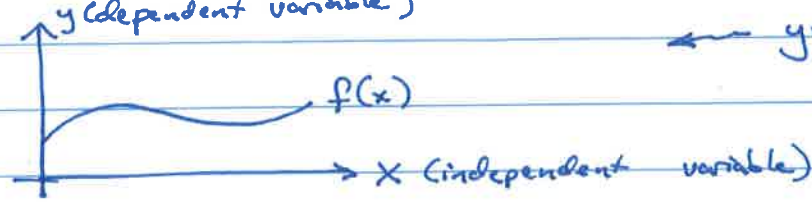
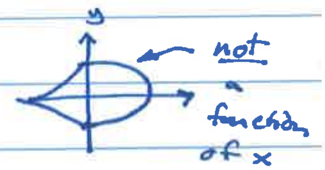
Multivariable Calculus

Most of you have a good handle on what a function is:

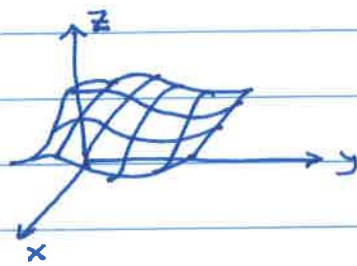


$\leftarrow y = f(x)$

General rules: functions are single valued
(i.e. $x \to$ exactly one $f(x)$)



In 2-Dimensions: $z = f(x, y)$



x & y are independent
z is dependent var.

In a right handed coordinate system z is up, y to the right, x is out of the page.

In N-dimensions $z = f(x_1, x_2, x_3, \ldots x_N)$

$x_1 \cdots x_N$ are all independent variables that f maps on to z

Example: Thermodynamic state functions:

$P(N, V, T) \leftarrow$ pressure of a gas as a function of N atoms, Volume, & Temperature

State functions predict one thermodynamic variable if the others are known:

$$P(N,V,T) = \frac{N k_B T}{V}$$ (k_B = Boltzmann's constant)

Other examples:

→3,3

- 2-D Gaussian : $z = e^{-x^2-y^2}$
- Complex sin : $\sin(z) = \sin(x+iy) = \sin(x)\cosh y + i\cos(x)\sinh(y)$

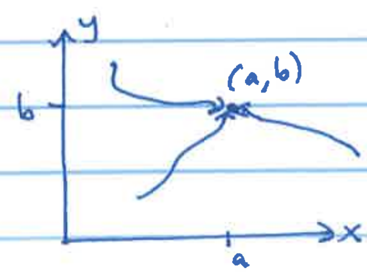
-2π,2π
-π,π

- Phase Diagrams ($G(T,P)$ ← Gibbs Free Energy)
- Protein backbone torsional angles (i.e. Ramachandran plots → probability of ϕ, ψ angles → $p(\phi,\psi)$)

Limits of multi dimensional functions

$$\lim_{(x,y)\to(a,b)} f(x,y) = \ell$$

If the limit of $f(x,y)$ exists at $x=a$ and $y=b$ then $\lim_{(x,y)\to(a,b)} f(x,y) = \ell$ is independent of the path along which (x,y) approaches (a,b)



All paths must yield the same value of $\lim_{(x,y)\to(a,b)} f(x,y) = \ell$

or the limit does not exist.

Properties of limits

- Addition & Subtraction

$$\lim_{(x,y)\to(a,b)} [\alpha f(x,y) \pm \beta g(x,y)] = \alpha \lim_{(x,y)\to(a,b)} f(x,y) \pm \beta \lim_{(x,y)\to(a,b)} g(x,y)$$

- Multiplication:

$$\lim_{(x,y)\to(a,b)} f(x,y)\, g(x,y) = \lim_{(x,y)\to(a,b)} f(x,y) * \lim_{(x,y)\to(a,b)} g(x,y)$$

- Division:

$$\lim_{(x,y)\to(a,b)} \frac{f(x,y)}{g(x,y)} = \frac{\lim_{(x,y)\to(a,b)} f(x,y)}{\lim_{(x,y)\to(a,b)} g(x,y)}$$ for

$$g(x,y) \neq 0$$

Continuity:

A function is continuous at (a,b) if

1) $f(x,y)$ is defined at (a,b)
2) $\lim_{(x,y)\to(a,b)} f(x,y)$ exists
3) $\lim_{(x,y)\to(a,b)} f(x,y) = f(a,b)$

In general, wavefunctions and other physically measurable objects are continuous.

Partial Derivatives

$$f_x = \frac{\partial f}{\partial x} = \lim_{\Delta x\to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x}$$

$$f_y = \frac{\partial f}{\partial y} = \lim_{\Delta y\to 0} \frac{f(x, y+\Delta y) - f(x,y)}{\Delta y}$$

Example:

$$f(x,y) = 2x^3 + 6xy + y^2$$

$$\frac{\partial f}{\partial x} = \lim_{\Delta x \to 0} \frac{2(x+\Delta x)^3 + 6(x+\Delta x)y + y^2 - 2x^3 - 6xy - y^2}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \frac{6x^2\Delta x + 6x\Delta x^2 + 2\Delta x^3 + 6y\Delta x}{\Delta x}$$

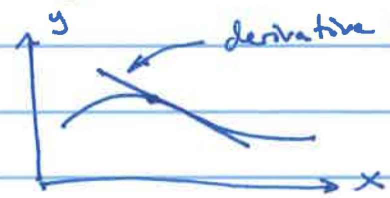
$$= \lim_{\Delta x \to 0} 6x^2 + 6x\Delta x + 2\Delta x^2 + 6y$$

$$= 6x^2 + 6y$$

A partial derivative is determined by differentiating with respect to one variable while regarding all other variables as constants.

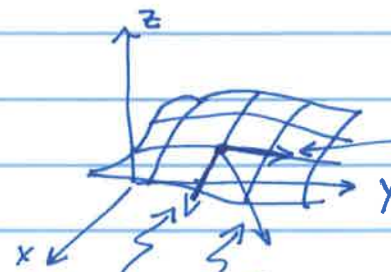
What is a partial?

For a regular function (in 1D)



derivative tells us the slope of the function in 1-D.

In multiple dimensions, the slope has a direction too!



$\left(\frac{\partial f}{\partial y}\right)_x$ = slope if we walk along y axis only

Downward Slope

$\left(\frac{\partial f}{\partial x}\right)_y$ = slope if we walk along x axis only

To find that downward slope we first find each of the partial derivatives, i.e. we hold y constant and find the slope along x:

Example 1

$$f(x,y) = e^x \sin(xy)$$

$$f_x = \left(\frac{\partial f}{\partial x}\right)_y = e^x \sin(xy) + e^x \cos(xy)\, y$$

$$f_y = \left(\frac{\partial f}{\partial y}\right)_x = e^x \cos(xy)\, x$$

Example 2 from thermodynamics

$$P = \frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

← i.e. how does pressure change with increasing temperature (holding Volume constant)?

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2}$$

Now you try it. A better model for realistic gases is called the van der Waals equation:

For one mole of gas, this is:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$P(V,T)$

a & b are constants that depend on which gas we have.

Find: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$$

Higher order partial derivatives

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial x^2} = f_{xx}$$

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y^2} = f_{yy}$$

these tell us about the curvature along particular axes.

Functions of multiple variables also allow Mixed partial 2^{nd} derivatives.

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial x \partial y} = f_{yx}$$

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial y \partial x} = f_{xy}$$

Example: Let: $f(x,y) = xy^2 + e^{x^2 y}$

$$f_x = y^2 + e^{x^2y}(2xy)$$

$$f_y = 2xy + e^{x^2y}(x^2)$$

$$f_{xx} = e^{x^2y}(2y) + 2xy\, e^{x^2y}(2xy) = e^{x^2y}(2y + 4x^2y^2)$$

$$f_{yy} = 2x + x^2 e^{x^2y} x^2 = 2x + x^4 e^{x^2y}$$

$$f_{xy} = 2y + 2x e^{x^2y} + x^2 e^{x^2y}\, 2xy = 2y + 2x(1+x^2y)e^{x^2y}$$

$$f_{yx} = 2y + 2x e^{x^2y} + 2xy\, e^{x^2y} x^2$$

$$= 2y + 2x(1+x^2y)e^{x^2y}$$

Note that $f_{xy} = f_{yx}$.

Theorem: If f_{xy} & f_{yx} are continuous at (a,b) then $f_{xy} = f_{yx}$ at (a,b); otherwise f_{xy} & f_{yx} may not be equal.

Example: $G = G(P,T) \equiv$ Gibbs Free Energy

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad = \text{the entropy}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad = \text{the volume}$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$ ← equivalence of cross partial derivatives

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$ ← one of Maxwell's Relations

This is important as S is hard to measure, but P, T, & V are easy to measure!

Chain Rules for Partial Derivatives

Suppose we know that u depends on x & y $u = u(x,y)$ but that both x & y are functions only of t: $x = x(t)$ $y = y(t)$

If we want to know how u depends on time, we could 1) substitute $x(t)$ & $y(t)$ in and get $U(t)$, or use the chain rule:

$$\frac{dU}{dt} = \left(\begin{matrix}\text{How does } U \\ \text{depend on } x\end{matrix}\right) * \left(\begin{matrix}\text{How does } x \\ \text{depend on } t\end{matrix}\right) + \left(\begin{matrix}\text{How Does } U \\ \text{depend on } y\end{matrix}\right) * \left(\frac{dy}{dt}\right)$$

that is:

$$\frac{dU}{dt} = \frac{\partial u}{\partial x}\frac{dx}{dt} + \frac{\partial u}{\partial y}\frac{dy}{dt}$$

This is the chain rule of partial differentiation.
provided $\frac{\partial u}{\partial x}$ & $\frac{\partial u}{\partial y}$ are continuous and
$x(t)$ & $y(t)$ are <u>differentiable</u>.

Note that $u(x,y)$ and $U(t)$ are different functions!

<u>Example</u>:

$$\left.\begin{aligned} u(x,y) &= x^2 y \\ x(t) &= te^{-t} \\ y(t) &= e^{-2t} \end{aligned}\right\} \quad U(t) = t^2 e^{-4t}$$

<u>Another example</u>:

$$u(x,y) = x^2y + xy^2$$
$$x(t) = te^{-t}$$
$$y(t) = e^{-t}$$

$$\frac{\partial u}{\partial x} = 2xy + y^2 \qquad \frac{dx}{dt} = e^{-t} + t(e^{-t})(-1) = e^{-t}(1-t)$$

$$\frac{\partial u}{\partial y} = x^2 + 2xy \qquad \frac{dy}{dt} = -e^{-t}$$

$$\therefore \quad \frac{dU}{dt} = \left(\frac{\partial u}{\partial x}\right)\left(\frac{dx}{dt}\right) + \left(\frac{\partial u}{\partial y}\right)\left(\frac{dy}{dt}\right)$$
$$= (2xy + y^2)(e^{-t}(1-t)) + (x^2 + 2xy)(-e^{-t})$$

Substituting in x & y:

$$= (2te^{-2t} + e^{-2t})(1-t)e^{-t} + (t^2e^{-2t} + 2te^{-2t})(-e^{-t})$$

$$= e^{-3t}\left[(2t+1)(1-t) - t^2 - 2t\right]$$

$$\frac{dU}{dt} = e^{-3t}\left[2t + 1 - 2t^2 - t - t^2 - 2t\right]$$

$$= e^{-3t}\left[1 - t - 3t^2\right]$$

The <u>same</u> result can be obtained by substituting $x(t)$ & $y(t)$ into U and then differentiating the whole mess with respect to t.

Now, imagine

$$u = u(x_1, x_2, \dots x_N) \quad \text{and} \quad x_i = x_i(t) \quad \text{for } i = 1 \dots N$$

$$\frac{du}{dt} = \frac{\partial u}{\partial x_1}\frac{dx_1}{dt} + \frac{\partial u}{\partial x_2}\frac{dx_2}{dt} + \dots \frac{\partial u}{\partial x_N}\frac{dx_N}{dt}$$

This is the general N-dimensional case of the partial derivative chain rule.

Getting the total dependence on other variables:

Suppose $u = u(x, y)$ and $y = y(x)$

In this case, u is really a function of a single variable:

$$\frac{du}{dx} = \frac{\partial u}{\partial x}\frac{dx}{dx} + \frac{\partial u}{\partial y}\frac{dy}{dx}$$

<u>explicit</u> dependence of u on x

implicit dependence of u on x

$$\frac{du}{dx} = \frac{\partial u}{\partial x} + \overbrace{\frac{\partial u}{\partial y}\frac{dy}{dx}}$$

$\frac{du}{dx}$ = <u>total</u> derivative of u wrt. x

An example:

$$u = y \sin x \qquad \text{where} \qquad y = xe^{-x}$$

$$\frac{\partial u}{\partial x} = y \cos x$$

$$\frac{\partial u}{\partial y} = \sin x \qquad\qquad \frac{dy}{dx} = e^{-x} - xe^{-x} = (1-x)e^{-x}$$

$$\therefore \quad \frac{du}{dx} = y\cos x + \sin x \; e^{-x}(1-x)$$

$$= xe^{-x}\cos x + \sin x \; (1-x)e^{-x}$$

Again, you can get the same result by substituting $y \leftarrow xe^{-x}$ first and then taking the x derivative of u.

An incredibly important case involves transforming between coordinates: $u = u(x,y)$ $\quad x = x(s,t) \quad y = y(s,t)$

s & t might be a different coordinate system (r, θ)

$$\frac{\partial u}{\partial s} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial s} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial s}$$

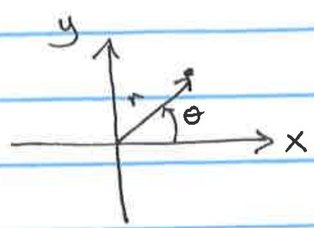
$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial t}$$

these tell us how u depends on the new coordinates

Example: Laplacian in 2-D (measures curvature of a surface at x & y)

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

related to kinetic energy of a wavefunction



We might want to know how to describe $\nabla^2 f$ in polar coordinates

We'll look at the special case where $r = a =$ constant

In this case ∇^2 depends only on θ:

$$\nabla^2 f(x,y) = \frac{\partial^2 f}{\partial x} + \frac{\partial^2 f}{\partial y^2}$$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial x} \quad \longleftarrow \text{chain rule}$$

but $\theta = \tan^{-1}\frac{y}{x}$

so $$\frac{\partial \theta}{\partial x} = \frac{1}{1+y^2/x^2}\left(\frac{-y}{x^2}\right) = \frac{-y}{x^2+y^2} = \frac{-y}{a^2}$$

$$= \frac{-a\sin\theta}{a^2} = \frac{-\sin\theta}{a}$$

$\therefore$

$$\frac{\partial f}{\partial x} = -\frac{\sin\theta}{a}\left(\frac{\partial f}{\partial \theta}\right)$$

To get the 2nd derivative we do it again:

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)\cdot\left(\frac{\partial \theta}{\partial x}\right)$$

$$= -\frac{\sin\theta}{a}\left[\frac{\partial}{\partial \theta}\left(-\frac{\sin\theta}{a}\frac{\partial f}{\partial \theta}\right)\right]$$

$$= \frac{-\sin\theta}{a}\left[-\frac{\sin\theta}{a}\frac{\partial^2 f}{\partial \theta^2} - \frac{\cos\theta}{a}\frac{\partial f}{\partial \theta}\right]$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\sin^2\theta}{a^2}\frac{\partial^2 f}{\partial \theta^2} + \frac{\sin\theta\cos\theta}{a^2}\frac{\partial f}{\partial \theta}$$

By the same procedure, we get:

$$\frac{\partial^2 f}{\partial y^2} = \frac{\cos^2\theta}{a^2}\frac{\partial^2 f}{\partial \theta^2} - \frac{\sin\theta\cos\theta}{a^2}\frac{\partial f}{\partial \theta}$$

$$\therefore \quad \nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = \frac{1}{a^2}\frac{\partial^2 f}{\partial \theta^2}\left(\sin^2\theta + \cos^2\theta\right)$$

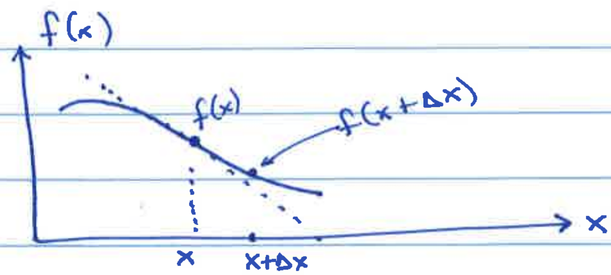
$$\nabla^2 = \frac{1}{a^2}\frac{\partial^2}{\partial \theta^2}$$

If you relax the $r =$ constant condition, you can find:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}$$

Differentials & total differentials

In one dimension, we can approximate a future value of a function if we know the current value of the slope:



We do this by relaxing the limit of Δx:

$$f'(x) = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

$$f'(x) \approx \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

$$f'(x)\Delta x \approx f(x+\Delta x) - f(x)$$

Or:

$$f(x+\Delta x) \approx f(x) + f'(x)\Delta x$$

$$\approx f(x) + \left(\frac{df}{dx}\right)_x \Delta x$$

Or: $\Delta f = f'(x)\,\Delta x$

When Δx is very small, the approximation is very good:

Example $\sin(0.1) \approx \sin(0) + \cos(0)\cdot 0.1 = 0.1$

$= 0.09983$ (actual value)

The notation we use for this is:

$$\underset{\text{differential of } f}{df} = \underset{\text{derivative of } f \text{ with respect to } x}{f'(x)} \; \underset{\text{differential of } x}{dx}$$

In 2-D, we can write something very similar called the <u>total differential</u>

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

That is, df = amount f will change if we change both x & y by small amounts dx & dy

In many dimensions:

$$df = \left(\frac{\partial f}{\partial x_1}\right) dx_1 + \left(\frac{\partial f}{\partial x_2}\right) dx_2 + \dots \left(\frac{\partial f}{\partial x_n}\right) dx_n$$

<u>An example:</u> $P(T, V) = \frac{RT}{V}$ ← ideal gas law

dP = how much will pressure change if we change T <u>and</u> V simultaneously

$$= \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\boxed{dP = \frac{R}{V} dT - \frac{RT}{V^2} dV}$$

Exact vs. Inexact differentials

13.5

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

If the mixed derivatives in this expression

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

are equal this is called an exact differential.

If they aren't it is called inexact.

Examples: $df = \underbrace{\pi r}_{\left(\frac{\partial f}{\partial h}\right)} dh + \underbrace{\pi h^2}_{\left(\frac{\partial f}{\partial r}\right)} dr$

Test:

$$\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial h}\right) \stackrel{?}{=} \frac{\partial}{\partial h}\left(\frac{\partial f}{\partial r}\right)$$

$$\frac{\partial}{\partial r}(\pi r) \stackrel{?}{=} \frac{\partial}{\partial h}(\pi h^2)$$

$$\pi \stackrel{?}{=} 2\pi h \quad \longleftarrow \text{inexact}$$

Another: $df = \underbrace{\pi r^2}_{\left(\frac{\partial f}{\partial h}\right)} dh + \underbrace{2\pi r h}_{\left(\frac{\partial f}{\partial r}\right)} dr$

Test:

$$\frac{\partial}{\partial r}\left(\frac{\partial f}{\partial h}\right) \stackrel{?}{=} \frac{\partial}{\partial h}\left(\frac{\partial f}{\partial r}\right)$$

$$\frac{\partial}{\partial r}(\pi r^2) \stackrel{?}{=} \frac{\partial}{\partial h}(2\pi r h)$$

$$2\pi r \stackrel{?}{=} 2\pi r \quad \longleftarrow \text{exact}$$

Exact: dU, dG, dH, dS ← thermodynamic state functions

Inexact: $đq$, $đw$ ← heat & work.

Reverse Differentiation → for Exact differentials

We can also go backwards. If we are given a total differential, we can usually determine the function:

$$dP = \underbrace{\frac{R}{V}}_{\substack{\text{must be} \\ \left(\frac{\partial P}{\partial T}\right)_V}} dT - \underbrace{\frac{RT}{V^2}}_{\text{must be } \left(\frac{\partial P}{\partial V}\right)_T} dV$$

V not allowed to change

So: $$\int \left(\frac{\partial P}{\partial T}\right)_V dT = \int \frac{R}{V}\, dT$$

integrating should get us within an undetermined ~~[illegible]~~ f(V) of P:

$$P = \frac{RT}{V} + f(V)$$

Now we match this up to $\frac{\partial P}{\partial V}$ by taking partial with respect to $\underline{V}$:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} + \frac{df(V)}{dV}$$

But this must be $= -\frac{RT}{V^2}$ from total differential

$\therefore$ f(V) can only be a constant

$$\therefore \quad P = \frac{RT}{V} + \text{constant}$$

How do we know this constant = 0 ?

$P \rightarrow 0$ as $V \longrightarrow \infty$, so the constant must be 0.

Some examples:

$$df = \underbrace{\pi r^2}_{\left(\frac{\partial f}{\partial h}\right)_r} dh + \underbrace{2\pi r h}_{\left(\frac{\partial f}{\partial r}\right)_h} dr$$

$$f = \int \left(\frac{\partial f}{\partial h}\right)_r dh + g(r) = \int \pi r^2 dh + g(r) = \pi r^2 h + g(r)$$

$$f(r,h) = \pi r^2 h + g(r)$$

Does this check out? $\longrightarrow$ $\left(\frac{\partial f}{\partial r}\right) = 2\pi r h + g'(r)$

yes, it does! $= 2\pi r h$ $\leftarrow$ must be const.

Differentials are often used in error analysis:

$V = \pi r^2 h$ $\longleftarrow$ volume of a cylinder

what's the uncertainty in volume (V) if

$r = 8.00 \pm 0.050$ cm

$h = 10.00 \pm 0.050$ cm

$$dV = \left(\frac{\partial V}{\partial h}\right) dh + \left(\frac{\partial V}{\partial r}\right) dr$$ $\longleftarrow$ $\boxed{\text{How much can V change if we make an error in r \& h?}}$

$$= \pi r^2 dh + 2\pi r h\, dr$$
$$= \pi (8)^2 (0.05) + 2\pi (8)(10)(0.05)$$
$$= (64 + 160)\pi (0.05) \qquad = (224\pi)(0.05)$$
$$= 35.19 \text{ cm}^3$$

(Here $V = \pi r^2 h = \pi (8)^2 (10) = 2010.62 \text{ cm}^3$

$\therefore \quad V = 2010.62 \pm 35.19 \text{ cm}^3$

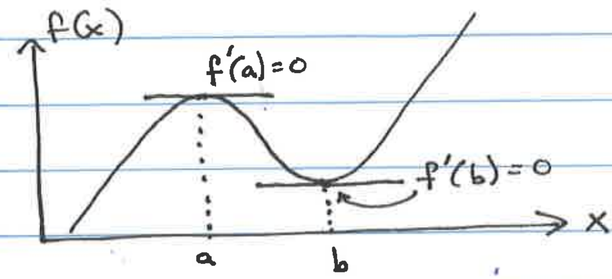
$V \pm dV$ $\longleftarrow$ dV helps find error bars

Maxima & Minima

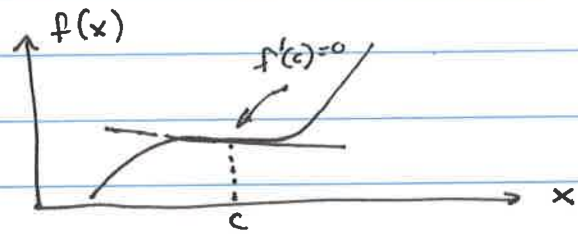
Critical points occur where the first derivative of a function is equal to zero:

$$\frac{df}{dx} = 0 \qquad \text{i.e. where } f'(c) = 0$$

In 1D, this corresponds to the location of a local minimum or maximum of the function:



or where the function is locally flat

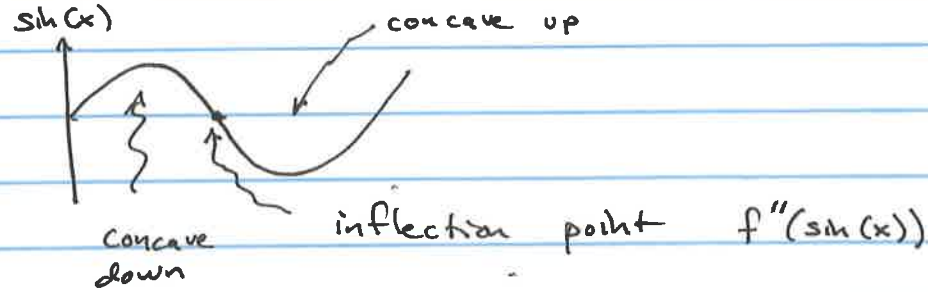


The 2nd derivative test can tell us what kind of critical point we have:

1. If $f''(a) < 0$ then $f(x)$ has a local maximum at $x = a$
2. If $f''(b) > 0$ then $f(x)$ has a local minimum at $x = b$
3. If $f''(c) = 0$, then no conclusion can be drawn without some further analysis

Inflection points

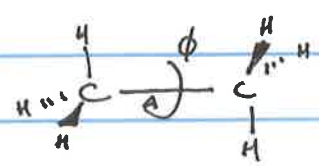
If $f''(c) = 0$ then c might be an inflection point. An inflection point is where a function shifts from "concave-up" on one side to "concave-down" on the other



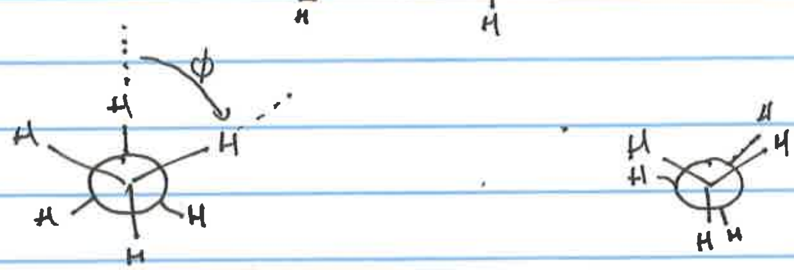
Note that $f'(x)$ at an inflection point is not 0.

Here's an application that is directly relevant to chemistry: Alkane conformations

H_3C-CH_3

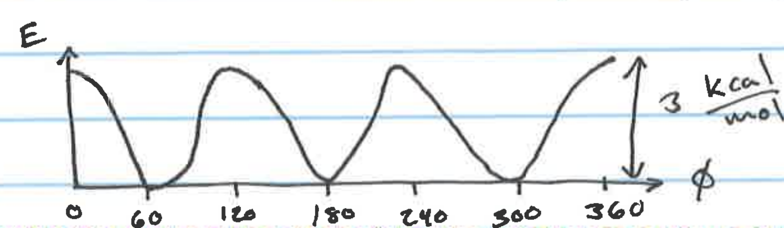


ϕ is the torsion angle for hindered rotation in ethane



staggered conformation
$\phi = 60°, 180°, 300°$

eclipsed conformation
$\phi = 0°, 120°, 240°, 360°$

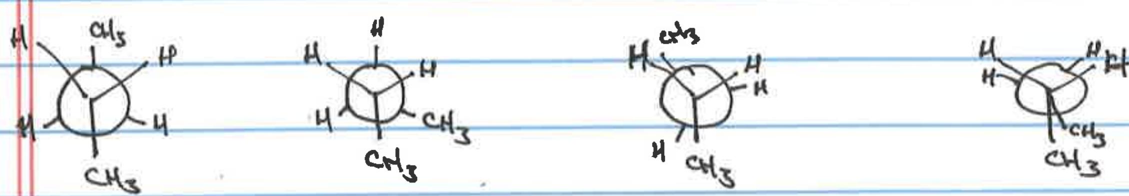


The local minima on this plot correspond to stable conformations

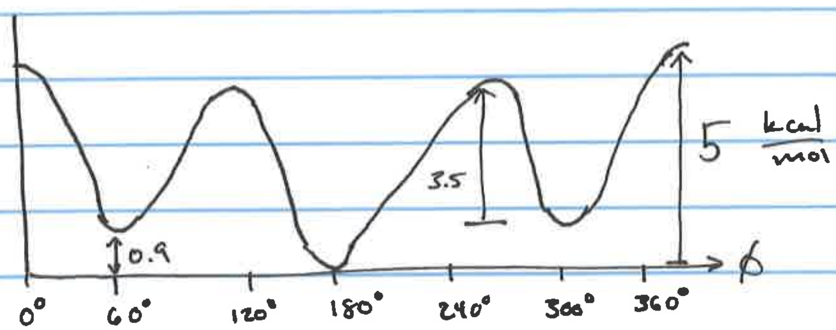
The local maxima correspond to transition states.

Things aren't always so symmetric:

$$CH_3 - CH_2 \overset{\phi}{-} CH_2 - CH_3$$



"Anti"	"Gauche"	"Eclipsed Gauche"	"Eclipsed"
$\phi = 180°$	$\phi = 60°, 300°$	$\phi = 120°, 240°$	$\phi = 0°, 360°$



Finding maxima & minima of functions (particularly energies) is essential to understanding molecular structures & reaction rates.

Functions of more than 1 variable

$c = (a,b)$ is a critical point of $f(x,y)$

if $\frac{\partial f}{\partial x} = 0$ at (a,b) and $\frac{\partial f}{\partial y} = 0$ at (a,b)

A critical point is not necessarily a local minimum or maximum

$$f(x,y) = x^2 - y^2$$

$$\left.\begin{aligned} \frac{\partial f}{\partial x} &= 2x \\ \frac{\partial f}{\partial y} &= -2y \end{aligned}\right\} \therefore (0,0) \text{ is a critical point.}$$

Let's consider x & y separately:

$f(x,0) = x^2$ which has a minimum @ $x=0$

$f(0,y) = -y^2$ which has a maximum @ $y=0$

How is this possible?

Mathematica: Plot3D[x^2 -y^2, {x,-2,2}, {y,-2,2}]

The point $(0,0)$ is a saddle point

The 2nd Derivative test in 2 variables.

$\frac{\partial f}{\partial x} = 0$ at (a,b)

$\frac{\partial f}{\partial y} = 0$ at (a,b)

Define $\quad D \equiv f_{xx}(a,b) f_{yy}(a,b) - f_{xy}^2(a,b)$

$f(a,b)$ is a

1. Local minimum if $f_{xx}(a,b) > 0$ & $D > 0$
2. Local maximum if $f_{xx}(a,b) < 0$ & $D > 0$
3. A saddle point if $D < 0$
4. If $D = 0$, no conclusion can be drawn without further analysis.

Example: $\quad f(x,y) = \ln(x^2+y^2+2)$

$$\left.\begin{aligned} \frac{\partial f}{\partial x} &= \frac{2x}{x^2+y^2+2} \\ \frac{\partial f}{\partial y} &= \frac{2y}{x^2+y^2+2} \end{aligned}\right\} \quad (0,0) \text{ is a critical point}$$

$$f_{xx} = \left.\frac{\partial^2 f}{\partial x^2}\right|_{(0,0)} = \left.\frac{(x^2+y^2+2)(2) - (2x)(2x)}{(x^2+y^2+2)^2}\right|_{(0,0)} = 1$$

$$f_{yy} = \left.\frac{\partial^2 f}{\partial y^2}\right|_{(0,0)} = \left.\frac{(x^2+y^2+2)(2) - (2y)(2y)}{(x^2+y^2+2)^2}\right|_{(0,0)} = 1$$

$$f_{xy} = \left.\frac{\partial^2 f}{\partial x \partial y}\right|_{(0,0)} = \left.\frac{(x^2+y^2+2)(0) - (2x)(2y)}{(x^2+y^2+2)^2}\right|_{(0,0)} = 0$$

$$D = f_{xx} f_{yy} - f_{xy}^2 = (1)(1) - 0^2 = 1$$

$$f_{xx} > 0 \quad \& \quad D > 0$$

so $(0,0)$ is a local minimum

Another example: $f(x,y) = \frac{1}{2}x^2 - xy$

$$\left.\begin{aligned} \frac{\partial f}{\partial x} &= x - y \\ \frac{\partial f}{\partial y} &= -x \end{aligned}\right\} \quad (0,0) \text{ is a critical point}$$

$$\left.\begin{aligned} f_{xx} &= 1 \\ f_{yy} &= 0 \\ f_{xy} &= -1 \end{aligned}\right\} \quad D = (1)(0) - (-1)^2 = -1$$

$f_{xx} > 0$ and $D < 0$

so $(0,0)$ is a saddle point

Global vs. Local minima & maxima

Consider the function:

$$f = e^{-(x^2+y^2)} \cos(3x)\sin(3y)$$

Plotting the function shows many critical points

```
f = Exp[-(x^2 + y^2)] Cos[3 x] Sin[3 y]
Plot3D[f, {x, -3,3}, {y,-3,3}]
```

Some of the points are local maxima, but only one of these is the global maximum

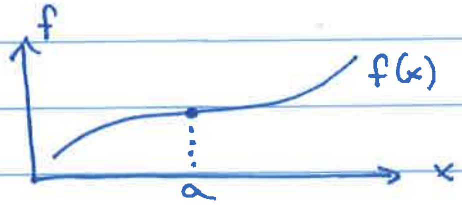
Some of the points are local minima, but only one of these is the global minimum.

Global minima are special in chemistry. These correspond to the thermodynamically stable structures on an energy surface.

Finding global minima is an incredibly difficult problem and is responsible for a very large fraction of the scientific computing done today.

Your next HW will ask you to think up ways for the blind hiker to find the lowest valley. Can you figure out a good method that will work on all terrains?

Taylor's formula in several variables



Given $f(a)$, $f'(a)$, $f''(a)$, $f'''(a)$ we can predict $f(x)$ at points far from a:

$$f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f'''(a)}{3!}(x-a)^3 + \dots$$

$$= \sum_{k=0}^{\infty} f^{(k)}(a) \frac{(x-a)^k}{k!}$$

= Taylor expansion of f about $x=a$

This formula assumes f & all of its derivatives are continuous in the region of interest

- If $a=0$, this is called the Maclaurin expansion
- If only a few terms are used, we get an approximation

$$f(x) \approx \sum_{k=0}^{N} f^{(k)}(a) \frac{(x-a)^k}{k!}$$

- The approximation gets better as $x \to a$

Example: Expand $f(x) = e^x$ about $x=0$

$$\left.\begin{aligned} f^{(0)} &= e^x \\ f^{(1)} &= e^x \\ f^{(2)} &= e^x \\ &\vdots \end{aligned}\right\} \qquad f(x) = \sum_{k=0}^{\infty} 1 \frac{x^k}{k!}$$

$$= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

Taylor's formula for a function of 2 variables

$$f(a+h,b+j) = f(a,b) + \left(h\frac{\partial}{\partial x} + j\frac{\partial}{\partial y}\right) f(x,y)\Big|_{a,b}$$

$$+ \frac{1}{2!}\left(h\frac{\partial}{\partial x} + j\frac{\partial}{\partial y}\right)^2 f(x,y)\Big|_{a,b}$$

$$+ \cdots$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!}\left(h\frac{\partial}{\partial x} + j\frac{\partial}{\partial y}\right)^k f(x,y)\Big|_{a,b}$$

This has some unfamiliar (operator) notation, so to illustrate $f(x,y)$ up to quadratic order:

$$f(x,y) \approx f(a,b) + (x-a)f_x(a,b) + (y-b)f_y(a,b)$$

$$+ \frac{(x-a)^2}{2} f_{xx}(a,b) + \frac{(y-b)^2}{2} f_{yy}(a,b) + \frac{2(x-a)(y-b)}{2} f_{xy}(a,b)$$

Example

Expand e^{xy} about $(0,0)$ up to quadratic order

$$\left.\begin{array}{ll} f_x = y e^{xy} & f_{xx} = y^2 e^{xy} \\ f_y = x e^{xy} & f_{yy} = x^2 e^{xy} \end{array}\right\} \text{ all } = 0 \text{ at } (0,0)$$

$$f_{xy} = e^{xy} + xy\, e^{xy} \qquad = 1 \text{ at } (0,0)$$

So: $$e^{xy} \approx 1 + (x-a)\cdot 0 + (y-b)\cdot 0 + \frac{(x-a)^2}{2}0 + \frac{(y-b)^2}{2}\cdot 0 + \frac{2(x-a)(y-b)}{2}\cdot 1$$

$$e^{xy} \approx 1 + \frac{2(x-0)(y-0)}{2}\cdot 1$$

$$e^{xy} = 1 + xy$$

Lagrange Multipliers

Goal: find extrema of a function $f(x_1, x_2 \dots x_N)$
subject to a constraint $g(x_1, x_2 \dots x_N) = 0$

We'll start with an example:

$$f(x,y) = x^2 + yx$$ ← find the minimum subject to $y = x+2$

- Boring method that only works for a few variables: substitute $y = x+2$ into f and minimize with respect to x:

$$f = x^2 + yx = x^2 + (x+2)x = 2x^2 + 2x$$
$$\frac{df}{dx} = 0 = 4x + 2 \implies x = -\frac{1}{2}$$
$$y = x+2 \implies y = \frac{3}{2}$$

- Wrong method (ignore constraints)

$$\left.\begin{array}{l} \frac{df}{dx} = 2x + y = 0 \\ \frac{\partial f}{\partial y} = x = 0 \end{array}\right\} x = y = 0$$ ← not right location!

- Most powerful method: Lagrange Multipliers

function of interest: $f(x,y)$
constraint equation: $g(x,y) = 0$

1. Define

$$F(x,y) = f(x,y) - \lambda g(x,y)$$ ← Lagrange Multiplier

2. Find $\frac{\partial F}{\partial x} = 0$ and $\frac{\partial F}{\partial y} = 0$

which give critical x & y in terms of λ

3. Determine λ from constraint equation

Back to our example:

$$f(x,y) = x^2 + yx$$
$$g(x,y) = y - x - 2 = 0$$

rewrite constraint to be $= 0$

Step 1:

$$F(x,y) = x^2 + yx - \lambda(y - x - 2)$$

Step 2:

$$\frac{\partial F}{\partial x} = 2x + y + \lambda = 0 \qquad \frac{\partial F}{\partial y} = \underbrace{x - \lambda = 0}_{\boxed{x = \lambda}}$$

$$2\lambda + y + \lambda = 0$$
$$\boxed{y = -3\lambda}$$

Step 3:

$$y - x - 2 = 0$$
$$-3\lambda - \lambda - 2 = 0$$
$$-4\lambda = 2$$
$$\lambda = -\tfrac{1}{2} \quad \therefore \quad \boxed{x = \lambda = -\tfrac{1}{2}, \; y = \tfrac{3}{2}}$$

The Lagrange multiplier works with any number of variables $f(x_1, x_2, \ldots x_N)$ and multiple simultaneous constraints

$$\left.\begin{array}{l} g(x_1 \ldots x_N) = 0 \\ h(x_1 \ldots x_N) = 0 \end{array}\right] \text{ constraint equations}$$

$$F(x_1 \ldots x_N) = f(x_1 \ldots x_N) - \lambda g(x_1 \ldots x_N) - \mu h(x_1 \ldots x_N)$$

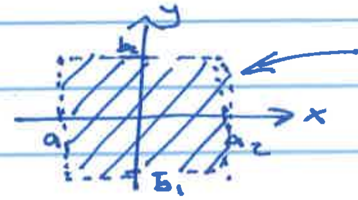
The procedure is the same

1. Find critical points in terms of λ, μ
2. Use constraint equations to Determine λ, μ

Multiple Integrals

$$I = \int_{a_1}^{a_2} \int_{b_1}^{b_2} f(x,y)\, dx\, dy = \int_{a_1}^{a_2} dx \int_{b_1}^{b_2} dy\; f(x,y)$$

where $dx\,dy$ is an infinitessimal unit of area in the x-y plane



Bounded area in the x-y plane

I is the net volume between the surface, $f(x,y)$, and the x-y plane itself.

Example:

$$I = \int_0^a dx \int_0^b dy\; (x^2 + 4xy)$$

Do y first, treating x as a constant:

$$\int_0^a dx \left[x^2 y + 2xy^2 \right]_0^b = \int_0^a dx \left[x^2 b + 2xb^2 - 0 - 0 \right]$$

$$= \int_0^a dx\; (x^2 b + 2xb^2)$$

$$= \left[\frac{x^3 b}{3} + x^2 b^2 \right]_0^a$$

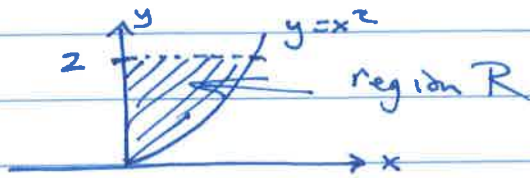
$$= \frac{ba^3}{3} + a^2 b^2 - 0 - 0$$

$$= \frac{ba^3}{3} + a^2 b^2$$

Another example, this time with a bounded region that is <u>not</u> rectangular

$$I = \iint_R dx\, dy \;\; x^2 y$$

R is the region in the xy plane bounded by $y = x^2$ and $y = 2$ with $x \geq 0$ and $y \geq 0$



We'll integrate y first, and then x:

$x^2 \leq y \leq 2$ and $0 \leq x \leq \sqrt{2}$

$$I = \int_0^{\sqrt{2}} dx \int_{x^2}^{2} dy \;\; x^2 y$$

$$= \int_0^{\sqrt{2}} x^2\, dx \int_{x^2}^{2} dy \;\; y$$

$$= \int_0^{\sqrt{2}} dx \;\; x^2 \left[\frac{y^2}{2}\right]_{x^2}^{2}$$

$$= \int_0^{\sqrt{2}} dx \;\; x^2 \left[2 - \frac{x^4}{2}\right] = \int_0^{\sqrt{2}} dx \left[2x^2 - \frac{x^6}{2}\right]$$

$$= \left[\frac{2x^3}{3} - \frac{x^7}{14}\right]_0^{\sqrt{2}} = \frac{2(2)^{3/2}}{3} - \frac{2^{7/2}}{14}$$

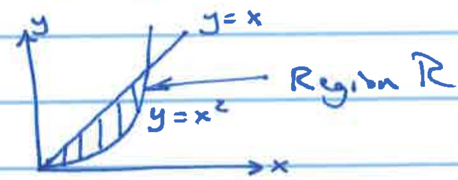
$$= \frac{16}{21}\sqrt{2}$$

In general, integrate y then x: $\displaystyle\int_a^b dx \int_{y_1(x)}^{y_2(x)} f(x, y)\, dy$

It is also perfectly reasonable to integrate x first in some cases:

$$I = \int_\alpha^\beta dy \int_{x_1(y)}^{x_2(y)} dx \; f(x,y)$$

<u>Example:</u> R is in the first quadrant, bounded by $y = x^2$ & $y = x$



$$I = \iint_R x \; dx\, dy$$

$$I = \int_0^1 dx \int_{x^2}^{x} dy \; x$$

$$= \int_0^1 dx \; x\Big[y\Big]_{x^2}^{x}$$

$$= \int_0^1 dx \; x\left[x - x^2\right]$$

$$= \int_0^1 dx \; x^2 - x^3$$

$$= \left[\frac{x^3}{3} - \frac{x^4}{4}\right]_0^1$$

$$= \frac{1}{3} - \frac{1}{4}$$

$$= \frac{1}{12}$$

$$I = \int_0^1 dy \int_y^{\sqrt{y}} dx \; x$$

$$= \int_0^1 dy \left[\frac{x^2}{2}\right]_y^{\sqrt{y}}$$

$$= \int_0^1 dy \left[\frac{y}{2} - \frac{y^2}{2}\right]$$

$$= \left[\frac{y^2}{4} - \frac{y^3}{6}\right]$$

$$= \frac{1}{4} - \frac{1}{6}$$

$$= \frac{1}{12}$$