Chemical Principles II

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Demonstration of Boltzmann Distribution

Ok, so we have seen that when the energy levels are different then the particle distribution also will be different, so when we talked about (flo) non interacting particles in two different boxes we saw that the particles were equally distributed then when we calculated for in different types of particles in different energy levels and there after we calculated the probability distributions of particle being in a particular level what we found is that as the energy increases the number of particle decreases.

In an exponential manner for the classical particles which are distinguishable and that is what is known as Maxwell-Boltzmann distribution and then we went on and showed that for Bosons which are in distinguishable particles but can occupy in a several particles can occupy in one level has a different type of distributions call Bose Einstein distribution and then we showed that for Fermi fermions which have half integrals spins and they are in distinguishable but only two of them can be in the same level maximum two of them can be in the same level in that case there was a different Fermi derived distributions that took place.

Now I will show you one demonstration of our simulations done by my PHD student rahman with the help of Abhijeet to make the movie is that we showed that when we use different energies in different boxes then no longer we are going to get the same distributions of the particles.

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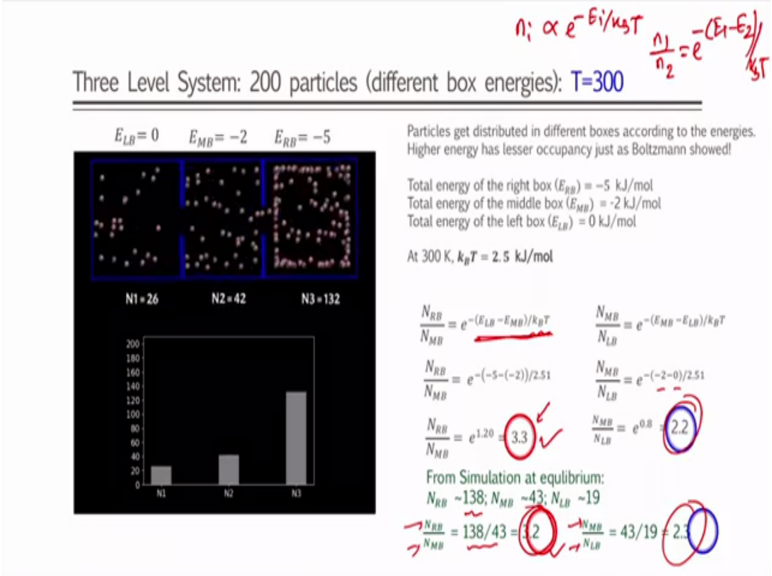

So here there are 3 boxes, 1 box is having 0 energy another is minus 2 another is minus 5 and you see initially the particles all start from middle and they get distributed in other 2 boxes, now we will wait for some time for the simulation to continue the stimulation typically use Lennard Jones of particles without any interactions but in this particular case we have used interactions in two of the boxes they are given by here these units are in kilojoule per mole that we going to show.

What you are observing here is that no longer the distribution of particles in 3 different boxes is same, the distribution is no longer same and rather we see that there are more particles on the right box than in the middle box than in the left box when the system reaches equilibrium and you know that systems reaches equilibrium and the entropy becomes maximum, so therefore an entropy will be maximum when the particle distribution will follow Maxwell-Boltzmann distribution which means in this case an exponential distribution.

So as you mentioned the 3 different boxes have 3 different values of energy that means a particle face different energy values and the temperature is kept at 300 kelvin which is very important and at 300 kelvin the k B T value, k B is Boltzmann constant k B T for 1 mole comes to be around 2 point 5 kilojoule and when you calculate now using Boltzmann distribution the number of particles in the right box divided by a number of particles in the left box then you will get this.

Because let us say your n i is proportional e to the power minus E i by k B T in that case then n 1 by n 2 will become e to the power minus E 1 minus E 2 by k B T and that is what we are showing here and we put the values and we get around 3 point 3 times of the right box will have a 3 point 3 times of the middle box and then we compare middle box with the left box again use the same energy the energy values that are there mentioned minus 2 is for the middle box and 0 for the left box and what we get is 2 point 2.

Now let us compare with the equilibrium values of the simulations which are right now there approximately, so at equilibrium which is calculated by averaging over 3 nanoseconds stimulation at the end of equilibriums period of the simulation we are not going to go into detail of that but we have taking cares so the average number is coming out to be 138 for the right box and 43 for the middle box and 19 for the left box and when we (rat) take the ratios of the number we get 3 point 2 for the ratios of right box and middle box and we get 2 point 3 for the ratios of the middle box and the left box.

So this is just from the simulations and this is what we expect from the Boltzmann Distribution based on the energy of individual boxes and you see remarkably these values 3 point 3 and 3 point 2 are very close and 2 point 2 and 2 point 3 are also very close, 2 point 2 and 2 point 3 are very close and 3 point 2 and 3 point 3 are very close, so what we are what we see here what I demonstrate here is that when there will be different energies then the particle will occupy according to Boltzmann distributions if it has the distinguishable properties which and the classical particles we know that to that has a distinguishable properties and therefore it is following that particular distribution.

Another important thing about the Boltzmann distribution is that the energy scale by k B T which mean is that if the temperature increases then this factor so if temperature increases then 1 by k B T becomes smaller and therefore this factor become smaller so even if the energy difference is higher if the temperature becomes higher than the experimental factor reduces and that will essentially which means that this ratio that you have observed will actually reduce which means that particle will start occupying higher and higher energy levels.

So exactly the same stimulation is done at a higher temperature 700 kelvin to show you what happens.

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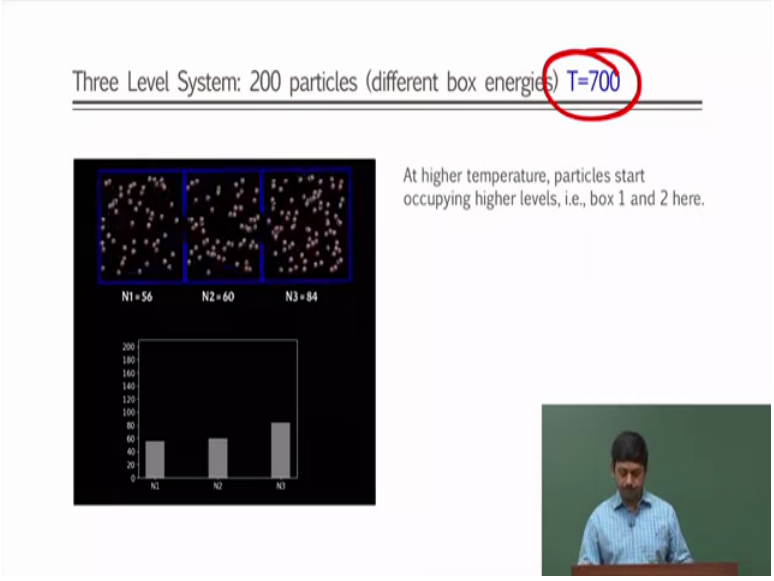

So you see at higher temperature again we start from the same number only thing is that note down that the temperature is now 700 kelvin, so what we expect is that the energy difference will whatever energy difference was there the effect of that will be reduced at that higher temperature particles start occupying and yes low and be hold the number of particles at 3 different boxes are becoming equal now, so it is should not be exactly equal should be you know little bit different however we expect them to have lesser difference compare to what we observed in 300 kelvin.

Now switch your imagination further and take it to a very low temperature what do you expect? When you go to even lower temperature the difference is will keep on increasing and now if you go on and on and go to almost like you know 0 kelvin temperature what you expect is that the difference will become infinite, so e to the power minus 1 by 0 which means e to the power minus infinite which will which means that other boxes should not have in everything will collapse to 1 level and that is what we known as the third law of thermodynamics which says that the temperature at t equal to 0 the entropy value will go to 0 although we know that it is taken to be 0 or perfect crystalline system but statistical mechanic says that at you know very low temperature it actually a can collapse to 1 particular state and we know for Boson switch for which all the (part) you know several particles can occupy the same level we have that Bose Einstein condensation at a very low temperature.