Computational Physics
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Lecture – 52
Molecular Dynamics Analysis Part 02

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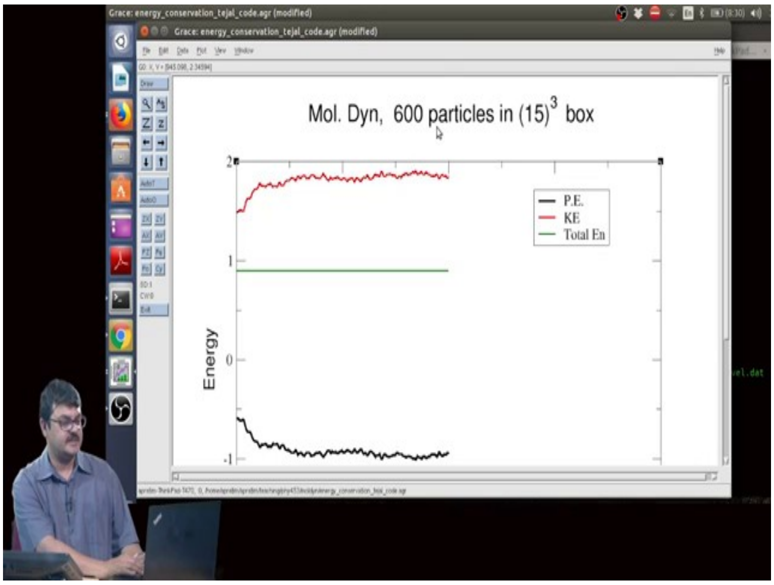

And that is exactly what I plan what I have done and I plan to show you for 600 particles. So, this is a molecular dynamic simulations 600 particles in a 15 cube box I have introduce the particles randomly.

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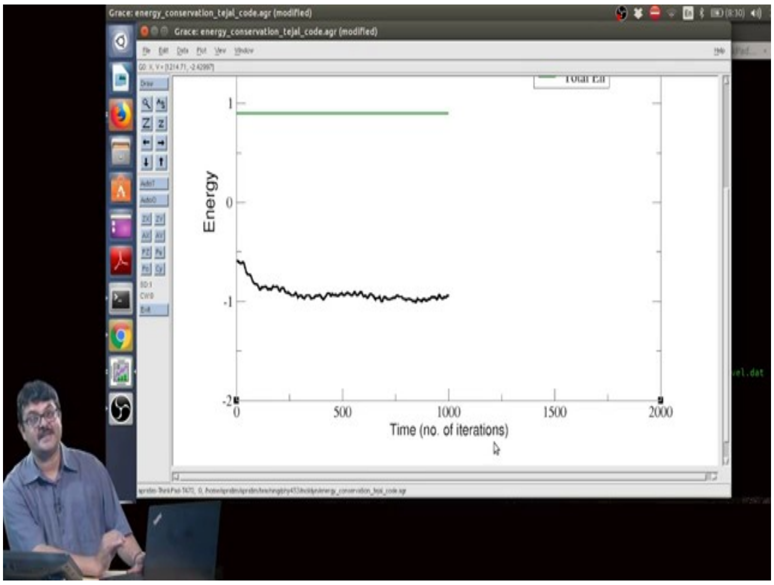

You can do it in a lattice does not matter, I have looked at it in a time; time is a misnomer actually what I have plotted is number of iterations. But if you multiply the number of iterations by dt which delta t then you essentially get the real time right. And what I have on the so this is on the x axis I have looked at it up 2000 iterations, you can also look at the energy and showed in the I look at the black curve is the potential energy, red curve is the kinetic energy and blue curve is the total energy.

What is what are other particles doing here, you see the initial kind potential energy of the system was some value closed to 0.6 minus 0.6. So, basically I had started of the system, so that quite a few particles are within the potential well. So, there is some negative potential energy, but as the particles move around they move to closer to the center of the well depending upon what kinetic energy they have an initiative position.

So, you see that the total potential energy is decreasing and fluctuating about some average, this too short and iteration to claim that it has least equilibrium. But as the potential energy decreases what you see is that the kinetic energy increases thankfully. The kinetic energy starts from plus 1.5 this is all per particle energy per particle it starts from 1.5, because that is how we had chosen or rescaled the total velocities when we had introduced the particle.

When we had introduced the velocity of particles in the box it starts from 1.5, but as the potential energy decreases the kinetic energy decreases to a certain value. But thankfully the total energy remains conserved do you see it is a perfect straight line right. How straight is straight? So, let us just zoom in.

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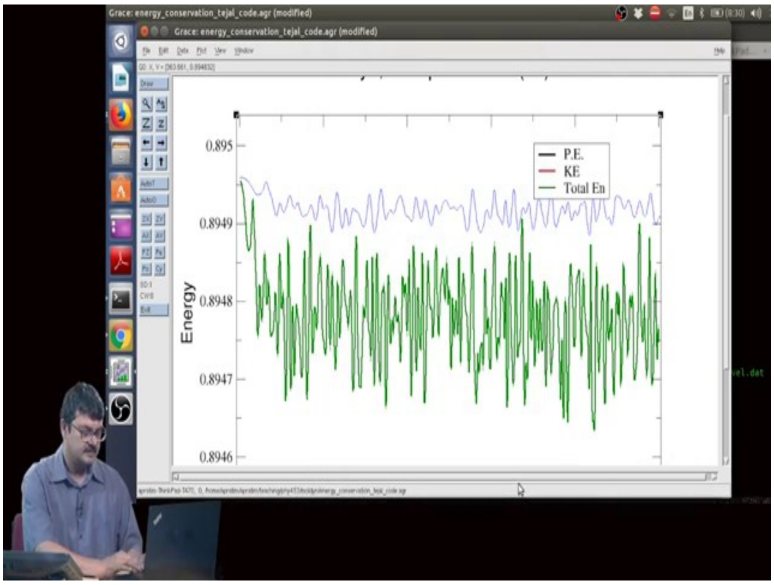

Now here you see some slight wiggles coming up and if you zoom in further you see that there are significant wiggles energy is conserved. But only up to the say fourth place of decimal and why is that because we are chosen d t equal to 0.005 whole square. So, your energy calculation is accurate up to a 0.005 whole square right, which is basically the close to the fourth place of decimal and you see energy fluctuations.

Now if you had done the you had repeated this simulation starting from the same initial condition, but with dt the integration time constant haft 2.0025 which I have already done then what you would get is something like this. So, this blue curve is the total energy of the system for d t equal to 0.0025, what you would see is that the fluctuations in energy are abode even by I estimate for no.

Of course, you can quantify it you can calculate the fluctuations in energy quantitatively standard division of the mean energy once it has least equilibrium. You can see that the fluctuation in energy by I estimate is about one fourth here, you have half dt the accuracy in energy has gone by dt by 2 previous dt by 2 whole squares. So, this is one fourth right that is exactly what you see. However, if you look like this so this is plotted a number of iterations.

I ran that the previous code for the same time. So, since I increase I decrease dt the number of iterations I increased to double, but I did not plotted was with respect to time. But I plotted with respect to iterations and you see within this scale the total energy remains perfectly constant right and only when we zoom in can we see the fluctuations. And this is exactly what you should test for your code yourself and ensure that energy is conserved to the fourth place of decimal fifth, it will it depends upon the value of dt as I told you right and so that this is a quick test.

Now, let me focus on this you see that the kinetic energy the kinetic energy started from 1.5 per particle, you wanted to set the kBT to be one. So, the kinetic energy per particular by equi partition theorem has to be 3 by 2 kBT per particle kinetic energy. But it has increased which means effectively that the average kinetic energy has increased means that the average temperature of the system has increased and you want to study the system at an appropriate temperature.

So what do you need you need a thermo stat you need a way. So, that you can rescale the velocities to the by the right amount, so that the average kinetic energy of the system remains at whatever value you want it to be right.

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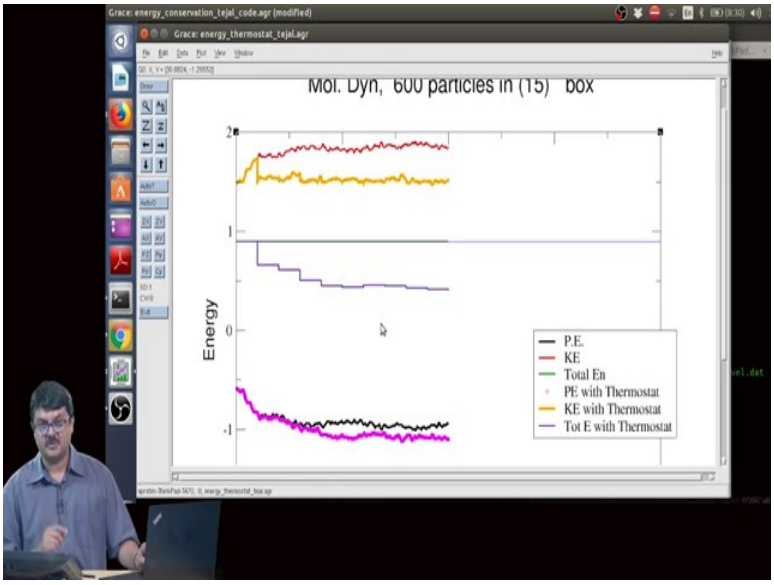

So, I will discuss the algo of the thermostat soon, but what I have done is implemented the thermo stat. So, what I am doing is already implemented the thermostat I shall discuss the algorithm soon after, what I have done is every time you update the velocity after a few iterations. Once the kinetic energy starts to increase I reset the velocities, so that the kinetic energy as reset to 1.5 sorry 3 by 2 kBT.

And then again kinetic energy starts to fluctuate after 100 iterations in this case after every 100 iterations I have reset the kinetic energy, so that the average kinetic energy of the system at that iteration is reset to 1.5 kBT. Now as the MD goes on the particles are going to move around and kinetic energy is going to change again, is potential energy is being changed to kinetic energy kinetic energy is going to be changed to potential energy and so on and so forth.

So, kinetic energy will slightly increase decrease it can do whatever, but you basically set it after every 100 iterations I am setting it back to 1.5 kBT. And after a few iterations you see that the average kinetic energy is fluctuating about an average even with the reset. Here you can clearly see it even here you can just about make out let me zoom in, you see here there is a district jump here I have reset it here I have reset it here I have reset it. So, I am resetting the kinetic energy every hundred steps. What are the consequences?

The consequences is that since the velocity of the particles has changed, the amount of displacement has change the potential energy initially follows the same graph trajectory as without thermostat as in this black curve. But since every time the you are changing the velocity the displacements are different, the potential energy flow also changes differently. So, it is basically path has changed.

Potential energy here is being not being rescheduled only the kinetic energy is being rescaled every 100 iterations. So, every for every 100 iterations the energy remains conserved. But when you reset the kinetic energy the total energy of the system also automatically gets rescaled to this value and here you call the thermostat again where you rescale the velocities.

So, the kinetic energy gets rescaled, the total energy gets rescaled. Again between this step and this step you will see that the energy is conserved up till about it is conserved to the accuracy of delta t whole square. But in between sorry, but whenever you call it the thermostat the total energy also gets rescaled right.

And you see here that basically here the energy rescaling is not much initially it is much more as the particles move around as the kinetic energy increases. Here it had basically stabilized to some value which is much higher than kBT not much higher, but whatever value near to and here due to rescaling you see that the total energy also fluctuates about the average. So, basically and between every two resetting the energy is conserved. How does one now implement the thermostat? So, that is let us the so that is the topic of our discussion and let us return to the board.

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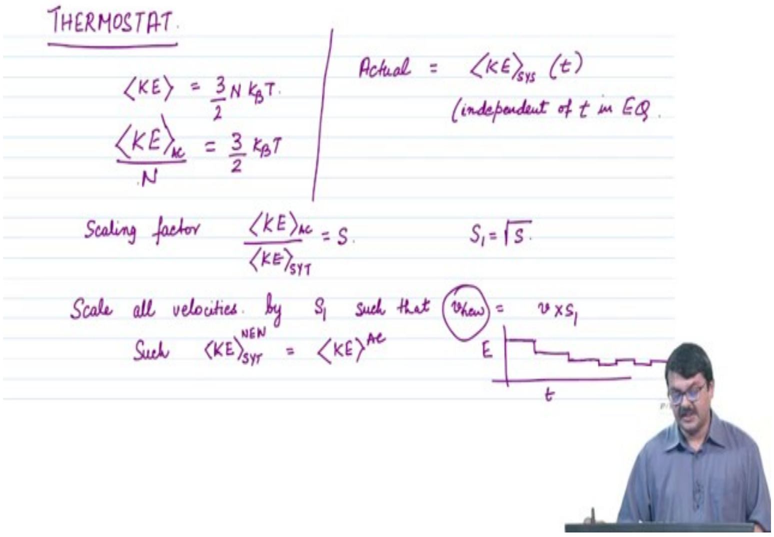

So, coming back to how the Thermostat works we shall be taking the help of the so called equi partition theorem ok. Just what is the thermostat, a thermostat is tool a computational tool which keeps the temperature of the system constant. So, in the real system an air conditioner would be a thermostat, because it keeps the temperature of the room fixed at say 25 degree centigrade.

So here what do we want we want to study in computationally a system which is maintained at a certain temperature right. So, when I say temperature it means that energy is no longer conserved, if there is excess kinetic energy due to which basically the temperature increases because of equal partition theorem. We are using equal partition theorem to calculate the temperature and then basically as we saw yesterday that as the particles started moving around in space, more there was a decrease in the potential energy in the system due to which there was an increase in the kinetic energy of the system.

And as a consequence the temperature the instantaneous temperature increases ah. What do we want we want to look at a system where the average kinetic energy of the system is maintained at a fixed value at 3 by 2 and kBT right kb being the Boltzmann's constant. Which would also mean that the temperature of the system is maintained. Now you are calculating and so the kinetic energy at each instant in time as the particle moves you are calculating the kinetic energy.

Remember temperature is related to the average kinetic energy, so a time average of the kinetic energy. But as we saw yesterday even as the system evolves starting from the initial condition the kinetic energy itself was increasing. So, even the average would increase. So, the average so the temperature would also increase and our aim is to keep the temperature fixed. So, the kinetic energy can fluctuate about an average value, but it should not change, because we want to study say a canonical system.

So, the simplest there are many thermostats which are discussed in literature and in the literature of computational physics I shall discuss the simplest one. And in the simplest one all that was does is as the kinetic energy increases say one simply rescales the kinetic energy to the right value, right means at the value that we want at the value that a is determined by kBT which we want to fix. We want to rescale the kinetic energy to it is appropriate value.

So, we will essentially take out kinetic. So, we were decreasing the kinetic energy you can decrease the kinetic energy and fix it to the appropriate value. So, you are taking out energy from the system right. Now going back going to the details. So, suppose the kinetic energy per particle here you want to maintain it you have fixed kBT and it should be a 3 by 2 kBT, you had fixed kBT to be one in the simulation. So, we want the average kinetic energy of the system per particle in the denominator per particle to be a 1.5 instead it was increasing.

So, what was the actual kinetic energy it was some kinetic energy which was increasing as a function of time. So, that is why I have put it as a function of time and once a system has reached equilibrium the kinetic energy should fluctuate instantaneously, but the average should be independent of the time. What one could do is define a so called Scaling factor.

So, you want to basically reduce the kinetic energy, you want to reduce the kinetic energy of the system. So, that this relationship is maintained right how much should you reduce it by that is the question we are asking ok. So, that is by this so for that we have to calculate this scaling factor, which is the kinetic energy actual that is the one we want that is the one we want fixed in the simulation.

Note the average sign it can fluctuate though because potentially and kinetic energy will exchange among each other. But the average kinetic energy suppose this is the one we want to maintain which is 3 by 2 kBT. The actual one is starts from the initial condition KE this subscript stands for system that is what you are actually seeing and then you can calculate this pre factor S.

So, suppose your actual kinetic energy is we want to be 3 by2 kBT, the actual one you see has become two right. The actual kinetic energy has become two kBT being one and then this factor is basically 1.5 by 2 right. Y ou can calculate the square root of S which you call S 1 right. And now if you scale all the velocities of the system by S 1 right then you would see that.

So if you so sorry this is wrong if you scale all the velocities of the system by S 1 right. So, basically S 1 is a quantity less than 1 all velocities are being decreased, because you are multiplying every velocity by number lower than 1. Then if you calculate the kinetic energy with this new value of the velocity, you will see that it is basically the kinetic energy of the entire system has been reset to the right value instantaneously right.

So, every particle; every particle you are rescaling the velocity of each particle by and getting a new velocity which is lower than the previous velocity. And basically we will see that the kinetic energy of the entire system has become the one which you want. Now you could do this every 100 iterations say I mean how many iterations after you should do will depend the value of dt right.

It has to be significantly the kinetic energy has to significantly change the micro state has to significantly change and if you see the kinetic energy is increased you rescale it back. And then let the particles move around with this new values of the velocity and still if you see that the average kinetic energy is again increased over a 100 iterations rescale it back to the right one.

So, the velocity of the system further decreases more energy has gone out of the system, that the particles move around with the in space. So, that again potentially there is exchange of energy between kinetic energy and potential energy. And then again if the kinetic energy increases you set it back to one. So, you keep on doing this till you see that the kinetic energy is now fluctuating about in average value right. So, you take out kinetic energy.

On the other hand you could also have potentials. So, yesterday we saw that they were attractive potentials the particles were slightly farther apart and the starting and as the molecular dynamics simulation started as it started as the position started evolving. The particles were essentially coming closer to each other towards the potential energy minima. So, the potential was decreasing hence kinetic energy was decreasing.

Now, if you have a purely repulsive interaction right or you start with a extremely densely packed system. It is also possible that the kinetic energy could decrease it is not an impossibility, then potential energy is increasing and kinetic energy is decreasing. Then again you use this appropriate expression to rescale. Now if kinetic energy is decreasing and you want it is kinetic energy per particle you wanted to be 1.5 kBT and you see that it is decreasing, then you again we scaled by this factor.

Now, kinetic energy this a the term on the numerator will be larger than the kinetic energy of the system. So, you are going to scale the velocities up to maintain the right temperature. Now, when you are calling the thermo stat say after every 100 iterations or say after every 500 iterations, you are basically taking out energy from the system because you are rescaling the kinetic energy. But in between these two steps energy will be conserved.

So, when you apply the thermostat suppose you update the velocity and calculate the kinetic energy and every five hundred steps, check whether the kinetic energy has deviated significantly from the desired value then you rescale and then you change you are essentially changing the energy of the system the total energy of the system as well right. But in between the calling of two thermostats the energy will be conserved.

So if you notice in yesterdays class there was also the plot of the energy and that basically was fixed for some time the kinetic energy and potential energy were changing. And when you call the thermo stat it decreased there was a jump in the energy and again it was constant conserved energy and when you call the thermo stat again it was there was a jump there was a decrease in the total energy because you are taking out kinetic energy.

It could also be an increase depending upon the system and finally, it would go something like this and then it would basically reach equilibrium right and then you can start measuring the statistical quantities ok. So, you have to read to the average potential till the potential energy fluctuates more than average. The kinetic energy fluctuates about an average and then you could say that the system has reached equilibrium and then you can start measuring statistical quantities which we shall discuss in the next class.

How to calculate statistical quantities what are the interesting quantities one could calculate ah. Throughout till now I have been talking about time and mass equal to 1 and kBT equal to 1 right. So, without worrying what these things mean so let us discuss units.

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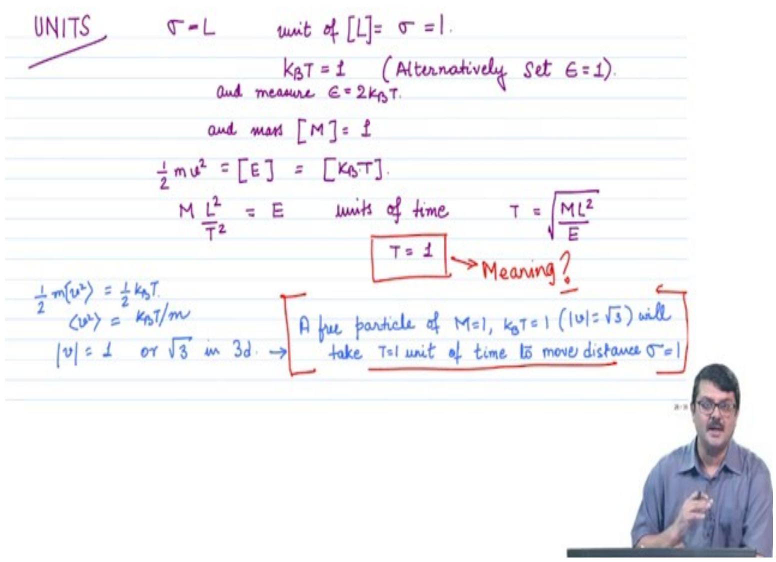

So, that is the basically the topic of the next our next topic of discussion. So, to low we have been saying that the size of the spears the Lenard Jones particles is 1 kBT is equal to 1. So, everything we set equal to 1 and then we said we are talking about some time and one does not know what this time means, it is again a d t is 0.005 in what units one does not know. So, let us discuss this topic. So now, I said that were measuring all lens in units of sigma the diameter of the particle, the size of the box is 30 times sigma or 15 times sigma right. So, that was the unit of length.

The unit of energy we had set as kBT. So, all other units so when you say epsilon is a 1, it means that it is epsilon is 1 times kBT right and we had also set mass equal to 1. Now if you set the values of mass length and energy then you automatically get the units of time let me explain. So, suppose half mv square [noise, so half mv square is equal to E right, I mean the kinetic energy and it has units of kBT.

You can also write it like this ML square by L square which is basically I am writing it in dimensions and it has dimensions of energy right ml square by T square has dimensions of energy and then you can write the dimension of time in terms of M L square by E square root right and if you have chosen M equal to 1 and L equal to 1 and kBT the unit of energy to be 1, then time comes out to be 1.

But again what does it mean it means? So, when time T equal to 1 it means essentially that a free particle of mass M equal to 1 with kinetic energy kBT or energy and kinetic energy is of course, related to kBT kBT equal to 1 and velocity of root 3 will take approximately T equal to 1 unit of time to move a distance sigma equal to 1. So, here I have used again half mv squared all that we are using is equipartition theorem right, because basically if kBT is equal to 1 then we will order b equal to 1 right, half mv square average equal to half kBT or rather 3 kBT by 2 if it is moving in 3 dimensions.

So, basically when T equal to 1 it means that to move a length of the diameter of a particles sigma equal to 1, diameter of a particle with k if kBT equal to 1. So you fix the average kinetic energy of the system you fix the average velocity of the system and a mass of 1 will take one time unit to cross the entire diameter let us actually put numbers.

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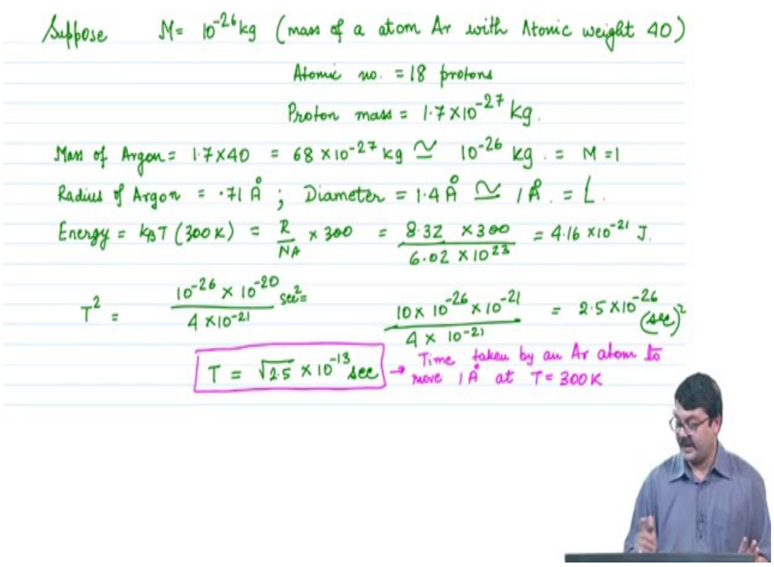

Now, suppose we were looking your particle which you are modelling in your molecular dynamic simulations is an argon an argon gas particle right. So, argon gas particle has a mass atomic mass atomic weight of 40, one proton is basically 1.7 into 10 to the power minus 1.7 into 10 to the power minus 27 kg. So, the atomic number of argon is 18 which means it has 18 protons and the rest of them is neutrons right. So, the mass of argon can be calculated to be 1.7 in to 40.

So, it is basically this into 40 which is approximately we are calculating order of magnitude. So, it is approximately 10 to the power minus 26 kg with some pre factors which we are ignoring. You are setting this equal 1 or you can actually set with all the numbers you can set that mass equal to 1. So, you are measuring all of their masses in units of the argon mass right.

So, you are setting 10 to the power minus 26 kg or if you want to be very precise this value which is the atomic mass of argon, you are setting that equal to 1 right. Radius of argon is 0.71 angstrom the diameter is 1.4 angstrom and this length you are setting it to be 1 ok. So, you are measuring when you say that your box size is 13 30 in some units in units of the diameter of your particle. So, if your length if the diameter is 1.4 angstrom then the assimilation box size is 30 into 1.4 angstrom.

Yesterday in our computer code we had used the box size to be 15. So, the box size is 15 into 1.4 angstroms right. Energy we have discussed in a Ising model as well can be calculated the value of kBT in at 300 Kelvin is R by NA, R being the gas constant n a being the Avogadro's number and that comes out to be 4.16 into10 to the power minus 21 Joules, this unit of energy you are setting to be 1.

Now, if you want to calculate T square. So now, we had so if you set everything equal to 1 we had got T equal to 1. So, what does T equal to 1 mean? So, here I am just writing the order of magnitude. So, this is mass 10 to go minus 26 this says l square. So, suppose you take 1 angstrom to be 1 unit of length or you can exactly put in the numbers 1.4 10 to the minus 10 meter.

So that is what I have put in here 10 to the power minus 10 meter square l square and this and on the denominator you have the value of kBT and then so if you put in all these values you see that you get T square to be 2.5 into 10 to the power minus 26 seconds, because now everything has units. So, this is so many seconds or rather second square because you are calculating T square right and then T it comes out to be root 2.5 10 to the power minus 13 seconds.

What does it mean that an arguing gas with at a temperature 300 Kelvin on an average has such velocities, that to cross a distance of 1.4 angstrom or 1 angstrom because I have not used the pre factors I am just you were talking about order of magnitude, it would take 10 to power minus 13 seconds to cross 1 angstrom, at the velocities it will have at T equal to 300 Kelvin right.

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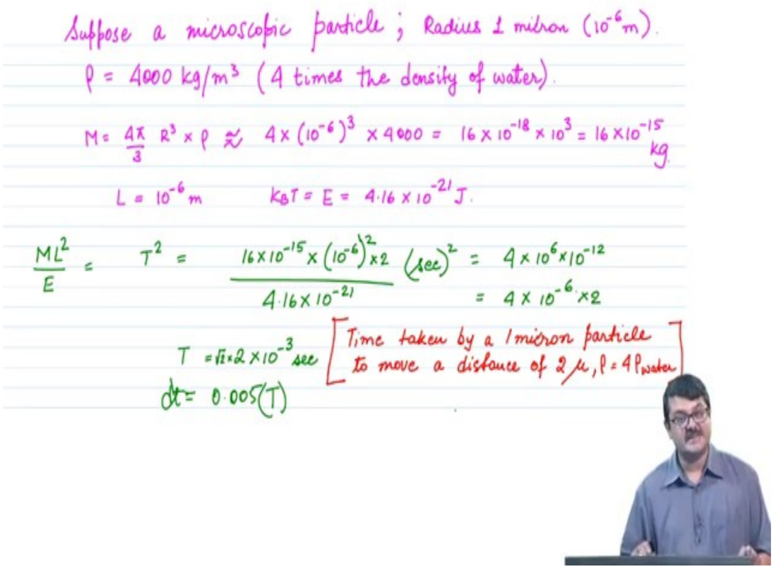

Let us take suppose you have instead of argon you are modelling some microscopic particles because L equal to 1. So, we were doing in dimensionless units now suppose you put the dimension of L to be not 1.4 angstrom, but radiuses 10 to the power minus 6 meters 1 micron size. So, you are looking at the particles moving around some suspended gas particles in air, you were you were not looking at the atomic scale you are looking at the molecular dynamics atom of much larger particle of size 10 to the power minus 6 meters 1 micron.

And suppose the density of that particle was 4000 kg per meter cube which is essentially 4 times the density of water, because if you write it in kg per meter cube the density of water is 1000 kg per meter cube right. Then you can calculate the mass you can calculate the mass of the particle 4 pi r cube, so 4 pi by 3 r cube into the density. So, we can calculate the mass assuming we are calculating an order of magnitude. So, pi and 3 cancels say and you can get the mass of such a big micron size particle to be 16 into 10 to the power minus 15 kg right.

Here I missed out the units where this is kg because we worked in SI units. The mass of an argon atom was 10 to the power minus 27 kg or 10 to the power minus 26 kg, here we are looking at a much larger particles. So, the mass is much larger I hardly surprising. The unit of length which we had set equal to 1 we is 10 to the power minus 6 meters microns kBT remains the same because we are looking at the same temperature.

And you put it back in this formula T square equal to ML square by E and you get essentially the value of time, the unit of time which you had set equal to 1 to be root to into 2 into 10 to the power minus 3 it is a milliseconds right. There we were getting 10 to the power minus 13 seconds here it is milliseconds, what does it mean? What does T equal to 1 mean? It means that the time taken by a 1 micron particle which is maintained.

So, 1 micron particle and of course, the many of them they are colliding with each other. But 1 micron particle which is maintained at a temperature of 300 Kelvin for it to move 1 micron which is the diameter or 2 microns, which is the diameter of the particle it will take milliseconds or we can put in the numbers and get the exact numbers.

But this is the physical picture this is what it means, when I say L equal to 1 M equal to 1 and kBT equal to 1 and time equal to 1. So, this is your unit of time equal to means now so many milliseconds and when you say that your dt is 0.005. It means that dt it means that essentially that your d t is 0.005 into T which has been set to 1 right. So, this into milliseconds square root 2 into 2 10 to the power minus 3 milliseconds. So, that is what the value of d t is your integration time constant right.