

Statistical Thermodynamics for Engineers
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Lecture 04
Combinatorial Analysis for Statistical Thermodynamics

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Statistical Thermodynamics for Engineers
Lec4

Combinatorial Analysis for
Statistical thermodynamics

am \rightarrow discrete energy
levels
for molecular
systems

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Distinguishable objects

1. In how many ways
N identical but
distinguishable objects
be placed

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1.7 In how many ways
 N identical but
 distinguishable objects
 be placed in M

different containers
 with a limit of one
 object per container



$$N \leq M.$$

→ First object can be
 placed in any of the
 M containers

→ Second object
 $(M-1)$ containers

$$W_1 = M(M-1)(M-2)\dots(M-N+1)$$



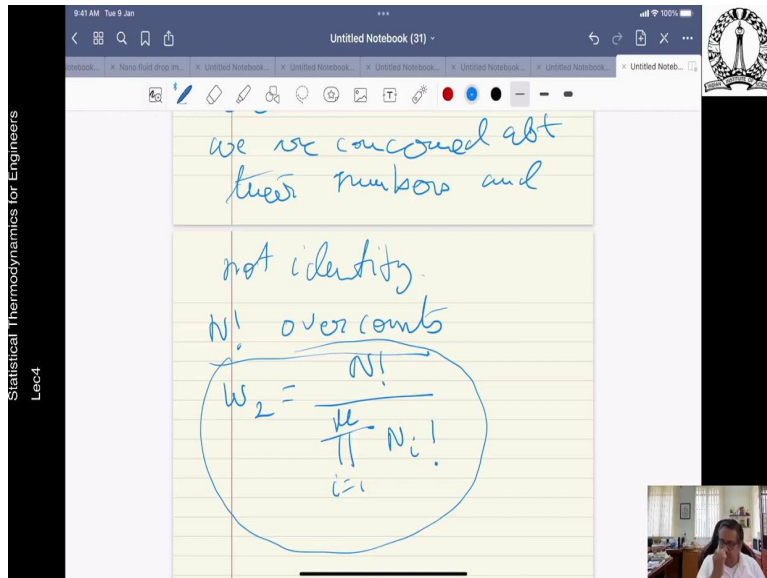
$$W_1 = \frac{M!}{(M-N)!}$$

2.) In how many ways
may N identical, distinct
objects be placed in
 M different containers each
but



objects are placed in
 M different containers each
but in container holds
exactly N_i objects
Total # of permutations
for N objects is $N!$.
However within each
container permutations
are irrelevant





Welcome to Lecture 4 of the statistical thermodynamics for engineers. So, in this particular class, we are going to first start doing what we call the combinatorial analysis or statistical thermodynamics. So, in this particular pane as we stated previously that in quantum mechanics ultimately what is quantum mechanics to this establishes the relevance that why we are studying this that the quantum mechanics we already say that dictates that the energy levels are discrete.

So, discrete energy levels for molecules systems so, this is this we already did in our first class, well later on see that the energy level is not only thing it has something called energy states as well, but we will see that a little bit later and that energy states are called (ϵ_i) (01:22), but for the time being.

Let us take a pause a little bit of a pause and let us try to see that how we can establish some statistical techniques before we delve into what are the energy levels and what are the energy states. So, we will come to that in a little bit later. So, first before doing this, let us look at something called distinguishable it has established a few concepts like distinguishable objects. So, what do we mean by distinguishable objects?

So, distinguishable objects, I have got basically three significant cases each of this can be considered by posing slightly different fundamental query. So, let us take the first one. So, the subject is distinguishable objects in which you can distinguish the objects from one another. So, let us ask the question that in how many ways N identical but distinguishable we should go objects be placed in M different containers with a limit of one object per container.

So, you got the point. So, the question that we fundamentally want to address over here is that in how many ways in identical but distinguishable objects can be placed in N different containers with a limit of one object per container. So, the limitation of one object per container requires that your N should be less than equal to M , M is greater than N in this particular thing cannot happen.

So, what happens here the first object can be placed in any of the M containers? The second object can be placed in N minus 1 container; the third object can be placed in M minus 2 containers in any of those two containers. So, that if I write it properly so, the first object can be placed in any of the M containers.

Similarly, the second object you take the second object that can be placed in M minus 1 container, correct and so on and so forth. So, the total number of ways becomes if I write it as W_1 what does it become M into M minus 1 into M minus 2 so long and so forth M minus N plus 1, in other words, W_1 becomes M factorial divided by M minus N factorial.

So, this is the first way I think we understood it very clearly that when there are these kinds of objects and they are N containers, they can be arranged the number of ways in which they can be placed is given by this. Now, let us ask the second question again with distinguishable objects. Here the question is in how many ways may N identical distinguishable objects be placed M different containers, those parts are all the same containers such that i th containers holes exactly in N_i objects.

So, you got the question right previously we said there should be like N different M objects are placed in N different M containers that such that is the limit of one object per container here we have stating that N identical but distinguishable objects are placed in M different containers such that the i th container contains N_i a number of objects.

So, we know for sure, in this particular case, it is if we analyze the problem the total number of permutations for N objects is N factorial but however within each container the permutations are irrelevant as we are only concerned with their number rather than their identity since, we are concerned about their numbers and not identical.

So, we are on the cover we do not want to differentiate between Ram and Shyam we do not want to differentiate like that we just are concerned about the number. So, even though N objects can be permuted in N factorial ways, but within a particular container, that permutation does not really matter. So, hence what happens is that this N factorial, so, therefore overcomes it overcomes a number of ways in which this arrangement can happen.

So, therefore, we have to correct so, therefore, the number of counts because if I write it as W_2 this becomes N factorial then it becomes 1 to M N_i factorial understood the point. So, this then becomes this overcomes. So, now, therefore, to get the real answer we have to divide by the individual permutation that happens within the containers we have to take that out. So, this is the ultimate result that you should get. So, these are for N distinguishable objects arranged in M containers such that i th container that contains in N_i number of objects.

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$\prod_{i=1}^M N_i!$

3.7 or identical, distinguishable
Objects be placed in
 M different containers
with no limitation on
the # of objects per
 C_i

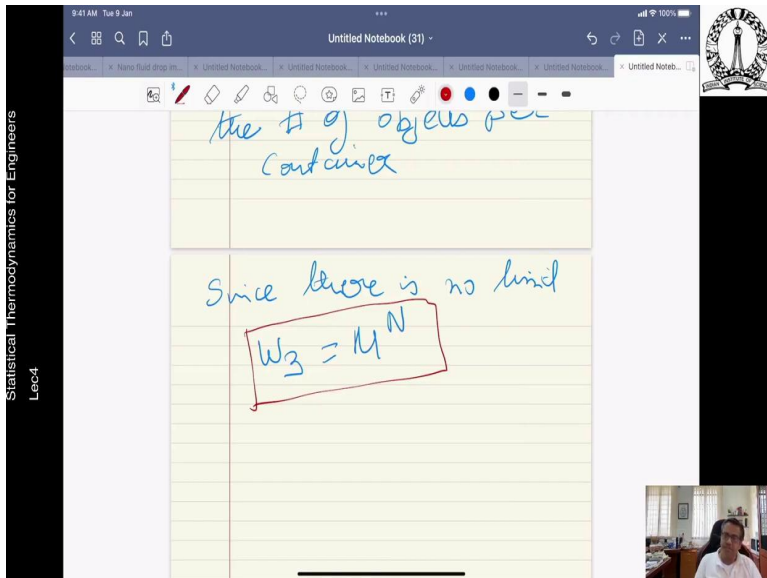
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the # of objects per container

Since there is no limit

$$W_3 = M^N$$


A screenshot of a digital notebook interface. The top bar shows the time as 9:41 AM on Tuesday, January 9th. The notebook title is "Untitled Notebook (31)". The page contains two lines of handwritten text in blue ink: "the # of objects per container" and "Since there is no limit". Below the second line, the equation $W_3 = M^N$ is written and enclosed in a red rectangular box. The notebook interface includes a toolbar with various drawing and editing tools. In the bottom right corner, there is a small video feed of a person.

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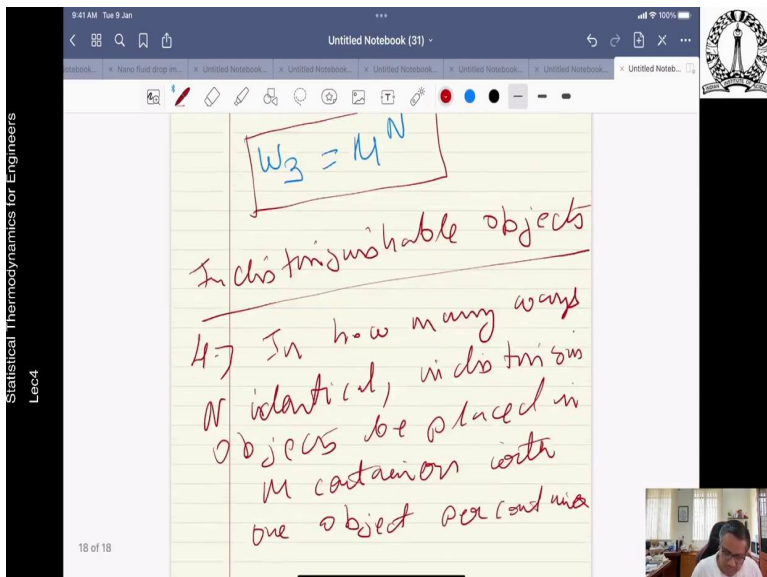
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$$W_3 = M^N$$

Indistinguishable objects

4.7 In how many ways
 N identical, indistinguishable
objects be placed in
 M containers with
one object per container

18 of 18



A screenshot of a digital notebook interface, similar to the one above. The top bar shows the time as 9:41 AM on Tuesday, January 9th. The notebook title is "Untitled Notebook (31)". The page contains the equation $W_3 = M^N$ in blue ink, enclosed in a red rectangular box. Below the box, the text "Indistinguishable objects" is written in red ink and underlined. Further down, a question is written in red ink: "4.7 In how many ways N identical, indistinguishable objects be placed in M containers with one object per container". The notebook interface includes a toolbar with various drawing and editing tools. In the bottom left corner, the page number "18 of 18" is visible. In the bottom right corner, there is a small video feed of a person.

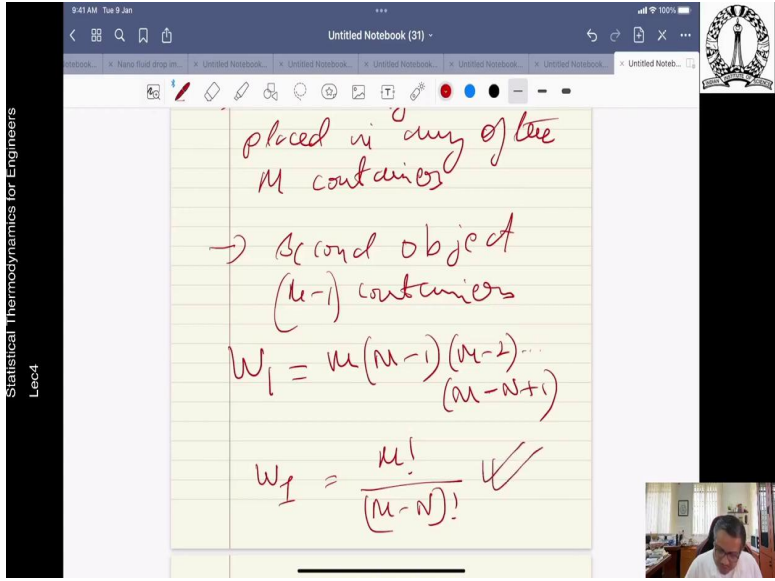
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placed in any of the M containers

→ second object $(M-1)$ containers

$W_1 = M(M-1)(M-2)\dots(M-N+1)$

$W_1 = \frac{M!}{(M-N)!}$ ✓

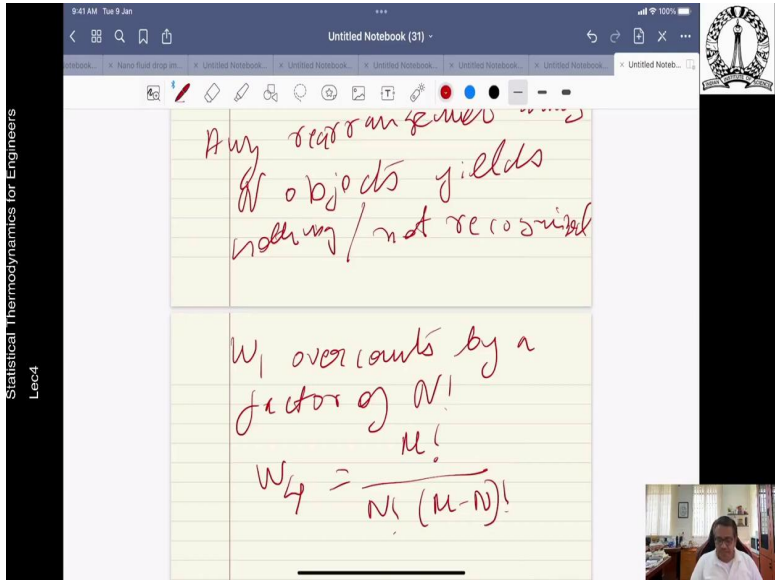


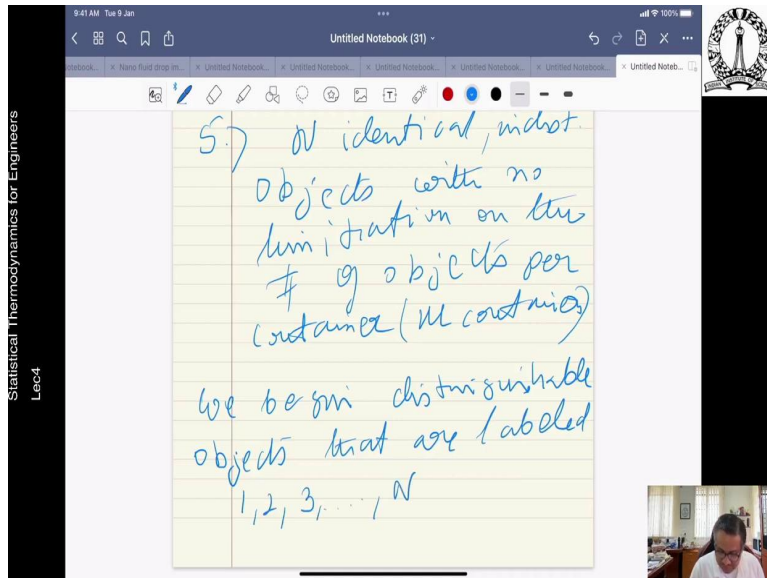
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Any rearrangement of objects yields nothing / not recognised

W_1 overcounts by a factor of $N!$

$W_4 = \frac{M!}{N!(M-N)!}$





So, therefore, this brings to the third question. So, the third question once again the question is the same and how many ways N identical distinguishable we should all objects be placed M different containers with no limitation. Now, the question is with no limitation on the number of objects basically number of objects per containers.

So, here therefore, the answer is since there is no limit it becomes fairly easy your W_3 becomes M raised to N . So, this brings the third possibility. So, for distinguishable objects therefore, there can be like three types of questions that you have fundamental queries and we will see how they are linked with quantum mechanics, the statistics of the quantum mechanics and answer is pretty clear that these are the three different ways the number of ways in which the objects can be arranged in N different containers.

So, this brings us then to indistinguishable objects so, there are therefore now two cases of significance that we can ask that same way that we asked the question with the distinguishable objects here we asked the question for indistinguishable objects asked named it is 4 so, in how many ways the question is N once again identical now, it is indistinguishable objects be placed the M containers with one object per container.

So, this is a imposition. So, now, for indistinguishable objects any rearrangement among the N objects is cannot be recognized. So, therefore, the W_1 that we saw previously that overcomes the number of ways in which indistinguishable objects can be arranged by a factor of physically M factorial.

So, if we look at the first case here so, that was the case if you recall this was the total number of arrangements that we had. Now, because the objects are indistinguishable now, so, any rearrangement among N objects yields $(N!)$ (13:48) that means it is not recognized you cannot differentiate as a result of that your $W1$ overcomes.

So, and overcomes by a factor of N factorial $W4$ there $W4$ is written as M factorial it is almost similar divided by N factorial. So, this is a new one and M minus N factorial. So, as you can see, so, this is the way this is the same question as question one except that the objects are indistinguishable now.

Now comes the fifth and more or less the final query that we will do over here once again it is N identical indistinguishable object the same question with no limitation on the number of objects per container and there are M containers. So, it is the same question as three $(M!)$ (15:15). Now, this is a fully unconstrained let us look at the little bit carefully these are indistinguishable objects, there is no limitation on the number.

So, it is almost like saying that lets us actually initially assume that distinguishable objects are labeled as 123456 up to n . Now, let us now arrange these objects in our role with M containers basically separated by partitions. Basically, you are putting partitions and so, that is an example that you can think of. So, let us put it writing say we assume say we begin by stating obvious that special initially assumed that distinguishable as a M indistinguishable objects and they are that are labeled 123 upto N .

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objects that are 1 each
 $1, 2, 3, \dots, N$

| | | | | |
|---------|------|---|-----|----------|
| 1, 2, 3 | 4, 5 | 6 | ... | $N-1, N$ |
| ① | ② | ③ | | ④ |

↳ partitions identify the containers.
 N objects, $(M-1)$ partitions

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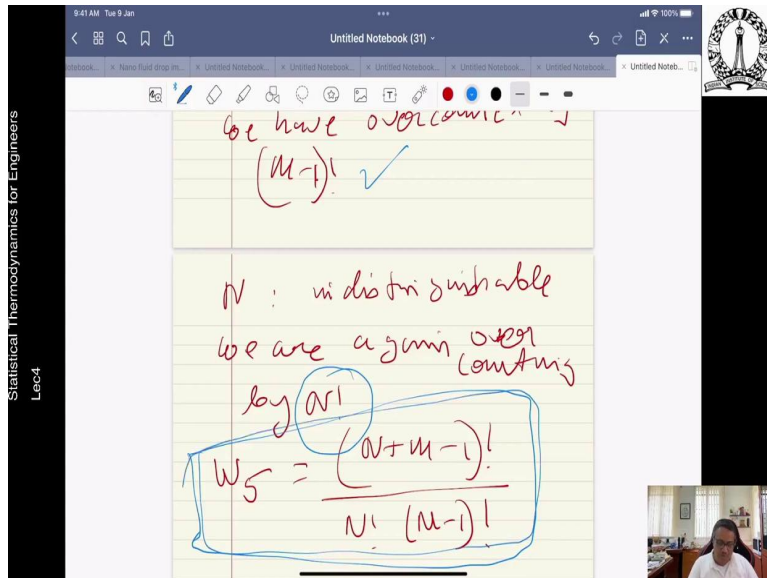
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partitions

$(N+M-1)$
 $(N+M-1)!$ → total # of ways
rearrangements can be made

we have overcounted by $(M-1)!$

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Now, let us arrange this N objects if you look at it, arrange these N objects in a row with M containers identified as partition. See, this is a partition 4 5, (())(16:46) another partition 6 is there is another partition that goes on then N minus 1 is one partition is something like this. So, these partitions are basically the container partitions and that we have put. So, these partitions basically identified by the containers (())(17:18).

So, this is one example, I mean this is just to put a perspective that how such arrangement can be made. So, you can see 123 up there in partition one (())(17:30) container then 4 5 and second container so, this is first container second container (())(17:35). So, now, regardless of your actual arrangement the maximum number arrangement amount from all M objects, so, there are N objects as you can see over here and then there are N minus 1 partition so, there are N objects M minus 1 partitions there are M minus 1 partitions.

So, the total number of objects if we just put it that way is this. And that by interchanging the partitions and all those things you know this maximum number of re arrangements that can be made is there for N plus 1 factorial is the total number of ways in which rearrangements are the maximum number this is the maximum double number of ways in which the rearrangements can be made.

So, but however, interchanging the partitions produces no new arrangement, you can just change the partitions does not result in anything. So, therefore, we have over counted by M minus 1 is the first overcome and since N objects are actually indistinguishable on the top of that.

N objects are also indistinguishable. So, that means, we are again over counting by N factorial. So, therefore, the total number of ways in which this arrangement can be made is N plus M minus 1 factorial divided by N factorial into M minus 1 factorial. So, you understood the premise of this particular problem is this firstly, as you let us assume all objects are distinguishable and we label them 1 2 3 4 5 and then we have the partitions also those are also like objects.

So, now, we arrange them in whatever order like this order that you see over here. So, this is one arrangement. Now, similarly, by changing the partitions and the objects together, we can get this number of maximal arrangements that are possible, but since this partitions can be interchanged it does not produce any new arrangements. So, therefore, we have over counted by N minus 1 because partitions are indistinguishable to begin with.

Now, the objects are also indistinguishable. So, therefore, again the rearrangement among the objects also does not say everything is 1 or everything is 2. So, there is no new arrangement that can be made just by changing the objects. So, therefore, we are gain over counting by N factorial. So, therefore, this becomes the total number of arrangements that are possible. So, for this, so we have considered therefore 5 cases.

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$$W_5 = \frac{(N+M-1)!}{N! (M-1)!}$$

5 cases (1-5) → 3 are for arr.
 ↳ 2 ident.

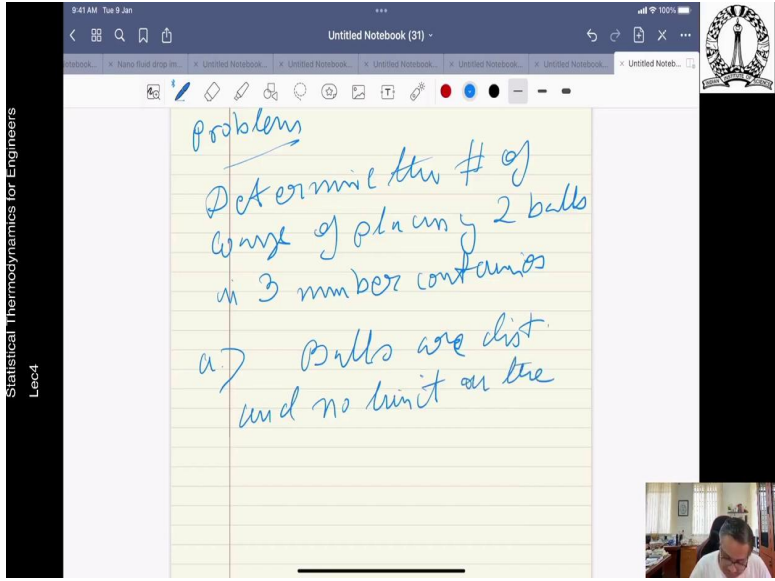
Case (3-5) → essential for what we care going to attempt

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problems

Determine the # of ways of placing 2 balls in 3 number containers

a) Balls are dist. and no limit on the



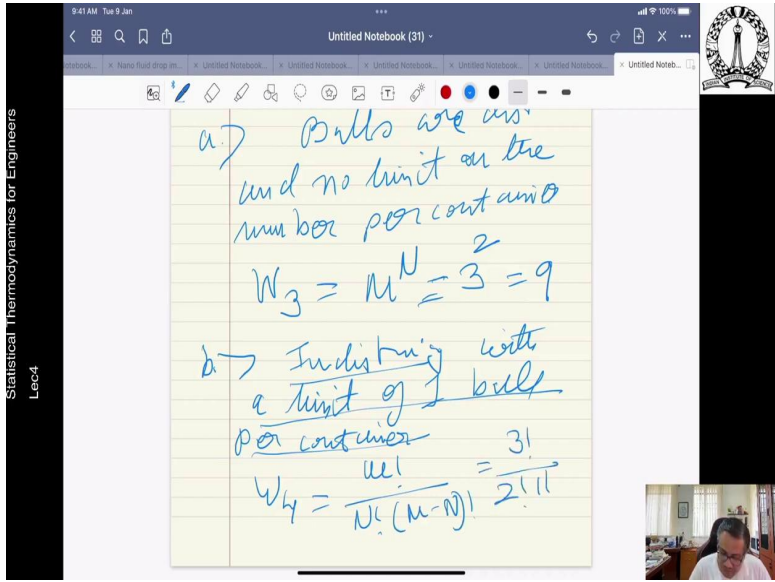
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a) Balls are indist. and no limit on the number per container

$$W_3 = M^N = 3^2 = 9$$

b) Indisting with a limit of 1 ball per container

$$W_3 = \frac{M!}{N!(M-N)!} = \frac{3!}{2!1!}$$


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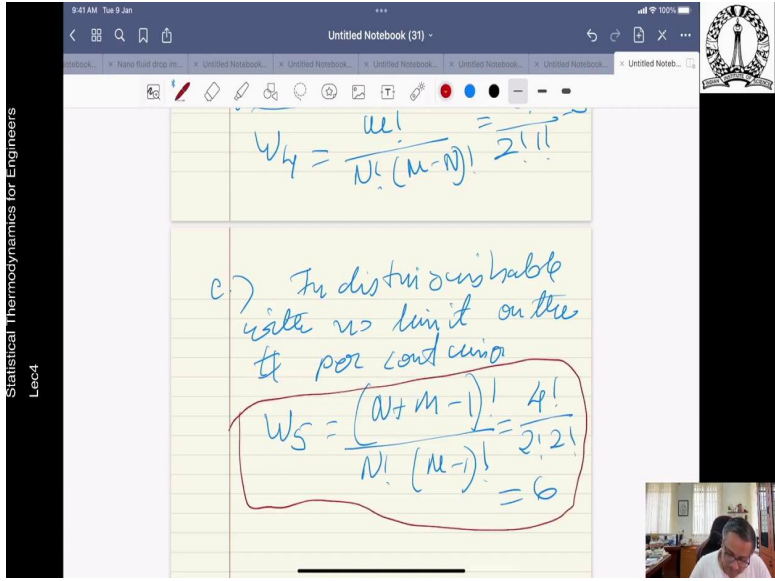
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$$W_4 = \frac{4!}{N!(M-N)!} = \frac{24}{2!2!}$$

c) In distributions with no limit on the # per container

$$W_5 = \frac{(N+M-1)!}{N!(M-1)!} = \frac{4!}{2!2!} = 6$$



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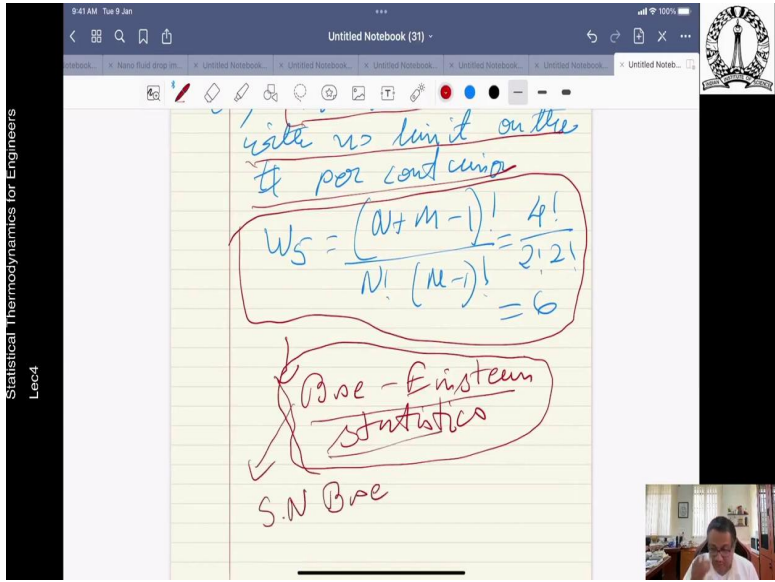
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write no limit on the # per container

$$W_5 = \frac{(N+M-1)!}{N!(M-1)!} = \frac{4!}{2!2!} = 6$$

Bose-Einstein statistics

S.N Bose



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a) Balls are distinguishable and no limit on the number per container

$$W_3 = M^N = 3^2 = 9$$

b) Indistinguishable with limit of 1 ball per container

$$W_4 = \frac{M!}{(M-N)!} = \frac{3!}{2!} = 3$$

5 cases 1 to 5, which form of those cases 3 are for distinguishable objects and 2 are indistinguishable objects. So, these are the five cases that we have done out of these cases 3 to 5 is what is of relevance the cases 3 to 5 will be essential, what we are going to do next essential for what we are going to attempt after we learn a little bit of the quantum mechanics, so, 3 to 5 is the essential (22:02).

So, 3 to 5 or what 3 to 5 was, 3 was N identical distinguishable objects listed N different containers with no limitation on the numbers for containers any number can go in a container that is case 3. Case 4 is N identical indistinguishable objects for limit of 1 for containers. And case number 5 was the same thing N identical indistinguishable objects.

Once again where there are no limitations on the number per container. So, let us just look at a simple problem the problem is to get an idea for determine the number of ways of placing 2 balls M 3 number containers, 3 number of containers such that let us take the first case a, where the balls are distinguishable and no limit on the number per container.

So, this is basically your case 3. So, it is given as M raise to the power N in this case there are 3 containers, 2 balls altogether the result is 9, 3 raised to the power 2 this is 9, you can also put all these 9 cases and see for yourself what will happen now, if I take the second case that the balls are indistinguishable now with a limit the limit of 1 ball per container.

So, this becomes your case 4 and these balls are indistinguishable with a limit of 1 ball per container. So, this now becomes a W4 which is if you recall is M factorial N factorial M minus N factorial. So, this is basically 3 factorial divided by 2 factorial and 1 factorial. So, this is 3 you can see the number of ways have kind of reduced in this particular case.

And then comes if you can consider another point which is C which is basically the balls are ones again indistinguishable with no limit the standard is no limit on the number per container. So, that becomes your W5 case W5 case that becomes a critical N plus M minus 1 factorial divided by N factorial M minus 1 factorial does take into account to overcome $(())(25:37)$.

So, 4 factorial divided by 2 factorial and 2 factorial this becomes 6 so the answer becomes 6. So, this is just example problem. Now, case a, where the balls are distinguishable and then there is no limit and the number per container this has got a formal name is called the Boltzmann distribution we will see later Gaussian distribution when the balls are indistinguishable with a limit of one ball per container, this is has got of name it is called Fermi direct statistics that is a Boltzmann statistics.

So, this is Fermi direct statistics the last one which is indistinguishable with no limit on the number per container this is called the Bose Einstein statistics. So, Boltzmann statistics deals with objects which are distinguishable which can be placed in M containers, containers means you will see what containers actually means in terms of statistical thermodynamics, but assume that there are these are particles which are distinguishable and then there is no limit on the number per container then that is called the Boltzmann statistics.

And that is your W3 over here, when the objects are particles becomes indistinguishable and with a limit of 1 per container then that is called the Fermi direct statistics and your electrons all other things follows Fermi direct statistics and then when they are indistinguishable with no limit on the number of particles or balls for container that is called the Bose Einstein statistics. So, this is SN Bose and this is the famous Bose Einstein statistics that we are talking about.

So, just by looking at some analysis and taking analysis from your everyday life just by objects or balls or whatever you can think of, we can kind of draw $(())(28:08)$ (Panelo) to the corresponding elements in statistical thermodynamics. And exactly we are going to next cover that what are energy levels what are energy states.

And how these things can be manipulated and what will be the different types of things that you get when you read about energy states and energy levels what is degeneracy and stuff like that and then we are going to work out the Boltzmann statistics also called Maxwell Boltzmann statistics and the parameter X -statistics and the Bose Einstein statistics and see that how from a probabilistic point of view from a permutation point of view from a combinatorial point of view, how we can evolve some of this statistics that we can (())(28:51) now, to real particles to real systems. So, this is the end of your Lecture 4 we will now meet you again in lecture 5.