Colloids and Surfaces Prof. Basavaraj Madivala Gurappa Department of Chemical Engineering Indian Institute of Technology-Madras

Lecture-04 Source, Synthesis and Characterisation of Colloids

(Refer Slide Time: 00:14)

So far	 NPTEL
 Definition of colloids Motivation to study colloids Definition of colloidal dispersions Classification of Colloids Stability of Colloids 	

Ok, so this is a class 3, so this is what we have done so far ok. We looked at the definition of colloids, motivations to study them, definition of colloid dispersions, classification and the stability ok.

(Refer Slide Time: 00:33)



So, what we will do in today's lecture is hopefully 2 things one is to look at source of colloidal particles. That is to tell you a little bit about where do they come from you know and then followed by that we will talk a little bit about a characterization of colloidal dispersions, I have a long list of things. So, I will try to introduce each of these terms to begin with and then I will tell you a little bit about you know the definition.

And what are the typical methods that people use for finding these you know physical and chemical properties of colloids ok. And most of the content that I am going to do is taken from Coulson and Richardson's chemical engineering series, ok. That is the particulate systems and particle technology chapter 13, ok.

(Refer Slide Time: 01:23)



So, any thoughts about the source of, so where do the colloidal particles come from ok. The first topic, ok.

(Refer Slide Time: 01:45)



So, the answer for that would be I mean it could come from any process right there could be an industrial process, you know you could have may be things like say size reduction for example, you have larger particles and you are trying to break them into smaller sizes. In that process you know you could get particles which are again in this you know colloidal length scale right, you could you know.

That could happen through industrial processes which could also come from vehicle emissions you know the lot of stuff that comes out you know from the vehicles. I give an example of burning of candles right the other lecture ok. So, it could come from burning of things like that I can add one more to the list d you could have from natural resources right, ok. Like I was talking about this bacteria, virus, ok or you know the latex, rubber latex and things like that right. So, you could also have you know particles from any source ok.

(Refer Slide Time: 02:55)



But however as I showed right the particles that come when you burn candle, I had shown a picture in which I said that you know they are of course each particle is colloidal length scale. But then you know there were very complex right ok, the particles that are produced in any of these processes are they are they have a very complex shape and structure ok right.

(Refer Slide Time: 03:27)



So, that is because their formation occurs in not so well controlled environment ok. Because when you burn you know candle right, so you have oxygen you have you know. So, essentially the environment around the candle burning process is not very well controlled, ok there could be fluctuations in temperature and stuff like that, right. That is what leads to the formation of such complex particles of different you know structure, sizes and shapes and things like that ok.

(Refer Slide Time: 04:09)



So, of course you know there is a lot of interest in studying such particles right because one could be interested in looking if you look at industrial processes right. So, one could be interested look at to assess the health hazard right. So, that you know one could be interested to

ask a question as to what will happen if there are fine particles that are producing an industrial process and then if we inhale them and things like that, right.

So, the particles that are produced by each of these processes are important, ok. There are people who were trying to look at health hazards of such things, people who are trying to look at fate and transport of aerosols. For example you know how do these particulate matter that are emitted because of you know vehicular emission you know how do they, how are they carried around you know how are they you know present in the environment stuff like that.

And of course people have also used particles that come from the sources as I was telling to design what are called super hydrophobic surfaces and so on and so forth, right. So, of course particles from such origin are important, there is a interest to look at these systems. But in colloid science what people are looking at are what are called as model particles, ok, what are mean by model particles, is that these are particles of well defined size, shape and surface properties, ok.

So, if you really want to investigate fundamentally a particular phenomena in colloidal science, what you do is, you go to these model particles which essentially are particles of well defined size, shape and surface properties, ok, so that is the need ok.



(Refer Slide Time: 06:08)

And again how do you get these particles, actually a lot of particles are commercially available you know you do not have to worry about synthesizing them. They are commercially available what you are given is an example of 4 different types of particles A and B, these are actually silica particles ok. And if you look at the again the length scale, they are you know, some 100 nanometer, so this is about 100 nanometer right, it is 100 nanometer.

So, if you look at these particles there may be about 30 nanometer in dimension and these are about 50 nanometer in dimension ok. They are kind of sold and by a commercial name called Ludox particles, you can buy them, they come in liters and liters not very expensive. And these two are examples of silica particles SiO_2 and this is a polystyrene ok and as you can see they are very homogeneous, uniform you know exactly similar size ok.

So, you can buy them and then design experiments to study whatever colloidal phenomena that you would like to ok. So, that is one source of you know a model particles which people have been using for several years to study in a lot of interesting phenomena and colloids.





Of course, you can synthesize them in the lab, ok, so these are some examples of synthesis from our lab. So, these are all you know synthesized by different people in the lab by well defined procedures are available in the literature, ok, this is not invented by us, so things are already existing. So, all that you have to do is follow these procedures and then know systematically and then you know control condition.

And you will be able to produce you know the particles of the spherical in shape or elliptical in shape these 2 right. So, the first set of particles, these are example of again silica particles which are produced by a technique called Stober synthesis, ok. Again, this is the name of the scientist who found this technique for making these particles.





Now, so this particular Stober synthesis it is a very simple reaction, it will involve water, some ammonia, ethyl alcohol and a reagent called TEOS, that is tetraethyl orthosilicate, ok that is a source of your Si in the particles ok. Ultimately I am going to get SiO₂ particles ok. And just by playing with the concentration of you know these reagents I can actually produce particles of very different sizes, ok.

And there is a lot of work that has gone in you know in the development of this synthesis procedure. It actually involves 2 reactions, a hydrolysis reaction and a condensation reactions, if you want to more details you can refer to the literature. But what people have done is they have come up with the correlations that I can use for designing particles of a particular size.

So, this Dp is a size of the particle that I am generating by this Stober synthesis. And you know I can control that by so it depends on the concentration of the water that I am using ok, that is these 2 right. And of course the parameters A and B which in turn depend on the concentration of the TEOS ammonia, you know and a few other things right. So, therefore if you want a particle of a particular size, what I can do is I can choose my reagents in appropriate proportions.

And then actually designed particles of different sizes ok, so that is about Stober synthesis. These elliptical particles that I was talking they are obtained by a again a very simple technique called force hydrolysis ok. Again it is a very simple chemical reaction which involves again iron salt you know water you know and a few other reagents, ok. And if you are interested again more you can read up literature.

So, I do not want you guys to know the procedure for synthesis but I just want to tell you that look there are things available in the literature which you can read up and then follow up. And then essentially make model colloids of your choice in the laboratory ok. And the last one is by a simple technique which anybody could do in the lab is called is nano precipitation ok.



(Refer Slide Time: 11:26)

It is a very simple process ok.

(Refer Slide Time: 11:29)



All that involves is that I take a solution ok and this solution contains it is the solution of a polymer, it could be polystyrene, it could be you know PMMA or you know PVA any polymer, ok it does not matter ok. And that is dissolved in a solvent, so that I get a homogeneous solution of this polymer in the solvent. Now what I do is I take this and I add a drop of that into another container which has another solvent, another fluid which is a non solvent for the polymer ok.

So, initially the polymer is dissolved in a what is called as a good solvent that means, this is all one in which the polymer dissolves completely, I am able to get a homogeneous solution. And I take that solution and added to into a fluid ok and the fluid is a non solvent for polystyrene, that means this polymer does not like to be in that solvent ok.

(Refer Slide Time: 12:41)



So, as soon as you do that and then if you stir it, you essentially have generation of spherical particles ok. That is because the polymer does not want to be in water and it precipitates out and it precipitates out as spherical particles ok. Again there is lot of literature can read up a little bit about it ok.





So, what we are done in our lab is to use this polystyrene waste ok, this is what is called as EPS expanded polystyrene that comes as a packing material, right. For a lot of electronics that you buy, ok you can take that and you can dissolve that into solvent such as THF tetrahydrofuran. Acetone, Lutidine does not matter any solvent in which the polymer dissolves, you do that, ok you get a homogeneous solution and simply add that to water.

And you can actually precipitate these particles, ok and I can control the of course I cannot make particles of single size. As you can see, there are different sizes ok there are ways by which I can control that as well. But I can play with the polymer concentration ok, I can play with the amount of water that I am using for precipitation and I can play with the mixing speed right. So, what has done here is when I added I am mixing it rigorously right I can you know, play with the mixing speed. And thereby I can actually control you know the size of the part that I am able to generate ok.

(Refer Slide Time: 14:21)



So, this is again some you know information about you know the source of particles where do we get them from you know and how to synthesize in the lab right. Following that, we will move onto defining or characterizing colloidal dispersion ok. So, now the moment I have a colloidal dispersion ok, that is dispersion of these particles in a fluid right. Now I may have to worry about several different physical, chemical or physicochemical properties of both the particles as well as the dispersion right.

So, if you talk about the particles themselves ok one may be interested to know what is the size of the particle, ok, what is it is, shape, right And of course the density of the particle is important you know it is a useful quantity that you should know for several different things as we will see little later ok.

(Refer Slide Time: 15:36)



Specific surface area, ok which is essentially defined as the surface area of the particle divided by mass of the particle, right. That is your ok specific surface area ok or if you want to call it as surface area you know specific or something like that ok. So, that is the surface area of the particle divided by the mass of the particle and it typically will have units of meter square per kg or you know meter square per gram right ok.

And this quantity is actually useful if people are trying to use colloidal particles for adsorption studies and things like that right where the surface area becomes important ok. So, one may also be interested to look at the properties of the dispersion itself ok. So, for example one maybe interested in look at the density of the dispersion ok. One could also be interested look at what is called as a volume fraction of particles in the dispersion right, ok which is defined as phi.

Typically people refer to it as phi ok is volume of particles in the dispersion divided by the total volume of the dispersion right ok, that is how it is defined, ok. The lower this number is that means the concentration of particles in your dispersion is smaller ok and higher this number is the concentration of the particles in your dispersion is higher, right.

(Refer Slide Time: 17:30)



Now have you heard of this term grafting density, somebody heard of this term no, ok. If you look at the images that I showed of these particles, right, ok. These are all solid particles right. In some cases, people work with particles which looks something like this ok. This is your solid particle ok and on the surface they can put some long chain molecules ok. These long chain molecules are can be put by 2 different ways one is by doing a chemical reaction.

If I know what is the surface chemistry of the particle, if I know what is the surface of the particle is made up of, I can take a long chain molecule, I can design a reaction. So that these chains kind of get attached onto the surface ok there are you know ways of doing that, ok. Or what I can do is I can have a particle a solid particle and I can add in some long chain molecules which can physically adsorb you know it is not a chemical reaction, ok.

However there is a physical interaction maybe you could think about maybe an attraction or you know something like that. Because of which you will invariably have particles which have some molecules on the surface, ok. When you have cases like that, that means when you have a chemical modification to the surface to give no chemical grafting, ok or a physical grafting which is more because of the adsorption of you know some molecules on the surface.

You can actually define what is called as a grafting density which essentially is defined as the number of molecules of these number of molecules that you have put on the surface divided by

the surface area ok. This is number of molecules ok maybe per particle, that means if I have a particle ok and if I say that look you know I have put in I do not know some 10 chains ok. And if I say that you know the particle surface area is like say for example say 100 micro meter square ok this is example.

Then you grafting density is going to be 10 divided by 100 micro meter square right. So, typically this will have units of you know some per you know micro meter square or meter square or something like that, right. So, that is your grafting density, we will tell you a little bit about why this you know chemical grafting or physical adsorption is important as we go along.

But at this point what is important is that there are particles which may have some long chain molecules on the surface and one would be interested to know what is the number of molecules on the surface of these particles. And that is characterized by a quantity which is what is called as a grafting density ok.





Now that I have mentioned what is grafting density, you should be able to guess what is surface charge density right, what do you mean by any thoughts, surface charge density. So, the surface charge density as the name itself says become important if you have particles which have charges right, I could have a negatively charged particle you know or I could have a positively charged particle ok.

If I know the number of charges on the particle surface ok, typically surface charge density is will have units of Coulumb per meter square right. And that you know the so this essentially comes from the total charge on the particle surface, ok. If I have like say 100 like say charges for example say that you know I have a particle surface where my surface group COO - ok.

If you have 100 such groups, ok, then the charge that is going to be on the particle surface is going to be 100 times the charge of the electron, right. That is your total charge on the particle surface divided by again the surface area of the particle will tell you what is the surface charge density, ok.

(Refer Slide Time: 23:12)



So, before we talk a little bit about you know what is surface charge density, what I will do is I will tell you a little bit about the origin of surface charge. So, where do this charge on the particle surface come from ok. There are different mechanisms that by which the particles can get as charged. One is by what is called as dissociation of charged or they say dissociation of surface groups.

So, what I mean by this is that see the synthesis chemistry right you know the people who do colloidal particle synthesis. The chemistry is so advanced that you know you can make particles with well defined charged groups on the surface you know what I can do is. If I may ask

somebody they will be able to give me a polystyrene particle which has COOH groups on the surface.

They will be able to give me polystyrene particles with maybe SO_3H group on the surface ok. Now, what happens when you have such particles in water, the moment I put such particles in water, what will happen is. These, the groups that you have it dissociate and it will leave out H+ ions in solution ok. So, therefore that happens for all the groups that are there on the surface ultimately you will end up with a particle that has a charge.

Therefore the dissociation of surface groups is one of the mechanisms by which the particles can acquire charge, ok that is one mechanism.

(Refer Slide Time: 25:13)



Now, the second mechanism that you can think of one of the simplest ways is dissociation of surface group right. Any other examples that you can think of or any other means by which the particles can get charged. Polarization then you are bringing what is it, it is a polar molecule you are saying that the particles themselves are made up of something that is polar in nature. See, when we talk about charge right, you are talking about the charge on the surface, right.

So, I mean polarization of course will lead to you know the regions where there is more charge, regions where they are less charged ok. Typically we talk about something like that when it

comes to molecules right. When it comes to particles you know itself you know, I do not think people think about this polarization as a. So, what people can do is there are cases by which, so this is you know shifting of electron crowd's right.

But there are cases where I can of course polarize the particle but if I put them in electric field and things like that, you can do that, ok. But you know in pure solutions, there are other mechanisms by which the particles can acquire charge, ok. So, the second example I am going to give you is by if I have say particles right. Now say these are not functionalized particles, they are homogeneously smooth right.

Then what you do is I can add different things to this fluid right, I have a colloidal dispersion ok. I can add a charged polymer ok or I can add a charged surfactant or I could add in some reagents which have some positive or negative ions, ok. So, what happens is in such a case all these things that I have added, ok they can go and adsorb onto the particle surface. And if I have you know charged polymer, so charged polymer I am going to represent it something like this, it is a long chain molecule.

But it may have some surface groups, right because it is a charged things, it has charges. Therefore I can invariably end up with a particle that has adsorbed macromolecules, adsorbed poly electrolytes which can give rise to charge on the particle. Similarly I could have a case where I have a particle and a surfactant that I add you know it can have a charge groups you know either positive or negative ok.

Thereby the particles can acquire charge because of either the adsorption of polymers charged polymers or adsorption of surfactant or adsorption of charged ions itself ok. There could be a physisorption or chemisorption adsorption of charges onto the particle surface ok. And ions onto the particle surface and that could lead to the charges on the particle surface, ok. So, therefore people think about these 4 different mechanisms by which the particles can acquire charge. And once you are dealing with charged particles in a fluid, therefore it makes sense to characterize them for surface charge density ok.

(Refer Slide Time: 29:12)



So, I have some examples listed here again whatever I wrote up in a schematic form, this is example where you know you have a group which is $SO_3 OSO_3$ - ok, that gives negative charge. And you have a NH2 NH + group here right that gives a positive charge on the particle surface. This is a case where there is adsorption of you know H + or OH - ions which can make the particle positive or negatively charged ok.

Or the surfactant molecules or adsorb or the charge polymers that adsorb ok. So, you can you know think about these different ways by which the particles can acquire a charge ok.



(Refer Slide Time: 30:04)

What can you say about this quantity, surface heterogeneity, have you thought of this, surface heterogeneity, some other. So, she says there is some of the surface or the particles, some other ok, so she is saying that look I have a particle ok. And she says that some of the surface you know may have positive charges ok, some of the surface may have negative charges ok, yeah. So, this is an example of a surface heterogeneity but in this case this is an example of what is called as a surface charge heterogeneity right.

So, therefore surface heterogeneity can be of 2 types, one is physical surface heterogeneity or it could be chemical surface heterogeneity, ok. The physical surface heterogeneity refers to cases where I may not have a perfectly smooth surface, I could have a particle where the things are rough ok, the surface is not atomically smooth ok. It has some undulations in the surface, there could be hills and valleys, right.

And there is an example where you have a physical heterogeneity or you could have a case like this where I have patches on the particle surface where things are positively charged. And patches were negatively charged or you could also have a case where I can have a patch which is hydrophilic, I could have a patch which is hydrophobic right, these are examples of cases where you can think about a chemical heterogeneity and one also needs to characterize them for this ok.

So, this is you know the last point is a bit more complex to characterize such things. Of course there are indications in the literature as to how do we characterize such things especially the chemical heterogeneity. The physical heterogeneity, the surface roughness you know how to do it, ok but however the chemical heterogeneity is still you know something that people are still trying to study, ok, yeah right yeah, yeah maybe I will talk a little bit about that maybe in the next class ok.

Yeah you can think about them as so what he is trying to talk about is that look I can have a particle ok where some part of the surface has some chemistry ok and other part has some other chemistry ok. Of course that will come into case where you have a broadly right it can say that you know this is a particle which has a surface heterogeneity, in this case it is a chemical heterogeneity, right.

So, yeah, you can think about particles like that as well. So, any questions so far all these terms are they clear. The particle size, shape, density, specific surface area, grafting density, charge density and heterogeneity.

(Refer Slide Time: 33:59)



Now let us so I would not spend a lot of time on this but maybe one class or maybe one and a half class ok. So, first characterizing particles for size and shape ok, so how do we do that. So, I somebody has given me a colloidal dispersion ok and then they will ask you to find out what is the size of the particle or shape of the particle that you have in the dispersion ok, what do we do, what is that.

She says dynamic light scattering ok, microscopy techniques anything else microscopy technique, dynamic light scattering technique, anything else ok. There are also techniques called static light scattering right ok. Again in microscopy you have optical microscopy also electron microscopy, right. Again electron microscopy you have scanning electron microscopy and transmission electron microscopy right.

But what technique that you use for measuring the particle size ok, depends and if you have any a priori knowledge about a typical sizing that you may have in the dispersion if you know that. Then you can choose one of the techniques appropriately ok, that means you know if the particles are a few microns in size then I would go for optical microscopy ok. If typically dynamic light scattering technique you know of course if you look at the manufacturer's specification they say you can measure sizes from 1 nanometer to you know close to about ok 8 to 10 micrometers, ok.

And if you look at static light scattering technique, you can measure sizes all the way from 10 nanometer to you know a few millimeters itself ok, very large size range. Of course electron microscopy is you know suited especially transmission electron microscopy suited when you are looking at particles which are nanometer length scale, right. So, we would not go into the details of all these techniques, I just want to mention that there are techniques available in the literature. And you should be able to characterize particles for size as well as shape, ok.

(Refer Slide Time: 37:23)



Now, so what you are looking at is a schematic where what can you say about this schematic. These are particles of they look very same size right, they look like the diameter of each of the particles that you have looks exactly the same, right.

(Refer Slide Time: 37:50)



And of course you can make such particles in the lab, ok. And so such particles where the particles are of identical size, they are refer to what is called as mono-disperse particles ok. That means, so all these particles are of exactly same size ok. But however I showed you this example of a nano precipitation right. If you looked at the microscopy image carefully these particles were of different sizes, right.

(Refer Slide Time: 38:34)



Of course, there are other you know examples, so this is done by a again a Stober synthesis which can give very uniform particles like this. However if your reactions are not controlled, if you are not careful in doing your synthesis you know what will happen is you will end up with the particles like this ok, where you have particles of very different sizes ok. When you have particles of this kind ok such a dispersions we can say that they are what are called as polydisperse.

That means you have particles of different sizes that exist in your dispersion ok. Now, if you look at the first case right mono-disperse, if I want to completely characterize you know the particles for shape, I can just say that look you know there are spherical particles and then there are of same size and that is my size ok, I can characterize them like that, ok. However when you have you know polydisperse samples you talk about what is called as a mean size ok.

And of course you also talk about what is called as a standard deviation right, how much does this mean size ok deviate, right.

(Refer Slide Time: 40:09)

The particles have been sorted into categories called classes with a narrow range of dimensions, each class is represented by the mid- point of the interval and the number of particles in each class n _i is known					
Class boundaries < d < (µm)	Class mark d, (µm)	Number of particles	Fraction of total number in class $f_{s,c}$	Total number with $d < d_p$ n_{E_p}	
0-0.1	0.05	7	0.018	7	
0.1-0.2	0.15	15	0.038	22	
0.2-0.3	0.25	18	0.045	40	
0.3-0.4	0.35	28	0.070	68	
0.4-0.5	0.45	32	0.080	100	
0.5-0.6	0.55	70	0.175	170	
0.6-0.7	0.65	65	0.163	235	
0.7-0.8	0.75	59	0.148	294	Ter
0.8-0.9	0.85	45	0.113	339	
0.9-1.0	0.95	38	0.095	377	
1.0-1.1	1.05	19	0.048	396	Mining Andrews
0.55 0.65 0.75 0.85 0.95 1.05 1.15		70 65 59 45 38 19 4	0.175 0.163 0.148 0.113 0.095 0.048 0.010	170 235 294 339 377 396 400	A BAL

So, again what people do is, you can get microscopy images like this ok, I have there are methods by which I can find out the size of each particles that I have in the sample ok. And typically you do that for a large population of particles 50 not enough, 100 not enough, 1000 not enough ok. So, when I say that I just want to go back to these techniques right, I said that people do dynamic light scattering and static light scattering and these microscopy techniques, right.

One of the a very important difference between the light scattering techniques and microscopy techniques is that when you do your size analysis you are focusing on a very small region of your

sample in microscopy ok. That means you look at this right this is an image from microscopy, right all you have is you know maybe 20, 30 particles, right. Of course I can play with a magnification I can get large number of particles in this window.

However when you do analysis people typically limit the number of particle that they analyze to maybe 50, 100, 200 something like that ok. However when you look at light scattering techniques, what happens is that you have a sample ok in which there are particles ok. And you have a beam of light ok that falls onto the sample ok. And then what you do is, it basically is when you say a beam of light has some dimension, right.

People talk about you know 0.1 millimeter beam and things like that ok. Now people talk about what is called as a scattering volume ok. So, in that volume even if I take a very dilute dispersion like say 0.001% particles. The number of particle that you are going to have is if you say like say silica particles of 50 nanometer diameters ok. You can roughly calculate and show that the number of particles could be of the order of 10 power 15 or 10 power 13 some numbers like that.

That means, so the number of the size that you obtain by light scattering it is an average of a large of size that you know the scattering that occurs because of a large number of particle that are in that volume ok. Therefore the sizes that one report from light scattering technique would are more representative of the sample that you dealing with than the techniques in which you use microscopy, ok.

So, that is ok, so we will come back to that, now if you have a way of you know finding out the size of the particles, then maybe I will stop here, ok. So, I think this is about time, so I just stop here, so what we will do is we will continue with the characterization in the next class, hopefully I will try and finish up the characterization by the next lecture itself, yeah, good, thanks.