

Chemical Kinetics and Transition State Theory

Professor Amber Jain

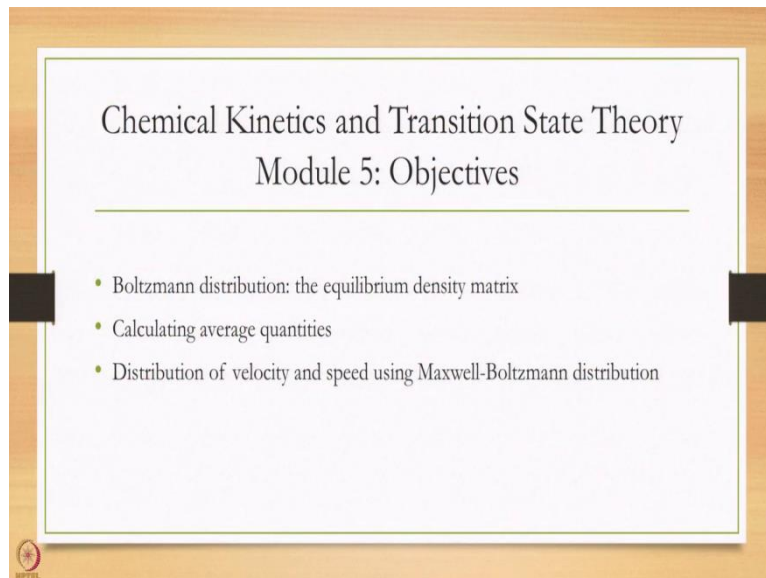
Department of Chemistry

Indian Institute of Technology, Bombay

Lecture 05

Boltzmann distribution: A story of Hamilton, Liouville and Boltzmann

(Refer Slide Time: 00:15)

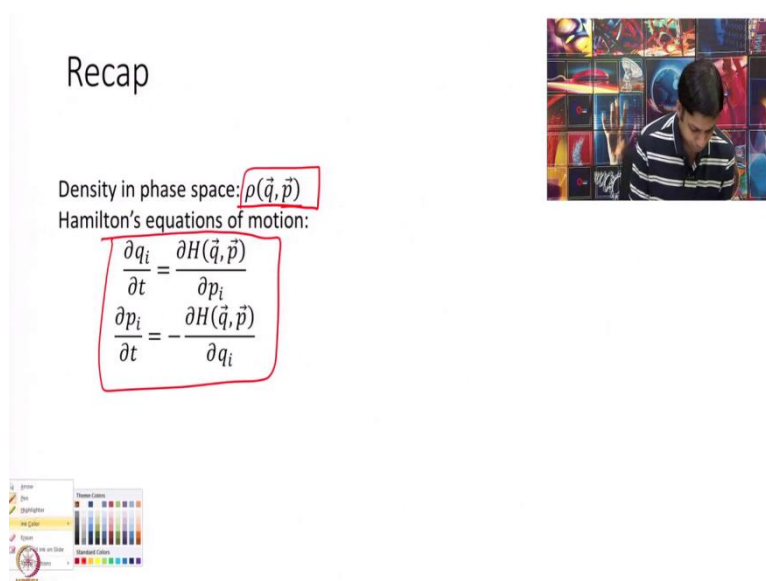


Chemical Kinetics and Transition State Theory
Module 5: Objectives

- Boltzmann distribution: the equilibrium density matrix
- Calculating average quantities
- Distribution of velocity and speed using Maxwell-Boltzmann distribution

Hello and welcome to module five of Chemical Kinetics and Transition State Theory. Today we are going to use the dynamics and phase space that we learnt in the last module and calculate what is the equilibrium density matrix, this is a very famous relation which is attributed to Boltzmann. We will use this equilibrium density matrix to calculate average quantities and then we will calculate the Maxwell Boltzmann relation.



(Refer Slide Time: 00:57)



Recap

Density in phase space: $\rho(\vec{q}, \vec{p})$

Hamilton's equations of motion:

$$\frac{\partial q_i}{\partial t} = \frac{\partial H(\vec{q}, \vec{p})}{\partial p_i}$$
$$\frac{\partial p_i}{\partial t} = -\frac{\partial H(\vec{q}, \vec{p})}{\partial q_i}$$


So, just a quick recap in the last module, we looked at the density in phase space $\rho(q, p)$, this density is the density of finding the system at the given point in space which is (q, p) and again (q, p) represents the phase space. We also derived, not derived really but verified the Hamilton's equations of motion given by these equations $\partial q_i / \partial t$ is $\partial H / \partial p_i$ and $\partial p_i / \partial t$ is $-\partial H / \partial q_i$ very symmetric looking equation.

(Refer Slide Time: 01:50)

Density of states: dynamics

Liouville's theorem: $\frac{d\rho(\vec{q}, \vec{p}, t)}{dt} = 0$

Full differential.
& not $\frac{\partial}{\partial t}$ X

Interested students can find a concise proof at http://www.pmaweb.caltech.edu/~mcc/Ph127a/Lecture_3.pdf

So, we will move forward with this and what we want to find now is how does density matrix changes with time I have told you how q and p changes with time, good, but as I have mentioned in the last module, we are really not interested in dynamics of q and p completely because it's a very very large space, I am more interested in finding the dynamics of ρ .

So, we are going to assume one statement, the derivation can be slightly mathematical and complex. So, we are not going to cover that in this course, it is called the very famous Liouville's theorem, another very famous mathematician and he was also exploring the dynamics of our nature, the differential equations that govern our nature and he figured out one very strange and powerful theorem which is called the Liouville's theorem $d\rho/dt$ is 0.

I must here emphasize this is a full differential I have not made a mistake, this is a full differential with respect to time and not partial differential. So, this is not partial differential for those interested students who want to read a proof of this I have provided a link here. This is one of the rather concise proofs, the proof, there can be more complex proofs coming from divergence theorems that you can also look at, but this one will give a proof in a rather simple

language. So, if you are interested you can look at this proof you do not have to. First let me tell you what this Liouville's theorem mean. What am I talking about? What the implication of this Liouville's theorem is let me draw a one dimensional phase space.

Well, there is no one dimension it's always 2D q and p . So, I have a one-dimensional system which is only q and the corresponding momentum p . What this is saying is let us look at some point in this phase space. And essentially let's look at a little box here of length δx and length δp and I have some density of particles in this box and we are going to look at δx and δp being very small.

Liouville is asking the question, fine I have this very small box. How does this box changes with time? How does this box evolves with time? Ok So, each particle in this box is having some dynamics and I end up getting a new box that perhaps looks like this with some new δq prime and with some new δp prime, Liouville says that $\delta q * \delta p = \delta q' * \delta p'$.

So, the volume of this little box does not changes with time, it can get reconfigured, its shape may change, but the volume will not. And in retrospect that's not a very strange thing really, is it? What we are saying is that the number of particles is effectively conserved, we are starting with some particles, well, they may expand or contract a little bit, but the net volume does not changes, its shape may change.

So, well, that might be intuitive or non-intuitive depending on you, but we do have a rather mathematical proof of this and in this course we are not going to write the proof, we are not going to cover the proof, but we will assume this statement to be true and we are going to look at the consequence of this theorem.

(Refer Slide Time: 06:30)


Density of states: dynamics

$\rho \equiv \rho(\vec{q}, \vec{p}, t)$

Liouville's theorem: $\frac{d\rho(\vec{q}, \vec{p}, t)}{dt} = 0$

$$\frac{d\rho(\vec{q}, \vec{p}, t)}{dt} = \frac{\partial \rho(\vec{q}, \vec{p}, t)}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \sum_i \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} = 0$$

$$\rho_{eq} : \frac{\partial \rho_{eq}}{\partial t} = 0 = \sum_i \frac{\partial \rho_{eq}}{\partial q_i} \frac{dq_i}{dt} + \sum_i \frac{\partial \rho_{eq}}{\partial p_i} \left(-\frac{\partial H}{\partial q_i} \right) = 0$$

$$= \sum_i \left[\frac{\partial \rho_{eq}}{\partial q_i} \frac{dq_i}{dt} - \frac{\partial \rho_{eq}}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0$$


So, let us analyse this $d\rho/dt$, $d\rho(q, p, t)$ we are being more formal over dt is given by you remember your chain rule it is given by 3 partial differentials, $\partial\rho/\partial t + \sum_i \frac{\partial\rho}{\partial q_i} \frac{\partial q_i}{\partial t} + \sum_i \frac{\partial\rho}{\partial p_i} \frac{\partial p_i}{\partial t}$. So, here and here I have dropped the brackets just for notation ease, but at all points, the ρ is the same as $\rho(q, p, t)$.

So, this is corrected for all ρ we are interested in ρ_{eq} . That's what we are trying to find in this module and play around with it. So, ρ_{eq} in the last module, we specified an important property of this, which is that ρ , $\partial\rho_{eq}/\partial t$ is 0 that is ρ_{eq} does not explicitly depends on time, it depends only on q and p that is the very meaning of equilibrium.

So, I can get rid of this term, this whole thing is 0 by Liouville's theorem. So, I end up with only this equation, for equilibrium if ρ is non-equilibrium then $\partial\rho/\partial t$ may not be 0. Well, what about it we get an equation let us massage this equation a little bit more and what we get is.

So, this differential equation will hold true only for equilibrium density matrix. So, now we will put in the Hamilton's equations of motion for dq_i/dt and $\partial p_i/\partial t$. So, I will get this is $= \sum_i \frac{\partial \rho_{eq}}{\partial q_i} \frac{dq_i}{dt}$ and $\frac{dq_i}{dt}$ look back into your notes. This is $= \frac{\partial H}{\partial p_i}$ over ∂p_i and $\frac{dp_i}{dt}$ you can again look back into your notes. This is $= -\frac{\partial H}{\partial q_i}$. This is equal to 0. Let me just take this equation and write it slightly cleaner. I will take the summation together of these two terms. I will take the negative outside and I get this equation.

(Refer Slide Time: 10:20)

Density of states: equilibrium

$$\sum_i \left(\frac{\partial \rho_{eq}}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho_{eq}}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0 \quad \text{--- (1)}$$

$$\rho_{eq} = N \cdot e^{-\beta H(\vec{q}, \vec{p})}$$

Verify that ρ_{eq} satisfies the above equation (1)



So, I have this equation that I have just copied here in this slide. What do I do with this equation? As it turns out, we can solve this equation and the solution is slightly hard. So, in this course, we are simply going to state you the solution, the solution is $\rho_{eq} = \text{some } N \cdot e^{-\beta H}$ and H is a function of (q, p) .

So, I will leave this as an assignment problem to you, this will be one of the assignment problems to verify that ρ_{eq} satisfies the above equation. So, you have to substitute ρ_{eq} in this above equation, take its derivative with respect to q_i and p_i and show that this sum over i will come out to be 0.

(Refer Slide Time: 11:42)

Identification of β

$\rho_{eq} = N \cdot e^{-\beta H}$

in statistical mechanics: $\rho_{canonical}(E_i) = N \cdot e^{-\beta E_i}$

$\beta = \frac{1}{k_B T}$ $k_B \equiv$ Boltzmann constant.

$\beta = \frac{1}{k_B T}$

So far, what we have got is ρ_{eq} is $N \cdot e^{-\beta H}$, where β is a constant so far, I have not specified what β is. But this particular ρ_{eq} might be reminding you of something very specific in statistical mechanics, you must have seen the distribution from a different perspective for canonical ensemble, some constant into $e^{-\beta E_i}$ at a particular E in that a statistical mechanics, β was $1/kT$ where k_B is the Boltzmann constant, you have to be as famous as Boltzmann to get a constant after you.


Note that H is the equivalent of energy. It's a function, but that is what gives me the energy. So, we note these two equations. And we will postulate that β is $1/kT$ for us, even in this equation.

(Refer Slide Time: 13:27)

Comments on Boltzmann distribution

$$\rho_{eq}(\vec{q}, \vec{p}) = N e^{-\beta H(\vec{q}, \vec{p})}$$

- This distribution holds at equilibrium.
- This is an averaged distribution: for a finite system, the distribution at any given time might deviate from the Boltzmann distribution.
- If the size of the system is increased, or the distribution is averaged over long time (at equilibrium), the Boltzmann distribution will be obtained.



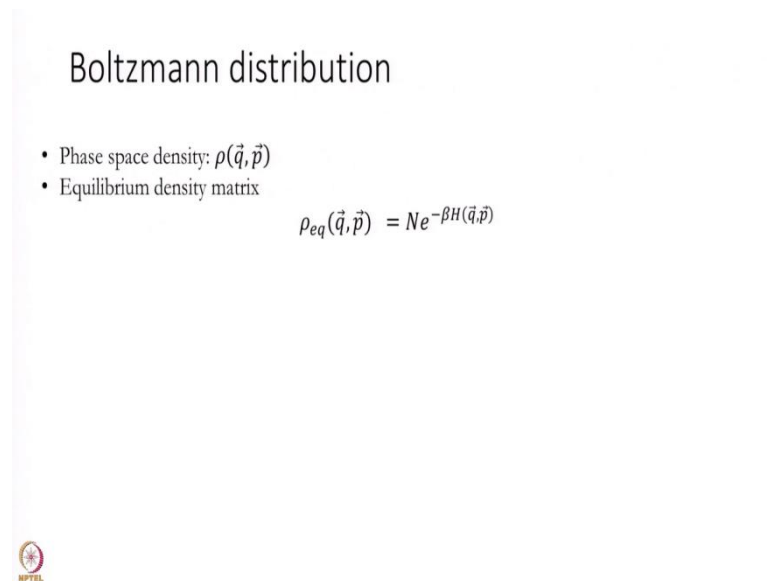
So, with this I want to make a few comments on this distribution, this distribution is called the Boltzmann distribution. This distribution holds only at equilibrium. Never ever make the mistake of assuming this distribution out of equilibrium, out of equilibrium I have no idea what this ρ might be, that's for a totally different course.

Another somewhat confusing point that might appear to you, this ρ is a statistical answer, it is a highly averaged answer. What I mean by that? Suppose, I take a small system, I take a box with a thousand gas particles in it and I find the distribution of q and p at a given instant of time that distribution might not follow this Boltzmann distribution.

However, if you increase the size of this system, instead of using thousand, I use million, I use billion, I use 10^{23} , I use 10^{100} . So, as this number keeps on increasing, my distribution will tend to this Boltzmann distribution, or if you do not want a large system, you may ask that is all good and fine, but my system is finite only after all in this room that I am sitting in, I have a finitely many number of gas particles will Boltzmann distribution not hold in it, it will if you average over time.

So, for even a finite size of particles, if I take the distribution at different snapshots of time, I find it at some time T_0 , I find it again at time T_1 , I again keep on doing it, and average them, I am going to get back this distribution. This is by the way called the Ergodic hypothesis, just an extra bit of information.


(Refer Slide Time: 15:41)



Boltzmann distribution

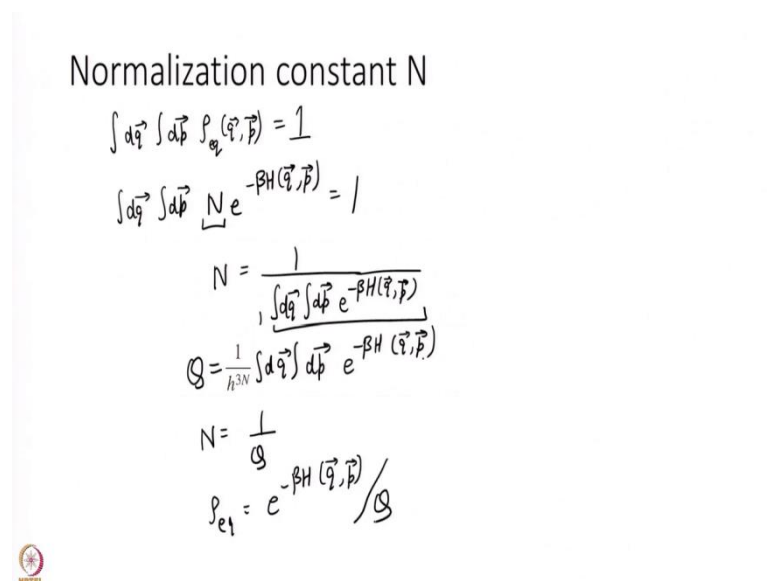
- Phase space density: $\rho(\vec{q}, \vec{p})$
- Equilibrium density matrix

$$\rho_{eq}(\vec{q}, \vec{p}) = N e^{-\beta H(\vec{q}, \vec{p})}$$




So, what we have got? Is this Boltzmann distribution in phase space. It's very famous, I have just written it out clearly here.

(Refer Slide Time: 15:49)



Normalization constant N

$$\int d\vec{q} \int d\vec{p} \rho_{eq}(\vec{q}, \vec{p}) = 1$$
$$\int d\vec{q} \int d\vec{p} N e^{-\beta H(\vec{q}, \vec{p})} = 1$$
$$N = \frac{1}{\int d\vec{q} \int d\vec{p} e^{-\beta H(\vec{q}, \vec{p})}}$$
$$Q = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p} e^{-\beta H(\vec{q}, \vec{p})}$$
$$N = \frac{1}{Q}$$
$$\rho_{eq} = \frac{e^{-\beta H(\vec{q}, \vec{p})}}{Q}$$



Let us get into what is the normalisation constant N now, so one property that we had listed is integral over all phase space will always be 1. Well, this should also be true for equilibrium density matrix, if it's true for any ρ , ρ_{eq} is just a special case of a density matrix, this must also be true. So, I get $\int d\vec{q} \int d\vec{p} N e^{-\beta H}$. N is a number, it's a constant.

So, I take it out of the integral and I get $N = 1 / \int d\vec{q} \int d\vec{p} e^{-\beta H(\vec{q}, \vec{p})}$. As it turns out, this integral that you are looking at is a very important integral. This is called the partition function whole of statistical mechanics is dependent on this integral and we can calculate any property we

want in statistical mechanics using this partition function. So, at the end, I get $N = 1/Q$ or $\rho_{eq} = e^{-\beta H(q,p)}/Q$.

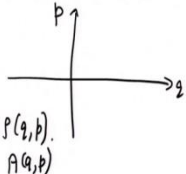
(Refer Slide Time: 17:37)

Average quantity:
integral over phase space

1D example:

$A(q, p)$


$\langle A \rangle = \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \rho(q, p) A(q, p)$



3N - dimensions:

$\langle A \rangle = \int d\vec{q} \int d\vec{p} \rho(\vec{q}, \vec{p}) A(\vec{q}, \vec{p})$

$\int d\vec{q} \int d\vec{p} \equiv \int_{-\infty}^{\infty} dq_1 \int_{-\infty}^{\infty} dq_2 \dots \int_{-\infty}^{\infty} dq_N \int_{-\infty}^{\infty} dp_1 \dots \int_{-\infty}^{\infty} dp_N$



So, now we will look at if I have this ρ_{eq} , what do I do with it? Can I comment on something useful out of this ρ_{eq} ? And the answer is to calculate any useful property you always average over phase space. Again, I do not care about where each particle is, I also usually do not care about a property at a given point in phase space, I want to calculate an average quantity like temperature.

So, once more a reminder of our 1D example, I have let's say q and p . And I have some quantity, some function defined over q and p . And I want to find the average of A , what am I going to do? Well, I will $\int dq$, I will $\int dp$, over all possibilities, I will find the probability that I am at that (q, p) that is given by $\rho * A(q, p)$.

So, that's our usual trick of finding averages, we find this property that I want to find average over at that given (q, p) , I find what is the probability that I am at that point and then I just integrate over all phase space. So, in general, for an N dimensions, well let me write $3N$ dimensions, I get average of some quantity A where A is some function of (q, p) to be an $\int dq \int dp \rho(q, p) A(q, p)$. Ok

So, I have calculated an average quantity now. And once more just to remind you, $\int dq \int dp$ is a shorthand dq_1 $-\infty$ to $+\infty$, $-\infty$ to $+\infty$ of dq_2 till $-\infty$ to $+\infty$ of dq_N , $-\infty$ to $+\infty$ of dp_1 $-\infty$ to $+\infty$ of dp_N , it should be $3N$.

So, I am integrating over every possible coordinate and momentum and rather than writing this rather ugly and long many integrals, I denote it $\int d\vec{q} \int d\vec{p}$.

(Refer Slide Time: 20:40)

Example: average momentum $\langle p \rangle$

In 1D: (q, p) ; $\rho_{eq}(q, p) = \frac{e^{-\beta H(q, p)}}{Q}$

$H = \frac{p^2}{2m} + V(q)$

$Q = \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta H}$

$\langle p \rangle = \frac{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp p \cdot \rho_{eq}(q, p)}{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp p \cdot \frac{e^{-\beta H(q, p)}}{Q}}$

$= \frac{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp p \cdot e^{-\beta H}}{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta H}}$

So, let us take an example again let us revert back to 1 dimension and let us find what is average momentum, we have a property which is p . So, a is p now, and I want to ask you the question what is average momentum at equilibrium. So, we will use the prescription that we had. So, in 1D (q, p) and $\rho_{eq}(q, p)$ is given by $e^{-\beta H}(q, p)$ divided by a partition function Q . So, we will simplify this a little bit my Hamiltonian is given by $p^2/2m$ which is the kinetic energy $+V(q)$. Ok

And q is $\int dq \int dp$ this $e^{-\beta H}$. So, the average over momentum as defined in the last slide is $\int dq \int dp p$ the quantity I want, into ρ_{eq} . So, let's substitute these quantities that I have written ρ_{eq} is $e^{-\beta H}/Q$ and I will substitute the Q here in this equation.

So, I get $\int dq \int dp p e^{-\beta H}$ divided by something that will look very similar. So, Q is a number Q I have taken out of these integrals and substituted $Q = \int dq \int dp e^{-\beta H}$ in all of these places, I have limits from $-\infty$ to $+\infty$. Let me put all these integrals there $-\infty$ to $+\infty$. So, how do we calculate this? How do we simplify this?

(Refer Slide Time: 23:15)

Example: average momentum $\langle p \rangle$

$$\begin{aligned} \langle p \rangle &= \frac{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta H} p}{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta H}} = \frac{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta [p^2/2m + V(q)]} p}{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta [p^2/2m + V(q)]}} \\ &= \frac{\int_{-\infty}^{\infty} dq e^{-\beta V(q)} \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m} p}{\int_{-\infty}^{\infty} dq e^{-\beta V(q)} \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m}} \leftarrow \begin{aligned} f(p) &= e^{-\beta p^2/2m} \cdot p \\ f(-p) &= -f(p) \end{aligned} \end{aligned}$$

$$\langle p \rangle = 0$$

So, let me just write down what I had got in the last slide, dq $-\infty$ to $+\infty$ dp $-\beta H * p$ and now we are going to substitute our Hamiltonian here. And that Hamiltonian was $p^2/2m + V(q) * p$. Quite the same I am not going to, I am going to stop writing integral limits.

So, we will open this exponential and note that this is equal to, so I have taken the part that is dependent only on q on the $\int q$ only. And the part that is dependent on p only in the $\int p$ and in the denominator, I do the same this looks like a complex integral to solve, how do I do it? It's actually trivial to solve. This is actually equal to 0. Why? You ask? Well, you see, this cancels with this. This is easy. These look bit nasty. But you note that the numerator, this is, this function that is there.

What you notice is that this is an odd function. So, $f(-p) = -f(p)$. And what do you know about integrating an odd function over all space? It is equal to 0. So, the numerator is 0, and so the whole thing becomes 0. But well, this is perhaps you already something you expect, don't you? The average momentum should be 0.

It doesn't matter, at thermal equilibrium all directions are equivalent so the particle has equal tendency of moving forward as going backward. It does not mean that every particle is at rest, the average is 0.

(Refer Slide Time: 26:14)

Question challenge
Average kinetic energy

Do you expect that the average kinetic energy per atom for helium gas be larger, smaller or equal to compared to that of argon gas at some temperature T ?

(A) Larger (B) Smaller (C) Equal (D) I do not know

Note: There is no link, please pause the video and think about the answer, the answer will be displayed on the screen shortly. Please pause the video now and work out the answer yourself

Question challenge
Average kinetic energy

Do you expect that the average kinetic energy per atom for helium gas be larger, smaller or equal to compared to that of argon gas at some temperature T ?

(A) Larger (B) Smaller (C) Equal (D) I do not know

Answer: Option (C)

So, I have a question challenge for you. Can you estimate what the average kinetic energy is going to come out? So, let's assume I have two different chambers at same temperature T , one filled with helium and other filled with argon, what do you think will be the average kinetic energy per atom for these two chambers?

So, take a moment, think about this answer very carefully. Go to the link that is provided here and provide your answer there for an immediate feedback. Do you think the helium gas will be larger, for helium it will be smaller or both will be equal And if you do not know be honest, and you can write you do not know, this is all anonymous. So, take a pause and answer this question.

So, we will quickly look at how to solve this question. Well, they have to be equal. That's my claim, we are going to prove it mathematically. But we already know they must come out equal, how? Because the average kinetic energy is essentially related to temperature. And two boxes connected to each other of whatever molecules they are filled within helium, neon, argon, nitrogen, hydrogen atmosphere, whatever.

At equilibrium, the average kinetic energy must be equal because the temperatures are equal. So, we are going to prove this statement this intuition that I have. So, we are going to calculate the average kinetic energy $p^2/2m$ now, just like we had calculated the average p .

(Refer Slide Time: 28:03)

Example:


Average kinetic energy $\left\langle \frac{p^2}{2m} \right\rangle$

$$\begin{aligned} \left\langle \frac{p^2}{2m} \right\rangle &= \frac{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \left(\frac{e^{-\beta H}}{Q} \right) \cdot \frac{p^2}{2m}}{\int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp e^{-\beta [p^2/2m + V(q)]} \cdot \frac{p^2}{2m}} \\ &= \frac{\int_{-\infty}^{\infty} dq e^{-\beta V(q)} \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m} \cdot \frac{p^2}{2m}}{\int_{-\infty}^{\infty} dq e^{-\beta V(q)} \int_{-\infty}^{\infty} dp e^{-\beta p^2/2m}} = \frac{1}{2} k_B T \end{aligned}$$

Assignment problem

Useful integrals

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

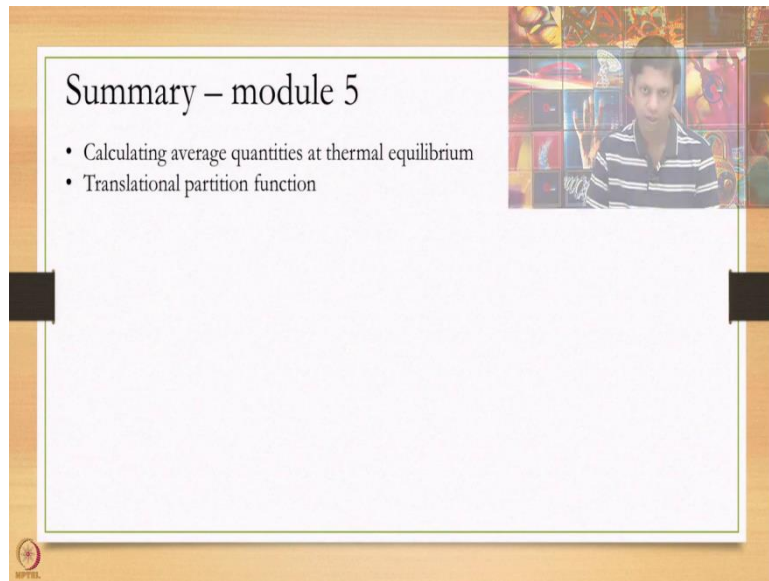
$$\int_{-\infty}^{\infty} dx x^2 e^{-ax^2} = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$


So, now we will play the same tricks as well $\int dq \int dp$ over all space. That's your $\rho_{eq} * p^2/2m$. So, just like we did in the for average momentum, we will separate these and write the Hamiltonian and the denominator will be the partition function which looks very close to the numerator, but not exactly.

And we again do this separation of q and p . So, I get $-\infty$ to $+\infty$ dq $2m * p^2/2m$, $dq - \beta V(q) \int p$, $e^{-\beta p^2/2m}$. So, the first thing that you notice that the potential term exactly cancels. So, it might my gas might even be interacting, it might be hydrogen, it might be whatever gas you want, even water vapour the potential term will exactly cancel.

And so, we have to solve these nasty integrals that are here. So, to solve that, I have provided you the integrals here. So, use those, plug them in and calculate these. So, this is going to be another assignment to be able to solve these integrals using the provided integrals and you have to show that this is $= \frac{1}{2} k_B T$, so $1/2\beta$. So, this is another assignment problem.

(Refer Slide Time: 30:28)



Summary – module 5

- Calculating average quantities at thermal equilibrium
- Translational partition function

So, we will stop here, what we have today looked at in this module is how equilibrium density matrix comes about from the fundamental equations of motion. We have skipped a few steps in the proof, we do not derive the Liouville theorem completely, but it is to motivate where does this partition, where does this density matrix comes about. Ok

So, you do not need to know get details of the proof that we have not covered, but what you need to know is what is the origin of this equilibrium density matrix, we have used this equilibrium density matrix to calculate average quantities, we have looked at average momentum and average kinetic energy today. So, with that we will stop today and in the next module, we will look at one of the very famous distribution, which is the distribution of speeds. Thank you very much.