Advanced Thermodynamics and Molecular Simulations

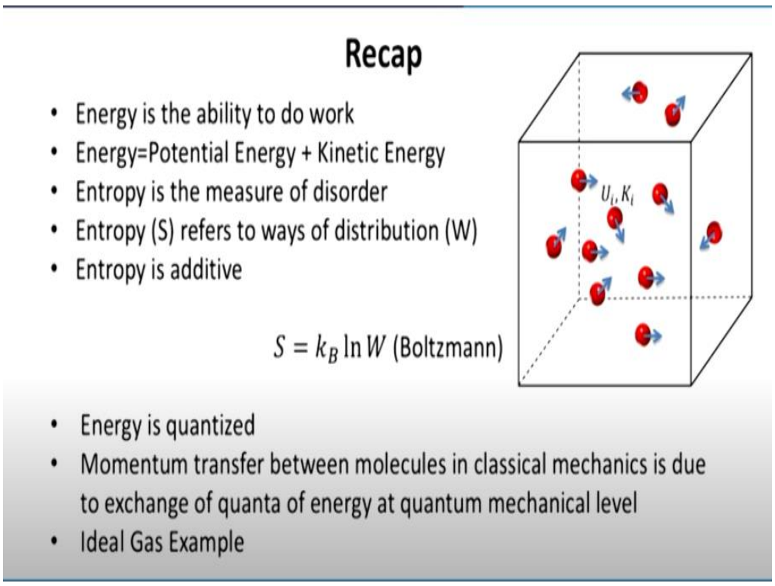
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture - 03
Probability and Probability Distributions

Hello, all of you. So in the last lecture, we have been discussing the idea of energy and entropy. In this lecture, I will introduce the basic notion of probability and how will that be important to thermodynamics, we will see but already we have discussed in the last lecture, that entropy is about disorder and we know that if I want to characterize disorder, then probability is probably the best way of doing it. So in today's lecture, I will basically recap the ideas of probability that you may have already had in the high school or before undergrad and in the following lectures, we will see how these ideas actually get into the description of thermodynamics.

So a quick recap of what we had covered in the last lecture, we said that energy is the ability to do work. Energy is a sum of potential and kinetic energy, that description is always valid. However, when we go to the level of molecules, then the kinetic energy and potential energy of molecules translates to or sums to the energy of an entire system of molecules and then the entropy basically refers to how the energy is being distributed among the molecules in the system and then we said that entropy actually refers to the ways of distribution that are possible.

(Refer Slide Time: 01:57)

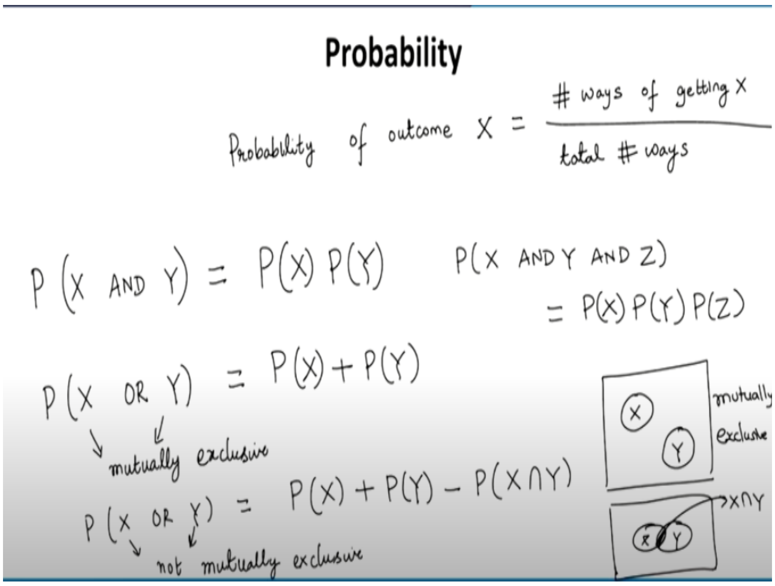


And then we argued that entropy must be additive that means that if I have two halves of system, the entropy of the two halves must add in the system that is formed by making these two halves together and that gave to the idea of Boltzmann that entropy can be a logarithmic function of the ways of distribution, because it satisfies the idea of additivity, and then finally, we discussed the idea of quantization of energy and then we said that momentum transfer in classical mechanics is because of exchange of quanta at quantum mechanical level. And finally, we discussed the ideal gas example.

So today I am, as I said, I will step back a bit and talk about the basic notion of probability and in the following lecture, we will see how it will be useful for the description of thermodynamics.

So what do we mean by probability? So the way we typically define is that portability is always refers to outcome of an experiment where there can be more than one possible outcome, right? So what we say is that the probability of an outcome, and let me say the outcome as some outcome X.

(Refer Slide Time: 03:10)



This can be anything depending on what actual experiment we are doing and this actually means the number of ways in which I can get that particular outcome and divided by the total number of ways or total number of possible outcomes that are possible in the experiment, right.

$$Probability\ of\ outcome\ X = \frac{\#number\ of\ ways\ of\ gettingX}{number\#ways}$$

So probability by definition is normalized. If I sum over the probability of all the outcomes, it is going to be equal to 1, because the number of ways of getting X for all possible outcomes will sum to sum to 1, sum to total number of ways, and that is why P is equal to 1, okay.

So now that refers to one particular experiment. But if I for example talk about two different experiments or two different outcomes, then we can talk about logical rules of probability. For example, if I am interested in an outcome X and an outcome Y. So maybe in two different experiments, I am looking at X happening in one experiment and Y happening in other experiment. In that case, the probability is defined as the multiple of the PX and PY and this can be generalized to more than two outcomes as well for example, P(X and Y and Z) will be equal to P(X), P(Y), P(Z). And you can have even more than three outcomes.

$$P(X \text{ and } Y) = P(X)P(Y)$$

Or

$$P(X \text{ and } Y \text{ and } Z) = P(X)P(Y)P(Z)$$

The other thing we can define is if I look at a particular experiment, and if I ask an or criteria that whether this or that happens, in that case, the probabilities get added. And we will do examples in a minute. So if I talk about the P(X or Y) then it is P(X) + P(Y).

$$P(X \text{ or } Y) = P(X) + P(Y)$$

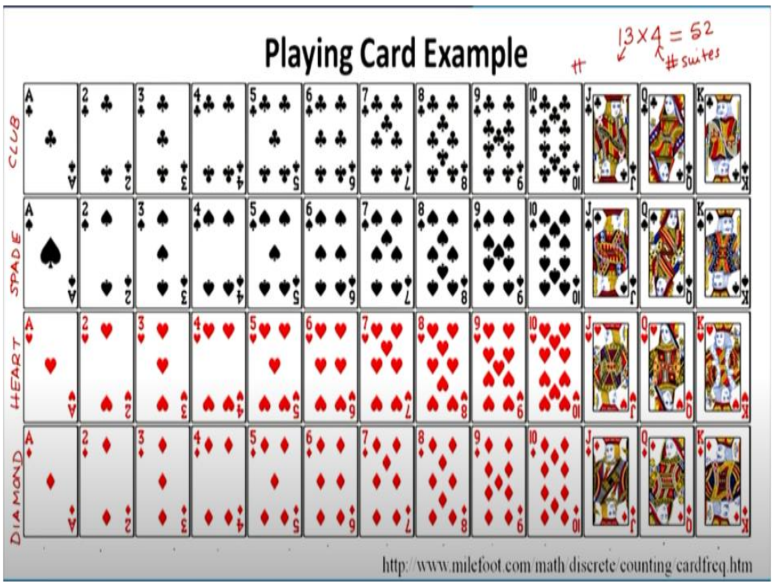
However, there is a small catch whenever we say that, we assume that both X and Y are mutually exclusive that means, both of them cannot happen together. If on the other hand, if both are not mutually exclusive, in that case we will add P(X) and P(Y) and we will subtract the case when both X and Y happen together that can correspond to the idea of intersection in set theory. And the way it goes like is clear to understand using this Venn diagrams.

So let us say for example, this box represents all possible outcomes of an experiment. And let us say this is my outcome X. This refers to the number of ways in which X can happen. And these refer to the number of ways in which Y can happen. In that case, both X and Y since they do not overlap, these are mutually exclusive. On the other hand, when I say it is not exclusive, in that case, X and Y has a reason of overlap, which correspond to the intersection of X and Y and we will do these cases as we go along. Alright.

(Refer Slide Time: 07:55)

So the best way to understand probability for any of us is to look at very simple daily life examples. Let us say for example, playing card or flip of a coin we do not have to really go into thermodynamics to understand probability. So this is for example a game of a playing card, most of you have played it. If you have not played it, I will discuss like what the game is all about and the essential thing to remember in this particular game is that there are 52 cards, right and all the games of playing card pretty much deals with these 52 cards, and these two cards comes in four suits this is what is discussed here.

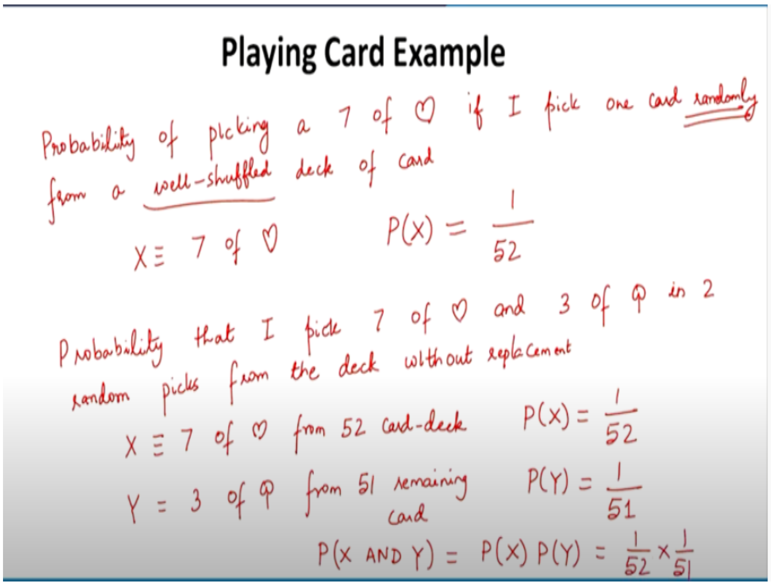
(Refer Slide Time: 08:29)



So this guy is referred as a club, these black guys are referred as the spade. So there are two types of black cards. One is a club one is a spade, and then we have two red card. One is a heart and one is a diamond. And then we have numbered cards 2, 3 4, 5, 6, 7, 8, 9, 10 and then we have colored cards, jack, queen, king and we also has one ace. Typically, the ace is assigned more importance than the other cards but that again it is detail. So the basic idea is that we have 13 multiplied by 4, 52 cards, where 4 is the number of suits. And 13 is the number of cards in every suit that includes nine numbered cards 2 to 10, three colored cards, jack, queen, and king and then finally an ace, right.

So now for example, if I have a well shuffled pack of cards, the shuffling part is very important because we are talking about entropy and then we said that entropy is a measure of disorder and what does disorder correspond in a playing card case. It corresponds to the case where the deck is perfectly shuffled that means, if I pick any card from the deck, it can be any of these 52 cards the assumption is that of course, all the cards are in the deck. And when I pick from any particular location, it will have equal probability to be any of these 52 cards.

(Refer Slide Time: 10:50)



So then, if for example, I ask you that what is the probability of picking a 7 of heart if I pick one card randomly from a well shuffled, and I want to emphasize the word well shuffled only when it is like well shuffled, only when there is no cheating involved, then only the probabilities are going to be equal for any card. So in that case, what is our outcome? Our outcome is getting a 7 of heart and what is the probability of that happening? The probability is number of ways in which I can get that. So there is only one 7 of heart in the deck. So the number of ways of doing that is one and total number of ways is 52. Because there are 52 different cards in the deck. So any of that is possible, right?

$$P(X) = \frac{1}{52}$$

So now for example, I want to look at something like X and Y. And the question can be that what is the probability that I pick 7 of heart and let us say 3 of spade in two random picks from the deck, right. And let us say for the time being I say that I pick one card first. And that should be my 7 of heart. And then I pick one card next, and that should be my 3 of heart. The order is important here, right?

Let us say for example, if I phrase the problem, like I pick two cards, and what is the probability that one is 7 of heart and second is 3 of spade, it becomes a different problem, because then the order is not important. But if the order is important, in that case I have two outcomes. . One is X that is same as earlier, picking a 7 of heart from a pack of 52 cards. And that probability is

$$P(X) = \frac{1}{52}$$

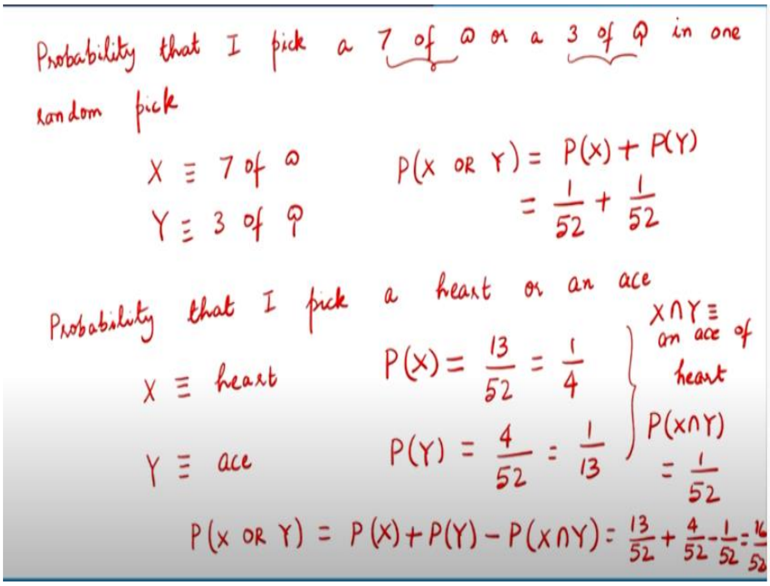
But now once I have picked that card, then I only have 51 cards in the deck remaining provided that I am not doing a replacement of the card back in the deck and I am shuffling it again. So here I am also meaning to say the deck without replacement. All these specifications are extremely useful. So in that case, the Y become the probability of picking a 3 of spade from 51 remaining cards. And what is the probability of that happening? Again, there is only one 3 of spade in the remaining card provided I have not picked it earlier in the first time itself. But if I have picked earlier, then the first event did not happen anyway. So that is already excluded. So for the second time, it is one way of picking the 3 of spade and there are 51 total ways of doing it.

$$P(Y) = \frac{1}{51}$$

And therefore, the probability that this happens that is P(X and Y) is going to be

$$P(X \text{ } and \text{ } Y) = P(X)P(Y) = \frac{1}{52} \text{ } x \frac{1}{51}$$

(Refer Slide Time: 15:40)



Let us look at now a case when we look at an OR operation. So let us say the question I now ask is, what is the probability that I pick a 7 of heart or a 3 of spade in one random pick, again from a well shuffled deck. And in this case, now we have two outcomes, X is a 7 of heart and Y is a 3 of spade and then we are talking about a probability of X or Y. And we have to check first whether X and Y are mutually exclusive. And we can see they are because both of them are not possible because they are two different cards. So this is going to be

$$P(X\ or\ Y) = P(X) + P(Y) = \frac{1}{52} + \frac{1}{52}$$

On the other hand, if we do a slightly different problem, and I ask that what is the probability that I pick a heart or an ace. And now you see, the number of outcomes become more than 1 because first of all, there are 13 hearts, there are 13 cards of every suit. So there must be 13 cards there. So in this case, my X becomes picking a heart and therefore,

$$P(X) = \frac{13}{52} = \frac{1}{4}$$

The second outcome is an ace and again there is not a single ace, there are four aces, one of each suit. So the probability of that happening is 4 divided by 52, that is 1 over 13.

However, now these two events are or these two outcomes are not mutually exclusive there is a case where the card can be both an heart and an ace, when it is an ace of heart in that case, what we have actually is an intersection of X and Y and the probability of that to happen is again there is only one ace of heart. So that should be

$$P(X \cap Y) = \frac{1}{52}$$

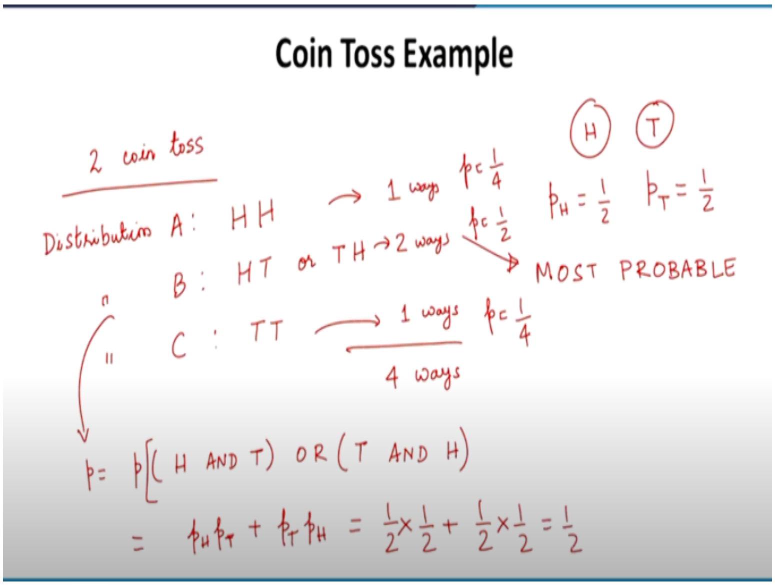
And therefore, for the case when the outcomes are mutually not exclusive, in that case, we are going to have P(X or Y) is equal to

$$P(X\ or\ Y) = P(X) + P(Y) - P(X \cap Y) = \frac{13}{52} + \frac{4}{52} - \frac{1}{52} = \frac{16}{52}$$

So I hope these ideas of adding or multiplying probabilities are clear but now we can look at a slightly more elaborate way of using probabilities and that is where the idea of distributions come into existence, which is what is more important for the purpose of thermodynamics. So let us take a different example, the playing card case, we had 52 different outcomes and I would say that was more complicated than the case we will discuss now.

Let us look at an coin toss example.

(Refer Slide Time: 20:41)



So we toss a coin, that is typically happens in any game, to decide which team will play first and the outcomes in that case is that it can be either a head or a tail and the probability of getting a head is 1 by 2, and probability of getting a tail is 1 by 2.

$$p_H = \frac{1}{2}$$

$$p_T = \frac{1}{2}$$

So in reality, if I do two tosses, we can get 2 heads, we can get 2 tails, and we can get 1 head and 1 tail right and this is what refers to the distributions of various outcomes, right. So for example, in the 2 coin toss case, there are 3 possible distribution- one distribution is a head and a head, the second distribution is a head and a tail. Now there are two possible ways here either the head comes in the first toss or the head comes in the second toss and unlike the playing card example, let us say the order is not important. Then there are two possibilities we can have a head first and tail second or a tail first and a head second and both of them will give me the same distribution one head and one tail. And then there is a third distribution that is having 2 tails.

So if I have to ask the probability of these three distributions, or I ask the number of ways of doing that, the way to look at it is the first one is going to be possible in only one way. So we get a head in the first time, and we get a head also in the second time. This one as you already discussed, it is going to be possible in two ways. And again, this one is possible is in only one way. So total number of ways in this case, if I combine the two coin tosses becomes four. So we are doing two times the experiment, every time we can get two outcomes. So in total, we have four possible outcomes or four possible ways of distribution and out of these four in two ways, we are getting 1 head and 1 tail and in two other ways, we are getting either heads or either tails, right.

So all we can say is that the distribution when we have 1 head and 1 tail is the most probable distribution because probability of this to happen is 1 by 4. Probability of this to happen is 1 by 2. Probability of this to happen again is 1 by 4. This we can also get by using the multiplication rule. So two heads means I get a head first, multiply it by, I get a head again the probability of these two events, which is 1 by 2 multiplied by 1 by 2, which is 1 by 4.

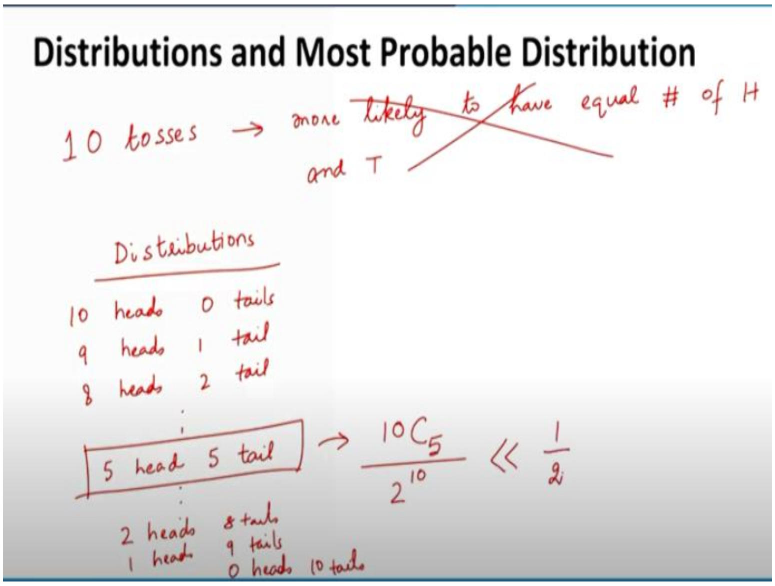
In the second case, there are two ways of doing it. So we either get a head first, or we get a tail first and if I get a head first, then I get a tail second, if I get a tail first I get a head second. So essentially, we multiply 1 by 2 with 1 by 2 for these two cases, and then we have two cases so it becomes 1 by 4 multiplied by 2 that is equal to 1 by 2. So in this case, we are combining both and operation and or operation. So more specifically, what we are doing is the probability in this case, is the probability of getting a head in the first toss and a tail in second or a tail in first and head in second. So for the cases, when it is and we multiply, and p H and p T are both equal to 1 by 2. And in the or case we add, which is why we get the answer as 1 by 2.

$$p = p[(H \ and \ T) OR (T \ and \ H)$$

$$p = p_H p_T + p_T p_H = \frac{1}{2} x \frac{1}{2} + \frac{1}{2} x \frac{1}{2} = \frac{1}{2}$$

Now here is an interesting part. What do we expect if I repeat this experiment more number of times. Let us say for example if I do 20 tosses, is it going to be more likely to have equal number of head and tail? Or is it going to be less likely? And the answer is more difficult than it appears.

(Refer Slide Time: 26:55)



So although by intuition, we expect that if I do 10 tosses, it should be more likely, just because I am doing it many times to have equal number of head and tail. Although we think that should be true, but it is not actually true and the reason is the following. If I again list out the possible distributions, then the number of ways in which we can have 5 head and 5 tails are not going to be 1 by 2 of the total number of ways, it is going to be much smaller than the total number of ways.

And now if I count the number of ways in which I can have equal number of head and tail, what we find is that it is going to be possible in $^{10}C_5$ way where C refers to the combinatorial because I do not care about the order. I can get 5 head in the first 5 tosses. In the last 5 tosses I can get heads in the first toss, third toss, fourth toss, seventh toss and so on, all I care is I should have 5 heads out of 10. And the number of ways to do that is $^{10}C_5$ that is to pick 5 numbers from 10 numbers, they are the number of ways.

So this is the number of way of this and if I count the total number of ways I can do the experiment or I can get the outcomes, we can see for every toss we have two outcomes. So if I do two tosses, the number of outcomes becomes 4 or the number of ways becomes 4. If I do 3 it becomes 8 and if I do 10 times it is going to be 2 to the power 10. And what you find is this number is going to be much smaller than 1 by 2 that is what we have got in the two toss example, okay.

So as we increase the number of tosses, what we observe is that it is going to be lesser and lesser likely to have equal number of head and tail. But what I will discuss in the next lecture is that even though the probability of having equal number of head and tail has decreased, the probability of the fraction of head becoming equal to 0.5 or close to 0.5 has increased and that is the whole idea that is where thermodynamics is built on, right. So we should not be looking at the number of heads, we should be looking at the fraction of heads and actually not exactly the same fraction, but near about the same fraction.

So if I say rephrase the question and say that what is the probability that we have roughly half the number of heads and that probability will increase as we increase the number of tosses and this is what we will discuss in the next lecture.

So basically to summarize, in this lecture, I have basically defined or did a recap on the ideas of probability. I have defined how the probabilities can be combined for the logical AND and OR operation. And then finally, we have discussed an example of a coin toss where we discussed the idea of distributions. So with this I conclude here.

Thank you so much.