Computational Physics

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Lecture - 56
Molecular Dynamics Diffusion Constant Calculation Part 01

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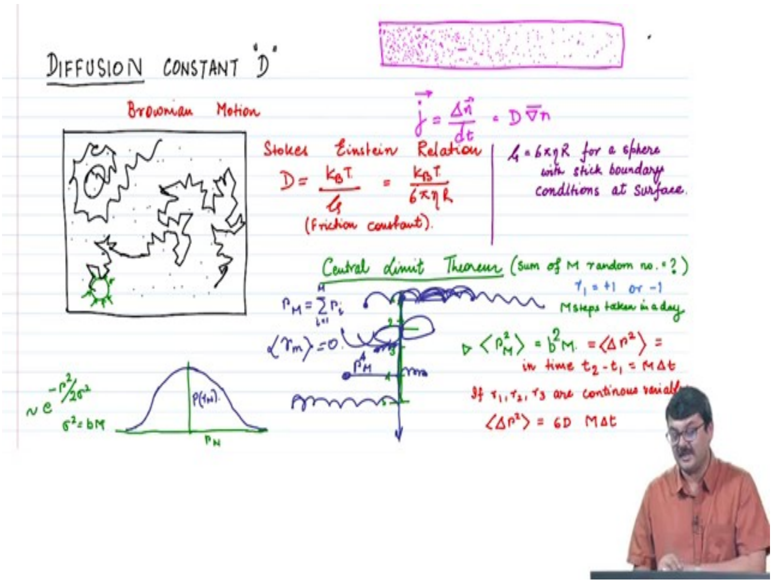

So, now we will discuss the idea of Diffusion and calculate Diffusion Constant ok, this is a dynamical quantity. But before the calculation of the diffusion constant and the algorithm, let I will remind you or take you through a general discussion of diffusion and so, that we exactly know what we are calculating, how we were calculating and then we shall discuss the implementation of the algorithm as it has been happening in the past, ok. So, when you talk of the word diffusion I would like you to think about Brownian motion, which you might have heard even in your class 11 and 12.

What is the idea? Suppose there is a particle dispersed in a fluid, so there is a fluid some pollen grain or some microscopic particle and it is basically floating around in a fluid and what happens; it does some random jiggly motion. So, and why does it do it? So, basically if this is your particle, microscopic particle and these small dots are say water particles; what is happening is that in a very microscopic instance of time? There are large number of particles, water particles which are hitting this green particle right, I mean the microscopic particle due to which it does a random motion.

So, basically the diffusion is it is acted upon as a sum of all these collisions which are happening with a water particle, there is a net force and the particle suppose move in this direction in an instant of time delta T. In the next instant of time delta T, large number of other water particles hit this green particle and then suppose it moves in another random direction say this one right. And in the next one it moves in some other direction say this one and as a consequence what you are going to see is basically this particle goes on doing.

So, what happens is, that this particle goes and doing a random walk in space. So, it is moving here and then here and then here somewhere here along this line and so on so forth, right. And after some time, it lands up here right, and where it will land up you can not exactly predict. So, if you had exactly, not exactly another identical particle dispersed in the fluid say somewhere here, then it would do it is own random walk in space and would land up somewhere in space after some time, right.

And in diffusion what you can predict is, the average displacement that a particle undergoes in a certain time T. You cannot specifically say that this particular particle is going to land up in this point in space after some time T. But, you can say if I had 1000 particles and it was undergoing Brownian motion, then some would displaced from it is original position by say x, some other one some other particle would get displaced from it is original position by say x 1, some third particle by x 2 and so on so forth, and you can calculate an average of the net displacement.

Now if you calculate really the net displacement some particles will move to the right, some particles will move to the left, some particles will move to the up, some particles will move down. And if you calculate the net displacement, averaged over many particles after time T, you will get 0, right. But at the same time some part, they would have got displaced.

So, the quantity to calculate is not the net displacement, but net displacement square, because then if something is moving in the negative direction and something is getting moving in the positive, some other particle is moving in the positive direction. So, when you take delta displacement square, both the negative and positive give a contribution and you can calculate how much has been net displacement square average in time T.

Now in your college you might have also studied diffusion in a slightly different context, and the typically you might have also heard about the word diffusion constant. Particularly when you have suppose fluid in a box somewhere and suppose you have now dispersed particles inside the fluid; and at one end you have a higher density, and at some other end you have a lower density. And then what you say is that well after some time this is a non-equilibrium situation, because the density is not uniform. And there will be a net current of particles moving from left to the right, from the region of high density to the region of low density.

So, basically particles on an average will move from left to right and you can say that is a particle current, j should be a vector and that is equal to delta n by d t, which is how many particles are moving in a particular direction in unit time, in a small time d t. And that is related in your statistical physics course if you had one as D some diffusion constant into grad n; grad n is the gradient in and the change in density right. So, this is gradient in n is a vector, hence del n del t is a vector and the current is a vector, right.

Now, Einstein managed in 1905 in a landmark paper showed that the Brownian motion that you study in class 12 and this diffusion of particles from left to right. There are actually correlated. Why do these particles move from left to the right, again there is a huge number of bombardment of smaller particles or with each other and as a consequence each is doing a random walk right, it is moving in random directions.

And the probability of it moving to the left or right is the same, but here there is a larger number of particles in the more dense region; as a consequence a larger number of them also end up moving to the right, right and because of Brownian motion, there is nothing more than Brownian motion happening. And he showed that the D, the diffusion constant, the diffusion constant of this is equal to K B T the thermal energy by zeta; where zeta is the friction constant.

What is friction constant? You might have come across the friction constant when you were doing the stokes flow experiment in your lab, where basically you have a column of the liquid and you drop a small sphere inside it. It finally, reaches it is steady velocity right due to the frictional drag and the gravity and so on so forth. And you might have heard that if it is a sphere the frictional force acting on that sphere is 6 pi eta R, right, that is the friction constant into V, the velocity of the particle in steady state right. And you might have done the buoyancy, so there you have.

So the gravity is acting in the direction towards the ground; the viscous force which is 6 pi eta A v or friction constant into v is acting in the up direction, up towards the sky and we have the buoyant force and so on and so forth. So, it is that friction constant right, it is a property of the particle and it depends upon the viscosity in which it is moving and r the radius.

Now, friction constant, the friction constant is basically equal to 6 pi eta R only for a sphere with stick boundary conditions at the surface; if the water is sticking to the, if the water at the surface of the sphere is moving along with the sphere and it has the same velocity locally as the surface of the sphere at that point in space, right.

But in general, if it is a non spherical object, you do not have 6 pi eta R; you might have a different functional dependence, it might be a more complicated looking equation. And in general that friction constant which we identify as 6 pi eta R for a sphere, we shall call it keep it general as zeta right, some friction constant is, some property of that particle. And diffusion constant Einstein showed is related to K B T by zeta. So, if you know the zeta and the temperature you can calculate the diffusion constant.

On the reverse side, if you can somehow experimentally measure or computationally calculate the diffusion constant and you know at what temperature you are doing the experiment, you can have an information about zeta, the friction constant of that particle; and if it is a sphere you can calculate your radius of that particle from this relationship.

Now, why does diffusion happen? You can see that diffusion is related to K B T, thermal energy, right. So, here what is essentially happening is, base all the particles have their own kinetic energy, they are moving around in space right, getting kicked around and because of the thermal energy they start to move and when they get kicked by other particles they change their direction.

So, in Brownian motion, what we have discussed or what you might have learnt is that, you have a typically a pollen particle or a micron size particle, big particle relative to the atomic size fluids. Now, suppose let us start taking a smaller and smaller particle, the particle the bigger particle which was dispersed in the fluid, let us take other particles which is smaller. So, as you keep it taking it smaller, you can take it to the limit where it is one of those particles of the fluid, right. Those particles are also interacting by a potential with it is neighboring particles, it has thermal energy, it is getting kicked around, it is interacting with particles, exchanging potential energy and kinetic energy whatever we were discussing for our molecular dynamics simulations.

And those particles also will do a essentially a Brownian motion, while it is interacting and bouncing with other particles; if it is not bouncing with other particles, if it is not colliding with other particles, then it would move in straight line for some time and then get a collision.

So, the amount of collisions, the number of collisions how often it gets kicked around, the smaller particle is basically a function of the density, right. And if you increase the density, you will have a lower value of net displacement in time t; because there have been less collisions, it can move over further distances that is what you have in a gas. But even gas particles though they are kicked around less frequently, they do diffuse around in space, in the air, right.

Now, I have been throughout saying that these particles move around, they move around randomly being kicked around can we have an estimate of how much they move in time t, and that essentially is the diffusion constant, and having an estimate of how much they move in time t.

So, to discuss that rather than talk about this Brownian motion and 3 D where particles are being kicked around in all possible directions, exchanging kinetic energy and potential energy. Let us talk about a simpler problem get an estimate how we expect these particles to behave, how much displacement we expect them to behave. And then come back and approach this problem ok, to have a quantitative idea of how diffusion constant is defined macroscopically, how it is calculated microscopically and then we shall go back to the algorithm.

So, now, to understand diffusion, we talk about a slightly separate problem, where we shall use the so called central limit theorem, ok. You might have heard about it in the mathematics and essentially it deals about how a sum of M random numbers behaves.

So, if is random number between 0 and 1; how does it behave or let us talk about a slightly different case; suppose the random number is between minus 0.5 and plus 0.5 and it you add large number, M number of random numbers and what would be the behavior of such a sum, ok.

Let us talk, even a about a simpler case; now suppose there is a man ok. So, this is typically called the drunken man random walk problem; now suppose there is a man on day one, starts from the bar and he is so drunk that he cannot decide whether he has to move a step towards the left direction or towards the right direction, ok.

So, he does takes a step in either to the left or to the right with equal probability, ok. And suppose the length of his steps is A 1, 1 in some units, 1 meter say ok, 1 meter or 1 foot does not matter; suppose it is plus 1 in some units. So, if he moves to the right so, you say that he has moved plus 1 and if he has moved to the left, suppose you say that he has moved minus 1.

Now this guy knows somehow that he has to take M steps to reach his home, but since he is so drunk and since he is doing a random walk, he is like to reach home in M steps in a particular direction. So, what does he do? So, if he is really doing a random walk; what will happen is, basically he will take, he will basically take suppose a step in the right direction and then maybe he takes another step in the right direction. But after that his forgotten in which direction he has to move and he takes a step in the suppose minus 1 in the left direction, which is minus 1 and each of his steps are exactly of the same length.

And then he takes a step again to the right to reach back here, and then back here and so on so forth; and he could even reach somewhere here and so on so forth. So, you can measure his net displacement. So, you can calculate so called r M. So, r M is the sum of these M random steps, some of them are in the plus direction, some of them are in the minus direction. So, it is basically sum of r i to M right and this is r i. So, r i can be plus 1 or minus 1. So, on day one suppose he reaches somewhere. On day two again he starts a random walk suppose he first does moves to the left and then back here and then here and then here and then here and then here and so on so forth.

So, on the second day he will have another next net displacement r M from the point of origin or from the bar wherever, right. And now you can calculate such things for 1 2 3 4. So, this is day, this is the number of days, so you can do this for say 1000 days or

10000 days, so every day he does one random, walk. Now, if you average over 10000 days say right or number of days going to infinity, actually going to infinity; then you will see on half of the days, he lands up towards the right home from his starting point sorry.

And on half of the days he lands up on the left of from where he started off right, on an average the net displacement will be 0; if you really average, really well over infinite number of days, right. So, this is not as I discussed before in a different slightly different context; the net displacement of this part, of this man who is doing a random walk in space along a certain line. We are just talking about a 1 D case and then we can later extrapolate the same ideas to 3 D's, hence we are talking about 1 D at the moment.

So, talking about this man, on half of the days is moving to the left, half moving to the right and even the displacement, some days he could take us to the right, on some other day he could end up taking a large number of steps to the left, net displacement I am talking. On some days he could land up relatively after taking M steps, relatively close to his start starting point. On some other days he could land up relatively close to his starting point, ok.

And we however, we want to have an estimate of how much would be the net displacement. And as I said that, r M average will be equal to 0; however, on each day if we take r M square, right. So, even if he has moved to in the negative direction, if his displacement is in this direction by some value r M on day 4, right. And if you take the square of that and then take an average, then you will get a positive number.

And by Central Limit theorem and in case you do not know please look it up in the books, then you can find that on the sum of such M random numbers or each of which is of value plus 1 or minus 1, you will have r M square average equal to. Note, here is a square r M square average equal to b, b is the size of the step which you have taken to be 1. So, here you can put b to be 1, but you can also take b to be 2 meters, if he is a giant and he can take 2 meter steps somehow and so, it is r M square equal to b into number of steps, right.

If we had moved in a straight line, in one particular direction then r M square would have been proportional to the number of steps square right. The displacement would be proportional to M and the r M square average would be proportional to M square b square M square. But, since is doing a random walk right, his net displacement will be r M square into here there is it should be b square, two dimensionally match; because this has dimensions of displacement length, this has to have dimensions of displacement into M is the number of steps, right. So, this r M square was basically how much he has moved on each day and you are taking an expectation value over large number of days, right.

And if we now think of the same problem where instead of a drunken man taking plus 1 steps or minus 1 steps you think of this to be a particle moving on the left or to the right by a random process in one directions right, then you can think of it. And say delta r square delta r being the displacement square average will be in time t 2 minus t one in a certain time m times the delta t delta t be the time of motion right. Here, I introduced time in the previous one we just talked about m steps.

Now, suppose each of these m steps take time delta t, right. So, in M steps the total amount of time elapsed is M delta t. If you are talking about a particle the net displacement is net displacement square average over many random walks. You can average over many random walks or take an ensemble average you have identical copies of a particle you have 1000 particles you are following the random walk of each particle you can also do that.

So, there is an average is a statistical average whether you take a time average or a ensemble average delta r square average is proportional to M delta t or proportional to the time elapsed.