

Lecture 20: Process modeling & balance laws

- Process modeling, structure and methodology
- Balance laws
 - Mass balances
 - Mass balances for multi-component systems

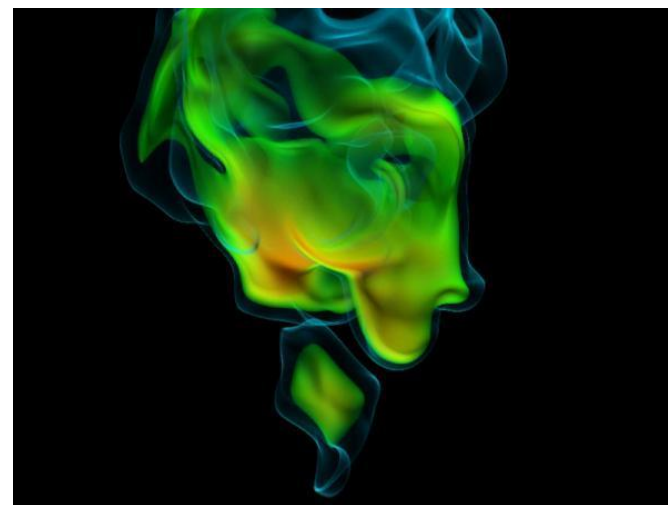
Book: 10.4, 11.1-11.4

What are process modeling and balance laws used for?



Process modeling & balance laws:

- Basically, modeling of anything that changes in the physical world.
- In this context, we will be concerned with **fluids** (liquids and gas) in (chemical) **process systems**

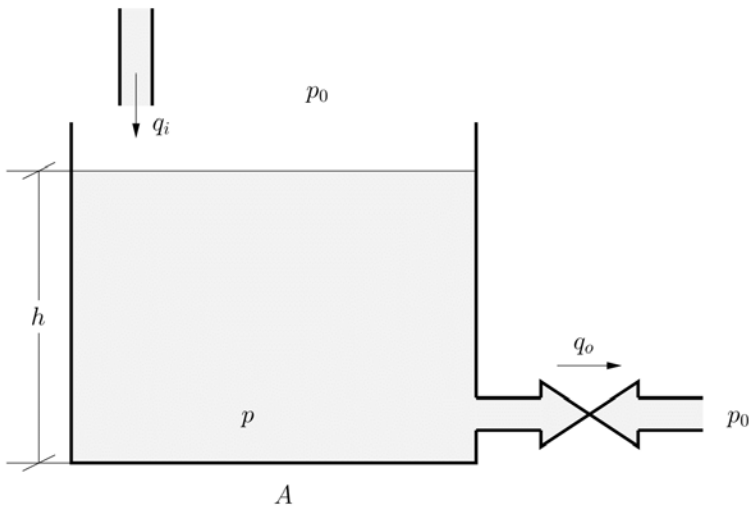


Autoignition of hydrogen in a turbulent hot air coflow

Process modeling: Structure and methodology

- Goal of process modeling: **Construct mathematical models of the process under study.**
- These mathematical models consists of process variables (**variables** and **parameters**) and the **equations** that link these

Process



Process variables

(variables and parameters)

- **Level**
 - Variability: Variable
 - Symbol: h
 - Value: 1.1
 - Unit: m
 - ...
- **Area**
 - Variability: Parameter
 - Symbol: A
 - Value: 2.2
 - Unit: m^2
 - ...
- ...

Process equations

$$\frac{dh}{dt} = \frac{1}{A} (q_i - q_o)$$

$$q_o = C\sqrt{p - p_0}$$

$$p = p_0 + \rho gh$$

Number of equations must match number of (unknown) variables.

Process equations

- Balance laws

- Mass
- Momentum
- Energy
- ...

- Constitutive equations

- For (generalized) flows
- Thermodynamic equations of state (e.g. ideal gas law)
- Phenomenological relationships (e.g. between friction force and flow in a pipe)
- ...

- Constraints

- Geometric relationships
- Equilibrium conditions
- ...

Also called «closure relations» as they «close» the balance laws (such that #equations = #variables)

Example Tank:

$$\frac{dm}{dt} = (w_i - w_o)$$

$$q_o = C\sqrt{p - p_0}$$

$$p = p_0 + \rho gh$$

$$V = Ah$$

$$m = \rho V$$

Process variables

- Thermodynamic state variables

- Mass, pressures, levels, ...
- Velocities
- Temperatures
- ...

- (Generalized) flows

- Transport (single phase)
- Exchange (between phases)
- Sources (reactions)
- ...

- Phenomenological coefficients

- Viscosity
- Reaction rates
- Valve constants
- ...

- Geometric dimensions

- Lengths, Areas, Volumes
- ...

Example Tank:

h, ρ, p, p_0

q_i, q_o

C, g

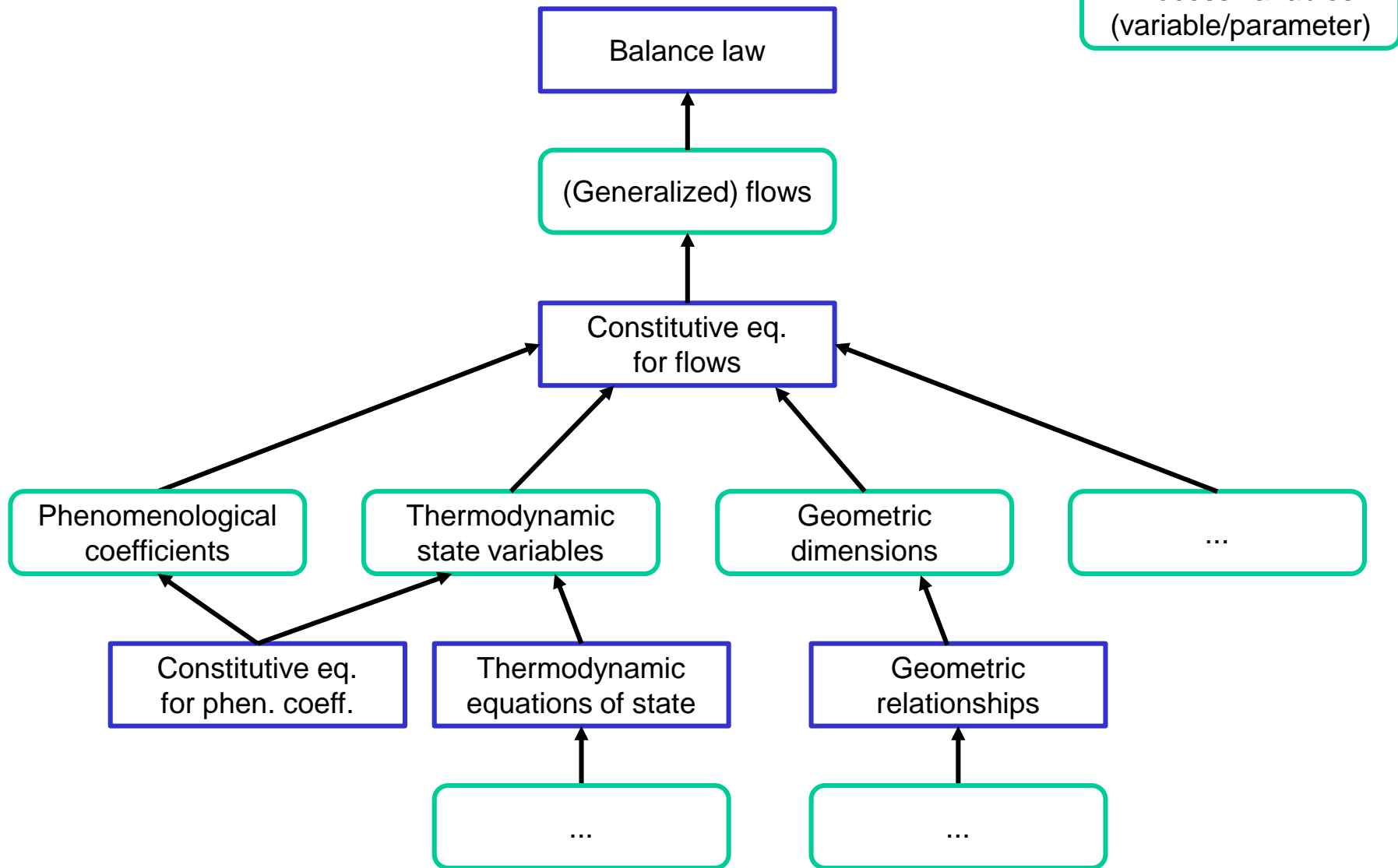
A

$$\frac{dh}{dt} = \frac{1}{A} (q_i - q_o)$$

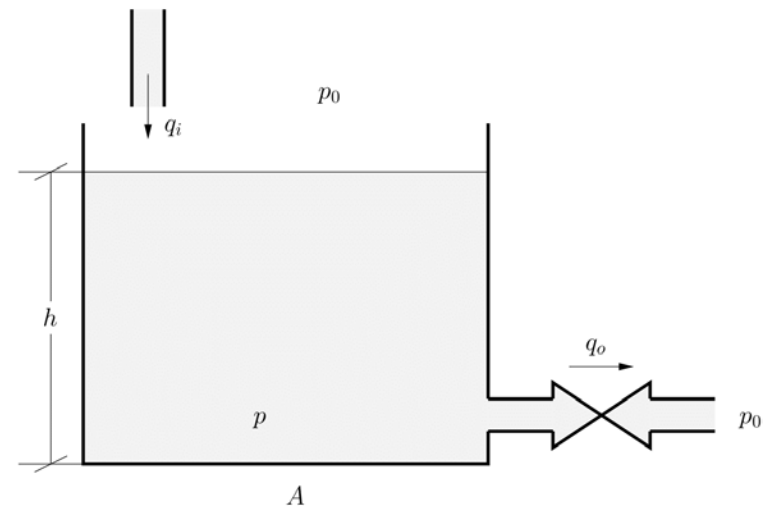
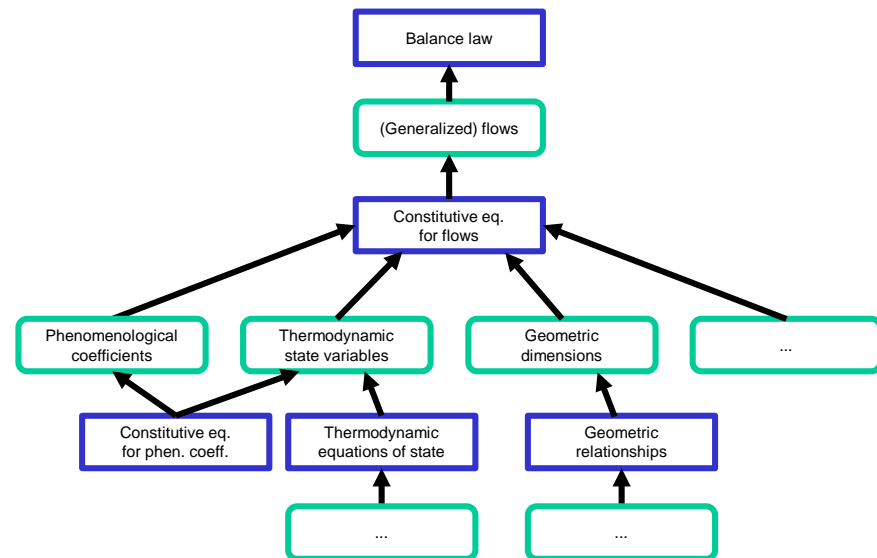
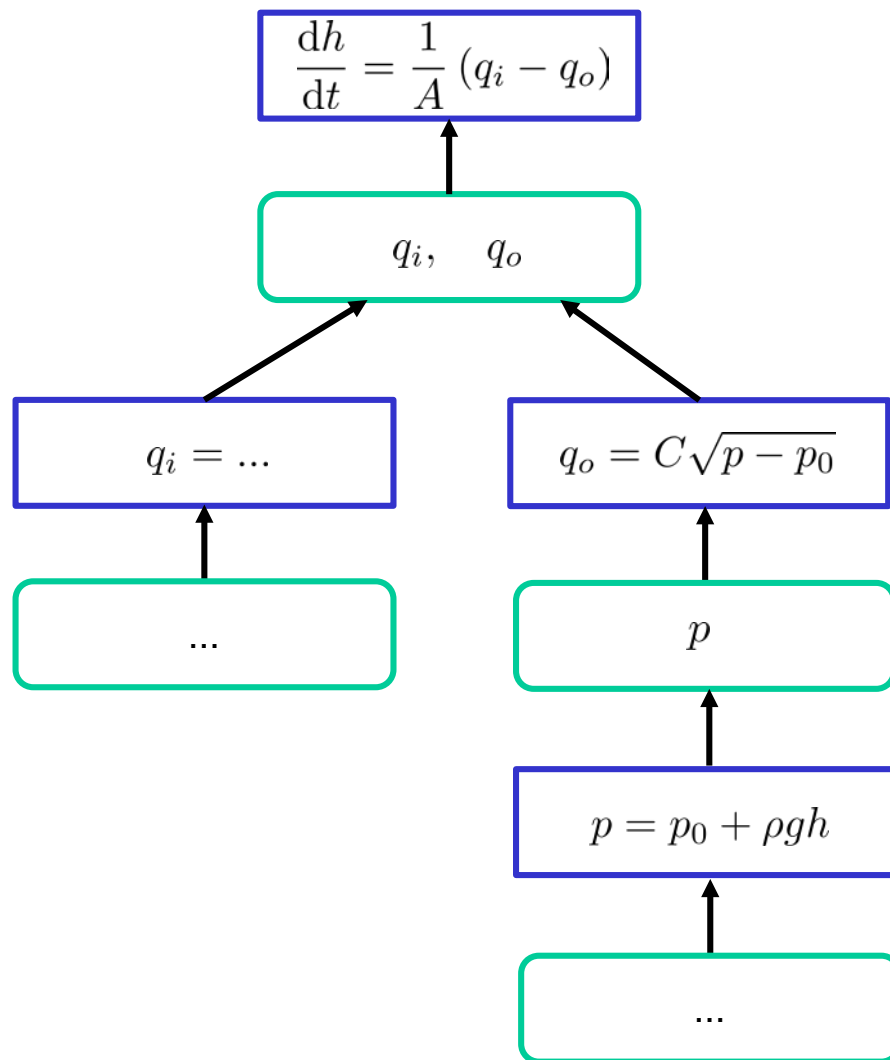
$$q_o = C\sqrt{p - p_0}$$

$$p = p_0 + \rho gh$$

Structure of process models



Example: Tank



BALANCE LAWS

Physical balance principles are based on

Conservation laws

That a physical property is *conserved*, means that it will remain constant in a closed system

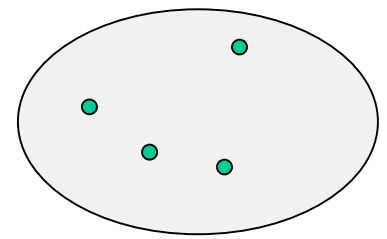
The following physical quantities are conserved:

- Mass
- Energy
- Momentum (norsk: impuls)
 - Linear and angular

No one has ever observed that conservation laws have been violated

- Conservation laws are exact laws

The basic physical principles



Consider a volume consisting of a **fixed** number of fluid particles, with total mass m , total momentum \vec{p} and total energy E . From basic physics (conservation laws), we know the following principles hold:

- Conservation of mass (mass balance):

$$\frac{dm}{dt} = 0$$

- Newton's second law (momentum balance)

$$\frac{d\vec{p}}{dt} = \vec{F}$$

Also holds for angular momentum, $\vec{h} = \vec{r} \times \vec{p}$:

$$\frac{d\vec{h}}{dt} = \vec{r} \times \vec{F} = \vec{T}$$

- First law of thermodynamics (conservation of energy, energy balance):

$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

Rate of heat flowing into volume from surroundings $\rightarrow \dot{Q}$
 \dot{W} Rate at which work is done by the body at surroundings

State variables for process systems

- What variables are relevant as state variable(s) for balance laws based on conservation of mass (that is, mass balances)?
 - Mass
 - Density
 - Moles, and mole concentration
 - Derived quantities: Pressure, level, ...
 - (number of particles, etc.)
- For energy balances:
 - Internal energy
 - Temperature
- For momentum balances
 - Linear or angular momentum
 - Velocities

Extensive and intensive properties

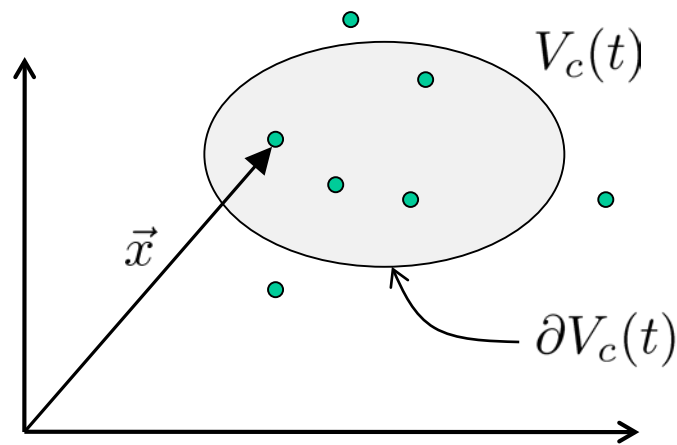
- We must choose properties (thermodynamic variables) to describe our process, and these are either *intensive* or *extensive*
- Intensive properties are scale invariant (does not change if we divide a volume in two), while extensive variables are proportional to amount of material
- In this course, we use mostly *mass-intensive* properties/variables (that is, we measure amount of material with mass):

Extensive properties	Symbol	Unit	Intensive properties	Symbol	Unit
mass	m	kg	1	-	-
volume	V	m ³	specific volume	v	m ³ /kg
internal energy	U	J	specific internal energy	u	J/kg
enthalpy	H	J	specific enthalpy	h	J/kg
entropy	S	J/K	Specific entropy	s	J/K/kg

- What alternatives are there to mass-intensive?
- Is temperature an intensive or extensive property? Pressure? (yes and no...)

The concept of control volume

- We use a control volume for separating what we are interested in from the rest of the world (surroundings)
- Generally, material flow into (or out of) the control volume, across the surface



Extensive Property B of one particle

$$dB = \rho(\mathbf{x})\beta(\mathbf{x}, t)dV$$

Summed over all particles in $V_c(t)$

$$B = \iiint_{V_c(t)} \rho(\mathbf{x})\beta(\mathbf{x}, t)dV$$

- We are interested in
 - knowing how the extensive property B varies inside the control volume
 - **or** (equivalently?) how the intensive property $\beta(\mathbf{x}, t)$ varies inside the volume
- Control volumes can move or change shape, but we will assume they are **fixed** (more on this in fluid mechanics)

Lumped vs distributed modeling

- If we do *lumped modeling*, we assume that intensive properties are constant (or averaged) over the control volume

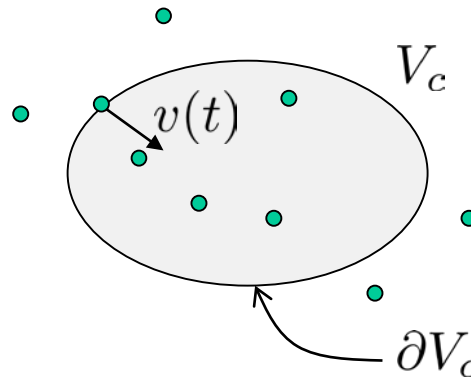
$$B = \iiint_{V_c} \rho \beta(\mathbf{x}) dV = \iiint_{V_c} \rho \bar{\beta} dV = \bar{\beta} \iiint_{V_c} \rho dV = m \bar{\beta}$$

- The balance laws used for lumped modeling are the *integral* (or *macroscopic*) balance laws
 - Formulated for extensive (e.g. mass), or averaged intensive (e.g. average temperature), variables
- The alternative to lumped modeling is *distributed* modeling, where we are interested in how $\beta(\mathbf{x}, t)$ varies as a function of position \mathbf{x}
- The balance laws for distributed modeling are the *differential* balance laws

(This course: Mainly lumped modeling and integral balance laws)

The balance laws I

- Assume a **fixed** control volume (of arbitrary size and shape), where fluid flows across the control volume



$$B = \iiint_{V_c} \rho \beta(\mathbf{x}, t) dV$$

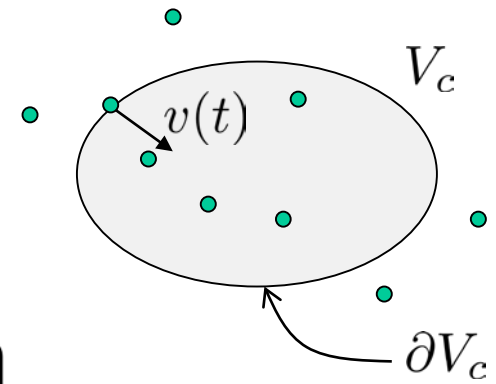
- The general integral (macroscopic) balance law for B is

$$\frac{d}{dt} B = \left\{ \begin{array}{l} \text{transfer of } B \text{ through} \\ \text{surface } \partial V_c \text{ by} \\ \text{fluid flow (convection)} \end{array} \right\} + \left\{ \begin{array}{l} \text{other effects that} \\ \text{transfer } B \text{ into } V_c \\ \text{(indep. of fluid flow)} \end{array} \right\}$$

The balance laws II

- **Mass balance** (without reactions/phase transfer)

$$\frac{d}{dt}m = \left\{ \begin{array}{c} \text{transfer of mass into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\}$$



- **Momentum** (note: momentum is a vector)

$$\frac{d}{dt}\mathbf{p} = \left\{ \begin{array}{c} \text{transfer of momentum into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\} + \left\{ \begin{array}{c} \text{generation of momentum} \\ \text{in } V_c \text{ due to forces} \\ \text{acting on } V_c \end{array} \right\}$$

- **Energy**

$$\frac{d}{dt}E = \left\{ \begin{array}{c} \text{transfer of energy into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\} + \left\{ \begin{array}{c} \text{transfer of energy into} \\ V_c \text{ by heat transfer} \\ \text{and by work} \end{array} \right\}$$

Mathematical formulation of convection

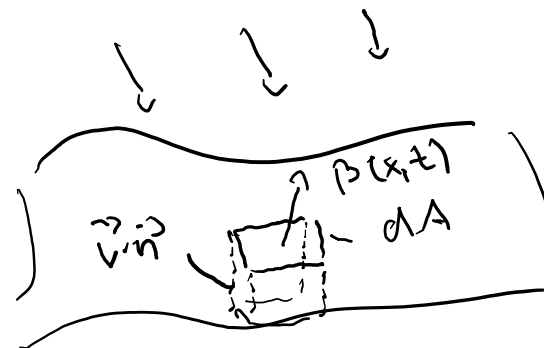
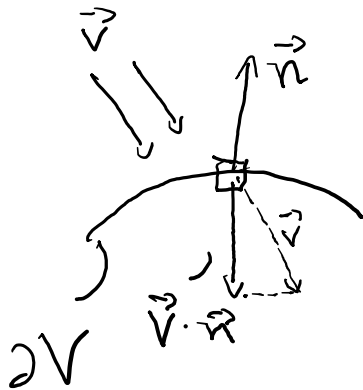
$$\frac{d}{dt}B = \underbrace{\left\{ \begin{array}{l} \text{transfer of } B \text{ through} \\ \text{surface } \partial V_c \text{ by} \\ \text{fluid flow (convection)} \end{array} \right\}} + \left\{ \begin{array}{l} \text{other effects that} \\ \text{transfer } B \text{ into } V_c \\ \text{(indep. of fluid flow)} \end{array} \right\}$$

$$- \iint_{\partial V_c} \rho \beta \vec{v} \cdot \vec{n} dA$$

$$\vec{v} \cdot \vec{n} \cdot dA$$

fluid flow
across dA

$\hat{=}$ volumetric
flow
rate



Inflow of B through dA :

$$- \rho(x,t) \cdot \beta(x,t) \vec{v}(x,t) \cdot \vec{n}(x,t) dA$$

Mathematical formulation of mass balance

- For mass, the intensive variable is $\beta(\mathbf{x}, t) = 1$

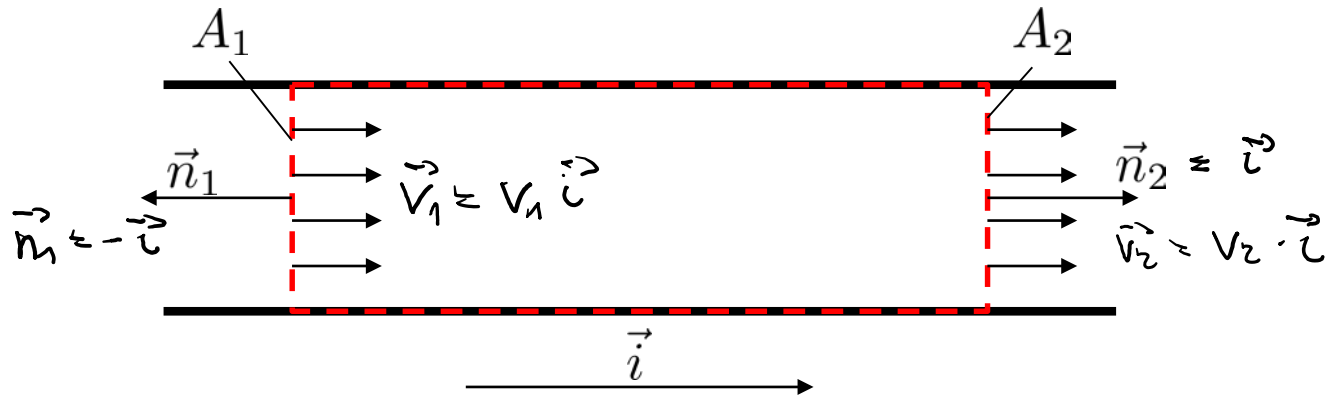
$$\frac{d}{dt}m = \underbrace{\left\{ \begin{array}{c} \text{transfer of mass into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\}}_{-\iint_{\partial V_c} \rho \beta \vec{v} \cdot \vec{n} dA}$$

$$\frac{d}{dt}m = \frac{d}{dt} \iiint_{V_c} \rho dV = - \iint_{\partial V_c} \rho \vec{v} \cdot \vec{n} dA$$

- Often, we have one (or more) «point inflows» $\omega_{in,i}$, and outflows $\omega_{out,i}$. Then mass balance can be formulated as

$$\frac{d}{dt}m = \sum_i w_{in,i} - \sum_i w_{out,i}$$

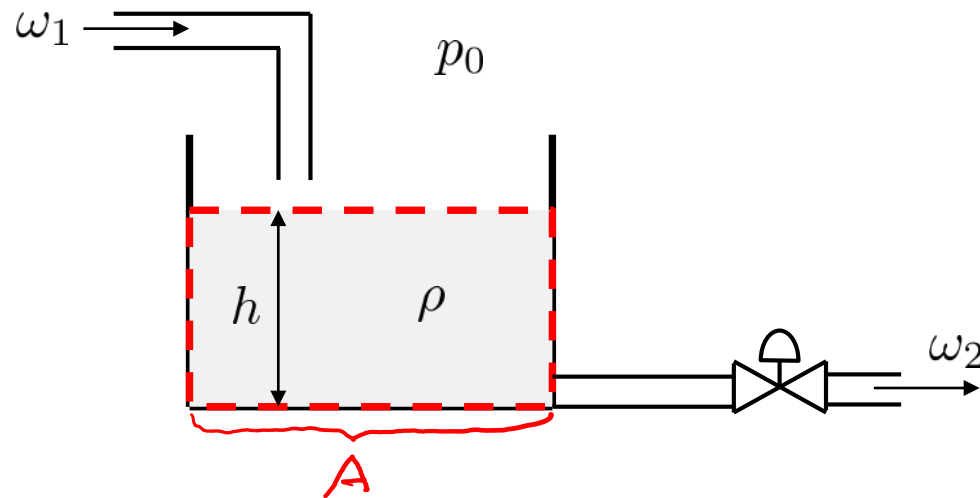
Example: Flow in a pipe



$$\begin{aligned}
 - \iint_{\partial V_c} \rho \vec{v} \cdot \vec{n} dA &= - \iint_{A_1} \rho_1 \vec{v}_1 \cdot \vec{n}_1 dA - \iint_{A_2} \rho_2 \vec{v}_2 \cdot \vec{n}_2 dA \\
 &= \rho_1 v_1 A_1 - \rho_2 v_2 A_2 \\
 &= \dot{W}_1 - \dot{W}_2
 \end{aligned}$$

$$\frac{dm}{dt} = \dot{W}_1 - \dot{W}_2 = \rho_1 q_1 - \rho_2 q_2$$

Example: Tank



$$q_2 = C_d A_v \sqrt{\frac{2}{\rho} \Delta p}$$

$$\begin{aligned} \Delta p &= p_0 + \rho g h - p_0 \\ &= \rho g h \end{aligned}$$

mass balance: $\frac{dm}{dt} = \omega_1 - \omega_2$

$$m = \rho A \cdot h$$

$$\frac{d}{dt} (\rho A h) = \omega_1 - \rho C_d A_v \sqrt{\frac{2}{\rho} \Delta p}$$

$$\frac{d}{dt} h = \frac{1}{\rho A} \omega_1 - C_d \frac{A_v}{A} \sqrt{2 g h}$$

Mass-type balance laws with generation

- Assume B is an extensive variable «equivalent to» mass
 - that is, mass of a component in a volume, or number of molecules of a component, number of particles, etc.
- These types of mass balance laws can have *internal generation*:

$$\frac{d}{dt}B = \sum_i W_{\text{in},i} - \sum_i W_{\text{out},i} + W_{\text{generated}}$$

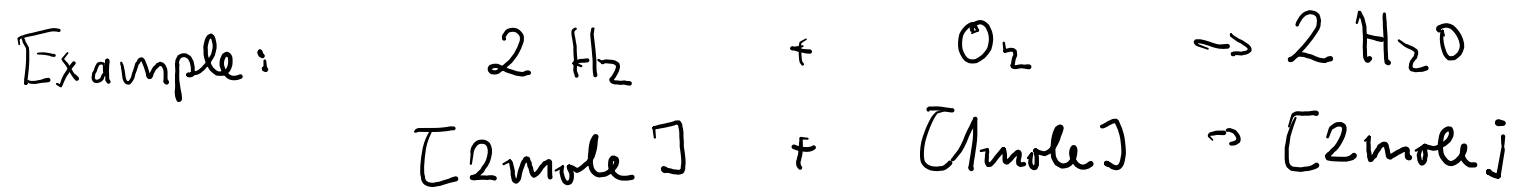
- More generally, if the local rate of generation of B is r_B :

$$\frac{d}{dt}B = \frac{d}{dt} \iiint_{V_c} \rho \beta dV = - \iint_{\partial V_c} \rho \beta \vec{v} \cdot \vec{n} dA + \iiint_{V_c} r_B dV$$

Multi component system : $k = 1 \dots n$ Components $\left[\frac{kg}{m^3 s} \right]$
↓
 density component ρ_k ; local production rate r_k
 Balance equation for component k :

$$\frac{d}{dt} \iiint_{V_c} \rho_k dV = - \iint_{\partial V_c} \rho_k \vec{v}_k \cdot \vec{n} dA + \iiint_{V_c} r_k dV$$

Chemical reactions I



- Sometimes easier with amount of molecules than with masses
- Amount of molecules is measured in mol and the symbol n_k

1 mole: $6.022 \cdot 10^{23}$ particles

→ Moleculebalance instead of massbalance

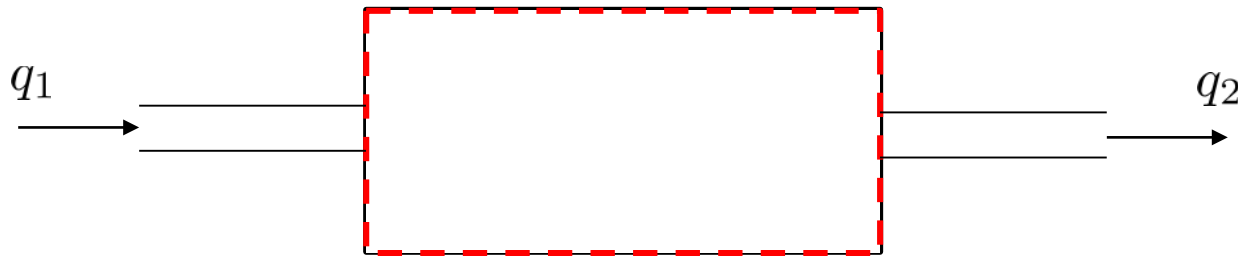
$$n_k = \frac{m_k}{M_k} \quad M_k: \text{mole mass} \left[\frac{\text{kg}}{\text{mole}} \right]$$

Molebalance

Define: $c_k = \frac{n_k}{V} = \frac{\rho_k}{M_k}$; $\frac{1}{\hat{r}_k} := \frac{\Gamma_k}{M_k}$

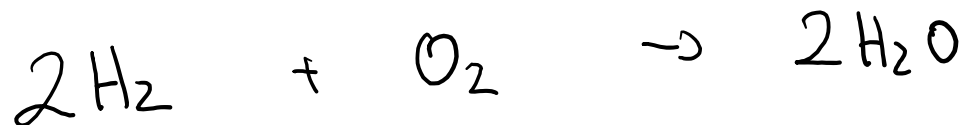
$$\frac{d}{dt} \iiint_{V_c} c_k dV = - \iint_{\partial V_c} c_k \vec{v} \cdot \vec{n} dA + \iiint_{V_c} \hat{r}_k dV$$

- Example:



$$\frac{d}{dt} n_k = \frac{d}{dt} (c_k \cdot V) = q_1 c_{1,k} - q_2 \cdot c_{2,k} + \hat{r}_k V$$

Chemical reactions II

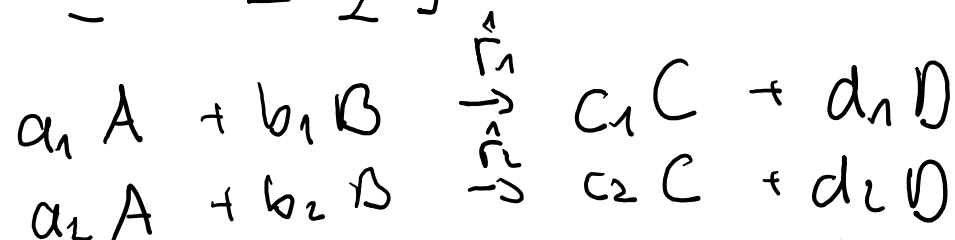


Stoichiometric
coefficients

-2 -1 +2

$$\dot{\underline{C}} = \begin{bmatrix} -2 \\ -1 \\ 2 \end{bmatrix} \hat{r}(c)$$

Several reactions:



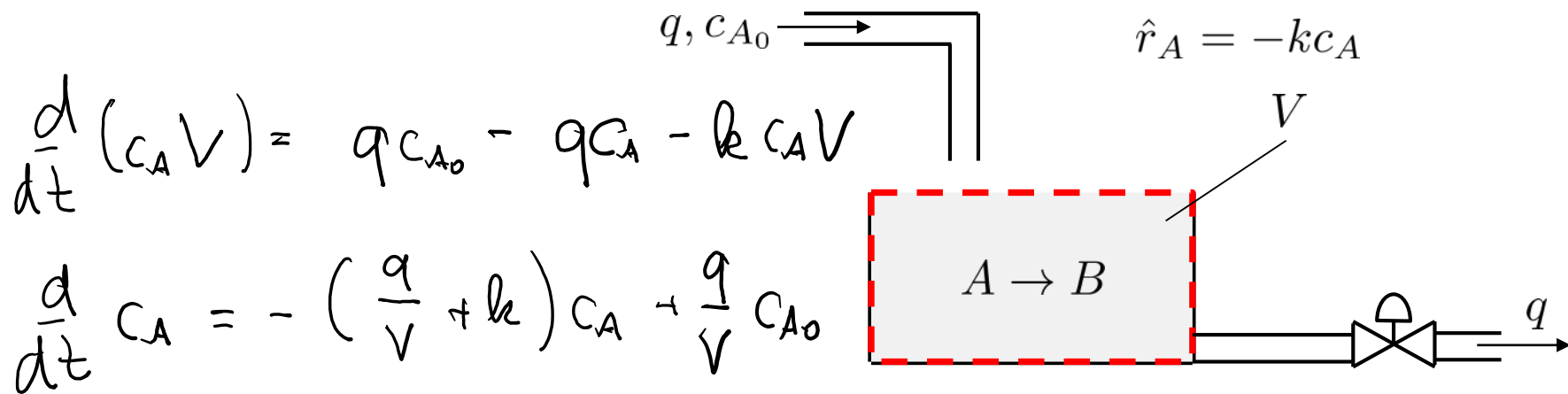
$$\underline{C} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix}$$

stoichiometric matrix $\Gamma = \begin{bmatrix} a_1 & a_2 \\ b_1 & b_2 \\ c_1 & c_2 \\ d_1 & d_2 \end{bmatrix}$

In closed system:

$$\dot{\underline{C}} = \Gamma \underline{\hat{r}} \quad \underline{\hat{r}} = \begin{bmatrix} \hat{r}_1 \\ \hat{r}_2 \end{bmatrix}$$

Example: Reaction in tank



For B:

$$\frac{d}{dt}(c_B V) = 0 - q c_B + k c_A V$$

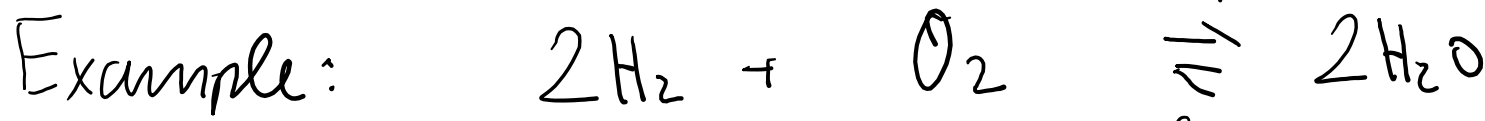
or

mass balance

$$\begin{aligned}
 0 &= \dot{m}_{A0} - (\dot{m}_A + \dot{m}_B) \\
 &= \dot{m}_{A0} M_A - \dot{m}_A M_A - \dot{m}_B M_B \\
 &= \dot{c}_{A0} M_A - \dot{c}_A M_A - \dot{c}_B M_B
 \end{aligned}$$

Chemical reactions III

In general : $\hat{r}_k = f(c_1, \dots, c_n, T)$



$$\hat{r}_{\text{O}_2} = -\gamma_1(T) c_{\text{O}_2}^2 c_{\text{H}_2}^2 + \gamma_2(T) c_{\text{H}_2\text{O}}^2$$

$$\hat{r}_{\text{H}_2} = 2 \hat{r}_{\text{O}_2} \quad ; \quad \hat{r}_{\text{H}_2\text{O}} = -2 \hat{r}_{\text{O}_2}$$

$$k_1 = \gamma_1(T) c_{\text{H}_2}^2 c_{\text{O}_2}$$

$$k_2 = \gamma_2(T) c_{\text{H}_2\text{O}}^2$$

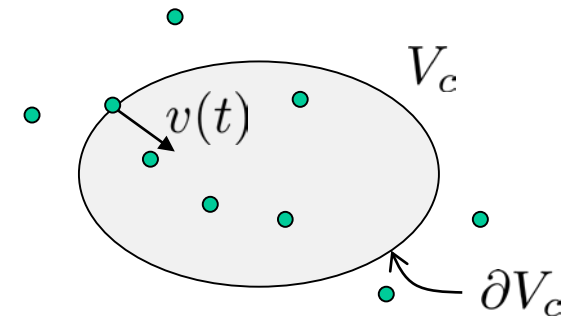
• Closed tank: $\frac{d}{dt} \iiint_{V_c} c_k dV = - \iint_{\partial V_c} c_k \vec{v} \cdot \vec{n} dA + \iiint_{V_c} \hat{r}_k dV$

$$\frac{d}{dt} c_k = \hat{r}_k$$

$$\frac{d}{dt} c_{\text{O}_2} = -\gamma_1(T) c_{\text{H}_2}^2 c_{\text{O}_2} + \gamma_2(T) c_{\text{H}_2\text{O}}^2$$

$$\Delta n_{\text{H}_2} = -\Delta n_{\text{H}_2\text{O}} = 1/2 \Delta n_{\text{O}_2}$$

The momentum balance



- In words

$$\frac{d}{dt}\mathbf{p} = \left\{ \begin{array}{c} \text{transfer of momentum into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\} + \left\{ \begin{array}{c} \text{generation of momentum} \\ \text{in } V_c \text{ due to forces} \\ \text{acting on } V_c \end{array} \right\}$$

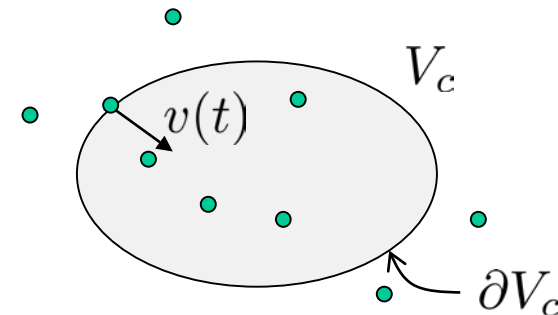
- Mathematically

$$\frac{d}{dt}\vec{p} = \frac{d}{dt} \iiint_{V_c} \rho \vec{v} dV = - \iint_{\partial V_c} \rho \vec{v} \vec{v} \cdot \vec{n} dA + \vec{F}^{(r)}$$

where $\vec{F}^{(r)}$ is resultant force on fluid in control volume

(often: gravity (hydrostatic) and/or friction (hydrodynamic))

The energy balance



- In words

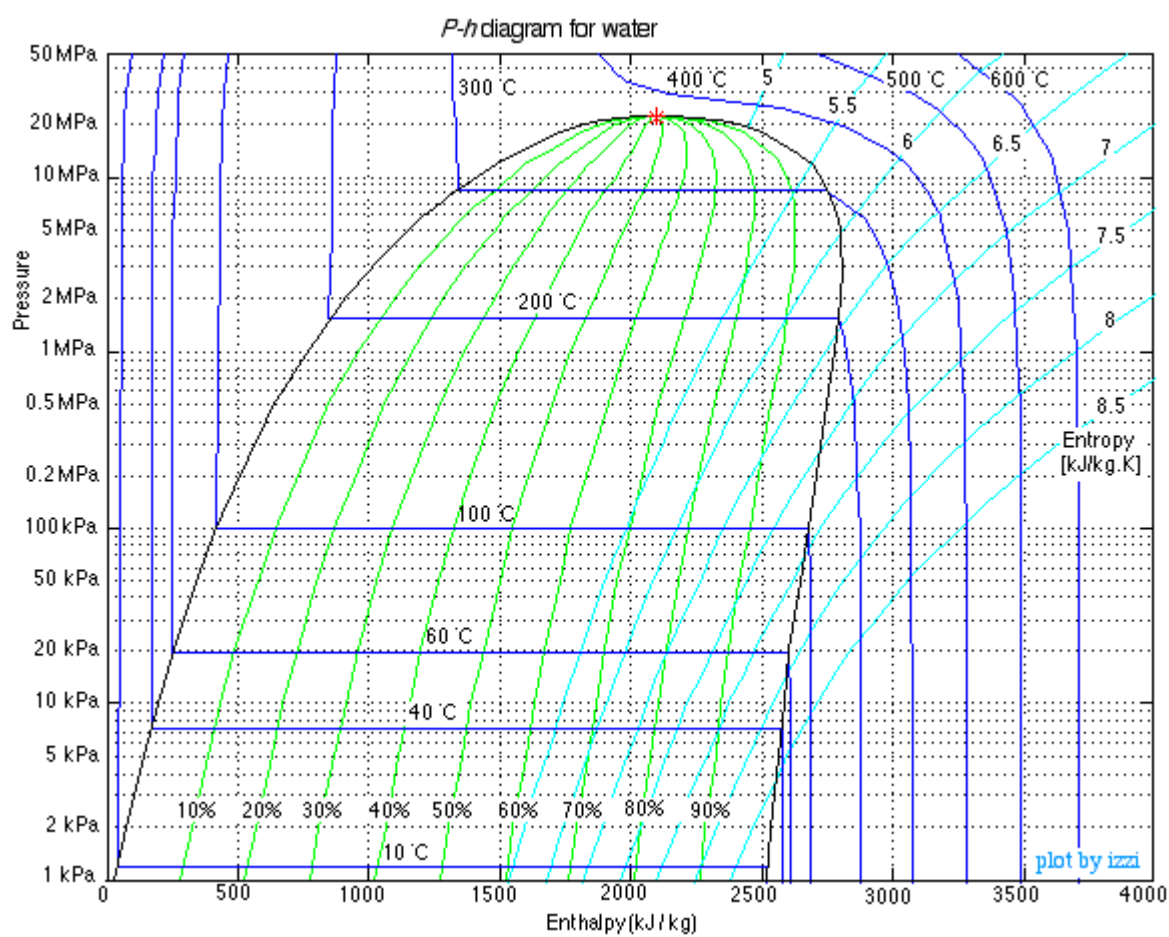
$$\frac{d}{dt}E = \left\{ \begin{array}{c} \text{transfer of energy into} \\ V_c \text{ by fluid flow} \\ \text{across surface } \partial V_c \end{array} \right\} + \left\{ \begin{array}{c} \text{transfer of energy into} \\ V_c \text{ by heat transfer} \\ \text{and by work} \end{array} \right\}$$

- Mathematically

$$\frac{d}{dt}E = \frac{d}{dt} \iiint_{V_c} \rho e dV = \underbrace{- \iint_{\partial V_c} \rho e \vec{v} \cdot \vec{n} dA}_{\text{Energy flow by convection}} + \dot{Q} - \dot{W}$$

- What is the energy of a fluid?

P-h-diagram for water



Homework

- Read 11.1-11.2
- Formulate a momentum balance for a pipeflow with friction

