Advanced Thermodynamics and Molecular Simulations
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Lecture – 42
Pair Potentials

Hello all of you, so in the last class I gave you some overview of particle simulations and multi-scale simulations. We have been discussing the theoretical basis of Monte Carlo and molecular dynamics in the last week and before that as well, but now I was talking more in practical terms how this methods are going to be applied at different length and time scales and how do they compare to the quantum chemistry and continuum simulations.

So, today I want to get back to the particle simulations and especially molecular dynamics but before that, I will discuss the idea of pair potentials or how we represent the interactions it turns out that this part of the simulation is also same as that is done in the Monte Carlo simulation. Except that, in Monte Carlo we are interested in the energies as opposed to forces in the case of Molecular dynamics.

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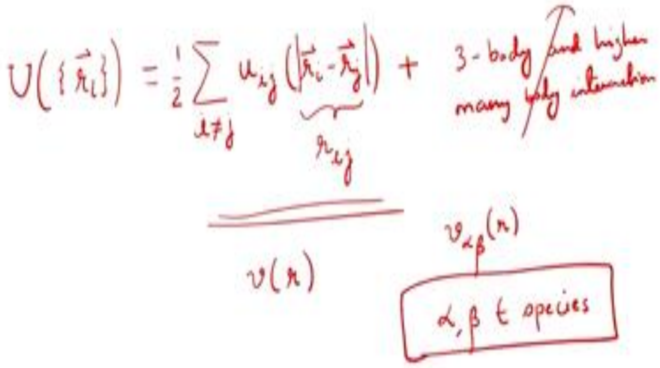

$$U(\{\vec{r}_i\}) = \frac{1}{2}\sum_{i\neq j} u_{ij}(\underbrace{|\vec{r}_i-\vec{r}_j|}_{r_{ij}}) + \text{3-body / and higher many body interaction}$$

$$v(r) \qquad v_{\alpha\beta}(r) \qquad \boxed{\alpha, \beta \in \text{species}}$$

So, I have been telling you that I can represent the energy of a system that is not under influence of any external force as a function of the coordinates of the molecules in the system or particles in the system I use the notation of generalized coordinates but I will develop in Cartesian coordinates from the time being but the same idea will apply also in generalized coordinates and this I said I can represent in terms of the pair interactions that is, going to be a function of specifically the distance or displacement vector but in most cases we really interested in just the magnitude of that.

$$U(\{\vec{r_i}\}) = \frac{1}{2}\sum_{i\neq j} u_{ij}\left(|\vec{r_i} - \vec{r_j}|\right)$$

And,

$$\left|\vec{r_i} - \vec{r_j}\right| = \{r_{ij}\}$$

There are in principle, three body and higher many body interactions, which are typically ignored in most simulations. Assuming that, these interactions are going to have lesser effect than compared to the two body interactions. But there are cases especially whenever we look at the condensed media like solids and, all that these interactions in sometimes are at least comparable importance to two body interactions. In some cases, these are the dominant interactions but as long as we are dealing with liquids and gases we are typically okay with using just the pair interactions or two body interactions.

In some sense, the three body interaction effect of three body interaction or higher body interactions can be incorporated in the two body terms because, when I develop a potential for this here in some sense, it is kind of fit to represent the behavior we are interested in. So, we should not think of the as the actual two body interaction in the system, this is some sort of an effective two body interaction we are trying to represent. So, in some sense we can basically fit the behaviour using the two body interaction itself and in that case this model applicable even when the three body interacts are significant enough but in most cases we are dealing with situations where the higher many body interactions beyond two body interactions are much lesser in comparison to two body interactions.

So, essentially we are interested in pair potential of the form, v(r) as long as we are dealing with a monoatomic or a single species system a single component system in that case, we are happy with only one function v of r. In general we can think of something like $v_{\alpha\beta}$ (r), where α and β are different species in the system.

So, for a monoatomic gas, for example, we are happy with a single function and this is the example that I want to start with.

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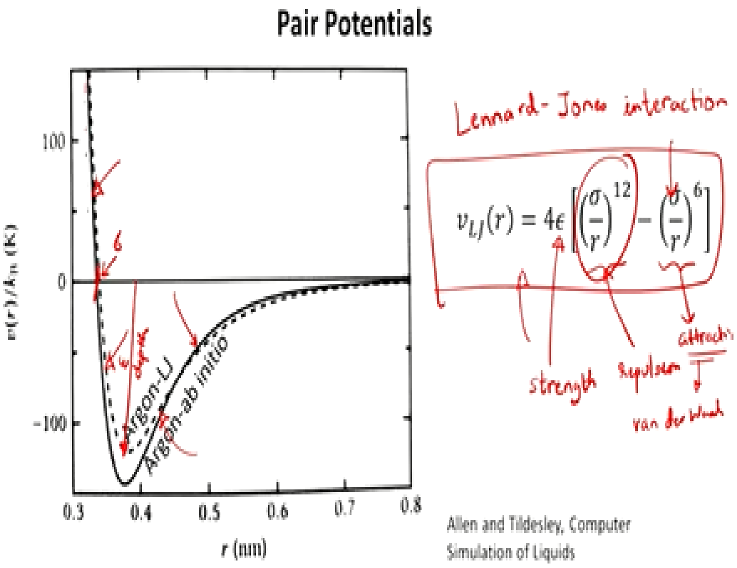

Pair Potentials

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

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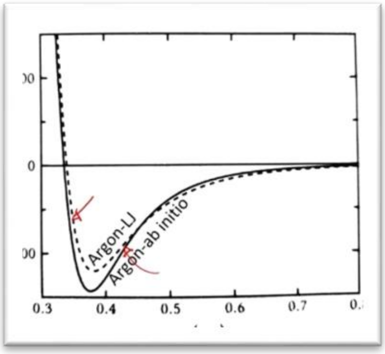
So, this is the pair potential for an argon gas that is indeed monoatomic, it is a noble gas and this bold line that you see here is what that has been obtained using an ab initio calculation, ab initio means that we are actually doing a quantum mechanical simulation to evaluate the potential. So, this is like in some sense first principle on the other hand, this dashed line is a potential of form that I have listed here that is fit to this particular data and this particular form is called the Lennard Jones interactions.



And you can see that of course, the ab initio should have been the way to go but that must be time consuming of time to compute that but let us say if someone has done that and now I want to study argon in various circumstances, I can simply use this fitted potential as opposed to the actual ab initio potential and this is the whole motivation of using force fields that I will come to eventually but let us focus just on the idea of pair potentials here because in the case of argon there is only one pair potential, because all there is only one component in the system and that too is monoatomic.

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

So, if you look at this carefully this epsilon here represent some sort of the strength of the interaction or the depth of this well and the first term that is a positive term that represents the repulsion, this is the part that you see here and the second term is the attraction, and this is this part that you see here this comes from basically a Van der Waals interaction and it has been shown theoretically or there are theories that source that Van der Waals interactions would go like 1 by r to the power 6. So, there is a clear basis for using the second term here. There is not so much clear basis for the first repulsive term, why should we have a power 12, in fact there are potentials like with having power 9 there or an exponential term there, the key idea is whatever potential we are going to use that should not allow for the overlap.

So, this for example is the value of sigma here so beyond sigma we are going to have a positive value and within I would say a very small distance less than sigma the potential becomes so high that any overlap is kind of prevented, so this is broadly the reason why we are using the first term and this is numerically convenient because once I have the sigma by r to the power 6, I can evaluate sigma by r to the power 12 by simply squaring it.

So, one of the things that should be kept in mind, whenever we think of any potential is how simple it will be to evaluate that since we have to do many, many of these computations in every molecular simulation step and, therefore this particular simpler potential reliabily captures, I would say the behavior of argon and also, even though we are not doing a full ab initio calculation, we can fit my epsilon value and sigma value in a manner that it represents reliably the potential we are interested in. Of course, we could use a more complicated from function and then also we can get a better fit and then that but we have to keep in mind how much computational expense it adds to and if the expense is relatively large then in that case we should go for the simpler potentials like the Lennard Jones potential they turns out Lennard Jones is pretty good for a wide variety of systems not only the argon.

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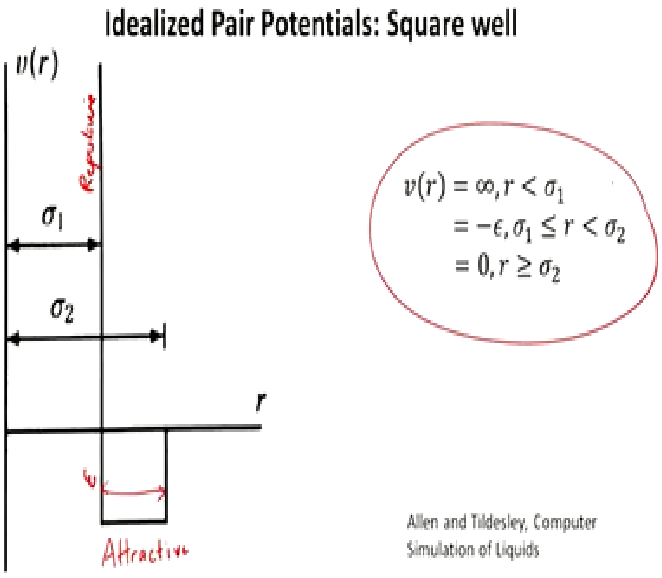

Idealized Pair Potentials: Square well

$$v(r) = \infty, r < \sigma_1$$
$$= -\epsilon, \sigma_1 \le r < \sigma_2$$
$$= 0, r \ge \sigma_2$$

Allen and Tildesley, Computer Simulation of Liquids

There are even simpler potentials and we give an example in the description of the Monte Carlo simulation. For example, we can use a hard sphere potential in this case there is no attraction whatsoever between the spheres but you have is simply a repulsion for distances less than sigma that is the overlap distance. This was the Van der Waals gas that we studied. So, in mathematical forms we can say that for r less than sigma the potential is infinite and for r higher than equal to sigma this pretty much goes to 0. This would represent the system where there is no Van der Waals attraction between the, between those species and we are using the fact we are using an assumption that whatever species, we have that is approximated by a sphere.

So, this kind of a try model, but it works great for many systems. The next thing that one can do and that is again simpler than the Lennard Jones potential is one can use a square well. So, in this case, you not only have the repulsive part but you also have an attractive part again with some depth epsilon. But now, that epsilon is the same over distance up to some sigma 2 and beyond that it goes to 0. So, this is clearly a simplification of the Lennard Jones potential. So, we are assuming there is an attraction, attraction is over a short range and the magnitude of attraction in the range of sigma 1 to sigma 2 is minus, minus epsilon. This is what is represented in the mathematical form right here.

$$v(r) = \infty, r < \sigma_1 = -\epsilon, \sigma_1 \le r < \sigma_2 = 0, r \ge \sigma_2$$

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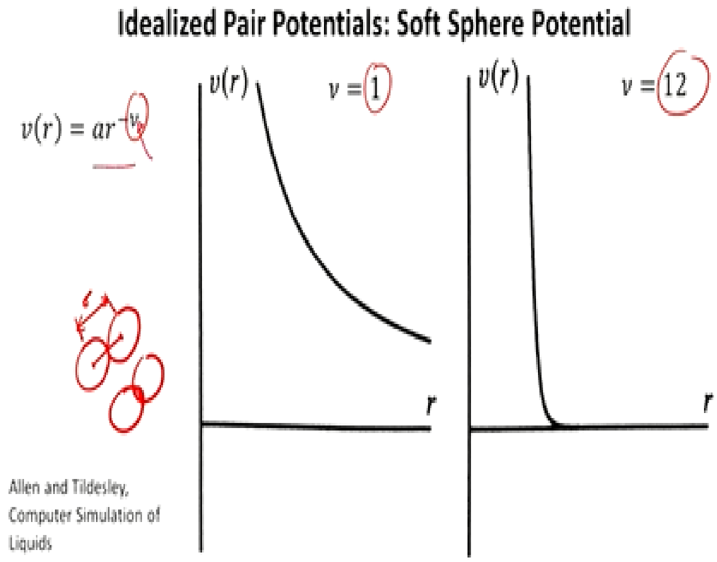

Idealized Pair Potentials: Soft Sphere Potential

$v(r) = ar^{-\nu}$

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And then we can go ahead and think of other potentials let us say for example; I can think of a soft sphere potential where little bit of overlap is allowed in the system but a large overlap is prevented and I can control how much overlap is allowed.

Now, before we think of these kinds of potentials, let me again come back to the point just for the last time of what exactly we mean by an overlap. So, in our kind of a model we are saying that we have, two is spheres and every time we come less than their closest separation we are basically having some sort of an overlap. Now, what will that overlap correspond to for an atomic system? So, what we have to we had in mind is that since we have a represented the atom by an sphere, it does not mean that the atom is start behaving like a rigid sphere, atom indeed if you look at there, you will find an electron cloud. So, an electron clouds can very well overlap on the repulsion will come in the picture when two nuclei come together because then there is a strong nuclear repulsion. Electron cloud themselves will not provide as much resistance like as hard spherical balls that I am putting in therefore that assumption of a hard sphere may appear to be more natural in certain cases where you really want to prevent the two balls to come together but, in the case of atomic system that may not be appropriate because, the electron clouds can very well come together. It is not meaning that electrons are sitting on top of each other, it only means that the electron density of the two clouds they superimpose and therefore you will have higher electron density, I mean if overlap did not happen, how can we have any chemical reaction for example, in system may not modeling chemical reaction, but the point is should be noted that the atomic systems do not really have that hard sphere kind of like limitation on the overlap and therefore in more cases than not soft sphere models are actually not only easier to implement but also more convenient because, that represents the cases where some overlap is allowed. Of course large overlaps when nuclei come together or when the electron-electron repulsions are pretty high that should be analyzed but there should not be an infinite repulsion at some imaginary contact distance.

So, this is what is represented using here and we have a way to control the amount of repulsion that we can have so in this particular case, I can tune the variable or parameter μ and I can basically simulate different degrees of the penalty to an overlap. And, I can control the softness of potential so as to speak.

Now, if we compare the last two potentials with the soft sphere potential, what you notice is for both these cases what we have is that the derivative dv by dr is going to be discontinuous very true here and that is true also here. That is not a problem as per say in the Monte Carlo method but in molecular dynamics, if you recall I was telling you that we are interested in finding forces and how do we find the forces?

Forces are going to be something like a gradient of the energy and the gradient will require derivative with respect to r, so therefore we will get discontinuous forces, in the case of a hard sphere potential or for a square well potential. This will lead to numerical difficulties in the calculation of the forces you may get a discontinuous derivative and that is not what you really desire to have this will add to some artifacts in the final results and therefore it is more convenient in molecular dyn-mics to go for soft sphere potentials that is not really a problem in Monte Carlo because in Monte Carlo, if there is an overlap happening I can always reject that kind of a move. I will not let that happen in molecular dynamics, it is not a possibility once two atoms or two particles come together and there is an overlap there is no going back there is no rejection in a molecular dynamic so as to speak. So, in that case it is better to use a soft sphere potential because in that case the derivatives are continuous and we never get in the regime of the overlap or infinite forces we can have small overlaps, but do not give you infinite forces.

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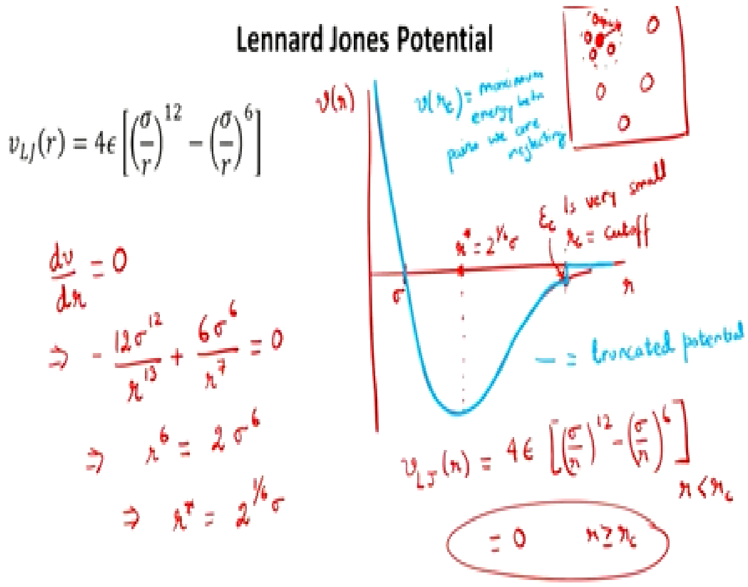


Lennard Jones Potential

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\frac{dv}{dr} = 0$$

$$\Rightarrow -\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} = 0$$

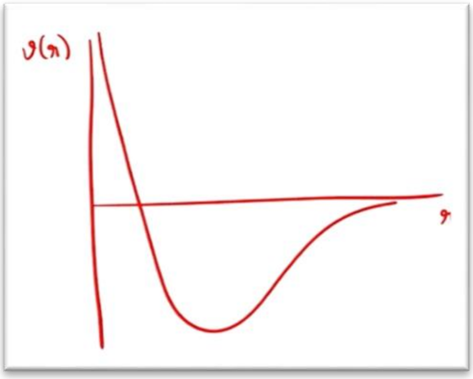
$$\Rightarrow r^6 = 2\sigma^6$$

$$\Rightarrow r^* = 2^{1/6}\sigma$$

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad r < r_c$$

$$\boxed{= 0 \quad r \geq r_c}$$

So, with this particular idea, I want to come back again to the Lennard Jones potential because this is the most used potentials in molecular simulations and let me look at this potential, in somewhat more detail. So, I am looking at, v r versus r and the shape as I said like this-



The first thing I want to check is at what point we get a minima here. We already have said that this will cross the axis at r equal to sigma. This you can see from here because if I put r equal to sigma here, you will get v equal to 0 but then the point where, the minima happens is different from that and this we can evaluate by doing-

$$\frac{dv}{dr} = 0$$

which is going to be something like-

$$-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} = 0$$

and this is going to give me something like-

$$r^6 = 2\sigma^6$$

and this gives me the-

$$r^* = 2^{\frac{1}{6}}\sigma$$

So, this is where we get the minimum value, I was also telling you that in typically in Monte Carlo simulation and we told you a code and I didn't go into details there, but I mentioned that it is not really wise to compute this pair potential over all possible pairs and the reason is that the vr will go to small values eventually. So, you can define some sort of a cutoff beyond which the value of v or the energy value let me call that some ϵ_c. The energy value at this particular point that becomes very small and beyond that point I should essentially cut off the potential. The reason why we will do that is by doing that the potential that we are modeling is something like this. So-

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

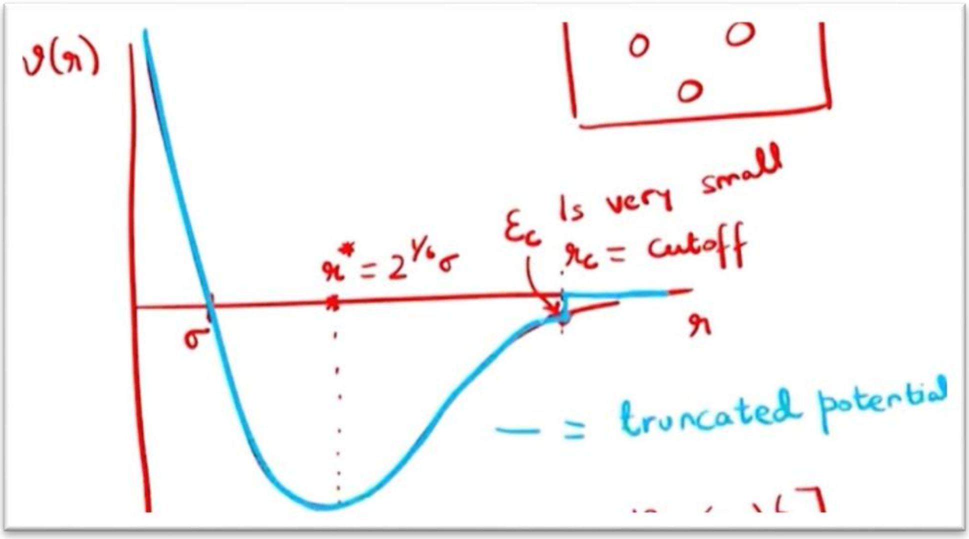
for r less than that r_c the cutoff that we have defined and it is equal to 0 for r greater than equal to r_c.

So, now in our simulation whenever we are computing the energies, of course, there is a step where we compute the distance between the pairs and using the distances I compute the forces. I was telling you that the force computation or energy computation is the most expensive step. So, in Monte Carlo, we are computing the paired energies in MD where computing the forces but nonetheless after the distance computation if we can say that if distances happen to be more than that cut off distances my v(r) equal to zero. That means I will not do an energy computation for pairs which are at distances more than the cutoff distance.

So, let us say for example, if you have a simulation box and I am looking at this particular particle and, this for example is my cutoff distance then I will only look at pairs for this black particle which are lying within a radius of r_c that is sphere of radius of r c with just a center at the particular interest.

So, we are not interested in this guy forming pairs with anything else in the system that will really reduce the number of force computations that we have to do and, that is going to introduce some error to us to speak provided that error is small we are happy with it.

So, let us see what that error should be how much of what should be my value of r_c where we can say that we are good to go. So, the way to look at it is I can look at the modified potential now that looks something like this. So, this is what I referred as a truncated potential.



So, the error in the truncated potential depends on the value of ϵ at r_c or the value of v at r_c. So, vr_c is something that defines the maximum energy between pairs we are neglecting.

Now, here is a small trick that is that is used there. We know that, if there was no interaction between the particles in the system the particles will carry some thermal energy even if there is an interactions the particles carry that thermal energy along with whatever interactions we have and, thermal energy of particles scales like something like ϵ_t which is like, k_BT.

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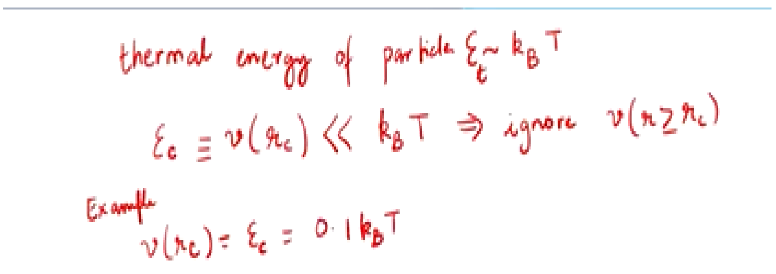


thermal energy of particle $\epsilon_t \sim k_B T$

$\epsilon_c \equiv v(r_c) \ll k_B T \Rightarrow$ ignore $v(r \geq r_c)$

Example

$v(r_c) = \epsilon_c = 0.1\, k_B T$

So, when do we think that interactions will result in deviations from the ideal gas behavior, so ideal gas law, we assume that the molecules are known interacting and they are moving by virtue of their thermal energy. Now, we are trying to incorporate the effect of interactions for a real system. Now, those interactions you may imagine will be important only when the strength of them is significantly higher than the thermal energy. If the strength is significantly less than thermal energy, then in that case the interactions will have pretty much no consequence on the final outcome.

So, let us say for example, there is interaction between particles in an ideal gas model but the interactions are so small that the particles thermal energy dominates over that in that case the particles will continue to move randomly. This is the assumption that we make in the ideal gas model, that it is not that we there is no interaction but the interaction is very weak in comparison to thermal energy. This is what where you will apply an ideal gas model too, whenever you will have two components in the system, they will always be some interaction but, if the interaction happens to be very small in comparison thermal energy, then we can ignore that.

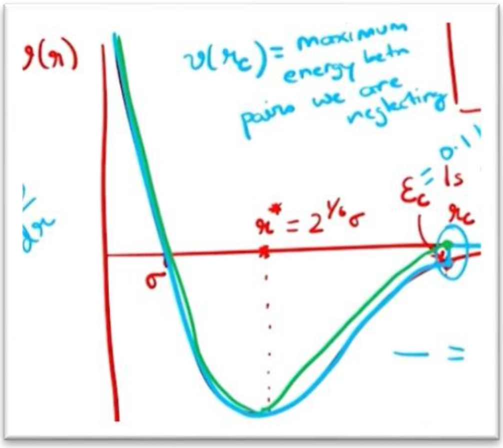
So, using this particular idea, what we say is my ϵ_c or the value of v at r_c; if it is significantly less than my k_BT. Then, I can ignore v of r where r is higher than equal to r_c and this is precisely what we use in our simulation. So, we say for example, I will choose my cut off as something like 0.1 k_BT that is say that now the interactions have decreased to 10% of thermal energy.

So, clearly that is the regime where interactions will stop playing much role and clearly the other pair interactions which are for r less than r_c; are significantly higher in comparison to these pair interactions, so other parent interactions will continue to operate they will do what they are doing but only the payers beyond are greater than r_c are pretty much removed for the computation. So, there is some error will get to that but that error is going to be very small.

So, that means that I will use something like ϵ_c as my 0.1 k_BT and now 0.1 is just a number I can think of 0.5 this is how you want to go about it and typically this basically gives me a criteria for r_c for most typical systems r_c like 2.5σ gives me the ϵ_c pretty small. Of course, it depends on the ϵ as well but nonetheless for this particular form of the potential it turns out that 2.5σ or 3σ is pretty much works for most of the cases, but the way to find it is we can evaluate the value of potential at r_c whatever you are picking and makes your that it is significantly smaller than the thermal energy of the system.

So, now I was telling you about discontinuities and in MD I am interested in dv by dr, although the original potential was not giving me a discontinuity in the derivative the truncated potential does because there is a discontinuity introduced at the particular point.

So, the way to do about it is we slightly shift the potential such that it becomes continuous at the particular point, we discussed that point earlier also when we are doing the code. So, we form a new potential that looks like this. So, at this particular point I basically subtract the v of r_c from vr and we get a new potential that looks something like this.



Although, I have not done a very good drawing what you can notice is that this is much smaller in comparison to that and in reality it is going to be very, very small because ϵ is typically much larger when you have Van der Waals attractions. So, in that case, you will make some error by doing that but that error is going to be very small and by doing this we are making sure that my dv by dr is continuous and therefore we can also use it for molecular dynamic simulations.

Even for Monte Carlo, even though there is no discontinuity in the energy, it turns out that the presence of a truncation is not a very wise thing to do. It may give rise to some artifacts it is always a good idea to use a shifting and truncation together.

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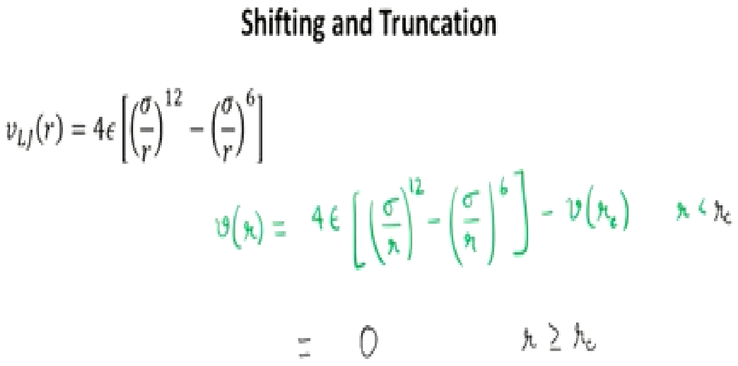

Shifting and Truncation

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$v(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - v(r_c) \qquad r < r_c$$

$$= 0 \qquad r \geq r_c$$

So, therefore, the potential now you work with is something like this, so we have-

$$v_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - v(r_c)$$

so at r_c this pretty much goes to 0. For r less than and this is equal to 0 for r higher than equal to r_c.

So, now we have managed to write a Lennard Jones potential that is not only efficient because there is a cutoff that is been implemented there, but also it is giving me a continuous function when we compute the derivative dv by dr and this is what is one of the most standard function.

So, again if this particular idea is kind of confusing to you it is always go back to the original comparison of the argon case that I have been discussing and you may recall that ultimately whatever function that we had the functional form that we had that was fit to an experimental data or some ab initio data that we had to get the parameters ϵ and σ.

So, we should not assign too much importance to the math that we are giving because anyway, whatever functional form we are using is as good as the fit that we are doing so ultimately it is not that we have a physical basis for doing what we are doing but we are simply picking a functional form that fits the behavior that we get from ab-initio simulations or experimental data and this is ultimately the motivation that we should have and we think about the force fields although, this may give rise to arbitrary mathematical forms that may not have some physical significance in the case of Lennard Jones, the first term clearly has no physical significance there is no reason why we should have 1 by r to the power 12, the second term has

1 because we have 1 over r to the power 6 and that is same as how Van der Waals interactions decay but nonetheless even with some non-physical forms if we are able to capture the behaviour the true behavior we get from a ab initio calculations or more detailed calculations, then we are good to go and this is the motivation why we use the force field spot.

The next lecture we will see how can, we use some more tricks around the cuts off distance to make our codes more efficient and then I will discuss the idea of the force fields which are used for description of molecular systems.

So, with that I want to conclude here. Thank you.