Computational Physics
Dr. Apratim Chatterji
Dr. Prasenjit Ghosh
Department of Physics
Indian Institute of Science Education and Research, Pune

Lecture – 58
Molecular Dynamics Diffusion Constant Calculation Part 03

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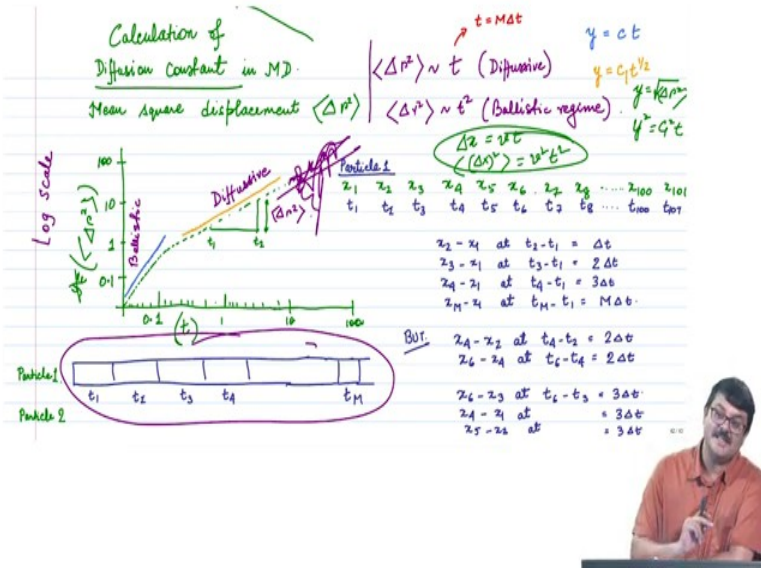

A small detail, I do not know whether you will have time to implement it. Now, delta t when I plot it for short times you can have an array just the way I have written here and of course, if the average over different number of particles and different number of times where you will write down x 2 minus x 1 at a certain position of the array and so on so forth.

What one can typically do is take an array with delta t equal to 1 2 3 4 5 6 so on for small time displacements because if you need an array if you receive the position of all the particles for around 1 million and you have 5000 particles and you are saving them for 1 million time the array to calculate the diffusion constant. The amount of space, the memory, the array that you have to take to save the position of all these particles is extremely large it is 1 million times 5000 right.

Whereas, specially at long times you do not need to save the difference in positions at each time right. You can save it every 100 iterations and or every 1000 iteration specially when you are looking at differences the displacements and 10000 at displacement at number of iteration differences of 10000. So, you do not need to save it at 10000 iterations, 10001 iterations, 10002 iterations specially since you are using a log scale what you could did well do is save the difference in positions at 10000 iterations, 20000 iterations, 30000 iterations, 40000 iterations and then thus averaged displacement over that.

For small times however, you shall need to save the displacement at each instant in time that is what we will give you this part right where as for this part you can have a different array where you save the positions only after every 10000 or say after every 1000 iteration and then you are done right and to calculate the difference in the positions. Now, there is one more thing you should keep track of.

Now, if you just give the positions of the particles remember that, but over long times particles are going to cross periodic boundary conditions right. So, if you just save the positions and calculate x 2 minus x 1 they are likely to get wrong values of x 2 minus x 1 because the particle might have started out somewhere in space then cross the periodic boundary condition and after say 1 million iterations it is somewhere close to it is starting point.

So, whereas, x 2 minus x 1 should be relatively a large number depends upon the diffusion constant as well actually the due to the presence of periodic boundary conditions can give you a misleading answer. So, what you should save is not the position of the particles, but every time you update the position in your update position subroutine, there itself you should be keeping track about what is the displacement in time delta t, what is the displacement in time 2 delta t.

So, this displacement, where what I am talking about is really the v t plus half a t square and not calculated from x 2 minus x 1. So, you have to keep track of the displacement and not the positions. If you make this mistake you want to get ridiculous values of the diffusion constant, you are not going to get the diffusive regime please think about it ok.

So, you have to incorporate the periodic boundary conditions in your calculation of your mean square displacement and what you really need is the displacement and not difference in positions because that could give a misleading answer .

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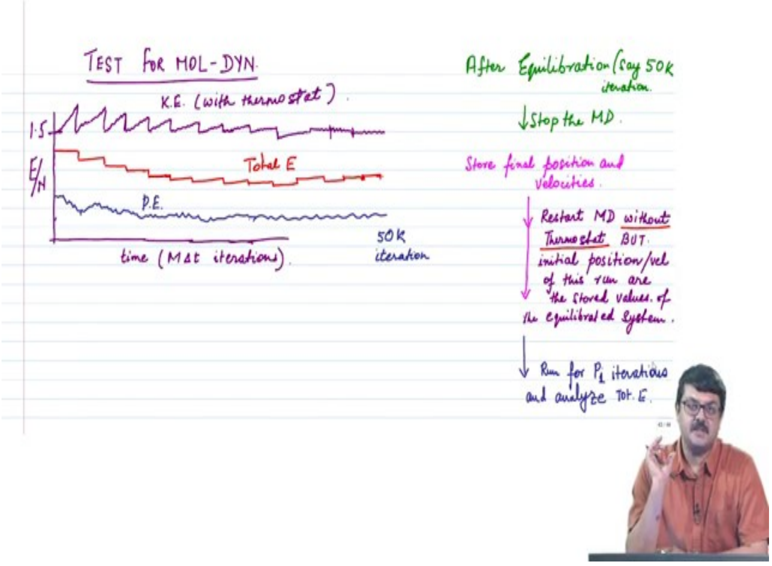

TEST FOR MOL-DYN.

After Equilibration (say 50K iteration.

↓ Stop the MD.

Store final position and velocities.

↓ Restart MD without Thermostat BUT initial position/vel of this run are the stored values of the equilibrated system.

↓ Run for P_1 iterations and analyze Tot. E.

So, finally, I will end this lecture with a test for molecular dynamics simulations. You know molecular dynamic simulations even the update of positions and velocities specially the calculation of forces, especially if you have complicated forces much more complicated than the Lennard Jones we discussed errors can creep in the calculation of forces. And, one needs a very robust test to ensure that your molecular dynamics simulations is working correctly even before you go to calculate statistical quantities ok.

So, this is something which you do not typically find in the books, but this is a test by which you can me dou v dou any tiny errors that might remain due to whatever the delta t naught working or some small errors at the cut off whatever be the errors this is the test by which you can really catch any tiny error ok. So, let us start in discussing the test in greater detail.

Now, what you have already told and what I have already shown in one of my previous recordings that when you start from a random initial condition and start a molecular dynamics, then you have an initial position you often need to switch on the thermostat, you need to switch on the thermostat right and in that case as the particles move around and exchange kinetic energy and potential energy with each other.

The kinetic energy could keep on increasing as a consequence plotting the energy particle now the energy is going to look like this I mean it is that it is constant and it is conserved for a certain amount of time till you call the thermostat and then the energy readjust itself, it could drop, it could go up as well, but most cases you see a drop and then energy again remains constant for some time and then it drops and then it remains constant for some time and so on so forth.

The drop is fast towards the initial it was the initial start of after the initial start of the simulation, but gradually it goes into a flat line and then energy could either slightly increase or decrease as you call the thermostat. And, correspondingly the kinetic energy typically grows up, but when you call the thermostat it is readjusted energy per particle to 1.5 kbt assuming kbt to be; kbt to be equal to 1 of course, a kbt is higher.

This will be 1.5 kbt and then as the MD goes on the kinetic energy increases and then drops again and drops again and so on and so forth. And this drop in the kinetic energy relatively decreases as you further run the MD system and the system goes towards equilibrium and once equilibrium is reached what you see is basically kinetic energy fluctuates about an average even as you call the thermostat there is very tiny nearly jumps in the kinetic energy which are not discernible in this scale where you have plotted the kinetic energy the total energy and the potential energy.

So, all that you have been growing is this scaling the kinetic energy to reach the equilibrium for which total energy has been adjusting itself, but typically the potential energy does not show any jump. However, the kinetic energy increases because thermo potential energy being converted to kinetic energy. Typically at least for the Lennard Jones case I want to see some decrease in the average potential energy of the system as the simulation goes on as the particles readjust themselves and sit close to the potential minima and it could form clusters of particles as well it depends upon the density and then it starts to fluctuate about the equilibrium.

So, that is how you identify equilibrium right that the kinetic energy, the potential energy and the total energy is fluctuating about an average value and after this point you can calculate the average value and calculate the statistical equilibrium energy, the potential energy, the kinetic energy at that temperature after it has reached equilibrium, yes.

Now, this is the standard molecular dynamics simulations. Now, what one should do for the tests? I am for I am basically, discussing a test for molecular dynamics. The first thing you do is you start with the system within the presence of a thermostat and allow the system to equilibrium. Suppose, the system takes around 50000 iterations after the system reaches equilibrium.

Then you stop the MD you just stopped the MD because your aim is to test whether you your code is working perfectly. Of course, if you wanted to measure some things you could continue with the MD. And, after the stopping the MD you could store the final position and velocities after now equilibrated configurations. Now, you have the positions and velocities of all the particles written in two different files or maybe was same file.

Now, what you have to do is starting from this positions and velocity. So, your initial you are going to restart the MD you want to restart the MD, but the initial position and the velocities of all the particles have to be the stored positions after equilibrium ok. And, now you switch off the thermostat you comment out the thermostat line and you restart the MD with the initial position and velocities of the equilibrated configuration and run the MD without the thermostat and say for P iterations; P being 1000 iterations.

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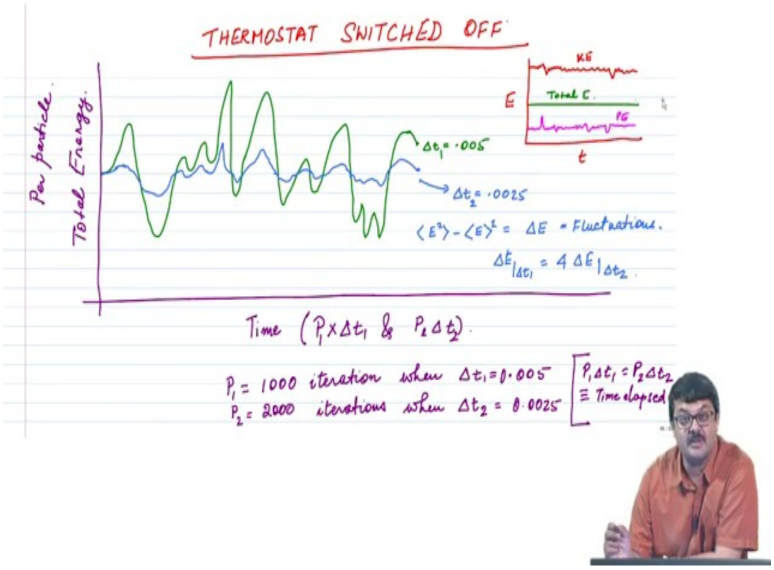

What will you see is the thermostat switched off that the total energy is absolutely constant, the potential energy is fluctuating and correspondingly energy whenever energy potential energy shows a peak kinetic energy which will show a corresponding dip. And whenever potential energy shows a peak, the kinetic energy could show a dip and so on and so forth right that is how you have the total energy constant especially if you look at it in the same scale where you have plotted kinetic energy, total energy per particle and the potential energy per particle on the same graph.

But, if you decided to zoom in at the total energy and zoom in really in great detail so that basically as I discussed before that the energy is going to remain constant, but it is going to fluctuate at the scale of delta t square. So, if your delta t is 0.005, suppose you zoom into 10 to the power minus 5 or something like that because right at 10 to the minus 6 or 10 to the minus 5 then what are you going to see you are going to see fluctuations in the total energy this green line suppose right fit that delta t equal to 0.005.

Now, if you restart the simulation from the same initial condition as before which is that equilibrated positions and velocities so, you are starting exactly from the same initial condition as before, but with a delta t the integration time to be half that of the previous value which is 0.0025 say and you run since you have integrate since you have a lower value of the delta time the integration time constant to run it for the same time, you have to run it for 2000 iterations if your previous number of iterations was 1000.

So, that the total time elapsed in that test run you are testing the molecular dynamics simulations with 1000 iterations or whatever be the number P 1 number of iterations. So, that P 1 delta t 1 it remains P 2 delta t 2 where delta t 2 is the smaller integration time constant.

And, now you plot the total energy again and zoom in of course, at this scale it is going to remain it is going to appear to remain exactly on top of each other because the total energy is constant all right and but if you zoom in then you are going to see that the trajectory of the energy in this graph where you are plotting total energy per particle versus time the length of the simulation the time elapsed in the simulation short run is the same, then it is going to exactly follow these peaks and dips in the energy look at this blue line right you are going to reproduce it in your simulations.

And, so you see that wherever there are peaks there are peaks also here, but the height of the peaks or the depth of the valleys wherever there is a dip that is around one fourth that of the previous value is basically that the fluctuations in energy. What is fluctuations in energy? E square average minus E average square, which you can calculate for both these two cases right. The fluctuations in energy the delta E, so, basically we are saying that the delta E with larger delta t 1 is 4 times that of the delta E the fluctuations in energy with the smaller integration constant.

And, this is 4 times because you have half the integration. Of course, if you had made it one third than this relation would be 9 times. So, the fluctuations in one would be 9 times than the other than the one with the smaller integration time constant right. Now, and the average of the two energies will be exactly the same. It will absolutely follow the path.

On the other hand, if there is a bug somehow so, then you will see that this does not follow the exact path the average will not be exactly on top of each other it might be shifted in some way if. This would be extremely tiny mistakes which can creep in. And, so, that is what tests for that is how I mean if this works perfectly there you can be we can be assured that you do not have a bug in your code.

Of course, if you keep on increasing delta t say 2.01 say then you will see that the integration itself is not working properly, the energy shows a shift, the particles move around and basically sit on top of each other because the Newton’s equations of motion are not being integrated properly. As a consequence the MD is going to show an error; two particles can come too close to each other form or face a very large value of the force because it has moved unphysically close to each other which will lead them to be kicked and sent away from the box and you typically get a code dump, your code stops running.

And, so depending upon the potential you have to choose a suitable value small value of the integration constant, the sharper your potential, the smaller integration constant you have to choose right. Well, the last thing I think I need to tell you and which I might have forgotten to tell you is often for equilibrating your system you switch on the thermostat in a molecular dynamics, but after the system has equilibrated whether you keep the when you are calculating your statistical quantities of interest.

Now whether you keep the thermostat on or off depends upon the physics of the problem, depends upon what you want to study if you want to study the system in a micro canonical ensemble where there are no energy fluctuations allowed, then you keep the thermostat off and then the energy will be perfectly conserved.

On the other hand if you are fine looking at the system in a canonical system, canonical ensemble then you can study your system with a thermostat switched on which will maintain the right temperature. Anyway, since the system is already equilibrated even if you switch off the thermostat, there will be only extremely small deviations from the right value of temperature which you can use calculating the which you can calculate using the equi-partition theorem.

So, it is basically going to fluctuate about an average because whatever extraneous kinetic energy and potential energy exchange was there that you have already taken it out using the thermostat right. So, this basically brings out to the end of this course of molecular dynamics simulations and end of this course.

Of course, there are many kinds of thermostats there were lot of other things which can be calculated using molecular dynamics, but we hope that with this amount of at least got some exposure to molecular dynamics and in more general various computational techniques, various flavours of them, various kinds of problems which can be solved, so that in future whenever you need to solve a computational problem you are will be capable to read up there algorithm from a book or learn it from your supervisor and be able to implement it on the code.

Very importantly, you always need to use your physics intuition to devise tests, why should you believe that your code which you have written is working correctly. There are more often than not bugs there are always bugs and one has to always device tests such as conservation of energy, conservation of momentum, whether density is uniform or law or not, whether you are getting correct this is a behaviour or not and or even better test like the one we discussed to ensure that you are getting the right code.

Moreover, even while you are calculating statistical physics statistical quantities whether you have a got a good average or not all these have to be tested using ideas of physics. And, whatever problem you do in your future wherever you use computational physics you have to use your background intuition, the background science of physics or whatever to somehow test whether things are right or not and then only then go ahead and calculate non-trivial quantities which will be of interest for the future right. With that word of advice I shall end this course.

And, thank you for your attention.