

Introduction to Statistical Mechanics
Prof. Girish S Seltur
Department of Physics
Indian Institute of Technology – Guwahati

Module No # 01
Lecture No # 02
Combinatorics and Entropy

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What we have covered so far...

- Prerequisites for the course.
- A historical timeline of notable events and milestones in the development of the subject.
- Zeroth Law, First Law and the Clausius and Kelvin form of the Second Law of thermodynamics.
- The equivalence of the Clausius and the Kelving forms of the Second Law.
- Meaning of microstates and macrostates.
- Boltzmann's definition of entropy.

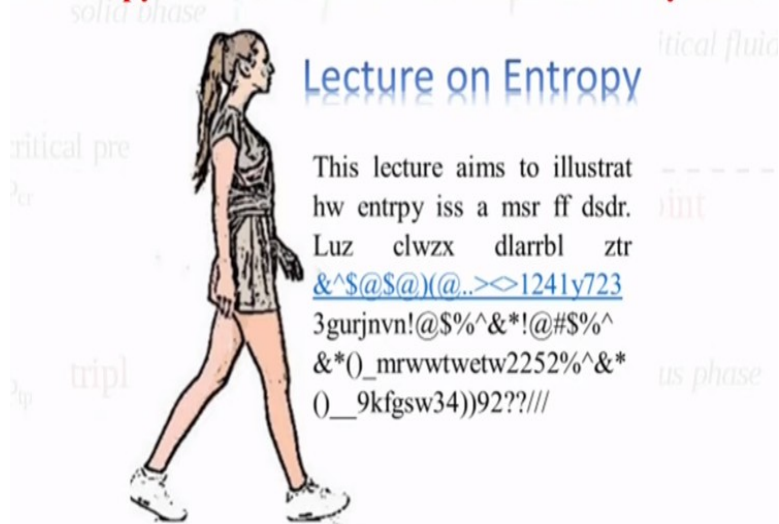
So let us see what we have covered so far, so we started with the prerequisites for this course. I really want all of you to take this somewhat seriously because if you do not have prerequisites you please make an effort to acquire them so the other thing we discussed was a historical timeline of notable event and milestones in the development of the subject. The other thing we discussed was the zeroth law, we mentioned the zeroth law of first law and we mentioned and discussed to some extent the Clausius and Kelvin's form of the second law of thermodynamics.

Then we also made an effort to prove the equivalents of the Clausius and Kelvin forms of the second law then we went on to discuss or you know explain the nature of the meaning of microstates and macrostates of a thermodynamic system. Then finally we ended with the definition or the Boltzmann definition of the entropy of a thermodynamic system. You see that the definition of entropy from the point of you of Boltzmann is it is basically a combinatorial quantity it is all about counting the number of microstates subject to certain constraints.

So now I want to discuss another facet of entropy that is often mentioned in various courses and other discussions of thermodynamics and statistical mechanics namely that entropy is a measure of the disorder of the system, so we really want to understand if that is really true or to what extent is that true. So I am going to show you a sequence of slides somewhat amusing I should admit ,you will see that the notion of disorder is actually somewhat vague and imprecise compared to the definition that Boltzmann gave okay. So let us get on with it, so the question is entropy a measure of the disorder in the system.

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Is entropy a measure of the “disorder” in the system?

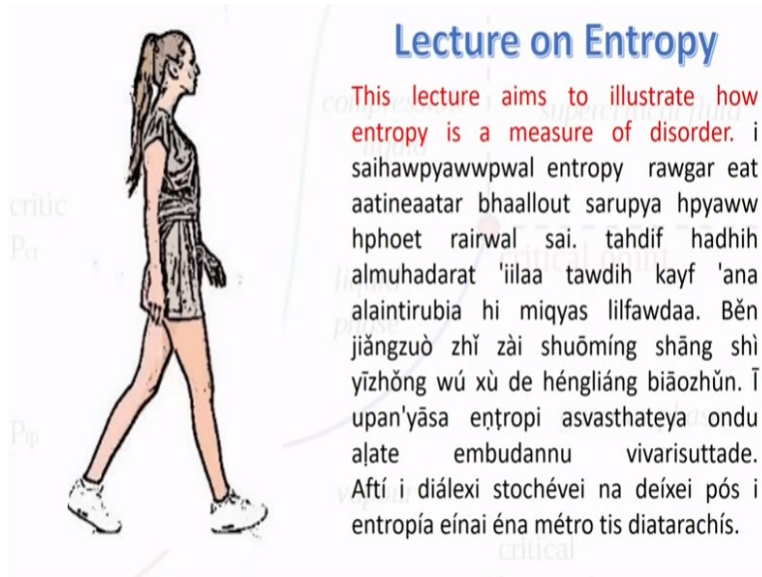


So imagine that there is a lecture on entropy which you know this lady wants to attend and then you see the advertisement for the lecture on entropy it starts off it is meaningful it starts off by saying ‘well this lecture aims to illustrate’ and then later on it becomes less and less intelligible and finally it becomes all sorts of nonsense so the question is you know if I ask yourselves can you spot phrases that are ordered and phrases that are disordered and to whatever extent and meaning that you can attribute that to?

You would probably immediately jump up and say well the first few words with the first sentence the first line may make sense then after that it makes a little less sense and later on it makes no sense at all. So you would kind of instinctively probably think of the first line as being ordered and the later lines as being disordered or the whole paragraph kind of tends towards chaos.

So however I want to point out that this is a certain bias that we have which is called which you know I call it as a bias of coarse graining, okay. So let me discuss what I mean by that so let me give you a slightly different example but a similar one.

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So it starts of you know this lecture aims to illustrates how entropy is a measure of disorder it is in perfectly grammatical English. But then the very next sentence has the word entropy but the rest of it does not seems to make any sense and the third sentence makes no sense at all it does not have any word that I can relate to and fourth one similarly does not have anything and the fifth one vaguely has a certain word like entropy.

So you see then if I ask you the same question you would still probably say that well this is also a paragraph which is mostly chaotic except the first sentence which is in red which is ordered and it make sense. But then I have to point out to you that this is a bias because actually each of this sentences say exactly the same thing but in different languages. So I cannot remember which one is which but I will tell you for example the one the penultimate sentence is in the south Indian language of Kannada.

And the third sentence is in Arabic it says exactly the same thing mainly this lecture aims to illustrate how entropy is the measure of disorder so it is someone who knows only Arabic only and does not know any of the other language would in fact call this a paragraph chaotic but the

ordered sentence would not be the English sentence but rather the Arabic sentence which is the third one.

So it is important for you to understand that you know what we call as a ordered collection of microstates is actually a human bias okay. So let me give you another example.

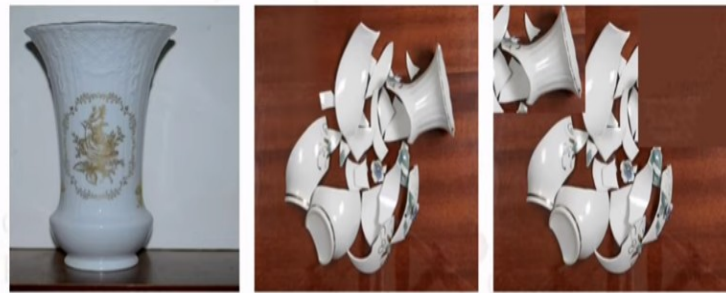
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So this is a vase which is not broken and on the right you see a vase that is broken so now I can ask myself and others you know which one is ordered and which one disordered you would probably instinctively say that well the vase that is not broken is ordered the one that is broken is disordered and why would you say that. So you would probably say that because the number of ways in which you can take a vase that is not broken and break it is infinitely more or enormously more compared to the way in which you can take a broken vase and convert it back to a real vase.

So you see here we are able to see the bias that we are talking about see what we have labeled as ordered is precisely one set of microstate it is one microstate if you like you take all the collection of all the pieces as microstate and it is precisely one microstate but the disordered a state is a vague notion because there are too many different ways in which a vase can be broken and yet we all have decided to lump all those different ways in which the vase can break. And we have called all of that disordered so that is the bias that I am talking about.

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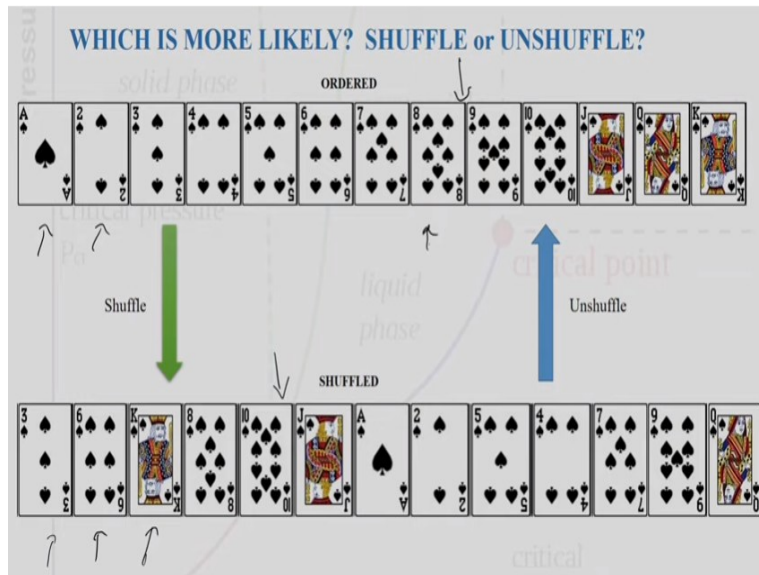
ORDERED - TYPE II

ORDERED - TYPE III

It is our human bias which thinks of the unbroken vase as ordered. This is because the broken phase is not one but countless distinct configurations, each as unique as the unbroken phase.

So instead what we really should probably do is that instead of calling the broken vase disorder we should really call it you know ordered of type 1 and this is ordered of type 2 and if you rearrange the pieces that are broken that would be the ordered of type 3. So there is no such thing as the disordered phase okay.

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So as I told you earlier that it is our human bias that makes us think that a broken vase is disordered whereas a unbroken vase is ordered so I just if you recall I showed you earlier three pictures and I suggested that rather than calling the broken vase as disordered and the unbroken vase as ordered we should simply call of them ordered except they are of different types. So you

can in fact a similar bias is seen in the next example ,imagine I have hand of cards that is shown here so it starts with ace of spades and then the two of spades and so on and hence so forth.

So it is ace 2, 3, 4, 5, 6 up to king so they are all complete spades so now I ask myself so this is an un-shuffled then suppose I shuffle this hand what will I get? I will get shuffled hand so let me ask myself this question which is more likely suppose i have a un-shuffled hand and I shuffle it I get an shuffled hand or is the reverse more likely ,I start with an un-shuffled hand and I shuffle it and will I get an ordered hand.

So suppose I ask you that question you will probably not hesitate in answering that it is more likely for un-shuffled hand to become shuffled rather than the reverse but then if you pause and think about it there is nothing in fact both are equally improbable. See the reason is because see just as this sequence of cards is a unique sequence ,see this particular sequence that I have which is called un-shuffled it is actually also an equally unique sequence see there is a first card 3 the second card is 6 and the third card is king.

So this is as unique as this so there is nothing you know un-shuffled about this , this is just another way of ordering a set of cards and so is this. So as a result if I ask myself what are the chances if I start with this sequence and I shuffle my cards that I get exactly this sequence the chances are extremely unlikely but then so is the reverse. So I start with this sequence and I shuffle the cards the chances that I get back this sequence is equally unlikely.

So in that sense so what we are doing in statistical mechanics is we are actually coarse graining by saying that this is ordered and anything that does not resemble this sequence is disordered or so basically we classify them all as shuffled but it is shuffled is not one sequence of cards but rather a whole bunch of sequences of cards which are not resembling this sequence.

So in that coarse grain sense so if you lump a whole bunch of sequences as shuffled then it becomes fairly obvious that you know it is overwhelmingly more likely for an un-shuffled hand to become shuffled then it is for the reverse to happen. Because the un-shuffled hand is actually not one sequence of card with a whole bunch of sequences and so that way the irreversibility creeps in.

So that is actually the origin of second law of thermodynamics according to Gibbs. So I hope I have made it clear that you know the idea that entropy is measure of disorder is only in this sense that we have decided to coarse grain our notion of what a disordered hand is. So if you lump a whole bunch of states together and choose not to distinguish between them then it is true that an ordered state is overwhelmingly likely to become an unordered state then it is further reverse to happen.

So in fact Gibbs correctly pointed out that it is this bias that makes us believe that entropy of a system which you know second law of thermodynamics which says that the entropy of the system increases with time, that is another formulation of second law which I did not discuss till now but that is the second law of thermodynamics which says that if you have an isolated system where nothing comes in nothing goes out and you look at the entropy of that system it either does not change with time or it increases with time.

So the reason for that according to Gibbs is because we choose to define entropy in this coarse grain sense. So, we choose to purposely ignore the subtle variations of the microstates between different possibilities and we lump all of them as a huge classe as a disordered state and we do not care about anything else. So let me get to this you know calculations of you know let us try to learn how to get some numbers out actually calculate entropy as a number. So you know that a Boltzmann explained to us that entropy is nothing but logarithm of the number of microstates subject to certain constraint.

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Playing cards example

A standard deck of playing cards has two colors – black and red.
 There are 26 distinct cards of each color.
 Imagine I have a hand which has N cards.



There are $C(26, N_1) = \frac{26!}{(26-N_1)! N_1!}$
 ways of getting N_1 black cards in hand.

There are $C(26, N - N_1) = \frac{26!}{(26+N_1-N)! (N-N_1)!}$
 ways of getting $N - N_1$ red cards in hand.

Thus the entropy of the system is

$$S(N, N_1) = \text{Log}[C(26, N_1)C(26, N - N_1)]$$

$$= \text{Log}\left[\frac{26!}{(26 - N_1)! N_1!} \frac{26!}{(26 + N_1 - N)! (N - N_1)!}\right]$$

The entropy $S(N, N_1)$ is a function of the macrostate described by the two macroscopic quantities (N, N_1) . Note that each macrostate corresponds to many possible microstates.

So now here is a deck of hand of playing cards, so now you know that a standard deck has two colors black and red and there are 26 distinct cards of each color. So imagine I have a hand that has a N cards and now imagine that hand has N_1 black cards and the rest are red cards. So $N - N_1$ red cards and N_1 black cards, so now I can ask myself you know if there is a standard deck sitting on my table, I pick cards one by one what are the chances that I will end up with the hand that has N_1 black cards and $N - N_1$ red cards?

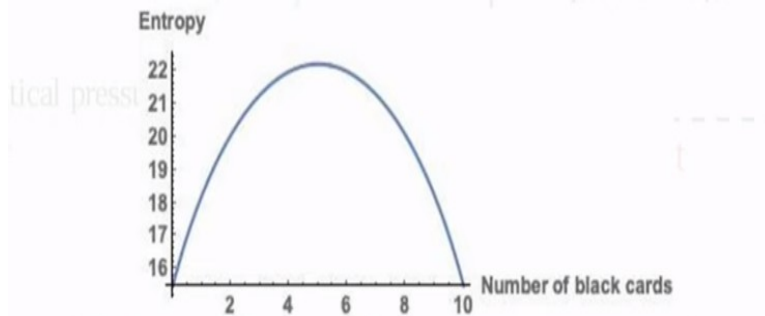
So the answer is clearly it is a simple combinatorial problem and it is just the you know the binomial coefficient or the $C_{N_1}^{26}$ which is the number of ways in which N_1 black cards can end up in your hand and $C_{N-N_1}^{26}$ is the number of ways in which the remaining cards can end up in your hand. So now the entropy of the system so the number the overall number of ways this can happen is really the product of these two numbers and now according to Boltzmann the entropy of the system is the logarithm of this overall number of ways in which you can get this hand from a standard deck of cards.

So as you can see I have written the formula here the entropy is the logarithm of the product of these two numbers. So now what I am going to do is i'm going to plot, so before I plot so let me point out what are the microstates and what are the macrostates actually the microstates have been subsumed in the combinatorics so that mean I have a huge number of micro states with which lead to this huge combinatorial number like $C_{N_1}^{26}$ so they are hidden there but then what are the macrostates, the macrostates are these two numbers N and N_1 .

So the macrostate is described by this collection of two numbers one is the total number of cards the other is the number of black cards. So by implication the number of red cards is the difference between the two. So now you can see that each macrostate really corresponds to a huge number of microstates.

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For example with 10 cards in hand, we may plot the entropy versus the number of black cards.



We can see that the entropy peaks when there are 5 black cards and 5 red cards in hand. The entropy is minimum (but not zero) when all the cards are black or none of the cards are black. The entropy increases with the increase of the number of black cards initially and then falls as the number of black cards approaches the total number of cards.

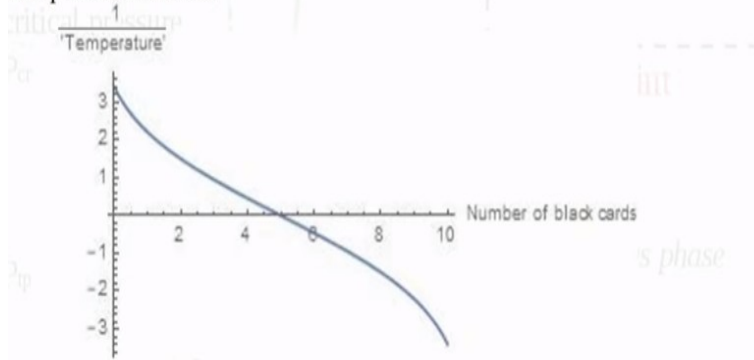
So now let me plot this entropy versus the number of black cards, so you suppose I have 10 cards in my hand and I can plot number of entropy which I have previously defined and you can see that it starts off being small, the entropy is not 0 but it is you know it is not 0 but the entropy is 0 it means there should be precisely one way of achieving that hand. So but we know that even if you know you have no black cards at all, if all the cards in your hand are red there is still many ways in which you can get that hand because after all there are only 10 cards, 10 red cards in your hand but your deck has 26 red cards.

So obviously there is still many ways in which you get that hand, so even if you start off with no black cards at all which is the origin of this plot. So you still have an appreciable entropy and as you increase the number of black cards then entropy goes up and it reaches a peak and then it comes down and when you have only black cards in your hand it again becomes the same as what it was when you have no black cards in your hand.

So this is very characteristic of systems where there is a limit to how many cards there are over this how many energy levels there are for example later on we will see that if there is an upper limit to the microstates that you are looking at, then it is always the norm that the entropy initially increases then comes down. So in fact one can define later on we will see that there is something called the temperature of the system that one can define and here also we may define the temperature as basically the reciprocal of the slope of this plot.

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We may define a type of thermodynamic potential which we generically call "temperature" which is the inverse of the slope of this plot. This temperature is positive sometimes and negative at other times. This is a common occurrence in systems where the entropy is not a monotonic function of its independent variable.



So if you make this plot and find this slope and plot the reciprocal versus the number of black cards you can see that the temperature of the system initially is positive then when the number of black cards is equal to the number of red cards the entropy, the temperature rather goes to 0 and then it becomes negative. So in fact you should not be alarmed by negative temperature because a negative temperature is simply a symptom of the system not having enough microstates at the upper end of the spectrum.

So that means as you increase the number of you know say the black cards in this example, that you run out of states you do not run out of it fully but then you will run out of it quite rapidly and which explains the way the reason why a temperature again you know the entropy comes down and as a result the slope is negative which makes the temperature negative.

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Staircase example

- A microstate is described by n_1 people (all different individuals) standing on the first step, n_2 people standing on the second step and so on until the last M -th step.

- The total number of people on the staircase is

$$n_1 + n_2 + \dots + n_M = N$$

- The potential energy of the microstate is ($w h$ is the weight of one person times height of one step)

$$w h n_1 + 2 w h n_2 + \dots + M w h n_M = U$$



So now let me get to another example which is also illustrative of the notion of entropy and also temperature and that is the example of a stair case where imagine there are n_1 people standing on a staircase and imagine that stair case has say M steps capital M steps. So imagine a microstate where there are n_1 people and notice that people are all different individuals so they are all ,they have different names, different genders they are all different people.

So they are all standing on different steps and there is not restriction let us assume that how many people can stand on a step. So imagine that is a very wide staircase there is no, there's plenty of room or anyone you know as many people as you want can stand on a step. So now imagine that the n_1 people standing on a first step n_2 people standing on the second step until you reach the last step.

So now the total number of people on the stair case therefore is the sum of n_1 , n_2 and n_3 and so on up to n_M and that is constrained to be equal to N so let us assume that the total number of people is fixed nobody enter an or exits that hall where the stair case is present so the you only have a fixed number of people they are all standing on the staircase. So now you can ask yourself what is the potential energy of this microstates so imagine that all the steps are of equal height and all the people of the persons have the same weight.

So this is just for simplicity so as a result each person contributes wh to the potential energy you know if they are standing on the first step for example. So now the total potential energy of the

system is the number of people standing on the first step which is n_1 times the potential energy of the first step which is w into h . So again then you have to add that to the number of people standing on the second step which is n_2 and you have to multiply that with the potential energy of the second step which is twice wh and so on and so forth until you reach the last step.

So notice that we are assumed that there is a last step that means that the total number of steps is fixed so in fact this is going to lead to a behavior similar to the behavior we saw earlier in this example, with the deck of cards so you will see that the entropy increases and then comes down. So we expect similar behavior in this stair case example simply because the total number of steps is fixed.

So later on we will see an example where this is not the case and infinitely many steps, right now let us assume that there are finitely many steps which is M and let me ask myself how many ways are there of redistributing these N different people on this M steps such that their total potential energy is U . So now what we have to do really is solve this mathematical question namely solve this equation.

So we should be able to solve the equation $n_1 + n_2 + \dots + n_M = N$, okay so now let us get to the next example which is that of a staircase. So imagine that there is a staircase on which there are several people standing, so I am going to assume that the people are all different individuals so each person is different, they are you know different genders, they have different names and so on but let us assume they all weigh the same for this example.

So let us assume that there are M number of steps and each step has the same height, so now I am going to ask myself you know I am going to describe a microstate where there are n_1 people standing on the first step and n_2 people standing on the second step and so on until the M -step until the last M th step. So of course by implication we will assume that there is no plenty of room on each step so there is no restriction on how many people can stand on each step.

So now however the restriction that finally emerges is that because the total number of people is fixed which is capital N . So I have to make sure that the microstate that I am looking at which is described by these number $n_1 + n_2 + n_3$ up to n_M . So they have to have the property that if I add them all up I should get the total number of people on all the steps put together. Now I can ask

myself I have a further constraint rather ,that is I am going to demand that not only should the number of people be fixed.

I also demand that their potential energy put together should be U which is fixed ,so now you see let me count the potential energy of this combined system of people standing on the stair case. So now you see n_1 is the number of people standing in the first step and on the first step the potential energy is w times h and w is the weight of each person and h is the height of the each step which will assume is common to all the steps, so all steps are of the same height h .

So now n_1 times wh is the potential energy of people standing on the first step and the potential energy of people standing on the second step is n_2 times $2wh$ because the potential energy of the second step is $2wh$. And potential energy of the last step is Mwh in the number of people standing on the last step is n_M . So that is this this equation that I am talking about so you see I have now 2 equations and several unknowns and these are all my unknowns and I have to obviously there are too many unknowns and too few equations.

So obviously I will get a huge number of solutions but then the only restriction now is that n_1, n_2, n_3 and so on are all integers and they are greater than or equal to 0. So now in principle I have to list all the possible solutions of these two equations and then I count how many solutions there are and that will be the total number of microstates and according to Boltzmann if I take the logarithm of that quantity of that number what I get is basically the entropy of the system.

So now these two equations actually a special case of what are called Diophantine equations which is named after a Greek mathematician who lived in antiquity.

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- These two equations are a special case of what are sometimes known as Diophantine equations. These are called Frobenius equations (not to be confused with the Frobenius method of solving ordinary differential equations with non-constant coefficients).

- *Historical aside:* An algorithm for solving Diophantine equations with two integer unknowns n_1, n_2 :

$$\epsilon_1 n_1 + \epsilon_2 n_2 = U$$

where ϵ_1, ϵ_2 and U are integers was invented by Āryabhaṭa (476–550 CE). This method was given the name **Kuṭṭaka** by his successor Bhāskara I (c. 600 – c. 680).

A wasteful way of finding the entropy is to list all the solutions of these two simultaneous Diophantine equations and count how many there are. There are many codes available in languages such as Python and Mathematica to do this. But we really don't need to list all the microstates we just want a quick way of counting how many there are. For this there is a separate analytical method which will be described later. If N and U are small numbers, these solutions can be enumerated explicitly which is what we do in the next few slides.

But then I have to point that well before Diophantius a special case of this equation with 2 unknowns n_1 and n_2 where ϵ_1, ϵ_2 and U being integers, so all these are integers all these are integers and positive and this there is a method for solving this in terms of unknowns n_1 and n_2 given ϵ_1, ϵ_2 and U and this was invented by Aryabhata in the forth to fifth century and this method was later explained properly by his successor Bhaskaracharya who lived in 600 AD and 680 AD.

So this is just I just want to point out because the algorithm were actually first invented long before Diophantus himself wrote down his equation in a general way. And this special case of Diophantine namely the one that I am staring at right now these they are actually called Frobenious equations so they are a special case of Diophantine equation and you should not confuse that with the Frobenious method of solving ordinary differential equation with non-constant coefficients okay.

So a not so good way of solving these Diophantine equations of Frobenious equations is to list all the solutions of these equations and then count how many they are and you know take the logarithm and you get the entropy and if you really want to do it this way there are codes available in languages such as python Mathematica and so on that can do this. But later on we will see in this course that it is not really necessary to list all the solutions rather you can count the number of solutions without actually listing them and that there is an analytical method for

doing this which I am going to describe subsequently and that is called the generating function method.

But however coming back to the wasteful way of doing it, so if the number of people on the steps are small and the number of steps are also small. So as a result the potential energy is small so we can actually without much effort list all the possible solutions of these two Frobenius equations and then take the logarithm and get the entropy and so that can be done by hand and that is something probably in some of exercises I will be encouraging you to do that by asking you to do repeat this calculation for you know 5 steps in 6 people and that sort of thing okay.

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Take a specific example with 2 steps and 3 people.

$$n_1 + n_2 = 3$$

All three people can be on the first step, or one person can be on the first step and two can be on the second, two can be on the first and one can be on the second or all three can be on the second.

In the first case the potential energy is $U = 3 w h$

In the second case the potential energy is

$$U = w h + 2 \times 2 w h = 5 w h$$

In the third case the potential energy is

$$U = 2 w h + 2 w h = 4 w h$$

In the fourth case the potential energy is

$$U = 3 \times 2 w h = 6 w h$$

So now let us take an specific example with two steps and 3 people so now you see the constraint that I have is that the number of people is three and the number steps is two which is described by the index there so that two steps and 3 people. So what are the ways in which I can manage this, so you see all three people can be on the first step or one person can be on the first step and two can be on the second or two can be on the first step and one can be on the second step or all three can be on the second step.

So these are the only possibilities, but notice that the people are all different so it is going to also effect the way in which we count. So in the first case the potential energy is when all people stand all the people means they are only three people they are all standing on the first step the

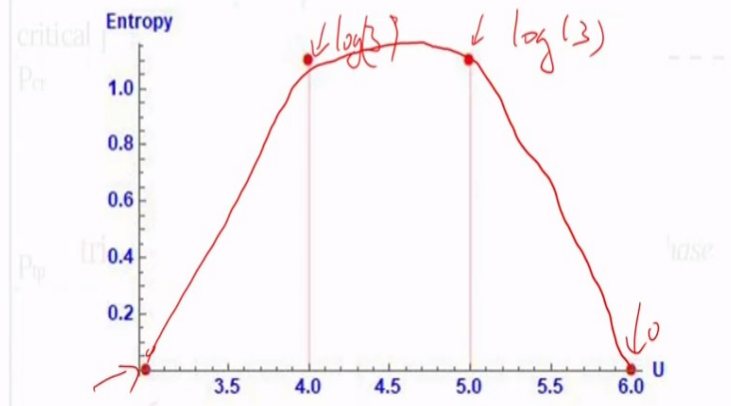
potential energy is $3wh$. Now in the second case the potential energy is wh because there is only one person standing on the first step and that two people standing on the second step so that means two people two times potential energy of the second step which is $2wh$ which is $5wh$.

So similarly if you look at the third case, in the third case there are two people standing on the first step and one person standing on the second step so it is two times wh for the first step and one times $2wh$ for the second step and that makes it $4wh$ for the third case. As the final case is when the potential energy is such that all the people are or all the people means all the three people there they are all standing on the second step.

So in which case the potential energy is 3 people times the potential energy of the second step which is $2wh$. So you can write a list plot or you know point plot of the entropy because the entropy is now every discrete object because so few people and so few steps so you see.

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In the staircase example, all people are distinct individuals. This means there are 3 different ways in which the potential energy can be $U = 4wh$ or $5wh$. This means the entropy versus potential energy would be similar to the earlier example – has regions with positive as well as negative temperature.



So if the energy of the system is you know wh so I am just thinking of you know a simple example, so if I have taken wh to be 1 actually so if when wh is 1 so what are the possibilities for the energies, you can see that the smallest possible energy is really 3. So and the largest possible energy is 6 so it is the values of U on the x axis is going to be 3, 5, 4 and 6 are rather 3, 4, 5 and 6, so on the x axis you have only these possibilities 3, 4, 5 and 6 and on the y axis you have the entropy which is the logarithm of the number of ways in which the energy can be 3, 4, 5 and 6.

So let us see how many ways there are in which the energy can be 3, so when can you get 3wh as the energy that is when all the people are standing on the first step, all 3 people are standing on the first step. So there is only one way in which you can do that you just simply make all 3 people stand on the first step. But however in the second case you know there is one person standing on the first step and two people standing on the second step and there are three ways of doing this because you know notice that people are all different.

So you can make George stand on the first step you know Aditya stand on the second step and Sourav stand on the second step so you have three people but then you can interchange you can Sourav stand on the first step and George stand on the second step you get a different of configuration so because the people are all different, so you get different ways of doing that, different ways of achieving the potential energy 5 wh and how many there are of doing this clearly there are 3 ways of doing it because you know you just have to decide whose stands on the first step and then other two are forced to stand on the second step.

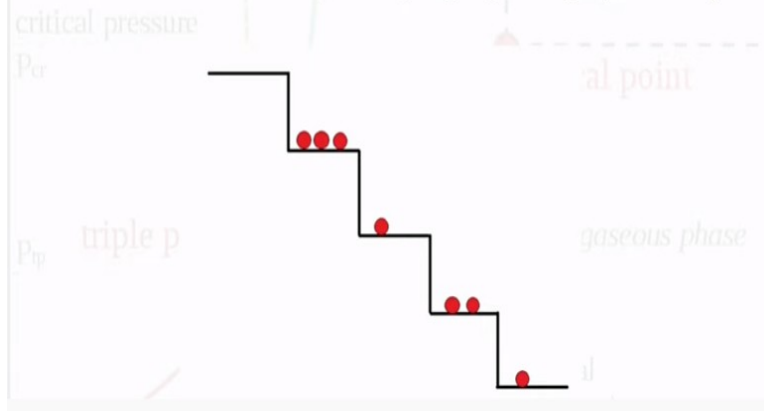
So same in the case of the third example where you force one person to stand on the second step and the other two are force to stand on the first step so that three ways in which you can select the person you want to make stand on the second step. So as a result when the potential energy is 4 or 5 the number of ways of doing it is 3 so when the entropy is $\log 3$ in these two examples.

So as a result you see whether entropy is 0 because there is only one way of doing it when the energy is 3 and there is only one way of doing it when the energy is 6 but there are 3 ways of doing it when the energy is 4 or 5, so as a result the entropy is $\log(3)$, $\log(3)$ there and 0 here and 0 there. So you see as a result even here the entropy increases then flattens out then again decreases and becomes 0 so this is reminiscent of what we saw earlier namely in this example, the playing cards example it has a similar feature.

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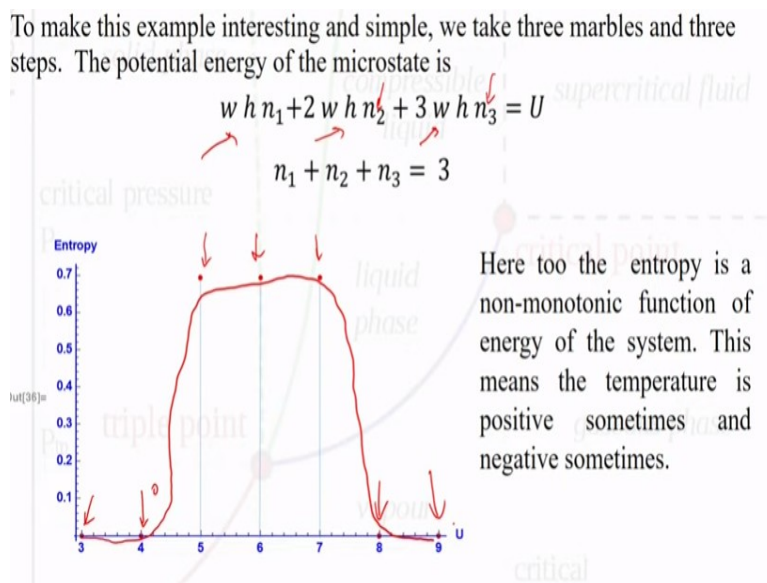
Marbles example

Instead of people, imagine there are identical marbles. In this example, since all marbles are the same, we are going to get a slightly different plot.



So now let me give you a slightly different stair case example, instead of people imagine there are identical marbles, in other words the people where all different you know you had George, Aditya, Sourav they are different people but then imagine there are identical marbles. So when there are marbles you know the countings are going to be different because they are all identical. So here is a typical microstate that I am looking at so you have one marble on the first step and then two marbles absolutely identical on the second step and one marble on the third step and three marbles on the fourth step and so on.

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So in this example for the sake of being concrete let me take three marbles and three steps so what are the constraints that I am looking at, I am looking at this constraint that the total number

of people, the number of persons should be 3. So the number of persons is 3 so $n_1 + n_2 + n_3$ should be 3 but I also want the total potential energy of a system to be fixed which is U . So how do I achieve that you know I have three steps so you know the first step has potential energy wh so and then n_1 people there which is my microstate n_1, n_2, n_3 is my microstate.

So you have wh into n_1 is the potential energy of the first step then $2wh$ is the potential energy of the second step and then two people there and $3wh$ is the potential energy on the third step and in 3 number of persons on the third step and here too I can count and here too you can find that when the energy is you know either 3 or 4 that the number of ways in which you can do you know just precisely one in which case the entropy is actually 0.

So however when it is 5, 6 or 7 you can figure out what it is ,its going to substantial but certainly not, see notice that it is different from the, so this plot is not exactly the same as the people example, so there here the more energy is where the entropy is actually 0 but here too you see that even though it is slightly different because the marbles are all identical unlike the other example where the people are all different but here too we have a common feature namely the entropy is actually increases ,flattens out then again decreases.

So here you see that here too the temperature is actually positive for some of the values of U and then again negative for some other values of U and this is a symptom as I said of a system where you know the number of steps or number of energy levels or whatever you want to call it when that is fixed. So when you have some restriction you know when there is no room at the top as it where when it becomes crowded at the top ,then the entropy goes down because you cannot really that the number of ways in which you can do things starts to diminish.

And you do not have many options left and as a result the entropy shrinks to 0 finally. So however if you do not like the situation and you do not want the entropy to shrink to 0 there is a way of doing this and that is you do not restrict the number of steps. So what you say is that you know I have a endless staircase, of course I have a fixed number of marbles or fixed number of people but I do not restrict on how high they can stand. So I have an endless staircase, so now I am asking myself that imagine that I have 10 people on the endless staircase.

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Marbles on an endless staircase

In the earlier examples, the temperature was positive sometimes and negative sometimes. The main reason for this is there is a maximum energy of the system in each of these examples. This is why now we consider another example - an infinite staircase. Consider 10 identical marbles.

$$n_1 + n_2 + n_3 + \dots = 10$$

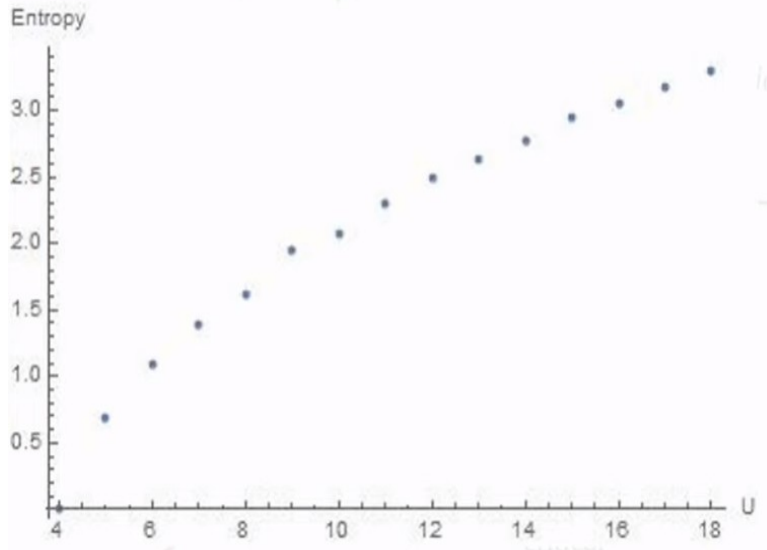
$$w h n_1 + 2 w h n_2 + 3 w h n_3 + 4 w h n_4 + \dots = U$$

It is possible to write a code in some programming language such as Mathematica to find the number of ways in which this may be accomplished given the value of U as some integer multiple of $w h$.

But in this example I have chosen marbles rather than the people because it is easier to do it with marbles because I do not have to distinguish between them. So I am talking about marbles now, so you have 10 marbles on endless staircase and as by now you should know how to write down these constraint equations, the Frobenius equations as it were and the first Frobenius equations is the total number of particles which is forced to be 10.

And the total potential energy and I won't repeat the arguments here and it is going to be U so again you can write a code for this I think you should do it yourself because I do not want to be biased towards any particular any particular language I prefer a language called Mathematica which is very nice for this sort of thing but I am you know I am not recommending any particular programming language you could work in Python or MATLAB, they are all equally good.

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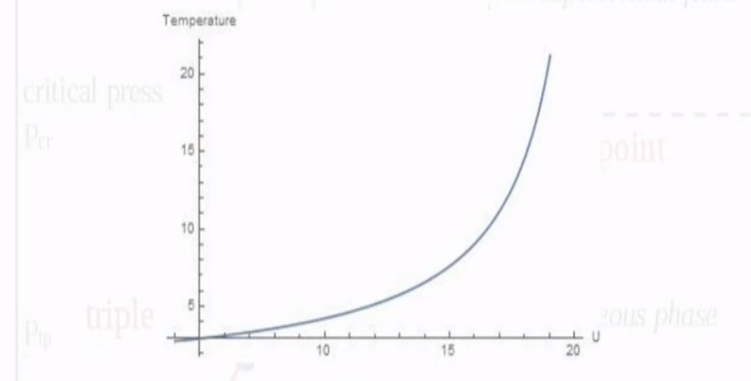


But whatever it is you could simply go ahead and try and solve these equations and when you do you get this plot so you can plot the number of the energy of the system versus the entropy of the system so you see the entropy actually increases monotonically, it never goes down ,it increases with energy okay.

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The temperature (for reasons that will be explained in the next few lectures) of the collection of marbles is defined as:

$$T = \frac{1}{\partial S(U,N)/\partial U}$$



It is easy to see that the temperature is a monotonic function of the total energy U

So now you can plot the temperature which is defined as the reciprocal of this slope of the earlier plot so it is going to look like this and notice that it is always positive. So the temperature is increasing and positive always so indicating that the entropy is a, you know non decreasing function of energy. So that is a symptomatic of a system where the there is no upper bound to the total number of energy levels or there is no upper bound to the energy of the system itself.

So if there is no upper bound to that energy there is no crowding at the top and there is lot of room at the top so entropy can, you can rearrange the microstates to get a entropy which is a non-decreasing function of the energy.

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Quantum objects

- Indistinguishability is a hallmark of quantum mechanics. In classical physics it is always possible to track a particle in motion and thus tell it apart from the others. In quantum mechanics, you can never be sure since you can only measure the position or momentum but not both. This means that two particles can be present with the same momentum but undetermined positions and we cant tell them apart since we don't know where each one is – we only know their common momentum.
- In quantum mechanics, indistinguishable particles are typically fermions or bosons. The example of identical marbles on an infinite staircase is an example of bosons (discussed earlier). We could also add a restriction to this example which would then describe fermions. The restriction could be - there cannot be more than one fermion on a given step of the staircase.

$n_1 + n_2 + n_3 + \dots = 10$
 $wh n_1 + 2wh n_2 + 3wh n_3 + 4wh n_4 + \dots = U$
 $n_1, n_2, n_3, \dots = 0, 1 \leftarrow \text{FERMIONS}$

So let me now give a name to the objects that I have been calling marbles so notice that the marbles are actually indistinguishable objects and indistinguishability is a hallmark of quantum mechanics so you do not have indistinguishability in classical physics because it is ,you can always, so if you have a you have a particle a classical particle moving you can always tell it apart from the others because you can you can know the position and momentum of each particle separately in principle you can know what it is.

And you can follow each particle around and so there is no way in which you can confuse that particle with some other particle because no two particles can be not only in the same position but have the same momentum. If two different classical particles have the same momentum and same position they had better be the same particles. So, however in quantum mechanics you cannot really do that you can either track the position or you can track the momentum.

So if you decide to track the position then you cannot be sure that you are looking at the same particle because you can have the another particle with the same position with the different momentum but then you will confuse that for the same particle because they have the same

position. So the point is that indistinguishability is the hallmark of quantum mechanics, now indistinguishable particles in quantum mechanics come in two types one of them are called Fermions the other called Bosons.

So the example of identical marbles that I gave you earlier where there is no restriction on how many particles there can be on each step of the staircase is an example of Bosons. So you can have another example of Fermions where there is restriction namely you say that I only allow a maximum of 1 marble on each staircase. So either I will leave that step empty or I allow only one marble to occupy that step of the stair case.

So in which case you have a total number of, so now your Frobenius equations become this is which is of course the constraint that the total number of marbles is 10 and the second one is as usual the total potential energy is U and the important constraint which tells you that these are fermions is that the number of marbles on each step is either 0 or 1. So that is a lot to swallow so in this hour we have learnt a lot hopefully but one common thread among all the ideas that you have learned in the last one hour is that you know you have this Frobenius equations that you are forced to solve by hand and you are forced to enumerate all the solutions rather wastefully just to count how many there are so Boltzmann tells you that if you somehow by hook or crook know the number of solutions of these Frobenius equations the logarithm of that number is the entropy. So if you are only interested in entropy it is wasteful to list all the solutions but in this last one hour we have done just that, we have used simple example with small number of particles small number of you know steps and then we have decided to explicitly enumerate all the solutions and count them explicitly.

So in the next lecture I am going to tell you a very clever analytical way of side stepping or avoiding having to list all the solutions of this Frobenius equations. So there is an analytical way, a clever one of counting now many solutions there are without actually listing all the solutions. Let us call the generating function method and that will be subject of the next hour of lectures.