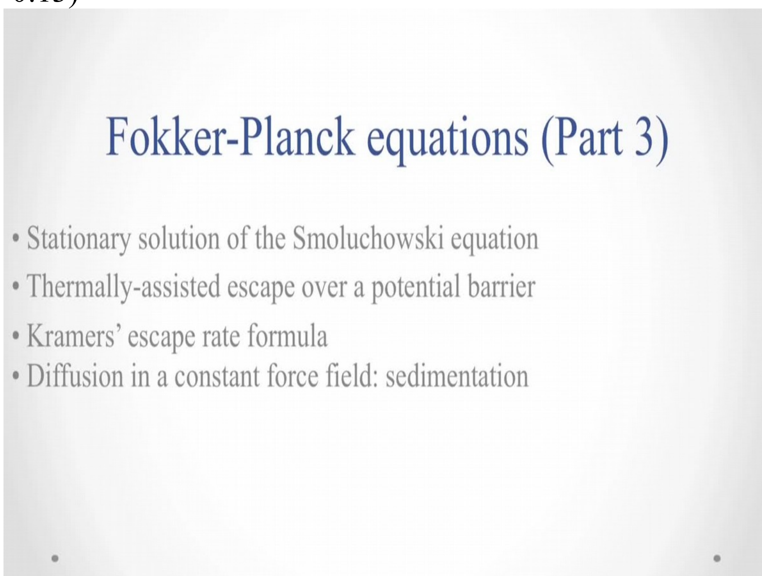
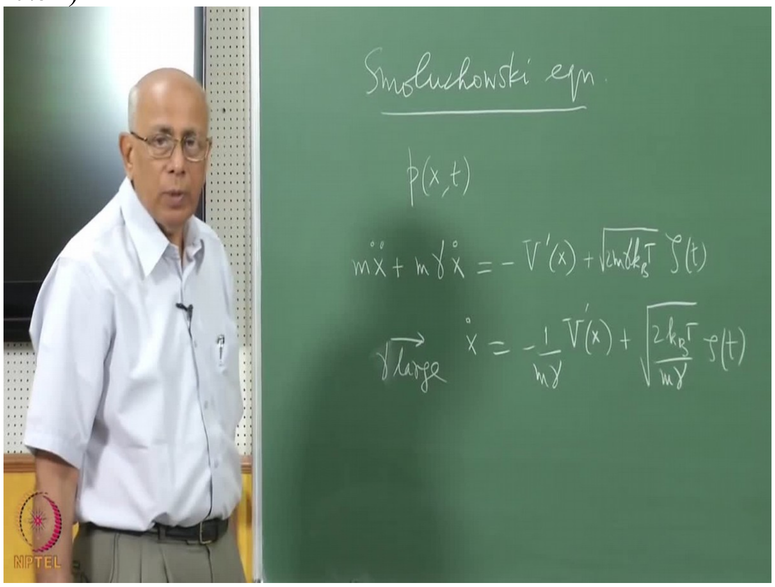
Non-equilibrium Statistical Mechanics
Professor V. Balakrishnan
Department of Physics
Indian Institute of Technology Madras
Module No 01
Lecture 19: Fokker-Planck equations (Part 3)

(Refer Slide Time: 0:13)



Right. So today what we will do is to look at one of the most important consequences of the equation for the density, probability density function for diffusion enough potential. It is called the smoluchowski equation as you know and we will derive from it other really important consequence. It is something which has wide range of applications. So to recall you what this smoluchowski equation was, we are looking at a one-dimensional variable X like the position of a diffusing particle on the X axis.

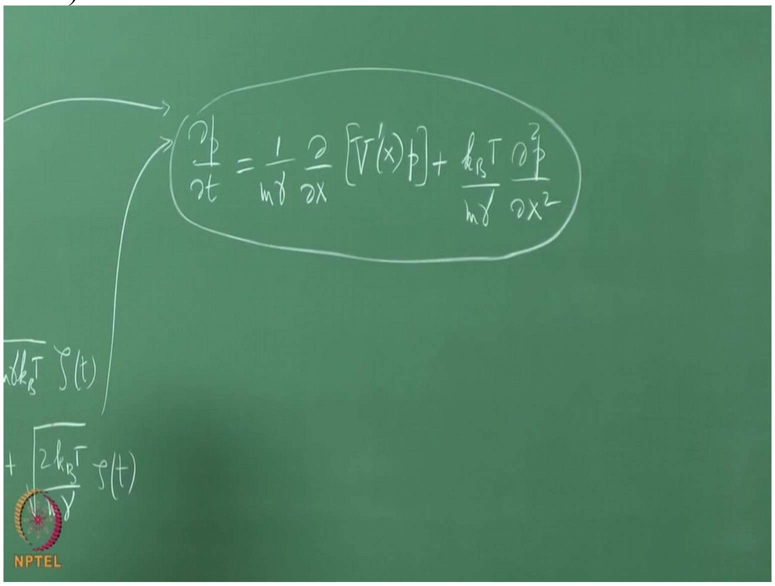
(Refer Slide Time: 0:51)

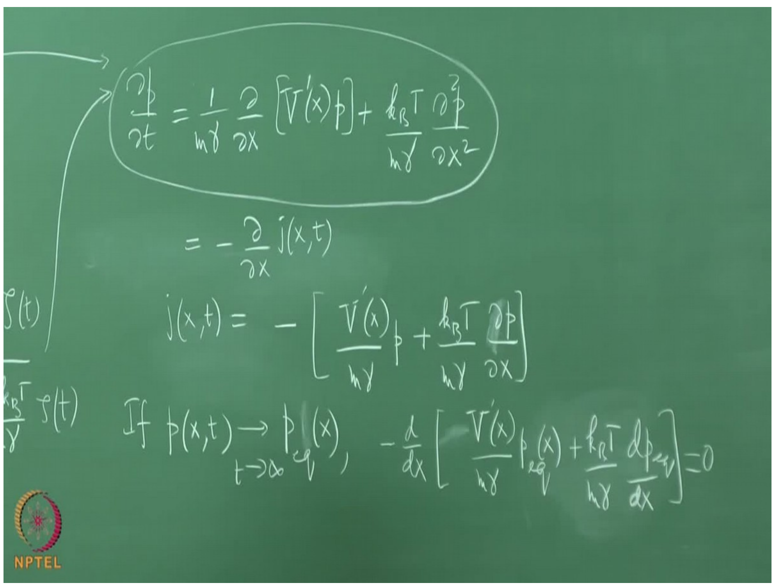


And then the smoluchowski equation was the equation for the probability density function P of X, T which is derived from the general Lounge equation in the high friction limit. So if you recall the equation in high friction limit the actual Lounge equation was MX double dot + M gamma X dot was equal to - the force on the particle which is V prime of X. And then there was a noise term which was essentially square root of 2M gamma K Boltzmann T times the white noise, the delta correlated white noise with unit strength here.

And then this went over in the high friction limit. So gamma large it went over to this equation, X dot is - 1 over M gamma V prime of X + the square root of this divided by gamma. So it is twice K Boltzmann T over M gamma times zeta of T. Now that is a Lounge equation in one variable with this drift term and that diffusion term. So it immediately follows that this quantity P of X, T, this conditional density with some initial condition satisfies the corresponding diffusion equation in the presence of a potential which we call the smoluchowski equation.

(Refer Slide Time: 2:34)





So this I think implies that delta P over delta T was equal to - the drift term, the derivative of it. So it is 1 over M gamma delta over delta X V prime of X times P, + the first-term + the diffusion term which is K Boltzmann T over M gamma. It is a square of this divided by 2, the G squared over 2 part times delta 2P over delta X2. This is the smoluchowski equation. This equation here is a smoluchowski equation. Okay. One of the questions, important questions is, is there a steady-state or equilibrium distribution at all? So let us start at that point.

If at all there is such a distribution we are saying that P of X, T if tends as T tends to infinity tends to P equilibrium of X, then this quantity, P equilibrium of X must satisfy an ordinary differential equation with this set equal to 0. And that equation of course is 1 over, is K Boltzmann T. It is the following. Before that, before I write this, notice that this equation because this is a derivative, it can be pulled out on the right-hand side, could be written as equal to - delta over delta XJ of X, T, some current.

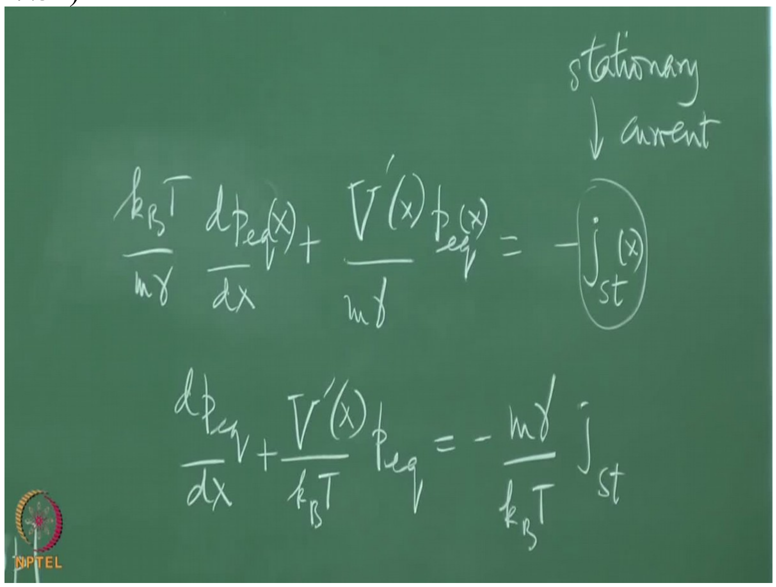
So this equation has the form of a continuity equation, delta rho over delta T + divergence of J equal to 0. So it has got exactly that form but this J was X, T equal to - whatever is inside this D over DX here. So it is - V prime of X over M gamma P inside there + K Boltzmann T over M gamma delta P over delta X. All I have done is to write out delta over delta X outside and then times this bracket here. So this if you like is the current, the probability current.

And now if P of X, T tends to P equilibrium of X as T tends to infinity, then it means delta P over delta T is 0 and therefore, this quantity here, D over DX of this guy must be equal to 0 okay. So this will imply that D over DX of this fellow is 0, so it says D over DX of - V prime of X over M gamma. - D over D X of V prime of X + K Boltzmann T, I want to retain these factors for a minute as you will see why. DP equilibrium over DX times P equilibrium.

So let me write these factors out carefully. P equilibrium of X + K Boltzmann T over M gamma DP by DX must be equal to 0. Which means that this quantity is a constant. And if it is a normaliseable distribution, then we would say the constant is 0. It is 0 at infinity, so 0 everywhere. And then you would get a sample solution for P equilibrium of X. On the other hand, it is conceivable that we could look at this as a problem in which you have a steady flux of many particles coming in with standard flux.

And you know, there is some complicated potential these particles are riding through under thermal agitation as well and then there is a flux outwards. So there is a stationary current. So it is possible there is a stationary current in the problem which we do not know as yet.

(Refer Slide Time: 7:32)

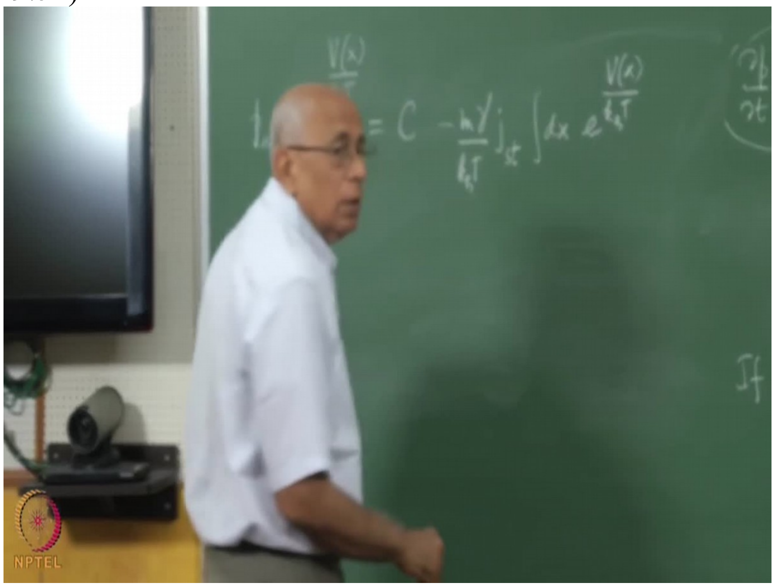


So the general solution is not that this quantity equal to 0 but that this quantity is equal to a constant, right? So this means that the general solution is that V prime of X over M gamma P equilibrium of X. Or let us write the derivative term 1st. So K Boltzmann T over M gamma DP equilibrium over DX + V prime of X P equilibrium divided by M gamma is equal to - J stationary. So this is some stationary current. Because it is stationary, it is a function of X alone just as these fellows are all functions of X. That is the general solution to this equation right.

So what does that imply? It says DP equilibrium over DX + V prime of X over K Boltzmann T P equilibrium is equal to - M gamma over K Boltzmann T J stationary. And if it is a flux which is moving smoothly, constant, uniform flux, it is a constant, the constant is a some number then right? So you can pull that out and you have to solve this equation with this constant, as some constant right. And what is the general solution to this equation? Well, it depends on the initial condition but suppose I have an arbitrary initial condition, I will integrate this equation without specifying an initial condition with an integration constant put in there.

So the general solution to this equation pretending for a minute that we know this J J stationary. So pretending that we know this constant, we will determine it in a self consistent way is the following.

(Refer Slide Time: 9:54)



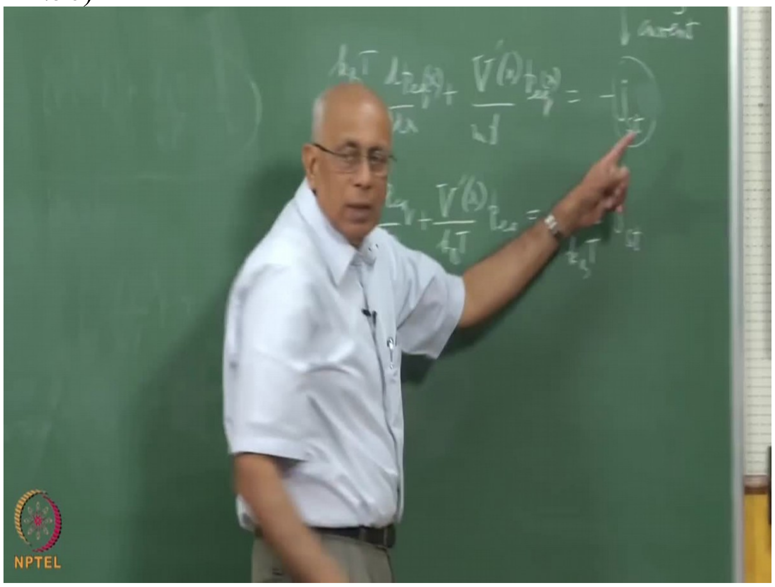
So it says, P equilibrium of X E to the power you have to integrate E to the integral PDX this is a function P which is V of X over KT. So this says P equilibrium E to the V of X over K Boltzmann T is equal to some constant, integration constant - M gamma over K Boltzmann T J stationary whatever that number is times an integral DX E to the integral PDX. So E to the power V of X by K Boltzmann T. That is the solution okay. And if I move this factor to the right-hand side, then it is this. E to the - V of X over K Boltzmann T.

So notice, we still have to do this integral and we do not know what this V of X is in general. But formally we can write the solution down. If you tell me and you measure a steady flux at some point in the X axis and then you say that that number is J Stationary. Pardon me?

Student: J could depend on X?

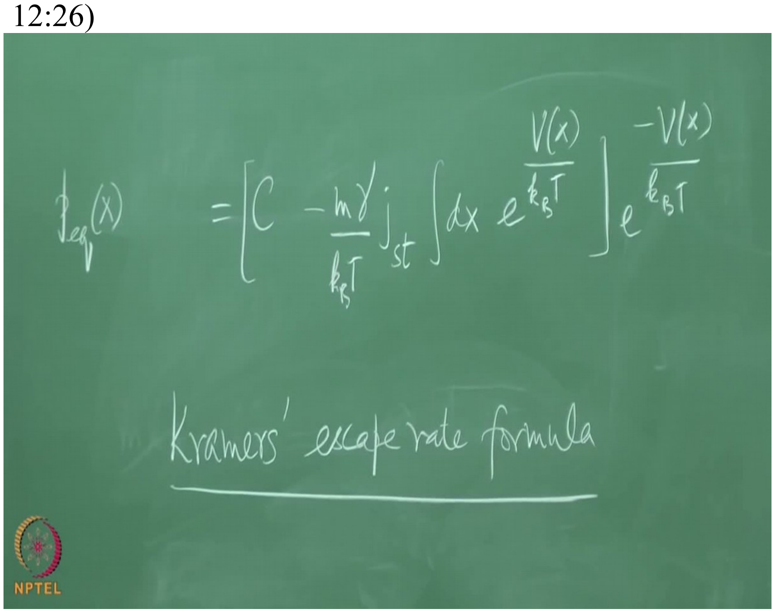
Professor: No, I am saying that it is a stationary current, it is a constant. D over DX of something is equal to 0 which implies this something is equal to a constant. J stationary has to be a constant because it will have to satisfy the continuity equation right and the P corresponding P is 0 and derivative is 0. So J stationary has to be a constant. Sorry, this is wrong.

(Refer Slide Time: 11:56)



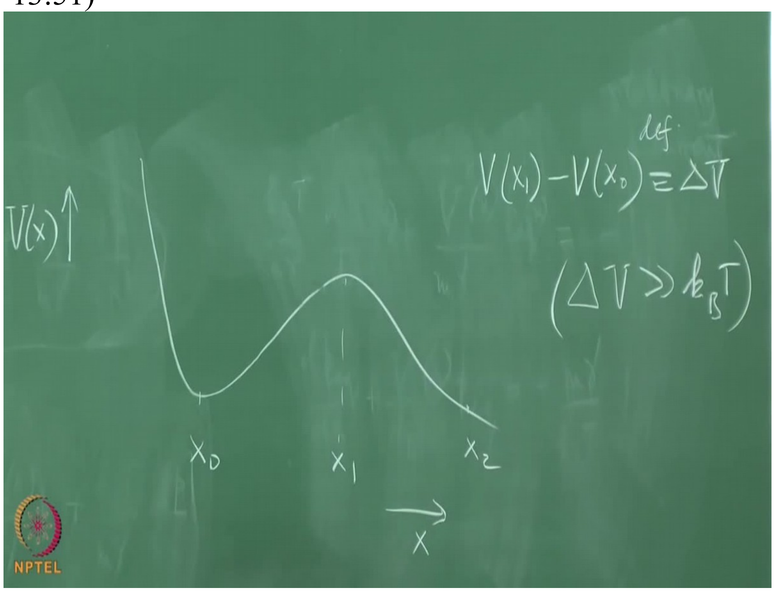
This is wrong. Yes, I should not have put that X there. It is a constant. So that is the formal solution. And to write it down explicitly, you have to give me some boundary conditions. You have to tell me at X equal to what other point, some X not or something, you will tell me what this is and then in terms of that, I determine T, put this side. Okay. Now let us apply this solution to a very crucial problem.

(Refer Slide Time: 12:26)



And this problem is called Kramer's escape rate formula and we are going to derive this formula okay. Now the formula itself envisages the following. Suppose you have a particle moving in a potential and the potential has ups and downs and so on and at some point, it encounters a minimum of the potential. You would expect that the concentration of particles is very high in the minimum, very low in the maxima of the potentials and somewhere in between between the extremes right. Now you could ask, because there is thermal agitation, particles have been kicked all time, is there a possibility that a particle might jump over the barrier and go to the other side of a maximum okay? And if so, at what rate is it doing? So the general scenario envisaged it is the classical thermally assisted process, completely classical. So it is the analogue of quantum mechanical tunnelling. Tunnelling happens because of quantum physics. There is no classical tunnelling at all but the following can happen.

(Refer Slide Time: 13:51)



Let us suppose that the V of X looks like this. There is a minimum somewhere and then there is a maximum and then it goes off in this fashion. Okay. So if I schematically say, this is V of X vs X on this side, you could ask, if I start with a particle here, at what rate will it have flow outwards across the maximum to the other side. At what rate will it escape the barrier? Now you could ask, why should it escape the barrier? Well, if you put a particle here with this 0 kinetic energy, it is just going to remain here but remember, it is being buffeted by thermal agitation.

So all the while there is kicks which are moving the particle and now the question is what is the escape rate going to be? It is a hard problem if you have quantum mechanical tunnelling and if your KT is so high, this is an energy scale in the vertical side, is so high that the barrier is not even visible to it. But what happens if KT is much smaller than the height of the barrier? So that is the question we are going to look at. Let us give some names to these points. So let us say, this point is X not, this point is X1, some point here is X2 and I want to know, what is the rate of escape of particles if there is a steady flux coming in from one side from the region around X not to a point like X2. So this is the question we would like to answer.

Student: (())(15:22).

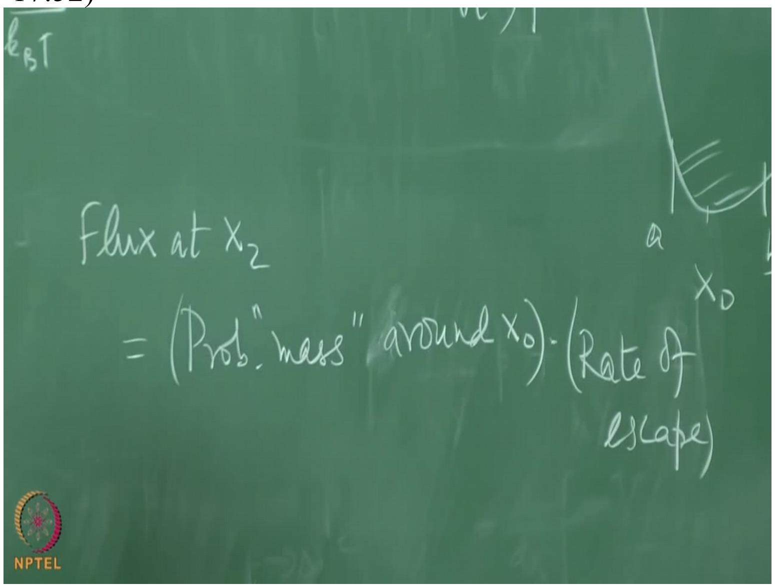
Professor: Yes so I am not worried about what happens here. I would like to know, what is the rate at which particles escape the minimum, can go across the maximum and get to the other side of it. Precisely where on the other side, is in a relevant detail, I can compute it for any point okay. The assumption is that V of X1 - V of X not which I will call Delta V. This is the definition of the barrier height with the maximum - the minimum. That is the height of the barrier. The assumption is, that is much bigger than the energy imparted by a single thermal agitation, by KT, much greater than KT. So Delta V much much greater than K Boltzmann T.

That is the regime we are interested in. Now you can see why this is going to be a tricky problem. Because you have a particle here. Imagine, it has got 0 kinetic energy. It gets kicked to the right by thermal agitation KT, typically KT energy, it goes up a little bit but then it gets kicked back and so on. It will oscillate about this point, move randomly about this point. To get it across this barrier, in some fashion, you have to coherently kick it with a lot of KTs all in one direction. So it is very improbable, it is very improbable but it is a nonzero probability and the question is to calculate what it is. Yes?

Student: (())(17:06)?

Professor: Yes, so we are going to make that, we are going to say there is a constant flux of particles coming in. So for some given constant flux, what is it? In fact we are going to do something better. We are going to argue and we know this that the equation, the diffusion equation obeyed by the concentration of particles is the same as the diffusion equation obeyed by the probability density for a single particle if they are not all interacting with each other. It is the same diffusion equation. So in a sense, either I talk about the concentration of particles here or I talk about the probability mass of the particles here.

(Refer Slide Time: 17:52)



So I am going to ask a general question. I take particles in some region, A to B. And I ask, how many particles are there? It is same as the integral of the probability density, equilibrium density from A to B. And I ask, what is the flux at a point like X2? And the answer is that the flux at X2 on the right-hand side is equal to the probability mass around X not multiplied by rate of escape of each particle. So I find the constant rate of escape of each particle, multiply that by the probability mass and that is the flux at X2. I am interested in computing this rate of escape.

Now you can see that this is a paradigm for a large number of processes. Any thermally assisted process which involves an activation barrier is precisely this problem. For instance, if you have molecules here and you have reaction, chemical reaction, and there is an energy barrier against this reaction. So the molecule here has to kick the molecule there in order for the reaction to happen but there is an energy barrier in between. Then the rate of this reaction is going to depend on the rate at which this escapes the barrier and gets there.

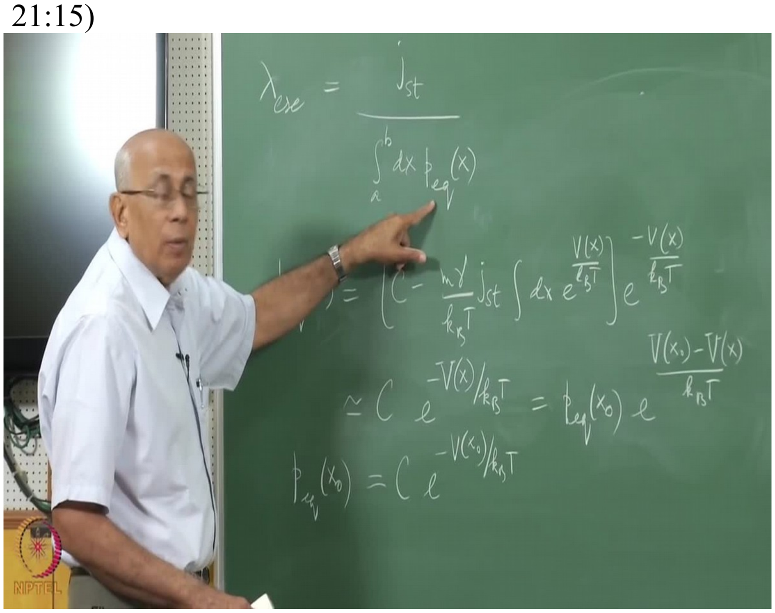
So in that sense, this is a very general formula. Now the question is, how is it going to depend on this height and how is it going to depend on the temperature given the fact that this height is much much greater than the temperature? So that is the question that we are going to answer and that is going to give was the final answer for this rate of escape which is called the Kramer's escape rate formula. So it surely has to do with the shape of potential here, the shape of potential there and so on. They are going to play a role, the height of this potential barrier is also going to play a role.

Student: (())(20:16)

Professor: It is biased in the sense that the moment you have potential, it is biased at every point. And that is the reason why in the smoluchowski equation, you got a drift come. So the drift term is acting like an X dependent bias if you like. There are times when it will be favourable to one direction, favourable to the other. It depends on V of X, V prime of X. We will look at the problem of a constant bias like gravity. We will do that at the end but here we have got a much more general question.

And right now we are looking at the problem of an escape over a barrier. So definitely the potential is assumed to have a minimum and a maximum and we would like to compute these quantities here. So the rate of escape is what we want to compute but 1[st] we need to compute the probability mass. So let us remember this formula.

(Refer Slide Time: 21:15)



The rate of escape, Lambda escape rate is equal to flux at X2, that is the stationary current. So this is J stationary divided by the probability mass around the point X not. So divided by an integral from A to B DX P equilibrium of X, so this is what we want to compute and we are going to make a number of approximations in doing this because the formula is an approximate and you will see how good the approximation is as we got. Now 1st step. Now we already found the formula for P equilibrium and you have to tell me what it is. It was if I recall right, it was C - M gamma over K Boltzmann T no times an…

Student: J stationary integral.

Professor: J stationary integral DX E to the power V of X over K Boltzmann T. This is an indefinite integral. So it is a function of X. Multiplying E to the - V of X over K Boltzmann T. But you see we need to do this to do, to find this, we need to find what is J stationary. So this fellow is sitting right here in this thing here. But now I am going to argue that this J stationary is small, is negligible because that is a small flux. How many particles do you expect to come out here? It is a highly improbable thing.

So to leading approximation except you cannot kill it here. Then of course, there is nothing but anything which comes from here, goes up, goes to higher-order in J stationary. So to leading order in the denominator, we are going to kill this here. So this is approximately equal to C E to the - V of X over K Boltzmann T. So I want you to understand clearly that this is self consistent. This whole thing is an approximate formula. We are finding the leading contribution under these conditions. So this going to give you higher-order terms including it.

But in the leading order, this is what it is. But there is a unknown constant sitting here. How are we going to determine that? Well, if this is true, then it is immediately clear that P equilibrium of X not whatever that be, whatever that be, at the minimum of the potential, is equal to the same constant C E to the - V of X not over K Boltzmann T right?

Student: (())(24:18)

Professor: I do not care, I do not care. You specify what A should be, what B should be because you will see that this answer is going to become independent of A and B due to the nature of the integrant as you will see in a minute. In just a minute we will come to that. So P equilibrium is this quantity and the ratio of the two Cs cancels out. So you could also write this as equal to P equilibrium of X not which is itself unknown times E to the power V of X not - V of X over K Boltzmann T. So I got rid of this but in favour of this constant. Now I need to integrate. Yes?

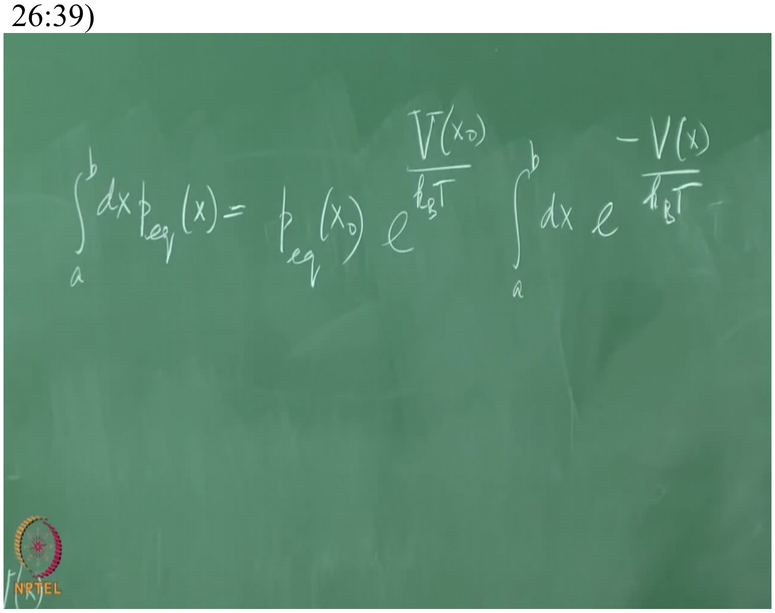
Student: (())(25:12)?

Professor: At any point. So what is happening is, what we are envisaging is way out here, you are going to insert particles at stationary rate and they are going to come out at the stationary rate but the question is, how is this barrier affecting that J stationary? Yes, it will depend on the X will depend on this flux. It is a constant, it is independent of X because that is how we defined J stationary. It was the integration constant on the right-hand side right?

We had D over DX, this current, this DP whatever it is equal to 0 and therefore that whatever in the bracket is equal to a constant and that has got the significance of a current, some stationary current right? So the question is how is this barrier affecting it? So essentially what we are asking is finally, the final question is, given that the A particle starts here, what is the probability that it is going to be formally assisted to get out of here? Okay even if you wait for a long long long time what is going to be the probability?

All right. So we have a formula for P equilibrium but integrate it from A to B. Let us do that.

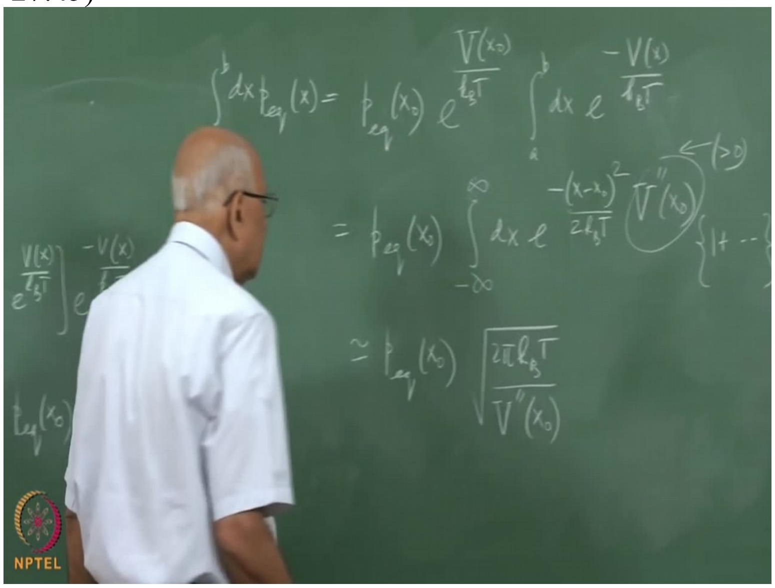
(Refer Slide Time: 26:39)

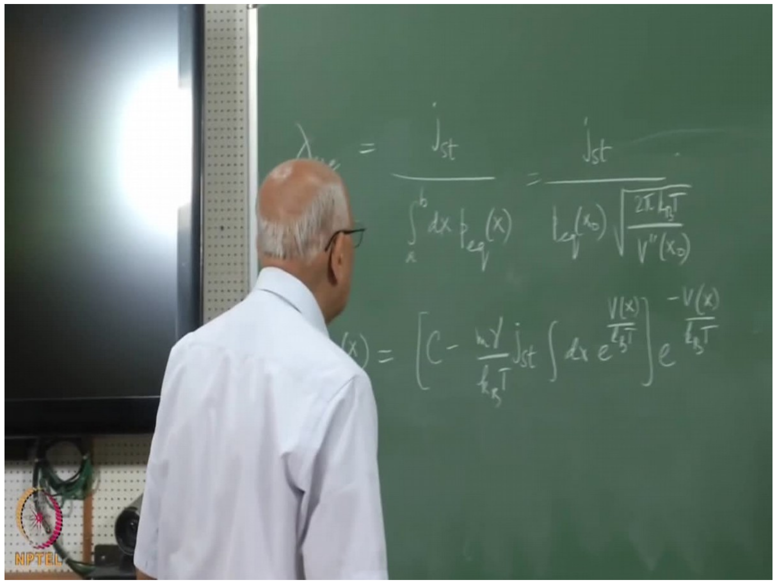


Therefore integral A DX P equilibrium of X, this is a constant, so it comes out. P equilibrium of X not E to the power, V of X not comes out. And then you have to integrate integral from A to B DX E to the - V of X K Boltzmann T. We have to do this integral. Now look at the nature of this integration. You have got E to the power, the function in a neighbourhood of the minimum at this point right? So whenever V of X not, V of X is large, this integral die dies down because of E to the - and the largest contribution will come from the minimum of the potential because that is where V of X out there has this integral is going to make sense.

It is going to be nearest, E the 0 which is 1 right?

(Refer Slide Time: 27:45)





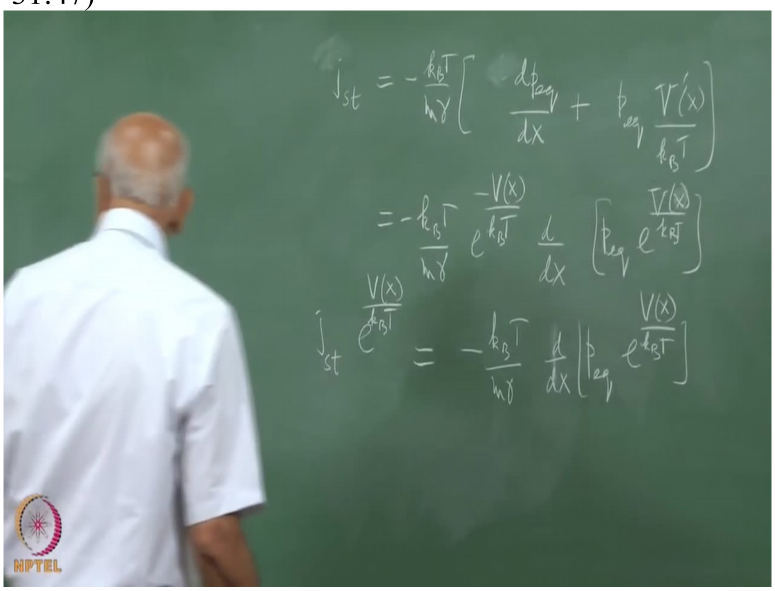
So this means you can write V of X equal to V of X not + X - X not V prime of X not which is 0. So this is now a straightforward Gaussian integration. That is 0 + X - X not whole squared over 2 factorial V double prime of X not + higher-order terms. And they are all sitting in the exponent. So this means, you can take this out. We can write as P equilibrium of X not E to the - the leading term is V of X not which cancels this, goes away and then you have an integral A to B DX E to the - X - X not whole square over 2 oh, there is a K Boltzmann T also.

So K K Boltzmann T here and then V double prime at X not into 1 + higher terms because I can write the next term, the cube term by taking it out down here, by expanding the exponent but the leading contribution comes from here. That is like a Gaussian integral and in a Gaussian integral, the bulk of the integration comes from the maximum of the potential. And due to the - AX square, the bulk of the contribution comes from the point near the origin. And the rest of it is exponentially down. So this is a standard approximation.

It is called, it goes by many names, it is the starting point or something called the method of steepest descent, the method of mother phase method and so on, saddle point method. It has got many many names. We are looking at the simplest version of it okay. And then in the same spirit, you can actually extend this integral from - infinity to infinity because again, the contribution comes from just the centre, everything else is exponentially down. So the dependence on A and B is gone over here.

And we know the formula for this. E to the - AX squared is square root of pi over A from - infinity to infinity provided A is positive. That it is. KT is positive and this is at a minimum of the potential. So the 2nd derivative is positive. We are sure about that. So this quantity here is greater than 0. So this is P equilibrium of X not and then this exponential factor is gone, square root of 2 pi K Boltzmann T divided by V double prime of X not. That is a denominator. So this is equal to J stationary divided by P equilibrium of X not square root of 2 pi K Boltzmann T over V double prime X not. We set that aside okay. It is going to come because we still have to find J stationary right? We still have to find J stationary. So how are we going to do that? Well we have got to go right back now and put things in. So how are you going to find J stationary? We have a formula for, we need a formula for this guy.

(Refer Slide Time: 31:47)



We have this fellow sitting here. What are we going to do next? How are we going to find J? D you have to remind me of this equation. J stationary pardon me?

Student: - V prime of X…

Professor: Yes, 1 over M gamma.

There is a - sign, so there is a DP equilibrium over DX. So let us pull out KBT here. + P equilibrium times there was another term, V prime.

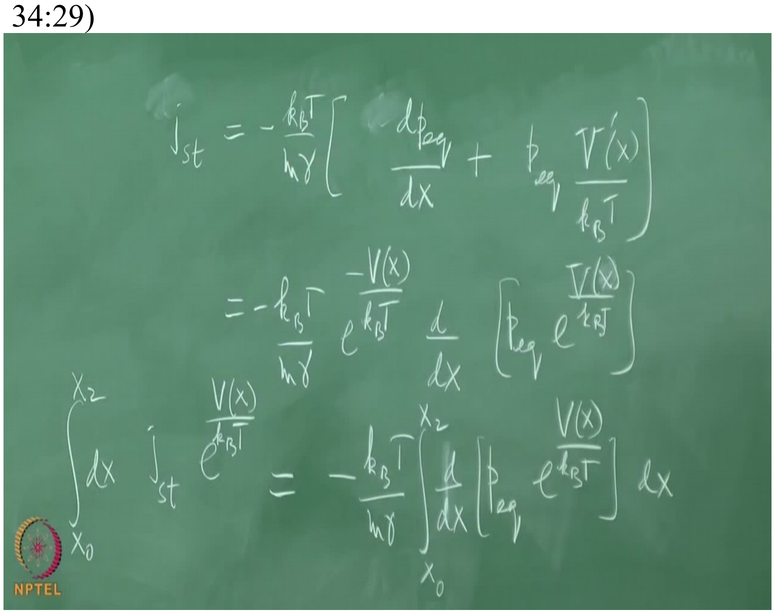
Student: (())(32:32)

Professor: Exactly.

So that was J stationary, right which is equal to - KBT over M gamma I will write this as a total derivative. So I can write this as D over DX times D over DX of P equilibrium times E to the power V of X by K Boltzmann T because it looks like a total derivative. If I do this, I get DP over DX times the exponential + P equilibrium times V prime divided by KBT but I should now compensate for that E to the. E power - V of X over KBT. So I rewrite it in this form. Therefore, J stationary multiplied by E power V of X over KBT is therefore equal to - KBT over M gamma D over DX P equilibrium E the V of X over KBT.

If I get this right with all the factors and so on, it will be a miracle because I want to be careful about the factors and not make a mistake somewhere because then it means the formula, I know the final end product formula. That is very easy to remember. So I just want to make sure I get all the factors right. Okay.

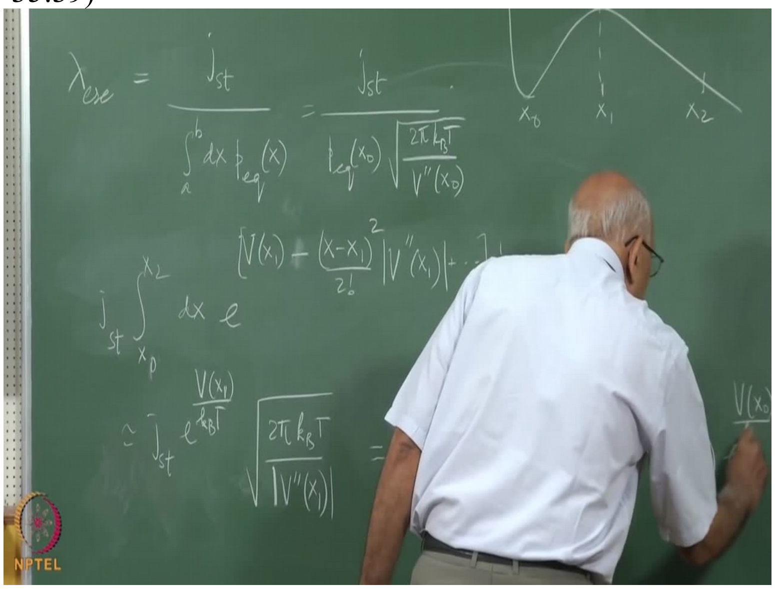
(Refer Slide Time: 34:29)

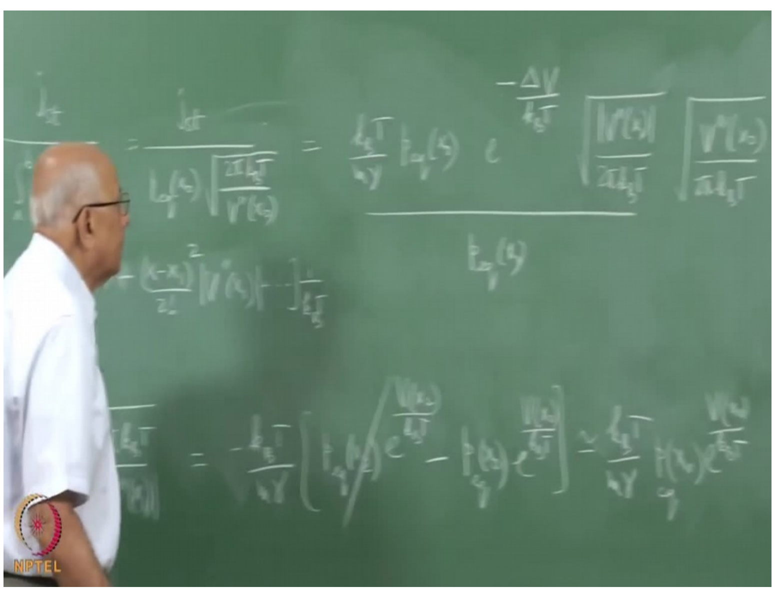


And now let us integrate this from remember the geometry, we have a thing like this and then went off. This fellow was X not, this was the peak X1 at this point and then we looked at some point X2 here. So let us integrate this from X not to X2 all the way.

Let us integrate DX from X not to X2. Let us integrate this. So this is integrated, X not X2 DX. So remember, this is some horrible function. We do not know what it is but I am go except that it has a shape like this and I am going to integrate it from X not to X2. What is appearing on this side is E to the VX with a + sign. So again this is going to contribute the maximum at the maximum of the potential. Elsewhere, it is going to drop down very very rapidly right?

(Refer Slide Time: 35:39)





So now let us write this therefore as integral from X1 to X not to X2 J stationary out there and then DX E to the V of X, let us do an integration saddle point Gaussian integration around the maximum of the potential X1. So I will write this as E the power V of X1 and again the 1st derivative is 0. So the next tem is X - X1 whole square over 2 factorial V double prime at X1 + higher-order terms, the whole thing divided by KT. That is the left-hand side which is approximately equal to J stationary E to the V of X1 over K Boltzmann T times a Gaussian integral. But it has got a + out here.

However, you are at a maximum and therefore, the 2nd derivative is guaranteed to be negative. So therefore I can write this as modulus and there is a - sign here. That integral is equal to square root of pi over A in the formula, square root of 2 pi K Boltzmann T divided by modulus of V double prime of X1. That must be equal to on the right-hand side, this integral out here from X not X2 of a total derivative right? So this is equal to - K Boltzmann T over M gamma times always have to do is to write now P equilibrium at X2 E to the power V of X2 over K Boltzmann T - P equilibrium of X not E to the power V of X not over K Boltzmann T.

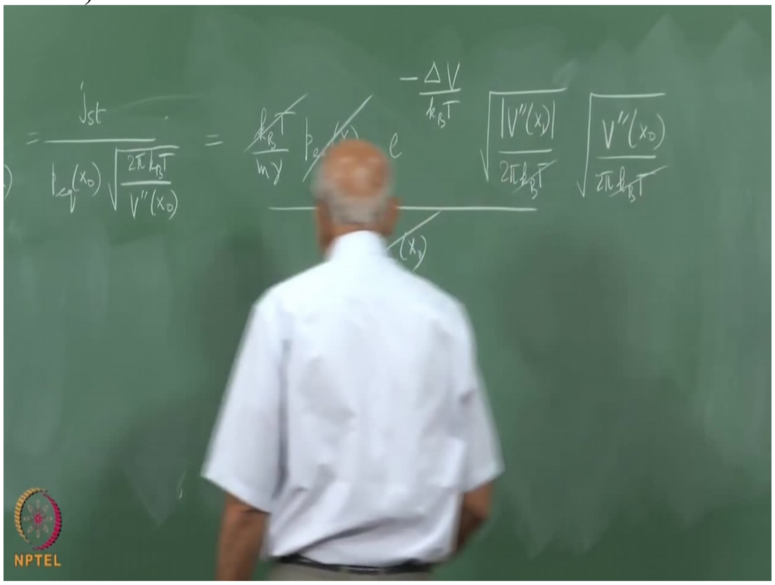
Is there a + sign or a - sign? There is a + sign. It is a + sign (())(38:18). I am not too thrilled by that. That is okay, that is okay. We have to go where it takes us. Now the probability itself at any point is vanishing out here like X2. Most of the probability mass is sitting in here, out here. Therefore compared to this term, this term is negligible. Potential is concerned, they do not make a difference. They are of the same weight. So these factors are of the same model but this thing here is much smaller than that okay?

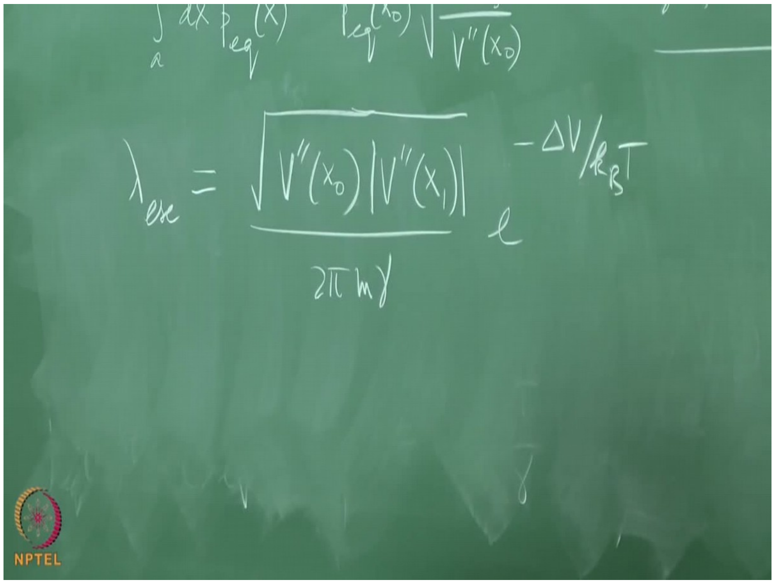
It is very improbable that you find something at X2. So we neglect this and you get approximately this thing here is approximately K Boltzmann T over M gamma times P of equilibrium of X not E to the power V of X not over K Boltzmann T and we are nearly home. So this says, J stationary, take everything to the right-hand side and this therefore is equal to K Boltzmann T over M gamma P equilibrium of X not is still sitting there. I move this factor to the right-hand side, it comes with a - sign and this is a + sign here.

So E to the power - Delta V at last over K Boltzmann T, that is sitting there. And then take this to the right-hand side. So square root of modulus V double prime of X1 divided by K Boltzmann T divided by this guy, the whole thing divided by P equilibrium of X not and then this factor. So I can again write this oh there is a 2pi right? And then this goes up in the numerator once again. So this is V double prime of X not divided by 2 pi K Boltzmann T. And notice P equilibrium of X not cancels out. We do not know this number.

We are not able to compute that number without actually solving that full equation and finding out what the steady-state solution is but it mercifully cancels out.

(Refer Slide Time: 41:09)





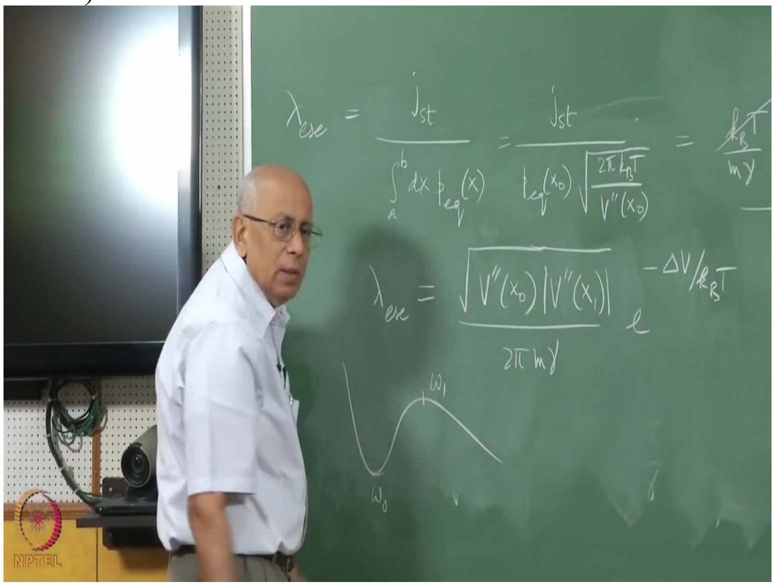
The T cancels out as well. So the K Boltzmann T cancels this and this. So we finally get this lambda escape equal to square root of V double prime of X not modulus V double prime of X1 divided by 2 pi M Gamma E the - Delta V over K Boltzmann T. This is the Kramer's escape rate formula. So it tells you that the rate at which this escape happens depends exponentially on the barrier height with a 1 over KT. That is precisely of the Arrhenius form and as you know, this is an extremely sensitive function of the temperature. A small change in the temperature changes things enormously, the rates of chemical reactions which are thermally assisted, changes enormously with the temperature for a given barrier height.

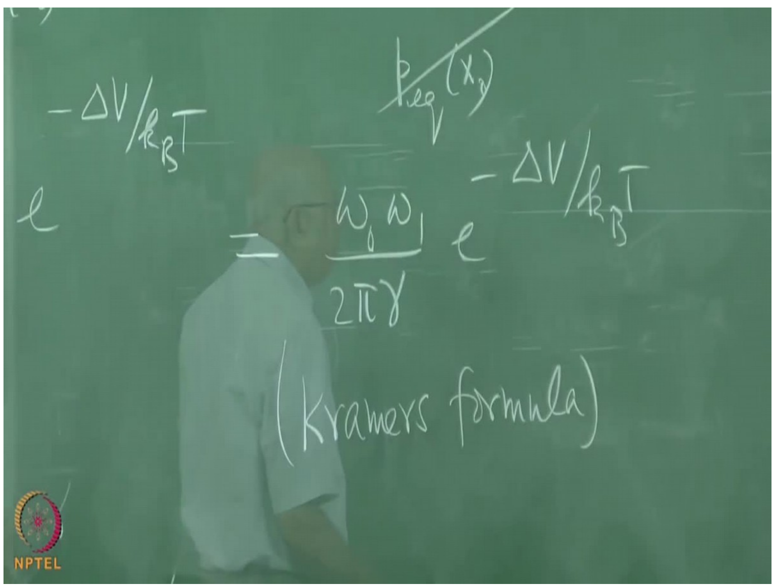
Similarly once you increase the barrier height, this exponentially becomes more difficult to happen. It justifies post-facto assumption that the probability is actually pretty small, the escape rate is pretty small. But this is indeed non-perturbative in the sense that it is not power series in Delta over KT or anything like that. It is actually this is an exponential form in 1 over T okay. That is why chemical reactions require very high temperatures in general unless of course you have enzymes.

Otherwise, given just think about it. Every time you take in food, your system actually breaks down these complex molecules and makes other complex molecules but when you cook food, you do so at a very very high temperature. That is how much energy it takes to break those bonds down right. On the other hand, you ingest this food and your stomach does it actually effortlessly apparently at 37 Celsius. So it would have come down enormously, the rate of reaction but it is working because there are enzymes. But this temperature dependence of the Arrhenius formula, this thermally activated processes is very typical.

Multiplied by these factors here, now geometrically of course, these are curvatures point of the potential at that point. So you can write this in a very compact way. That is the way it is normally written.

(Refer Slide Time: 43:45)





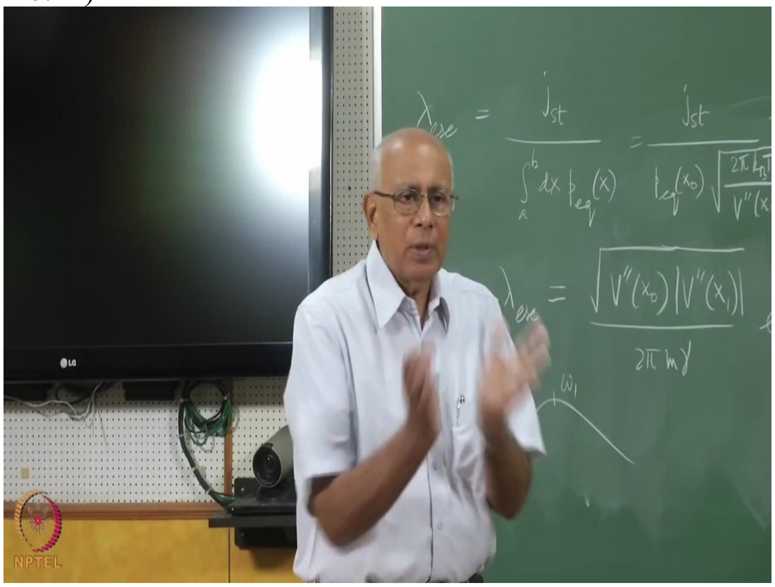
You can say well, if I have a potential like that, around this point, this curvature can be subsumed in the frequency of harmonic oscillations about this minimum. So let us call that frequency omega not around the point X1 X not. And similarly, this is an inverted parabola. So let us call the frequency of this inverted parabola, the harmonic approximation, let us call that frequency omega 1. Then of course, this curvature here, V double prime this is equal to, this thing here it is M omega not square and this is M omega 1 square and the M cancels that way. So this gives you a nice little formula. It is omega not omega 1 over 2 pi Gamma E to the - Delta V over K Boltzmann T. This is the Kramer's rule. That is a simple derivation ofthis formula. Now we can put in all the various complications and so on. For instance, you could ask what happens if this is potential barrier height is brought down, KT is made larger? What happens if you have more singular potential and so on? What happens if you have quantum tunnelling assisting this formal process?

These are complicated questions but they do have physical applications, physical importance. But in the simplest instance, this is the way the Kramer's formula is derived. The ingredients in it are the curvature at the minimum, the curvature at the maximum of the potential at the height of the barrier, at the bottom of the barrier and the energy difference, the potential difference with the temperature appearing here. This is a very mild dependence on temperature, powers and so on. But the pre-factor as it turns out in the leading approximation is not even temperature dependent.

Yes, now we have assumed that things are, curvature exists, it is finite, et cetera, et cetera. So you will have to do those case-by-case.

Student: (())(46:09).

(Refer Slide Time: 46:12)

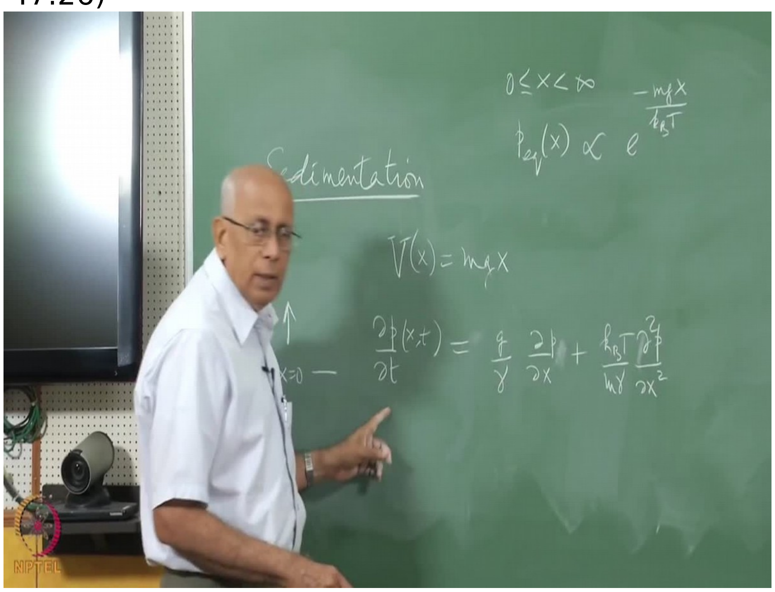


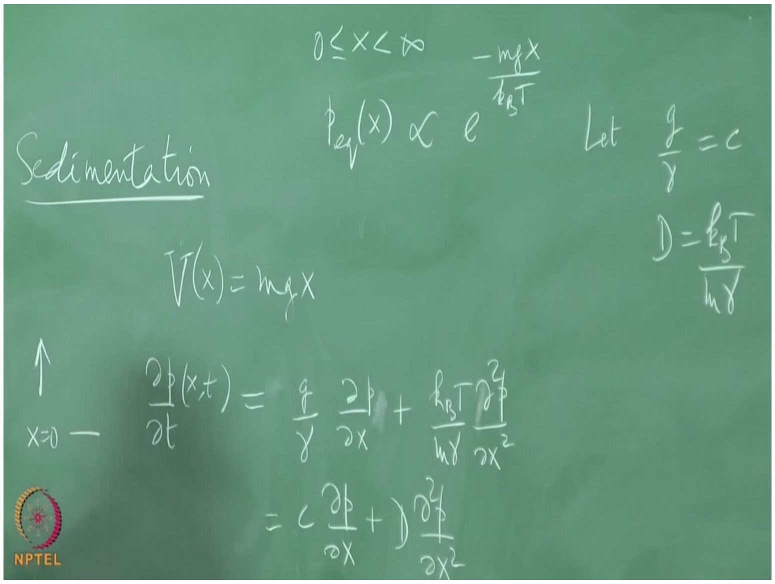
Professor: Yes or if it is a (gestures by hands). But this is the generic case.

You could ask what if V double prime is also 0 and it is a very flat 4^{th} order potential and so on. I leave you to play with those things and find out but the trick essential trick is the Gaussian trick okay. The next problem we are going to look at is what happens in a constant force feed. I said we would do this and then go back to the smoluchowski equation. That is a linear problem, it is relatively simple. Again I call attention to the fact that what we have done is a self consistent calculation.

We assumed that there is a stationary current which is nonzero, a stationary flux and then we kind of found it by a self consistent way, by a sequence of approximations knowing beforehand that the the equilibrium density at beyond the barrier is actually going to be quite small because of this barrier. How small? Exponentially small by the height of this barrier. And one should have expected this because the only energy scale in the problem is this and of course, the height of the barrier. So this is got to be some function of the ratio. Let us look at the problem of sedimentation.

(Refer Slide Time: 47:26)





Again, let us convert it to a one-dimensional problem. And now this time, let us do it under gravity just so that we have a physical picture. This is X equal to 0 and the X axis moves upwards in this fashion and the potential is MGX. So V of X in this problem with reference to the floor level. And we have a particle diffusing in a column in one dimension up there, that big fluid column, infinite say semi-infinite and then we ask, what will be the equilibrium distribution of the probability density or the density itself like volume of gas assuming the whole thing is at constant temperature?

That is not true of the real atmosphere but assuming that, you are going to get an exponential distribution something which probability of finding it at a height X is going to decay exponentially with the height. That is called the barometeric distribution and we can actually write it down. It is very clear that you will have P equilibrium of X and X by the way 0 less than equal to X less than infinity. So we go in the vertical direction. This is proportional to E to the power - MGX over K Boltzmann T. That is the Boltzmann factor, the Hamiltonian is going to have P square over 2M + MGX and E to the - with the Hamiltonian, the X part of it is precisely this.

One should expect that. So let us write the exact equation down for the actual probability density using the smoluchowski equation. So Delta P over Delta T XT is equal to 1 over M Gamma Delta over Delta X V prime of X but V prime of X is just MG with a - sign right. - V prime of X. So - MG right? The force is in the downward direction times P full P. There is no X because that got differentiated out. So it is actually an easier problem than the Fokker Planck equation was for the velocity process or the OU process. + the usual thing KT over M gamma D2 P over DX2. I have already had a - V prime of X right?

Student: And this became a + V prime of X there (())(50:31)?

Professor: This will become, of course, this becomes +. Let us see the dimensions are okay?

This is G over Gamma and it should have dimensions of a velocity LT in those because there is an L here and a T here which it does. This is LT to the - 2 and this is LT T to the - 1. So it is LT inverse which is the speed. So let us give it a name. Let G over Gamma be equal to C. It has got dimensions of velocity speed, so let us call it C. And this is our old friend D. Of course we can immediately write down what the equilibrium distribution is. It is precisely this because I pull out this is equal to 0, I pull out a D over DX and whatever is in the bracket is the current and that current must 0 at infinity.

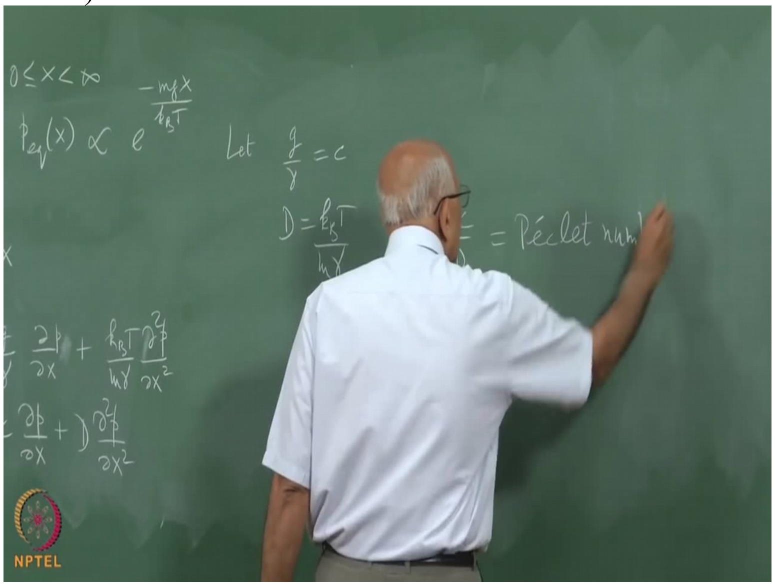
It is a constant in any case and therefore you end up with the distribution. You have to normalise it. From 0 to infinity, you integrate and the answer is KT over M and G, whatever it is times the exponential. So that is the barometric distribution. But our interest here is in some things like…

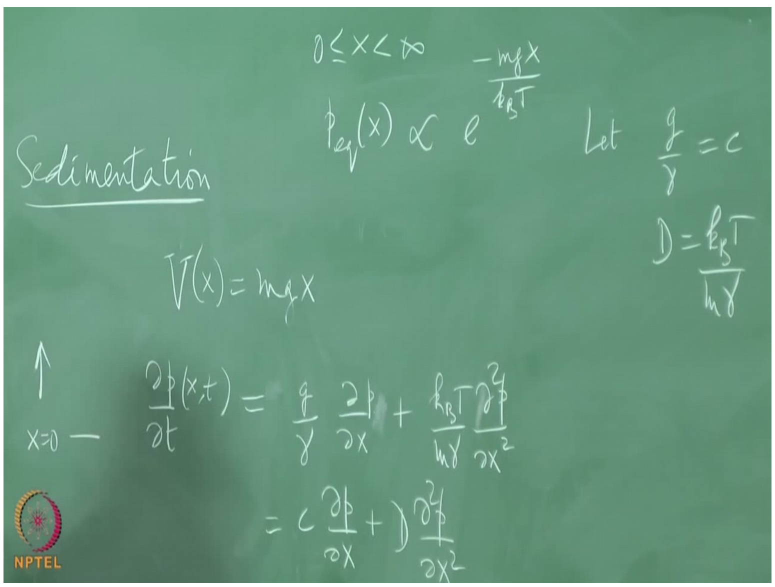
Student: Time-dependent?

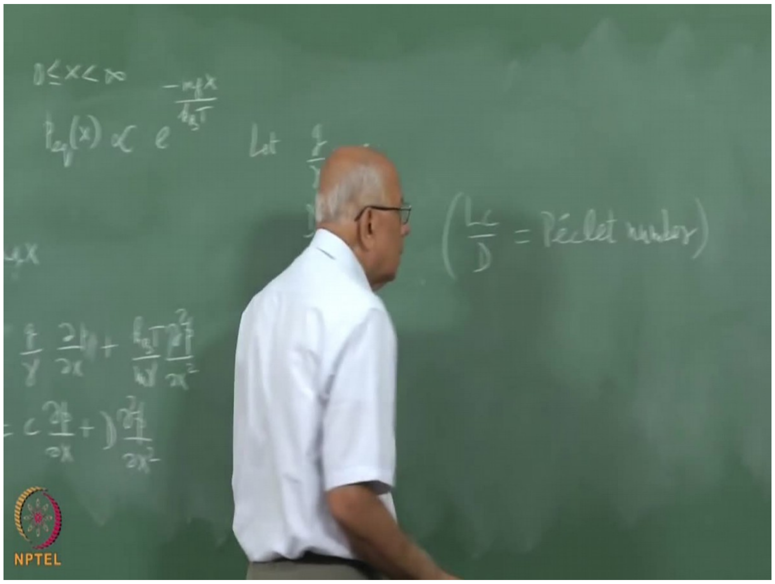
Professor: Well, I would like to get the full time-dependence if possible but 1st let us see what this stationary thing actually is like. Notice that if I call so this is equal to C Delta P over Delta X less D times D2P over DX2 where this C is given by that and D is KT over Gamma as usual.

Now you can form if you had for instance a finite column then there is one more microscopic length scale in the problem which is the length of this fluid column. Then you can form a dimensionless number.

(Refer Slide Time: 52:49)



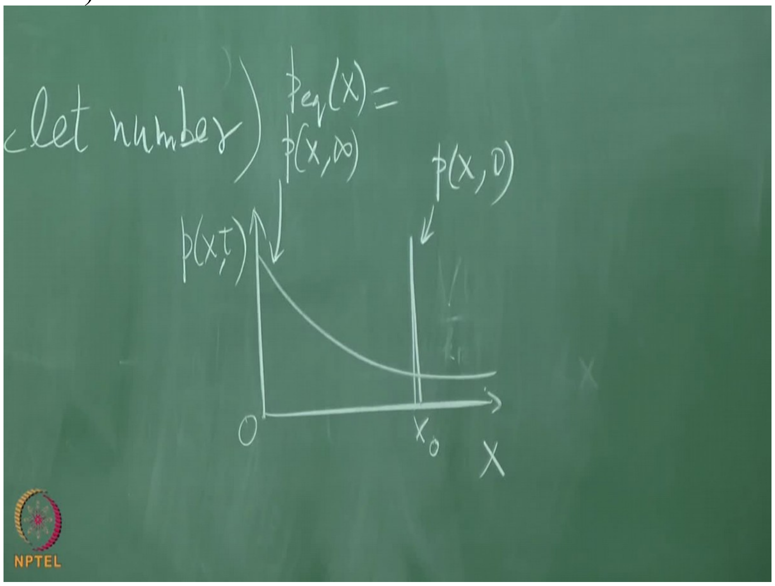


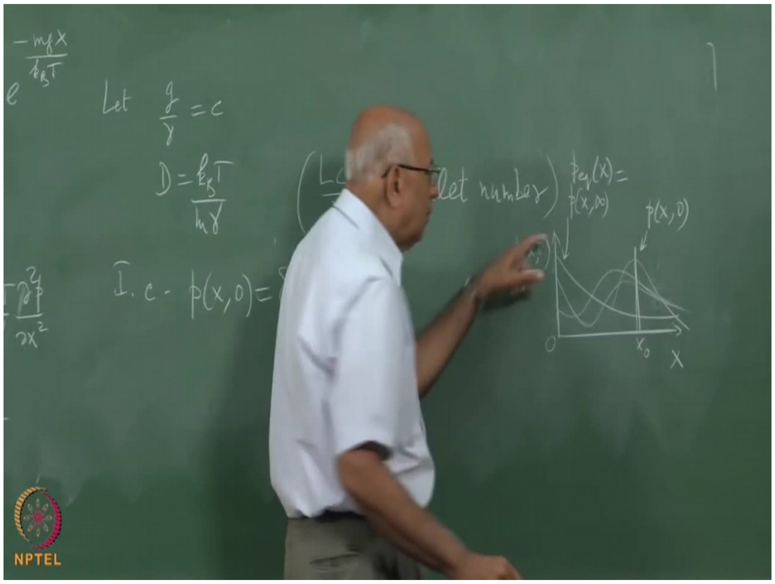


So you can form LC over D. If this column extended to a height L from 0 to L for instance then this quantity has got dimensions of, this is L and that is LT inverse. So this is L square T inverse, this is L square T inverse okay. So that is a dimensionless number and it will govern the motion fluid dynamics under a constant field of force. It has got a name. Is anyone familiar with this name here? All these dimensionless numbers in fluid dynamics have specific names like the Reynolds number you are familiar with. This is called as the Peclet number and it plays a role in fluid dynamics (())(53:44).

So we have settled the equilibrium distribution. It is this. Notice Gamma cancels out in it, as it should. There is no role for it in that. Dimensionally, it cannot exist in P equilibrium. This in fact cancels out. As you pull it out of the bracket and set the rest equal to 0, then you just get KT over MG which is what happens here. Now what about the exact solution? What would it look like? I am not going to solve it here now but what would this actually look like? It depends on the initial condition. So we have to specify the initial condition and the boundary conditions .

(Refer Slide Time: 54:30)

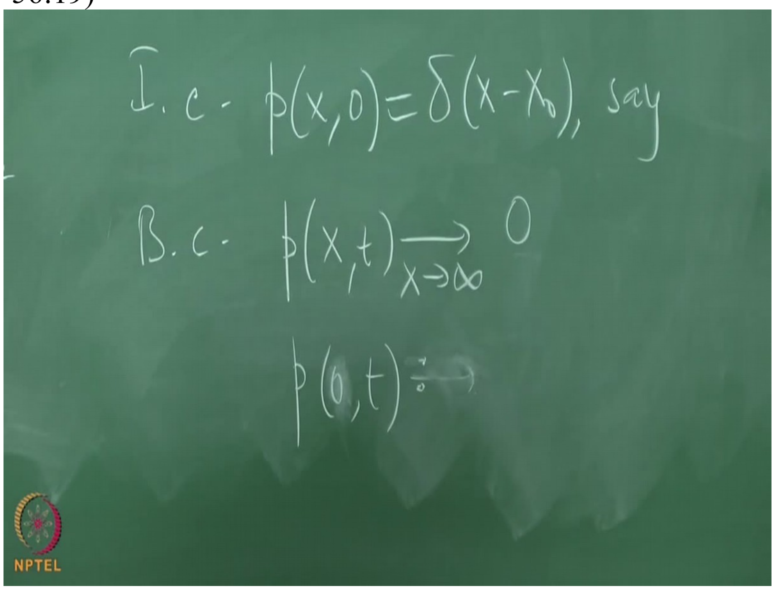




So the initial condition P of X0 equal to some Delta of X - X not same. So if I plot this P of XT as a function of X, initially it is a Delta function at X not. Remember, you cannot go to the left of X equal to 0, nor can P be negative. As T increases and becomes infinite, this thing goes to the asymptotic exponential distribution P of X0 and this distribution is P of X infinity which is P equilibrium. This thing. It is an exponential thing. So the question is how does this Delta function spike at T equal to 0? How does it spread out and become this exponential with a peak at 0 no matter what X not is?

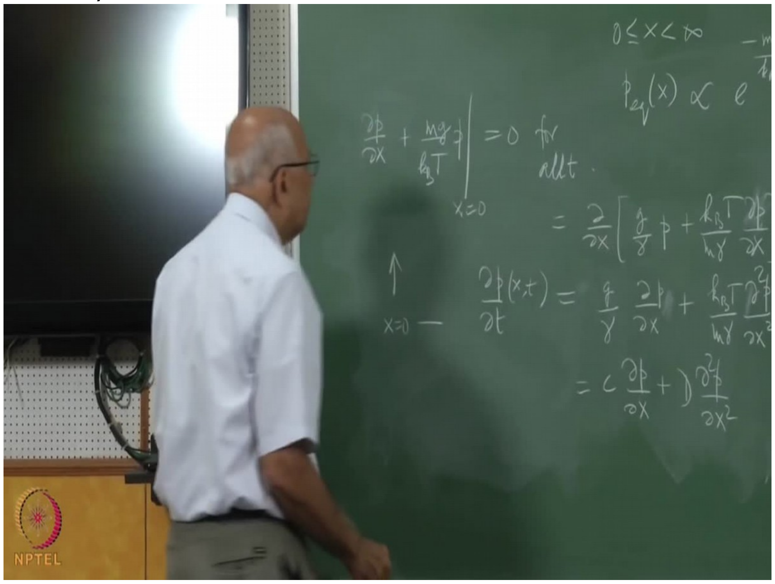
So clearly, sort of physically you can see that initially immediately it will start diffusing. So it will do something like this and then the peak mean meanwhile starts shifting to the left. So it will start doing this but then there is a bounce back. Anything that hits this cannot go there. So it will probability mass and will bounce back and gradually as this shifts left, it becomes more and more pronounced and this gets flatter and flatter and eventually it goes through this. So clearly there is reflection at X equal to 0 which is obvious because under this diffusion process, particles are going to hit the floor and they cannot go through the floor. There is no leakage through the floor. So what is the boundary condition for this?

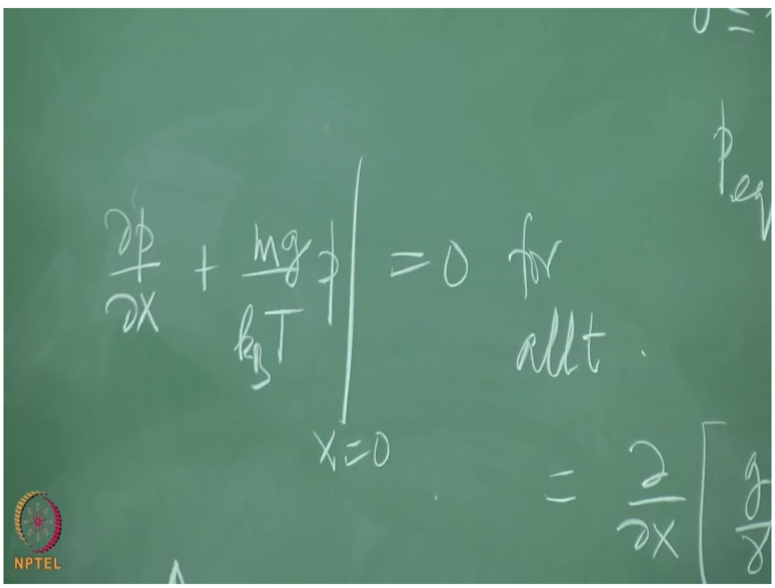
(Refer Slide Time: 56:19)



So the boundary condition is P of XT tends as X tends to + infinity, this tends to 0. It is a normalisable distribution. So the probability density must go to 0 as X goes to infinity. What is the boundary condition at the origin at at X equal to 0? So P of 0T, what is the condition on this? It is not 0. It is not 0. At any arbitrary time, this probability density is not 0. In fact at T going to infinity, all the probability mass, much of it is concentrated here. But the current is 0. And what is the boundary condition? And everything lies in the boundary condition. If you have understood that, then job is done. So remember that the current here, you pull out at D over DT and the Gamma.

(Refer Slide Time: 57:25)





So you can write this as equal to this whole side as Delta over Delta X of G over Gamma P + K Boltzmann T over gamma Delta P over Delta X and - this quantity is the current and we want the current at the floor to be 0. So it is a the boundary condition at VC at 0 is Delta P over Delta X, the Gamma goes away + MG over K Boltzmann T P equal to 0 at X equal to 0 for all. Okay. So sometimes that is a reflecting boundary condition. If you discretise this and read it as a random walk problem, it says the moment you come to 0, the particle cannot go to the left.

So anything which tries to go to the left, has to go to the right. So the probability of a jump to the right is + V. You have to impose that as a boundary condition at 0. So it is the current that goes to 0, not the probability density itself. That does not go to 0. So given that, you have to solve this equation. I am going to leave this as an exercise. I will mention what the solution is. It is messy to write down. How would you do this? Well, you can do the, you can solve the full partial differential question.

We know the initial condition, we know T runs from 0 to infinity, we know X runs from 0 to infinity. So take Laplace transform with respect to time and then you get an ordinary 2nd order differential equation. This is a constant coefficient and so is this. So you can find a solution for the Laplace transform. You have to translate. You know the initial condition out here. We know the Laplace transform of the time derivative, it is S times the transform of this - the initial value. It becomes a green function equation for whatever is the Laplace transform and then you have to invert that okay.

So there would be various error functions etc etc. And then after that, you have to invert the Laplace transform. But the problem is doable, exactly solvable. But we have extracted all the physical information from it. Now the rest of the matter (())(60:14). All right. So let me stop here today.