Computational Physics
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Lecture – 57
Molecular Dynamics: Diffusion Constant Calculation Part 02

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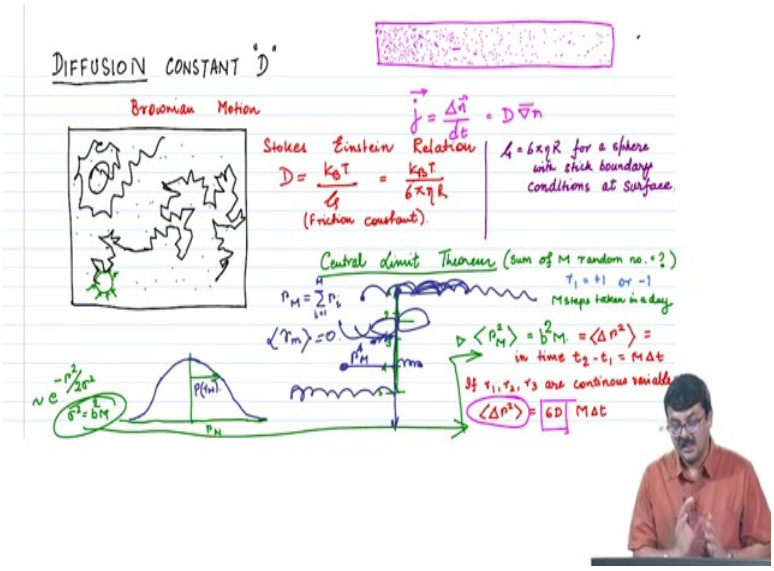

Now, you can think that there are three random walks happening in the three directions instead of 1D. Now, I am trying to increase it I want you to extrapolate 1D random walk into 3D random walk where each of the directions are different and then again you can calculate in 3D the net displacement square average, mean squared displacement. Displacement, square of the displacement mean of the displacement; mean square displacement, that is actually the standard term, will go as linearly with t.

Now, let us take a step forward. Till now, we had been talking of cases in 1D where all the steps where off the same length right plus 1 or minus 1; plus 1 meter or minus 1 meter whatever. If, suppose, a particle was moving sometimes to the left and sometimes to the right, and sometimes up and north, on each of these steps were of different size. Why could it be of different size?

Now, suppose let us come back to this Brownian motion. So, a particle is moving in some random direction with a certain velocity v, some particle is colliding earlier in time

is colliding earlier in time and changing its direction or it is moving in a different direction if you like and some other particle is taking larger amount of time to have a collision or it has a higher velocity, in the same time it can move larger distance say and then it collides again.

So, each of this length of the step; the each of the values of these random numbers which we were summing up the each of the step is different; some particle is moving a small distance, some particle is moving a large distance. And, there it is undergoing collisions and it is constantly changing directions and yet you can calculate the so called mean square displacement which is displacement square average.

And, if you take the average, when the particle has moved over a very large distances undergone a large number of collisions then this quantity will be again proportional to M delta t which is the amount of time elapsed and by convention we say the proportionality constant is 6D; 6D, D being the diffusion constant. So, diffusion constant is essentially measuring the pre-factor 6D is by convention. So, the diffusion constant is essentially measuring the amount of displacement squared average due to a large number of collisions by t, that is the definition of the diffusion constant, ok.

So, where these collisions are happening due to interactions between particles, now having given this background, let us think of our Lennard Jones particles. What is happening for these Lennard Jones particles we were doing in molecular dynamics? They are moving around in space you have, so, each is moving around the different velocities for time delta t you are updating the position, it is going and colliding with some other Lennard Jones particles which is getting attracted and if it comes too close, it is basically feels the repulsion between two Lennard Jones particles feeling.

This repulsion between two Lennard Jones particles is nothing more than a collision. So, two particles are coming together they are getting attracted in space, but as they come close together there is a strong repulsive force acting due to which they again start to fly back apart from each other. That is basically nothing more than a collision right. You are basically following the collision between a large number of n particles, right.

Then you can ask the question given my certain density at a certain simulation box and given the interaction how much on an average does the particle get displaced in a certain

time t in M delta t steps; M delta t is now that integration constant with the time integration constant that you were using in your MD calculations, right.

And, thereby of course, you already know that if you increase the density, the number of collisions will be more it will collide more frequently than displacement will be more and hence the diffusion constant will be less. From Einstein's relationship you can also know right that basically if you increase the temperature, the kinetic energy the velocity of all of these particles are going to be more they are going to collide more. But, on an average they are going to get displaced even more.

So, that is the notion you already have from your Brownian motion that if you increase the temperature of the fluid the Brownian particle micron sized right in the MD we were working with all particles of the same size. But, the same physics is happening in the Brownian motion as well where you have a micron size particle dispersed in the fluid. And, there again if you increase the temperature this particle is going to be hit with higher velocities from the fluid particles due to which the effective force that it is going to feel in a certain time it is going to be more.

So, it is going to get displaced more on an average and as a consequence it is diffusion the amount of displacement is going to be the more right then that is what says that D equal to K B T by zeta. More the K B T more the diffusion, more the mean square displacement in the same amount of time, right. So, this is the background physics. I hope you have understood it. With this pictures so, this is the quantity we are trying to capture or calculate through diffusion constant.

The last thing I wanted to tell you before we go to actual algorithm and calculation of the diffusion constant. So, if you have got the physics of it that it is already known by the central limit theorem that well this is the so called mean displacement mean square displacement in time t, but if you plotted the distribution of displacements. Distribution of displacements for a large number of particles or the same person the same drunken man on a large number of days you would find that it is you would find, that it is a Gaussian.

So, if you have a random walk if you have a random numbers and you sum them up, the sum of the random numbers the sum of M number random numbers would follow Gaussian like this, e to the power minus r square by 2 sigma square. What is 2 sigma

square? It is the standard deviation of that sigma square is the standard deviation of that Gaussian and this sigma square is nothing, but b square M, the thing we discussed here or rather here, right.

So, it is a measure. So, that is the average mean square displacement square is what sits here and it is a Gaussian with the standard deviation sigma where sigma square equal to P square m right, you plot the distribution of displacement that will be a Gaussian like this, ok.

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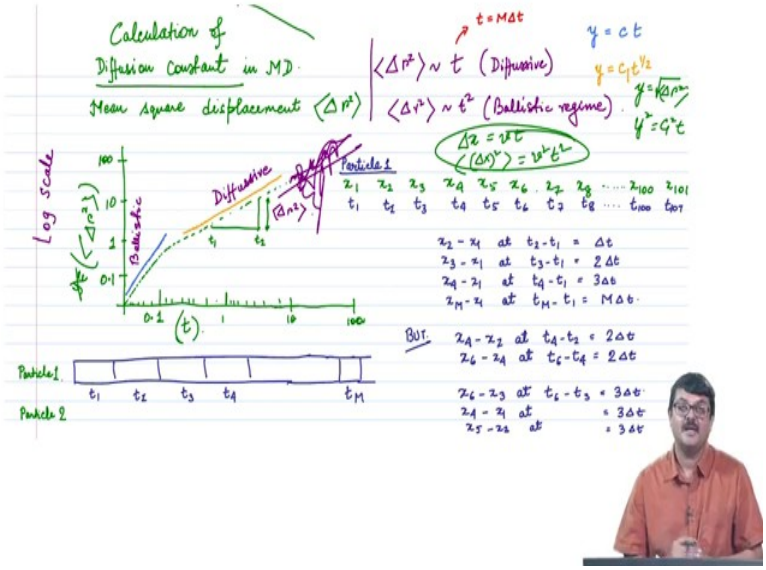

Now, coming to the calculation of the diffusion constant in molecular dynamics simulations; so, now let us just discuss this. What you have already learnt in the previous just in the previous slide what is discussed is that delta r squared the mean squared is displacement delta r square average that goes as time. So, that changes linearly as time and the proportionality constant is 6 D essentially in the diffusive case right.

Now, if you manage to calculate delta r square average and we will discuss how we will do that averaging. From extremely small times what does extremely small times means over dt and so, you have you are n molecular dynamics you can calculating in one time unit in time d t, the particles are taking a displacement they are moving in space and, we are of course, updating the velocity.

Now, if you take the really smallest to this time dt and take the average over many particles and over various time units and you plot this delta r square average, the mean square displacement it is called MSD versus time yeah. And you plot it in log scale which means here 0.1 equidistant away is 1, equidistant away is 10, then you have 100 and again, in the time it starts from 0.005 or 0.001 whatever dt is to 0.1, 1, 10 and 100.

So, this is the so called log scale and in whatever software you are using you can use the log scale. And, if you plot it like that you will see that first the mean square displacement MSD will go as a straight line like this where the slope will be delta r square will go as t square and that is the so called ballistic regime. And only after sometime around 1 I mean it really depends upon the density and the interaction, because for different interactions you will have different diffusion constant as well right. There decide the range of the interaction there where this purely repulsive attractive or whatever.

So, the diffusion constant will also depend upon the interaction and only after a certain time which is dependent both on the density of the particle as well as the interaction due, does the MSD reach the diffusive regime, where delta r square goes as t. Now, why is that? Why do you see that? I mean all that I have been discussing in the last slide has been only the diffusive regime the point is this.

So, now we are doing in a molecular dynamic smaller particles are moving around in space as a function of time and every particle also has an inertia, it has a mass it has a kinetic energy, right. Now, when it moves it has it is own inertia half mv square right, due to that it has a certain speed, velocity. It is moving in a certain direction and it is moving basically because of its inertia. Of course, that is being it is velocity is also getting updated and changed due to interaction with the other particles.

But, at extremely small times, it is almost like moving under the influence of other particles, under the influence of forces from other particles, but it also has its inertia so that the net displacement goes as t square, right. So, it basically is coming from x equal to v t delta x equal to v t, t is the time elapsed and delta x square average will go as v square t square average I am sorry. There is no t square average is like velocity.

At only at slightly longer times right do the effect of the half a t square and acceleration and the interaction and the collision they come up. At extremely small times the displacement is essentially dominated by such terms and hence delta r square average the

mean squared displacement and you see that delta r square average goes as t square ,right. This is called the ballistic regime and if you plot a y equal to ct where y is basically delta r square average, you plot some other curve here you will see that the slope of this curve will go as y goes as c t.

Whereas, in the diffusive regime for reasons that we discussed earlier basically y square y will go as c to the power half, where y is root delta r square average this is slightly wrong and the this is what it is and this will go as t to the power half or y square will go as c 1 square t right that is what we have been discussing where delta r square average goes as t. So, that is the thing.

So, so the way you calculate diffusion constant is identified the ballistic regime, identify the diffusive regime from there you calculate delta r square average. This in; this has been statistically average to calculate mean square displacement and we shall discuss about the averaging. And, after this statistical averaging when you plot this will be a straight line with the appropriate slope. Calculate delta r square average, calculate t 1 minus t 2 and delta r square average minus sorry, divided by 6 t 2 minus t 1, the time elapsed gives the diffusion constant d right and that is what we discussed in the previous slide, ok.

So, all that is you great, but what you actually have is basically the position of particles at different times, right. And, how do you calculate mean square displacement average? Now, you are going to have an array. Suppose, for particle 1 and at time t 1 and t 2 and t 3 and the difference between t 2 and t 1 is delta t, because you have just updated the position and t 3 minus t 2 is delta t because you have updated the position again and so on so forth.

And, you basically write the position x 1 at time t 1 for one particle and x 2 at time t 2 here and x 3 at time t 3 here. So, basically suppose at different times t 1, t 2, t 3, t 4, t 5, t 6 at different times and these different bins of the array you save the positions x 1, x 2, x 3, x 4, x 5, x 6 and so on up till x 100 x 101 and so on so forth for particle number 1, right.

Now, if you wanted to calculate for a particular particle the net displacement in time delta t you would have to do; what you have to do? You have to do x 2 minus x 1 that is the net displacement in time t 2 minus t 1 which is nothing, but in your MD delta t, right.

And for the net displacement at a larger time so, t you can calculate x 3 minus x 1 which is the displacement net displacement at time t 3 minus t 1 which is nothing, but equal to 2 delta t after 2 delta t so, what is the net displacement.

And similarly, we can calculate x 4 minus x 1 which will give you the displacement at after 3 delta t for a particular particle 1 and if you calculate x m minus x 1 it will give you the displacement for particle 1 after M delta t's, at time equal to M delta t. But you need to do a statistical averaging right, because you want to do it over many random number or random walks.

x 4 minus x 2 will also give you the displacement at time after time spent equal to 2 delta t just like x 3 minus x 1 was giving you the net displacement after time 2 delta t. Similarly, x 4 minus x 2 will also give you the displacement not the average you have to average over the displacement. That is what we are after? We are after mean square displacement. The question is you can calculate the displacement, you can take the square how do you calculate the mean. So, the part we had we are discussing is actually how to take the mean, how to get a quick and good value of the mean this expectation value these angular brackets.

So, you also get a net displacement at if you calculate x 4 minus x 2, if you calculate say x 6 minus x 4 that is the time difference of t 6 minus t 4. You again they do get a displacement for the same particle at time 2 delta t and you can average over those. Similarly, for time t time elapsed equal to 3 delta t, you can calculate x 6 minus x 3. I am written x but, it is in three-dimensional x and x 4 and x 3 these are going to be vectors. You can calculate x 4 minus x 1 right, at 3 delta t that will also give you a displacement of the same particle; you have basically shifted the origin of the averaging.

Similarly, x 5 minus x 2 will give you the displacement at after 3 delta t and you can average over all of this for a single particle. Moreover you can also average and calculate similar quantities for particle number 2, particle number 3, particle number 4, particle number 5 and so on so forth. So, not only for a single particle you can calculate these averages at different times right and you can differ calculate different times in the way like you can use x 2 minus x 1. But, you can also use suppose x 3 minus x 2, x 4 minus x 3, similarly for 2 delta t and similarly for 3 delta t up till long times where M can be large it can be 100 or it can be 1000 and so on and so forth right.

Not only you can average over the trajectory of a single particle you can also average over the trajectory of all the particles in the system right and thereby you calculate mean. So, that is what the mean is you are taking averages over different points in the same of over the trajectory of a single particle, moreover the trajectory over different particles.

Now, the thing to notice is that when M is large; suppose, M is I do not know 10 lakhs 10 lakhs iterations right. So, which is and then the time elapsed is 10 lakh into dt if you are taking dt to be 0.005 what the time. Then, you are unable to average so well from a single trajectory because, if m is 10 lakh suppose I have run the simulation itself for 10 lakh iterations then m minus.

So, when m is 10 lakh 1 million essentially; 10 lakh is 1 million then for the net displacement at a very large time when number of iterations is 1 million, you have only one point, you cannot average because for one particle you have. And, you have run the simulation for only 1 million iterations say, then from one particle you have only one difference. So, you have you like in other cases for smaller time differences you could average over x 6 minus x 3 and x 9 minus x 6 for 1 million iteration. So, last times you are unable to average value right, because are you do not have so many points you cannot have so many differences from the same trajectory. However, you can average over different particles.

So, while getting the average at short times is relatively simple, because you have so many differences from the same trajectory, getting an average out for diffusion for mean square displacement for large distances is difficult and you would either have to do a molecular dynamics simulations with different initial conditions. An average over not only the mean square displacement over different particles over the trajectory of different particles, but you can have a independent runs of the molecular dynamics simulations. So that basically you can get a good average over different independent trajectories of the particles with different velocities and different positions.

So, give 10 independent runs each with different initial conditions and let the particles run and only then can you calculate the mean square displacement at large times. And, if you do not have a good value of the mean square displacement at large times, what you would see is that at large times this means square displacement essentially undergoes

fluctuations like this. So, you do not get a clean straight line, unless you get a good clean straight line you cannot calculate the diffusion constant, right.

So, this is the ideal case scenario if when you have averaged really well, but if you do not average well you are going to get all sorts of random behavior when you calculate the mean square displacement at large times. So, one has to be careful about that and since these things require large long runs to calculate the mean square displacement at long time and you have to average over large number of particles.

And, of course, this is the basic molecular dynamics typically you would calculate much more interesting quantities of interest from a molecular dynamics simulations, but these are the simplest ones. You need the neighbor list because you want the code to run fast and over long in large number of iterations over large number of particles.