Mathematics Methods and Thermodynamics

Classical Thermodynamics II

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Class Overview

- Exact Differentials
- Legendre Transform
- Maxwell Relations

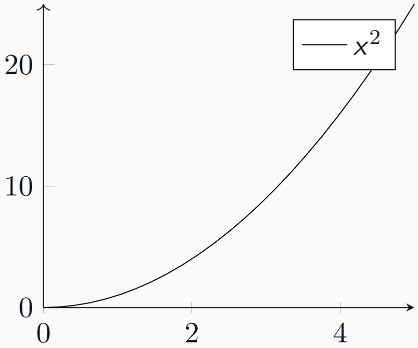
Differentiation

- Inexact differentiation is the difference between path functions. They have no anti-derivatives and therefore are not integratable.
- Exact Differentiation is the differentiation you are all familiar with. This is the difference between state functions.

Differentiation

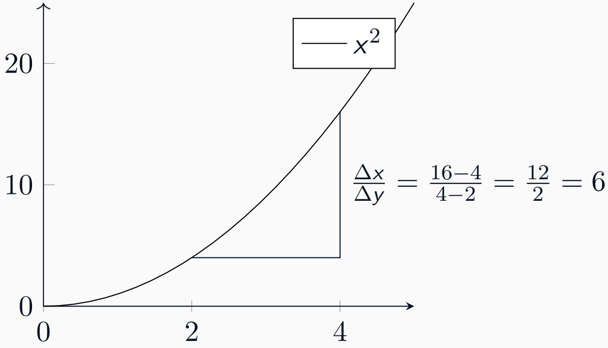
Exact differentiation (or just differentiation), is the gradient of a curve.

We can work out an approximate gradient by taking the differences $\frac{\Delta y}{\Delta x}$



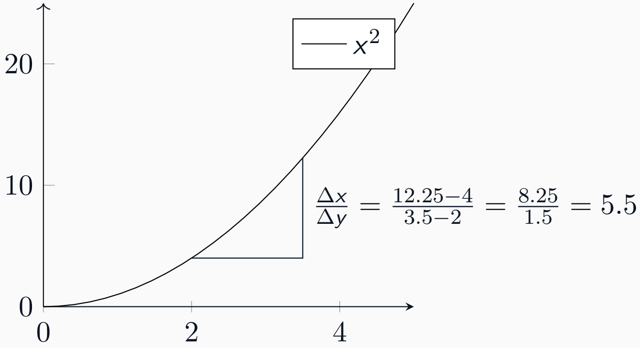
Differentiation

Here at $x = 2$ the gradient is approximately $\frac{\Delta y}{\Delta x} = 6$



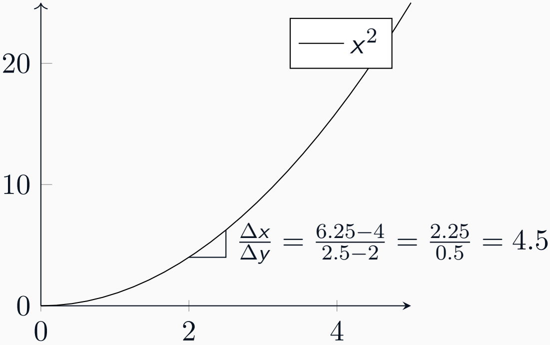
Differentiation

By decreasing the Δ we get a more accurate gradient. Here at $x = 2$ the gradient is approximately $\frac{\Delta y}{\Delta x} = 5.5$



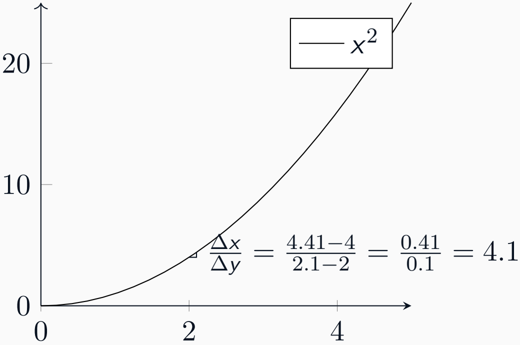
Differentiation

A Δ of 0.5 gives the gradient as approximately $\frac{\Delta y}{\Delta x} = 4.5$



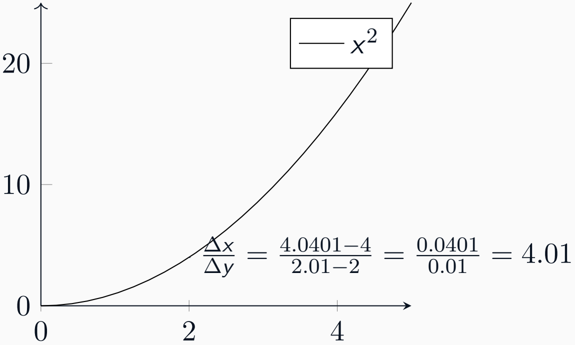
Differentiation

A Δ of 0.1 gives the gradient as approximately $\frac{\Delta y}{\Delta x} = 4.1$



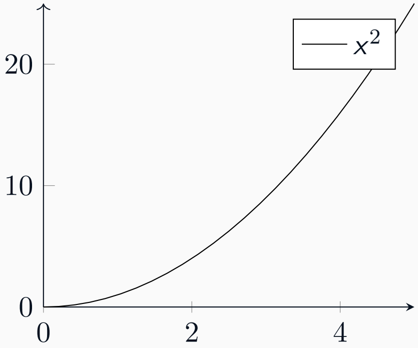
Differentiation

A Δ of only 0.01 gives the gradient as approximately $\frac{\Delta y}{\Delta x} = 4.01$



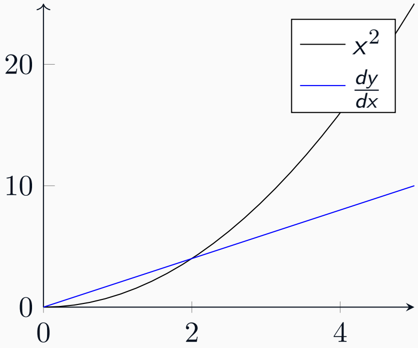
Differentiation

You could see from the previous graph that we were converging towards 4, which happens to be $2x$ which as you all know is the derivative of x^2.



Differentiation

To get the true gradient we do not take a difference using $\frac{\Delta x}{\Delta y}$ but instead we use dy and dx which represents infinitesimal changes $\frac{dx}{dy}$.



Differentiation

- When differentiating we only care about the gradient
- This means that the information about the intercept is lost

$$\frac{d}{dx}x^2 = \frac{d}{dx}\left(x^2 + a\right)$$

- This becomes important when we are performing the anti-derivative (integration) as we must recover this lost information

Differentiation

- We are going to go over some of the most common differentiations, and the various rules you can apply to the more complex ones.
- There are several ways to represent differentials for a function $f(x)$
  - Leibniz's notation
$$\frac{d}{dx}f(x)$$
  - Newton's notation
$$\dot{f}(x)$$
  - Lagrange's notation
$$f'(x)$$
  - Euler's notation
$$Df(x), \quad D_x f(x)$$

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Higher Derivatives

- It is also possible to differentiate an already differentiated curve
- Higher derivatives can be represented in the following ways
  - Leibniz's notation

$$\frac{d^2}{dx^2}f(x)$$

  - Newton's notation

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Mixed Derivatives

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$$\frac{d^2}{dxdy} f(x, y), \quad \frac{d^3}{dxdy^2} f(x, y)$$

  - Lagrange's notation

$$f_{\prime}^{\prime}(x, y), \quad f_{\prime\prime}^{\prime}(x, y)$$

  - Euler's notation

$$D_{xy} f(x, y), \quad D_{xyy} f(x, y)$$

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Derivatives

- Each notation can be used interchangeably, but some are clearer than others under certain circumstances
- I will predominantly use the Leibniz's notation as it is more flexible being able to handle multiple mixed derivatives.
- You can use any notation you feel is appropriate

Derivatives - Rules

- Just like in integration any constant can be taken outside

$$f(x) = cg(x), \quad \frac{d}{dx}(f(x)) = c\frac{d}{dx}(g(x))$$

- Variables raised to a power can be treated as follow

$$f(x) = cx^n, \quad \frac{d}{dx}(f(x)) = cnx^{n-1}$$

- Sums can be treated separately

$$f(x) = g(x) + h(x), \quad \frac{d}{dx}(f(x)) = \frac{d}{dx}(g(x)) + \frac{d}{dx}(h(x))$$

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Derivatives - Rules

- The exponent is very simple to differentiate

$$f(x) = \mathrm{e}^x, \quad \frac{d}{dx}(f(x)) = \mathrm{e}^x$$

- More generally it is

$$f(x) = a^x, \quad \frac{d}{dx}(f(x)) = a^x \ln(a)$$

- While the logarithm differentiates as follows

$$f(x) = \ln(x), \quad \frac{d}{dx}(f(x)) = \frac{1}{x}$$

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Derivatives - Rules

- For the trigonometric functions we have

$$f(x) = \sin(x), \quad \frac{d}{dx}(f(x)) = \cos(x)$$

$$f(x) = \cos(x), \quad \frac{d}{dx}(f(x)) = -\sin(x)$$

$$f(x) = \tan(x), \quad \frac{d}{dx}(f(x)) = 1 + \tan(x)^2$$

Derivatives - Rules

- For the inverse trigonometric functions we have

$$f(x) = \operatorname{asin}(x), \quad \frac{d}{dx}(f(x)) = \frac{1}{\sqrt{-x^2+1}}$$

$$f(x) = \operatorname{acos}(x), \quad \frac{d}{dx}(f(x)) = -\frac{1}{\sqrt{-x^2+1}}$$

$$f(x) = \operatorname{atan}(x), \quad \frac{d}{dx}(f(x)) = \frac{1}{x^2+1}$$

Derivatives - Rules

- Products should be treated with the product rule, this may need to be done several times

$$f(x) = g(x) \times h(x)$$

$$\frac{d}{dx}(f(x)) = \frac{d}{dx}(g(x)) \times h(x) + g(x) \times \frac{d}{dx}(h(x))$$

- For division use the quotient rule

$$f(x) = \frac{g(x)}{h(x)}$$

$$\frac{d}{dx}(f(x)) = \frac{\frac{d}{dx}(g(x)) \times h(x) - g(x) \times \frac{d}{dx}(h(x))}{h(x)^2}$$

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Derivatives - Rules

- Substitutions (change of variables) are handled with the chain rule

$$f(x) = g(h(x)),$$

$$\frac{d}{dx}(f(x)) = \frac{d}{dx}(h(x)) \times \frac{d}{dx}(g(h(x)))$$

This one is very useful, for example

$$f(x) = \mathrm{e}^{-3x^3}$$

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We can substitute with this

$$u(x) = -3x^2$$
$$f(u(x)) = \mathrm{e}^{u}$$

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Applying the chain rule

$$\frac{d}{dx}(f(u(x))) = \frac{d}{du}(f(u)) \times \frac{d}{dx}(u)$$

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$$f(x) = \mathrm{e}^{-3x^3}$$

Gives this

$$\frac{d}{dx}(f(u(x))) = \mathrm{e}^{u} \times (-6x)$$

Derivatives - Rules

- These rules will cover most of differentiation
- For anything more complex I recommend, some algebra software such as:

  Wolfram Alpha Free online algebra solver (amongst many other things)

  Matlab Commercial software to solve matrix manipulations, data plotting and algebraic expressions

  Maple Commercial software similar to Matlab, but with an easier interface

  sympy A free python library to solve mathematical expressions

Derivatives - Examples

- Here are some examples of some differentials using the various rules given before
- Product rule

$$\frac{d}{dr}\left(r^2 \mathrm{e}^{-r}\right)$$

$$u = r^2 \qquad v = \mathrm{e}^{-r}$$

$$\frac{d}{dr}(u) = 2r \qquad \frac{d}{dr}(v) = -\mathrm{e}^{-r}$$

$$\frac{d}{dr}\left(r^2 \mathrm{e}^{-r}\right) = \frac{d}{dx}(u)\, v + u \frac{d}{dx}(v)$$

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- Chain rule

$$f(x) = \cos\left(3x\right) + \sin\left(2x^2\right)$$

$$u = 3x \qquad v = 2x^2$$

$$\frac{d}{dx}(u) = 3 \qquad \frac{d}{dx}(v) = 4x$$

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- Here are some examples of some differentials using the various rules given before
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- When dealing with multiple derivatives you can think of it as two separate differentiation steps

$$\frac{d^2}{dxdy}\left(f\left(x,y\right)\right) = \frac{d}{dy}\left(\frac{d}{dx}\left(f\left(x,y\right)\right)\right)$$

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$$\frac{d^2}{dxdy}\left(2y^3x^2 + xy\right)$$

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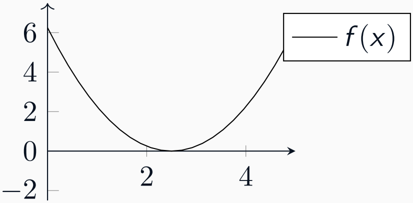
Derivatives - The second derivative

- While the first derivative $(\frac{d}{dx}(f(x)))$ gives the gradient of a function the second $(\frac{d^2}{dx^2}(f(x)))$ gives the gradient of the gradient
- This is useful to tell us the direction of the curve. As in if the is concave or convex



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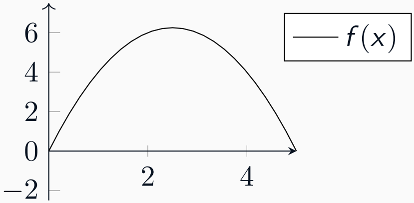

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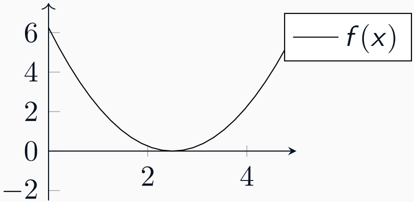

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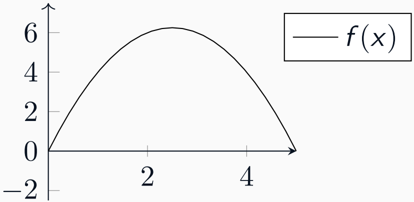

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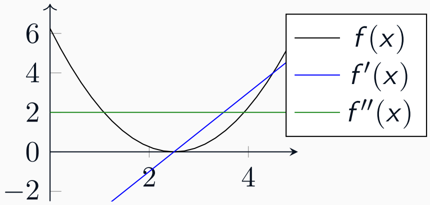
- For a convex curve the second derivative is positive
- For a concave curve the second derivative is negative



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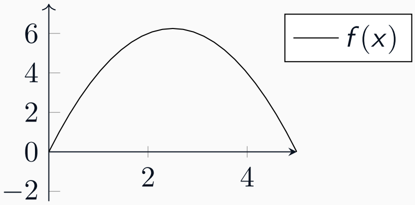

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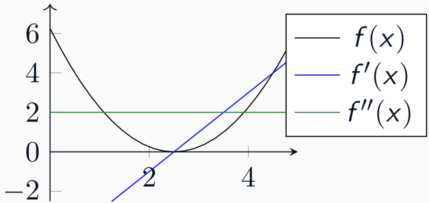

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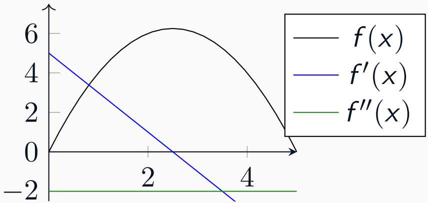

Concave

Class Overview

- Exact Differentials
- Legendre Transform
- Maxwell Relations

Transforms

- What is a transform?
- A transform is a way of changing a function while still ensuring it containing the same information
- Common transforms include:
  - Legendre Transform
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Legendre Transforms

- The Legendre transform is a way of representing a function in terms of its differential
- It is used in classical mechanics to derive the Hamiltonian
- Used in thermodynamics to derive the chemical potentials

Legendre Transforms

- For a Legendre transform to work certain conditions must be met
  1. The function must be "well behaved"
  2. It must have a derivative
  3. The function must be convex. If it is concave then define a new function such that $\widetilde{f}(x) = -f(x)$

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- You will see a function described as “well behaved” a few times throughout physical chemistry
- What however is a “well behaved” function?
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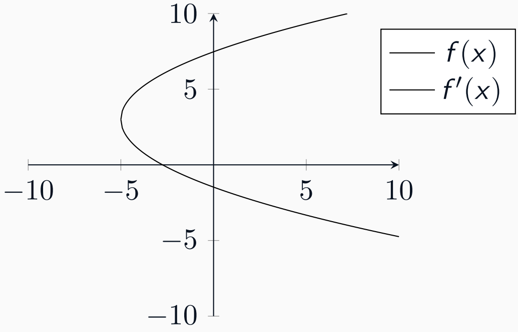

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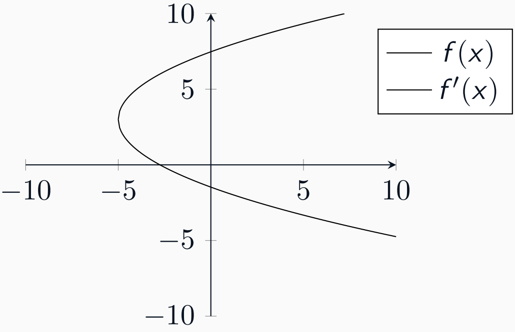

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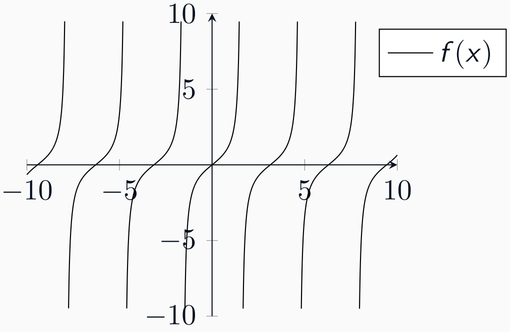

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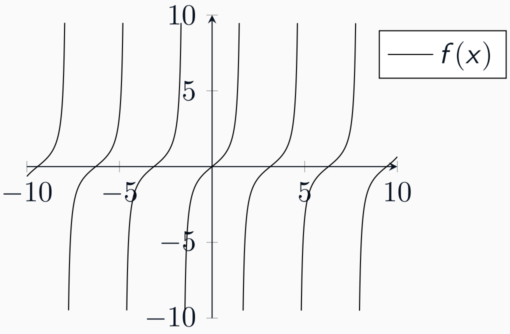

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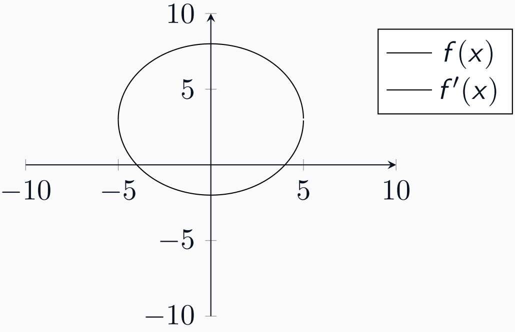

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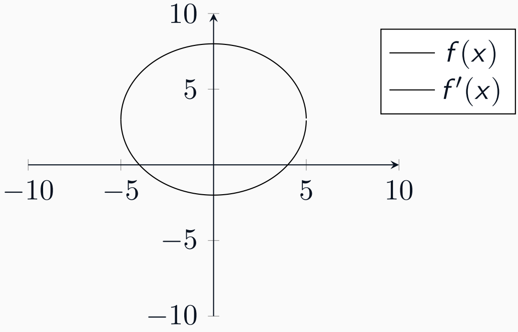

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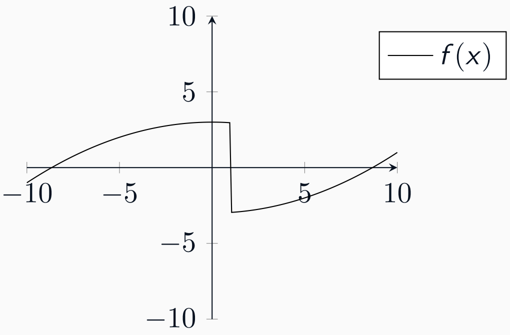

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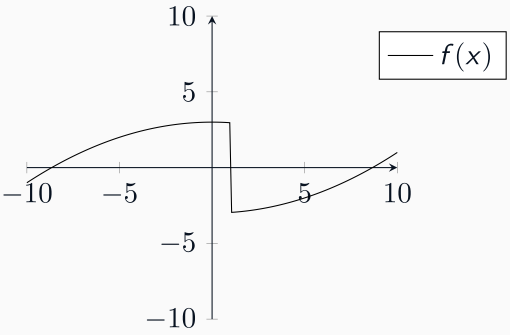

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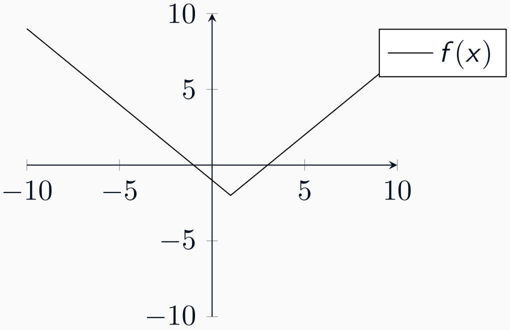

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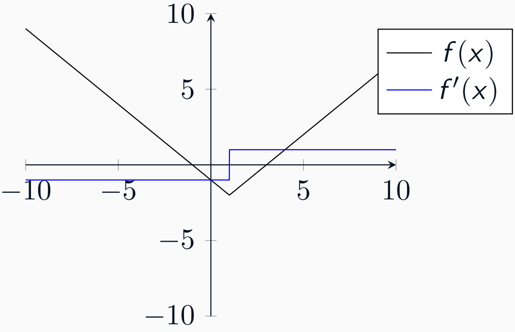

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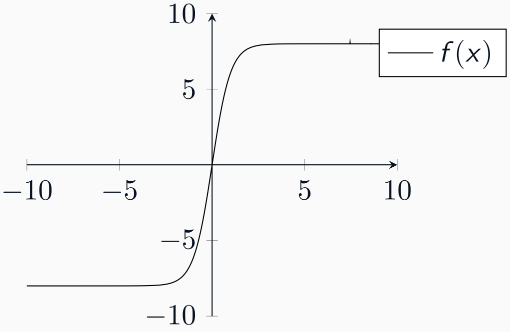

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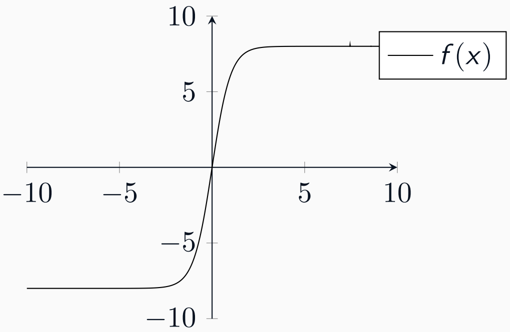

Legendre Transformation

- To perform a Legendre transformation there are a few relatively simple steps
  1. Check that $f(x)$ is "well behaved" and that it is convex
  2. Define a new function $p(x)$ such that $p(x) = f'(x)$
  3. Rearrange $p(x)$ in terms of x, call this $x(p)$
  4. Define a new function $g(p)$ that represent the negative $y-$intercept of the tangent of line from $f(x)$.
  5. Write the formula in terms of p
  $$g(p) = p \times x(p) - f(x(p))$$

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  $$p(x) = \text{Gradient at point } x$$
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     Tangent at point x is given by
     $$y = mx + c$$
     $$y = p(x)x + c$$
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     To find the intercept we use the information we know. The at x, $y = f(x)$
     $$f(x) = p(x)x + c$$
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Legendre Transformation

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- What is the Legendre transform of $f(x) = x^2$
  1. $f(x)$ is well behaved and $\frac{d^2}{dx^2}(f(x)) > 0$
  2. $p(x) = f'(x) = 2x$
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  2. $p(x) = f'(x) = 2x$
  3. $x(p) = \frac{p}{2}$
  4. $g(x) = p(x)x - f(x) = 2x \times x - x^2 = x^2$
  5. $g(p) = \left(\frac{p}{2}\right)^2 = \frac{p^2}{4}$
- The Legendre transform of x^2 is $\frac{p^2}{4}$

Legendre Transformation

- Here is the example from the pre-test
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Legendre Transformation - Overview

- Legendre transform represents a function in terms of its derivative without losing information
- To perform a Legendre transform the function must be:
  - "Well behaved"
  - Convex
  - Have a derivative
- The inverse of a Legendre transform is a Legendre transform

$\hat{L}$ Legendre operator

$$\hat{L}(f(x)) = g(x)$$

$$\hat{L}(g(x)) = f(x)$$

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Legendre Transformation - In Thermodynamics

- A thermodynamic system can be described by its internal energy $U(S, V)$
- Unfortunately entropy is hard to measure, it would be good if we could instead rerepresent this in terms of T which is much easier to measure
- We can do this with a Legendre transform

Legendre Transformation - In Thermodynamics

- We apply a Legendre transform to represent it

$$g(p) = p \times x(p) - f(x(p))$$

- Lets write down what each of these parts is equivalent to

$$f(x) = U(S, V)$$

$$p = T$$

$$x(p) = S(T)$$

- The Legendre transform is thus

$$g(T) = T \times S(T) - U(S(T), V)$$

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Legendre Transformation - Duel Differentials

- Consider a generic function with 2 independant variables $f(x,y)$
- Its differential is $df = \left(\frac{\delta f}{\delta x}\right)_y dx + \left(\frac{\delta f}{\delta y}\right)_x dy$
- If we perform the Legendre transform $f(x,y) \to g(x,v)$ can we calculate the transform of $df \to dg$ as well
- Lets define $u = \left(\frac{\delta f}{\delta x}\right)_y$ and $v = \left(\frac{\delta f}{\delta y}\right)_x$
- Such that $df = udx + vdy$, the variable u and x are Legendre transform pairs, (similarly v and y) also know as conjugate pairs

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Legendre Transformation - Duel Differentials

- Lets apply the transform of $y \to v$

$$g = f - vy(v)$$

- Then it follows that

$$dg = df - d(vy)$$

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- We can compute $d(vy)$ with a simple product rule

$$d(vy) = vdy + ydv$$

- We therefore arrive at

$$dg = udx + vdy - (vdy + ydv)$$

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Legendre Transformation - In Thermodynamics

- Now to actually use what we just learned
- Recall that internal energy is hard to measure but that its change is not
- We learned last week that this change in internal energy is

$$dU = \delta q + \delta w$$

Which for a reversible process undergoing only expansion work becomes

$$dU = TdS - PdV$$

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- This looks very similar to above

$$df = \left(\frac{\delta f}{\delta x}\right)_y dx + \left(\frac{\delta f}{\delta y}\right)_x dy$$

- Instantly we learn that

$$\left(\frac{\delta U}{\delta S}\right)_V = T$$

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Legendre Transformation - In Thermodynamics

- Now if we perform the Legendre transform of $\hat{L}(U) = F$
- We also know how to transform dU to dF

$$dU = TdS - PdV$$

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Legendre Transformation - In Thermodynamics

- Let us say that we are able to measure entropy in the internal energy $U(S, V)$
- But instead of V we would like to represent it in terms of pressure P, as pressure is easier to control

Legendre Transformation - In Thermodynamics

- Again this can be done with a Legendre transform

$$g(p) = p \times x(p) - f(x(p))$$

$$f(x) = U(S, V)$$

$$p = -P$$

$$x(p) = V(P)$$

- The Legendre transform is thus

$$g(P) = U(S, V(P)) - P \times V(P)$$

The reverse in sign is a consequence of defining $p = -P$

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Legendre Transformation - In Thermodynamics

- This if you recall from last week is enthalpy (H)

$$H = PV - U$$

- Which we now also know its dH

$$dH = TdS + VdP$$

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Legendre Transformation - In Thermodynamics

- As one last change lets say we didn't like S or V in $U(S, V)$, instead preferring T and P
- In this case we can perform the Legendre transform on both the conjugate pairs

$$g(P) = U(S(T), V(P)) - TS(T) + P \times V(P)$$

- This is known as the Gibbs Energy G

$$G = U - TS + PV$$

- dG is given as

$$dG = -SdT + vdP$$

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Legendre Transformation - In Thermodynamics

- Starting from the Internal energy we can arrive at all of the thermodynamic potentials through Legendre transforms

$$\begin{array}{c c} & S \longrightarrow T \\ \begin{array}{c} V \\ \downarrow \\ P \end{array} & \begin{bmatrix} U & F \\ H & G \end{bmatrix} \end{array}$$

$$F = U - TS$$

$$H = PV - U$$

$$G = U - TS - PV$$

Legendre Transformation - In Thermodynamics

- We can also arrive at all the derivative functions

$$dU = TdS - PdV$$

$$dF = -SdT + PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

Class Overview

- Exact Differentials
- Legendre Transform
- Maxwell Relations

Maxwell Relations

- Maxwell's Relations are a set of relations that defines the relationships between the derivatives of T, V, P and S.
- They are all obtainable from the thermodynamic potentials
- The most common 4 derived from U, F, H and G are

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$
$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$
$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$
$$-\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$$

Maxwell Relations

- To derive the relations we start from one of the thermodynamic potentials

$$U(S, V)$$

$$dU = TdS - PdV$$

- Recall from earlier that

$$df = \left(\frac{\delta f}{\delta x}\right)_y dx + \left(\frac{\delta f}{\delta y}\right)_x dy$$

- Therefore

$$\left(\frac{\delta U}{\delta S}\right)_V = T$$

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Maxwell Relations

- The order of applying second derivatives is unimportant therefore

$$\frac{d}{dy}\left(\frac{\delta f}{\delta x}\right)_y = \frac{d}{dx}\left(\frac{\delta f}{\delta y}\right)_x$$

- It follows that

$$\frac{d^2}{dVdS}(U) = \frac{d^2}{dSdV}(U)$$

$$\frac{\delta}{\delta V}\left(\frac{\delta U}{\delta S}\right)_V = \frac{\delta}{\delta S}\left(\frac{\delta U}{\delta V}\right)_S$$

$$\frac{\delta}{\delta V}T = -\frac{\delta}{\delta S}P$$

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

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$$\frac{\delta}{\delta V}T = -\frac{\delta}{\delta S}P$$

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

Maxwell Relations - Summary

- The four most common Maxwell Relations
- Each of which can be derived from the thermodynamic potentials

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$
$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$
$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$
$$-\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$$

Summary

- We have covered various derivatives that you may find helpful including
  - Powers $\frac{d}{dx}ax^n = anx^{n-1}$
  - Exponents $\frac{d}{dx}\mathrm{e}^x = \mathrm{e}^x$ and logarithms $\frac{d}{dx}\ln(x) = \frac{1}{x}$
- We have covered also covered several useful rules for derivates
  - Product rule $\frac{d}{dx}uv = du \times v + u \times dv$
  - Quotient rule $\frac{d}{dx}\frac{u}{v} = \frac{u \times v - u \times dv}{v^2}$
  - Chain rule $\frac{d}{dx}f(u(x)) = \frac{df}{du}\frac{du}{dx}$

Summary

- Legendre transforms can represent convex functions in terms of their $y-$intercept without loosing information
- These transforms are used to acquire Hamiltonians in classical mechanics and thermodynamic potentials in classical thermodynamic
- The maxwell relations, relate physical and natural derivatives. They can be derived from second derivatives of the thermodynamic potentials.