Introduction to Polymer Physics
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Lecture-26
Molecular Dynamics Simulations, Review of Thermodynamics

Welcome guys, so in the last class we have discussed the Monte Carlo methods and some practical tips of doing Monte Carlo simulations and today I will briefly touch on the molecular dynamics simulation method that is an alternative simulation method employed for polymer simulations and other simulations and then I will transition into some ideas from thermodynamics because we are going to build thermodynamics of polymer solutions. So some part I will discuss will be useful for simulations we have discussed and some part will set the ground for what we will cover next the polymer solution theory.

So in the Monte Carlo method if you recall, the idea was that you will make trial displacements and accept or reject them based on the energy change that results from the trial displacement that is not the only way to get the equilibrium behaviour of system. An alternate and the most common method is the molecular dynamics or MD simulation, that is based on a very different idea gives you a very similar kind of result of course that gives you a variety of more results that Monte Carlo does not give you, but at least most part of what we have discussed can be gotten both from a Monte Carlo simulation or from molecular dynamics simulation.

So here again just like we did for a Monte Carlo simulation, we start with a simulation box and we assume that whatever we want to simulate in the connection of particles or the polymer chain whatever you want to simulate is contained within the simulation box just like we did earlier from Monte Carlo simulation. So we assume say a polymer chain is contained in the simulation box. Now however what we do if we don’t look at the energy of this confirmation what we look at is how much force is being experienced by each of the bead and using Newton's laws of motion that tells me F=MA we update the position of particles. So it is like a system of particles which are simply moving by Newton's laws of motion. So the equation we are solving here is-

$$\vec{F}_i = m_i \vec{a}_i \, where \, i = 1,2,\ldots\ldots\ldots\ldots n$$

Now we take the second derivative which gives me the position which is indeed a vector.

$$\vec{F}_i = m_i \frac{d^2 \vec{x}_i}{dt^2}$$

Now we know the initial positions because it can be guess, we need to know the forces acting on each of the particle the beads in this particular case ok. So if I look at the force that is acting on the particle i in that force is the sum over the pair interaction forces that involve a pair of particle including the particle i.

$$\vec{F}_i = \sum_{j \neq i} \vec{F}_{ij}$$

$$\int ¿$$

$$U = U_{elastic} + U_{¿}$$

$$\vec{F}_i = -\vec{\nabla}_R U = \frac{\partial}{\partial \vec{x}_i} U$$

So we take a derivative of the total energy with respect to position of this bead that gives me the forces and then we know the forces are also some of interaction forces and using the forces we can update the position of particles and we can continue doing it ok. So unlike in the Monte Carlo case where I can accept or reject a trial, in the molecular dynamics methods there is no such thing, we do not accept or reject every move is simply accepted. We know the forces acting on the particle. So we get a new position based on those forces and all the thing here is as soon as the particles move the forces are being changed. So if I take my time step to be like large enough and if I compute the new position based on the value of forces at previous time step then within that time step the forces are being changed which are not being accounted for. So the time step must be a small enough to say this again in terms of expression I am interested in the new position $t+\Delta t$ that will of course depend on the old position at xt and the forces acting at time t-

$$\vec{x}(t+\Delta t)=f(\vec{x}(t),\vec{F}(t))$$

Here Δt must be small enough since $\vec{F}$ will change from t to Δt.

Although as a opposite to a Monte Carlo method there is no stochastic term involved at least can what we have discussed so far but the main issue is the time in step has to be very small enough. However there is a key thing here that we did not have in the Monte Carlo simulation. In the Monte Carlo simulation we only talked about the position of particles, the movements we were making where somewhat artificial in nature.

So we give a random displacement and see whether the energies are going to a lower value or not or whether it is following the Boltzmann distribution or not. In this case however we track both the position and velocity of the particle because since we have a time there right so we can talk about the velocity of particle as a-

$$\vec{v}=\frac{d\vec{x}_i}{dt}$$

So molecular dynamics for the same reason captures both static and dynamic properties of chain whereas Monte Carlo method does not captured the dynamic behaviour it only captures the static behaviour.

Nevertheless it turns out that if I run the molecular dynamics simulation long enough ultimately it will go to similar equilibrium that we achieve in a Monte Carlo simulation. That is to say that if I again simulate a polymer chain again we will have some equilibrium phase followed by a production phase R_g^2 and again eventually these will start fluctuation around average value and this is what we report as R_g^2. So although the methods are apparently very different, the end result in terms of static properties come out to be the same. If however I look at dynamic properties that depend on velocities like the diffusion coefficient it turns out molecular dynamics can give you a diffusion coefficient Monte Carlo cannot because there is no time actual time in the Monte Carlo simulation, but first hand properties almost both these methods can be used interchangeably.

There are also computational advantages of molecular dynamics it is it can be easily parallelised there are many parallel molecular dynamic codes, Monte Carlo on the other hand is difficult to parallelise. One advantage of Monte Carlo simulation however is since we can take larger steps in any case the steps are artificial, so I can really make larger displacement in any go and so I can go to equilibrium position rather faster, if I am very far from there. In MD the time is steps are restricted by the numerical error I am making when I am updating the position. So I really cannot take longer time steps because numerical errors will be very high, in the Monte Carlo simulation there is no numerical error if I use a larger time step larger displacement because in any case we are not doing the true dynamics system.

So if we want to equilibrate systems which are hard to equilibrate or if I want to equilibrium from position that is very far from equilibrium or configuration very far from equilibrium in that case Monte Carlo is typically preferred, it is relatively easier to code compared to MD as well. On the other hand if I want to have efficiency of a parallel code, if I want to get some dynamic properties to get those particular things then in that case I will go for the MD method.

So now let me talk something about thermodynamic ensembles that is used both Monte Carlo simulation and molecular dynamics simulations before I do that let me recap some thermodynamics that will be useful also for that will discuss next.

So the first concept is there are 4 energy function- when we say that I will use a Gibbs energy or enthalpy or internal energy or Helmholtz free energy. We are talking about different energy functions, all of which characterize the energy of the system, but the systems are different when we are looking at these 4 energy functions. So we have energy functions U, H, A, G. Here

$$U \equiv Internal\,Energy\,,H \equiv Enthalpy\;A \equiv Helmholtz\,free\,energy \wedge G \equiv Gibbs\,Free\,Energy$$

Now ultimately I am not interested in the actual or absolute values of energy, we are interested in the change in energy due to certain process based on that we say whether the process is available or not or determine the work done or work required carried for the process. The easy way to remember is this-

$$U \equiv TS - PV + \mu N$$

Here T is a temperature, S is entropy, P is the pressure, V is the volume, μ is the chemical potential and N is the number of particles. And this T and S, P and V and μ and N are referred as conjugate variables. So P is conjugate to S, P is conjugate to V, μ to conjugate to N and then we can write others as-

$$H \equiv U + PV = TS + \mu N$$

$$A \equiv U - TS = -PV + \mu N$$

$$G \equiv H - TS = \mu N$$

Then there is a particular rule that is known as the Gibbs Duhem rule which we will not derived but the basic idea behind the rule is very simple. So we will look at this conjugate variables and identify that which of these variables are extensive variables and which of these variables are intensive variables and all I do is I will get rid of the intensive variables inside the derivative and extensive will be outside the derivative. Based on this rule we can write-

$$SdT - VdP + Nd\mu = 0$$

So the total derivation dU after cancelling out becomes-

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu = 0$$

$$dU = TdS - PdV + \mu dN$$

Similarly we can write other energies as well-

$$dH = dU + PdV + VdP$$

$$so, dH = TdS + VdP + \mu dN$$

$$dA = dU - TdS - SdT$$

$$so, dA = -SdT - PdV + \mu dN$$

$$dG = dH - TdS - SdT$$

$$so, dG = -S\,dT + VdP + \mu dN$$

So now we have this pretty much derived the 4 relations that characterised 4 energy functions U, H, A and G. So I want to note down a thing here. The first thing I mentioned about the conjugate variable. If I look at this particular relation what is appearing inside the derivative is the one that you are actually controlling, what is appearing outside the derivative is the one that you are writing it as a function of that controlling variable because if I think of integrating this I will integrate it in terms of the variables that appear inside the d or derivative. So I have to write my variable as a function of those variables. So other way to say that is what I am saying here U is a function of S, V, N because I will write T as a function of S, P as a function of V, U as a function of N because ultimately even we integrate using S, V, N, that is disappearing inside the derivative d.

Similarly for H now we have S, P, N, so H is a function of S, P, N, A is a function of T, V, N and G is a function of P, T, and N. So use of this energy function their functions is the following it depends on what the system is like which variables are you controlling inside the experiment and which variables of course the conjugate variables will be a function of those variables that were controlling but you do not control them explicitly.

So when I am talking about Gibbs free energy are typically employed in a scenario where I am working at a constant temperature and constant pressure the idea is I can control the temperature and pressure value, I can specify the temperature and pressure value and the corresponding values of entropy and the volume will be determined for the temperature and pressure that I have I am controlling what taken as constant in the process.

If on the other hand I am looking at a constant volume, constant temperature process or if I am controlling the volume and temperature, in that case I will have pressure as a function of volume, entropy as a function of temperature again and I can control the temperature and volume. Keep in mind that there is a bit of a confusion here when we say that we work at a constant temperature and pressure because in that case if I look at dG the first two terms are 0, so what does it mean that temperature and pressure are controlling variables, all it means is a I can conduct at the temperature and pressure I specify that is to say that I can systematically vary the temperature and pressure in the experiment and I can look at the conjugate variables as a function of that change that is the variable that you are controlling, that is the variable that you will write all the other variables or function.

This is what you have to keep in mind this is why we have 4 energy functions, all of them come from the same thermodynamic origin, the way they differ in what exactly are they are a function of which 3 variables I have chosen to be the independent variables, of course the other 3 will be the dependent variables and it must be in pairs so you cannot make a combination of say T, S and V because as soon as you specify temperature the entropy is automatically specified as a function of temperature, you cannot vary both temperature and entropy independently similarly you cannot vary both pressure and volume independently and you cannot vary both chemical potential and number of particles independently they must work in pairs you can only choose 1 each from these 3 pairs as the controlling variable or as the 1 that is held constant other 3 must be found as a function of this on the 3 that we have chosen.

So based on this there is an idea of ensembles that is used in in thermodynamics and also in simulations. So we write internal energy as a function of S, V, N enthalpy as a function of S, P, N and Helmholtz free energy as a function of T, V, N and Gibbs free energy as the function of T, P, N and they define the simulations that I am conducting. If I am doing a simulation where the pressure and temperature are the variables I am controlling, then in that case as the number of particles I am doing what is known as N, P, T simulation. Where I can specify both the pressure and the temperature as soon as I specify the pressure volume is not being specified, that would mean the volume will change in the simulation ultimately when we reach equilibrium the volume will starts fluctuating around the average the pressure is the one that I am controlling, the volume is being calculated as a function of that pressure. So NPT simulation is also known as NPT ensemble is also known as an isothermal- isobaric ensemble then we are also do NVT simulations which is referred as a canonical ensemble, we can also do the first case and NV and S actually we call it NVE simulation where the number of particles, the volume and energy are being held fixed energy anyway gives you the entropy this is known as micro canonical ensemble. Of course we can form 4 ensemble for it but that is not are not used and then there is something called grand Canonical ensemble that correspond of controlling variable μVT and we can construct energy function that will be basically in terms of μVT but you are following the rule we take one each from the from 3 pairs and also by the Gibbs Duhem rule, we know that all that we cannot be intensive variables because if I take all intensive the sum is 0, so one of them must be extensive, so here V is the one with extensive and μ and T are both intensive.

So depending on like what I am looking at I can make a choice of ensemble. Let us say for example I want to know the behaviour of system at a certain pressure. For example water at 1 bar I will do a simulation that is in NPT ensemble and I will let the volume fluctuate, on the other hand if I want to know the water at a density of say 1 gram per litre I do not care about the pressure I will keep the volume fixed or the numbers per unit volume fixed and I will let the pressure vary or fluctuate eventually any way it will start fluctuating around an average value. So depending on what kind of experimental scenario I am trying to model I can pick up the ensemble that I am choosing. However there is one thing to note here that by design the Monte Carole method is for the NVT ensemble that is Canonical ensemble and by design the MD method is for NVE ensemble.

If I want to do simulations in different ensemble I may have to use what is known as a thermostat and a Barostat. So let us say I want to use MD for NVT. Now I want to control the temperature. So I will use something known as a thermostat that will help me control temperature and thermostat although have a clear experimental log in simulation implemented bit differently and I will not going to tell here. Similarly and I am doing say NPT I will need a thermostat and also a Barostat again I will not put details here, but we have to keep in mind that if I am doing simulations in different ensembles we need something beyond what I have already discussed in the case of Monte Carlo and MD algorithm. For the MD case the programming comes out to be a bit difficult. So we will we can you can use a standard software like LAMMPS that is one of the most commonly used software but the MC anyway is easier to code, so we can program in any language that you are used to.

So with this I want to stop here and in next class we will take the thermodynamics discuss ion further and talk about the solution thermodynamics building up towards the thermodynamics of polymer solutions.

Thank you.