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**PROFESSOR:** So today's topic is liquid gas condensation and throughout this course I have already mentioned two different perspectives on the same phenomenon, transition between liquid and gas. One perspective was when we looked at the phase diagram even in the first lecture I mentioned that if you look at something like water as a function of pressure and temperature it can exist in three different phases. There is the gas phase, which you have at high temperatures and low pressures. At low temperatures and high pressures you have the liquid phase. And of course at very low temperatures you also have the possibility of the solid phase.

And our concern at some point was to think about the location of the coexistence of the three phases of that was set as the basis of the temperature, 273.16. Actually what you're going to focus now is not this part of the phase diagram but the portion that consists of the transition between liquid and gas phases. And this coexistence line actually terminates at what is called the critical point that we will talk about more today at the particular value of  $T_c$  and  $P_c$ .

An equivalent perspective that we have looked at that and I just want to make sure that you have both of these in mind and know the relationship between them is to look at isotherms. Basically we also looked at cases where we looked at isotherms of pressure versus volume. And this statement was that if we look at the system at high enough temperatures and low enough pressures so let's say pick this temperature and scan along a line such as this, it would be equivalent over here to have some kind of an isotherm that is kind of potentially a distorted version of an ideal gas hyperbola.

Now if we were to look at another isotherm that corresponds to this scan over here then what would happen is that it will cross this line of the coexistence, part of it

would fall in the liquid phase, part of it would fall in the gas phase. And we draw the corresponding isotherm, it would look something like this. There would be a portion that would correspond to being in the liquid. There would be a portion that would correspond to being in the gas. And this line, this point where you hit this line would correspond to the coexistence.

Essentially you could change the volume of a container and at high volumes, you would start with entirety gas. At the same pressure and temperature you could squeeze it and some of the gas would get converted to liquid and you would have a coexistence of gas and liquid until you squeezed it sufficiently, still maintaining the same pressure and temperature until your container was fully liquid. So that's a different type of isotherm. And what we discussed was that basically there is a coexistence boundary that separates the first and the second types of isotherms. And presumably in between there is some trajectory that would correspond to basically being exactly at the boundary and it would look something like this.

This would be the trajectory that you would have at  $T_c$ . The location  $P_c$  is the same, of course, so basically I can carry this out so there is the same  $P_c$  that would occur here. And there would be some particular  $V_c$  but that depends on the amount of material that I have. OK?

So we are going to try to understand what is happening here and in particular we note that suddenly we have to deal with cases where there are singularities in our thermodynamic parameters. There's some thermodynamic parameter that I'm scanning as I go across the system. It will not be varying continuously. It has these kinds of discontinuities in it. And how did discontinuities appear and how can we account for these phase transitions given the formalisms that we have developed for studying thermodynamic functions.

And in particular let's, for example, start with the canonical prescription where I state, let's say that I have volume and temperature of a fixed number of particles and I want to figure out thermodynamic properties in this perspective. What I need to calculate is a partition function and we've seen that the partition function is

obtained by integrating over all degrees of freedom which are basically the coordinates and momentum of particles that make up this gas so I have to do  $d^3 p_i$ ,  $d^3 q_i$ , divide by  $h^3$ , divide by  $n!$  because of the way that we've been looking at things, of energy so I have  $e^{-\beta H}$  that has a part that is from the kinetic energy which I can integrate immediately. And then it has a part that is from the potential energy of the interactions among all of these particles. OK?

So somehow if I could do these integrations-- we already did them for an ideal gas and nothing special happened but presumably if I can do that for the case of an interacting gas, buried within it would be the properties of this phase transition and the singularities, et cetera. Question is how does that happen? So last time we tried to do shortcuts. We started with calculating a first derivative calculation in this potential and then try to guess things and maybe that was not so satisfactory. So today we'll take another approach to calculating this partition function where the approximations and assumptions are more clearly stated and we can see what happens.

So I want to calculate this partition function. OK? So part of that partition function that depends on the momentum I can very easily take care of. That gives me these factors of  $1/\lambda$ . Again as usual my  $\lambda$  is  $h/\sqrt{2\pi m k T}$  and then I have to do the integrations over all of the coordinates, all of these coordinate integrations and the potential that I'm going to be thinking about, so again in my  $U$  will be something like  $\sum_{\text{pairs}} V(q_i - q_j)$ , where the typical form of this  $V$  as a function of the separation that I'm going to look at has presumably a part that is hard-core and a part that is attract. Something like this. OK?

So given that potential what are the kinds of configurations I expect to happen in my system? Well, let's see. Let's try to make a diagram. I have a huge number of particles that don't come very close to each other, there's a hard-core repulsion, so maybe I can think of them as having some kind of a size-- marbles, et cetera, and they are distributed so that they cannot come close to each other. More than that are zero and then I have to sum over all configurations that are compatible where

they are not crossing each other and calculate  $e^{-\beta u}$ .

So let's try to do some kind of an approximation to this  $U$ . I claim that I can write this  $U$  as follows- I can write it as one-half, basically this  $i < j$ , I can write as one-half all  $i \neq j$ , so that's where the one-half comes from. I will write it as one-half but not in this form, as an integral  $\int d^3r \int d^3r' \sum_n \rho(r) \rho(r')$  of  $r - r'$  where  $\sum_n \rho(r)$  is sum over all particles asking whether they are at location  $r$ . So I can pick some particle position here-- let's call it  $r$ -- ask whether or not there is a particle there, construct the density by summing over everywhere. You can convince yourself that if I were to substitute this back over here, the integrals over  $r$  and  $r'$  can be done and they sit  $r$  and  $r'$  respectively to sum  $q_i$  and  $q_j$  and I will get back the sum that I had before. OK?

So what is that thing doing? Essentially it says pick some point,  $r$ , and then look at some other point,  $r'$ , ask whether there are particles in that point and then sum over all pairs of points  $r$  and  $r'$ . So I changed my perspective. Rather than calculating the energy by looking at particles, I essentially look at parts of space, ask how many particles there are.

Well, it kind of makes sense if I coarse-grained this a little bit that the density should be more or less the same in every single box. So I make the assumption of uniform density-- I shouldn't say assumption, let's call it an approximation of uniform density in which I replace this  $\rho(r)$  by its average value which is the number of particles per [INAUDIBLE]. OK? Then my  $U$ -- I will take the  $\rho$ 's outside. I will have one-half  $\rho^2 \int d^3r \int d^3r' v(r - r')$ .

Again it really is a function of the relative distance so I can integrate over the center of mass if you like to get one factor of volumes so I have one  $\rho^2 V$  and then I have an integral over the relative coordinate  $d^3r$ -- let's write it as  $4\pi r^2 dr$ , the potential as a function of separation. Now the only configurations that are possible are ones that don't really come closer than wherever the particles are on top of each other, so really there is some kind of a minimum value over here. The maximum value you could say is the size of the box but the typical range of

potentials that we are thinking is much, much less than the size of the box. So for all intents and purposes I can set the value of the other part of the thing to infinity.

So what I'm doing is essentially I'm integrating this portion and I can call the result of doing that to be minus  $u$ . Why minus? Because it's clearly the attractive portion in this picture I'm integrating. And you can convince yourself that if I use the potential that I had before-- yes, the last time around it was minus  $u_0 r_0$  over  $r$  to the sixth power, but this  $u$  is actually the  $u_0$  that I was using times  $u_0$  but I will keep it as  $u$  to sort of indicate that it could be a more general potential. But the specific potential that we were working with last time to calculate the second virial coefficient would correspond to that. So essentially I claim that the configurations that I'm interested will give a contribution to the energy which is minus whatever this  $u_0$ --  $u$  is  $n^2 V$  divided by 2.

Now clearly not all configuration has the same energy. I mean that's the whole thing, I have to really integrate overall configurations. I've sort of looked at an average contribution. There will be configurations where the particles are more bunched or separate, differently arranged, et cetera, and energy would vary. But I expect that most of the time-- I see something like a gas in this room, there is a uniform density typically.

The fluctuations in density I can ignore and I will have a contribution such as this. So this factor I will replace by what I have over here. What I have over here will give me  $e^{-\beta u}$  to the minus  $\beta u$  density squared actually I can write as  $N^2$  over  $V^2$  squared, one of  $V$ 's cancel here, I have  $2 V$ . OK?

So that's the typical value of this quantity but now I have to do the integrations over all of the  $q$ 's. Yes?

**AUDIENCE:** In terms of the approximation you made--

**PROFESSOR:** Yes.

**AUDIENCE:** --the implications are that if you have a more complex potential--

**PROFESSOR:** Yes.

**AUDIENCE:** --you'll get into trouble with for a given sample size, it will be less accurate. would you agree with that?

**PROFESSOR:** What do you mean by a more complex potential? Until you tell me, I can't--

**AUDIENCE:** I mean I, guess, and usually-- I mean, I guess if you had like multi-body or maybe the cell group.

**PROFESSOR:** OK. So certainly what I have assumed here is a two-body potential. If I had a three-body potential then I would have a term that would be density cubed, yes.

**AUDIENCE:** But then you would-- my point is that-- and maybe it's not a place to question-- for a given sample size, I would imagine there's some relation between how small it can be and the complexity of the potential when you make this uniform density assumption.

**PROFESSOR:** OK. We are always evaluating things in the thermodynamic limit, so ultimately I'm always interested in  $m$  and  $v$  going to infinity, while the ratio of  $n$  over  $v$  is fixed. OK? So things-- there are certainly problems associated with let's say extending the range of this integration to infinity. We essentially are not worrying about the walls of the container, et cetera. All of those effects are proportional to area and in the thermodynamic limit, the ratio of area to volume goes to zero. I can ignore that.

If I bring things to become smaller and smaller, then I need to worry about a lot of things, like do particles absorb on surfaces, et cetera. I don't want to do that. But if you are worrying about complexity of the potential such as I assume things to be radially symmetric, you say, well actually if I think about oxygen molecules, they are not vertical. They have a dipole-dipole interactions potentially, et cetera.

All of those you can take care of by doing this integral more carefully. Ultimately the value of your parameter  $u$  will be different.

**AUDIENCE:** But I guess what I'm getting at is you deviate from the-- if you're doing it-- if we're back when computers are not as fast and you can essentially approach the

thermodynamic limit and you're doing a simulation and you want to use these as a tool--

**PROFESSOR:** Mm-hmm?

**AUDIENCE:** --then you get into those questions, right?

**PROFESSOR:** Yes.

**AUDIENCE:** But this framework should still work?

**PROFESSOR:** No. This framework is an approximation intended to answer the following question-- how is it possible that singularities can emerge? And we will see shortly that the origin of the emergence of singularities is precisely this. And if I don't have that, then I don't have singularities. So truly when you do a computer simulation with 10 million particles, you will not see the singularity. It emerges only in the thermodynamic limit and my point here is to sort of start from that limit.

Once we understand that limit, then maybe we can better answer your question about limitations of computer simulations. OK? So I've said that there's basically configurations that typically give the [INAUDIBLE]. But how many configurations? I can certainly move these particles around. And therefore I have to see what the value of these integrations are. OK?

So I will do so, as follows-- I will say that the first particle, if there was nobody else-- so I have to do this integration over  $q_1, q_2, q_3$ , and I have some constraints in the space that the  $q$ 's cannot come closer to each other than this distance. So what I'm going to try to calculate now is how this factor of  $v$  to the  $n$  that you would have normally put here for ideal gases gets modified. Well I say that the first particle that I put in the box can explore the entire space.

If I had two particles, the second particle could explore everything except the region that is excluded by the first particle. The second particle that I put in can explore the space minus the region that is excluded by the first two particles. And the last, the end particle, the space except the region that is excluded by the first  $n$  minus 1. This

is an approximation, right?

So if I have three particles, the space that is excluded for the third particle can be more than this if the two particles are kind of close to each other. If you have two billiard balls that are kind of close to each other the region between them is also excluded for the first particle. We are throwing that out and one can show that that is really throwing out things that are higher order in the ratio of  $\omega$  over  $V$ . So if you're right, this is really an expansion in  $\omega$  over  $V$  and I have calculated things correctly to order of  $\omega$  over  $V$ .

And if I am consistent with that and I multiply all of these things together, the first term is  $V$  to the  $N$  and then I have  $1 - \omega$  plus  $2\omega$  plus all the way to  $N - 1$   $\omega$  which then basically sums out to  $1 + 2 + 3$  all the way to  $N - 1$ , which is  $N - 1$  over  $2$  in the large  $N$  limit. It's the same thing as  $N$  squared over  $2$  and this whole thing is raised to the power-- OK this whole thing I can approximate by  $V - N\omega$  over  $2$  squared. There are various ways of seeing this. I mean one way of seeing this is to pair things one from one end and one from the other end and then multiply them together.

When you multiply them you will have a term that would go be  $V$  squared, a term that would be proportionate to  $V\omega$  and would be the sum of the coefficients of  $\omega$  from the two. And you can see that if I pick, say,  $\alpha$  term from this side  $N - \alpha$  minus one term from the other side, add them up, the  $\alpha$ s cancel out,  $N$  and  $N - 1$  are roughly the same, so basically the square of two of them is the same as the square of  $V - N\omega$  over  $2$ . And then I can repeat that for all pairs and I get this. Sorry.

So the statement is that the effect of the excluded volumes since it is joint effect of mutually excluding each other is that  $V$  to the  $N$  that I have for ideal gas, each one of them can go over the entire place, gets replaced by  $V - \text{something}$  to the power of  $N$  and that something is  $N\omega$  over  $2$ . Plus higher orders in powers of  $\omega$ . OK? So I will call this a mean field estimate. Really, it's an average density estimate but this kind of approximation is typically done for magnetic systems and in



that context the name of mean field has stuck. And the ultimate result is that my estimation for the partition function is  $1$  over  $N$  factorial  $\lambda$  to the power of  $3N$   $V$  minus  $N$   $\omega$  over  $2$  raised to the power of  $N$  because of the excluded volume and because of the Boltzmann weight of the attraction between particles I have a term which is  $e$  to the minus  $\beta U N$  squared over  $2V$ . OK?

So the approximations are clear on what set of assumptions I get this estimate for the partition function. Once I have the partition function, I can calculate the pressure because  $\log z$  is going to be related to free energy, the derivative of the free energy respect to volume will give me the pressure, and you can ultimately check that the formula is that  $\beta P$  is the  $\log Z$  by  $dV$ . That's the correct formula. And because we are doing this in the canonical formalism that I emphasized over here, let's call this  $P$  that we get through this process  $\beta P$  canonical. OK?

So when I take  $\log z$ , there's a bunch of terms and I don't really care about because they don't have  $V$  dependence from  $N$  factorial  $\lambda$  to the power of  $3N$ , but I have  $N$  times  $\log$  of  $V$  minus  $N$   $\omega$  over  $2$ . So that has  $V$  dependence. Take the derivative of  $\log$  of  $V$  minus  $N$   $\omega$  over  $2$ , what do I get? I get  $V$  minus  $N$   $\omega$  over  $2$ .

The other theorem when I take the  $\log$  I have a minus  $\beta U N$  squared over  $2V$  so then I take a derivative of this  $1$  over  $V$ . I will get minus  $1$  over  $V$  squared so I have a term here which is  $\beta U$  over  $2 N$  squared over  $V$  squared. OK? Let's multiply by  $kT$  so that we have the formula for  $P$  canonical.  $P$  canonical is then  $N k T V$  minus  $N$   $\omega$  over  $2$  and then I have-- I think I made a sign over here-- yes the sign error that I made is as follows-- note that the potential is attractive so I have a minus  $U$  here. So when I exponentiate that, it becomes a plus here and will be a plus here and therefore I will have a minus here and I will have a minus  $U$  over  $2$  times the density squared. OK?

So what did we arrive at? We arrived at the van der Waals equation. OK? So we discussed already last time around that if I now look at the isotherms pressure volume at different temperatures, at high temperatures I have no problem. I will get

things that look reasonable except if I have to terminate at something that is related to this excluded volume, whereas if I go to low temperatures, what happens is that the kind of isotherms that I get have a structure which is kind of like this and incorporates a region which violates everything that we know about thermodynamics, is not stable, et cetera. OK?

So what happened here? I did a calculation. You can see every step of the calculation over there. Why does it give me nonsense? Everything that you need to know is on the board. Suggestions? Yep?

**AUDIENCE:** The assumption of uniform density in a phase transition?

**PROFESSOR:** Right. That's the picture that I put over here. If I draw the box that corresponds to what is happening over there, what's going on in the box? So there is a box. I have particles in it and in the region where this nonsense is happening, what is actually happening in reality? What is actually happening in reality is that I get some of the particles to condense into liquid drops somewhere and then there's basically the rest of them floating around as a gas. Right?

So clearly I cannot, for this configuration that I have over here, calculate energy and contribution this way. So coexistence implies non-uniform density. OK? So what do we do? I want to carry out this calculation. I want to stay as much as possible and within this framework and I can do it, but I need to do one other thing. Any suggestions? Yes?

**AUDIENCE:** Try to describe both densities simultaneously?

**PROFESSOR:** Try to describe both densities--

**AUDIENCE:** You know the amount of liquid and the amount of vapor on average--

**PROFESSOR:** I guess I could. I have an easier way of doing things. OK. So the easier way that I have on doing things is we have emphasized that in thermodynamics, we can look at different perspectives. Problem with this perspective of the canonical is that I know that I will encounter this singularity. I know that.

There's phase diagrams like this exist. Whereas if I use this prescription I have one. So what's the difference is this prescription is better mind in terms of pressure and temperature. So what I want to do is to replace the canonical perspective with what I will call the isobaric-- it's the Gibbs canonical ensemble. In this context it's called isobaric ensemble where rather than describing things at fixed volume, I describe things at fixed pressure.

So I tell you what pressure, temperature, and the number of particles are and then I calculate the corresponding Gibbs partition function. Why does that help? Why that helps is because of what you see on the left side diagram is if I wanted to maintain this system at the fixed pressure rather than a fixed volume, I would replace one of the walls of this container with a piston and then I would apply a particular value of pressure.

Then you can see that a situation such as this does not occur. The piston will move so that ultimately I have a uniform density. If I'm choosing my pressure to be up here, then it would be all liquid. If I choose my pressure to be down here, it will be all gas. So I have this piston on top.

It does not tolerate coexistence. It will either keep everybody in the gas phase or it will compress, change the volume so that everybody becomes liquid so what I have done is I have gotten rid of the volume. And I do expect that in this ensemble as I change pressure and go through this line, there is a discontinuity that I should observe in volume. OK?

So again just think of the physics. Put the piston, what's going to happen? It's going to be either one or the other. And whether it is one or the other, I'm at uniform density and so I should be able to use that approximation that I have over there. OK?

So mathematics, what does that mean? This Gibbs version of the partition function in this isobaric ensemble, you don't fix the volume you just integrate over all possible volumes weighted by this  $e^{-\beta P V}$  that does the Laplace transform from one ensemble to the other of the partition function which is at some

fixed volume,  $V, T, N$ . OK? And for this we use the uniform density approximation.

So my Gibbs partition function, function of  $P, T$  and  $N$  is the integral  $0$  to infinity  $dV e^{-\beta P V}$  and I guess I have what would go over here would be  $\log Z$  of  $V, T, N$ . OK? Again this is answer to previous question, I am in the thermodynamic limit. I expect that this which gives essentially the probabilities or the weights of different volumes is going to be dominated by a single volume that makes the largest contribution to the thermodynamics or to this integration. But this integration should be subtle point like so what I would do is I will call whatever is appearing here to be some function of  $V$  because I'm integrating over  $V$  and I'm going to look for its extreme. So basically I expect that this because of this subtle point will be  $e^{-\beta \psi(V)}$  that maximizes this weight. OK?

So what I have to do is I have to take the  $\psi$  by  $dV$  and set that to  $0$ . Well part of it is simply minus  $\beta P$ . The other part of it is  $\log Z$  by  $dV$  but the  $\log Z$  by  $dV$  I have up there. It's the same  $Z$  that I'm calculating. It is  $\beta P$  canonical.

So this is none other than minus  $\beta P$  that I in this ensemble have set out, minus this  $\beta P$  canonical that I calculated before which is some function of the volume. Again, generally, it's fine. We expect the different ensembles to correspond to each other and essentially that says that most of the time you will see that you're going to get the pressure calculated in this fashion and calculated canonically to be the same thing. Except that sometimes we seem to have ambiguity because what I should do is given that I have some particular value of pressure that I emphasize exists in my isobaric ensemble, I calculate what the corresponding  $V$  is by solving this equation.

What is this equation graphically? It says pick your  $P$  and figure out what volume in these canonical curves, intersected. So the case that I drew has clearly one answer. I can go up here I have one answer. But what do I do when I have a situation such as this? I have three answers.

So in this ensemble I say what the pressure is and I ask, well, what's the volume? It says you should solve this equation to find the volume. I solve the equation graphically and I have now three possible solutions. What does that mean?

All this equation says is that these solutions are extrema. I set the derivative to 0. The task here is to find if I have multiple solutions, the one that gives me the largest value over here. So what could be happening? What is happening is that when I'm integrating as a function of  $V$ , this integrand which is  $e^{\psi(V)}$ . Right?

An integrand in the curve let's call these curves over here number one. In the case number one there's a clear solution is if I'm scanning in volume, there is a particular location that maximizes this side of  $V$  and the corresponding volume is unambiguous. If I go and look at the curve let's say up here let's call it that case number three. For case number three it also hits the blue curve unambiguously at one point which is at much lower volume and so presumably I have a situation such as this for my number two.

Now given these two cases it is not surprising that the middle one, let's say number two here, corresponds to a situation where you have two maximums. So generically, presumably, case number two corresponds to something such as this. OK? There are three solutions to setting the derivative to 0.

There are three extrema. Two extrema correspond to maxima. One extrema corresponds to the minimum and falls between the two and clearly that corresponds to this portion that we say is unstable. It's clearly unstable because it's the least likely place that you're going to find something. Right?

Not the least likely but if you go a little bit to either side, the probabilities really increase. Yes?

**AUDIENCE:** I think your indices don't correspond on the plot you've just drawn and on the [INAUDIBLE]. Like 1, 2, 3 in parentheses, in two different cases they don't correspond to it.

**PROFESSOR:** Let's pick number one.

**AUDIENCE:** Number one is when we have a singular maximum is the biggest.

**PROFESSOR:** With the biggest volume, yes?

**AUDIENCE:** No. Number two should be--

**PROFESSOR:** Oh, yes. That's right. So this is number three and this is number two. And for number two I indicated that there are maxima that I labelled one, two, and three without the parenthesis that would presumably correspond to these. OK? So then you see there is now no ambiguity.

I have to pick among the three that occur over there, the three solutions that correspond that occur from the van der Waals equation. The one that would give the highest value for this function  $\psi$ . Actually what is  $\psi$  if you think about this ensemble? This ensemble is going to be dominated by  $-\beta P V$  at the location of the  $V$  that is thermodynamic.

This  $Z$  is  $e^{-\beta E}$ , so there's a  $-\beta E$  and there's  $\omega$  which gives me a  $\beta T S$ . So it is this combination of thermodynamic quantities which if you go and look at your extensivity characterization is related to the chemical potential. So the value of the  $\psi$  at the maximum is directly related to the chemical potential and finding which one of these has the largest value corresponds to which solution has the lowest chemical potential.

Remember we were drawing this curve last time around where we integrated van der Waals equation to calculate the chemical potential and then we have multiple solutions for chemical potential. We picked the lowest one. Well, here's the justification. OK? All right.

So now what's happening? So the question that I ask is how can doing integrals such as this give you some singularity as you're scanning in say pressure or temperature along the lines such as this? And now we have the mechanism because presumably as I go from here to here the maximum that corresponds to the liquid volume will get replaced with the maximum that corresponds to the gas volume or vice versa.

So essentially if you have a curve such as two then the value of your  $Z$  which is also

$e^{-\beta U_N}$  as we said is determined by the contribution from here or here. Well, let's write both of them. I have  $e^{-\beta \psi}$  corresponding to the  $V$  of the gas plus  $e^{-\beta \psi}$  corresponding to  $V$  the liquid. Now both of these quantities are quantities that in the large  $N$  limit will be exponentially large. So one or the other will dominate and the mechanism of the phase transition is that as I change parameters, as I change my  $P$ , I go from a situation that is like this to a situation that is like this. The two maxima change heights. OK?

It is because you are in the large  $N$  limit that this can be expressed either as being this or as being the other and not as a mixture because the mixture you can write it that way but it's a negligible contribution from one or the other. This is the answer I was giving in connection with computer simulations. Computer simulations, let's say you have 1,000 particles. You have  $e^{-\beta U}$  1,000 times something,  $e^{-\beta U}$  1,000 times another thing, and if you, for example, look at the curves for something like the density you will find that you will start with the gas density. You ultimately have to go to the liquid density in the true thermodynamic limit there will be a discontinuity here.

If you do a computer simulation with finite end, you will get a continuous curve joining one to the other. As you make your size of your system simulated bigger, this becomes sharper and sharper, but truly the singularity will emerge only in the  $N$  goes to infinity limit. So phase transitions, et cetera, mathematically really exist only for infinite number of particles. Well, of course, for  $10^{23}$  particles the resolution you would need over here to see that it's actually going continuously from one to the other is immeasurably small. OK? Any questions about that?

I guess there was one other thing that maybe we should note. So if I ask what is the pressure that corresponds to the location of this phase transition, so what is the value of the pressure that separates the liquid and gas, the location of the singularity? I would have to find  $P_c$  from the following observation, that that's the pressure at which the two  $\psi$ 's,  $\psi$  of the gas is the same thing as the  $\psi$  of the liquid. Right? All right. Or alternatively, the difference between them is equal to 0. OK?

And the difference between-- I can write this kind of trivially as the integral of the derivative of the function. So  $dV d\psi$  by  $dV$  integrated between the  $V$  of the liquid and then the  $V$  of the gas. That integral should be 0.  $d\psi$  by  $dV$  we established, is this quantity. It is beta integral from  $V$  liquid to  $V$  gas  $dV P$  canonical of  $V$  minus this  $P$  transition that I want, has to be zero. OK?

So what do I have to do? Since that we identify the location of your  $P_c$  such that if you integrate the canonical minus this  $P_c$  all the way from the  $V$  of the gas to  $V$  of the liquid, this integral will give you 0. So this is the Maxwell construction that you were using last time. Again, it is equivalent to the fact that we stated that really this object is the same or related to the chemical potential, so I'm requiring that the chemical potential should be the same as I go through the transition. Yes?

**AUDIENCE:** Could you repeat why minus finite size does not in phase transition?

**PROFESSOR:** OK. Yes. So let's imagine that I have two possibilities that appear as exponentials but the number that is appearing in the exponential which is the analog of  $N$  makes one of them to be positive so I have  $e$  to the  $Nu$  and the other to be negative. So my object would be something like this. OK? Then what is this? This is related to a factor of 2 to hyperbolic cosine of  $Nu$ . OK?

So this is like some kind of a partition function and what we are interested is something like the log of this quantity. And maybe if I take a derivative with respect to  $u$  of this I will get something like the tangent of  $Nu$ . OK? So some kind-- something like a tangent and  $u$  would be something like the expectation value of this quantity. It's either plus  $u$  or minus  $u$  and it occurs-- so the average of it would be  $e$  to the  $Nu$  minus  $e$  to the minus  $Nu$   $e$  to the  $Nu$  plus  $e$  to the minus  $Nu$  and so  $u$  would be some kind of an expectation value of the quantity such as this.

Now what is this function look like the function tangent. So for positive values it goes to plus 1, for negative values it goes to minus 1 and it's a perfectly continuous function. It goes to 0. All right? That's the tangent function. Now suppose I calculate this for  $N$  of 10, this is the curve that I drew. Suppose I draw this same curve for  $N$



of 100.

For  $N$  of 100 I claim that the curve will look something like this because the slope that you have at the origin for the tangent grows like  $N$  so basically becomes steeper and steeper but ultimately has to saturate one or the other. So what-- for any, for even  $N$  of 1,000 then it's a finite slope. The slope here is related to 1,000  $U$  1,000, but it's finite. It is only in the limit where  $N$  goes to infinity you would say that the function is either minus 1 or plus 1 depending on whether  $U$  is positive or negative.

So the same thing happens as I scan over here and ask what is the density? The density looks precisely like this tangent function. For finite values of the number of particles the density would do something like this. It is only for infinite number of particles that the density is discontinuous. Yes?

**AUDIENCE:** Sir, on the plot which you drew initially on that board, what are the axis over which this scans?

**PROFESSOR:** Over here?

**AUDIENCE:** Yeah. Just what values are physical values?

**PROFESSOR:** OK. Pressure, right? So what I said was that if I scan across pressure what I will see is a discontinuity, right? So if--

**AUDIENCE:** You said that this is the result of a numerical experiment with finite number of particles. So what is the parameter of the experiment, and what is the result.

**PROFESSOR:** We have the density so you could have, for example, exactly the situation that I--

**AUDIENCE:** [INAUDIBLE]?

**PROFESSOR:** Pressure. This box that I'm showing you over here, you simulate on the computer. You have a box of finite volume, you put a piston on top of it, you simulate 1,000 particles inside.

**AUDIENCE:** OK. Thank you.

**PROFESSOR:** Then you scan as a function of pressure, you plug the density. Now, of course, if you want to simulate this, you have to increase both the number of particles and the volume of the box so that the average density is fixed and then you would see something like this. OK? Any other questions? OK, let's stick with this picture.

I kind of focused on the occurrence of the singularity, but now let's see the exact location of the singularity. So I sort of started this lecture by labeling  $P_c$ ,  $T_c$ ,  $V_c$ . Well, what are their values? OK.

So something that you know from stability is that the isotherms are constrained such that  $\Delta P \Delta V$  has to be negative. OK? Or writing  $\Delta V$  as a function of  $V$  or  $\Delta V$ , this is  $dP$  by  $dV$  along an isotherm  $\Delta V$  plus  $d^2P$  by  $dV$  squared along the isotherm  $\Delta V$  squared-- this is one-half plus one-sixth  $d^3P$   $dV$  cubed along the isotherm and so forth. This whole thing has to be negative. OK?

Now generically I pick a point and a small value of  $\Delta V$  and the statement is that along the isotherm this derivative has to be negative. So generically what I have is that  $dP$  by  $dV$  for a physical isotherm has to be negative and indeed the reason we don't like that portion is because it violates the stability condition. Well, clearly that will be broken at one point the isotherm that corresponds to  $T$  equals to  $T_c$  is not a generic isotherm. That's an isotherm that at some point it comes in tangentially.

So there is over here a point where  $dP$  by  $dV$  is 0 and we already discussed this. If  $dP$  by  $dV$  is 0 then the second derivative in such an expansion must also be 0. Why? Because if it is nonzero, irrespective of whether it is positive or negative, since it multiplies that  $V$  cubed, I will be able to pick a  $\Delta V$  such that the sign will be violated by the  $\Delta V$  of positive or  $\Delta V$  of negative. And clearly what it says is that over here the simplest curve that you can have should not have a second order term which would be like a parabola but should be like a cubic. And that the sign of the cubic should be appropriate the negative so that  $\Delta V$  to the fourth is always positive, then you have the right thing. OK?

So given that information I have sufficient parameters, information to calculate what the location of  $P_c$ ,  $T_c$ ,  $V_c$  are for the van der Waals or other approximate equation of state such as the one that you will encounter in the problems. So let's stick with the van der Waals so the van der Waals equation is that my  $P$  is-- actually let's divide by  $N$  so it would be volume per particle so I have introduced  $V$  to be the volume per particle which is the inverse of the density, if you like, so that is intensive.  $V$  minus-- there's some excluded volume, let's call it through the volume  $b$  and then I have minus something that goes like the inverse of this excluded volume, let's write it as  $a$ .

Just I write those two parameters as  $a$  and  $b$  because I will be taking many derivatives and I don't want to write anything more complicated. OK. So that's the equation. We said that the location of this critical point is obtained by the requirement that  $dP/dV$  should be 0 so what is that? It is minus  $k_B T$  divided by  $V$  minus  $b$  squared plus  $2a$  over  $V$  cubed so I took one derivative. And the second derivative is now constrained also, so that's going to give me plus  $2k_B T$   $V$  minus  $b$  cubed minus  $6a$   $V$  to the fourth. OK?

Now if I'm at a critical point-- so I put  $c$  over here, this will be 0, and this will also be 0. So the conditions for the critical point are that first of all  $k_B T_c$  divided by  $V_c$  minus  $b$  cubed should be  $2a$  over  $V_c$  cubed and  $2k_B T_c$   $V_c$  minus  $b$  to the fourth power should be  $6a$  divided by  $V_c$  to the fourth power. Hmm? So this is two equations for two unknowns, which are  $T_c$  and  $V_c$ .

We can actually reduce it to one variable by dividing these two equations with each other. The division of the left-hand sides will give me  $V_c$  minus  $b$  in the numerator divided by 2 in the denominator. The ratio of these two is simply  $V_c$  over 3. That's a one variable equation. Yes?

**AUDIENCE:** Where you have written the equations in terms  $V_c$  minus  $b$  and  $V_c$ , it should come in different powers. So our first equation should be  $V_c$  minus  $b$  squared.

**PROFESSOR:** Yes.

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** OK. Magically the ratio does not get affected and therefore neither does the answer which is  $V_c$  which is  $3b$  so that's one parameter. I can substitute that  $V_c$  into this equation and get what  $k_B T_c$  is. And hopefully you can see that this will become  $2b$  squared, which is  $4b^2$  so this gives me a factor of  $8a$ , ratio of these will give me one factor of  $b$ , so that's  $k_B T_c$ .

And then if I substitute those in the first equation, I will get the value of  $P_c$  and I happen to know that the answer-- oops, this is going to be  $27$ , I forgot because  $3^3$  will give me  $27$ . And  $P_c$  here will give me  $27$  also. I believe  $b^2 a$  and there will be a factor of  $1$ . OK. OK?

Really the only thing that actually I wanted to get out of this, you can do this for any equation of state, et cetera. Point is that we now have something to compare to experiment. We have a dimensionless ratio  $P_c V_c$  divided by  $k_B T_c$ . So I multiply these two numbers, I will get one-ninth. And then I have here a factor of  $8$  so the whole thing becomes a factor of  $3/8$  which is  $0.375$ . OK?

So the point is that we constructed this van der Waals equation through some reasonable description of a gas. You would imagine that practically any type of gas that you have will have some kind of excluded volume so that was one of the parameters that we used in calculating our estimation for the partition function, ultimately getting this  $\omega$ . And there's some kind of attraction at large distance that's been integrated over the entire range, here was this factor of  $U$ . You would expect that to be quite generic.

And once we sort of put this into this machinery that generic thing makes a particular prediction. It says that pick any gas, find its critical point-- critical point occurs with for some value of  $P_c$  density or inverse density,  $V_c$ , and some characteristic [INAUDIBLE] pressure  $k_B T_c$ . This is a dimensionless ratio you can calculate for any gas and based on this semi-reasonable assumption that we made, no matter what you do you should come up the number that is around this. OK?

So what you find in experiment? You find that the values of this combination from 0.28 to 0.33, so that's kind of a range that you find for this. So first of all, you don't find that it is the same for all gases. There is some variation. And that it's not this value of 3/8.

So there's certainly now questions to be asked about the approximation, how you could make it better. You could say, OK, actually most of the gases, you don't have spherical potentials. You have things that are diatomic that shape may be important. And so the estimation that we have for the energy for the omega et cetera is too approximate.

There is something to that because you find that you get more or less the same value in this range for gases that are similar, like helium, krypton, neon, argon, et cetera, they're kind of like each other. Oxygen, nitrogen, these diatomic molecules are kind of like each other. OK? So there is some hope to maybe get the more universal description.

So what is it that we're after? I mean the thing that is so nice about the ideal gas law is that it doesn't matter what material you are looking at. You make it sufficiently dilute, you know exactly what the equation of state is. It will be good if we could extend that. If we could say something about interacting gases that also maybe depends on just a few parameters.

So you don't have to go and do a huge calculation for the case of each gas, but you have something that has the sense of universality to it. So clearly the van der Waals equation is a step in that direction, but it is not quite good enough. So people said, well, maybe what we should do is increase the number of parameters, because currently we are constructing everything based on two parameters, the excluded volume and some integrated attraction. So those are the two parameters and with two parameters you really can only fit two things.

What we see that the ratio of  $P_c V_c$  over  $k T$  is not fixed, it's as a range, so maybe what we should do is to go to three parameters. So this whole is captured by the search for law of corresponding states. So the hope is that let's do a three

parameter system. Which parameters should I choose? Well, clearly the different systems are characterized by  $P_c$ ,  $T_c$  and  $N_c$  at critical point, so maybe what I should do is I should measure all pressures, made them dimensionless by dividing by  $P_c$  and hope that there is some universal function that relates that to the ratio of all temperatures divided by  $T_c$ , all densities or inverse densities divided by the corresponding  $V_c$ .

So is there such a curve so that that was a whole and you go and play around with this curve and it is with this suggestion and you can convince yourself very easily that it cannot be the case. And one easy way to think about it is that if this was the case, then all of our virial expansions and all of the perturbative expansions that we had should also somehow collapse together with a few parameters. Whereas all of these complicated diagrams that we had with the cycles and shapes and different things of the diagrams are really, you can calculate them. They're completely independent integrals. They will give you results that should not be collapsible into a single form.

So this was a nice suggestion what in reality does not work. So why am I telling you this? The reason I'm telling you this is that surprisingly in the vicinity of this point it does work. In the vicinity of this point you can get the huge number of different system gases, krypton, argon, carbon dioxide, mixtures, a whole lot of things. And if you appropriately rescale your pressure, temperature, et cetera, for all of these gases, they come together and fall on exactly the same type of curve of over here. OK?

So there is universality, just not over the entire phase diagram but in the vicinity of this critical point. And so what is special about that, and why does that work? OK? So I give you first an argument that says, well, it really should work. It shouldn't be a surprise. And then show that the simple argument is in fact wrong.

But let's go through because we already put the elements of it over there. So let me try to figure out what the shape of these pressure versus volume curves are going to be for isotherms that correspond to different temperatures close to  $T_c$ . So what I

want to do is to calculate  $P$  as a function of volume, actually there's reduced volume by the number of particles, and  $P$  and I'll do the following. I will write this as an expansion but in the following form--  $P$  of  $V_c$   $T$  plus  $dP$  by  $dV$  at  $V_c$   $T$  times  $V$  minus,  $V_c$  plus one-half  $V^2$   $P$  by  $dV$  squared at  $V_c$   $T$  minus  $V_c$  squared plus one-sixth  $d^3P$   $dV$  cubed at  $V_c$  and  $T$   $V$  minus  $V_c$  cubed and so forth.

So it's a function of two arguments. Really it has an expansion in both deviations from this critical point along the  $V$  direction so going away from  $V_c$  as well as going  $T$  direction, going to away from  $T_c$  but I organize it in this fashion and realize that actually these derivatives and all of the coefficients will be a function of  $T$  minus  $T_c$ . So for example  $P$  of  $V_c$  and  $T$  starts with being whatever value I have at that critical point and then if I go to higher temperatures the pressure will go up. So there's some coefficient proportional to  $T$  minus  $T_c$  plus higher order in  $T$  minus  $T_c$  and so forth and actually I expect this  $\alpha$  to be positive.

The next coefficient  $d^2P$  by  $dV^2$   $V_c$   $T$  what do I expect? Well, right at this point  $dP$  by  $dV$  there's slope. This has to be 0 for the critical isotherm. So it starts with 0 and then if I go and look at a curve that corresponds to high temperatures because of the stability, the slope better be positive. So I have a  $T$  minus  $T_c$  plus our order that I know that  $\alpha$  is positive because of  $\alpha$ --  $\alpha$  is negative because of stability. So let's write it in this fashion. OK?

What about the second derivative? Well, we said that if I look at the point where the first derivative is 0, the second derivative better be 0, so it starts also with 0. And then there's some coefficient to order of  $T$  minus  $T_c$  and then higher order and actually I don't know anything about the sign of  $P$ . It can be both positive or negative, we don't know what it is.

Now the third derivative there is no reason that it should start at 0. It will be some negative number again in order to ensure stability and there will be higher order terms in  $T$  minus  $T_c$  what we have is structure such as this. So putting everything together the statement is that if I look in the vicinity of the critical point, ask what should pressure look like? You say, OK, it has to start with a constant that we called

Pc. It has this linear increase that I put over there.

The first derivative is some negative number that is proportional to  $T - T_c$  multiplying by  $V - V_c$ . The third coefficient is negative-- oh and there's also a second-- there's the second order coefficient and then there will be high order terms. So there should be generically an expansion such as this. Say, well, OK, fine, what have we learned? I say, well, OK, let me tell you about something that we're going to experimentally measure.

Let's look at the compressibility,  $\kappa$ .  $\kappa$  is  $-\frac{1}{V} \frac{dV}{dP}$  evaluated at whatever temperature you are looking at. So if I look at this-- actually I have stated what  $\frac{dP}{dV}$  is.  $\frac{dV}{dP}$  will be the inverse of that, so this is going to give me in the vicinity of this critical point  $V_c$  a  $T - T_c$ .

So the statement is this is now something that I can go and ask my experimentalist friends to measure, go and calculate the compressibility of this gas, plot it as a function of temperature, and the prediction is that the compressibility will diverge at  $T$  goes to  $T_c$ . OK? So the prediction is that it is  $1/(T - T_c)$ . OK. So they go and do the experiment, they do the experiment for a huge number of different systems, not just one system, and they come back and say it is correct. The compressibility does diverge but what we find is that irrespective of what gas we are looking at, and this is a very universal, it goes with an exponent like this. OK?

So question is maybe you made a mistake or you did something or whatever, really the big puzzle is why do such different gases all over the spectrum and even some things that are not gases but other types of things all have the same diverges? Where did this number 1.24 come from? OK?

**AUDIENCE:** So there isn't a range like there was 0.375. It all depends on 1.24.

**PROFESSOR:** All hit 1.24. Irrespective of [? order. ?] It's a different quantity, though. I mean, it's not the number, it's an exponent. It's this, a functional form.

Why did this functional form come about? Another thing that you predict is the shape of the curve at  $T_c$ . So what we have said is that at  $T$  close to  $T_c$ , the shape of



this isotherm is essentially that  $P - P_c$  is cubic, it's proportional to  $V - V_c$  cubed. And the way that we said that is OK at that point there's neither a slope nor a second derivative, so it should be cubic.

They say, OK, what do you find in experiment? You go and do the experiment and again for a whole huge range of materials all of the data collapses and you find the curve that is something like this, is an exponent that is very close to 5 but is not exactly 5. And again, why not 3 and why is it always the same number 5? How do you understand that?

Well, I'll tell you why not 3. Why not 3? All of the things that I did here was based on the assumption that I could make an analytical expansion. The whole idea of writing a Taylor series is based on making an analytical series.

Who told you that you can do an analytic series? Experiment tells you that it is actually something non-analytic. Why this form of non-analyticity? Why it's universality? We won't explain in this course. If you want to find out come to a 334.