

Thermodynamics And Kinetics of Materials

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Lecture 14

Concepts of Statistical Thermodynamics - 1

So, welcome to this week's lecture. Today, I will discuss, first we will discuss statistical thermodynamics or the concept that connects the atomistic understanding of materials to the thermodynamic principles. See for example, we have so far discussed the macroscopic thermodynamic parameters such as for example, U, volume, internal energy, volume, entropy, then mole number and of species, then for example, temperature, pressure, even heat capacity C_v or C_p . So, all these were macroscopic thermodynamic description and basically these are all macroscopic measures of materials. However, when we talk of materials, we talk of an atomistic description where, so atomistic description of matter of materials where we tell that any material is composed of atoms, right, any material is composed of atoms or molecules and we also tell for example, when there is an atom, then that atom has a position in space that is I have to define some coordinates. So, for example, if I tell say I consider a monatomic gas, then what I will do, I will first consider that it is composed of these atoms in a container, we will consider a container inside this container, we will consider a bunch of molecules, gas molecules and when you consider these gas molecules or gas atoms because these molecules are basically at the single atom because it is a monoatomic gas, for example, helium, so helium or argon, neon, so these inert gases basically are monoatomic and each atom when we describe what we tell, its mass.

Statistical Thermodynamics

- Connect the atomistic understanding of materials to thermodynamic principles

Macroscopic thermodynamic parameters

- U, V, S, N, T, P, C_v or C_p

Atomistic description of materials

- atoms/molecules

Monoatomic gas - helium, argon, neon

Atomistic description

- mass of each atom m
- position in space x, y, z
- velocity \vec{v}
 v_x, v_y, v_z

Macroscopic equation of state

$PV = NRT$

U, V

1 mole of Gas atoms
- 6.023×10^{23} of atoms

Translational Kinetic Energy

$$= \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

So, when we describe a monoatomic gas in atomistic description, if I give an atomistic description, then I specify mass of each atom and that mass of each atom say let us consider it as m , then I specify the atom's position in space with respect to a coordinate system position in space. So, position in space requires 3 coordinates, right, x , y and z , it is a 3 dimensional description of matter, right, we are 3 dimensional, so basically we have to use 3 dimensions to describe an atom of a monoatomic gas right in a container and to specify the position of that atom, to specify the position of that atom, we require the position coordinates x , y and z . Similarly, the gas atom for example is moving around, right, it is moving around as a kinetic energy, it is a translational kinetic energy, if you remember in a previous lecture I have talked about translational kinetic energy, vibrational kinetic energy, rotational kinetic energy, so think the translational kinetic energy again if I have to describe the translational kinetic energy of an atom or a molecule, what I have to specify, I have to specify the velocity, velocity or momentum, so if I velocity of the, if I have to describe its velocity, so for each atom I have to describe its velocity, so if I have to describe velocity v , okay, and if for each atom if I have to describe that velocity v is a vector, so it has again position is a vector, so it has 3 coordinates right x , y and z , again velocity v it is a vector, it has 3 coordinates v_x , v_y and v_z and once we have specified all of these, I can basically write the translational kinetic energy, so if I can basically write the translational kinetic energy which is half $m v_x^2$ plus half $m v_y^2$ plus half $m v_z^2$. Now each atom, now this is the most important part that each, the most important part in atomistic distribution is that each atom has its own position in space, each atom has its own velocity in space defined by the v_x , v_y and v_z and the atoms say for example if this is gas atom and these are enclosed in a container then these atoms will be colliding with the walls of the container and it will change its velocity, it will change its velocity direction, so but if I have to now equivalently describe something like an internal energy, I require some sort of an average of over this entire collection of atoms and this entire collection that I am talking about is a very large collection of atoms, for example if it is just a 1 mole, if I think of 1 mole of gas atoms, what I am describing is like 6.023×10^{23} , as you know this is Avogadro number of atoms, so it is a massively large number of atoms that are occupying even if I am considering only 1 mole of atoms, if we are considering a container that contains 1 mole of gas atoms or monoatomic gas atoms, I have so many atoms and each of these atoms has a unique position in space, it has a unique velocity and now we have to find out how we can calculate an average velocity and that average velocity will basically give me an average translational kinetic energy assuming again these atoms are not interacting, if they interact then we have to basically also discuss the interaction force between them. However, when it look at the thermodynamic, the macroscopic thermodynamic description, we talk about an energy that energy is like the total energy of all these atoms that are enclosed in the container, we talk about its volume, so which is basically describe the volume of the container itself, when a gas is enclosed in a container, then the gas is spread all over the container and as a result the volume of the gas is nothing but the volume of the container and then we have to think of right mole number is like 1 mole and but 1 mole contains so many atoms and finally, when we do all of these, when we do all these analysis, I need to connect this U and V and we will get some very easy constitutive law, say for example, PV

equals to nRT where n is the mole number, R is the universal gas constant, T is temperature, V is volume and P is pressure. Now, this is a macroscopic one, macroscopic constant equation of state. So, how do we arrive at this from this microscopic world of so many atoms, each atom having its own position and velocities what I will describe and I will also describe, say for example, we have defined something called entropy, I have described something called entropy, entropy S , which is a function of U , V and M . Again, so entropy S again is a macroscopic thermodynamic parameter, which is a function of macroscopic extensive variables like internal energy, volume and mole number.

Entropy $S(U, V, N)$

$S \leftrightarrow C_V \text{ or } C_P$

$dS \geq \frac{\delta Q}{T}$

$S, C_V \text{ or } C_P \rightarrow \left\langle m, x, y, z, v_x, v_y, v_z \right\rangle$

Statistical mechanical description of matter which relates microscopic quantities to macroscopic thermodynamic parameters

Equipartition Theorem

Relation between temperature of a system with its average energies

Every atom of an inert noble gas that is in thermal equilibrium at T has an average translational kinetic energy $\frac{3}{2} k_B T$ $k_B = R/N_A$

- Boltzmann's constant

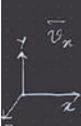
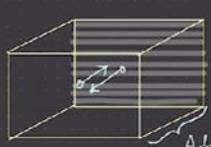
Then we also told how S is connected to say for example, C_V or C_P that is the heat capacities at constant volume or constant pressure, what is the connection between them that also we discussed and then we discussed also for example, how is S related to heat transfer and we have described for example, dS is greater than equal to δQ by T . So, we have described various thermodynamic means various macroscopic parameters to describe all these macroscopic parameters. Now, how is S for example, related to what is connection of S or what is the connection of C heat capacity C_V or C_P to the position and the velocity or more precisely the momentum, we have M also of each atom and this we are taking on a large we can think of this pointed brackets as the enclosing brackets as some sort of an average of the collection of atoms. This average of the collection of atoms how are they related to this S or heat capacities what we have to explore and that is why these lectures. So, these lectures will basically give you elements of a very important idea and that is called statistical mechanics. This will give you statistical obviously statistics is required when you have a large population of something. In this case we are dealing with a large population of particles. So, this will basically tell you a statistical mechanical description of matter. So, this is a very basic means introduction I am not this is not like a course on statistical mechanics. So, we are looking at the elements of statistical thermodynamics that are useful to connect. So, we are looking at the elements of the thermodynamics that are useful to connect this macroscopic quantities to the microscopic quantities like the mass of atom or the position of these atoms in space and then different species type atomic species type and all of these we want to give a. So, that is why we are giving a

statistical mechanical discussion of matter which relates microscopic quantities basically microscopically if I can define some quantities some averages these microscopic averages will be related to macroscopic thermodynamic parameters. So, this is what we are going to do. Now, we know so first thing that I can start with is like equipartition theorem. We have told that there is a relation between temperature of a system and its average energies. It gives you a relation between temperature of a system and its average energies. Every atom of an inert noble gas that inert noble gas you can think of like it is the closest to the approximation of ideal gas inert noble gas which is monoatomic and which is also not as much interacting. So, these are these inert noble gases are the closest approximation to this concept of ideal gas. Ideal gas is a concept that we have drawn basically this ideal gas concept what gives you a very simple equation of state. It also gives you a very simple non-interacting description of these atoms. So, when we tell that the atoms are non-interacting there is only thing that these atoms are doing is these atoms are moving with a velocity and either this is a point some position in space and if you want to this idealization can be achieved in reality if we consider an inert noble gas at certain temperatures and pressures. Now, there what we are telling in the equipartition theorem is every atom of this inert noble gas that is in thermal equilibrium at temperature T has an average translational kinetic energy which is $\frac{3}{2} k_B T$. So, where k_B is the Boltzmann's constant and k_B is related to the gas constant by R by N_A which is R is the universal gas constant divided by the Avogadro number which gives you k_B . So, every atom of an inert noble gas that is in thermal equilibrium at temperature T has an average translational kinetic energy which is $\frac{3}{2} k_B T$. And this is something that when you start with that this is where first the molecular interpretation or atomistic interpretation of temperature of energy comes in because we are talking about kinetic energy that is translational kinetic energy is the if you think of an ideal gas or an inert noble which is again an example is an inert noble gas the closest approximation to ideality. So, in that case what we are ignoring is the interactions between the atoms we are ignoring the interactions between the atoms we can ignore the interactions between the atoms and we are telling that the internal energy of this collection of monatomic gas atoms is basically coming from its translational kinetic energy and this translational kinetic energy is $\frac{3}{2} k_B T$. Now, if I have to basically show that this indeed is so that means the kinetic energy which is $\frac{1}{2} m \bar{v}^2$ now \bar{v} when I am talking about \bar{v} , \bar{v} is an average of over the collection of this atom.

Kinetic energy: $\frac{1}{2} m \bar{v}^2$

\bar{v} - Average velocity of a collection of atoms

$$= \frac{1}{2} m \bar{v}_x^2 + \frac{1}{2} m \bar{v}_y^2 + \frac{1}{2} m \bar{v}_z^2$$

$$= \frac{3}{2} k_B T$$



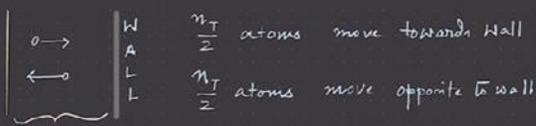
Volume $V = \Delta l A$

$A \rightarrow$ area of cross section

$n_T = n N_A$

- no. of gas molecules

Over a time period Δt , on an average,



\bar{v}_x - rms velocity along $+x$

$-\bar{v}_x$ - rms velocity along $-x$

m is the mass of atom

Change in momentum upon elastic collision with wall

$$m \bar{v}_x - (-m \bar{v}_x) = 2 m \bar{v}_x$$

So, or collection means you can call it an ensemble average or the average of the collection. So, it is an average velocity it is an average velocity of collection of atoms and the average is taken over a very large number and that very large number as I told you for example is like the Avogadro number which is 6.023 into 10 to the power 23 it is a very large number of particles or atoms and over which each so each atom is moving with some velocity and we are taking an average of all of these and we are calling it the and from there only we are calculating the average translational kinetic energy which is half $m \bar{v}^2$ which is again in terms of the components half $m \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$ right. So, you have $\bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$ which basically has to be 3 by 2 k_B . Now, if I want to basically understand it I can think of a one dimensional say I have a three dimensional description of matter. So, this is my y axis, this is my x axis, this is my z axis. So, this is z and this is y. Now, think of we are this there is this gas molecule hypothetical gas atom which is moving and this is the wall of the container right we are talking about and wall perpendicular to the motion of this atom. This atom is moving in one dimension along x direction. Now, it has some velocity v_x and when it hits the wall it has a velocity which is minus v_x right. So, and the volume can be described by so if I have taken this container or this box which has this dimension Δl this Δl is the dimension that is along the so basically I will do one thing I will make a little correction here I will tell that this is my. So, if I look at this Δl so I can think of this as my x axis, this as my y axis and this as my z axis and so this is the positive v_x and this is minus v_x right. So, basically an atom moving towards the wall is moving along negative x direction and then when it hits the wall collides with the wall and comes back then it is moving the positive x direction right. We can tell any of these right we can specify any of these directions. So, basically it is a one dimensional problem. So, we are looking at positive x direction and negative x direction right. So, we are looking at the direction towards the wall and direction away from the wall but in the same along the same x axis. Now, but we are also considering this cross sectional area. See this analysis the analysis that I am trying to present is a very very simple analysis and this analysis although we will do it in one along one dimension we will extend it to three dimensions. So, I have this total volume which is nothing but this Δl times the cross sectional area. So, this is Δl times the cross sectional area A is the cross sectional area right. So, this is the cross sectional area that I am talking about which is basically perpendicular to

delta right this area is perpendicular to delta. So, this is the cross sectional area of the wall right that I am talking about. And there is the same cross sectional area that the atom is experiencing. So, this is basically Δl times A . And I am telling the total number of atoms the total number of atoms N is the total number of gas atoms or gas molecules is nothing but N , N is the mole number times Avogadro number right. Mole number times Avogadro number gives you the total number of atoms, total number of gas atoms. Now, what we are telling is over a time period Δt . So, this atom is moving over a time period Δt . So, this is moving here and then it comes back and then again maybe there is a wall on this side and again it moves back and forth. So, over a time period a small time period Δt on an average there will be. So, now, we are looking at a collection of atoms let us think of this total number of atoms A . So, on an average if you think of all these gas molecules colliding with the wall and coming back then N by 2 atoms are moving towards the wall half of the atoms half of the total number of atoms is moving towards the wall and half of the total number of atoms is moving opposite to the wall right. So, half of the so, on an average over some time period we are telling that N by 2 atoms N is the total number of atoms N by 2 or half of that population of atoms is moving towards the wall and half of its population is moving opposite to the wall right. And again as I told you it is an average velocity the average velocity the now this is the definition that we are thinking of root mean square velocity right. It is a mean. So, we are looking at like the root mean square measure. So, that means mean square means we are talking about V_x^2 V_x^2 1 plus. So, basically if I look at the V_x average. So, basically this is like this. So, if I look at V_x average I can think of like this V_x average is equals to root over of. So, for each atom V_x^2 1 square plus V_x^2 2 square plus dot. So, V_x^2 N square by the number. So, this can be N which is nothing, but N . So, in this case it is N . So, it is a root mean square. So, that means it has to be divided by N and then we are taking the square root. So, that basically defines my root mean square average velocity RMS. So, this is RMS root mean square RMS measure right. Root mean square measure of the average velocity average velocity along x direction or the x component of velocity root mean square x component of velocity is different like this. So, you have the root mean square velocity along plus x which is V_x bar and then there is also root mean square velocity along minus x right. So, you have a velocity towards the wall a velocity away from the wall right after colliding. So, this is along plus x and one is along minus x and m let us assume m to be the mass of the atom. Now, since it is a monoatomic gas and it is a say for example, neon gas or argon gas then it is like basically all atoms are argon right. So, they are all identical atoms in terms of the chemical nature and they have the same mass.

Rate of change of momentum

$$= \frac{2m\bar{v}_x}{\Delta t} \quad \Delta l - \text{distance}$$

$$\Delta l = \bar{v}_x \Delta t$$

$$V = \Delta l \cdot A = \bar{v}_x \Delta t A \quad V = A \bar{v}_x \Delta t$$

$$F = \frac{A \bar{v}_x \Delta t}{V} \cdot \frac{n_T}{2} \cdot \frac{2m\bar{v}_x}{\Delta t}$$

Pressure

$$P = \frac{F}{A} = m \frac{\bar{v}_x^2}{V} \cdot \frac{n_T}{2}$$

$$n_T = n N_A$$

$$PV = m n N_A \frac{\bar{v}_x^2}{2} \quad N_A \rightarrow \text{Avogadro number}$$

But $PV = nRT$ — Equation of state

$$= m n N_A \frac{\bar{v}_x^2}{2} \quad \text{Microscopic description}$$

$$k_B = \frac{R}{N_A}$$

$$m \frac{\bar{v}_x^2}{2} = \frac{R}{N_A} T = k_B T$$

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$$

the probability of motion along each direction is equal

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$$

$$\bar{v}^2 = 3 \bar{v}_x^2$$

So, m is the mass of each of these atoms right. Now, if you think of that \bar{v}_x is the root mean square velocity along the plus x axis minus and minus \bar{v}_x is the root mean square velocity along minus x then the change in momentum. So, we are assuming that the collision is completely perfectly elastic that is it does not lose any velocity anything it just or momentum it just goes and hits the wall the gas atom goes and hits the wall and then it comes back with the same velocity means same magnitude, but in the opposite direction. So, then the change in momentum is nothing but $m\bar{v}_x$ minus of minus $m\bar{v}_x$ right because this is minus there is a minus \bar{v}_x and plus \bar{v}_x . So, this becomes $2m\bar{v}_x$ right the change in momentum is $2m\bar{v}_x$. Now, if I look at rate of change of momentum right if you think of Newton's second law what we look at rate of change of momentum which we will relate to force. Now, rate of change of momentum is $2m\bar{v}_x$ by Δt because we are looking at a we are analyzing our time period of Δt right in this interval this all this is happening. So, over this time period the rate of the change of momentum is $m\bar{v}_x$ $2m\bar{v}_x$ and then if I divide by Δt then what we get is the rate of change of momentum and that is nothing but the force according to Newton's second law right it is nothing but the force which is equal to from Newton's second law. Now, if you see this very carefully if you look at the force you first have to understand what is this volume and now as I want to tell you Δs if you look at Δl which is the distance right it is the linear distance travel then Δs Δl is basically velocity times time right distance equals to velocity into time right Δl equal to $\bar{v}_x \Delta t$ thus the volume can be written as a $\bar{v}_x \Delta t$. So, what we did is volume was Δl times a . Now, Δl I am writing in terms of the root mean square velocity $\bar{v}_x \Delta t$ times a right. So, this becomes $\bar{v}_x \Delta t a$. So, I have just rearranged I have written it as a $\bar{v}_x \Delta t$ right. So, now you have a $\bar{v}_x \Delta t$ and we have if I look at force I will consider only half the molecules right. So, I am considering half the molecules is moving along one direction and the half the molecules are moving on the other direction. So, if I am thinking of a force exerted by the atoms on the wall then I am considering only half the molecules that are moving towards the wall. So, then we have this Nt by 2 and if you see $2m \bar{v}_x$ by Δt $2m \bar{v}_x$ by Δt is so I have a by Δt missing here is my rate of change of momentum and if you see this a $\bar{v}_x \Delta t$

is volume and this is volume by volume. So, I have just written it here and you have this N_t by 2 right N_t is the total number of atoms. So, if I have that then the force exerted per unit area which is basically the pressure on the is F by A which is if you see you have V_x bar here and V_x bar here. So, this becomes V_x bar squared and then m and 2 and 2 cancels. So, you have $m V_x$ bar squared and then you have N_t by V . So, this 2 and this 2 cancels right this 2 and this 2 cancels this and this cancels. So, you have this term and this term now Δt and Δt cancels. So, you have A is there but p is what we are considering is p which is force by area which is basically this is nothing but pressure. Pressure is force by area force by the cross sectional area which is $m V_x$ bar squared N_t by V correct. So, N_t by V N_t by 2 is the number of total number of atoms that are basically exerting the force on the wall right at any point of time because half of it is moving towards the wall creating the pressure on the wall and then it is moving back right it is moving away from the wall. So, now N_t as we have discussed earlier is N , N is the mole number. So, N_t goes to N times the Avogadro number right N_A is the Avogadro number. So, then what we can write is p and here there is V , V is volume right it is the volume of the which is basically $A v_x$ bar Δt is what I have expressed, but it is also Δl times A right which is nothing but V_x bar Δt by A . Now, if you see you have this volume here and the total number of atoms here. So, if I take volume on this side then it becomes pV equals to $m N$, N why because there is a N_t which is equal to $N N_A$ right. So, m is the mass, m is the mass, N is the number of moles and then N_A is Avogadro number and this is V_x bar square. So, pV equals to this expression, p is a average means on an average or macroscopic thermodynamic quantity, V is another macroscopic thermodynamic quantity and see this is the microscopic quantity, this is another microscopic quantity, this is mole number, but it is multiplied by the Avogadro number which is the Avogadro number of molecules for 1 mole of atoms. Then you have and we know that macroscopically the equation of state can be written as pV equals to NRT which is nothing but $m N N_A V_x$ bar square and k_B here is if I define k_B or Boltzmann's constant as R by N_A which is universal gas constant by the Avogadro number then what we get is $m V_x$ bar square is R by N_A into temperature right. If I compare this equation which is the equation of state, so this is my equation of state for the ideal gas and this we got from the microscopic description. If we relate them what we get is that pV is nothing but or $m V_x$ bar square sorry $m V_x$ bar square right pV is equal to NRT , pV is equal to also this. So, if I equate this NRT equals to $m N N_A V_x$ bar square I can write this. So, NRT equals to $m N N_A V_x$ bar square and N and N I can cancel and I have mass here, N_A here, R and T . So, if I take R so if I have T here and instead of R I will use R by N_A because I am taking this N_A this side. So, if I take that this side then I will remove N_A here. So, what happens? Rearranging what we get is $m V_x$ bar square equals to R by $N_A T$ which is nothing but k_B Boltzmann's constant T . So, $m V_x$ bar square equals to R by $N_A T$ or $k_B T$. So, we have $m V_x$ bar square similarly likewise if I extend to three dimensions then what happens? We get since V bar square on average this is like a root mean square velocity, root mean square velocity which has all these components so root mean square, x component of velocity, root mean square, y component of velocity, root mean square, z component of velocity and the probability. So, basically there since there is no anisotropy here there is no anisotropy movement along each direction along each direction whether it is along x direction whether it is

along y direction or whether it is along say x is this and y is this. So, this is x direction, this is y direction and this is z direction and we free tell that probability of moving along any of this directions is equal then \bar{v}_x equal to \bar{v}_y equals to \bar{v}_z right that is what I am telling because there is no anisotropy there is no preference along one particular direction right. So, it is all equally probable if it is all equally probable \bar{v}_x and \bar{v}_y and \bar{v}_z this is the components of the root mean square velocity. The root mean square velocity components are all equal then \bar{v} square is nothing but according to this relation \bar{v} square is nothing but $3\bar{v}_x$ square. Now, if it is $3\bar{v}_x$ square we have already proved that $m\bar{v}_x$ square equals to $k_B T$. So, $m\bar{v}_x$ square equals to $k_B T$ and average energy of each atom for example is nothing but half $m\bar{v}$ square \bar{v} square which is nothing but equal to half m . Now, \bar{v} square I have seen that the energy in \bar{v} square is nothing but $3\bar{v}_x$ square. So, half m $3\bar{v}_x$ square which is basically $\frac{3}{2} m\bar{v}_x$ square, but we have proved that $m\bar{v}_x$ square is nothing but $k_B T$. So, this is $k_B T$. So, this is $\frac{3}{2} k_B T$ right. So, basically the average energy per mole is basically so this is like per atom. So, if I think of per atom this is like energy per atom which is $\frac{3}{2} k_B T$. Now, U per mole is N_A times e which is N_A which is the Avogadro number times $\frac{3}{2} k_B T$ which is equal to $\frac{3}{2} k_B T$. Since, R equals to or since, k_B equals to R by m right or R equals to N_A times k_B right. So, we get this. Now, we know this description we understand this and we have also shown this, but we did not go through all the detail here, but we can immediately now realize that there is this molecular interpretation of internal energy which I have described a little bit previously, but here we give you some sort of a derivation or description it is not a derivation as such the derivation is much more involved, but it at least gives you the connection between this $\frac{3}{2} k_B T$ and the on an average the kinetic energy. Now, what about entropy? Now, entropy as we have seen is entropy is increasing for an irreversible process, entropy of an isolated system increases when the process is irreversible otherwise the change in entropy is 0 and all of this stuff we have talked about, but what is the microscopic understanding of entropy right. So, we want to again give this connection between the microscopic world of atoms and the macroscopic thermodynamics. In microscopic thermodynamics S is a very very important quantity right, entropy is a very very important quantity. We talk about the second law which is nothing, but dQ we can write it as dQ reversal equal to $T dS$ then we call talk about locus inequality and we also talk about the different properties of entropy right. Entropy vanishes at absolute 0 Kelvin then entropy is a monotonically increasing function of energy which is differentiable right and continuous, but what about the molecular interpretations right. So, here we will try to describe that in terms of arrangement or configurations. So, let us look at different types of atomistic configurations. Let us think of this very simple description of 4 A atoms and you have 4 boxes right you have 4 boxes here box 1, box 2, box 3 and box 4. Now, I am talking or considering 4 A atoms all of these are identical or indistinguishable and I am telling that how many ways I can arrange this 4 A atoms among these 4 boxes. So, the answer is I have 4 boxes and I have 4 atoms and since these are indistinguishable there is only this there is only one way you can put this 4 A atoms right there is only one way. So, they are since they are indistinguishable. Similarly, let us think of B atoms now. So, basically I am talking about 2 different atomic species. So, I have one is A, A is like copper and another is B is like nickel and or say say neon and argon.

$$m \overline{v_x^2} = k_B T$$

Average energy of each atom

$$u_a = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m 3 \overline{v_x^2}$$

$$U (\text{per mole}) = N_A \langle E \rangle = \frac{3}{2} m \overline{v_x^2}$$

$$\langle E \rangle = \frac{3}{2} k_B T$$

$$= N_A \cdot \frac{3}{2} k_B T$$

$$= \frac{3}{2} RT \quad \therefore k_B = \frac{R}{N_A}$$

Connection between the microscopic world of atoms & macroscopic thermodynamics

$\delta q^{rev} = T ds$

A	A
A	A

B	B
B	B

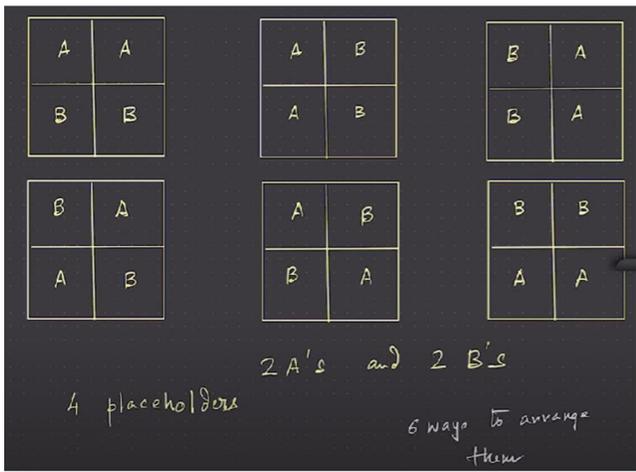
4 A atoms
4 A's are identical
or indistinguishable

B atoms
Are there distinguishable?

A — distinguishable from B

So, something like that ok. So, it can be a gas mixture, it can be also it can be solid, it can be liquid. So, but these are 2 different atomic species, but if I consider B alone and if I consider the same box with this 4 4 placeholders. So, I have this one placeholder 1 placeholder 2, 3 and 4 and I have 4 B atoms all of which are identical right all of which are indistinguishable among themselves. Although A and B can be identified, B alone cannot be identified or A alone cannot be identified or the basically they are all identical. One A cannot be distinguished from the other A, one B cannot be distinguished from the other B, but A can be distinguished from B right. So, you have B atoms and A atoms even for B atoms the same idea holds right. So, 4 B atoms you can only arrange in one way if they are all identical. So, whether it is A atoms or B atoms you can arrange only in one way right. If you are only considering one of these atoms we are considering 4 A atoms or 4 B atoms right. Then the arrangement there is only one way to arrange these atoms among this 4 placeholders. However, as I told A is this in distinguishable right it is distinguishable from B, we can distinguish A from B right A and B are different distinguish means I can I am telling A and B are different. Now, if A and B are different and I have 2 A atoms and 2 B atoms think about it 2 A atoms and 2 B atoms and look at this description. So, I have like 2 A's on the top and then 2 B's on the bottom and then 2 A's this way and 2 B's on the so on the left side and 2 B's on the right side. Then I have the reverse thing right B A B A and all of these that we have drawn. So, B A and A B or A B B A and B B on the top shelf and A A on the bottom shelf. So, these are the 4 placeholders and I have found that there are 1 2 3 4 5 6 6. So, 4 placeholders 2 A atoms 2 B atoms A atoms and B atoms are distinguishable. We are finding 6 ways to arrange right 6 ways. So, we are finding 6 ways to arrange right 6 ways to arrange them right. So, there are 6 ways to arrange them. Now, think of this if I have all atoms that are distinguishable they are all different species means A is different from B which is different from C which is different from C which is different from D which is different from D. Now, you have A B C D now this A B C D these are 4 different species and these we have to arrange among 4 placeholders 4 empty placeholders. Then there are 4 factorial ways or 4 factorial ways or 24 ways to arrange them. So, find out why so you have like if you put an A here so A so basically I can tell you this way A can be placed in any of the 4 empty placeholders. Then B can be arranged in any of the 4 empty placeholders in 3 ways right in the remaining in the 3 empty

placeholders. This once I have placed an A so basically I can place A in 4 ways right A can be placed in any of the 4 ways these are all empty right A can be here or A can be here or here or here right. So, if I once I have placed an A I cannot place the A right. So, A can be placed in 4 ways. So, basically if I tell there are 4 empty placeholders so A can be placed in any of the 4 ways. So, if I tell there are 4 empty placeholders so A can be placed in any of the 4 empty placeholders. Now you have remaining 3 empty placeholders. So, B can only be arranged in 3 ways right because the 3 remaining empty so basically 3 remaining empty spots right remaining placeholders. Now once I have arranged or placed B then there are only 2 2 remaining right 2 remaining placeholders where I can place placeholders that are empty where I can basically take any of these 2 or I can put a C then I have only 1 remaining right 1 remaining placeholder for B. I can do it in with starting with C I can do it starting with B you will basically get it the same I mean same type of arrangement. So, you have 4 ways to put any of these 4 atoms like 4 species we have 4 distinguishable atoms remember these are 4 distinguishable atoms. So, we have 4 distinct atoms. So, we have 4 distinguishable atoms. And we have 4 empty placeholders. Now if A can be placed in 4 ways B can be placed in the remaining 3 placeholders and C can be placed in the remaining 2 placeholders. So, you have 4 times 3 times 2 times 1 and that is your number of arrangements that are possible right 4 times 3 times 2 times 1 which is basically nothing but 4 factorial right this is nothing but a 4 factorial number of ways right because n factorial because to n times n minus 1 times n minus 2 dot dot dot then 3 2 right that is n factorial definition of n factorial. Now we have as you can see there are 4 empty placeholders and 4 atoms and these are all distinguishable. Now since they are all distinguishable A can be placed in or B can be placed in any of the 4 ways then the remaining A can be placed in any of the 3 ways and C can be placed in any of the 2 remaining placeholders empty placeholders and D can be placed in any of the 3 ways. So, which ever way you start with you will always end up with 4 factorial number of ways or 24 ways. However, if you look at the previous example we could only see 6 ways to arrange them why because 2 A atoms are identical and 2 B atoms are identical although A and B are distinguishable.



A B C D - 4 distinguishable atoms
4! ways
= 24 ways
Why?
 $n! = n \cdot n-1 \cdot n-2 \cdot \dots \cdot 3 \cdot 2 \cdot 1$
different
A - B - C - D
A can be placed in any of the 4 empty placeholders, B can be arranged in 3 ways in the 3 remaining placeholders, 2 remaining placeholders, 1 remaining placeholder
 $4 \times 3 \times 2 \times 1 = 4!$

So, there are only 2 distinct means if you think of that A and B this is the these are the 2 distinct cases right means I can identify A from a B, but I cannot identify A from an A or B from a B and as a result the number of ways have reduced to 6 from 24 if A B C D all of them were there and there were 4 boxes or 4 placeholders then we have 24 ways, but if you have 2 ways and 2 ways I have 6 ways. So, this is where comes the idea of combination and the idea of arrangement of particles in different ways and if I am looking at if we are not considering the order of arrangement then what this idea comes in is from statistics and this is called combinatorics and in combinatorics we actually solve such problems that how many ways I can arrange some red balls and blue balls among some 4 empty boxes. So, many such combination or 10 empty boxes how many ways I can arrange a deck of cards and all of these basically is in the field of combinatorics and this combinatorics gives us an idea of number of ways of this different or distinct arrangements and these arrangements basically give us an idea to interpret entropy. This is something that I will come to here. So, for example the problem that we are talking about say what is the problem which basically the problem here is statistical mechanical or statistical interpretation. We are trying to come up with a statistical interpretation. of entropy which is a macroscopic thermodynamic parameter and we know this entropy is basically nothing but it basically is a way means or entropy basically describes irreversibility. Entropy is always increasing if the process is irreversible if the process is reversible the change in entropy is zero.

Problem - Statistical interpretation of entropy

Arrange n_1 elements of type 1
 n_2 elements of type 2
 n_3 elements of type 3
 n_k elements of type k
in n positions.

Each type is distinct or distinguishable from the other

$$n_1 + n_2 + n_3 + \dots + n_k = n$$

Macrostates

Statistical thermodynamics - probable states of particles in a system

Macrostate \equiv state in macroscopic (Statistical Thermodynamics) thermodynamics U, V, N

Microstate denotes the state of all particles in a system

Now, when I am talking about statistical interpretation of entropy remember we have moved away from that definition of entropy increasing and stuff but we are looking at arrangements we are looking at configurations. So, somehow we will make a connection between them and I think the idea is that Boltzmann looked at all this looked at this idea and then he came up with a very interesting hypothesis and that hypothesis neatly fits with the macroscopic thermodynamic description. So, we will try to describe that how these configurations or these arrangements can basically give you this macroscopic quantity called entropy or how are these connected. So, we will so that is the problem. The problem is first but the problem can be now subdivided. So, we have this problem of n_1 elements of type 1, n_2 elements of type 2, n_3 elements of type 3 and n_k elements of type k. So, n_k elements of type k. So, it can be like k species think of k different atomic species.

Now, k different atomic species are there. So, type 1, type 2, type 3, type 4 like these are like different types of atoms and we have total n positions or n placeholders. Now, each type is distinct or distinguishable from the other that means type 1 is distinguishable for type 2, type 2 is distinguishable for type 3 and so on but among n_1 elements. So, we have this n_1 atoms of type 1 say this n_1 atoms are indistinguishable or identical and n_2 atoms are indistinguishable or identical. Now, when I am looking at this arrangement we are also telling that these n positions are there and these elements are there and there is this additional constraint and the constraint is this that sum of all these elements that the number of these elements. So, n_1 of type 1, n_2 of type 2, n_3 of type 3 and n_k of type k . So, sum of all of these add up to the number of placeholders that are available. The number of empty slots that are available is n and n_1 plus n_2 plus n_3 plus dot dot plus n_k is nothing but n . So, that is the constraint. That is the constraint that we have and we want to find these arrangements these different arrangements that is the entire crux of the problem. So, for that we will define something called a macro state and so we will define something called a macro state and we also define something called a micro state. So, in statistical thermodynamics where we deal with the large number of particles like large number of atoms, large number of particles then it gives you probable states of particles in a system. Probable states means probable arrangements or probable configurations of particles in a system. What are the different probable configurations? Now, macro state basically tells it is very much identical the state in macroscopic thermodynamics. When we describe a state in macroscopic thermodynamics of a simple system what we use we tell that it has this type of internal energy, it has a fixed volume, it or fixed mole number and we tell that this is the total internal energy of the system and stuff. So, in macro state basically we will see that it is very much equivalent to the state in a in the macro state in statistical thermodynamics. I will give an example. It is equivalent to the state that we define in macroscopic thermodynamics. So, macro state is defined in statistical thermodynamics. Now, we will find this obviously we have to find a connection between them but I am now telling you that this macro state will basically be equivalent to the state that we define in macroscopic thermodynamics. Like in simple systems it is like we define it using some u v n very similarly macro state is described. But micro state now this is the interesting part micro state denotes the state of all particles. So, it denotes all the particles it denotes the state of all each of these particles present in the system. So, denotes the state of all particles in a system that is what is described by micro state.

Isolated system comprising of a gas occupying a given volume V at equilibrium
 — Macrostate

Position and velocities of all gas molecules within the system at any instant of time
 — Microstate

Macrostate passes through many microstates

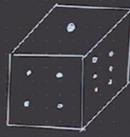
Example

Use two standard (unbiased) dice that are six sided.

Labels 1-6

Roll both dice

Outcome - sum of numbers on both die faces



Dice I	Dice II	} Microstates
2	6	
6	2	
5	3	
3	5	
4	4	

Sum: 8 - A macrostate

So, let us look at an example think of an isolated system. So, you have an isolated system comprising of a gas occupying a given volume v at equilibrium. So, isolated system comprising of a gas occupying a given volume v . So, it is basically a gas in a container and it is at a given volume v at equilibrium. So, it is an isolated system. So, some of the internal states are already defined. There is an isolated system means it does not allow any heat transfer or mass transfer and we have this gas which is occupying a given volume and it may be in some thermal equilibrium or it may be its own there is may be some the constrained equilibrium we can describe say for example, you can give a temperature we can give a pressure already we have given a volume of the gas. So, that basically describes this micro state that is an example of a macro state. So, we are thinking of an isolated system that contains a gas and a given volume v and that is the macro state. This is at equilibrium, but now if I have to define the micro state of this gas then we have to define position and velocities. There is a positions and velocities of all gas molecules within the system at any instant of time. So, there may be that means there will be a large number of microstates. So, basically a macro state which is an overall outcome which is like some gas occupying a given volume v at equilibrium and that gas has lots of atoms right. It is like an Avogadro number of atoms or more than. So, if I have two moles like two into Avogadro number of atoms and all these atoms we have to specify the position and velocity at one instant at any instant of time and see think of this when I am observing a macro state the macro state passes through many many micro states right. Many many instantaneous micro states are there and all of these micro states average is what is going to give you the idea of macro state right. So, that is the idea. So, for example we can think of again micro state and macro state if we again come back to statistics and the problem of counting right. See when we talk about combinatorics the number of ways of arranging stuff or number of way right number of configurations possible and number of arrangements with the constraint or exploding repetitions and stuff then what we come back to is the problem of counting. So, we can consider some kind of combinatorics or in statistics and we call it this is statistical because we are dealing with a very large number of outcomes right. But if we consider some slightly smaller number of outcomes and we can consider the problem of deck of cards or dice or a coin then basically many of these understand things means many of these ideas of micro state macro state becomes more and

more clear. Say for example so I am just giving you this example of use two standard unbiased dice. Unbiased means if you have biased dice then there is a possibility that see in a dice you have 1, 2, 3 there are 6 faces and each face is level with like 1, then 2, then 3, 4, 5 and 6 right. So, 1, 2, 3, 4, 5, 6 are the 6 are the levels on the 6 faces. Now if I roll a dice if it is an unbiased dice there is an equal probability of 1 by 6 for getting either 1 or 2 or 3 or 4 or 5 or 6. However, if it is biased then there is might be a little more probability to obtain a 6 or a 1 than 2 or 3 or 4 means I am just talking about one example of biased. So, basically we have to make sure that the dice that we have are unbiased right. So, there is an equal probability of obtaining any of these like 1, 2, 3, 4, 5, 6. So, this is the dice that one example of a dice and so we take two of these we take two of the standard dice and then we roll them right. We roll them and this rolling is nothing but the experiment that we are doing. So, we are doing and the outcome of this rolling is something that we are looking at that the outcome is what is going to define the state. So, the outcome in the previous case was the isolated system in equilibrium having a volume V containing a gas with a volume V right. So, that is that was the outcome. So, here the outcome that I am talking about I can think of an outcome we have these experiments the experiment cells rolling this two unbiased dice right and we also know that you have 1, 2, 3, 4, 5, 6 these are the levels that are on each face of the dice and of both dice right. So, now if that is so then if I tell the sum of numbers on both die faces gives you. So, we have this both die and we are telling that the sum of numbers is given. So, for example, a sum 8 is given. So, if I telling that sum 8 so the experiment should have an outcome of 8 how many ways I can roll the dice. Now, this outcome of 8 is defining the macro state or the state right the outcome of volume V is defining the macro state. So, exactly the sum 8 is the macro state. So, the sum of the numbers on these faces of these two dice should add up to 8. Now, if I am looking at that how many ways you can get 8. So, 8 is the macro state or 8 is the outcome that we are looking at, but how many ways we can are basically going to define my micro states right. How many ways we can is going to define my micro states. So, if you look at that if you look at that. So, if you look at the how many ways it is going to connect my micro states then you will see that if I have to get a sum of 8 for these two dice roll then basically if dice 1 has a number 2 then the dice 2 should have a number 6. If the dice 1 has number 6 then the dice 2 should have number 2. Similarly, 5, 3, 3, 5 or 4, 4. So, these 5's there are 5 possibilities or which will give rise to a sum of 8. There are only 5 possibilities that will give rise to a sum of 8 and sum of 8 that the sum of the outcomes of this dice roll that some of the sum of whatever is the level on the dice that sum should add up to 8 that is the macro state, but there are 6 micro states that will give the outcome of 8 right. So, now you can understand the micro state is the instantaneous restriction and over all micro states we have to choose over the so basically one macro state will pass through several micro states. These micro states are telling that this macro state is possible right. So, sum of 8 is the macro state and there are 5 1, 2, 3, 4, 5 micro states that basically gives you the macro state right. So, we will describe this further in the next lecture ok. So, I am stopping it here now, but I will in the next lecture I will continue with this idea. Thank you.