Basic Statistical Mechanics
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Lecture – 21
Ideal Monoatomic Gas: Microscopic Expression of Translational Entropy Part 4

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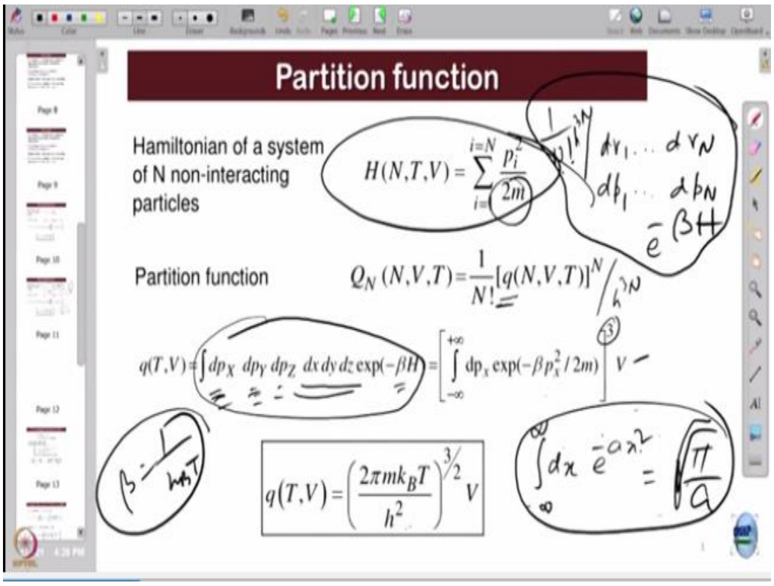

Partition function

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

$\frac{1}{N!\,h^{3N}}\int dr_1\ldots dr_N\, dp_1\ldots dp_N\, e^{-\beta H}$

Partition function $Q_N(N,V,T)=\frac{1}{N!}[q(N,V,T)]^N/h^{3N}$

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

$\beta=\frac{1}{k_BT}$

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

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

So now, I will go and start take you through the okay; so we now calculate the partition function of the system and you can, you just look at it that we wrote down this ideal gas, so ideal gas is the total Hamiltonian is the just kinetic energy, ideal gas means the particle does not interact with each other, so we do not have any potential energy, If you do not have any potential energy, then it is just kinetic energy.

And kinetic energy means it is just sum over as we shown in this equation here it is just that) now, I want to get the; so why that means that I want to get the partition function and as I have shown the partition function here is 1 over N ! and h to the power 3N then dr1, drN, then dp1, dpN e to the power - β h, so this would be the partition function.

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

Now, look at this partition function, there is no interaction, so position of the atom, so I have this like I have taken a monatomic gas (spheres) and they do not interact with each other like an argon or a noble gas in low density and then interestingly, if I do that then each particle they do not interact with each other, so they are completely disjoint. If they are completely disjoint I can separate them out.

That means this indication dr1 and dr2, dr3 are not coupled, dp1, dp3 are not coupled, so I have essentially N integrations; identical N integrations was a product, like these are just product, so then I have e to the power N and then I have h to the power 3N here and so this is then my partition function where q is now given by this integration of dpx, dpy, dpz, dx, dy, dz e to the power -β H, this is the partition function of a single particle.

And then that I can now do because dx dy dz, in β h there is no position, so I can just integrate over dx dy dz and I can get volume V , this clear that this volume V comes out and I have to evaluate this integral which is this Gaussian integral and I can do that Gaussian integral, (this integral I can do because just bear with me for a minute), this is I know that -∞ to ∞, dx e to the power – ax^2 is root over π by a, I know this integral that integral is used here.

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

Then if you do that this integral then becomes there are three integrals, there are three because dpx, dpy, dpz are independent of each other because kinetic energy p; one particle is px square plus py square pz square, so they are again uncoupled so, I think Gaussian integrals and that integral I can do, so then I know root over this, so this is 3 of them and each comes with root, then and there are 2m, so 2m goes over 2π m k_BT.

And k_BT is there β is 1 over k_BT, so when I do that I get this, so this is the partition function of a single molecule in ideal gas, this is the single particle partition function this quantity, the single particle partition function, okay, so that thing is done, so then we can now go back and construct the next partition next, okay.

$$H(N,T,V) = \sum_{i=1}^{i=N} \frac{p_i^2}{2m}$$

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

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

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

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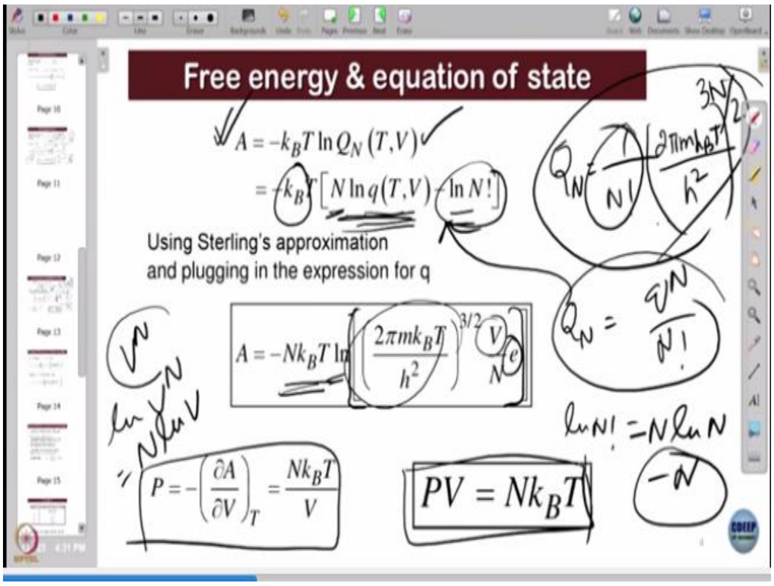

Free energy & equation of state

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

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

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

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

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

$$PV = Nk_BT$$

$Q_N = \frac{1}{N!}\left(\frac{2\pi m k_BT}{h^2}\right)^{3N/2}$

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

$\ln N! = N \ln N$

$-N$

V^N

$\ln V^N$

$N \ln V$

So, now we got the partition function and the partition function $Q_N$is 1 over N ! and then 2 π m k_BT by h square 3 N by 2 this is the partition function. So, now we know that from canonical ensemble we have done that in lecture I think 4th or 5th that free energy equal to - k_BT lnQ_N this quantity, so now we can put the Q that we this Q here, so then we get - ln this becomes - ln N !.

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

And this become N, this is Q to the power N, so N ln Q, so and this is trivial right, that means Q_N equal to Q to the power N by N ! that thing is used here, now we put the value of Q there which we derived before, so we get the ln N !, Sterling's approximation is made, so ln N ! equal to N ln N - N. If we do that this - N actually shows up here as A and we already have V, so Q is already have this N 3N/ 2.

So, I bring out that, so I have a N here, so this the only 3 by 2, so N comes out, so N k_BT here, this k_BT and Q to the power N, Q is Q to the power N that brings it N, so N k_BT ln then 2π m k_BT by h square 3 by 2 V, this is multiplied by whole thing here V by N because they separate it out ln V and the one is this comes from these things, you can just work it out the basic things which you will find, we will work out and find, okay.

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

So, important thing to understand now that everything is in logarithmic, so I have a logarithmic here, so there will be logarithmic β because it is V to the power N, so that comes from the volume integral and so ln that part is ln V to the power N, so that becomes ln V. So, now I can calculate from here the pressure, I can calculate the pressure from here and that is by thermodynamic relation pressure - dA by dV T.

And then you can do that look at the; let us do these things here, so this is ln, so then I break it out like ln this term plus V by ln, so it just ln V dA dV then that N is there, this just goes out and I get the 1 over V term the ln V, so ddV ln V 1 over V, so Nk$_B$ T in front so Nk$_B$T by V by doing the derivative, then PV by Nk$_B$T, so this is the ideal gas law. So, now I have a microscopic derivation of PV equal to Nk$_B$T which was surmised by doing experimental; enormous amount of experimental studies and also what comes out from Maxwell, Boltzmann kinetic theory of gases.

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

$$PV = Nk_BT$$

But here there is no kinetic theory of gases, no collisions with the wall, no cross section that we have done you have to do the collisions of the wall with the kinematic description, we did not take any kinematic description anywhere, we did have a kinetic energy of course but we do not have a kinematic description but this is very important to understand that this is the pressure of the system of molecules which is contained in a volume V, this is really magical this derivation.

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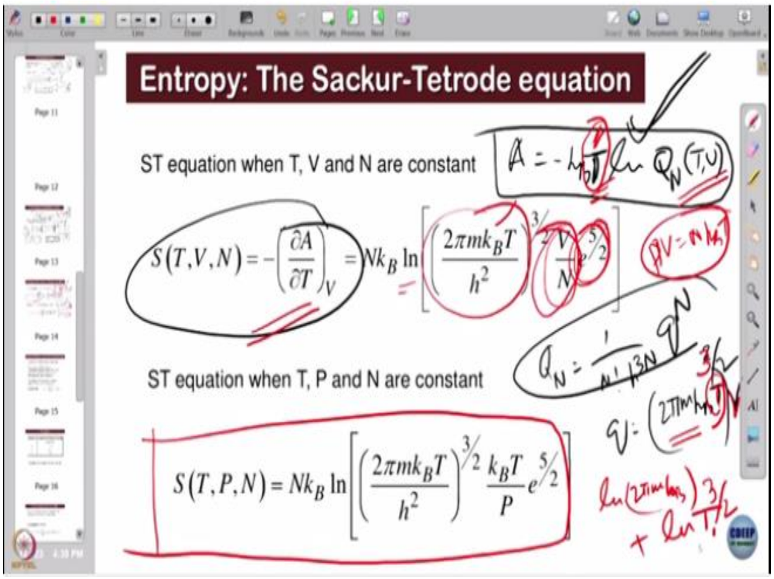

Entropy: The Sackur-Tetrode equation

ST equation when T, V and N are constant

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

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

$$PV = Nk_BT$$

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

ST equation when T, P and N are constant

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

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

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

Next what goes on something even more magical ; now we are doing something really very, very important and this is something one of the major reason of reviewing this class once more and also we will do that in the diatomic gas also, there are certain very far reaching consequences and we do not, actually these kind of jumps that it comes from almost nowhere because we did not expect such a beautiful relation.

So, early in our derivation or study of a for such a major area of research, so the formidable area of research like in statistical mechanics which is actually as I told you again is one of the 2 major disciplines of our thinking, our theory, our understanding of huge number of phenomena, the very, very first class I spent fully on describing that thing okay. So, now we have the partition function and now we have the free energy.

Because we have the free energy A equal to; we have this beautiful relation, now I know entropy because I know entropy by this, I know entropy A is equal to - dA by dT, I have aQ_N , I know the Q_N because I know Q_N is 1 over N ! h to the power 3N q to the power N and q I know is 2 π m k $_B$T 3 by 2 and volume V, I know everything, so I know Q_N and q is the single particle.

And then I know free energy exactly and then I can now calculate entropy, I can calculate the absolute value of the entropy, it is very important because thermodynamics cannot do, now yes you can say okay, I can get it from ideal crystalline all these things but this is okay but you know everything have to be done numerically. Now, I can do that and the beauty of this thing is now that if I do, I take now look at this.

I show, I take Q_N, I take ln of this thing, now look at that so, a free energy has temperature in two places; one is in temperature T, this is one, another place it has is in temperature T here in q here, so when I have to take this derivative, I have to take care of this temperature and I have to take care of this temperature, okay. Now, I do that first one is easy, dA/dT just this goes off, I have kBT ln Q_N T V and this is Q_N T, V, great.

That is why 2 π m kBT by h square all these things come in, wonderful now, I have to do the second derivative that now I come here and do the derivative here okay, now as I told you it is not Q to the power N, so N comes out I have a q and I have to take the temperature derivative of this q okay, then ln q, so then I do ln q, then ln 2 π m k_B plus ln T, I have a k_BT sitting in front, when I do that okay.

So, now I can take that derivative, I can do this derivative on this quantity and I can then I combine the terms, this you can do yourself and is left as an exercise, you can do it yourself and you will get that entropy, just do it yourself it just takes a couple of minutes, then you get that this quantity this entropy, so this part temperature part is ln Q, the ln is here and q is here 2π mk_B T and that is the volume V, this volume V is here, V by N.

And so everything remains the same except e becomes 5 by 2 because 1 extra terms comes in, 3 by 2 N comes because this derivative this 3 by 2 that comes out, so then that T 3 by 2 here, so when you take the derivative of that then 3 by 2 comes out and T becomes 1/2, the T becomes 1/2 then you have a T to the power; this becomes T to the power 1/2, you have the T here, so you combine that T that becomes 1/2 here after taking derivative.

So that become T to the power 3 by 2 again, so you combine get 3 by 2, you are left with one 3 by 2 term that your one term, you can combine and get e to the power 5 by 2, so the main thing is to combine and you can get that term, so this is the then, this is an exact expression for an entropy, a highly nontrivial equation which is this thing that entropy of N number of ideal gas law is Nk_B ln 2π m k_BT 3 by 2 k_BT by P.

Now, this V by N one can use now, PV equal to Nk_BT ideal gas law, PV Nk_BT and then you remove V by N, bring it here, so it becomes k_BT by P, this is more useful because most of the time at a constant pressure not at constant volume and we know the number of particles and if we know and at temperature, constant temperature, constant pressure constant N, so this more of an experimental thing.

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

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

Then this is an exact expression of the entropy of the system, beauty of it is the following; the V by N that comes here when you do the calculations is a very important thing, very important to understand from that, that what makes everything an extensive quantity. So, the entropy that I have here is just for entropy is portion of N as it should be, everything else inside is an intensive property.

The temperature is an intensive property, pressure is an intensive property, so the entropy is extensive because it is proportional to N but this is a beauty of an equation, it is called Sackur-Tetrode equation, it is obtained called ST equation, this is equation which is one of the; so you now, the basic idea of my telling all these things again in great detail is to give you an idea how the statistical mechanics flows, just like in quantum mechanics you do particles in a box you learn that how you solve Schrodinger time independent Schrodinger equation by putting boundary values.

And when you do that low and behold discrete energy levels appear and then immediately find a news of that particle in a box explaining the spectra of butadiene or conjugated polymers, then you go harmonic oscillator and low and behold you can get some idea of the vibrational spectroscopy, rigid rotator you get rotational spectroscopy, those are very preliminary, very simple things that we solve time independent solving equation.

But we get back huge amount of information as if without doing any work that you are getting such formidable and very fundamental things, this is essentially analogous to particular box or harmonic oscillator we will use harmonic oscillator immediately now but important thing to know that we are getting PV equal to Nk_BT, we are getting an expression a beautiful expression of entropy and absolute value of entropy although ideal gas but it will find lot of use in even today this research, this equation finds a lot of use.

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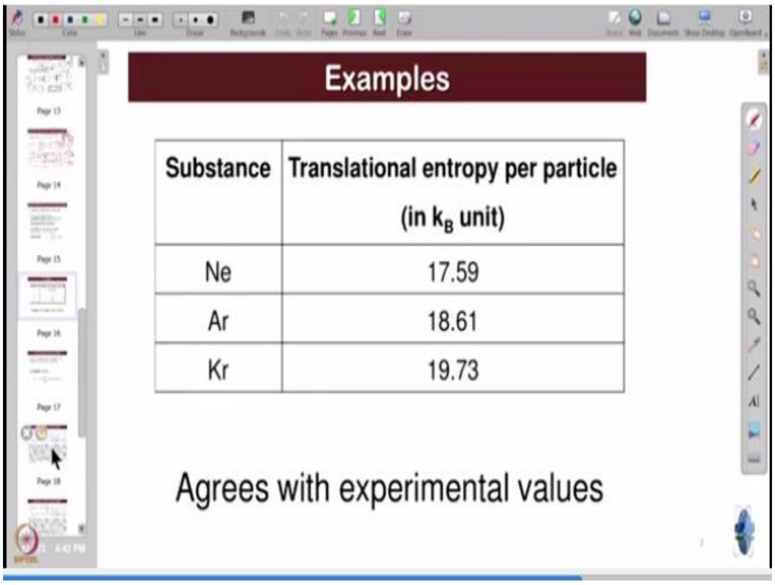

Examples

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

Agrees with experimental values

So, one can now calculate the translational entropy, this is called translational we have taken only translation into account so entropy, the values of the; absolute value of the entropy, see in thermodynamics, it cannot give you absolute value of the entropy, absolute value of the entropy, this is the neon, argon and krypton in atmospheric pressure.

But then atmospheric pressure of course is probably not a; but whatever condition is not written here, (I do not remember) but the experimental condition that we can calculate this translation into the particle, then we can experimental way of finding the entropy and it agrees with the experimental values of this entropy of these 3 gases, they are very similar to each other.

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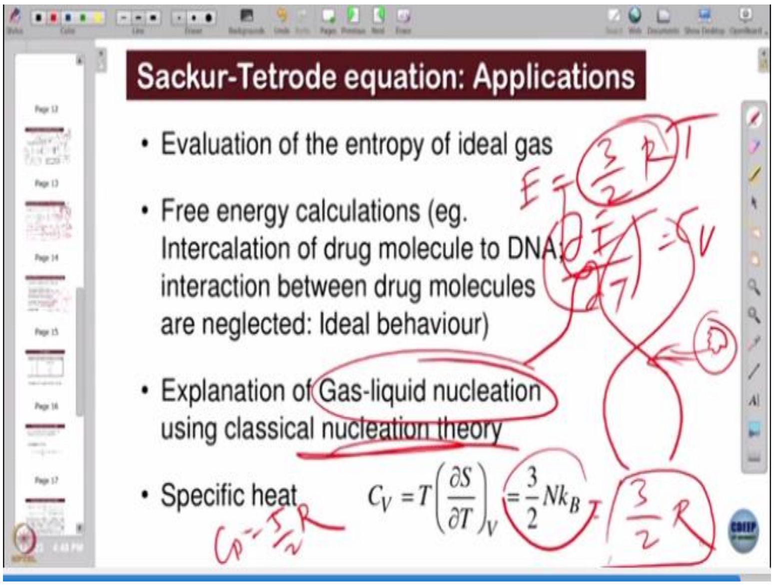

Sackur-Tetrode equation: Applications

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

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

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

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

So, now I will just want to tell you why these things are so important and so what are the Sackur-Tetrode equation; one of the important applications of Sackur-Tetrode equation of modern times is this quantity which is the very recently has been used by several people that you want to calculate that how a drug goes into you know minor or major groups of DNA and that is very important to know.

Because of many chemotherapeutic drugs they go and bind to many other drugs, bind to DNA is the target of many, many therapeutic studies and so we need to know what is the binding energy of this molecule, drug molecule, this is now done in the following way that you consider your drug molecule; the drug molecule is going to go and bind to minor major group of the DNA.

So, now this has a lot of entropy in the ideal, when it is in solution now, in this solution we can treat it as an ideal gas because a single drug molecule are very low density (drug molecule that goes and combines to these the DNA), so that we need to know the entropy, loss of entropy of the drug when it binds there, so we need to know the what is the entropy of this molecule in solution that is why Sackur-Tetrode equation is used.

Then you want to do for example, gas liquid nucleation; in a low temperature a gas is going to go to bubble to form a bowl like in atmosphere to form nucleation, then one need to calculate how much entropy the gas particles are losing in order to form the bubble because you know once from a bubble, it moves very slowly and it moves as one particle, so N number of gas molecules like water, forms and goes, form the water droplet then is a huge amount of loss of entropy.

So that actually resists formation of the droplet, formation of the cloud bubbles and particularly that is why high temperature when the water molecules are still there but they have lot of entropy and they will not form the bubble, they will not nucleate, they will not nucleate to form a water droplet which can form as a rain. So, entropy of these water molecules in the gas phase it is not just translation entropy, this is a rotational entropy, it is a vibration entropy we will talk of that.

So, all those entropies play very important role, so this is done by this gas liquid nucleation is a huge area of research and in the study of this nucleation against this entropy, this in the nucleation theory again this entropy that we derived today finds use. Now, finally to end this part that specific heat 3/2 R ,that’s very trivially derived now, you go to Sackur-Tetrode equation, do the dS/dT, then you will find that it just becomes 1 over Nk_BT by T that T cancels.

And you get C_v equal to 3/2 R and that is one of the; PV equal to RT along with the ideal gas law, C_v equal to 3/2 R and C_p is 5/2 R and that is because another way to derive, E equal to 3/2 RT that you know, then dE/ dT C_v, this is C_v and that is 3/2 R that is the derivation that we you know from the kinetic theory of gas but this is the derivation here coming from entropy directly with the entropy, so it is the alternate derivation same result.

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

$$C_V = \frac{dE}{dT} = \frac{3}{2} R$$

And is since my equipartition theorem is involved, I cannot say it is more fundamental because equipartition theorem is as fundamental. This is a statistical mechanical derivation starting from partition function, so this is about the ideal gas law, monotonic gas and ideal gas law that I wanted to do again in order to tell you the take you through a second time the things.