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PROFESSOR:

Let's start. Any questions? We've been gradually building up thermodynamics, culminating in what I call the most important fundamental relation, which was the E is $T dS$ plus $J_i dx_i$. And essentially we said that this was some statement of conservation of energy. where there's a heat component that goes into the system, and there's a work component. And actually, we ended up breaking the work component into a mechanical part and a chemical part, which we wrote as $\mu_\alpha dN_\alpha$. I guess if I don't write the sums, the summation convention is assumed.

Now, this gave us an idea of what a thermodynamic system is, in the sense of how many coordinates do we need in order to place the system in equilibrium somewhere in some coordinate space. And we said that we can just count the number of variables that we have on this side. And indeed, for the case of energy, the natural set of variables would be S , x , and N . And given some place in the coordinate system that is S , x , and N , you could find a point that corresponds to that thermodynamic equilibrium state.

Now, having gotten this fundamental relation, we can manipulate and write it in different fashion. And in particular, for example, you can write the S is dE by dT , minus $J_i dx_i$ over T , minus $\mu_\alpha dN_\alpha$ over T . So you could in principle express everything rather than in terms of entropy-- which in some circumstances may not be the right variable-- in terms of the energy content of the system and the variables that you need in order to make work type of changes on the system.

And we saw that other versions of it is possible. So for example, we could rearrange. Rather than looking at E , we could look at E minus TS , the quantity that we call F . And then dF would look very much like the original equation. Rather than $T dS$, we would get minus $S dT$. And clearly, for this quantity F , the natural variables

are T , x , and N . And there were other types of these functions that we construct.

So basically at this stage, we have a formula that tells us how to navigate our way in this space of things that are in equilibrium. And by taking various derivatives of equilibrium functions with respect to each other, we can express other ones. And via this methodology, we can relate to many different things to each other and have mathematical relations between physical observables.

So following up on that, we then ask what are some other mathematical forms that we can look at. And one set of forms followed from extensivity. And we saw that if we were under circumstances such that we were to multiply all of the extensive variables by some factor-- 2, 3, whatever-- and the energy content would increase by that same factor, then we could in fact integrate the equation and drop the d 's and write it in this fashion-- $T S + \sum \mu_i N_i$, regarding these as kind of vectors.

And importantly, that told us that the intensive variables were not independent of each other. And you had relationship that you-- $S dT + \sum J_i x_i dJ_i + N d\mu$ where α is 0. And last time, I did one calculation using this Gibbs-Duhem relation that I repeat. And that was for a gas isotherm. Isotherm corresponds to dT goes to 0. And the analogue of hydrostatic work for a gas was minus P for J . So this becomes minus $V dP + N d\mu$. If you have one component, it goes to 0. And we said that this gives us the relationship along an isotherm. So for a fixed T , $d\mu$ by dP is V over N . I'll come back to that shortly.

Towards the end of last lecture, I mentioned that we can get a number of other so-called Maxwell relations by noting that mixed second derivatives are independent of the order of taking derivatives. So that if you have some df of x and y written as df by dx at constant y plus df by dy at constant x , then the order of the second derivatives, which would be obtained by taking either a derivative of the first term with respect to y or the second term with respect to x -- doesn't matter which order.

So let's start with our initial equation. And for simplicity, let's think of cases where we have a fixed number of particles so that we can write dE as $T dS + \sum J_i dx_i$. So this looks like this dF that I wrote before for you. And I can identify temperature as dE by

dS at constant x , and each one of the forces J_i as dE by dx_i at constant S . And all of the J 's that are not equal to i kept fixed.

And then, since the second derivative is irrespective of order, I can form the second derivative with respect to the combination $S x_i$ into a different fashion. I can either take a derivative over here-- I already have derivative with respect to S giving me T , so I will get dT by dx_i , essentially at constant S -- or I can take the derivative of this object. I already have the x derivative, so I take the S derivative. So I have dJ_i with respect to S at constant x .

So this is an example of the Maxwell relation. And just to remind you, we can always invert these derivatives. So I can invert this and say that actually, if I had wondered how the entropy changes as a function of a force such as pressure at constant x , it would be related to how the corresponding displacement to the force changes as a function of temperature. So you would have a relationship between some observable such as how the length of a wire changes if you change temperature rapidly, and how the entropy would change as a function of pressure, or corresponding force, whatever it may be.

Now, what I would like to remind you is that the best way to sort of derive these relationships is to reconstruct what kind of second derivative or mixed derivative you want to have to give you the right result. So for example, say somebody told me that I want to calculate something similar-- dS by dJ , let's say at constant temperature. How do I calculate that?

A nice way to calculate that is if I somehow manipulate so that S appears as a first derivative. Now, S does not appear as a first derivative here, but certainly appears as a first derivative here. So who says I have to take E as a function of state? I can look at the second derivative of F .

So if I look at F , which is E minus TS -- and actually, I don't even need to know what the name of this entity is, whether it's F , G , et cetera. All I know is that it will convert this to minus $S dT$ -- the TS that I don't want, so that S appears now as a first derivative.

Now I want to take a derivative of S with respect to J . If I just stop here, the next term that I would have is $J_i dx_i$. And the natural way that I would construct a second derivative would give me dS with respect to x_i . But I want the S with respect to J_i . So I say, OK, I'll do this function instead. As I said, I don't really care what the name of these functions is. This will get converted to $x_i dJ$.

Now I can say there is this first derivative-- d of minus S with respect to J_i at constant T is the same thing as d of minus y with respect to T at constant J . So I can get rid of the minus sign if I want, and I have the answer that I want. It is dx_i by dT at constant J -- at constant-- yeah, T -- J . And you can go and construct anything else that you like.

Let me, for example, try to construct this entity we already calculated. So let's see. What can I say about $d\mu$ by dP at constant temperature, and I want to calculate that via a Maxwell relation? So what do I know? I know that dE is $T dS$ minus $p dV$. Good. Oh, I want to have μ in the play, so now I have to add μdN .

That's good, because I have μ as a first derivative. I have it over here. But I have P as a first derivative, whereas I want P to appear as the work element, something like dP . So what I will do is I will make this d of E plus pV . This converts this to plus $V dP$ plus μdN . That's fine, except that when I do things now, I would have calculated things at constant S . And I want to calculate things at constant T . That's not really important. I do a minus ST . This becomes minus $S dT$.

And then I have a function of state-- I don't care what it's called-- that has the right format for me to identify that $d\mu$ by dP at constant N and T , along an isotherm of a fixed number of particles, is the same thing as dV by dN at constant P and T . So that's my Maxwell relation.

So why didn't I get this result? Did I make a mistake?

AUDIENCE: [INAUDIBLE].

PROFESSOR: Louder.

AUDIENCE: Is this valid for extensive systems?

PROFESSOR: Yes, this is valid for extensive system. I used extensively in the relation of this. And here, I never used extensivity. But if I have a system that I tell you its pressure and temperature, how is its volume related to the number of particles? I have a box in this room. I tell you pressure and temperature are fixed. If I make the box twice as big, number of particles, volume will go twice as big. So if I were to apply extensivity, I would have to conclude that this is the same thing as V over N , and I would be in agreement with what I had before.

Any questions? Yes.

AUDIENCE: What about the constraint of constant P N T [INAUDIBLE]?

PROFESSOR: OK. Actually, constraint of constant P N T is important because we said that said there it is a kind of Gibbs-Duhem relation. And the Gibbs-Duhem relation tells me for the case of the gas that the S dT minus V dP plus N $d\mu$ is 0. And that constraint is the one that tells me that once you have set P and T , which are the two variables that I have specified here, you also know μ . That is, you know all the intensive quantities. So once you set P N T -- the constraints over there-- really, the only thing that you don't know is how big the system is. And that's what's the condition that I used over here.

But it is only-- so let me re-emphasize it this way-- I will write dV by dN is the same thing as V over N , only if I have P N T here. If I had here P N S , for example, I wouldn't be able to use this.

I was going to build this equation to say, look at the elements of this. This part we got from the first law, the temperature we got from the zeroth law, and this we got from the second law, which is correct, but it leaves out something, which is that what the second law had was things going some particular direction. And in particular, we had that for the certain changes that I won't repeat, the change in entropy to be positive.

So when you are in equilibrium, you have this relationship between equilibrium state functions. But in fact, the second law of thermodynamics tells you a little bit more than that. So the next item that we are going to look at is, what are the consequences of having underlying this equality between functions of state some kind of an inequality about certain things being possible and things not being possible? And that relates to stability conditions.

And I find it easier to again introduce to you these stability conditions by thinking of a mechanical analogue. So let's imagine that you have some kind of a spring, and that this spring has some kind of a potential energy that I will call ϕ as a function of the extension x . And let's say that it's some non-linear function such as this. There is no reason why we should use a hook and spring, but something like this.

Now, we also discussed last time what happens if I were to pull on this with some force J . So I pull on this. As a result, presumably it will no longer be sitting at x , because what I need to do is to minimize something else-- the function that we call H -- which was the potential energy of the spring plus the entity that was exerting the force. So if I were to make it in the vertical direction, you can imagine this as being the potential energy of the mass that was pulling on the spring.

So what that means is that in the presence of J , what I need to do is to find the x that minimizes this expression. Once essentially the kinetic energy has disappeared, my spring stops oscillating and goes to a particular value. And mathematically, that corresponds to subtracting a linear function from this. Actually, what will it look like? Let's not make this go flat, but go up in some linear fashion so that at least I can draw something like this.

So what I need to do is to minimize this. So I find that for a given J , I have to solve $d\phi/dx = J$. But especially if you have a spring that has the kind of potential that I drew for you, you start increasing the-- so basically, what it says is that you end up at the place where the slope is equal to the derivative of the potential function. What happens if you start increasing this slope, if it is a non-linear type of thing, at some point you can see it's impossible. Essentially, it's like a very flat noodle. You pull on it

too much and then it starts to expand forever.

So essentially, this thing that we are looking for a minimum, ultimately also means that you need to have a condition on the second derivative. $d^2 \phi$ by dx squared better be positive actually, I have to take $d^2 H$ by dx squared. I took one derivative to identify where the location of the best solution is. If I take a second derivative, this became essentially the J . J is a constant. It only depends on the potential energy.

So it says independent of the force that you apply. You know that if the shape of the potential energy is given, the only places that are accessible are the kinds of places where you take the second derivative and the second has a particular sign. So this portion of the curve is in principle physically accessible. The portion that corresponds to essentially changing the curvature and going the other way, there's no way, there's no force that you can put that would be able to access those kinds of displacements. So there is this convexity condition.

This was for one variable. Now suppose you have multiple variables-- x_2 , x_3 , et cetera. So you will have the potential energy as a function of many variables. And the condition that you have is that the second derivative of the potential with respect to all variables, which forms-- and if there are n variables, this would be an n by n matrix. This matrix is positive definite. What that means is that if you think of this as defining for you the bottom of a potential, in whatever direction you go, this would describe the change of potential for you. The first order change you already set to 0 because of the force J . The second order change better be positive. So this is the condition that you would have for stability, quite generally mechanically.

And again, this came from the fact that if you were to exert a force, you would change the energy by something like $J \Delta x$, which is certainly the same thing that we have here. This is just one component that I have been focusing on. And so ultimately, I'm going to try to generalize that to this form.

But one thing that I don't quite like in this form is that I'm focusing too much on the displacements. This is written appropriately using this form. And we have seen over here that whether or not I express things in terms of the displacements or in terms

of entropy, temperature, conjugate forces, et cetera, these are all equivalent ways of describing the equilibrium system. So I'm going to do a slight manipulation of this to make that symmetry between forces and displacements apparent.

So the generalization of this expression that we have over here is that once I know the potential energy, the force in this multi-component space is df by dx_i . So in this multi-component space, I have some J , and there's a corresponding x . They're related by this.

Now, if I were to make a change in J , there will be a change in the position of the equilibrium. And I can get that by doing a corresponding change in the derivative. The corresponding change in the derivative is the second derivative of ϕ with respect to $x_i x_j \delta x_j$, sum over J . So what I'm saying is that this is a condition that relates the position to the forces. If I make a slight change in the force, there will be a corresponding slight change in the position. And the changes in the position and the force given by this equilibrium condition are related by this formula.

Now, you can see that that sum is already present here. So I can rewrite the expression that is over here using that formula as $\delta x_i \delta J_i$, sum over i -- better be positive. So this expression is slightly different and better way of writing essentially the same convexity condition, stability condition, but in a manner that treats the displacements and the forces equivalently.

And I'm going to apply that to this and say that in general, there will be more ways of manipulating the energy of a thermodynamic system, and that having the system reach to equilibrium requires the generalization of this as a $\delta T \delta S$, plus sum over $i \delta J_i \delta x_i$, plus sum over α , $\delta \mu_\alpha$, δN_α -- to be positive.

And you may say I didn't really derive this for you because I started from mechanical equilibrium and stability condition and generalized to the thermodynamic one. But really, if you go back and I use this condition and do manipulations that are compatible to this, you will come up with exactly this stability condition. And I have that in the notes. It is somewhat more mathematically

complicated than this, because the derivatives involve additional factors of $1/T$. And you have to do slightly more work, but you will ultimately come with the same expression. OK?

You say, why is that of any use? It is possible that you've already seen a particular use of this expression. Let's look at the case of a gas-- one component. You would say that the condition that we have is that $\Delta T \Delta S - \Delta P \Delta V + \Delta \mu \Delta N$ has to be positive.

Let's even be simpler. Look at the case where ΔT is 0, ΔN equals to 0, which means that I have a fixed amount of gas at a particular temperature. So I could have, for example, a box in this room which is in equilibrium at the same temperature as the temperature of the room. But its volume I'm allowed to adjust so that the pressure changes. So in that process, at a particular temperature, I will be finding a particular curve in the pressure volume space.

And the reason that I drew this particular way is because I have the condition that $-\Delta P \Delta V$ better be positive, so that if I have P as a function of V , then I know that dP is dP by $dV \Delta V$. And if the product $dP dV$ is positive, then this derivative dP by dV has to be negative. This has to be a decreasing function. And another way of saying that is that the compressibility-- κ_T , which is $-1/V$, the inverse of this dV by dP at constant T -- has to be positive. So this is a curve where dP by dV is negative.

Fine, you say. Nothing surprising about that. Well, it turns out that if you cool the gas, the shape of this isotherm can change. It can get started. And there is a critical isotherm at which you see a condition such as this, where there's a point where the curve comes with 0 slope.

So you say that for that particular critical isotherm occurring at T_C , if I were to make this expansion, the first term in this expansion is 0. You say, OK, let's continue and write down the second term-- $1/2 d^2 P$ by dV squared at constant P times ΔV squared.

Now the problem is that if I multiply this by ΔV -- which would have made this into ΔV squared and then this into ΔV cubed-- I have a problem because ΔV can be both positive or negative. I can go one direction or the other direction. And a term that is a cubic can change sign-- can sometimes be positive, can sometimes be negative, depending on the sign of that. And that is disallowed by this condition. So that would say that if an analytical expression for the expansion exists, the second derivative has to be 0.

And then you would have to go to the next term-- $d^3 P / dV^3$. And then ΔV -- you would normally write ΔV cubed, but then I've multiplied by ΔV on the other side. We'd have ΔV to the fourth. ΔV to the fourth you would say is definitely positive. Then I can get things done by having to make sure that the third derivative is negative.

And you say, OK, exactly what have you done here? What you have done here is you've drawn a curve that locally looks like a cubic with the appropriate sign. And so that's certainly true that if you have an isotherm there the compressibility diverges, you have a condition on second derivatives. And you probably have used this for calculating critical points of van der Waals and other gases. And we will do that ourselves. But it's actually not the right way to go about, because when you go and look at things experimentally with sufficient detail, you find that these curves at this point are not analytic. They don't admit a Taylor expansion. So while this condition is correct, that the shape should be something like this, it is neither cubic nor a fifth power, but some kind of a non-analytic curve.

AUDIENCE: Could you repeat last statement?

PROFESSOR: That statement, in order to fully understand and appreciate, you have to come to next term, where we talk about phase transitions. But the statement is that the shape of the function in the vicinity of something like this is ΔP is proportional to ΔV to some other gamma that is neither 3 nor 5 nor an integer. It is some number that experimentally has been determined to be of the order of, I don't know, 4.7. And why it is 4.7 you have to do a lot of interesting field theory to understand.

And hopefully, you'll come next semester and I'll explain it.

AUDIENCE: So your point is that gamma is not [INAUDIBLE].

PROFESSOR: Gamma is not-- so the statement is, in order for me to write this curve as something ΔV plus some other thing-- ΔV^2 -- plus some other thing-- ΔV^3 -- which we do all the time, there is an inherent assumption that an analytical expansion is possible around this point. Whereas if I gave you a function y that is x to the $5/3$, around x of 0, you cannot write a Taylor series for it. OK?

Essentially, this stability condition tells you a lot of things about signs of response functions. In the case of mechanical cases, it is really that if you have a spring, you better have a force constant that is positive, so that when you pull on it, the change in displacement has the right sign. It wants to be contracted. And similarly here, you are essentially compressing the gas. There's a thermal analogue of that sine which is worth making sure we know.

Let's look at the case where we have a fixed number of particles. And then what we would have is that our dE is $T dS$ plus $J_i dx_i$. I am free to choose any set of variables. The interesting set of variables-- well, OK. So then stability implies that $\Delta T \Delta S$ plus $\Delta J_i \Delta x_i$ with the sum over i is positive.

Now, I can take a look at this expression and choose any set of variables to express these changes in terms of. So I'm going to choose for my variables temperature and x_i . You see, the way that I've written it here, S , T , J , x appear completely equivalently. I could have chosen to express things in terms of S and J , T and J , S and x . But I choose to use T and x .

All right, so what does that mean? It means that I write my ΔS in terms of dS by dT at constant x dT , plus dS by dx_i at constant T and other x_j not equal to i , Δx_i .

I also need an expression for ΔJ_i here. so my ΔJ_i would be dJ_i by dT at constant x , ΔT , plus dJ_i with respect to x_j at constant T , an appropriate set of J 's, Δx_i -- Δx_j . Sum over J implicit here.

I substitute these-- ΔS and ΔJ -- in the general form of the stability condition to get constraints applicable to combinations involving ΔT and Δx . So I have to multiply ΔS with ΔT . I have to multiply ΔJ_i with Δx_i here. Yes?

AUDIENCE: So here, J is not equal to i . And then which one is J ? [INAUDIBLE].

PROFESSOR: OK. So let's say that I have S that is a function of-- I have x_1 and x_2 . So here, I would have derivatives dS by dx_1 times Δx_1 . I would have derivatives dS by dx_2 times Δx_2 . In both cases, T is kept fixed. In this case, additionally, x_2 is kept fixed. In this case, additionally, x_1 is kept fixed. That's all. OK?

So let's do that multiplication. We multiply a ΔT here and we get dS by dT at constant x , ΔT squared. We get here a term which is $\Delta T \Delta x_i$, multiplying dS by dx_i at constant T , and the others that I don't bother to write. But I note that I will get another term that is $\Delta x_i \Delta T$ from the second term, whose coefficient is dJ_i by dT at constant x . And I group those two terms together. And finally, we have the last term here, which is $\Delta x_i \Delta x_j$, dJ_i by dx_j , constant T .

And the constraint for all of these stability conditions that I have written, I have to be in the minimum of a potential. Any deviation that I make better lead to an increase in this combination, which is kind of equivalent to being at the minimum of some kind of potential energy. If you do some manipulations, this is also equivalent to being at the maximum of some entropy function.

Now, let's look at that manipulation a little bit. Now, I happen to know that this form will simplify a little bit. And that's why I chose this combination of variables. And the simplification that will happen is that this entity is 0. So let me show you why that entity is 0. And that relies on one of these Maxwell relationships that I had. So let's find the Maxwell relation that is applicable to dS by dx_i at constant T , which is what I have over here.

OK, let's again start with dE being $T dS$ plus $\sum_j \mu_j dx_j$. I'm at fixed number of particles. I don't need to write the other term-- $U dN$. Unfortunately here, S is not the first derivative. So what I will do is I will look at $E - TS$. That's going to turn this into

minus $S dT$. Good. $J_i dx_i$ is exactly what I want because this will tell me something about the derivative in this fashion.

dS by dx_i at constant T is equal to what? It's taking the things in this fashion, which is dJ_i by dT at constant x . Good. So I can see that the sum total of these two terms is 0. And that's exactly what I have here. So this is 0 by Maxwell relation. OK? OK

So having set that to 0, I have two terms. One of them is this entity that goes with ΔT squared. And the other is this entity-- sum over i and J , Δx_i , Δx_j , dJ_i , dx_j , constant T . And this-- for any choice of Δx 's and ΔT 's-- for any choice, it better be positive.

So in particular, given this nice form that I have over here, I can certainly choose all of the Δx 's to be 0, because I do things at constant displacement. And then what I have is that the whole thing is proportional to ΔT squared and some coefficient. So that coefficient better be positive.

So entropy should always be an increasing function of temperature at constant displacement. And the consequence of that is that heat capacities measure at constant displacement. So this is the heat capacity-- C_x . The general definition is you put some amount of heat into the system at constant displacement. So I have to specify the procedure by which heat is applied to the system and see how much this temperature changes.

I can in principle do this sufficiently stability so I can measure precisely the changes in temperature infinitesimally. And then I can use the relationship between dQ and reversible heat-- so dS at constant x dT . And dS by dT at constant x is precisely the entity that we have looked at-- to be positive.

So in the same way that a spring is stable-- if you pull on it, its extension should increase a little bit. And so the coefficient that relates the change in displacement corresponding to the change in force has to be positive for stability. Heat capacities must have this positivity in the sense that if you add heat to a system, its temperature should go up. If it went the other way, it would actually also violate the

second law of thermodynamics. Yes?

AUDIENCE: I'm a bit confused about the J notation that we used. The initial equation that we start has only-- it deals with i, but where does J come from?

PROFESSOR: This equation. Which equation? Up here?

AUDIENCE: So index J is just a dummy variable? [INAUDIBLE] that dE equals $T dS$ equals $J_i dS_i$.

PROFESSOR: OK. Fine. So let's start from here. And part of the confusion is that I'm not really consistent. Whenever I write an index that is repeated, there is a so-called summation convention that you may have seen in quantum mechanics and other courses which says that the index that is repeated twice is summed over. So when I write $a_i b_i$, using the summation convention, what I mean is, sum over all possible values of i, a_i , b_i .

So what I meant here is that there may be multiple ways of doing work on the system. So there could be pressure, there could be spring, there could be magnetic work. And if I do mechanical work on the system, the change in energy is the sum total of all different ways to do mechanical works, plus the heat that is supplied to the system. So that's statement number one.

Now, I did something else here, which is that when I take a derivative of a function that depends on multiple variables-- so f depends on x_1, x_2, x_3, x_n -- then if I look at the change in this, any one of these variables can change by an amount that is dx_i . And if the second variable changes, there is a corresponding contribution, which is df with respect to the second variable. And I have to add all of these things together. So if I'm again inconsistent, this is really what I mean, that when you do a change in a function of multiple variables, you would write it as dx_i, df by dx_i . If you use the summation convention, I have to really sum over all possibilities.

Now, suppose I took one of these things, like df by dx_3 . So it's one of the derivatives here. And I took another derivative, or I looked at the change in this function. This function depends also on variables x_1 through x_n . So I have to look at the sum over

all changes with respect to x_j of df by dx_j .

So you can see that automatically, I have kind of assumed some of these things as I write things rapidly. And if it is not clear, you have to spend a little bit of time writing things more in detail, because it's after all kind of simple algebra. Yes, did I make another mistake? Yes?

AUDIENCE: Oh, not a mistake, just--

PROFESSOR: Yes?

AUDIENCE: When you were talking about mechanicals, you had a non-linear spring. You start pulling on it. At some point, it just increases.

PROFESSOR: If it is a non-linear spring, yes, that's right.

AUDIENCE: Can you provide example of thermodynamic system which, upon some threshold action upon it, becomes unstable?

PROFESSOR: OK. I think I more or less had that example. Let's try to develop it a little bit further. So I said that typically, if I look at the pressure volume isotherms of a gas, it looks something like this. And I told you that there is actually some kind of a critical isotherm that looks something like this. And you may ask, well, what do things look below that for lower temperatures? And again, you probably know this, is that this is the temperature below which you have a transition to liquid gas coexistence. And so the isotherms would look like that.

Now, it turns out that while these are true equilibrium things-- you would have to wait sufficiently long so that the system explores these isotherms-- it is also possible in certain systems to do things a little bit more rapidly. And then when you go below, you will see a kind of remnant of that isotherm which kind of looks like this.

So that isotherm would have portions of it that don't satisfy these conditions of stability. And the reason that you still get some remnant of it-- not quite the entire thing. You get actually some portion here, some portion here-- is because you do

things very rapidly and the system does not have time to explore the entire equilibrium. So that's one example that I can think of where some remnants of something that is like that non-linear noodle takes place.

But even the non-linear noodle, you cannot really see in equilibrium. You can only see it when you're pulling it. And you can see that it is being extended. There is no equilibrium that you can see that has that. So if I want to find an analogue of that non-linear noodle showing instability, I'd better find some near-equilibrium condition. And this is the near-equilibrium condition that I can think of.

There are a number of cases. And essentially, you've probably heard hysteresis in magnets and things like that. And by definition, hysteresis means that for the same set of conditions, you see multiple different states. So not both of them can be or multiple of them can be in equilibrium. And over some sufficient time scale, you would go from one behavior to another behavior. But if you explore the vicinity of the curves that correspond to these hysteretic behavior, you would see the signatures of these kinds of thermodynamic instabilities.

There was one other part of this that maybe I will write a little bit in more detail, given the questions that were. Asked It is here I looked at this general condition for the case where the δx 's were 0. Let's look at the same thing for the case where δT equals to 0, because then I have the condition that the J_i by the x_j , δx_i , δx_j should be positive. And this was done at constant T .

And to be more explicit, there is a sum over i and J in here. So if I'm doing things at constant temperature, I really have the analogue of the instability condition. What I have here, it is the same thing as this one.

And if you think about this in a little bit more detail-- let's say I have something like a gas. We have two ways of doing work on the system. I have dJ_1 by dx_1 . I have dJ_2 by dx_2 . I have dJ_1 by dx_2 . I have dJ_2 by dx_1 . Essentially, this object, there are four of them. And those four I can put into something like this.

And the statement that I have written is that this 2 by 2 matrix, if it acts on the

displacement δx_1 δx_2 on the right, and then gets contracted on the left by the same vector δx_1 , δx_2 , for any choice of the vector δx_1 δx_2 , this better be positive. This is for two, but in general, this expression is going to be valid for any number.

Now, what are the constraints that a matrix must satisfy so that irrespective of the choice of this displacement, you will get a positive result? Mathematically, that's caused a positive definite matrix. So one of the conditions that is certainly immediately obvious is that if I choose the case where δx_2 is 0, then the diagonal term that corresponds to that entity better be positive. So a matrix is positive definite if for every one of the diagonal elements, I have this condition.

So this is actually something that we already saw. In the case of the gas, this would be something like minus dP by dV at constant temperature-- be positive. This is the nature of these isotherms always going one way that I was drawing.

AUDIENCE: Question.

PROFESSOR: Yes.

AUDIENCE: You're not summing over alpha now, are you? Or are you--

PROFESSOR: Yes, I'm not. And I don't know how to write. [LAUGHS] Let's call it δJ_1 , x_1 . So all diagonal elements must be positive, but that's not enough. So I can write a matrix that has only positive elements along the diagonal, but off-diagonal elements such that the combination will give you negative values of this culmination for appropriate choices of δx_1 and δx_2 . The thing that you really need is that all eigenvalues must be positive.

It is not that easy to write down mathematically in general what that means in terms of multiple response functions. That's why this form of writing is much more compact and effective. It basically says, no matter what combination of elements you choose, you are at the bottom of the potential. You should not be able to go away from it.

AUDIENCE: So the second statement is necessary and sufficient condition?

PROFESSOR: This statement is necessary but not sufficient. This statement is equivalent to the meaning of what is a positive definite matrix. It is sufficient. Yes?

AUDIENCE: Is there any physical interpretation to diagonalizing that matrix?

PROFESSOR: It depends on the kind of the formations that you make. Like if I was really thinking about a gas where I allow some exchange with the surface or something else so that ΔN is not equal to 0, the general form of this matrix in the case where I have pressure volume would be something like this. I would have minus dP by dV . I would have $d\mu$ by dN . I would have dP by dN . I would have $d\mu$ by dV . And I would have to make sure that this matrix is positive definite, so I know certainly that the compressibility by itself has to be positive.

$d\mu$ by dN also has to be positive. But if I allow changes both in volume and the number of particles, then because of these off-diagonal terms, I have additional constraints. So for appropriate changes, it is sufficient to look at the diagonal terms. But for the entire set of possible transformations, it's not. Yes?

AUDIENCE: If you look at different ways to do the work on the system-- so in this case, change volume, change number of particles, if you're saying forces have different dimensions, and if diagonalization of these metrics corresponds to inventing some new ways of acting on the system which are a linear combination of old ways like change volume a little and change particles--

PROFESSOR: Change the number of particles, yes.

AUDIENCE: Those are pretty weird manipulations, in terms of how to physically explain what is diagonalization matrix.

PROFESSOR: OK. There is a question of dimensions, and there's a question of amount. So maybe what you are worried about is that if I make one them volume and the other pressure, one is extensive, one is intensive, and the response functions would have to carry something that is proportional to size.

But then there are other conditions, let's say, where all of the variables are intensive. And then it's moving around in the space that is characterized, let's say, by pressure and chemical potential from one point to another point. And there is some generalized response that you would have, depending on which direction you go to. So essentially, I could certainly characterize various thermodynamic functions in this space P, μ .

And what I know is that I cannot write any function in this two-parameter space that would be consistent with the thermodynamic principles of stability. I have to have some kind of convexity. So certainly, what typically-- let's say again, going back to my favorite example here-- what people do and what we will do later on is we specify that you have some particular pressure and volume of an interacting gas. And there is no way that we can calculate the thermodynamic properties of that system exactly.

We try to construct a free energy as a function of these variables. And that free energy will be approximate based on some ideas. And then we will see that that free energy that I construct in some places will violate the conditions of stability. And then I know that that free energy that I constructed, let's say on the assumption that the box that I have is uniformly covered by some material, that assumption is violated.

And maybe what has happened is that part of the volume is a liquid and part of the volume is gas. So we will do precisely that exercise later on. We will choose a pair of variables. We will try to construct a free energy function out. We make the assumption that the box is uniformly occupied with the gas at some density.

Based on that, we estimate its energy, entropy, et cetera. We construct a free energy function out. And then we will see that that energy function violates the compressibility condition at some point. So we know that, oh, we made a mistake. The assumption that it is uniformly occupying this box is wrong.

All right, any other questions? Yes?

AUDIENCE: One of the things that confuses me about thermodynamics in general is the limits of its applicability. We think of it as being very general, applying to many different systems. For example, if we had two bar magnets and we had the north pole close to the south pole of the other one, and I thought of the magnetic field in between, is it conceivable to think of that as a thermodynamic system?

PROFESSOR: You can think of the magnet as a thermodynamic system. And you can certainly look at two of them, including the electromagnetic field that surrounds them. And there would be some conditions, like if you were to jiggle these things with respect to each other-- and you would maintain the entire thing in a box that prevented escape of electromagnetic waves or heat to the outside-- that eventually this jiggling of the two magnets will lead to their coming to equilibrium but at a higher temperature. So this is what I'm saying.

So imagine that you have-- let's for simplicity think of, again, one big magnet that you don't move, and one small magnet here that you externally jiggle around. And then you remove the source of work. You wait for a while. And then you find that after a while, this thing comes to an equilibrium.

You ask, where did that kinetic energy go to? You had some kinetic energy that you had set into this, and the kinetic energy disappeared. And I assume that there are conditions that the kinetic energy could not have escaped from this box. So the only thing that could have happened is that that kinetic energy heated up the air of the box, the magnet, or whatever you have. So thermodynamics is applicable in that sense to your system.

Now, if you ask me, is it applicable to having a single electron spin that is polarized because of the magnetic field and some condition that I set it to oscillate, then it's not applicable, because then I know some quantum mechanical rules that govern this. There may be in some circumstances some conservation law that says this with oscillate forever. If it doesn't oscillate forever, there's presumably a transition matrix that says it will admit a particular photon of a particular energy. And I have to ask what happened to that photon.

So what we will see later on is that thermodynamics is very powerful, but it's not a fundamental theory in this sense that the quantum mechanics that governs the spins. And the reason that this works for the case of the magnet is because the magnet has billions of spins in it-- billions and billions of spins, or whatever. So it is the of large numbers that ultimately allows you to translate the rules of motion into a well-defined theory that is consistent with thermodynamics.

AUDIENCE: I know that my question seemed off-topic. But the reason why I asked about this particular system is because I would think that it doesn't have a positive compressibility. Like if you pull the two magnets apart very slowly, the force pulling them together decreases instead of increasing like with the rubber band.

PROFESSOR: OK. It may be that you have to add additional agents in order to make the whole system work. So it may be that the picture that I had in mind was that you have the magnet that is being pushed up and down. And I really do put a number of springs that make sure there exists an equilibrium position. If there is no mechanical equilibrium position, then the story is not whether or not to thermodynamic applies. It's a question of whether or not there is an equilibrium.

So in order for me to talk about thermodynamics I need to know that there is an eventual equilibrium. and that's why I actually recast the answer to your question, eventually getting rid of the kinetic energy of this so that I have a system that is in equilibrium. If there are things that are not in equilibrium, all bets are off.

Thermodynamics is the science of things that are in equilibrium.

Other questions? All right, so there is only one minor part of our description-- rapid survey of thermodynamics-- that is left. And that's the third law of thermodynamics and that has to do something with the behavior of things as you go towards the limit of the zero of thermodynamic temperature. And I think we will spend maybe 10, 15 minutes next lecture talking about the third law of thermodynamics.

Probably from my perspective, that is enough time with respect towards the time we spend on the other laws of thermodynamics, because as I will emphasize to you also, the third law of thermodynamics is in some sense less valid than the others.

It's certainly correct and it is valid. It is just that its validity rests on other things than what I was emphasizing right now, which is the large number of degrees of freedom. You could have a large number of degrees of freedom in a world that is governed by classic laws of physics, and the third law of thermodynamics would be violated. So it is a condition that we live in a world that is governed by quantum mechanics that tells us about the third law, as we will discuss next time.