Introduction to Statistical Mechanics
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Lecture no. #13
Van der Waals fluid

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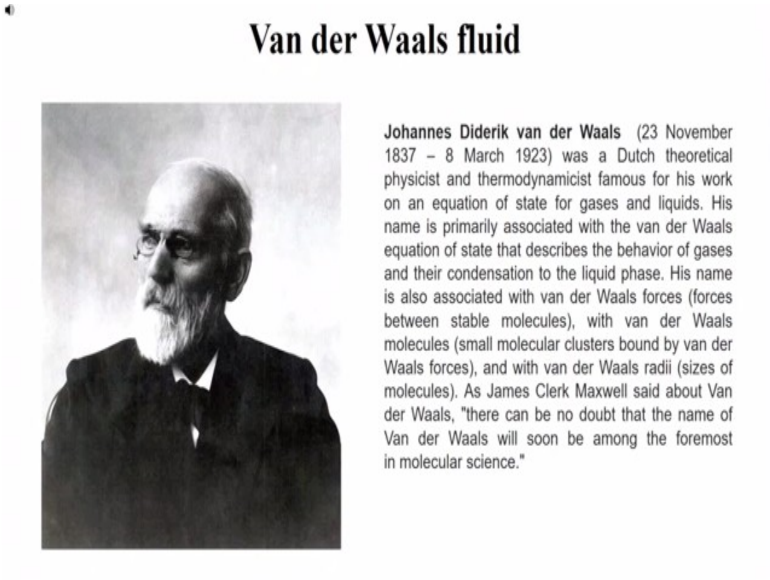

Van der Waals fluid

Johannes Diderik van der Waals (23 November 1837 – 8 March 1923) was a Dutch theoretical physicist and thermodynamicist famous for his work on an equation of state for gases and liquids. His name is primarily associated with the van der Waals equation of state that describes the behavior of gases and their condensation to the liquid phase. His name is also associated with van der Waals forces (forces between stable molecules), with van der Waals molecules (small molecular clusters bound by van der Waals forces), and with van der Waals radii (sizes of molecules). As James Clerk Maxwell said about Van der Waals, "there can be no doubt that the name of Van der Waals will soon be among the foremost in molecular science."

Okay, so let us begin a new topic, which is Van der Waals fluid. So Van der Waals fluid is an example, a simple, the simplest example of a non ideal gas basically what, you know ideal gases, classical ideal gases specifically, they remain gases regardless of what pressure you apply or how much you will lower the temperature, never going to change phase. So, however, in real life, all gases are going to either liquefy, or solidify depending upon how much temperature you lower or how much pressure you apply and so on. So if you want to know if you own the subject of statistical mechanics to have any relevance to real life. You had better be studying gases that can in principle liquefy, even in theory. So, because we know in practice in reality they do liquefy and, and even solidify. So the question is, how would you go about studying a non ideal gas. So, in general what we talked about in this chapter in this section is a fluid.

So fluid is anything that flows. So by definition it excludes solids. So I am going to only focus on two phases, that is one is the gaseous phase and the other is the liquid phase. So the idea is to come up with a model, a simple model that describes a fluid. So that means a phase, which could be a gas. But then if you do appropriate things to it, such as lower temperature or apply more pressure then, in principle, it could also become a liquid.

So I want to be studying such a system, mathematically and using the methods of statistical mechanics and thermodynamics that I have learned till now. So the question is, how would I do that. So the first person to do it in a satisfactory way was the Dutch physicist Johannes Van der Waals, so you can see from this. This picture that I have displayed, that he lived between 1837 and 1823. And so his main contribution was to what is called a Van der Waals equation of state.

For a Van der Waals fluid. So Van der Waals fluid as the simplest, you know, caricature of a real fluid that you see in real life. So let us, let us go ahead and discuss what Van der Waals fluid is, ok.

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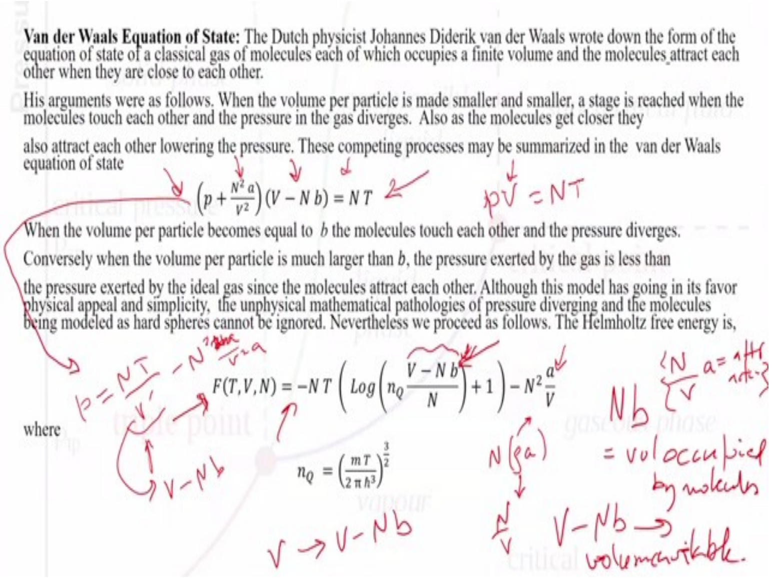

Van der Waals Equation of State: The Dutch physicist Johannes Diderik van der Waals wrote down the form of the equation of state of a classical gas of molecules each of which occupies a finite volume and the molecules attract each other when they are close to each other.

His arguments were as follows. When the volume per particle is made smaller and smaller, a stage is reached when the molecules touch each other and the pressure in the gas diverges. Also as the molecules get closer they also attract each other lowering the pressure. These competing processes may be summarized in the van der Waals equation of state

$$\left(p+\frac{N^2 a}{V^2}\right)(V-N\,b)=N\,T$$

When the volume per particle becomes equal to b the molecules touch each other and the pressure diverges. Conversely when the volume per particle is much larger than b, the pressure exerted by the gas is less than the pressure exerted by the ideal gas since the molecules attract each other. Although this model has going in its favor physical appeal and simplicity, the unphysical mathematical pathologies of pressure diverging and the molecules being modeled as hard spheres cannot be ignored. Nevertheless we proceed as follows. The Helmholtz free energy is,

$$F(T,V,N)=-N\,T\left(Log\left(n_Q\frac{V-N\,b}{N}\right)+1\right)-N^2\frac{a}{V}$$

where

$$n_Q=\left(\frac{m\,T}{2\,\pi\,\hbar^3}\right)^{\frac{3}{2}}$$

So Van der Waals equation of state so the basically before I get to the equation of state let me tell you what the fluid, it actually is. So, Van der Waal imagined that ,he imagined the usual gas that means we which has all these molecules. And unlike an ideal gas, which only interacts with the walls of the container. So he said that, you know, we should also be considering the idea that when the molecules approach each other. Then, when they are sufficiently close they can attract each other so the idea is that they, they have a certain short rain attractive interaction, which contributes basically to the lowering of the energy because it is attractive. So there is a kind of lowering of energy, and the amount by which it gets lowered, that is the is proportional to the density of particles so that the the lowering per particle is proportional to the density of particles so that is what we postulate, and the other thing.

Which is concomitant again with this idea as I see each molecule. He assumed had a certain finite volume. So, so as a result, the volume actually that is available to the fluid is the total volume in the box minus the volume occupied by the molecules. So, these are the two postulates that winder was made about his real fluid. So you can see that that is kind of captured in this free energy so it easier to start in terms of the free energy.

So the idea is that you replace the volume. So, if, if I did not have this b and this a if I put a and b to 0. So what i am going to be describing is the perfectly ideal classical gas. So now, the idea is to systematically modify the free energy of an ideal gas to, to be able to start describing a non ideal fluid. So the question is how do you do that? So the way you do that is to, you know, adopt or incorporate both the postulates of Van der Waals.

So the first postulate is that the volume available to the fluid is not the volume of the box which is V, but rather it is the volume of the box minus the volume occupied by the molecules. So the Nb, b is the volume occupied by each molecule, then Nb is the volume occupied volume occupied by the molecules all the N molecules, okay. So, as a result V-Nb is the volume available to the fluid. So that is why here in. So, in the free energy expression wherever there is V.

I am going to substitute V-Nb so implying that the volume available to the fluid is now less. So, so i am going to systematically modify the free energy of an ideal classical gas to obtain the free energy of a non ideal gas. So how would I, so this is how I do it so the. The first postulate, which is replace V by V-Nb. The other thing I should not forget to do is incorporate the idea that there is an attractive interaction between the molecules, which basically lowers the energy.

So it is the attractive interaction per particle is actually proportional to the density times A. So this is the attractive interaction. The amount by which the energy gets lowered. So a is some constant, which is measures the strength of the attractive interaction. And it is clearly proportional to that density so more molecules there are per unit volume, the more attraction there is clearly, they are going to all come closer, more easily and then there is more attraction, so it is proportional to the density. So the free energy is extensive so it is proportional to N.

But then there is also a intensive quantity which is which is basically tells you the attractive energy of the attractive interaction, which is proportional to the density times a constant which signifies the strength of the interaction, rho itself is N/V okay. So if you swallow this if you accept that this is a valid modification of the ideal gas free energy. Then you can go ahead and ask yourself what are the consequences of this modification.

So happens that you can work out the equation of state so once you know the free energy you can do your usual thermodynamics and work out the equation of state, and you end up with this. So, this is the usual starting point, that people use to describe Van der Waals fluid. So, it has its usual feature namely that I have replaced the volume so this is just PV. So this has a very familiar ring to it, that is it is PV = NT, is the usual classical ideal gas equation.

So all I have done is modified this in this fashion. So I have replaced the volume of the fluid / the volume available to the fluid, and that is volume minus the volume occupied by the molecules. The volume of the box, which is V minus the volume available to the fluid which is volume of the box - the volume occupied by the molecules which is Nb. So the other thing I have to make sure is that there is the idea that it is that interactions are attractive.

So that basically what it does is it lowers the pressure on the walls. So, so if you calculate the pressure, it comes out to be. So from here if you calculate the pressure on the walls of the container. it is less than what it is for the ideal gas so in fact it is going to be

$$p = NT/V' - N^2/V^2a$$

okay. So you see it is less than, it is less than what you normally expect it to be, normally expected to meet this, this is the pressure acting on the wall.

So in the absence of interaction with the molecules did not attract each other if they do not add if they just had some size, which is b, but they did not attract each other, you know, the pressure they would exert on the wall would simply be NT by the volume available to the fluid which is V dash which is V-Nb. However, in addition to having a finite size. If the molecules also attract each other. Then, because they attract each other, they will not exert as much pressure on the walls as they would if they did not attract each other.

And as a result, the pressure gets lowered. So in fact, you do not have to be, can either start with this. Or you could start with this and derive this to the same thing. Okay, so i will allow you to use whatever interpretation you wish. So you can either start with us, or and try to derive this to,in other words, you can start with the equation of state and derive the free energy, or you can start with the free energy and try to derive the equation of state.

So now let us now focus on the equation of state. This called Van der Waals equation of state.

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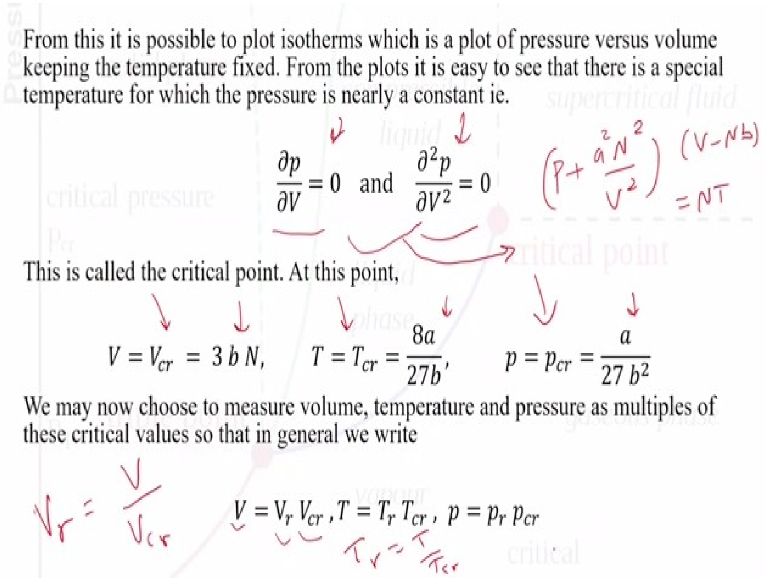

From this it is possible to plot isotherms which is a plot of pressure versus volume keeping the temperature fixed. From the plots it is easy to see that there is a special temperature for which the pressure is nearly a constant ie.

$$\frac{\partial p}{\partial V} = 0 \quad \text{and} \quad \frac{\partial^2 p}{\partial V^2} = 0$$

$$\left(P + \frac{a^2 N^2}{V^2}\right)(V - Nb) = NT$$

This is called the critical point. At this point,

$$V = V_{cr} = 3\,b\,N, \qquad T = T_{cr} = \frac{8a}{27b}, \qquad p = p_{cr} = \frac{a}{27\,b^2}$$

We may now choose to measure volume, temperature and pressure as multiples of these critical values so that in general we write

$$V_r = \frac{V}{V_{cr}} \qquad V = V_r\,V_{cr}\,, T = T_r\,T_{cr}\,,\ p = p_r\,p_{cr}$$

$$T_r = T/T_{cr}$$

So now i am going to point out to you that this has a very curious feature, which is not shared by, which is not present in actually in a classical ideal gas and that is the existence of what is called a critical point so critical point is a particular value for the volume of the gas and particular value for the temperature, and therefore also for the pressure, such that the pressure, near the critical point is a constant.

So in other words, when you are near the critical point the pressure does not change. So if you plot isotherms that means you fix the temperature, and you plot pressure versus volume. So, you will see that there is a region. there is a certain temperature at which the pressure becomes independent of the volume. And so if the pressure is independent of the volume. It is effectively, saying that the first derivative and the second derivatives are 0.

So in other words it is nearly independent of the volume. So, so, pressure is sort of flat, it is nearly constant, so you can use this, you can use your equation of state, the Van der Waals equation of state. And you can go ahead and use this to calculate what this means, what are the critical points so i am going to leave a lot of this to homework and exercises later on. Now that I have everything so so that you will be. you will also have an opportunity to follow along.

In fact, you should be doing this, as I said already, you should not think of this as a story, and you should follow along by proactively working out the claims that I am making and making sure that they are valid. Okay. Now if I insert, or if I incorporate these two ideas into this Van der Waals equation of state. I can show that basically, this implies that there is a critical volume. And there is a critical temperature, and therefore there is a critical pressure.

If you combine the Van der Waals equation of state, you will see that there is a critical pressure as well. So now it is very convenient because now you see these critical volumes critical temperature, they all depend upon b's and a's, b's and a's were not there, the b's and a's are what make the gas non ideal. So if the b's and a's were not there, so there will not be any critical point. So b's and a's tell you that basically the gas is non ideal.

So now, assuming it is there. I can start measuring my volume in the units of the critical volume, the critical volume times some dimensionless number which is called V_r. So basically V_r is nothing but, the volume of the box, times the critical volume. Which is, which is dimensionless so in other words it is like measuring the volume of the box in units of the critical volume so same with temperature I am going to measure the temperature in units of the critical temperature and same with pressure, i am going to measure pressure and units of critical pressure. So if I decide to do this,

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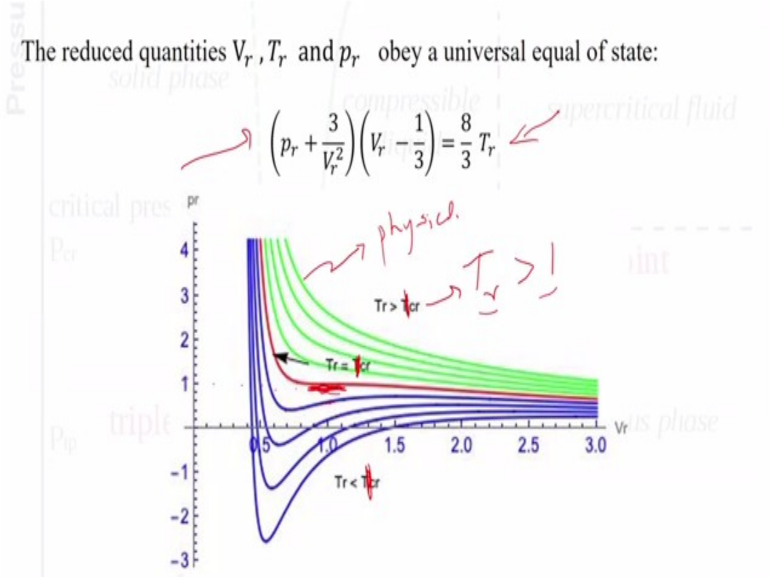

The reduced quantities V_r, T_r and p_r obey a universal equal of state:

$$\left(p_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3} T_r$$

You will see that I can rewrite Van der Waals equation of state in this very nice way. So now notice that this equation, this is called the reduced equation of state. It does not have any a's or b's so in fact they are all hidden in those P_r's and V so they are not explicitly there. So, so i am just measuring the reduced pressure so the pressure in the units of the critical pressure.

So that means, you see the a's and b's basically tell you different values have a correspond to different strengths of attraction, that is present in the guests so they correspond to different types of gases, for example. So different gases will have different values of a which is the inter molecular attraction strength. But then the reduced equation of state is universal, that is an independent of a, it is independent of b which is the size of each molecule.

So b is different. It means that the molecules are either bigger or smaller. So you can see that the reduced equation of state which is this is also independent of the size of the molecules. So, this equation of state, pretty much describes a generic Van der Waals fluid which is insensitive to the details of what that fluid really is, besides the fact that it is Van der Waals fluid so it does not matter how big the molecules does not matter how strong the attractive interaction between molecule is, regardless of that it is all those different types of gases are still described by the same equation of state already, this is called the reduced equation of state. So, and this is this idea that a whole bunch of different gases can be described by what is essentially the same equation of state goes by the name of correspondence principle so it is something, it is called a correspondence principle.

Alright, so now I am going to go ahead and because now i have rendered everything dimension less. I can go ahead and plot the isotherms. so isotherms are laws of pressure versus volume, keeping temperature fixed. So you can see in this plot that if. So if I make the. So sorry this is, this is one,I mean in in dimension less units, this is one. This is one say if the reduced temperature is greater than one, so that means that temperature is greater than the critical temperature.

So, that means that basically. So the green plots represent pressure versus volume for fixed temperature, greater than 1. So, as you go here the temperature is more and more, and then the critical temperature. So as you lower the temperature, you will see that you will reach a stage where in this region the pressure becomes constant so this is basically the, this is, this is, tr =1. So the critical temperature so the critical temperature.

The, the pressure is independent of the volume so this plot is flat, right there. So now, if you lower the temperature, even further. So that means $T_r < 1$, so the temperature is less than the critical temperature. So you will see that the pressure versus volume becomes somewhat unphysical. So, the reason why it is on physical is because if you apply pressure you expect the volume to reduce. But here, what happens is that there is a region in which from here to here.

It actually as you increase the pressure the volume also increases which is unphysical. So, after a long time it again becomes physical, so you see this is a completely physical. There is nothing unphysical about this because pressure is monotonically decreasing at a fixed temperature. If you increase the pressure you expect the volume to decrease. So, so you see that is consistent with these green lines are perfectly valid and intuitively obvious.

But then the blue lines are somewhat unphysical here. So, that is telling you that there is something you know that that there is something lacking in this Van der Waals model that. That there are regions in which the model breaks down, basically. But then, all is not lost you can still salvage the important physics. By adopting this point of view that. So, and let me go to the next slide,

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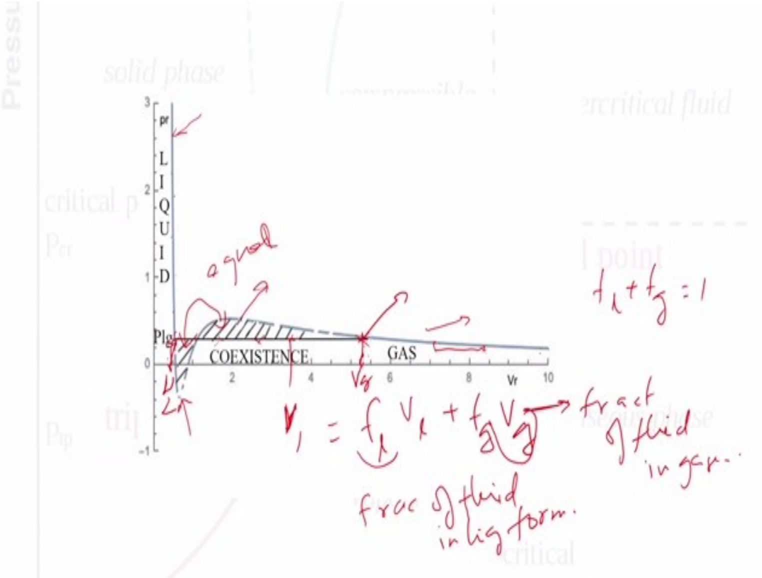

I will tell you how we salvage the these plots and still extract physically meaningful ideas.

So now i am going to pick one of those plots one of the blue plots, where the temperature is below the critical temperature so the reduced temperature is less than 1. And then I am going to carefully plot the reduced temperature versus the reduced volume, and then it looks like this. So, you see, in this region, I have written liquid, so these points signify that the phase that I am looking at is a liquid phase and why is that because, you see.

Even though the pressure is changing dramatically here, because the y axis is the pressure. The volume is hardly changing so that is a characteristic of a liquid so it is incompressible. So, you change the pressure a lot, where the volume does not change much. So that is what happens to a liquid. So if you take for example, you know, you just take a glass of water and, you know, you try to apply pressure to it, its volume is hardly going to change.

So that is typically what a liquid. But then if you come here in this other extreme. So here, you know, even a very small change in pressure causes a huge change in volume. So the plot is nearly flat. It implies that if you change pressure from here to this this value so if you change from this value to this value, the pressure changes very slightly where the volume changes enormously. So that is characteristics of a highly compressible fluid.

Highly compressible fluid is a gas. So, therefore, this, this particular region of the plot is occupied by gas. So now what happens in between is what is interesting. So you see I told you that this region where the pressure increases with volume is unphysical. So, it so happens that the factors of all region that on physical which you can cross out in the following way. So, I tell you why to adopt this procedure so the procedure is the following.

You draw a horizontal straight line, such that, the shaded area. These two shaded areas are equal so they kind of cancel out. So in other words, you make sure that this shaded area is the same as the shaded area. Okay, so you draw a straight line size that these two shaded areas are equal, and the straight line is signifies a certain particular pressure. So in that is what I have been noted as Plg. So, Plg is basically the pressure of liquid gas coexistence so the.

So on this so the claim now is that the Van der Waals equation of state, which now if you literally plot it without any modification namely if you simply plot this blindly, it is going to look like this so it is going to look like. It is going to start from a high value and then come down again go up again come down. But then, I have told you that parts of this is unphysical. So the parts that are unphysical is what I have written here from here to here is some physical.

So how do I make it physical? How do I rectify this? The idea is that you simply join this, these two points by a straight line in such a way that this area is same as that area. So then the actually the physical plot now therefore is, as usual, the Van der Waals fluid plot from here to here is given by the Van der Waals equation of state, and also from here to here is still given by Van der Waals equation of state, but this is something i have done by hand.

So I have drawn a horizontal line. So these three pieces put together is the correct equation of state so that is the claim. So what does this physically mean so physically it means that this region there is liquid because it is incompressible. From here to here it is liquid. Because incompressible from here to here it is gas because it is highly compressible, but then from here to here, you see it is, it stands to reason that there is a coexistence.

That means that the pressure is fixed. So the, the pressure becomes fixed so that the liquid gas coexistence pressure so there is some, some particular so I think given temperature. there is a particular pressure at which liquid and gas can coexist. And that pressure, you can have, you know, volume can be either this or this. You know the volume is this that means all the fluid is in the liquid form. So if the volume is this, then that means all the fluid is in gaseous form.

But if the volume is somewhere in between. It means that part of the fluid is in. So, liquid form part of it is in gaseous form so you can in fact write so if this is your volume of your fluid. So you can always write this $f_l v_l + f_g v_g$. So this is your this is your v_g, and this is your v_l . So, here is vl. So this is the fraction of the fluid that is in f_l is the fraction of the fluid that is in liquid form. So the fraction of fluid and liquid form, and sorry f_g is the fraction of fluid as an gaseous form. So, that you can kind of tune from 0 to 1. So, $f_l + f_g = 1$. So you can tune it to go from fully liquid to fully gas. And in between, you have the coexistence region, and the coexistence happens at a particular pressure, which is a function of the temperature of the fluid. So the temperature is less than the critical temperature, there will always be coexistence between liquid and gracious states, so that is this.

I mean that is basically the essence of the Van der Waals fluid. So the one that you know the ideal guys equation of state is oversimplified it is too simplistic. It does not capture the real life situation. And then the next best thing you can do is, you know, and describe it by something which is not too complicated like Van der Waals equation of state but then, because it is so simple. It also unfortunately becomes slightly unphysical.

Which you will have to have done physical aspects of the Van der Waals equation of state namely, this region, you will have to reinterpret and fix it by hand. And this is how you fix it.

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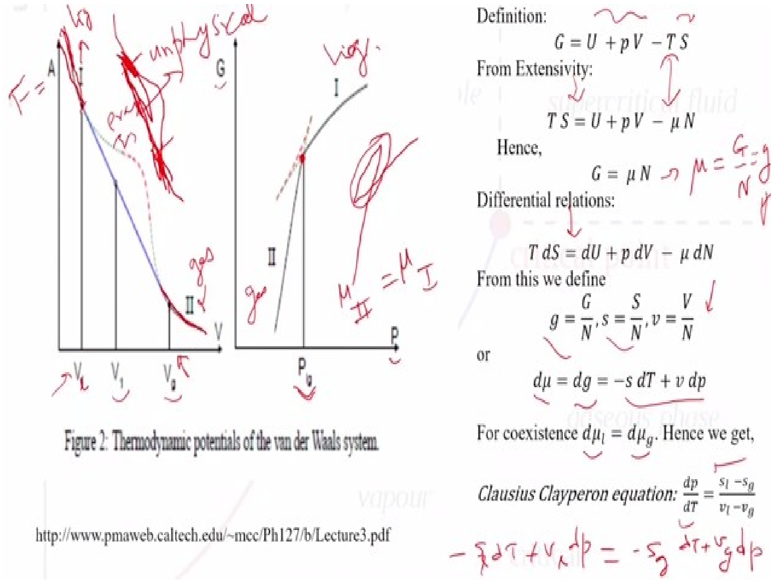

Figure 2: Thermodynamic potentials of the van der Waals system.

http://www.pmaweb.caltech.edu/~mcc/Ph127/b/Lecture3.pdf

Definition:

$$G = U + pV - TS$$

From Extensivity:

$$TS = U + pV - \mu N$$

Hence,

$$G = \mu N \rightarrow \mu = \frac{G}{N} = g$$

Differential relations:

$$T\,dS = dU + p\,dV - \mu\,dN$$

From this we define

$$g = \frac{G}{N}, s = \frac{S}{N}, v = \frac{V}{N}$$

or

$$d\mu = dg = -s\,dT + v\,dp$$

For coexistence $d\mu_l = d\mu_g$. Hence we get,

Clausius Clayperon equation: $\frac{dp}{dT} = \frac{s_l - s_g}{v_l - v_g}$

$$-s_l\,dT + v_l\,dp = -s_g\,dT + v_g\,dp$$

Okay, so now you can go ahead and, you know, do the same thing. Not only can you plot the isotherms. You can also plot the helmholtz free energy which either I have called it as f or sometimes it is called A. So, you see, I can plot it versus volume.

Again, for a fixed temperature. So I can plot the free energy versus volume for fixed temperature. And here you can see the same thing that this is the vl which is the when all the volume is in the liquid form and vg which is when all the volume is in gaseous form, so in other words the liquid is fully gaseous here. And it is fully liquid. And in between. It is the liquid and gas is a coexisting so. So you see, here also so this plot is basically from the Van der Waals formula.

So that just blindly from the formula if you plot, if you plot this formula. In other words, I've told you what it is. This formula so if you simply plot a fixed temperature and you plot it versus volume. This is your remote free energy. So if I simply plot it, it is going to look like this it is going to look like this. So the point is that this region is unphysical so this bump here is unphysical. So, so this this region is unphysical. So the question is how do you fix this?

So just like the fixed here, fix this by drawing a straight line here also we are going to we are gonna find a tangent here. we are going to find a tangent there so kind of joined this by two tangents that is going to work out. Basically this you draw a tangent to this says that, and then you erase this part so you erase this. And you say the Helmholtz free energy is really this plot which is given by the formula and this plot is given by the formula.

And this I joined by hand so there is like a straight line which is because I joined it by hand. So this is how I, you know, modify the Van der Waals formulas to describe physically correct fluid. So the mathematical formulas, unfortunately, break down for certain values of the parameters. So I like to fix it by hand so this is how I choose to fix it. Now, it is more illuminating, you know, you might be wondering this is very mysterious, why should I be fixing it this way.

How do you know that this is the correct way of fixing the unphysical aspects, so that can be better explained if you plot the Gibbs free energy versus pressure. Okay, so for fixed volume so you already know I told you what genre transformation is basically the Helmholtz free energy is the Legendre transformed version of entropy so in other words the entropy is a function of internal energy, volume, and the number of particles.

So if you trade the internal energy, with temperature, using Legendre transformation, you get a potential, which is the Legendre transform of entropy. Which is basically Helmholtz free energy, to the Helmholtz free energy is now attempt functional temperature, volume and number of particles. So you can go ahead and do one more transformation one more Legendre transformation, where you also transform the volume you trade the volume with pressure.

So, so the idea is, of course, now we have a system, you have a fluid, where the walls of the fluid are not rigid. So they, they are flexible so the fluid comes to an equilibrium with the surroundings so the pressure equalizes between the fluid and its surroundings. And then it can also exchange energy with the surroundings. So, the temperature of the fluid and the surroundings also equalize. So, so as a result the free energy that is available in such a situation is known as Gibbs free energy.

And we have been successful in showing that Gibbs free energy is basically given by the enthalpy, which is U+pV-TS. And we know from the extentivity of the entropy. That was called I think the fundamental relation of thermodynamics which is basically the extensivity of entropy allowed us to write this so if you combine these two equations, you will see that the Gibbs free energy is actually very directly related to the chemical potential.

So in fact the chemical potential is nothing but Gibbs free energy per particle. So, this is denoted by g. So the chemical potential of the system is nothing but Gibbs free energy per particle. So, coming back to this idea that. So, this II signifies gas. This the Roman numeral II signifies gas and Roman numeral I signifies liquid. So, here also. So this is gas, and this is liquid. So you can see that if I say if I plot g versus p for a fixed volume.

What is going to happen is this, this plot suppose I plotted using the Gibbs free energy derived from Van der Waals formulas I successfully derive his free energy. So I already know the Helmholtz free energy then it is just one more step to derive Gibbs free energy. And if I derive Gibbs free energy. it is and I try to plot it it is going to look quite ugly it is going to look like this. it is not going to be a single.valued. So that is how the plot is going to look like.

So the point is that this region is un physical. So the idea is that you kind of snip this off, so there is a kink there, so there is some something special happening. So it is basically it is telling something special happening right there and what is special is basically the coexistence. So you see that, at this point, the gas, which is this region coexist with the liquid in this region. So they touch heres to touch the touch, when the pressure is exactly Plg so what does touching mean?

Touching basically means that the chemical potential of region 2 is same as chemical potential because chemical potential is nothing but Gibbs free energy per particle. So basically, equalizing the chemical potential that signifying that you know when the liquids, the molecules of the liquid evaporate and become gas or the molecule of the gas condense and become liquid so there is a kind of the the phases in the different phases, the number of particles are not fixed.

In other words, even though the total number of particles in the liquid +gas is fixed but the number of molecules of the liquid is not fixed. Because some of it can evaporate and become gas, and some of the molecules of the gas can condense and become a liquid, so you know that when particle exchange is allowed. So what equalizes the chemical potential So,here instead of particles exiting to the environment.

And what is happening is that the particles are exiting from one phase into another, and vice versa. So as a result, the chemical potentials of the two phases equalize. So that is pretty much what is happening here, so they equalize when the pressure is a certain value, which is liquid gas coexistence pressure. So coming back to these formulas. So, you can see that I can use the differential relation also, which tells me that this is basically the second law of thermodynamics if you like for reversible processes. It tells you that

$$Tds=dU+pdV-\mu dN$$

now, if I use this idea that gives free energy power particles G/N and entropy per particle as S/N and volume per particles V/N. The differential changing the chemical potential is basically given by the differential changing against Gibbs free energy per particle, and you can convince yourself that this is given by this formula. And now, because the liquid and gas part of it should be equal.

So I just told you that the liquid chemical potential should be same as gas chemical potential, you can equate these two and you can derive the coexistence curve. So the coexistence curve is basically the pressure versus temperature at a fixed volume. So the coexistence curve is given by what is called the Clausius Clapeyron equation, which is obtained by equating $dT+v_ldp$ with gas $dT+v_gdp$ so if you solve for dp/dt you get this first basically the change in entropy from the liquid.

Entropy per particle with liquid and gas phases, divided by the basically the volume per particle which is the inverse of the density. So the change in the density of the liquid and gas regions times the chain in entropy is effectively the rate of change of pressure with temperature.

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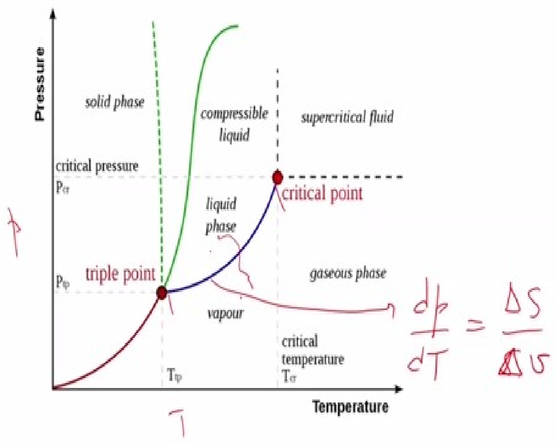

https://www.thoughtco.com/definition-of-triple-point-604674

So basically that is what this is the coexistence is pressure versus temperature. So the slope of the coexistence, dp/dt is the slope of this curve.

So this is, I mean, see this blue thing is only, you know, this the only coexistence part of this, this is a realistic phase diagram it is called, the realistic phase diagram only this blue curve can be captured by this analysis that I have described in now because after all the border the blue curve is the gas and liquid coexistence region. So that is all I can describe for the rest of it also describes solid, so which I cannot capture using the Van der Waals equation.

The Van der Waals equation captives only the liquid and gas coexistence , so this blue curve. So, the triple point is when the solid also coexist with liquid and vapor. So, the idea is that you can see that the slope of this is described by so that dp/dt of this is basically described by that Clausius Clayperon equation, this curve you can derive you know Van der Waals idea. Up to this point so this is the critical point which also is captured by Van der Waals theory.

Okay, so the rest of it is not captured by Van der Waals theory. So, but then this is the realistic face diagram. So I want you to stare at this. And so this is all I will have time to discuss in this course because you know actually deriving this phase diagram from realistic theoretical first principle theory is very difficult. And I will not attempt it okay. So, in the next class we will discuss another topic, which is called Pauli paramagnetism**.** So hope you will join me for the next class. Thank you.