[SQUEAKING] [RUSTLING] [CLICKING]

GIAN PAOLO BERETTA: So welcome back from spring break. We're still talking about mixtures. We spoke about mixing and separation. And we're going to talk today about stratification. But I want to spend the first few minutes answering a question that I had from a colleague who was following the lectures online and asked me a nice question about, how can we do separation at constant temperature and pressure?

You remember that we did the entropy of mixing by mixing gases. And we obtained this formula for the entropy of mixing. Then we also spoke about the fact that we could have done the mixing in a better way in terms of thermodynamics. We could have done it reversibly and, therefore, extract the adiabatic availability of this situation-- or this state with respect to this mixed state.

We also spoke about computing the minimum work of complete separation of a mixture when in mutual equilibrium with a reservoir, which keeps it at the same T and p. And we found that the minimum work is equal to the difference in the Gibbs free energy of the separated final state from the initial mixture state.

So this diagram shows graphically what the problem is. So we have a mixture, and we want to separate it. And if the mixture is in-- and we want to separate it at fixed temperature and pressure so that, in the end, it will remain in mutual equilibrium with the thermal reservoir, which is at this same temperature.

Now, if the mixture is an ideal mixture of ideal gases, we found that the initial state and the final state, they have the same temperature. And also, they have the same energy. But of course, they don't have the same entropy. So the separated state, we call it B here, as lesser entropy than the mixed state.

So in order to separate, we have to remove at constant energy this entropy to go from here to here. So removing entropy from a system requires another system that picks up that entropy. And that's why we need the reservoir. But the reservoir, which starts at this state here, cannot just pick up the entropy. In order to pick up some entropy, we need to give it, also, some energy.

And so to pick up this amount of entropy, this is the amount. TR times that entropy is the amount of energy that we must give to the reservoir. Of course, these are minimal amounts because we are considering the reversible process, which is the optimal. So the question is, how can we go-- can we do this?

One possibility-- it's on the next slide, so I'll switch back and forth between this and the next-- is to make a process like this. We take first the mixture and cool it down to this state, C. Of course, we have to do it reversibly. So we will use a machinery to do that. And so in order to cool it down, we change the state.

We need the machinery to consume some work, which is equal to the available energy of this state, C, which is colder than the reservoir. But as you remember, the graphic representation of available energy is given by this segment from here to here with respect to this reservoir. So even if it is colder than the reservoir, it has a positive available energy. And finally, then we will do an adiabatic-- a work only, so a weight process, that takes us from here to here.

And this is the sequence. So here is a machinery, which cools down the mixture from the initial temperature to that temperature T, TC. And in order to do that, the machinery needs to consume work, which is equal to the available energy of state C. And while doing that, it will transfer an amount of heat to the thermal reservoir, which is equal to this work because the mixture-- no, sorry, I take it back-- which is going to be different-- to be given by this much. So it's not equal to that work, sorry.

And once we have the mixture prepared in that state, then we can perform our work-only process, like weight process, using semi-permeable membranes that will-- for example, this membrane, which is permeable only to particles, to the black particles, is initially here. Then it's pulled down by the weight. So it compresses the gray particles to their, say, half of the volume.

And then also, this other membrane, which is permeable to the gray particles only, it's on this side here. And then the weight going down here, so consuming work, will push the black particles to their half. So it will do sort of a partial compression of those. In doing that, we go from here to here. So we spend the weights, the sum of the weights. Energies of the weights is the adiabatic availability of this state here.

So this is a possibility to perform. Of course, it requires membranes. It requires reversible processes. So it's not very practical. So many times in practice, when you need to really separate things, you can also use chemistry, chemical engineering and solvents that would extract this substance you're interested in from your mixture.

And then once it has been separated, then you have to recover your solvent so that it is not consuming the solvent-- which could be a physical solvent. Or it could also be a chemical solvent. Or maybe not. That's not a proper word, but to give the idea, something that would preferentially interact and react chemically with one of the components. And then you have to reverse that reaction in order to recover your solvent after you have separated.

But even if you do it chemically, and if the final states are these ones, and your solvent is a dummy variable, so to speak, of the process in the sense that it's cyclic, it goes back to its initial state and remains, therefore, pure at the end, then this still represents the minimum work of separation. And so it is referenced also in order to compute the second-law efficiency of that actual separation process. So let's go now to this problem of stratification.

And we are interested, for example, in the stratification of gases in the atmosphere, like oxygen, nitrogen, CO_2. So remember that we started by saying that for these kind of problems, like in the bulk-flow state model, we model the energy of the substance as given by the energy which is proper of the stable equilibrium state for the given entropy, volume and amounts of the substance, plus a potential energy, which in the case of uniform gravitational field is, as we all know, m gz.

And the mass, of course, depends on the composition. So the local mass of the fluid parcels changes with elevation due to changes in composition. The chemical potentials in this situation are substituted by-- the role of the chemical potential is played by the total potential, which is still the derivative of the energy with respect to the amounts. But now the amounts appear not only here, but also in the mass. And that gives rise to an additional contribution to the potential. So we have the chemical potential plus the gravitational potential.

And so we have-- the sum of the two is the total potential. That is what enters in the conditions for mutual stable equilibrium between fluid parcels and, therefore, also between layers of fluids, parcels of fluids, that find themselves at different elevation in the gravity field. So in order to impose mutual stable equilibrium, we will impose equality of chemical potential-- I'm sorry, total potentials between two layers at different elevations.

We will assume instead, as an approximation, that although we are not going to assume that the temperature is completely uniform, so we are not-- we want to go beyond the model of an isothermal atmosphere, we will assume that the temperature changes, but that the local changes are irrelevant or can be, say, neglected for this computation of the chemical equilibrium.

So in order to apply these, we have to write these chemical-- these total potentials. And the total potentials are written, one, at elevation z plus dz, and the other at elevation z. And of course, we need to use this double contribution, chemical plus gravitational. For the chemical part, we will assume ideal mixture behavior. So the chemical potential is given by the pure component chemical potential, at the same temperature and pressure, plus RT log of the mole fraction of that component.

And then here we have the gravitational contribution and the line above has the z plus dz contribution. So in order-- since these two must be equal, you do some manipulation. You also remember that, since here, we have the difference between the chemical potential at z plus dz-- at the pressure, that belongs at z plus dz, and that at the elevation z.

Here enters the partial derivative of mu with respect to the pressure, which is the specific volume. And that's why in the end, this is what we are left, is the specific volume, dp plus RT, the derivative of the logarithm of the mole fraction, plus the Migdz. And Mi, of course, are the molecular masses of the various components.

So we have one equation like this for each component because all components can be exchanged between layers. And this is actually true, also, for the pure substance. So if you have a pure substance, so just one component, this equation becomes this one. And if you recognize that the specific-- that the molar mass divided the specific volume-- and remember, this is specific volume molar.

So M over v is the density. So this equation becomes dp equals minus the density times g times dz, which leads when you integrate to the Bernoulli equation of static fluid mechanics. But you can also apply it, for example, for a gas. So for a gas, the specific volume is not constant.

So you shouldn't put the-- you should remember that v is RT over p. And therefore, you can integrate RT over p. So you get dp over p on this side. And you have Mg over RT on the other side. You can integrate. So this becomes the derivative of the logarithm. That's why the exponential here.

And on the right-hand side, depending on whether your temperature is fixed or not-- if it is not fixed, you have to integrate in dz the inverse of the temperature. So this is the equivalent of the Bernoulli equation for a gas, which gives you the exponential pressure decay with height for an ideal gas in the gravity field.

If you have a mixture instead, and the mixture is of gases, we can play the same. And here is a similar expression, but it is-- you get one expression like this for every constituent. And this is the partial pressure. So you compute these partial pressures, which also go down exponentially with z, but there is a coefficient of the exponential that depends on the molar masses. So the heavier particles, the heavier molecules, go down faster than the lighter molecules. And so their partial pressures go down faster.

For example, oxygen is molecular weight 32, molecular oxygen. And nitrogen, molecular nitrogen, is 28. So that difference, 28 versus 32, makes it so that the partial pressure of oxygen goes down more rapidly than that of nitrogen with elevation. And therefore, as you go high, the percentage--I mean the mole fraction of oxygen diminishes from about 21% at sea level to lower levels at higher elevations. We'll see a graph in a moment.

Once you have the partial pressures, of course, since this is a mixture of ideal gases, we can use Dalton's law. And by adding them, you get the total pressure. So you see how, also, the total-- you can compute also how the total pressure goes down in the atmosphere. You can-- also, here, we did it for a liquid, for a pure liquid. You can also do it for a mixture of liquids. It's the same. You start from the same equation. Only that now, for the liquid, the specific volume is constant if you can apply the incompressible fluid model.

And so you-- this is the equation to be integrated. And you can combine these two because you have one equation for each constituent. You can combine them into this equation here and integrate. And here is the result of the integral. This is the mole fraction of constituent one at elevation z. Of course, the other constituent has a mole fraction, 1 minus y1.

This is the ratio of the specific volumes of the pure components. These are the difference in the densities in the pure components. This is the molecular weight of one component. And this, again, is z over the temperature. Or if the temperature is varying, it's the contribution of the varying temperature.

Now, in Canvas, you will find an Excel file that I am sharing where I do this calculation, where I made these plots. So I'm considering air. And I'm using an air made of only four constituents, nitrogen, oxygen, argon, and CO2. And I assume that at the elevation of the Mauna Loa laboratory, which is at 3,400 meters, this is the composition. I expressed them in ppm's, parts per million. So today, the ppm's of CO2 is 425 up there.

Of course, the mole fractions are 32 and so on, 44 for CO2. And this is the expression that we use in order to compute the partial pressures. And this Cz is that integral. Or actually, it is a nondimensionalized integral of the temperature. And for the temperature, I am assuming the actual measured temperatures. But there is something fishy here because it should be 1 minus az here. So there is something wrong in this denominator in the integral.

But that's the temperature distribution that I'm assuming, which is the average measured temperature that is found in the handbooks of chemical physics. People have measured the average temperature in the atmosphere. It goes down about six and a half degrees Kelvin per kilometer of elevation.

People have also measured the pressure as a function of elevation. And this is the correlation. p0 is the sea level pressure. And z is the elevation in kilometers. And we are not using this. We just use it as a check for our calculation. So this formula here is these triangles on the spot here, which, as you already see, match pretty well, almost exactly, our estimate based on this calculation here.

So by substituting that-- by doing this integral, which can be done, and then computing the function Cz and using the mole fraction-- the mole molecular weights, you find the partial pressures. For example, 0.8, this is the partial pressure of nitrogen. Zero elevation is at sea level. 3.4 is Mauna Loa. And this is the top of Mount Everest, 8.-- I forget now, 8,500 something meters.

So you see the partial pressure of nitrogen goes down. This is oxygen. It also goes down. And of course, the sum of the two plus the sum also of the others, argon and CO2 have such low partial pressures that they-- in order to visualize them, I multiply them by a factor of 60 for argon and a factor of 1,000 for CO2.

So this one is CO2, the green. No, I'm sorry. This is-- the green is argon. And the blue one is CO2. This is the value measured at Mauna Loa. But as you see, at sea level, the value is much higher. And at Mount Everest, it's much lower. These are the mole fractions.

But before we go to the mole fractions, oh, you sum up the partial pressures and you get the total pressure, which is this other curve. So the reason why, at the top of Mount Everest, the air is thin is twofold. One is that-- the main one is that the pressure is about 0.32, so it's 32% So every time you breathe, you take in only-- the volume of the lungs, they're more or less the same. So you take in 1/3 of the air.

Plus, there is the second order effect, which has to do with the molecular-- the composition. That as you see, the mole fraction of nitrogen goes up and that of oxygen goes down. But see, it goes down very slightly. And so instead of 21%, you get maybe 20% or 19%. The effect is more important for CO2. The mole fraction changes quite a bit with elevation. So if you measure 425 ppm's at Mauna Loa, at sea level, it's over 500.

Now, this is just the beginning, of course, of things that you can calculate along these lines. And so I wanted to point to you this website, which is called Climate 4 You, which contains a lot of measurements, historical measurements, of CO2, temperatures, all sorts of comparisons.

So I'm not going through details of these plots, only to show you that I'm sure you've seen this many times. This is the CO2 going up along the years. This is from 1955 to the last month. This is, what, January? And this is the various ways to measure the average temperature. Many labs, many universities, have their own ways of averaging over six months, one month or one year, and so on. So you get smoothed lines or peaks. Anyway, this gives the idea that the temperature is indeed going up.

And of course, not only the atmospheric temperature, but also, this is the temperature of the upper layers, say the first hundred meters of the oceans, which is the layer in which there is a lot of mixing due to turbulence. So it's an average where, of course, the reason I'm bringing this up is that between that layer and the atmosphere, there is that tendency to reach mutual equilibrium for the various gases, including CO2, because CO2 gets dissolved in water.

And then also, CO2 being a higher molecular weight molecule, has the tendency to go down. So once it reaches-- the modeling of the first layers are sort of complicated by the chemistry because CO2 gets ionized, solvated into bicarbonates and then carbonates. And so you also need a chemical equilibrium, which is something that we have not done yet.

But eventually, when you go at about 450 meters of depth, CO2 becomes liquid also. So you get a liquid-liquid mixture. And from that point on, that stratification formula that we derived for liquids could be applied in order to see how the CO2 concentrates in the bottom layers of the oceans where, in fact, there are literally lakes of supercritical CO2. And it's actually a major place where a lot of the carbon in the planet is stored.

These other plots represent-- compare these CO2 oscillations with temperature of the oceans and/or of the atmosphere. They also tend to show a delay from the peaks in the temperatures of the ocean and atmosphere and the peaks in the CO2. So many people are speculating about the origin of these-- because, as you know, of course, by burning fossil fuels, we produce CO2 that goes into the atmosphere.

And a good part of that, maybe half or almost, let's say, 40% of it, goes into the ocean through this equilibrium. But of course, we are concerned about the amount that stays because it's a greenhouse gas. Actually, just to mention that just the other day, there was an article on MIT Tech Talk or-- about people concerned about this new or little mentioned gas, which is 24,000 times more powerful than CO_2 in terms of greenhouse gases, which is, I think, some sulfur hexafluoride.

Now, that molecule, though-- I tried to read quickly through that article. I couldn't find-- they mention how much it's produced by the various countries, but it doesn't mention the concentrations, how many ppm's we have in the atmosphere. They also say that it is very stable in the atmosphere. And I'm sure they have their reasons to say that. On the other hand, a heavy molecule by gravity tends to go down.

So I haven't found yet-- I don't think these people of the Climate 4 You website have already done-- collected data about that particular molecule. But I'm sure that soon they will because they're very keen at keeping updated with all the various news. And also, this graph reports the solar activity as measured by the sunspots, solar spots. And there is a cyclic activity. And this activity is related to some effects on the cosmic rays and the formation of clouds.

So this also-- a lot of people who study climate change are studying the connection between this kind of solar activity and the clouds because the clouds, as you know, are the source for cooling of the planet via the albedo because they reflect some of the light away. So by controlling clouds, cloud formation, you could also control global warming. So enough for the advertisement of this website, which, of course, it's not an advertisement, but it's simply mentioning, because it's a good source of scientific data.

Back to stratification. Here is another problem, which is very similar to the one that we've done with gravity, which is centrifugal force. If you have a fluid, which is static with respect to a rotating reference frame, you know that there is a force like gravity that pushes you-- pushes the heavy particles towards the exterior.

And, well, it turns out that you can model this kind of-- it's not really a force. It is a fictitious-- an apparent force. Apparent forces can be represented by a negative potential energy. If we assume an energy like this, and instead of mgz, we use the mass times the angular velocity times the r squared, this is the negative potential energy, we get a total potential, which has this negative contribution.

And then if we consider the mutual equilibrium between two layers at different distance from the center of the axis of rotation, so you impose that the chemical potential here and there are equal, again, we assume, a mild effect of temperature, but not completely uniform temperature.

So we do-- yeah, you go over the same steps. And here, there is an error definitely here because there should be a 1/2 m omega squared r dr here, I think. So I need to correct that. Yeah, it is something like this. So this is the general one that applies for all substances, for each substance of the mixture. If you don't have a mixture, but a pure substance, you get an equivalent of the Bernoulli equation for the statics, for the fluid statics here.

So here, the pressure goes, again, exponentially. As you go down the centrifugal force, there is no minus sign here. So the pressure goes up. It's opposite, then, the gravity field for a gas and for a liquid. It goes up exponentially for the gas and parabolically for a liquid. And then, again, you can apply the same formula to find the partial pressures in gas mixtures or the mole fractions in liquid mixtures. I skip the details because they are exactly parallel, and with the case of gravity.

I mention this because in the energy business, centrifuges are important because they are used, for example, to separate, to enrich, the uranium from the natural concentration in the isotope 233 (I meant, 235) which is the fissile nucleus, which is 0.71%. You need to take it up to 3% or 3.5%, depending on the reactors.

And in order to do that, you make this react with an hexafluoride. And then you put them into this centrifuge, which separates the small difference between the molecular weight of the 235 and the 238 isotopes. That minute difference is enough to separate the gas. So you'll find more of the 238 towards the outside.

And then, of course, this is not completely static. Otherwise, you wouldn't have any yield in the process. So you need to do the extraction. And the extraction complicates things because of secondary flows and so on. So these are just details. But there is this nice article in *Scientific American,* if you're interested, that does all that, very well explained.

And then, of course, so you have to run one centrifugal. From one, you get slightly enriched. You put it in the next stage and so on. And this is how many stages you need in order to obey-- obtain a correct cascade so that you get 3% uranium, 235 up here. You get depleted uranium, just 0.2%, from a feed, which is the natural composition.

And then of course, you'll read about the fact that, also, these depleted uranium is problematic because it's kept in some cylinders somewhere nearby these separation plants. And sometimes, there are accidents also there because these steel containers get rusted. And so there is a lot of cost associated with not only the separation, which is energy consuming, but also keeping the sites safe.

In spite of all these costs, the cost of nuclear energy is still competitive, very competitive. And so many countries are using it. And of course, a good part of the investment is also into doing some kind of control and management of the wastes, and the byproducts, and so on. And these costs can be huge.

I just mentioned, for example, that in Italy, we had a referendum in 1989 that banned all the nuclear power plants. We had a few. And one was already-- was just built. And that one, in order to keep it closed, you cannot just close it and get away. It still has, after 40 years-- no, 35 years, I think it has about 200 people working there just to keep it, how do you say, stopped, not working, offline.

Yeah, there is another very similar problem that can then be done with exactly the same logic that we have done for gravity and centrifugal field. Now, this is for an electric field. And this also gives us a chance to introduce the electrochemical potential. Electrochemical potential is one in which you have that your fluid parcels also contain charged particles.

So if we denote the charge by q, the q, the charge, is given by how many particles you have times the charge per particle. So z is in terms of the charge of the electron. So for example, sodium plus is an ion that has z equal to plus 1 because it has the charge of an electron, but of the opposite sign. So it's a plus 1. An electron has a charge minus 1. z is minus 1 for the electron.

And F, this F, is called the Faraday constant. And it is the charge of a mole of electrons. So each electron has a charge, which is given by this-- I've reported all these digits because, a couple of years ago, it has been decided by the international system of units, I think, by somebody, that these are the digits to be used. So there is no dot, dot, dot, as there used to be.

And also, for the Avogadro's number, that's the number you should use. And this is also for the Boltzmann constant. All right, so if you take an Avogadro's number, so you multiply this times this, you get the Faraday constant. And the product is something like 96,500 coulombs per mole, something like that. Whereas, of course, you know that-- remember that if you multiply Avogadro's number times Boltzmann constant, you get the gas constant.

So you shouldn't be confused by the fact that we call it the gas constant. And then you apply it to liquids and solids because, after all, it's just the Boltzmann constant. It also happens to play an important role in gases, but not only in gases. So calling it the gas constant is a bit misleading and perhaps confusing.

Anyway, so this is the charge of a mixture with this many constituents, each one of them having a certain partial charge. And the energy that you have to add to the energy proper of the stable equilibrium state of the noncharged components is equal to the charge times the value of the electrostatic field. So phi is the field.

And as you remember from your physics, once you have a field, the conservative field, you take the gradient and minus the gradient of the field. It gives you a vector because the gradient is a vector operator. And so you apply it on a field which varies with position. And minus the gradient is called the electric field. It's a vector.

So the bold x here means x, y, z. It's a location in space. And the bold in these symbols means that they are vectors. It's true that, also, these n's are also vectors, but they are not vectors in x, y, z, but it's simply a list of numbers. So yeah, but I hope you'll not get confused by these details.

So when you do-- when you compute conditions for mutual equilibrium, as usual, we have this derivative of energy with respect to the amounts. But also here, the amounts now are not only in this stable equilibrium state, non-charged part of the energy of your fluid parcels, but it's also on this side. And the charge depends on the n's.

So that's when you do the partial derivative with respect to n. You pick up from here z and F, which is then multiplied by the value of the electrostatic field. And so this is the electrostatic contribution. And this is the chemical contribution. And that's the total, which is in this business called electrochemical potential.

All right, so the analog of the problem that we've considered is that now you have an electric field. So suppose you have some charges or a mixture of charges or charged particles, for example, a solution in which you have electrolytes-- in an electric field. So the electric field is directed. I made it for analogy, like gravity, like the same direction of gravity, so that this is x.

All right, same logic. Apply the equality of chemical potential between these two layers using now this formula for the total potentials. Sorry, I said chemical. That should be total potentials. And after the details, this is what you obtain. This is the expression, specific volume, dp RT times the derivative of the logarithm of the mole fraction.

And here is the contribution of the gradient of the electrostatic field. So this is minus the electric field dotted into dx. This is true also for the pure substance. So if you have a pure substance, so it's just one-- say, a charge in some electric field, charged particles in electric field, you get equations which are similar to the ones we obtained for gravity.

But of course, typically, you don't have only charges of one kind. You have mixtures of charges. And so this is the expression for the partial pressures if they are in the gas phase. Or if you are in solution, so if your charges are in an electrochemical solution, and you want to compute how the concentration changes as you move along the direction of the electric field, this is how this formula integrates. You can also do it for a variable temperature.

For the simplest example here, suppose you have the plates of a condenser. Or, say, an anode and a cathode. And you will have some charge carries, so particles with charge that are between these two. So if the plates of a condenser are close enough, the electric field (I meant, potential) phi varies linearly from the value of field (potential) in one plate and the value on the other plate. So you get a linear phi. So the electric field, which is the derivative, the gradient in the x direction is the derivative with respect to x, is constant.

And if you apply those formulas for the liquid case, the mole fraction comes out to be exponential. So the plus-- the positive charges will have a concentration that decays as you get far from the negative electrode because they like to stay near the negative. And the negative charges decay exponentially as you go far from the positive electrode.

All right, so now we can move to another interesting topic that is one of-- what happens when mixtures of various components boil, or condense, or freeze? So we are first going to do something with ideal models. And then we'll say something about nonideal models.

You remember we talked about the Lennard-Jones potential. I'm not spending much time on this again. This can be, through molecular dynamics or Monte Carlo numerical simulations, a way to model substances. In fact, you can model a pure substance with just those parameters.

There are, I think, if not thousands, maybe hundreds of articles that have played this game in recent years because of the advances in molecular dynamics. And so people have developed this pseudo substance that is called the Lennardjonesium. So it's the Lennard-Jones pure substance, where you play with non-dimensionalized properties.

For example, this is the nondimensionalized density. It's number density, so particles per unit volume. This is the nondimensionalized temperature. And there has been a dispute for a while about, for example, how the critical point is characterized.

But now there is a very nice article in Wikipedia under this title. That's where I also took these plots, they're very nice, which summarizes and explains the details of these calculations. So the critical point of this fluid is given by-- it's like a universal fluid, no? So it's given by these values.

So once you fix-- you take your substance, and you think that your substance is correctly described by a value of epsilon and a value of sigma, then you know that that substance will have this critical temperature, this critical pressure, this critical volume. So that means, also, that this is a way in which you can infer the values of those epsilons and sigma for a given substance.

If you know the substance and you, therefore, know-- because people have measured the critical pressure and critical temperature, you can make a system of these two equations and obtain the epsilon and the sigma that properly correct-- that properly get you to the critical values of T and p.

Unfortunately, there are only two parameters, the epsilon and the sigma in this model-- they are not enough to make the model universal because the most difficult one to model is the volume, the critical volume. So if you match temperature and pressure, then you're going to be likely off the critical volume.

In fact, for example, if you compute pv over RT, like the ratio, the ideal gas ratio, at the critical point, since these values are fixed, you take these ratios, it becomes dimensionless. This is called the compressibility factor, typically denoted by Z.

And for the Lennardjonesium this is the number. If this model was universal, all substances would have this number for this critical ratio. That's not really true because, for example, if you go water, it's pretty off. It's 0.23 instead of 0.31. Helium 4, it's 31, so it's pretty good. Argon, also. CO2 is off.

So there is missing-- this says that the Lennard-Jones model is incomplete. It's a very good starting place, but it's incomplete, possibly due to the fact that, especially when you get to the liquid phase, the Lennard-Jones considers only pairwise interactions. And instead, when the molecules get close to one another, also, three body interactions may become-- may have a role, and they are not accounted for in this model.

But you can predict condensation and boiling. You can predict the fact that the substance below the critical temperature doesn't like to stay in certain regions. So it prefers to separate into a liquid and a vapor phase. And also, it predicts pretty well the surface tension. So you can measure the surface tension.

For example, here, it shows it as a function of temperature. This is the interfacial energy of the molecules that live in between the liquid and the vapor on the other side. So they are in a-- in order to stay there, which is a more uncomfortable location to be, they have more energy.

So the surface energy can be interpreted as the extra energy that the molecule needs to stay on the interface, and which therefore-- Also the triple point can be computed. And you can compute the volumes at the triple point, where you get the solid, the liquid, and the vapor coexisting. So you can compute what is the specific volume that they have. This is the volume of the solid.

You can compare the volume of the solid because these are-- after all, it's a model of some kind of soft spheres. And you want to compare how they fill the volume. You know, if you take spheres and you try to pack them in a given volume, you're not going to fill the entire volume because, of course, there is the void between one and the other.

So you can do perfect packing, and the perfect packing has-- let's see, where is that? I didn't write it here. Yeah, here, the volume of completely packed spheres is this one, is 1 over the square root of 2 times the volume of the particles. So it means that the other 30% of the volume is the empty space between the various spheres.

So here, the triple point, the model predicts that the solid is not completely packed. It's 1.5, the completed packed volume. The liquid is 1.7. It's better packed than the solid (I meant, the solid is better packed then the liquid). And of course, in the vapor, the vapor has a much higher volume per particle, 800.

Here, you compute the compressibility factor for the vapor at the triple point. You find that it is approximately 1, very close to 1. That means that already there, the vapor behaves pretty much as an ideal gas because you see pv equals RT. And then these are plots that show what other parameters you can play with in order to adjust, but also to make the numerical calculation less heavy.

For example, by truncating the potential and saying, well, beyond a certain distance, so instead of having small digits, I'll just put it 0. That makes-- that induces some errors, and this kind of error, or maybe errors, but may also be considered as an additional tool with which you can gain that extra parameters to play so as to fit, also, the volume.

All right, so this is one-- this is the numerical world. In the old times, physics couldn't enjoy these numerical possibilities. And so there was a lot of physical thinking. And van der Waals, in his PhD thesis, for which he got the Nobel Prize in 1910, developed this simple model with, again, two parameters, only two parameters, like Lennard-Jones.

b is the covolume. So it's related to sigma, say. And a is related to the force of attraction. So it's related to the epsilon of the Lennard-Jones. And this is two ways of writing the van der Waals equation of state, which is an improvement with respect to the ideal gas law.

If you set a equals 0 and b equals 0, you get pv equals RT, which accounts also for the attractive forces and for the fact that the volume available to the molecules is not the entire volume because, especially in the liquid phase, the volumes themselves--I mean the particles themselves occupy some volume. And so that's not volume available for the other particles.

So that's the physical intuition behind this. Once you have an expression like this, which is an equation of state, so we have a function of volume between volume pressure and temperature. As you remember from the initial lectures, you can compute the compressibilities, the coefficient of-- this is isothermal compressibility, the isobaric expansion, which enter also in the Mayer relation, which gives you the difference between the specific heat at constant pressure and constant volume.

So by doing those derivatives with this equation of state, here is what you get. For example, in the limit-- for vapor states, in the limit, not the ideal gas limit, but in the limit of vapor, in such a way that the covolume is-- the volume available to the particles is much greater than the covolume. And also, the particles live far away from each other, so that the attraction is also small.

Then these approximate. You get an ideal equation of state. You get cp minus cv equals R. So that's the Mayer relation for ideal gases. You don't get exactly 0 for these things. So you get corrections, which are useful to represent non-ideal gas behavior. For example, this is the Joule-Thomson coefficient, which is the derivative of temperature with respect to pressure at constant enthalpy, which is useful when you expand a gas and a throttle to compute, whether it is going to heat up or cool down.

Well, or you can also compute the critical point because, as I will show in a moment-- or actually, let me show it now. If you draw the isotherms, for example, at constant temperature-- this is a pressure versus volume diagram. And these are the isotherms. So in the ideal gas state, pv equals RT. So if T is constant, pv equals constant. So this would be an equation of a hyperbola.

As you see, as you go lower in temperature and also in pressure, these isotherms get distorted. And at one stage, there is one isotherm, which we call the critical isotherm, in which there is-- in which the first order derivative goes to 0 and you have a flex. But you can apply the model, also, below that. So this is what the van der Waals isotherms would look like. It goes up and down.

Now, if you remember when we did the Le Chatelier-Brown principle, we found that one of the stability conditions were that this compressibility is greater than 0 and, therefore, the derivative, the first derivative-- along an isotherm, so at constant T, the derivative of p with respect to v, which is the slope of these curves, should be negative.

So here, yeah, it goes down. It's negative. Here, it goes down. It's negative, negative. Here it goes to 0. And then the derivative goes up, positive, positive, positive, until here, and then it keeps going down. So this region here, where the derivative of the isotherm is, where the slope is negative (I meant, positive), does not satisfy this stability condition. It's an unstable situation. That's the situation in which your particles don't like to stay and they prefer to separate into a dense phase and into a non-dense phase, which is the vapor.

Now, going back to the previous slide, using the model, we can also compute the chemical potential. The chemical potential is important because, for example, when we have mutual equilibrium between phases, we need equality of chemical potential. So even for a pure substance, if you have the liquid and the vapor in mutual equilibrium, they have to have the same chemical potential, equality of chemical potential, not only of temperature and pressure.

So you can compute the chemical potential with the van der Waals model by integrating the usual derivative that we use often. The derivative of mu with respect to p is equal to the specific volume. So mu is equal to-- you integrate over pressure. So you have an integration constant, which depends on temperature only, and then an integral of v in dp.

Then you do this integral by parts. So this could be also pv minus integral of p in dv. And since p is given here by the van der Waals equation, you can do that integral. And the result is that the chemical potential is a constant of integration times a function of T and v, this function of T and v.

We don't know that constant, c of T, but we can reason even without knowing it by using the fact that we know that when you have liquid and vapor in equilibrium, the chemical potentials of the two phases must be equal. Not only, but also the pressure and the temperature.

So if I have-- so I have two conditions, equality of pressure. So pf is equal to pg. And that's the saturation pressure. That's what we call the saturation pressure when we have a liquid and a vapor in equilibrium. So that gives us-- by substituting, here pvdW means substituting this expression here for the pressure.

So we get one equation, where the unknowns are two. It's the volume of the liquid phase and the volume of the vapor phase. The temperature is a given. So that's one equation that derives from the condition of equality of pressures. Then equality of chemical potentials says that the chemical potential of the liquid is equal to that of the vapor.

So you see the constant of integration goes away. And you have this equality, where the function f is this function here. So now I have a system of two equations for a given temperature, from which we can solve for the specific volumes of the two phases in mutual equilibrium.

And so once I have computed that volume, either vg or vf, I can compute this function f. And I can express the chemical potential-- or actually, the difference between the chemical potential and the chemical potential at saturation as f minus-- so in other words, I'm using the chemical potential at saturation to express these integration constant.

So this is what is done on this other graph. We plot mu minus mu sat. So essentially, that it is that function, f at Tv minus f at T vg. It is a function of temperature, and volume, and so on. So for an isotherm, here is how they look. If I am above the critical point, it's a continuous monotone function.

But when we get to the critical point, we get to the beginning of something that is kind of a discontinuity. Let's look at it far away from the critical point. So let's look at it for this isotherm, this one. So the chemical potential goes like that. It gets to this point, where it crosses the chemical potential for the vapor. So it's the one computed from the other side.

At this point here, the two chemical potentials are equal. The pressures are equal. The temperature are equal. So that is the stable equilibrium state. And it corresponds to having vapor in these conditions with this specific volume and liquid in that condition. That's the saturated liquid. That's how the mixture likes to separate. This is the stable situation.

However, you see that these van der Waals curves continue down, continue down, without violating the stability condition. The derivative, this derivative here, is still negative. So these are still somewhat stable. They are not fully stable, but they are somewhat stable. They are metastable.

And also on this other side, here the derivative is negative. And it corresponds to this branch of the chemical potentials that goes up there. Then you get a switch in which the derivatives of the pressure, the stability condition, gets violated. And it corresponds to this. This is what happens to the chemical potentials.

So for example, if I wanted to-- if I plot that thing a bit enlarged here, and let me consider this value of pressure, I have three values of the chemical potential. So the chemical potential for the van der Waals has three values. And notice that here we are plotting mu minus mu sat. And remember that for a pure substance the chemical potential is the Gibbs free energy.

So this one of the three points is the one that has the minimum Gibbs free energy that corresponds to the stable equilibrium state. And the stability condition is met by, first of all, having that the derivative of p in dv at constant T is negative. And second, the condition of equality of mutual equilibrium between the two phases.

This other one, the intermediate state is metastable. It satisfies only the condition that the dpdv is less than 0, but not the equality of chemical potentials. And this other one is unstable because it doesn't satisfy that.

So what's the metastable situation, somewhere here? If I'm somewhere here, I have a liquid that doesn't realize yet that it would be more stable by evaporating. Or maybe a liquid that, in order to evaporate, needs to form the first little bubble. And forming a bubble in a liquid requires energy because you require the surface energy, the interfacial energy. So you need energy to do that.

And that is why these metastable states are feasible in practice and experimentally. If you manage to-- for example, here you have a liquid, which in stable conditions at a given temperature. And then you lower the pressure. So you decrease the pressure suddenly. Then your liquid finds itself at a lower pressure at the same temperature down here.

It is superheated with respect to that pressure. And therefore, its stable situation would be to become-- to evaporate. But in order to evaporate, it needs some energy to form that interfacial, that initial bubble. And in fact, the moment it gets that energy, maybe from some noise, from some vibration, from some cosmic ray or particle that provides that energy to form that surface, what happens?

You see, consider it, again, a plot having to do with the Gibbs free energy. This state here, with respect to the stable state, has this much extra free energy because that's the metastable state. So this extra free energy is there. The moment you have provided the initial trigger to nucleate the first bubble, then it becomes an explosive process, the collapse from the liquid to the vapor because all this free energy is there, available, is made available to form additional surface, additional bubbles, and all that.

So you only need to tell the liquid that it is in that metastable state, and it will start and burst into-- and the same is on the other side. On the other side, if you are here, so this-- this was a liquid. And this is the vapor. The same here. Here is the metastable, this is the unstable, and this is the stable.

See, you get this much free energy as soon as you have-- actually, I think I misspoke. You have to turn around all what I said because, when I'm here, this was the vapor. This is the vapor up to here. So this is the metastable vapor. And what I said before had to do with the liquid. So the liquid is here. So this is the metastable liquid. Let me write it down, metastable vapor. And this is, instead, metastable liquid.

Also, here-- so this is the unstable. Also here, you get-- also for the vapor. You get, again, the-- now, for the vapor, of course, the energy is not needed to form the first bubble, but the first drop. And as soon as you form the first one and the system realizes that there is a more stable state, it will use all the free energy to redistribute fast that free energy in order to form the surface that is needed to form those drops in order to condense.

Now, this phenomena have been worth another two Nobel prizes. So one is the one by Wilson, who invented this method. It's called the cloud chamber. And the other two, Glaser, the bubble chamber. These are both ways to detect elementary particles. These were the initial ways in which you could-- I think also, somehow, similar ideas are used today in more modern detectors.

But see, what happens is that in the cloud chamber, you form a subcooled metastable vapor. So you form something like that. And in the bubble chamber, instead, you form a superheated liquid. So they are sort of symmetrical devices. And then you wait for these particles that you want to measure, you want to visualize.

These particles deposit energy. Typically, they ionize the liquid or the vapor in which they travel. And that ionization energy is what triggers the formation of either the bubbles, or the drops. So in this case, you form little drops, like the drops that you see in the clouds.

In fact, this is the same phenomenon, whereby some part of cloud formation is triggered by cosmic rays. As you know, the Earth is continuously hit by a flux of cosmic rays. These are charged particles with a lot of energy that come. And when they hit the atmosphere, they provide-- and the atmosphere has some water vapor in it.

But that water vapor didn't have enough energy to form the droplets to-- the cosmic rays provide that energy, and that triggers the formation of the clouds in that neighborhood. And here it is the same. Then after-- and, of course, these-- then you have to light-- to put the light in a particular way so that you visualize these traces, these trains of droplets that have formed.

So the last thing on the van der Waals is, well, OK, then what happens if we instead are in the unstable region. So suppose you start from an unstable. Suppose you manage to-- so how can you do this, prepare a sample in a state which is unstable? Well, you have to do it quickly.

For example, you remember this is the pressure. So you can go very quickly down in pressure. And therefore, your-- so from supercritical or from above the saturation curve, you just quench or you cool down quickly. Although, cooling is more difficult because cooling requires extracting heat.

And heat is kind of a slow thing to do experimentally. But you can do it in thin samples, like between two glasses, two small glasses, like in the chemistry labs. And therefore, by cooling that, somehow, it cools immediately the entire surface of the fluid. It doesn't require too much time because it's a thin layer of fluid.

In any case, suppose you have-- these are numerical simulations, very nice. And there are three cases. One is the middle one, is when you drop into this region here, the unstable region, with the critical specific volume. So this is the critical point. You cross the critical point.

And then you have a development of, how do you say, a pattern. First, initially, the mixture-- I mean not the mixture-- Your substance is homogeneous, and then it begins to separate. The separation is in terms of bicontinuous. So you see the blue particles are all connected to the blue particles, the red particles to the red regions.

Whereas, if you are off critical, you form either bubbles, the red things are bubbles, or drops. But what is most important is that this phenomenon occurs very quickly because, again, of this important free energy that is there and is available to form all these interfacial regions, initially small.

And then after a while, once you have formed all that, then the system will try to coalesce in order to reduce the surface tension, reduce the surface area. And so the two bubbles will form a bigger bubble so that the surface area goes down. And that is a way to go down in free energy.

And, yeah, time is up. I think I forgot to say, but the word spinodal appears all over, that this curve here, that is the locus of the points inside that separate the region between unstable and stable. It's called the spinodal curve, spinodal curve. And for van der Waals, you can even compute its equation, which is this one. Yeah, enough for today.