Thermodynamics: Classical to Statistical

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Lecture - 14

Macroscopic and microscopic states; Boltzmann distribution; Canonical partition function

Today we will discuss macroscopic state and microscopic state. For that we first consider a container (Figure 1) of ideal gas molecules of volume V containing Avogadro number of molecules (N_A).

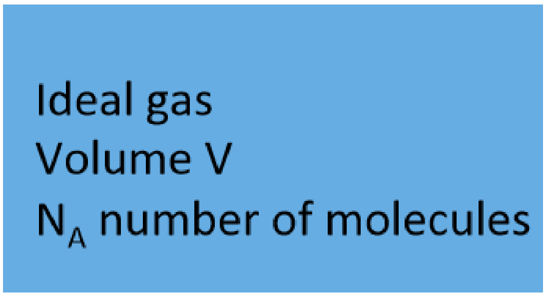

Figure 1

This a description of macroscopic system. So, macroscopic systems are characterized by few variables like pressure, volume, temperature, etc. So we can observe what is the pressure here, what is the temperature here etc. But, the description in terms of microscopic parts requires the specification of the state of each individual particle. So while we discuss about macrostate, there we did not consider what is the contribution of the pressure for each and every particle here. But, the description in terms of microscopic parts requires the specification of state of each and individual molecule. Now the number of molecules we considered here is in the order of Avogadro number. And for each particle or molecule we need to know at least 3 position coordinates and 3 Momentum coordinates. So total 6 variables we need to know for each particle. We have used Avogadro number of particles here. So typically we need 6×10^{23} variables. Thus, to specify the microscopic state of the system, it is convenient to work on a 6N dimensional space of coordinates and momentum of N particles. This 6N dimensional space is called phase space of the system, and microstate is simply a point in the phase space and the macroscopic state on the other hand corresponds to a large number of microstates and it depends the volume in the phase space. We can say it in this plot here (Figure 2).

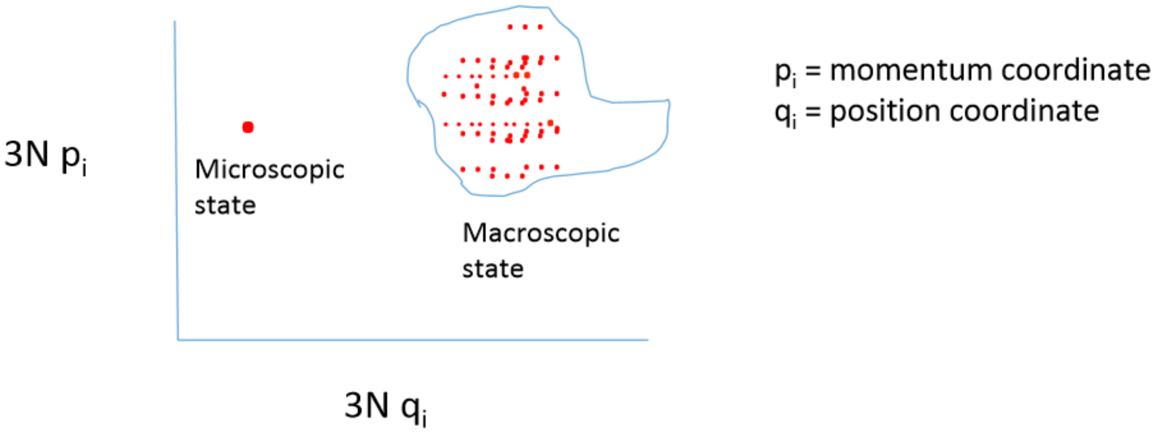

Figure 2

Now, if we specify the total energy, suppose total energy is say E on the N particle in system. It allows for a large number of microstates corresponding to this macrostate. So as we see that we have 6N dimensional space here, so here we plotted 3N number of momentum coordinates versus this 3N number of position coordinates and microscopic state is only a point in that phase space. On the other hand, the macroscopic state, it is volume in the volume in the phase space. If you considered a particle, consider a particular microscopic state of the system and watch how it evolves in time. We will be obtaining phase trajectories. Now, we will here consider two examples for better understanding of macrostate and microstate. Suppose we are flipping 2 coins (Figure 3), so one possibility is first coin comes with head and second coin comes with tails. So this is the first occurrence here. Then next occurrences is first for first coins, first coin we get tails and for the next second coin we get heads. So for this macrostate means one head and one tail, we have 2 microstates, first we have head then tails or tails heads, like this. Similarly, for macrostate HH means for both coins if we get head. So for this macrostate we have only one microstate. For HT or TH we get 2 microstates. We can also get tails both the coins, so for this one we get for this macrostates, macrostate we define by TT here, we get 1 microstate. So we have total 3 macrostates. What are those macrostates? One head one tail is one macrostate, both the heads is another macrostate and both the tails is the third macrostate. And how many microstates we have? We have 4 microstates. Because macrostate HT contains 2 microstates, like HT and TH. Next we take another example (Figure 4). We have suppose 4 balls and then we have 2 rooms or 2 baskets or whatever you say. And these balls they are identified by different colors. Now, if I ask you, you put 4 balls in different manner, what are the

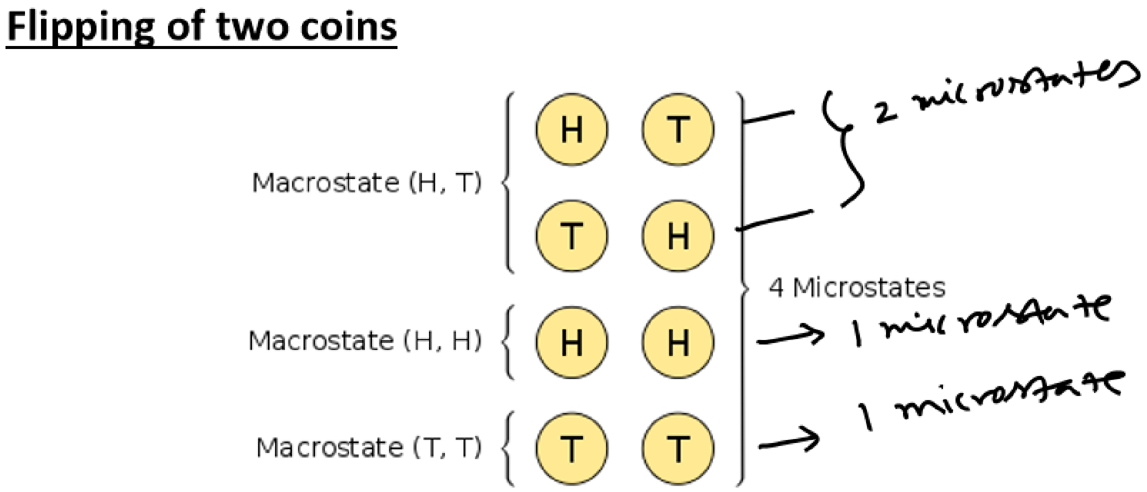

Figure 3

possibilities? First possibility is all 4 balls are in the first room and there is no balls in the second room. So this is one macrostate possible. So this macrostate, 1 microstate is possible.

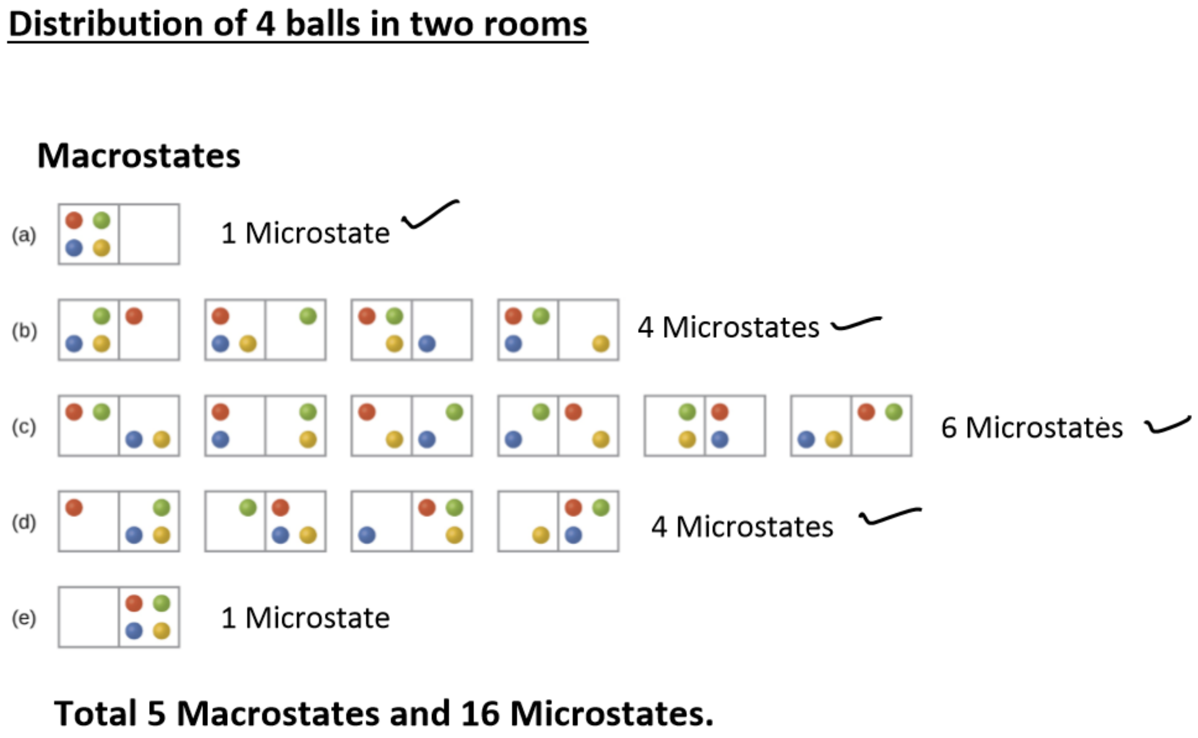

Figure 4

Then we can have blue, red and green ball in one room and the red ball in second room. And now we can change the ball, means 3 ball in first room and 1 ball in second room. So for this kind of arrangement we get 4 microstates. Now we can have both rooms we can have the equal number of balls means 2. If we rearrange the balls so we gets 6 different possibilities here and then in the fourth case. Suppose we put 1 ball in the first room and 3 balls in the second room and for this case we get 4 different possibilities. And the last case, the first room is empty and the second room contains all the 4 balls. So how many macrostates we have now? We have we have 5 macrostates, and how many microstates are there? We have 16 microstates. Like, for the first macrostate we have only 1 microstate. For the second macrostate we have 4 microstates. For third macrostate we have 6 microstates. For fourth macrostate, we have 4 microstates. And for the fifth macrostate we have only one microstate. So, now we understand what is macrostate and what is microstate.

Next we start with Boltzmann factors. So now, we discuss Boltzmann factors. All of you know Schrodinger equation. The Schrodinger equation, for N body system is,

$$\hat{H}\Psi_j(1,2,3,\ldots) = E_j(N, V)\ \Psi_j(1,2,3,\ldots) \text{ ---------------(1)}$$

Where, $j = 1, 2, 3, \ldots$. = no of microstates

So basically what we consider here is we consider a cubic box containing N number of ideal gas molecules and so we have one container here and the volume of the container is V, and edge length of each edge of this box is ‘a’. So for this kind of systems, so this is our system here (Figure 5), we are considering.

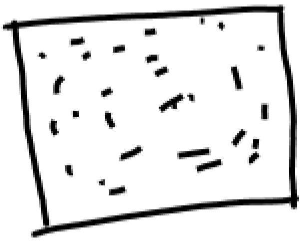

Figure 5

So we are considering a system is like a cubic box containing N number of ideal gas molecules and volume of the container is V and edge length of the box is a. So V is nothing but a^3. And for this kind of systems, we write the Schrodinger equation like equation 1, and $j = 1, 2, 3, \ldots$, these are microstates. Now, for this special case of ideal gas, since ideal gas that do not interact with each other, we can write, E_j, the function of N and V, we will discuss why E_j depends on or how does E_j depend on N and V, number of particles and volume V. If you go back and check, Schrondinger equation and this 1, 2, 3 they represent the coordinate of particle one, the coordinates of particles 2, coordinate of particle 3, etc. Now, Ej is like this,

$$E_j(N,V) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \ldots.. + \varepsilon_N \text{ -----------(2)}$$

So, this is our equation 1. And we can say this is our equation 2. What at are those ε_1, ε_2, etc are the individual molecular energy. Number of particles it means N number of particles. So E_j depends on number of particles. So that is how the independency of E_j comes here. And we can add them the molecular energy levels. Because we are considering here ideal gas. Now for example, if we consider the monoatomic ideal gas in that container, presented above presented here or considered here, if we ignore the electronic states and focus only on the translational states, then εj's are just the translational energy given by like this,

$$\varepsilon_{nx,\ ny,\ nz} = (h^2/8ma^2)\ (n_x^2 + n_y^2 + n_z^2)$$

Since, we consider a 3 dimensional box we get this expression. So this is related to you know the particle in one dimensional box. So this is for the energy value for the energy expression for particle in 3 dimensional box. Now, how does the V dependency comes. Now the V dependency comes, if we see the expression here, we see that there is one term called a^2. So in the above expression, we have a term a^2 in the denominator and we know and a is nothing but $V^{1/3}$, we considered cubic box. So it says, or it depicts the volume dependency of E_j. So now we know how does E_j depends on N and depends on V. So what is our goal? So we want to know the probability that a system will be in the j_{th} state having energy or with energy E_j. So we want to know the probability. Because if we know the probability then we can calculate the average quantity with the help of the discussion that we discussed in the last class. For this we consider a huge collection of systems in contact with a heat reservoir at a temperature T. Each system that collection has the same values of N, V and T, but is likely to be in different quantum States, consistent with the values of N and V. Such a collection of systems is called an ensemble.

So, what is the definition of ensemble? We will just define ensemble. It is an idealization consisting of a large number of mental copies sometimes infinitely many. So we consider many many or huge number of or large number of mental copies of a system, considered all at once each of which represents a possible state that the real system might be in. Since, we considered constant N, V, T. So we are basically describing Canonical ensemble (Figure 6).

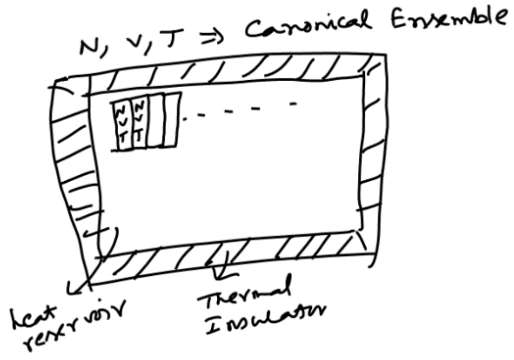

Figure 6

So in Canonical ensemble number of particles, volume of the system and the temperature are fixed. Now, basically what is ensemble? If we represent a pictorially, we will get like this. So these are the mental copies of our system. And they all are having constant N, V, T. So let me draw it again little bit in better manner. So we have like this. So all are having in same number of particles, volume and temperature fixed, etc. So we have heat reservoir here, and if we just put one insulator here, whole thing is isolated from the surroundings. So we have thermal insulator. So these are all mental copies. So our goal is to find a state j having energy E_j and for that what is the probability? That is our goal.

We are defining one quantity a_j, which is number of systems in the state j with energy E_j. How many systems are there in the j state having energy E_j? That we called a_j. And A, represents total number of the systems in the ensemble. And this A is very large number usually. The relative number of systems in the states with energy E_1 and E_2 must depend on E_1 and E_2. So we can write,

$$a_2/a_1 = f(E_1,E_2)\text{----------} (3)$$

So what is a_2 and a_1? So a_2 is the number of states having energy E_2, and a_1 is the number of states having energy E_1. Since, energy is a quantity that depends or that must always be referred to a zero of energy. In equation 3, must be of the form a_2 by a_1 is function of difference in their energy. Because energy is a quantity that must always be referred to a zero of energy, so we need to conside zero of energy. So the dependence on E_1 and E_2 in equation 3 must be of the form,

$$a_2/a_1 = f(E_1 – E_2)\text{----------} (4)$$

Now this equation 4, is true for any two energy states. Thus, we can write,

$$a_3/a_2 = f(E_2 – E_3) \text{ and } a_3/a_1 = f(E_1 – E_3)$$

Again,

$$a_3/a_1 = (a_2/a_1)(a_3/a_2)$$

$$f(E_1 – E_3) = f(E_1 – E_2)\, f(E_2 – E_3) \text{ ----------}(5)$$

The above equations 5 is very similar to

$$e^{x+y} = e^x e^y$$

$$\text{So, } a_2/a_1 = e^{\beta(E1 – E2)} \text{ -----------}(6)$$

So in general, β is a constant and we will later see that β is inversely proportional to absolute temperature or we can write β is $1/k_BT$, where, k_B is Boltzmann constant. Later we will prove it. In general equation 6 can be written as

$$a_m/a_n = e^{\beta(En - Em)} \text{-----------}(6)$$

$$\text{So, } a_m \,\alpha\, e^{-\beta Em)}$$

$$a_m = ce^{-\beta Em)}$$

where, c is a proportionality constant. So what is the value of c? We will see it.

$$a_j = c\, e^{-\beta E_j(N,V)}$$

What is the value of 'c'?

$$\sum_j a_j = A = c \sum_j e^{-\beta E_j(N,V)}$$

$$\Rightarrow c = \frac{A}{\sum_j e^{-\beta E_j(N,V)}}$$

$$a_j = \frac{A\, e^{-\beta E_j(N,V)}}{\sum_j e^{-\beta E_j(N,V)}}$$

$$\Rightarrow \frac{a_j}{A} = \underset{\substack{\Downarrow \\ \text{probability of state 'j' having energy } E_j(N,V)}}{p_j(N,V,\beta)} = \frac{e^{-\beta E_j(N,V)}}{\sum_{\substack{j \\ (\text{states})}} e^{-\beta E_j(N,V)}}$$

So, this is how we calculate the value of c and calculate the probability ($p_j(N, V, \beta)$) of state j, having energy $E_j(N,V)$.

So what you obtained so far? We obtained,

$$p_j(N,V,\beta) = \frac{e^{-\beta E_j(N,V)}}{\sum_{\substack{j \\ (\text{states})}} e^{-\beta E_j(N,V)}}$$

So what is our goal? Our goal is to get the probability of state j having energy E_j that we arrived here. So this is expression for that. And the denominator we have, we define it as Q. And this Q is known as canonical partition function.

$$\sum_{\substack{j \\ (\text{states})}} e^{-\beta E_j(N,V)} = Q(N,V,\beta)$$

So our expression of Pj, now reduces to like this,

$$\mathbf{P_j(N, V, \beta) = (e^{-\beta Ej(N,V)}) / Q(N, V, \beta)}$$

Since, we have obtained the expression for P_j, we can calculate various thermodynamic quantities.