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Good afternoon. So the last time we have done the definition of a simple system model. It's very important because we acquire the so-called macroscopic limit which holds when we deal with many particles in a container and which is the framework in which most of thermodynamics has been developed until maybe 20 years ago. And so we will review just quickly what we've done. Remember that the issue here is that walls cause rarefaction effects because the density of particles must go to 0 at the wall.

In most frameworks, we have seen some examples. And so these rarefaction effects are important. Like here, because when I remove a partition, they leave sort of a hole or a rarefaction area that will spontaneously be filled by the particles as they realize that the wall is not there anymore. And so if you remove the wall, you get a spontaneous and, therefore, irreversible process that takes you, as represented on the E versus S diagram, from this state to that state.

And this is an irreversible spontaneous process. Later on today, we will talk about-- just in a few minutes-- about going also up this way. But for the moment, let me just recall that in the limit of many particles, the stable equilibrium state curve for the composite system divided into two partitions, gets closer and closer to the stable equilibrium state curve for the system with the same particles but no partitions. And therefore, also the rarefaction effect is smaller, and it becomes negligible as we have several particles.

In fact-- yes, we have seen some examples in that paper that I pointed to you where there are 10 to the fifth particles. But that is at extremely cold temperatures, I believe. Whereas at normal temperatures, as soon as you have maybe 10, 20 particles, these rarefaction effects become already pretty negligible. And that's why we can use the many particle-- the simple system model-- for most systems, not only macroscopic, but also mesoscopic and even microscopic as long as you don't go to just few molecules.

And the idea is that in that limit you can neglect essentially the effect of inserting or removing partitions from a stable equilibrium state. Mathematically, that is equivalent to assuming that the fundamental relation is a homogeneous function of first degree in all of its variables, meaning this. And as we said, from that mathematical condition which represents the physics that we said, we gain one relation, which is the Euler relation, which I was unable to prove with the previous viewgraph.

So here is a new viewgraph which does a better job. This is the condition. And in order to prove it, yeah, here is a proof. You just have to take the partial derivative of both sides with respect to λ . And so on the left-hand side, there is no λ . So the partial derivative is 0. And on the right-hand side, it's λ times U.

So it's U plus λ times the derivative of U with respect to the first variable, which is the temperature evaluated at the same independent variables, times the derivative of this argument here that is S over λ , which does depend on λ . So the derivative is S over minus λ squared and so on for the other derivatives. And here is what you get. And now, in this expression here, if you set λ equal to 1, out comes the Euler relation.

You can also take from this the fact that the partial derivatives of the fundamental relation are homogeneous functions of degree 0. In other words, see, there is no λ multiplying in front. So the temperature of a system with given S , V , and n is equal to the temperature-- of course, we're talking about stable equilibrium states-- for a system in which the S , V , and n 's are divided by the same number. As long as it's the same number, it will be the same temperature. So that means small or large, as long as the relative amounts are equal, you get the same temperature for the stable equilibrium states.

So that's the Euler relation. And we have proved that-- thanks to the Euler relation-- we can define specific properties, which, for example, is the specific energy-- is the energy divided by n -- And then, we can see how this specific property is a function of the other specific properties-- the specific entropy, specific volume, and the mole fractions, which are the specific amounts of constituents. And, as we see here, there is a lot of n dependence, but we proved that the partial derivative of U with respect to n is equal to minus 1 over n squared times this quantity.

And this quantity, you remember, is what we called the Euler free energy. It's the characteristic function. In fact-- And this is still valid also for small systems. Here is how we define the Euler free energy. And here is its differential from which, for example, we can see that the amount of one constituent is equal to the partial of the Euler free energy with respect to the chemical potential of that constituent when you hold fixed the temperature, the pressure, and the chemical potentials of all the other constituents.

So if you have a reservoir that keeps temperature, pressure, and also chemical potentials-- except this one-- by changing the chemical potential and measuring the amounts, you can measure the Euler free energy. This might be a possible procedure to measure this for small systems using molecular dynamics. Well, here, what we have done in the previous slide in order to compute the derivative of energy with respect to the amounts-- the derivative of the specific energy with respect to the amounts-- at fixed specific entropy volume and mole fractions-- to find that it is minus 1 over n times the Euler free energy.

We have done it also for these other properties. And those derivatives turn out to be all equal, at least for those that are-- for the specific properties that emerge from the Legendre transform of the energy version of the fundamental relation. They all come out to be Euler free energy divided by n squared negative. Whereas for the entropy, it's minus 1 over T of the same result.

So since in the limit of many particles, there may be also significance here that you are left with an n at the denominator, which for many particles grows up, and whereas this is the specific Euler free energy per particle. So this may be an indication already that this dependence goes down with n . In any case, again, these relations may be ways to measure the Euler free energy for small systems, of course. Because in the large system limit, the Euler free energy goes to 0. The Euler relation is equivalent to setting Eu equals 0.

So now, let's go back to this issue of partitioning a system-- a small system, so a few particles. And we want to see if there is a cost in dividing the system, which is in a stable equilibrium state in this one, and producing another stable equilibrium state of the system with λ partitions in each of which there is the same amount. It has the same volume and also the same entropy. And the overall entropy must be the same.

If we do this, we can go from here to there in a reversible weight process. And if we go from partitioned to without partition, you see we go down. So we extract the adiabatic availability, essentially, of that state that is generated the moment we remove those partitions. The moment we remove these partitions, this is not anymore the stable equilibrium state curve because we've changed the system. So the stable equilibrium state curve becomes this one.

So yes, we could let thing evolve spontaneously. So the system will evolve spontaneously at constant energy, generating entropy by irreversibility. But if we are a good enough and fast enough-- faster than irreversibility-- we could attempt to extract this adiabatic availability and go all the way down at constant entropy to reach this stable equilibrium state. But this also says that if I want to go from here and introduce the partitions in a weight process since I cannot go leftward in the weight process, the first time I reach the stable equilibrium state of the system curve of the system with partitions is here.

So this is the first available-- I mean reachable-- partitioned state. Others could be up here. And so as I go from here to there, I need to spend at least this much work or energy from the weight in order to introduce those partitions. And physically, you can think of the idea that since there are refraction effects at the wall as you introduce the partition, the partition moves the particles away because it has to create that space. And that is work.

Of course, the mathematics of the same idea is that you can compute the work to introduce those λ partitions, which is the minimum work to go from 0 to-- from just 1 to λ . It's the maximum you can extract if you go from λ to 1. And it is the difference between the energy here, which is E_λ , which is λ times the energy of each partition. So it's E_1 . E_1 is the system with-- the fundamental relation of the system without partitions, that you evaluate at the values of the entropy, volume and amounts that are present in one partition.

So E_λ minus E , and this is instead E_1 -- fundamental relation of the system without partitions evaluated at the value of the entropy of the overall system, which is the sum of all the entropies. It's essentially λ times the entropy that is in each partition. So this is this difference. And, for example, we could see how it changes as we go from λ to $\lambda + 1$, or-- which is essentially the same-- from λ to $\lambda - 1$ -- so minimum work to add or remove one partition.

And notice that it's not exactly so obvious because when I add one λ , it's not that I just have to push in. I have to also rearrange the particles in the other λ s so that they are all divided in equal amounts. But with that understanding, if you see that this work-- so that's essentially the work of going to $\lambda + 1$ minus the work of going to λ partitions divided by 1, and this is a fancy way of writing 1.

But to make this ratio look like the partial derivative of W with respect to λ and since we have an expression for W , we can take the partial derivative with respect to λ . Do the math, and out comes that that work is the Euler free energy of each partition in the λ subdivided system. So that's another physical interpretation of the Euler free energy. OK, good.

So now that we have the simple system model, there are a number of results that you have seen in previous courses of thermodynamics. So I will do a very brief review of those because it also helps brushing up a bit, considering that the other day you didn't remember the value of γ for air. So the first idea is that of an extensive property. And here, notice I keep repeating these titles. This is now within the simple system model.

What do we mean by an extensive property? For example, the energy is an extensive property. This is precisely the mathematical definition of a simple system model. Now, the homogeneity of first degree of the function that represents-- that was for the energy. This is for-- Any other function that has that property, we call it extensive. And you can prove that examples--

In the list of these extensive properties, you find energy, of course. We find entropy. We find volume, the amounts, the total amount, which is the sum of the amounts of the various different constituents, the enthalpy. Enthalpy is not an additive property. Because if you have two systems that are at different pressures-- enthalpy is $U + PV$ -- the P is different, and, therefore, U and V are additive. But the P that is different doesn't make that linear combination of U and V additive.

But if you have a simple system in which you can assume that-- you see these independent properties are all divided by the same number, we have said before that the partial derivatives of the fundamental relation, including temperature and pressure, do not change if you change with this particular change of variables. And that is why you find the enthalpy here in this list. It is extensive. Also, the Gibbs free energy is missing in this list, but it is another example, as well as the specific heat capacities and the mass.

Now, if I take any two extensive properties and take the ratio, I obtain specific properties. So, for example, the first line here represents the specific properties when I divide. So these are the molar specific processes because I divide by n . Or I could have the mass specific properties when I divide by m . Or I could have the volume specific properties when I divide by V . For example, the mass divided by the volume is the density. Of course, they are related between one another.

And sometimes here I try to differentiate by using a different symbol like the star here is there just in case you need to make sure that you don't get confused. But in most of the treatments, once you set the definition and the context makes it clear that you're working with a mass specific properties, you just use a lowercase letter without the star, and you let the context define what you're doing.

For example, the amounts if you divide them by n , you get the molar fraction. I'll use the letter y_i , but not everybody uses that letters. If I have the mass-- so I take take the number of particles i multiplied by their molecular weight-- capital M_i -- of particles i and divide by the total mass, that becomes the mass fraction of that constituent. If I divide the amount of constituents by the volume what I get is the concentration of those constituents, which in the chemistry business sometimes is also denoted this way. This is the volume concentration of particles of type i .

So notation varies depending on the various fields in which you apply thermodynamics. Remember that we define extensive property when for the properties there is a relation like this, but there is a λ here multiplying. If there is no λ like as we have said for the partial derivatives of the fundamental relations-- so for T, P and the chemical potentials but also for all of the specific properties that we just defined-- you can prove that there is no λ there, and this relation holds. We call these properties intensive properties.

Also here, I have to warn you that I may be using a definition which might differ from what you've seen elsewhere, so just be careful when you see the word intensive property. Check how the author defines that intensive. This is our definition. There are many properties. So we said not just T, P and chemical potentials but also all the specific properties. All right, so if you take the list of the values of all these intensive properties, which is usually an infinite number of properties, but most of the times, there is a smaller set of independent properties.

The list of all properties of this kind for a stable equilibrium state is called the intensive state. And you can show that if you have the intensive state and you also have the value for one extensive property, then you have completely fixed the state. So you must-- in order to get the state-- we're talking about stable equilibrium states within the simple system model-- if you want the state, you can start from the intensive state and add an extensive property.

The other idea that is a very important consequence of the simple system model is that the fact that you can add and remove partitions allows you to describe a stable equilibrium states in which you have the coexistence of parts of the system that are in different intensive states. For example, think of a pot with water inside, and it's on the stove. And so you have heating below, and there is boiling. And as you know boiling will produce bubbles. These bubbles will go to the surface and may generate drops. If the boiling is sufficiently vigorous, it generates drops.

So this is a-- it's not really a stable equilibrium state, but you can approximate the properties with those of a stable equilibrium state at least after a while that you have stopped the heating. So you don't have-- as you get a sort of uniform temperature, uniform pressure. But you still have some drops and bubbles-- drops in the vapor and bubbles in the liquid. So this is a complicated system to describe. But conceptually, the simple system model allows you to do the following.

I can imagine to take another pot-- my model pot, so to speak. It's a mental image of that thing. And let me take a physical partition that runs at the interface between liquid and vapor. And, as you know, inserting that partition doesn't cost. So you already see that that doesn't cost means you are neglecting-- the simple system model is neglecting also the surface tension effects. Because that interface does matter, but not within the simple system model.

So I can take this and think of putting it here. And then I take another bubble and-- sorry, let me put them up here. So I take all the bubbles, and I put them there. And I also need to change the shape a bit so that it fills the same space. And also here, this I can take larger areas--

so essentially, all the continuous area that doesn't contain drops-- and put it there. So eventually, what I managed to do is to put all the vapor here and all the liquid here. Usually we use these letters to represent that.

So I've generated two regions in which there are no inhomogeneities. Whereas here, the inhomogeneity stems from the fact that, as you know, there is a huge difference in density, for example, which is one of the intensive properties-- like a factor of a thousand between the density of the liquid and the density of the vapor. So this is an inhomogeneous or heterogeneous situation that can be represented, certainly not in a uniform intensive state. But I can group the various intensive states that are present in my multiple phase state into just areas that we call phases that are locally homogeneous.

So the f phase is the collection of all the parts of my system that have the same intensive state, like the liquid, high density. And this g is the collection of all the other parts that share this other intensive state. And if you have a triple point-- suppose you also have ice here because we are at the proper pressure. If I have also ice, I need also to produce a third phase. So that defines the idea of phase.

And then, as you know, there is this famous Gibbs phase rule. And here is how it follows. All right, one way of looking at it is-- let's see what happens-- Let's choose this set of variables that are the variables that describe this equilibrium state, temperature and pressure I select them because I assume that all the various parts are in-- the various phases must be in mutual equilibrium. Therefore, they must be at the same temperature for the overall system to be in a stable equilibrium state. Because, as we said, we consider the overall system as a composite of the phases, and they are in mutual equilibrium.

So the conditions for mutual equilibrium are equality of pressure because they can exchange volume, equality of temperature because they can exchange energy, and equality of chemical potentials. The intensive states that are present here-- the number of independent properties that define intensive state is this much. It's T , p , plus the composition of each of the phases because-- yeah, here I consider a simple situation in which the substance is only water.

But you could have also a mixture. We will do that as we approach the second part of the course. This is very useful for that part. So these are the base variables. However, they are not all truly independent because, first of all, the mole fractions by obvious definition must sum up to 1. So for each of the phases-- for example, for the summation here I only have r minus 1 mole fractions that are independent because the last one can be computed as 1 minus the summation of the others. Plus, we also have the fact that the chemical potentials must be equal.

So I need to have equality of chemical potentials between the phases for each of the constituents that can be exchanged. And here, there are no membranes or things that disallow the exchange of types of particles. They can all be exchanged. And therefore, I have to satisfy the chemical potential equality for mutual stable equilibrium for each type of constituents. You see, actually here, the reason why I have chosen as candidates for independent variables-- temperature, pressure, and the mole fractions-- because we proved that the chemical potentials are functions of this T , P , and y .

And as we know, from the chemical potentials we can compute-- we will see that we can compute all the properties-- at least, yeah, all the properties-- because we proved that the chemical potentials are derivatives of the Gibbs free energy, which is one of the characteristic functions, Legendre transforms of the fundamental relation. All right, so now it's just a matter of counting. How many do I-- did I start with? So it's q times r -- is the mole fractions-- plus 2, temperature and pressure. Then I have to subtract q relations because of this condition here. And then, I have to subtract as many equations I have here.

Now, the equal sign-- each equal sign counts for an equation. So I have q phases. So it's q minus 1. And I have r lines here because I have one line like this for each type of constituent. So it's q minus 1 times r . And then, so if you subtract from that 2 plus rq -- subtract q and subtract q minus 1 times r -- you are left with this r plus 2 minus q which is the so-called variance. It's the real number of independently variable intensive properties. And this is assuming that we have no chemical reactions.

If we also have chemical reactions, we will see that there is one additional equation, which we will call the chemical equilibrium condition for each independent reaction in play in your system. And so you will have to subtract also-- let's call it z , the number of independent chemical reactions. We have to subtract z to get the actual variance.

For example, we take a pure substance like water. So pure substance means only one mole fraction. And, of course, one mole fraction is equal to 1. That's 100% of that substance. So that's not really a variable. The Gibbs phase rule says that the independent variables are 3 minus q . So, for example, if I have a single phase-- now, single phase means that it's all water, for example, homogeneous. It means that at every point in my stable equilibrium state, no matter where I go and make my little partition, I will find an intensive state that is equal to everywhere else.

So it's homogeneous. Single phase is homogeneous-- same intensive state everywhere. So with q equals 1, one phase, the variance is 3 minus 1. So it's 2. That means that if I have a liquid state, and I want to change that stable equilibrium state to a neighboring stable equilibrium state, I can move in two directions. I can change two variables. So I can change, for example, the temperature and the pressure independently.

If I have two phases like this-- well, without the ice-- and I want to move to another neighboring stable equilibrium state with the same two phases, so, for example, liquid and vapor. I want to move to an adjacent stable equilibrium state, again, with liquid and vapor. I cannot do it by arbitrarily changing both the temperature and the pressure. I can change only one, and the other must be tuned-- the change of the other must be tuned in a proper way because I need to follow the condition imposed by the chemical potential equality, which is written here.

I need that chemical potential equality to remain satisfied. And, therefore, if I change T , that imposes a change in p . And, in fact, this relation between temperature and pressure for two-phase states is what we call the saturation relation. Pressure and temperature are related by saturation. If I have three phases, and I want to move from a stable equilibrium state with those three phases to another stable equilibrium state with the same three phases and different temperatures or pressure, I cannot.

Because the variance is to 0. There are no neighboring states with different values of T and p . Because the equality of the chemical potential here, see I have two equalities and the two variables are T and p . So that fixes uniquely the value of T and p at which you can have those three phases. That's the triple point. This is better represented, for example-- this is the pressure temperature diagram for water. So if we have-- in this area-- this is the vapor area.

And if we have some vapor in this state, I could move to adjacent conditions in which I still have vapor, but different pressure and temperature. And I can move in both directions here. So I have two directions in which I can move. That's the meaning of variance. Variance equals 2. Along here are the line of coexistence of liquid. So inside the liquid also the variance is 2 and also inside the solid. These are the homogeneous single phase states. Along this curve, which is represented by the P saturation relation between pressure and temperature, we have the coexistence of liquid and vapor.

And as you see, the variance is 1. If I want to move to a neighboring equilibrium state with different pressure, I also have to adjust the change in temperature so as to follow this curve up to the critical point. Above that, there is no distinction between the liquid and the vapor phase. And therefore, it is possible, as you know, to go all the way from liquid to vapor and vice versa by going this path in which there is no sharp-- there is no two-phase conditions. So the liquid becomes smoothly vapor and vice versa without phase separation.

But if you go from here to there at a certain stage, like we do when we boil, we boil at constant atmospheric pressure. So I think-- let's see where is it? There should be one somewhere for-- but one bar is atmospheric pressure more or less. So if I go from here, and then I heat up at constant pressure, I move to the right in the diagram. At a certain stage, I'll reach the two-phase condition in which the water begins to boil. And, as you know, the temperature gets stuck to that value until it's all boiled. And then, you can still heat up, and the temperature will begin to increase.

So here, essentially when you have the two phases, the only way in which the system likes to stay in equilibrium is to separate into vapor and liquid. Triple point is this one. As you know, there is no adjacent values of temperature and pressure, but there are other triple points. If ice has many stable, but some are also metastable. For example, ice IV is not present here because it's metastable. But these are stable forms, and, therefore, you may find several triple points.

You can have no more than three coexisting phases for a pure substance because the variance cannot go negative. Now, remember that we gave these relations that allow to reconstruct the fundamental relation and, in particular, energy, entropy, and enthalpy, which is useful for bulk flow applications. When you start from-- if you have the expressions of how the coefficient of thermal expansion-isobaric expansion, isothermal compressibility, heat capacity of constant pressure-- how these things depend on T and p. And these were the relations. If we have a pure substance, for example, we could simply divide by the mass that we have in our system. And so we can rewrite. So E becomes little e, which I write u because we said that we use the letter u for energy just to remind ourselves that we are within the simple system model.

So the heat capacity becomes the specific heat or specific heat capacity. The volume becomes a specific volume here and here. And so you get these expression that allow you to compute for any substance-- any pure substance in the simple system model-- the various properties. And from that, we have some extreme, simple examples that-- simple behaviors that we call ideal behavior. The first one is the ideal incompressible solid or fluid model in which we assume that the specific volume is approximately constant because of the incompressibility. It is not strictly true because the solid, as you know, can be compressed.

The Young's modulus of elasticity describes precisely that. But for some applications, for some purposes, for thermal aspects, you may neglect that change in volume. And if you can neglect that change in volume, then the compressibility and the coefficient of expansion are approximately zero.

So if you take the limit and assume that they are exactly zero and that they go to zero in such a way that from the Mayer relation you also have that it doesn't-- so it is well behaved, because there is a ratio in the Mayer relation-- there is a ratio, where there is an αp , I think squared at the numerator divided by κT . And so you have a zero over zero.

So if that limit is appropriate, then the specific heats become equal. And you can show that they are also just a function of temperature. How do you show that? Well, here it is. If κ and α are zero, this coefficient here is always zero. So that means that the internal energy is a function of temperature but not a function of pressure.

And since the specific heat at constant volume is the partial of the energy with respect to temperature, it is also a function of temperature. Since u is a function of T only. And if we go here for entropy-- let's do also for entropy. So if α is equal to zero, entropy is a function only of the temperature. It's not true for the enthalpy, though. If α is equal to zero, the enthalpy depends on both temperature and pressure.

So for a liquid, enthalpy depends on T and p . And here is the expressions for the du , ds , dh , which come from these relations here when you substitute these assumptions for-- sorry. Whoops. Whoa. OK. All right. Of course, from these expressions, if you need to compute the differences, you just do the integral because c varies with temperature. Do some integrals. Sometimes you're lucky and the specific heats are not functions of temperature.

Then in that case, if in the range of your application, you can assume constant specific heat. The integral is easy, and sometimes you also call that a perfect behavior. It's perfect only for the purpose of the calculation, because it makes it easy. Not that there is anything better from the physics point of view. Now, the ideal gas model is another, of course, very well-known and useful model. If you assume this relation for the equation of state.

We already proved that κT is one over the pressure, αp is one over the temperature, and the Mayer relation becomes that c_p is equal to c_v plus R . In that case, let's go back once more here. Since α is $1/T$, this coefficient in front of the pressure variation is zero, so it means that the enthalpy is a function of temperature only.

And here also for the energy, κ is $1/p$. So p times $1/p$ is 1 . α is $1/T$, so T minus-- T times 1 is 1 , so 1 minus 1 is zero. So also the energy as a function of temperature only. Whereas for the entropy, this α is $1/p$. And from that, you see that the entropy, in the case of an ideal gas, is a function of both temperature and pressure. And here you can integrate-- I mean, this is how that formula appears-- comes out.

And if you use the Mayer relation to switch from-- sometimes it is useful instead of working with the specific heat at constant pressure, using that of constant volume because maybe in your problem, one of these variables remains zero and so you can choose either of these alternatives. And again, if the specific heats are not function of temperature, which happens in some cases, then you can integrate easily. Otherwise you have to do the integrals. I didn't write them explicitly.

Within the ideal gas model, you may realize that the way the molecules of the gas accumulate or carry the energy is mainly through their degrees of freedom. So certainly there is the translational and the rotational degrees of freedom. And then if you go to sufficiently high temperatures, you also have the vibrational degrees of freedom as well as the electronic degrees of freedom. So at relatively low temperatures, not too low, the vibrational and electronic degrees of freedom are less active.

There is sufficient ability for your molecules to accumulate whatever energy has to be distributed within the system by using the translational and rotational structure. And each degree of freedom contributes to the specific heat a factor of $1/2$. You remember the famous $1/2kT$. That's the energy that is carried. It's the equipartition energy that is carried by each degree of freedom at equilibrium.

So if you divide by T , if you take the derivative with respect to T , you are left with $1/2$ of k . And k is the Boltzmann constant which, when you multiply it by the Avogadro's number, becomes the gas constant R . So for a gas that only has translational degrees of freedom, so the molecules are point-wise and can move in the three directions, you have the three translational degrees of freedom, so you have $1/2$ of R contribution for each of them.

So the specific heat contributed by those degrees of freedom is just $3/2$ of R . And then if this is c_v , then c_p is c_v plus R . So the $3/2$ becomes $5/2$. Gamma, this famous ratio of specific heats, is therefore 5 over 3 , which is 1.67 . Now other molecules, for example, oxygen or nitrogen, they're biatomic. And these molecules also have the ability to put energy, yes, in the vibration.

But most importantly-- here, we said that we are interested in the rotation. So the rotation of the molecule. So if you look at the principal axis of this thing here, the moment of inertia for rotation is large in two directions and very small in the other one. Because when the molecule rotates along the axis of alignment of these two atoms, it doesn't have-- since the atoms are concentrated in very small radii, the mass is concentrated there.

So the moment of inertia is small. So if you multiply the moment times the angular velocity, probably squared. Since that M is important only in the two directions where the molecule rotates perpendicular to the axis of alignment, and so you have only-- in this molecule with aligned atoms, you have only two additional degrees of freedom in which the molecule can carry the energy. And that's why you go from 3 , plus 2 , to 5 . $5/2$.

And that makes gamma equals 1.4 . This is typical of oxygen, nitrogen, and therefore air. More complex molecules like H_2O where the atoms are not aligned but enjoy the possibility of storing energy also in the rotations, in the three principal axis of rotation, all three have a non-negligible moment of inertia. And therefore, you add another three. 3 plus 3 halves makes $6/2$. That's gamma equals 1.33 .

For example, the products of combustion-- also H_2O has a similar. And as the products of combustion are mainly done with the-- well, not exactly, because you have CO_2 -- but OK. Let's say that if you have water and carbon dioxide, then they both belong to these categories. If you have-- like most of the times, also air you are somewhere in between here and there. So it's a weighted sum of 1.4 and 1.33 .

So these numbers allow you, just by looking at the molecule, to get a good rough, immediate idea of what the specific heat is. But of course, as you go higher in temperatures, the various thresholds, you can activate also the various vibrational modes of the molecule. And even higher, you can also shift the electrons from the lower shell to the higher shells, and that adds to specific heat. So the specific heat, as we are interpreting it as, is the capacity, represents the capacity of our molecule to store the energy.

Yeah, these are expressions that are often used when you assume isentropic change. So if the entropy doesn't change, you just set from those equations here that the entropy remains constant, then you get these expressions. And since R is c_p minus c_v , that's how you can express the setting equal to zero, these in terms of just the ratio of the heat capacities. Gamma. That's why gamma appears here. Now, going back to two phases.

Well, actually, how do we prove this relation here that connects the pressure and the temperature? This is called the Clausius-Clapeyron relation, and it gives the slope of the saturation line on that pressure temperature diagram that we have shown before. It allows you to compute it using the ratio of the enthalpy of the change of phase and the volume of the change of phase and the temperature.

And the way you obtain this relation is, well, it follows again from the condition of equality of chemical potentials of the single substance we have, water, in the two phases. So it's this relation here. So one way to write it is to take the differential of the left-hand side and put it equal to the differential of the right-hand side.

So it's the $d\mu$ because we have-- the differential of $d\mu$ can be written if you-- this is not written in terms of the differential, but you can see that it also represents a differential. This is the Gibbs-Duhem relation. OK? But it's also viewed as the differential of the chemical potential as a function of temperature and pressure. And the Gibbs-Duhem relation shows that the partial derivatives of μ with respect to T is minus s and partial derivative of μ with respect to p is v . OK?

So if I want to move from a state in which I have these two phases coexisting, one and two could be liquid and vapor or ice and water or vapor and ice. And I want to move to another state in which I change the temperature, therefore also change the pressure. Then it means that the two differentials-- also, the change in chemical potential must be the same so that if they were equal at the beginning, they are equal also after, and therefore the two phases are still in mutual equilibrium.

So if you equate $d\mu_1$ with $d\mu_2$ here-- so eliminate these two because they must be equal-- and you see you get a relation between dT and dp that involves the differences in the specific entropies for the two phases and the differences in the specific volumes, which are the coefficients here. Then how do we go from here to there?

Well, again, the equation, the equality for mutual equilibrium of the chemical potentials, remember that the chemical potential for a pure substance is equal to the Gibbs free energy. Specific Gibbs free energy. So it's h , which can also be written as enthalpy minus Ts . OK? This is true only for the pure substance.

So if the chemical potentials are equal, it means that h minus Ts must be equal in the two phases, and therefore, in this equality I can extract T . And it's equal to the ratio of the enthalpy of the change of phase over the entropy of the change of phase. And so I can substitute-- instead of the entropy, I put the enthalpy of the change of phase divided by T .

Let's be more specific. Suppose we just have liquid and vapor, and then how do we compute the properties of a system in which I have two phases. Or three. Well, as we said, thanks to the simple system model and this idea of inserting and removing partitions for free, we have represented this kind of complex situation into a simpler one. It is a composite system of as many subsystems as there are phases. In the slide here, we have only two. It's a composite system.

So for the properties of the composite system, the additive properties, it's easy. For example, the volume. That's the volume of one plus the volume of the other. The energy is an additive property, so it's the energy of one phase plus the energy of the other. The entropy also is an additive property. The entropy of one plus entropy of the other. The enthalpy, here it's also-- in general, it is not an additive property, but here, because both systems have the same pressure, then it becomes additive.

And then we would be done, except that in terms of expressing how much of the substance we have in one phase and how much we have in the other, sometimes it is often use-- I mean, sometimes it's useful to work in terms of fractions. So we call, for example, vapor fraction or steam quality. The ratio, the amount of mass that is in the vapor phase over the overall mass of our system.

And by doing that and substituting in-- dividing here in these properties, the additive properties, we can compute the specific properties in terms of this mass fraction and of the specific properties that characterize each of the phases at that temperature and pressure. So these are typically called with the subscript g and f, and the difference is called the vaporization-- So for example, h_{fg} is the enthalpy of vaporization. s_{fg} is the entropy of vaporization.

And if we go back to this expression here where 2 and 1 is f and g, this says that the temperature is equal to the ratio of the enthalpy of vaporization over the entropy vaporization. These properties v_g and v_f are listed in the steam tables for water or, in the equivalent of the steam tables for other substances. Or maybe they are represented by correlations.

For example, the steam tables that were developed by Keenan and Keyes and in the '30s, 1930s, were based on correlations with some 40 parameters that were used to correlate the experimental data for water over the full range of applicable-- I mean-- important values. So we need a lot of experimental data. And with those 40 parameters, you can actually construct the entire steam tables.

Now pictorially, you can represent properties of substances. Of course, yes, you could do it in at most a three dimensional visualization. And pictorially, this is what an energy versus volume versus entropy diagram would look. So it's like, remember the E versus S diagram? All right? Here we also add volume. So if I fixed volume, this curve here is the curve that we usually would represent on an E versus S diagram for that particular value of the volume.

Here is for another value of the volume. We fix the entropy, then you have energy versus volume and you follow this line. The slope of this line is the negative of the pressure. Whereas the slope of that one is the temperature. Notice that when we have, for example, at the triple point, the triple point, which is a point on the pressure temperature diagram, becomes a planar region of triangular shape called the triple point triangle here. Because--

It's true that you can have the three phases only at one particular set of values of p and T, but you may have many different states like that. For example, you may have more ice, less water, and so on. So all the various combinations give you two mass fractions. So you got two degrees of freedom and you can span within that triangle. For example, here you have almost only vapor.

Here you have almost only liquid and here almost only solid, and in between, you have all the possible combinations. This is the region for liquid and vapor coexistence. This is solid and vapor coexistence. This is the value of the critical isotherm. So this is points that are the same temperature equal to the critical temperature. And above that critical isotherm, we change name from vapor. We call it gas. There is no real physical distinction.

But conventionally, we usually use the term gas where something like the ideal gas applies. Now, if you-- this is a pictorial representation. If you try to do it for water with the real property using the steam tables, this is how it looks. And you have to realize that since the specific volume spans over how many, maybe eight orders of magnitude in the interesting parts, not only because there is a factor of 1,000 between the density of the specific volume of the vapor and the liquid, but also, as you-- so that would account only for three orders of magnitude here.

But at lower pressures, this difference becomes even more important. It's inconvenient. You cannot do this on a linear scale. So you see this, which is supposed to be straight lines, become distorted into exponentials because we have used a logarithmic scale for the specific volume. So this is still the triple point triangle. And excuse the Italian here, but that was done for a booklet I have in Italian.

Obviously working with three dimensional diagrams is not useful, so most people who work with water have a diagram of this sort, which is called the Mollier diagram, in the form of a poster on the wall of their offices. And this is how they compute the properties of water. And this is how-- I'm sure you've probably done some homeworks perusing this diagram in the old days of your undergraduate thermodynamics. This is another view. It's like pressure versus volume.

Yeah. So I should change this because I forgot to update this. The reason I'm mentioning this is because sometimes-- yes. So in order to do this calculation here, I needed all the 40 parameters that Keenan used for the steam tables to obtain the real properties of water in the full range, including drawing these lines. So this is the true thing for water. There is a much simpler model that covers, at least qualitatively, the liquid vapor state, which is the Van der Waals equation of state.

Which looks like pV equals RT . If it weren't for this additional term here and this additional subtracting term here, this would be the ideal gas equation. So Van der Waals, with a simple modification of the equation of state for a gas, for a perfect gas, for an ideal gas, correcting the volume, we're subtracting the covolume. So it's essentially something that represents the volume not available to the particles, because the particles themselves occupy some volume.

And this one that has to do with the attractive forces that happen-- that are important. And we'll return to this, for example, when we talk about the Lennard-Jones potential. The electrostatics of molecules make it such that the electrons are attracted by the nuclei of the other molecule, and so there are some attractive forces up to a certain stage. And so this makes an additional contribution here.

So if you use this expression here, it gives you a curve which is similar to the actual curve for the actual substance. Of course, we cannot match everything. So one way is to choose. It does entail a critical point. And the critical point for the Van der Waals has these values that depends on the values of a and b .

If I choose to select a and b using the actual values for water, for the critical pressure and the critical temperature, I get two values of a and b so I can have a representation of water. It's not exactly good because there is also an expression for the Van der Waals models of the specific volume at the critical point, which is also a combination of a and b . And if I use these values, it will not match. So that's already a first error that I do.

But you see that sometimes simple models capture, at least qualitatively, part of the physics. It actually captures also an additional interesting part. These curves here are the isotherms. OK. So this is the critical isotherm. And these are the other isotherms. As you go farther away from the saturation region or the two phase region, this becomes an hyperbola, and that's the ideal gas behavior.

But the interesting thing happens here inside. Somehow this model allows you to extrapolate also inside of the saturation dome. And so you may go this way. Then the model takes you up and then down again. So we go to a minimum and a maximum here. So that suggests that for as much as this equation represents some physics, it may be possible to have states this way.

The only problem is that they are not stable equilibrium states because, you see, if you impose the equality of chemical potentials here, if you look at the chemical potential, the equality is obtained only if you stop here with the liquid and you start here with the vapor. And this is why when you do things in practice and you boil water here in noisy situation, this is exactly the path that is followed.

The liquid realizes that there is a vapor with the same chemical potential in which it could boil and stay in mutual equilibrium with. But in a less noisy environment, you could also go down here. So it is possible to generate these that would be metastable states, states in which the liquid didn't realize yet that there is a vapor in which it could transform. And also going back to the other side, if you could go up this way, the vapor can go in metastable, supersaturated.

It means it remains vapor even in the region where, in a noisy environment, it would condense. And this is actually experimentally achievable only up to this dotted line. This dotted line is called the spinodal curve. It is the locus of all the minima on this side and the maxima on that side.

And this is because to the left-- so outside, in this region between the spinodal curve and the saturation dome, in this region, the conditions for stability, those second derivatives that we have developed, are still satisfied. So the liquid can exist there. And of course, it is not completely stable, so it's metastable. So if you give it a perturbation which is large enough, it will collapse. It will jump.

The liquid will immediately flash into vapor or the vapor will condense explosively into liquid. In this flashing and - oh, I don't know. Senior moment. I don't remember the name of the collapse. It's a typical phenomenon that can cause the erosion of, for example, blades of steam turbines. Cavitation. Thanks.

All right. Because the vapor goes to this region and then it immediately realizes that it has to condense, and it does it in an abrupt way. That's a shock that creates a damage to the structure. OK. All right. Yeah. We still have a few moments. Maybe we can go ahead with what we-- the subject that we left on the side, but now we have to return. We did the first part, and today we'll do just a little bit more.

Remember, we were talking about exergy and this second law efficiency. We talked about cogeneration the last time and you told me that MIT has cogeneration, which makes me very happy, and district heating. OK. So now that we have developed the simple system model and the bulk flow model for the exchange of mass, we can ask the question.

If I have a certain flow at certain conditions, say, pressure, temperature, and therefore enthalpy, entropy, and possibly also in this case I forget about gravitational potential and kinetic energy. So we ask ourselves, what is the maximum work that I can obtain by using that flow in a given environment? And here I use the environment in two ways. The first way is that I want my machinery to process the flow without accumulating the material.

So the mass that goes in must also go out and must be given to the environment. And I will give it to the environment at conditions where I have extracted as much as I could. So when it is mutual equilibrium with the environment, essentially, at least from the thermal point of view and typically also the pressure point of view. So the environment here provides also an ambient pressure.

And the other way is that I need the environment as a dump for dumping the entropy, because if I have to change the state of my flow from one to this ambient-- to environmental conditions, most likely it will have to change entropy from s_1 to s_a . And that change of entropy, suppose it's a reduction in entropy. It means that I have to extract entropy from the flow. That's the purpose of the machinery. And of course, the machinery will have to give it somewhere because the machinery operates cyclically.

It cannot go accumulate entropy. So the environment is there to accept at least the entropy that I must extract from the flow in order to exploit it. But it may also be there to dump also the entropy that may be produced by irreversibility, by the machinery. But if we are asking for the maximum we can do, we suppose the machinery is reversible so at least that contribution of the entropy produced by irreversibility is not there.

And so this is the setup. As usual, you solve the problem by making an energy balance and an entropy balance and setting the entropy produced by irreversibility equal to zero. This is the result. So the maximum work is the linear combination of changing enthalpy and changing entropy represented here. This is called the exergy of the flow of that bulk flow state with respect to an environment temperature T_a and with outlet conditions that are ambient conditions denoted by a .

Of course, I may also have the opposite problem. It's exactly the same situation. Simply that now I don't want to exploit a certain bulk flow state one, but I want to produce a bulk flow state which is at conditions different from mutual equilibrium with the environment. For example, this is material processing, or maybe I want to heat up some water. What is the minimum work that is needed by this machinery to do it?

Well, again, we use the environment in two ways. We take the material from the environment. For example, we go to a mine for raw materials or we go to a lake or reservoir, the water reservoir for fresh water, and we also use the environment as a provider of the entropy that may be needed in order to achieve that task. Because if the bulk flow conditions one have more entropy than ambient conditions, then I need to give entropy to this flow.

And that entropy, the best way to do it is not to generate it by irreversibility, but that is to get it from the environment. For example, when we heat up water from 20 degrees to, say, 60 degrees, I mean Celsius, yes, we could also do it without the environment. We just could use an electric boiler. The electric boiler would use some work, dissipates it by Joule effect so as to generate the entropy necessary to heat up the water. OK?

Doesn't use the environment. Whereas this reversible situation is like a heat pump setup in which I do take the entropy from the environment and the environment gives me that entropy only if I take also some energy. And that energy gets pumped to my fluid, and that fluid will receive exactly the entropy and the energy needed in order to go from here to there. This is, again, the same exergy as before. OK. Well, I think time is up, isn't it? So we'll take it from here next time.