Numerical Methods and Simulation Techniques for Scientists And Engineers

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Lecture 22
Molecular Dynamics

So, here we are going to look at the last chapter a ah simulation chapter on molecular dynamics we have already looked at one of them called the Monte Carlo and this is the other one that we see called as a molecular dynamics.

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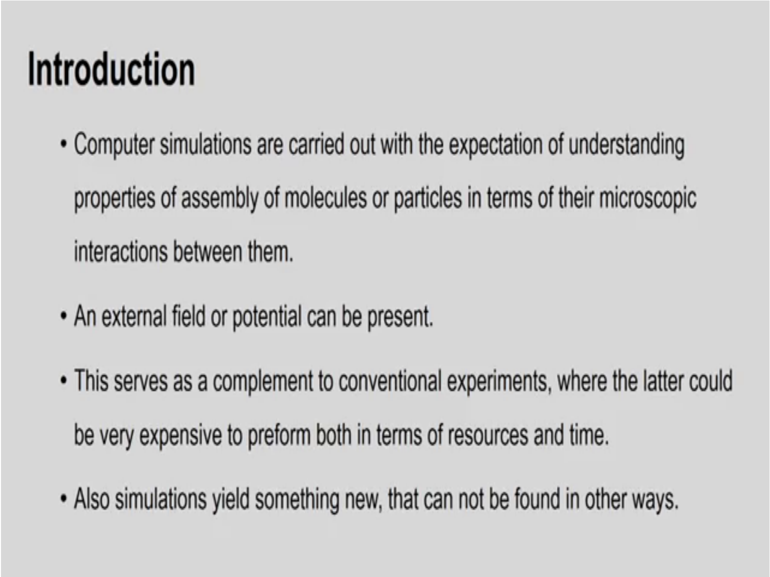

Introduction

- Computer simulations are carried out with the expectation of understanding properties of assembly of molecules or particles in terms of their microscopic interactions between them.
- An external field or potential can be present.
- This serves as a complement to conventional experiments, where the latter could be very expensive to preform both in terms of resources and time.
- Also simulations yield something new, that can not be found in other ways.

So, let us give a short introduction of what molecular dynamics is and how the simulation etcetera are carried out what is it based on what are the pitfalls and what are the advantages and so on. And we have already said this first slide has is just for repetition and to remind you that why simulations are important. The computer simulations are of course carried out with the expectation of understanding properties of molecules or a large number of particles which are interacting with each other via macroscopic you know interactions between them ok.

So, they are talking to each other or they are interacting with each other by certain a potential the potential the form of the potential or the force involved will have to be decided by the nature of the system or this nature of the particles. If you are talking about an atomic system there will be some kind of force. So, if you are talking about molecular system you are talking about a different kind of force and if you are talking about matching with the spectroscopic data then we might really need another kind of force and so on okay.

In either of these cases we may have an external field that is present or an external potential that could be present it is not necessary for that in fact we would leave it out of our discussion of having a an external field or a potential to be present but nevertheless it could be there and it does not harm the ah simulations in any way. This serves as a complement to conventional experiments which we have discussed at length that sometimes the performing the real experiments can become very hazardous and can become very expensive in terms of the resource the computer resources or the manpower that is involved.

Or it could be you know also very expensive in terms of the time which could take you know even months and years of simulation in order to find a certain conclusion for a for a given problem. Whereas this these experiments the computer experiments can be performed without having us to spend that much of time and the results also can be analyzed in a you know within a reasonable time.

The simulations are likely to yield something new what I mean is that sometimes some correlations sometimes some physical properties which are not directly achievable in experiments so that with simulations have a lot of value. And we have seen that earlier having seen Monte Carlo so why do you want to see molecular dynamics.

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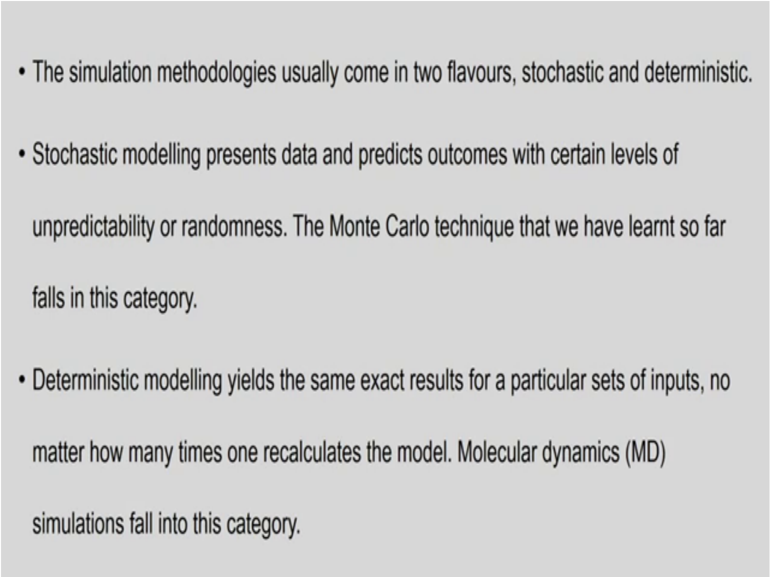

- The simulation methodologies usually come in two flavours, stochastic and deterministic.
- Stochastic modelling presents data and predicts outcomes with certain levels of unpredictability or randomness. The Monte Carlo technique that we have learnt so far falls in this category.
- Deterministic modelling yields the same exact results for a particular sets of inputs, no matter how many times one recalculates the model. Molecular dynamics (MD) simulations fall into this category.

And the reason being that the simulation methodologies usually come in two flavours one being the stochastic and the other is the deterministic. So, the stochastic modelling that presents data and predicts outcome with certain levels of unpredictability or randomness we have seen this we have taken a set of data points which are taken from a known distribution but random points these are random points being taken.

And if you take all the random points with equal probability then we see that it is a normal distribution or rather crude Monte Carlo. Whereas if we take them with certain you know bias however the bias actually goes away as the number of points become too large and these are seen in the Monte Carlo technique, that we have seen and the Monte Carlo technique actually falls in this category of stochastic modelling.

So, this is one word that we are coming across which we have not mentioned this is to distinguish what we are going to learn here on the deterministic modelling that is another class which is the same exact results for a particular set of inputs. And no matter how many times one actually calculates the model. So, you are going to get the same set of you know output every time you give the same inputs and that is all the case with a stochastic modelling.

You are likely to get a different slightly different maybe and there is an unpredictability for the Monte Carlo technique this is called as the molecular dynamics. The molecular dynamics fall into this category. So, what our MD simulations so Monte Carlo is abbreviated as MD and this is done everywhere. So, it is MD simulations is a very common colloquial word used in this particular context.

So, the basic idea of MD is to explore the behaviour of a physical system by computing with significant accuracy the trajectories of individual particles constituting the system. So, you have a large number of particles and these particles are interacting with each other’s through certain potential okay which could be Coulomb potential which could be some other kind of potential as I said that one can have an external field which or an external potential.

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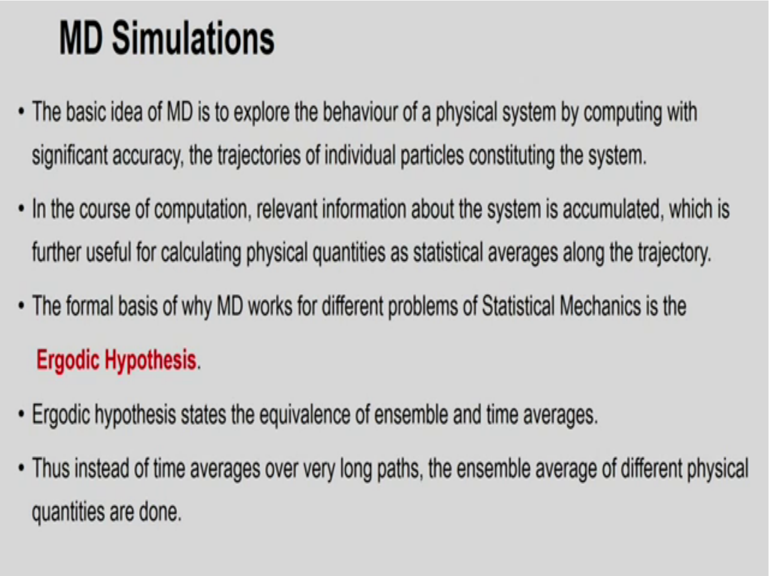

MD Simulations

- The basic idea of MD is to explore the behaviour of a physical system by computing with significant accuracy, the trajectories of individual particles constituting the system.
- In the course of computation, relevant information about the system is accumulated, which is further useful for calculating physical quantities as statistical averages along the trajectory.
- The formal basis of why MD works for different problems of Statistical Mechanics is the **Ergodic Hypothesis**.
- Ergodic hypothesis states the equivalence of ensemble and time averages.
- Thus instead of time averages over very long paths, the ensemble average of different physical quantities are done.

But that could be you know sort of skipped at this moment. In the course of the computation relevant information about the system is accumulated okay. So, the particles are moving they are not stationary they are made to evolve according to certain equations of motion. Now these equations of motion are to be solved pertaining to certain you know conditions or boundary conditions as we have learned and these differential equations will give us finally the trajectory of the particle of the system rather which is a set of particles not a single particle.

But a set of particles which have an interaction between them previously for studying these other you know the initial value and the boundary value problem we have always talked about one particle or one you know sort of entity of the system. And wanted to see that how it evolves with time. Here we in addition to that we have a large number of particles and these particles are interacting with each other.

So, we want these information to be calculated as physical quantities which come out as statistical averages along that trajectory okay. So, the formal basis of why MD works for different problems of statistical mechanics is the what is called as the Ergodic hypothesis. This is a concept that is very common or fundamental to statistical mechanics. So what it says is that the ensemble average of a system is same as the time average.

So a time average can be actually replaced by the ensemble average let us see what we mean by that, suppose you have a gas an ideal gas which has is in a volume say which is there are these particles constituting the gas and there is a certain a pressure volume and temperature of the gas and the pressure occurs because these molecules of the gas is continuously exerting pressure or colliding with the walls of these irregular shaped boundary that we have considered.

And volume is the volume of these regular irregular shape boundary that we are talking about and temperature comes out because of the kinetic energy of the molecules okay. So, this is the equal partition theorem says that per harmonic degree of freedom the kinetic energy or the energy total energy is per degree of freedom is at thermal equilibrium equal to half KT.

Now the particles of the gas are of course moving and they are interacting with each other they could be interacting via some really complicated potentials or they could only be interacting with each other when the meet that is they sort of move or flow as non-interacting particles and then they sort of undergo a solid sphere or a hard on collision elastic collision. And then they change their directions and sort of this is you know goes on in the system.

So as the system you wait for the system to evolve the system comes with a different configuration if we are able to you know identify the molecules or the atoms constituting this gas somehow by either colouring them or naming them. Then we will find a different configuration at every different instant of time in which case the pressure volume temperature etcetera or other physical parameters they would be functions of time.

And this is what again goes against the spirit of a equilibrium stack make where we actually when we talk about a pressure or a volume or our temperature these are often the or rather these are always the equilibrium quantities and they do not depend on time. Now in order to have these that then cannot be we cannot quote things which are functions of time yet we want their equilibrium values.

So this Ergodic hypothesis is proposed where it says that let me make several mental copies of this system so this is the system of an ideal gas at a given some pressure volume and temperature and so on. So, if I make several mental copies of this gas and say that and they are called as ensembles. So, that we understand that as time progresses if we make really large number of these ensembles then the gas or rather the system would actually visit some ensemble or the other during its course of evolution okay.

So which means that we are making an assumption that our system is actually travel cursing or visiting all these different ensembles or the mental copies that we have made of the system in our mind. And then if we wait for long enough and kind of assume that the system has visited all the mental copies or the ensemble then instead of taking a time average we can take an ensemble average.

So, taking a time average and ensemble average would be same and we would get you know by taking this ensemble average we would get the equilibrium properties of the system and then there is no time dependence. So, this is called as Ergodic hypothesis. And the Monte Carlo simulations they crucially depend upon this hypothesis. So, as I said that that instead of time averages over very long paths the ensemble average for different physical quantities are done okay.

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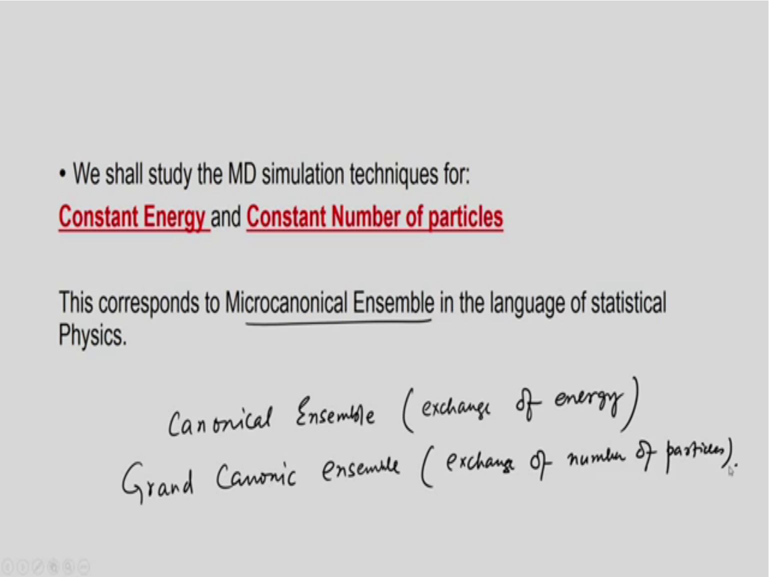

- We shall study the MD simulation techniques for:

Constant Energy and Constant Number of particles

This corresponds to Microcanonical Ensemble in the language of statistical Physics.

Canonical Ensemble (exchange of energy)

Grand Canonic ensemble (exchange of number of particles).

Here we shall really study at the most rudimentary version of this MD simulation because it is not a really a specialized course it says a course which gives you an overview of the different numerical techniques. So, will restrict ourselves to constant energy and constant number of particles and ah if you are aware of statistical mechanics. So, if you have learned statistical mechanics at the undergraduate level then you know that this corresponds to what is called as a micro canonical ensemble.

And in a canonical ensemble the system is actually if it is put in a thermal contact with a temperature bath. Temperature bath is an object which even if you or that is in contact with the when it is in contact with the system ah the system can exchange energy with the bath the temperature of the bath does not change but and the finally the system comes in equilibrium with the bath by exchanging energy okay.

And this is called canonical ensemble and when you also x relaxed the colour trained of keeping the number of particles to be same that is called as a grand canonical ensemble alright. So, I just give you an example to say this room is very big and I have a cup of tea in the on my on my table and I would not drink it. But since it is a little hot I cannot immediately drink it or all of it and I keep it on the table.

Now the as I as a time progresses the tea will get become colder and colder but the temperature of the room does not rise. So, the whole room is like a temperature bath and the tea is like our system which is which could be an ideal gas and so on. So, these are some ensembles that one talks about as I told that the three of them one is called as a micro canonical which is already said and then we can have a canonical ensemble which talks about exchange of energy and there is also a grand canonical ensemble which talks about exchange of the number of particles all right.

So we will restrict ourselves to the simplest case which is for a given you know energy so the energy is same the number of particles is same there is no bath. So, the system cannot exchange energy with a bath so it is an isolated system so to say.

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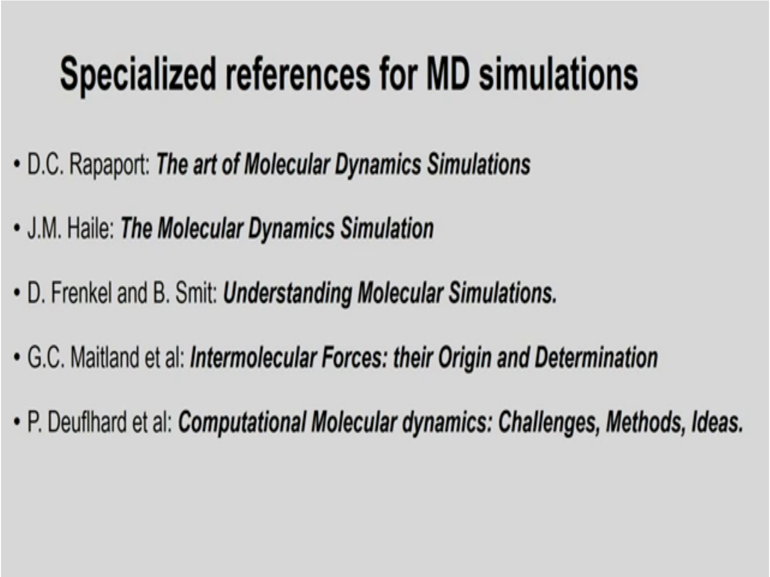

Specialized references for MD simulations

- D.C. Rapaport: ***The art of Molecular Dynamics Simulations***
- J.M. Haile: ***The Molecular Dynamics Simulation***
- D. Frenkel and B. Smit: ***Understanding Molecular Simulations.***
- G.C. Maitland et al: ***Intermolecular Forces: their Origin and Determination***
- P. Deuflhard et al: ***Computational Molecular dynamics: Challenges, Methods, Ideas.***

Once again we reiterate that this is really very rudimentary introduction of the subject and there are lots of specialized references not only the five that I have listed but very large number of them and one can go through this if one is interested or one takes it up for further specialized studies. They are these Rapaport's book on the art of molecular dynamic simulations or Hale on the molecular dynamic simulation again Frankel and Smit understanding molecular simulations. Maitland Et al, on the intermolecular forces of origin and determination and Deuflhard on the computational molecular dynamics challenges methods and ideas ok.

So these are very brief introduction of the subject now let us get into the details or rather the technical details of this particular topic of molecular dynamics.

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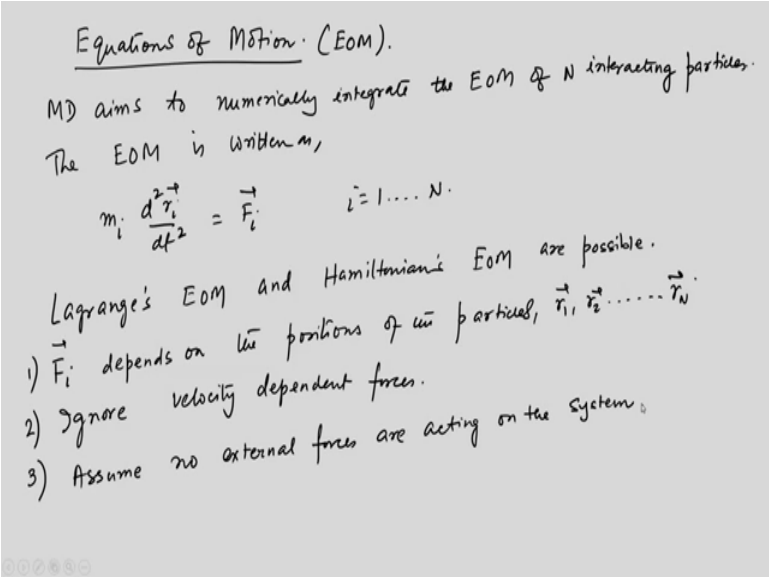

Equations of Motion. (EOM).

MD aims to numerically integrate the EOM of N interacting particles.

The EOM is written as,

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i \qquad i = 1 \ldots . N.$$

Lagrange's EOM and Hamiltonian's EOM are possible.

1) $\vec{F}_i$ depends on the positions of the particles, $\vec{r}_1, \vec{r}_2 \ldots \ldots \vec{r}_N$.

2) Ignore velocity dependent forces.

3) Assume no external forces are acting on the system.

So, what we have to solve is what are called as the equations of motion. So, we need to generate trajectories for a given system of particles and in short this called as a EOM. So, the MD aims to numerically integrate the equation of motion of N interacting particles. So, this EOM is written as m i d2 r i dt2 equal to F i where i equal to 1 to n, now remember this is called as a Newton's equation of motion all of you are familiar with right from you know maybe class 6th or 7th or 8th maybe.

However it is not the only equation of motion that we know we have Lagrange's equation of motion, we have Hamilton's equation of motion and so on. Lagrange's equation of motion is the second-order whereas the Hamilton's equation of motion is a first-order equation. So, anything would do but we are mostly familiar with this so we are starting with this as a equation of motion and we have N particles capital n is a number of particles.

So let us just remind you saying that the Lagrange's EOM and Hamilton's EOM are possible. So, if I depends on the positions of the particle it can depend upon other things but let us just talk about only positions of the particle and ignore velocity dependent forces. So, when you have velocity dependent forces when you have a damping term or if you are talking about a charged particle in an electromagnetic field that also has potential or rather the force of course depends upon velocity.

And so there are complications there so we ignore these velocity dependent forces. And so these are the positions of the particles are given by r 1 r 2 and r n. And third is that assume no external forces are acting on the system okay. So, these are the main feature of what we want to do so this is the equation that we want to solve and as I said that this could have been solved even otherwise by in the spirit of solving just a differential equation.

But now imagine that there are these interacting particles and this interaction has to be taken into account okay.

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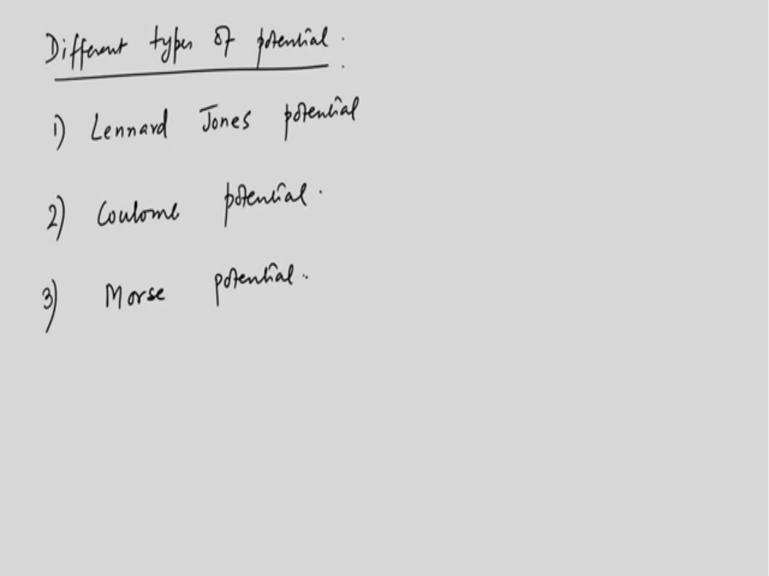

Different types of potential:

1) Lennard Jones potential
2) Coulomb potential.
3) Morse potential.

So, we can talk about different kind of potential and a few potentials that we are going to consider is the following which is mostly therefore you know molecular interactions. So, one is called as so one is called as a Lennard-Jones potential and for charged particles one can have a Coulomb potential and you know the vibrational spectra of atoms they can be described by what is called as a Morse potential okay. We will see briefly what they are mostly going to talk about Lennard-Jones potential.

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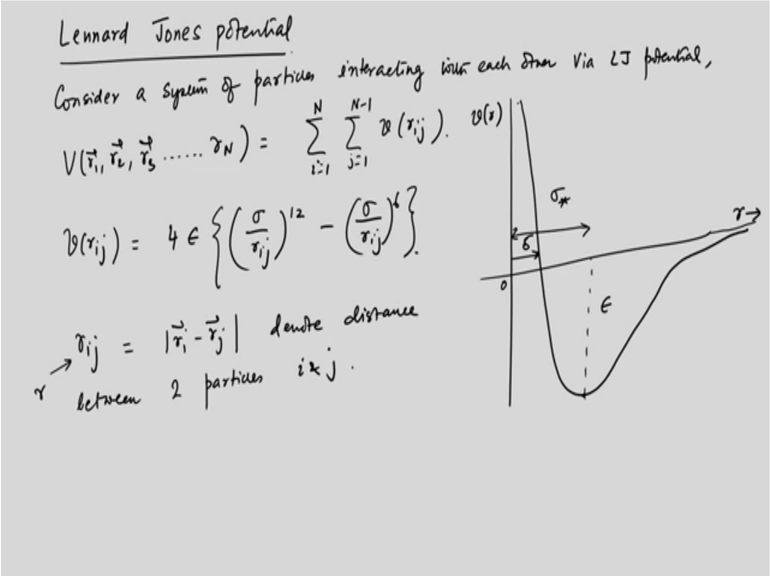

Lennard Jones potential

Consider a system of particles interacting with each other via LJ potential,

$$V(\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots\ldots r_N) = \sum_{i=1}^{N} \sum_{j=1}^{N-1} v(r_{ij}).$$

$$v(r_{ij}) = 4\epsilon \left\{ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right\}.$$

$r \nearrow r_{ij} = |\vec{r}_i - \vec{r}_j|$ denote distance between 2 particles i & j.

So, let us write down Lennard-Jones potential, so I consider a system of particles interacting with each other via Lennard-Jones potential. So, V r1 r2 r3 etc r n is takes a form where i equal to 1 to N j equal to 1 to N -1 just leaving that one particle and then there is a V r ij and where V r ij takes a form 4 epsilon this is very conventional to write it this way it is a sigma by r ij 12 - sigma by r ij 6 and this called as a 612 potential because of these powers 6 and 12 where r ij it is equal to ri – rj, so, that is the distance between i and j it only depends on the distance and not individually on this ri and rj.

And so they denote the distance or magnitude of the distance i and j and so if you actually plot this it takes a form as more like it so this is your V of r and this is r so I am writing that ri - rj for a moment as r so this one is written as r. And so this is the form so what it says is that it is very strongly repulsive at short distances and very weakly attractive at large distances okay. So, there is the form of the potential and this is the distance the unit of distance is Sigma and this is a particular point we will find out what this write down this as something like a sigma star or some such notation that is given here.

This has a depth of epsilon where epsilon is the one that you it appears that the as a coefficient of these bracketed term. So, there is 4 epsilon, so this is the that and this is the distance r so at as r goes to 0 as the to you know molecules they come very close to each other there is an enormous you know repulsion and as they go away from each other there is a weak very weak attraction. And this attraction asymptotically vanishes when the distance between the two molecules that become very large. So let us see some features of these potential.

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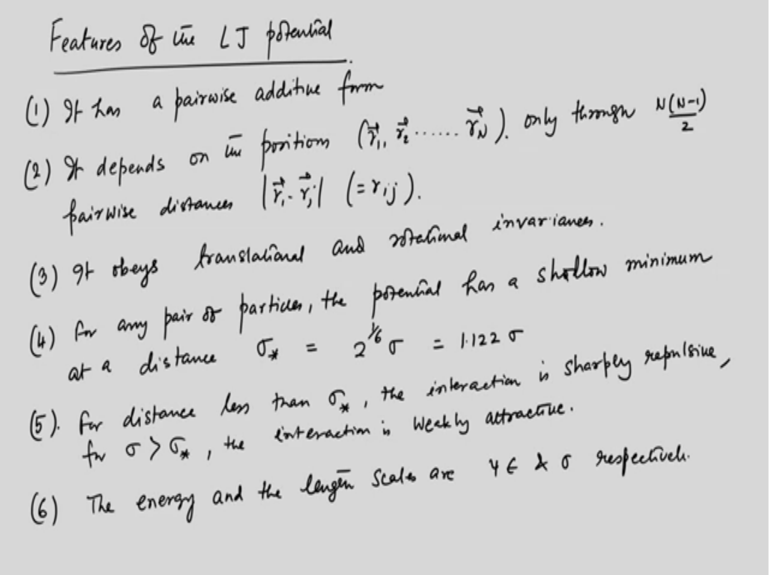

Features of the LJ potential

(1) It has a pairwise additive form

(2) It depends on the positions ($\vec{r}_1, \vec{r}_2 \ldots\ldots \vec{r}_N$). only through $\frac{N(N-1)}{2}$ pairwise distances $|\vec{r}_i - \vec{r}_j|$ $(= r_{ij})$.

(3) It obeys translational and rotational invariances.

(4) For any pair of particles, the potential has a shallow minimum at a distance $\sigma_* = 2^{1/6}\sigma = 1.122\,\sigma$

(5). For distance less than σ_*, the interaction is sharpley repulsive, for $\sigma > \sigma_*$, the interaction is Weekly attractive.

(6) The energy and the length Scales are 4ϵ & σ respectively.

So, let us just write it as LJ, so LJ potential then are chose so it has a pairwise additive form what we mean is the following that there are two sums i and j and this is pairwise additive and so these two additions are referred to as being pairwise additive. So, it depends on all the positions of the particles only through N into N - 1 by 2. So, there are you are summing over really n of those particles a pairwise distance.

So, these are number of pairwise distances ri - rj which is of course equal to r ij okay you know the sum of N numbers is N into N - 1 by 2 and so these are n particles so they this form of the potential depends upon these number of these many number of N into N - 1 by 2 numbers of pairwise distances it obeys translational and rotational invariances okay. For any pair of particles why translational because it is ri - rj and because it is a magnitude even its rotationally invariant okay.

So, even if you rotate the system then it does not matter because it is just the magnitude of the distance. so there is no angle involved etcetera. For any pair of particles the potential has a shallow we have not of course quiet shown it as shallow but it is a shallow minimum at a distance Sigma star which is equal to 2 to the power 1 by 6 Sigma which is equal to 1.122 Sigma. So, this is the equilibrium distance of this so this is called as the equilibrium distance.

And this has a value which is 1.1 to 2 times this of course shown it with a lot of you know over-exaggerated it but this is not too far away from this and it is a very shallow potential which you have shown it as a lot of depth because of to show these distance and all that, 5 is for distances lesser than the interaction is sharply repulsive and for Sigma to be greater than Sigma star the interaction is weakly repulsive sorry weakly attractive.

So very important thing here is that the energy and the length scales are 4 epsilon and Sigma respectively.

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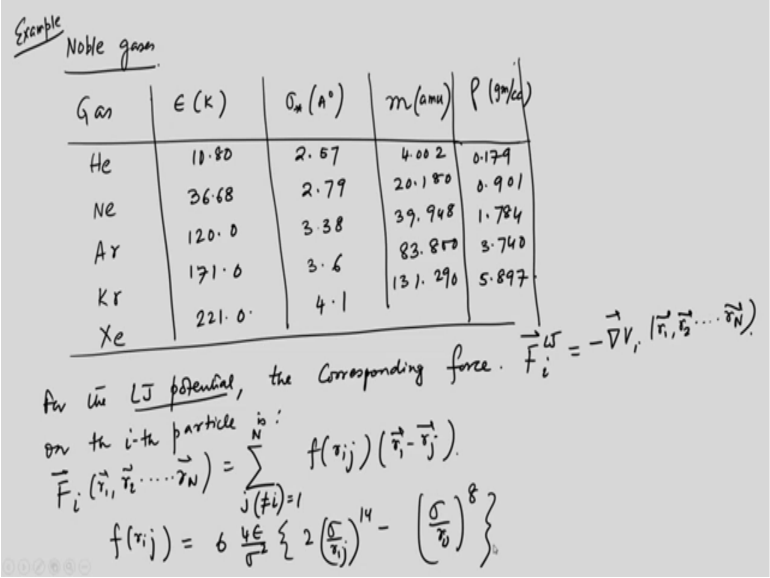

Example

Noble gases.

Gas	ϵ (K)	σ_* (A°)	m (amu)	ρ (gm/cc)
He	10.80	2.57	4.002	0.179
Ne	36.68	2.79	20.180	0.901
Ar	120.0	3.38	39.948	1.784
Kr	171.0	3.6	83.800	3.740
Xe	221.0	4.1	131.290	5.897

For the LJ potential, the corresponding force. $\vec{F}_i^{LJ} = -\vec{\nabla} V_i (\vec{r}_1, \vec{r}_2 \dots \vec{r}_N)$

on the i-th particle is:

$$\vec{F}_i(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) = \sum_{j(\neq i)=1}^{N} f(r_{ij})(\vec{r}_i - \vec{r}_j).$$

$$f(r_{ij}) = 6\,\frac{4\epsilon}{\sigma^2}\left\{2\left(\frac{\sigma}{r_{ij}}\right)^{14} - \left(\frac{\sigma}{r_{ij}}\right)^{8}\right\}$$

So, let us write down certain values for the noble gases this is an example. So, gas, so this is helium, neon, argon, Krypton and xenon okay. This is epsilon in Kelvin this is Sigma star in Angstrom and this is m this is in not in grams this is in mu and finally the density which is in gram per cc okay. So, this is 10.80 this is 36.68 this is 120.0, 171.0, 221.0 where the Sigma stars in angstrom are 2.57, 2.79, 3.38, 3.6, 4.1.

So, it is between 2.52 4.1 in for these cases and the masses are 4.002, 20.180, 39.948, 83.800 and 131.290. Similarly for the densities it is equal to .179 in gram per CC .901 1.984 and 3.740 5.897 okay. So, it is important to you know see that for the Lennard-Jones potential the corresponding force which is given by let us call it f Lj which is equal to - grad Vi or we decided to you know write it as okay so on a given so this is and this is like r 1 r 2 r n on the ith particle is given by so let us write that, so let us write Lj here and the i here.

Let us just drop this Lj for the moment and then write this as r 1 r 2 r n and this is equal to j 0 equal to i, so this is not equal to i can be j which is not equal to i equal to 1 to N f r ij and ri - rj ok where f r ij this is equal to 6 for epsilon by Sigma square 2 Sigma by r ij to the power 14 Sigma by r ij whole to the power 8 and so on okay.

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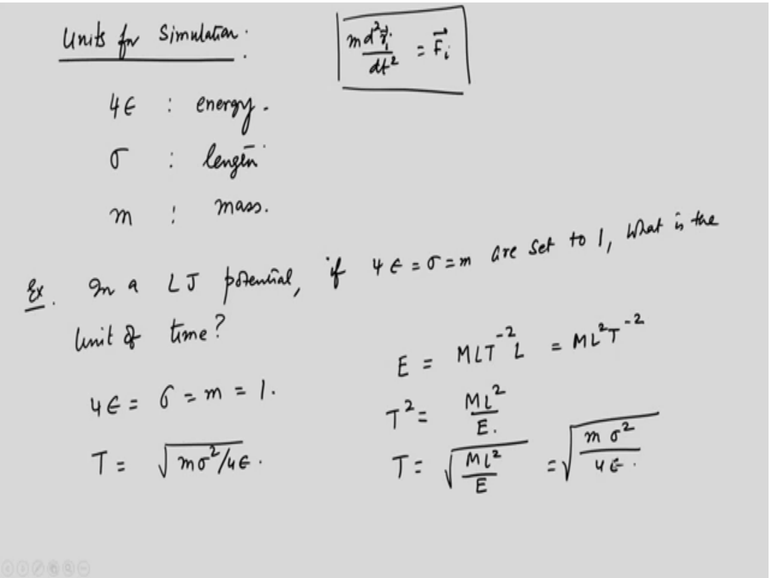

Units for Simulation:

$$\boxed{m\frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i}$$

4ϵ : energy.

σ : length

m : mass.

Ex. In a LJ potential, if $4\epsilon = \sigma = m$ are set to 1, what is the unit of time?

$4\epsilon = \sigma = m = 1.$

$T = \sqrt{m\sigma^2/4\epsilon}.$

$E = MLT^{-2}L = ML^2T^{-2}$

$T^2 = \frac{ML^2}{E}.$

$T = \sqrt{\frac{ML^2}{E}} = \sqrt{\frac{m\sigma^2}{4\epsilon}}.$

So, maybe a note on the units for the simulation so using conventional units for this simulation, a MD simulation is actually inconvenient because one is that the numbers could be so small or the so large that it will introduce difficulty for the computers to handle those numbers. And that is the reason that one has actually come up with natural units for these so we have 4 epsilon is the unit for energy Sigma for length and m for the mass okay.

And remember that this is the equation of motion that we have talked about so this mass is important. And so if you are given a simple problem that what is in a LJ potential if 4 epsilon equal to Sigma equal to m equal to 1 is set so this is are set to 1 what is the unit of time that is the question okay. So, we have 4 Sigma equal to a sorry not for Sigma is 4 epsilon equal to Sigma equal to m equal to one and time is then in root over m Sigma square by 4 epsilon.

Let me tell you how because energy has got say we just talked about potential energy which is MGH so M G is acceleration due to gravity so we will write it as M L T -2 okay because length by you know it is a meter per second square so it is that is the way it is LT -2 and H is again length so we are talking about MGH nevertheless even take 1/2 MV square also does not matter so finally you land up with M L Square t to the power -2 alright.

And we want T so we have a T square here which is equal to ML square by E and so T is equal to root over ML square by E and this is equal to M is M L square is Sigma square and E is for epsilon and that is how it is M Sigma square by 4 epsilon.

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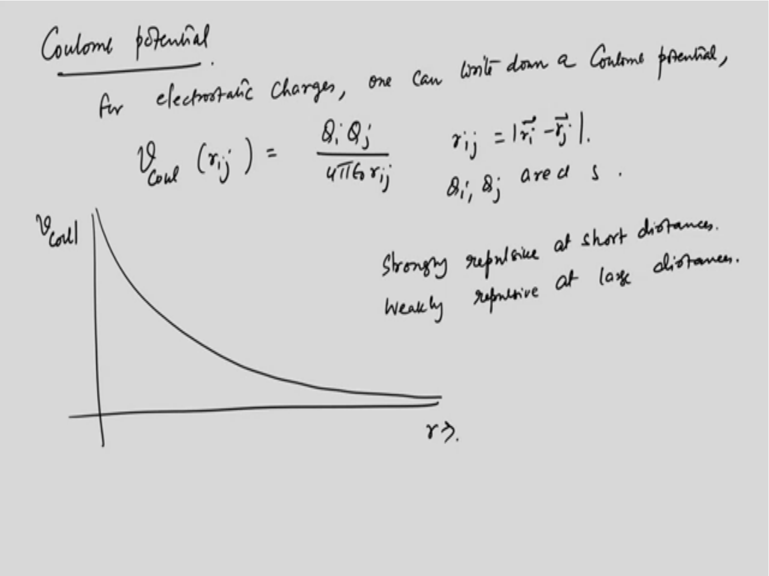

Coulome potential.

for electrostatic Charges, one can write down a Coulome potential,

$$V_{Coul}(r_{ij}) = \frac{Q_i Q_j}{4\pi\epsilon_0 r_{ij}} \qquad r_{ij} = |\vec{r}_i - \vec{r}_j|.$$

Q_i, Q_j are cl s.

Strongly repulsive at short distances.
Weakly repulsive at large distances.

Let us quickly look at two more potential so we have Coulomb potential which we are very familiar with, so if one has charged particles then one for electrostatic charges, we can write down a Coulomb potential which is of the form of the V Coulomb rij again for the pair of particles Qi Qj divided by 4 PI epsilon zero r ij and again r ij it is equal to ri- rj so, again it depends on the distance between the two particles.

And the Qi and QJ are the electrostatic charges. So, this is a different kind of potential than what we have already seen it is of course a false off asymptotically and so this is a V Coulomb ends function of r so it is actually strongly repulsive at short distances and becomes weakly repulsive at large distances.

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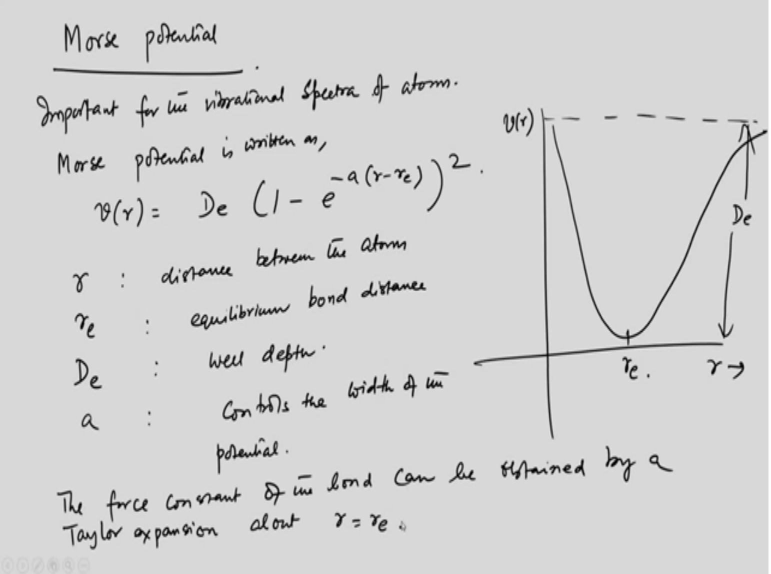

Morse potential.

Important for the vibrational Spectra of atom.

Morse potential is written as,

$$V(r) = D_e \left(1 - e^{-a(r-r_e)}\right)^2.$$

r : distance between the atom
r_e : equilibrium bond distance
D_e : well depth.
a : Controls the width of the potential.

The force constant of the bond can be obtained by a Taylor expansion about $r = r_e$.

And let us also look at another one called as a Morse potential. So, it is important for the vibrational spectra of atoms okay. So what happens is that you can have the vibrational spectra as well from the harmonic oscillator potential. But this is better than the harmonic oscillator potential in terms of having in an harmonic term so there is an N harmonic term being present and Morse potential is written as Vr equal to some De 1 - exponential r - re whole square, so r is the distance between the atoms, re is a equilibrium bond distance, De is the well depth and a controls the width of the potential.

So one can actually talk about so this is your so this is De which appears as a coefficient of this term so this is V of r and versus r so see that there is harmonic part there. So, this is re and also one can get a force constant which is the you know the elastic modulus of the atoms can be obtained by a Tailor expansion about r equal to re okay. So, these are the different potentials that one can talk about for which would generate a force field which gives you an interaction between the particles with their atoms or molecules or something else.

And then one can solve the equations of motion with some conditions and we will see the details of the solution according to certain algorithm in the next discussion.