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Lec 20: Sackur-Tetrode Equation, Density Matrices

Welcome to this new part of the course on statistical mechanics. We will be talking about quantum statistics or quantum statistical mechanics, and so far, we have seen classical statistical mechanics—the formalism of it, which mainly included the calculation of the partition function. From there, one can derive the free energy, entropy, specific heat, magnetization, susceptibility—pretty much everything that an experiment or a physical system can reveal about itself. So, we have examined several such systems and calculated various physical properties of these systems. We have not made any mistake and those classical statistical mechanics seem perfectly fine.

It is only that at large temperature. So the temperature has to be large and in addition to that we will also pose another constraint on the density of particles in some time. But before that we wanted to study now quantum stat-mech which should include the indistinguishability of particle. So far, in classical statistical mechanics, the particles were distinguishable. Each particle of the gas, ideal gas as if they were distinguishable and we could you know identify them either by their name or by their colour or by texture or something.

Now, that is not possible here. Now we of course did not make a mention of this particle in a gas or that particle in a gas. What we mean by identification or by the distinguishability is that if you actually interchange two particles. This is taken as a new state and in quantum mechanics it is not a new state it only differs by a phase factor and the phase factor could either be 1 or minus 1 and things like that which means that This exchange of two particles in a quantum mechanical system has to be dealt with care and it does not give you a new state of the system or new microstate of the system and it is related to the original state by just a phase factor.

is the crux of indistinguishability that we have to talk about or we have to incorporate in our system and develop the quantum statistical mechanics. This is the main idea of quantum statistical mechanics that the indistinguishability was not taken into account in

classical mechanics and which was fine as we have said earlier that at large temperature or at very low densities, of the particles will show how the density come into the picture. Those things that we have learnt earlier, they all seem fine. Now we have to modify each one of them and incorporate this indistinguishability.

Okay. And a step towards that had already been taken by this Sackur-Tetrode equation. So, we will just briefly introduce the Sackur-Tetrode equation or which is a formula for the entropy of an ideal gas monatomic ideal gas. But before that, let us try to go a little history of how quantum mechanics was developed and what necessitated the introduction of quantum ideas, which were preliminarily done by a large number of people. Let us say only we are going to talk about Planck of these very large number of people who have contributed significantly to the development of the subject.

So, the way quantum mechanics developed is that there was this black body radiation which was seen that you have the intensity versus the wavelength that for these black bodies they seem like this which means that the intensity of the emitted radiation versus the wavelength of the radiation is by it looks like this non-monotonic curve that I show here. And this was a bit of a surprise because why it shows a non-monotonic behavior because this part was nicely explained earlier and this part is nicely explained earlier as well. So, there are two monotonic functions: one we call Wien's law, the other is called as a Rayleigh-Jeans law. And these two actually nicely explain the either the lower lambda region or the higher lambda region, but none of them actually have a upturn and going down. And so what we are talking about is that you take a metal.

And you heat it up and initially when you start heating it up it starts getting hot first is become it becomes red hot and then it becomes white hot and so on which means that the intensity of the emitted radiation actually changes its wavelength from some red to blue and so on or to white and so on so forth. So, that means that these intensity of the emitted radiation versus wavelength when you try to plot it, it shows this formula and so the Vien's and the Rayleigh-Jeans law they were unsuccessful in showing the upturn and actually reproducing the experimental observations. And Planck came and fixed it a bit out of desperation and also you know by his intuition that what should it be and he said that look I mean all these the emission or absorption of electromagnetic radiation happens in terms of packets which are called as photons or these packets or this quantum of this radiation is they are called as photons. And so all these exchanges, either emission or absorption by any body in presence of an electromagnetic radiation, it happens in the unit

of h nu or h cross omega. And then he wrote down a distribution function which correctly reproduces the intensity of the radiation.

So you calculate the average energy with that distribution. We have seen how average energy is calculated with the aid of a distribution. So, Planck gave you a distribution formula and then you plug in this h cross omega multiplied by that by that distribution and integrate over all frequencies or all wavelengths I mean frequency and wavelength are related. And then you can get this, you multiply it by the speed of light, which is C or the speed of the electromagnetic radiation and you get the intensity. So, the intensity correctly gets reproduced by this.

And this was a birth of quantum theory. But now we are not here to discuss really the development of quantum theory, but the Sackur-Tetrode equation, which was the first step towards understanding of these indistinguishability of particle and working out the entropy of a monatomic ideal gas correctly by taking into account this indistinguishability. So, that was like the first step which was independent completely independent of this Planck's radiation formula or Planck's ideas. and it is also independent of this you know the Einstein's concept of quantization for the photoelectric effect and so on.

So, it is really an independent effort from the thermodynamic point of view or from the statistical mechanical point of view that such a development had taken place and we will actually talk about this. this equation or the formula for the entropy of the monotony gas, okay. So, this is not relevant. So, let me just rub it out and let us write down Sackur-Tetrode equation. As the name suggests, there are two people Sackur and Tetrode that they have independently actually came up with this equation.

in about 1912. So, it is more than 113 years or 112 years from now. And so, what they did was that they wrote down the entropy of a gas monatomic gas. And the way they did it is that they have taken this z, which is a function of t, let us write it as beta. And this is like sum over k exponential minus beta e k.

I am writing it as ek where ek is equal to h cross square k square over 2m where it is p is equal to h cross k. So, which means that all these things were already you know in place and these the fact that we are using h cross there was a hint in fact it was initially developed from the micro canonical perspective. However, we are doing it from the canonical point of view. So, once you write this down and have to evaluate it, what you do is that you convert it into an integral and you write this down as e to the power minus

beta E k. and then you have a dk and this is nothing but equal to V over 2 pi whole cube and sorry whole cube and 4 pi square and then you have a 0 to infinity and you have a k square e to the power minus beta h cross square k square over 2m and a dk. okay and really there is nothing new that we have done we have simply trying to calculate the canonical partition function and once we do that I will not show you this derivation but you can do it yourself this is very simple this is you know a double derivative of the Gaussian formula that we have already given.

So, what we can say is that if you have a quantity like this. x square e to the power minus x square or alpha x square, say alpha x square dx from, say, 0 to infinity or minus infinity to plus infinity. We should put a factor of half because we have already halved this interval, and it is a d 2 d alpha 2, and then we have an exponential minus alpha x square dx from 0 to infinity, and this is nothing but the square root of pi over alpha, okay, with this half factor included there. So, we can, we can do these, integral and, can land up with this, simple formula for n particles.

So, for, so this for one particle, so for n particles, Now, there is a correction factor that they this occurrent approach they introduced which gives a V to the power n and this n factorial and then a 2 pi m kT. divided by H square whole to the power 3 N by 2. So, this is the total partition function, and you can write it as the one-particle partition function. So, this is the canonical partition function where there is a permutation, this N factorial being used.

$$\text{Sackur - Tetrode equation}$$

$$Z_1(\beta) = \sum_K \exp\left(-\beta \mathcal{E}_K\right).$$

$$= \frac{V}{(2\pi)^3} \int e^{-\beta \mathcal{E}_K} \, d\vec{K} = \frac{4}{(2\pi)^3} 4\pi^2 \int_0^\infty K^2 e^{-\frac{\beta \hbar^2 K^2}{2m}} \, dK.$$

$$\mathcal{E}_K = \frac{\hbar^2 K^2}{2m} \qquad p = \hbar K.$$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} \, dx$$
$$\frac{1}{2} \frac{d}{d\alpha^2} \int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx$$
$$\rightsquigarrow$$
$$\sqrt{\frac{\pi}{\alpha}}.$$

for N particles
$$Z = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3N/2}.$$

$$F = -k_B T \ln Z = -N k_B T \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{\hbar^2}\right)\right]$$

And this is just to make sure that each of those exchanges of particles does not give you a distinct state, but it is actually the same state with some phase factor. So, this N factorial cuts down the number of permutations possible for such exchanges. And because these exchanges are included here, this should correspond, or rather should take into account, the indistinguishability of particles and should give you the correct formula for any of these parameters that you are interested in, particularly the entropy that they were interested in the quantum mechanical limit, okay. So, again, you can use F equal to minus KT log Z and one can find out what the free energy is, which comes out as minus NKT log of V over N and a plus 3 by 2 log of T. plus 1 plus 3 by 2 log of this, just writing it taking this log and so on, and there is an H square and there is a big bracket here.

So, that is the free energy that one gets and you can also write down the partition function. which you can do it either by you know from the this Z itself or what you can do is that you know that this is nothing but equal to 3 by 2 NKT and then of course, your S is equal to E U minus F by T U minus F by T. And this gives you a nice formula, which is a correct formula because of the reason that we have seen last day. So, this is V over N plus 3 by 2. log of 2 pi m k T and h square plus 5 by 2 and so on.

So, this is the formula for that and then S over n k or which is n k is often written as R the universal gas constant is equal to V over n lambda cube 5 by 2 and we just write it lambda with a lambda t where lambda t is called as a thermal de Broglie wavelength and this has a form which is given by h over root over 2 pi m k t okay. And this will play some role in distinguishing classical STATMEC from quantum STATMEC. And we will come to that in just a while. And so the gas is really still classical.

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

$$S = \frac{U - F}{T} = N k_B \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right) + \frac{5}{2} \right] \quad (Eq. \ 1)$$

$$\frac{S}{N k_B} = \ln\left(\frac{V}{N \lambda_T^3}\right) + \frac{5}{2}$$

λ_T : Thermal de Broglie wavelength

$$= \frac{h}{\sqrt{2\pi m k_B T}}$$

It is still a classical gas with Correct Counting!

However, this n factorial that is included in the partition function that excludes over counting that is you know the exchange of particles that is that gives rise to a new state that is not taken into account by this n factorial. Gibbs paradox, it was similar to the spirit of how the Gibbs paradox was fixed, which we have discussed last day and in which inside the expression for entropy, this N was introduced or N factorial was introduced and then Stirling's approximation was applied and which gave rise to the correct formula. for the entropy at least in terms of its extensiveness, okay. And here you can see that the extensiveness is maintained that is if you increase N, V and E by a factor, by a certain factor, the entropy enhances or rather gets multiplied by that factor as well, okay. So even though it is like we are doing it on a classical gas, classical ideal gas, but this correct counting is being introduced.

So I write that because it is an important comment. and I told you what this correct counting means that is to you know exclude the over counting of states due to the exchange of the particle. All right, so this is called as the Sakur-Tetraud equation and then if you really apply to the Gibbs paradox with this entropy, so this entropy let us call it as the equation 1 and this equation 1 would be applied to Gibbs paradox that is mixing of gases. So we again just draw that same picture just to remind you that you have N1 V1 T and N2 V2 T that is there at the same temperature and we are allowing the mixing of the two gases. So this goes from a situation when the partition is removed.

And you have still T and then N1 plus N2 and V1 plus V2. So this is before mixing and after mixing. we have 2 ideal gases there in the 2 chambers and these chambers have these number of particles volume and temperature to be given by N1 V1 T and N2 by 2 T and after they are mixed there is this T is still the same and then N1 plus N2 and V1 plus V2. So, the available volume is that. So, S initial is we have written it initial even earlier.

So, this is equal to I am just using this, the number of modes or you can write it as Nk. So, it is N1k and log of V1 by N1. 3 by 2 log T we can combine these all the other constant into C. This other constant is also an important quantity in the context because that gives you some S0 or the entropy that is you know independent of all these. relevant parameters.

So, this is the first one for the first gas, and then it is NK, and then we have a log of V2 by N2 plus 3 by 2 log of T. Plus some constant again, which is independent of all these things. So, we can simply add them up, and what we get is the N1 plus N2 K, and then we have log of now what we do is that we replace V by by the equation of state which is

PV equal to NKT and then we have this as P KT over P. So, this is replacing this and then we have a 3 by 2 ln T plus some constant, okay. So, this is the initial entropy of the gas, that is before mixing, and the final entropy of the gas, which is easy to determine.

Mixing of gases.

$$S_{initial} = N_1 k_B \left[\ln \frac{V_1}{N_1} + \frac{3}{2} \ln T + C \right] + N_2 k_B \left[\ln \frac{V_2}{N_2} + \frac{3}{2} \ln T + C \right]$$

$$= (N_1 + N_2) k_B \left[\ln \left(\frac{k_B T}{P} \right) + \frac{3}{2} \ln T + C \right]$$

$$S_{final} = (N_1 + N_2) k_B \left[\ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) + \frac{3}{2} \ln T + C \right]$$

So, that is corresponding to N1 plus N2 number of particles. So, we have N1 plus N2 into K, and then we have log of V1 plus V2 divided by N1 plus N2 and then you have a 3 by 2 log of T, which would remain constant, and plus some C. Now, you see that if you again use the equation of state, that is a pressure at V1 plus V2 equal to some N1 plus N2 KT then what we see is that we get S initial equal to S final, which I should get. So, the idea was to start taking care of the over counting right from the beginning at the definition of the this partition function and hence arrive at this expression for entropy which is known as the Sackur-Tetrode equation.

And this equation not only has the extensive nature. Now, you see that the extensive nature is inbuilt here and this called as equation 1 is called as Sackur-Tetrode equation. Alright, so this is the equation and as we said that this has been in terms of historical development, it has a lot of value because it was developed independently of either Einstein's photoelectric effect or the Planck's distribution formula, it was purely from a thermodynamic point of view. So, either you can do it from a microcanonical perspective. Here, we have shown it from a canonical perspective.

In the microcanonical perspective, you would have calculated the number of microstates and taken the log of that multiplied by K to get the entropy directly. Here, of course, we have gone through the canonical path and have calculated the entropy. The entropy is not only extensive when you have these two identical gases kept in two chambers, and they are allowed to mix, there should be no change in entropy, which is what— So, the entropy of mixing, which we have defined earlier, is 0, which means there is a correct result, okay.

$$P(v_1 + v_2) = (N_1 + N_2) k_B T$$

$$\boxed{S_{initial} = S_{final}}$$

$$\Delta S = 0. \qquad \underline{Correct \; result\,!}$$

So, in the classical gas, if the overcounting is properly taken into account, it gives you the right entropy, and that is what this equation tells you, okay. All right, so let us now go to few differences between classical STATMEC and classical and quantum STATMEC will write it together. Okay, so how do we sort of enumerate the differences? And there are many differences, in fact, and we are just highlighting some of the important ones and the ones that are of relevance to us. All right, so we need to, of course, as you understand, some of the classical ideas that we have developed,

they need to be modified in order to incorporate the indistinguishability of particles, okay. One of the things that is of importance is that the positional coordinates, momenta, and energy are quantized in quantum mechanics, okay. And this quantization should actually take the scale of the Planck's constant h or h cross, the h cross is equal to h over 2 pi, okay. So, most of the time, you know, this is used, this h cross is used or even in some cases h is used. Now, you have to understand that there are quantization in some sense, even in classical physics, in classical electrodynamics and so on.

If you remember that if you take an organ pipe and want to know the frequencies, how the frequencies are, they behave or you want to take out different notes in the flute that you are familiar with. And there are these nu over 2L or nu over 4L are the quantization of the frequencies where L is the length of the flute or that organ which emits sound. So, these are quantizations that are there and whenever you solve a differential equation pertaining to certain boundary condition, you are bound to get such quantizations. you know quantization if I if you remember that if you have solved Laplace's equation for say

for example, either dielectric or magnetic material you got those results as you know these some constants and then some function of R and then some PL cos theta where these are called the Legendre polynomials and so on. So, this else each of the allowed else are going to be solutions for this problem.

So, a superposition of all of them they are also solutions of the problem and so these L equal to 1. So, I am particularly talking about this Legendre polynomial for the this Laplace's equation. So, it is a T L cos theta where L equal to 0, L equal to 1 or L equal to 2 etcetera they allowed solutions and then you can also superpose them to get a solution which is the most general solution for this particular problem. So, for example, your V of r by solving a Laplace's equation, it gives you some form, if I remember it correctly, it is like a l r l plus b l by r l plus 1 and a p l cos theta.

and this is a solution for both the electrostatic potential or as a magnetic potential if you are talking about a magnetic case, magnetic scalar potential and each of these else can take values as I said 0, 1, 2. So, it seems that there is a quantization or there is a discreteness there as well in the solutions. We are not talking about this kind of discreteness—the discreteness in energy or the discreteness in the angular momentum should carry a scale that is equal to Planck's constant, which is h or h-bar, okay. So, that is one important thing. The second important thing is that we know that Q and P can be independently defined in classical mechanics.

However, Q and P cannot be independently defined because of the uncertainty relation that we have. So, this delta Q delta P should be of the order of h cross or one can write it a little more correctly as less than h cross by 2. There is got nothing to do with the accuracy of the experiment. This is very inherent to the system and every canonical, every set of canonical observables have to follow this uncertainty relation, okay, which could be, you know, J phi or it could be J means the angular momentum and the angle, corresponding angle. Angle of variable rather, and energy and time.

So, delta e delta t is again this follows this relation delta e into delta t is equal to or less than equal to h cross by 2 delta j delta phi which angular momentum and phi is the angular variable, they also would conform to this. So, now let us take an example for say particle in a box. So, we have particle in a box and this is the first thing that you always see. So, what it says is that the potential is 0 inside and these walls are infinitely high.

So, this V equal to actually infinity so, the which means that the particle is confined and it cannot escape on either side and while it is inside there is no potential that it feels ok.

So, it is like a free particle which is allowed to go anywhere between this and it is associated with a wave and so on and then we know that the quantization for this. comes as P n or the momentum is quantized as 2 pi over L n h cross and so on, so where n is an integer. Okay, there is no extra degree of freedom. We actually have lost the position or positional degree of freedom, but it does not matter to us because this N can be actually found out as PNL divided by 2 pi h cross.

and there is no information about Q, but when you actually do this sum over N or sum over all the steps, you can do an integral over this N and this is equal to nothing but, so this L by 2 pi h cross. dP and which is nothing but equal to I mean dQ dP by H. This is just a simple example for particle in a box where even if you do not see the positional degree of freedom that is actually there and this L is you know it takes into account this positional this uncertainty there and so on. So, in short what we want to say is that if you if you remember that P and Q are two points in the not two points just a point in the phase space in the P Q space there is a point here which is called as P 0 Q 0. OK. And it's a sharply defined point.

Differences between Classical & Quantum Stat Mech.

(1) q, p, E are quantized.

$$\Delta q \cdot \Delta p \le \frac{\hbar}{2}.$$
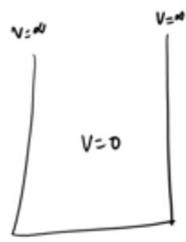
$$p_n = \frac{2\pi}{L} n \hbar$$

n: an integer.

$$n = \frac{p_n L}{2\pi \hbar}.$$

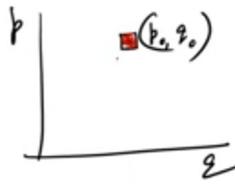$$\sum_n \to \int dn = \frac{L}{2\pi \hbar} \int dp = \int \frac{dq\, dp}{h}$$

(p, q)

$$\hbar = \frac{h}{2\pi}.$$

$P_\ell (\cos\theta)$

$$\ell = 0, 1, 2 \cdots$$

$$V(r) = \sum_\ell \left(A_\ell r^\ell + \frac{B_\ell}{r^{\ell+1}} \right) P_\ell (\cos\theta).$$

(p_o, q_o)

And, you know, we have developed much understanding of how to do an ensemble average, how to define ensembles, and how to actually reconcile the statement of Liouville's theorem, etc. All in this description. And so because of this uncertainty relation now this point actually acquires a bit of fuzziness and it is let me draw it with the colour and this is that is now the area of this fuzzy object which now looks squarish is a multiplication of delta Q and delta P which is of the order of h cross. That is where the

correspondence between classical mechanics and quantum mechanics they are that is how they are established that a point now becomes fuzzy and acquires certain region of space with an area equal to h or h cross. Alright, so let us look at some more differences with them and with between the two and let us just talk about this two very importantly which we have told many times earlier and as well as today is the indistinguishability of particles.

So exchange of two particles does not give rise to a new state. okay this has to be properly taken into account okay in classical mechanics it was classical statistics it was taken as it would have given rise to a new state and so on okay so even within that this exchange statistics is called as the exchange statistics so one needs to define an exchange statistics and this exchange statistics gives rise to two kinds of particles 1 is called as a fermions which upon changing their mutual positions they pick up a negative sign that is a phase which is equal to pi and there are other kind of particles which do not pick up a sign and they or rather this pick up a phase which is equal to 0. So, this 0 and pi phase because of the interchange of particles that give rise to two kinds of you know particles quantum particles that we have to talk about and these two type of quantum particles have very different properties like for example, fermions obey

Pauli exclusion principle which means that no 2 fermions with the same quantum number can occupy a given energy state. So, this is called as a Pauli exclusion principle and because of that you know, are picking up a negative sign, one can write down the wave function or many particle wave function for the fermions as a Slater determinant, we will see all of that and bosons actually have no problem in occupying any number basically no constraint on the number of particles occupying single particle states. So, this is a more stringent condition because you see that if two fermions cannot allow one given energy state that is like putting a hardcore condition that one electron if it is already there or one fermion if it is already there electrons are fermions.

It is already there then another electron or another fermion cannot come so that puts a constraint and this constraint gives rise to a large number of very interesting properties of for fermions which are not observed for bosons. On the other hand since bosons actually like being together in fact we will show that this number fluctuation for bosons they indicate that they actually like being together this gives rise to another very important phenomena which has been observed experimentally called as a Bose-Einstein condensation. So, they will all be part of our discussion on statistical mechanics. We just want to mention it here.

2) Indistinguishability of particles.

Exchange of two particles does not give rise a new state.

→ Exchange statistics

→ Fermions (Fermi-Dirac statistics)

→ Bosons (Bose-Einstein statistics).

⇒ Fermions obey Pauli's exclusion principle.

Bosons have no problem in occupying single particle state.

So, these obey Fermi-Dirac statistics, and these obey Bose-Einstein statistics. And what could be more differences or other differences? One can really think that in classical mechanics, one really talks about solving Newton's equations of motion. So, Newton's laws and they would really mean all the three laws that we are aware of and this means that F is equal to you know dP dt equal to M d2 X dt2. And this means that if you solve this differential equation by integrating it twice, you can get X of T if you know the nature of F that is acting on the system.

And this is what is done in the numerical procedure is followed in what is called as a molecular dynamics simulation and so on. So, one really sort of builds up X1 T1 at X2 T2. and all the way till X n T n, so that sort of you know fixes the trajectory of the particle that it takes in the influence or under the effect of this force that acts on the system. On the other hand, in quantum mechanics, one talks about the Schrödinger equation. We are, of course, talking about non-relativistic mechanics.

So, where it is written as minus h square by 2m and we write it in three dimensions. So, it is del square psi is called a Laplacian operator plus V of r psi, psi is a function of a vector r. And vector r can be x, y, z or r theta phi depending on what kind of symmetry the system has. And this is e psi r. You can write it as the time dependent equation is written as ih cross del del t of psi r. and one solves this equation and we are only sort of familiar with solving it you know in known situations where there is a closed solution the time independent part of it mostly and that is what you see in the first course of quantum mechanics that you solve it for a number of problems such as particle in a box such as hydrogen atoms such as harmonic oscillator

and maybe more sort of systems such as say linear potential instead of harmonic potential and linear potential which gives rise to airy functions and so on. And some of these

things are easier to do using an approximate method. For example, this linear potential or a slowly varying potential is usually done using WKB approximations. So, we can solve this in a variety of situations and in a very different type of arbitrary situation even this one particle Schrodinger equation is not solvable and one may resort to techniques, numerical techniques to solve this differential equation once again just like the Newton's laws. And one finally gets what is known as psi r. And in this particular case, it's if you take a time dependent, there's really a psi rt, v is taken to be time independent in the sense the potential is also time dependent.

Then, of course, you cannot solve this equation unless you have a very specific kind of time dependence, which is, you know, periodic time dependent then there are different methods of solving this things called as a Floquet formalism and so on so forth okay. So, what you find out is that you find out these Psi of RT By itself, which is the solution of this differential equation, by itself psi of RT does not have any physical significance, okay. It only acquires physical significance if you talk about the quantity called probability density and probability, which is given as Psi of RT mod square or probability current density. which is defined as say J which is like RT and this is if I remember the pre factors correctly it is like this.

$$(3) \qquad \text{Newton's laws:} \qquad \vec{F} = \frac{d\vec{p}}{dt} = m\frac{d^2\vec{x}}{dt^2}$$

$$x(t) \qquad\qquad x_1(t_1), \; x_2(t_2) \; \cdots \cdots \; x_n(t_n).$$

Schrödinger equation.

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t) = E\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r}).$$

$$\psi(\vec{r},t)$$

Probability density — $|\psi(\vec{r},t)|^2$

Probability current density — $J(\vec{r},t) = \frac{\hbar}{2mi}\left[\psi^*(\vec{r},t)\vec{\nabla}\psi(\vec{r},t) - \vec{\nabla}\psi(\vec{r},t)\psi^*(\vec{r},t)\right]$

So, it is a Psi star RT del Psi RT minus del Psi RT so Psi star. where Psi is the wave function, which is, in general, complex, and by itself, as I said, Psi is just a mathematical function. It has no physical meaning, but when you talk about this mod Psi squared, it

acquires a physical meaning that denotes the probability of finding a particle in a certain region of space and time, which is R and T, and one can also calculate this probability current density if you know this Psi and Psi star. So, Psi is, in general, complex, as you can understand, so that is why Psi and Psi star could be distinct. which will tell you that the probability current density would exist if Psi is completely real in certain situations, which it does, as you solve this particle barrier penetration problem. If you have the wave function to be completely real, there is no current associated with it, and it is called an evanescent wave instead of a propagating wave. Okay, so another very important thing is that two kinds of averages appear. What do I mean by two kinds of averages?

One is, of course, the quantum mechanical average, which is the—we will just see in a while—what is a quantum mechanical average. And we also have a statistical average or the ensemble average—okay, statistical or the ensemble average. So instead of just one average, which is the ensemble average in classical statistical mechanics, here one needs to worry about two kinds of averages, or there's a double averaging that comes into the picture, where the quantum mechanical average or the expectation values of operators also have to be taken into account. And as well, you need to average over the ensembles. So this is something that we are going to discuss.

(4) Two kinds of averages.

        (i) Quantum Mechanical average.

        (ii) Statistical (ensemble) "

Now, let us see that what is the limiting case of quantum statistical mechanics or quantum mechanics, quantum stat mech maybe. That is the one that we have learned so far. Are they all wrong, or in some limiting case, is it true? We have said that in the limiting case it is true, but let us see it more carefully, and so we write this delta X delta P is equal to of the order of h-cross. You can write it h-cross by 2 or less than h-cross by 2—they mean the same thing. So, say this one, delta X for a particle—okay, for a point particle or for a particle with some finite dimensions—what could be a delta X? So, if you think of just a small, you know, billiard-ball-like structure, which has a radius R, so the maximum uncertainty—or the maximum uncertainty in the measurement of the position—is the radius itself.

So, this delta X—the maximum delta X—is, say, for example, like the R, which is the size of the object. It can be a cubic object or it can be a spherical object. Just for, you know, convenience, we have taken it to be a spherical object, but it can be a cubic object as well. And this one—this P is the momentum, which is, you know—so the classical limit demands that these quantities should be much, much greater than R into P should be much, much greater than h-cross, right? Because if h-cross is comparable to this product, then we are in the quantum regime. And we are talking about the classical limit of this. So, R cross R dot P should be equal to you know H. So, R you know should be much much greater than H over P or H cross over P does not matter.

So, this is this H over P is of the order of lambda where lambda is called as a de Broglie wavelength. So what de Broglie proposed is that when it was fairly clear at the beginning you know era of quantum development of quantum physics that there are particle descriptions and there are wave descriptions of the same experiment like for examples photons they undergo interference experiments Young's double slit experiments or diffraction. which show up the wave phenomena, whereas there are Compton effect and there are photoelectric effect, which shows the particle phenomena, because you apply the conservation of energy and so on, as if they are like hard billiard balls, they are electron is colliding with photons or, you know, particles. In situations where they are really taken as hard spheres, and you talk about the energy and momentum conservation relation—of course, we talk about these as elastic scatterings—there has to be a reconciliation between the wave description and particle description. De Broglie came up with exactly that when he said the momentum of a particle P, which is equal to MV in the non-relativistic case, should be related to the wavelength of the wave through this relation, okay?

So, lambda is equal to h over p is what he said and this is called as a de Broglie wavelength. So, it is h over p if we ignore this h cross and h which is simply a factor of 2 pi then this is really equal to much greater than the wavelength associated with the wave. So, the size of the particle has to be very large compared to a wavelength that could be associated with the particle. So, this is the classical limit. Now, if you think of gas or a sort of system and try to fill up the system by all these hard spheres or for just for a moment thing that we have cubes, which have a volume equal to R cube.

and we need n such R cubes there could be a fourth third factor if you you know take into account the sphere but let us forget that and so R cube into n should be equal to V. So, we have a system with a volume V and we are completely filling it up with objects that have

volume R cube and n of them that are going to fill this entire volume. So, this tells you that R is equal to which is V by N to the power one-third. So, this is R to the I mean R equal to V by N to the power one-third. So, this is V by N is nothing but inverse of the density. So, there is a density to the power minus one-third that comes here and this when you apply equipartition theorem.

So you have a 1 over 2m and P square this is equal to some E which is equal to some 3 by 2 KT and that tells you that this P is equal to like a root over 3m KT. So, this lambda that you get is H over P and this is like root over 3 m KT. Well, we have written it with the thermal de Broglie which is slightly different than that and so, the where classical limit is valid when this V by N hold to the power one-third is much, much greater than H this particular thing, okay. So, this is what we have told.

So, this condition translates to so, R much, much greater than lambda that translates to so, we have calculated R which is V by N whole to the power one-third and we have also calculated lambda which is H divided by 3 m KT. So, putting it into this r much much greater than lambda we get root over h divided by 3 m kT okay. So, this tells one thing that the classical limit is valid 1 when temperature is high which means the thermal effects dominate over the quantum effects and the other is that we have the density to be small. So, the density is here, which is N divided by V is equal to the density.

$$\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{\sqrt{3mk_BT}}$$

Classical limit is valid

(i) T is high

(ii) density to be small.

So, when the density is small, that is inverse of this is small, then of course, this is going to be valid or when temperature is large. So, the limit of the quantum statistical mechanics is the classical statistics. So, classical statistical mechanics is obtained as a limiting case of quantum stat mech. So, which means that at very large temperature the distinguishability goes away and the particles become indistinguishable. okay and at very low temperature the indistinguishability test sets in which means that the particles are to be treated alike and you cannot you know give a sort of name texture or color to each of the particle that are under consideration okay I will stop here.

Amen.