Functional of Computational Materials Modelling
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LAMMPS Exercises - 3

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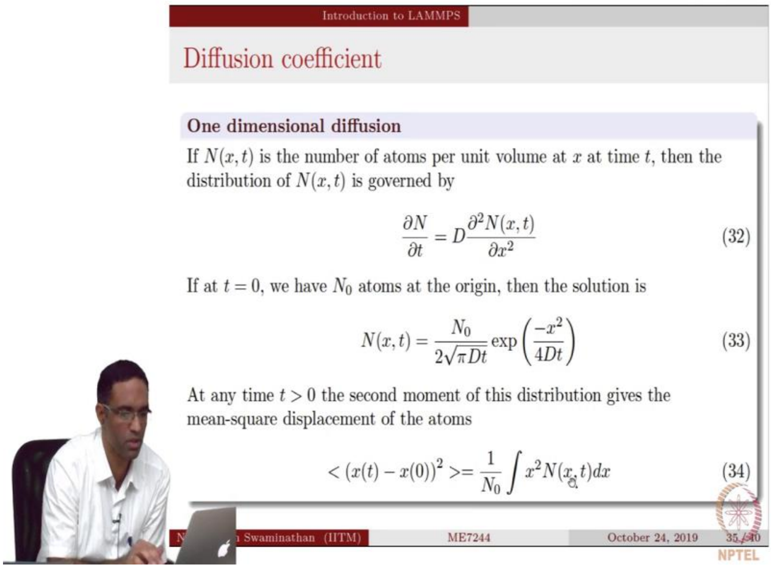

Introduction to LAMMPS

Diffusion coefficient

One dimensional diffusion

If $N(x,t)$ is the number of atoms per unit volume at x at time t, then the distribution of $N(x,t)$ is governed by

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N(x,t)}{\partial x^2} \qquad (32)$$

If at $t = 0$, we have N_0 atoms at the origin, then the solution is

$$N(x,t) = \frac{N_0}{2\sqrt{\pi D t}}\exp\left(\frac{-x^2}{4Dt}\right) \qquad (33)$$

At any time $t > 0$ the second moment of this distribution gives the mean-square displacement of the atoms

$$< (x(t) - x(0))^2 >= \frac{1}{N_0}\int x^2 N(x,t)dx \qquad (34)$$

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So, let us begin. Good Afternoon. We have seen several applications of the fix command and the compute command for calculating the radial distribution functions, the velocities and things like that. And then also averages them over specific time intervals and plotted them in previous two classes. Another important aspect that we can generally obtain from molecule dynamic simulation is the diffusion coefficient or the self-diffusion coefficient of the atoms. So, this does not require any explicit chemical potential or mass gradient to be provided to the system to see the atoms move. This is just qualitative measure of how, how much the atoms may actually be diffusing in the system over a given period of time.

So, when you want to compare systems then it gives you a good indication as to how whether, whether atoms in krypton are moving faster or whether atoms in argon are moving faster and things like that. So, what we have to compute is what is referred to as the mean square displacement of the atoms in a system. And if you plot the means square displacement of the items over time and the slope of the mean square displacement atom is basically proportional to actually the diffusion coefficient. So, we will see a very, the, the actual theory that tells us this that the main square displacement is proportional to the diffusion coefficient is comes very much later in statistical mechanics.

So we will have to know a lot of background in order to actually understand exactly why it turns out that way. So, instead of going through all those details, I have just put forth some simple qualitative derivation which actually gives us the same result for one dimensional system and then we will extend it to three dimensional systems. So, if you consider one dimensional diffusion, so if you have say N is basically the total number of atoms that is percent per unit volume at a particular point, a particular point in space say x at a given time t then its distribution is actually governed by this differential equation, the rate of change of N with respect to t is diffusion coefficient times dou square N by dou x square.

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N(x,t)}{\partial x^2}$$

So, if at time t equal to 0, we have certain N 0 number of atoms placed right at the origin and then if you let it, if you let the atoms diffuse then they will eventually, the concentration at the origin will start decreasing and they will start spreading out, like for example, a drop of ink that is dropped on a plate of say what right, if you drop a drop of ink right in the centre it will start spreading out. So, if you solve the differential equation for this boundary condition or initial condition, it so happens to have this particular solution where the evolution of N with respect to time is nothing but N naught times some exponential minus x square type of function which is basically a Gaussian function.

$$N(x,t) = \frac{N_0}{2\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right)$$

So, initially it will peak like this and as time progresses, the peak from its narrow appearance will start appearing, will start broadening out. So, at any time t greater than 0 the second moment of this distribution.

$$< (x(t) - x(0))^2 >= \frac{1}{N_0} \int x^2 N(x,t) dx$$

So basically, x square times N of x dx divided by N naught is basically nothing but the square of the, mean of the square of the distance that the particular atom has actually travelled from its initial position. So, this is a one-dimensional expression.

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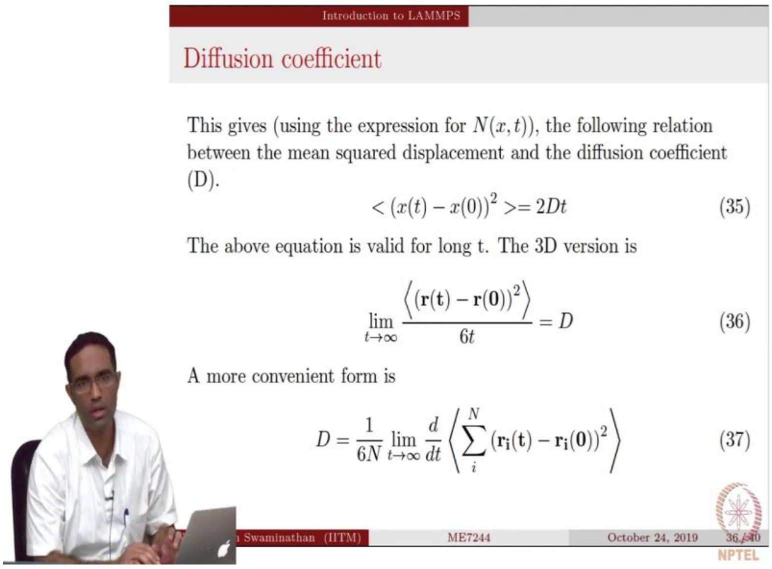

Introduction to LAMMPS

Diffusion coefficient

This gives (using the expression for $N(x,t)$), the following relation between the mean squared displacement and the diffusion coefficient (D).

$$< (x(t) - x(0))^2 >= 2Dt \qquad (35)$$

The above equation is valid for long t. The 3D version is

$$\lim_{t\to\infty} \frac{\left\langle (\mathbf{r(t)} - \mathbf{r(0)})^2 \right\rangle}{6t} = D \qquad (36)$$

A more convenient form is

$$D = \frac{1}{6N} \lim_{t\to\infty} \frac{d}{dt} \left\langle \sum_i^N (\mathbf{r_i(t)} - \mathbf{r_i(0)})^2 \right\rangle \qquad (37)$$

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So if you actually solve plug the value of N of x into this expression 34 here and solve you happen to get the mean square displacement is eq the average mean square displacement is actually equal to 2 times Dt.

$$< (x(t) - x(0))^2 >= 2Dt$$

Then, of course, this is this expression is actually valid for extremely long periods of time and the above equation is 1 and if you look at the 3D version of it, all you have to do is divide by 6. So, in the limit of extremely large t, the mean square, the mean square displacement of the atoms divided by 6t is actually the diffusion coefficient of the atoms.

So, here this is x of t, so basically since we are talking only about one dimensional diffusion, so r of t minus r of 0 the whole square averaged over, say all the atoms in the system is basically nothing but the square of the distance that that particular atom has travelled at time t from its initial configuration, average over all the atoms in the system. So, it is actually a function, this expression here is actually a function of time, the mean square displacement is actually a function of time. And if you divide it by 6t, so here it is 2Dt, so if it is going to be a three dimensional system, it happens to be 2 this the exact expression for a 2 dimensional system is 2 times 2 times Dt.

So, if N is equal to 3, it happens to be six times Dt, so you get this expression for the diffusion, self-diffusion coefficient of a system.

$$\lim_{t\to\infty} \frac{\left\langle (\mathbf{r}(\mathbf{t}) - \mathbf{r}(\mathbf{0}))^2 \right\rangle}{6t} = D$$

So, in molecular dynamics, a more convenient form is used where you say 1 by 6N and you plot the mean square displacement. So, you basically calculate the current position of an atom at time t from its initial position, you calculate the distance that it has travelled, square it, do this for all the atoms in the system. Basic assumption is that all the atoms are essentially the same atoms, so they would behave essentially the same way and you get better statistics.

And you once you average it over all the atoms in the system, you take the slope of this mean square displacement versus time curve and divide it by 6 times N, you essentially get the, this is for one atom and then summed over all the atoms divided by N which is essentially averaged over all the atoms divided by 6 of that particular slope will essentially give you the diffusion coefficient.

$$D = \frac{1}{6N} \lim_{t\to\infty} \frac{d}{dt} \left\langle \sum_{i}^{N} (\mathbf{r_i}(\mathbf{t}) - \mathbf{r_i}(\mathbf{0}))^2 \right\rangle$$

So, this is a very brief and rough overview of how this expression might have come about, the details you can take a look at some statistical mechanics book and you will find it there. But this course, this part of the course is not about teaching you how to derive this but to see how we can calculate the mean square displacement with LAMMPS.

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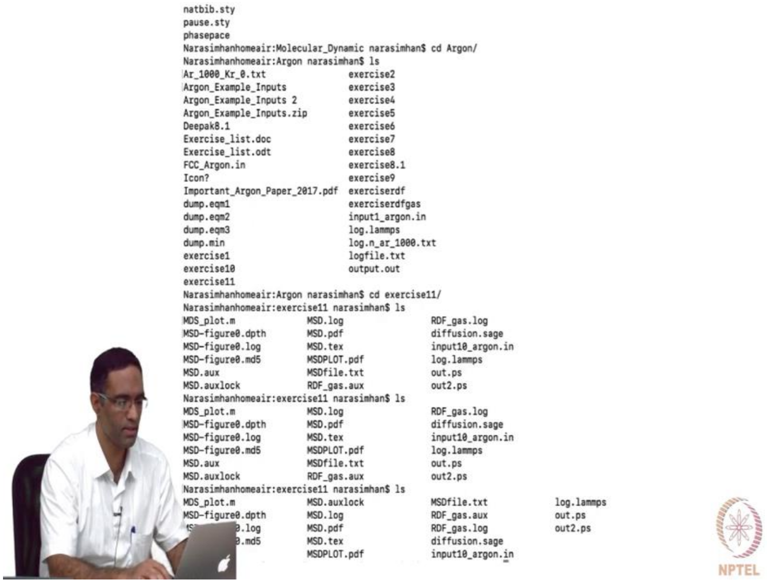

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pause.sty
phasepace
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Narasimhanhomeair:Argon narasimhan$ ls
Ar_1000_Kr_0.txt              exercise2
Argon_Example_Inputs          exercise3
Argon_Example_Inputs 2        exercise4
Argon_Example_Inputs.zip      exercise5
Deepak8.1                     exercise6
Exercise_list.doc             exercise7
Exercise_list.odt             exercise8
FCC_Argon.in                  exercise8.1
Icon?                         exercise9
Important_Argon_Paper_2017.pdf exerciserdf
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dump.eqm3                     log.lammps
dump.min                      log.n_ar_1000.txt
exercise1                     logfile.txt
exercise10                    output.out
exercise11
Narasimhanhomeair:Argon narasimhan$ cd exercise11/
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MDS_plot.m              MSD.log                 RDF_gas.log
MSD-figure0.dpth        MSD.pdf                 diffusion.sage
MSD-figure0.log         MSD.tex                 input10_argon.in
MSD-figure0.md5         MSDPLOT.pdf             log.lammps
MSD.aux                 MSDfile.txt             out.ps
MSD.auxlock             RDF_gas.aux             out2.ps
Narasimhanhomeair:exercise11 narasimhan$ ls
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MSD.auxlock             RDF_gas.aux             out2.ps
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MSD-figure0.dpth        MSD.log                 RDF_gas.aux             out.ps
MS       0.log          MSD.pdf                 RDF_gas.log             out2.ps
         0.md5          MSD.tex                 diffusion.sage
                        MSDPLOT.pdf             input10_argon.in
```

```
#==========================================================================
mass 1  39.948  #<Mass of atom type 1 is 39.48 [mass units grams/mole]>
pair_style      lj/cut  20.0    # 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 a
tom 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)
fix relaxbox all  box/relax iso 1.0
minimize 1e-10 1e-9 100000 100000 #<Minimize the energy using a conjugate gradient step.
#==========================================================================
#Provide an initial maxwellian distribution of velocity corresponding to temperature 5K
velocity all create 600 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
thermo_style custom step time cpu temp pe ke etotal press vol#<Print the thermodynamic information >
thermo 1000
#run 1
run 10000
unfix 1
fix 1 all npt temp 300 300 0.1 iso 1.0 1.0 1.0
#run 1
run 50000
unfix 1
#-------
#Check for equilibrium
fix 1 all nve
#run 1
run 10000
unfix 1
#-------
#
log MSDfile.txt
compute msdisp all msd com yes
variable tt equal time
variable mtt equal time-${tt}
fix 1 all nve
thermo_style custom v_mtt c_msdisp[1] c_msdisp[2] c_msdisp[3] c_msdisp[4]#<Print the thermodynamic information
 >
```

So, this is done in exercise 11. This is the exactly same input file as the previous exercise which is 10. And the only difference that I have done is, the only thing that I have done is after relaxing the system completely, say fix 1 all nve run 10000 was the last nve and after that we did another nve fix in order to compute the radial distribution function. But now I am going to now compute the mean square displacement. So, what, one of the things that happens is we are going to have to print out the mean square displacement. So, I would like for me to, I would like the code or the script to print out only the mean square displacement information in a separate file and not along with everything else because, it cumbersome for me to open that file and delete all the previous steps and look at only what I want.

So, what I do is, I just say log (MSDfi) MSDfile dot txt, so at this (ins), from this instant on, it will start printing information in a new file. So, I say compute msdisp all MSD, MSD is basically the, MSD and come is equal to yes basically specifies that the, the where it calculates the velocity it removes this velocity of the centroid of the system, if at all there is any, so that is what it does. So, and then I am running this then I am running the nve fix right here, so all these calculations are done after these variables have been defined. So, these this (comp), this mean square displacement is actually compute over this nve right here. And I say thermo style and I give a variable, I will tell you what this variable is in a second.

And then I print out c underscore msdisp 1 disp 2 and disp 3 and disp 4 which is basically the mean square displacement along the x, the y, the z and the magnitude of the mean square displacements. What I have done here is since this time here is not actually going to start from 0, but it is going to start from finite value, because I have run a lot of simulation above this. I just define a simple calculation here, where I say tt is equal to time and then say my time my mtt is equal to time plus dollar tt which essentially subtracts the current time from the, the from the previous time and hence this will this variable, when it prints out it will start printing out from 0. So, then it is nice to plot this entire thing.

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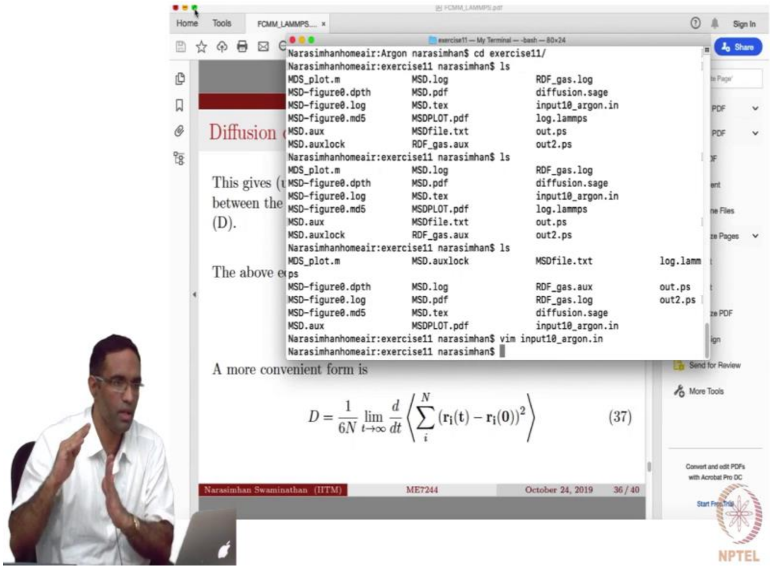

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Narasimhanhomeair:exercise11 narasimhan$ ls
MDS_plot.m              MSD.log                 RDF_gas.log
MSD-figure0.dpth        MSD.pdf                 diffusion.sage
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MSD.aux                 MSDfile.txt             out.ps
MSD.auxlock             RDF_gas.aux             out2.ps
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MSD.aux                 MSDfile.txt             out.ps
MSD.auxlock             RDF_gas.aux             out2.ps
Narasimhanhomeair:exercise11 narasimhan$ ls
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ps
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MSD-figure0.log         MSD.pdf                 RDF_gas.log             out2.ps
MSD-figure0.md5         MSD.tex                 diffusion.sage
MSD.aux                 MSDPLOT.pdf             input10_argon.in
Narasimhanhomeair:exercise11 narasimhan$ vim input10_argon.in
Narasimhanhomeair:exercise11 narasimhan$ 
```

A more convenient form is

$$D = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\left\langle\sum_{i}^{N}(\mathbf{r_i(t)}-\mathbf{r_i(0)})^2\right\rangle \qquad (37)$$

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One of the, one of the another things that you should notice is that when I am trying to do this mean square displacement, I am running it over at least 2 or 3 orders of magnitude more number of time steps than what I did for other simulations. So, it might have reached equilibrium, but if I want to look at the region in the MSD versus t plot, where the diffusion coefficient is actually proportional to the time then I will have to wait long enough for this diffusion, for this relationship to actually show up. So…Yeah?

Student: the variable diffusion. So in this case we declare tt equals to time and mtt equals to time when it is infinite So in this case like how it is executed, because like every time when you say execute line 48 and then line 49, it is going to give 0, right?

Professor: No, tt equals time and then I said dollar tt, at this particular instant of time, tt is going to have the value of time that it currently, what about the value of time it is currently. Then when I say the (word), when I use time, it is actually current time minus dollar tt. So, always the time that was stored in tt will actually be used.

Student: So that is the same as 48, for 48, is there change?

Student: You are not printing tt in thermostat, so it can never be print out

Professor: You are only calculating v minus mtt. mtt is the only thing that is being calculated, so it will never print out.

Student: If time is constant…

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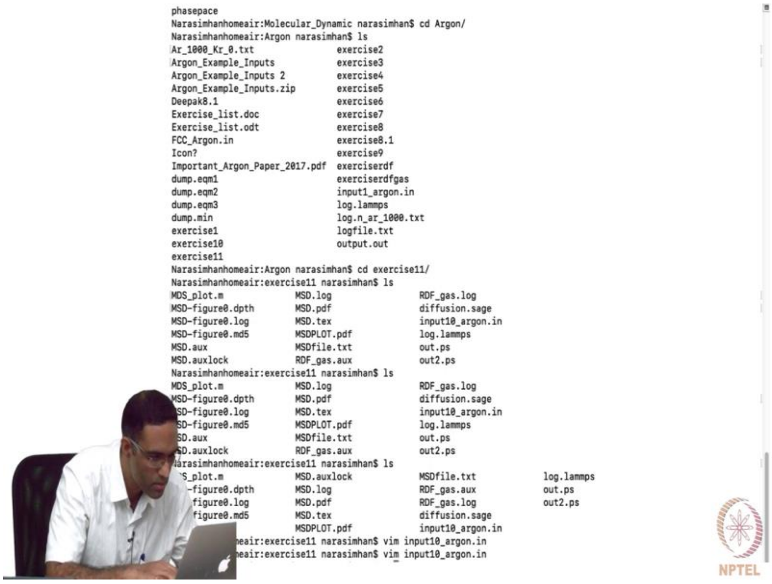

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phasepace
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Exercise_list.doc               exercise7
Exercise_list.odt               exercise8
FCC_Argon.in                    exercise8.1
Icon?                           exercise9
Important_Argon_Paper_2017.pdf  exciserdf
dump.eqm1                       exerciserdfgas
dump.eqm2                       input1_argon.in
dump.eqm3                       log.lammps
dump.min                        log.n_ar_1000.txt
exercise1                       logfile.txt
exercise10                      output.out
exercise11
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MSD.auxlock             RDF_gas.aux             out2.ps
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SD.aux                  MSDfile.txt             out.ps
SD.auxlock              RDF_gas.aux             out2.ps
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-figure0.dpth           MSD.log                 RDF_gas.aux             out.ps
figure0.log             MSD.pdf                 RDF_gas.log             out2.ps
figure0.md5             MSD.tex                 diffusion.sage
                        MSDPLOT.pdf             input10_argon.in
eair:exercise11 narasimhan$ vim input10_argon.in
eair:exercise11 narasimhan$ vim input10_argon.in
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19996.188     74608350     74172901     76765309 2.2554656e+08
19996.288     74608821     74173183     76765690 2.2554769e+08
19996.388     74609294     74173467     76766069 2.2554883e+08
19996.488     74609769     74173751     76766448 2.2554997e+08
19996.588     74610245     74174036     76766826 2.2555111e+08
19996.688     74610724     74174321     76767202 2.2555225e+08
19996.788     74611207     74174602     76767578 2.2555339e+08
19996.888     74611693     74174882     76767955 2.2555453e+08
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19997.188     74613154     74175713     76769093 2.2555796e+08
19997.288     74613639     74175990     76769473 2.255591e+08
19997.388     74614123     74176268     76769854 2.2556024e+08
19997.488     74614606     74176547     76770235 2.2556139e+08
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19997.688     74615572     74177099     76770996 2.2556367e+08
19997.788     74616055     74177370     76771375 2.255648e+08
19997.888     74616542     74177641     76771755 2.2556594e+08
19997.988     74617030     74177913     76772136 2.2556708e+08
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19998.188     74618005     74178457     76772896 2.2556936e+08
19998.288     74618493     74178730     76773276 2.255705e+08
19998.388     74618976     74179002     76773656 2.2557163e+08
19998.488     74619456     74179275     76774036 2.2557277e+08
19998.588     74619933     74179548     76774417 2.255739e+08
19998.688     74620411     74179824     76774799 2.2557503e+08
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```

At tt, tt has a constant value now. So, so, if you look at the file, I do not know where the file is. It looks like this and this is the this is the first column is basically the time and it is going to or 20000, 20000 what, 20000 picoseconds is the time. It is huge, 20000 picoseconds is a very, very long time, but you need that time in order to actually see the diffusive regime and be able to calculate the diffusion coefficient.

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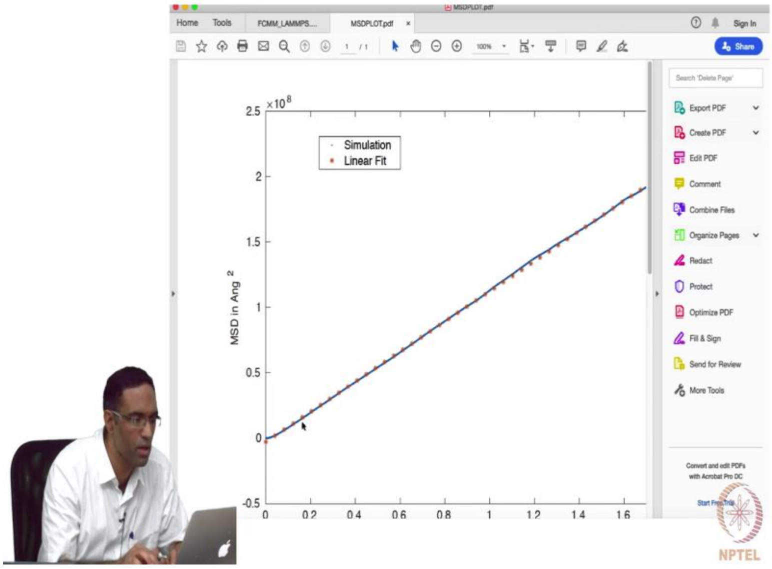

So, when you do this, this is how it looks. So, in this region, at extremely small times, so so this this plot shows two things, one is actually the continuous looking line which is basically from the simulation and then the, the thing that is marked which is basically a linear fit over this. So, if you look at it very, very carefully, here the fit is actually not so good, this this this is this this start asterisk mark is basically the linear fit whereas it starts off a little bit flat. So so, you need to make sure that you are running your MSD simulations for long enough, of course it does not have to be such a long time for, for this system, this is just for illustration purposes and it is only 4000 atoms and this simulation completes within the reasonable time frame.

But when you are looking at larger systems then you have to be careful as to how long you want to run this simulation. So, once you run this simulation, we can obtain, sorry I am not able to open MATLAB. You can actually perform the calculation and check the value of, so so this MSD not only does it, it (gives), it also the command, the compute command MSD, it also averages it over all the atoms. So, one of the things that you do not need to do is, after calculating the MSD, you just need to calculate the slope and divide it by 6, you do not need to divide it by the total number of atoms that is present in the system.

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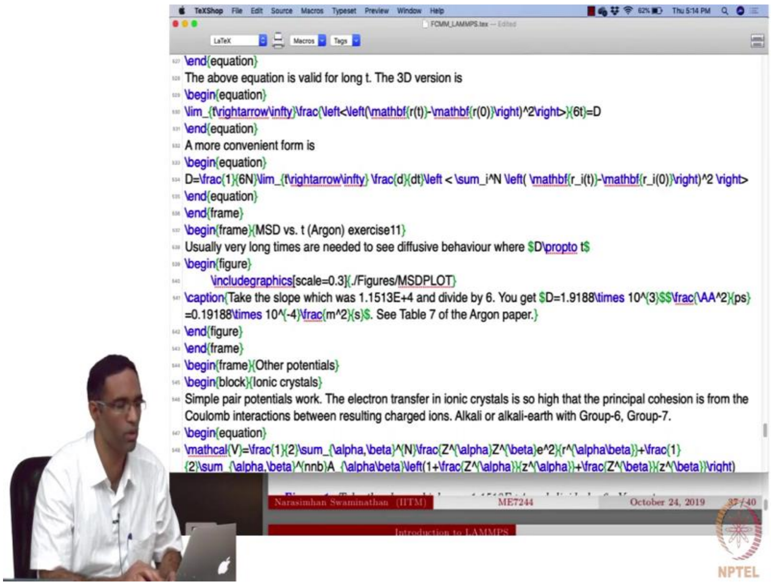

```latex
\end{equation}
The above equation is valid for long t. The 3D version is
\begin{equation}
\lim_{t\rightarrow\infty}\frac{\left<\left(\mathbf{r(t)}-\mathbf{r(0)}\right)^2\right>}{6t}=D
\end{equation}
A more convenient form is
\begin{equation}
D=\frac{1}{6N}\lim_{t\rightarrow\infty} \frac{d}{dt}\left < \sum_i^N \left( \mathbf{r_i(t)}-\mathbf{r_i(0)}\right)^2 \right>
\end{equation}
\end{frame}
\begin{frame}{MSD vs. t (Argon) exercise11}
Usually very long times are needed to see diffusive behaviour where $D\propto t$
\begin{figure}
	\includegraphics[scale=0.3]{./Figures/MSDPLOT}
\caption{Take the slope which was 1.1513E+4 and divide by 6. You get $D=1.9188\times 10^{3}$$\frac{\AA^2}{ps}
=0.19188\times 10^{-4}\frac{m^2}{s}$. See Table 7 of the Argon paper.}
\end{figure}
\end{frame}
\begin{frame}{Other potentials}
\begin{block}{Ionic crystals}
Simple pair potentials work. The electron transfer in ionic crystals is so high that the principal cohesion is from the
Coulomb interactions between resulting charged ions. Alkali or alkali-earth with Group-6, Group-7.
\begin{equation}
\mathcal{V}=\frac{1}{2}\sum_{\alpha,\beta}^{N}\frac{Z^{\alpha}Z^{\beta}e^2}{r^{\alpha\beta}}+\frac{1}
{2}\sum_{\alpha,\beta}^{nnb}A_{\alpha\beta}\left(1+\frac{Z^{\alpha}}{z^{\alpha}}+\frac{Z^{\beta}}{z^{\beta}}\right)
```

So, I have some caption here, it is just not turning out. I did the calculation and I compared it to our paper that I just shared with you. Let me show you the values here. So, what I get is I get a value of, I get a value of slope which is about 1.1513E to the 4, I just have to divide it by 6 and I get a diffusion coefficient of about 1.9188 times tend to the times tend to the 3 angstrom per picosecond, angstrom square, actually angstrom square per picosecond which is approximately equal 0.19188E to the minus 4 meter square per second.

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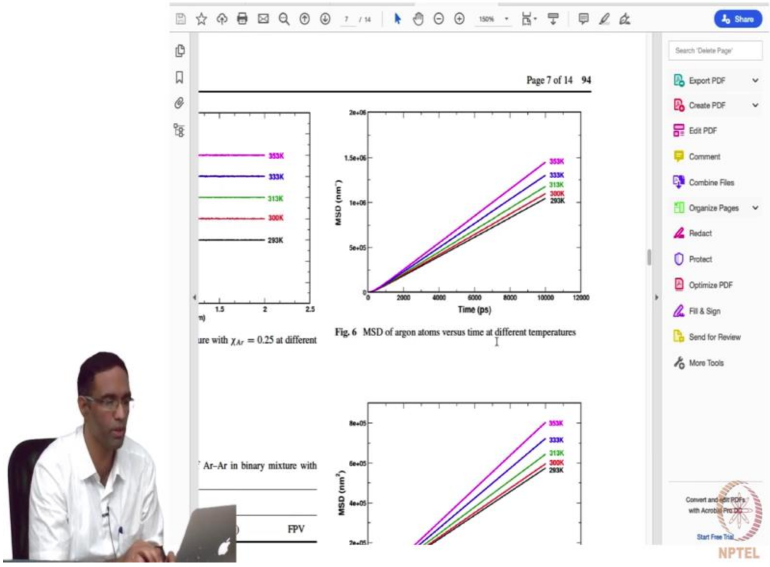

ure with $\chi_{Ar} = 0.25$ at different

Fig. 6 MSD of argon atoms versus time at different temperatures

Ar–Ar in binary mixture with

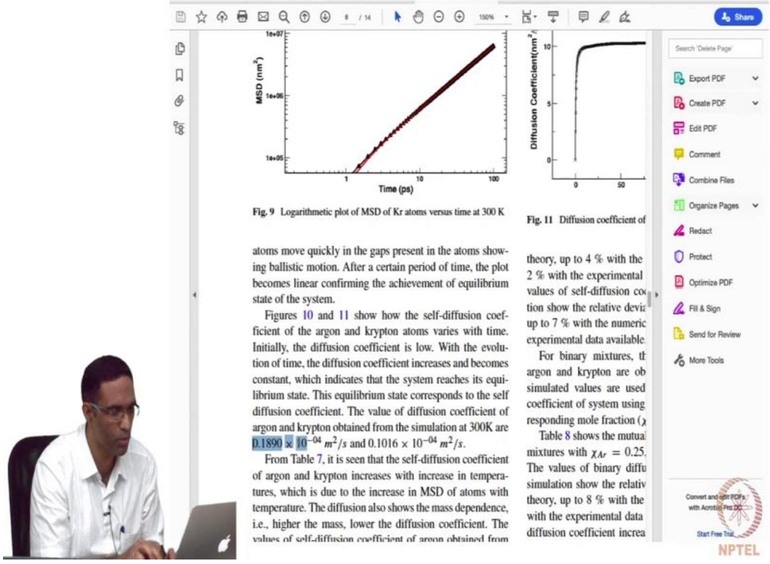

Fig. 9 Logarithmetic plot of MSD of Kr atoms versus time at 300 K

Fig. 11 Diffusion coefficient of

atoms move quickly in the gaps present in the atoms showing ballistic motion. After a certain period of time, the plot becomes linear confirming the achievement of equilibrium state of the system.

Figures 10 and 11 show how the self-diffusion coefficient of the argon and krypton atoms varies with time. Initially, the diffusion coefficient is low. With the evolution of time, the diffusion coefficient increases and becomes constant, which indicates that the system reaches its equilibrium state. This equilibrium state corresponds to the self diffusion coefficient. The value of diffusion coefficient of argon and krypton obtained from the simulation at 300K are $0.1890 \times 10^{-04}\ m^2/s$ and $0.1016 \times 10^{-04}\ m^2/s$.

From Table 7, it is seen that the self-diffusion coefficient of argon and krypton increases with increase in temperatures, which is due to the increase in MSD of atoms with temperature. The diffusion also shows the mass dependence, i.e., higher the mass, lower the diffusion coefficient. The values of self-diffusion coefficient of argon obtained from

theory, up to 4 % with the
2 % with the experimental
values of self-diffusion co
tion show the relative devi
up to 7 % with the numeric
experimental data available

For binary mixtures, th
argon and krypton are ob
simulated values are used
coefficient of system using
responding mole fraction (χ

Table 8 shows the mutual
mixtures with $\chi_{Ar} = 0.25$
The values of binary diffu
simulation show the relativ
theory, up to 8 % with the
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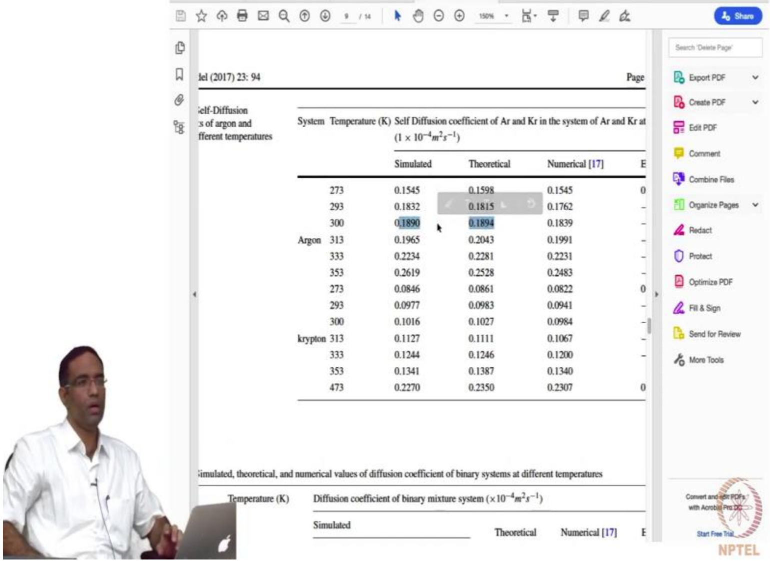
diffusion coefficient increa



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elf-Diffusion
s of argon and
fferent temperatures

System	Temperature (K)	Self Diffusion coefficient of Ar and Kr in the system of Ar and Kr at $(1 \times 10^{-4} m^2 s^{-1})$			
		Simulated	Theoretical	Numerical [17]	E
	273	0.1545	0.1598	0.1545	0
	293	0.1832	0.1815	0.1762	–
	300	0.1890	0.1894	0.1839	–
Argon	313	0.1965	0.2043	0.1991	–
	333	0.2234	0.2281	0.2231	–
	353	0.2619	0.2528	0.2483	–
	273	0.0846	0.0861	0.0822	0
	293	0.0977	0.0983	0.0941	–
	300	0.1016	0.1027	0.0984	–
krypton	313	0.1127	0.1111	0.1067	–
	333	0.1244	0.1246	0.1200	–
	353	0.1341	0.1387	0.1340	
	473	0.2270	0.2350	0.2307	0

imulated, theoretical, and numerical values of diffusion coefficient of binary systems at different temperatures

Temperature (K)	Diffusion coefficient of binary mixture system $(\times 10^{-4} m^2 s^{-1})$			
	Simulated	Theoretical	Numerical [17]	E

So, if you look at the, the argon paper. I have shared this paper also with you, right? The argon paper. If you look right here, they have basically made the exact same plot, this is exactly what we had for 300 Kelvin and it is a very small region where it is nonlinear, actually this is maybe a couple of picoseconds actually. So, you should make sure that you are running it reasonably long time to make sure that you see the diffuser regime. And the value that they get is about 0.1890E to the minus 4 which is quite close to what we have got and it is compared in this table as well.

So, so, you can try to do this for krypton and other noble gases. And in this is paper, there is also a, there are also techniques that is given how, as to how you can actually simulate the mixture of gases, a combination of both argon, krypton and so on. So, these things can also, this paper can also teach you how to do that. Should not be very complicated to understand how to model the behaviour of a mixture of these ideal gases. So, please take a look at this article and try to simulate as many plots as you can from this paper. It is a very good learning experience.

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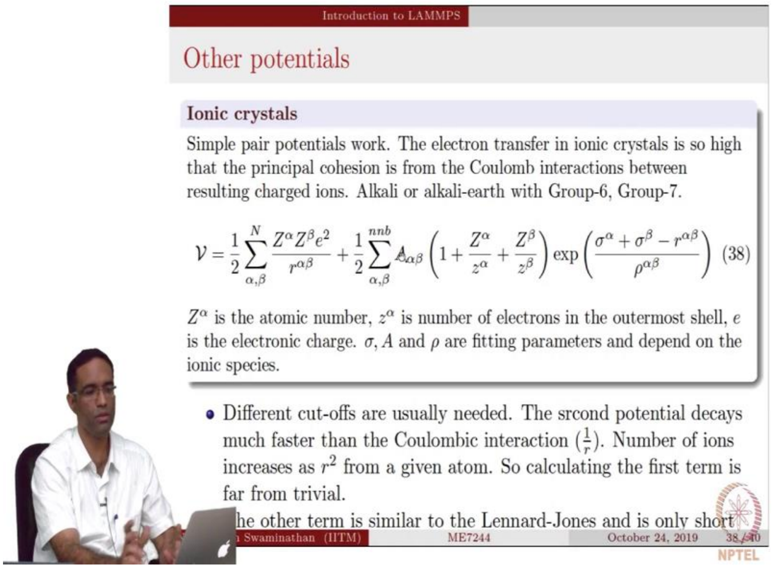

Introduction to LAMMPS

Other potentials

Ionic crystals

Simple pair potentials work. The electron transfer in ionic crystals is so high that the principal cohesion is from the Coulomb interactions between resulting charged ions. Alkali or alkali-earth with Group-6, Group-7.

$$\mathcal{V} = \frac{1}{2}\sum_{\alpha,\beta}^{N}\frac{Z^\alpha Z^\beta e^2}{r^{\alpha\beta}} + \frac{1}{2}\sum_{\alpha,\beta}^{nnb} A_{\alpha\beta}\left(1+\frac{Z^\alpha}{z^\alpha}+\frac{Z^\beta}{z^\beta}\right)\exp\left(\frac{\sigma^\alpha+\sigma^\beta-r^{\alpha\beta}}{\rho^{\alpha\beta}}\right) \quad (38)$$

Z^α is the atomic number, z^α is number of electrons in the outermost shell, e is the electronic charge. σ, A and ρ are fitting parameters and depend on the ionic species.

- Different cut-offs are usually needed. The srcond potential decays much faster than the Coulombic interaction ($\frac{1}{r}$). Number of ions increases as r^2 from a given atom. So calculating the first term is far from trivial.
- he other term is similar to the Lennard-Jones and is only short

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So, now there are the only interatomic potential we have looked at so far is basically the Lennard-Jones potential and it is a pair potential. And, and many other potentials also, although they do not usually model ideal gases, say for example, solids, they are also pair potentials and apparently, they do very good jobs. Let us take for example, one type of potential which is called as the Born Huggins Mayer potential, Born Mayer potential, it is useful in ionic crystals.

So, ionic crystals, what happens is that the bonding that is existing between the atoms is essentially ionic and the long-range interaction between the charged ions is so effective that it is, effectively that it is the only part effectively important by enlarge. And then you just need to have some other short-range potential which is a pair potential, which will just take care of the electron-electron repulsion that is existing between the atoms. So, the bond potential, the particular potential looks like this and it is generally used to model ionic crystals where you have mixture of alkali or alkali earth metals with Group-6, Group-7.

So, basically oxygen sulphur, Group-6, Group-7, chlorine and all those halogens basically. So, this potential looks like this, so you have a part which takes care of coulombic interactions and another part which is basically a short-term interaction existing between the atoms. Now this part contains both repulsion and attraction depending upon the state of charges between the interacting ions, whereas this is exclusively repulsion. So here, you have, capital Z is basically the atomic number, small z is basically the number of electrons in the outermost shell of the particular atom, e is the electronic charge, sigma a and rho are the fitting parameters and depend on the specific ionic species that you are talking about. So, for sodium there will be something.

$$\mathcal{V} = \frac{1}{2}\sum_{\alpha,\beta}^{N} \frac{Z^{\alpha} Z^{\beta} e^{2}}{r^{\alpha\beta}} + \frac{1}{2}\sum_{\alpha,\beta}^{nnb} A_{\alpha\beta}\left(1 + \frac{Z^{\alpha}}{z^{\alpha}} + \frac{Z^{\beta}}{z^{\beta}}\right)\exp\left(\frac{\sigma^{\alpha} + \sigma^{\beta} - r^{\alpha\beta}}{\rho^{\alpha\beta}}\right)$$

So, one of the important aspects that is, that makes this potential little bit difficult is the following. So, this this part the part that is concerned with repulsion, short range repulsion, is pretty straightforward and there is no special treatment that is actually required in order to evaluate this. This is just rapidly decreasing potential. And it is also exponentially decaying which means that the potentials go to 0 quite fast. So, if you are sitting at the atom and trying to evaluate the energy due to some other atom then you only need to consider so much distance from that atom when you are calculating this portion of the interatomic potential, because it it is exponentially decaying.

However, this one is not like that. This is actually having a 1 over r decay, so having A 1 over r decay which is must slower than this. And as you increase r, as you go far away from given atom, the total number of atoms that you have to basically consider increases as r square. So, this component of the interatomic potential is extremely tricky. And the cut-off that you have to give for this interatomic potential and this interatomic potential can actually be different. Now, this computation of this is actually quite challenging and people have developed a lot of smart ways to actually see how to compute this, so that you can finally cut-off radius in such a way that within that cut-off radius this, this term should actually converge to some value, but this actually converges out actually over a very large distance.

So, we are not going to talk about how it is done inside LAMMPS. I will just say that whenever you are using ionic crystals, you have to make sure that the cut-off for this is large enough that your energies are going to converge. So, there may be some, there may be some trial and error that might be important for you to do if you are working with new systems in order to figure out, figure that out. Is that okay? So, that is with respect to the potential and these are of course fit to reproduce some property of the material.

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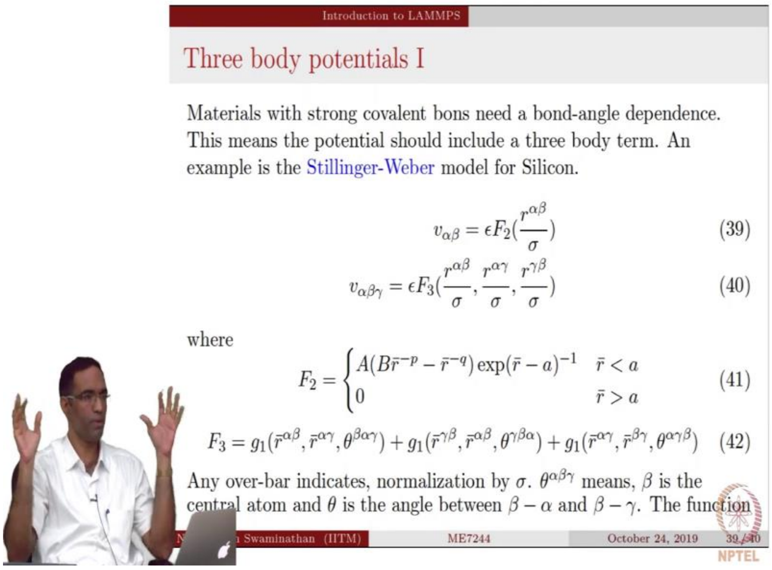

Introduction to LAMMPS

Three body potentials I

Materials with strong covalent bons need a bond-angle dependence. This means the potential should include a three body term. An example is the Stillinger-Weber model for Silicon.

$$v_{\alpha\beta} = \epsilon F_2(\frac{r^{\alpha\beta}}{\sigma}) \quad (39)$$

$$v_{\alpha\beta\gamma} = \epsilon F_3(\frac{r^{\alpha\beta}}{\sigma}, \frac{r^{\alpha\gamma}}{\sigma}, \frac{r^{\gamma\beta}}{\sigma}) \quad (40)$$

where

$$F_2 = \begin{cases} A(B\bar{r}^{-p} - \bar{r}^{-q})\exp(\bar{r} - a)^{-1} & \bar{r} < a \\ 0 & \bar{r} > a \end{cases} \quad (41)$$

$$F_3 = g_1(\bar{r}^{\alpha\beta}, \bar{r}^{\alpha\gamma}, \theta^{\beta\alpha\gamma}) + g_1(\bar{r}^{\gamma\beta}, \bar{r}^{\alpha\beta}, \theta^{\gamma\beta\alpha}) + g_1(\bar{r}^{\alpha\gamma}, \bar{r}^{\beta\gamma}, \theta^{\alpha\gamma\beta}) \quad (42)$$

Any over-bar indicates, normalization by σ. $\theta^{\alpha\beta\gamma}$ means, β is the central atom and θ is the angle between $\beta - \alpha$ and $\beta - \gamma$. The function

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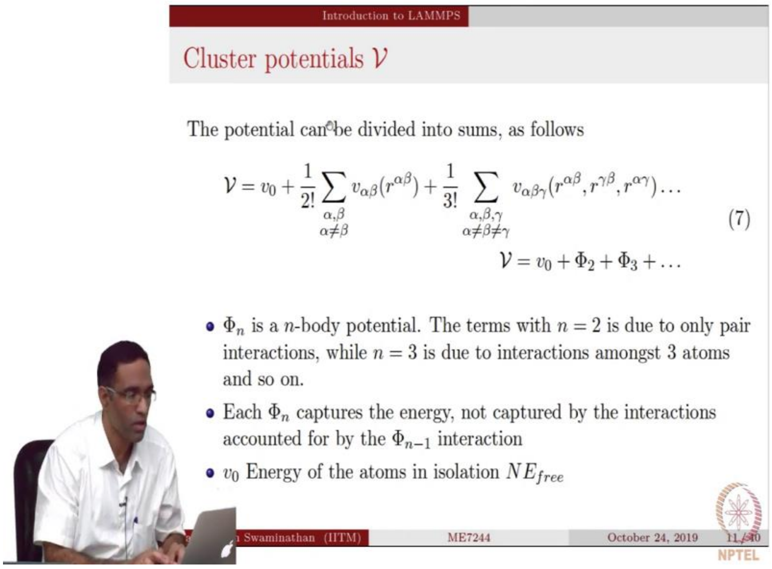

Introduction to LAMMPS

Cluster potentials $\mathcal{V}$

The potential can be divided into sums, as follows

$$\mathcal{V} = v_0 + \frac{1}{2!}\sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} v_{\alpha\beta}(r^{\alpha\beta}) + \frac{1}{3!}\sum_{\substack{\alpha,\beta,\gamma \\ \alpha\neq\beta\neq\gamma}} v_{\alpha\beta\gamma}(r^{\alpha\beta}, r^{\gamma\beta}, r^{\alpha\gamma})\ldots \quad (7)$$

$$\mathcal{V} = v_0 + \Phi_2 + \Phi_3 + \ldots$$

- Φ_n is a n-body potential. The terms with $n = 2$ is due to only pair interactions, while $n = 3$ is due to interactions amongst 3 atoms and so on.
- Each Φ_n captures the energy, not captured by the interactions accounted for by the Φ_{n-1} interaction
- v_0 Energy of the atoms in isolation NE_{free}

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Now, whatever we saw was a 2-body potential. There are many other 2-body potentials, all of them have different names and different parameters to determine depending upon the problem, but they are all fundamentally the same thing, there is not anything different. Now, when you talk about the next potential, so when I talk about 2-body, 3-body, I would like to point, point out to this expression we have seen earlier, this expression that we have seen earlier, this is the reference and this is the 2-body term, this is the 3-body term and so on. So, 3-body term essentially depends on 3 atoms, so the distance between alpha beta, beta gamma and alpha gamma. 4-body means even more and so on.

So, the class of pair potentials comes under this and if you have additional potential the 3-body potential comes into picture and one example of that is the Stillinger-Weber potential which is used to model solids with, with a strong covalent bond. Like for example, carbon germanium, silicon, diamond structures and these materials are very often modelled using this Stillinger-Weber potential. The potential turns out to be quite complicated and it results in about 7 to 8 fitting parameters which you have to find in order to match experimental results. So, it consists of a 2-body term plus F3, so v suffix alpha beta is basically the 2-body term in that expression that I just showed you before. v suffix alpha beta gamma is basically the 3-body term and it depends on all these, it depends on the distance between each of these individual atoms.

So, F2 which is basically the 2-body term simply depends upon the position and this power p power q which looks just like your Lennard-Jones potential except that it is p and q are not 12 and 6 and you have this additional exponential r bar minus a term creeping in. And as long as r bar is less than A then you have to have this potential, otherwise it is 0. And the 3-body term is a sum of g1, g2 and g3 and each of this is depending on alpha beta, alpha gamma, whereas this one depends on, it is it is a function, there is a functional form, but in that functional form you need to substitute the distances between alpha beta, alpha gamma and then gamma beta, alpha beta and so on.

$$v_{\alpha\beta} = \epsilon F_2(\frac{r^{\alpha\beta}}{\sigma})$$

$$v_{\alpha\beta\gamma} = \epsilon F_3(\frac{r^{\alpha\beta}}{\sigma}, \frac{r^{\alpha\gamma}}{\sigma}, \frac{r^{\gamma\beta}}{\sigma})$$

where

$$F_2 = \begin{cases} A(B\bar{r}^{-p} - \bar{r}^{-q}) \exp(\bar{r} - a)^{-1} & \bar{r} < a \\ 0 & \bar{r} > a \end{cases}$$

$$F_3 = g_1(\bar{r}^{\alpha\beta}, \bar{r}^{\alpha\gamma}, \theta^{\beta\alpha\gamma}) + g_1(\bar{r}^{\gamma\beta}, \bar{r}^{\alpha\beta}, \theta^{\gamma\beta\alpha}) + g_1(\bar{r}^{\alpha\gamma}, \bar{r}^{\beta\gamma}, \theta^{\alpha\gamma\beta})$$

So, g1 is just one functional form which looks something like that,

$$g_1(\bar{r_1}, \bar{r_2}, \theta) = \begin{cases} \lambda \exp(\gamma(\bar{r} - a)^{-1} + \gamma(\bar{r_2} - a)^{-1})(\cos(\theta) + \frac{1}{3})^2 & \bar{r_1} < a \text{ and } \bar{r_2} < \\ 0 & \text{otherwise} \end{cases}$$

so g1, each g depends on alpha beta and alpha gamma, two distances and one angle. So, if you are sitting on alpha, the distance between alpha beta and alpha gamma and with this as a centre, the angle that is existing between them is basically theta super fix beta alpha gamma. So, how this needs to be read is I am sitting on atom alpha, I am drawing a vector from alpha to beta, alpha to gamma and measuring the corresponding distance in between, corresponding angle in between. So, these are just general functions.

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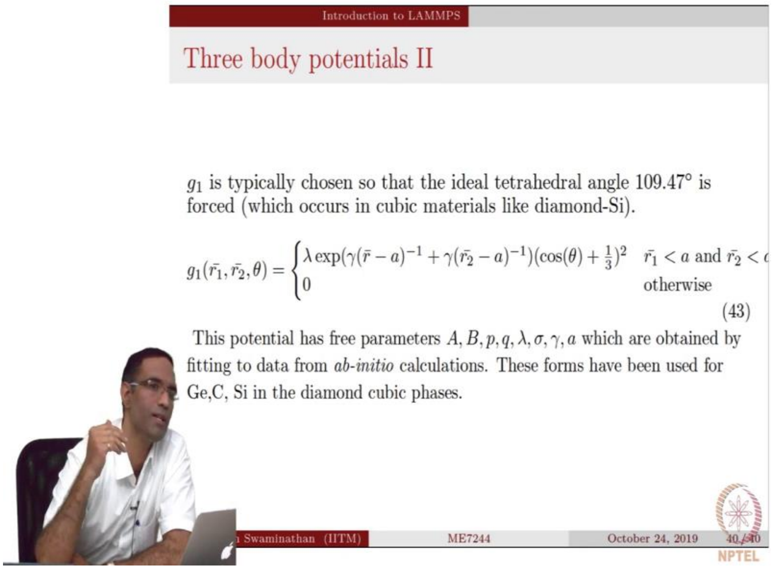

Introduction to LAMMPS

Three body potentials II

g_1 is typically chosen so that the ideal tetrahedral angle 109.47° is forced (which occurs in cubic materials like diamond-Si).

$$g_1(\bar{r_1}, \bar{r_2}, \theta) = \begin{cases} \lambda \exp(\gamma(\bar{r} - a)^{-1} + \gamma(\bar{r_2} - a)^{-1})(\cos(\theta) + \frac{1}{3})^2 & \bar{r_1} < a \text{ and } \bar{r_2} < \\ 0 & \text{otherwise} \end{cases} \tag{43}$$

This potential has free parameters $A, B, p, q, \lambda, \sigma, \gamma, a$ which are obtained by fitting to data from *ab-initio* calculations. These forms have been used for Ge,C, Si in the diamond cubic phases.

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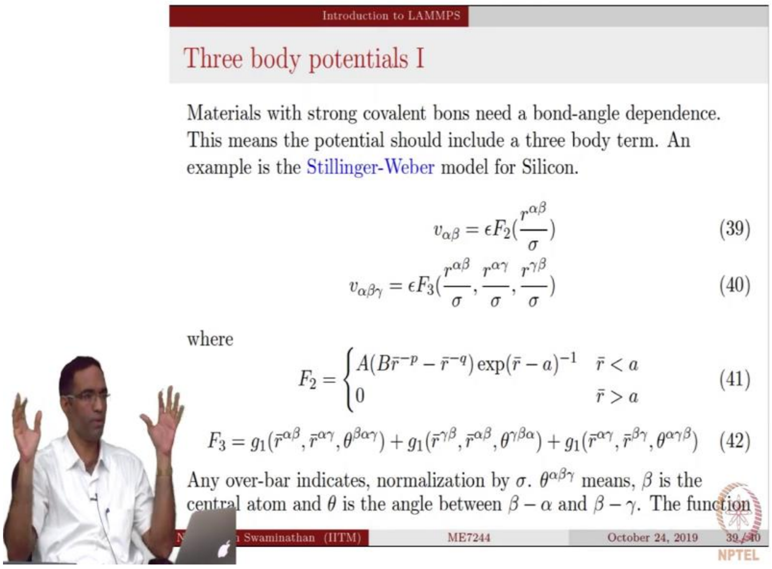

Introduction to LAMMPS

Three body potentials I

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where

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$$F_3 = g_1(\bar{r}^{\alpha\beta}, \bar{r}^{\alpha\gamma}, \theta^{\beta\alpha\gamma}) + g_1(\bar{r}^{\gamma\beta}, \bar{r}^{\alpha\beta}, \theta^{\gamma\beta\alpha}) + g_1(\bar{r}^{\alpha\gamma}, \bar{r}^{\beta\gamma}, \theta^{\alpha\gamma\beta}) \tag{42}$$

Any over-bar indicates, normalization by σ. $\theta^{\alpha\beta\gamma}$ means, β is the central atom and θ is the angle between $\beta - \alpha$ and $\beta - \gamma$. The function

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And for silicon diamond silicon, this potential is used a lot. And the form of the interatomic potential looks like this, so there is additional parameters, here is lambda and then gamma and then you have a cos theta plus 1 by 3 the whole square term. So, if you look at silicon diamond silicon, if you know the structure of it carefully, it basically forms a tetrahedron. There will be a silicon and then there is a silicon on top and then there is a silicon that is right here forming a tetrahedron and the angle between this and this would higher on 9.5 degrees, the angle of the tetrahedron angle.

That is the cos of that angle is actually 1 by 3. So, this term here is basically forcing that angle that is existing between these bonds to actually be higher on 9.47 degrees. So, this potential will have about 8 parameters which are again obtained by fitting data to match the material properties. So, we will try to see if we can do some examples for Stillinger-Weber potential and later on we will look at other types of potentials also. Now, the question is it is always, yes?

Student: Why is there a dependence on?

Professor: So, the question now is, is it always possible for us to actually have potentials by just adding 4-body terms and 5-body terms and so on. So, it so happens that people have actually stopped with 3-body terms. And there are very few works which actually consider 4-body interactions in materials. So, the next thing that people developed was, for many systems it is not sufficient for us to actually just consider or cut off or trunket off the potential at 2-body or 3-body, the other terms also are important, but they happen to make things a little bit complicated, simple because now once you have 4-body terms, you will have to consider the distances between alpha beta, beta gamma, gamma delta and all the combinations that are there. It becomes very very cumbersome.

So, they developed a potential that is referred to as functionals, functional potentials. So, we will look at that in a little bit, in some, give you a brief introduction to that and describe two potentials that is associated as functionals, basically the Tersoff potential and the embedded atom potential are these functionals. So, we will try to do some examples based on them as well.