Mathematics for Chemistry

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Lecture – 6

We have defined vectors, we have defined vector spaces, we have defined functions of vectors and then we have also defined derivatives of functions of vectors with respect to vector quantities. And if you recall we defined three kinds of derivative; one was called a gradient, the other was called divergence, and the third was called curl. And each of these quantities will appear in various areas of theoretical chemistry and you will encounter them at various points during your during your studies. Now, let us look today at the physical significance of each of these quantities starting with a gradient.

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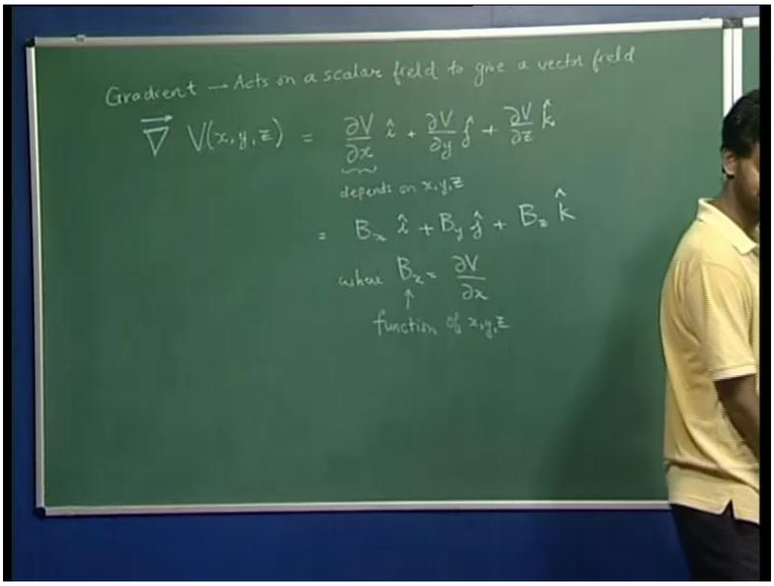

So, to recap the gradient operator is defined in the following way, gradient acts on a scalar field to give a vector field. So, suppose you had a scalar fields called V. So, scalar field is just a can be thought of as a multiple variable function as a function of many variables. And now the gradient is denoted by this gradient of V is defined as by dou V plus dou V by dou z, so here we have the gradient it operates on a scalar field to give a vector field. So, what you get is a, the vector has 3 components and remember that each of these components depends on x, y and z.

So, what you get you can call it if I call it, where dou x and since V is a function of x, y, z this will also be a function of x, y, z; similarly, we can write b y and b z. So, you say that the three components of the gradients are nothing but the derivatives of V with respect to x, y, z. Now, we are going to look at the physical significance of the gradient, gradient is something that you will encounter innumerable times during your studies and other area areas of chemistry.

So, I will just give some understanding about what does that mean to take a gradient of a of a scalar field. So, the first physical significance that we are going to give is that a gradient is related to what is called a directional derivative. So, what do we mean by a directional derivative, now I will try to motivate the idea of directional derivative, a directional derivative comes into play when you are looking at functions of many variables.

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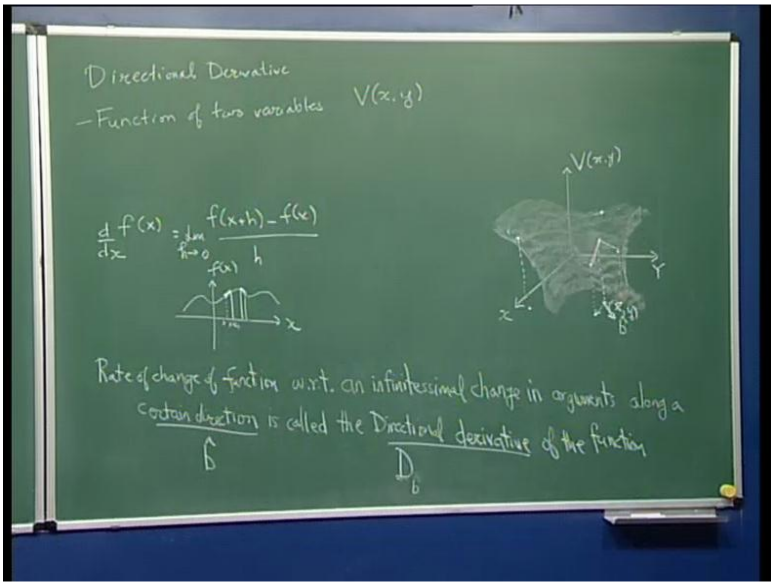

So, let us start example function of 2 variables V of x y, so now you might ask the question, so the way you might plot this function is you will say that I will put, I will call this a x axis, call this a y axis. And for any point on this on the x y plane I have a certain value of V, so it might be here. So, for this point this might be the value for another I might get another value and so on, so for each point I will get a certain value and if I connect all those values I will get some sort of surface.

So, I will get some sort of surface, which represents V of x y, so V of x, y is represented by a surface like this. Now we want to mean, what it means to take a derivative of V so derivative if you recall from for a function of one, you had f of x then you will say that d f of x by d x is equal to f of x plus h x divided by h limit is h tends to 0. So, it is a rate of change of the function as you change x by the small interval. So, in this case you just had x in one direction and you will f of x which will plot.

And the derivative will be suppose you want to find the derivative of this point you will see the value of the function here minus the value of the function here divided by this, so that will give you the slope here. And similarly, if you find the derivative here you will get a slope in this direction. So, you can calculate the derivative here the derivative will be negative, here it will be positive, because the slope is upward and the slope is downward. But, wherever you are the change in x is only going from x to x plus h, so you just go an interval h in the forward direction.

Now you come to this case you have a function of two variables so suppose I have a point x y. So, for each pair of x and y I have the function has a certain value. So, you just come up and you find out where it intersects this surface and that is the value of the function. So, similarly if you are if you are somewhere here your function might have a value of somewhere around here. So, depending on where if you go upwards where this surface cuts this line is the value of the function, now how do you understand.

Now, if you want to define a derivative with this point, if you want to define the derivative of the function here you have to see how the function changes as you change it is argument. So, you sit at this point now you can change it is arguments so let us say you can either increase y keeping x fixed or you can increase x keeping y fixed. So, you can either go in this direction or in this direction or you go in this direction. If you go in this direction, then at this point if your function has some value here, then you will define this will be related to the derivative.

If you come in this direction if at this point you see the value of the function somewhere here then your derivative will be will be this much. So, the derivative depends on which direction you are going and there is no reason for you to go just along x or y you can go along any arbitrary direction. You just have to go a small interval and you see how the function changes and that defines a derivative in that direction, so the idea of a directional derivative is that you go in some direction in this x y plane and you see how the function changes see the rate of the function in a certain direction.

So, the idea of directional derivative is the rate of change of function with respect to infinitesimal change in arguments along a certain direction. So, this is called the directional derivative, rate of change of a function with respect to an infinitesimal change in argument along a certain direction is called the directional derivative of the function; along this direction that your change the arguments. So, if this direction if this direction is denoted by a unit vector b that points along this direction.

So, for example, if you are changing in this direction then a unit vector in that direction is b, then this directional derivative you use the symbol for the directional derivative use the symbol D b. So, D b tells you what is the rate of change of the function as you go an infinitesimal distance along the b direction, so how is the derivative related to this directional derivative. So, this directional derivative is actually very closely related to the derivative and to the gradient infact. So, the question is how is the directional derivative related to the gradient of the function.

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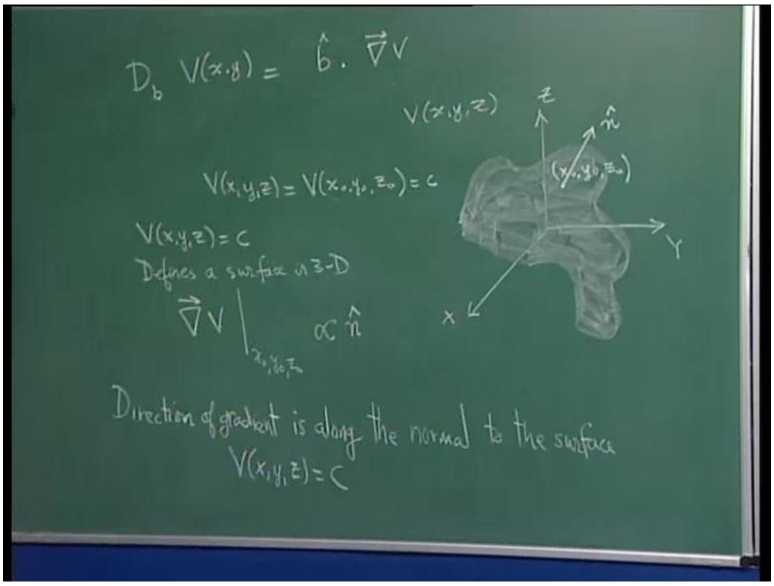

So it is not hard to show that the directional derivative of the function recall my function, if I had a function V of x y is equal to b hat dot gradient V. So, if I want to find the directional derivative along any direction I just take a dot product of a unit vector in that direction the gradient. So, you can imagine how this is a very useful quantity you can imagine that you have this function of two variables and this looks like a some surface, so you can think of it as a mountain and valley example.

So, you can imagine that as you change x and y you have z which is changing in the form of in the form of mountains and valleys. And you are sitting somewhere and you can ask how does my height change as I move in this direction or how does my height change as I move in this direction or how does my height changes I move in this direction. And if you want to calculate that you just calculate the gradient at this point and you take a dot product with a unit vector in whichever direction you are going.

So, for example, you might go very steeply in one direction and very gradually in one direction and to know to and the directional derivative will contain information about that. So, the gradient can be thought of as a something that who's dot product with a unit vector use the directional derivative in that direction. There is another way to understand the meaning of the gradient and this is a gradient can be thought of as something called a surface normal.

So, it is a surface normal and the way to understand this is to think of, if you have the gradient at this point this is probably best illustrated with using a three dimensional example. So, yes this is best illustrated with a three dimensional example, so what I will do it is in the following way, so suppose I had a function of x, y, z now suppose I had a function V of x, y, z.

So, v of x, y, z I cannot show it on this plot because I have only three axis but now suppose I take V of x, y, z is equal to V of x 0, y 0, z 0. So, where x 0, y 0, z 0 is sum point and you, so this has some value. So, the value of the function at some point x 0, y 0, z 0 is c. Now this v of x, y, z equal to c this defines a surface in three dimensions. So, V of x y z equal to c is a equation of a surface in three dimensions and this surface can be closed it, can be open it has some form.

Now, this surface will pass through the point x 0, y 0, z 0, so the point x 0, y 0, z 0 will lye on the surface, because V at x 0, y 0, z 0 is equal to c. So, all the points where V, V of that point is equal to c lye on this surface and so since clearly the point x 0, y 0, z 0 will lie on this surface. Now, you look at the surface at the point x 0, y 0, z 0 and you draw a normal. So, this is the normal to this surface at the point x 0, y 0, z 0 and it is not and you can show that the gradient of V at this point x 0, y 0, z 0, evaluated at x 0, y 0, z 0 is proportional to n.

In other words the gradient is vector and the direction of the gradient vector is along this surface normal at this point. So, the question is you might ask which direction does a gradient point and you can immediately see that you can say that you look at this surface of constant V draw normal to the surface at this point and this represents only the direction of V of grad V normal to the surface. So, the direction of the gradient is along the normal to the surface V of x y z equal to constant and this surface as we had already mentioned it passes through the point x 0, y 0, z 0.

So, at this point the direction of the gradient will be normal to this surface at x 0, y 0, z 0. Now, we can come back to our two dimensional example what happens in two dimensions does this does this picture hold in two dimensions and the answer is yes it does hold in two dimensions.

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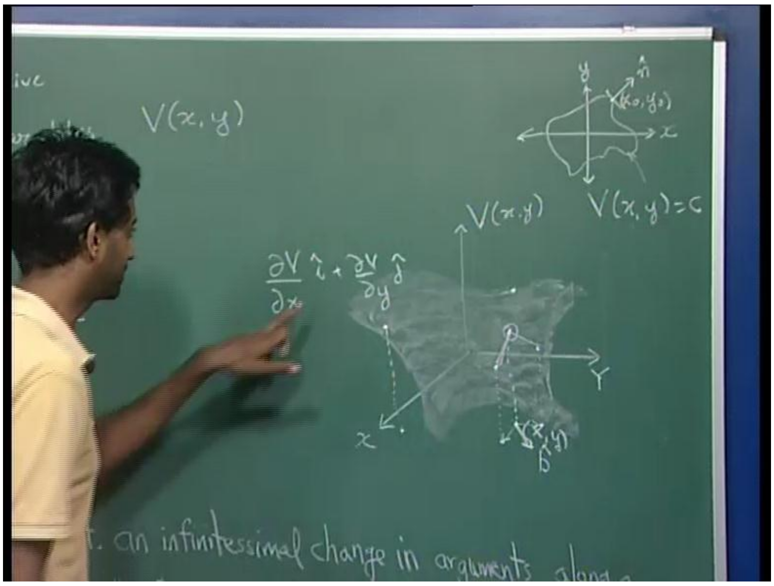

So, in two dimensions the, if you have x and y, V of x y equal to constant this defines a curve in this x y plane, so it defines a curve in this x y plane that could be close, it could be open it looks like this. So, this is v of x y equal to constant and if this curve passes through the point x 0, y 0, then the gradient will be along the normal to this curve at this point, so it draw normal to the curve with this point and this is the direction of the gradient.

So, it holds even in two dimensions it is probably easier to see it in this with this three dimensional example but it holds even for two dimensions. So, in two dimensions a surface where V of x y is constant is given by a curve in this x y plane it is just a function of x y. So, you have some function of x y equal to constant, so it is a curve in the x y plane and at any point you can draw normal to this curve which will also be in the x y plane and that is the direction of the gradient.

So, notice that the gradient in this has two components j and this represents a vector that has a certain direction and that direction is exactly the same as this normal. So, we have looked at two ways of understanding the gradient there is a third way to understand that is closely related to that we discussed. So, first we said that the gradient is related to the directional derivative and the second idea we said is that the gradient points along the surface normal. So, now we can combine these two ideas to say that the direction of the gradient. So, when you move in different directions you have different values of the directional derivative.

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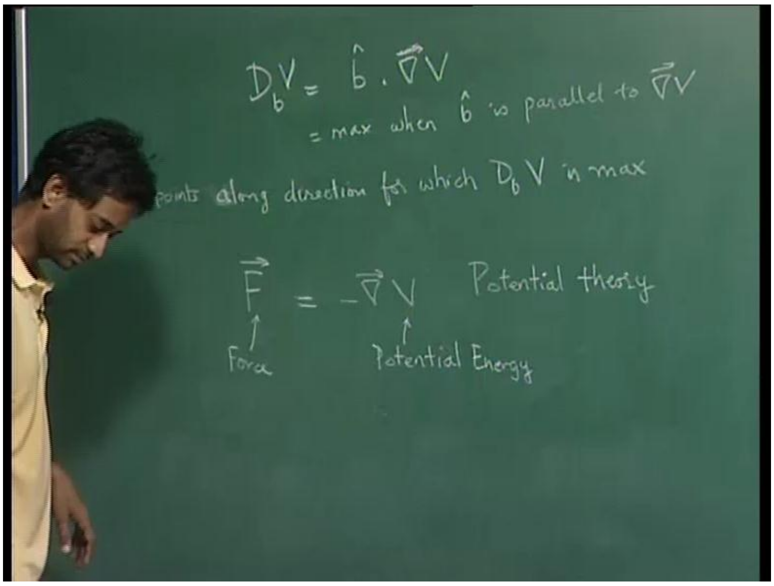

So, the directional derivative D b grad v, so the directional derivative of V is given by this. And so along directions you have different values of this directional derivative and the direction along which this derivative is maximum, this derivative will be maximum when b and grad V are pointing in the same direction, when b vector is parallel to the gradient vector this directional derivative is the largest. So, therefore, so this is maximum when d is parallel to grad V.

So, this implies that if somebody asks you what is the direction of grad V you will say that it is that direction along which the directional derivative is maximum. So, when the directional derivative is maximum, so it along direction for which is maximum. So, in other words you can say that gradient points along the direction for which this directional derivative is maximum. So, essentially if you can think of it this way that if you have this mountains and valleys kind of picture of your function of two variables then you go in different directions.

Suppose you want to know what is the direction of the derivative at any point, you try to move in this direction, in this direction, the direction along which the function changes the fastest is the direction of the gradient. So, the gradient points along the direction where the rate of change of the function is the largest or in other words where this directional derivative is the largest. Now, the gradient operator plays a very important role in multi variable calculus and one application, which we will discuss at the after the next lecture is that of potential theory where in which the gradient plays an important role.

Now it is just to give you an idea one of the there are many kinds of forces, which are called as conservative forces, which can be expressed as negative gradient of a of a potential. So, those forces that can be expressed in this form or called as conservative forces and these are almost ubiquitous in both physics and chemistry and so the existence of a potential allows you to say that the force is conservative and when and if you have conservative forces then there are some theorems on how to calculate the work done by a conservative force.

So, this is the topic of potential theory, which we will come back to when we are discussing the applications of the gradient operator, so this is this case this is force this is potential energy, so this is one application of gradients that you will see that you will encounter many times. Next let us look at the divergence and let us see if we can get some sort of handle on understanding what this divergence is…

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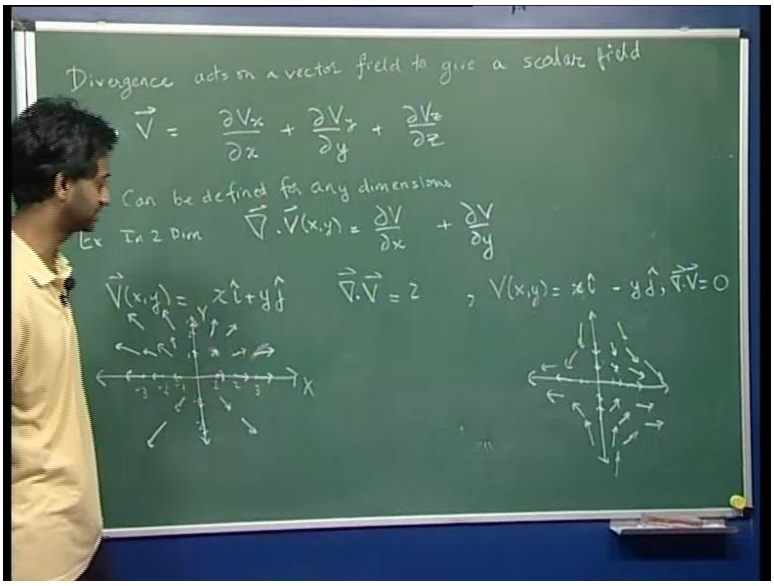

Now to do that let us start with the definition of divergence and if you remember it acts on a vector field to another vector field. And the definition of divergence is suppose del cross v is equal to sorry it does not give another vector field, it gives a to give a scalar field, so the divergence acts on vector field to give a scalar field. So, you can write the definition of the divergence as del dot v is d v x by d x plus d v y, so each of these are partial derivatives.

So, now how do we understand this quantity and to understand this first thing we notice that this can be defined for any dimensions. So, let us do example in two dimensions this is the, I think this should not be this is the definition of the of the divergence. So, let us look at examples of certain functions so let us take suppose V of x y is equal to x i plus y j, then you can immediately see that del dot v is 2, so del dot v equal to 2. Now let us say plot V of x y so in order to plot it we do, so we consider the x y axis and at each point you show the direction of this vector.

So, if you had a point, if I call this point 1, 2, so this point is x equal to 1 y equal to 0 and when x equal to 0 y equal 0 V of x y is just 0. So, it is just a a vector of length 1, along this direction, when x equal to 2 y equal to 0, this is a vector of twice a length, when it is 3 it is of thrice the length. Similarly, when it is minus 1 it is vector in this direction it is length increases. So, these arrows represents the direction of the vector field and the length of the arrow is proportional to the magnitude of the vector field.

So, these are vector arrows that represents this vector field at each point, so the value of the vector field at this point is represented by this arrow. So, you can extend this to the y direction and to the z direction and I am sorry to the minus y direction and you can even extended to other points. Let us say here you have x component is 1, y component is 1, so you have a the resultant the net vector points along in this direction.

And you it is not hard to see at this point the net vector will point along this direction if you take a point at 2, 1 the x component is 2, the y component is 1. So, you have a vector pointing along this direction and here you will have a vector pointing along this direction. In other words it is not hard to show that all these vectors they point radially outward and you can show it in this direction to and in all directions you can show this so here also it will be pointing.

So, what I have done is, I have shown a representative plot of this vector field and now we notice at the divergence is 2, which is not equal to 0 and the way to think of it is that you will look around the center and you see that the that the arrows seem to be increasing outwards it looks as, so there is a net flow of arrows outwards and this is what tells you that the divergence is not equal to 0.

So, the fact that you have a net flow of arrows outwards tells you that the divergence is not equal to 0, so the arrows are increasing in size and growing outward. So, it has so you have a source of arrows here and then they are slowly they are increasing and they are increasing both in length and they are all pointing outwards. So, the divergence is non zero. On the other hand if I had V of x y equal to x i minus y j now the divergence of this field, so in this case divergence is equal 0 and if you plot the field in this case what you will find is that along the x direction it is still the same but along the y directions it points out here the it points inwards.

So, along the y direction it points inward and if you look if you look along in if you look let us say at x equal to y. So, x equal to y equal to one in this point you can you can easily see that it points along x minus y, so it points along this direction. Similarly, if you go if you go to this point it will point along this direction and if you go to x equal to 1 y equal 2 it will point along this direction and if you go to x equal to 2 y equal to 2 it will point along this direction.

So, it seems to come this way and go out this way. Similarly, in this side you can show that it will go, so it seems to go similarly, this direction you can show that it will go and in this direction it will go. So, what you see is that is that in some directions the vectors are flowing in some directions they are flowing out. So, as a net result this point really does not act like a source of vector and therefore, the divergence of such a field will be 0. So, the divergence in some way is related to the net flow of these vectors and the flow is defined where the vectors change length.

So, the length of the vectors are changing the fact that they are longer here and shorter here that is the reason for getting a non zero divergence. Now, let us look at an example of where the divergence appears in some physical theory and theory that we will look at is the theory of hydrodynamics or which is one example of physical transport that we will study that you probably have studied or you will study in some of the courses.

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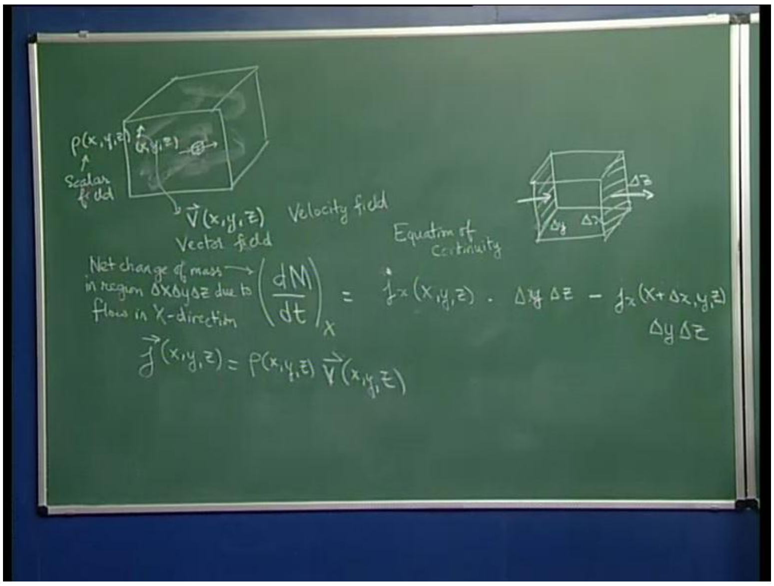

So, in hydrodynamics you think of suppose you have a volume and you have a fluid inside this volume and the fluid need not be stationery the fluid is moving. So, at each point the fluid has a velocity and the density of the fluid at each point is different, so at each point there is a density rho of x, y, z which is a scalar field and there is also a velocity. So, there is also a velocity of x y z, so you can ask which is a vector field? So, at any point x, y, z, so this point is x, y, z and at this point you have a local density and a local velocity field.

So, this is the velocity, so this is a scalar field and this is a vector field and it is these two fields that are fundamental in hydrodynamics. Now, you can ask a question suppose I had a volume d x, d y, d z suppose I had a or probably I should use the volume delta x, delta y, delta z. Suppose I had a volume delta x, delta y, delta z and I want to ask what is the net amount of fluid that flows into this volume. So, this is imagine that this is a very small volume lying somewhere in the fluid.

So it could be some volume like this here and you want to ask now what happens is that there is fluid flowing in and fluid flowing out and you want to ask what is the net, what is the rate of change of matter in this fluid. Now, because the mass of the fluid is a conserved quantity, so the total mass of the fluid has to be conserved. So, what you can say is that the rate of change of matter into the fluid should be equal to the net current.

So, how the amount of matter in this volume changes should be equal to matter flowing in minus matter flowing out and this leads to an equation called the equation of continuity. So, the idea is the following now you can ask in the x direction the net flow of matter so net mass flow in the x direction across this area delta x delta y is equal to the current in the x direction times is area across which this matter is flowing is this area which is given by delta y times delta z.

So, the current is the flow of matter per unit area per unit time, so you can say that d M by d t has to be in the x direction has to be equal to the current in the x direction. So, then you can ask what is the current. So, the current is a vector filed which is given as the product of the rho z. So, it is a product of the scalar field for the density times the vector field for the velocity so the product of a scalar times a vector is a vector; so it is a vector field that is given by this quantity.

So, it really measures how much fluid is flowing, so if the density is very high, the current will be high or if the velocity is very high the current will be high so then the rate of change of mass due to flow in the x direction per unit time will be given by the current times delta y times delta z which is the area. So, now this is the current that is flowing in if this is the positive x direction this is flowing in at x, then you have some current that is flowing in at x plus delta x.

So, minus j x of x plus delta x, y, z delta y delta z, so the net change of mass should be equal to this to this difference between due to the current flowing in and the current flowing out. And you can write this you simplify this expression as x to remind you this is the and this d m by d t in the x direction I can simplify this and write this as.

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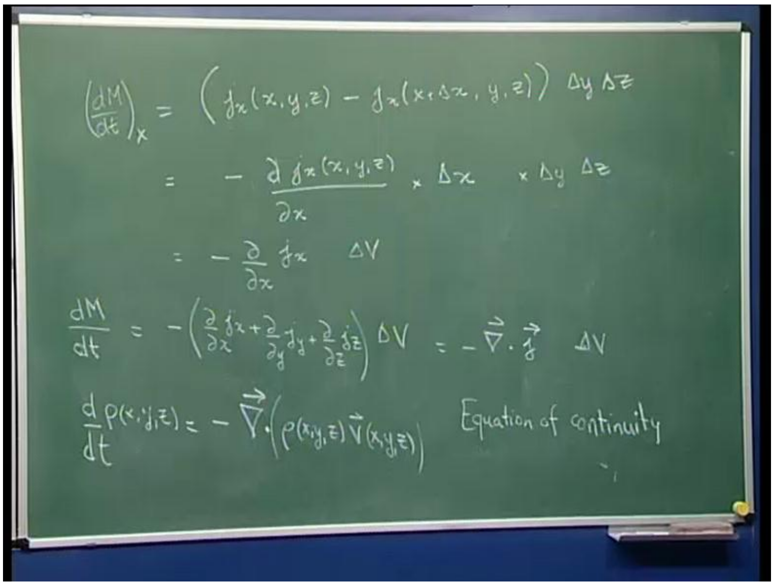

And now this if this delta x is very small, so if this volume element is very small, then this difference this is j of x plus delta x minus j of x. So, that is this is nothing but minus partial derivative of j x of x, y, z into delta x so this whole quantity you can write it in this form and you have to multiply by delta y delta z. So, in other words you can write this as minus j x delta v.

Now similarly, I can write similar expressions for d M in the y directions with it will be d by d y of j y and similarly, I can write d m by d t in the z direction as d by d z of j z. And if I add all of them up I can write d by d M d t is equal to minus times delta v and I can write this as minus the divergence of j into delta v and if I take this delta v on the left hand side and use the fact that m divided by delta v is nothing but the density. So, then I can write d by d t of rho which is the function of x, y, z is equal to minus del dot.

Now, I can substitute for j for j I can write j equal to rho times v, so del dot rho v and this is called the equation of continuity. Now, the important point about the equation of the continuity is that equation of a continuity only takes into fact that your total mass is the conserved quantity. So, the total change in mass should be related to how much mass is flowing in to and how mass is flowing out. So, it is just a statement about the fact that your total mass is the conserved quantity, so you are not creating extra matter by any process.

So, the flow of a fluid does not create any extra matter. So, this is an example of a place where the divergence appears and so you can you can imagine that you depending on the way the fluid flows depending on the properties of your of your v and rho this divergence can be zero or it can be non zero. Now, this is an example of an application of a divergence the equation of continuity we wrote it for the mass. So, that involves the rho but you can write similar equation of continuity for momentum flow and also for energy flow, which because momentum an energy of a fluid are also conserved quantities and these are things that you will see in any course on hydro dynamics.

Now, suppose I have a field that has let us say this current suppose this current has divergence zero at every point then such a field is called a solenoidal field, so a solenoidal field has divergence zero at every point. So, finally, I will just I will just mention briefly about the curl and to give the an example of the physical significance of the curl we will take another example of a field with a non zero curl.

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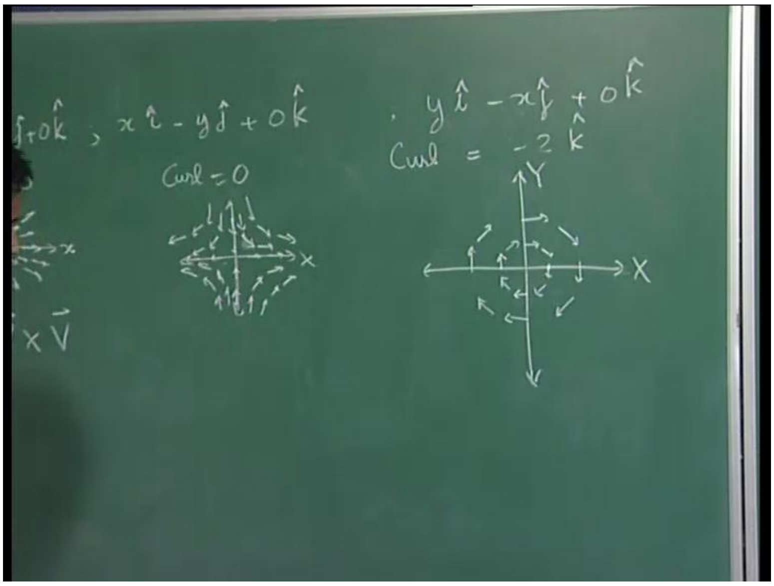

So, remember we had we had plotted these fields x i plus y j and we had plotted x i minus y j and now the curl equal to curl of v equal to del cross. So, since this is a cross product operation it is unique to three dimensions, so you need a three dimensional vector v in order to think of a curl. Now, suppose I take a to make this a three dimensional vector I make it 0 k, so the k component is 0, so these are vectors in the x, y plane. And now these two vectors if you calculate the curl, so curl equal to 0 and if you remember this the first field had a this property that it looked like this.

So, the first field x i plus y j in the x y plane it seemed to look like this and the curl was 0 and the and the other field that we talked about seemed to look like and both these fields had curl 0. Now, suppose instead of having this field I had a field y i minus x j, now the curl of this you can show this that the curl should be minus 2 k. So, the curl is related to the derivative with respect to with respect to x of this quantity minus the derivative with respect to y of this quantity, so the curl will turn out to be minus 2 k.

Now, if you look at the at this field, so y i minus x k. So, if you are at this point then it points in this direction similarly, if you are if you are here then it points along minus x. So, it points along minus x this way, so you can show easily that in each direction it points.

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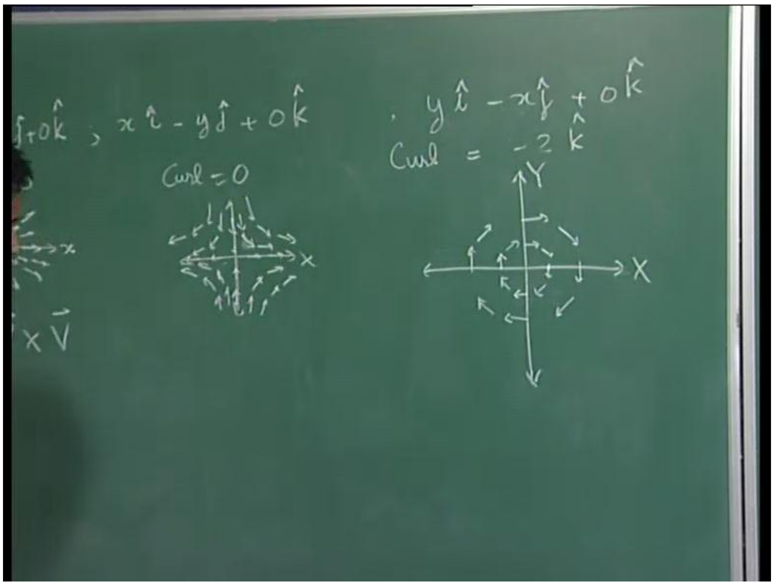

So, this will point the other way, so if you plot this field what you will get is the following, when x equal to 1 y equal to 0 then this points at along minus j. So, this is minus j it points along this direction, when x equal to 0 y equal to 1 it points along plus i when x equal to 0 y equal to minus 1 then it points along minus i. And similarly, when x equal to x equal to minus 1 y equal to 0 then it points along plus j and you can show in between that that it will form and the vectors will get longer as you go higher up.

So, what you notice is that unlike these fields, this field seems to have a net rotation in this direction and that is what gives it a non zero curl. And since a rotation is from is in the counter clockwise direction along y to x the sign of the curl is negative. So, far I hope I have tried to show you some of the physical significances of the gradients in divergence and curls and one of the best ways to learn more about these gradient divergence and curl is to actually plot various functions.

Now, as you can see it is not that simple to plot these functions it is very tedious and so you what I encourage you to use various programs like mathematic or mat lab or plot or whichever plotting program you have, usually in some of the modern plotting programs you can plot vector fields and scalar fields and you can actually get a get a physical field for what these various quantities are.

Thank you.