Two Phase Flow and Heat Transfer
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Lecture No: 16
Molecular Perspective of Two Phase Flow

Hello welcome to the sixteenth lecture of Two Phase Flow and Heat Transfer. Today we will be discussing about molecular dynamics.

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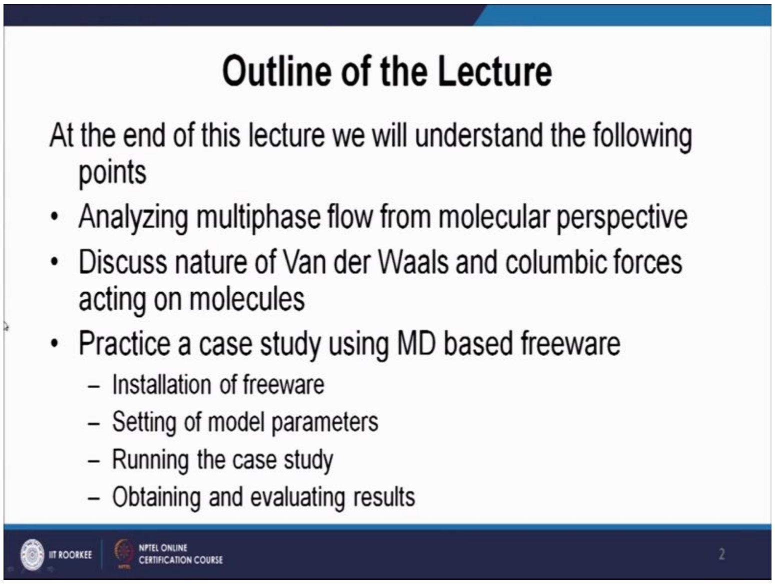

Outline of the Lecture

At the end of this lecture we will understand the following points

- Analyzing multiphase flow from molecular perspective
- Discuss nature of Van der Waals and columbic forces acting on molecules
- Practice a case study using MD based freeware
  - Installation of freeware
  - Setting of model parameters
  - Running the case study
  - Obtaining and evaluating results

So at the end of this lecture we will understand the following points. First we will be understanding multiphase flow from molecular perspective. We will discuss the nature of Van der Waals and columbic forces acting on the molecules. Then we will practice a case study based on molecular dynamics based freeware. There we will see how to install the freeware, how to set up the model parameters, how to run the case study and finally the analysis of the results also we will be showing you over here.

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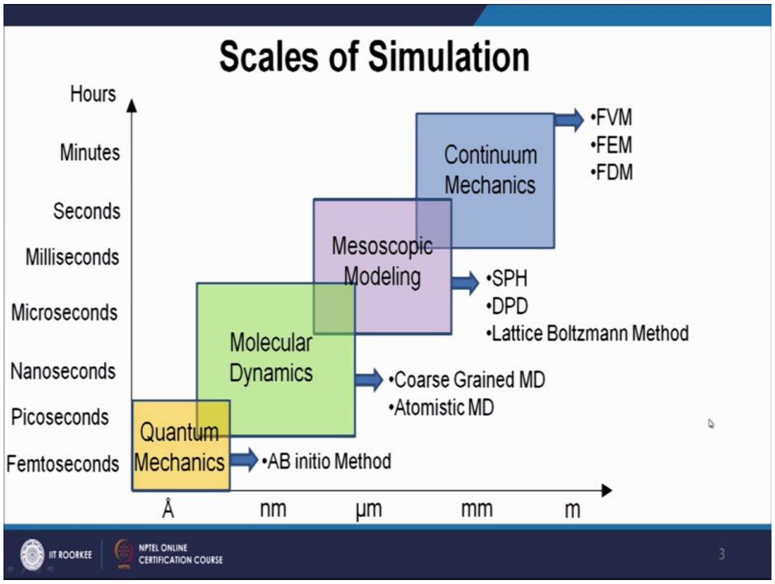

Scales of Simulation

- •FVM
- •FEM
- •FDM

- •SPH
- •DPD
- •Lattice Boltzmann Method

- •Coarse Grained MD
- •Atomistic MD

- •AB initio Method

To start with let us see where molecular dynamics lies in case of the scales of the problem okay. So here you see i have presented a pictorial view of the scale of the scale of the problem in the abscissa and here time in ordinate. So, you can find out a very fast and low scale or small scale phenomena is being understood by quantum mechanics. Whereas once you increase the length scale as well as increase the time scale, we can come to the molecular nature of the matter and then once you move upwards the extreme higher scale or engineering scale or extreme highest time or engineering time will be giving us the continuum mechanics what we see around okay.

So in between we are also having another concept which is called mesoscopic which bridges us the molecular nature to your continuum nature. There are different methodologies for continuum mechanics. These come under the periphery of your computational fluid dynamics but to name a few over here we are having finite volume, finite element and finite difference methodology. In previous few lecture I have shown you some mesoscopic technologies like Smoothed Particle Hydrodynamics and Lattice Boltzmann method like LBM. There are few more called DPD ,Dissipative Particle Dynamics also.

Now in this lecture we will be concentrating in this green block, where we will be understanding the molecular features of the matter okay. So what will be doing, we will be trying to find out the properties or behavior of the matter based on the atomistic calculations as well as coarse grain molecular nature okay. So these we will be finding out it is lying in the range of nanometers and the time level will be something around nanosecond to picosecond okay. So let us see for doing a molecular dynamics simulations what things are necessary. So here you see at the center I have shown you the molecular simulation model okay and then it is supported by 4 parts over here actually.

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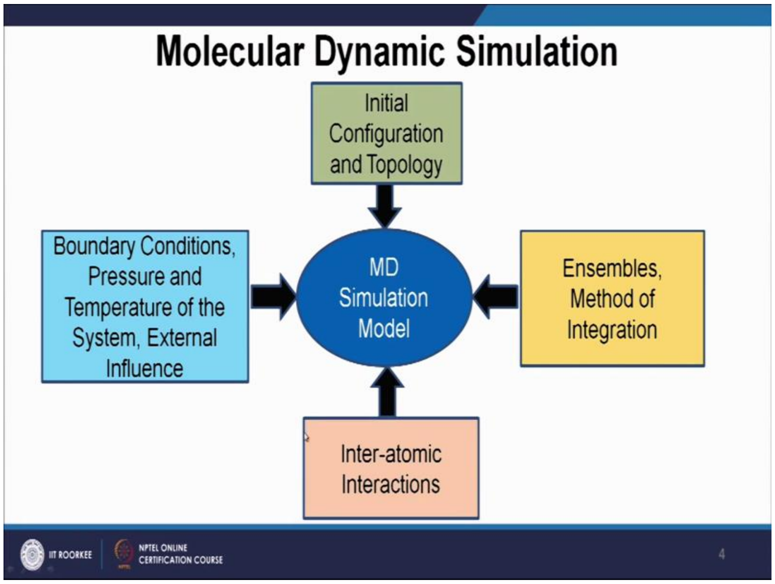

Molecular Dynamic Simulation

Initial Configuration and Topology

Boundary Conditions, Pressure and Temperature of the System, External Influence

MD Simulation Model

Ensembles, Method of Integration

Inter-atomic Interactions

To set up a molecular simulation you need to do all these 4 features. To begin with first you need to create the configuration and the topology. So configuration and topology means with what type of molecular structure we will be starting our simulation, the fluid molecules we need to construct or the surface structures we need to construct so those will be coming over here configuration and topology okay. Then we need to decide that what inter atomic interactions we are considering. So you know different molecules whenever they will be applying forces amongst themselves so there different inter atomic interactions okay.

Whether that is columbic interaction, whether there is potential Lennard Jones type of interactions so those things will be decided over here in this block where interactions will be actually finalized. Apart from that we have to also give some sort of ensembles, that means we need to decide that which quantity we are actually going to fix up ;whether it is number of the molecule, temperature of the molecule, pressure of the molecule so those will be decided in this ensembles. Also we need to decide in this point what will be the method of integration that means any computational fluid dynamics simulation we know that it advances with time right.

So, what will be the time advancement integrations that will be decided over here in this block. Apart from that problem to problem we know that boundary conditions pressure and temperature of the system and if you are having some external influence like you know magnetic field or electric field. So those things will be also needed also need to be given in the simulation okay. So, all these 4 blocks will come into pictures in case of a molecular simulation. So let us see that what type of inter atomic interaction you are having first. So if you if you think about know very common fluid like water.

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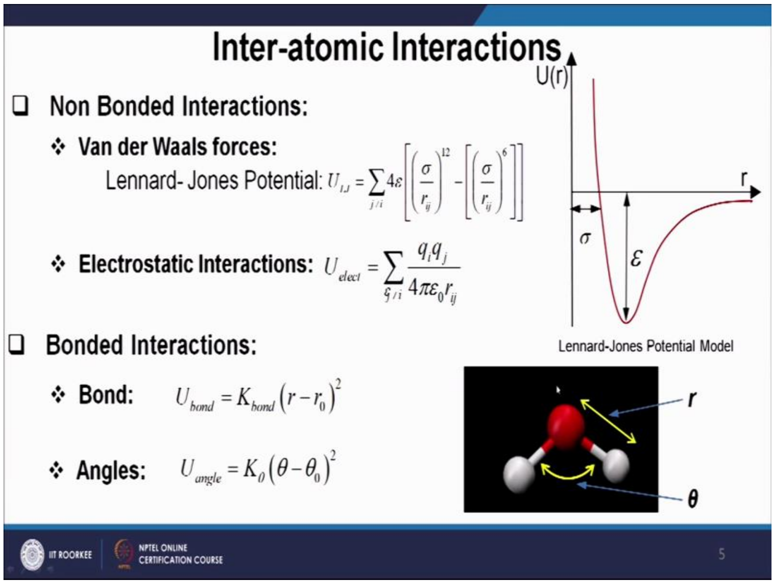

Inter-atomic Interactions

❑ **Non Bonded Interactions:**

- ❖ **Van der Waals forces:**
  Lennard- Jones Potential: $U_{I,J} = \sum_{j/i} 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$
- ❖ **Electrostatic Interactions:** $U_{elect} = \sum_{j/i} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$

❑ **Bonded Interactions:**

- ❖ **Bond:** $U_{bond} = K_{bond}\left(r - r_0\right)^2$
- ❖ **Angles:** $U_{angle} = K_\theta\left(\theta - \theta_0\right)^2$

So here I have shown you water, you see this red colored molecule, red colored atom is actually your oxygen and here we are having 2 hydrogen connected by the covalent bonds okay. Now, this water structure will be having fixed armed length for the OH bonds as well as fixed angle okay between 2 OH bonds okay. So this is a common nature of the water molecule. Now this water molecules will be doing multiple inter atomic interactions.

For examples, 1 water molecule if it is doing some sort of interaction with another water molecule. So those will be called as non bonded interaction because those water molecules are not connected via bond okay. So non bonded interactions we will be finding out between 2 water molecules or 2 dissimilar are 2 non-connected molecules okay. So there are various types of forces which will be applicable as you know non bonded interactions.

Few I have named over here. First 1 which will be applicable is called Van der Waals force, so between 2 molecules always will be having some sort of attraction or repulsion. That is guided by Lennard Jones potential okay. Lennard Jones potential comes out in this fashion, the potential u okay lj symbolizes Lennard Jones will be actually summation of j =! i that means j =! i means this will be not acting whenever we are considering interaction with the own molecule okay with the same molecule.

So j =! i means apart from this molecule, present molecule, all other molecules will be coming into consideration for this Lennard Jones potential. Then we are having over here a nature of you see, 4 into epsilon then sigma /r ij, where r ij is actually the mutual distance between the molecules to the power 12 minus sigma by r ij to the power 6 okay. If you try to plot this u verses this r ij, so uij verses r ij this will look like something in this fashion.

So you see at very small distance between the molecules of interest you will be finding out that the potential is very high. So that means whenever the molecules are coming very close to each other you will be finding out their facing very high negative repulsive force okay. And these goes to 0 almost 0 whenever they are very far away apart okay. So this type of Lennard Jones potential we apply as Van der Waals force.

Apart from that if the molecules are charged in nature. Then you will be finding out electro static interactions are also coming into place so that we use the columbic law of forces. So electro static potential will be something around summation of once again j =! to i qi qj /4 pi epsilon 0 r ij where epsilon 0 is the permittivity for the for the vacuum okay. And qi and qj are their respective charges stored in the molecules okay. r ij is their mutual distance.

Apart from that this non-bonded interaction, we can also have bonded interactions. I have already shown you that if you are having some covalent bonds in your molecular structure then you will be finding out that they are the supposed to keep some fixed length okay between the bonds and then between the atoms in the bonds and they will be keeping some angle between the bonds also.

Now it can be like this that due to some external force or field you will be finding out that these bonds are being stretched or angles between the bonds are actually being twisted. So there can be some torsional stress or there can be some stretching stress also. So depending on that you may find out that whatever nominal r and theta needs to be maintained that will not be maintained and some other values will be coming. So due to that there will be some sort of torsional potential and stretching potential. So the stretching potential can be written as u bond = k bond.

So this is some constant we keep for different molecules. So this we are having some chemical charts from where you can get these constant for the potential r - r0. Here r0 is that, what you can say equilibrium gap between the atoms in the bond okay square okay. Similarly for torsion we can write down u angle = k theta, theta - theta0 whole square. Here also theta0 is the nominal angle in case of equilibrium okay between the bonds okay.

And k theta is once again constant can be found out from chemical properties of the molecules okay. So, next let us see that apart from this, in the other block I have shown you that next we need to give the boundary conditions. So here let us discuss about different boundary conditions available in molecular dynamics. So first I will be showing you that we are having periodic boundary condition.

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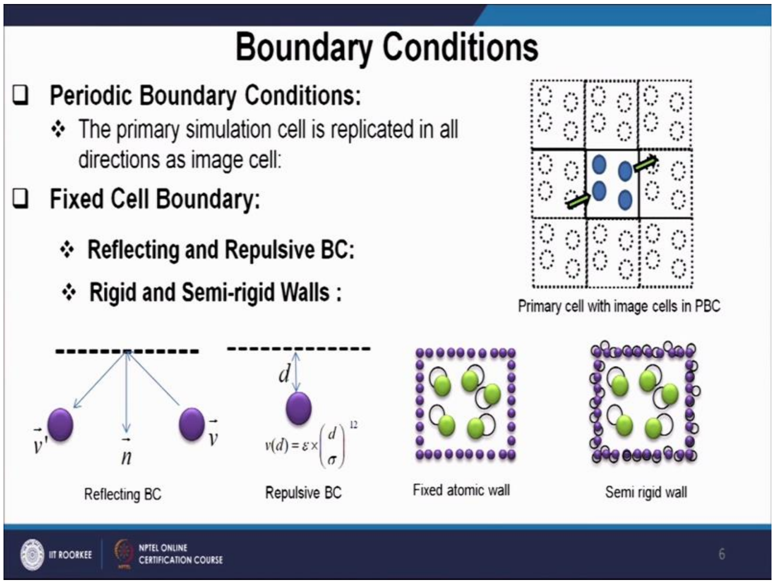

Boundary Conditions

- ❑ **Periodic Boundary Conditions:**
  - ❖ The primary simulation cell is replicated in all directions as image cell:
- ❑ **Fixed Cell Boundary:**
  - ❖ **Reflecting and Repulsive BC:**
  - ❖ **Rigid and Semi-rigid Walls :**

Primary cell with image cells in PBC

Reflecting BC

Repulsive BC

Fixed atomic wall

Semi rigid wall

So, usually molecular dynamics simulations are done for a very small domain because number of molecules will be high for simulation of 1 engineering problem. So what we do, we squeeze the domain and considered that the domain is being repeated elsewhere. So we need to keep a periodic boundary condition for this kind of simulation. Now what does this periodic boundary condition means?

Let say here we are having a cell which we are considering for our simulation. So what will be doing over here let say 1 molecule is entering over here through this boundary. So that molecule whenever it will be entering at the same time another molecule will be also going out from the opposite boundary. So it is like this, from 1 boundary someone will be entering, from the opposite boundary same amount of mass of the molecules will be going out with equal velocity okay.

So this kind of things we call as periodic boundary condition and this kind of boundary condition we apply very frequently for molecular dynamics. Apart from that we also give some boundary conditions like fixed cell boundary. Now, fixed cell boundaries can be of multiple types. So based on the amount of reflection we divided it by 2 types, reflective and repulsive boundary condition. So here I have given you example of reflective and repulsive boundary condition here you see.

Reflective means it will be obeying all the laws of optical reflection okay. So angle of incidence will be equals to angle of reflection all these things it will be obeying. In case of repulsive, we will be finding out that it is getting some force okay from the wall. Whenever it is getting near to the wall, it will be getting some force okay. So that it will not be you know, colliding with a wall. So let us say here we are having the wall depending on the distance between the wall and the molecule, you will be finding out it is getting some potential okay.

So less the distance then you will be finding out the potential is increasing okay. Apart from that depending on the rigidity of the wall this fixed cell boundary can be divided into 2 types, rigid and semi rigid walls. So here I have given 1 schematic of rigid and semi rigid. So here you see all these violet colored dots are actually wall molecules and you can find out that due to motion of the inner molecules, none of the wall molecules are changing their position. So this is an example of rigid wall. On the other hand, over here you see due to the motion of the inner molecules the wall molecules are changing their shapes.

So this violet colored dots are the initial conditions of the wall molecules and the circular corresponding positions are actually the final positions of the wall molecules. So you can see wall molecules are actually moving okay due to the interaction of the inner molecules. So this is one example of some sort of semi rigid wall okay. Though it will not allow the inner molecules to go outside through this wall boundary but the wall boundary can, you know deflect depending on the potential of the inner molecules okay.
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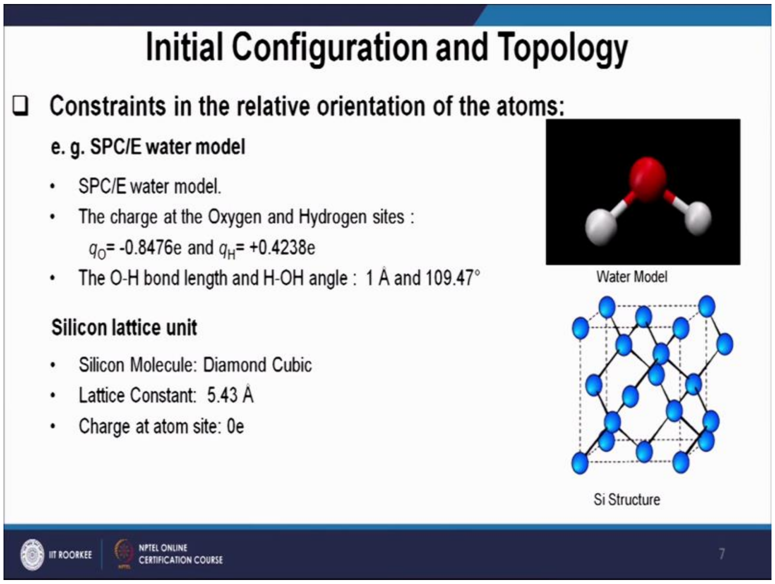

Initial Configuration and Topology

☐ **Constraints in the relative orientation of the atoms:**

e. g. SPC/E water model

- SPC/E water model.
- The charge at the Oxygen and Hydrogen sites : q_O= -0.8476e and q_H= +0.4238e
- The O-H bond length and H-OH angle : 1 Å and 109.47°

Silicon lattice unit

- Silicon Molecule: Diamond Cubic
- Lattice Constant: 5.43 Å
- Charge at atom site: 0e

After discussing these boundary conditions, let us see the initial configuration and the topology which is also very important for molecular dynamics. As I have mentioned, so for deciding the topology at the beginning we need to give whatever potentials and distances necessary for the molecules. So here I have shown you a water molecule and silicon molecule okay. For example, because majority of the electronic applications in 2 phase flow we place water droplet on silicon and do little bit of micro fluidic applications. So here I have shown you, we basically use for water spc/ e model okay.

Because many times we find out for micro fluidic application electric field is very, very important. So in those cases spc/ e, e symbolizes electric field actually works well. So let me tell you what are the characteristics of this spc/ e water model? So what we do in case of spc /e water model, we give the charge to the oxygen and hydrogen molecules. So you see we give oxygen -0.8476 of multiplied by electron charge and then in case of hydrogen we give + 0.4238 multiplied by the electron charge. So you see this qH is exactly half of the q in magnitude and opposing signs.

So this remains this mixed water as a whole neutral and you know all the charges will be balanced. Next what will be the bond length that means r0 and what will be the bond angle between H-oH that means the theta0 those values we said as 1 Angstrom as r0 and 109.47 degree for theta 0. Similarly for silicon molecule what we do, we consider a diamond cubic structure and we decide the lattice constant will be 5.43 Angstrom. So between 2 silicon molecules we are having distance of 5.43 Angstrom okay and usually for this type of application we considered the silicon is having no charge okay. So we give silicon atom charge is 0*e okay.

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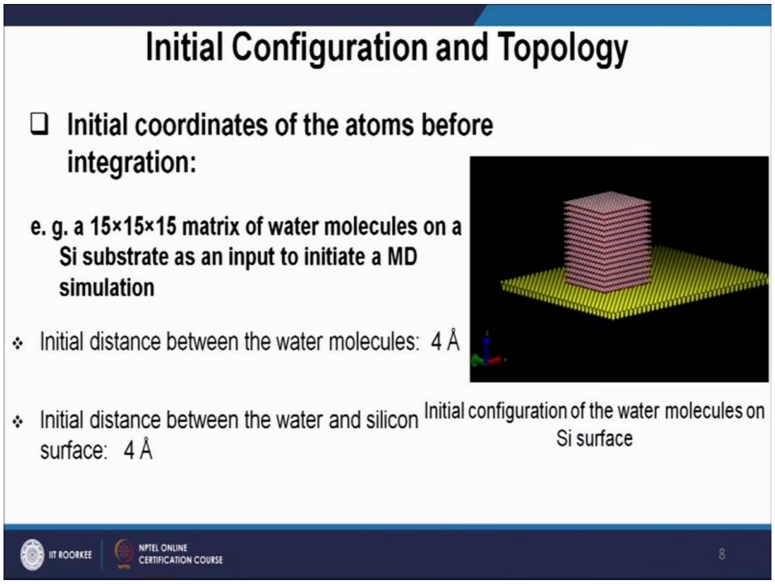

Initial Configuration and Topology

- ☐ **Initial coordinates of the atoms before integration:**

e. g. a 15×15×15 matrix of water molecules on a Si substrate as an input to initiate a MD simulation

- ❖ Initial distance between the water molecules: 4 Å
- ❖ Initial distance between the water and silicon surface: 4 Å

Initial configuration of the water molecules on Si surface

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Next let us see that how we can place the initial configuration for simulation. Here I have shown you that we place this yellow colored molecules are actually your diamond cubic structure of your silicon molecules okay. And over that we have created 1 water box. So you can find out the red colored things over here whatever you find out those are actually your oxygen and white colored atoms are actually hydrogen okay.

So what we do initially for a setting up a simulation. Here I have given you 1 example of a water box over a silicon substrate. So I have taken 15 x 15 x 15 matrix of the water molecules as a box over the silicon substrate okay. And then initial distance between the water molecules we have kept as 4 Angstrom. Remember, this is not the bond length or r0 this is actually between 2 water molecules we have kept 4 Angstrom okay.

And initial distance between the water and silicon surface is also kept as 4 Angstrom. So here this will be the figure for the initial placement okay. Next let us see what different ensembles and integration methodology we follow. There are various ensembling methodologies amongst of which I have named here 3.

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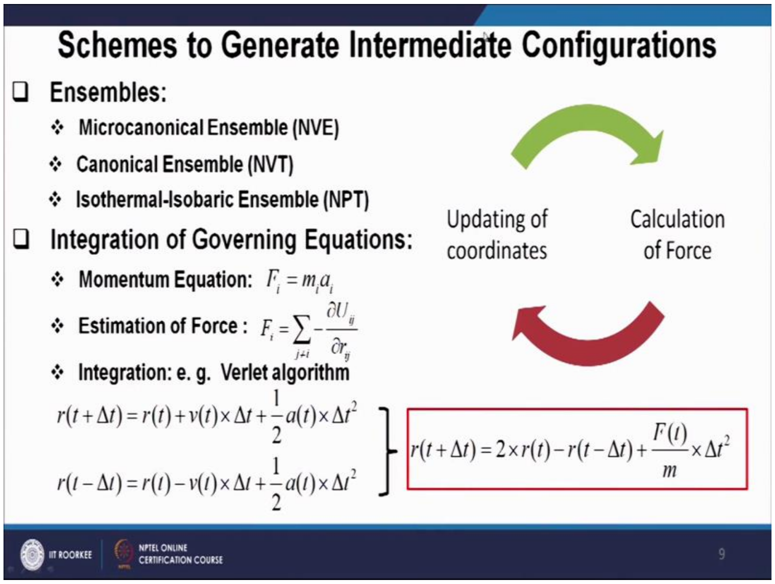

Schemes to Generate Intermediate Configurations

☐ **Ensembles:**

- Microcanonical Ensemble (NVE)
- Canonical Ensemble (NVT)
- Isothermal-Isobaric Ensemble (NPT)

☐ **Integration of Governing Equations:**

- Momentum Equation: $F_i = m_i a_i$
- Estimation of Force : $F_i = \sum_{j \neq i} -\frac{\partial U_{ij}}{\partial r_{ij}}$
- Integration: e. g. Verlet algorithm

$$\left.\begin{aligned} r(t+\Delta t) &= r(t) + v(t)\times\Delta t + \frac{1}{2}a(t)\times\Delta t^2 \\ r(t-\Delta t) &= r(t) - v(t)\times\Delta t + \frac{1}{2}a(t)\times\Delta t^2 \end{aligned}\right\} \boxed{r(t+\Delta t) = 2\times r(t) - r(t-\Delta t) + \frac{F(t)}{m}\times\Delta t^2}$$

The first 1 is micro canonical ensemble. In this micro canonical ensemble the number volume and energy of the molecules will be being conserved okay. Similarly we are having approach like canonical ensemble where number volume and temperature, not energy is being conserved. We are having isothermal isobaric ensemble also,here we will be keeping number, pressure and temperature constant okay.

So you can choose any of the ensembles. Next if you see the governing equations, so we know that for particulate nature or molecular nature it will be always boiling down to Newton's second law. If we write down Newton's second law for molecular structure i, molecule number i. So it will be Fi, the force acting on the molecule is actually mass of the molecule multiplied by the acceleration of the molecule okay. So from the potentials we can calculate what is the force acting on that in this fashion.

So Fi will be summation of all the potential addition of all the potentials non-bonded and bonded potentials. del /del r of that potential you can give as force okay. Now once we get the force we can find out what is the acceleration okay. And using that acceleration we can find out the next position of the molecule, so that we do using Verlet algorithm.

So Verlet algorithm already I have described to you but let me give you 1 quick outlook over here. So r (t + delta t) we can find out based on r (t) v (t) and a (t) okay. So in this fashion, so r (t) + v (t) *delta t. v (t) is nothing but the velocity of the molecular time t half of a(t) which is acceleration of the molecule at time t multiplied by delta t square.

In a similar fashion r (t) - delta t that means the previous time step, the history time step = r (t) – v (t) + multiplied by delta t + half of a (t) *del t square. These are coming from you know, your Taylor series expansion once again. Now if you add this 2 then you will be getting r (t +delta t) = 2* r (t) – r (t - delta t) + F(t) / m*delta t square.

Here intentionally what we have done, we have eliminated v (t). Because v (t) nowhere we are calculating. We are always finding out F(t). So a(t) has been actually replaced by F(t) / m okay. So once we know the F then quickly using this 1 and the previous knowledge of the positions of the molecule. We can find out the next position of the molecule.

Next let us see, what are the different free wares available for doing simulation of a molecular dynamics? There are few well established free wares like you know, LAMMPS, GROMACS, NAMD, MDYNAMIX okay. But today I will be giving you an overview of LAMMPS simulation okay.
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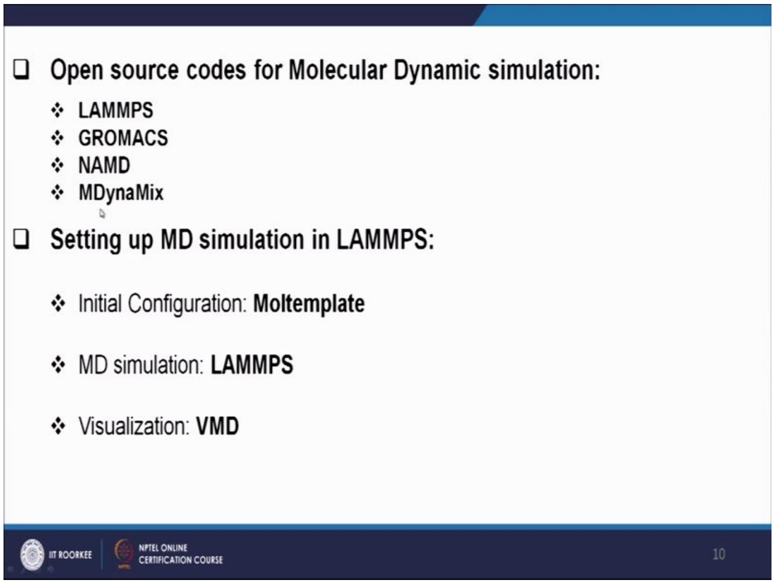

- ☐ **Open source codes for Molecular Dynamic simulation:**
  - **LAMMPS**
  - **GROMACS**
  - **NAMD**
  - **MDynaMix**
- ☐ **Setting up MD simulation in LAMMPS:**
  - Initial Configuration: **Moltemplate**
  - MD simulation: **LAMMPS**
  - Visualization: **VMD**

So this is very robust software for molecular dynamics simulations. So let us see how LAMMPS works. Now, to setup a molecular dynamics simulation in LAMMPS, we need to consider actually 3 different segments. So first for fixing of the topology and initial configurations of the molecule, we need to go for a software called Moltemplate then the whole molecular dynamics simulations is being done in LAMMPS and finally for the visualization, you can take any external software.

Here I will be showing you the software called VMD okay. First let me show you how to install LAMMPS because this is very, very important.

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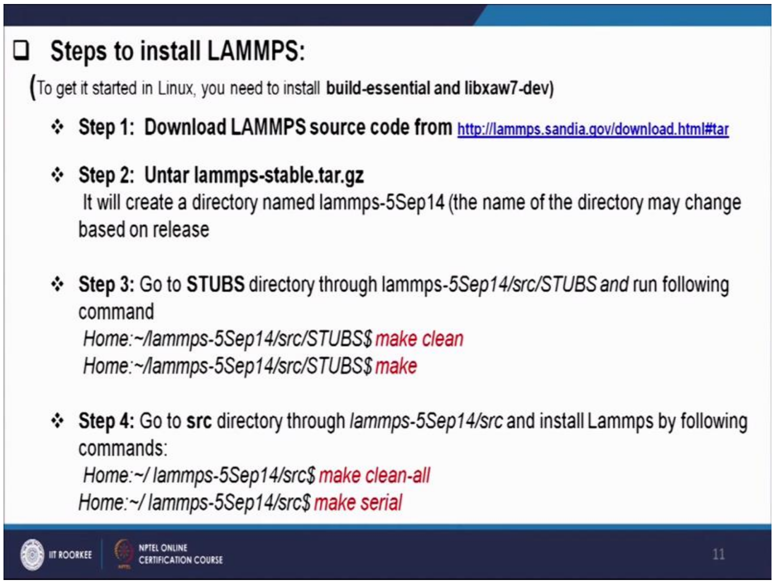

☐ **Steps to install LAMMPS:**

(To get it started in Linux, you need to install **build-essential and libxaw7-dev)**

- **Step 1: Download LAMMPS source code from** http://lammps.sandia.gov/download.html#tar
- **Step 2: Untar lammps-stable.tar.gz**
  It will create a directory named lammps-5Sep14 (the name of the directory may change based on release
- **Step 3:** Go to **STUBS** directory through lammps-*5Sep14/src/STUBS and* run following command
  Home:~/lammps-5Sep14/src/STUBS$ make clean
  Home:~/lammps-5Sep14/src/STUBS$ make
- **Step 4:** Go to **src** directory through *lammps-5Sep14/src* and install Lammps by following commands:
  Home:~/ lammps-5Sep14/src$ make clean-all
  Home:~/ lammps-5Sep14/src$ make serial

So first, what we need to do, you need to find out or you need to download the LAMMPS source code from the LAMMPS website that has been developed by Sandia national lab okay. So you can download it. As it is freeware, from there before that you need to resolve some dependency. So dependencies I have written over here. So those things you can resolve. After that it will be downloading as some tar.gz files.

So you need to untar that one. So already I have shown you in the previous few lectures that how to untar a file, zipped file. So you can untar that one. So once you untar, it will be creating a directory like LAMMPS then hyphen and the date will be coming. So one example of the date structure I have shown you over here 5Sep14. So it can be changing depending on the date of download. Next we need to go to STUBS directory of this LAMMPS folder.

Whatever you have downloaded the destination is like this LAMMPS folder then go to src then in between that will be getting a STUBS directory. So once you go to STUBS directory by you know, using cd, whatever I have told you earlier in a Linux platform. Then what you need to do, you need to do first give the command as make clean and then make okay.

So it will be making your code okay ready for use. Then we need to install the software by going to the src directory. So src directory is once again if you go 1 level up from the STUBS directory, you can reach to src directory and then there you type this command make clean all and then make serial now, make serial will be enabling you to run the codes in serial okay. Here I have discussed the installation of the other software like VMD.

So VMD once again you can download from some website. The website ID I have given over here. This is freeware, so first once again you have to unzip this one because all the software will be actually in the zipped format to minimize the space then you need to configure the source file.
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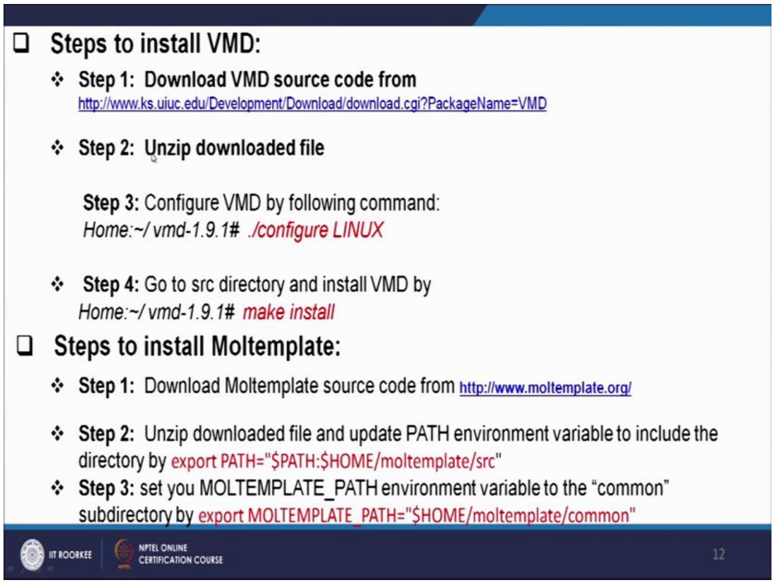

☐ **Steps to install VMD:**

- **Step 1: Download VMD source code from** http://www.ks.uiuc.edu/Development/Download/download.cgi?PackageName=VMD
- **Step 2: Unzip downloaded file**

  Step 3: Configure VMD by following command:
  Home:~/ vmd-1.9.1# ./configure LINUX
- **Step 4:** Go to src directory and install VMD by
  Home:~/ vmd-1.9.1# make install

☐ **Steps to install Moltemplate:**

- **Step 1:** Download Moltemplate source code from http://www.moltemplate.org/
- **Step 2:** Unzip downloaded file and update PATH environment variable to include the directory by export PATH="$PATH:$HOME/moltemplate/src"
- **Step 3:** set you MOLTEMPLATE_PATH environment variable to the "common" subdirectory by export MOLTEMPLATE_PATH="$HOME/moltemplate/common"

So configuring this one we need to give for configuring this one, we need to give the command like this .#configure Linux then you have to install by giving the command make install okay. So VMD will be installed. Similarly Moltemplate for the initial topology and configuration you have to download the Moltemplate from this website, www.Moltemplate.org then unzip it okay and set the path of the environmental variable and you have to include this path using in your environmental variable export path = $path : $Home then home Moltemplate/src okay.

At the end you said the Moltemplate environmental variable also to the common subdirectory by export Moltemplate path home/moltemplate/common okay. Next let me go to the simulation methodology. So first what will be doing over here, I will be showing you that we have done in Moltemplate. So this is the Moltemplate file. Over here main points I have highlighted. You see over here, we have shown the oxygen, hydrogen and hydrogen h1 and h2 are the 2 hydrogen atoms. So, first values are their charge 0.08476, .4238, .4238. And then next 3 positions are their locations x, y and z coordinates okay.

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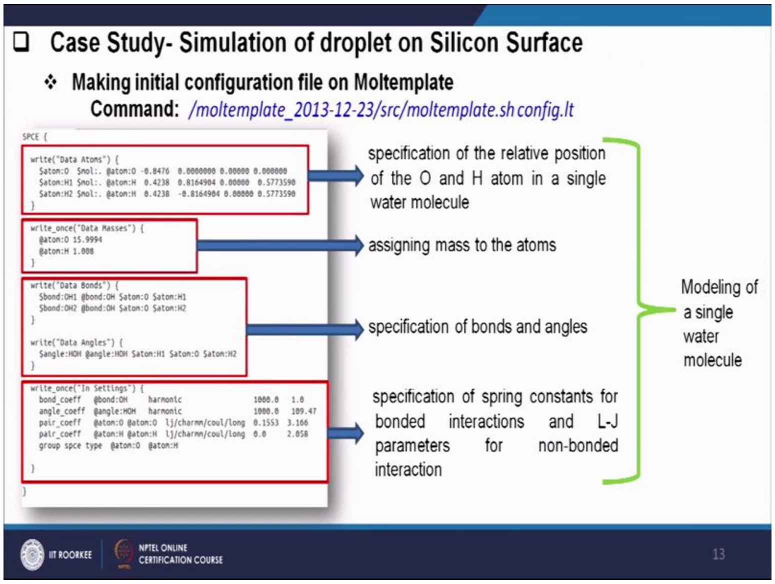

- Case Study- Simulation of droplet on Silicon Surface
  - Making initial configuration file on Moltemplate

Command: */moltemplate_2013-12-23/src/moltemplate.sh config.lt*

```
SPCE {
  write("Data Atoms") {
    $atom:O  $mol:. @atom:O -0.8476  0.0000000 0.00000 0.000000
    $atom:H1 $mol:. @atom:H  0.4238  0.8164904 0.00000  0.5773590
    $atom:H2 $mol:. @atom:H  0.4238  -0.8164904 0.00000 0.5773590
  }
  write_once("Data Masses") {
    @atom:O 15.9994
    @atom:H 1.008
  }
  write("Data Bonds") {
    $bond:OH1 @bond:OH $atom:O $atom:H1
    $bond:OH2 @bond:OH $atom:O $atom:H2
  }

  write("Data Angles") {
    $angle:HOH @angle:HOH $atom:H1 $atom:O $atom:H2
  }
  write_once("In Settings") {
    bond_coeff   @bond:OH     harmonic                    1000.0   1.0
    angle_coeff  @angle:HOH   harmonic                    1000.0   109.47
    pair_coeff   @atom:O @atom:O  lj/charmm/coul/long  0.1553  3.166
    pair_coeff   @atom:H @atom:H  lj/charmm/coul/long  0.0     2.058
    group spce type  @atom:O  @atom:H


  }
}
```

specification of the relative position of the O and H atom in a single water molecule

assigning mass to the atoms

specification of bonds and angles

specification of spring constants for bonded interactions and L-J parameters for non-bonded interaction

Modeling of a single water molecule

So depending on the angular location 109.9 degree and their angular location 1 Angstrom, angular length 1 Angstrom this coordinates will be calculated okay. Then we have given the mass of the hydrogen and oxygen also. So for oxygen we have given 15.9994 and for hydrogen we have given 1.008. We have also selected, what will be the bonds and angles. So bonds are selected between OH1 and OH2 and the angle has been selected between OH1 and OH2 okay.

So that angle will be theta0 okay. Then we have specified that what will be the spring constants dependent on the l j potential. So here for OH we have consider that k r will be actually 1000 and r0 will be 1 and for the bond angle, the angle will be 109.47 and k theta we have selected as 1000 once again okay. Now for O and H the Lennard Jones potential that means sigma and epsilon are selected like this okay. In the next one, I have shown you for silicon.

So once again you, that silicon is having a structure like this. So you can always calculated by knowing the coordinate position of the silicon. So here I have given the coordinate position by the way for charge we have given all 0 of first column,you can see all are having 0 and their corresponding locations after that we have given.

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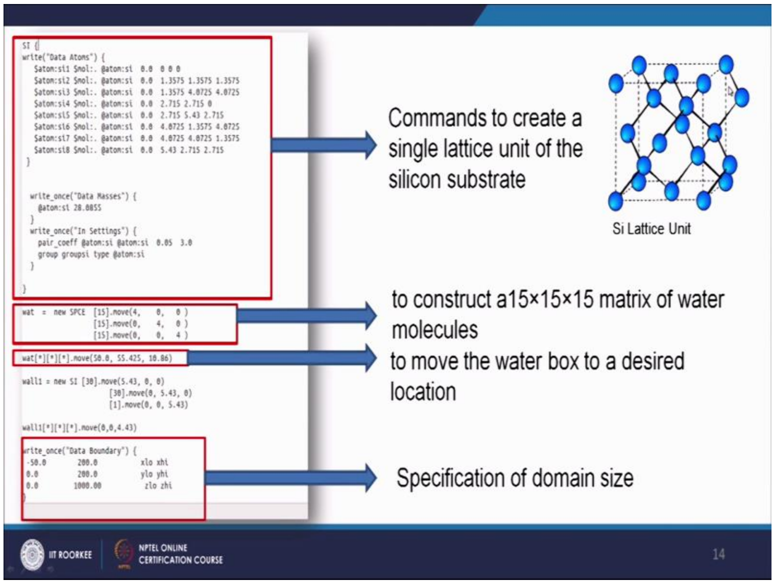

```
SI {
write("Data Atoms") {
   $atom:si1 $mol:. @atom:si  0.0  0 0 0
   $atom:si2 $mol:. @atom:si  0.0  1.3575 1.3575 1.3575
   $atom:si3 $mol:. @atom:si  0.0  1.3575 4.0725 4.0725
   $atom:si4 $mol:. @atom:si  0.0  2.715 2.715 0
   $atom:si5 $mol:. @atom:si  0.0  2.715 5.43 2.715
   $atom:si6 $mol:. @atom:si  0.0  4.0725 1.3575 4.0725
   $atom:si7 $mol:. @atom:si  0.0  4.0725 4.0725 1.3575
   $atom:si8 $mol:. @atom:si  0.0  5.43 2.715 2.715
 }


  write_once("Data Masses") {
    @atom:si 28.0855
  }
  write_once("In Settings") {
    pair_coeff @atom:si @atom:si  0.05  3.0
    group groupsi type @atom:si
  }

}
wat  =  new SPCE  [15].move(4,    0,   0 )
                  [15].move(0,    4,   0 )
                  [15].move(0,    0,   4 )
wat[*][*][*].move(50.0, 55.425, 10.86)

wall1 = new SI [30].move(5.43, 0, 0)
                     [30].move(0, 5.43, 0)
                     [1].move(0, 0, 5.43)

wall1[*][*][*].move(0,0,4.43)

write_once("Data Boundary") {
 -50.0       200.0          xlo xhi
 0.0         200.0          ylo yhi
 0.0        1000.00          zlo zhi
}
```

Commands to create a single lattice unit of the silicon substrate

Si Lattice Unit

to construct a15×15×15 matrix of water molecules

to move the water box to a desired location

Specification of domain size

Here the silicon atomic mass we have given as 28.0855 and we have also setup that what will be the Lennard Jones potential over here for the silicon 0.05 and 3.0 okay then we have created a box of having 15 water molecules. So, 15 x 15 x 15 in each direction in this fashion. So 15 and then we have given the initial position as 4, 0, 0 in x direction and then in y direction also 15 molecules. So 0, 4, 4 and z direction 0, 0, 4. So it is 15x 15 x 15 box.

Then we have moved the water box on desired position to place it over the silicon substrate by some location. So these are optional. So you can give any value over there and then we have said the domain size. You can see the domain size is starting from -50 to 200 for the x direction, 0 to 200 for the y direction and for the z direction because the z direction will be very high we have to see the droplet dynamic. So it will be 0 to 1000 okay.

Next let us see the simulation of the LAMMPS file. So this is your LAMMPS file. Previous 1 was Moltemplate file. Here important thing is that what we are doing; we are setting up all those parameters over here. First we are specifying the unit okay, unit is real unit.

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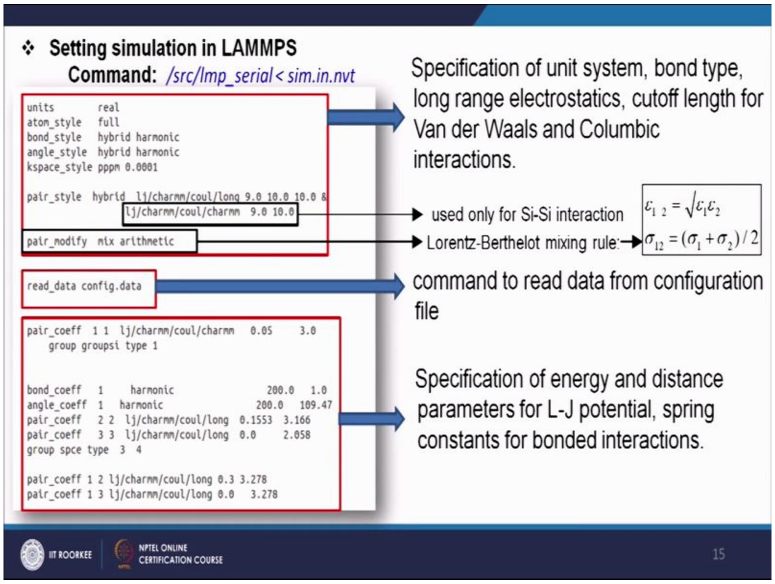

❖ **Setting simulation in LAMMPS**

Command: */src/lmp_serial< sim.in.nvt*

```
units         real
atom_style    full
bond_style    hybrid harmonic
angle_style   hybrid harmonic
kspace_style pppm 0.0001

pair_style  hybrid  lj/charmm/coul/long 9.0 10.0 10.0 &
                    lj/charmm/coul/charmm  9.0 10.0

pair_modify  mix arithmetic
```

Specification of unit system, bond type, long range electrostatics, cutoff length for Van der Waals and Columbic interactions.

used only for Si-Si interaction $\varepsilon_{1\,2} = \sqrt{\varepsilon_1 \varepsilon_2}$

Lorentz-Berthelot mixing rule: $\sigma_{12} = (\sigma_1 + \sigma_2)/2$

```
read_data config.data
```

command to read data from configuration file

```
pair_coeff  1 1  lj/charmm/coul/charmm   0.05     3.0
   group groupsi type 1


bond_coeff   1     harmonic                  200.0   1.0
angle_coeff  1   harmonic                  200.0   109.47
pair_coeff   2 2  lj/charmm/coul/long  0.1553  3.166
pair_coeff   3 3  lj/charmm/coul/long  0.0     2.058
group spce type  3  4

pair_coeff 1 2 lj/charmm/coul/long 0.3 3.278
pair_coeff 1 3 lj/charmm/coul/long 0.0   3.278
```

Specification of energy and distance parameters for L-J potential, spring constants for bonded interactions.

Then bond type, bond type is actually hybrid harmonic bond type and angle will be decided by hybrid harmonic. We are also giving the Van der Waals and columbic interactions and cutoff potentials over here like this. So you see for any particles will be having your lj potential will be having the lower maximum point and higher maximum point as 9 and 10 and for columbic potential we will be having only 10.

Now for only silicon will be having you know, there will no columbic interactions, you will be having only lj potential. So these will be 9 and 10. Now using mix arithmetic, we are defining the lj potential for this similar material. We used this type of formulation for epsilon and sigma. So if you are having 2 dissimilar materials, having epsilon and sigma.

So epsilon 1 2 can be calculated as geometric mean and sigma 1 2 can be calculated as arithmetic mean okay. So these are given by Lorentz Berthelot mixing rule. So this by adding this line will be mix arithmetic you can activate this rules okay. Then we will be reading the config data, which has been generated by Moltemplate using this one using this line and finally will be setting the lj potential.

So though we have given lj potential in Moltemplate file, if we want to change in LAMMPS file that we can do over here, you see here we have changed for k we have krn k theta. Earlier we have chosen 1000 here we have given 200 and 200. Similarly for different types of atoms hydrogen and oxygen and silicon; here we have given 1 as your hydrogen molecule atom, 2 as your oxygen, and 3 as silicon one. So you see here, we have given all the potentials. Potentials mean epsilon and theta values over here okay. For different molecule atom 2 atom interactions okay.

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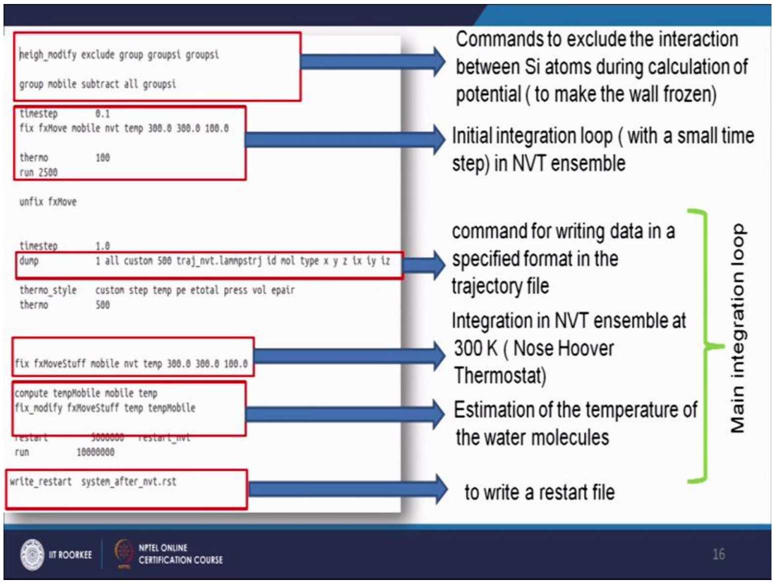


```
heigh_modify exclude group groupsi groupsi

group mobile subtract all groupsi

timestep        0.1
fix fxMove mobile nvt temp 300.0 300.0 100.0

thermo          100
run 2500

unfix fxMove


timestep        1.0
dump            1 all custom 500 traj_nvt.lammpstrj id mol type x y z ix iy iz

thermo_style    custom step temp pe etotal press vol epair
thermo          500


fix fxMoveStuff mobile nvt temp 300.0 300.0 100.0

compute tempMobile mobile temp
fix_modify fxMoveStuff temp tempMobile

restart         5000000   restart_nvt
run         10000000

write_restart  system_after_nvt.rst
```

Commands to exclude the interaction between Si atoms during calculation of potential (to make the wall frozen)

Initial integration loop (with a small time step) in NVT ensemble

command for writing data in a specified format in the trajectory file

Integration in NVT ensemble at 300 K (Nose Hoover Thermostat)

Estimation of the temperature of the water molecules

to write a restart file

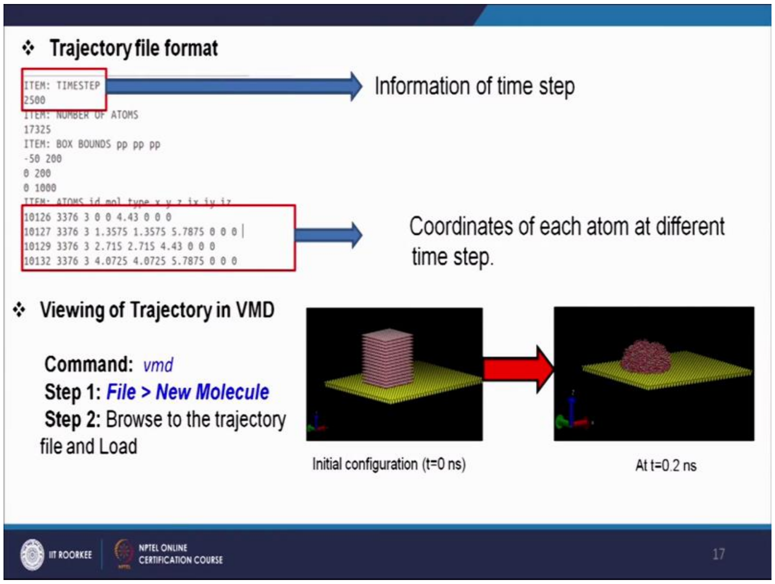
Main integration loop

Next, here what we have done, we have created a domain. So domain is something like this you see we have created a domain called si groups, silicon group and we have excluded this silicon group from the whole groups. So we are not considering the movement of the silicon over here okay. And then we have given the instruction for running the simulation. So time step is created as 0.1.

And here if temperature increases due to interaction so for correction we are using thermo after every time 100 times. How thermo will be working, that we have given over here using fix move stuff mobile nvt. So this is our n symbol actually what we need to take. So this will be keeping the temperature fix at 300 at a step of 100 Kelvin’s. So 300 kelvin temperature will be always kept fixed. You can dump the results in some outside files.

So that you can see later on using VMD and you know it will be running out for this much time step okay. And it will be writing a restart file you are having something problem in between. Next whatever file you will be writing after the simulation, so you will be actually reading that using VMD. So this is a typical example of VMD file. So at the beginning, you will be finding out what is the time step and then you will be having a long data over here I have shown a shorten one.

(Refer Slide Time: 30:46)



❖ **Trajectory file format**

```
ITEM: TIMESTEP
2500
ITEM: NUMBER OF ATOMS
17325
ITEM: BOX BOUNDS pp pp pp
-50 200
0 200
0 1000
ITEM: ATOMS id mol type x y z ix iy iz
10126 3376 3 0 0 4.43 0 0 0
10127 3376 3 1.3575 1.3575 5.7875 0 0 0
10129 3376 3 2.715 2.715 4.43 0 0 0
10132 3376 3 4.0725 4.0725 5.7875 0 0 0
```

Information of time step

Coordinates of each atom at different time step.

❖ **Viewing of Trajectory in VMD**

Command: *vmd*

Step 1: ***File > New Molecule***

Step 2: Browse to the trajectory file and Load

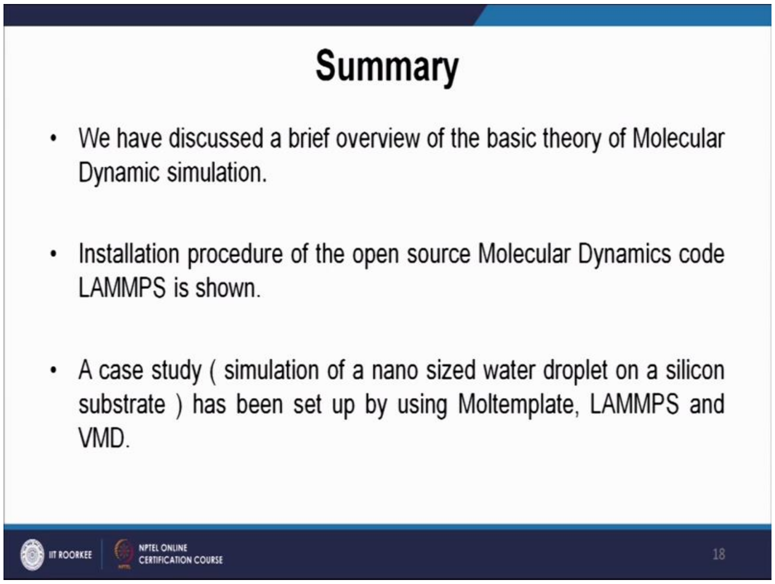
Initial configuration (t=0 ns)

At t=0.2 ns

So here you will be finding out the item number then atom type and then you will be finding out the molecular mass type x, y, z that means x coordinate, y coordinate and z coordinate and ix, iy and iz. So those are actually indices for x, y and z. So here I have shown you 1 typical example. So we have started with a water box and you can find out at the end of solution, you will be getting a water droplet placed over the silicon.

This is after 0.2 nano second okay. So in this way you can setup 1 simulation in LAMMPS and you can obtain the result okay. Let us summarize.

(Refer Slide Time: 31:34)

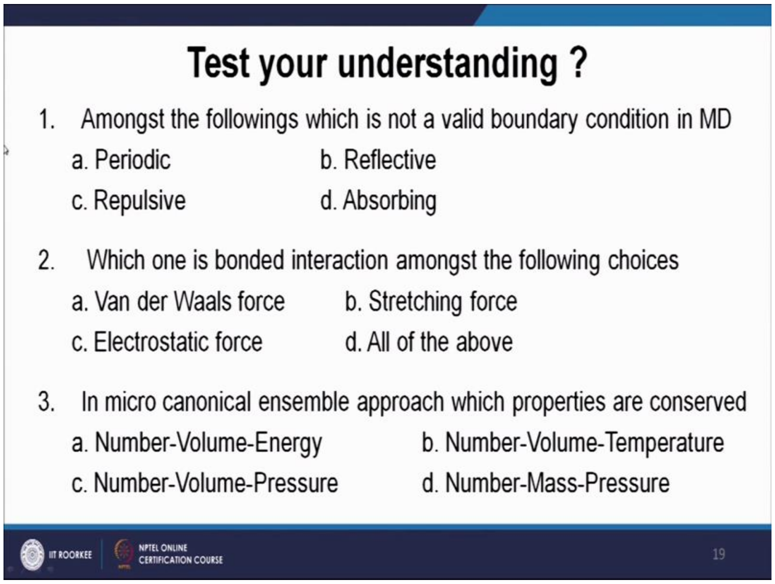


Summary

- We have discussed a brief overview of the basic theory of Molecular Dynamic simulation.
- Installation procedure of the open source Molecular Dynamics code LAMMPS is shown.
- A case study (simulation of a nano sized water droplet on a silicon substrate) has been set up by using Moltemplate, LAMMPS and VMD.

So we have discussed briefly, what is the basic theory of molecular dynamics. Installation procedure for molecular dynamics code LAMMPS we have shown. And setting up the simulation also we have shown in this way. We have actually done a case study of simulation of nano sized water droplet over a silicon substrate. We have used Moltemplate, LAMMPS and VMD to setup the simulation, perform the simulation and see the results . Let us test your understanding at the end of this lecture. So as usual you are having 3 questions.

(Refer Slide Time: 32:06)



Test your understanding ?

1. Amongst the followings which is not a valid boundary condition in MD
   a. Periodic b. Reflective
   c. Repulsive d. Absorbing
2. Which one is bonded interaction amongst the following choices
   a. Van der Waals force b. Stretching force
   c. Electrostatic force d. All of the above
3. In micro canonical ensemble approach which properties are conserved
   a. Number-Volume-Energy b. Number-Volume-Temperature
   c. Number-Volume-Pressure d. Number-Mass-Pressure

So first 1, amongst the following which is not a valid boundary condition in MD? We have discussed elaborately about the boundary conditions. So conditions are, first periodic, second reflective, third repulsive, and fourth absorbing okay. So most of the names you have heard, so you have to find out the odd one. So correct answer is absorbing there is nothing called absorbing boundary molecular dynamics.

Next question, which 1 is bonded interaction amongst the following choices. So we are having 4 choices, Van der Waals force, stretching force, electrostatic force, all of the above okay. Which 1 is bonded interaction okay? So bonded interaction obviously is stretching force okay. Which is nothing but k r *r-r0 whole square okay.

Then in micro canonical ensemble approach which properties are conserved. So micro canonical ensemble approach, so that means it is nothing but nve. So we are having 3 options number-volume energy, number-volume temperature, number-volume pressure and number-mass-pressure okay. So as it is nve, so number volume energy is the correct answer. So with this I will be ending this lecture, thank you.