Week 8

Functions

Integrals, Parametric Functions, Multi-variable Functions

F. Sorin (MX)

Ecole Polytechnique Fédérale de Lausanne

Reminder

- We discussed the concept of functions and defined limits, continuity and derivability thanks to fundamental definitions.

- We showed in particular how the fundamental definition of the differentiability of a function can be used to find the derivative of some common functions.

$$\forall \varepsilon > 0, \exists \alpha > 0, \forall h \in I, |h| < \alpha \Longrightarrow \left| \frac{f(x+h) - f(x)}{h} - l \right| < \varepsilon$$

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

- We introduced the need for the common tangent construction in phase diagrams, and gave an example of a power function in the Lennard-Jones potential.

- We then insisted on the concepts of Taylor series and Taylor expansion.

$$\forall x \in I, f(x) = \sum_{k=0}^{n} \frac{x^k}{k!} f^{(k)}(0) + \frac{x^{n+1}}{(n+1)!} f^{(n+1)}(c)$$

- For physical models, the arguments in functions must be a-dimensional !

Overview

- Taylor expansion example
- Primitives and definition of integrals
- Basic integration techniques
- Curve and surface calculation
- Parametric functions
- Multi-variable functions - Thermodynamics

Next week:

- Multi-variable functions continued
- Deriving the atomic diffusion equation
- Fourier transforms

Physical representation of chemical bonds

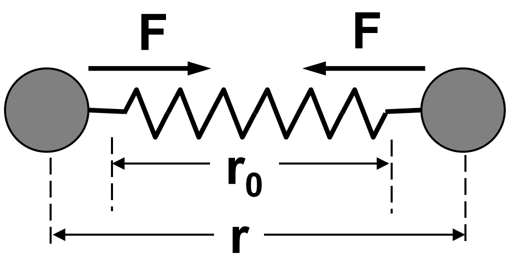
A simple model to physically apprehend the bond between atoms: the Lennard-Jones potential.

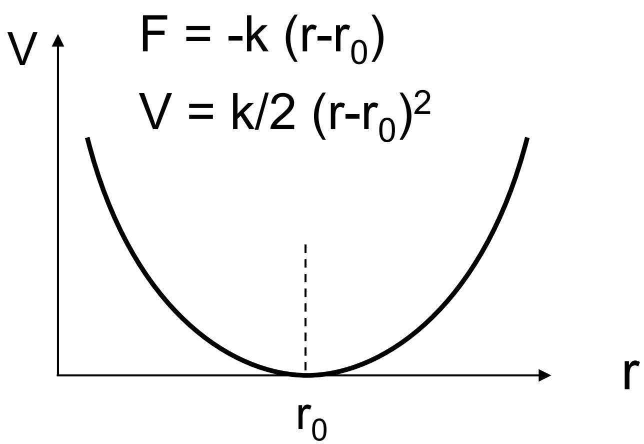
A Conservative force (the work done on an object does not depend on the object's path) can be derived from this potential:

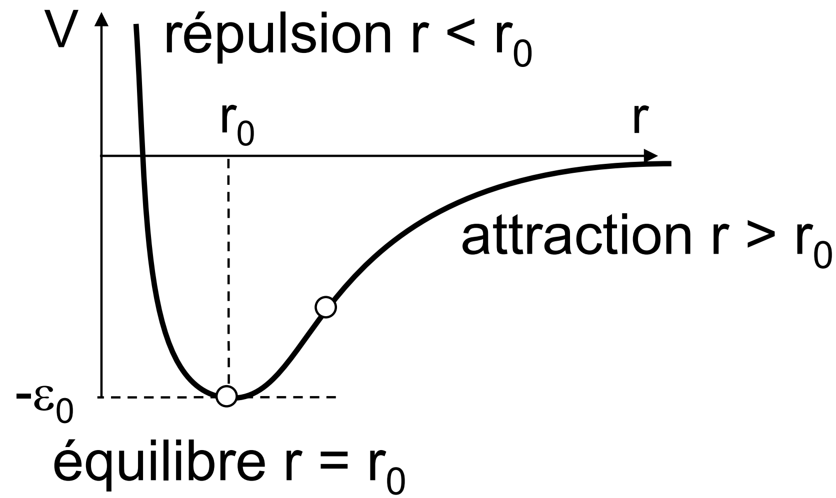
$$\vec{F} = -\overrightarrow{grad}\, V$$

Potential of Lennard-Jones:

$$V = \varepsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^{6} \right]$$







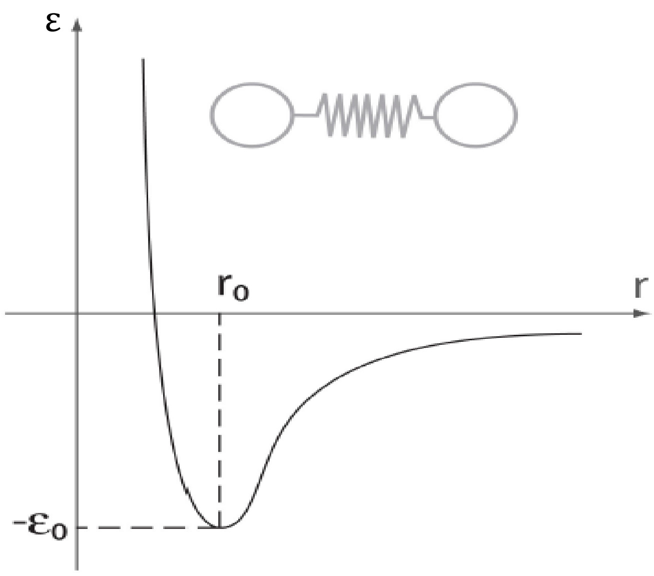
Physical representation of chemical bonds

- A gradient is a vector that looks into the change of a quantity over the different directions:

$$\vec{F} = -\overrightarrow{grad}V = -\frac{\partial V}{\partial x}\vec{x} - \frac{\partial V}{\partial y}\vec{y} - \frac{\partial V}{\partial z}\vec{z}$$

- Along a vector $\overrightarrow{e_r}$ and a distance called *r,* we have:

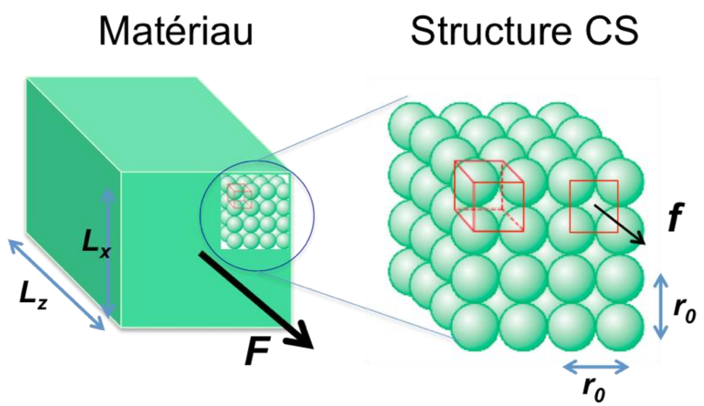
$$\vec{F} = -\frac{\partial V}{\partial r}\overrightarrow{e_r}$$

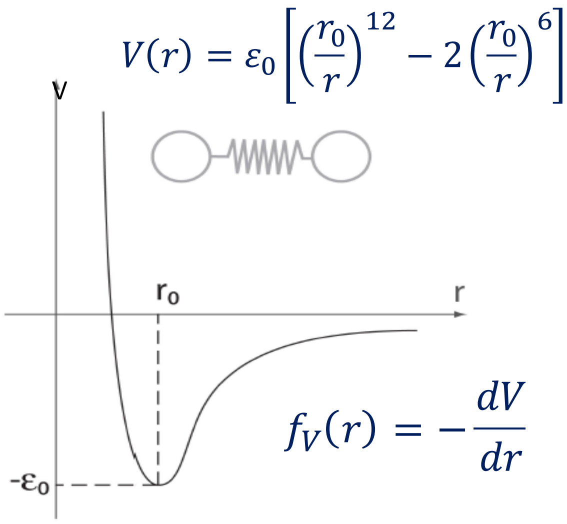


- The derivative has hence a lot of physical meaning: for small r, when atoms get close to each other, the potential increases significantly, from which derives a force that is repulsive, away from the increase of the energy, hence the minus sign in front of the gradient.
- As atoms are pulled apart, an attractive force brings the atoms back together into a more stable, low energy state.
- At the equilibrium condition, the forces equalize and the change of potential is zero.

Example: Linear Hooke's law

- From the fundamental definition, several operations on the differentiation of functions can be demonstrated.



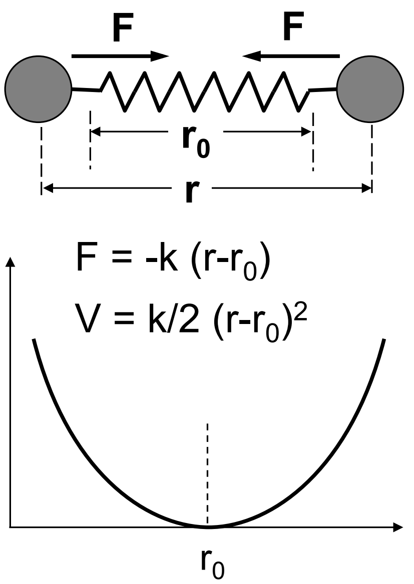


$$\frac{df_{ext}}{dr} = \frac{12\epsilon_0}{r^2}\left[13\left(\frac{r_0}{r}\right)^{12} - 7\left(\frac{r_0}{r}\right)^{6}\right] \quad \text{So,} \quad \frac{df_{ext}}{dr}(r_0) = \frac{72\varepsilon_0}{r_0^2}$$

$$f_{ext}(r) = \frac{dV}{dr} = 12\epsilon_0\left(-\frac{r_0^{12}}{r^{13}} + \frac{r_0^6}{r^7}\right) \qquad \epsilon = \frac{\Delta L_z}{L_{0z}} = \frac{\Delta r}{r_0}$$

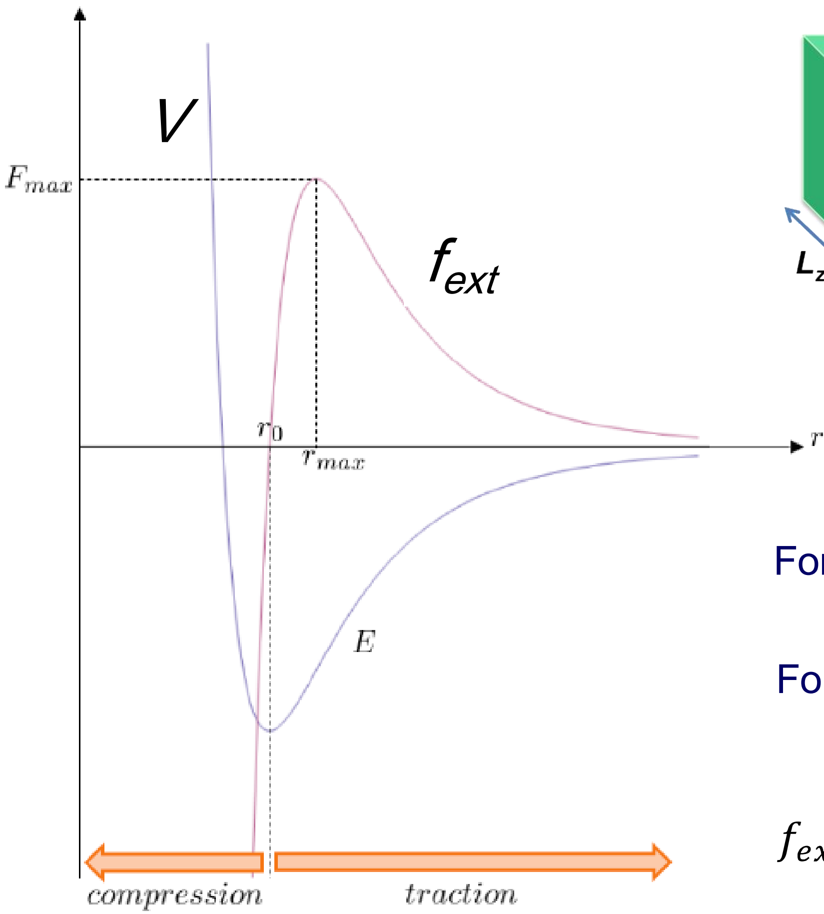
$$f_{ext}(r) = f_{ext}(r_0) + \left.\frac{df_{ext}}{dr}\right|_{r=r_0}(r - r_0) = \frac{72\varepsilon_0}{r_0^2}(r - r_0)$$

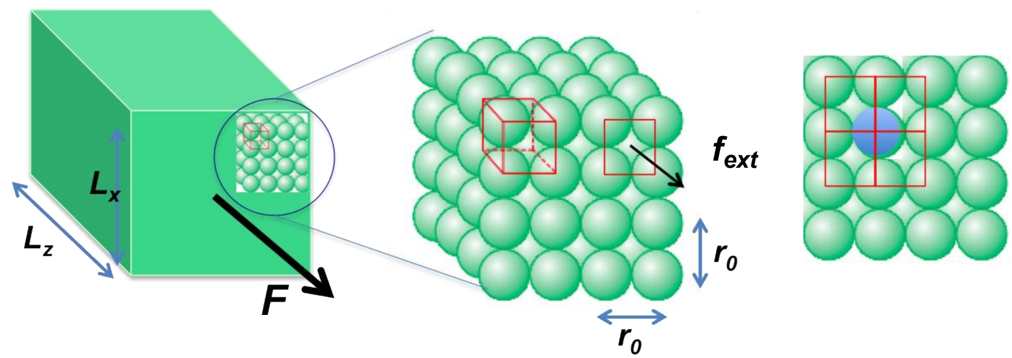
$$\sigma = 72\frac{\varepsilon_0}{r_0^3}\epsilon \qquad \text{or} \qquad \sigma = E\,\epsilon$$



Example: origin of plasticity

- The maximum force represents the force when the bond is breaking and the material should deform.
- Metals however deforms at stresses much lower than the value found in theory.





$$V(r) = \varepsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^{6} \right]$$

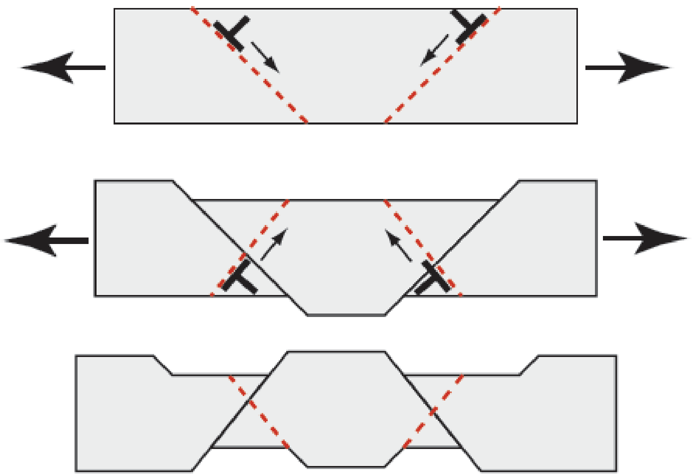
Force associée au potentiel: $f_V(r) = -\frac{dV}{dr}$

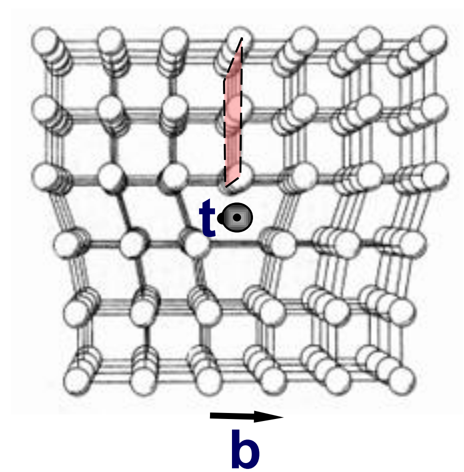
Force extérieure appliquée: : $f_{ext} = - f_V$

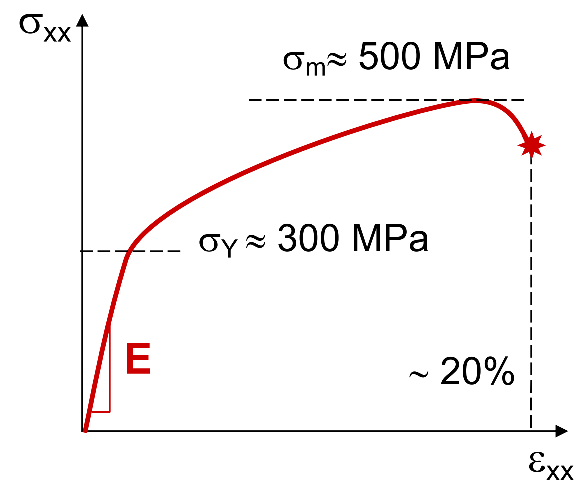
$$f_{ext}(r) = \frac{dV}{dr} = 12\epsilon_0 \left(-\frac{r_0^{12}}{r^{13}} + \frac{r_0^6}{r^7} \right) \qquad \sigma_m^{LJ} = \frac{E}{27}$$

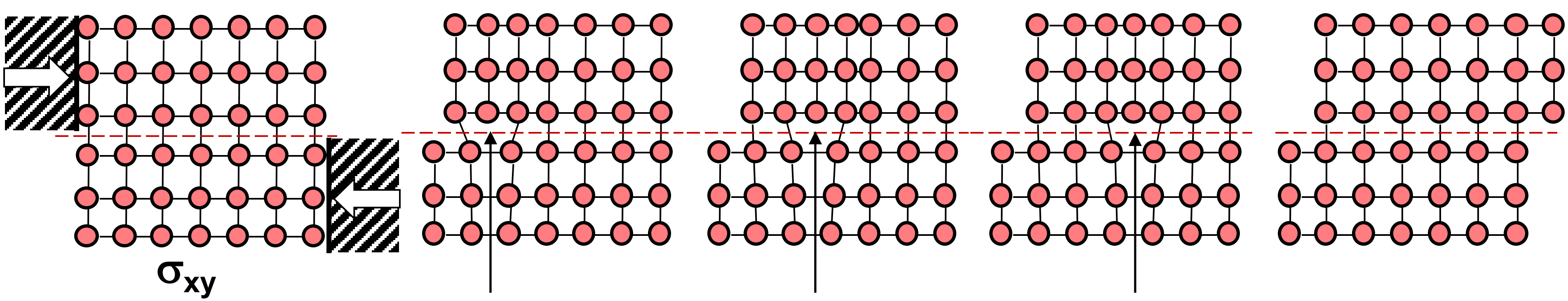
Example: origin of plasticity in metals

- The plastic deformation in metals is not due to individual bonds breaking but rather the movement of linear defects – dislocations – that can move at low stress applied.



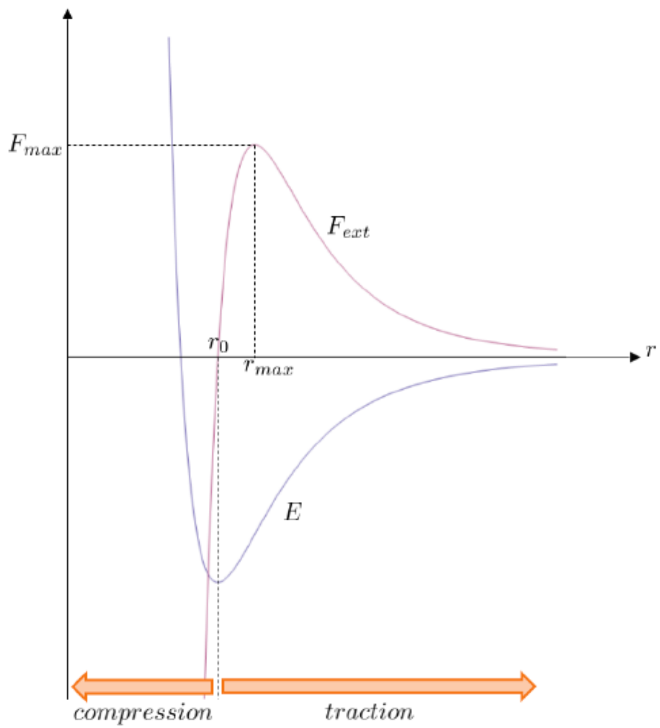






Work needed to break a bond

- What work one needs to perform to separate two atoms in a bond ?



$$W_{ext} = \int_{r=r_0}^{+\infty} F_{ext}(r)\,dr = \int_{r=r_0}^{+\infty} -F(r)\,dr$$

$$= \int_{r=r_0}^{+\infty} \frac{dV}{dr}\,dr = \int_{r=r_0}^{+\infty} dV = [V(r)]_{r=r_0}^{r\to+\infty}$$

$$\lim_{r\to\infty} V(r) - V(r_0) = 0 - (-\varepsilon_0)$$

$$W_{ext} = \varepsilon_0$$

- Did the work performed depend on the path taken to bring the atoms to infinity ?

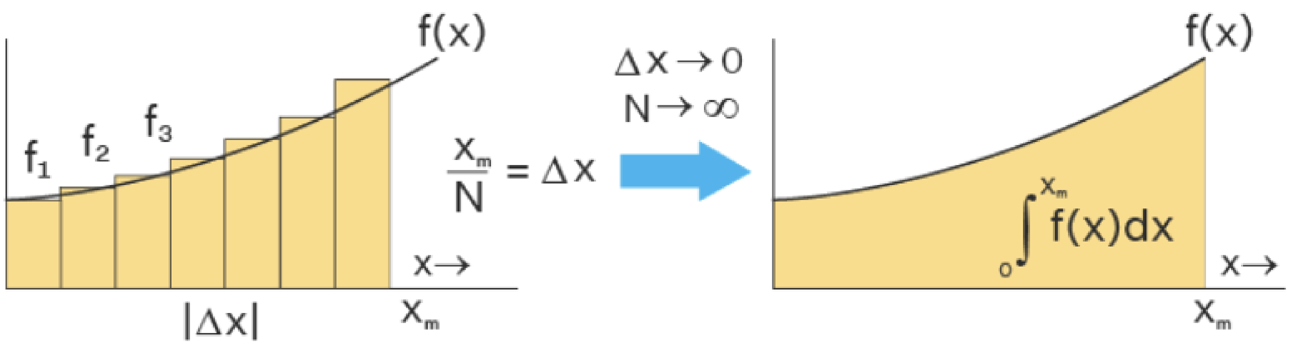
Primitives and integrals

- Given F and f two functions continuous and differentiable over $I \subset \mathbb{R}$, F is a primitive of f if $\forall x \in I, F'(x) = f(x)$
- If F is a primitive of f, $\forall \lambda \in \mathbb{R}\ or\ \mathbb{C}, F + \lambda$ is a primitive of f.

- Fundamental theorem: F and f two functions continuous and differentiable over $[a, b] \subset \mathbb{R}$, the area under the curve $f(x), x \in [a, b]$ is written, and verifies:

$$F(b) - F(a) = \int_a^b f(x)dx$$

- Riemann's interpretation gives an intuitive understanding of a rather bizarre fact !

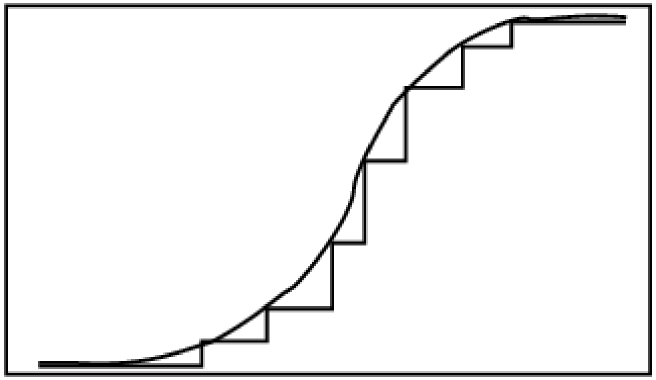


$$\text{Area} = \int_0^{X_m} f(x)dx = \lim_{\Delta x \to 0} \sum_{i=1}^{N} f_i(x)\Delta x$$

Primitives and Integrals

- One builds the concept of integration in different ways, the Rieman integral approach being very intuitive and closely linked to how we use integrals in engineering and materials Science.

- A few results are important to build this theory, as a reminder:
  - Stair-case functions are piecewise continuous functions over an interval in $\mathbb{R}$.
  - Every continuous function can be approximated by stair case functions, i.e. it can be the limit of a sequence of stair-case functions.
  - Every bounded function $f: [a, b] \to \mathbb{R}$, that is continuous (actually almost continuous everywhere) over $[a, b] \subset \mathbb{R}$, is Rieman-integrable, i.e:



$\forall \varepsilon > 0, \exists \varphi, \psi$ stair case functions such that $\varphi \leq f \leq \psi$ and $\int_a^b (\psi - \varphi)(t)\, dt < \varepsilon$

- More generally, let's consider an interval $[a, b[$ $(0 < a < b \leq +\infty)$, and f a function $[a, b[\to \mathbb{R}$, that is integrable on every closed interval in $[a, b[$. If we consider the function $F(x) = \int_a^x f(t)\, dt$

If $\lim_{x \to b} F(x) = l$, hence exists and is finite, then $\int_a^b f(t)\, dt$ converges and $\int_a^b f(t)\, dt = l$

Primitives and Integrals

- Let f be a continuous real-value function defined on a closed interval [a, b]. Let F be the function defined, for all x in [a, b], by

$$F(x) = \int_0^x f(t)dt$$

Then F is uniformly continuous on [a, b] and differentiable on the open interval (a, b), and

$F'(x) = f(x)$ for all x in (a, b) so F is an antiderivative (or primitive) of f.

- The form expressed above is an indefinite form, also written $\int f(x)dx$
- Definite forms is an integral over a defined interval that returns a number.
- Every continuous function has an anti-derivative, actually an infinity of them shifted by a constant.
  - The difficulty is to find antiderivatives and integrate functions !
  - Two techniques: substitution and part integration
- Important practical use of integrals:
  - Calculate surfaces, volumes… and length !
  - Sum infinitesimal time steps and length / surface / volume: work, fluxes…
  - Sum over densities (of states, of probabilities…)
  - Differential equations
  - Functions defined with integrals: Laplace and Fourier transforms

Common integration rules

$$\int_a^b f(x)\,\mathrm{d}x = \int_a^c f(x)\,\mathrm{d}x + \int_c^b f(x)\,\mathrm{d}x$$

$$\int_a^b k f(x)\,\mathrm{d}x = k\int_a^b f(x)\,\mathrm{d}x \quad (k = \text{constant})$$

$$\int_a^b f(x)\,\mathrm{d}x = -\int_b^a f(x)\,\mathrm{d}x$$

$$\int_a^a f(x)\,\mathrm{d}x = 0$$

$$\int_a^b [f(x) + g(x)]\mathrm{d}x = \int_a^b f(x)\,\mathrm{d}x + \int_a^b g(x)\,\mathrm{d}x$$

Integration by parts

$$\int_a^b u(x)v'(x)\,\mathrm{d}x = [u(x)v(x)]_a^b - \int_a^b u'(x)v(x)\,\mathrm{d}x$$

Integration by substitution

The integrand is a function of a function; the inner function is taken as the new variable.

$$\int_a^b f(g(x))\,\mathrm{d}x = \int_{g(a)}^{g(b)} f(u)\frac{\mathrm{d}u}{g'}$$

By substitution

$$u = g(x)$$

Common antiderivatives

$f(x)$	$\int f(x)\,\mathrm{d}x$	$f(x)$	$\int f(x)\,\mathrm{d}x$
c	cx	$\dfrac{1}{x^2+a^2}$	$\dfrac{1}{a}\tan^{-1}\dfrac{x}{a}$ or $\dfrac{-1}{a}\cot^{-1}\dfrac{x}{a}$
x^n	$\dfrac{x^{n+1}}{n+1} \quad (n \neq -1)$	$\dfrac{1}{x^2+2ax+b}$	$\dfrac{1}{\sqrt{b-a^2}}\tan^{-1}\left(\dfrac{x+a}{\sqrt{b-a^2}}\right)$ $(b > a^2)$
$\dfrac{1}{x}$	$\ln\lvert x\rvert \quad (x \neq 0)$	$\dfrac{2x+a}{x^2+ax+b}$	$\ln\lvert x^2+ax+b\rvert$
e^x	e^x		
a^x	$\dfrac{a^x}{\ln a} \quad \begin{pmatrix} a > 0 \\ a \neq 1 \end{pmatrix}$	$\sqrt{ax+b}$	$\dfrac{2}{3a}\sqrt{(ax+b)^3}$
$\ln x$	$x\ln x - x \quad (x > 0)$	$\dfrac{1}{\sqrt{ax+b}}$	$\dfrac{2}{a}\sqrt{ax+b}$
$\dfrac{1}{x-a}$	$\ln\lvert x-a\rvert$	$\dfrac{1}{\sqrt{a^2-x^2}}$	$\sin^{-1}\dfrac{x}{a}$
$\dfrac{1}{(x-a)^2}$	$-\dfrac{1}{x-a}$	$\sqrt{a^2-x^2}$	$\dfrac{x}{2}\sqrt{a^2-x^2}+\dfrac{a^2}{2}\sin^{-1}\dfrac{x}{a}$
$\dfrac{1}{x^2-a^2}$	$\dfrac{1}{2a}\ln\left\lvert\dfrac{x-a}{x+a}\right\rvert = \begin{cases} \dfrac{-1}{a}\tanh^{-1}\dfrac{x}{a}, & \lvert x\rvert < \lvert a\rvert \\ \dfrac{-1}{a}\coth^{-1}\dfrac{x}{a}, & \lvert x\rvert > \lvert a\rvert \end{cases}$		

Common antiderivatives

$f(x)$	$\int f(x)\,\mathrm{d}x$	$f(x)$	$\int f(x)\,\mathrm{d}x$
$\frac{1}{\sqrt{x^2+a^2}}$	$\ln\left(\frac{x+\sqrt{x^2+a^2}}{\lvert a\rvert}\right)=\sinh^{-1}\frac{x}{a}$	$\frac{1}{1-\sin x}$	$-\cot\left(\frac{x}{2}-\frac{\pi}{4}\right)=\tan\left(\frac{x}{2}+\frac{\pi}{4}\right)$
$\sqrt{x^2+a^2}$	$\frac{x}{2}\sqrt{x^2+a^2}+\frac{a^2}{2}\ln(x+\sqrt{a^2+x^2})$	$\frac{1}{1+\cos x}$	$\tan\frac{x}{2}$
$\frac{1}{\sqrt{x^2-a^2}}$	$\ln\left\lvert\frac{x+\sqrt{x^2-a^2}}{a}\right\rvert=\cosh^{-1}\frac{x}{a}$	$\frac{1}{1-\cos x}$	$-\cot\frac{x}{2}$
		$\tan x$	$-\ln\lvert\cos x\rvert$
$\sin x$	$-\cos x$	$\tan^2 x$	$\tan x-x$
$\sin^2 x$	$\frac{1}{2}(x-\sin x\cos x)=\frac{1}{2}\left(x-\frac{\sin 2x}{2}\right)$	$\cot x$	$\ln\lvert\sin x\rvert$
$\frac{1}{\sin x}$	$\ln\left\lvert\tan\frac{x}{2}\right\rvert$	$\cot^2 x$	$-\cot x-x$
$\frac{1}{\sin^2 x}$	$-\cot x$	$\sin^{-1} x$	$x\sin^{-1}x+\sqrt{1-x^2}$
		$\cos^{-1} x$	$x\cos^{-1}x-\sqrt{1-x^2}$
$\cos x$	$\sin x$	$\tan^{-1} x$	$x\tan^{-1}x-\ln\sqrt{1+x^2}$

Common antiderivatives

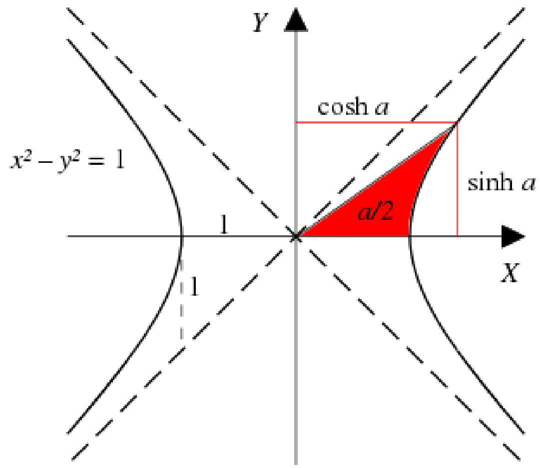
$f(x)$	$\int f(x)\,\mathrm{d}x$	$f(x)$	$\int f(x)\,\mathrm{d}x$
$\cos^2 x$	$\frac{1}{2}(x+\sin x\cos x)=\frac{1}{2}\left(x+\frac{\sin 2x}{2}\right)$	$\cot^{-1} x$	$x\cot^{-1} x+\ln\sqrt{1+x^2}$
$\frac{1}{\cos x}$	$\ln\left\lvert\tan\left(\frac{x}{2}+\frac{\pi}{4}\right)\right\rvert$	$\sinh x$	$\cosh x$
$\frac{1}{\cos^2 x}$	$\tan x$	$\cosh x$	$\sinh x$
		$\tanh x$	$\ln\lvert\cosh x\rvert$
$\frac{1}{1+\sin x}$	$\tan\left(\frac{x}{2}-\frac{\pi}{4}\right)$	$\coth x$	$\ln\lvert\sinh x\rvert$
		$\sinh^{-1} x$	$x\sinh^{-1} x-\sqrt{x^2+1}$
		$\cosh^{-1} x$	$x\cosh^{-1} x-\sqrt{x^2-1}$
		$\tanh^{-1} x$	$x\tanh^{-1} x+\ln\sqrt{1-x^2}$
		$\coth^{-1} x$	$x\coth^{-1} x+\ln\sqrt{x^2-1}$

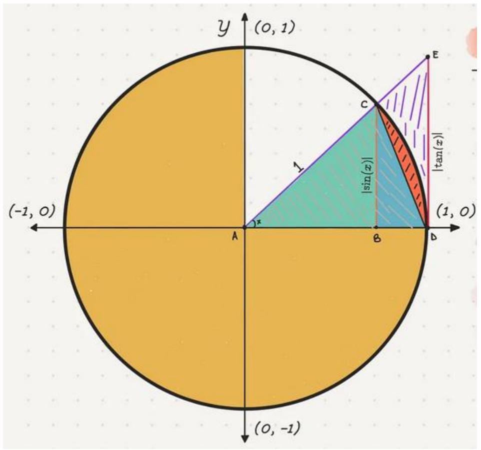
- Functions that are integrable but with no antiderivatives that can be expressed with usual functions (powers, inverse, trigonometric, exponential, logarithmic etc..):
  - e^{-x^2}; $\frac{\sin(x)}{x}$; $\frac{1}{\ln(x)}$….

Practical use of integrals: surface, volumes… and lengths !

- Calculating Surfaces: Hyperbolic functions

  - $cosh(x) = \frac{e^{x}+e^{-x}}{2}$
  - $\sinh(x) = \frac{e^{x}-e^{-x}}{2}$
  - $tanh(x) = \frac{\sinh(x)}{\cosh(x)}$
  - $cosh^{2}(x) - sinh^{2}(x) = 1$
  - $\frac{d}{dx}(cosh^{-1}(x)) = \frac{1}{\sqrt{x^{2}-1}}$



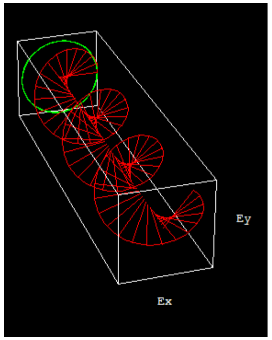


- Parametric functions:

Functions represented in the (x,y) plan, or at higher dimensions, can often be defined by a paramter (time, angle….).

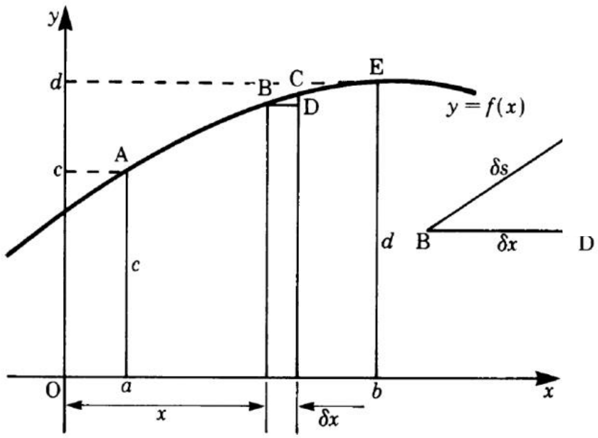
Example:
- Hyperbolic functions
- Light polarization:

$$\vec{E}_x(z,t) = E_{0x}\cos(kz - \omega t)\,\vec{x}$$
$$\vec{E}_y(z,t) = E_{0y}\cos(kz - \omega t + \varepsilon)\,\vec{y}$$



Arc length and Curvature

- Calculation of Arc length

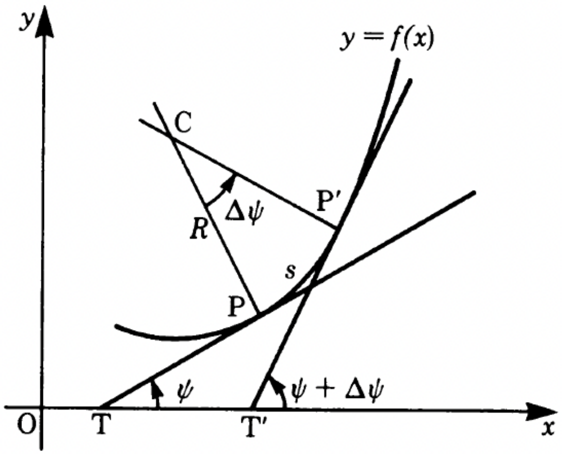


$$\left(\frac{\delta s}{\delta x}\right)^2 \approx 1+\left(\frac{\delta y}{\delta x}\right)^2 \quad \text{or} \quad \left(\frac{\delta s}{\delta y}\right)^2 \approx \left(\frac{\delta x}{\delta y}\right)^2 + 1$$

$$\frac{\delta s}{\delta x} \approx \sqrt{1+\left(\frac{\delta y}{\delta x}\right)^2} \quad \text{or} \quad \frac{\delta s}{\delta y} \approx \sqrt{1+\left(\frac{\delta x}{\delta y}\right)^2}$$

$$s = \int_a^b \sqrt{1+\left(\frac{dy}{dx}\right)^2}\,dx = \int_a^b \sqrt{1+f'(x)^2}\,dx$$

- Curvature



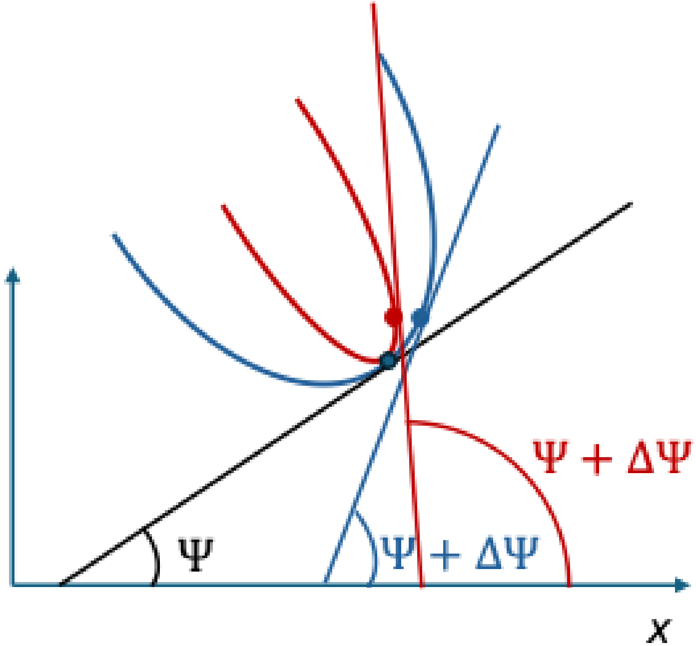
The curvarture is defined as $\kappa = \frac{1}{R}$

where R is given by: $R = \frac{\mathrm{d}s}{\mathrm{d}\psi}$

$$\frac{\mathrm{d}s}{\mathrm{d}\psi} = \frac{\mathrm{d}s}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}\psi} = \frac{\mathrm{d}x}{\mathrm{d}\psi}\sqrt{1+(y')^2}$$

$$R = \frac{\mathrm{d}s}{\mathrm{d}\psi} = \frac{\left[1+(y')^2\right]^{3/2}}{y''}$$

Curvature



$\Delta s = \Delta s$

$\Delta\Psi = \kappa \Delta s$

$\Delta\Psi = \kappa \Delta s$

$$\kappa = \frac{d\Psi}{ds}$$

$$\Rightarrow R = \frac{ds}{d\psi} = \frac{ds}{dx} \times \frac{dx}{d\psi}$$

$$\frac{ds}{dx} = \sqrt{1+y'^2} \qquad (y = f(x)).$$

$$\cdot \tan\psi = \frac{dy}{dx} = y'$$

$$\left((\tan x)' = \frac{1}{\cos^2 x} \right).$$

$$\cdot \frac{d(\tan\psi)}{dx} = \frac{d\psi}{dx} \times \frac{1}{\cos^2(\psi)} = y''$$

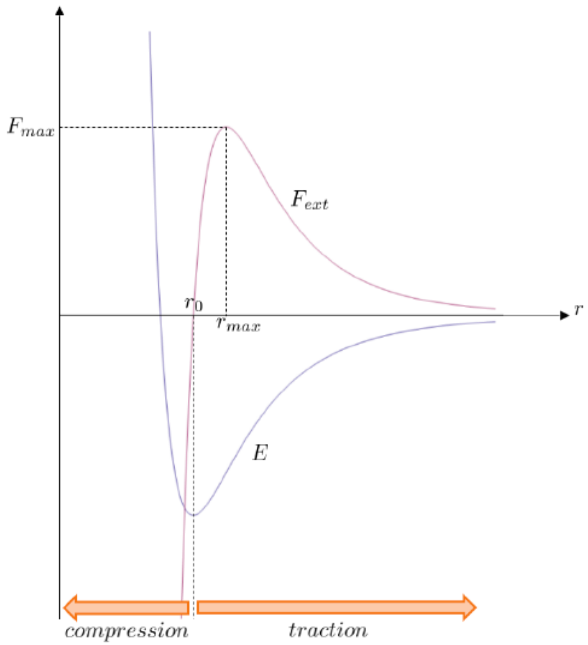
$$\frac{1}{\cos^2\psi} = \frac{\cos^2\psi + \sin^2\psi}{\cos^2\psi} = 1 + \tan^2\psi = 1 + y'^2$$

$$\Rightarrow \frac{d\psi}{dx}(1+y'^2) = y'' \Rightarrow \frac{d\psi}{dx} = \frac{y''}{1+y'^2} \Rightarrow \frac{dx}{d\psi} = \frac{1+y'^2}{y''}$$

$$R = \frac{ds}{d\psi} = \sqrt{1+y'^2} \times \frac{1+y'^2}{y''} = \frac{(1+y'^2)^{3/2}}{y''} \Rightarrow \boxed{\kappa = \frac{y''}{(1+y'^2)^{3/2}}}$$

Work needed to break a bond

- The work required to break a bound and bring an atom from equilibrium to infinity:



$$W_{ext} = \int_{r=r_0}^{+\infty} F_{ext}(r)\,dr = \int_{r=r_0}^{+\infty} -F(r)\,dr$$

$$= \int_{r=r_0}^{+\infty} \frac{dV}{dr}\,dr = \int_{r=r_0}^{+\infty} dV = [V(r)]_{r=r_0}^{r\to+\infty}$$

$$\lim_{r\to\infty} V(r) - V(r_0) = 0 - (-\varepsilon_0)$$

$$W_{ext} = \varepsilon_0$$

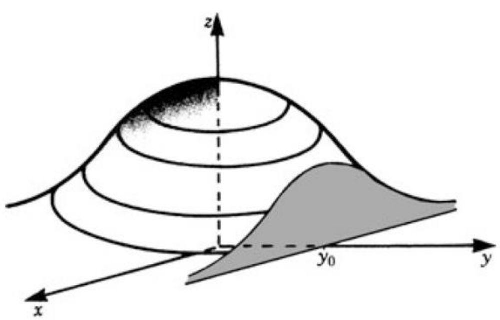
- Did the work performed depend on the path taken to bring the atoms to infinity ?
- A central force being conservative, it derives from a potential (as we saw). It is hence an exact differential and the work should not depend on the path.
- In an orthonormal coordinate system like the spherical one, a central force is given by $\boldsymbol{F} = F(r)\boldsymbol{e_r}$. The work is hence always directed along $\boldsymbol{e_r}$ and regardless of the path, we will have $W_{ext} = \int_{r=r_0}^{+\infty} F_{ext}(r)\,dr$.

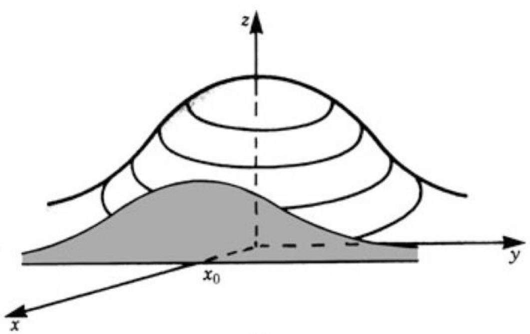
Multiple variable functions

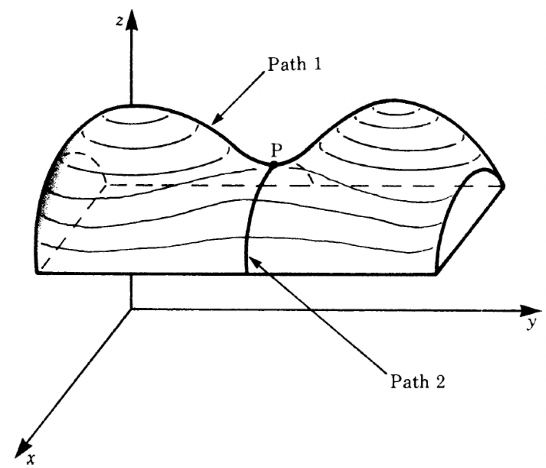
- All continuous functions of one variable we manipulate have antiderivative, and most of the times can be differentiated over extensive domains.

They hence form "exact differential", that is the integration over an infinitesimal change of variable dx is not dependent on the path, since we consider an algebraic path and not its absolute value.

- For multi-variable functions that we commonly encounter in materials science, it is more complex because paths to go to a point (x,y) are plenty.







- All the discussions we had regarding the continuity, limit and differentiability of single variable function can be extended to n-variable function in $\mathbb{R}^n$.

- Continuity:

$$\forall \varepsilon > 0, \exists \alpha > 0, \forall x \in I, d(x, x_0) < \alpha \Longrightarrow d(f(x), f(x_0)) < \varepsilon$$

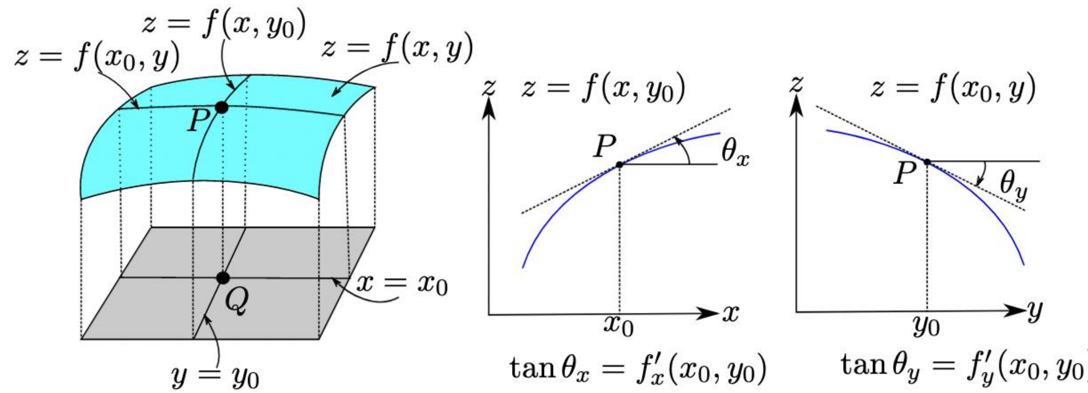
Exact and Inexact differentials

- Partial differentiation

Multi-variable functions will be studied usually by looking at how they vary when changing only one variable at a time:

$$\frac{\partial f}{\partial x}(x_0, y_0) = \frac{d}{dx} f(x, y_0)\Big|_{x=x_0}$$

$$\frac{\partial f}{\partial y}(x_0, y_0) = \frac{d}{dy} f(x_0, y)\Big|_{y=y_0}$$



with

$$\frac{\partial f}{\partial x}(x_0, y_0) = \lim_{h\to 0} \frac{f(x_0 + h, y_0) - f(x_0, y_0)}{h} \qquad \frac{\partial f}{\partial y}(x_0, y_0) = \lim_{h\to 0} \frac{f(x_0, y_0 + h) - f(x_0, y_0)}{h}$$

- Higher order Partial differentiation

Since partial derivatives of a function are also functions of several variables, they can be differentiated with respect to any variable. For a function of two variables:

$$\frac{\partial f}{\partial x} \longmapsto \frac{\partial}{\partial x}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial x^2}, \quad \frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial y\,\partial x}$$

$$\frac{\partial f}{\partial y} \longmapsto \frac{\partial}{\partial x}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial x\,\partial y}, \quad \frac{\partial}{\partial y}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial y^2}$$

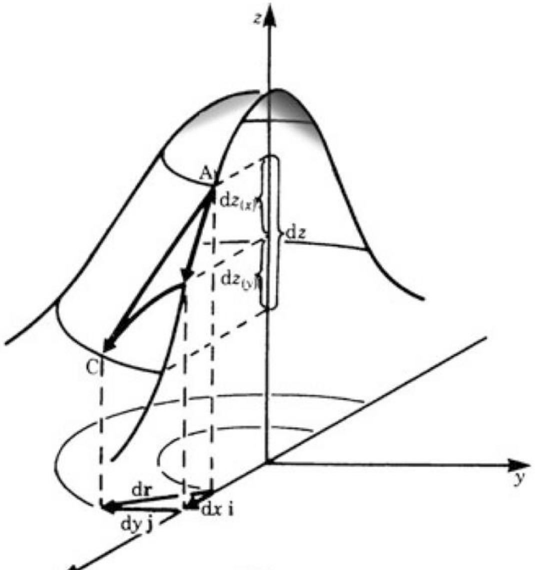
Exact and Inexact differential: Multiple variable functions

- Differentiability:

If a function *f* defined on an open set I of $\mathbb{R}^n$, *f* is differentiable in I if all its partial derivatives exist and are continuous.

- Clairaut's theorem:

If a function f defined on an open set I of $\mathbb{R}^2$, and if all the partial derivatives of f exist and are continuous, then: $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$



(b)

This is the case for most functions we handle !

- Differential form and total differential:

A differential form is an expression of the type

$$Q(x, y)\ dx + P(x, y)dy$$

In some open domain of a space, a differential form is an *exact differential* if it is equal to the total differential of a differentiable function f in an orthogonal coordinate system, ie:

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

In that case, it is an exact differential and since f is differentiable and has continuous partial derivatives, we must have: $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$

Exact and Inexact differential

- An other way to look at it is the following:

A differential form $Q(x,y)dx + P(x,y)dy$ is an exact differential if and only if: $\frac{\partial Q}{\partial y} = \frac{\partial P}{\partial x}$

- This is a very convenient result and great test !
- One can then find a function f such as $Q(x,y) = \frac{\partial f}{\partial x}$ and $P(x,y) = \frac{\partial f}{\partial y}$
- Examples: $ydx + xdy$; $ydx + 2xdy$
- An exact differential have integrals that are path independent: $df = \boldsymbol{\nabla f . dr}$

$$\int_A^B \boldsymbol{\nabla f . dr} = f(B) - f(A)$$

- Inexact differential are not path independent, which is the case for most work produced and heat exchange in thermodynamics functions:
    - State functions are exact differentials
    - Exchange functions are often inexact differentials that depend on the integration path.
    - Example: for a compressible system, the reversible mechanical work differential is: $\delta W = -pdV$. Is it an exact differential ?

Multiple Integrals

- The Riemann integrability for the one-variable cse can be extended to the case of n-variables.
- In particular if f is bounded and continous (or continuous almost everywhere), on a bounded, closed »Jordan-measurable » region, then f is Riemann integrable over this region.

- Change of variables:

Let T : $x = g(u, v)$, $y = h(u, v)$ be a transformation that maps a closed bounded region S in the uv-plane onto a region R in the xy-plane. Assume that T is one-to-one on the interior of S and that g and h have continuous first partial derivatives there. If f is continuous on R, then:

$$\iint_R f(x,y)dxdy = \iint_S f(g(u,v), h(u,v))|J(u,v)|dudv$$

- Where $J(u,v) = det\begin{pmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{pmatrix}$

- Definition: for $\mathrm{f} = (f_1, \ldots., f_n)$ n functions from $\mathbb{R}^n$ to $\mathbb{R}^n$, the jacobian matrix is given by:

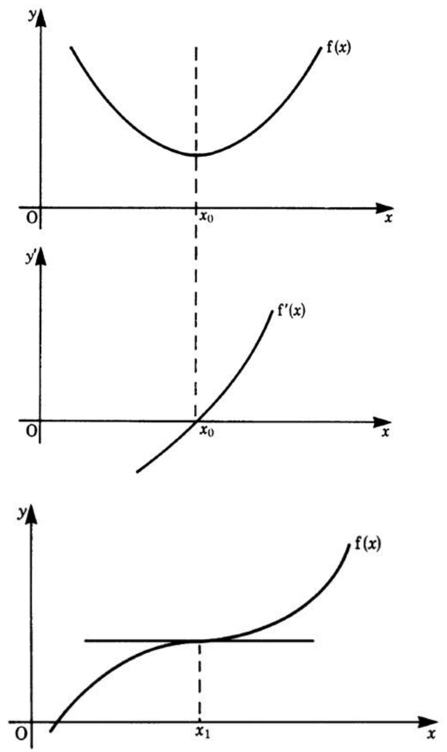
$$J(f) = \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \cdots & \frac{\partial f_n}{\partial x_n} \end{pmatrix}$$

Reminder: one-variable functions

- Successive derivatives can help evaluate in a finer way the change of functions, and in particular if they have a maximum or a minimum locally.

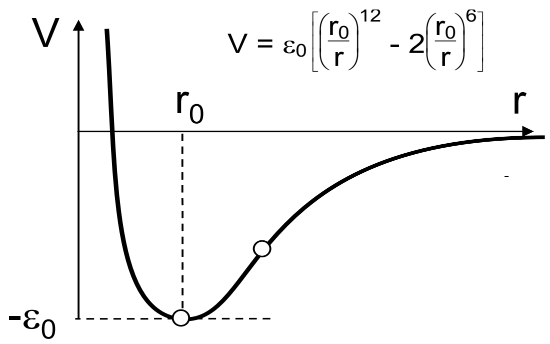
- For a function to have an **extremum at a point x_0**, it is necessary that $f'(x_0) = 0$. It is however not sufficient.
- It must also be such that $f''(x_0) > 0$ (convex) or $f''(x_0) < 0$ (concave).

- A point of inflexion is such that $f''(x_0) = 0$, marking where the concavity of a function changes.
  We must also have $f'''(x_0) \neq 0$ (for example $f(x) = (x-1)^4$).

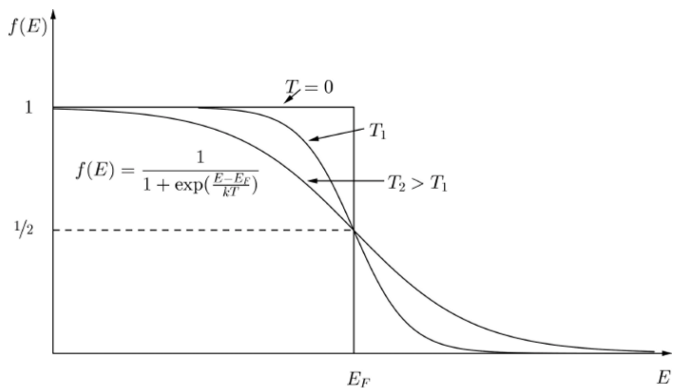


Examples:

Lennard-Jones potential: bonds



Electrons Occupancy



Extremum and Saddle Points

- Extremum:
  - A multi-variable function $f: \mathbb{R}^n \to \mathbb{R}$ admits a local maximum at a vector point $\boldsymbol{x_0}$ if there exists a small region $I \subset \mathbb{R}^n$ near that point for which $\forall \boldsymbol{x} \in I, f(\boldsymbol{x}) \leq f(\boldsymbol{x_0})$

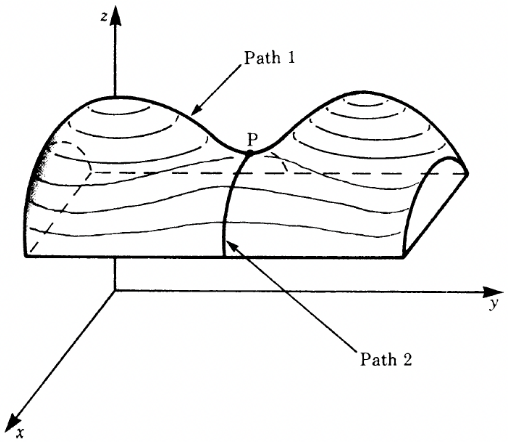
  Which you can write: $\exists \alpha \in \mathbb{R}, \forall \boldsymbol{h} \in \mathbb{R}^n, d(\boldsymbol{x_0}+\boldsymbol{h}, \boldsymbol{x_0}) < \alpha \to f(\boldsymbol{x_0}+\boldsymbol{h}) \leq f(\boldsymbol{x_0})$

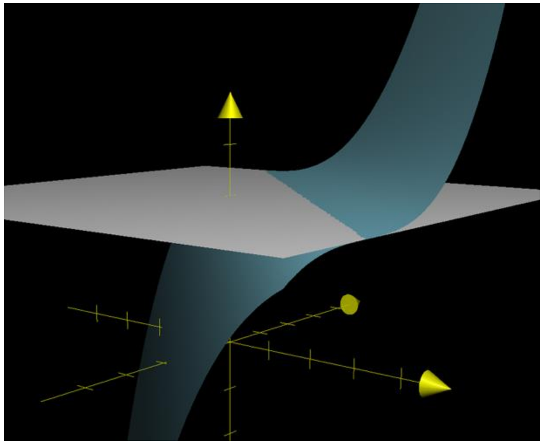
  - $f: \mathbb{R}^n \to \mathbb{R}$ admits a local minimum at a vector point $\boldsymbol{x_0}$ if there exists a small region $I \subset \mathbb{R}^n$ near that point for which $\forall \boldsymbol{x} \in I, f(\boldsymbol{x}) \geq f(\boldsymbol{x_0})$

- At a local maximum or minimum, we must have: $\forall i, \frac{\partial f}{\partial x_i}(\boldsymbol{x_0}) = 0.$

- For a two variable funciton: $\frac{\partial f}{\partial x}(x_0, y_0) = \frac{\partial f}{\partial y}(x_0, y_0) = 0.$

- This condition is however not sufficient !





Extremum and Saddle Points

- To look for a condition for an extremum, we can look at the expansion of a at least three times differentiable function $f\colon \mathbb{R}^2 \to \mathbb{R}$ around a point (x_0, y_0) :

For h and k small, we have:

$$f(x_0+h, y_0+k) - f(x_0, y_0) = h\frac{\partial f}{\partial x}(x_0, y_0) + \mathrm{k}\frac{\partial f}{\partial y}(x_0, y_0) + \frac{k^2}{2!}\left(\left(\frac{h}{k}\right)^2 \frac{\partial^2 f}{\partial x^2}(x_0, y_0) + 2hk\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0) + \frac{\partial^2 f}{\partial y^2}(x_0, y_0)\right) + o(h^2, k^2, hk)$$

- At an extremum: $\frac{\partial f}{\partial x}(x_0, y_0) = \frac{\partial f}{\partial y}(x_0, y_0) = 0$, and so:

$$f(x_0+h, y_0+k) - f(x_0, y_0) = \frac{k^2}{2!}\left(\left(\frac{h}{k}\right)^2 \frac{\partial^2 f}{\partial x^2}(x_0, y_0) + 2\left(\frac{h}{k}\right)\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0) + \frac{\partial^2 f}{\partial y^2}(x_0, y_0)\right) + o(h^2, k^2, hk)$$

- We hence have a quadratic function in $\frac{h}{k}$: $\left(\frac{h}{k}\right)^2 \frac{\partial^2 f}{\partial x^2}(x_0, y_0) + 2\left(\frac{h}{k}\right)\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0) + \frac{\partial^2 f}{\partial y^2}(x_0, y_0)$

Which will be positive or negative for all h,k, if and only if it has no roots, ie if the determinant is strictly negative:

$$\left(\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0)\right)^2 - \left(\frac{\partial^2 f}{\partial x^2}(x_0, y_0)\right)\left(\frac{\partial^2 f}{\partial y^2}(x_0, y_0)\right) < 0$$

Extremum and Saddle Points

- So there is an extremum at (x_0, y_0) if and only if

$$\frac{\partial f}{\partial x}(x_0,y_0) = \frac{\partial f}{\partial y}(x_0,y_0) = 0 \text{ and } \left(\frac{\partial^2 f}{\partial x \partial y}(x_0,y_0)\right)^2 - \left(\frac{\partial^2 f}{\partial x^2}(x_0,y_0)\right)\left(\frac{\partial^2 f}{\partial y^2}(x_0,y_0)\right) < 0$$

It is a minimum if $\frac{\partial^2 f}{\partial x^2}(x_0,y_0) > 0$ and $\frac{\partial^2 f}{\partial y^2}(x_0,y_0) > 0$

It is a maximum if $\frac{\partial^2 f}{\partial x^2}(x_0,y_0) < 0$ and $\frac{\partial^2 f}{\partial y^2}(x_0,y_0) < 0$

- Link with an eigen value criteria:
  - The Hessian matrix is a matrix of functions: $H(x,y) = \begin{pmatrix} \frac{\partial^2 f}{\partial x^2}(x,y) & \frac{\partial^2 f}{\partial x \partial y}(x,y) \\ \frac{\partial^2 f}{\partial x \partial y}(x,y) & \frac{\partial^2 f}{\partial y^2}(x,y) \end{pmatrix}$
  - The real matrix $H(x_0, y_0)$ is symetric ! From the spectral theorem, it has real, orthogonal eigen values ! And, it can be diagonalized.
  - The determinant at (x_0, y_0) is then:

$$\det\big(H(x_0,y_0)\big) = \left(\frac{\partial^2 f}{\partial x^2}(x_0,y_0)\right)\left(\frac{\partial^2 f}{\partial y^2}(x_0,y_0)\right) - \left(\frac{\partial^2 f}{\partial x \partial y}(x_0,y_0)\right)^2$$

Extremum and Saddle Points

- The condition $\left(\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0)\right)^2 - \left(\frac{\partial^2 f}{\partial x^2}(x_0, y_0)\right)\left(\frac{\partial^2 f}{\partial y^2}(x_0, y_0)\right) < 0$ is then equivalent to the condition $\det\big(H(x_0, y_0)\big) > 0$.
- Since the real matrix $H(x_0, y_0)$ can be diagonalized, if λ_1 and λ_2 are its eigenvalues, we must have $\det\big(H(x_0, y_0)\big) = \lambda_1 \lambda_2 > 0$, and so necessarily λ_1 and λ_2 are of the same sign.
- If λ_1 and λ_2 are negative, we have a local maximum (the trace is negative, and so will be second derivatives).
- If λ_1 and λ_2 are positive, we have a local minimum.

- If $\det\big(H(x_0, y_0)\big) < 0$, ie if λ_1 and λ_2 are of oppposite sign, **we have a Saddle point**.

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

It means that the concavity of f is opposite in the x and y directions, hence the second term is negative leading to an overall positive expression.

- If $\left(\frac{\partial^2 f}{\partial x \partial y}(x_0, y_0)\right)^2 - \left(\frac{\partial^2 f}{\partial x^2}(x_0, y_0)\right)\left(\frac{\partial^2 f}{\partial y^2}(x_0, y_0)\right) = 0$, we don't have enough information to tell with only the second derivative.

- Note that one can write: $f(\boldsymbol{x} + \Delta \boldsymbol{x}) = f(\boldsymbol{x}) + \nabla f(\boldsymbol{x})^T . \Delta \boldsymbol{x} + \frac{\mathbf{1}}{\mathbf{2}} \Delta \boldsymbol{x}^T . \mathbf{H}(\mathbf{x}) . \Delta \boldsymbol{x} + o(\|\Delta \boldsymbol{x}^2\|)$

SUMMARY

- We reviewed important concepts regarding the mechanical properties of metals, via using Taylor expansion and integration of the Lennard-Jones potential.
- We reviewed the concept of primitive (or antiderivatives) and of Riemann integrals.
- We defined the primitive in terms of an integrable function, and reminded the rules for integration and common primitives.
- We then showed examples of using integrals to calculate length and surfaces, number of free electrons in a semiconductor, and the work done to break a bond.
- This led us to discuss the difference between exact and inexact differentials.
- We also reminded a few results regarding multi-variable functions, and the conditions when one can switch the order for integration, differentiation, and limits.

- Next class:
  - We will these concepts to precisely derive the diffusion equation for atomic diffusion and introduce Fourrier transforms
  - We will also study Laplace transforms.