Colloids and Surfaces
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Lecture-06
Characterisation of Colloidal Particles-II

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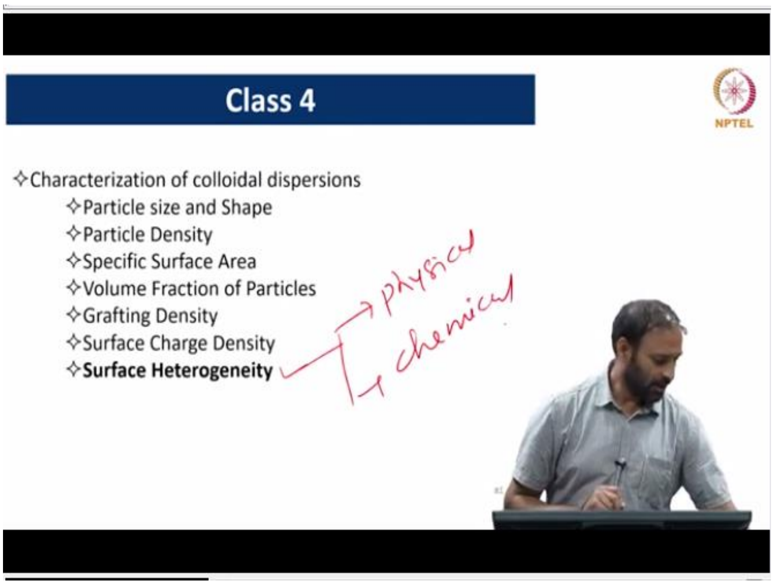

Class 4

- Characterization of colloidal dispersions
  - Particle size and Shape
  - Particle Density
  - Specific Surface Area
  - Volume Fraction of Particles
  - Grafting Density
  - Surface Charge Density
  - **Surface Heterogeneity**

→ physical
→ chemical

We will move on to the grafting density okay. So, we have kind of defined this parameter in the last class. So, this becomes important if you are going to have particles okay which have some long chain molecules that you have on the surface right and the grafting density okay you can call it a sigma g if you want to you know okay is defined as what did we say number of grafted molecule per particle divided by surface area right you know.

In this case if it is a spherical particle is pi D p square ok, how do we get that some random thoughts as to how do we get this thing, see one of the technique that people use in the literature is something like this okay.

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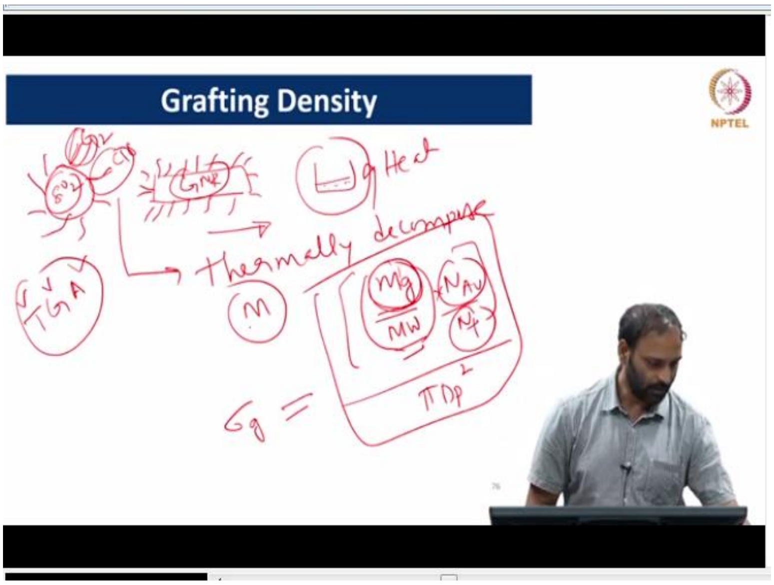
Grafting Density

So, typically when you take these particles that have these molecules right okay, say that I have a silica particle Si O 2 or you know I could have a maybe a gold nano rod okay which again may have these things in the surface right, what I can do is I can take a known quantity of the sample ok, and then I can subject it to a heating process okay. Now when you have silica particles or gold nano rods we know that you can heat them to a fairly high temperature.

They would not decompose, however these long chain molecules that you have you know it could be C 18 chains you know or it could be C 12 chains or something like that okay, what will happen is, if you are heating a sample to a you know what you do is you take a sample which has a known amount of particles. And you start heating it okay. Now when you start heating it at some you know characteristic temperature all these grafted molecules can thermally decompose okay.

What you do is because you have particles of known mass right and then you know this is typically there is a technical TGA right thermo gravimetric analysis in which what you can do is you can take a sample I can you know heat it at a controlled rate you know control temperature okay. As you do that what you do is you look for the change in the mass okay. So, these molecules start decomposing at a particular temperature and the decomposition ends at a particular temperature okay.

Therefore if you know the temperature range where they decompose and you basically estimate what is the change in the mass okay that occurs in that temperature window, I can actually get what is the total mass of all the grafted molecules that I have in the sample okay. If that is the total mass of the grafted you know chemical species that you have in the sample if that is your mp okay or mg okay that divided by the molecular weight of the grafted species what will it give macro environment, it will give me the number.

No, no it will give me the moles right, it will give me the, the moles of the grafted molecules that I have in the sample that multiplied by Avogadro number will give you what is the number of molecules okay. Number of molecules of the grafted molecules on all the particle that I have in the sample right, I divide this by the number of particles that you have in the sample okay.

That will give me what is the number of grafted molecule per particle right and that divided by your surface area, if it is a spherical particle it is pi D p square that is what will give me sigma g that is the grafting density okay. That is how it is typically done there are other ways of doing it okay in this simple TGA base analysis what you do is you calculate what is the characteristic in a mass change that is associated with a particular chemical species.

That is either grafted onto the particle by a covalent bond or physically adsorbed and you measure what is the mass corresponds to those species that divided by the molecular weight right. Multiplied by Avogadro number will give me the total number of molecules that I have in the entire sample divided by the number of particles okay divided by your surface area will give you what is the grafting density okay. So, the next one that is specific that is surface charge density okay.

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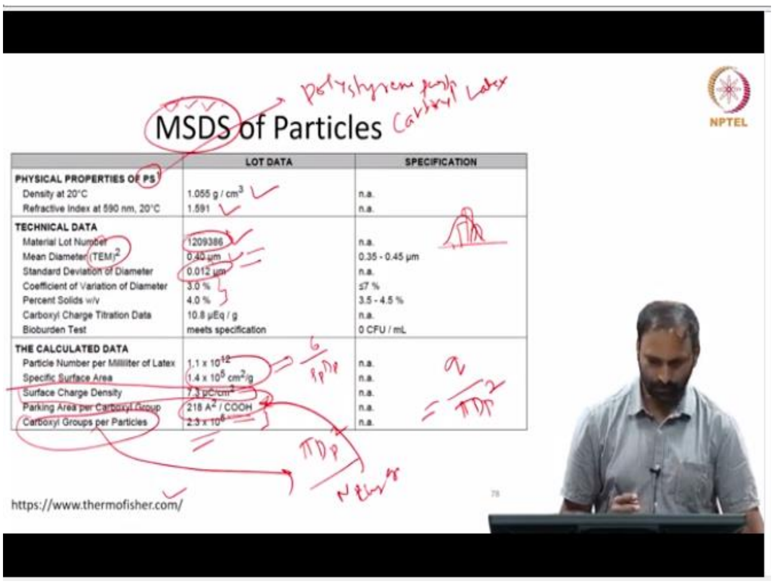

MSDS of Particles

	LOT DATA	SPECIFICATION
PHYSICAL PROPERTIES OF PS[1]		
Density at 20°C	1.055 g / cm^3	n.a.
Refractive Index at 590 nm, 20°C	1.591	n.a.
TECHNICAL DATA		
Material Lot Number	1209386	n.a.
Mean Diameter (TEM)[2]	0.40 µm	0.35 - 0.45 µm
Standard Deviation of Diameter	0.012 µm	n.a.
Coefficient of Variation of Diameter	3.0 %	≤7 %
Percent Solids w/v	4.0 %	3.5 - 4.5 %
Carboxyl Charge Titration Data	10.8 µEq / g	n.a.
Bioburden Test	meets specification	0 CFU / mL
THE CALCULATED DATA		
Particle Number per Milliliter of Latex	1.1 x 10^{12}	n.a.
Specific Surface Area	1.4 x 10^5 cm^2/g	n.a.
Surface Charge Density	7.3 µC/cm^2	n.a.
Parking Area per Carboxyl Group	218 A^2 / COOH	n.a.
Carboxyl Groups per Particles	2.3 x 10^6	n.a.

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So, before we do that I have taken an MSDS right, people who work with any chemicals you would have heard this right MSDS material safety data sheet right. So, like for any chemical there is also MSDS you know or a data sheet for particles okay and this is a typical data sheet I have taken it for from a website okay. So, if you look at this is actually for a PS okay polystyrene particles.

Let us look at what all do they give, they give you the density of the particle okay 1055 kg per meter cube, refractive index they give you a lot number okay, all the particles that you buy are kind of identified by this number that means people can get this lot number and then you know whether it is supplied here or elsewhere in the world you will get particles of exactly identical you know nature right.

The mean diameter that is measured by TEM okay that is the standard deviation right something like this which is obtained by I said right you get this histogram you know I can fit a distribution function I can get the, the mean size and the standard deviation hmm, there are other few parameters you can think a little bit about it. I would like to highlight this quantity of course they also show what is the specific surface area right.

I said you know for spherical particles it is 6 divided by rho p into D p right you can get that and this is the surface charge density okay 7.3 micro coulombs per centimeter square right. I said that the surface charge density is defined as the total charge q okay on the particle surface divided by again the surface area which for a spherical particle is pi D p square okay, that is how it is obtained okay.

And there are other 2 nice parameters you can think about packing area per carboxyl group okay. So, if you look at the surface area is pi D p square right, that will give you the total surface area okay. Now if I divide that by the number of the charge group that I have in the surface okay. This is an example of what is called a carboxyl latex, that means it has carboxyl groups on the surface okay.

And if I know so they also give you this quantity right carboxyl groups per particle, that means on the carboxyl you know on the particle surface there are 2.3 into 10 power 5 number of molecules right, number of charge groups okay. Therefore this pi D p square divided by N p okay number of you know this number of charge groups okay number of charge groups will give you this quantity right that is area per carboxyl group okay.

So, all these parameters are important you know if you really trying to do good set of experiments with your colloidal particles you should worry about every physical and chemical properties of your particles okay only when you do that okay only when you have a complete characterization of your particles that is when you know your experiments in terms of designing.

And you know in terms of interpreting the data that you get out of the experiments is becomes more meaningful okay when you have such a characterization like that okay.

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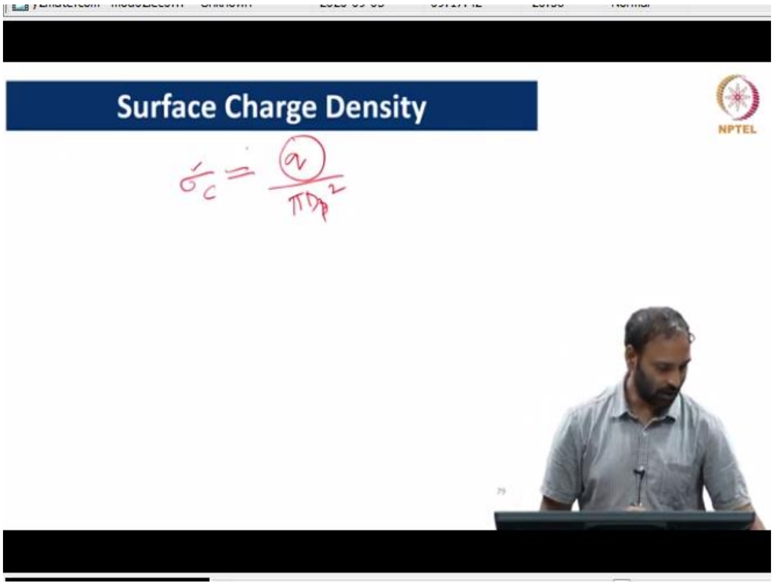

Surface Charge Density

$$\sigma_c = \frac{\textcircled{Q}}{\pi D_p^2}$$

So, with that again we have already defined the surface charge density okay. So C for charge sigma for density, so which is defined as the q, the total charge that the on the particle surface divided by a pi D p square right. Now there are different ways by which you can get q we will talk a little bit about that this in detail a little bit later.

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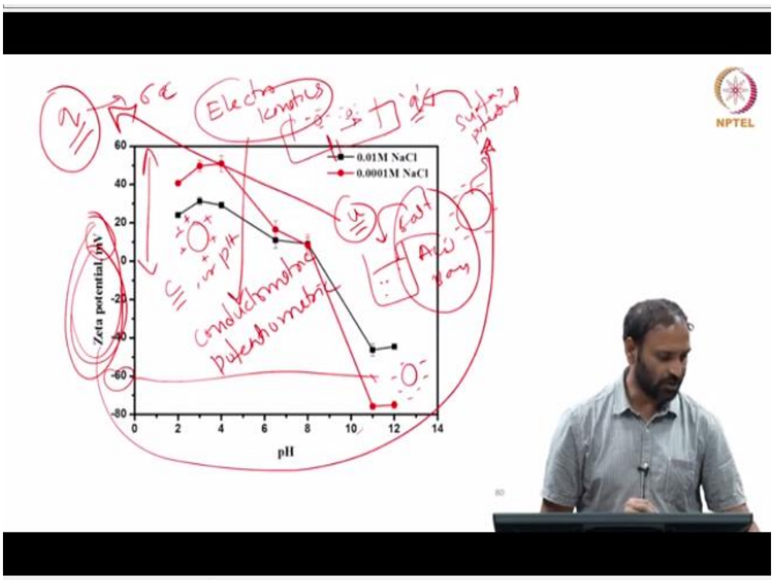

At this point I know how many of you heard of a parameter called zeta potential, have you heard this parameter zeta potential okay. So, just to tell you in a simplistic term if I make. So, this zeta potential kind of tells you something about the charge of the particle okay. If the zeta potential is positive okay that means the particles are positively charged okay. The zeta potential is negative you know like here right, they are negatively charged okay.

And this is a unit of milli holes okay, we will learn that whenever you are working with charged particles in a fluid it turns out that the mathematical treatment okay becomes much simpler if you not work with charge but a quantity called surface potential okay and again we will define what is surface potential in a while okay. So, this zeta potential for all practical purposes can be taken as a surface potential and okay that is somehow related to q okay.

Let us put it that you know this way at this point okay. Now there are methods by which I can measure surface potential okay or the zeta potential and from that there are ways by which I can get q and once I have q I can get you know the charge density okay. So, typically this zeta potential is actually measured by a technique called electrokinetics okay in which what you do is I have a dispersion of particles either positively charged or negatively charged okay.

And you apply a voltage okay and you make them move okay whenever you have a charge species it does respond to the electric field that you apply okay and depending upon the velocity with which they move okay. There are you know I can measure what is called the velocity which is the particles move okay and from that I can back calculate what is the charge in the particle okay let us put that there you know that way at this point okay.

There are other methods of measuring it not only electro kinetics there are ways by which people do what is called a conductometric titration okay or potentiometric titrations okay in which what you do is you take a dispersion of particles. And then you add a salt okay or an acid or a base and then you measure the change in the conductivity or pH okay and the way this conductivity and pH changes okay as a concentration of the this you know the electrolyte or the acid or base changes from that you can actually calculate you know.

The charge on the particle okay and once you have that I can actually calculate what is the surface charge density. The last parameter surface heterogeneity I have mentioned that there are 2 types of heterogeneity right a physical and a chemical heterogeneity.

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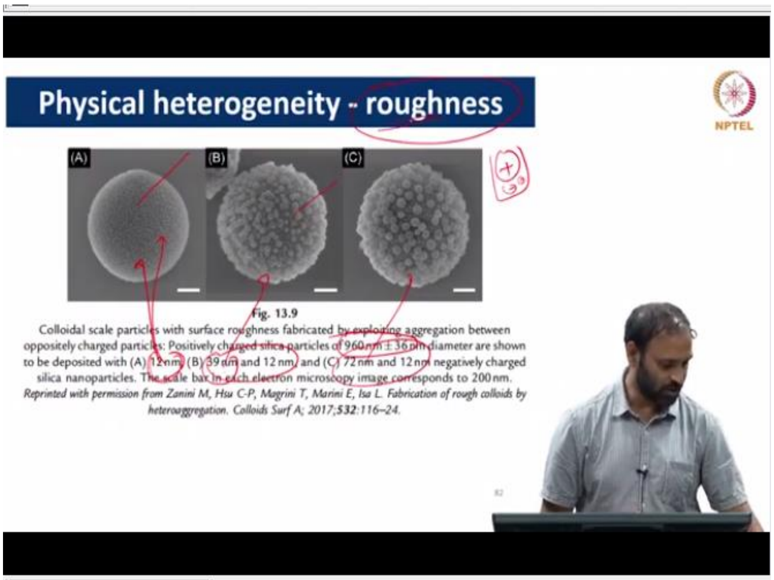

Physical heterogeneity - roughness

Fig. 13.9

Colloidal scale particles with surface roughness fabricated by exploiting aggregation between oppositely charged particles: Positively charged silica particles of 960 nm ± 36 nm diameter are shown to be deposited with (A) 12 nm, (B) 39 nm and 12 nm, and (C) 72 nm and 12 nm negatively charged silica nanoparticles. The scale bar in each electron microscopy image corresponds to 200 nm.

*Reprinted with permission from Zanini M, Hsu C-P, Magrini T, Marini E, Isa L. Fabrication of rough colloids by heteroaggregation. Colloids Surf A; 2017;***532***:116–24.*

An example of a physical heterogeneity is particles that are rough okay, what you are looking at is a nice example where what has been done is they have taken 960 plus or minus 36 nanometer size particles or large particles, they are put into a solution which has 12 okay 39 okay or a mixture of you know 39 and 12 okay and 72 + 12 okay. So, these are examples where I have a positively charged particles.

I have a large personally charged particle, they are put into a solution which have negatively charged particles okay or different sizes okay, in one case only 12, second case a mixture of 39 and 12, a third case a mixture of 72 and 12 and because they are oppositely charged, these smaller particles are going to get deposited on the surface of larger particles right, just because of the electrostatic interactions.

And thereby they are able to get particles which have different roughness right, in this case very small scale of roughness, in this case you have roughness of different of different degree if you want to call it okay. Now once you have particles like this I would have to characterize such particles also for roughness okay.

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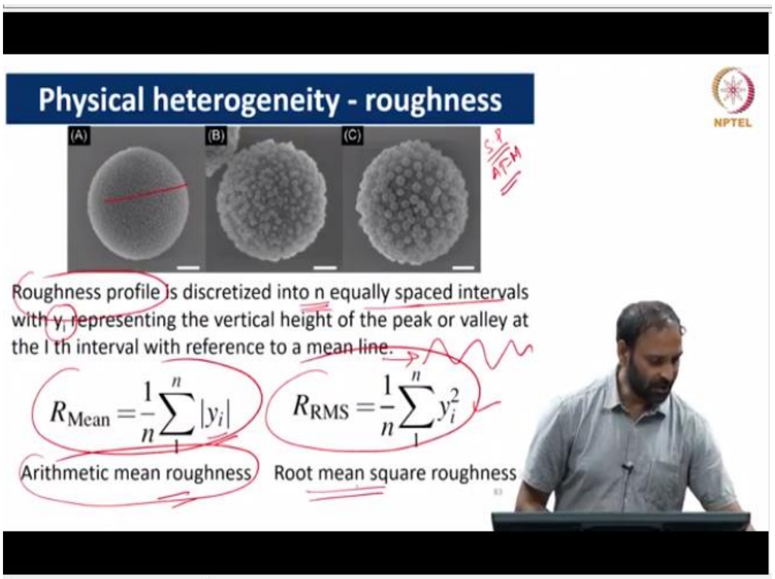

Physical heterogeneity - roughness

Roughness profile is discretized into n equally spaced intervals with y_i representing the vertical height of the peak or valley at the I th interval with reference to a mean line.

$$R_{\text{Mean}} = \frac{1}{n}\sum_{1}^{n} |y_i|$$

Arithmetic mean roughness

$$R_{\text{RMS}} = \frac{1}{n}\sum_{1}^{n} y_i^2$$

Root mean square roughness

So, what people do is people typically use techniques such as surface profilometry which is an interference based technique for measuring the heterogeneity of the surface okay or people can use AFM atomic force microscopy or any other technique okay and then what you get is what is called a roughness profile okay. This is as simple as if I have a surface like this.

And if I draw a line what I am going to have is I am going to have hills and valleys right. They are going to be hills and valleys okay and you get what is called a line profile okay and then you kind of discretize it and then you look at your discretize into n equally spaced intervals and then look at what is the height of the hills and the valleys okay. So, therefore if you do that and from this the height of the peak or the valley I can get what is called a arithmetic mean roughness okay.

Arithmetic mean roughness which is simply 1 over n sigma of 1 to n okay the average you know the size of this height or the valley right or you can get what is called as a root mean square roughness ok by this simple formula right. So, therefore if you have particles that have physical roughness okay or you know a physical heterogeneity one of the ways of quantifying such a thing would be measuring what is called the arithmetic roughness or a root mean square roughness okay.

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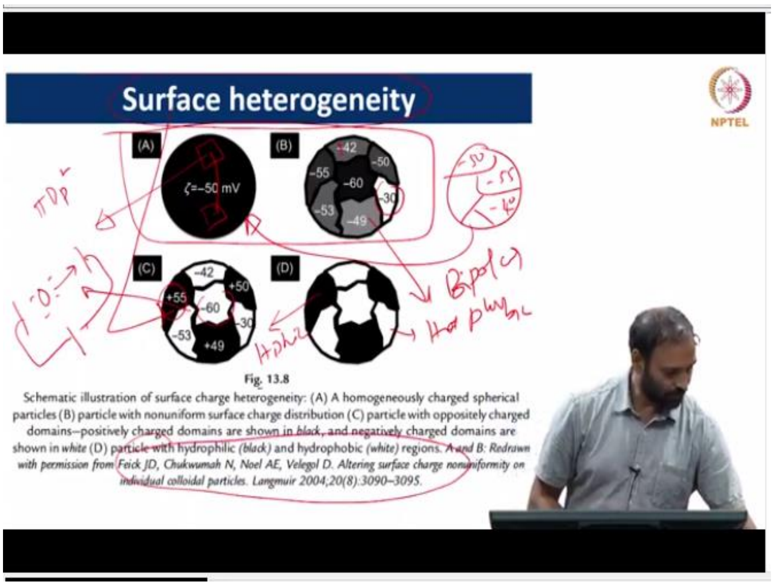

Surface heterogeneity

Fig. 13.8

Schematic illustration of surface charge heterogeneity: (A) A homogeneously charged spherical particles (B) particle with nonuniform surface charge distribution (C) particle with oppositely charged domains—positively charged domains are shown in *black*, and negatively charged domains are shown in *white* (D) particle with hydrophilic *(black)* and hydrophobic *(white)* regions. *A and B: Redrawn with permission from Feick JD, Chukwumah N, Noel AE, Velegol D. Altering surface charge nonuniformity on individual colloidal particles. Langmuir 2004;20(8):3090–3095.*

Similarly we kind of roughly touched upon this point that this could also be what is called as a surface heterogeneity, what you are looking at is an example in this case where you have a particle which is homogeneously charged okay what I mean by homogeneously charged is that we looked at it quantity right carboxyl groups per particle okay. Now what I can do is I can do a similar exercise.

And I can go back and ask you a question as to I have a particle whose surface area is pi D p square right, I can take different regions you know I am going to take a small section on the particle surface, I can ask a question as to what is the total number of carboxyl groups in that area I go to a different location I consider the same area again and I can ask a question as to what is the number of carboxyl groups okay.

If that number here and here or anywhere across the sample is exactly same that will give you a surface which is chemically homogeneous okay. Of course you could have cases where I could have a particle which is similarly charged but I could have you know if this is my average data potential I could have - 50 here or it could be - 55 in some region or - 40 in some region okay.

That will still is an example of a case where I have a surface heterogeneity, that means there are pockets on the particle surface where the zeta potential is not same okay or you could have designed experiments where I could have a particle where some case you know some regions the particles are possibly charged that may have positive zeta potential and some region may have negative okay.

That is again an example where this is an example of a particle what is called bipolar particles, that means these are particles which have both positive charges and negative charges on the particle surface okay or you could have cases where I have some region which is hydrophilic or hydrophobic right. This is an example of a surface heterogeneity but chemical heterogeneity.

And such things are more difficult to characterize okay, it involves more advanced techniques you know for example you know I was talking about this electrophoresis right you could have a case where I have a charged particle which may move in a particular direction when you apply a electric field. However, if you have particles which have you know heterogeneity like this whereas the patches where these things are positively charged negatively charged such particles could rotate in the electric field okay.

You could use exploit properties like that and you can actually characterize the particles for chemical heterogeneity okay, but that is you know it involves more advanced techniques more involved kind of work. So, if you are interested to know a little bit more about this you can read up some references that is here okay.

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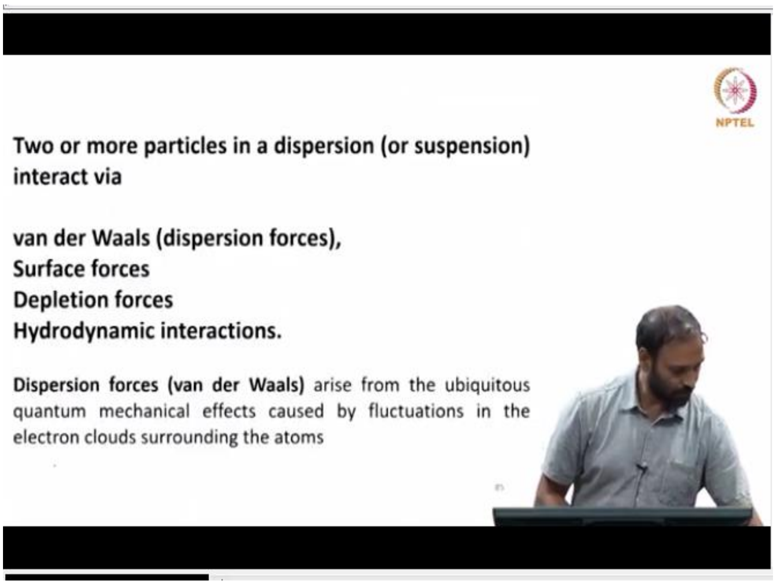

Two or more particles in a dispersion (or suspension) interact via

van der Waals (dispersion forces),
Surface forces
Depletion forces
Hydrodynamic interactions.

Dispersion forces (van der Waals) arise from the ubiquitous quantum mechanical effects caused by fluctuations in the electron clouds surrounding the atoms

Okay with that I think we will end with the characterizing the particles we will try and talk about a few of the other things in the next lecture okay.