THERMODYNAMIC CHARACTERIZATION OF TECHNOLOGIES
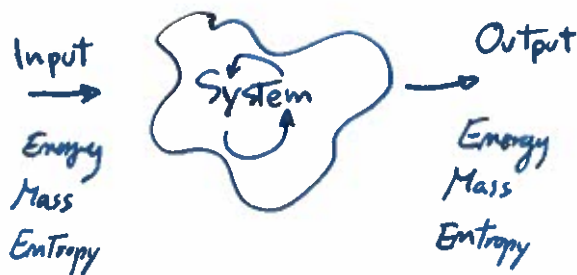

What do we need to characterize a technology / process?

1) Mass Balance → Mass is conserved $\sum \dot{m}_{in} = \sum \dot{m}_{out} + \dfrac{dm_{cv}}{dt}$

2) Momentum Balance → Navier-Stokes equations, fluiddynamic

3) Energy Balance → First Law, thermodynamics $dU = \delta \tilde{Q} - \delta W$

4) Thermodynamic constraints → Second law, thermodynamics
$$\dot{Q} - \dot{W} = \dot{m}_{out}\left(h + \frac{v^2}{2} + gz\right)_{out} - \dot{m}_{in}(h + ..$$
$$dS \geq \delta Q/T$$

5) Characteristic equations → Equation of state $pV = m\mathcal{R}T$ ideal gas thermodynamics

Mass transfer k_c , $J = -D\dfrac{dc}{dt}$ Fick's laws

Kinetics $r = k_r \prod_i c^{m_i}$

Heat transfer $q' = -k_t \dfrac{dT}{dx}$

SHORT RECAP OF THERMODYNAMICS

↳ 4 Laws of thermodynamics : what you cannot do when converting heat into work

Zeroth law — you cannot ignore the temperature of your heat engine

First law — you cannot win, the best you can do is break even (you cannot exert more work than the heat content).

Second law — you cannot break even, unless you reach $T = 0$ K

Third law — you cannot reach $T = 0$ K in a reasonable amount of time

◦ Extensive / Intensive properties [A property is a macroscopic chacteristic of a system to which a mechanical numerical value can be assigned at a given instant]

U , Q , W , (any capital) **EXTENSIVE**   generic $K = \sum_s K_s$

u , q , w , (any small letter) **INTENSIVE**   intensive properties are not additive and the value is independent of the size

$$u = \frac{U}{m} \left[\frac{kJ}{kg}\right] \qquad q = \frac{Q}{m} \left[\frac{kJ}{kg}\right]$$

↳ Open / Closed system

Closed system (or control mass)   a closed system always contains the same matter. No mass transfer across its boundary
  ↳ Piston

Control Volume (or open system)   a region with fixed boundaries where mass may cross the boundaries
  ↳ A combustion chamber

$M = const$

Air → ☐ → Gas   fuel →

$$\frac{dM}{dt} = \sum_i \dot{m}_{in} - \sum_s \dot{m}_{out}$$

$$\dot{m}_{fuel} + \dot{m}_{Air} = \dot{m}_{gas}$$

↳ Energy transfer by HEAT and by WORK

Heat is defined as the form of energy that is transferred between two systems by virtue of a temperature difference

Q [kJ] q [kJ/kg] $Q = \int_{t_1}^{t_2} q\, m\, dt$

Work : work is an energy interaction between two systems. If the energy being exchanged is not heat, it must be __work__.

$$W \ [kJ] \qquad w = \frac{W}{m} \ \left[\frac{kJ}{kg}\right]$$

Heat and Work are __energy transfer mechanisms__ between a system and its surroundings :
- both are boundary phenomena
- systems posses energy, not heat or work
- both are associated with a process, not a state (no properties !)
- both are path functions

Path functions have inexact differentials designated by the symbol δ

$$W_{1\to 2} = \int_1^2 \delta W$$

$$W = \int_1^2 p \, dV \qquad \underline{\text{Volume work}} \qquad\qquad W = m g (z_2 - z_1) \quad \text{gravitational work} \quad \ldots$$

↳ Phases of a pure substance and phase change processes

Substances exist in different phases :

    Solid : molecules arranged in a 3D pattern (lattice) - fixed position

    liquid : molecules are no longer in a fixed position but they can rotate and translate freely

    gas : molecules are far apart from each other, no molecular order in place

There are many cases where two phases coexist in equilibrium

Compressed liquid → not about to vaporise

Saturated liquid → about to vaporise

Saturated vapor → about to condense

Superheated vapor → not about to condense

At a given pressure, the temperature at which a pure substance changes phase is called Saturation Temperature, T_{sat}

At a given temperature, the pressure at which a pure substance changes phase is called saturation pressure, P_{sat}
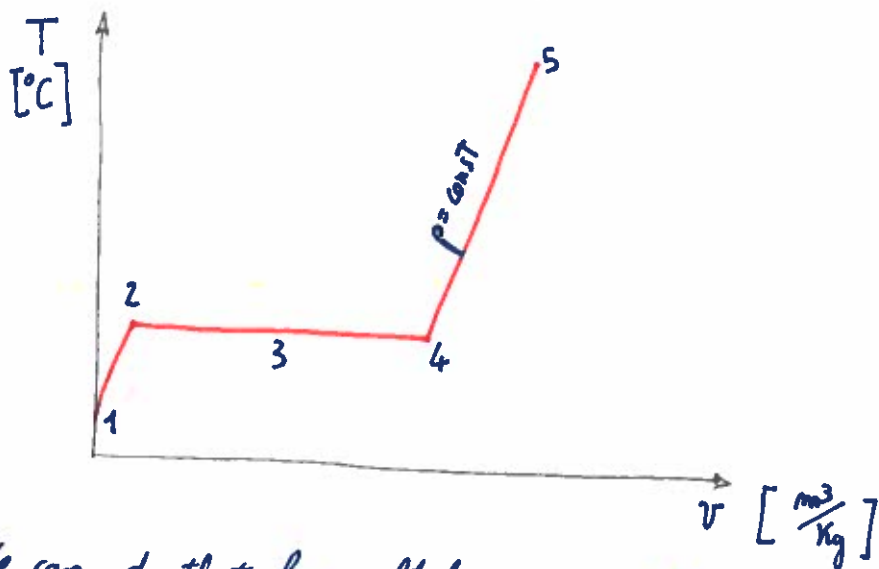
↳ At During a phase-change process, pressure and temperature are dependant properties $\qquad P_{sat} = f(T_{sat})$

P_{sat}

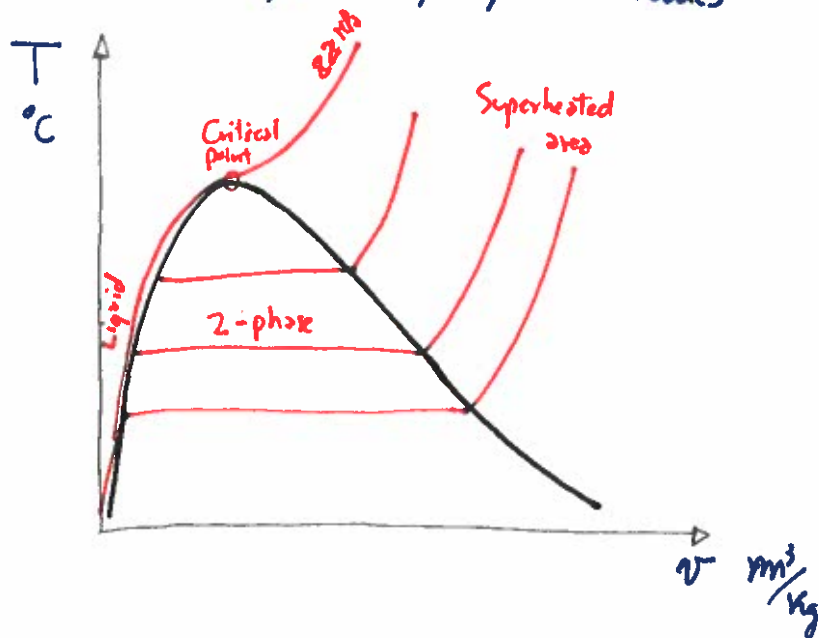Liquid-Vapor saturation curve

T_{sat}
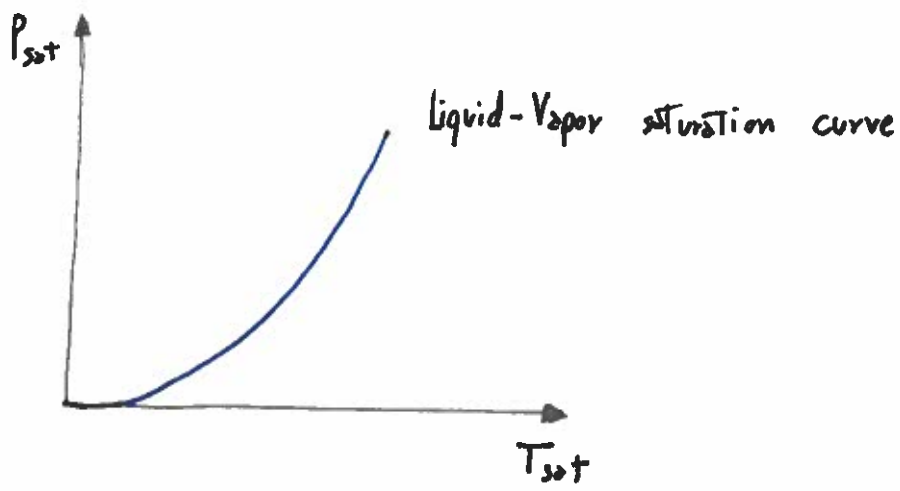
↳ Property diagrams for phase-change processes

Thermodynamic diagrams are used to represent the thermodynamic states of a material

Let us analyze the T-v diagram of water

T [°C]

5

2

$p = const$

3

4

1

$v \left[\frac{m^3}{kg} \right]$
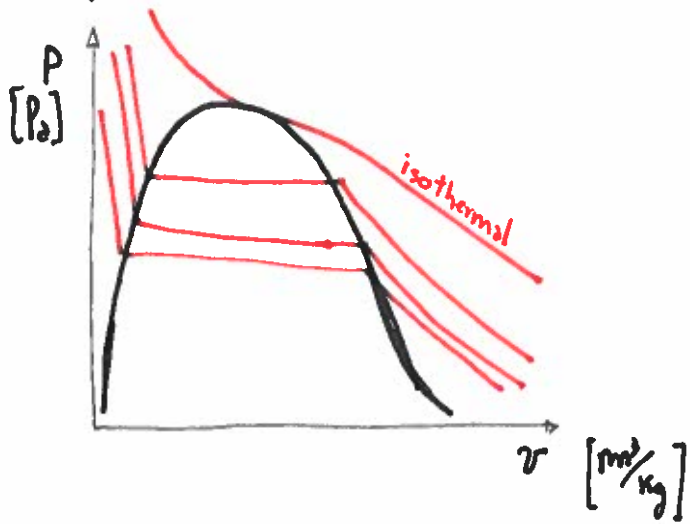
1: compressed water (ℓ)

2: saturated water (ℓ)

3: 2-phase water (ℓ+ѕ)

4: saturated vapor (ѕ)

5: superheated steam (ѕ)

We can do that for multiple pressure values

T °C

22 Mb

Critical point

Superheated area

liquid

2-phase

$v \ \frac{m^3}{kg}$

We can produce similar plots for other combinations, as T-s, T-h, p-v

P [Pa]

isothermal

v [m³/kg]

The phase diagram T-p is particularly useful to visualize the different phases

P

solid phase

T_{cr}

supercritical fluid

liquid phase

Critical point

P_{cr}

Triple point

gaseous phase

Vapour

T
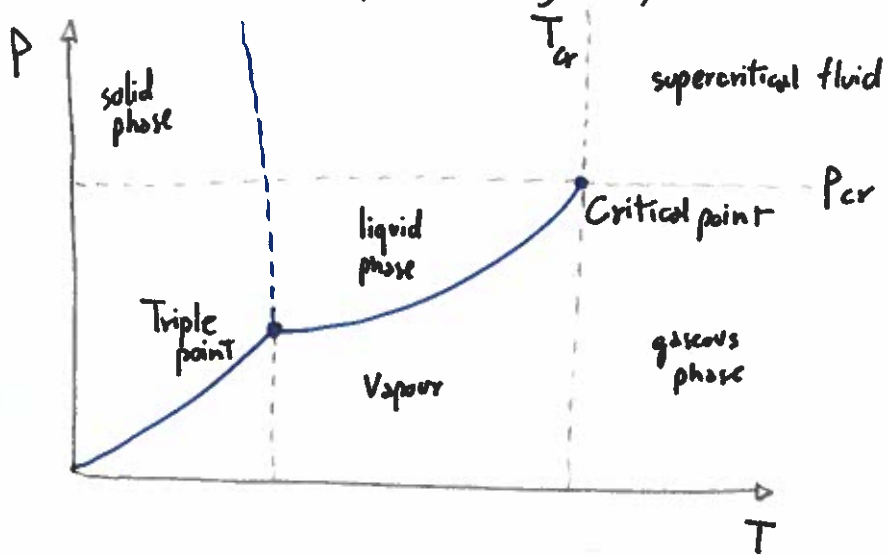
THERMODYNAMIC EQUILIBRIUM

Thermodynamic equilibrium: a system has no unbalanced potentials or drivers to promote a change of state. The state of a system in Thermodynamic equilibrium remains unchanged for all time.

$\hookrightarrow$ It implies the system must be in thermal, mechanical, chemical equilibrium, and phase equilibrium.

Thermal equilibrium: a system is at uniform Temperature, and is at the same temperature of its surroundings. Moreover, it does not receive radiative heat.

$$T_s \qquad T_\infty \qquad T_s = T_\infty$$

Mechanical equilibrium: the pressure throughout the system is uniform, and there are no unbalanced forces at the system boundaries.

Chemical equilibrium: the composition of any present species is unchanging with time.

Phase equilibrium: amount of a substance in any one phase does not change in time

We want to derive a framework for the computation of chemical equilibrium. Let's go back to the definition of the TdS equations:

$$U = U(S, V, m_i) \Longleftrightarrow \text{ if } S \text{ is continuous, differentiable, monotonically increasing with } U$$
$$\text{[then } S = S(U, V, m_i) \text{ can be inverted to } U = U(S, V, m_i)$$

$\hookrightarrow$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, m_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, m_i} dV + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial m_i}\right)_{S, V, m_{\neq i}} dm_i$$

All partial derivatives are intensive properties

- if only heat is provided to the system $\quad dU = \left(\frac{\partial U}{\partial S}\right)_{V, m_i} dS = T dS \qquad T = \left(\frac{\partial U}{\partial S}\right)_{V, m_i}$

  $dV = 0 \quad dN = 0$

  $\underbrace{}_{\text{temperature}}$

- if only mechanical work is available for exchange $\quad dU = \left(\frac{\partial U}{\partial V}\right)_{S, m_i} dV = -p\,dV \qquad p = -\left(\frac{\partial U}{\partial V}\right)_{S, m_i}$

  $dS = 0 \quad dN = 0$

  $\underbrace{}_{\text{pressure}}$

- if only chemical work is available for exchange $\quad dU = \left(\frac{\partial U}{\partial m_i}\right)_{S, V, m_{\neq i}} dm_i = \mu_i\,dm_i \qquad \mu_i = \left(\frac{\partial U}{\partial m_i}\right)_{S, V, m_{\neq i}}$

  $dS = 0 \quad dV = 0$

Therefore, we obtain:

$$dU = TdS - pdV + \sum_{i=1}^{C} \mu_i \, dm_i$$

U depends on the quantities S, V, m_i: some of these are not very practical if one wants to measure variables in a real environment (e.g. measure S?). We can therefore derive new potentials to describe the system, for example that depend on T and p or other quantities.

We make use of Legendre Transformation: $f(x) \longrightarrow f^*(p)$

$$f^*(p) = f(x) - xp \quad \text{where} \quad p = \frac{df(x)}{dx}$$

$$f^*(p) = f(x) - \frac{df(x)}{dx} x$$

Replace S,V with T,p

$$U(S, V, m_i) \longrightarrow G(T, p, m_i)$$

First $U(S,V,m_i) \longrightarrow H(S, p, m_i)$

$$\underset{x=V}{\underset{f(x)}{}} \qquad \underset{p=?}{\underset{f^*(p)}{}} \qquad \longrightarrow \qquad p = -\left(\frac{\partial U}{\partial V}\right)_{S,m_i}$$

$$H = \underset{f(x)}{\underbrace{U}}, \underset{x}{\underbrace{-V \cdot}} \underset{P}{\underbrace{\left(-\frac{\partial U}{\partial V}\Big|_{S,m_i}\right)}} = U + pV \longrightarrow dH = dU + pdV + Vdp = TdS + Vdp + \sum \mu_i dm_i$$

Then $H(S, p, m_i) \longrightarrow G(T, p, m_i)$

$$\underset{x=S}{\underset{f(x)}{}} \qquad \underset{}{\underset{f^*(p)}{}} \qquad \longrightarrow \qquad p = \left(\frac{\partial H}{\partial S}\right)_{p,m_i} = T$$

$$G = H - TS \qquad \therefore \text{Gibbs Free Energy}$$

$$dG = dH - d(TS) = dH - TdS - SdT = -SdT + Vdp + \sum \mu_i dm_i$$

$$\mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,p,m_{s \neq i}} \qquad \underline{\text{Chemical Potential}}$$

Let's now derive the condition for equilibrium. From the second law, we know that a system can evolve only in the direction of increasing entropy

$$(dS)_{isolated} \geq 0$$

$$dS + dS_{\text{E}} \geq 0 \qquad dS_E = \frac{dq_{\text{E}}}{T} = -\frac{dQ}{T} \longrightarrow dS \geq \frac{dQ}{T}$$

or: $dQ \leq TdS$

from the 1st thermodynamic principle $dU = dQ - pd_gV \Rightarrow dQ = dU + pdV$

$dU + pdV - TdS \leq 0$

Let's look at the case where the temperature T and pressure p of the system are fixed

$dU_{p,T} + d(pV)_{p,T} - d(TS)_{p,T} \leq 0$

$d(\underbrace{\underbrace{U + pV}_{H} - TS}_{G}) \leq 0$

$\boxed{dG_{p,T} \leq 0}$ $\longrightarrow$ $(dG)_{T,p} < 0$ The system will evolve

$(dG)_{T,p} = 0$ The system will be at equilibrium

After introducing:

$\hookrightarrow$ The standard state Gibbs function ΔG°_T for $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$:

$$\Delta G^\circ_T \equiv \left(\nu_C g^\circ_{C,T} + \nu_D g^\circ_{D,T} - \nu_A g^\circ_{A,T} - \nu_B g^\circ_{B,T} \right)$$

$\hookrightarrow$ The equilibrium constant K_p

$$K_p = \prod_i a_i^{\nu_i} \Rightarrow \text{ideal gas } K_p = \prod_i (x_i)^{\nu_i}$$

$$K_p = \frac{x_C^{\nu_C} \cdot x_D^{\nu_D}}{x_A^{\nu_A} \cdot x_B^{\nu_B}}$$

And some algebra, we find that chemical equilibrium at constant pressure and temperature can be expressed as:

$$\Delta G^\circ_T = -RT \ln K_p$$

or

$$K_p = \exp\left(-\frac{\Delta G^\circ_T}{RT} \right)$$

$G = H - TS$

or $K_p = \exp\left(-\frac{\Delta H^\circ}{RT} \right) \cdot \exp\left(\frac{\Delta S^\circ}{R} \right)$

Conditions that favor products:
1. $\Delta H^\circ < 0$ exothermic reaction
2. $\Delta S^\circ > 0$
The system energy lowers and the entropy increases.

For $\Delta G^\circ_T > 0 \Rightarrow -\frac{\Delta G^\circ_T}{RT} < 0 \Rightarrow K_p < 1 \Rightarrow \frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{\nu_A} x_B^{\nu_B}} < 1$ Reactants are favored

For $\Delta G^\circ_T < 0 \Rightarrow$ Products are favored

DERIVATION OF BERNOULLI EQUATION

The Bernoulli equation is an approximate relation between pressure, velocity, and elevation. It is valid for steady, incompressible flow where net frictional forces are negligible.

Bernoulli's equation can be derived in multiple fashions, for example:

1. From the first law of thermodynamics applied to a control volume

2. The conservation of momentum for a fluid particle moving along a streamline

Case 2 can either be directly applied forth along the distance s on a streamline or as simplification of the more rigorous Euler Equation for inviscid fluids (itself a simplification of Navier-Stokes equation).

Let us start with the first case

Derivation of Bernoulli from 1st Law of Thermodynamics

We first write (recall) the energy balance for a generic control volume:

| The time rate of change of the energy content in the CV | = | The net rate of energy transfer into the CV by heat and work transfer | + | The flow rate of energy in of the Control surface by mass flow | − | The flow rate of energy out of the control surface by mass flow |

$$\frac{dE_{cv}}{dt} = \dot{Q} - \dot{W}_{cv} + \sum_i \dot{m}_{in_i}\left(h + \frac{v^2}{2} + gz\right)_{in_i} - \sum_j \dot{m}_{out_j}\left(h + \frac{v^2}{2} + gz\right)_{out_j}$$

We can derive the Bernoulli equation plugging in a series of simplifications in the energy balance equation.

a) Single Stream $\sum \dot{m} \rightarrow \dot{m}$

b) Steady State $\rightarrow \dfrac{dE_{cv}}{dt} = 0$

c) Flow is ideal with no irreversibilities (e.g. friction) $\rightarrow$ total mechanical energy is conserved

d) Absence of turbines / pumps $\rightarrow \dot{W}_{cv} = 0$

We obtain:

$$\dot{m}\left(h + \frac{v^2}{2} + gz\right)_{in} + \dot{Q} = \dot{m}\left(h + \frac{v^2}{2} + gz\right)_{out}$$

Now, as $h = u + pv$ → Internalb energy + Flow work → associated to the energy required to push the fluid into/out of system
↳ associated to the movement of molecules/or chemical bonds

$$\dot{m}\left(u + pv + \frac{v^2}{2} + gz\right)_{in} + \dot{Q} = \dot{m}\left(u + pv + \frac{v^2}{2} + gz\right)_{out}$$

If the mechanical energy is conserved, we need to have

$$\dot{m}\left(pv + \frac{v^2}{2} + gz\right) = const \quad , \text{ and therefore } \quad \dot{Q} = \dot{m}\left(u_{out} - u_{in}\right)$$

or, in other words, an increase in internal energy corresponds to, and only to, heat transfer into/out the CV. None of the other terms is associated to a change in internal energy. We therefore obtain

$$\dot{m}\left(pv + \frac{v^2}{2} + gz\right)_{in} = \dot{m}\left(pv + \frac{v^2}{2} + gz\right)_{out}$$

or

$$\left(\frac{P}{\rho} + \frac{v^2}{2} + gz\right)_{in} = \left(\frac{P}{\rho} + \frac{v^2}{2} + gz\right)_{out} \quad \rightarrow \quad \frac{P}{\rho} + \frac{v^2}{2} + gz = const$$

If we allow for mechanical energy loss, Bernoulli's equation is extended to:

$$\dot{m}\left(\frac{P_a}{\rho} + \frac{v^2}{2} + gz\right)_{in} + \dot{W}_{pump} = \dot{m}\left(\frac{P}{\rho} + \frac{v^2}{2} + gz\right)_{out} + \dot{W}_{turbine} + \dot{E}_{loss}$$

where: $\dot{E}_{loss} = \dot{m}\left(u_{out} - u_{in}\right) - \dot{Q}$

Derivation of Bernoulli from Conservation of Momentum

Let's first derive this from a simple 2D case with a force balance along a streamline.
First, in a 2-D case, the acceleration a is composed of a streamwise acceleration a_s and a normal acceleration $a_n = \frac{v^2}{R}$.

Let us take the velocity V of a fluid particle as function of the distance along the streamline s and of the time t, $V = v(s, t)$. It follows:

$$dV = \frac{\partial V}{\partial s} ds + \frac{\partial V}{\partial t} dt$$

Steady flow

$$a_s = \frac{dV}{dt} = \frac{\partial V}{\partial s}\frac{ds}{dt} + \frac{\partial V}{\partial t} \cancel{=} \frac{\partial V}{\partial s} V = V \frac{dV}{ds}$$

Streamline, Steady flow
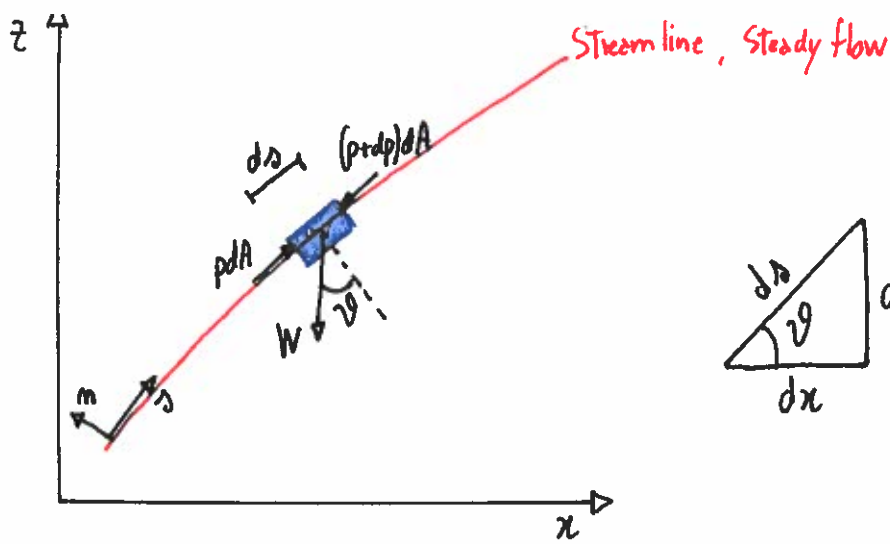
$$\Sigma F_s = \bar{m} a_s \qquad \text{Conservation of linear Momentum (Newton's second law)}$$

$$p dA - (p + dp) dA - W \sin \vartheta = m V \frac{dV}{ds} \qquad \text{Hp: Net frictional forces are negligible}$$

Now, we recognize that: $m = \rho \cdot \underset{fluid}{Volume} = \rho \, ds \, dA$

$$W = m g = \rho g \, ds \, dA$$

$$\sin \vartheta = \frac{dz}{ds}$$

and therefore:

$$\cancel{p dA} - \cancel{p dA} - dp \, dA - \rho g \cancel{ds} dA \cdot \frac{dz}{\cancel{ds}} = \rho V \cancel{ds} dA \frac{dV}{\cancel{ds}}$$

$$- dp \cancel{dA} - \rho g \cancel{dA} dz = \rho V \cancel{dA} dV \qquad \text{dividing by } \frac{1}{dA \rho}$$

$$- \frac{dp}{\rho} - g dz = V dV \qquad \text{and recognizing that} \quad V dV = \frac{1}{2} d(v^2) \quad \overbrace{- v \times [\nabla \times v]}^{\text{irrotational} = 0}$$

we obtain: $\qquad + \frac{dp}{\rho} + \frac{1}{2} d(v^2) + g dz = 0$

Integrating along the streamline, between position 1 and 2: $\int \frac{dp}{\rho} + \frac{v^2}{2} + gz = const$

or: $\int_1^2 \frac{dp}{\rho} + \frac{1}{2} (V_2^2 - V_1^2) g (z_2 - z_1) = 0$

if the fluid is incompressible $\int \frac{dp}{\rho} = \frac{1}{\rho} \int dp$

$$\frac{P}{\rho} + \frac{V_0^2}{2} + gz = const$$

This is equivalent to the general conservation of energy for systems that do not involve any conversion of mechanical energy and internal energy to each other.

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LIMITATIONS ON THE USE OF BERNOULLI

It is important to underline the restrictions on Bernoulli's applicability and observe the limitations on its use. Here we provide a list of key limitations:

Steady State — Bernoulli is applicable to steady flow, and shall not be used during Transient start-up and shut-down or periods of change in the flow conditions. An unsteady form exists:

$$\int \frac{dp}{\rho} + \int \frac{dV}{dt}\, ds + \frac{v^2}{2} + gz = const$$
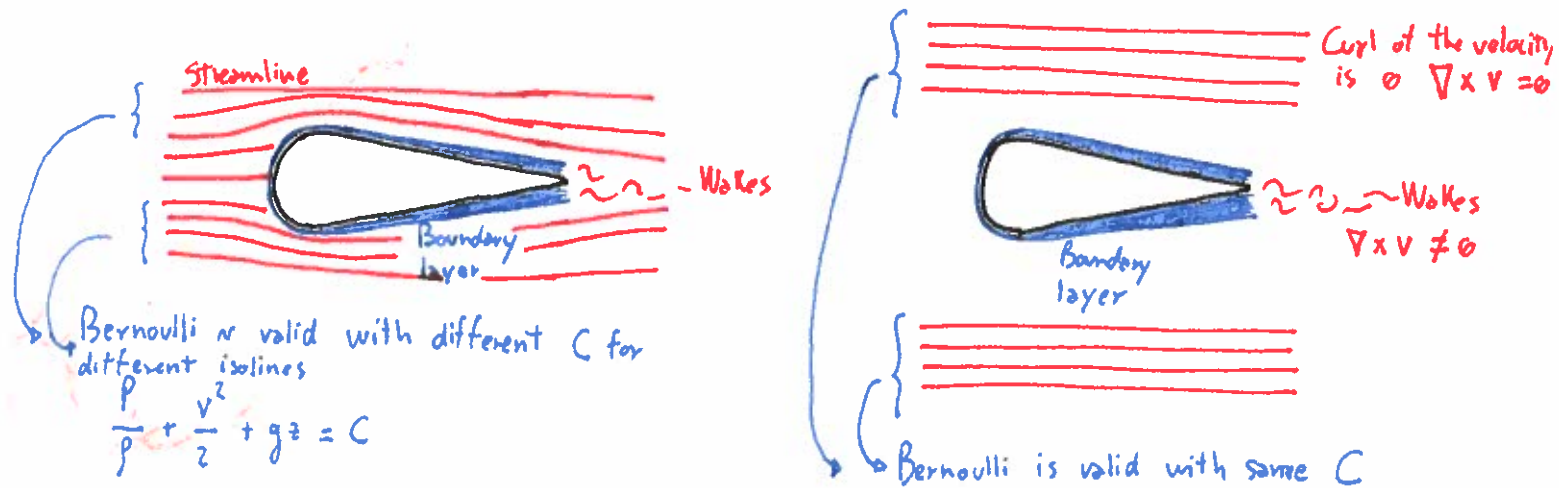
Frictionless flow — Every flow involves some friction: frictional effects may or may not be negligible. Frictional effects are generally negligible for short flow sections with large cross sections, especially at low velocities. Frictional effects are also significant near solid surfaces ⟶ Bernoulli is applicable along a streamline in the core region of the flow, but not along a streamline close to the surface.

Flow along a streamline — Bernoulli is applicable along a streamline, and the values of the <u>constant</u> varie for different streamlines.
However, when the flow is irrotational — there is no vorticity in the flow field — the value of the constant is the same across streamlines.

Bernoulli ∼ valid with different C for different isolines

$$\frac{p}{\rho} + \frac{v^2}{2} + gz = C$$

Bernoulli is valid with same C

Curl of the velocity is 0 $\nabla \times V = 0$

$\nabla \times V \neq 0$ ∼ Wakes

Wakes & Boundary layer ⟶ Bernoulli is not valid

Incompressible flow — Bernoulli is derived using $\rho = const$ and thus the flow is incompressible. This condition is satisfied by liquids, and by gases at Mach numbers less than ∼ 0.3

No shaft work — A machine would indeed break the streamline and interact with the energy of the particle of fluid. The energy equation can be used in this case

No large temperature difference — Bernoulli should not be used for cases where the density varies enough with temperature.

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Example of application Bernoulli's Equation

Static, Dynamic, and Stagnation pressure

$$\frac{P}{\rho} + \frac{v^2}{2} + gz = const \qquad \text{or} \qquad P + \rho\frac{v^2}{2} + \rho gz = 0$$

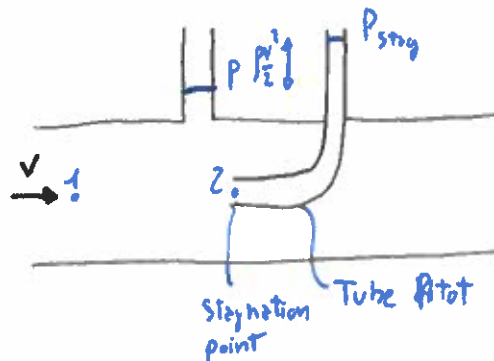Each term has pressure units and thus we can define:

P: <u>static pressure</u>, or thermodynamic pressure of the fluid

$\rho\frac{v^2}{2}$: <u>dynamic pressure</u>, or the pressure rise when the fluid in motion is stopped isentropically

ρgz: <u>hydrostatic pressure</u>, it accounts for the elevation effects on pressure

$$P_{tot} = P + \rho\frac{v^2}{2} + \rho gz$$

$$P_{Stagnation} = P + \rho\frac{v^2}{2}$$

Stagnation point   Tube Ptot

If we write Bernoulli's equation between 1 and 2

$$P_{tot_1} = P_1 + \rho\frac{v_1^2}{2} + \rho gz_1 = P_{tot_2} = P_2 + \rho\frac{v_2^2}{2} + \rho gz_2$$

Now: $v_2 = 0$, $P_2 = P_{stagnation}$

$$z_1 = z_2$$

$$\longrightarrow \quad P_1 + \rho\frac{v_1^2}{2} = P_{stag} \qquad v_1 = \sqrt{\frac{2(P_{stag_1} - P_1)}{\rho}}$$