Microscale Transport Processes

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Lecture No. # 38

Electrohydrodynamic Atomization

I welcome you to this lecture of electrohydrodynamic atomization, which is also commonly referred as electro spray.

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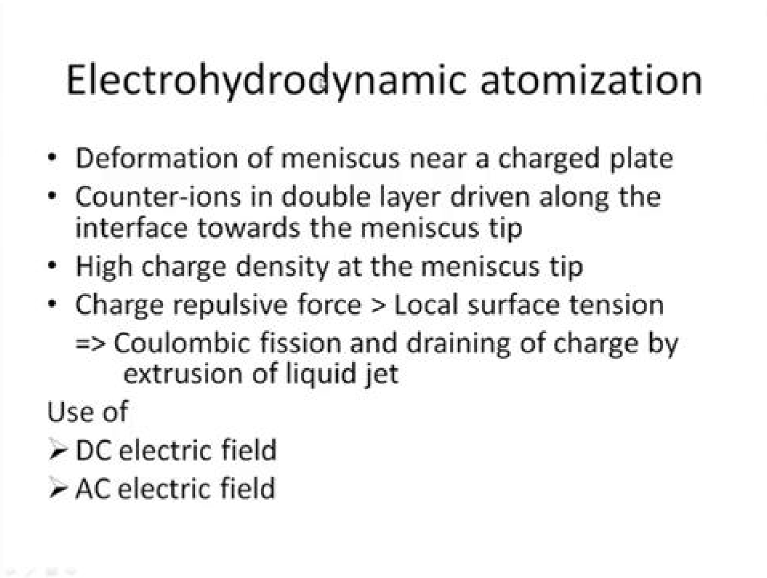

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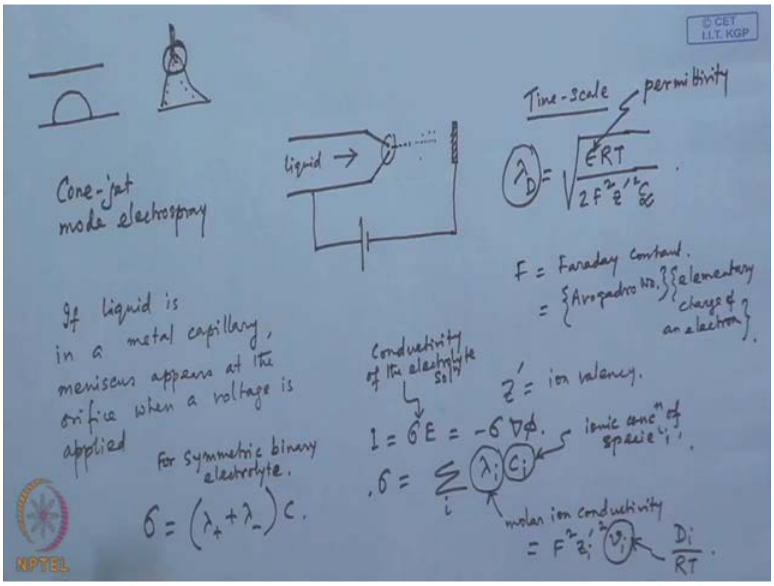

What we have here in thisslide is,there is a deformation ofmeniscus near a charged plate. What we mean by this is, ifthere is a liquid sitting there, and ifyou bring a charged plate next to it, you see that the meniscus is deformed, by that what we mean is thatyou will see that the meniscus takes the shape like. Thisdeformation ofmeniscus near a charged plate that happens, because counter ions in double layer driven along the interface towards the meniscus tip I mean the thisoneimmediateevent that happens, because ofthis deformation ofmeniscus is that counter ions is, counter ions in double layer driven along the interface towards the meniscus tip.

And what eventually, this will lead to is a high charge density near this meniscus tip,high charge density at this meniscus tip.When this charge repulsive force, when this is greater, when this charge, ifthis repulsive force ifI look at the slide, when thischarge repulsive force is greater than the local surface tension,then we generally see something called acolumbic fission and draining ofcharge by extrusion ofliquid jet. So, what eventually, what this means is that you have a droplet, and that has because ofthe presence ofthis electric field, there is a high charge density at the meniscus tip.

And then this meniscustip,there would be this charge repulsive force within this tip when it is higher than the local surface tension this droplet cannot hold that portion. There would be A Columbic fission and the only way, the charge can drain is, ifthere is a liquid jet that excludesfrom this tip.Now, this idea has been used in something called A Cone jet modeelectrospray.What is done in this cone jet mode electrospray is, there is a metal capillary,this is the end ofthe cone and then there isa grounded plate.Now, you have here,this is the electric; this is the circuit that you have. So, whatyou see here is that the liquid jet emanates from this tip and this liquid jet breaks down in to small droplets.

So, what you have here. So, what we are trying to do here is; what we are saying here is ifliquid is coming from this side, ifliquid isin a metalcapillary,then A Conical; then a meniscus appearsat the orifice I mean to say this place. At the orifice, when a voltage is applied across this point and this point. So, then automatically there would be a meniscus appearing. So, what we see here is that;what we will see here at the, this point is that there will be a double layer forming here.And what is important at this point is,something called time scale, in this operation there isit is important to look into the time scale.

What I mean by this is that, this double layer it has certain time to form there would be there would be something called a charge relaxation time. I mean you have to; when you apply the voltage there would be the charge, they have to align themselves next to the wall that requires certain amount oftime and that time is different. Ifyou expect an electron to align or ifyou expect an ion in an electrolyte to align or ifyou expect a polymer,big polymer molecule to align that time is different.

So, it requires certain time and at the same time you have something called an hydrodynamic timescale, where I meanthe liquid is flowing. So, how much time it takes for the liquid to flow through this capillary?So, ifthis timescales are not matched properly, then you cannot expect there to;there,then equilibrium exist in that double layer and it is important to have that equilibrium existing in the double layer.Now, ifyou try to; ifwe try to look at the time the, this relaxation time that, I have been talking about ifI look into it further.

If,what I see here is that this electric double layer I think by now, you all know that this electric double layer that has something called aDebye length.That is given by lambda D is equal to square root ofepsilon R T divided by 2Fsquare Z prime square C infinity. And you know, what are these terms? Because we have already discussed in connection with electroosmosis,Fis here the faradayconstant, which is nothing butthe product ofAvogadronumber and elementarychargeofan electron.

So, these two product ofthese two quantities, that is Fand this Z prime is the ion valency, that is how we look at it and. So, in this case we have a lambda D,which is called aDebye length.Now, I expect the ion to travel over these lambda D,I mean ifwe; ifthis equilibration ofdouble layer. Ifthat has to happen, we ion has to travel over this distance. So, what we see on the other hand is that,acurrent can be written as sigma into E which is nothing butthis quantity where sigma is given as sum offor all components lambda iC i.

What is sigma here? Sigma is, let me point out Ihere we have tonote two terms which are important one is epsilon, which is permittivity that we have already studied in connection with electroosmosis. On the other hand this sigma is basically the conductivity.This sigma isconductivityoftheelectrolyte solution. So, this is permittivity and this sigma is the conductivity. So, conductivity isreciprocal ofthe resistance. So, you can see,iis equal to sigma into E and E is del ofphi.

So, this we understand and then sigma; I mean how? Where the conductivity is coming from? Ifwe look at it, then this sigma is basically the molar ion conductivity. That lambdaiis equal to; lambda iis molar ion conductivity as far as this i-th, ion is concerned and this C iis ionic concentration ofspeciesi.Now, ifwe are looking at a symmetric binary electrolyte with ion concentration ofC. So, ion concentration ofC, ifyou are looking at then, you write sigma as equal to lambda plus lambda minus into C.

So, this is forsymmetric binaryelectrolytewith ion concentration C.Now, here we have another term that is lambda i. So, we understand sigma, we understand C i.Now, lambda ior in otherhere; we are talking about lambda plus and lambda minus. This lambdaIagain intern, one writes lambdaias I said is molar ion conductivity that is equal toFsquareZ iprime square vi,where this viis, intern therelated to the diffusivity ofthe ion v iis equal to D I divided by R Tso, this molar ion conductivity.So, that will have a faraday’s constant and the valency that part is taken care ofand then a velocity, which is arising from the diffusivity ofthat particular ion.

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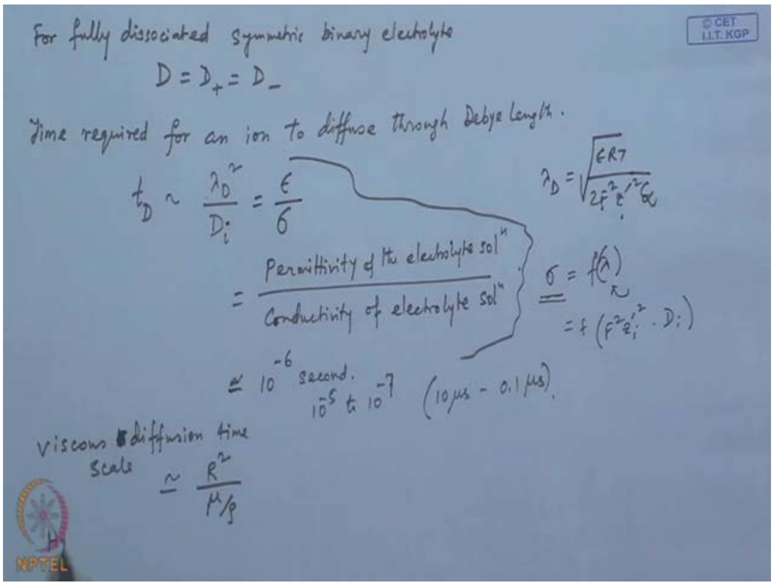

Now, for a fully symmetric, for fully dissociated symmetric binary electrolyte, ifI write or ifI go to the next page,for a fully symmetricfor sorry for fully dissociated symmetricbinary electrolyteD is equal to D plus is equal to D minus. We are talking about D iso, here, since we have brought in this lambdaplus and lambda minus for symmetric binary electrolyte.So, by the same token, you will have D plus and D minus and both would be equal to D for a fully dissociated symmetric binary electrolyte. So, we given this information now, ifsomebody tries to find out, what is the time required?Ifsomebody wants to find out, what is the time required for an ionto diffusethroughDebye length?

So, that can be given by in that case,t D let us say, that would be close to lambda D square divided by D i.This D iis thediffusivity ofcomponent ofspeciesI,ofthat; ionidiffusivity ofthat, through that D by layer and lambda D is the length.I meanbasically we are talking about a length scale and the velocity at which, that will go through that length scale and from that you are trying to find out; we are trying to find out, what would be the time?What would be the order oftime required for an ion, to go through this distance?So, that is basically lambda D square by D iand if,somebody works with these I mean; I have already we have talked aboutlambda D here, what is lambda D?

Lambda D is square root ofthis quantity that we have already; we have studied this earlier as well andthis part is the sigma. So, ifsomebody works with these and this sigma intern is related to the D i. So, ifsomebody works now, weto find out, what would be the lambda D square by D iin this case? You will find that lambda D square means, you had lambda D as square root of epsilon R T by 2Fsquare Z prime square C infinity. So, this lambda D square means, this square root would be gone and on the other hand ifyou look at, what you have in sigma? You will find that sigma Contains, those other terms, there as well sigmacontains lambda.

Sigma is a function oflambda and then lambda, this is the molar ion conductivity and that contains these Fsquare Ziprime square etcetera and then you have D i.So, ifsomebody works through this, we will find out that, this all these terms will cancelout. This Fsquare Z prime and here, you have sigma plussorry lambda plus and lambda minus for definition ofsigma. So, you will find that, this will cancel out and you will have this t D,left you are with t D is equal, this quantity is equal to epsilon divided by sigma. That means,this is the ratio ofpermittivityofthe electrolyte solution divided by the conductivityofelectrolytesolution.

Now, ifsomebody looks into what are the typical permittivity and typical conductivity ofthe materials that one works with, you will invariably find that, this is; this comes to about ten to the power ofminus six second. I mean of course, this is ofthe order I mean ten to the power minus six means, it can be between ten to the power minus five to ten to the power minus seven. That means,this is basically ten micro second to point one micro second. So, this is the time required for equilibration of anion, ifyouthrough thisDebye length.

Now, here you haveanother time scale see, what you are playingwith? Ifyou have to ifyou have to atomize this way; that means, you are having a liquid flow and at the same time you are developing some charges within this solution. So, ifyouexpect that these two;expect that the; that these equilibration within the Debye length happens, much faster than I mean much before the liquid is flown out ofit. So, then in that case this time scale has to be compared with, what you call? The viscoustime scale, viscous orthat complete term would be viscous diffusion time scalewhich typically referred as R square divided by mu by rhowhere R is the capillary dimension.So, this is typically a viscous diffusion time scale or ifsomebody wants to work with a, what you call?

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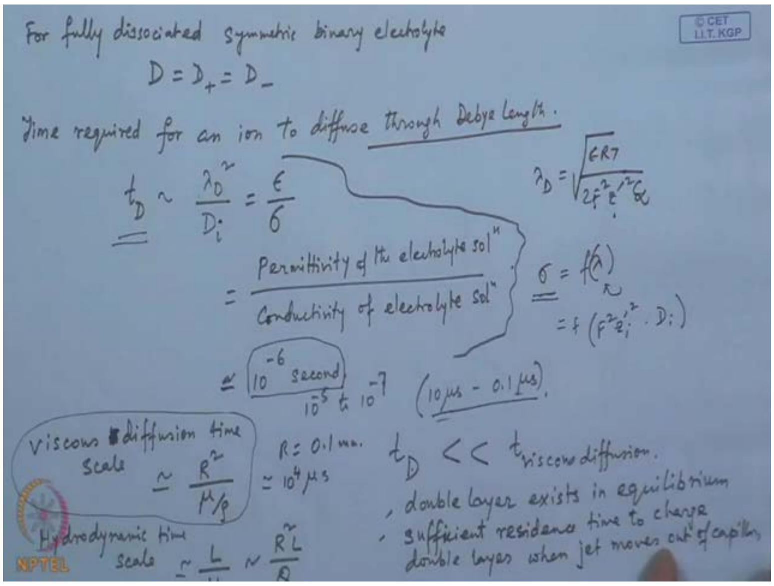

Hydrodynamic time scale, one can write it this way as well.Hydrodynamic time scalewhich would be equal to L.L is the length divided by mu, which is the velocity, which is something like R square L by Q.Q is the flow rate, R is the capillary dimension. So, that also possible, this hydrodynamic time scale and what you have to ensure is that, this viscous diffusion time scale,has to be greaterthan this. That means, this should be shorter, this t D the time required for theseionsto relax. Within this Debye length that has to be shorter by, at least couple oforders ofmagnitude because then in; that case, the flow will happen and the equilibration will happen instantaneously.

So, you do not have any issue withit, has not been equilibrated ions have not formed properly, butthe, you are forcing the flow to go out I mean it is not that way. So, then you can use the full potential ofthis mechanism. So, these time scales are extremely important I mean,ifI try to articulate this further, ifthis time scale. If,this t Dis much less than this viscous diffusion, ifthis is much less, what you can conclude from hereis that, the double layerexistsinequilibrium.

In other words the;so, what you conclude here is that, sufficient timesufficient I would say, residence timeto chargedouble layer,when jetmoves out ofcapillary. So, this isensured these issues are addressed, ifyou have this time scale. This is less than the viscous diffusion, fortunately this viscous diffusion typically. People have for say, for R is equal to say,ifyou are looking at0.1 millimeter, then these will come to the, these time scale. This viscous diffusion time scale typically will for conventional, for common materials that we handle this will come to about ten to the power four microsecond.

So, we were looking at 10 to 0.1 or may be 1 micro second. Ten to the power minus six second for thattime required for an ion to diffuse whereas, the viscous time scale is much higher. So, when this is much higher so; that means,the equilibration ofdouble layer will have I mean this time scale appears almost instantaneous compared to the flow ofthis liquid. The viscous as far as the, viscous effect is concerned and this is extremely important ifthese two time scales are not adjusted then you cannotleverage thisidea.

So,as a matter offact, I mean since we are into this relaxationtimescale I mean, we need to understand this time scale or rather we will address this time scale, once againat a later time.Because thesewe have;sofar, assumed that this is a DC electric field.Now,ifone has this AC ifthe; ifthere is AC field. If,there is another time scale involved, within the time scale the voltage changes. So, then that time scale also will become important for this mechanism. So, this AC time scale, an AC time scale,what defines AC time scale is a frequency? How many hertz?

So, what frequency you have?This the that is, that becomes important and then what we will try to do at this, at that time is, we are trying to find out, what is the R c time scale? Because see, this Debye, thetime required for adiffuse to Debye length. So, this double layer, that can be expressed as A Circuit like, a resistance and capacitance for example, a resistance and capacitancethey are acting parallel. Because this electric double layer that has its own resistance, arisingsince you have seen, there is a sigma involved and at the same time there would be some amount ofcapacitance as well.

So, you bring in that resistance capacitance type model I mean ininstead oflooking at the double layer, you simulate that with a R and c and find out, what is the time scale for that R C circuit? And that is referred as a R C time scaleso, this R C time scale will be compared I mean, ifyou had an AC fieldoperating then the that has its own time scale and how that?Where that stands with reference to the time scale ofthisdiffusion ofthis, ions?So, that is another aspect, another issue that will come up.

So, this…So, you…So, basically ifwe go back to I mean, where we started? We started this,we started on these, formation ofwe are trying to find a mechanism by which the electrospray will happen and we found that, there is an, there is a issue ofthis time scale we I mean that is appreciated.

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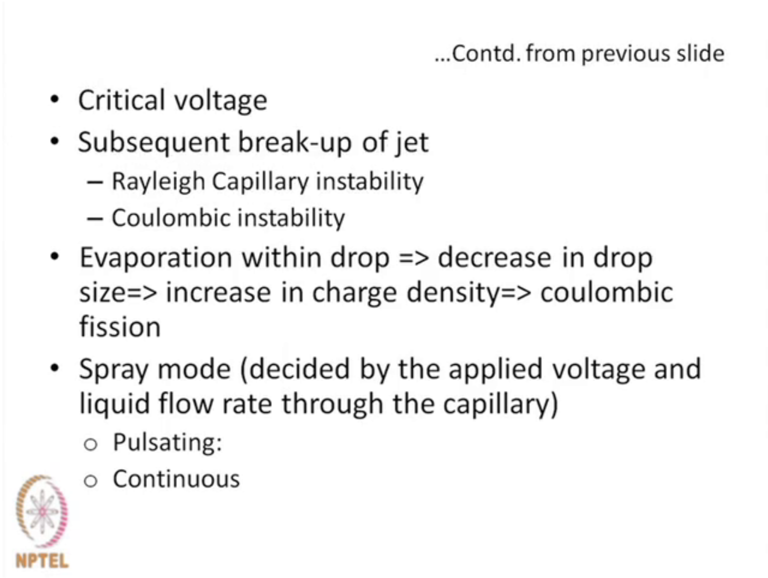

If,there could be and. So, ifI look at the slide, there could be the DC electric field or an AC electric field either way, it is possible. For DC electric field whatever, wetalked about is fine. For AC electric field, there is another time scale coming in because ofthe frequency.Now,what we must understand here is there exists something called A Critical voltage I meanof course, we are in this DC regime. I mean we first, we are talking about the DC field, not the AC field we will look into some ofthe aspects ofthese later.

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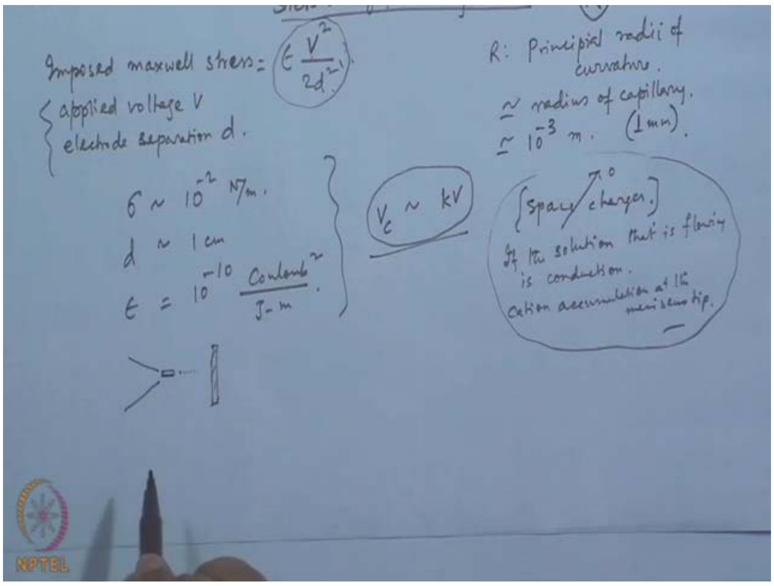

What we have here,is something called A Critical voltage. The critical voltage is,ifItry to derive it here, the critical voltagesee this, the liquid.Ifwe look at the liquid meniscus, that protrudesfrom the orifice.Ifyou assume that, this is basically ofthe shape ofa spherical cap.Ifthis is considered as spherical cap,then this is equal to, then this will be sigma by. So, then the stress arising from surface tensionthat is, equal to sigma by R.Where R is basically you know principle. Imeanyou understand what this is?This is ofthe same order as radius ofthe capillary.

We are doing just an order analysis here, I mean at what time well we need ten to the power five volt or ten to the power eight volt. That kind ofanalysis we are doing,it is not a rigorous analysis either and. So, this is ofthe order of,ifwe look; try to look at the order, this would be about ten to the power minus three meter. That means, we are talking about say 1millimeterand the if,somebody looks into the imposedMaxwell stress,then for applied voltage Vand electrode separation D,Maxwell stress imposed. Maxwell stress would be epsilon into V square byD square.

So, ifthisif,the stress arising from surface tension is greater than the Maxwell stress, then thatdroplet will not come out. So, this Maxwell stress this has to be greater thanthis quantity has to be greater than this sigma by R,then only the I meanwe are talking about the orderby order ofmagnitude. This has to be greater than this then, only you can expect the droplet to come out. So, ifthat is. So, then you can come up with a,what would be the critical voltage? I mean what is the minimum voltage that you should have?

So, ifwe equate this to and if,you remove two I mean ifyou. So, what ifwe try to find out the order? You can take sigma as ten to the power minus two Newton per meter.dis the distance between the two can be taken as say, one centimeterthat means, what distance we are talking about? We are talking about distance between the two electrodes, we are talking this distance. So, this distance is let us say, 1centimeter and then epsilon iscommonly taken as ten to the power minus ten coloumb square by joule meter. So, in that case, you will find this critical voltage. This critical voltage will come to the order ofkilovolt.

Sayit can,this is ofthe order ofkilovolt,not simple volt or notmegavolt. It will be ofthe order ofkilovolt. So, that is something. So, the there exists such critical voltage. So, you.So, ifsomebody wants to knowfor conventional applications,for conventional the materials that we have, ifwe want to create droplet by this mechanism. What kind ofvoltage we have to create between the electrodes? And this is something, which we havethere. So, there exists A Concept ofcritical voltage.

Of course this is,butjust an orderanalysisone important thing you must understand I mean ifyou do such, ifyou go by this kind ofthe route. What we are neglecting here is the space charges, because there would be if,the solution itself. Ifthe solution that is flowing ifthe…So, this part is, this is neglected. So, ifthe solutionthat is flowing is conducting ifthe solution, that is flowing is conducting, that meansthere would becation accumulationat the meniscustip.

So, there would be some difference, there would be some change to this critical voltage. So, for A Conducting solution thereifthe solution that is flowing is,it has its own space charge. So, that has to be. So, that will effectthis analysis.Now, once the jet comes out, once the liquid meniscus come out here, we haveanother issue here. Subsequent breakup ofjet, which is basically there are two ways,this jet can breakup. One is by Rayleigh capillary instability and the other is coulombic instability. Let us try to understand,do you have? This is the coneand the, this is from which the liquid is coming and this is the ground plate and a jet comes out ofthis.Now, this jet subsequently breakup into small droplets.

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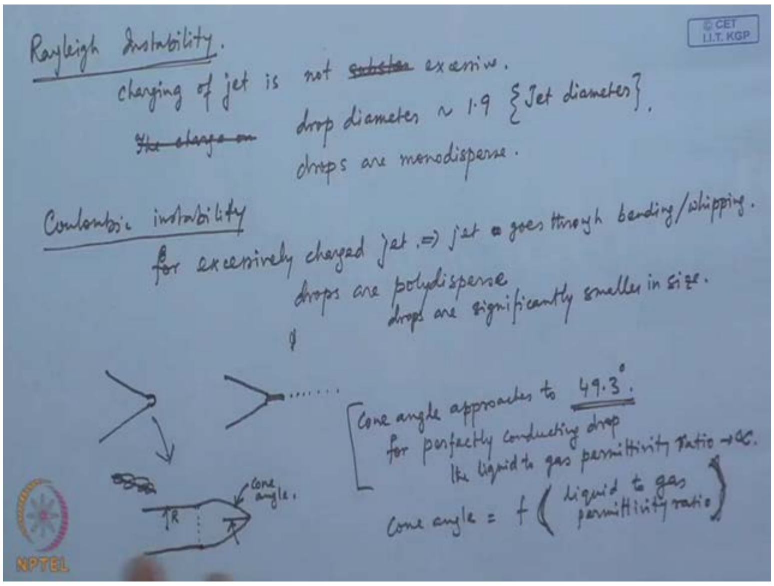

This breakup is possible by two mechanisms one I sayone we see here is that, this Rayleighcapillary instability other is the coulombic instability. The first type ofinstability, we haveseen already.We have studied herein the previous occasion this instabilitywill come into play, when the chargingofjetisnotnotnot substantial, not not excessive.So, this is the type ofbreakup ofjet. We have talked about it is exactly the same one. Basically you assume that the charge on the surface ofthat jet, does not contribute significantly to this instability.Here, in this type ofinstability the drop diameteis close to 1.9 times the jetdiameter anddrops are monodisperse.

So, basically that the Rayleighinstability that was, that is considered for breaking ofa jet, that has been modifiedfor the presence ofcharge and that the that. So, people have done analysis in that line and that type ofbreaking will happen, when the charging ofjet is not very high.So, in that case, there ismonodispersedrops are obtained by drop diameter is close to 1.9 times jet diameter.You know, we have already talked about these Rayleigh instability. How the jet diameter? How the drop diameterrelates to jet diameter? There would be a perturbation, that perturbation grows andthere is a from breaking ofjetinto smaller droplets. So, this we have done similar analysis, only the presence ofcharge has to beconsidered in that analysis nothing else.

The other type ofbreaking is referred as coulombic instability this is for excessively chargedjet. So, this is, this. When the jets are, jet is excessively charged that time thesuchcoulombic instability will come in. And these in this case the drops arepolydispersedand a jet undergoes basically.In this case jet goes throughbendingor whipping jet is,jet goes through these processes and a drops are polydisperse. However, here, the drops aresignificantlysmaller in sizeanother thing you mustappreciate here is that evaporation within drop. See, when the jet is,jet has come out ofthe capillary tip there will be evaporationwithin the drop and therefore, there will bedecrease in drop size.

If,there is evaporation then automaticallythere would be loss, evaporative loss and the drop size decreases.But charge does not decrease. So, there would be increase in charge density and as a result, ifthere is increase in charge density, there would be more possibility ofthis coulombic fission. So, once the drop forms, it could be that you the drop has formed by thisthe first one, first type ofinstability. Butwith evaporation there is decrease in drop and then there would be increase in charge density. So, there would be further coulombic fission; that means, further breaking ofdrops. So, that. So, this evaporation is thecause here. So, that you have tomake note of.

Now, when it comes to the spray mode, the spray ofthis there are two ways. It can be I mean twodistinct features can be observed here, one is called a pulsating mode another is continuous mode. In pulsating,this is decided by the applied voltage and liquid flow rate through the capillary. So, the,these are primarily the two parameters, two variables that control the spray mode and. So, you have the two methods one is pulsating another is continuous.

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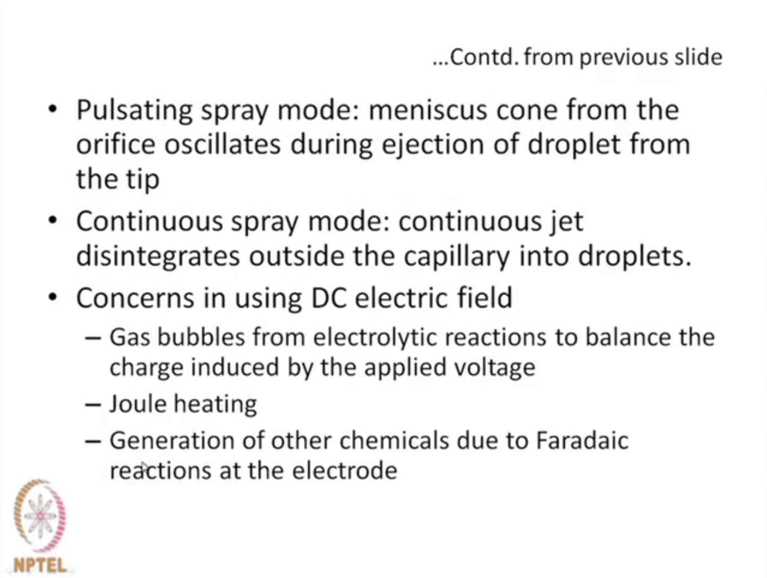

Now, what you have in pulsating spray mode is that, the meniscus cone from the orifice oscillates during ejection ofdroplet from the tip. So, anin on the other hand the continuous in the case ofcontinuous spray mode, continuous jet disintegrates outside the capillaryinto droplets. So, in one occasion we see, that ifthis is the cone, there is a meniscus coming out from the orifice and then this is released and then this one is meniscus goes back. So, meniscus cone from the orifice oscillates, meniscus cone comes out forms a drop and gain it goes back again another drop comes in. So, this drops are formed directly from this meniscus, that is a possibility, the other possibility could be A Continuous jet coming out and then that jet disintegrates intodroplets.

So, the; this one is referred asin this jar gun that they are referred as pulsating spray mode another is continuous spray mode. So, there is a difference between the two. In this connection, you mustunderstand one thing is that,thethere is a proposition here, is that. If,this is the capillary I mean we are talking about thisspray mode we are talking about this pulsating mode. We have that means, you are forming A Cone here,tailor has shown that, ifthis is the capillary, ifsay radius capital R and then it forms A Cone like this.So, this is the end ofthe capillary and then it forms A Cone like thisand this being the cone angle.

So (()) had this,there arescientificliterature, where it is shown that, this cone angle approaches this cone angle. So, we are talking about this for this pulsating mode, this cone angle approachesto 49.3 degree for perfectlyconductingdrop and the liquidto gas permittivityratiointo infinity. So, for these casesthis were shown that, this cone angle will takea value ofthis. So, in.In fact, cone anglecan be predicted fromthe liquid togaspermittivityratio. So, so from.So, this there would be. So, ifthis is the end ofthe capillary tip, there would be forming A Cone and this cone angle will be a function ofliquid to gas permittivity ratio. And theseat the limit,this is49.3 degree this has beenshownby the researcher already.

So, this is what we have as far as. So, these are the two modes, that we talked about and this is all, we have as far as thetwo rather that,the use of DC electric field is concerned in forming thedroplets.Now, there are certain concerns in using DC electric field because next what we would be talking about is the AC electrospray.And there are certain concerns in using this DC electric field.This, concerns are I can see number one is gas bubbles from electrolytic reactions to balance the charge induced by the applied voltage. So, that is one concern, which is already I mean we understand this,that is not athat is understandable. Second thing is joule heating, because this is a DC field and generation ofother chemicals due to Faradaic reactions at the electrode.

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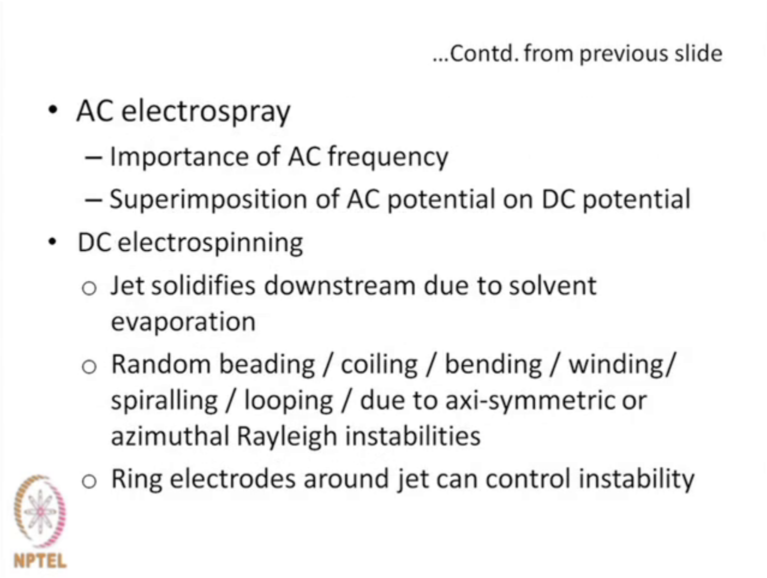

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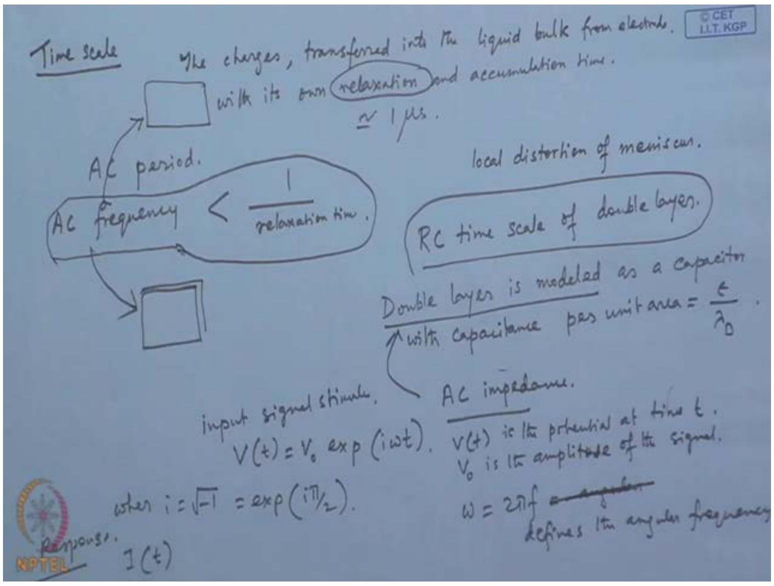

So, these are some ofthe concerns of DC electric field for whichthat there was an interest in using the AC field.Now, ifwe look at this AC electrospray,there arecouple ofmain issues, that I would be touching upon because otherwise this method is same and. You have this relaxation time and then there would be critical voltage an all everything would remain same. Only thing added on top here is the importance of AC frequency. So, importance of AC frequency, what we meant here is,thatthere exits anothertime scale.

So, that isthis time scale that is another time scale,which is coming which is from the electric field itself.I mean if,I try to revisit that issue once again, the charges transferredinto the liquid bulkfrom of course, from electrode.The charges transferred into the liquid bulk from electrode with its own relaxationand accumulation time.We showed that, this is ofthe order of 1 microsecond.Now, here you are imposing another AC period; that means, you are applying the voltage for certain time and for other times you are not applying I mean, you are go; going the other way.

So, ifthis AC frequency is less than 1 divided by this relaxation time, we are talking about. So, ifthe AC frequencyis less,ifthis AC frequency is less see there is an issue,it could be that we are looking at a local distortion ofmeniscus. That means,there is I mean you are applying a voltage, butyou are moving away from that. So, fast that simply the meniscus has distorted locally, butit has not gone to the culmination within that time frame. Culmination means forming ofa complete drop and going out.

So, you have to ensure that, this voltage is applied for sufficient time. So, that the,you are not simply talking about the local distortion ofthe meniscus. So, this AC frequencyculminationis linked with both these aspects. One is towardsthis AC frequency has to abide by thedemand from thatcharge relaxation point ofview and this AC frequency also has tobe in tune with. What is the viscous timescale? Because the it is, ifit is just a local distortion ofmeniscus that will not be sufficient.

So, what we would be looking at this point probably issomething called the R C timescaleofdouble layer that is something, which we have to look into.Now, ifwe try to understand, what is the R C timescale ofdouble layer? Then what we have to do here, is we need to understand, how this double layer works here?Typically double layeris modeledas a capacitorwith capacitanceper unit area is equal to epsilon divided by lambda D, epsilon you know is permittivity lambda D is the thickness ofthisdouble layer.

Now, this double layer;so in that case the double layer I meanthe ideally, I mean what they? Whatthe way it is looked into is, ifyou consider this as an ACimpedancethat is the ideal way ofhandling double layer. Because in that case, you will; ifyou have an input signalsomethinglike this where I is equal tothis quantity. So, ifyou give an input signal, where V naught is the amplitude ofthe signal,andV t is the potentialat time t and omega here is equal to 2 pi Fis the angular.I mean basically it is associated with the angularfrequency,in that case, what we will do?In fact, we will continue this analysis what we will do is, we will find out the correspondingresponse signal which is called an response signal.

So, V t is an input signal stimulus and this is the response signal,we will calculate and then we will calculate, what is called the complex impedance.So, I mean this is a very standard exercise for electric circuits,what we are trying to find? We will try to find out, what would be the R C timescale ofa double layer? And that has to relate to the AC frequency. I will try to at least touch upon the various issues in the next lecture and then, we will continueunderstandingthiselectrospray process and there is another very interestingphenomenon, which is I mean which is very close to this kind of,this use ofelectrode andproducingflow out ofit.Sothat, we willtouch upon in the next lecture thank you very much.