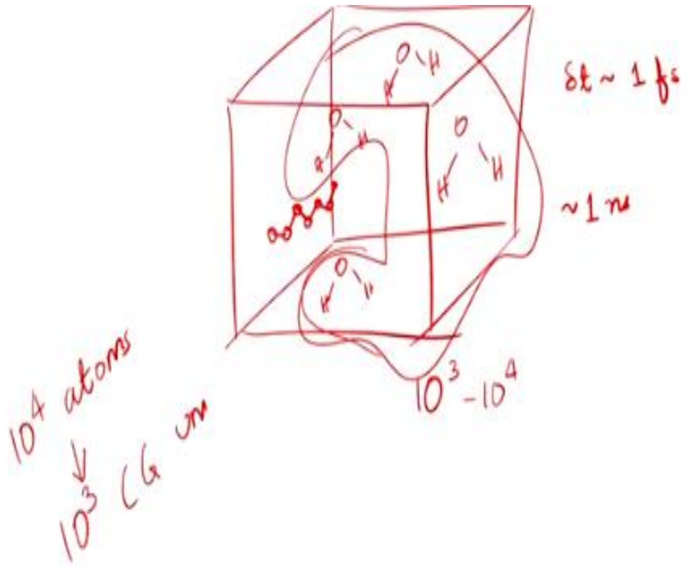
Advanced Thermodynamics and Molecular Simulations

Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture – 56
Tackling Time Scale Issues (Continued); Non-equilibrium Molecular Dynamics; Mesoscale Simulations: Langevin Dynamics and Brownian Dynamics, Kinetic Monte Carlo Simulations; Dissipative Particle Dynamics

Hello all of you, so in the last week we discussed the free energy calculations and towards the end of the last lecture I discussed briefly about the time Scales Issues when some methods that fall in this category particularly the methods come under the rear Events Simulations, non-equilibrium Simulations, and then finally mesoscale simulations. Before we come to those methods I will briefly touch upon what the time scale issues really is and then later on we will discuss the Langevin dynamics and Brownian Dynamic Simulations after that.

(Refer Slide Time: 01:03)



So, when we are doing typical Molecular Dynamic Simulations let us say of an atomic system the problem is that the time step that we can take is typically quite limited and the reason why it is so small is because we are trying to probe the motion of the molecules actually within the molecules and in that case we are pretty much limited by the vibration of the bonds the angle of the bonds and all these things that are happening at very, very small time scale and therefore if I really want to capture the true dynamics of a molecules we really have to work at a time scale or choose a time step such that it captures these effects the bond vibration, angle vibration the conformation changes because of that and so on and that really means that in typical Molecular Dynamic Simulations all we could to go is the times of the order of say 1 nanosecond because the δt is so small that we cannot really go very long times.

The second issue is that if I am looking at the liquid systems in most cases we have plenty of solvent molecules. Let us say while if I look at a solution of any compound we are basically simulating most of the time the solvent molecules as opposed to the compound itself, because the compound is present in for example water and at any significant density we will have quite a large number of water molecules to work with in typically the water molecules are being simulated are 10^3- 10^4 times larger than the molecules that we are interested in fact much more for dilute solutions and that really means that not only I am similar to the molecule. I am simulating plenty of solvent molecules in there.

Then we are interested in the equilibrium behavior and therefore we have to simulate long enough that we can get to the equilibrium behavior in Monte Carlo there can be some smarter ways where you can introduce dynamics that get us faster to equilibrium, but in molecular dynamics we have to follow the true dynamics of the system and that means that we are further limited in the equilibrium approach because it will take some time to achieve equilibrium and for that time we have to simulate the motion of all the molecules and we have plenty of them.

So, one of the ways that we can think about addressing this problem is why not simply take all the solvent molecules out of the box? We just consider the compound that is being considered because ultimately we are interested in that only that we could have done if the solvent was not playing any role between the interactions between the compounding question typically solvent mediates the interaction between the compound that is one thing that solvent does but solvent also basically have interactions with itself that contributes to the behavior of the entire solution and therefore we cannot simply remove the solvent L together in most of the cases and when we remove that the interactions are not very well captured.

Then what we can do is we can remove it at the expense of adding in some kind of an effective interaction that basically somehow accounts for the effects of removed solvent and this is where the Langevin Dynamics method fits in the essentially removes solvent but add some extra interactions that takes care of the solvent that has been removed or we can use what is known as Coarse Graining in which we can try to represent molecules into like smaller units then compare to the number of atoms in the molecules.

Let us say for example if you have 10^4 atoms I can say 10 of them form a CG unit or a Coarse Grain Unit. So, in sense you are simulating 10^3 CG units only, but of course now each of the each of the CG units contain 10 atoms and we are not simulating the atoms themselves. So, we have lost some resolution we are not looking at what is happening within those 10 atoms we are looking at what is happening between the CG units not the atoms itself.

So, not only we have lost the resolution, but also we have to somehow again get the effect of the atoms the interaction between atoms in our description of the Coarse Graining Process and that is not so trivial again and finally in many cases equilibrium is not what we are interested in so Molecular Dynamics is ultimately capturing the true dynamics.

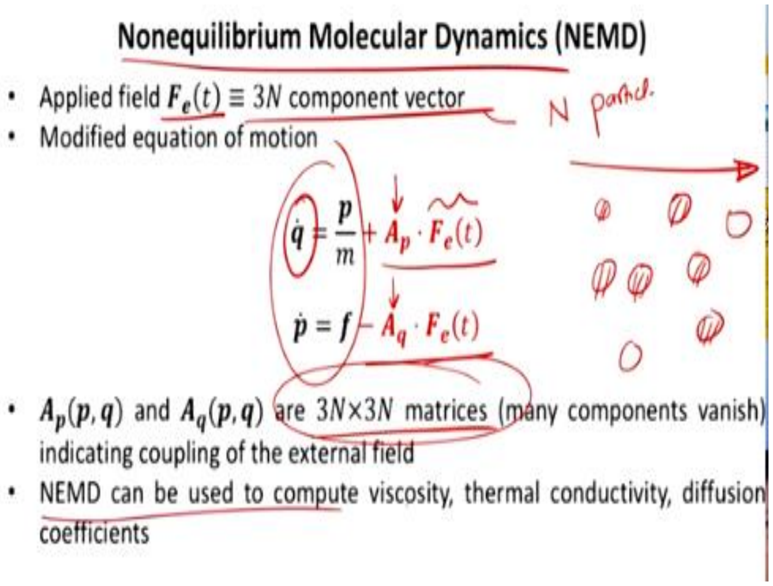
So, why not simulated for phenomena where there is no equilibrium let us say for example we have some external feel acting on the system and in that case clearly we can use Molecular Dynamics at least intuitively because Molecular Dynamics is in principle capturing the true dynamics of a system. The only problem is that when we use Thermostat or Barrostat that it is typical that the methods are particular to the equilibrium condition only and therefore in any case of an applied field we have to revise in the Molecular Dynamics methods to account for the non- equilibrium behavior that we are interested.

Having said that when we argue that when I start my simulations and until I reach equilibrium I do have an non-equilibrium part of my simulation but the problem is that since the initial state is something that we do not know that non-equilibrium part is something that we cannot assign much meaning to because that is based on the initial state that we have chosen, without the knowledge of the actual system configuration in most cases it is arbitrary.

So, although we have capturing an equilibrium behavior until we reach equilibrium that is not the kind of non-equilibrium behavior, we are typically interested in we are interested in non-equilibrium behavior in the presence of an applied field starting from unknown initial state and that is where the trouble comes in. So, basically the class of methods that will discuss try to look at these problems.

Where, time scale can be an issue and we really want to simulate the effect of applied field and the first method that I will discuss is category is known as the non-equilibrium molecular dynamics I will not try to go to the mathematical details of these methods, but I will like to just highlight what methods are out there and all of these requires quite a bit of reading to learn about the methods and to apply to practice they are quite detailed methods. Many of these methods are still developing and better approaches are coming in to improve these methods so it is an ongoing research I would say instead of being like a standard tools out there and many of these methods are not even implemented inside standard software so you may have to program with yourself and at least in the case of course graining the methods are not robust enough to be applied to any system that you want to stimulate.

(Refer Slide Time: 09:31)



Nonequilibrium Molecular Dynamics (NEMD)

- Applied field $F_e(t) \equiv 3N$ component vector
- Modified equation of motion

$$\dot{q} = \frac{p}{m} + A_p \cdot F_e(t)$$

$$\dot{p} = f - A_q \cdot F_e(t)$$

- $A_p(p,q)$ and $A_q(p,q)$ are $3N \times 3N$ matrices (many components vanish) indicating coupling of the external field
- NEMD can be used to compute viscosity, thermal conductivity, diffusion coefficients

So, the first class of methods is non-equilibrium molecular dynamics. So, in this case, we are interested in an external field that is being applied on the system let us say I call it by a vector F_e (t) and this is a 3N component vector corresponding to an n particle system so every particle can be experiencing not only the force due to other particles, but an applied force coming from the external field and that force will have 3 components for every particle so in total the course is going to have 3N components.

So, even though for example the electric field is going to be constant the actual force because of the electric field can be different on different particles in the system. Similarly for Magnetic Field or any other field that you can think of because it also depends on the properties of those particles. If it is completely passive that means the particles do not affect the forces in that case this becomes somewhat easy the force becomes constant but if it is somewhat active that means that if particles are playing a role on the forces acting on them in that case it becomes quite complicated, because the force is depend on the system configuration the coordinates of the particle and so on so forth.

Nonetheless we can start with the equation of motion that we had the classical equation of motion that we used for equilibrium molecular dynamics and add extra terms in the q dot equation and p dot equation.

$$\dot{q} = \frac{p}{m} + A_p \, .F_e(t)$$
$$\dot{p} = f - A_q . F_e(t)$$

The q dot for the derivative of the generalized coordinates that is the momenta, and p dot that is momenta derivatives. So, that is the acceleration really and in this case A_p and A_q are going to be 3N times 3N matrices, because F_e is a 3N matrix q_n is a 3N vector because you have 3 coordinates for every particle multiplied by n times and A_p and A_q essentially are telling me how the filled is coupling with the particle in the sense that how the position and momenta of the particle is coupled with the external field in the case as I said if it is a passive field that will be probably a constant but in other cases it has to be somewhat complicated.

But in most cases it is not really a very large matrix because many of the terms are 0 so we have a work with only the terms that are none 0 and that is the particular matrix so in that cases this matrices become somewhat tractable so as to speak.

So, using the idea of non-equilibrium molecular dynamics we can for example compute the viscosity the thermal conductivity and diffusion coefficient by doing simulations that somehow simulates the transfer processors because as we study in chemical engineering there are three kinds of processes the momentum transfer in which the variable that we work with is the viscosity then we have heat transfer particularly the conductive heat transfer where the variable we work with is thermal conductivity and then finally we look at mass transfer where the variable for diffusing mass transfer is the diffusion coefficient.

So, we can perform numerical experiments where in we have some momentum transport going on and measure the viscosity we can perform a heat transfer experiment numerically and compute thermal conductivity and we can perform the mass transfer experiments numerically in which we can compute the diffusion coefficient and in most cases we are going to be non-equilibrium simulations because viscosity is a property that is defined in the dynamic manner thermal conductivity is also dynamic property diffusion coefficient is defined at equilibrium in principle because at equilibrium also we have diffusion of molecules, but that is not always same as the diffusion coefficient out of equilibrium and therefore that can be also computed in a non-equilibrium simulation.

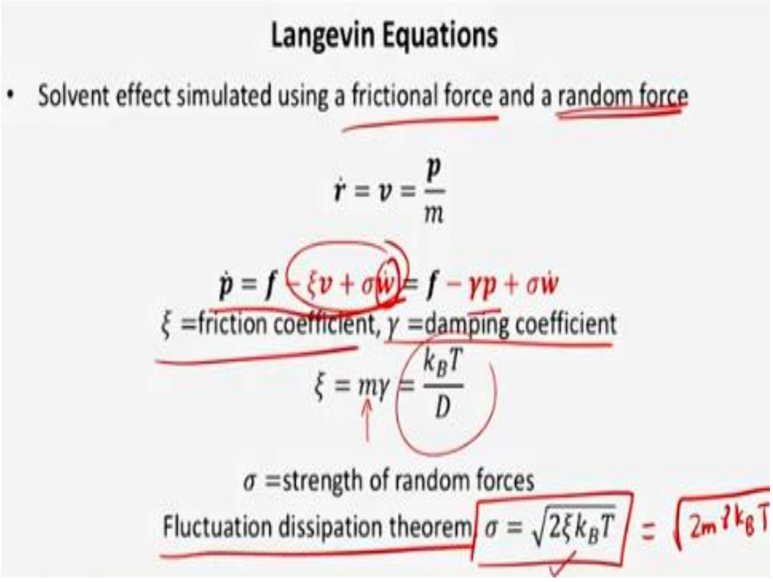
(Refer Slide Time: 14:07)

Mesoscale Simulations

- Reduce degree of freedom
  - Remove solvent
  - Coarse-Graining

The next class of methods are the mesoscale simulation methods. And here as I said the goal is to remove the degree of freedom and that we can do either by removing solvent or by doing some kind of coarse grain.

(Refer Slide Time: 14:22)



Langevin Equations

- Solvent effect simulated using a frictional force and a random force

$$\dot{r} = v = \frac{p}{m}$$

$$\dot{p} = f - \xi v + \sigma \dot{w} = f - \gamma p + \sigma \dot{w}$$

ξ =friction coefficient, γ =damping coefficient

$$\xi = m\gamma = \frac{k_B T}{D}$$

σ =strength of random forces

Fluctuation dissipation theorem $\boxed{\sigma = \sqrt{2\xi k_B T}} = \sqrt{2m\gamma k_B T}$

So, the first method in the category is the Langevin Equation that inhere that pretty much remove all the solvent from the system and we simulate the effect of solvent by adding two forces in the equation of motion, one is a frictional force or a drag force and other is a random force or the thermal energy of the system.

$$\dot{r} = v = \frac{p}{m}$$

$$\dot{p} = f - \zeta \mathrm{v} + \sigma \dot{\mathrm{w}} = f - \gamma p + \sigma \dot{w}$$

And these forces appear in the p dot equation as the red guys in here, the first is the frictional force that has a ζ that is a friction coefficient and the velocity of the particle and a σ that is the strength of random force and a random force term w dot that is the time derivative of a random force which is defined using what is known as a wiener process and γ is the damping coefficient that is basically related to ζ so we can write this equation in terms of like ζv or γp where in one case I am keeping the velocity and in the other case I am keeping the momentum in the frictional force term and therefore is ζ basically mass times γ so there are two ways of righting the equation for the frictional force term. And that particular term is defined as k_BT thermal energy divided by the diffusion coefficient as even in here.

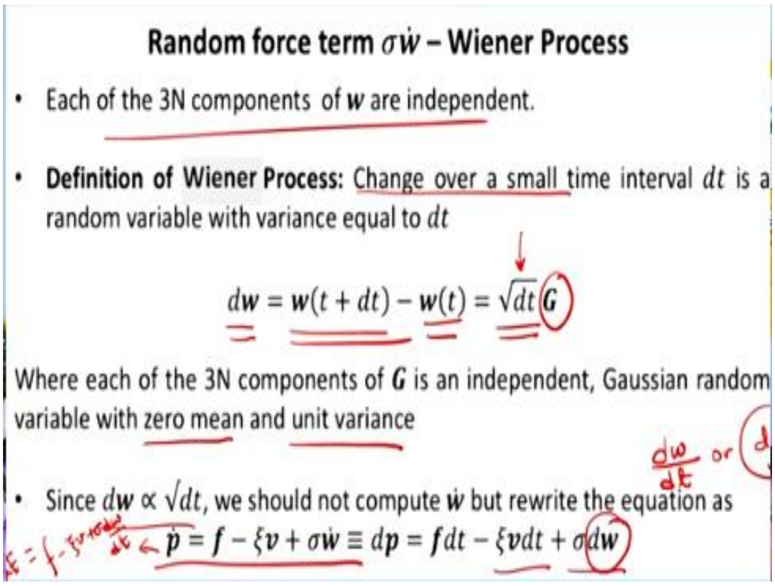
$$\zeta = m\gamma = \frac{k_B T}{D}$$

Finally there is a theorem called the Fluctuation Dissipation Theorem, that says that the strength of the random force should be a function of the ζ that is the friction coefficient or we can write in terms of gamma as something like 2m gamma k_BT because ζ and γ are related.

$$Fluctuation\ dissipation\ theorem, \sigma = \sqrt{2\zeta k_B T} = \sqrt{2m\gamma k_B T}$$

So, there is a relation between σ and ζ and that must be satisfied so the random force term is quite settle in here.

(Refer Slide Time: 16:27)



Random force term $\sigma\dot{w}$ – Wiener Process

- Each of the 3N components of $\boldsymbol{w}$ are independent.
- **Definition of Wiener Process:** Change over a small time interval dt is a random variable with variance equal to dt

$$d\boldsymbol{w} = \boldsymbol{w}(t + dt) - \boldsymbol{w}(t) = \sqrt{dt}\boxed{\boldsymbol{G}}$$

Where each of the 3N components of $\boldsymbol{G}$ is an independent, Gaussian random variable with zero mean and unit variance

- Since $d\boldsymbol{w} \propto \sqrt{dt}$, we should not compute $\dot{\boldsymbol{w}}$ but rewrite the equation as

$$\dot{\boldsymbol{p}} = \boldsymbol{f} - \xi\boldsymbol{v} + \sigma\dot{\boldsymbol{w}} \equiv d\boldsymbol{p} = \boldsymbol{f}dt - \xi\boldsymbol{v}dt + \sigma \boxed{d\boldsymbol{w}}$$

So, first of all this w has 3N components and in fact the time derivative w appears in the equation and all these 3N components are independent of each other and they are basically forming what is known as a Wiener Process and it is defined like this so if we look at the change in w over a small time interval dt it is going to be a random variable with the variance equal to dt that means if I look at the dw that is the change in w between times t plus dt to time t; It is going to be under root dt multiplied with another random variable G which is going to be a Gaussian random variable which 0 mean and unit variance.

$$dw = w(t + dt) - w(t) = \sqrt{dt}G$$

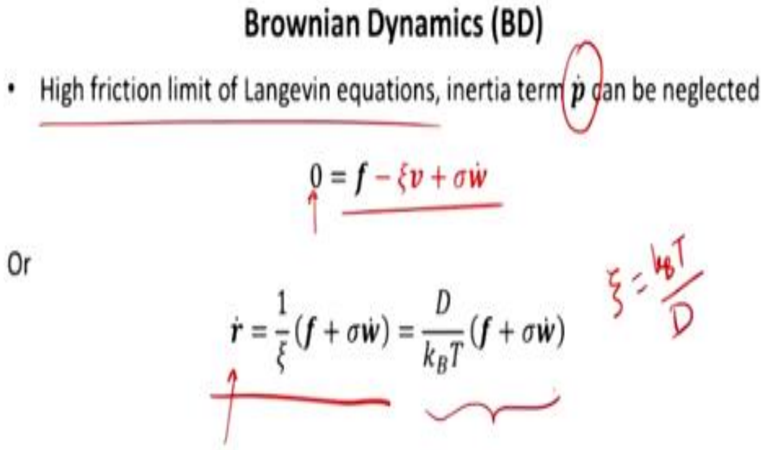
So, that if I square this I get dt and that becomes the variance in the Wiener Process. So, since the change in w is proportional to square root of dt we should better not work with dw by dt but we should work with dw directly and that means that we can change the way we write the equation slightly. So, that we do not have a compute the derivatives because w is a function of square root dt and numerically it will be more convenient if we work with dw directly and this is what we can do here. So, I write this equations we can note that this is equal to dp by dt is equal to f - ζv + σ dw by dt but I can also write it in the form dp is equal to fdt - ζvdt + σdw.

$$\dot{p} = f - \zeta v + \sigma\dot{w} \equiv dp = fdt - \zeta vdt + \sigma dw$$

So, that dw appears here as opposed to dw by dt that just convenient from numerical perspective and also because w is proportional to square root of dt. So, with this particular idea we basically numerically integrate the equation of motion there are methods out there similar to the velocity verlet method we had discussed but also taking care of the random post term and the frictional term that basically integrates the equation of motion.

A very similar idea is also used in the thermo stat known as the Langevin ThermoStat that is often used in Molecular Dynamics but Langevin dynamics itself is a whole different class of method that is used for the simulations of systems where I want to simulate at larger length and time scales since we remove solvent completely simulations are pretty quick in comparison to atomistic simulations.

(Refer Slide Time: 19:32)



Brownian Dynamics (BD)

- High friction limit of Langevin equations, inertia term $\dot{p}$ can be neglected

$$0 = f - \xi v + \sigma \dot{w}$$

Or

$$\dot{r} = \frac{1}{\xi}(f + \sigma \dot{w}) = \frac{D}{k_B T}(f + \sigma \dot{w})$$

$$\xi = \frac{k_B T}{D}$$

So, there is a method called the Brownian dynamics method which is going to be the high frictional limit of the Langevin equation, so at high friction what we can do is we can eliminate the inertia term, the inertia term is going to be negligible that is the p dot term that is basically mass times acceleration is going to be negligible in comparison to the friction term and therefore I can pretty much remove that it becomes 0 everything else is pretty much same as the Langevin equation.

$$0 = f - \zeta v + \sigma \dot{w}$$

Or,

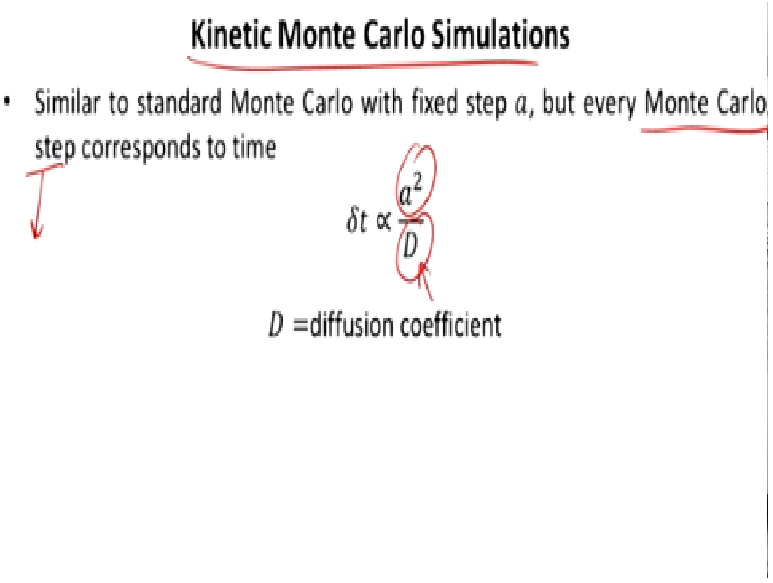
$$\dot{r} = \frac{1}{\zeta}(f + \sigma \dot{w}) = \frac{D}{k_B T}(f + \sigma \dot{w})$$

And what we then have is a simple first order differential equation in terms of the r dot that is the velocity of the particles acceleration is said to be equal to zero. And again using zeta equal to k_BT by d, I can also write in this particular form again the methods of numerical integration are very similar to Langevin equation but brownian dynamics is somewhat simpler because we are not dealing with a second order term we are solving a first order differential equation but it is only applicable when the friction offered by solvent is very large where we can ignore the inertia term or neglect the inertia term in the equation of motion.

One of the things that we have to kept in mind whenever we move from the atomistic simulation to Langevin Dynamics of Brownian Dynamics is the definition of time itself becomes somewhat arbitrary, so in Molecular Dynamics with the solvent and everything the time is well defined as soon as we remove the solvent, of course the motion is going to be faster because the solvent is not present there is no collision with solvent so molecules can go very easily because there is nothing in between them the solvent molecules are not there and therefore that may lead to somewhat speeding up of the motion of the molecules.

Now in some way the friction term is doing just that so it is basically slowing the molecules down. So, that the time scales remain comparable to what should be if the solvents were there, but then we have to really consider that also when we are looking at the time in comparison to the actual physical time and we have to carefully define our time step in a manner that is consistent with the friction term that we have added and the diffusion coefficient and the system under consideration. So, it really becomes one of the problematic areas in Brownian dynamic simulations.

(Refer Slide Time: 22:23)



Kinetic Monte Carlo Simulations

- Similar to standard Monte Carlo with fixed step a, but every Monte Carlo step corresponds to time

$$\delta t \propto \frac{a^2}{D}$$

D =diffusion coefficient

So, one of the methods that are that is pretty much similar to Brownian dynamics, but it approaches the problem from a Monte Carlo perspective is Kinetic Monte Carlo simulation method where essentially what we do is pretty much what we do in a typical Monte Carlo simulation or an equilibrium Monte Carlo simulations, for example we can perform a Monte

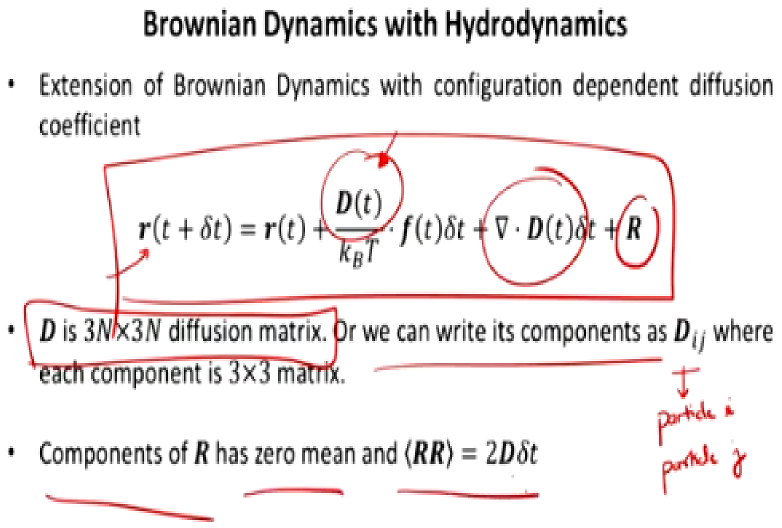
Carlo with a fixed step size A but then we associate certain time to every Monte Carlo step and saying that let us say if I do this Monte Carlo step I go in time with so much typically when I say a Monte Carlo is step in this case it refers to the trial movement of all the particles in the system and the δt happens to be proportional to the a square by D where a is my step size and D is my diffusion coefficient.

$$\delta t \propto \frac{a^2}{D}$$

Both in Brownian dynamics and in kinetic Monte Carlo scheme, the D is typically taken as constant but in reality the diffusion coefficient may also change as the simulation progress for example a system starts to aggregate now the diffusion coefficient is not going to be the same as the diffusion coefficient in the solution. Secondly, the diffusion coefficient that we are typically using are the self diffusion coefficient once we have a binary system or a ternary system there will be many mutual diffusion coefficient of species A going through species B and so on that really makes the process quite complicated.

So, the methods in principle are best suited for one component system where the diffusion coefficient can be approximated to be the same as the self diffusion coefficient and that is the quantity that is also given by the Einstein’s relation as soon as we have more than one component that is typical of us as chemical engineers we have to be careful what diffusion coefficient should go here and in principle we need to have methods that should account for the mutual diffusivities between the species and the concentration.

(Refer Slide Time: 24:38)



Brownian Dynamics with Hydrodynamics

- Extension of Brownian Dynamics with configuration dependent diffusion coefficient

$$\boxed{\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{\boldsymbol{D}(t)}{k_B T}\cdot \boldsymbol{f}(t)\delta t + \nabla\cdot \boldsymbol{D}(t)\delta t + \boldsymbol{R}}$$

- $\boldsymbol{D}$ is $3N\times 3N$ diffusion matrix. Or we can write its components as $\boldsymbol{D}_{ij}$ where each component is 3×3 matrix.

particle i

particle j

- Components of $\boldsymbol{R}$ has zero mean and $\langle \boldsymbol{R}\boldsymbol{R}\rangle = 2\boldsymbol{D}\delta t$

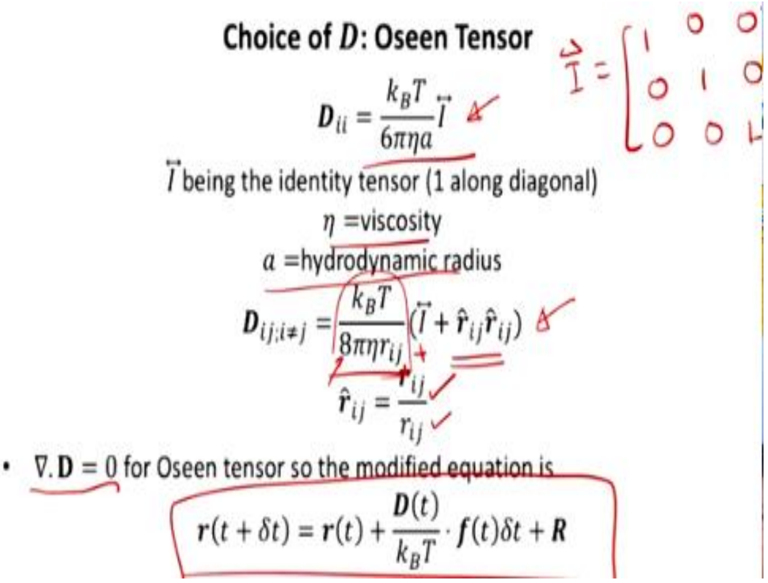
So, until so far we have accounted for only basic only two effects of solvent one is the friction offered by the solvent and other is the thermal motion of the solvent or the collisions of solvent with the solute, but in many cases particularly in the non-equilibrium scenarios the hydrodynamic interactions are also very important and in that case we have to revise the Brownian Dynamic Scheme to also account for the Hydro Dynamic Interactions and even though that is of more purpose in cases when we are having some kind of a flow situation that need not be the case even in thermodynamic equilibrium this hydro dynamic interactions can be important in certain cases.

So, in these cases one way to include that is to have a notion of a diffusion matrix that somehow accounts for the hydrodynamics of the fluid and we modify the equation of motion. Now, I am writing the numerical equation that we solve for instead of the actual equation of motion where the position of the particle is updated according to this rule where we have a diffusion matrix as opposed to the diffusion coefficient in the earlier equation and since it is going to be changing matrix change with time and with very variables in the system we also have one more term that is corresponding to del dot d that is the first to the changes in the diffusion coefficient.

$$r(t+\delta t) = r(t) + \frac{D\dot{(}t)}{k_B T}\, f(t)\delta(t) + \nabla . D(t) + \delta t + R$$

So, in this case this matrix takes care of the HIFX hydro dynamic interaction effects in the in this means particular case we can write the components of this matrix as something like D_{ij} which will refer to basically the particle i and particle j in the system and now since for both particle i and particle j they have three coordinates in x y and z direction this matrix for every particle will have three times three components nine components. So, in total we will have N into N matrix of 3 into 3 matrices or we can say we have 3N times 3N diffusion matrix so each component of the matrix typically is represented as D_{ij} that itself is a three times three matrix and there is a random term that has a zero mean very similar to what we had earlier and the correlation is given as 2D δt simply an extension of the idea when we had a constant diffusion coefficient.

(Refer Slide Time: 27:33)



Choice of D: Oseen Tensor

$\overleftrightarrow{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$D_{ii} = \frac{k_BT}{6\pi\eta a}\overleftrightarrow{I}$$

$\overleftrightarrow{I}$ being the identity tensor (1 along diagonal)

η =viscosity

a =hydrodynamic radius

$$D_{ij;i\neq j} = \frac{k_BT}{8\pi\eta r_{ij}}(\overleftrightarrow{I} + \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij})$$

$$\hat{\mathbf{r}}_{ij} = \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- $\nabla.\mathbf{D} = 0$ for Oseen tensor so the modified equation is

$$\boxed{\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{\mathbf{D}(t)}{k_BT}\cdot \mathbf{f}(t)\delta t + \mathbf{R}}$$

So, one of the choice of D is the Oseen Tensor this is not the only possible choice, the reason why we have multiple choices is because there are certain approximations involved in there and there are certain limitations of this particular tensor we are using and we can read more references to learn more about what is the problem with Oseen tensor but this is the one that is most commonly used.

$$D_{ii} = \frac{k_BT}{6\pi\eta a}\overleftrightarrow{I}$$

So, it contains basically two different expression for the pair of the same particle and pair of two different particles, for pair of the same particle the D_{ii} is given by k_BT by 6πηa multiplied with identity tensor where i is defined as essentially a diagonal one and all other off diagonal terms are zero, eta is the viscosity and a is the Hydro Dynamic Radius that can be found from experiments D_{ij} for i naught equal to j is given by something with a similar pre factor but there is an eight here again we have an identity tensor in the beginning and then we have the diad comprised of the unit vector for the distance between i and j or displacement vector between i and j the unit vector is defined as the displacement vector divided by the magnitude of the displacement between i and j.

$$D_{ij;i\neq j} = \frac{k_BT}{8\pi\eta r_{ij}}(\overleftrightarrow{I} + \widehat{r_{ij}}\widehat{r_{ij}})$$

The del dot D is zero for the Oseen Tensor that is the reason why it is commonly used because you may recall in the previous expression we had an extra term del dot d so for oseen tensor, it will not appear and the modified equation therefore if i drop that term is going to be this which is somewhat simpler because we have dropped of particular term from the expression.

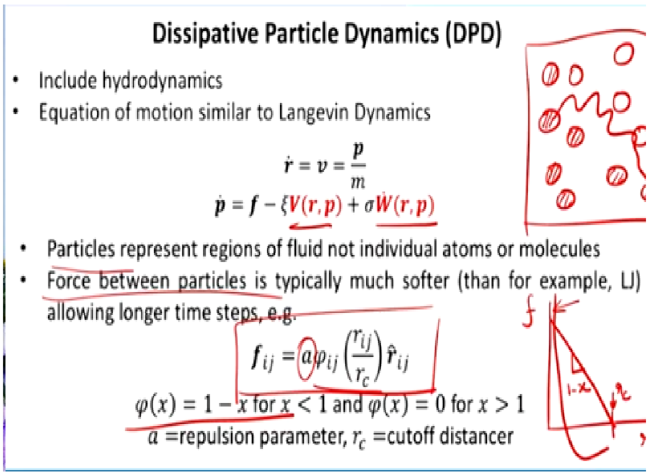
$$r(t+\delta t) = r(t) + \frac{D(t)}{k_B T}\ .\ f(t)\delta t + R$$

There is another method called the dissipative particle dynamics method that also accounts for hydro dynamic interactions. In this case again the equation of motion is similar to Langevin Dynamics but instead of V and W dot here we have functions of the position and momentum that I write as capital V and capital W in the earlier case to a simply the velocity of the particle and the wiener process but now both of these are a function of the position and momenta of the particles actually all the particles in the system.

$$\dot{r} = v = \frac{p}{m}$$

$$\dot{p} = f - \zeta V(r,p) + \sigma W(r,p)$$

(Refer Slide Time: 29:56)



Dissipative Particle Dynamics (DPD)

- Include hydrodynamics
- Equation of motion similar to Langevin Dynamics

$$\dot{r} = v = \frac{p}{m}$$
$$\dot{p} = f - \zeta \underline{V(r,p)} + \sigma \underline{W(r,p)}$$

- Particles represent regions of fluid not individual atoms or molecules
- Force between particles is typically much softer (than for example, LJ) allowing longer time steps, e.g.

$$\boxed{f_{ij} = a\varphi_{ij}\left(\frac{r_{ij}}{r_c}\right)\hat{r}_{ij}}$$

$\varphi(x) = 1 - x$ for $x < 1$ and $\varphi(x) = 0$ for $x > 1$

a =repulsion parameter, r_c =cutoff distancer

In this case the particles represent really the regions in the fluid, they may not be the individual atoms or molecules. So, what I mean in here let us say for example I am considering a fluid I am not really meaning that these particles are the ones which are being tracked but these are referring to special regions in the fluid that are moving together some kind of like collective motion of the entire reason of fluid so it is happening really at a measure scale, so there is not a very clear atomic scale analogue whenever we are doing a dissipative particle dynamic simulations and the reason why that happens is because the time scale for Hydro Dynamic Interactions are quite different from the time scales where molecular scale processes take place so although in principle they account for some effects like thermal fluctuations and so on and solute, solute interactions and so on but it does not really account for the detailed molecular resolution of these systems and many of that is missed by assuming that the particles are not really the molecules but regions of the fluid comprised of many molecules or atoms.

The force between these particles that we defined are typically much softer, one of the most commonly used form is the following. The force pretty much goes like this with distance linear form and that pretty much means that the particles can pretty much overlap unlike for example a Lennard Jones interaction where you have substantial repulsion at a small r between a very large repulsion once they convey very close. In this particular case there is not really very large repulsion even when we go to r equal to 0 and therefore what we can say is that the potential is very, very soft and the consequence of that is we can take larger or longer time steps in our simulations.

The reason why we could take only smaller time step is also because if I take a longer time step you can violate many overlaps or we can violate many hardcore of the molecules but in this particular case since we are working with softer potential the overlaps are being allowed, so the particles can move with much longer time step than we can take in a say a molecular simulation. So, with this particular idea I can define the force between the particles in one of these ways is this-

$$f_{ij} = a\varphi_{ij}\left(\frac{r_{ij}}{r_c}\right)\overbrace{r}\, ij$$

So, we have a repulsion parameter a, we define a function of r_{ij} by r_c where r_{ij} is again the distance between the particles r_c is some cutoff distance at which the force goes to zero. And the function phi is defined as 1minus x for x less than 1, that is pretty much the form of this is going like 1 minus x and zero after that so it goes to zero beyond r equal to r_c.

So, with this I want to conclude this lecture. In the next lecture we will discuss some more methods of mesoscale simulations that also tries to capture the effect of Hydrodynamics in somewhat different manner, thank you.