Computational Physics

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Lecture – 47
Molecular Dynamics Introduction Part 02

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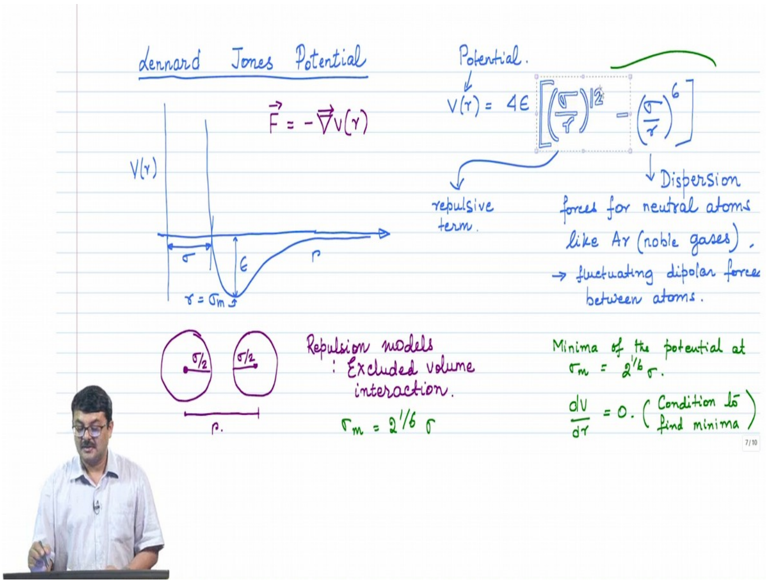

So, now let us come to the discussion of the force. So, for our studies for this module we will be using relatively short range force or the potential. I mean the force you basically take by a gradient of the potential and the potential that we shall be using for the purpose of the study is the so called the Lennard Jones Potential. And the expression of this Lennard Jones potential looks like this. So, v of r is equal to 4 epsilon, epsilon is a unit of energy it says the scale of the energy and into sigma to the power r, sigma is a parameter I shall explain what that means, minus sigma by r to the power 6.

So, this potential looks something like this all right. So, here you have I plotted v of r on the y axis and on the x axis is r and the functional form of the potential. When you plot this function it looks like very sharp sharply increasing potential for r less than equal to sigma ok. So, it is very fastly increasing after that there is a potential minima, there is some attractive potential this is negative here and then it gradually goes to 0 as r increases.

So, what does this potentially mean, I mean what does it signify? So, suppose that you had two particles right I mean you are calculating the interaction between two particles and there are spherical particles and of size of radius sigma by 2 ok. So, when they were at a distance r which is greater than sigma sigma so each is sigma by 2.

So, when they touch suppose these are those two particles and when they touch the distance between their centers would be exactly sigma. And at sigma you see that the potential is exactly zero. But as soon as the distance between particles becomes less than sigma, so basically less than the diameter there is an extremely fast increase in the repulsive potential right.

So, sigma by r to the power twelve is the repulsive potential and it increases extremely fast as basically the particles start to overlap. So, this is what basically is modeling the so called so this repulsive interaction is modeling the excluded volume interaction. What is the excluded volume interaction basically that two particles cannot sit are they are not allowed to sit on top of each other, because there would be basically if there are atoms or even there are particles.

If two two particles basically they exclude some volume in two particles cannot simply sit on top of each other, electrons would ripple electron from the two atoms they would ripple, ripple that two particles away from each other right. So, what does it say, so at distance less than sigma the potential is a sharply increasing, at up at a distance slightly more than r equal to sigma. There is an attractive weakly attractive interaction well weakly or not it really depends upon this value epsilon.

And at larger distances if these two particles go further and further apart there is a attraction, but it is very weak it is the potential is nearly tending towards 0 negative but 0. The minima of the potential; the minima of the potential is at a value of sigma m and you can calculate that, so we can calculate the position of the minima

So, how do you take the how do you calculate the maxima or minima of a certain function. So, here the function being v of r basically you take d v d r equal to 0 right and then solve for the value of r at which it is minima. So, basically d v d v d r equal to 0 is the condition of a maxima and minima and later you can check that it is a minima.

So, the value of sigma m comes out to be 2 to the power 1 by 6 sigma, sigma being the diameter of a particle or sigma by 2 is the radius of a particle. So, basically where does this expression for the potential come from. So basically sigma by r to the power6 is the so called dispersion forces between neutral atoms. So, basically if you have neutral atoms like argon noble gas where it has no net magnetic moment and so on and so forth and no charge and so on so forth.

So, basically what happens is that the center of the positive charge is the nucleus and the electrons they basically oscillate they move around in space due to which there are local, local in time effective dipoles which are formed and these dipoles are constantly fluctuating. I mean the strength of the dipoles are constantly fluctuating, because basically the charges are moving around and the center of charge of the electron cloud need not exactly match all the time on an average.

Of course, it matches but not locally and so basically because of this fluctuating dipoles two atoms or particles if you like they are because Lennard Jones is also often used to model weak attraction between larger particles. It is just a model and it is a good model system, but it works very well for argon.

Basically what you have is so when you have two atoms, because of these two fluctuating dipoles there is a weak attraction which is induced and which has been shown to go as sigma by r to the power 6 r to the power 6 right. And this so that is the origin of this minus sigma r to the power 6 weakly attractive term, this sigma by r to the power 12 is basically put ad hoc and the emails it should model the short distant extremely strong repulsion between particles right.

So, that two particles do not overlap and you see that it is increasing as r to the power 12. So, it is very fast decreasing as soon as r becomes less than sigma, if r becomes less than sigma sigma by r is a number greater than 1 and then it sharply do you increases. And it increases faster than r to the power sigma by r to the power 6 right. On the other hand when r is greater than sigma, so then sigma by r is a 0.5 to the power 3 and then it is 0.625 and so on so forth right. So, it well 25 to yeah.

So, basically if you take a small number and keep on powering it will go slow small to smaller and smaller values, basically if you take 0.1 whole square it is 0.01 0.1 whole cube is 0.001 and so on so forth. So, this basically dominates over this at large distances, but this dominates over this at short distances right, so that is what it is good.

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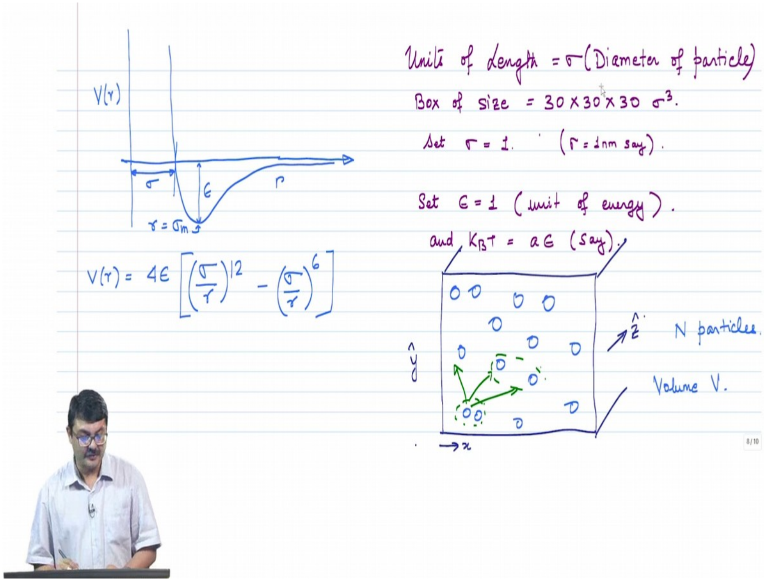

Now, you might have noticed that basically this point here where the potential goes to 0 is at sigma at when r equal to sigma. So, when they are just touching and that typically is set as the unit of length in our simulations, which means that you measure all other distances in terms of this value sigma ok. So, that is for the Lennard Jones if you have a different potential then you have to set it you set your units suitably. I mean here suppose you are modeling argon atoms suppose right, then sigma there would be some a few angstroms.

Now, in the computer you are not going to put in angstroms I mean we are not going to put 10 to the power minus 10 meters as units of your simulation, you set is sigma you say the diameter of the atom is set to 1. Whether it be 2 angstrom 3 angstrom whatever bit we set it equal to 1 and measure all other lengths the distance between particles in units of that.

Suppose you have a box size which you can choose to be 30 sigma 30 cross 30 cross 30 sigma, which means that the length of the box is 30 times the diameter of the particles right and then of course you have x y and z the three directions that 30 cross 30 cross 30 sigma. And well you can also set sigma equal to 1 nanometer, if suppose you are studying some system with a particle size of one nanometer of 1 micron whatever by 8 ah

So, you basically set that to be equal to 1 and measure all other distances in terms of that units. Similarly you can set epsilon what was epsilon, epsilon was the unit of energy if you remember it is this epsilon. You set epsilon to be equal to 1 the depth of the potential equal to 1 and then measure all other energies like thermal energy KBT in units of this in units of say KBT equal to some number times epsilon. And you set epsilon equal to 1 and then say where KBT is 2, if you set epsilon equal to one then a equal to 2.

So, the thermal energy is twice that of epsilon. By the way one thing which had forgotten to tell you in the previous slide is you might have noticed that the unit of energy has been written as 4 epsilon here. So, this is the unit of energy these numbers are of course, dimensionless sigma has diameter by r. So, the reason you right it like this is if you write it like this, then the depth of the potential at the minima becomes epsilon right. Now, if you have chosen it to be as well some other quantity suppose b.

So, if you had written b here then the depth of the potential at the minima would have been b by 4 right So, is the convention that you write the expression of the Lennard Jones and as 4 epsilon. So, that you know that the depth of the potential is epsilon and then all other energies like thermal energy. So, if you have very low temperature low thermal energy, then all particles would like to aggregate together because of this attractive interaction.

So, this attraction attractive energy would dominate the potential energy would dominate over the kinetic energy, kinetic energy because the kinetic energy is related to KBT right half m v square equal to half KBT for degree of freedom. So, or half m v square v is the speed then v square is 3 by 2 KBT if you take the three degrees of freedom right.

So that is the picture, so that is the discussion of the starting discussion for the potential and so what do you have you essentially have a simulation box like this all right. I have not plotted the box fully in the third direction the z direction, suppose this is y this is x and these blue things are basically particles Lennard Jones there are particles interacting by Lennard Jones interactions right.

So, each particle if you like so let us focus on this particle, this particle is interacting with this particle, this particle is interacting with this particle. But this particle is also interacting with this, this, this all other possible particles far away into the box, because this potential essentially goes to 0 only at infinity. It might have a very low value at higher distances, but still it is nonzero.

So, for each particle you have to calculate the potential the and the force of interaction between all of the particles in the box and similarly if you have n particles. So, N particle you have to calculate the force with N minus 1 particle and so on so forth it is basically N square calculation right. So, you have N particles in a box of volume v.

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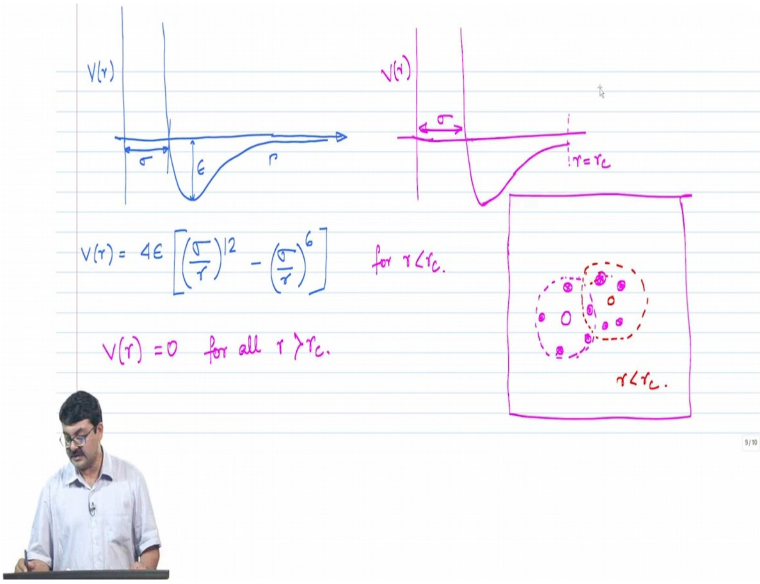

As I told you we are studying canonical ensemble we will be studying the system in a canonical ensemble right. Now, that is a bit of a problem why is it a problem, because extremely expensive it is if you have thousand particles then to calculate the force each time you have to do from 1 million force calculations right. Whereas, as I just told to you that basically at distances very far away a distances are much greater than sigma 3 sigma 4 sigma 5 sigma, here the value of the potential is rather weak and even if you calculate the forces you will see there are very weak forces acting between the particles. So, that is not really affecting the motion.

So, suppose that you had a particle here it is interacting with another particle here right. But the force of attraction is extremely weak it is effect will not I mean it will be felt, but overall statistically it will not make much of a difference. If you say that beyond a certain distance say r c beyond a certain distance r c say. So, you set that the potential is completely 0, you set the potential completely equal to 0. So, here the repulsive the strongly repulsive interaction stays the weak the attractive part of the interaction stays, but at r greater than r c.

So, instead of this figure the Lennard Jones you have essentially a modified Lennard Jones. So, that you say that you know what v of r beyond a certain cutoff distance r c cut off that is why there is r subscript c there is equal to 0 it is set to 0. So, then what happens what does it mean? So, it means that that suppose there is a particle this is a particle in question you have want to calculate the forces the potential of interaction between this particle and all of the particles in the box.

So, basically all the particles which are neighboring particles which are within a distance r c given by this dashed line, they feel some force some interaction potential. But beyond any particle which is suppose here or here which is greater than the distance r c between this particle feels is 0 force.

So, what do you get? You get that you do not have to calculate the expression of the force and the potential for a very large number of particles. If this is the your particle in question you are calculating the force only for suppose one two three four five particles, which are neighboring particles and not the force between this and this and all the particles which are far away.

Say calculation speed your calculation efforts or rather the calculation effort for the computed decreases significantly and it has been checked already by previous studies and you can check it to yourself as well that this slight change does not affect the physics much. Similarly if you are interested to calculate the force for suppose this red particle, all that you have to do is check out which particles are within a distance less than r c and calculated the force for only those particles right.

So, basically what you have now is that the expression for the Lennard Jone; Jones interaction gets modified to this. So, that v of r is the standard Lennard Jones term for r is less than equal to r c and v r equal to 0 for all r for all r r being the distance between two particles distance between the centers of two particles it is set equal to 0. So, that is very nice and good, but there is always a but and there is a problem.

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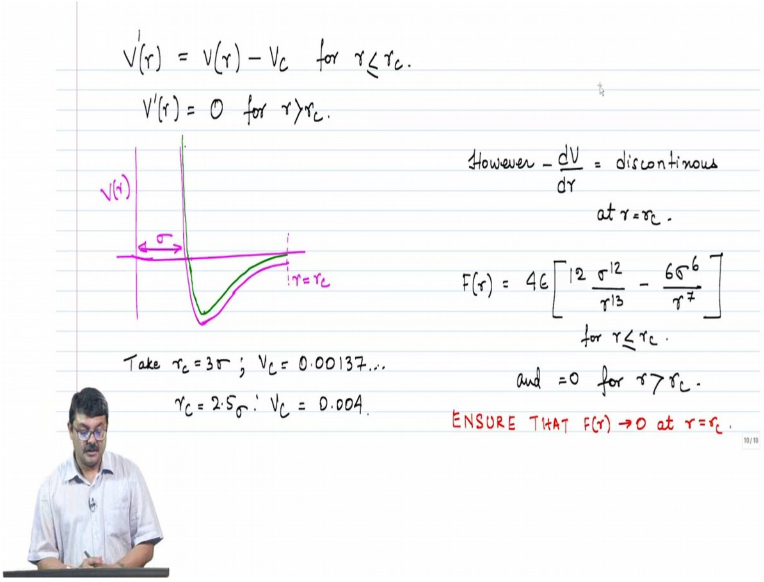

The problem is that basically the potential becomes discontinuous at r equal to r c. So, there is a certain potential here as a finite value of the potential here and suddenly there is a jump and the potential goes to 0 right, because we have cut it off was the solution ah. If probably the solution looks quite simple shift the potential off. So, that instead of having this magenta colored potential which you have also had a look at in the previous slide. You have this green curve right which I have just shifted up by how much by the value of the potential which was at this point.

So, suppose the value of the potential at r equal to r c was v c, you just shift the entire potential up you just subtract the value of v c from the entire potential that the own entire potential gets shifted up right. Then you can do your derivatives and calculate your force and so on and so forth.

So, then the potential at least goes smoothly to zero at r equal to r c and beyond that it remains 0. So, this is the potential becomes a continuous function, the expression for the potential then becomes v dash r right because your modified it. So, this was your original Lennard Jones expression for the potential and your new potential modified Lennard Jones potential becomes v r minus v c for r less than equal to r c and v dash r equal to 0 for r greater than r c.

Now, this quantity is continuous this function is continuous in the value even at r equal to r c it smoothly goes to 0, what are the values of r c you can take. So, suppose you took r c to be three sigma right three times sigma. So, if you are taking sigma equal to 1 you take r c equal to 3 sigma. So, that sigma by r is one by three then the value of v c would be 0.001.

So, basically it goes very quickly to zero at distances beyond 2 2 or 3 sigma 3 sigma, the value of the potential would be 0.00137. So, you can choose the value of v c here to be this right, you fix the cutoff right at the beginning; of the beginning of the code and shift the potential off you could as well have chosen r c equal to 2.5 sigma. What would be the advantage? It is basically you have to calculate the interaction between the particle of your interest and it is neighboring particles over a shorter distance. So, you will have a smaller number of neighbors over with which to calculate and the corresponding v c is you can calculate it is rather small it is 0.004.

So, the message is it goes rather quickly to 0 at these r c at r equal to 3 sigma or 2.5 sigma, you can choose your r c to be 3.5 sigma, there is nothing holy is you basically you just set it because the physics is not changing. Because the potential the shift in the potential is so low and at even higher distances the value of the potential would be even lower right.

So, you would think that it is quite nice and you can go ahead and do the simulations. And in fact if you were doing a Monte Carlo simulation you could just work with this where the potential smoothly goes to 0. So, if two particles are close together they feel a repulsion as they go further apart they feel some traction, but as they go further and further apart the particles the interaction between the particles becomes weaker. And image after some point at beyond r equal to r c, at r equal to r c becomes 0 and beyond that it remains 0.

Of course, as two particles are moving further and further apart from each other, this particle could meet some other particle which is at some other point in the box right. And then it would feel attracted to that and then it could come close to each other to that other particle, it could collide with it and move apart or steak depends upon the kinetic energy right. But it happens that for if you are doing molecular dynamics you have to work who not with a potential.

So, though I have been discussing the potential what you actually have to work with is the force, which is minus d v d r the expression for the force is by taking a derivative gradient of the potential right. And what is the expression if you had Lennard Jones potential then by taking the derivative this is what you would get you just take a d d r and correct for the.

So, you have a minus d v d r as definition of the force and you would get 12 sigma to the power 12and r to the power 13 minus 6 sigma to power 6 r to the power 7 right. So, take a derivative you would get a minus sign, but that this minus sign takes care of this. So, basically you again have this thing here and this thing here.

Now, you have taken the potential you have moved the potential smoothly to 0 at r equal to r c. But the thing you have to work with is not the potential but the force and that this function still remains discontinuous at r equal to r c. So, basically what is happening it is up two particles as they are moving further and further away from each other, they are feeling some weak attractive force and suddenly it goes to 0 right. There is a jump but there is a discontinuity in the potential.

So, we have to ensure that both the potential and the force goes smoothly to 0 at r equal to r c ok. It is not very difficult, but it will be take 10 minutes of your time and hence we will discuss this in the next class.

Thank you.