Computational Chemistry & Classical Molecular Dynamics

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Lecture – 29
Classical Molecular Dynamics – 2, Force Fields and Equations of Motion

Hello and welcome to this lecture on molecular dynamics, as we did last time we started classical molecular dynamics, I will just briefly reintroduce what we did last time. So this lecture will consist of introduction, system studied, potentials, equations of motions, periodic boundary conditions, minimum image convention, classical molecular dynamics and Monte Carlo Algorithms.

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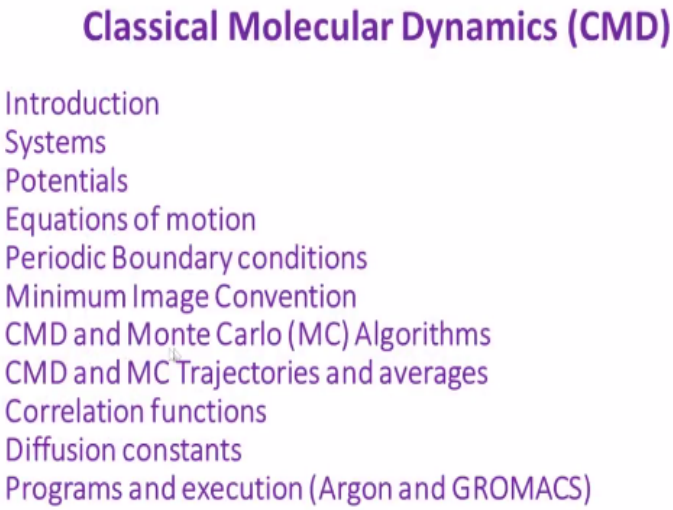

And also classical molecular dynamics and Monte Carlo trajectories and averages over these trajectories. We will also describe correlation functions, diffusion constant and we will execute Argon program first and afterwards we will introduce this public domain software GROMACS. So what are the main features of classical molecular dynamics?

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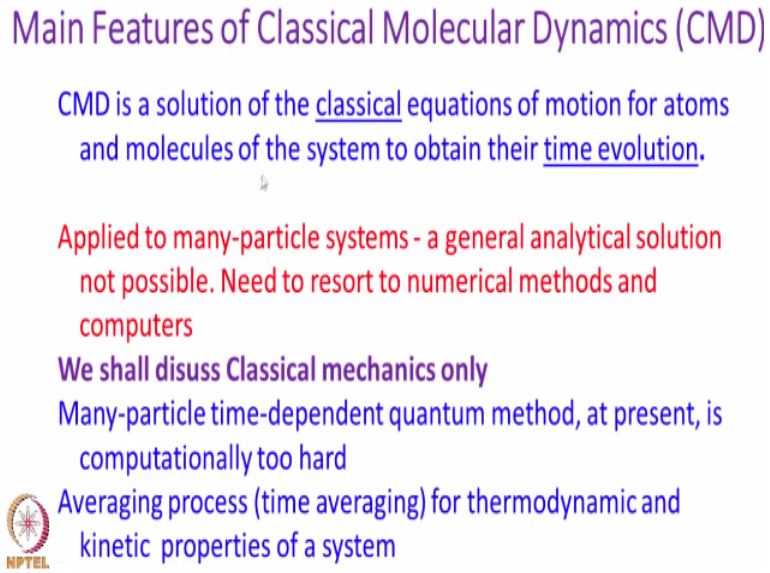

Now classical molecular dynamics is the solution of the classical equations of motion for atoms and molecules of any system to obtain it is time evolution. Now applied to many particle systems a general analytical solution is not possible because there are no formulae for solutions of position and momentum of all the particles as a function of time except for a 2 body problem like the earth and the sun or even a hydrogen atom.

For a hydrogen atom we have a quantum mechanical solution so since there are more than 2 particles we need to resort to numerical methods and of course computers. So for our purpose we will only discuss classical mechanics because the many particle time dependent quantum method at present is computationally very hard. Suppose you have 100 electrons and several nuclei to study them as a function of time is even today extremely difficult.

So after we evolve our system as a function of time we will do time averaging. Time averaging is nothing but averaging over different members of the trajectory that we have generated and once we average we will get thermodynamics and kinetic properties of the system so that is our main goal to do chemistry using classical molecular dynamics. So what are the kind of system that can be studied today? okay.

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Examples of Systems that can be studied by Molecular Dynamics

Simple liquids: atomic systems, ionic systems

Molecular Liquids and their mixtures

Ions and Hydrophobic particles in solvent mixtures

Macromolecules, biopolymers, membrabes

Reactive media

So today we can study simple liquids like atomic systems, ionic systems, ionic solutions, molecular liquids such as water, different solvents for chemistry, mixtures of these solvents. We can study ions and hydrophobic particles in solvent mixtures, macromolecules, biopolymers, membranes. We can even study reaction media of course all this will be with the classical mechanics as the approximation.

So there will be some errors and corrections, but if these corrections are less than 2 to 5% then we have a reasonable solution to the problem at hand, okay. So when we said we are studying liquids, so what is the range of fluids that we can study using classical molecular dynamics okay.

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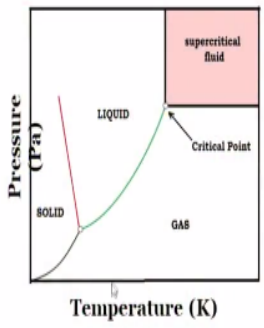
Range of Fluids that can be studied in CMD



For gases, virial coefficients were calculated in the past. They yielded an equation of state. The virial coefficients are integrals over intermolecular interactions.

$PV = nRT + BP + CP^2 + DP^3 + EP^4 +$ .....

So this is the standard phase diagram pressure versus temperature, okay, so extreme left low temperature and high pressure what you have is only a solid, okay. So once you have a solid there is hardly any motion. So you will not be studying any molecular dynamics in this region of space and when you go to very high temperatures, it is a gaseous system and when it is a very high temperature the system will behave closer and closer to an ideal gas.

So we would also not be interested in this because high temperature gaseous systems are of not great interest to chemistry today. So in chemistry what we are interested? We are interested in the liquids, because most reactions occur at room temperature or between 0 and 100. So we are interested in this liquid state and nowadays there is a lot of interest in the supercritical region. Supercritical region is the region where you are above the critical point, above the critical pressure and critical temperature of the system.

So super critical fluids are important because you can do lot of supercritical extraction solvation and movements of liquids are very fast in supercritical region. So this is also important. So most of our interest will be in this region okay. So in the early days that is 1950s, 40s, 60s we were interested in gases and they were interested in virial coefficients. So they were calculated in the past because this was the main activity between 1930 to 1960.

Because they did not have computers, so the only way you can correct the ideal gas equation of state. So this is my ideal gas equation of state PV = nRT. There will be many correction, so this is the first correction B, second correction C, third correction D, fourth correction E. So these are all coefficients which give corrections to my ideal gas equation of state and all these coefficients can be obtained in terms of intermolecular interactions.

So this entire classical molecular dynamics will be driven by these intermolecular interactions. So in the next few slides we will see what kind of intermolecular interactions are there. So once intermolecular interactions are known one can get the virial coefficients. So for many years they would study virial coefficients have different gases, but this virial coefficient expansion is not of use to liquids.

Because if I want to study a liquid I have to go to very high order of expansion, so because at liquids it is very non-ideal system, so you cannot explain equation of state for a liquid using this virial equation of state. So you have to go beyond this and that is why classical molecular

dynamics has become extremely popular because you can do corrections to ideality to very high orders in density.

So now let us look at some examples of systems under study. I am just giving some arbitrary examples; I am giving this example because this is of interest to me. So nowadays you know that nanochemistry has become very popular.

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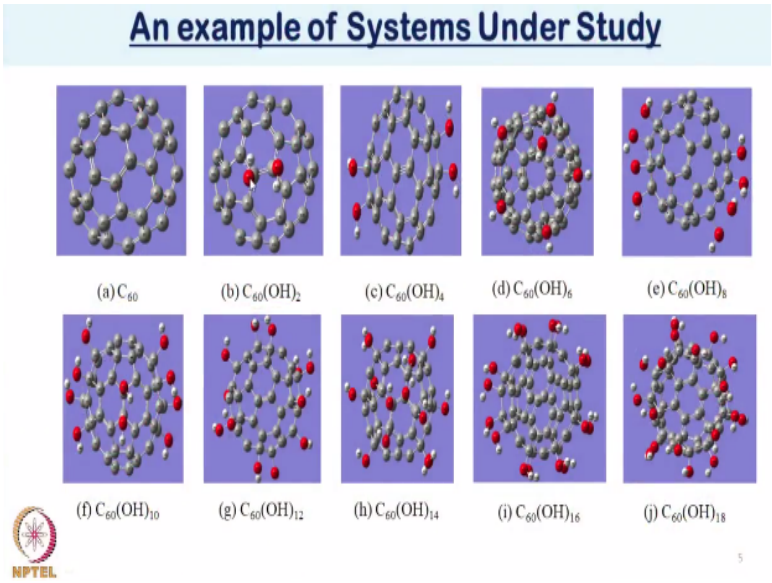

You have fullerene, fullerols with 2 carbons on which there are OH groups. This is a fullerol with 4 OH groups, fullerol with 6 OH groups. So these are all fullerols and these fullerols in different liquids can be studied using molecular dynamics and you get very interesting properties. One of the interest in this system was fullerols below 14 OH are not soluble in water, but 14 and beyond are soluble in water.

So can we predict this solubility using molecular dynamics, that was the problem that was studied and it turns out that by doing this calculations we can show that the free energy of solvation is negative beyond OH = 14 and free energy of solvation is positive for number of OH groups less than 14. So thus this very elementary technique of classical molecular dynamics can be used to predict many useful properties of these liquid systems.

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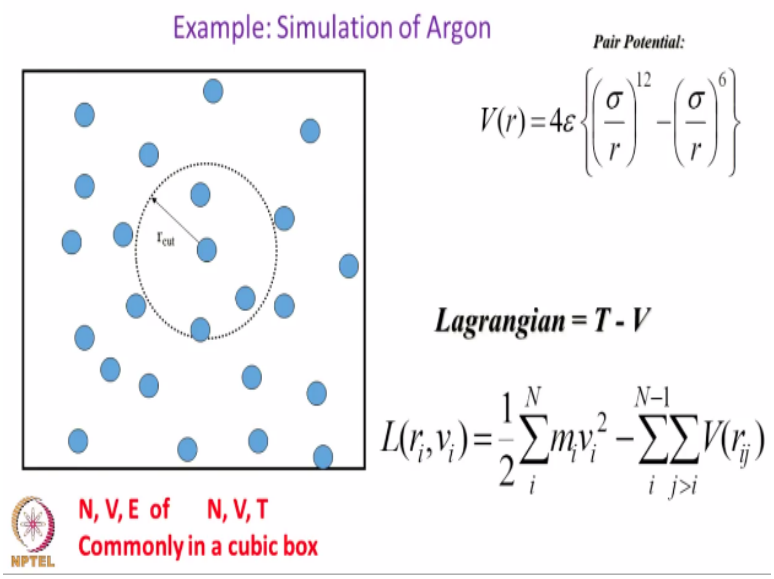

So now we will go to a very simple system, so this is simulation of argon. So you know that argon is generally a gas at room temperature, but at low temperatures you can get it as a liquid state and now we want to study the molecular dynamics of liquid argon. Now why liquid argon because all these particles are spherical because argon is monoatomic system so all the particles are spherical.

So if I have a good estimate of the size of this argon atom and if I know the interaction between 2 argon atoms, if I can find out a good formula for interaction then I have a case for doing dynamics using this potential. So one of the oldest potentials is this Lennard-Jones potential, very old and very well known. So this potential consists of an attractive term sigma/r to the 6th power.

This is an attractive term, now often we use r to the 6th, 1/r to the 6 as an attractive term because this is the dispersion interaction. All systems, all molecular systems when the distance between molecule is very large, so the dominant interaction at large distance is this dispersion interaction 1/r to the 6, so this is there for every system. So this is a very universal interaction, dispersion interaction is very universal.

Even if there are no charges between atoms you will always have a dispersion interaction and it is because of this dispersion interaction that you have situation where a gas turns into a liquid. If there were no dispersion interaction there will be no liquid state and now when the distance between molecules is small. So you know that when 2 molecules come very near each other so they cannot come less than some short distance.

So there is a repulsion term, so a standard practise is to use sigma/r to the 12th power as a repulsion, the main reason is that sigma/r to the 6 is my attraction, if I just square it. I will get sigma/r to the 12. So computationally it is very easy to calculate this sigma/r to the 12, therefore we use r to the 12 potential. In real life the potential is not sigma/r to the 12, but computationally it is very easy and it gives fairly good results so we continue to use this repulsion term.

So now once I have this interaction energy, this is a potential between 2 particles, between every 2 particles we will have this potential term. So when there are n particles each one will interact with the remaining n-1. So that is how we write this particular Lagrangian. Now Lagrangian is a term in classical statistical mechanics. So what a Lagrangian means that it is nothing but the kinetic energy of my system minus the potential energy.

So this is the Lagrangian, okay, so how do I read the Lagrangian as a collection of particles suppose this Lagrangian for ri and vi, so ri goes from 1, 2, 3, 4, all the particles in the system, so it goes from 1 to n, vi also each particle will have velocities, so there will be Lagrangian which depends on positions and velocities, so the formula is T –V, so how do I write it, 1/2 of i going from 1 to n mi vi square, this is the kinetic energy of all the particles.

And the interaction energy, so what is the interaction energy of n particles, first one interacts with n-1, second one will not only interact with the first one, will interact with all the remaining n-2. So what I am saying here, so since the first particle interacts with the second particle when I count the interaction for the second particle I will not count interaction between 2 and 1 again.

So that is why in this summation i goes from 1 to n-1 and j is always > i. So what does it do, it ensures that the total number of terms is n * n-1/2, so that is the total number of interactions between particles. So if I count 1 and 2 once I will not count 2 and 1 again. So now there are other ways of writing it, if you double count then you have to divide by factor of 2. So suppose I say i going from 1 to n, j going from 1 to n and i not equal to j, then I have to divide by 2 so that you get exactly 1/2 * n * n-1, so this is my Lagrangian.

So now what I have shown here, I have shown a cubic box actually it is a rectangle, but in real life very often we use a cubic box for simulations, why a cubic box, it is very easy to set up the box length. Because once I know the length in one dimension all 3 are the same. So I can do simulation in a cubic box far more easily but it does not mean you can do simulations only for a cubic box.

You can do simulations for different size, different types of boxes okay. So now there are 2 common methods of this simulation, one would be where I fix the number of particles in my system, the volume of my system and the energy. So this is one kind of simulation, which is commonly the molecular dynamic simulation, but in other systems or other situations I want to keep the number of particles, the volume and the temperature fixed.

So this is more like a Monte Carlo simulation which we will describe after we complete our molecular dynamics discussion.

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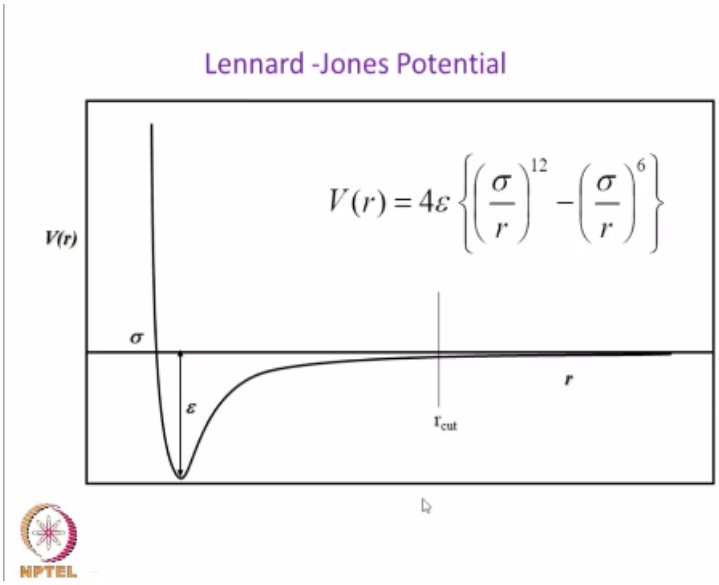

So now let us see this Lennard-Jones potential once again, so this Lennard-Jones potential consist of a repulsive term, you look at this repulsive term then it goes through a minimum then there is an attraction. At long distances the potential is always attractive, so this is my interaction. Now suppose you want to find out at what distance this derivative goes to 0. See this potential goes to 0 at this particular value.

So you can find that value of 0 by setting dV/dr = 0 and then you will find that r should be = 2 to the 1/6th * sigma to get the minimum value. You can do this calculation. Find out the

distance at which the potential goes to 0. Now what is sigma now? Sigma is the distance where the potential is 0. You see that when sigma = r so this is sigma/r will be 1 so 1 to the 12 – 1 to the 12 is 0.

So when sigma = r, the potential is 0. So for all distances less than sigma the potential is repulsive and for all distances greater than sigma the potential is attractive. So that is the meaning of this sigma and very often you can treat this sigma as some kind of a contact distance. So you may be familiar with this what is called a van der Waals radius. People want to talk of a distance at which 2 molecules almost touch each other, okay, that is called a van der Waals distance.

So sigma approximately represents the van der Waals distance for that object.

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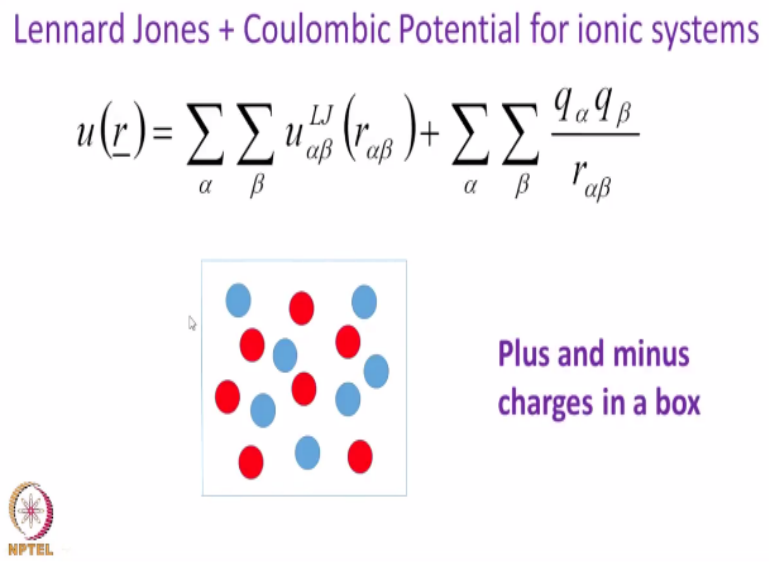

So now we considered only the Lennard Jones interaction. So this interaction is for systems for which there is no electrical charge, but you know that in real life molecules have positive and negative charges. So what do you do when there are positive and negative charges, these charges interact with each other as Lennard Jones particles because there will always be a very strong repulsion when the molecules come very close to each other.

And when the molecules are very far there is always this dispersion interaction. So this is universal, the long range repulsion, long range attraction, 1/r6 is universal, but if there are charges in addition to this Lennard Jones interaction there will be interaction due to the

charges on the sides. So what I have shown here the red colours let us say they are positive and blue colours let us say they are negative.

So there will be interaction between the plus and minus charges as well as the ++ charges okay. So now what is the total electrostatic interaction, it is interaction between all pairs of charges and this 1/r is my coulomb term. So I sum over all charges alpha going from 1 to 6 as well as, there will be between all pairs of interactions okay. So this should be between all pairs of interaction.

So finally each charge will interact with the remaining n-1 charges. So again there will be n-n/2 term in this case also. So this is the case of a system where there are electrostatic charges.

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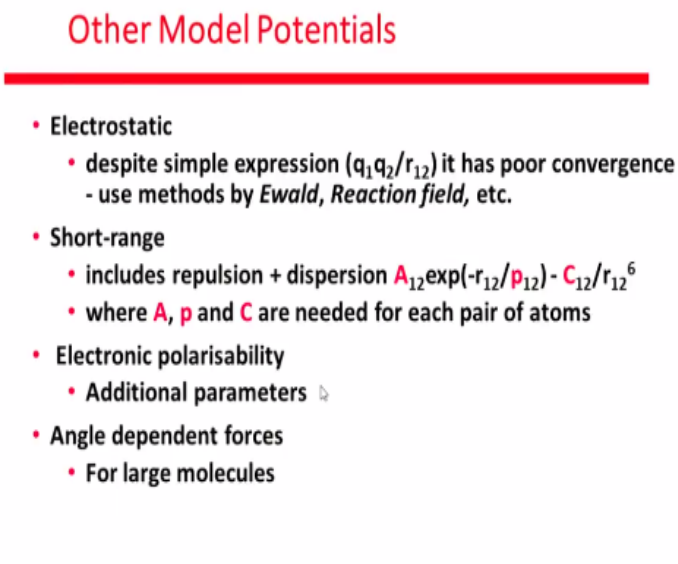

So now in addition to the electrostatic interactions so maybe I will comment on this because, the electrostatic interaction is q1 q2/r inside that box, but you know that if there is a box such as this, this box will not correspond to a liquid and we want the box to have properties of a liquid. So what is the way to make sure that it behaves like a liquid. I will surround this box on all sides by similar boxes.

So I will come to that convention just in a little while, so if this box is surrounded by many boxes like that. So each box has to interact with other boxes and you know that this Coulomb interaction 1/r is a very long range interaction. So that is if the distance between 2 particles is 1 angstrom the interaction will be of the order of 331 kilojoules per mole. If the distance is 10 angstrom it is 31 kilojoules per mole.

If the distance is 100 angstrom it is still 3 kilo calories per mole and 3 kilo calories per mole is a very large number, it is almost of the order of a hydrogen bond interaction. So when you have coulombic interaction. So it is not possible to neglect the interaction of other boxes that is why you have systems like this Ewald summation, there is something called a reaction filed.

I will not discuss this in great detail, but you will have occasion to use this when you do the GROMAC simulation because there you have to give parameters for the evolved, parameters for the reaction filed. So these will become important when you do more advanced calculation beyond liquid Argon. So now in addition to that sigma/r to the 12 so that was repulsion earlier okay, but there are many situations where the repulsion is explained in terms of an exponential repulsion, not a 1/r to the 12, so this is more realistic.

So in many situations the repulsion will be exponential repulsion, e to the –r12/some parameter minus this is my standard dispersion interaction. So this A, p and C are needed for each pair of atoms. So this is another way to calculate my interaction, this is not Lennard-Jones, it is an exponential repulsion and a normal dispersion interaction at long distance. So now in addition to this suppose a molecule has polarizability.

So polarizability means I have an object some other charge comes near this object then the entire charge gets redistributed. So in the earlier models when we studied plus, minus interaction we treat them as not polarizable, so that is the charge will not change at all, but very large objects like iodine, benzene. So when you bring a charge near these objects the charge redistribution occurs in those.

So polarizability becomes important, so then you have to have additional parameters then you have many situations where the forces depend on angles. So for large molecules there will be angle dependent forces and we will also discuss few examples of angle dependent forces.

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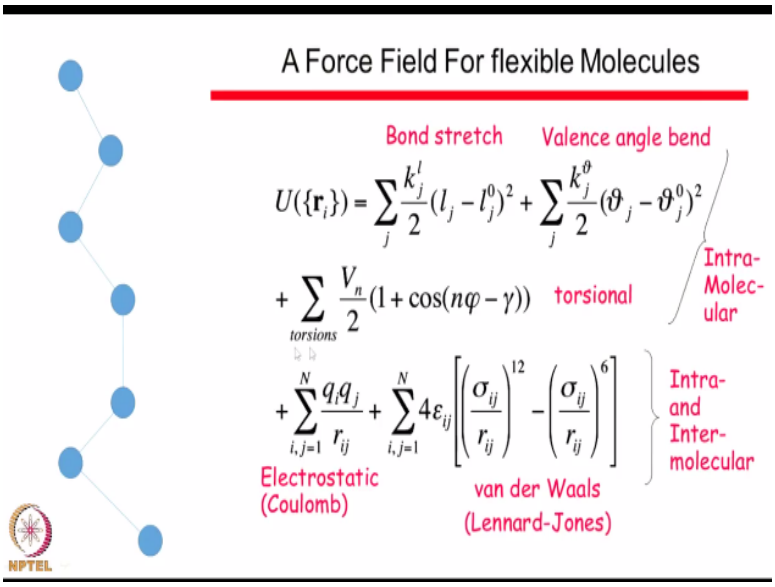

So now this is an example of a force field, so in all our simulations in the future this force field is the term which you will hear again and again. So what is this force field? Force filed is all the set of interactions, which are defined for my system. So now let me consider a flexible molecule, think of this flexible molecule. There are many atoms, there are many bonds connecting those atoms.

Now I want to define the interaction between these objects, so these interactions now will not only depend on inter particle distance between adjacent particles, but it will also depend on next adjacent particle and the third adjacent particle because there could be torsion, so you know you can bend this molecule across these 3 atoms, the whole thing can be bent, twisted. So there will be many interactions.

So I will just indicate a few of these interactions here. The first would be a bond stretch, what is the meaning of bond stretch, suppose in polymers or any molecule the bond length is never going to be exactly the same in all situation, the bond keeps on stretching or compressing between an average bond length. So this l0 is my average distance between the particles and in real life there is stretching as well as compression.

So there will be a term, it is like a harmonic oscillator, each bond can behave like a harmonic oscillator. So I have first term for bond stretch. So then there could be an angle bend. Suppose I have this molecule 1, 2 ,3, so this angle can bend that is suppose I have some angle here that angle can become larger and smaller. So there will be a term for valence angle bend. So this is my term for that angle bend.

So this also is written as a harmonic oscillator. What is a harmonic oscillator? Constant times the difference squared, so this is my harmonic. So in addition to this bend there will be a torsion, what is the meaning of torsion? Three is a bond 1, 2, 3 and there is a bond 2, 3, 4. So the 2, 3, 4 will rotate around 1, 2, 3, so that is my torsion. So the torsion also will depend when there is more than 3 atoms.

So these are all torsional interactions between the atoms in this. So between 1 and 2 there is no torsion, between 1, 2 and 2, 3 there is no torsion because it is only an angle bend, but it is 1, 2, 3 versus 2, 3, 4 there will be a torsion. So these are all torsional interactions and of course in addition to this intramolecular forces there will also be forces depending on the sites. Remember if these all have charges; each charge will interact with other charge.

This will be interaction between one molecule and the other, this will be van der Waals forces just as the earlier case okay. So this will be intra as well as intermolecular because. This particular 1, 2 will also interact with n and n-1. Suppose this n and n-1 come close to it, then again you will have Lennard-Jones interaction between that okay, between adjacent atoms also there is Lennard-Jones interaction and between 1 and n-1 there is also Lennard-Jones interaction and also this molecule will interact with the remaining molecules.

So there will be interactions between pairs of molecules as well. So we have to consider intra and intermolecular interactions in every situation.

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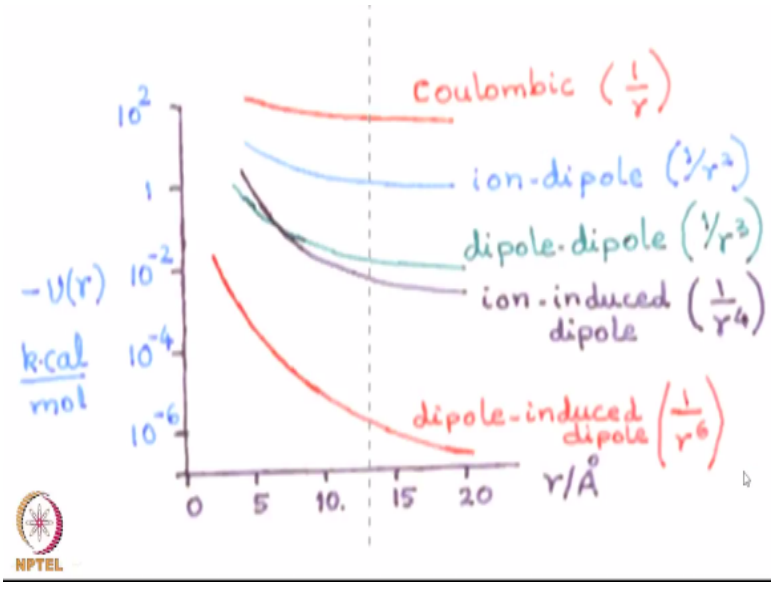

So this particular graph really tells you what is the nature of these interactions okay. So the coulomb interaction varies very slowly with distance you know, it varies, this is the logarithmic plot, I mean what is the meaning of a logarithmic plot, this is 10 raise to 2 then 1, 10 raise to -2, 10 raise to -4, 10 raise to -6. So this is changing very large, very significantly, okay, this is a logarithmic plot whereas this is a linear plot and angstroms 5, 10, 15, 20.

So this is a linear plot, so this is a logarithmic plot this side. So you see that coulombic interaction varies very slowly, ion-dipole varies as 1/r square, dipole-dipole varies as 1/r cube, ion induced dipole 1/r fourth, dipole-induced dipole okay, as well as your Lennard-Jones they all vary as 1/6. So you will see that these interactions like coulombic they vary very slowly. So you have to be very careful when I cut off these interactions.

Because whenever I have a box of some length and if I consider only the interactions inside that box what will happen to the interaction beyond that box? Coulomb I cannot neglect, whereas these others like induced dipole, dipole-induced dipole they are very weak. So I can neglect, okay, so this gives you a picture of interaction at a function of distance.

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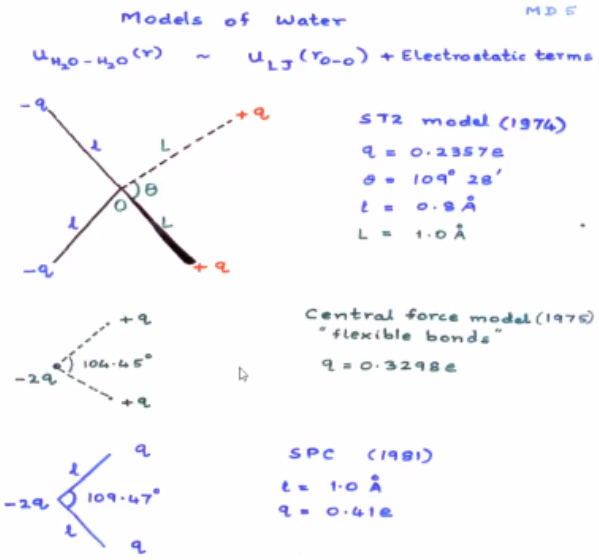

So now I will give you an example of a model of water. Water has been one of the objects which has been studied for a very large number of years because many reactions do occur in water, entire life exist because of water. So people have studied many models of water. One of the earliest models of water was called an ST2 model 1974, so there will be 4 charges okay, tetrahedral charges okay.

So theta = 109, that means it is a tetrahedral situation, there are 4 charges –q, -q, +q, +q, and a charge on the central oxygen. So this is a tetrahedral model of water. Then there is another model called a central force model. What is the meaning of a central force model there is a -2q charge on oxygen, +q charge on the hydrogens and now the bind angle is 104.45 okay?

So this is a central force model where I allow the bonds to be flexible, in this ST2 model the bond length does not change at all. Whereas in the central force model the bond lengths change as a function of simulation. As I simulate the bond length can change and even simpler model 1981, it is called an SPC model, there is -2q charge on oxygen, q and q on the hydrogen.

There is bond length, bond length is given by 1 angstrom and the bond angle is 109.47. Now when we have all these different models natural question will be which is a good model, okay, there really is no clear answer. So one way to approach this problem would be you do the complete simulation using these different models and see which model explains properties better okay and it may so happen that some properties are explained very well by SPC model. Some other properties are explained very well by ST2 model.

So this is really a very difficult task. So to understand chemistry properly you do have to make simulations with different models and come to a conclusion using all the models you know reality is really a combination of several models, you cannot say that one model is the best and another model is very poor, okay. So let me summarize briefly what we did, we discussed different intermolecular forces okay.

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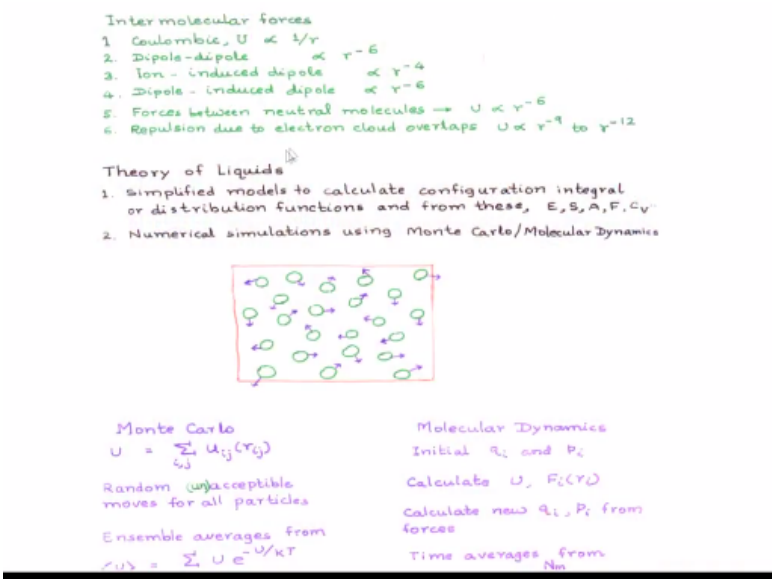

Then we also discussed a box and in that box I allowed particles to move okay, particles to move okay, then we studied, we discussed molecular dynamics in great detail of course, I did not discuss the algorithm. We also have a Monte Carlo simulation; I shall come to that after I finish molecular dynamics.

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$$m_i a_i = F_i$$

$$F_i = \sum_{j \neq i}^{N} f_{ij}$$

Newton's Equations of Motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v_i^{\alpha}}\right) = \frac{\partial L}{\partial r_i^{\alpha}}$$

Lagrange's Equations of motion

$$f_{ij} = -\nabla_i V(r_{ij}) = 24\frac{\varepsilon}{r_{ij}^2}\left\{2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\} r_{ij}$$

Lennard-Jones forces

Now before I conclude let us see what are the equations of motion for my dynamics. So you know that the Newton's laws are force = mass * acceleration and what is the force on each particle? Force on each particle is the force on that particle due to all the remaining particles okay, j not equal to i, i going from 1 to n, Fij, so force on each particle is the sum of the forces due to all the remaining particles and just as you have Newton's laws an equivalent form of equations of motion is the Lagrange's equations.

So this Lagrange's equation remember I have already defined what is L, L has been defined as T-V and Lagrange's equations d/dt of dL/dv alpha = dL/dr alpha. So you can take the Lagrangian and take these derivatives and see that the Lagrangian's equations are exactly equivalent to Newton's laws. Now why there are Lagrangian's equation in addition to newton's laws because for many situations using this Lagrange equation is more convenient than using the Newton's laws okay, especially when there are constraints.

Remember we have a bond length which is fixed, we have a bond angle that is fixed. So whenever we have constraints people use Lagrange equation. Now how do I calculate force between particle i and j. So this force is minus gradient of the potential. If I want the force on particle i this is want I want. I want the force on particle i due to particle j, so that is the derivate, derivate of the potential Vrij.

So how do I take the derivative, take the Lennard-Jones potential and take the derivative with respect to ri, so this is what I get. When I take the derivative of the Lennard-Jones potential what I get is 24 epsilon/rij square * 2 * sigma/rij to the 12 – sigma/rij to the 6 multiplied by the vector, see this rij it is a bold phase, it is a vector between i and j, unit vector. So the potential now is, this is the vector, not a unit vector, this is a vector between i and j because force is always a vector okay.

So this is the formula for the vector, I urge you to verify this formula, so in the next lecture I will continue different aspects of molecular dynamics. I will close this lecture at this point, thank you.