Basic Statistical Mechanics
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Lecture – 22
Ideal Monoatomic Gas: Microscopic Expression of Translational Entropy (Part 5)

So, we will continue initially, with the review of monatomic statistical mechanics of monatomic gas and then we will do the atomic gas today itself, we did it once before but we need to redo many other aspects because these are fairly detailed things. So, you can call it as a revision but it is more likely many new, new information will come in, in today's and; so in the study of statistical mechanics and study of any subject, which is bit mathematical and involving lot of equations; it is what going through these many times.

Like, when you used to derive equations, when you are a student one of the things that we are told and we did is that we derived the same thing many, many times that is the way; you do not memorize it but you derive it many times, you go through it many, many times; it is like painting, when you; in order to understand something and get it inside you deeply, you do like we do painting of the wall, you know you do several coats.

So, we will briefly and quickly go through few things and then we will go to the new things today, in a monatomic gas we will do two new things which we missed before, then we go to diatomic gases and we will do some old and some new.

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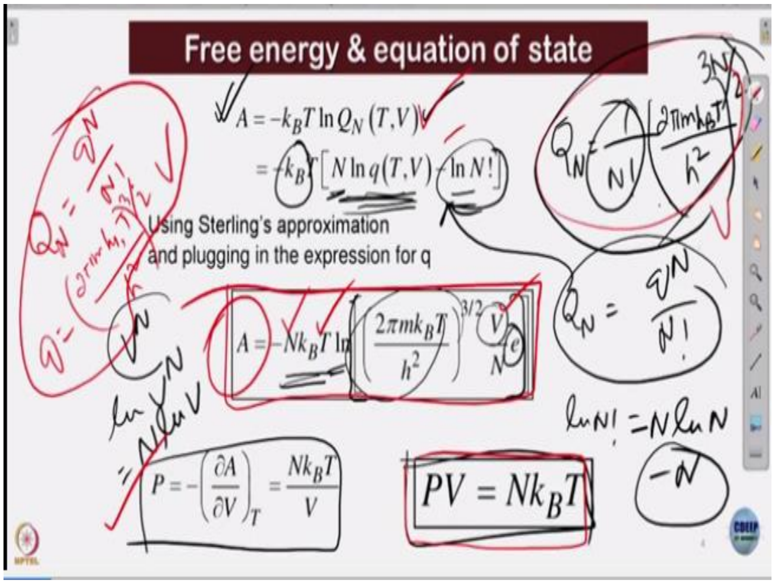

Free energy & equation of state

$$A = -k_B T \ln Q_N(T,V)$$

$$= -k_B T\left[N \ln q(T,V) - \ln N!\right]$$

Using Sterling's approximation and plugging in the expression for q

$$A = -Nk_B T \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{Ve}{N}\right]$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{Nk_BT}{V}$$

$$PV = Nk_BT$$

Now, in the last class we discussed first the partition function and the partition function is the thing that I have here on my board, the QN and QN coming from integration over the momentum and for A integration gives volume real space integration gives volume and then these essentially, then what happened that q; q that we derived it has contain this quantity and multiplied by the volume.

So, N particles we have now q to the power N and then we go in and we derived that, that the free energy, so all these details were done in the previous page. So we did that, that we wrote down Q_N is q to the power N /N ! and then we have the volume q to the power N /N ! and Q is this quantity that 2π mk$_B$T /h square to the power 3/2 and the volume V that was the quantity.

$$q(T,V) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

When that Q_N with this q is used in the statistical mechanical expression of free energy; statistical expression of free energy in - k_BT ln Q_N, Q_N is the canonical partition function, then we get this and then one get an expression of free energy in terms of N, total number of particles in the system temperature of the system and the volume of the system, this is really beautiful. An exact expression, a microscopic expression what is Helmotz free energy and that has; is a function of, A is a function of NVT and I have those dependents.

$$
\begin{aligned}
A &= -k_B T \ln Q_N(T,V) \\
&= -k_B T \left[N \ln q(T,V) - \ln N! \right]
\end{aligned}
$$

And we have, some very fundamental quantities like I have Boltzmann constant k_B, I have mass of the particle and I have the Planck's constant, okay. This is a beautiful, really beautiful expression these(in the box). Now, then I can calculate by using thermodynamic relation from these free energy, I can now calculate pressure, then another beautiful thing comes in that is equal to Nk_BT , we all know, the ideal gas law.

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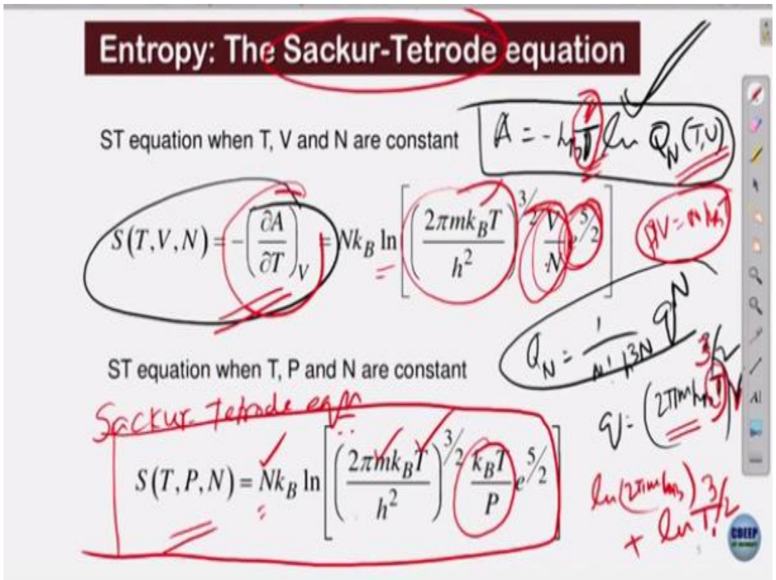

Entropy: The Sackur-Tetrode equation

ST equation when T, V and N are constant

$$A = -k_B T \ln Q_N(T,V)$$

$$S(T,V,N) = -\left(\frac{\partial A}{\partial T}\right)_V = Nk_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{V}{N} e^{5/2}\right]$$

$$PV = Nk_BT$$

$$Q_N = \frac{1}{N!\,\Lambda^{3N}} q^N$$

ST equation when T, P and N are constant

Sackur Tetrode eqn

$$S(T,P,N) = Nk_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P} e^{5/2}\right]$$

$$q = \left(2\pi m k_B T\right)^{3/2} V$$

$$\ln(2\pi m k_B)^{3/2} + \ln T^{3/2}$$

So, then the next what we did; we went on using that partition function and the Helmotz free energy, we get the entropy and the entropy then is obtained by $(dA/dT)_V$, the thermodynamic relation and now, we get a beautiful expression of entropy again, the expression of entropy includes the N, the number of particles, temperature T and when I remove V /N by using the ideal gas law, then it is in pressure.

$$S(T,V,N) = -\left(\frac{\partial A}{\partial T}\right)_V = Nk_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{V}{N} e^{5/2}\right]$$

$$S(T,P,N) = Nk_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P} e^{5/2}\right]$$

So, entropy suddenly is an exact expression of which depends on total number of particles in the system, the pressure of the gas and the temperature T, again I have the mass of the particles is a monatomic gas, or one gas, this can be generalized to binary mixture or three particles things, almost trivially. Then, what will happen; I have to say, I have argon and krypton, then I have a N argon here, number of argon will come in here.

And then mass of argon will come here, everything same, pressure remains the same, then I say N of the krypton and then again, mass of the krypton again, this is same, so is the ideal gas law here follows Raoult's law, so you add up the entropy multiplied by the number of them and if I say entropy per particle, then it will be mole fraction . So, the things to remember and things to really note that you have a number of particles N and we have the temperature T here.

And we have the pressure P here, if I have the volume there, volume here, this is the famous Sackur Tetrode equation which I discussed is used in many, many, many, many applications. But ; before I go, I really want to impress upon you the beauty of this equation, that this is where the temperature comes as 3 over 2, so if I combine temperature with this, it becomes T to the power 5 /2 and these are much less known and much less emphasized but these are some elegance but these are beautiful thing.

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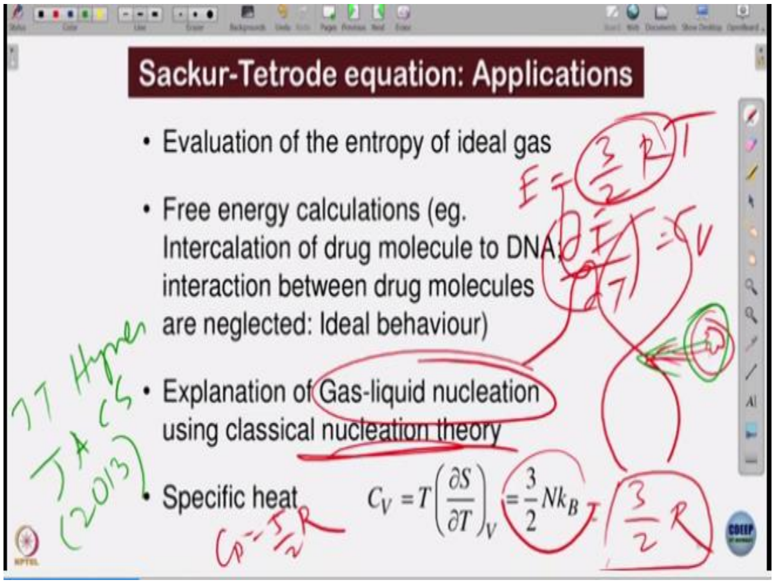

Sackur-Tetrode equation: Applications

- Evaluation of the entropy of ideal gas
- Free energy calculations (eg. Intercalation of drug molecule to DNA; interaction between drug molecules are neglected: Ideal behaviour)
- Explanation of Gas-liquid nucleation using classical nucleation theory
- Specific heat $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}Nk_B = \frac{3}{2}R$

$E = \frac{3}{2}RT$

$\left(\frac{\partial E}{\partial T}\right) = C_V$

$C_P = \frac{5}{2}R$

77 Hynes JACS (2013)

So, then we commented that we use this Sackur Tetrode equation in a drug DNA intercalation, we discussed this same that in that this drug is going into minor or major group and this is a very important problem in chemotherapy or many other drugs and then in doing the calculation, there is a beautiful paper by Charles then there is a paper beautiful paper on drug intercalation which you can do it in the name of JT Hynes, JACS , I think probably 2013 or so.

And with that this thing was used, the Sackur Tetrode equation was used to calculate the free energy integration and this is very important that we get the free energy of intercalation because that allows us to choose or select drugs this you know very, very important, then we use it extensively in the formation of water droplets in the cloud and that you know this entropy, when the water goes to form a droplet, a bubble water droplet which has to become rain that is lot of; loss of entropy.

Because instead of moving separately they are stuck together and a big mass and so, then the entropy decreases but that thing is used in many, many other thing, in nucleation, many, many other things.

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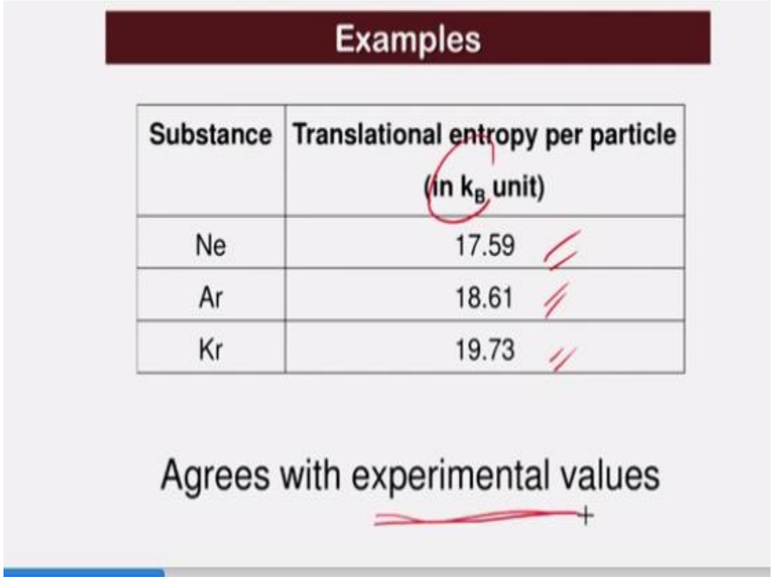

Examples

Substance	Translational entropy per particle (in k_B unit)
Ne	17.59
Ar	18.61
Kr	19.73

Agrees with experimental values

So, continuing now that I gave some numbers, you should always think in terms of numbers and in entropy, number is always in terms of these k_B unit that is called entropy unit in a Boltzmann constant. Now, this is under ambient conditions that means, they are expected the liquid state, the gas state, neon's entropy is this and argon is this, so they are pretty close to each other, this, this, this entropy and there with the whatever experimental values we have by integrating thermodynamic variables they agrees almost exactly with the experimental values.

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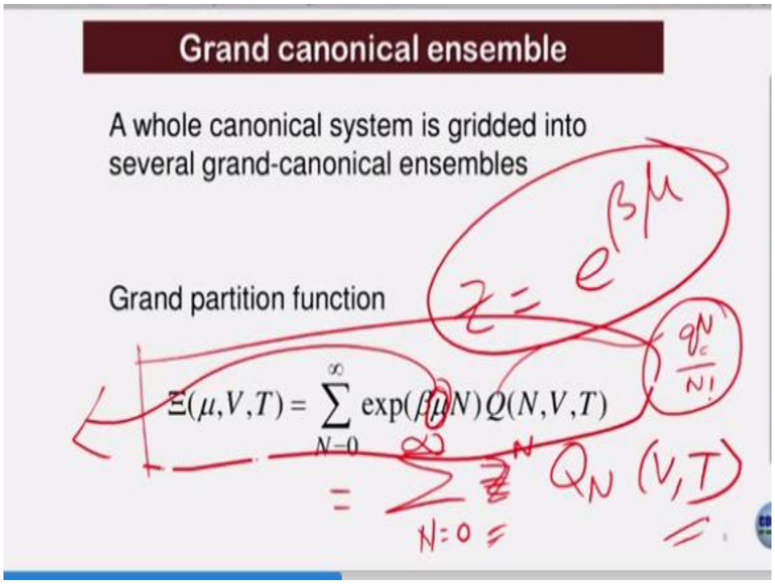

Grand canonical ensemble

A whole canonical system is gridded into several grand-canonical ensembles

Grand partition function

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \exp(\beta\mu N) Q(N,V,T)$$

$$= \sum_{N=0}^{\infty} z^N Q_N(V,T)$$

$z = e^{\beta\mu}$

$\frac{q^N}{N!}$

So, now we will do two simple calculations which we have not done before and there are very nice calculations, the simple calculations but they use some mathematics, so we now derived expression for pressure, we derived an expression for entropy, we derive an expression for free energy, we derived an expression for specific heat; $\frac{3}{2}R$ and $\frac{5}{2}R$ R, $\frac{3}{2}R$ comes just as I showed you from A and then $\frac{5}{2}R$ because you add R which comes from PV terms, h equal to e plus PV because C_p is dA; derivative of enthalpy.

And enthalpy comes with a PV, extra PV term, so that PV, then we replace PV /RT and we take the derivative, then 1R comes with adds to $\frac{3}{2}R$ and you get $\frac{5}{2}R$ that is a reason that CP is $\frac{5}{2}R$ and CV is $\frac{3}{2}R$, the PV terms, the extra PV terms that goes over to becomes R T in the per mole; 1 mole for ideal gas law. Now, we will do something we have discussed, the grand partition function but we have not used too much of grand partition function.

We will use a grand partition function later quite a bit but now, we are just somewhere about in the beginning of the Statistical mechanics course and but we have already getting many, many nice results but we will get one more nice results. The result that we used extensively in your freshman chemistry or in (()) (10:48) chemistry and but in solution chemistry or in undergraduate chemistry at least, I can personally say myself I found it boring.

And even now, teaching it sometime fairly boring, so there are lot of very nice books have come to make it easier but the problem of those physical chemistry equations is that they are introduced much of the time, they are not derived and example says a solvation, the concept of chemical potential, why the chemical potential goes at logarithmic term that comes as the definition.

But what we will do now it is not a definition, we will derive it from statistical mechanics more fundamental why; chemical potential shall goes logarithmic of density, it is a very important quantity, remember in your undergraduate study that we start what you know the chemical potential and is a very important quantity and in describing the flow of matter but that this proportional to logarithmic density.

So, if we keep low density, high density together, then matter flows from low density to high density and the driving force will be given by the logarithmic density and that is goes into the diffusion equation, ficks law and all these kind of stuff which we will do later, as we go and viewing in a little bit of time dependence statistical mechanics which is just wonderful subject.

So, what we did before that we did the grand partition function and grand partition function is this quantity that is can be, I wrote it also like that, these quantity and here the Z is the fugacity and μ is the chemical potential, so Z equal to e to the power β mu, so this is the relation between chemical potential and fugacity Z, we use the chemical potential and Z is the fugacity.

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \exp(\beta\mu N)\,Q(N,V,T)$$

$$z = \exp(\beta\mu)$$

So, this is the and remember that this Z or β μ comes, these in terms was a Lagrangian multiplier or Lagrange undetermined coefficient andμcame as the conservation condition that number of particle must be conserved, so you form from micro canonical ensemble to then you go into canonical ensemble, we introduced conservation of energy of my super system.

And that conservation of energy on the super system that means there is energy exchange between the system but in the super system which has been put by contact putting them in contact with each other, so that exchange energy and can attain a temperature T; however the conservation of the total thing was maintained, conservation of total energy of my super system.

And that conservation condition gave rise to β, the temperature β, the temperature term β, β is 1/ k_BT, it came as undetermined coefficient but it came as a conservation condition similarly, when you go to grand canonical partition function, then the chemical potential or fugacity came again as an undetermined coefficient but to take care of the conservation of the number of particles.

So, this is very, very important that they come very naturally from a very fundamental condition that is conservation of energy, conservation of number of particles that means they are not ad hoc. Now, then with that going, the way just like Q_N was sum over energy levels E to the power -βμk_BT, we get grand partition function as e to the power βμN andμNVT which is written here in another form.

So, now we will do something very interesting with that, before you do that if I now talk of ideal gas; in ideal gas I know Q now, Q is a quantity which goes as q to the power N /N !, this is the ideal gas or monatomic gas that means, I have an exact expression for Q, now those of you like mathematics, you can immediately see that this is something e to the power N and this is also something to the power N; Z is e to the power - β mu, so this is Z to the power N this quantity is Z

So, I have 1 to the power N and the Z, so Z, q multiplied and to the power N and divided /N ! and what does that remind you; that remind you that becomes nothing but an exponential function, so e to the power Zq, it becomes e to the power Zq.

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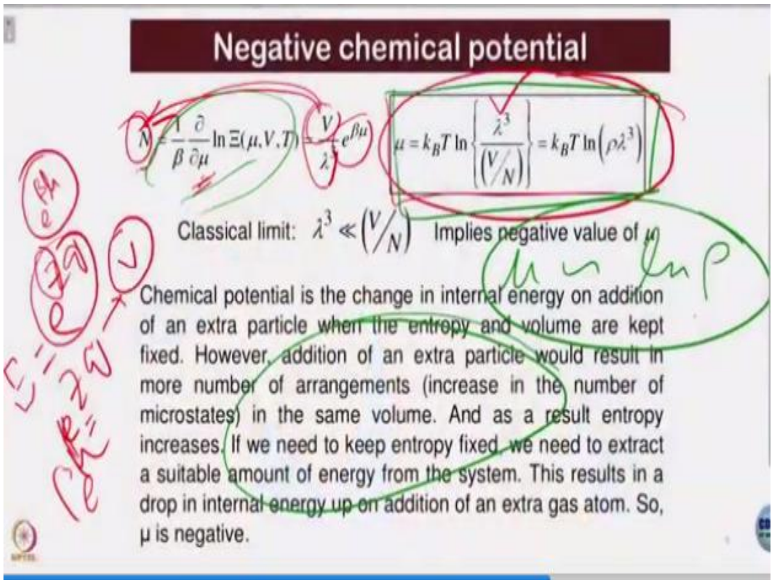

Negative chemical potential

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi(\mu,V,T) = \frac{V}{\lambda^3}e^{\beta\mu} \qquad \mu = k_BT\ln\left\{\frac{\lambda^3}{\left(V/N\right)}\right\} = k_BT\ln\left(\rho\lambda^3\right)$$

Classical limit: $\lambda^3 \ll \left(V/N\right)$ Implies negative value of μ

$\mu \sim \ln\rho$

Chemical potential is the change in internal energy on addition of an extra particle when the entropy and volume are kept fixed. However, addition of an extra particle would result in more number of arrangements (increase in the number of microstates) in the same volume. And as a result entropy increases. If we need to keep entropy fixed, we need to extract a suitable amount of energy from the system. This results in a drop in internal energy up on addition of an extra gas atom. So, μ is negative.

So, now and that so now, we know in; so I have an expression for grand partition function that is e to the power Zq and I know q, so this is the my grand partition function beautiful, so now I also know that chemical potential and number of particles are conjugate of each other and the exact relation between then is just like pressure is dA/dV, entropy is, dA /dT and everything like that, number is related to this grand partition function through A of chemical potential.

Now, when I put q and all these things here because this is e to the power β, Z it is again e to the power β mu, I add them here put them I take a log term and then this β you come;μcomes in front and then ln V will comes it and then I take the derivative of this quantity, then e to the power Zq, then it becomes, it comes out as Zq and q is a proportional to volume and Z is e to the power β mu.

Then, when I do that simple algebra, I get the derivative; the derivative of exponential is exponential brings β R down and when I do these things together, I get just this beautiful relation. So, now you see the volume V, the volume; if N becomes this quantity, so now I can take these V on that side or I can take V on that side, I can take N /V that becomes density and lambda q, so this whole part is taken there, so giving rise to be this term and is e to the power βμand then I take the logarithmic term and β becomes 1 over k_BT.

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi(\mu,V,T) = \frac{V}{\lambda^3}e^{\beta\mu}$$

$$\mu = k_B T \ln\left\{ \frac{\lambda^3}{\left(V/N \right)} \right\} = k_B T \ln\left(\rho \lambda^3 \right)$$

So, you can easily see that I get this beautiful relation, this beautiful relation (I like, so I use one more color), so these beautiful relation now, that means chemical potential is logarithmic of density, many times we write ln ρ which is not correct because you cannot put in dimensional quantity within logarithmic or you cannot put definitional quantity in exponential, so something is missing in these equations.

But in classical physical chemistry, we just write ln ρ we cannot not, there is always that function lambda cube there and or many times what we do; we do chemical potential with respect to one another space E, so another state, then delta μ term, then I have - ln and then I that becomes a ln A - ln B is ln A /B and then lambda cube cuts out, you get; ln ρ_1/ρ_2, so that is why lambda q is always kind of a silent player in all these things.

But I really want to impress upon you this beautiful relation that mu;µgoes as ln ρ, this is something which is hugely used. So, when I talk about non-ideality, so these are ideality, chemical potential is dependent on linear logarithmic dependence on density but when I talk of non-ideality now, the non-ideality we just introduced other activity coefficient and other quantities that is where this is where it enters all these things.

So, there is a very solid foundation of these things, these were actually; these terms were actually done in by Gibbs himself, so that is why in the thermodynamics of solution theory many, many things that Gibbs equation, Gibbs Duhem equation and all those stuff because this was worked out by Willard Gibbs himself. Now, so there is a little bit of writing here now that we let me you read through; chemical potential is the change in internal energy on addition of an extra particle when the entropy and that is given here, these you know these things.

However, an extra particle would result in more number of arrangements in the same volume as a result, entropy increases, so basically what one trying to tell here the chemical potential and that is how it is done in undergraduate textbooks, the chemical potential in ideal gas when their molecules are not interacting with each other is an entropic origin, it is very, very important to understand that.

Chemical potential and ideal gas is an entropic origin, so ideal gas law gives us a fantastic way to talk of entropy because you all you have this entropy and what we do then later, when you add interactions, many times we try to preserve the entropic term, the lnρ term like in remember, binary mixture, ideal entropy of mixing, what is that; that xi ln xi, so essentially ρ_i lnρ_i which has basically, the same structure ln ρ term coming and they multiplied by the relative weight of that lnρ term.

This is just, just beautiful things that the way they fit together but these are very important thing is talk here that it is the entropy that is the important player here because in ideal gas law, we do not have interaction energy but by entropy alone, we will get a huge number of phenomena and as again, I am repeated this part of entropy, we take; we try to take over when you do interacting systems, the real systems.

These are not real but very important just like particle in a box in quantum mechanics is important, harmonic oscillator is important, rigid rotator is important and then you go and start doing, after doing these things you start doing at ideal gas of ideal molecules here also, we will go toward complex systems okay.

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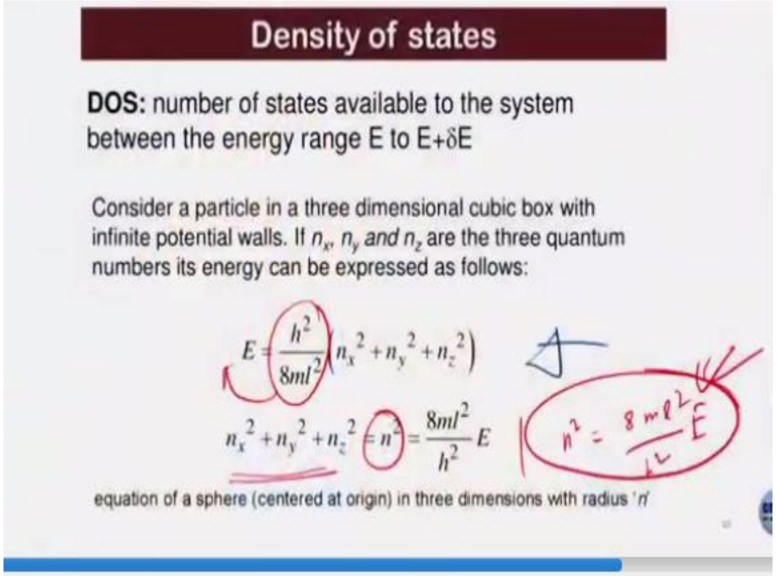

Density of states

DOS: number of states available to the system between the energy range E to E+δE

Consider a particle in a three dimensional cubic box with infinite potential walls. If n_x, n_y and n_z are the three quantum numbers its energy can be expressed as follows:

$$E = \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$n_x^2 + n_y^2 + n_z^2 = n^2 = \frac{8ml^2}{h^2}E$$

$$n^2 = \frac{8ml^2}{h^2}E$$

equation of a sphere (centered at origin) in three dimensions with radius '*n*'

So, now we now know, we want to go the and very important second calculation of the mono atomic gas, ideal monoatomic gas then with a lot of consequence, a result that is used extensively in for example, solid state physics and in spectroscopy, in conductivity of solids you know the electron gas and that kind of a problem where we need to know what is the number of density of states, how many number of quantum states between energy e; at energy e between e and de that is called density of states.

And it is very important how the density of states changes with energy and there is a simple trivial calculation but very nice calculation that let us go through that. Now, you have done quantum mechanics particle in a box and you know that the energy is given by this quantity that E is h square by 8ml square, nx square nx, ny, are the quantum number and their values are from 1, 2, 3, 4 . We discussed at length why, this quantum number starts from 1.

$$E = \frac{h^2}{8ml^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

And they are integer numbers; 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 like that now, this is a beautiful equation, now I realized if I can do a little bit messaging of that then nx square, nu square, nz square I can write it at n square, then that n square and I can take now these quantity on this side, then I can write and this is going to be very important; 8ml square /h square, I go there so and then n square becomes equal to 8ml square /h square internal energy.

$$n_x^2 + n_y^2 + n_z^2 = n^2 = \frac{8ml^2}{h^2} E$$

Now, this is I can call these as nx square, n square all these things like you know, x square plus y square plus z square equal to h square that is the equation of sphere, so this is the equation of sphere and then I will have something very interesting thing to do because this centered at origin in 3 dimension, now that becomes the radius now but I know the radius, I know the radius that radius in term is given by that okay.

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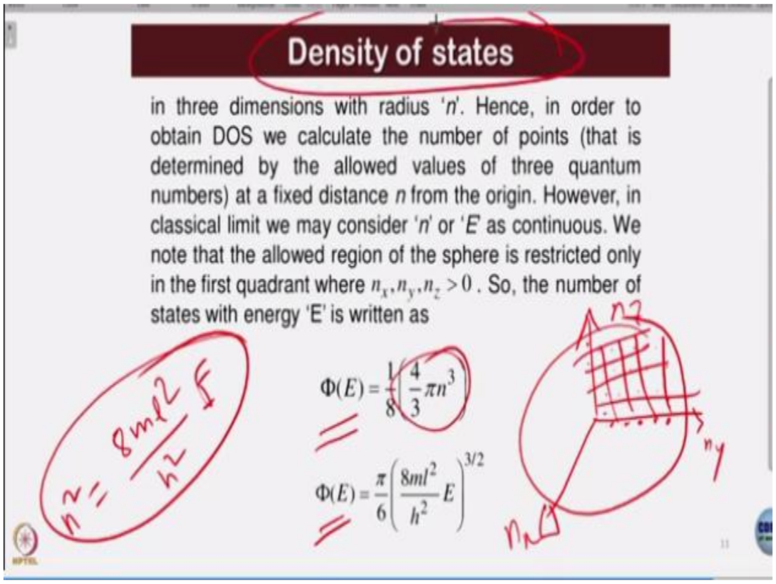

Density of states

in three dimensions with radius '*n*'. Hence, in order to obtain DOS we calculate the number of points (that is determined by the allowed values of three quantum numbers) at a fixed distance *n* from the origin. However, in classical limit we may consider '*n*' or '*E*' as continuous. We note that the allowed region of the sphere is restricted only in the first quadrant where $n_x, n_y, n_z > 0$. So, the number of states with energy 'E' is written as

$$\Phi(E) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

$$\Phi(E) = \frac{\pi}{6}\left(\frac{8ml^2}{h^2}E\right)^{3/2}$$

$$n^2 = \frac{8ml^2}{h^2} E$$

Now, one plays a very, very smart game and is that, we now one to consider that we have a sphere, hypersphere, let me consider to like that and now this is sphere, now in that sphere I have nx, ny, nz all has to be in the positive, I do not have nx, ny, nz negative, so if I say ny, nz and nx, now I want to calculate; now I say they are all; I point and then these are the point which I correspond to nx, ny, nz in that one part you know, one octant of that in the sphere; 3 dimensional sphere.

So, now I can now play this smart game, I said okay, the total number of states would be you know, these are very large, in order to calculate the total number of states all I need to do and this is a place unit 1 and this is the real crux of the matter that nx, ny and nz increases by 1, nx goes 1, 2, 3, 4; ny go 1, 2, 3, 4, so there is this grid that I am forming, I am all spacing 1, so that allows me to if I get the volume because of them, this unit thing the volume gets me total number of density; total number of states and that is what I do now.

And since 1/8 th of it , so I know the total number, total volume and total volume is this 4π/3n cube, n is the radius and n is the nx square + ny square + nz square and then I have these total number in all these region, all the one is 1, 8 4π /3 n cube that is just beautiful. So, now I also know what is the n, I just did in last class, my n is n square; n square is 8 ml square /h square E that I did in the last slide.

$$\Phi(E) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

So, n cube is then 8 ml square /h square /3 /2 this is just wonderful, so total number of states is increases as E to the power 3 /2, so it increases fairly rapidly and also what is very interesting that it depends not only on the energy, it also depend on the mass and it depends on the length of the box, remember l is the length of the box in this particle in a box model, so now but this is not the density of states, I am interested in density of states, it is not the density of states, these are total number of states.

$$\Phi(E) = \frac{\pi}{6}\left(\frac{8ml^2}{h^2}E\right)^{3/2}$$

Now, how do we calculate the density of states? what is the definition of density of states; the density of states is that you take the energy; the number of states with E and E plus dE that is the density of states and so you do it by taking derivative, you know this number, so it is increase from E to E + del E, is of course will be proportional to del E in a linear thing.

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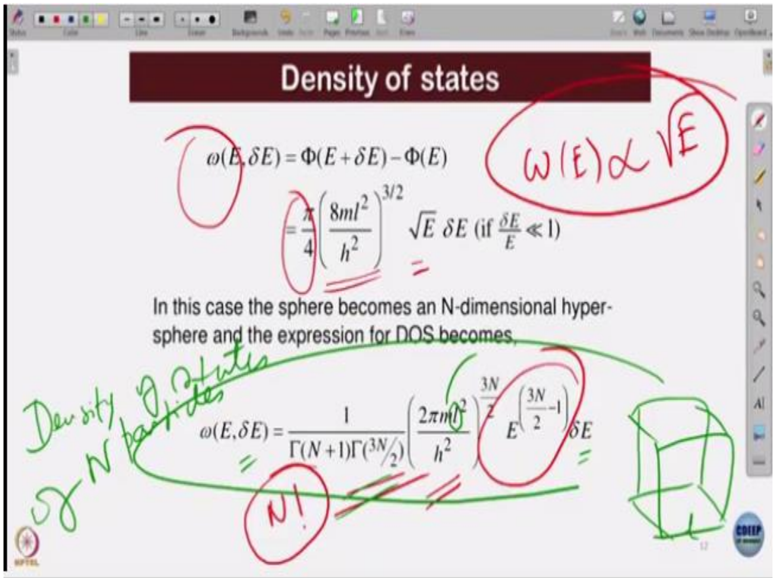

Density of states

$$\omega(E,\delta E)=\Phi(E+\delta E)-\Phi(E)$$
$$=\frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2}\sqrt{E}\;\delta E\;(\text{if } \tfrac{\delta E}{E}\ll 1)$$

In this case the sphere becomes an N-dimensional hyper-sphere and the expression for DOS becomes,

$$\omega(E,\delta E)=\frac{1}{\Gamma(N+1)\Gamma(3N/2)}\left(\frac{2\pi ml^2}{h^2}\right)^{\frac{3N}{2}}E^{\left(\frac{3N}{2}-1\right)}\delta E$$

So, now we do that little thing and this we get that density of this is Ω is the density of states fairly universal notation and then I get the derivative del E, I can divide by del E and these del E is here, when I do that, then 3 by 2 comes out and these 3 /2; these 3\ 2 comes here and that 3 cancel this and I get a 2 and 2 is here, so I get 4, so I get π /4 here, then 8ml square /h square remain untouched 3 /2.

$$\omega(E,\delta E)=\Phi(E+\delta E)-\Phi(E)$$
$$=\frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2}\sqrt{E}\;\delta E\;(\text{if } \tfrac{\delta E}{E}\ll 1)$$

And 3 /2 become root E; E to the power 3 /2 divided /E to the power 1/2 root E, so this is a beautiful result which shows that ωE goes as square root E, density of states in a particle in a box goes and this is very important this result as I told you, this is the result is used in many applications. Now, there is one more interesting result, very interesting result that comes now, we do not have 1 particle, we have n number of particles.

So, do not have a sphere, we have a hypersphere and in hypersphere now, you have the volume that is going as 3 to the power N /2 and then you can do exactly same derivative I said, 3N /2 becomes -1 and these, in the volume these gamma to the power 3N /2 and this is gamma N + 1 is nothing but our N ! and these comes in the volume of the 4 π / 3 that factor comes like that.

$$\omega(E,\delta E)=\frac{1}{\Gamma(N+1)\Gamma(3N/2)}\left(\frac{2\pi ml^2}{h^2}\right)^{\frac{3N}{2}}E^{\left(\frac{3N}{2}-1\right)}\delta E$$

And then and this is coming again from the particle in a box energy, so you now have the density of states of N particle systems, so this is the density of states of N particles in a cube of length l, so you have a cube in a hyper of length l and this beautiful thing now is ω E del E you can; it has to proportional to del E but del E is not the important quantity, important quantity is these N ! that comes from the same logic as partition function.

But this is the one which comes from the factors that come in the volume and E to the power 3, so now you can see a very, very important thing that we made already allude to in the statistical mechanics, in initial part that there is a huge number of states when you particularly when you go into high temperature, so number of states or density of states of N particle system scales as E to the power N and that is a very important result.

And this means, there is a huge number of states up there and these are exact result in an ideal gas law, exact result but either again and again, telling much of it goes over even in interacting system and this is the one which is used now in the conductivity problem and many other calculations of solid state physics where electrons are used as free particles and that is a very important model of solid state physics that free electron gas and when you are talk of free electron gas, we take the mass of electron M there.

And then we calculate these, we use these things in the particle in; okay, so this is what we wanted to talk of this beautiful thing of; in a way of classical and quantum, the beautiful interaction between quantum and statistical mechanics and then so we will take a short break and we will start on the diatomic.