Foundations of Computational Materials Modelling
Professor Narsimhan Swaminathan
Department of Mechanical Engineering
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Input script for LAMMPS 4

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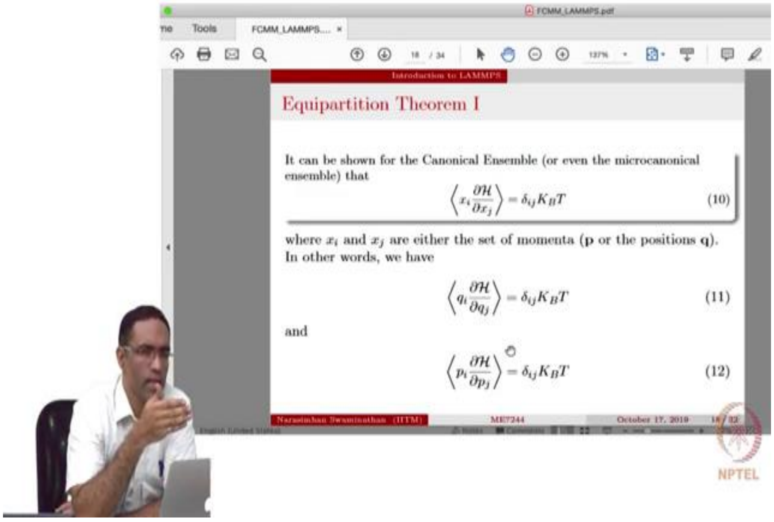

Introduction to LAMMPS

Equipartition Theorem I

It can be shown for the Canonical Ensemble (or even the microcanonical ensemble) that

$$\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \right\rangle = \delta_{ij} K_B T \quad (10)$$

where x_i and x_j are either the set of momenta ($\mathbf{p}$ or the positions $\mathbf{q}$). In other words, we have

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_j} \right\rangle = \delta_{ij} K_B T \quad (11)$$

and

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_j} \right\rangle = \delta_{ij} K_B T \quad (12)$$

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Good afternoon so, in the last class, whatever we looked at, I just want to relook at it once again and tell you some of the things that I missed out. First and foremost, I hope you all got the set of exercises on Moodle, all those exercises is what I am going to be repeating here and all of them pertain to argon. And the whole idea is to simply learn some simple techniques in LAMMPS, so as to be able to reproduce some of the things that we actually know. So in exercise two, one of the things that we did was we initialized the kinetic energy of a system, and then simply started evolving it in NVE.

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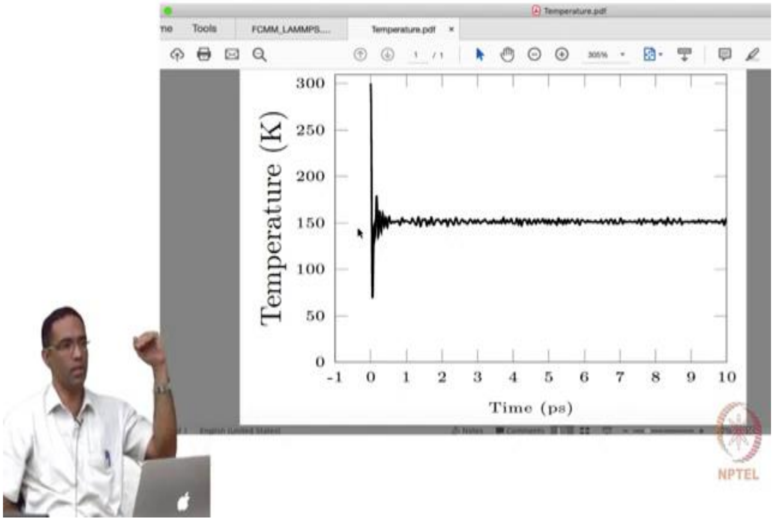

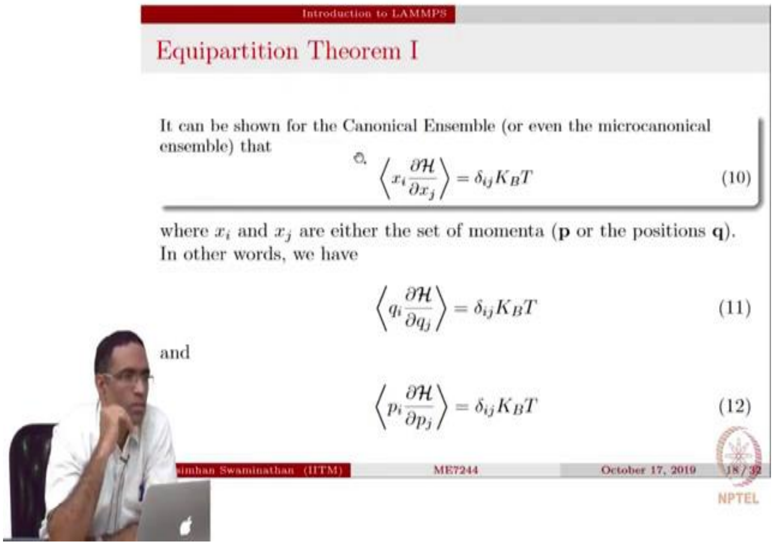

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And what we found is when we looked at the equilibrated structure, the temperature turned out to be half of what we set it to be. We set it to be 300 Kelvin, and then we started integrating it and then it turned out to be half the structure, I just told you that this is going to happen as if the atoms are actually going to be vibrating about their mean positions, basically exploring the harmonic region of their inter atomic potential. So, I want to show a simple mathematical means of seeing actually how that actually works.

In doing so, we will actually be introducing few results from statistical mechanics also, you do not need to know the proof of all of these things, but if you just follow my reasoning that will be more than enough. So, for example, so we have to talk about something called as the Equipartition theorem, which essentially tells you how the energy is essentially distributed amongst the various degrees of freedom that is available in the system. So, the first equation that you see on the slide, which says that the average of x i Dau h by Dau x j is equal to Del i j K B T, what does that mean?

It means that the ensemble average of this quantity is equal to Del i j K B T where K B is obviously the Boltzmann's constant and T is the temperature, x i and x j are actually either the position degrees of freedom or the momentum degrees of freedom. So, equation 10 can be written either as equation 11 or equation 12. So, q i times Dau h by Dau q h Del i j K B T, p i Dau h by Dau P j Del i j K B T, this is a result from statistical mechanisms, you can actually show and these brackets essentially means the face average or the ensemble average. So, if you want to quickly see what that means, I will just write it down but not necessarily the entire proof.

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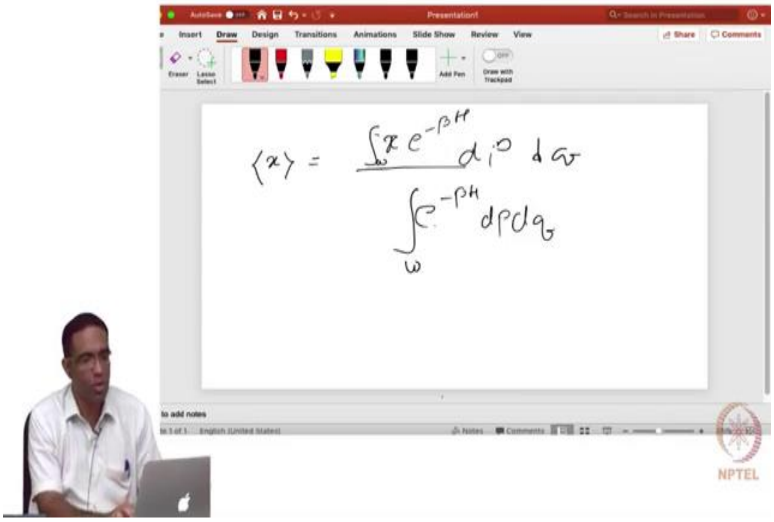
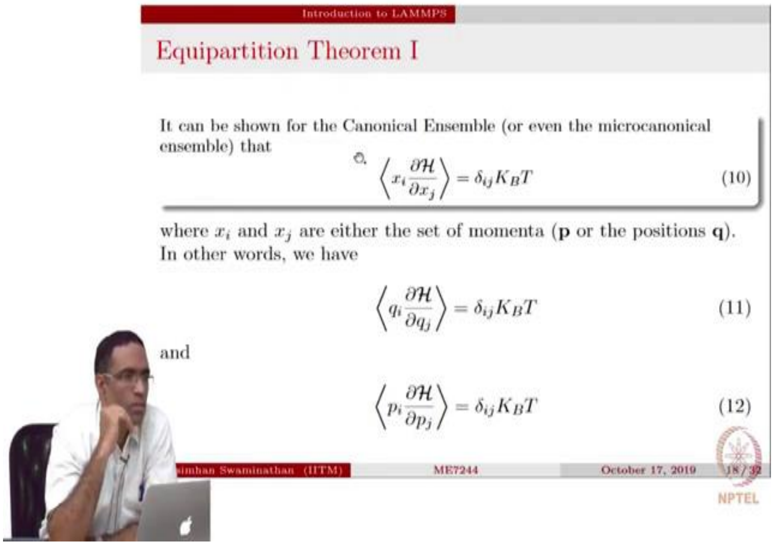


$$\langle x \rangle = \frac{\int_{\omega} x e^{-\beta H} dp\, dq}{\int_{\omega} e^{-\beta H} dp\, dq}$$



Introduction to LAMMPS

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What I meant to ask, if you want to calculate the average of some quantity, say x this means integral over the face space x, integral of the entire face space, that is what it means. So I have written a little bit badly, but you are able to follow what I mean by that. So, if you want to calculate the average of the energy, so you just have to find out what the energy is, what is the probability that particular energy is occurring. So that e x p minus beta h is essentially telling you the probability, so that particular quantity multiplied by e to the power minus beta h integrated over the entire face space divided by integrated over the entire face space e to the power minus beta h is essentially going to give you the average value of that quantity.

So, when I am talking about the average of this quantity, it means this quantity is going to replace the x in the PowerPoint slide that I just wrote down now. So when you do that, it happens that it is just Del i j K B T that means if q i and q j are the same only you have K B T, this can be proved rigorously in statistical mechanics. So, now let us take a look at equation 12 and expand it a bit. Now Dau h by Dau p j, h is basically what is h? Right Dau h by Dau p j is what? q dot.

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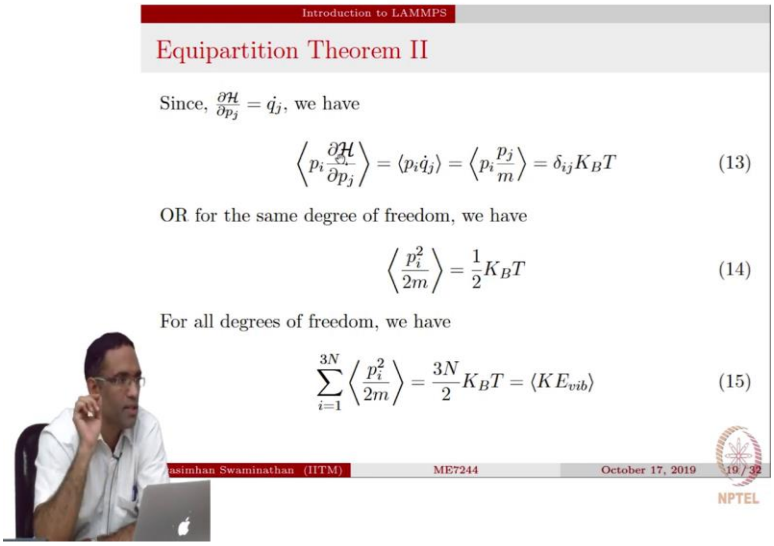

Introduction to LAMMPS

Equipartition Theorem II

Since, $\frac{\partial \mathcal{H}}{\partial p_j} = \dot{q}_j$, we have

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_j} \right\rangle = \langle p_i \dot{q}_j \rangle = \left\langle p_i \frac{p_j}{m} \right\rangle = \delta_{ij} K_B T \tag{13}$$

OR for the same degree of freedom, we have

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} K_B T \tag{14}$$

For all degrees of freedom, we have

$$\sum_{i=1}^{3N} \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{3N}{2} K_B T = \langle KE_{vib} \rangle \tag{15}$$

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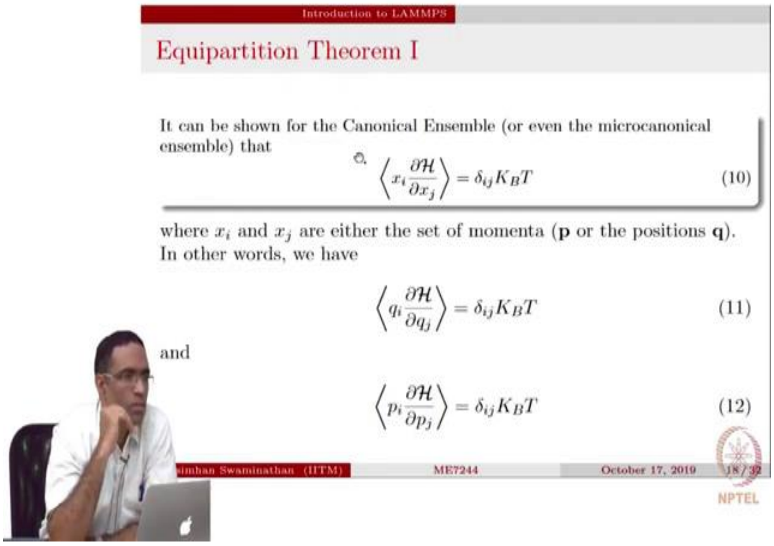

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So, if you rewrite it, you get p i times, the average of p i times q j dot is equal to which can be written as p i times p j divided by m, momentum divided by the mass is nothing but q j, just the time derivative of the position. And that happens to be equal to Del i j times K B T, and therefore, if we are talking about exactly the same degree of freedom of the system, it is equal to p i square divided by 2 m, the average of that quantity is actually equal to half times K B T. So, what this is saying is, what is p i square by 2 m? What does it look like? It looks like the kinetic energy that is associated with C p x of atom 1 or p x of atom, p y of atom 1, it could be anything.

It depends on the each degree of freedom, we are talking about one particular degree of freedom. So, the average kinetic energy that is associated with each degree of freedom turns out to be half K B T. So, if you are going to consider all the degrees of freedom that is existing for the entire system, then you can sum over the 3 N degrees of freedom that is available to the system and you happen to get summation over I equal to 1 to 3 N, the average of p i square by 2 m is equal to 3 N by 2 K B T, which is nothing but the average kinetic energy of the entire system that is associated with the vibration of the atoms.

So, this of course has come from the equipartition theorem which we are not proving right now, which I am expecting you to accept as it is. But if you accept that, that is actually a general thing, there is no assumptions that is gone in there. And so, even this one is quite general, there is no assumptions that we made as long as it is a classical system, we are talking about the kinetic energy of the system, this term is here is clearly the average kinetic energy associated with the system, and that is related to the temperature.

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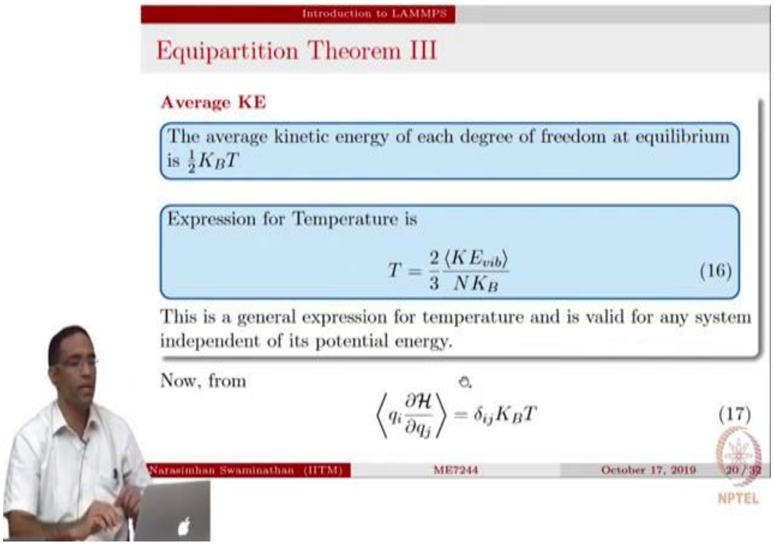

Introduction to LAMMPS

Equipartition Theorem III

Average KE

The average kinetic energy of each degree of freedom at equilibrium is $\frac{1}{2}K_BT$

Expression for Temperature is

$$T = \frac{2}{3}\frac{\langle KE_{vib}\rangle}{NK_B} \tag{16}$$

This is a general expression for temperature and is valid for any system independent of its potential energy.

Now, from

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_j} \right\rangle = \delta_{ij} K_B T \tag{17}$$

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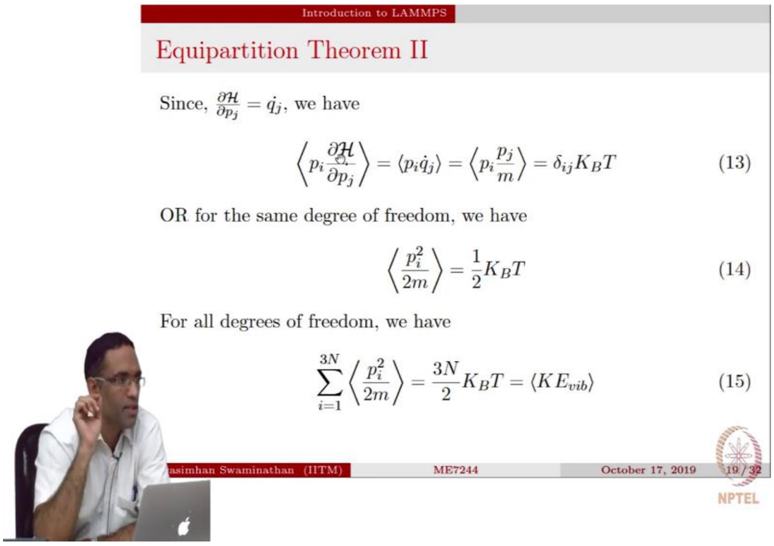

Introduction to LAMMPS

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So, the average kinetic energy of each degree of freedom at equilibrium turns out to be half K B T. And therefore, if you take a look at this expression and reorganize it a bit, you get the expression for temperature which is 2 by 3, the total kinetic or the average kinetic energy of the entire system divided by N times K B. So in this, this expression is quite general, you might have seen it for ideal gases, but in the derivation that we just made we did not make any assumption concerning the nature of the system.

Therefore, the expression for temperature for any system is always 2 by 3, the average kinetic energy of the system divided by n times K B. So, when molecular dynamics is actually calculating the temperature of the system and printing it out in the log file, it is actually using this expression. Now, if you take a look at the other expression right q i times Dau h by Dau q j Del i j K B T, then the only part of the Hamiltonian which explicitly depends on the coordinates is actually the potential energy, the kinetic energy it depends on the momentum, the potential energy only depends on the q's.

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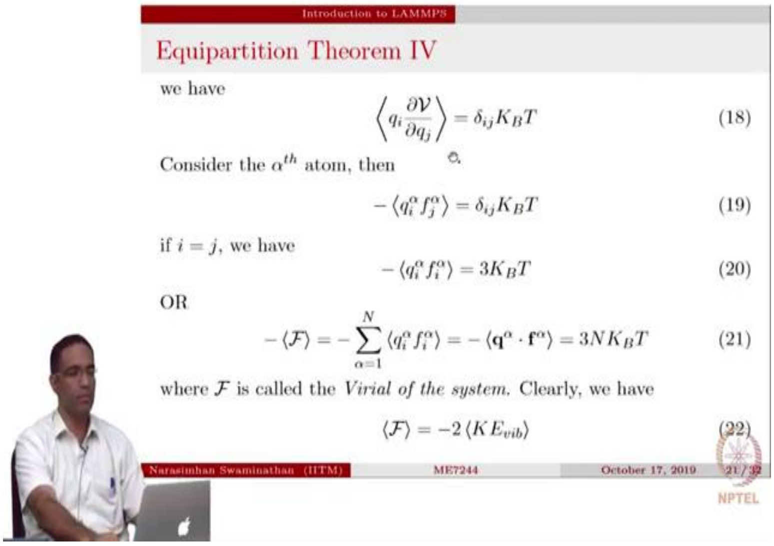


Equipartition Theorem IV

we have

$$\left\langle q_i \frac{\partial \mathcal{V}}{\partial q_j} \right\rangle = \delta_{ij} K_B T \quad (18)$$

Consider the α^{th} atom, then

$$-\langle q_i^\alpha f_j^\alpha \rangle = \delta_{ij} K_B T \quad (19)$$

if $i = j$, we have

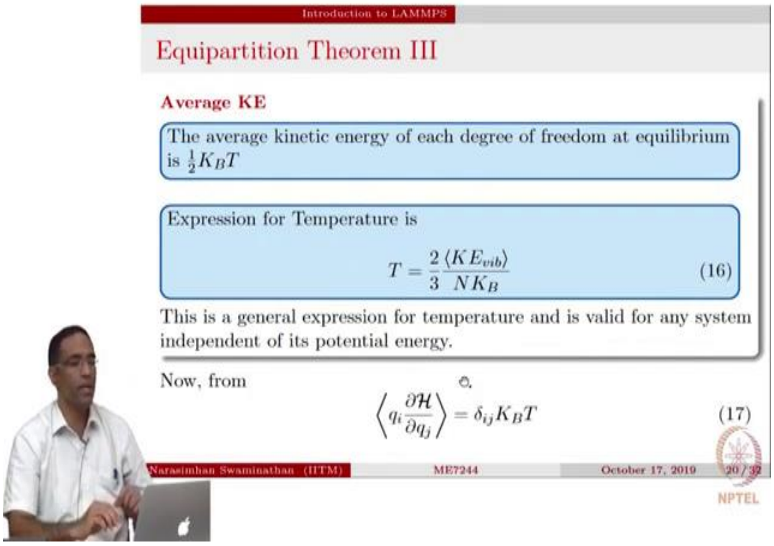
$$-\langle q_i^\alpha f_i^\alpha \rangle = 3 K_B T \quad (20)$$

OR

$$-\langle \mathcal{F} \rangle = -\sum_{\alpha=1}^{N} \langle q_i^\alpha f_i^\alpha \rangle = -\langle \mathbf{q}^\alpha \cdot \mathbf{f}^\alpha \rangle = 3 N K_B T \quad (21)$$

where $\mathcal{F}$ is called the *Virial of the system.* Clearly, we have

$$\langle \mathcal{F} \rangle = -2 \langle K E_{vib} \rangle \quad (22)$$



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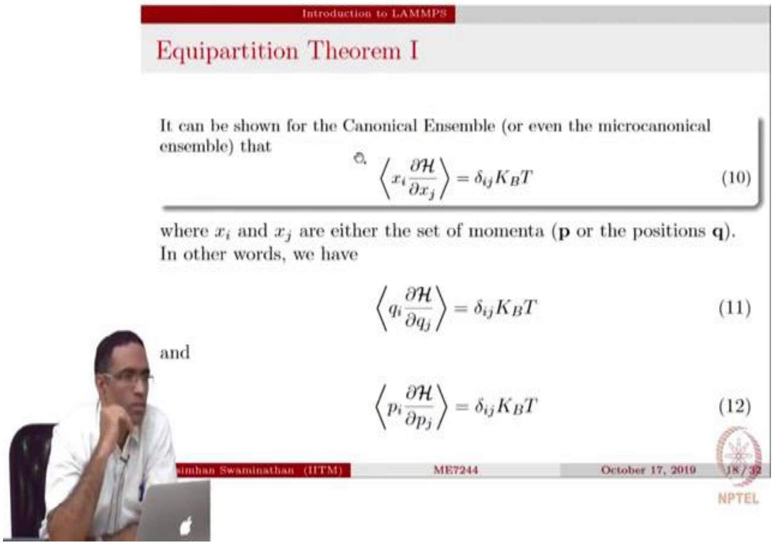

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So, we can write the previous expression as q i times Dau v by Dau q j is equal to Del i j K B T. Now, if you consider the, what is Dau v by Dau q j, what does it look like? The derivative of the potential with respect to position what should it force. So, if you consider the Alpha th atom and write down this expression Dau v by Dau q j must actually be the negative of the force by definition. So, you have your q i Alpha f j Alpha, the average of the quantity is equal to Del i j K B T, for i equal to j, you have q i Alpha f i Alpha the average of that quantity is equal to 3 times K B T.

So this quantity here and if you average it over the entire, if you sum it up over all the atoms of the system contained in the system, then you get expression 21 where you have, you know when you submit on both the sides you get basically 3 N K B T. So, this expression that you see right here is called as the Virial of the system and is represented by this f right here. So, clearly you have the average of this quantity f to be equal to minus 2 times the kinetic, the vibrational kinetic energy of the system. So, this is something to keep in mind, these are two consequences of the equipartition theorem of these two expressions.

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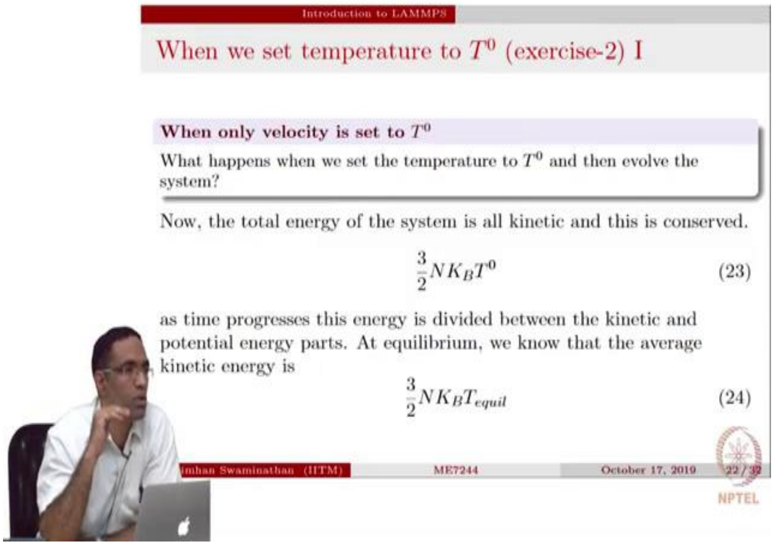

Introduction to LAMMPS

When we set temperature to T^0 (exercise-2) I

When only velocity is set to T^0

What happens when we set the temperature to T^0 and then evolve the system?

Now, the total energy of the system is all kinetic and this is conserved.

$$\frac{3}{2}NK_BT^0 \tag{23}$$

as time progresses this energy is divided between the kinetic and potential energy parts. At equilibrium, we know that the average kinetic energy is

$$\frac{3}{2}NK_BT_{equil} \tag{24}$$

Now, let us see what happens when we actually set the temperature of the system to T naught without actually displacing the atoms from their initial equilibrium positions. When we do that, the entire energy that has been dumped into the system is purely kinetic. So, the total energy of the system is 3 by 2 N K B T naught at the instant that we set, in exercise 2, is that is that okay? Are you able to accept that?

Now, this energy has to be maintained throughout the simulation that means, the kinetic energy that is being given to it must be somewhat portioned properly between the potential energy components and the kinetic energy components as the system evolves. So, as time progresses, this energy has to be divided between the potential energy and the kinetic energy component. And at equilibrium, once the system has reached equilibrium the average kinetic energy is known, it is going to be 3 by 2 N K B T equal which is going to be different from this temperature we set it to be initially.

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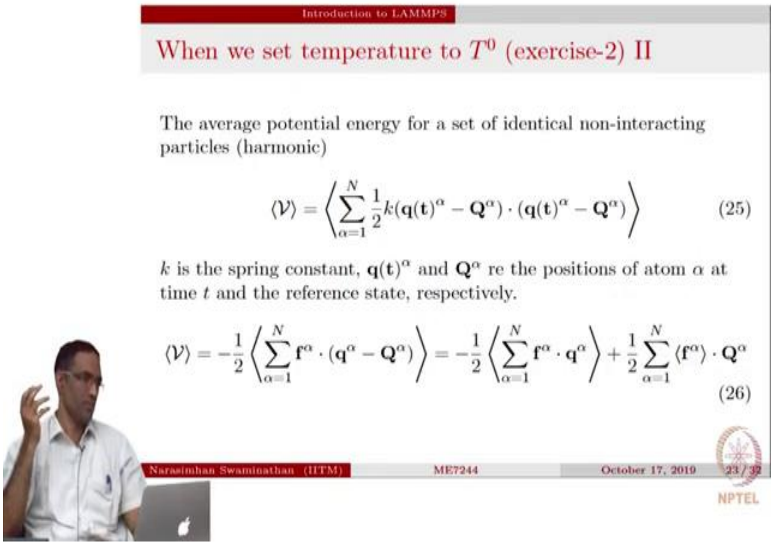

Introduction to LAMMPS

When we set temperature to T^0 (exercise-2) II

The average potential energy for a set of identical non-interacting particles (harmonic)

$$\langle \mathcal{V} \rangle = \left\langle \sum_{\alpha=1}^{N} \frac{1}{2} k(\mathbf{q(t)}^{\alpha} - \mathbf{Q}^{\alpha}) \cdot (\mathbf{q(t)}^{\alpha} - \mathbf{Q}^{\alpha}) \right\rangle \qquad (25)$$

k is the spring constant, $\mathbf{q(t)}^{\alpha}$ and $\mathbf{Q}^{\alpha}$ re the positions of atom α at time t and the reference state, respectively.

$$\langle \mathcal{V} \rangle = -\frac{1}{2} \left\langle \sum_{\alpha=1}^{N} \mathbf{f}^{\alpha} \cdot (\mathbf{q}^{\alpha} - \mathbf{Q}^{\alpha}) \right\rangle = -\frac{1}{2} \left\langle \sum_{\alpha=1}^{N} \mathbf{f}^{\alpha} \cdot \mathbf{q}^{\alpha} \right\rangle + \frac{1}{2} \sum_{\alpha=1}^{N} \langle \mathbf{f}^{\alpha} \rangle \cdot \mathbf{Q}^{\alpha} \qquad (26)$$

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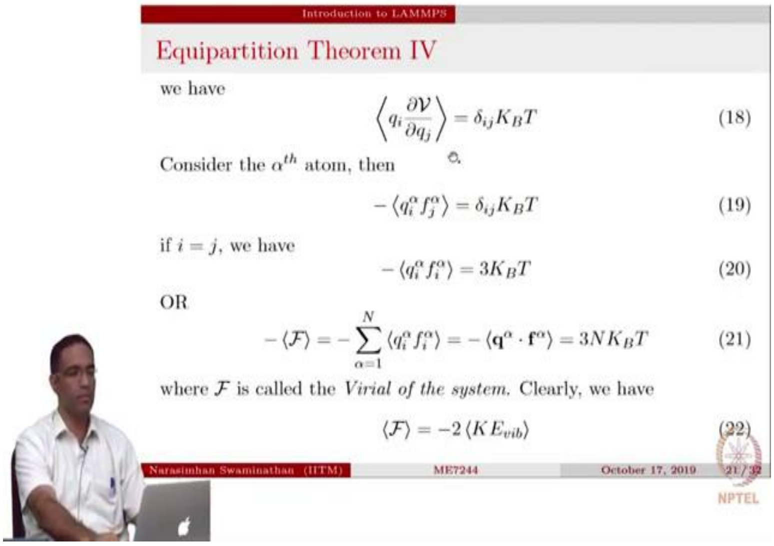

Introduction to LAMMPS

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$$-\langle \mathcal{F} \rangle = -\sum_{\alpha=1}^{N} \langle q_i^{\alpha} f_i^{\alpha} \rangle = -\langle \mathbf{q}^{\alpha} \cdot \mathbf{f}^{\alpha} \rangle = 3 N K_B T \qquad (21)$$

where $\mathcal{F}$ is called the *Virial of the system*. Clearly, we have

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So, now what is the average potential energy of the system? So, the average potential energy of the system is rather difficult to calculate under very general for us, if you assume general cases like Lennard-Jones or any other kind of potential it is difficult for us to calculate. Just for the purposes of illustration, I have taken a potential which is basically a set of non-interacting particles, where you have the atoms initially are there original equilibrium positions and any displacement from their initial positions gives it energy through the spring constant k.

So, the average energy of this potential energy of the system at any instant of time is given by this expression 25, where k is basically the spring constant, q is the position of the particle at any instant of time and capital Q Alpha is basically the initial position or the reference position from where it is actually moving to gain that energy. So, if you calculate the, so now, if you take a look at it, k times q minus Q Alpha is nothing but the force or negative of the force, spring force.

So, we have replaced that term with minus f Alpha dot q Alpha minus capital Q Alpha, and we want to take the average of that quantity. And if you look at this expression carefully, this is basically a constant, this Q Alpha is basically a constant, which is basically the reference position of that atom. And this becomes minus half times average of this dot product plus half times the average of this dot product because the average over q Alpha does not give anything because it is a constant.

Now, since the atoms are actually vibrating about their mean positions at equilibrium, this average force on every atom becomes 0 therefore, this quantity essentially vanishes. And this is related to the Virial that we just saw, it was very similar to that, this half the Virial, value of the Virial. So, the average potential energy of the system is negative half summation over all the atoms f dot Q. And since f dot Q is nothing but the Virial it is nothing but 3 N K B T or this entire thing becomes 3 N by 2 K B T.

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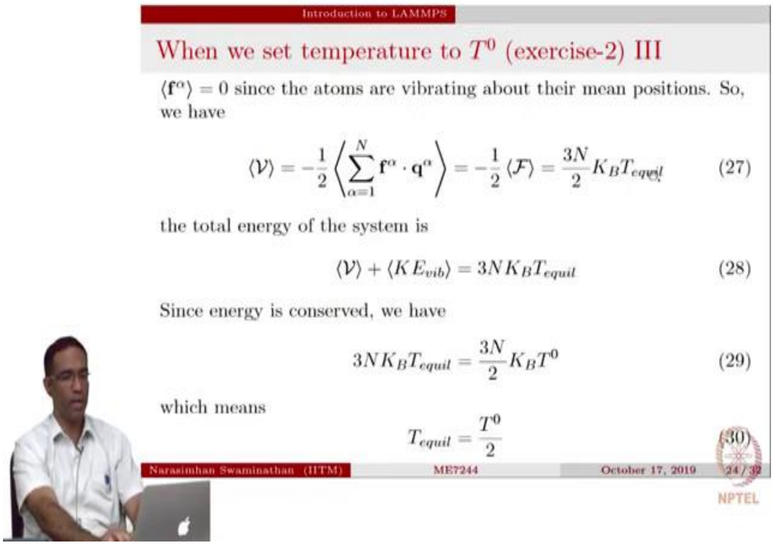

Introduction to LAMMPS

When we set temperature to T^0 (exercise-2) III

$\langle \mathbf{f}^\alpha \rangle = 0$ since the atoms are vibrating about their mean positions. So, we have

$$\langle \mathcal{V} \rangle = -\frac{1}{2}\left\langle \sum_{\alpha=1}^{N} \mathbf{f}^\alpha \cdot \mathbf{q}^\alpha \right\rangle = -\frac{1}{2}\langle \mathcal{F} \rangle = \frac{3N}{2} K_B T_{equil} \quad (27)$$

the total energy of the system is

$$\langle \mathcal{V} \rangle + \langle KE_{vib} \rangle = 3N K_B T_{equil} \quad (28)$$

Since energy is conserved, we have

$$3N K_B T_{equil} = \frac{3N}{2} K_B T^0 \quad (29)$$

which means

$$T_{equil} = \frac{T^0}{2} \quad (30)$$

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So, that is what I am trying to say here in equation 27. So the total energy of the system is nothing but the average energy at equilibrium is nothing but the average potential energy plus average kinetic energy and that has to be always conserved and is therefore equal to 3 N K B T times the, 3 N K B T times equilibrium. Since the energy is conserved, so we just added up these two this is nothing but 3 N by 2 K B T, this is also 3 N by 2 K B T and I am just adding them up and you get 3 N K B T equal. Since the energy is conserved, 3 N K B T equilibrium must be equal to the dumped in energy 3 N by 2 K B T naught which is the initial temperature that we set. So, when you look at this expression carefully, you will see that the equilibrium temperature becomes equal to half the temperature at which we set. So, this is a very, very simple way of showing explicitly that this equilibrium temperature that the system reaches is actually the half the set temperature.

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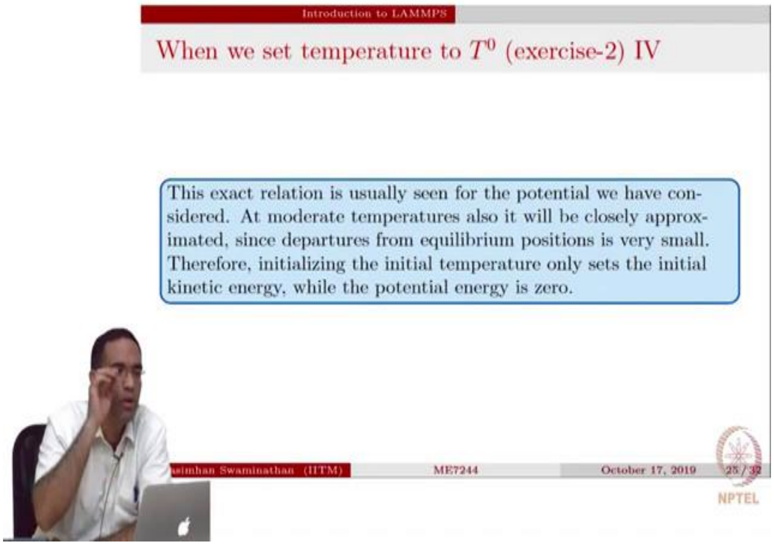

Introduction to LAMMPS

When we set temperature to T^0 (exercise-2) IV

This exact relation is usually seen for the potential we have considered. At moderate temperatures also it will be closely approximated, since departures from equilibrium positions is very small. Therefore, initializing the initial temperature only sets the initial kinetic energy, while the potential energy is zero.

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Now you have to remember that this exact relation.

Student: Is this result valid for all potentials?

Professor: This exact result is valid only for potentials which are like quadratic in q i and p i.

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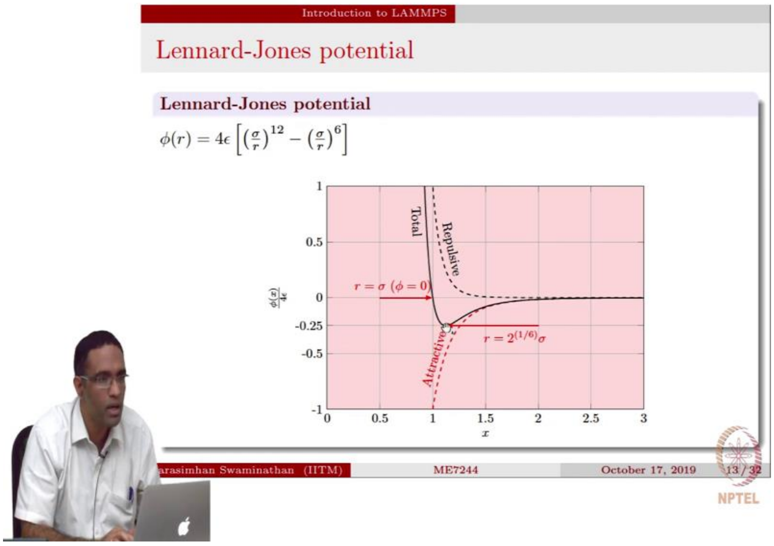

Introduction to LAMMPS

Lennard-Jones potential

Lennard-Jones potential

$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

arasimhan Swaminathan (IITM) ME7244 October 17, 2019 13 / 32

Or if you look at the Lennard-Jones potential, there is a small region here, where it is harmonic. So, anywhere if the atoms are just vibrating about that position, if the deviation from the position is not too much, even then your equilibrium temperature will settle down to T set by 2 approximate. So, this is some justification as to why that is happening.

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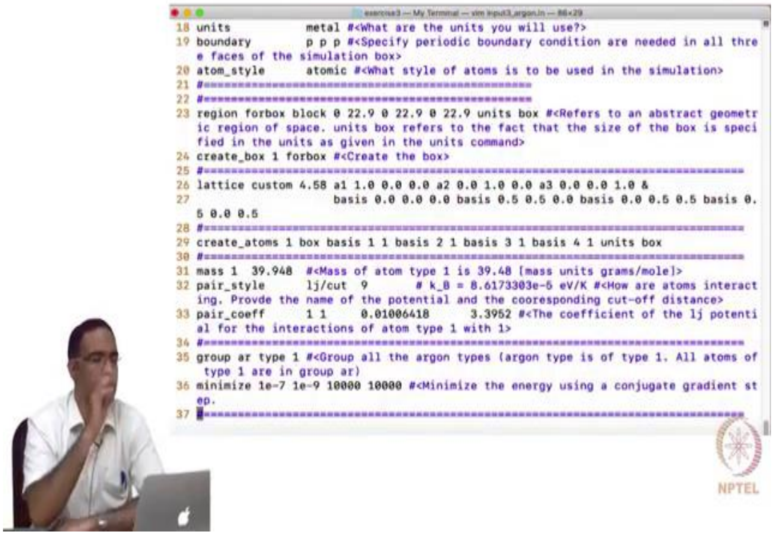
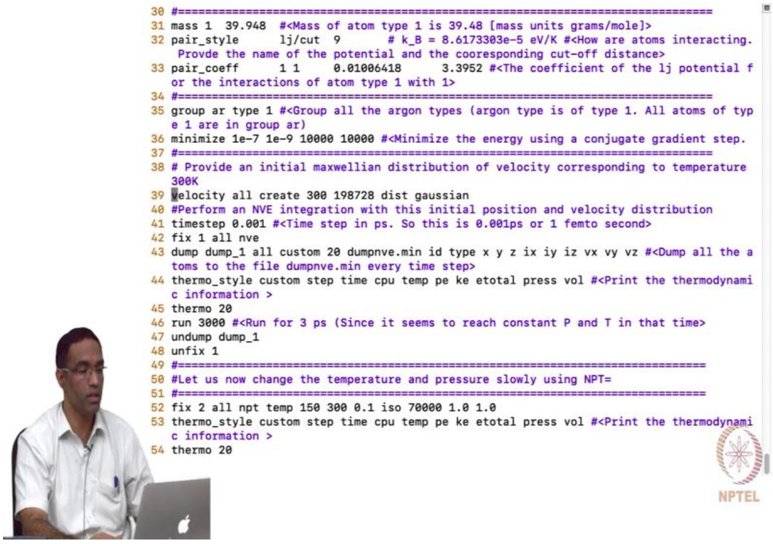
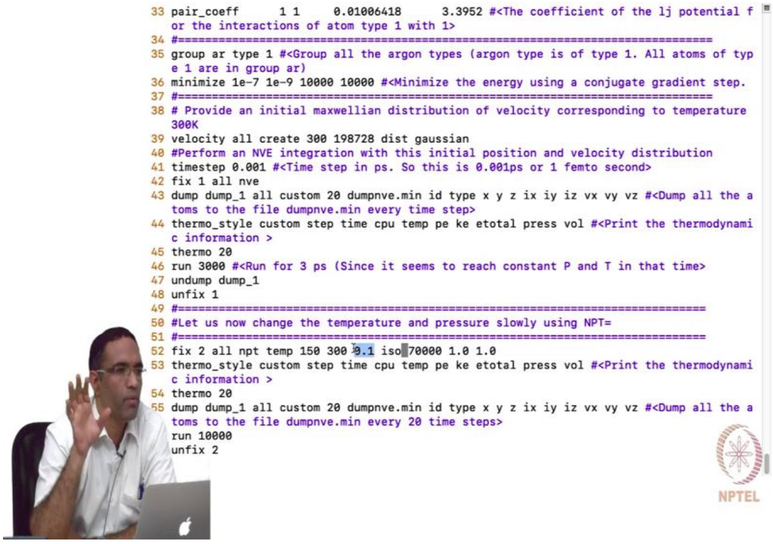


```
units           metal #<What are the units you will use?>
boundary        p p p #<Specify periodic boundary condition are needed in all three faces of the simulation box>
atom_style      atomic #<What style of atoms is to be used in the simulation>
#=================================================
#=================================================
region forbox block 0 22.9 0 22.9 0 22.9 units box #<Refers to an abstract geometric region of space. units box refers to the fact that the size of the box is specified in the units as given in the units command>
create_box 1 forbox #<Create the box>
#===============================================================================
lattice custom 4.58 a1 1.0 0.0 0.0 a2 0.0 1.0 0.0 a3 0.0 0.0 1.0 &
                    basis 0.0 0.0 0.0 basis 0.5 0.5 0.0 basis 0.0 0.5 0.5 basis 0.5 0.0 0.5
#===============================================================================
create_atoms 1 box basis 1 1 basis 2 1 basis 3 1 basis 4 1 units box
#===============================================================================
mass 1  39.948  #<Mass of atom type 1 is 39.48 [mass units grams/mole]>
pair_style      lj/cut  9       # k_B = 8.6173303e-5 eV/K #<How are atoms interacting. Provde the name of the potential and the cooresponding cut-off distance>
pair_coeff      1 1     0.01006418      3.3952 #<The coefficient of the lj potential for the interactions of atom type 1 with 1>
#===============================================================================
group ar type 1 #<Group all the argon types (argon type is of type 1. All atoms of type 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#===============================================================================
```



```
#===============================================================================
mass 1  39.948  #<Mass of atom type 1 is 39.48 [mass units grams/mole]>
pair_style      lj/cut  9       # k_B = 8.6173303e-5 eV/K #<How are atoms interacting. Provde the name of the potential and the cooresponding cut-off distance>
pair_coeff      1 1     0.01006418      3.3952 #<The coefficient of the lj potential for the interactions of atom type 1 with 1>
#===============================================================================
group ar type 1 #<Group all the argon types (argon type is of type 1. All atoms of type 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#===============================================================================
# Provide an initial maxwellian distribution of velocity corresponding to temperature 300K
velocity all create 300 198728 dist gaussian
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
undump dump_1
unfix 1
#==============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#==============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
```



```
pair_coeff      1 1     0.01006418      3.3952 #<The coefficient of the lj potential for the interactions of atom type 1 with 1>
#===============================================================================
group ar type 1 #<Group all the argon types (argon type is of type 1. All atoms of type 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#===============================================================================
# Provide an initial maxwellian distribution of velocity corresponding to temperature 300K
velocity all create 300 198728 dist gaussian
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
undump dump_1
unfix 1
#==============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#==============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every 20 time steps>
run 10000
unfix 2
```

So, now I want to take a look at the next exercise. I think, in the next exercise what I wanted to do was, I wanted to show you what happens when you simply use this fix called a fixed NPT and try our best to relax the system to a certain pressure and temperature. So, what I have done first is initially you create velocity of about 300 Kelvin distributed in a Gaussian manner, and then perform a NVE and now at the end of this run, the temperatures are not going to be around 300 Kelvin at all, they are going to be in fact somewhere around 150 Kelvin.

And then I just set fixed to all NPT, if it is temperature you ramp it up from approximately 150 Kelvin to 300 Kelvin with a T damp parameter of 0.1 And then if it is going to be, if it is a pressure, for the pressure you have different options that is available in LAMMPS. ISO means do it isotopically for all the faces like I mentioned in last class, from the current pressure that it is in, it was approximately 70000 bars to about 1 which is what we want and there is a corresponding p damp parameter.

So, this one and this one are the values are the corresponding T damp and p damp values, and there is a convention specified in the manual that, not a convention the default values, the values that you should use depends upon the time step. So, for T damp it is approximately about 100 times step and p damp is approximately thousand times the time step. In most of the cases that I have worked with these settings are sufficient. Very rarely will you actually have to change this.

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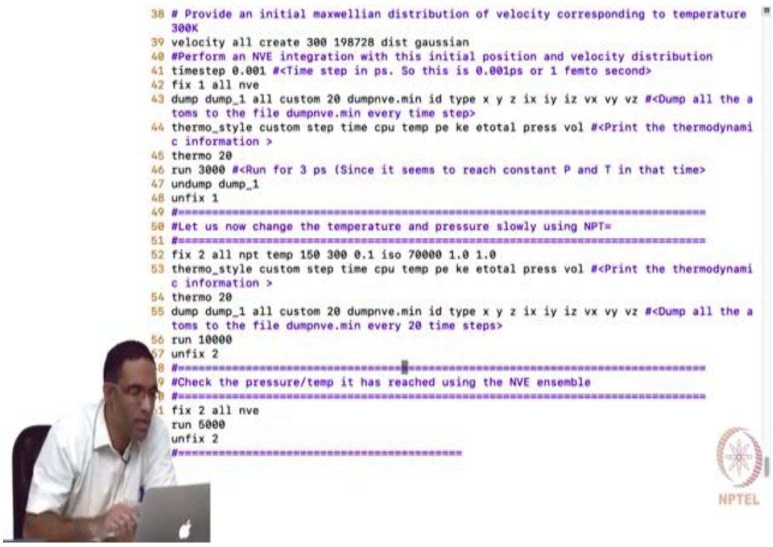

```
# Provide an initial maxwellian distribution of velocity corresponding to temperature
300K
velocity all create 300 198728 dist gaussian
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the a
toms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynami
c information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
undump dump_1
unfix 1
#=========================================================================
#Let us now change the temperature and pressure slowly using NPT=
#=========================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynami
c information >
thermo 20
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the a
toms to the file dumpnve.min every 20 time steps>
run 10000
unfix 2
#=========================================================================
#Check the pressure/temp it has reached using the NVE ensemble
#=========================================================================
fix 2 all nve
run 5000
unfix 2
#========================================
```

Now, the whole thing is after performing this NPT fix for about 10000 steps, so we have already done something for about 3000 steps right here, and then I am performing something for about 10000 steps. So, totally, the simulation has run for about 3 plus 10, 13 Picoseconds. After that, what I am trying to do is, I am trying to isolate the system from the surroundings and just to NVE and check if the temperature and the pressure that I have requested has actually reached the values that I wanted it, this fix is supposed to dump in energy and it is also supposed to change the dimensions of the box. So as to reach the required pressure and temperature.

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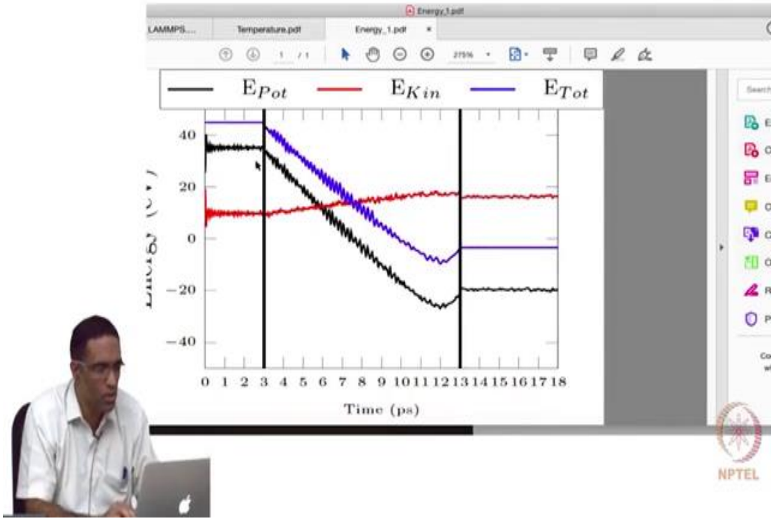

So now this is the energy so I mean, I did not describe what exactly these partitions mean here last class that is why I am showing it again. So you can see that the first 3 picoseconds, the total energy is a constant, this is energy variation or the entire simulation. So our simulation was divided into 3 parts; 3 picoseconds of NVE, 10 Picoseconds of NPT and then again 5 picoseconds of NVE. So, the first 3 Picoseconds illustrates the region where the NVE was carried out, so total energy is remaining constant and the kinetic energy and the potential energies are also shown here.

Then we have the NPT simulation, where several things are happening. So the kinetic energy is slowly increasing because we are ramping up the temperature, then the potential energy is decreasing and total energy is decreasing. And then again, I stopped all the NPT fixes and continued my NVE fix for another 5 Picoseconds and once again I see a constant energy and mildly fluctuating potential and kinetic energies. So, the whole thing is, the whole point is, whether this thing has actually reached equilibrium.

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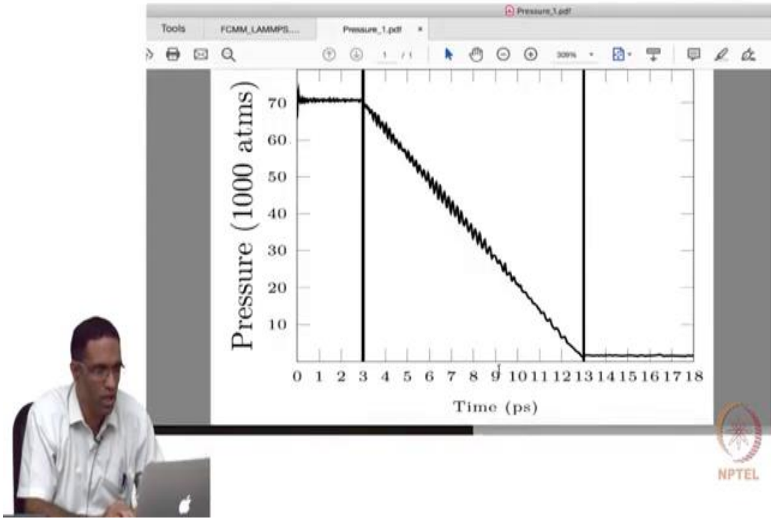

So, the pressure it started at 70000 atmospheres and it is somewhere here. So, this is not still 1 atmosphere, this is still in the order of about 1000 atmospheres because this is the scale is like going at 10, 20, 30, 40 and I have printed it in 1000 of atmospheres. So, although this appears to be small, this is not the pressure we want. So, you can take a look at the log file.

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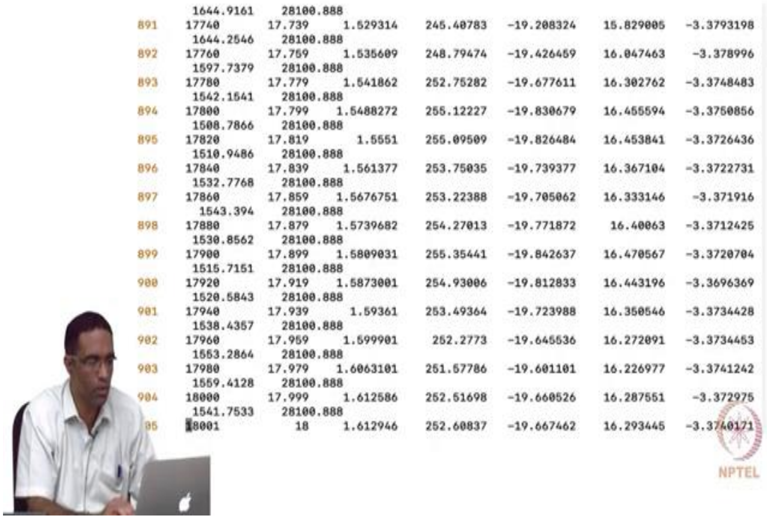
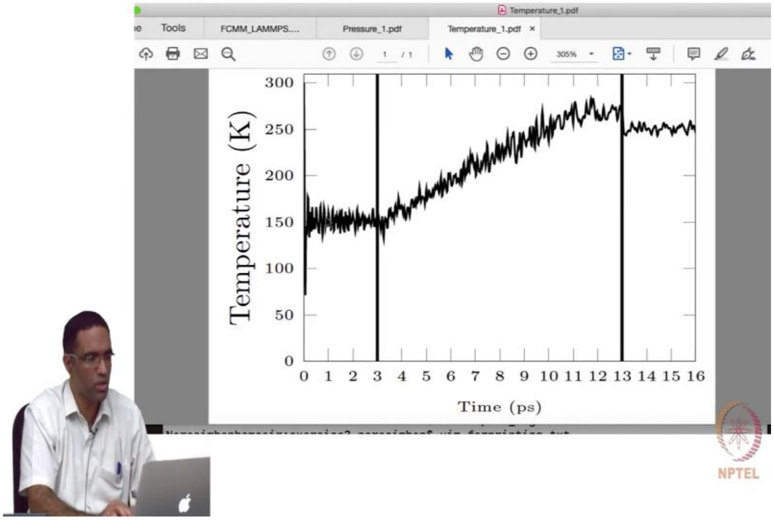


```
   1644.9161    28100.888
  17740        17.739     1.529314     245.40783   -19.208324    15.829005   -3.3793198
   1644.2546    28100.888
  17760        17.759     1.535609     248.79474   -19.426459    16.047463    -3.378996
   1597.7379    28100.888
  17780        17.779     1.541862     252.75282   -19.677611    16.302762   -3.3748483
   1542.1541    28100.888
  17800        17.799    1.5488272     255.12227   -19.830679    16.455594   -3.3750856
   1508.7866    28100.888
  17820        17.819       1.5551     255.09509   -19.826484    16.453841   -3.3726436
   1510.9486    28100.888
  17840        17.839     1.561377     253.75035   -19.739377    16.367104   -3.3722731
   1532.7768    28100.888
  17860        17.859    1.5676751     253.22388   -19.705062    16.333146    -3.371916
    1543.394    28100.888
  17880        17.879    1.5739682     254.27013   -19.771872     16.40063   -3.3712425
   1530.8562    28100.888
  17900        17.899    1.5809031     255.35441   -19.842637    16.470567   -3.3720704
   1515.7151    28100.888
  17920        17.919    1.5873001     254.93006   -19.812833    16.443196   -3.3696369
   1520.5843    28100.888
  17940        17.939      1.59361     253.49364   -19.723988    16.350546   -3.3734428
   1538.4357    28100.888
  17960        17.959     1.599901      252.2773   -19.645536    16.272091   -3.3734453
   1553.2864    28100.888
  17980        17.979    1.6063101     251.57786   -19.601101    16.226977   -3.3741242
   1559.4128    28100.888
  18000        17.999     1.612586     252.51698   -19.660526    16.287551    -3.372975
   1541.7533    28100.888
  18001            18     1.612946     252.60837   -19.667462    16.293445   -3.3740171
```



So this is what I printed out just the information. You see the, so the last column and is volume and the column before that is actually pressure, so this is the volume and this is the pressure. Still about 1540 bars, still not reached the required pressure that we want. The temperature also this region is NVE, so it was oscillating about 150 or from 300 and then it starts oscillating about 150, about 3 picoseconds. I stopped it at about 3 picoseconds because the NVE run that we carried out previously for a longer period of time seemed to show that at 3 picoseconds it that reached some equilibrium value so I do not have to continue that run for a longer period of time.

And then from 150 to 300 I have tried to ramp but I ramped it for about 13 Picoseconds, and then I stopped it and continued by NVE run. But when I continued my NVE run, the energy that was dumped into the system is still making it oscillate only at around 250 Kelvin, we still again when it comes to temperature, also we have not yet reached the required temperature that we require the thermostat to do, we want the system to be at 1 atmospheres and 300 Kelvin. But nonetheless, the pressure has still come down from 70000 bar to about 1500 bar. And like I showed you last class what is essentially happening during the NPT run is the expansion of this whole system. I think we saw that. Yes we saw that.

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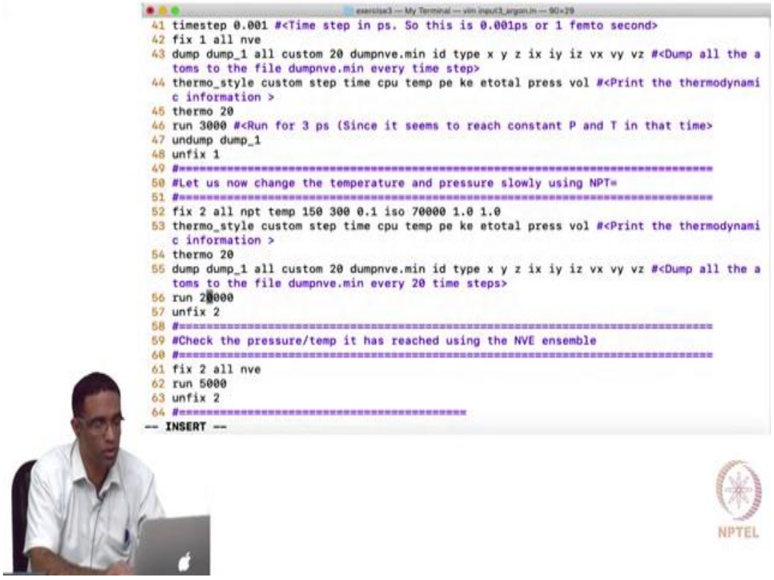

```
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the a
toms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynami
c information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
undump dump_1
unfix 1
#===========================================================================
#Let us now change the temperature and pressure slowly using NPT=
#===========================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynami
c information >
thermo 20
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the a
toms to the file dumpnve.min every 20 time steps>
run 20000
unfix 2
#===========================================================================
#Check the pressure/temp it has reached using the NVE ensemble
#===========================================================================
fix 2 all nve
run 5000
unfix 2
#========================================
-- INSERT --
```

Now, if you run it for a longer period of time, so for example, if I run this thing for say a longer period of time and look at the temperatures, it happens to be slightly better for 20000 or 30000 steps if I do this NPT it happens to be only slightly better, it is still not and even the pressure. For example, I just before coming here I ran it for about 50 Picoseconds, the temperature came to about 280 Kelvin and the pressure was still around 600 bars. So, sometimes you may have to run it for a very long time before you are actually able to achieve equilibrium. And you have to check it, how do you check for equilibrium in MD? How do you check for equilibrium, whether it has reached equilibrium or not?

Student: Kinetic energy?

Professor: You stop. The way I generally like to do it is, stop any exchange of heat or energy with the surroundings, I mean, stop any NVT, NPT fixes, and then do an exclusive NVE. So if the system has reached equilibrium with the surroundings, then its temperature and pressure should be what you want. Otherwise, it will just shift and show you a different value. There is another way by monitoring what is referred to as the velocity autocorrelation function, we will come to that a little bit later.

But qualitatively what that function is going to tell you is, how soon has this system lost memory of its initial configuration. So remember, you have set the initial velocities and initial positions. And the system is supposed to behave independent of that, no matter what initial configurations that you gave, or the temperature that you gave at equilibrium, it is supposed to behave independently of your initial condition, the velocity auto correlation function is one way by which you can check whether the system has lost any memory of its initial state. And that is another method by which you can actually check if the system has reached equilibrium.

But this method I like it because it is quite intuitive, simply because the definition of equilibrium is you have to isolate the system from the surroundings and see if things are changing that is the definition of equilibrium from thermodynamics and we are doing exactly that, we are stopping any NVT fix and we are performing an NVE fix, and NVE means an isolated system for a given input. Yeah.

Student: Sir, so autocorrelation becomes 0?

Professor: Yes, the autocorrelation function will become 0 as time progresses to suggest, it will oscillate about 0, we will see that if we have time.

Student: Sir what do you mean by memory of its previous state?

Professor: Not previous but initial configuration.

Student: Means you are referring to the memory of the…

Professor: Of the system itself of the bunch of atoms itself, it should not depend on. So, you say for example, let us consider you took a system, you initial this is a good way to probably explain that.

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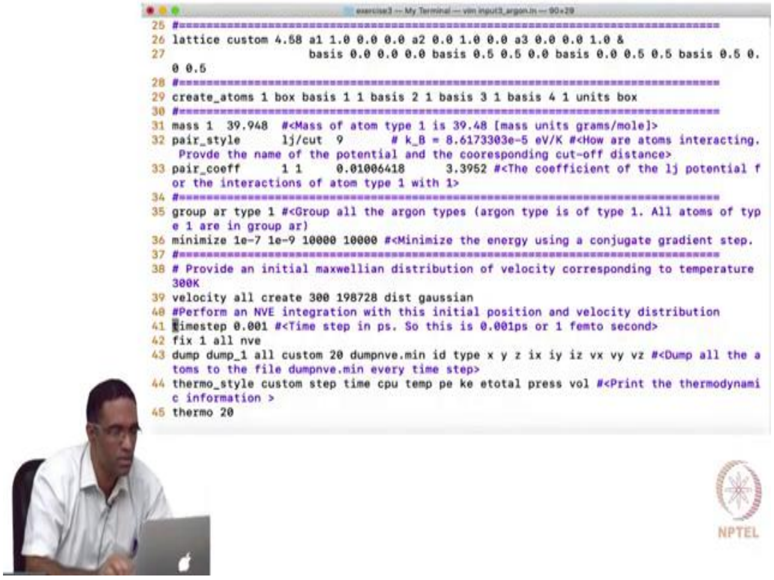

```
#===============================================================================
lattice custom 4.58 a1 1.0 0.0 0.0 a2 0.0 1.0 0.0 a3 0.0 0.0 1.0 &
                    basis 0.0 0.0 0.0 basis 0.5 0.5 0.0 basis 0.0 0.5 0.5 basis 0.5 0.
0 0.5
#===============================================================================
create_atoms 1 box basis 1 1 basis 2 1 basis 3 1 basis 4 1 units box
#===============================================================================
mass 1  39.948  #<Mass of atom type 1 is 39.48 [mass units grams/mole]>
pair_style      lj/cut  9       # k_B = 8.6173303e-5 eV/K #<How are atoms interacting.
 Provde the name of the potential and the cooresponding cut-off distance>
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or the interactions of atom type 1 with 1>
#===============================================================================
group ar type 1 #<Group all the argon types (argon type is of type 1. All atoms of typ
e 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#===============================================================================
# Provide an initial maxwellian distribution of velocity corresponding to temperature
300K
velocity all create 300 198728 dist gaussian
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the a
toms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynami
c information >
thermo 20
```

So, you initialize the velocity of the system in a particular way at 300 Kelvin using this random seed, if I change this random seed, it is going to get initialized in a different way. Yes or no? Different sets of atoms are going to have different velocities, and now I run the simulation. No matter what I give the initial condition, the equilibrium state of the system must not depend on these configurations, it should not. As time progresses, it should start exploring its equilibrium state and that will happen after some time. For example, 300 Kelvin start becomes 150 Kelvin not instantaneously, there it takes some time for it to become 150 Kelvin, if you look at that graph, it takes about, I do not know maybe a half a picosecond or something like that.

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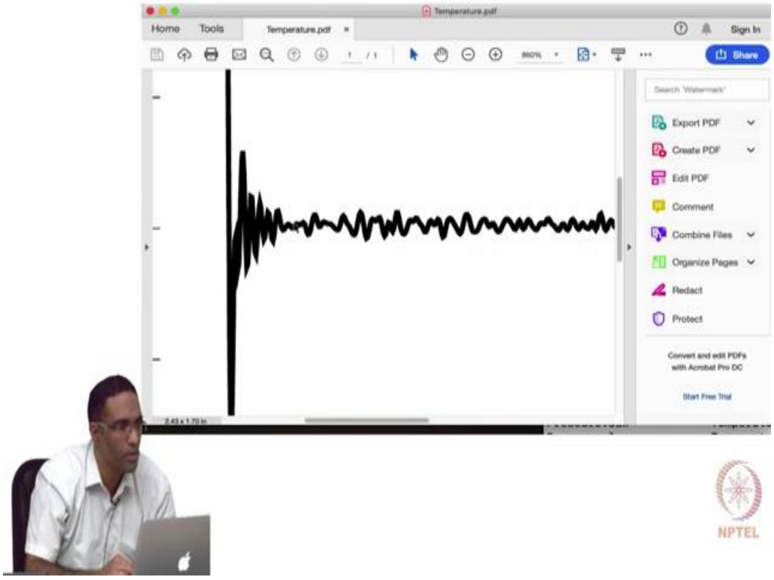

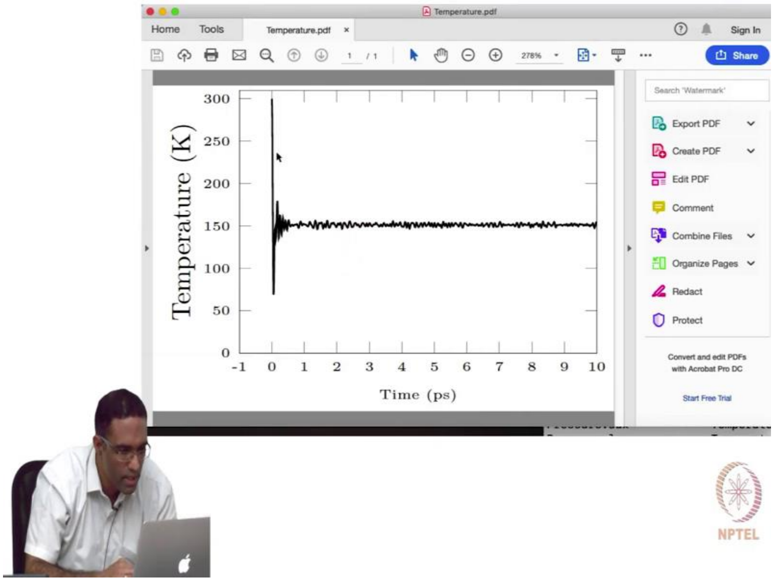

So, it takes some time for the vibrations to actually die out and reach 150 Kelvin. So, now, no matter what was the initialization of the velocities at this spot, it should always start reaching equilibrium. And once here, once it is starting exploring the space here, it is not possible for the system to tell you whether this state was initialized with random seed of 197248 or whether it was initialized with some other random seed. It has completely lost memory of its initial conditions, so that should happen to any system.

Student: Random seed should always be 6 digit?

Professor: Always be?

Student: Should it be 6 digit?

Professor: No no, some number, some integer you can give, it does not have to be any 6 digit number, I just gave something that came to my mind or I just type something without even looking at the keyboard actually.

Student: Can we give the same figure each time we do it?

Professor: Yes, because it is really not, computer is not that random yet, pseudo random. So yeah, so when you do it a little bit longer, when you just have NPT or after NVE, you just have NPT and do it a little bit longer, it still does not converge to the pressure and temperature that we require. So, this equilibration has to be done very carefully and in steps.

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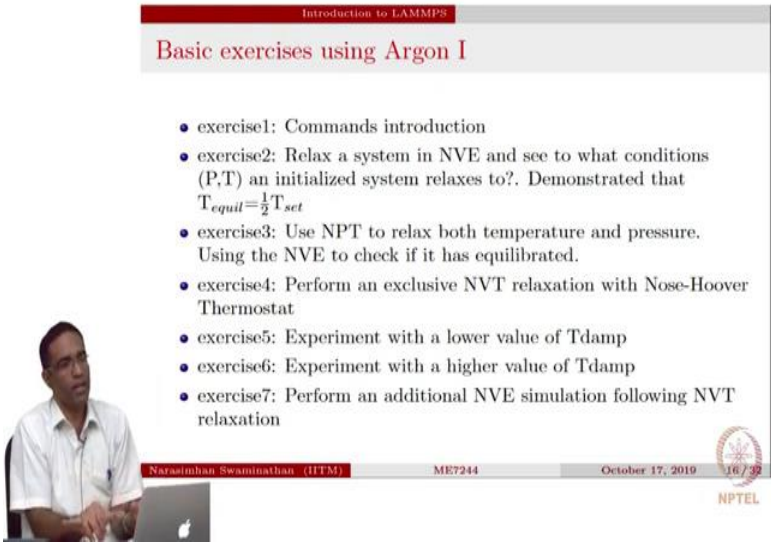

Introduction to LAMMPS

Basic exercises using Argon I

- exercise1: Commands introduction
- exercise2: Relax a system in NVE and see to what conditions (P,T) an initialized system relaxes to?. Demonstrated that $T_{equil}=\frac{1}{2}T_{set}$
- exercise3: Use NPT to relax both temperature and pressure. Using the NVE to check if it has equilibrated.
- exercise4: Perform an exclusive NVT relaxation with Nose-Hoover Thermostat
- exercise5: Experiment with a lower value of Tdamp
- exercise6: Experiment with a higher value of Tdamp
- exercise7: Perform an additional NVE simulation following NVT relaxation

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So the next thing what I am going to do is, I am just going to perform after this NPT I am going to perform an exclusive NVT relaxation using the nose hoover thermostat, no NPT just holding whatever volume was fixed, we will hold that whatever volume was created, we will hold that, what happened?

Student: What is Nose hoover?

Professor: Nose hoover what it is? It is a thermostat. So that is actually it is a methodology by which the dynamics of the system is changed. Even NPT is actually altered dynamics of the system, you have to add terms to the set of differential equations that you are solving so as to allow it to input heat or to change the volume. So nose hoover thermostat is a thermostat that is available in LAMMPS for you to implement a thermostat, basically increase the temperature that is it. Now, there is a lot of math, there is a lot of derivation to actually understand and see why this actually explores the NVT ensemble. Now this is not, I am not going to do that, but then that would be a coding course and it would require a different type of background in order to be doing that. We will see how to use it, we will see how to use the nose our thermostat and what it does for our system.

Student: Sir.

Professor: Yes.

Student: When we write the command fix 1 all NVE, what refers to the…

Professor: Fix ID.

Student: Okay, it refers to the fix ID.

Professor: Fix ID, which can be referred to later on in the script. So, if you say unfixed one, it means stop that, you can also say a fix some other name, you can say fix, I am NVE fix, you can say that, it is some name that you give, so that you can refer to it later on in the script.

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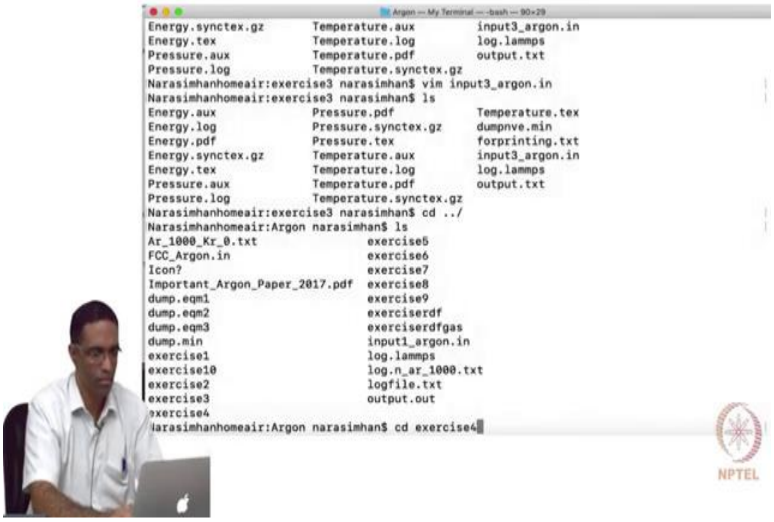
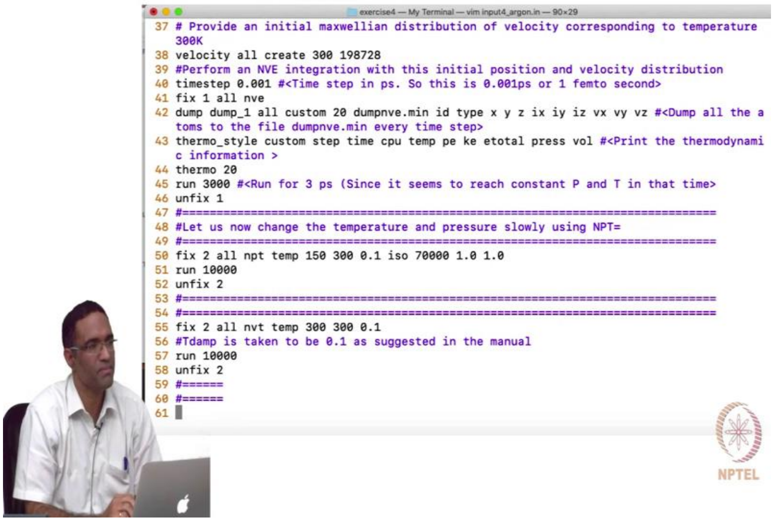


```
Energy.synctex.gz       Temperature.aux         input3_argon.in
Energy.tex              Temperature.log         log.lammps
Pressure.aux            Temperature.pdf         output.txt
Pressure.log            Temperature.synctex.gz
Narasimhanhomeair:exercise3 narasimhan$ vim input3_argon.in
Narasimhanhomeair:exercise3 narasimhan$ ls
Energy.aux              Pressure.pdf            Temperature.tex
Energy.log              Pressure.synctex.gz     dumpnve.min
Energy.pdf              Pressure.tex            forprinting.txt
Energy.synctex.gz       Temperature.aux         input3_argon.in
Energy.tex              Temperature.log         log.lammps
Pressure.aux            Temperature.pdf         output.txt
Pressure.log            Temperature.synctex.gz
Narasimhanhomeair:exercise3 narasimhan$ cd ../
Narasimhanhomeair:Argon narasimhan$ ls
Ar_1000_Kr_0.txt                exercise5
FCC_Argon.in                    exercise6
Icon?                           exercise7
Important_Argon_Paper_2017.pdf  exercise8
dump.eqm1                       exercise9
dump.eqm2                       exerciserdf
dump.eqm3                       exerciserdfgas
dump.min                        input1_argon.in
exercise1                       log.lammps
exercise10                      log.n_ar_1000.txt
exercise2                       logfile.txt
exercise3                       output.out
exercise4
Narasimhanhomeair:Argon narasimhan$ cd exercise4
```



```
# Provide an initial maxwellian distribution of velocity corresponding to temperature 300K
velocity all create 300 198728
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
unfix 1
#==============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#==============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
run 10000
unfix 2
#==============================================================================
#==============================================================================
fix 2 all nvt temp 300 300 0.1
#Tdamp is taken to be 0.1 as suggested in the manual
run 10000
unfix 2
#======
#======

```

So here everything until the spot remains the same. But now what I am going to do is, I am just going to say fixed to all NVT temperature from 300 to 300 with a T damp of about 0.1, and I am going to run it for about 10 Picoseconds. So what is either in difficulty you are looking at them and saying this is difficult, it is something complicated here or.

Student: Sir can you go to that NVT page? Should not the NVT contain two different means initial and kinetic energy, should not we get that?

Professor: Not necessary.

Student: Actual usages is there start from one temperature to another?

Professor: Yes, you can ramp it up or you can start at 300 and end at 300 also, both are fine. You see our initial temperature was what? 150. And we tried to reach 300 using this NPT, but it reached some 280 that was close enough to 300 so I am starting at 300 and ending at 300. Now, if there is a huge difference between the current temperatures at which the system is and the temperature to which you want to go to, then it is a good idea to ramp it up slowly. Otherwise you can actually give the starting temperature and the ending temperature to be the same value and basically what it does is, it tries to maintain the temperature of 300 Kelvin. So, this has been run to about 10 picoseconds.

Student: If you start from 280 or something to 300, then will it try to make sure it comes to 300?

Professor: Yes, 280 to 300 means it will come to 300 from it is trying going to try to make it to come to 300 from 280. Yeah, but the initial temperature that it is going to try to give us 280 and then slowly as a function of time it is going to ramp it.

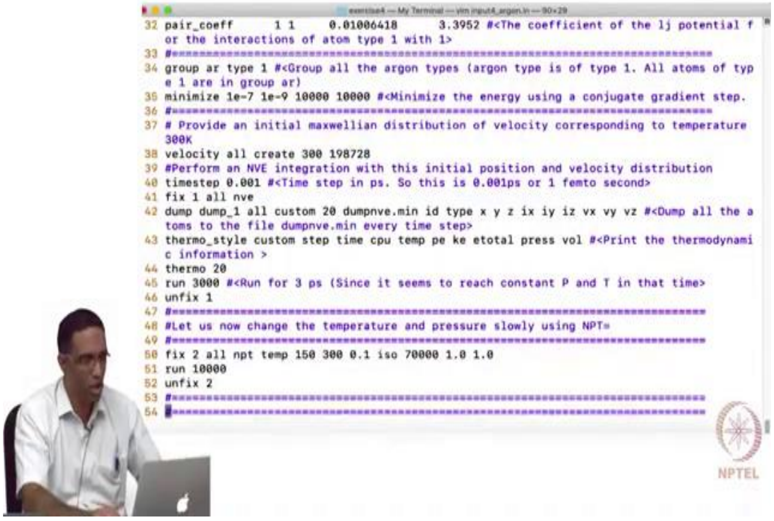
Student: Sir say of we increase the number of iterations of say 20000 also then this system is still the same? Because we are still it maintaining at 300 so it just reached 300 and say…

Professor: Yes, yes. So when I did this.

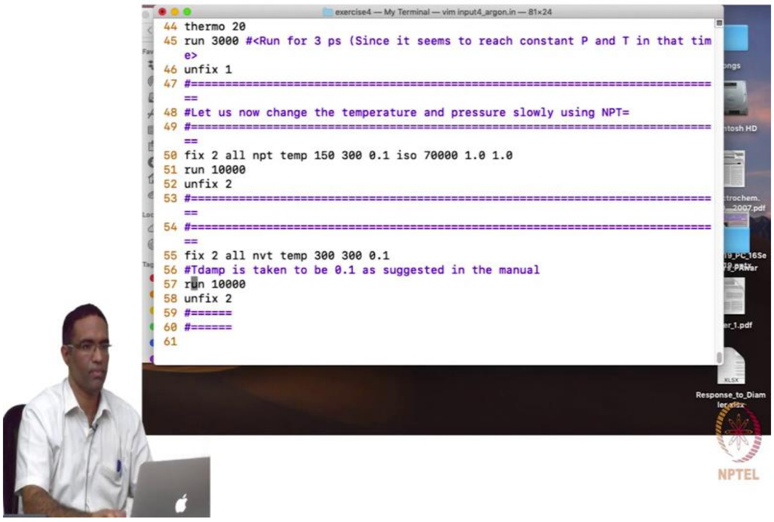
Student: Sir if the temperature is not changing then what is the NPT doing exactly?

Professor: No, it is trying to change the temperature, your system is not at 300 yet, it is still at some 250 or something know. See, this is exact this is just an extension of the exercise 3.

(Refer Slide Time 35:41)



```
pair_coeff      1 1     0.01006418      3.3952 #<The coefficient of the lj potential for the interactions of atom type 1 with 1>
#==============================================================================
group ar type 1 #<Group all the argon types (argon type is of type 1. All atoms of type 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#==============================================================================
# Provide an initial maxwellian distribution of velocity corresponding to temperature 300K
velocity all create 300 198728
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
unfix 1
#==============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#==============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
run 10000
unfix 2
#==============================================================================
#==============================================================================
```



```
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
unfix 1
#================================================================================
#Let us now change the temperature and pressure slowly using NPT=
#================================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
run 10000
unfix 2
#================================================================================
#================================================================================
fix 2 all nvt temp 300 300 0.1
#Tdamp is taken to be 0.1 as suggested in the manual
run 10000
unfix 2
#======
#======
```

Exercise 3 basically stopped here, there was a NPT run, where we tried to ramp it up from 150 to 300. And we observed the results and we saw that it was not reaching 300, it is something 200 Kelvin. I am just adding another fix to only ramp the Temperature. Yes

Student: Sir in the previous slide you said that the temperature reaches about 275 280, then why have you given 300 to 300 and shouldn't it be different?

Professor: Yeah. You can give 280 to 300 also, it does not matter. It will start from 280 and slowly ramp it up to 300 in this time step, before it reaches this time set if it happens to reach 300 then it will maintain 300 but that is not what it is going to do. If you say start temperature and end temperature, it means it will start at 280 and over that timeframe it will reach 300 Kelvin. Is that clear? But if you give 300 to 300, it is just going to maintain 300, it is just going to start at 300 and maintain that 300 value for the entire time period for which this fix is held.

Student: Sir can we reduce the number of iterations if it anyways starts from 300?

Professor: I did not follow you.

Student: If NVT we start from 300, so we can reduce the number of iterations, then how can get the temperature?

Professor: You can try this 10000 is not something that was derived just tried.

Student: What iteration will it need to bring it to 300?

Professor: What is it?

Student: In which step will it bring it to 300, is it the first step itself?

Professor: The first step it is going to put some heat into it to try to bring it to 300. But then as a function of time, enough energy may not have been pumped in for the entire system to have got 300. So, it has to continuously do it, there might be some see, what does temperature mean if the average temperature could be 300 but there could be higher and lower temperatures within the system, there might be heat transfer going on within the system, but that is not what you want. You want the entire temperature to be on an average oscillating about 300 Kelvin. So, it will start at 300 and try to maintain it at 300, if you do 300 initial and 300 end over the entire time period.

If you reduce the number of steps, you can try, it may reach it may give you an equilibrium set of 300 or it may not reach also, for example, if I just did this for one step, if I did this for just 1 step. Do you think it would be 300? It will not be 300. So, there is sufficient you have to give it sufficient time so that it reaches equilibrium with the bath that is pumping in heat to the system.

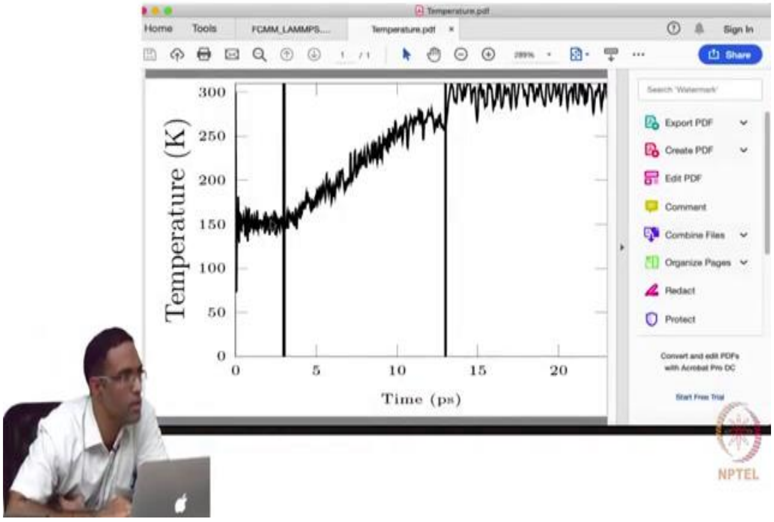
Student: So in the very first iteration it will try to make it 300 and maybe in the second iteration it will go to some…

Professor: It may go down again it can, it will fluctuate.

Student: But the very first equation will reach 300.

Professor: It will reach 30, yes. And if you set 280 to 300, the reverse iteration will be to, no it will start with 280 to 280 and it will go to 300 in that time span.

(Refer Slide Time 39:45)

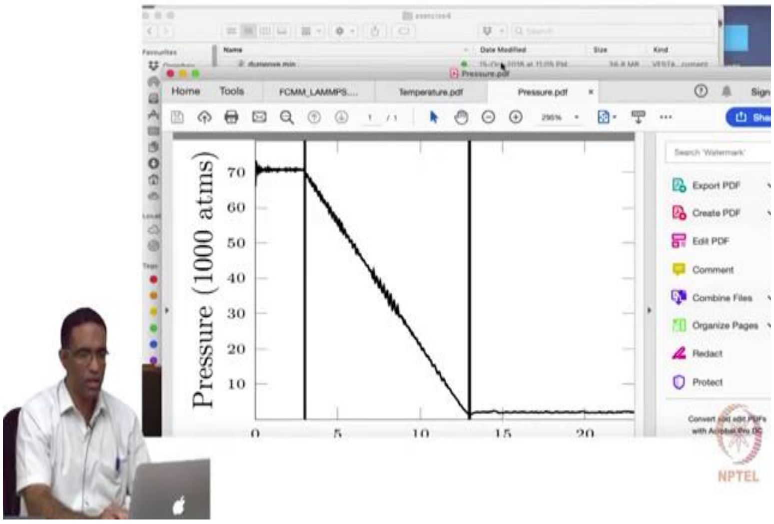


So now if you see, so this is our NVE part, this is the temperature as a function of time here. So, this is our NVE part, the first 3 Picoseconds, followed by 13 Picoseconds of our NPT which ended somewhere here and then I do NVT to try to make it oscillate about 300. And now?

Student: In the very first iteration it will reach 300 but it will not be in equilibrium if you are giving 1 as a…

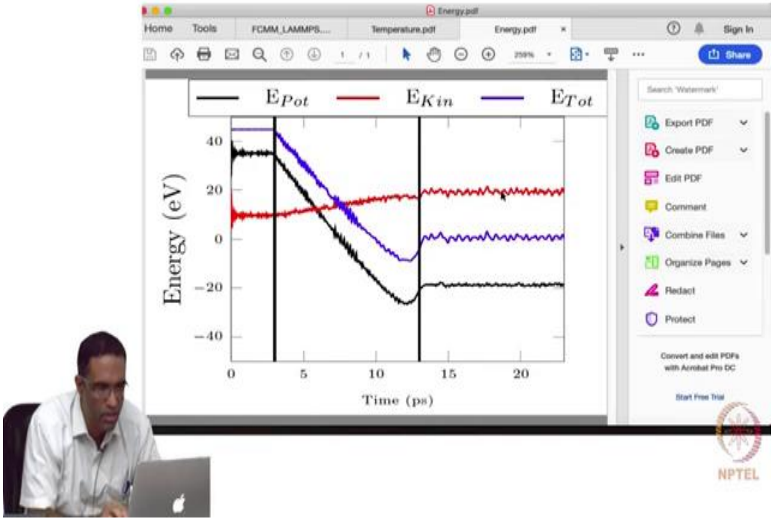
Professor: Yes, it will not be an equilibrium with the bath. Somewhat oscillating at about 300, definitely better than the value that it ended in previously. But of course, we will know this only when we stop this fix and do NVE run, otherwise we will not know. Now of course, what should happen to the pressure?

(Refer Slide Time 40:39)



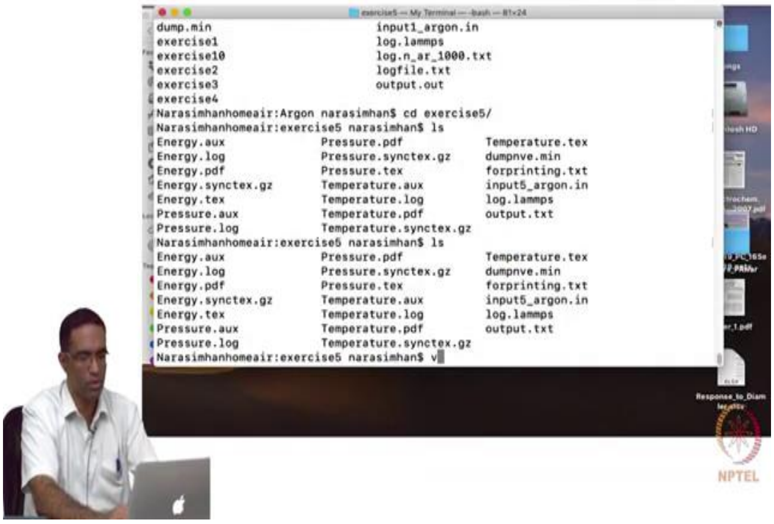
So the pressure is still not what we want obviously, it continues to be what it was. Actually, it cannot be what it was, it will change a little bit, because you are holding the volume fixed, and you are increasing the temperature a bit. The pressure is likely to increase a bit, so that is what we are observing here.

(Refer Slide Time 41:08)

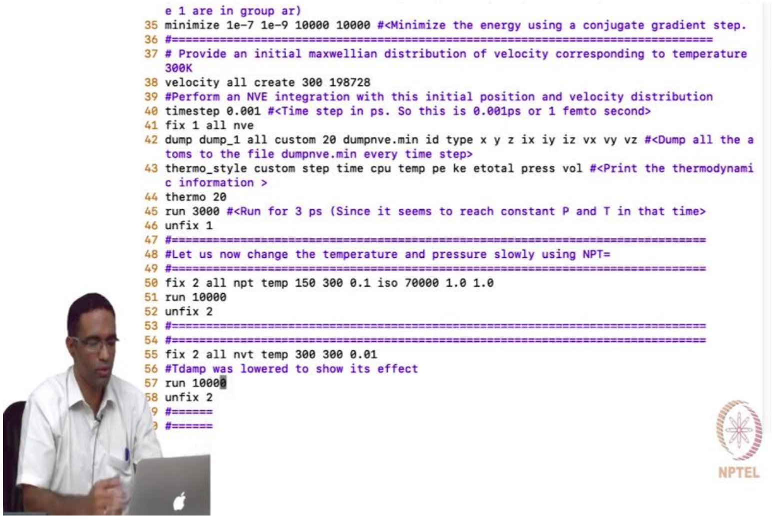


And there is nothing interesting to see about energy it looks exactly the same, this is the region where the NVT has been run. In the NVT all the energies are actually fluctuating, the total energy, the potential energy and the kinetic energy.

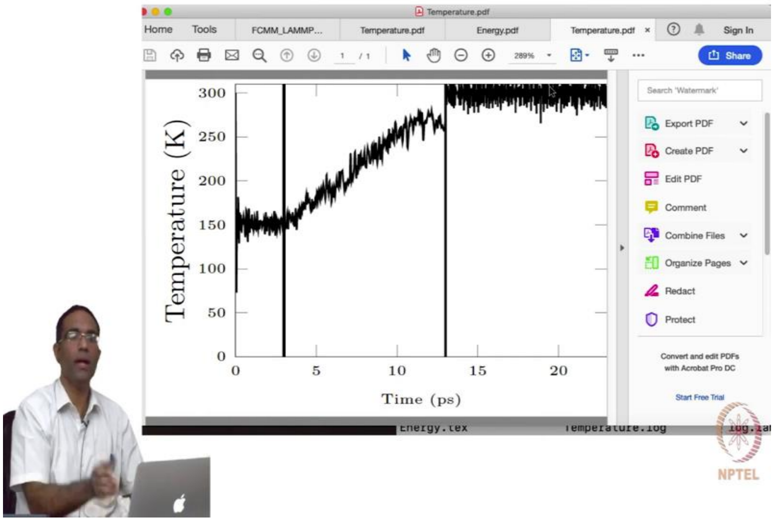
(Refer Slide Time 41:17)



```
dump.min                        input1_argon.in
exercise1                       log.lammps
exercise10                      log.n_ar_1000.txt
exercise2                       logfile.txt
exercise3                       output.out
exercise4
Narasimhanhomeair:Argon narasimhan$ cd exercise5/
Narasimhanhomeair:exercise5 narasimhan$ ls
Energy.aux              Pressure.pdf            Temperature.tex
Energy.log              Pressure.synctex.gz     dumpnve.min
Energy.pdf              Pressure.tex            forprinting.txt
Energy.synctex.gz       Temperature.aux         input5_argon.in
Energy.tex              Temperature.log         log.lammps
Pressure.aux            Temperature.pdf         output.txt
Pressure.log            Temperature.synctex.gz
Narasimhanhomeair:exercise5 narasimhan$ ls
Energy.aux              Pressure.pdf            Temperature.tex
Energy.log              Pressure.synctex.gz     dumpnve.min
Energy.pdf              Pressure.tex            forprinting.txt
Energy.synctex.gz       Temperature.aux         input5_argon.in
Energy.tex              Temperature.log         log.lammps
Pressure.aux            Temperature.pdf         output.txt
Pressure.log            Temperature.synctex.gz
Narasimhanhomeair:exercise5 narasimhan$ v
```



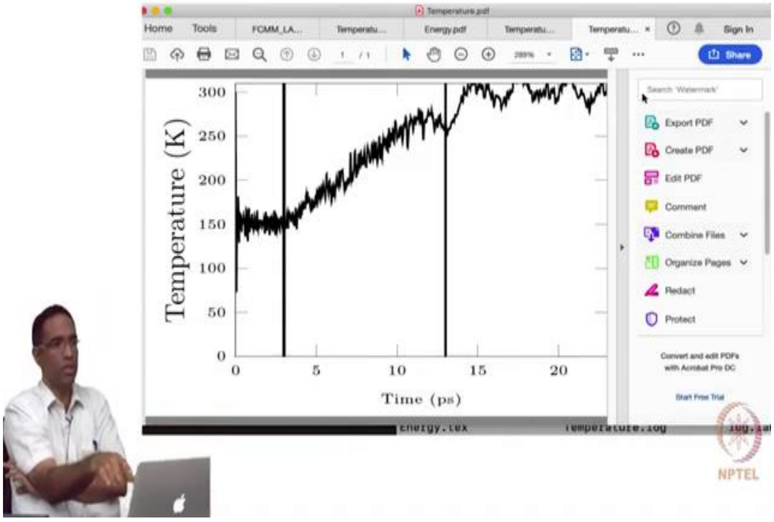
```
e 1 are in group ar)
minimize 1e-7 1e-9 10000 10000 #<Minimize the energy using a conjugate gradient step.
#============================================================================
# Provide an initial maxwellian distribution of velocity corresponding to temperature 300K
velocity all create 300 198728
#Perform an NVE integration with this initial position and velocity distribution
timestep 0.001 #<Time step in ps. So this is 0.001ps or 1 femto second>
fix 1 all nve
dump dump_1 all custom 20 dumpnve.min id type x y z ix iy iz vx vy vz #<Dump all the atoms to the file dumpnve.min every time step>
thermo_style custom step time cpu temp pe ke etotal press vol #<Print the thermodynamic information >
thermo 20
run 3000 #<Run for 3 ps (Since it seems to reach constant P and T in that time>
unfix 1
#============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
run 10000
unfix 2
#============================================================================
#============================================================================
fix 2 all nvt temp 300 300 0.01
#Tdamp was lowered to show its effect
run 10000
unfix 2
#======
#======
```



So now, it is important to see what this T damp does. So, like I told you previously the T damp value is about 100 times the value of the time step. So, in this case, I gave a slightly lower value of T damp so, if you change that value and if you run the simulation and you took a look at the temperature profile, somewhat changing it more frequently than what it was for the value of 0.1. So essentially, this is some parameter that is telling you how quickly you want the system to reach a temperature that you actually are desiring.

This is actually a parameter with which you have to for certain systems you may have to play with. And you will know whether this parameter is actually good or not only when it is, only when you have tested whether it has reached equilibrium or not. Temperature at least is okay, usually you will be able to reach equilibrium but pressure especially for solids you can have a hard time. It will, you will say one atmosphere, but it will take a very, very long time to reach that pressure and the fluctuations can be huge. So, in that instance there might be a need where you have to trick these P damp parameter a little bit.

(Refer Slide Time 42:39)



The next exercise I just do it for a slightly larger value of 0.5 for the T damp, this is exactly the same simulation except that I have changed T damp to 0.5 but you see that the oscillations are a little bit less frequent, which means you are giving it in more time for the system to actually reach the system to the desired temperature. The same behaviour is also observed for P damp, if you have larger values, it will look more like that, whereas if you have smaller values, it will fluctuate wildly about the temperature that you are requesting. And you will know whether that is right or wrong when you stop it and check for equilibrium.

Student: Sir also here also both of it is not desirable so..?

Professor: No, to bring it to equilibrium you may have to change these things a bit.

Student: So we need to find 1 which was slight previous first one like exercise 4?

Professor: Yes. Again, these are just visual conclusions that we have drawn. So, like I mentioned, you will know which of these things is right when you are testing for equilibrium otherwise, you will not know. Yeah.

Student: Overall this is big so does it mean it takes more time?

Professor: This might take more, this will take much more time, yeah.

Student: What type of values we should give so that it will be better?

Professor: Yeah correct, but there can be issues if you are lowering these values to a great extent also. There are some things that will break down if you are decreasing it to a ridiculously low value. So, you cannot do that too much.

Student: What will take more time?

Professor: What will take, so what happen, so if you give a larger value of T damp, you saw the temperature how it was equilibrating. It is like this, for a value of 0.01 it was like this. And for a value of 0.1 it looked like this. So I am illustrating what this T damp is doing to the temperature. Now what is desirable or what is not desirable you will know only when you are testing the system for equilibrium and seeing if it is reached the temperature that you want. So, basically after doing this exercise, after NVT you have to stop it and do NVE run to check whether the temperatures are oscillating about 300 Kelvin. Now, it may so happen that you have done it so slowly but you have done it for a fewer time steps that your system is still not reached equilibrium. You see what I am seeing? Your understanding what I am saying?

Student: It will become so slowly that still the system have not…

Professor: Reached equilibrium, but for the same time step I may be able to use a lower value of T damp which may bring the system to equilibrium in the same, for the same time period.

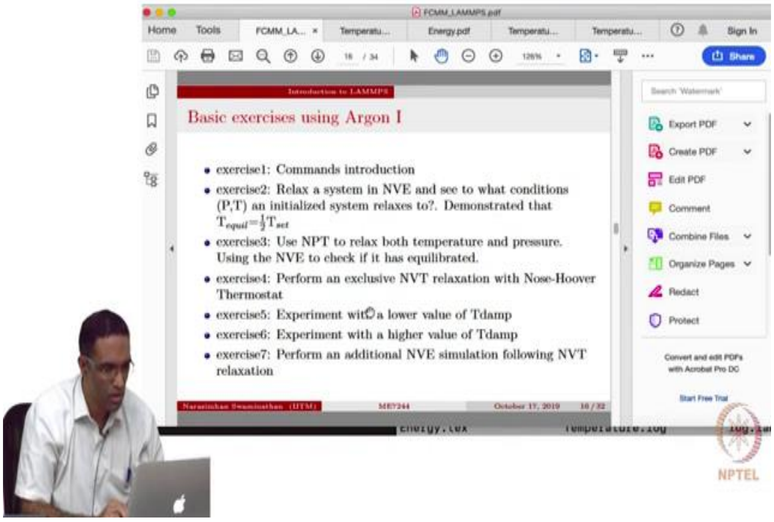
Student: So T damp is related to how fast heat is being pumped from the bar?

Professor: Correct, how fast you want your system to reach the temperature that you desire.

Student: Is the value of T damp is low and heat is being pumped?

Professor: Extremely fast. Is it ok?

(Refer Slide Time 46:22)



Introduction to LAMMPS

Basic exercises using Argon I

- exercise1: Commands introduction
- exercise2: Relax a system in NVE and see to what conditions (P,T) an initialized system relaxes to?. Demonstrated that $T_{equil} = \frac{1}{2} T_{set}$
- exercise3: Use NPT to relax both temperature and pressure. Using the NVE to check if it has equilibrated.
- exercise4: Perform an exclusive NVT relaxation with Nose-Hoover Thermostat
- exercise5: Experiment with a lower value of Tdamp
- exercise6: Experiment with a higher value of Tdamp
- exercise7: Perform an additional NVE simulation following NVT relaxation

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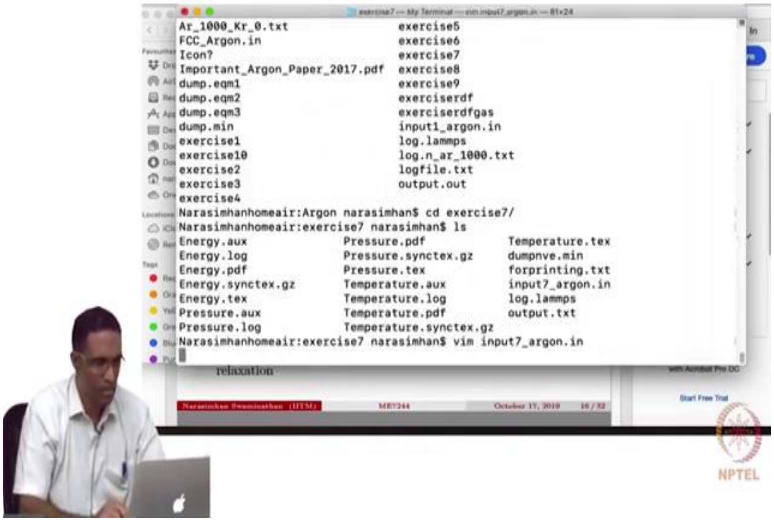
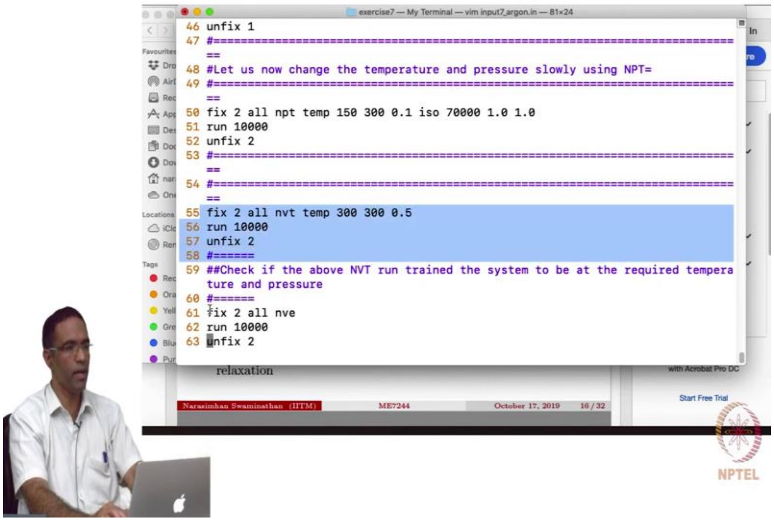


```
Ar_1000_Kr_0.txt                   exercise5
FCC_Argon.in                       exercise6
Icon?                              exercise7
Important_Argon_Paper_2017.pdf     exercise8
dump.eqm1                          exercise9
dump.eqm2                          exerciserdf
dump.eqm3                          exerciserdfgas
dump.min                           input1_argon.in
exercise1                          log.lammps
exercise10                         log.n_ar_1000.txt
exercise2                          logfile.txt
exercise3                          output.out
exercise4
Narasimhanhomeair:Argon narasimhan$ cd exercise7/
Narasimhanhomeair:exercise7 narasimhan$ ls
Energy.aux              Pressure.pdf              Temperature.tex
Energy.log              Pressure.synctex.gz       dumpnve.min
Energy.pdf              Pressure.tex              forprinting.txt
Energy.synctex.gz       Temperature.aux           input7_argon.in
Energy.tex              Temperature.log           log.lammps
Pressure.aux            Temperature.pdf           output.txt
Pressure.log            Temperature.synctex.gz
Narasimhanhomeair:exercise7 narasimhan$ vim input7_argon.in
```



```
unfix 1
#==============================================================================
#Let us now change the temperature and pressure slowly using NPT=
#==============================================================================
fix 2 all npt temp 150 300 0.1 iso 70000 1.0 1.0
run 10000
unfix 2
#==============================================================================
#==============================================================================
fix 2 all nvt temp 300 300 0.5
run 10000
unfix 2
#======
##Check if the above NVT run trained the system to be at the required temperature and pressure
#======
fix 2 all nve
run 10000
unfix 2
```

relaxation

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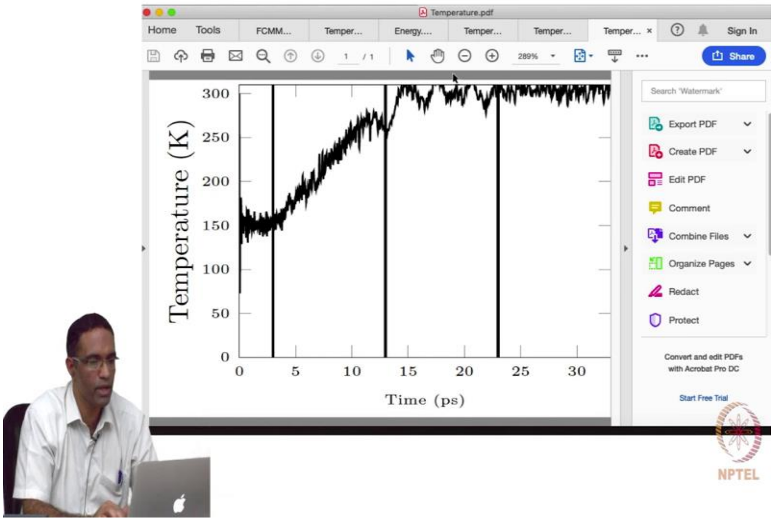
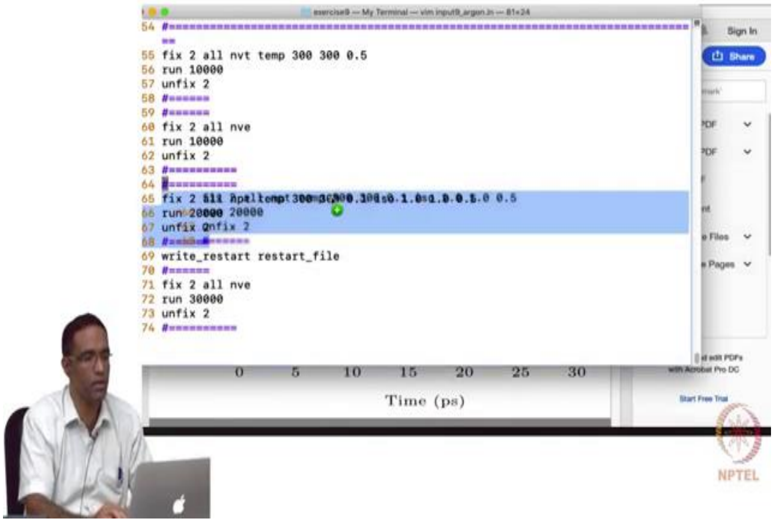


So then I say perform an additional NVE, so exercise 7 so let us go to exercise 6, what is exercise 6? That is also done so exercise 6. So in exercise 7 after doing this NVT I am checking if my system has actually reached equilibrium once again. So this was my NVT oscillation with T equal to 0.5, and then I am stopping it and I am checking if it is oscillating about 300 Kelvin. I am satisfied that it has reached equilibrium at 300 Kelvin, so I think it is at 300 Kelvin. Now, the pressure is still way off, we will still be way off, it will not be close to 1 atmospheres. So we need to perform additional NPT runs, now the 300 it was now previously what did we do? NPT from 150 to 300 and then you stopped it, it was not oscillating about 300.

(Refer Slide Time 48:21)



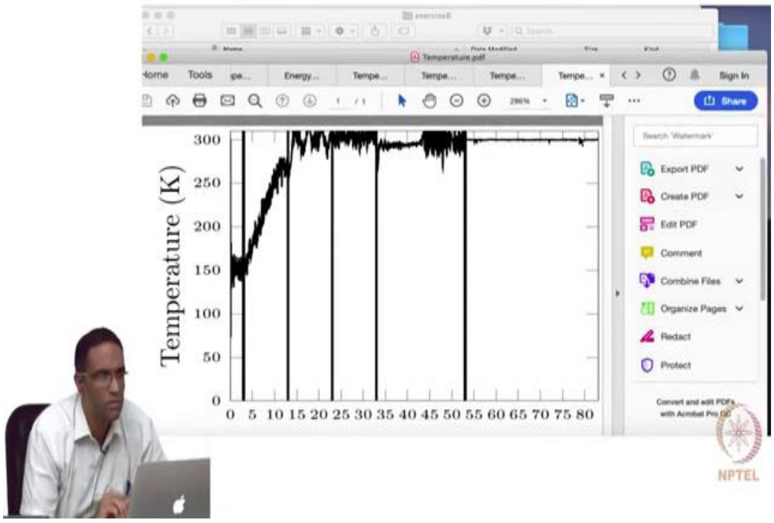
```
#===========================================================================
==
fix 2 all nvt temp 300 300 0.5
run 10000
unfix 2
#======
#======
fix 2 all nve
run 10000
unfix 2
#==========
#==========
fix 2 all npt temp 300 300 0.1 iso 1.0 1.0 0.5
run 20000
unfix 2
#==========
write_restart restart_file
#======
fix 2 all nve
run 30000
unfix 2
#==========
```

Now what we have done, we have exclusively just used NVT to bring only that, to make the temperature oscillate at about 300. So the system is well thermalized and is going to be at 300 Kelvin. Now I just if I use the NPT thermostat, I will reach the required, so what I do is after this run NVT, I check for something. After that I do once again NPT, but this time the temperature is 300 to 300 0.1 and ISO 1 bar and I have given arbitrary P damp parameter of 0.5. And then again I check whether the system has actually reached equilibrium, so…

Student: write_restart?

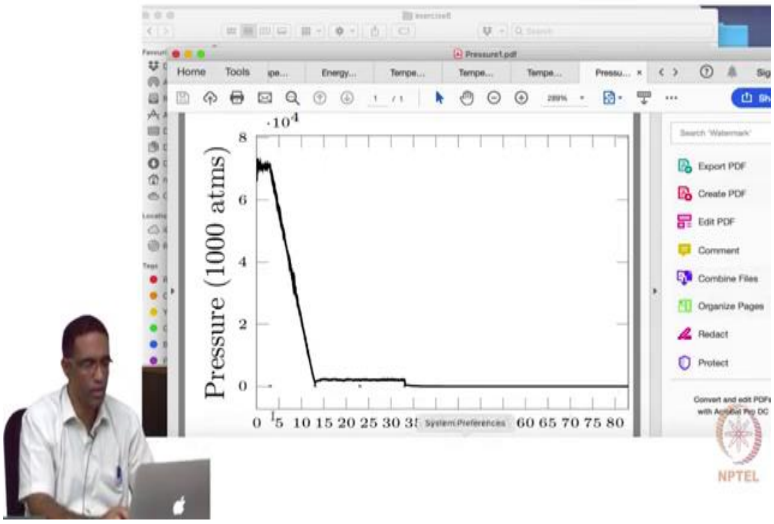
Professor: I will just come to it. I am just going to talk about it in a bit.

(Refer Slide Time 49:13)



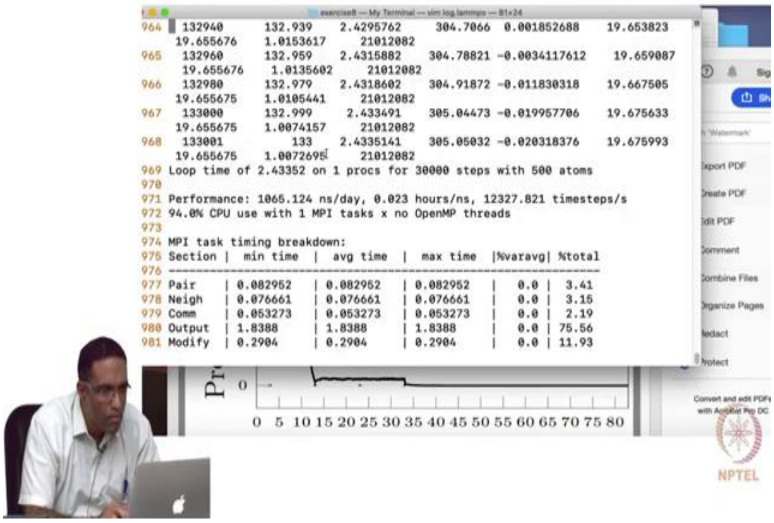
So that is the temperature, so temperature that it has reached.

(Refer Slide Time: 49:30)



And that is the pressure. So, now this is difficult to read, it looks like it is 0, because we started off at some insanely large value, it looks like it is 0.

(Refer Slide Time 50:08)



```
  132940      132.939   2.4295762    304.7066  0.001852688    19.653823
 19.655676    1.0153617     21012082
  132960      132.959   2.4315882   304.78821 -0.0034117612    19.659087
  19.655676    1.0135602     21012082
  132980      132.979   2.4318602   304.91872 -0.011830318    19.667505
 19.655675    1.0105441     21012082
  133000      132.999    2.433491   305.04473 -0.019957706    19.675633
 19.655675    1.0074157     21012082
  133001          133   2.4335141   305.05032 -0.020318376    19.675993
 19.655675    1.0072695     21012082
Loop time of 2.43352 on 1 procs for 30000 steps with 500 atoms

Performance: 1065.124 ns/day, 0.023 hours/ns, 12327.821 timesteps/s
94.0% CPU use with 1 MPI tasks x no OpenMP threads

MPI task timing breakdown:
Section |  min time  |  avg time  |  max time  |%varavg| %total
---------------------------------------------------------------
Pair    | 0.082952   | 0.082952   | 0.082952   |   0.0 |  3.41
Neigh   | 0.076661   | 0.076661   | 0.076661   |   0.0 |  3.15
Comm    | 0.053273   | 0.053273   | 0.053273   |   0.0 |  2.19
Output  | 1.8388     | 1.8388     | 1.8388     |   0.0 | 75.56
Modify  | 0.2904     | 0.2904     | 0.2904     |   0.0 | 11.93
```

If you now look at the log LAMMPS. What exercise we will be looking at? 1.00, so it has reached equilibrium at 1, this is at NVE, this is oscillating about 1 or so in the NVE ensemble. So the pressure has reached equilibrium, the temperature has also reached equilibrium. So we have our system, the argon gas at 1 atmosphere and at 300 Kelvin. Now you can go and check if P V is equal to N R T for the system and it will. So, multiply P and V here from the simulation and do N R T there and you will get your, it will satisfy the ideal gas law.