

Thermodynamics of Fluid Phase Equilibria
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Lecture – 13
Thermodynamic Calculus – 4

Welcome back, in the last lecture we derived Euler integrated fundamental equation, we will continue this exercise in this particular lecture I will start with Legendre transformation.

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The image shows a digital whiteboard with handwritten notes. At the top, the variables T and $-P$ are written. Below them, the Euler Integrated Fundamental Equation is written and boxed:
$$U = TS - PV + \sum_k \mu_k N_k$$
 Underneath the equation, it is labeled "Euler Integrated FE". Below this, the text "Legendre Transformation" is written and underlined. Underneath that, the natural variables (S, V, N) are listed. An arrow points from "CONST T & P" to the text "first derivation of $U(S, V, N)$ ". To the right of this, it says " $U(T, P, N)$ - will not have the same info". The whiteboard interface includes a toolbar at the top and a status bar at the bottom showing "21 / 68".

This is quite relevant or rather important. The reason being is that though our natural variable for example, for U is S, V, N though it is possible to control in principle this variable, but this is much more difficult in practice. The much more common variables which often used is temperature, because you can easily put your system in a control bar and maintain the temperature, you can also maintain the pressure by keeping it open to the atmosphere. So, thus the common variables which are of interest to us, which we can control much easily is constant temperature and pressure ok. Now our temperature and pressure appear as a first derivative of the fundamental equation $f u$.

So, in other word if we want just a function U as a function of T, P, N this is possible; however, this will not have the same information as in the original function ok. So, we will not have the same information thus we rather not use it. So, the one of the reason is

if we use integration in order to get such a function, we get a constant which is ambiguous variable; why ambiguous a and cannot be assigned certain information and as we lose the information by simply trying to use integration and I will try to explain it by a simple example. So, let us assume that we have just one function variable.

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$f(x) = x^2 + 2$
 construct a fn $f(w)$; $w = \frac{df}{dw} = 2x \Rightarrow x = \frac{w}{2}$
 $f(w) = \frac{w^2}{4} + 2 \equiv y \Rightarrow w = \pm 2\sqrt{y-2}$
 attempt to recover original $f(x)$
 $\frac{dx}{dy} = \frac{1}{w} \Rightarrow x = \int \frac{1}{w} dy$
 $= \int \frac{1}{\pm 2\sqrt{y-2}} dy$
 $= \pm \sqrt{y-2} + c$
 or $y = (x-c)^2 + 2$
 Unknown int. const.

A one variable based function f of x is x plus 2 plus 2. So, now, we are going to construct a function. So, we are going to construct a function f of w ok, such that w is the derivative of f ok. So, which means basically w is a df by dw , which is nothing, but $2x$ ok.

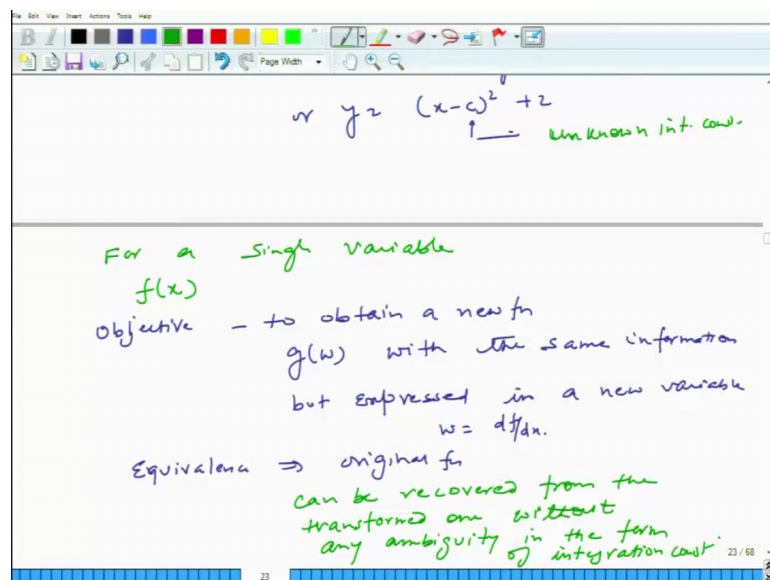
All this means x is w by 2. So, f of w is going to be w square by 4 plus 2 all right. Now we are going to attempt to recover original $f(x)$ ok. So, that is our objective now. So, w is nothing, but the derivative of the function. So, let us say this is y now. So, w is a function. So, what we are going to do is, let us assume that this is y which essentially means w is $2y$ minus 2 right.

Now this w itself is also committing as $del x$ by $del y$ this is nothing, but w which is can be written as x is integral of w , y and now w is back here we plug in here we get ok. This is equivalent to saying y minus 2 plus c or in other word y is x minus c square plus 2. So, this unknown integral constant constants are introduced here ok.

So, by simple integration we are going to get unknown constant, which means that we are not going to get the original function recovered here. So, which means this is not appropriate method in order to extract or change the variable ok. Because in this method we are not going to retain the information as we change the variable, but there is another method which allows you to do that and that is what we going to use it that is called the Legendre transformation

So, let us again assume single variable.

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For a single variable f of x , our objective is to obtain new function g of w let us assume that, with the same information as in the original function, but expressed in a new variable. So, what is available w which is a derivative of x first derivative of the original function. And same information means is equivalence is something which we can which means we can recover original function.

So, we can recover original function without any integration constant so; that means, can be recovered from the transformed 1 without any ambiguity ok, which can be which will be in the without any ambiguity in the form of. So, the equivalence is basically can be that we can recover the original function from the transformer without any ambiguity in the form of integration constant ok.

So, this can be done through mathematical operation which we are going to say or which we are going to describe subsequently Legendre transformation ok. So, I am going to prove it for only single variable. So, let us assume that. So, you have this $g(w)$ which is basically a transform function.

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The image shows a whiteboard with the following content:

$$g(w) = f - xw \quad \rightarrow \text{with the following props}$$

$$\left[\begin{array}{l} df = w dx \\ dg = df - x dw - w dx \\ dg = -x dw \end{array} \right.$$

- role of variable & derivative has been exchanged
- variable of the original fn is - derivative of the transform

To recover the original fn
 - apply LT for one more time.

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So, we are going to write it this as the original function minus x multiplied by first derivative of the function f that is x multiplied by w ok. So, this has the following property with the following property ok.

So, first of all df is $w dx$ right because that is by definition we are saying w is nothing, but the first derivative as well as dg is going to be df minus $x dw$ minus $w dx$ right and this is going to get cancelled. So, dg is nothing, but minus $x dw$ ok. So, what do you see when you look at this differentiation of f and g ? We see the following that the role of variable and its derivatives are switched between this function f and g . So, in the word role. So, in the word role of variable and derivative has been exchange; variable of the original function is now derivative of the transform ok.

Now, in order to recover in order to recover the original function, what we do is we simply apply the Legendre transformation for one more time ok. So, to recover the original function apply Legendre transformation for one more time ok..

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The image shows a whiteboard with handwritten mathematical notes. At the top, there is a toolbar with various drawing tools. The text on the whiteboard reads: "To recover the original in - apply LT for one more time". Below this, the differential equation $dg = -x dw$ is written. Then, the general solution $f = g - w (dg/dw)$ is shown. Finally, the specific result $f = g - w (-x) = g + wx$ is boxed.

$$dg = -x dw$$
$$f = g - w \left(\frac{dg}{dw} \right)$$
$$f = g - w (-x) = g + wx$$

So, dg is minus of xw all right. So, we are going to get a function g minus we are going to say this is again f the original function g , which can be written as g minus the variable is w . So, w times the derivative of that that is $\frac{dg}{dw}$. So, this is going to be g minus w and this is nothing, but minus of x .

So, you have g plus wx . So, this is how you are go get back the original form original function ok. Now having derived this having said that let us apply this concept to the function, which we just did in order to show that simple integration doesn't work. So, let us again use the same function. So, the example is $f(x)$ is equal to $x^2 + 2$.

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$$f(x) = x^2 + 2 \quad w = f' = 2x \Rightarrow x = \frac{w}{2}$$
$$g(w) = f - x \cdot f' = f - xw$$
$$= x^2 + 2 - \frac{w^2}{2}$$
$$g(w) = \frac{w^2}{4} + 2 - \frac{w^2}{2} = -\frac{w^2}{4} + 2$$

Apply LT

$$f = g + xw$$

$f(x)$ is $x^2 + 2$ all right and the w in this case is the derivative of f which is $2x$. So, what would be or $g(w)$ or g has a function of w is going to be f , minus the variable and the derivative of f which is nothing going to be $f - xw$. Now f is $x^2 + 2$ minus x is w by two. So, we are going to write w^2 by 2 and this is going to be w^2 by 4 plus 2 minus w^2 by 2 this is nothing, but minus w^2 by 4 plus 2 all right. So, this is your g of double.

Now, in order to obtain. So, this is our Legendre transformation which we apply to f of x now in order to get back that, we can obtain the original function we are going to apply a Legendre transformation to g , and let us see whether we are going to get back the original function or not.

So, if you apply apply again Legendre transformation. So, this is going to be let us say g plus x of w , that is what we showed here earlier ok. So, what is g here g is nothing but.

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$$g(w) = f - x \cdot f' = f - xw$$
$$= \frac{x^2}{4} + 2 - \frac{w^2}{4}$$
$$g(w) = \frac{w^2}{4} + 2 - \frac{w^2}{4} = -\frac{w^2}{4} + 2$$

Apply LT

$$f = g + xw$$
$$= -\frac{w^2}{4} + 2 + \frac{w}{2} \cdot w \quad (x = w/2)$$
$$= \frac{w^2}{4} + 2$$

$f(x) = x^2 + 2$ ORIGINAL FUNCTION

Minus w square by 4 plus 2 plus what is x? X is w by 2 and thus we are going to get the w square by 4 plus 2 which is nothing, but since x is w by 2 which is nothing, but we plug in here this is nothing, but x square by 2 plus 2 which is nothing, but the original function ok.

So, this is how we have shown that the Legendre transformation is something which we can apply in order to change the variable, keeping the information intact and now we can apply this Legendre transformation to thermodynamic functions.

So, I will stop here and take it in the next lecture application of Legendre transformation to thermodynamic function see you in the next class.