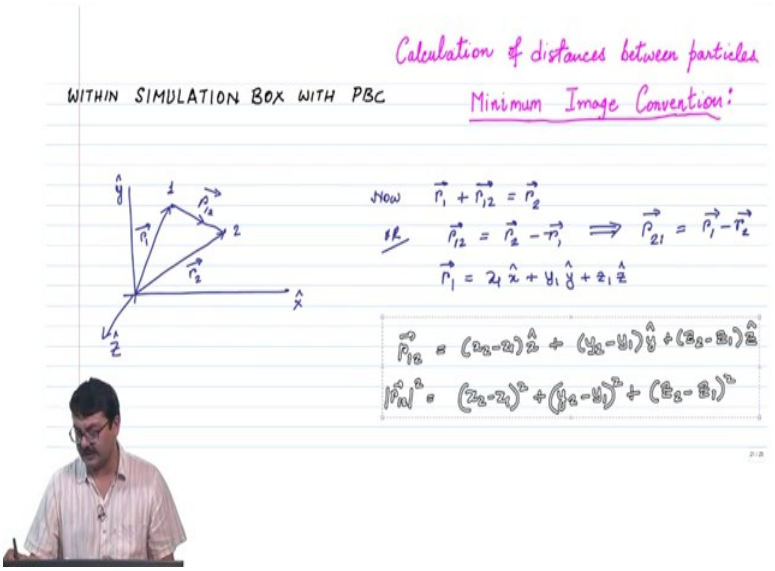
Computational Physics
Dr. Apratim Chatterji
Dr. Prasenjit Ghosh
Department of Physics
Indian Institute of Science Education and Research, Pune

Lecture – 50
Molecular Dynamics Details and Algorithm Part 03

(Refer Slide Time: 00:16)



Now, when you have a box, a simulation box with periodic boundary conditions implemented, then the distance the calculation of distances between particles in the simulation box becomes a problem. And one has to introduce the ideas of the minimum image convention to calculate the distance between particles, specially if they are near the edges of the box. So, let me explain.

So, suppose you have a box with the periodic boundary conditions. Now, let me explain. So, now, how do you usually calculate the distance between two particles or two points? So, suppose this is essentially x y z coordinate system and this is point number 1 and this is point number 2.

And then you would basically refer the position with respect to the origin here, as vector r 1 which basically denotes the position of particle 1, position r 2 which essentially

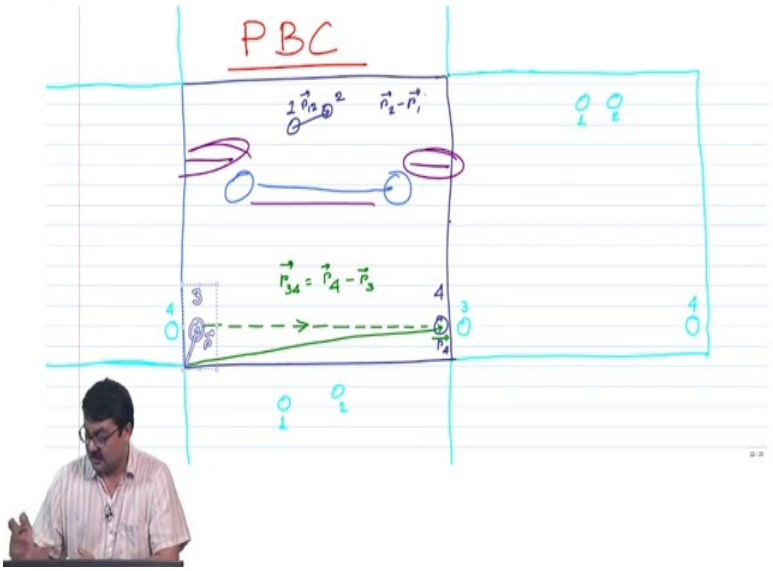
denotes, so r 2 denotes the vector which is the basically the position of particle 2 and this vector here is the vector joining particle 1 and particle number 2.

So, then one could easily write that r 1 plus r 12 equal to r 2, right, this would hold a simple vector. But then one can also write r 12 is r 2 minus r 1. So, r 12 is this vector joining position number 1 to 2 and that can be written as r 2 vector minus r 1 vector. Similarly, if you had a vector which is going from 2 to 1, so basically this r 2 to 1 right, which is exactly opposite that of the vector r 12 then this that is r 1 minus r 2 right. And then basically well what is r 1 you could write it as x 1 into x hat plus y 1 into y hat and z 1 into z hat and similarly you can write r 2 as well.

And then r 12, if you have to calculate it explicitly new simulation box where the origin is at 0 then you would do it x 2 minus x 1 x hat right, that is what is r 2 minus r 1 x 2 minus x 1 x hat y 2 minus y 1 y hat and z 2 minus z 1 z hat. And that is the vector going from here to here, that is r 12 vector. And of course, r 2 minus r 1 would be the vector with the opposite sign and it would point in the opposite direction.

And the magnitude of r 12 whole square the magnitude, right, so that is why I have used the wetter and the bar and whole square is x 2 minus x 1 whole square plus y 2 minus y 1 whole square plus the 2 minus at 1 whole square this is the standard knowledge what you have. And that is what you would how calculate the distances and the vectors and if the force acts along these vectors, then you can give the direction of the force vector, you can define a unit vector from all of this and that is how you would do your calculations.

(Refer Slide Time: 03:46)



But if you have a box with priority boundary conditions PBC, then a situation could get a bit more complicated. And let me explain. Now, suppose this deep blue is your main simulation box right and here is your particle number 1 and here is your particle number 2 and you can calculate r 12 exactly as we discussed in the previous slide and that is equal to r 2 minus r 1.

So, suppose these are relatively close together, close in space with respect to each other, but this is a box with periodic boundary conditions. And now suppose you had particle number 3 which is situated here right and particle number 4 which is situated here and these are the basically the two vectors r 3 and r 4 and then you would say well r 3 to 4, r 3 to 4 is this vector; is r 4 minus r 3 is no different from here.

But and there is a but, and a suppose its periodic boundary conditions; that means, you could imagine that if this particle number 4 goes out due to whatever attractive forces of, appropriate values of forces and velocities suppose it goes out in this direction right then you would put it back somewhere here, right, that is where you would put it back. And then it would overlap or it would sit on top of 3.

Now, as I said since you have a periodic boundary condition you can also imagine that the main simulation box which is marked in this dark blue is surrounded by identical copies of the box in all possible directions. Here I have shown on the right and on the left and on the top and on the bottom, but also you would have some box imaginary box

identical copies of the box which is basically setting into the plane and outside the plane, opposite to the plane of the screen right.

And then you would have these copies of 1 and 2 and if you like you could think that just near 4 you have a particle number 3 setting or you could also imagine that particle near this particle number 3 there is this particle number 4 setting which is essentially saying that you know this this and this are connected they are basically periodic boundary. So, from here you can directly go to there.

So, this is just a visualization of that aspect, right. And correspondingly, if particle 4 is situated here and particle number 3 is situated here the actual distance between these two particles if you even take this part and this part its actually relatively close. So, the distance is not this distance, it would be unwise of you to use this formula r 4 minus r 3 because that would give a very large distance.

I mean this is the vector and from there you can calculate the distance and if you calculate x 4 minus x 3 whole square plus y 4 minus y 3 whole square, I mean the way we discussed this basically this formula, the corresponding formula here then you would get a very large distance, but actually as you see and because this and this are essentially the same point in space, because they are connected because they are periodic boundary conditions the actual distance between 3 and 4 is much less. It is not the last distance that you see.

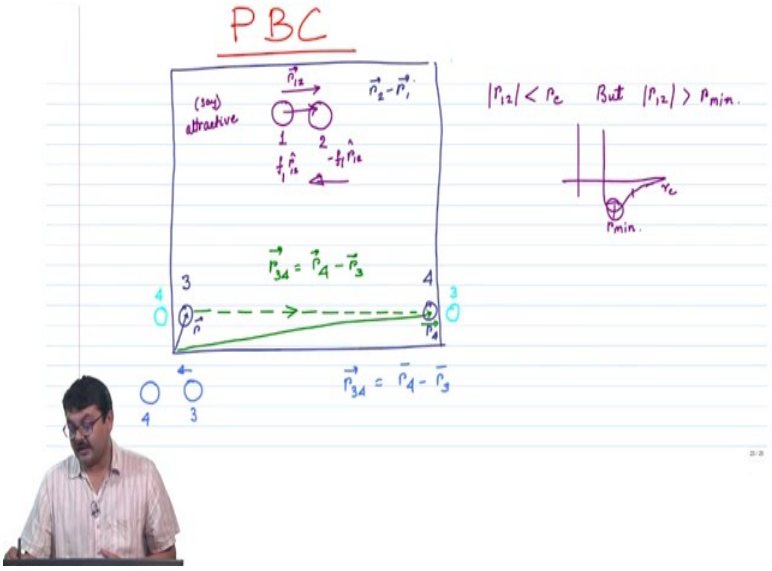
So, when you have a system with periodic boundary condition you have to ensure which is the minimum distance. If it is this then of course, you should take this distance, but as you as these particles, so as these particles. So, suppose the one particle is here and one particle is here then you have to check whether this is your minimum distance or this plus this is the minimum distance, right.

So, if the distance between the two particles becomes greater than half the size of the box or rather take the x direction if the x distance between ah the distance in the x component becomes greater than l x by 2, similarly when you calculate y 2 minus y 1 or y 4 minus y 3, if that distance becomes greater than l y by 2 and similarly in the z direction then the appropriate way to calculate the distance or you should correct for dx d x being x 4 minus x 3 d y being y 4 minus y 3.

So, we should not take this distance instead take this plus this distance. So, that is the so called minimum image convey. So, you should actually check which distances actually the minimum. And the reason is periodic boundary conditions, as I mentioned before because basically this is sitting close to r 3 though in within the simulation box it looks very far away, right.

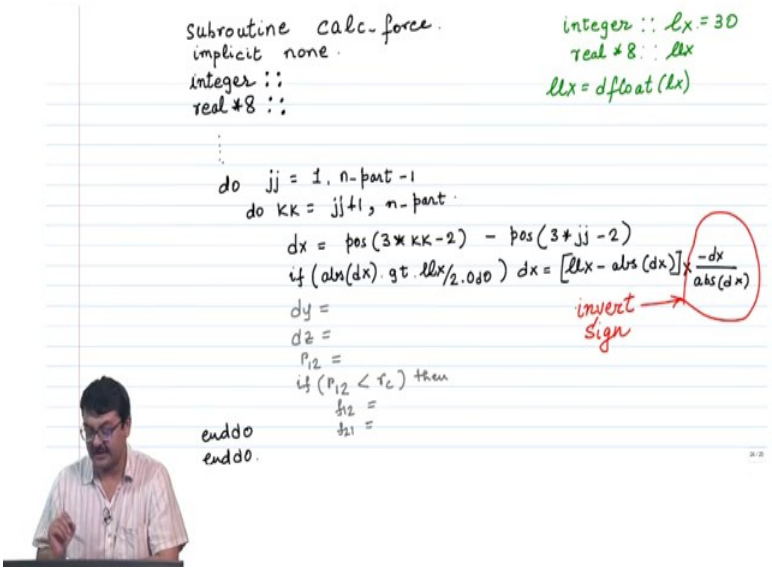
So, we should correct for this distance and use the minimum image convention to calculate the actual distance between particles. And this minimum image convention has to be implemented in all 3 independent directions.

(Refer Slide Time: 09:48)



But one has to be careful of one more thing and then and let me explain.

(Refer Slide Time: 09:52)



Now, suppose this is your particle number 1 and this is particle number 2, and they are interacting by Lennard-Jones interactions and this is the r 12 vector going from particle number 1 to 2. And suppose the magnitude of r 12 is such that r 12 is less than r c, so that there is an interaction the interaction is not 0, but r 12 is greater than r mean, so it is an attractive interaction, so attractive force. So, the this is your schematic Lennard-Jones potential diagram.

So, it says that r 12 somewhere here between r, so greater than r min and less than r c. So, as a consequence the force acting on particle number 2 will be in will be basically in this direction, similarly the force acting on particle number 1 will be in this direction in the direction of r 12, right and so that is how.

So, if these are two particles they have an attractive force, so they will start moving towards each other assuming they that they start from 0 velocity, there is no initial velocity, they would move towards each other, till they the distance between the particles become somewhere here where there will be a repulsive. Actually, a repulsive attraction will start acting as soon as the distance between particle becomes less than r min, right.

But imagine the same situation with essentially box particle number 3 and 4, right. So, if they are close to each other, 3 and 4 are close to each other if you have problems imagining you can draw particle number 4 here or draw particle number 3 here and as a consequence there is attraction between them, so particle number 3 will move towards

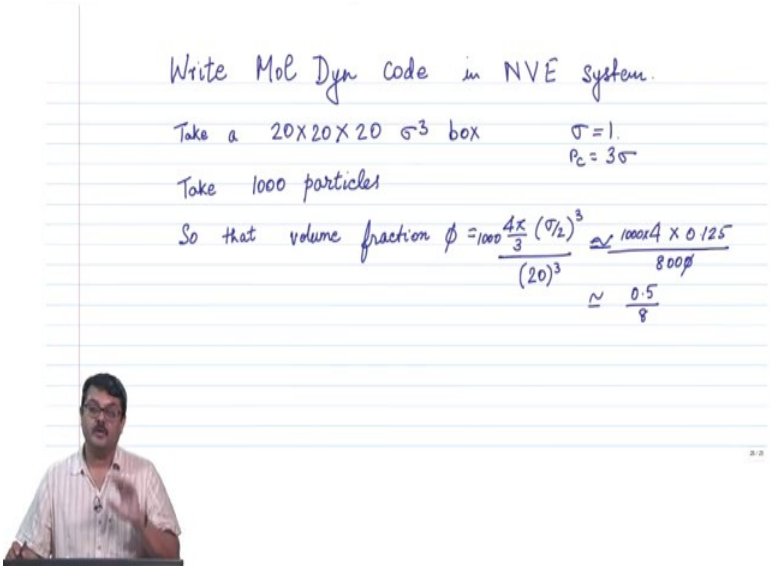
particle number 4 and particle number 4 will move towards particle number 3. But if you take this vector, right.

So, basically particle number 4 will move in this direction and particle number 3 should move in this direction. But if you consider r 3 4 to be the vector that is exactly opposite from the direction that you expect it to move and that is because of minimum image convention. In this case, because the distance between the particles within the simulation box when you calculate r 2 minus r 1 or rather x 2 minus x 1 and y 2 minus y 1, these distances are less than lx by two half the length of the box.

But here the distance at least in the x direction suppose this is the x direction is less is a much more than half the length of the box and then if you use just this formula to calculate the direction of the forces you will get a wrong answer. When you correct for the distance of minimum image convention you also have to correct for the vector because it is larger.

You have to basically ensure or calculate the vector using the minimum image convention because of this and this is attracted a 4 is not going to move in this direction, it is going to move in this direction towards particle number 3 which is sitting here, towards particle number 3 which is sitting here because this this distance is essentially the smallest distance and not this dashed green line, right.

(Refer Slide Time: 13:37)



So, the way you have to calculate distances while calculating the force, for periodic boundary conditions you have to basically do it when you were updating the position of the particle, when the particle goes out from the right side of the box put it back in the left, when the particle goes out from the top of the box put it at the bottom of the box.

But because of this because of periodic boundary conditions when you are calculating the distances between particles to calculate the force which is essentially in subroutine calc-force, the way you have to write the distance and the way you have to write the vectors is slightly different. Just I am showing you the basic schematics algorithm you will implement it in the code.

So, suppose you had the subroutine calc-force and you start with implicit none and this is the, and then you have your integer star 8 and you define various variables real star 8 and you define whatever variables you start on with the other definitions whatever you need to. So, when you are counting you want to calculate the force between every pair of particles. So, how do you write the loop?

So, jj is some dummy loop integer variable do; jj equal to 1 to n part minus 1. Why n part minus 1? Because you want to count every pair of particles only once right. So, 1 will interact with 2 3 4 5 6 7 8 so on so forth. Similarly, 2 will interact with 3 4 5 6 7 8 9 10. 4 will interact with 5 6 7 8 and so on so forth. So, the last, suppose you had 100 particles, so jj will run from 1 to 99 and kk this is another dummy variable will run from jj plus 1; so, if jj is 1, then jj kk will run from 2, jj being 1, 1 plus 1 is 2. If jj is 99, right then kk has to be jj plus 1.

So, you are basically only calculating the interaction between the 99th particle and the 100th particle. The interaction between 100th and the first, 100th and the second has been taken care of already, right. So, the loop should go like this. Just think about it a bit. And so, here you have your jj and you have your loop over so that you count every pair of particles. This is the end of the loop and if you were calculating the distances then dx would be pos 3 into kk minus 2, minus pos 3 in jj minus 2.

So, this is basically like calculating r 12 write the x component of r 1 and there we have to implement if absolute dx is greater than llx by 2. What is llx? Suppose, the size of the box in the x dimension was lx, just amazing equal to 30, then you could do mine then you could basically define a variable llx which is real star 8 and ll x is nothing but dfloat,

the real version of lx. So, basically if you define lx to in an integer variable, you have defined llx to be the same variable, but now in a float and a real.

So, if dx, the distance, the x distance between the two particles is greater than half the length of the box in the x direction, then dx equal to this is the minimum calculating the distance in the minimum image convention you are saying, ok, I want to wrap around the box and to calculate the distance. So, llx minus absolute value of dx because you do not know which particle is on the right and which particle is on the left right.

So, you really need to take the absolute value of dx, right. And then, so this is the correction for the distance the appropriate distance and dx by absolute dx with a minus sign basically changes the direction of the vector, right. So, if you have; if you have to invoke minimum image convention you have to correct and invert the sign of the as well to basically calculate the forces, correctly.

And that is basically what I explained here, that the particle 4 where if they have an attractive interaction will move towards this direction and particle 3 will move towards this duration and that is opposite to what you would get if you invoked just this in their normal way, right. I hope you have got these ideas. Just think it over a bit.

Now, with this background you will be able to write molecular dynamics code in the NVE ensemble, right. And so, basically energy is conserved and how to implement a thermostat we will discuss in next week you. What you could do is take 20 cross 20 cross 20 box, 20 cross 20 cross 20 sigma cube box because you have to mention the dimension, but you can take sigma to be 1 and r c to be 3 sigma.

And take 1000 particles in the box, put them in a lattice at the distances of 3 or 4 whatever well fit, you can also put them randomly, but then that is a more difficult thing. You could however try to do that, so that they do not overlap. And if you have 1000 particles in a 20 20 cross 20 box then the volume fraction will be 1000 into 4 pi by 3 sigma by 2, sigma by 2 radius; cube the radius of a sphere by 20 cube, right. This is the volume of all the boxes.

And if you assume pi n as an estimate pi n 3 to be equal then basically what you get is 1000 into 4 into 0.125. Why? Because sigma by 2 is 0.5, 0.5 cube is 0.125. The volume fraction is low, its less than 10 percent and less than 0.1, if you can calculate it this is a

weakly interacting system and you can choose epsilon to be 1, epsilon being the depth of the potential remember there is the 4 epsilon in the Lennard-Jones interaction and you can introduce the particles, give random velocities, ensure that the total momentum of the particles becomes 0.

Whatever is the total momentum of the particles you set it, you subtract the total momentum from each of the particles, so that the total momentum becomes 0, 0 here since you have real star 8 variables become means actually. Accuracy to the value 10 to a minus 16 and now you can calculate the force and because you know the positions and then you can basically run the simulation for say 10,000 iterations.

What should you see? You should see that starting from the whatever initial energy that you had the total energy will remain conserved that is basically what Newton's laws says. You have 1000 interactions, 1000 particles in a box, they interact with each other, they want to change kinetic energy, they are going to exchange kinetic energy and potential energy with each other, but total momentum will remain conserved because pairwise interaction whatever force is acting on this particle equal and opposite force is acting on that particle, so total momentum will remain conserved.

The accuracy of 10 to the minus 16, you could take dt, the integration constant to be 0.005. Units will be discussed next week. And well, you can just check out whether your total energy is conserved or not, even as potential energy and kinetic energy vary, right.

So, with that we shall come to the end of this class. And we shall continue from this point next week.

Thank you.