Statistical Mechanics
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Module No # 02
Lecture No # 06
Thermodynamics potentials

Welcome back! So just to recapitulate what we have been doing. We derived the one dimensional version of the entropy of a classical gas of molecules and made sure that it is extensive by taking into account the permutation of the number of particles thereby resolving what we called the Gibbs paradox.

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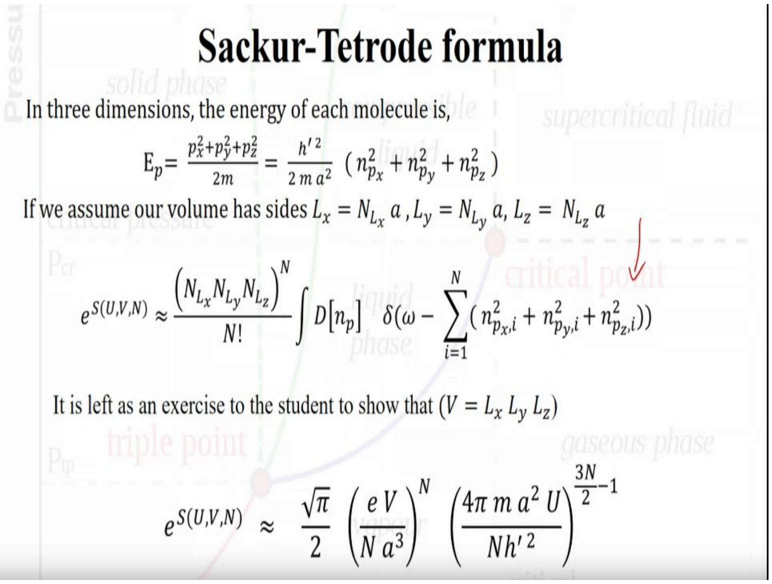

Sackur-Tetrode formula

In three dimensions, the energy of each molecule is,

$$E_p = \frac{p_x^2+p_y^2+p_z^2}{2m} = \frac{h'^2}{2\,m\,a^2}\,(n_{p_x}^2 + n_{p_y}^2 + n_{p_z}^2)$$

If we assume our volume has sides $L_x = N_{L_x}\,a$, $L_y = N_{L_y}\,a$, $L_z = N_{L_z}\,a$

$$e^{S(U,V,N)} \approx \frac{\left(N_{L_x}N_{L_y}N_{L_z}\right)^N}{N!}\int D[n_p]\;\delta(\omega - \sum_{i=1}^{N}(n_{p_{x,i}}^2 + n_{p_{y,i}}^2 + n_{p_{z,i}}^2))$$

It is left as an exercise to the student to show that $(V = L_x\,L_y\,L_z)$

$$e^{S(U,V,N)} \approx \frac{\sqrt{\pi}}{2}\left(\frac{e\,V}{N\,a^3}\right)^N\left(\frac{4\pi\,m\,a^2\,U}{Nh'^2}\right)^{\frac{3N}{2}-1}$$

I also encouraged you later on in this slide to do this or think of this as a homework namely find the entropy or generalize the one-dimensional example to three dimensions and get the what is known as the Sackur-Tetrode formula of the entropy of an ideal gas. So the way you do that is obviously very similar to what we were doing in 1D and that is it involves simply evaluating such an integral and the way you do this is to rewrite the Dirac Delta function as a Fourier transform and then you go ahead and do the rest.

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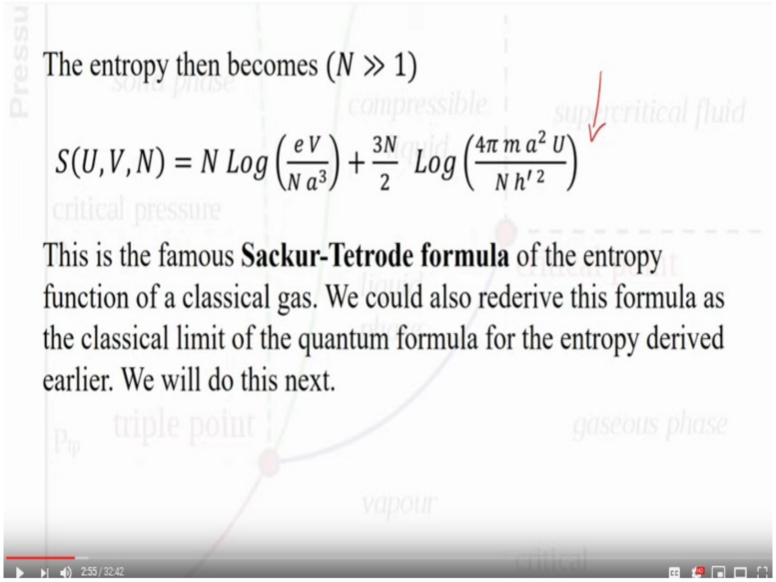

The entropy then becomes ($N \gg 1$)

$$S(U,V,N) = N\, Log\left(\frac{e\,V}{N\,a^3}\right) + \frac{3N}{2}\, Log\left(\frac{4\pi\, m\, a^2\, U}{N\, h'^2}\right)$$

This is the famous **Sackur-Tetrode formula** of the entropy function of a classical gas. We could also rederive this formula as the classical limit of the quantum formula for the entropy derived earlier. We will do this next.

So I am going to leave this to you as an exercise and when you finish with it you end up with this formula. And this is the famous Sackur-Tetrode formula of the entropy of a classical ideal gas. So notice that how we derived this in the traditional way namely the way it was done by the pioneers and that is to divide up the phase space into pixels and populate those pixels with the molecules and then learn how to count the various microstates subject to various constraints.

So that is the conventional way of doing it and that gave us Sackur-Tetrode formula. And of course there is a more sort of sophisticated way of doing the same thing and that is remember that we took great pains in deriving the entropy of a quantum ideal gas. And we could go ahead and use that expression and take the classical limit of that expression and also arrive at the same formula. So it is instructive to do it both ways so that you know the whole subject is self-consistent.

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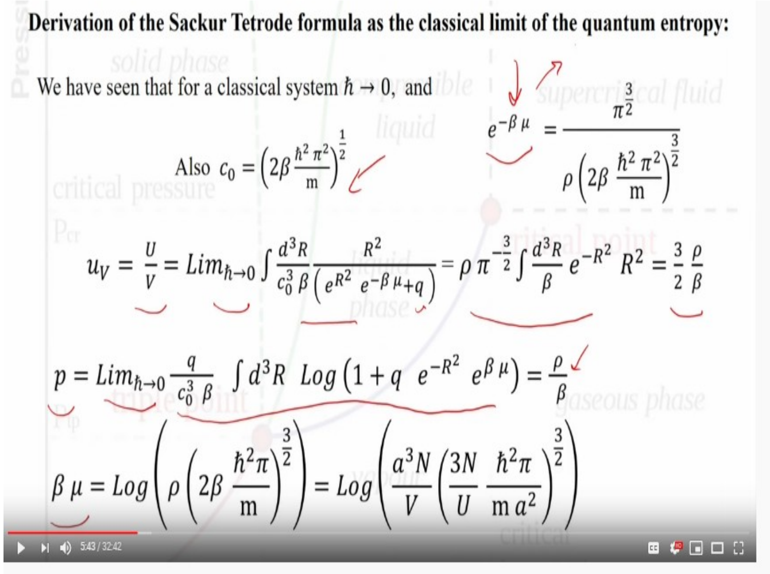

Derivation of the Sackur Tetrode formula as the classical limit of the quantum entropy:

We have seen that for a classical system $\hbar \rightarrow 0$, and $e^{-\beta\mu} = \frac{\pi^{\frac{3}{2}}}{\rho\left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{\frac{3}{2}}}$

Also $c_0 = \left(2\beta\frac{\hbar^2\pi^2}{m}\right)^{\frac{1}{2}}$

$$u_V = \frac{U}{V} = Lim_{\hbar\rightarrow 0}\int\frac{d^3R}{c_0^3\,\beta}\frac{R^2}{\left(e^{R^2}\,e^{-\beta\mu}+q\right)} = \rho\,\pi^{-\frac{3}{2}}\int\frac{d^3R}{\beta}\,e^{-R^2}\,R^2 = \frac{3}{2}\frac{\rho}{\beta}$$

$$p = Lim_{\hbar\rightarrow 0}\frac{q}{c_0^3\,\beta}\int d^3R\;Log\left(1+q\;e^{-R^2}\;e^{\beta\mu}\right) = \frac{\rho}{\beta}$$

$$\beta\,\mu = Log\left(\rho\left(2\beta\,\frac{\hbar^2\pi}{m}\right)^{\frac{3}{2}}\right) = Log\left(\frac{a^3N}{V}\left(\frac{3N}{U}\;\frac{\hbar^2\pi}{m\,a^2}\right)^{\frac{3}{2}}\right)$$

Alright so let us get on with it so how do we do that? So recall that in the case of classical if you want to take the classical limit of a quantum system you are compelled to choose the chemical potential in such a way that this quantity in fact this is called a reciprocal of fugacity, $e^{\beta\mu}$ is widely called fugacity. And so this would be reciprocal of fugacity or 1/ fugacity.

So and this is basically chosen to be proportional to h^{-3} . So that is because when you do this you are able to successfully handle the classical limit of a quantum system that we have shown this earlier. So as a result if I select this to be my constant c_0 and the energy density in the classical limit comes out to be this expression. So it is insensitive to whether it is bosons or fermions the moment you go to the classical limit you see the expressions do not care anymore whether you are describing bosons or fermions after all we are now entering the classical limit.

So when you do that you end up having to do this integral and then you get this expression for the energy per unit volume of a classical ideal gas. Now you could do the same thing with pressure and so you should understand why I am doing this first? Because if you recall the entropy expression really had all these things in it the energy density, energy per unit volume pressure and so on.

So I had better calculate these first so the pressure and of course these will be useful independently later on. So the pressure of a classical ideal gas is the $h \rightarrow 0$, Planck's constant tends to 0 limit of the quantum version of the same quantity. And when you do this, when you take this limit you end up with this expression this simple looking expression which of course now does not involve either q which determines whether it is not bosons or fermions nor does it involve h which is Planck’s constant.

All right so lastly we will also be needing something over βμ in our expression for the entropy has this quantity. And this Planck’s constant finally refuses to go away, you will see that the expression for the entropy still involves Planck’s constant and that should not come as a surprise.

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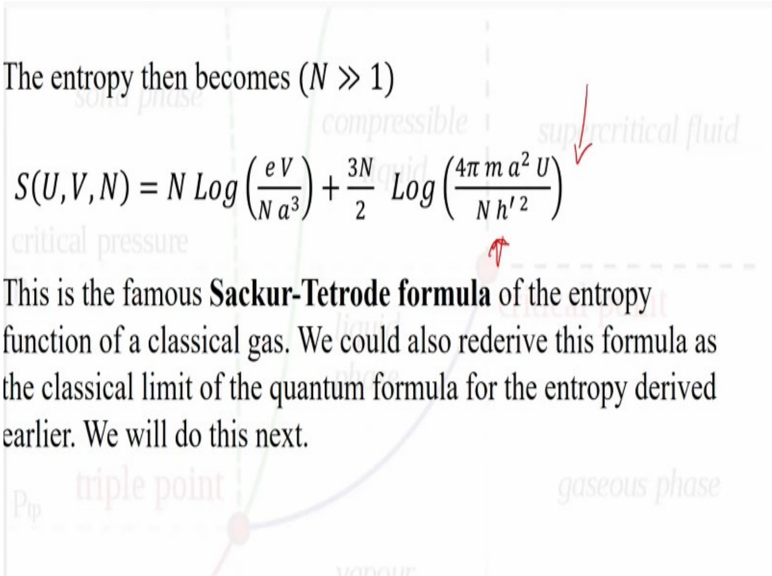

The entropy then becomes ($N \gg 1$)

$$S(U,V,N) = N\,Log\left(\frac{e\,V}{N\,a^3}\right) + \frac{3N}{2}\;Log\left(\frac{4\pi\,m\,a^2\,U}{N\,h'^2}\right)$$

This is the famous **Sackur-Tetrode formula** of the entropy function of a classical gas. We could also rederive this formula as the classical limit of the quantum formula for the entropy derived earlier. We will do this next.

Because if you recall in the earlier expression there was this h’ . Which really did not have any intrinsic meaning other than, what was this h’ if you recall it was the size of the pixel? So that means I divided up the phase space which is made of x coordinates and p coordinates into small bits and pieces of small squares and the area of each square small square and the area of each square small square was h prime.

Now of course that h’ being a square in phase space in one dimensional phase space has the dimensions of momentum times length. And that is of course there also the dimensions of Planck’s constant so you should not be surprised if there is some relation between the smallest pixel size that I have selected notice this is an artificial coarse graining and that it survives in this expression so it does not go away so we are stuck with it.

So now we are also similarly going to be stuck with Planck's constant even though we are studying the classical limit of an ideal gas. So we end up with this expression for βμ well in the classical limit and this what it is. It is just you know obtained by taking logarithm on both sides of this expression this was a choice we made in order to recover the classical limit.

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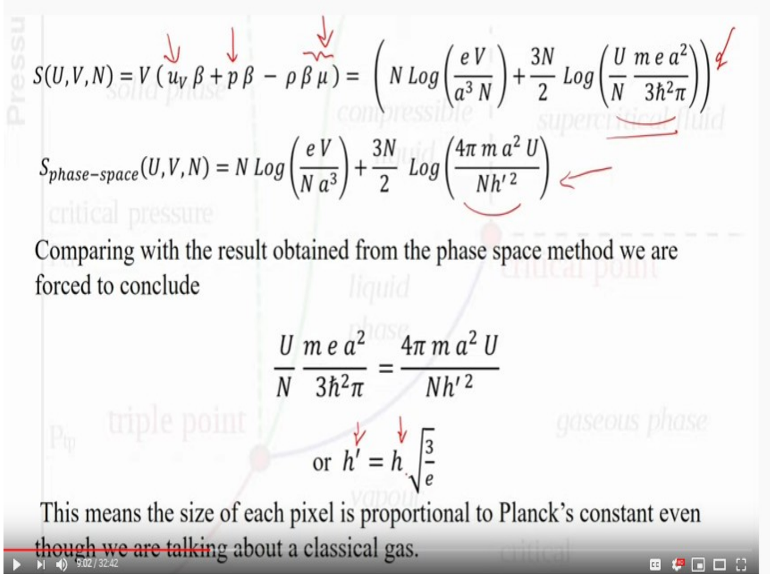

$$S(U,V,N) = V\,(u_V\,\beta + p\,\beta\ -\ \rho\,\beta\,\mu) = \left(N\,Log\left(\frac{e\,V}{a^3\,N}\right) + \frac{3N}{2}\ Log\left(\frac{U}{N}\,\frac{m\,e\,a^2}{3\hbar^2\pi}\right)\right)$$

$$S_{phase-space}(U,V,N) = N\,Log\left(\frac{e\,V}{N\,a^3}\right) + \frac{3N}{2}\ Log\left(\frac{4\pi\,m\,a^2\,U}{Nh'^2}\right)$$

Comparing with the result obtained from the phase space method we are forced to conclude

$$\frac{U}{N}\,\frac{m\,e\,a^2}{3\hbar^2\pi} = \frac{4\pi\,m\,a^2\,U}{Nh'^2}$$

$$\text{or}\ \ h' = h\sqrt{\frac{3}{e}}$$

This means the size of each pixel is proportional to Planck's constant even though we are talking about a classical gas.

All right so now let me go ahead and substitute all these expressions into the entropy functions. So notice that the entropy function has energy per unit volume which we have just derived, it has pressure which we have just derived and βμ which we have selected earlier. So we have derived the classical limits of the energy density of the pressure and of beta mu which we selected in order to make all this work.

And we substitute now all those expressions into this formula for the entropy of a quantum ideal gas in the classical limit and then we end up with this expression. So now what we are going to do, so this is the answer for the entropy of a classical ideal gas viewed as the classical limit of quantum entropy. So now notice that we have also derived the familiar Sackur-Tetrode formula directly by phase space counting and we got this expression.

Obviously we want these two expressions to be the same and then when we equate these two we see that means basically we equate the logarithms here and that effectively tells you that the size of the pixels or the area of that pixel that I was talking about is really related to Planck's constant h the original Planck’s constant not divided by 2π. So it is just proportional to some number times Planck’s constant.

So try as you might you will never be able to get rid of the effects of quantum mechanics completely. and so that is telling you that basically at the subatomic level there is some amount of quantum mechanics is going to survive no matter how hard you try.

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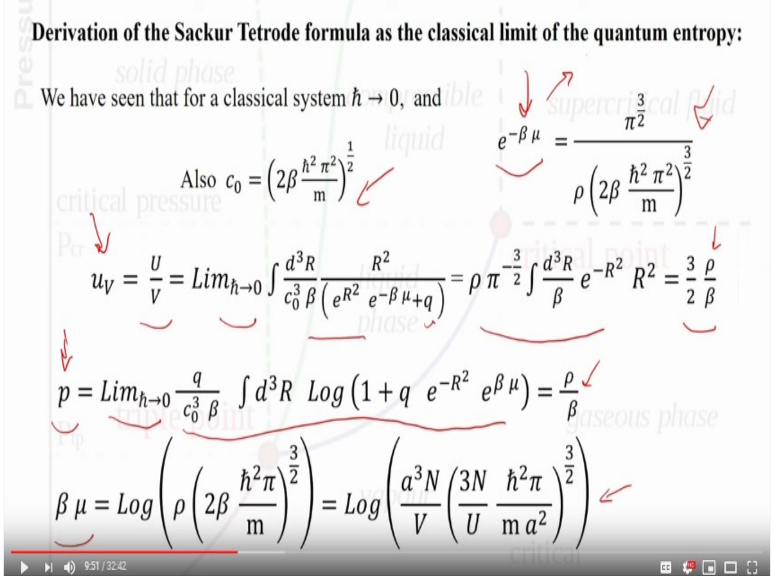

Derivation of the Sackur Tetrode formula as the classical limit of the quantum entropy:

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Also $c_0 = \left(2\beta\,\frac{\hbar^2\,\pi^2}{\mathrm{m}}\right)^{\frac{1}{2}}$

$$u_V = \frac{U}{V} = Lim_{\hbar\rightarrow 0}\int \frac{d^3R}{c_0^3\,\beta}\frac{R^2}{\left(e^{R^2}\;e^{-\beta\,\mu}+q\right)} = \rho\,\pi^{-\frac{3}{2}}\int \frac{d^3R}{\beta}\,e^{-R^2}\,R^2 = \frac{3}{2}\,\frac{\rho}{\beta}$$

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$$\beta\,\mu = Log\left(\rho\left(2\beta\,\frac{\hbar^2\pi}{\mathrm{m}}\right)^{\frac{3}{2}}\right) = Log\left(\frac{a^3N}{V}\left(\frac{3N}{U}\;\frac{\hbar^2\pi}{\mathrm{m}\,a^2}\right)^{\frac{3}{2}}\right)$$

So the expressions that we derived for p and energy per unit volume u_V is not merely to you know as an intermediate step for obtaining the entropy. But it is interesting in its own right because after all if you know that ρ is nothing but the number of particles per unit volume and then you can extract total energy by multiplying both sides by volume and recall that β was just inverse temperature.

So when you do that you gain an expression which is very familiar to you which is a total energy is

$$E = (3/2)\,NT$$

with of course the Boltzmann constant being set to one because I am measuring temperature and energy units as I have told you repeatedly earlier okay.

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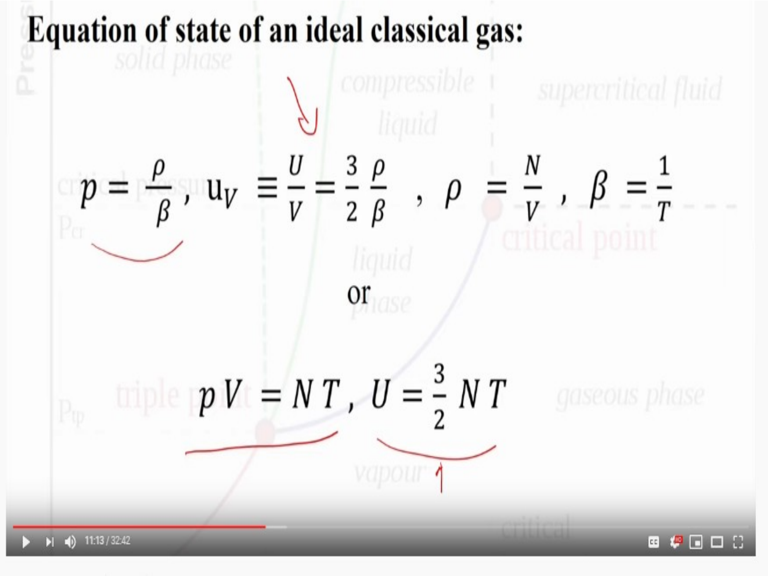

Equation of state of an ideal classical gas:

$$p = \frac{\rho}{\beta}, \; u_V \equiv \frac{U}{V} = \frac{3}{2}\frac{\rho}{\beta} \;, \; \rho = \frac{N}{V} \;, \; \beta = \frac{1}{T}$$

or

$$pV = NT, \; U = \frac{3}{2} NT$$

So that is precisely what I am getting here. So when I do that when I multiply both sides by V, I end up getting this familiar expression. So I had just derived this expression here which is P = ρ/ β. And then I rewrite it in terms of something more familiar namely temperature and volume and so on and you get this equation of state of a classical ideal gas pV = N kT but k is 1 so pV = NT.

So you see we have been successful in doing three things one is derive the equation of state of a classical ideal gas, find the relationship between the total internal energy of a classical ideal gas in terms of temperature and finally derive an expression for the entropy function of a classical ideal gas. So all these are extremely important calculations made possible only because we have understood statistical mechanics sufficiently well.

We have understood what entropy is and how it is related to counting the number of microstates subject to various constraints well we still have not fully understood what pressure and temperature mean other than the fact that it is you know the derivative of the entropy function relative to various other independent parameters. But that is a very mathematical and opaque way of thinking about it. So obviously there is a more physical meaning for pressure and temperature which we have not discussed yet and that is something I am going to do subsequently.

But that apart we have successfully written down the equation of state, total internal energy and entropy function of classical ideal gas.

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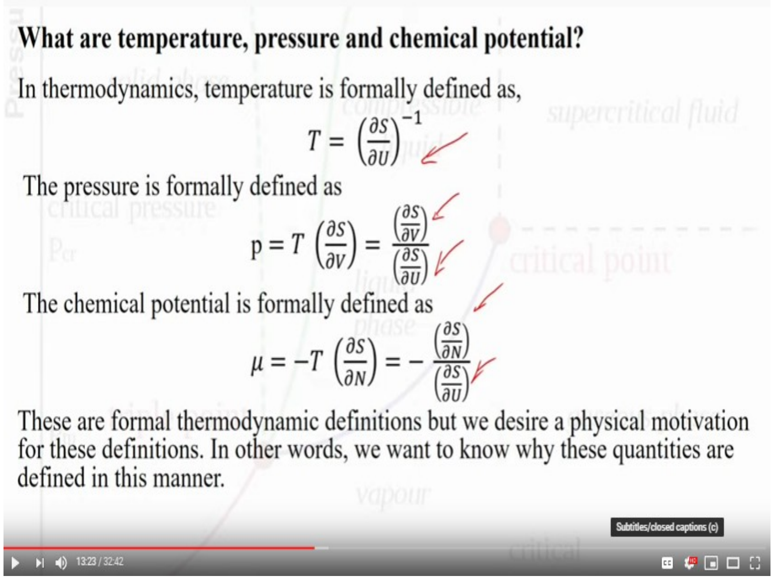

What are temperature, pressure and chemical potential?

In thermodynamics, temperature is formally defined as,

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1}$$

The pressure is formally defined as

$$p = T\left(\frac{\partial S}{\partial V}\right) = \frac{\left(\frac{\partial S}{\partial V}\right)}{\left(\frac{\partial S}{\partial U}\right)}$$

The chemical potential is formally defined as

$$\mu = -T\left(\frac{\partial S}{\partial N}\right) = -\frac{\left(\frac{\partial S}{\partial N}\right)}{\left(\frac{\partial S}{\partial U}\right)}$$

These are formal thermodynamic definitions but we desire a physical motivation for these definitions. In other words, we want to know why these quantities are defined in this manner.

So now let me get on to this question that I just mentioned namely what is temperature? What are these quantities? Other than the fact that they are simply you know that their derivatives formally in thermodynamics absolute temperature is defined as the rate of change of entropy with internal energy and it is the reciprocal of that the slope of the entropy function versus the internal energy the reciprocal of that slope.

So pressure is similarly defined as the ratio of these two slopes that means the slope of the entropy versus volume and a slope of entropy versus internal energy and similarly chemical potential is similarly defined in this way. So as a ratio of slopes of the appropriate slopes of the entropy function. So of course these are mathematical definitions it does not teach you anything about what it means physically after all we know that temperature has a very concrete physical meaning which we experience on a daily basis so does pressure maybe not chemical potential.

But unless you are you know a chemist or somebody who does laboratory experiments in chemistry well we do not experience that on a daily basis but pressure and temperature we always experience on a daily basis, all of us. So we had better be able to relate these formal mathematical definitions to something more tangible, okay.

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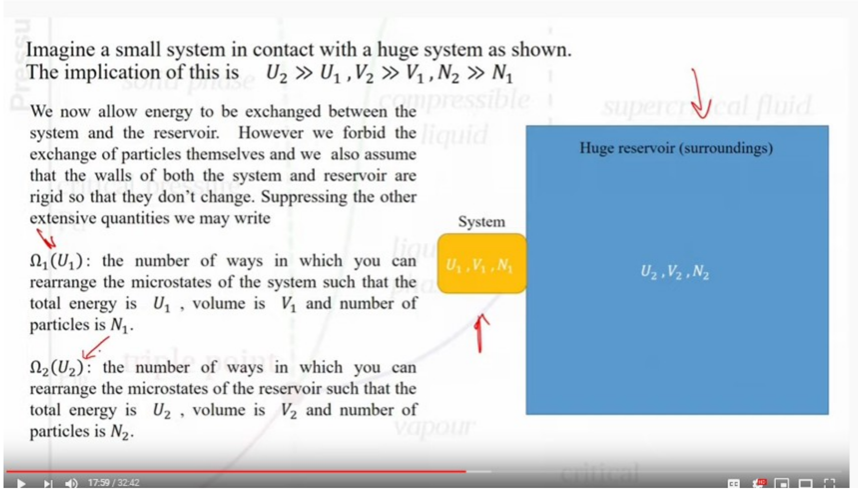

Imagine a small system in contact with a huge system as shown.
The implication of this is $U_2 \gg U_1, V_2 \gg V_1, N_2 \gg N_1$

We now allow energy to be exchanged between the system and the reservoir. However we forbid the exchange of particles themselves and we also assume that the walls of both the system and reservoir are rigid so that they don't change. Suppressing the other extensive quantities we may write

$\Omega_1(U_1)$: the number of ways in which you can rearrange the microstates of the system such that the total energy is U_1, volume is V_1 and number of particles is N_1.

$\Omega_2(U_2)$: the number of ways in which you can rearrange the microstates of the reservoir such that the total energy is U_2, volume is V_2 and number of particles is N_2.

Let me try and do that so in order to do this what we should be doing is imagining a system which say for arguments say let us assume that it contains energy U_1 and it has volume V_1 and a number of molecules in that system is N_1 . I am going to distinguish this system from what I call surroundings or reservoir so imagine that there is a system which is surrounded by some huge reservoir.

And that reservoir could be for example the atmosphere itself so you can have a system which could be a gas which is you know trapped in a container and its place in the Earth's atmosphere and the atmosphere itself is the reservoir and that gas that is trapped in your container is your system. So now what we are going to do is that we are going to allow the energy to be exchanged so we assume that the containers have rigid walls for example the containers of the gas that we have called the system has rigid walls.

So let us imagine they have rigid walls and we are going to also assume that it is not isolated in other words the system is not isolated it can exchange energy with surroundings so how do you accomplish that, with rigid walls it is very easy so all you do is you assume that your wall of your container that contain the gas are not thermally insulating so they are kind of thermally conducting walls.

So as a result heat can flow in and escape from the system so as a result energy gets exchanged the system and the reservoir so you allow that so as a result what is really fixed is not the total internal energy of the system which is which I have called U_1 but rather it is the sum of the total internal energy of the system plus the reservoir. So in other words that is going to be U_1 +U_2

which is fixed. So I am going to call that U, I am going to call $U_1 + U_2$ as U and so as a result U_2 is going to be $U - U_1$.

So imagine that Ω_1 is the number of ways in which you can rearrange the microstates of the system such that its total internal energy is U_1 and of course because the other ones are fixed so notice that my walls are rigid the walls of my system are rigid. So as a result the volume of the system is always fixed at V_1 and I do not allow particles to escape in or out of the system. So the number of particles is fixed as N_1 so same with the reservoir so the volume of the reservoir is fixed as V_2 which is enormous compared to V_1 and N_2 is the number of particles which is also fixed but it is also enormous compared to the number of particles in the system.

So now the only thing that is the other thing which is remaining is the internal energy which is not fixed so in other words U_1 is not fixed and U_2 is not fixed but their sum is fixed so in other words put together it is fixed but individually they are not fixed. So as a result I can suppress the volume label V_1 and the number of particles label N_1 because they are fixed so I am going to suppress that and I am going to refer to $\Omega_1 (U_1)$ as the number of ways in which I can rearrange my microstates of my system which is a gas.

So the number of ways I can rearrange my microstate such that the total internal energy is U_1 and of course the other parameters are what I just told you. So similarly I label $\Omega_2 (U_2)$ to be the total number of ways in which I can rearrange the microstates of my huge reservoir such that it is total internal energy is U_2 .

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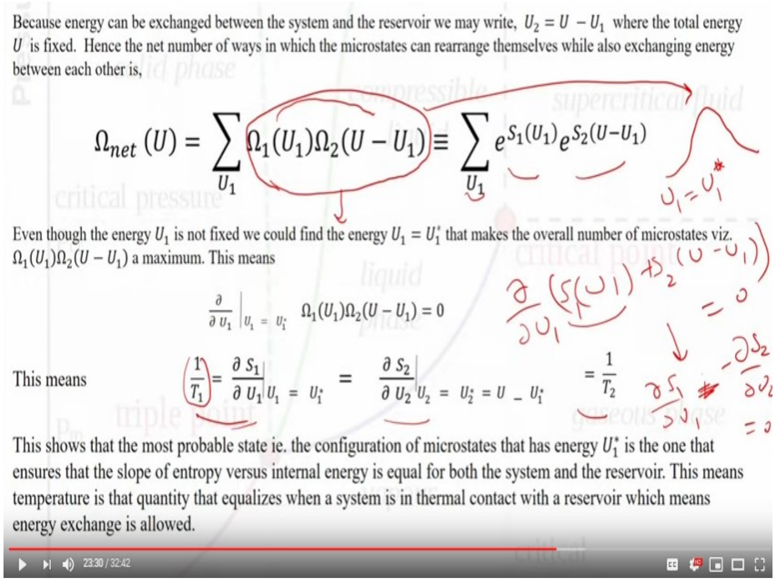

Because energy can be exchanged between the system and the reservoir we may write, $U_2 = U - U_1$ where the total energy U is fixed. Hence the net number of ways in which the microstates can rearrange themselves while also exchanging energy between each other is,

$$\Omega_{net}(U) = \sum_{U_1} \Omega_1(U_1)\Omega_2(U - U_1) \equiv \sum_{U_1} e^{S_1(U_1)} e^{S_2(U-U_1)}$$

Even though the energy U_1 is not fixed we could find the energy $U_1 = U_1^*$ that makes the overall number of microstates viz. $\Omega_1(U_1)\Omega_2(U - U_1)$ a maximum. This means

$$\left.\frac{\partial}{\partial U_1}\right|_{U_1 = U_1^*} \Omega_1(U_1)\Omega_2(U - U_1) = 0$$

This means $\frac{1}{T_1} = \left.\frac{\partial S_1}{\partial U_1}\right|_{U_1 = U_1^*} = \left.\frac{\partial S_2}{\partial U_2}\right|_{U_2 = U_2^* = U - U_1^*} = \frac{1}{T_2}$

This shows that the most probable state ie. the configuration of microstates that has energy U_1^* is the one that ensures that the slope of entropy versus internal energy is equal for both the system and the reservoir. This means temperature is that quantity that equalizes when a system is in thermal contact with a reservoir which means energy exchange is allowed.

So notice that because U_1 and U_2 are not fixed and their sum is fixed that the net number of ways in which I can rearrange the microstates of the combined system such that the total internal energy of both put together as U is this sum, so it is this the first product will tell me that if the system has U_1 energy there is the reservoir as $U – U_1$ energy then of course the overall number of ways of rearranging the microstates of both the systems in the reservoir put together is this product of Ω_1 Ω_2 .

But then I have to ask myself you know I have to repeat this calculation for various different U_1’s and then because you know for each U_1 there is going to be a certain way of doing it and for a different U_1 there is a certain other number of ways of rearranging the microstate and these are independent re-arrangements. So because there are independent I will have to add them all up in this fashion and get a net number of ways in which I can rearrange the number of microstates of both the system and the reservoir and rewritten in terms of entropy it is going to look like this.

Now what I am going to do is I am going to ask myself what is the most probable value of this U_1? So notice that you won is not fixed so it can fluctuate wildly because U_1 is being exchanged with the surroundings. But then I can still legitimately ask the question what is the most probable value of U_1. So clearly the most probable value of U_1 is that U_1 which makes this quantity a maximum so in other words we have to anticipate that if I plot this product as a function of U_1 it is going to peak at some U_1^* it is going to peak at this U_1^* and that is something that I refer to as the most probable value of the internal energy of my system.

So how do you determine that and the way you determine that is to simply you know differentiate this quantity and set it equal to 0 at U_1^* as you very well know that is how you find the extremum of a function and given that these omegas can be expressed in terms of the entropy that eventually amounts to doing this. So it amounts to equating the so notice that if I do it this way I can do it with the entropy for after all it is extremizing Ω products of Ω is the same as extremizing the log of the product of Ω s.

And then the derivative of the log is the suggest the entropies the sum of the entropies and the derivatives would then correspond to this sort of an expression equals 0. And when you do that you get this expression which is dS_1 / dU_1 so this is plus so here this is plus because if you take the log you get the sum of the entropies it is the Ω that is the product that is why if I take the derivative with respect to U_1 I get this plus and then notice that differentiating with respect to U_1 is same as differentiating with respect to U_2 which is $U - U_1$ and flapping this sign so the so in other words this going to be $-dS_2 / d U_2 = 0$.

So the extremum is achieved when you equate the slope of the entropy with respect to the internal energy of the system and the surroundings. So recall that this slope is nothing but the thermodynamic temperature and that is how we have defined thermodynamic temperature. So now you have a physical meaning for thermodynamic temperature so now you can also choose to alternatively define thermodynamic temperature as that quantity which equalizes when a system is allowed to be in contact with a reservoir and allowed to exchange energy.

So in other words the quantity that is common to the system and the reservoir in thermal equilibrium is precisely temperature or something related to it so in particular it depends on how you define it so we have chosen to define this as a reciprocal of temperature. So the temperature concept is basically a concept which just tells you that it is that attribute of a system which becomes the same as that corresponding attribute of the reservoir when the two are in thermal contact with each other and sufficient time is allowed to elapse so that they come to an equilibrium.

Alright so that is what temperature means intuitively also and so it is nice that we have successfully related a mathematical definition namely at the inverse of temperature being the slope of the entropy versus internal energy rather abstract and sort of opaque definition. And we have linked it to thermal equilibrium and how when two system and reservoir come into contact and the attribute that is common to the two is exactly what is known as temperature.

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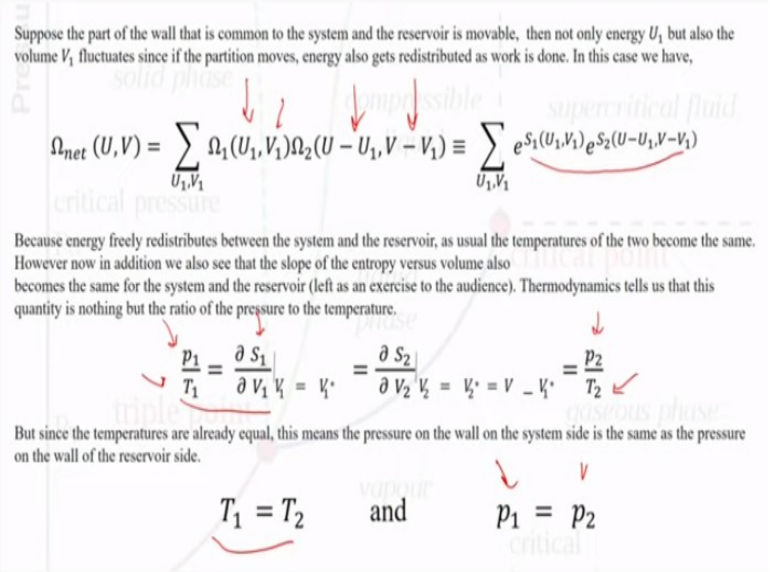

Suppose the part of the wall that is common to the system and the reservoir is movable, then not only energy U_1 but also the volume V_1 fluctuates since if the partition moves, energy also gets redistributed as work is done. In this case we have,

$$\Omega_{net}\,(U,V) = \sum_{U_1,V_1} \Omega_1(U_1,V_1)\Omega_2(U-U_1,V-V_1) \equiv \sum_{U_1,V_1} \underline{e^{S_1(U_1,V_1)}e^{S_2(U-U_1,V-V_1)}}$$

Because energy freely redistributes between the system and the reservoir, as usual the temperatures of the two become the same. However now in addition we also see that the slope of the entropy versus volume also becomes the same for the system and the reservoir (left as an exercise to the audience). Thermodynamics tells us that this quantity is nothing but the ratio of the pressure to the temperature.

$$\underline{\frac{p_1}{T_1} = \frac{\partial S_1}{\partial V_1}}\Big|_{V_1 = V_1^*} = \frac{\partial S_2}{\partial V_2}\Big|_{V_2 = V_2^* = V - V_1^*} = \frac{p_2}{T_2}$$

But since the temperatures are already equal, this means the pressure on the wall on the system side is the same as the pressure on the wall of the reservoir side.

$$\underline{T_1 = T_2} \quad \text{and} \quad p_1 = p_2$$

So you can go ahead and do the same thing with pressure, so with pressure of course what you have to do is that you have to make sure that you your walls the walls of your container are not rigid. So in other words the gas that is in the container is free to expand and contract. So you repeat this exercise where the total volume of the combined system of the system and the reservoir is fixed. So in other words $V_1 + V_2$ is constant which I call V so but V_1 and V_2 can change by themselves.

So of course you know if you allow for gases to expand and contract and naturally you know the work gets done and as a result the internal energy also gets exchanged whether you like it or not. So the mere fact that you allow for gases to expand the walls of the container to be not rigid implies that work gets done or is done on the system. So as a result that work gets transmitted to the internal energy of the system sometimes and as a result you cannot really have it is not easy to you know have a mechanism by which only volume changes but internal energy does not change.

So typically we end up allowing for both to get exchanged. And so that is why I have allowed for the internal energy to be exchanged and volume to be also exchanged. But however it is very easy to prevent molecules themselves from being exchanged. Because all you have to do is you know have an impenetrable wall where molecules cannot diffuse into the reservoir or molecules from the reservoir cannot diffuse into the system.

So that is easily accomplished so as a result I can ask similar questions about when is the most probable volume and when is the most probable internal energy achieved? And that is when this combined entropy get extremized. So in this case maximized so what I have to do is I have to find the so I am not going to repeat this calculation it is very similar to what we did earlier so if I do it for the volume I end up asserting that the slope of the internal energy with volume has to be equated in equilibrium to the slope of the internal energy of the volume of the reservoir.

So the system slope is equal to the reservoir slope. And notice that the slope of the entropy with the volume is nothing but the ratio of pressure and temperature. And it involves so as a result in at equilibrium you end up equating the ratio of the pressure and temperature of the system with the ratio of pressure and temperature of the reservoir. But notice that I have also allowed for energy to be exchanged so as a result the temperatures were anyway equal to begin with so because the temperatures were equal to begin with that implies the pressures are also equal.

So if in a situation where I allow both the volume and the internal energy to exchange then you see that there are two aspects or attributes of the system that become equal to the corresponding attributes of the reservoir and those two attributes are pressure and temperature ,well okay.

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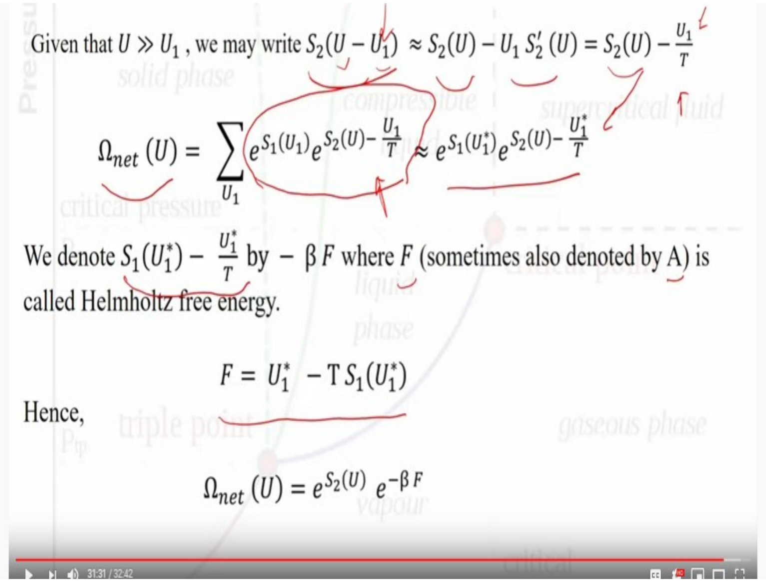

Given that $U \gg U_1$, we may write $S_2(U - U_1) \approx S_2(U) - U_1 S_2'(U) = S_2(U) - \frac{U_1}{T}$

$$\Omega_{net}(U) = \sum_{U_1} e^{S_1(U_1)} e^{S_2(U) - \frac{U_1}{T}} \approx e^{S_1(U_1^*)} e^{S_2(U) - \frac{U_1^*}{T}}$$

We denote $S_1(U_1^*) - \frac{U_1^*}{T}$ by $-\beta F$ where F (sometimes also denoted by A) is called Helmholtz free energy.

$$F = U_1^* - T S_1(U_1^*)$$

Hence,

$$\Omega_{net}(U) = e^{S_2(U)} e^{-\beta F}$$

There is further concept that is useful I really want to go back and ask myself what is this net way of rearranging the microstates of the combined system look like how does that look like? So all you have to do is go ahead and replace the entropy so notice that we have taken pains to point out the energy that maximizes this product that is e^{S1} e^{S2} is maximized at or close to $U = U_1{}^*$.

So the most probable value of the energy is the place at which this product gets maximized so it stands to reason that to a crude first approximation we may easily replace this summation we may ignore that we have to sum over all the energies rather we just make do with the energy which corresponds to the most probable value or the one that maximizes this. Of course at this stage it is not very convincing because I have to convince you that by doing this I would not be making a huge mistake by ignoring other energies that may be close to this most probable energy. So I will do that subsequently so we'll have to actually what is called compute are called fluctuations around the most probable state and then we have to convince ourselves that under suitable circumstances those fluctuations around the most probable state and then we have to convince ourselves that under suitable circumstances those fluctuations are suppressed and as a result we are justified in ignoring them in the first place. So you will have to take my word for it right now so I am going to ignore those fluctuations and assert that the most probable value for the energy is the only energy that matters and I am going to simply replace U_1 by $U_1{}^*$ .So because U_1 's are anyway very small compared to the total energy U, I can do a Taylor series of S_2 around $U_1 = 0$ and then I get this Taylor series.

So notice that this is same as asserting that this $S_2(U_2)$ which is the reservoir's entropy is same as the reservoirs entropy then the system has no internal energy at all minus the internal energy of the reservoir divided by the common absolute temperature this is just Taylor expansion Taylor series to first order in U_1. So now I am going to go ahead and substitute this expression here I have already done that here this is S_2. And then I end up getting this product which is S_1 $S_2(U_2)$ which I have written like the now of course I can pull this $S_2(U_2)$ outside and if I just focus on the most probable energy contributions.

So I end up with this difference that is the entropy of the system at its most probable energy minus the most probable energy divided by absolute temperature. So this is related to what is known as Helmholtz free energy. So we denote this by - F / T which is, β is remember it is 1 / T.

So we call this difference as - β F and F is sometimes it's also denoted by A it is some German word for work that starts with A.

So but anyway F and A are common letters that denote what we call Helmholtz free energy , so Helmhotlz free energy can be thought of as this difference of the most probable internal energy of the system minus the absolute temperature times the entropy of the system at its most probable internal energy. So I am going to stop here and in the next hour I am going to just continue with this and see if I can explain to you how to define other types similar to Helmholtz's free energy, other type of free energy which is related to allowing the gas to also expand and contract.

So here I have just allowed the internal energy to be exchange I did it did not allow volume to be exchanged or change at all. So you can do that and you get a different type of free energy and that is a topic for the next session and then we will continue from there ok thank you. Hope to join you next time.