colloids, liquid crystals & other mesoscopic constituents.

(e.g. colloids → dispersion of one phase into another; size range - 10nm - 100 μm)



So, when we had discussed the colloids we had said that the size range of for this is usually between 10 nanometres to 100 microns or between 1 nanometre to 100 microns and we had said that the size range applies to only one particular dimension, and not to the others. And the reason that happens is because something like a lamellar mycelia would be classified as a colloid even though this dimension can extend for maybe even 4 millimetres and even larger. So, it need not be constrained in the planar direction along the direction of the film, it need not be that, size need not be constraint, but it will still be a colloid.

So, these surfactants are extremely important in dispersion technology and they lead to formation of, they can easily help you make complex fluids. How would they help you do that? Let us take one example here perhaps, so let us say you have water and if you pour oil onto this, oil will form a separate layer and it will not be miscible inside the water. But you can help yourself if you have surfactants because what the surfactants can do, so this is water.

So, now you add surfactants along with oil and what can happen is you have many of the surfactant molecules where hydrophilic head is directed towards outside and here where all these hydrophilic tails are meeting, here you can have oil, because that part you have not really worried about so this could be oil. Obviously I am just drawing a schematic so these are not to scale or anything, so this is how you can disperse. So, this is your oil and this is your surfactant. And with this you can help the situation and you can actually make your oil disperse in that. So, you can create complex fluid systems, which are made of many different type of subsystems or sub materials.

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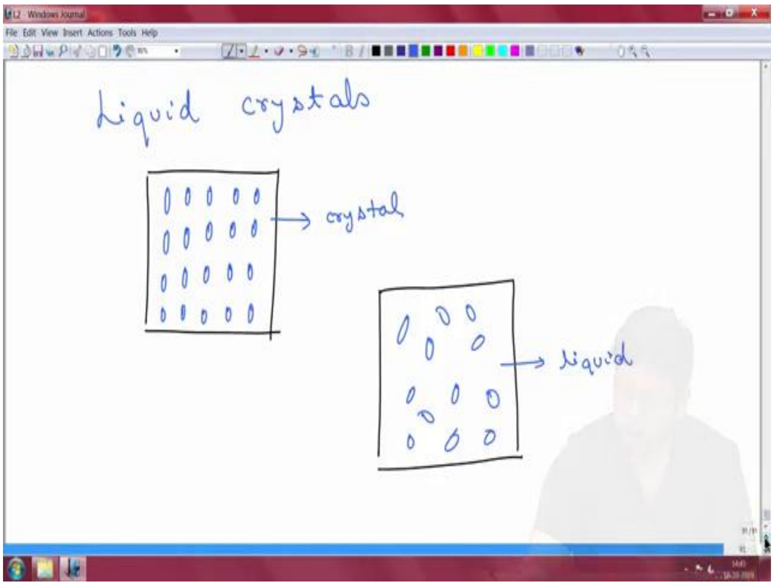

So, what we want to do one more so, while we are talking about example, so we talked about polymers, we looked at surfactants very briefly, and this one more last thing that I just briefly talk about, and those are liquid crystals because that is also another large family of materials that belong to this important category of soft materials. So now, when we had discussed this question of hard versus soft, we had said the hard condensed matter are basically things materials which are crystalline in nature.

And what does crystalline nature mean? It means that at the molecular at the atomic scale, the atoms are distributed in a very ordered fashion. So, they may perhaps they are in the form of a lattice and those lattice structures are very well placed and are in a periodic fashion so that gives rise to metals. Whereas, when you compare water, the water molecules are not placed in any lattice form, they are just occupying whatever space is available to them.

So, in a in a sort of opposite to that of crystalline metals, liquids simple liquids have a total disorder at the atomic or the molecular scale. So, there are materials which can actually lie somewhere in between, between that of a crystalline solid and that of a total disordered state. So for example, we will draw so let us say if you had if you wanted to make a crystal, you would place, let us say, you have some molecules that you are going to place and then you are going to place them in proper lattice structures so, this is an example of a pistol.

And a liquid Crystal basically, probably hopefully gives you an idea that it has the properties of both liquids and crystals. So, the order at the atomic or the molecular scale is somewhere in between that of perfectly crystalline system and a disordered system like water. So, you can have, so if this was for a liquid, there would be not be any positional order and no orientational order. So, this is a liquid type of system, so this is a crystalline system because you are positional and orientational order in this case because it deliberately drew things which are anisotropic in nature so the system is composed of these ellipses.

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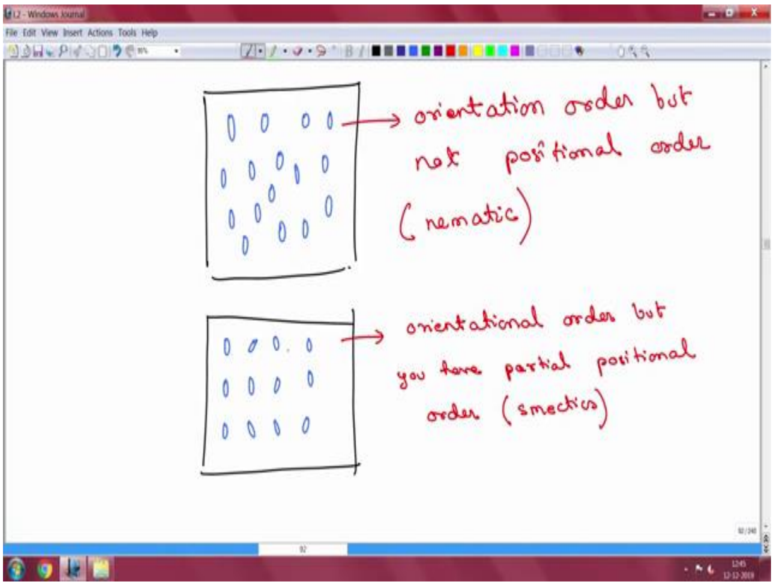
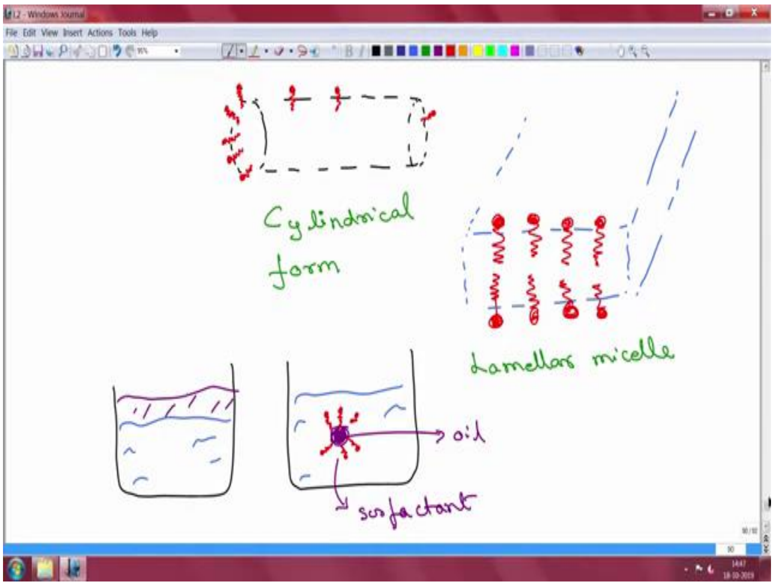


orientation order but not positional order (nematic)

orientational order but you have partial positional order (smectics)



Now, you can have something called a pneumatic liquid crystal where these are distributed such that they have orientational order but not necessarily positional order. So, let us say the ellipses are all pointed in a single direction, but they are not placed in any particular order, placement order is not there. So, this is a system which has orientational order, but not positional order, so this is what is also called a pneumatic. And there is another class of materials where you have orientational order. So that brings us to one more class of liquid crystals, where you have orientational order, but you have partial positional order also.

And although in this diagram it seems as if the positional order is there in large in a significant quantity. So, this class of materials is also called smectics. And although here in the drawing it would seem as if the positional order is significant. This is just a cross sectional view so, usually the partial positional order comes from slight positional order in one of the dimensions, but in the other two dimensions, the positional order is not there it is random, the distribution is random. So, this is a cross section in a dimension where the partial positional order is there, but let us just remember that in the other two dimensions it is not there.

So, what are we doing here, initially we had taken quantum mechanics perspective to everything where we disregarded the molecular scale nature of the soft material. And we discussed how there are various tests that you can do in a laboratory which can distinguish the behaviour of a viscoelastic material versus that of a perfect solid or perfect liquid. And that difference comes purely from an observational perspective, where you observe the response, the response observation. And then later on we said, we want to understand from our molecule perspective also why they are different.

So, once you start observe something from a molecular perspective, it actually becomes important to know what you want to discuss because every material would have its own molecular structure, which gives it viscoelasticity or a soft material characteristic. So, we looked at so you cannot have, it is very difficult to have a very generic microscopic perspective for soft materials. So, you have to look at individual systems so that is why we started off with one of the largest set of soft materials that we encounter, because they are heavily in use in the industry so we produce them in very large numbers and those are polymers.

And then along with that, we today we looked at surfactants and we also looked at liquid crystals. Very briefly we discussed liquid crystals, we are not going to go into too much depth here for this. But polymers we encountered in a little bit more depth because at a later point, we will go into the laboratory and we will also perform some experiments with those polymers so we want to understand how those polymers behave and what makes them so special, so for today, we will stop here.