Basic Statistical Mechanics
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Lecture – 19
Ideal Monoatomic Gas: Microscopic Expression of Translational Entropy Part 2

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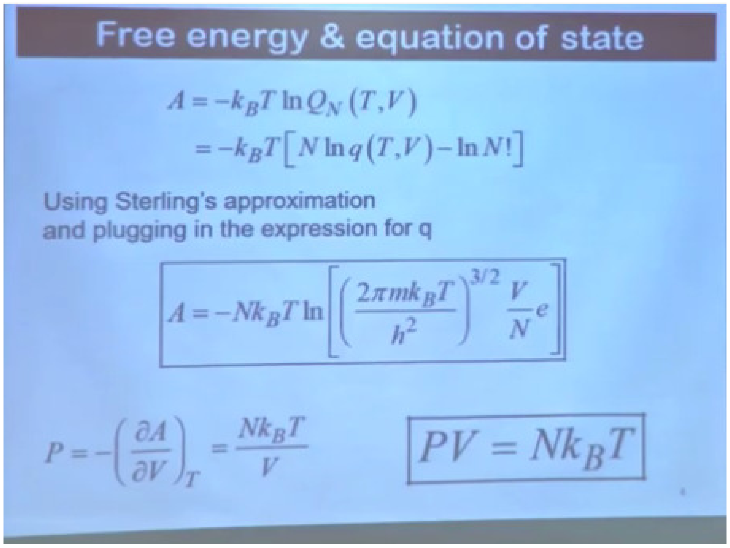

Free energy & equation of state

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

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

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

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{Nk_B T}{V} \qquad \boxed{PV = Nk_B T}$$

Now, then I have k_BT ln Q to the power N is N ln q, then because there Q to the power N and minus ln N factorial, this N comes because there is an exponent here in QN and these comes because of N factorial, then what is something is jumped here but I hope you will be able to do that I put now, Q to the power; this is my Q, so Q to the power N has becomes ln Q, so these become; what do we have in the last page, this quantity you have N ln N the N ln by e to the power N all these factors come here.

And these N becomes Nk_BT, these factor that is here with h square everything, these thing that ln V by N that ln V is not from there that comes that V comes from this V;

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

Using Stirling's approximation $N! = N^N e^{-N}$equation

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

EQUATION OF STATE

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

$$PV = Nk_B T$$

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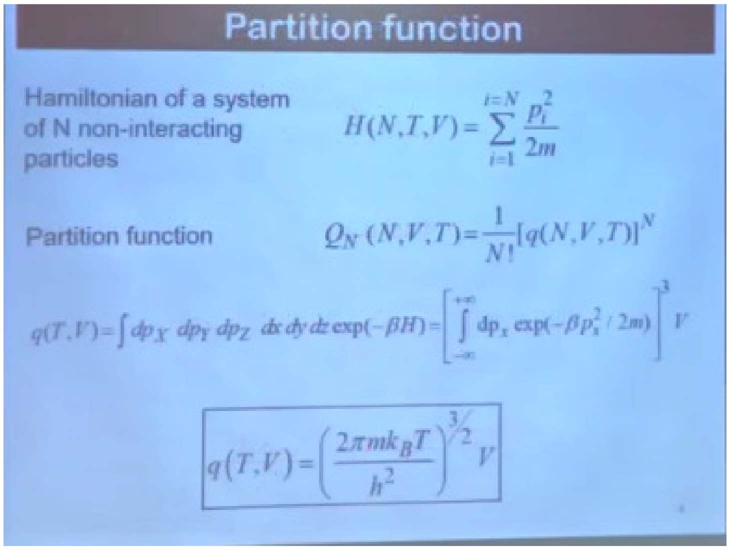

Partition function

Hamiltonian of a system of N non-interacting particles $H(N,T,V) = \sum_{i=1}^{i=N} \frac{p_i^2}{2m}$

Partition function $Q_N(N,V,T) = \frac{1}{N!}[q(N,V,T)]^N$

$$q(T,V) = \int dp_X\, dp_Y\, dp_Z\, dx\, dy\, dz \exp(-\beta H) = \left[\int_{-\infty}^{+\infty} dp_x \exp(-\beta p_x^2/2m)\right]^3 V$$

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

Sterling's approximation gives this factor V by N to the power e ie $N! = N^N e^{-N}$that is play the very, very important role as we see right now. So, if this is the free energy which is following from this, from there we get, we do this, this is a little unstable, from this then we get this, then we take the derivative with the pressure minus dA dV T and thermodynamics, there we get if you do that then all these things, since their log all of things these do not matter, these do not matter, I just get 1 over V because it is ln V 1 over V then gives Nk$_B$T by V and these

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

$$PV = Nk_B T$$

So, this is the ideal gas which are written down by people from Boyle's time from 1830s or 1840s something which he used, Maxwell used but there was no derivation, PV = RT was the kinetic theory of gas derived it by using, remember P equal to 1/3rd mN C square and then you put C square there, you get this quantity and but that is I told you kinetic theory of gas had this kind of strange set of assumptions within it, it does not interact.

But at the same time, it has a size and it is interacting with wall having an elastic scattering like a billiard ball, as a the basic idea that it is a non-interacting collection of particles and that gives rise to these ideal gas law was proven, so these are the as I told you in the beginning, these are beginning of the applications of statistical mechanics, so these one of the result.

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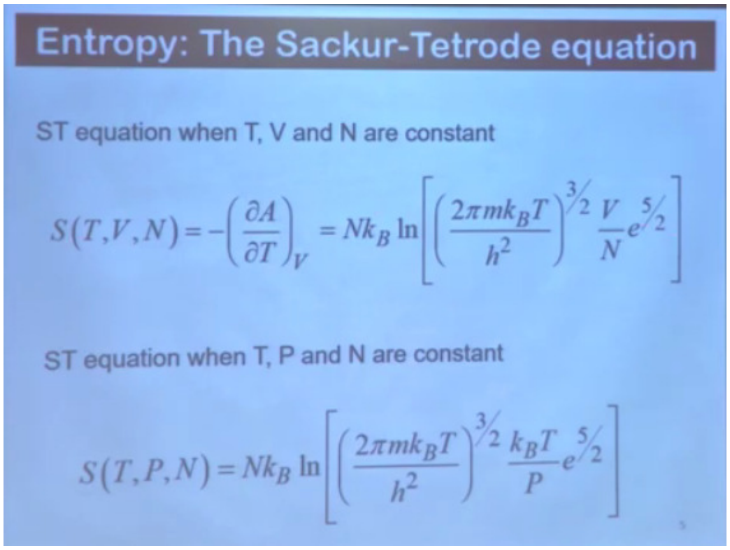

Entropy: The Sackur-Tetrode equation

ST equation when T, V and N are constant

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

ST equation when T, P and N are constant

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

Then this next result is that this is very, very important thing that I told you Sackur-Tetrode equation and this Sackur-Tetrode equation follows trivially, then you go now take with respect to entropy is negative temperature derivative of free energy, okay and that when you do, I take B dT what I can see what can happen, I can, it can, this is strictly 3 by 2 here so that will become T to the power of 5 by 2.

So, first term I take dA/dT, first term we will just take remove this term and have Nk_B ln 2 by k to 3 by 2 okay, then second term Nk_BT remains Nk_BT, I go and do derivative of this term. When I do ln there inside then all these things disappear, they are long terms, I do not have to take care of them, I have to take care of 3 by 2; 3 by 2 when I take a derivative, it become 3 by 2 comes out and it becomes 3 to the power 1 by 2.

Because ln T 3 by 2 1 over T 3 by 2 and then you can combine the and the 1 T there that comes in and that hits you with the 3 by 2, so that again become okay 1 by 2; this is 1 by 2, you hit by, again become 3 by 2 and when you do that ultimate result is 2 pi by; I am not deriving this, fairly trivial but you can do it because it is just ordinary derivation. So, these quantity, this is the expression of entropy of an ideal gas which plays very important role, we will show right now is called the Sackur-Tetrode equation.

This equation is given when the volume constant but I can use this equation within ideal gas, I can derive more useful equation which is this equation which is not given in your textbooks, you use volume PV equal to NkBT, so if PV T is V by N is equal to kBT by P and then kBT by P, okay so this is the one that is used because most of the time we are working with NPT on some book, NPT.

So, in that case this is the Sackur-Tetrode equation, so please ask me if there is any problem, if there any confusion in deriving this equation, everything clear, I am not doing it by line by line but I have explained to you how taking derivative of that you get this term coming out, log is preserved here because first is this term and then you have the k term, everything remains log and kBT ln terms remain, then that become 3 by 2 that is why 3 by 2 comes.

Then if multiplied by that is absorbed, the extra term that comes has been absorbed here, remember ln e 5 by 2 what is that, what is ln e 5 by 2; exactly 5 by 2, so that term these were absorbed the 3 by 2 factor, is absorbed, okay and so that is this is very elegant and nice result which as I told you in the beginning that is widely used these days, many, many cases is widely used, it is an amazing that Sackur-Tetrode result can find so much use.

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

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

And what is the more useful than these which is not usually given in textbook is this quantity, except one book uses that, that is why when researches write books or give courses this is little better, the one place I found, it is not in my query but I found it is in Ben Widom new little book for undergraduate statistical mechanics, very popular book just about 100 not even 100 pages probably.

But he did actually only up to diatomic gas and a little bit of that not beyond that, elementary level but he has this equation, I needed this equation because when you are doing nuclear theory of nucleation in a constant, this under this condition which is the experimental condition right, much of a time, then I needed that that is what I was very happy to be able to; I did it myself as very happy, the trivial state.

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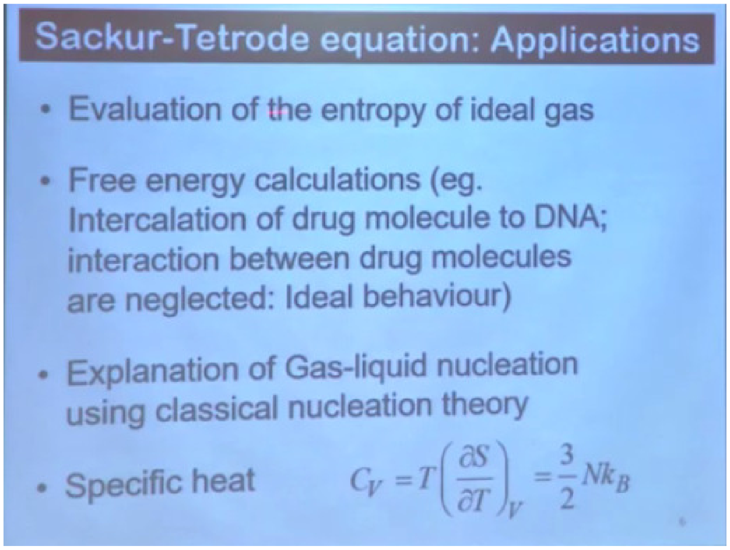

Sackur-Tetrode equation: Applications

- 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 $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}Nk_B$

But some time doing something new trivial is very nice okay, so Sackur-Tetrode equation there are many applications hierarchical, one is the evaluation of the entropy of ideal gas which is used in these, let me write down this, this is in toto from my stat mech book line by line probably the mistakes you find here will be mistakes will also be there so, please just go through the book once and let me know if there are any mistakes.

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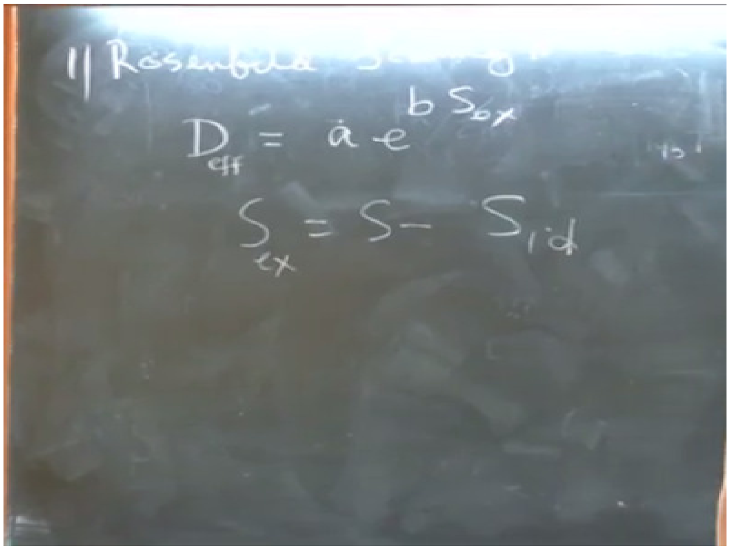

1| Rosenfeld scaling

$$D_{eff} = \dot{a}\, e^{b S_{ex}}$$

$$S_{ex} = S - S_{id}$$

So, the diffusion is called Rosenfeld scaling D, sometime I put D effective diffusion in an interacting system this a e to the power bS_{ex} and then S_{ex} is entropy minus ideal entropy, these one more applications which I have not written down because it was not written in the book, so this is as cut and paste from my book, so these beautiful relation is called Rosenfeld scaling, this is the lot of papers are being written on that on the last 5 years or 6 years.

And in liquid or dense gases, these equations works surprisingly well but so one plots this quantity against x, so you can understand one thing S ideal is the ideal, the maximum entropy that it can have, so because of correlations and order, entropy decreases, so S ex is negative more it becomes negative, more the diffusion decreases and it describes the results exceedingly well.

And where I was saying that where we have to use it in a gas liquid nucleation, there we needed this free energy calculation, G minus TS and when a low temperature gas is going into liquid, then the free energy of the gas has both entropy and enthalpy, you can make an approximate assumption that entropy of the gas is given this quantity and that is where a nucleation and it is widely used and you can, there is a book I forgot the name or several books on nucleation, you will see that use,

Now, a beautiful result I think it is done very badly that from here specificity is the temperature derivative of entropy right, dS/dT is specific heat TdS/dT and I can do that now, I can go, I do dS/dT, do the derivative here and then ln, there is no temperature here now to complicate things, so just ln T to the power 3 by 2 plus other things are here, they disappear when I take the derivative, I just have ln T to the power 3 by 2.

So that becomes just like before 3 by 2 and ln T becomes 1 by T and then I; it comes in denominator and then very interesting it comes in and leaves by 3 by 2 term just like before, then these T removes that T in the denominator, is it clear and then I have 3 by 2 comes from these 3 by 2, I have a Nk_B, so specific heat is just 3 by 2 Nk_B, when N is the Avogadro number, CV=3/2 R.

So, this is the derivation of the ideal gas law, so the 2; these are really beautiful stuff which everybody should know by heart because you will use them always, always when you start thinking about interacting system, start thinking with the ideal gas.

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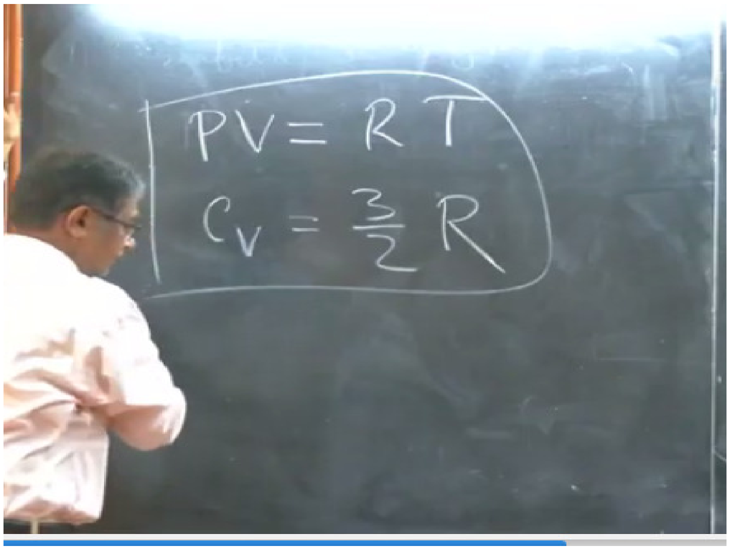

So, PV = RT, CV = 3/2 R , so these are the 2 things that we; so the things that you are under; first year undergraduate physical chemistry that comes out from a rather sophisticated thing but you of course understand when we introduce such a sophisticated thing, this was not the goal of statistical mechanics, this is kind of things on the way, these are kind of rewards you get.

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2} N k_B$$

But that is not you started, you did not start to explain an ideal gas, you start to explain interacting systems, we start by Newton's equation, where there are forces between atoms or molecules but these are the way we got and it just makes your life happy that you okay.

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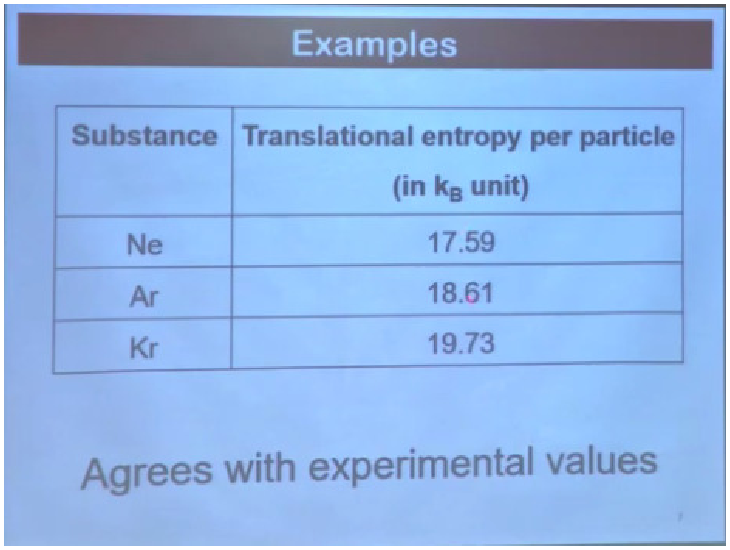

Examples

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

Agrees with experimental values

We understand what you are doing and we are on the right track okay, now some things which are really very nice you should know, so example; translational entropy per particle, these are huge that is what I am saying. So, neon this is 17.59, these are all given in my book, see most of these stat mech books are done not with too much affection or laugh of this ideal gas that is a change language to use.

But you should feel good about it, okay and asymptotically I can get the entropy from a low density neon that is durable and these are very nice agreement of the; why you chose neon, argon, krypton, can you tell me? One very good answer, second exactly, exactly, so they are the good example of ideal gas, so exactly that is a good answer yeah, so agrees with the experimental values, okay.

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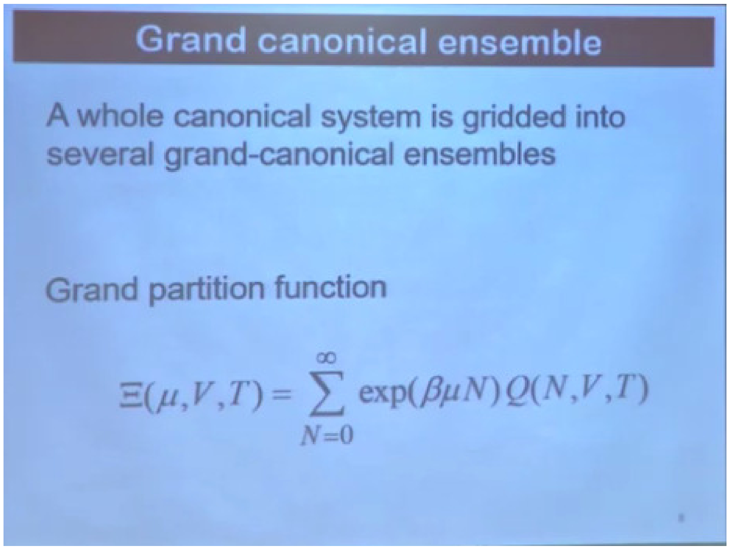

Grand canonical ensemble

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

Grand partition function

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

Now, if a canonical system gridded into then we can go to grand canonical which we did the other day, this is a grand canonical, sum over just mu N $k_B T$ right, so these are grand canonical partition function ie $\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp(\beta \mu N) Q(N, V, T)$

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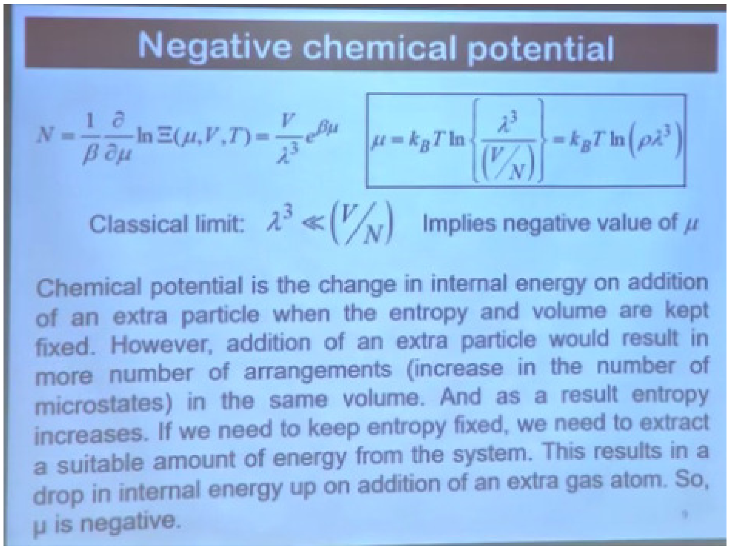

Negative chemical potential

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

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

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

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.

And then one can get the total number of particles and another expression for a chemical potential, this is extremely useful in the density functional theory, exceedingly useful. So, I can go from your grand canonical partition function, now I take the grand canonical partition with this way to chemical potential, the conjugate number, I get the average number of particles in the system, okay.

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

And then I can write it log up and make that into a density, I can bring V here, so N by V is density then I take the log then this is extremely useful quantity where chemical potential is given in terms of logarithm and you guys know that this is the expression undergraduate physical chemistry we use that chemical potential logarithm of density, you remember that.

Of course, we did not understand though Castellon is the best book on physical chemistry even Castellon that is where you can understand but even there was no need to it, why did we write chemical potential the first term in a non-interacting system lnρ, this is the beautiful equation that comes out. So, chemical potential is given in terms of density as a log vector, oh lambda is this; lambda is de Broglie length 2ΠmK$_B$T by h square, sorry, thank you very much. ie $\lambda = \left(\frac{2\pi m k_B T}{\hbar^2} \right)^{1/2}$

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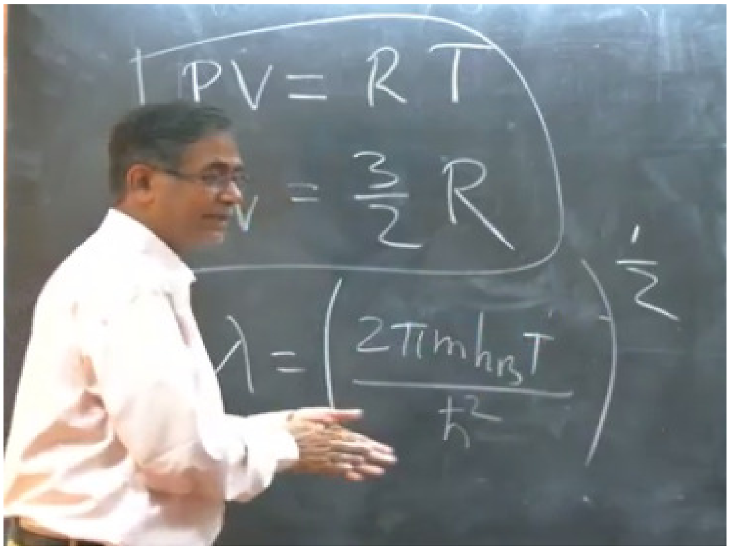

So, lambda is 2 pi m k$_B$T by h square, so let us say m, m, m, m L square by T square, then everything else, these also have m L square by T square, so I think this 1/2 that is the lengths de Broglie length that comes up naturally, when you do these things a length is always sitting there, I could have introduced and I should have introduced there but does not matter.

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

So, this is the beautiful result, gem of a result that chemical potential, so is the change in internal energy on addition of an extra particle when the entropy and volume are kept fixed, you know so all these things we do not need to do at this point, so we have got these important result and then another important result we write it down here. When I studied the reason I am so excited I am talking about it, when I studied statistical mechanics, nobody told us that these will be so important.

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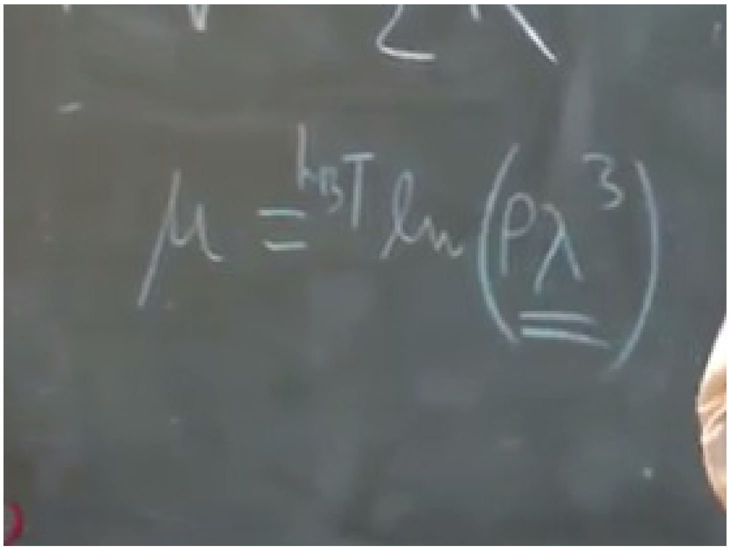

And we had to go back every time, chemical potential has to have the dimension of and this has to be dimensionless and this has to be dimensional energy okay, always keep a on dimension because you know if you cannot do analytical work, I am telling you when you go to a postdoc, you will be miserable shape, everybody expects because there they do it from, I have seen in my not so bright in American colleagues, my students they are very good in very basics.

$$\boxed{\mu = k_B T \ln\left(\rho\lambda^3\right)}$$

Because there has been; they repeat these things from 7th or 8th grade and all the way even after going to PhD level I had to take thermodynamics twice and there they take thermodynamics 10 times, so they just grind it into you, you better know how to do very simple things, okay yes, that is what we will do next.

Microcanonical is that because for getting the microcanonical you need to need the energy levels or the micro canonical any way I can do without, a omega you can calculate by integration over the phase space, when you do that exactly same result comes out for example, I want to get the that is the one I want to do next in a very elegant way, the elegant way also allows me to establish connection with; so what is omega?

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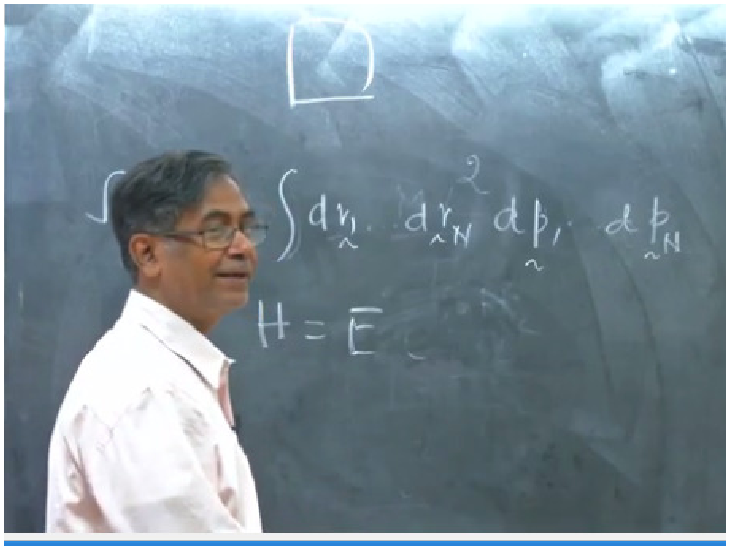

Omega is the volume of the phase space, so that means given a volume V and energy E, I have to now, it is a little difficult because say dr1 and I will do that this is a very good question that actually brings out why micro canonical is difficult, so I have the kinetic energy putting here now but when have NVE, I do not have this term at all instead I have H has to be equal to be E i.e H = E that constraint and that is a difficult constraint.

That means I am within a volume in phase space, so I have to impose that constraint that becomes very difficult we just did it in our in one of the calculation well, we did it also before many times but there is another way of doing it which is that in quantum mechanics gives you the energy levels where you can put this constant much more easily that is particle in a box and then you can get the micro canonical partition function quantum mechanically and that gives you essentially the same result, okay.