Multiphase and Reactive Flow Modelling

BMEGEÁT(MW17|MG27)

Part 1

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Active controls in this slide show

ℹ	• Link to related contents
?	• Definition, explanation or notation
▶|	• Jump to next section
|◀	• Jump back one section
▶	• Branch to other topics
◀	
⮌	• Go back to previous slide
⌂	• Go to main contents slide

Certain links do not work in the pdf version

⮌ ⌂

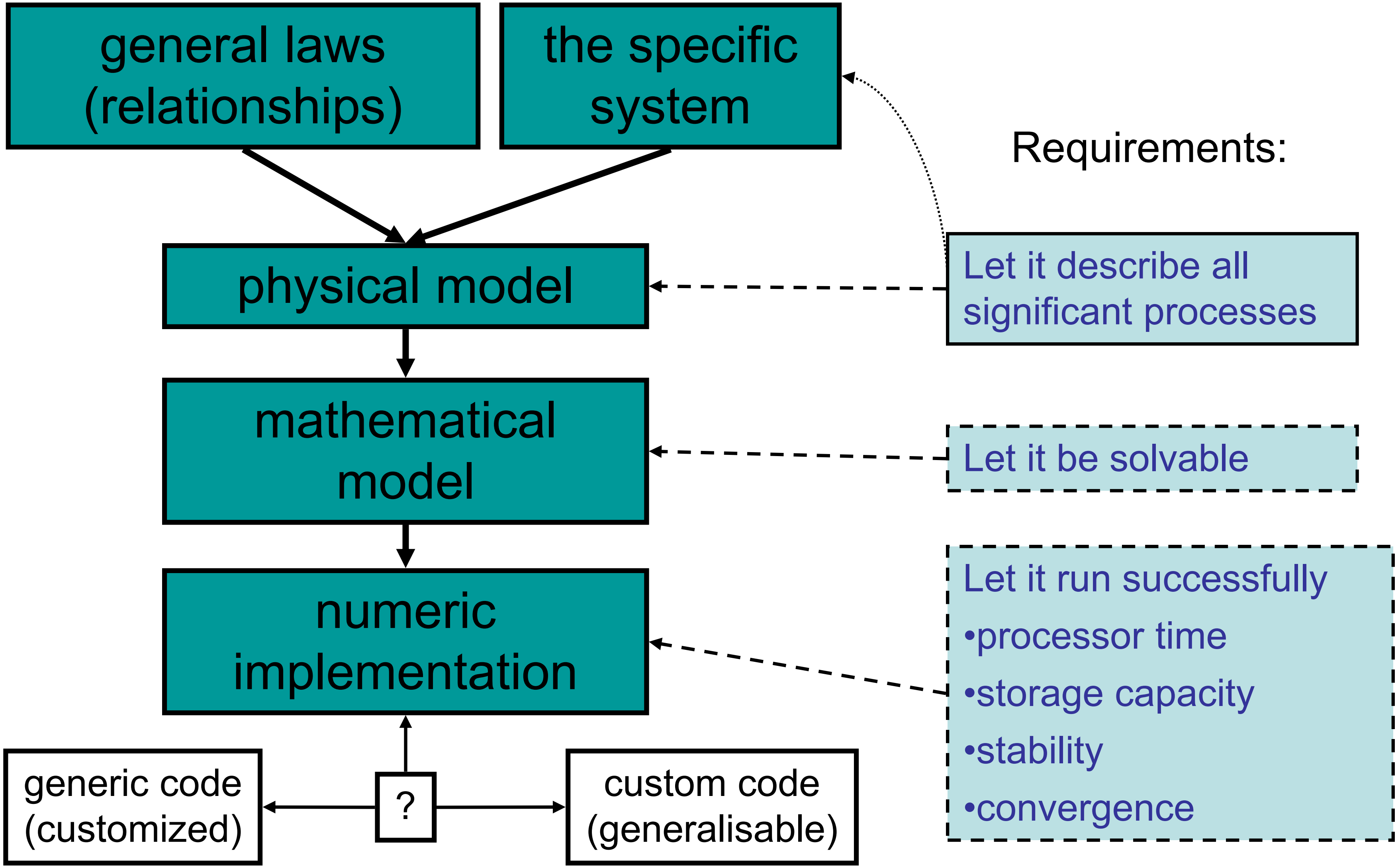
Contents

MODELLING CONCEPTS

What is modelling?

- Experimental modelling
- Theoretical modelling
  - Physical model layer
  - Mathematical model layer
- Numerical modelling

Model layers



general laws (relationships)

the specific system

physical model

mathematical model

numeric implementation

generic code (customized)

?

custom code (generalisable)

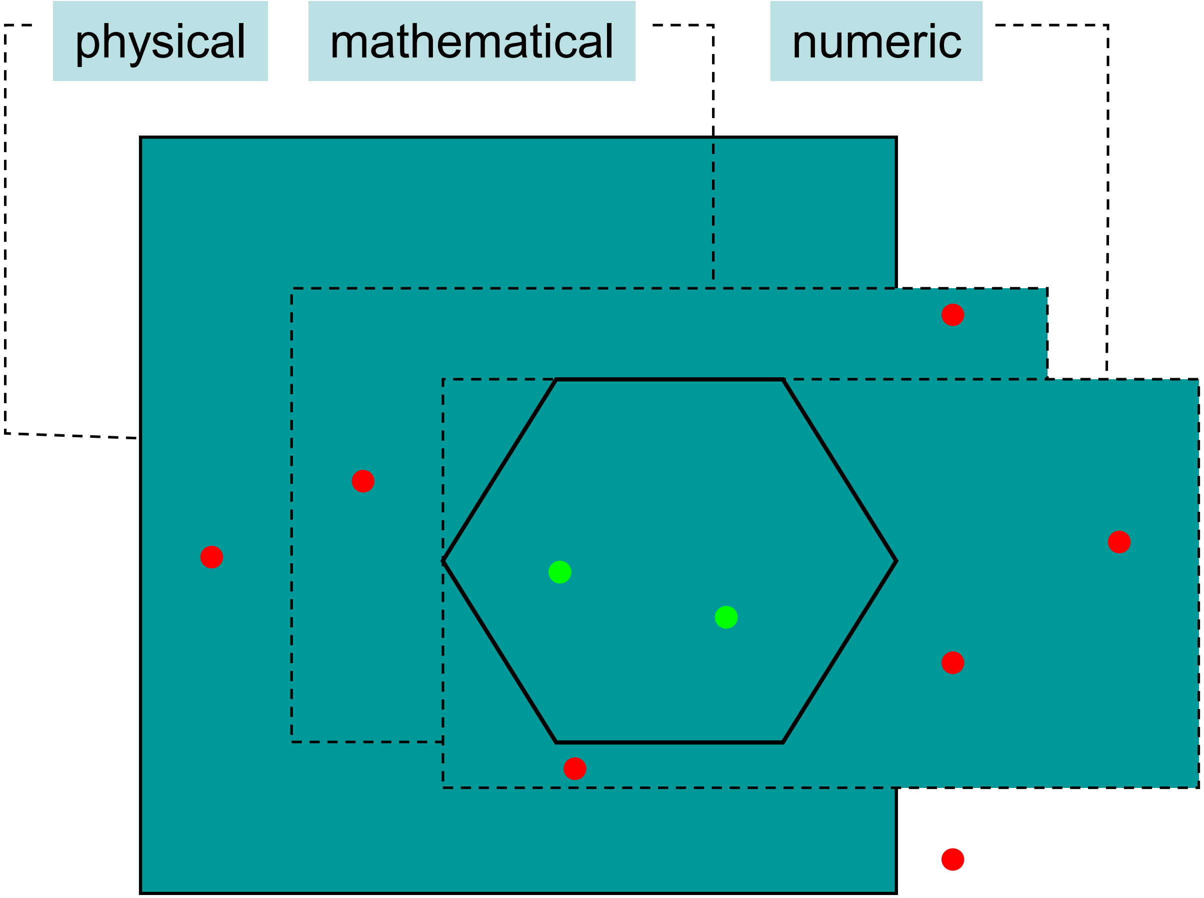
Requirements:

Let it describe all significant processes

Let it be solvable

Let it run successfully
- processor time
- storage capacity
- stability
- convergence

Relating model layers properly



physical

mathematical

numeric

self consistence

validity

- 🟢 good models
- 🔴 wrong models

Validation/verification is unavoidable in the modelling process!

•mistakes can be *proven*,

•reliability can only be *substantiated* by empirical probability

Creating a physical model

What are the significant processes?

- Include all the significant processes
- Get rid of non-significant ones

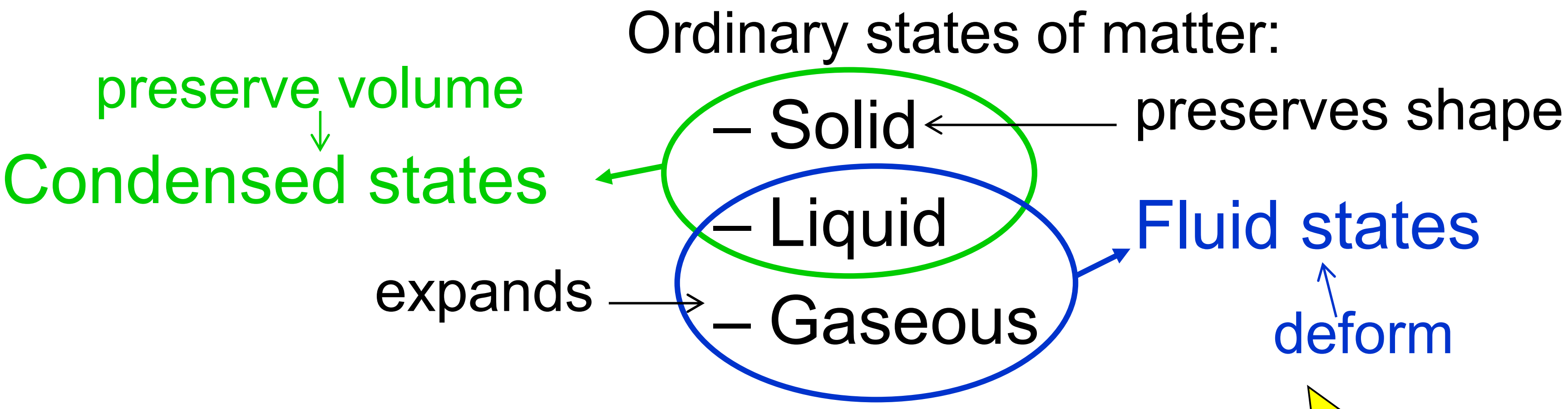
The dimensionless numbers help us with these!

- Classify the system based on the above

Notation
Terminology
Phenomena
Background knowledge

BASIC CONCEPTS

Classification of ordinary media



Ordinary states of matter:

- Solid
- Liquid
- Gaseous

preserves shape

expands

preserve volume

Condensed states

Fluid states

deform

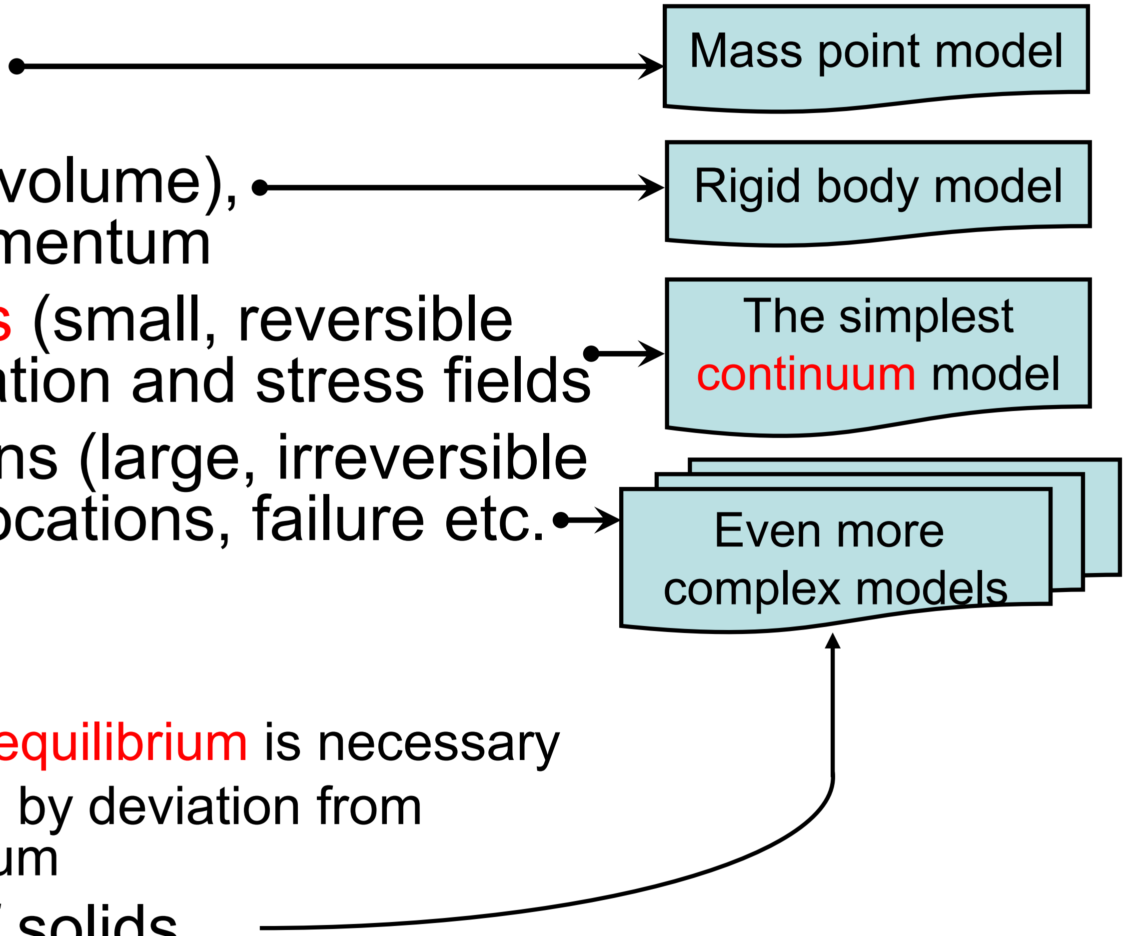
There also exist extraordinary states, like plasma, plastic and other complex materials

The property of *fluidity* serves in the definition of fluids

Properties and physical models of solids

Properties of solids:

- Mass (inertia), position, translation
- Extension (density, volume), rotation, inertial momentum
- Elastic deformations (small, reversible and linear), deformation and stress fields
- Inelastic deformations (large, irreversible and nonlinear), dislocations, failure etc.



Mass point model

Rigid body model

The simplest continuum model

Even more complex models

Modelled features:

1. Mechanics
   - Statics: mechanical equilibrium is necessary
   - Dynamics: governed by deviation from mechanical equilibrium
2. Thermodynamics of solids

Properties and physical models of fluids

Key properties of fluids:

- Large, irreversible deformations
- Density, pressure, viscosity, thermal conductivity, etc.

Only continuum models are appropriate!

Features to be modelled:

1. Statics
   - Hydrostatics: definition of fluid (pressure and density can be inhomogeneous)
   - Thermostatics: thermal equilibrium (homogenous state)
2. Dynamics
   1. Mechanical dynamics: motion governed by deviation from equilibrium of forces
   2. Thermo*dynamics* of fluids:
      - Deviation from global thermodynamic equilibrium often governs processes multiphase, multi-component systems
      - Local thermodynamic equilibrium is (almost always) maintained

Mathematical model of simple fluids

- Inside the fluid:
  - Transport equations

    Mass, momentum and energy balances

    5 PDE's for $p(t,\vec{\mathbf{r}}),\ \vec{\mathbf{u}}(t,\vec{\mathbf{r}})$ and $T(t,\vec{\mathbf{r}})$

    Primary (direct) field variables
  - Constitutive equations

    Algebraic equations for $\rho(p,T),\ \eta(p,T),\ k(p,T),\ \ldots$

    Secondary (indirect) field variables
- Boundary conditions

  On explicitly or implicitly specified surfaces
- Initial conditions

Some models of simple fluids

- $\rho = const\,,\ \mu = const$ → Stoksean fluid
- $\rho(p),\ \mu = const$ → compressible (or barotropic) fluid

  In both of these, the heat transport problem can be solved separately (one-way coupling):

  fluid dynamical equations → heat transport equation (1 PDE)

- $\rho(p,T),\ \mu(p,T),\ k(p,T),\ \ldots$ → general simple fluid

  Mutually coupled thermo-hydraulic equations:

  fluid dynamical equations ↔ heat transport equation

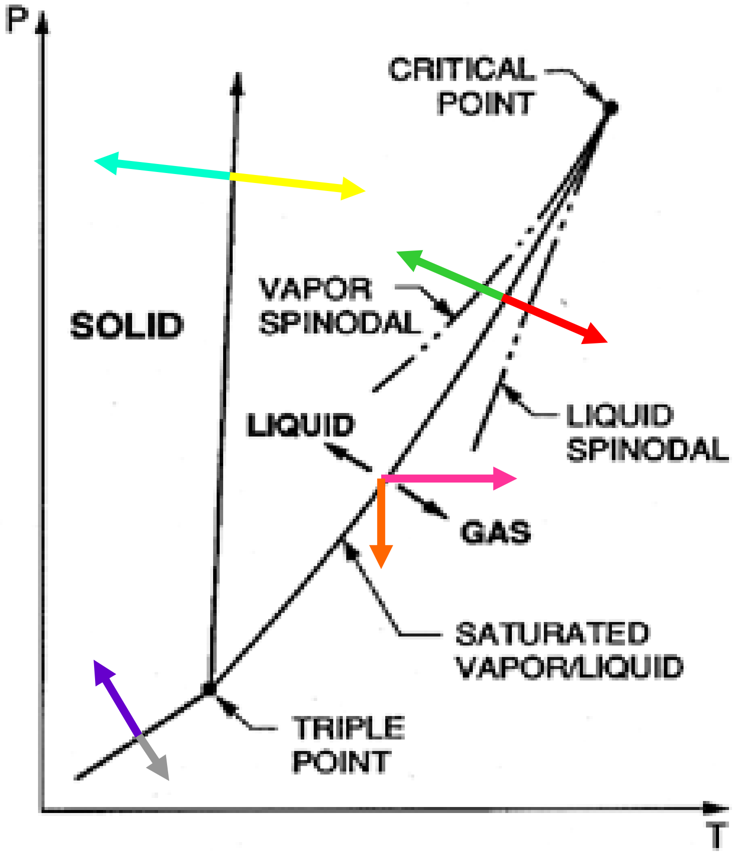
- Non-Newtonian behaviour etc. → models for complex fluids

Phase transitions

in case of a single compound

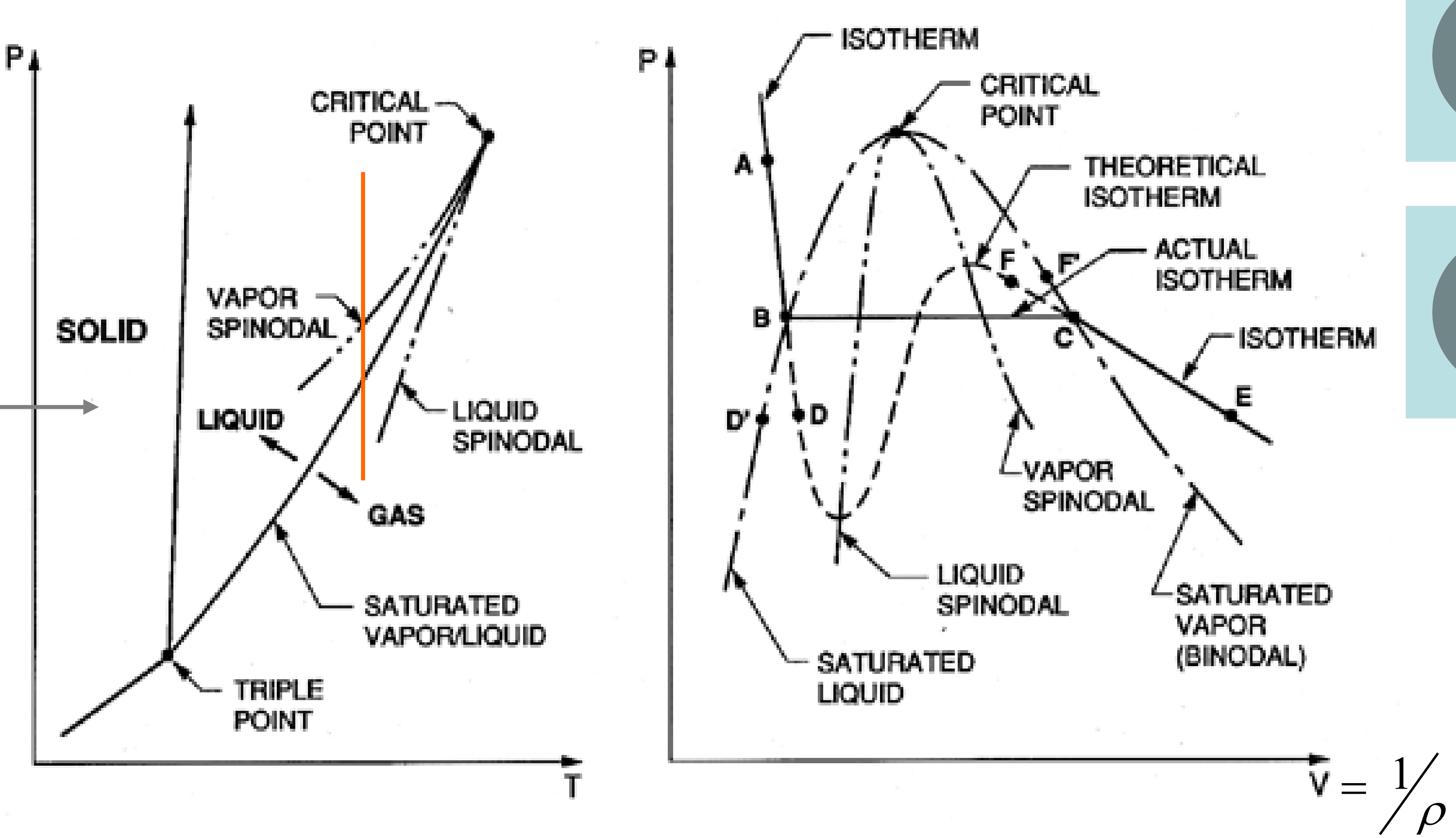
- Evaporation, incl.
  - Boiling
  - Cavitation
- Condensation, incl.
  - Liquefaction
  - Solidification
- Sublimation
- Freezing
- Melting

All phase transitions involve <u>latent heat</u> deposition or release



Typical phase diagrams of a *pure* material:

Several solid phases (crystal structures) may exist



In equilibrium 1, 2 or 3 phases can exist together

Complete mechanical and thermal equilibrium

Material properties in multi-phase, single component systems

One needs explicit constitutional equations for each phase.

For each phase (p) one needs to know:

- the thermodynamic potential $\mu^{(p)}(p,T)$
- the thermal equation of state $\rho^{(p)}(p,T)$
- the viscosity $\eta^{(p)}(p,T)$
- the heat capacity $c_p^{(p)}(p,T)$
- the thermal conductivity. $k^{(p)}(p,T)$

Conditions of local phase equilibrium in a contact point in case of a pure material

- 2 phases:

  $T^{(1)}=T^{(2)}=:T$

  $p^{(1)}=p^{(2)}=:p$

  $\mu^{(1)}(T,p)= \mu^{(2)}(T,p)$

  Locus of solution:

  a line $T_s(p)$ or $p_s(T)$, the saturation temperature or pressure (e.g. ‘boiling point´).

- 3 phases:

  $T^{(1)}=T^{(2)}=T^{(3)}=:T$

  $p^{(1)}=p^{(2)}=p^{(3)}=:p$

  $\mu^{(1)}(T,p)= \mu^{(2)}(T,p) = \mu^{(3)}(T,p)$

  Locus of solution:

  a point (T_t,p_t), the triple point.

Multiple components

- Almost all systems have more than 1 (chemical) components
- Phases are typically *multi-component mixtures*

Concentration(s): measure(s) of composition

There are lot of practical concentrations in use, e.g.

- Mass fraction (we prefer this!)

$$c_1 = m_1/m, \quad c_2 = m_2/m, \ldots \quad c_k = m_k/m, \ldots \quad \sum_k c_k = \sum_k m_k/m = 1$$

- Volume fraction (used in CFD and if volume is conserved upon mixing!)

$$\alpha_1 = V_1/V, \quad \alpha_2 = V_2/V, \ldots \quad \alpha_k = V_k/V, \ldots \quad \sum_k \alpha_k = \sum_k V_k/V = 1$$

- Mole fraction (used in case of chemical reactions and diffusion)

$$y_1 = n_1/n, \quad y_2 = n_2/n, \ldots \quad y_k = n_k/n, \ldots \quad \sum_k y_k = \sum_k n_k/n = 1$$

Multiple components

Concentration fields appear as new primary field variables in the mathematical model

One of them (usually that of the solvent) is redundant, not used.

$$c_k(t,\vec{\mathbf{r}}) \text{ for } k = 2,\dots,K$$

Material properties in multi-component mixtures

- One needs constitutional equations for each phase
- These algebraic equations depend also on the concentrations

For each phase (p) one needs to know:

- the thermodynamic potential $\mu^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the thermal equation of state $\rho^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the heat capacity $c_p^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the viscosity $\eta^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the thermal conductivity $k^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the diffusion coefficients $D_{k,\ell}^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$

Conditions of local phase equilibrium in a contact point in case of multiple components

- Suppose *N* phases and *K* components:
- Thermal and mechanical equilibrium on the interfaces:

$T^{(1)}=T^{(2)}=\ldots=T^{(N)}=:T$

$p^{(1)}=p^{(2)}=\ldots=p^{(N)}=:p$ 2*N* → only 2 independent unknowns

- Mass balance for each component among all phases:

$$\mu_1^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_1^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_1^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$

$$\mu_2^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_2^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_2^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$

$$\vdots$$

$$\mu_K^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_K^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_K^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$

K(*N*-1) independent equations for 2+*N*(*K*-1) independent unknowns

Phase equilibrium in a multi-component mixture

Gibbs’ Rule of Phases, *in equilibrium*:

$$\boxed{\#\text{phases} \equiv N \le \#\text{components} + 2 \equiv K + 2}$$

TD limit on the # of phases

If there is no (global) TD equilibrium: additional phases may also exist

- in transient metastable state(s) or
- in spatially separated, distant points

Miscibility

The number of phases in a given system is also influenced by the miscibility of the components:

- Gases always mix →

  Typically there is at most 1 contiguous gas phase

- Liquids maybe miscible or immiscible →

  Liquids may separate into more than 1 phases

  (e.g. polar water + apolar oil)

1. Surface tension (gas-liquid interface)
2. Interfacial tension (liquid-liquid interface)

(In general: Interfacial tension on fluid-liquid interfaces)

- Solids typically remain granular

Topology of phases and interfaces

A phase may be

- *Contiguous*

  (more than 1 contiguous phases can coexist)
- *Dispersed:*
  - solid particles, droplets or bubbles
  - of small size
  - usually surrounded by a contiguous phase
- *Compound*

Interfaces are

- 2D interface surfaces separating 2 phases
  - gas-liquid: *surface*
  - liquid-liquid: *interface*
  - solid-fluid: *wall*
- 1D contact lines separating 3 phases and 3 interfaces (at least)
- 0D contact points with (at least) 4 phases, 6 interfaces and 4 contact lines

Topological limit on the # of phases (always local)

Special Features to Be Modelled

- Multiple components →
  - chemical reactions
  - molecular diffusion of constituents
- Multiple phases → inter-phase processes
  - momentum transport,
  - mass transport and
  - energy (heat) transfer

across interfaces and within each phase.

(Local deviation from total TD equilibrium is typical)

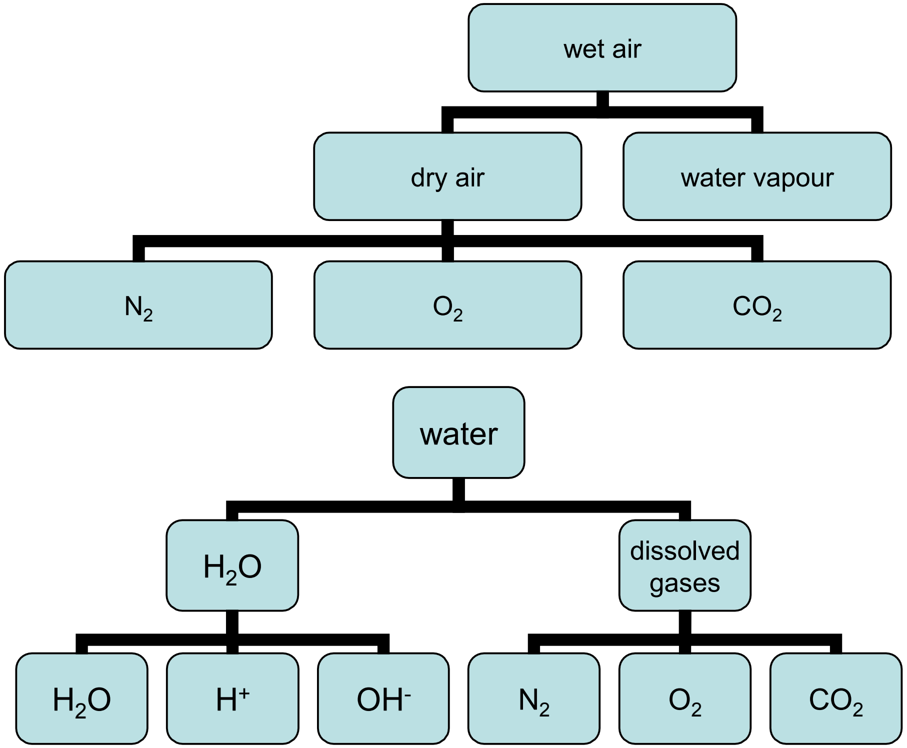
Are components = chemical species?

Not always:

- Major reagents in chemical reactions has to be modelled separately,
- but similar materials can be grouped together and treated as a single component
  - The grouping can be refined in the course of the modelling

Example:

components in an air-water two phase system



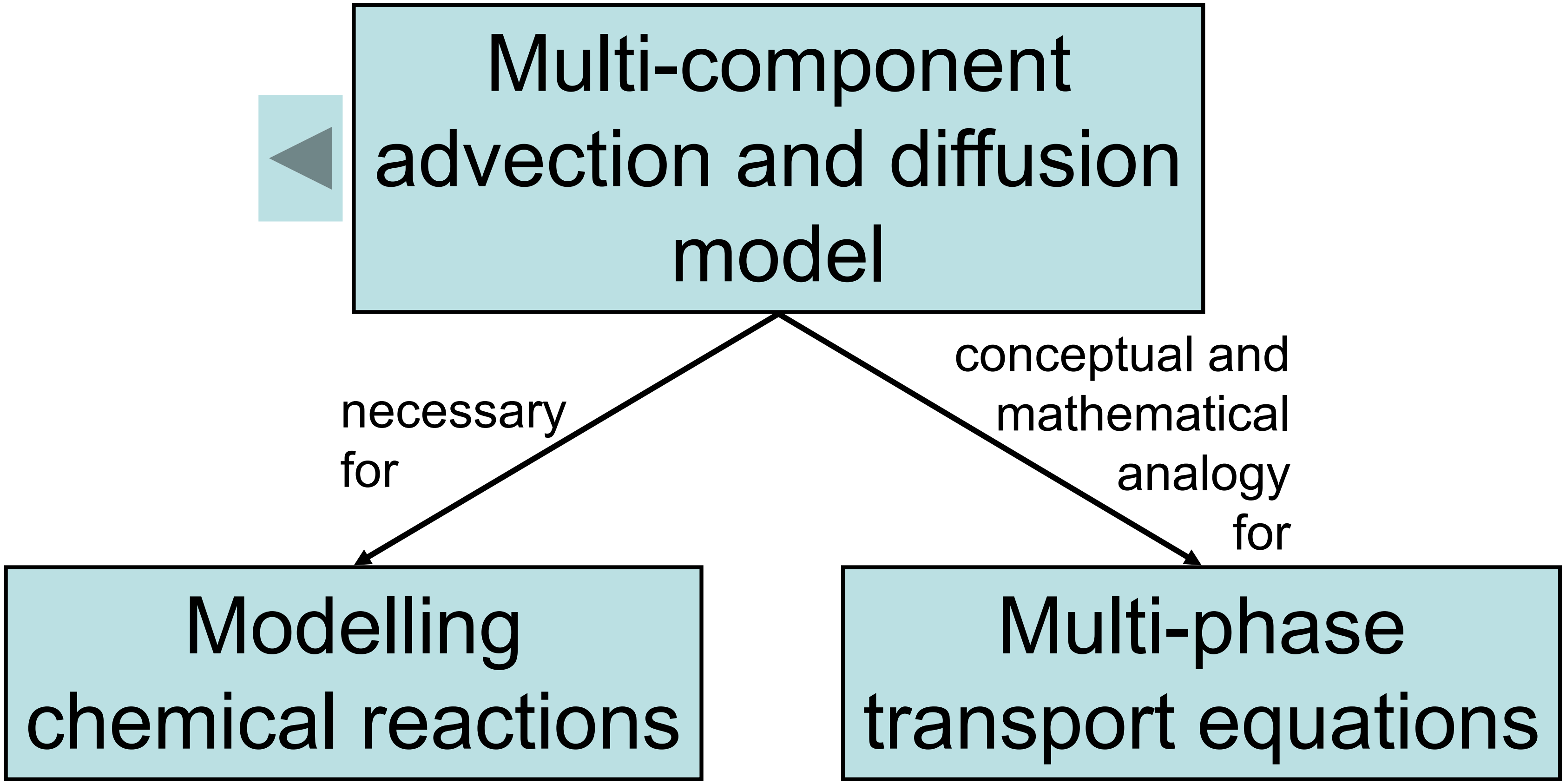
Governing equations

- Transport equations
- Chemical reaction modelling

MODELLING MULTI-COMPONENT FLUIDS

Multi-component transport

We set up transport equations for single-phase multi-component fluids



Multi-component advection and diffusion model

necessary for

conceptual and mathematical analogy for

Modelling chemical reactions

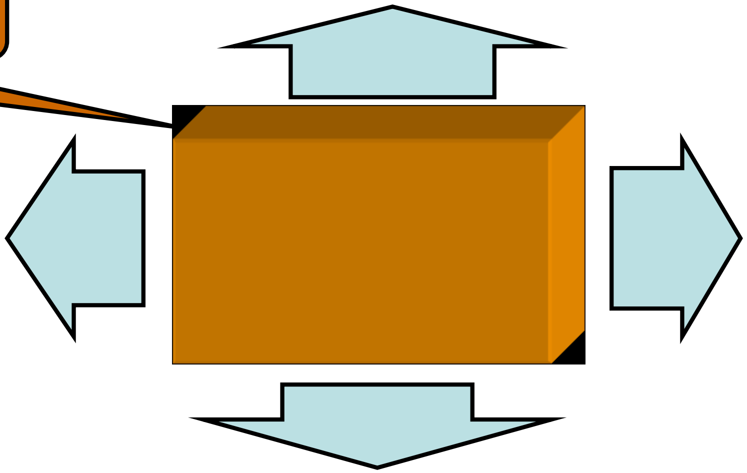
Multi-phase transport equations

Multi-component transport Outline

- Balance equations
  - Mass balance — equation of continuity
  - Component balance
- Advection
- Molecular diffusion
- Chemical reactions

Mass balance for a control volume

Eulerian (fixed) control volume in 3D



Mass inside: $m(t) = \iiint \rho(t, \vec{\mathbf{r}})\, dV$

Outflow rate: $J(t) = \oiint \vec{\mathbf{j}}(t, \vec{\mathbf{r}}) \cdot \mathbf{d}\vec{\mathbf{A}}$

Mass production rate: $Q(t) = 0$

Mass is a conserved quantity (in 3D):
no production (sources) and decay (sinks) inside

This is a conservation law

Integral form: $\frac{dm}{dt} = -J(t) + Q(t)$

Mass balance equation

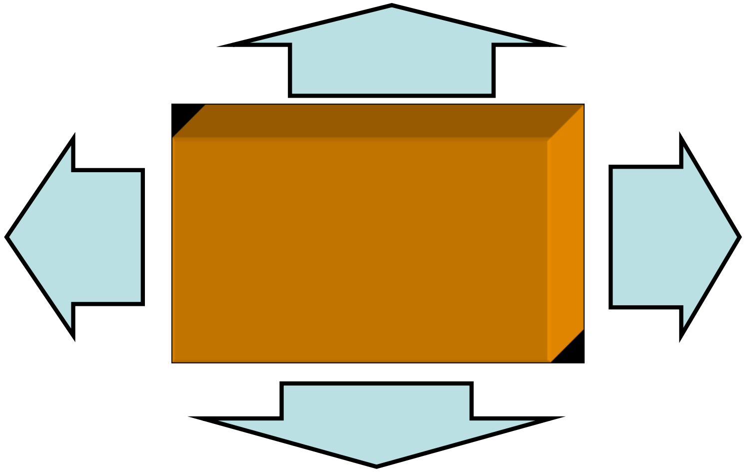
$$\Updownarrow \qquad \Updownarrow \qquad \Updownarrow$$

By definition:

Differential form: $\partial_t \rho + \vec{\nabla}(\rho\, \vec{\mathbf{u}}) = 0 \quad \leftarrow \quad \vec{\mathbf{u}}(t, \vec{\mathbf{r}}) := \vec{\mathbf{j}} / \rho$

Component mass balance

For each component:



Mass inside: $m_k(t) = \iiint \rho_k(t,\vec{\mathbf{r}})\,dV$

Outflow rate: $J_k(t) = \oiint \vec{\mathbf{j}}_k(t,\vec{\mathbf{r}}) \cdot \mathbf{d}\vec{\mathbf{A}}$

Mass production rate: $Q_k(t) = 0$

If component masses are also conserved, **then** no production (sources) and decay (sinks) inside

These are also conservation laws

Integral form: $$\frac{dm_k}{dt} = -J_k(t) + Q_k(t)$$

Mass balance equations

$$\updownarrow \qquad \updownarrow \qquad \updownarrow$$

By definition:

Differential form: $$\partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}_k\right) = 0 \leftarrow \vec{\mathbf{u}}_k(t,\vec{\mathbf{r}}) := \vec{\mathbf{j}}_k / \rho_k$$

The mass transport equations

$$\boxed{\partial_t \rho + \vec{\nabla}(\rho\, \vec{\mathbf{u}}) = 0}$$

$$\sum_k \quad \Uparrow$$

$$\forall k:\ \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}_k) = 0$$

$$\Updownarrow$$

$$\sum_k \rho_k = \rho, \quad \sum_k \vec{\mathbf{j}}_k = \sum_k \rho_k \vec{\mathbf{u}}_k = \vec{\mathbf{j}}$$

$$\rho_k = c_k \rho, \qquad \vec{\mathbf{j}}_k = \rho_k \vec{\mathbf{u}}_k = c_k \rho\, \vec{\mathbf{u}}_k$$

$$\vec{\mathbf{u}}_k = \vec{\mathbf{u}} + (\vec{\mathbf{u}}_k - \vec{\mathbf{u}}) = \vec{\mathbf{u}} + \vec{\mathbf{w}}_k$$

$$\partial_t (c_k \rho) + \vec{\nabla}(c_k \rho\, \vec{\mathbf{u}}) = -\vec{\nabla}(\rho_k \vec{\mathbf{w}}_k) = -\vec{\nabla}\vec{\mathbf{j}}_{\text{diff } k} \quad \Leftarrow \quad \vec{\mathbf{j}}_{\text{diff } k} := \rho_k \vec{\mathbf{w}}_k$$

advection ***diffusion***

$$c_k \left[\cancel{\partial_t \rho + \vec{\nabla}(\rho\, \vec{\mathbf{u}})}\right] + \rho \left[\partial_t c_k + \vec{\mathbf{u}} \vec{\nabla} c_k\right] = -\vec{\nabla}\vec{\mathbf{j}}_{\text{diff } k}$$

$$\boxed{\forall k: D_t c_k = \partial_t c_k + \vec{\mathbf{u}} \vec{\nabla} c_k = -\frac{1}{\rho} \vec{\nabla}\vec{\mathbf{j}}_{\text{diff } k}}$$

$$\sum_k \vec{\mathbf{j}}_{\text{diff } k} = \sum_k \rho_k \vec{\mathbf{w}}_k = \vec{\mathbf{0}}$$

Two ways of resolving redundancy

1. Pick exactly *K* mass transport equations and choose the *K* primary variables as follows:

$$k=1,\ldots K:\ \partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}\right) = -\vec{\nabla}\vec{\mathbf{j}}_{\mathrm{diff}\ k}$$

$$\partial_t \rho + \vec{\nabla}\left(\rho \vec{\mathbf{u}}\right) = 0$$

$$k=2,\ldots K:\ D_t c_k = -\left(1/\rho\right)\vec{\nabla}\vec{\mathbf{j}}_{\mathrm{diff}\ k}$$

2. If needed, calculate the remaining secondary variable fields from the algebraic relations:

$$\rho(t,\vec{\mathbf{x}}) = \sum_k \rho_k(t,\vec{\mathbf{x}})$$

$$c_k(t,\vec{\mathbf{x}}) = \rho_k(t,\vec{\mathbf{x}}) / \rho(t,\vec{\mathbf{x}})$$

$$c_1(t,\vec{\mathbf{x}}) = 1 - \sum_{k=2}^{K} c_k(t,\vec{\mathbf{x}})$$

$$\rho_k(t,\vec{\mathbf{x}}) = \rho(t,\vec{\mathbf{x}}) \cdot c_k(t,\vec{\mathbf{x}})$$

Typically, this is the solvent

For a binary mixture:

$$c_2(t,\vec{\mathbf{x}}) =: c(t,\vec{\mathbf{x}})$$

$$c_1(t,\vec{\mathbf{x}}) = 1 - c(t,\vec{\mathbf{x}})$$

Differential forms in balance equations

Conservation of *F*: $F(t)=\iiint \varphi(t,\vec{\mathbf{r}})dV=\iiint f(t,\vec{\mathbf{r}})\cdot\rho(t,\vec{\mathbf{r}})dV$

- equations for the density (φ)
  - general
  - only convective flux
- equation for the specific value (f)

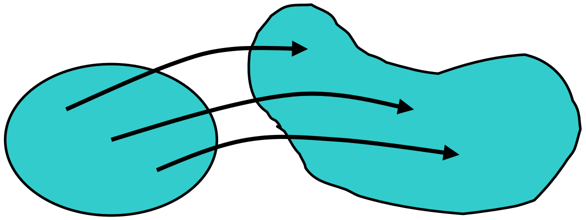
$$\partial_t\varphi+\vec{\nabla}\cdot\vec{\mathbf{j}}_F=0$$

$$\Downarrow \text{if } \vec{\mathbf{j}}_F=\vec{\mathbf{u}}\cdot\varphi$$

$$\boxed{\begin{gathered}\partial_t\varphi+\vec{\nabla}\left(\vec{\mathbf{u}}\cdot\varphi\right)=0\\ \Downarrow \text{if } m \text{ is conserved}\\ D_t f\equiv\partial_t f+\left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)f=0\end{gathered}}$$

These forms describe passive advection of *F*

Passive advection



- The concentrations of the fluid particles do not change with time:

$$D_t c_k \equiv \partial_t c_k + \left(\vec{\mathbf{u}} \cdot \vec{\nabla}\right) c_k = 0$$

- The component densities vary in fixed proportion to the overall density:

$$\partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}\right) = 0$$

- Computational advantage: The component transport equations uncouple from the basic fluid dynamical problem and can be solved separately and *a posteriori*
- The solution requires
  - Lagrangian particle orbits
  - Initial conditions (hyperbolic equations)

Simple diffusion models

- No diffusion → <u>pure advection</u>

$$\boxed{\vec{\mathbf{j}}_{\mathrm{diff}\;k} = \vec{\mathbf{0}}}$$

$$\begin{cases} \partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}\right) = 0 \\ D_t c_k = 0 \end{cases}$$

- <u>Equimolecular counter-diffusion</u>

Turbulent mixing

$$\boxed{\vec{\mathbf{j}}_{\mathrm{diff}\;k} = -\rho D \vec{\nabla} c_k} \text{ for constant } D \text{ and } \rho \rightarrow \begin{cases} \partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}\right) = D \nabla^2 \rho_k \\ D_t c_k = D \nabla^2 c_k \end{cases}$$

- <u>Fick's 1st Law</u>

for each solute if $c_k << 1 \; \left(k = 2, \ldots, K\right)$

$$\boxed{\vec{\mathbf{j}}_{\mathrm{diff}\;k} = -\rho D_k \vec{\nabla} c_k} \quad \text{constant } D_k \text{ and } \rho \rightarrow \begin{cases} \partial_t \rho_k + \vec{\nabla}\left(\rho_k \vec{\mathbf{u}}\right) = D_k \nabla^2 \rho_k \\ D_t c_k = D_k \nabla^2 c_k \end{cases}$$

but note that $\sum_{k=1}^{K} \vec{\mathbf{j}}_{\mathrm{diff}\,k} \neq \vec{\mathbf{0}}$

<u>Fick's 2nd Law:</u>
$\partial_t c_k = D_k \nabla^2 c_k$

Further diffusion models

Thermodiffusion and/or barodiffusion:

occur(s) at

- high concentrations
- high *T* and/or *p* gradients

For a binary mixture:

$$\vec{\mathbf{j}}_{\mathrm{diff}} = -\rho D\left(\nabla c + \left(k_T / T\right)\nabla T + \left(k_p / p\right)\nabla p\right)$$

Analogous cross effects appear in the heat conduction equation

$D \cdot k_T$:coefficient of thermodiffusion

$D \cdot k_p$:coefficient of barodiffusion

Further diffusion models

<u>Nonlinear diffusion model</u>

Cross effect among species' diffusion

Valid also at

- high concentrations
- more than 2 components
- low *T* and/or *p* gradients

(For a binary mixture it falls back to Fick's law.)

$$\vec{\mathbf{j}}_{\mathrm{diff}\,k} = \rho \cdot \sum_{\ell \neq k} \frac{M_k}{M} \cdot \frac{\widetilde{K}_{\ell k} - \widetilde{K}_{kk}}{\det(\mathbf{K})} \cdot \vec{\nabla} y_k$$

$$\widetilde{\mathbf{K}} = \mathrm{adj}(\mathbf{K})$$

$$K_{k\ell} = \frac{y_k}{D_{k\ell}} + \frac{M_\ell}{M_k} \cdot \sum_{s \neq k} \frac{y_s}{D_{ks}} \quad \text{if } k \neq \ell$$

$$K_{kk} = 0$$

$$y_k = \frac{M}{M_k} \cdot c_k : \text{mole fraction}$$

$$M = \sum_k y_k M_k \; : \text{mean molar mass}$$

$$D_{k\ell} : \text{binary diffusion coefficient}$$

$$D_{k\ell}(T, n, M_k, M_\ell) = D_{\ell k}$$

Further notes on diffusion modelling

- For internal consistency of the whole model
  - D has to be changed in accordance to the turbulence model (`turbulent diffusivity’)
  - Diffusive heat transfer has to be included in the heat transport equation
- In the presence of multiple phases, the formulation can be straightforwardly generalised by introducing the phasic quantities

$$c_k \rightarrow c_k^{(p)},\ \rho_k \rightarrow \rho_k^{(p)}, \vec{\mathbf{j}}_k \rightarrow \vec{\mathbf{j}}_k^{(p)},\ \vec{\mathbf{j}}_{\mathrm{diff}\,k} \rightarrow \vec{\mathbf{j}}_{\mathrm{diff}\,k}^{(p)},\ D_k \rightarrow D_k^{(p)} \ldots$$

The advection–diffusion equations

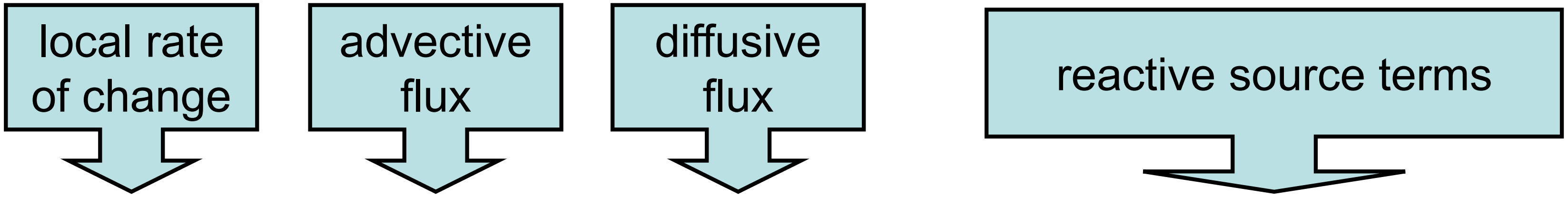
$$\overbrace{\partial_t\left(\rho\cdot c_k\right)}^{\text{local rate of change}}+\overbrace{\vec{\nabla}\left(\vec{\mathbf{u}}\cdot\rho\cdot c_k\right)}^{\text{advective flux}}=\overbrace{-\vec{\nabla}\cdot\vec{\mathbf{j}}_k}^{\text{diffusive flux}}$$

$$\Updownarrow \text{ since } m \text{ is conserved}$$

$$D_t c_k \equiv \partial_t c_k + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)c_k = -\frac{1}{\rho}\vec{\nabla}\cdot\vec{\mathbf{j}}_k \longleftarrow \boxed{\text{e.g. } D\cdot\nabla^2 c_k}$$

The component masses are *conserved* but *not passive* quantities

The advection–diffusion–reaction equations



local rate of change

advective flux

diffusive flux

reactive source terms

$$\partial_t(\rho\cdot c_k)+\vec{\nabla}(\vec{\mathbf{u}}\cdot\rho\cdot c_k)=-\vec{\nabla}\cdot\vec{\mathbf{j}}_k \quad +(\text{mass production rate density})$$

$\Updownarrow$ since m is conserved

$$D_t c_k \equiv \partial_t c_k + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)c_k = -\frac{1}{\rho}\vec{\nabla}\cdot\vec{\mathbf{j}}_k + (\text{local specific production rate})$$

The component masses are *not conserved* quantities

Reaction modelling
OUTLINE

!

Incomplete
without class
notes

1. Reaction stoichiometry
2. Reaction energetics
3. Reaction kinetics

Effects in the model equations:

- reactive source terms in the advection–diffusion–reaction equations
- reaction heat source terms in the energy (=heat conduction) equation

Chemical reactions

- *Chemical reactions* are <u>stochastic processes</u> in which a molecular configuration of atoms transitions into another configuration

Incomplete
without class
notes

A figure showing initial and final configurations and explaining the relevant energy changes is missing from here

Energetics

forward reaction: ΔE>0 energy released → *<u>exothermic</u>*

reverse reaction: ΔE<0 energy consumed → *<u>endothermic</u>*

A binary reaction

Stoichiometry

forward reaction

reactant → *products*

$H_2O = H^+ + OH^-$

product ← *reactants*

reverse reaction

$$\boxed{\forall k : \left|\nu_k\right| = 1}$$

Reagents and reaction products	
k	species
1	H_2O
2	H^+
3	OH^-

A template reaction

Stoichiometry

forward reaction

reactants → *product*

$2\ H_2 + O_2 = 2\ H_2O$

products ← *reactant*

reverse reaction

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

Reaction stoichiometry

Stoichiometric constants

- *forward reaction:*

  $+2\cdot H_2O - 1\cdot O_2 - 2\cdot H_2 = 0$

  $\nu_1 = +2,\ \nu_2 = -1,\ \nu_3 = -2$
- *reverse reaction:*

  $-2\cdot H_2O + 1\cdot O_2 + 2\cdot H_2 = 0$

  $\nu_1 = -2,\ \nu_2 = +1,\ \nu_3 = +2$
- for reactants: $\nu_k < 0$,
- ror reaction products: $\nu_k > 0$
- for *catalysts*: $\nu_k = 0$

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

$$\sum_k \nu_k \neq 0$$

The number of molecules <u>is not</u> conserved

Reaction stoichiometry

Stoichiometric constants

- *forward reaction:*

  $+\ 2\cdot H_2O - 1\cdot O_2 - 2\cdot H_2 = 0$

  $v_1 = +2,\ \ v_2 = -1,\ \ v_3 = -2$
- *reverse reaction:*

  $-2\cdot H_2O + 1\cdot O_2 + 2\cdot H_2 = 0$

  $v_1 = -2,\ \ v_2 = +1,\ \ v_3 = +2$
- for reactants: $v_k < 0$,
- ror reaction products: $v_k > 0$
- for *catalysts*: $v_k = 0$

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

$$\sum_k M_k \cdot v_k = 0$$

BUT: the total mass <u>is</u> conserved

Reactive source terms

Incomplete without class notes

One reaction process:

$$\forall k : \frac{dn_k}{dt} = \nu_k \cdot \dot{\xi}$$

reaction rate

Several reactions:

$$\forall k : \frac{dn_k}{dt} = \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

reaction rate vector

Possible units:

- mol/s,
- (mol/m^3)/s,
- (mol/kg)/s

$$\forall k : \frac{dm_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]} = Q_k(t)$$

$$\forall k : \frac{d\rho_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

$$\forall k : \frac{dc_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

reactive source terms

An alternative formulation:
summation over reaction pairs instead of individual reactions

$$\forall k : \frac{dm_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]} \right) = Q_k(t)$$

$$\forall k : \frac{d\rho_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]} \right)$$

$$\forall k : \frac{dc_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]} \right)$$

forward and reverse reaction rates

Reactive heat source terms in the energy transport equation

Energy released (or consumed) in the course of the reactions appear in the system as *reaction heat*.

The corresponding source terms in the energy balance (aka. heat transport) equation are:

$$\sum_{[r]} \Delta E_{[r]} \cdot \dot{\xi}_{[r]}$$

or, equivalently

$$\sum_{[r]} \Delta E_{[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]} \right)$$

energy released in reaction [*r*]

energy released in forward reaction [*r*]

Reaction kinetics

For a wide range of reactions the reaction rates look like this

$$\dot{\xi}_{[r]} \propto \left[\prod_i (c_i)^{\nu_i'}\right] \cdot \exp\left(-\frac{E_{\mathrm{act}[r]}}{R \cdot T}\right)$$

probability of the simultaneous presence of all reactant molecules

Typically, v_i’are the stoichiometric coefficients of the reactants

probability of the transition at the prevailing temperature

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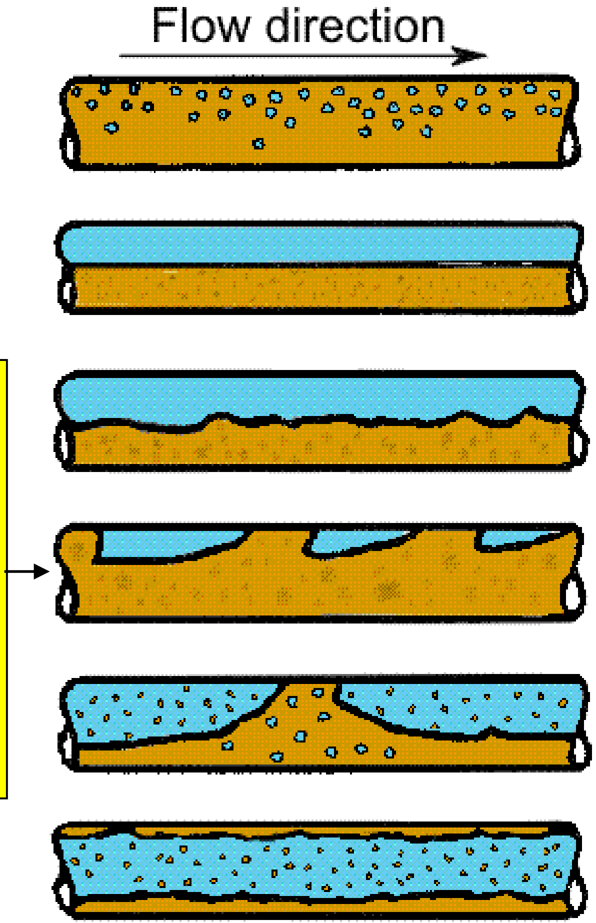
MULTI-PHASE FLUID SYSTEMS

Multiphase systems

- Multiphase pipe flows
  - Physical phenomena
  - Modelling approaches
  - Quantities pertinent to multiphase phenomena
  - Special measurement techniques

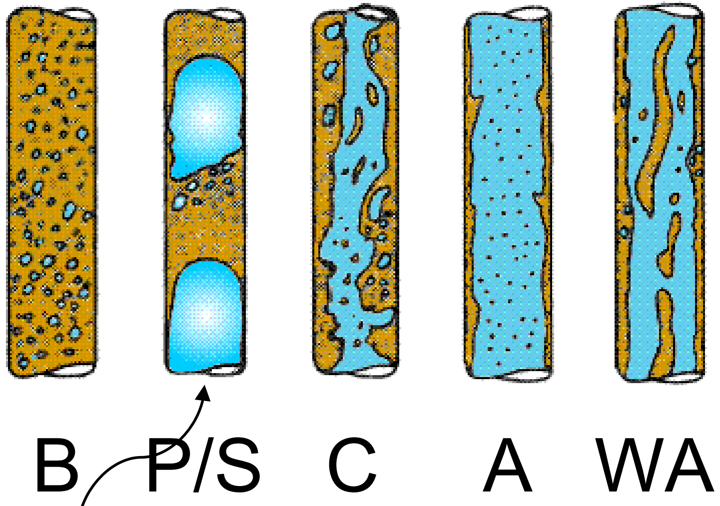
Horizontal gas-liquid flow patterns



Benjamin bubble

- Dispersed Bubble Flow
- Stratified Flow
- Stratified–Wavy Flow
- Plug Flow
- Slug Flow
- Annular–Dispersed Flow

Vertical gas-liquid flow patterns

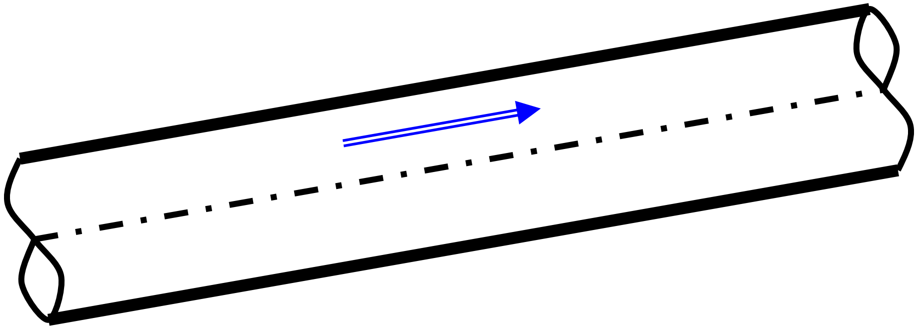


Taylor bubble

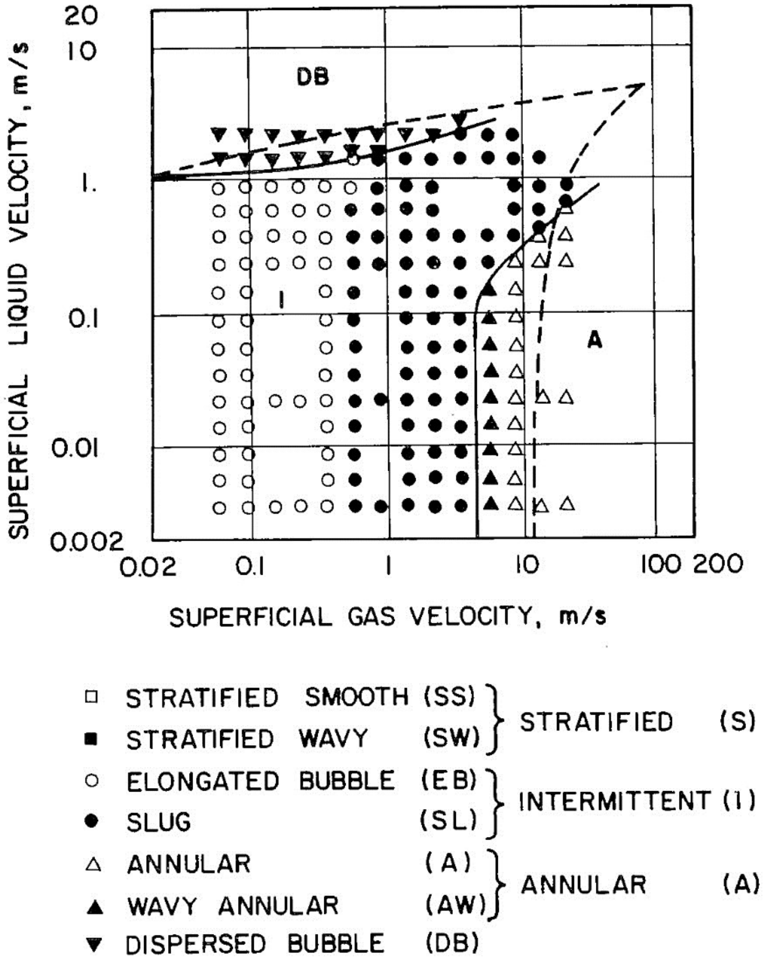
- Bubble Flow
- Plug or Slug Flow
- Churn Flow
- Annular Flow
- Wispy Annular Flow

See videos at www.thermopedia.com/videos

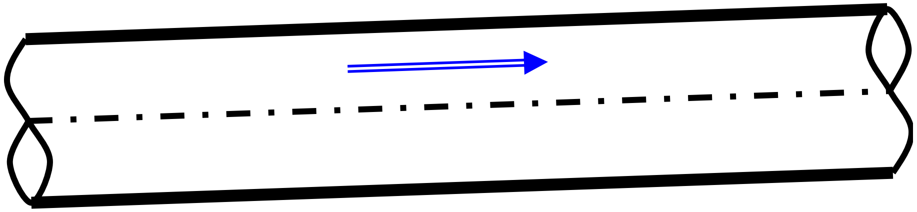
The effect of pipe inclination



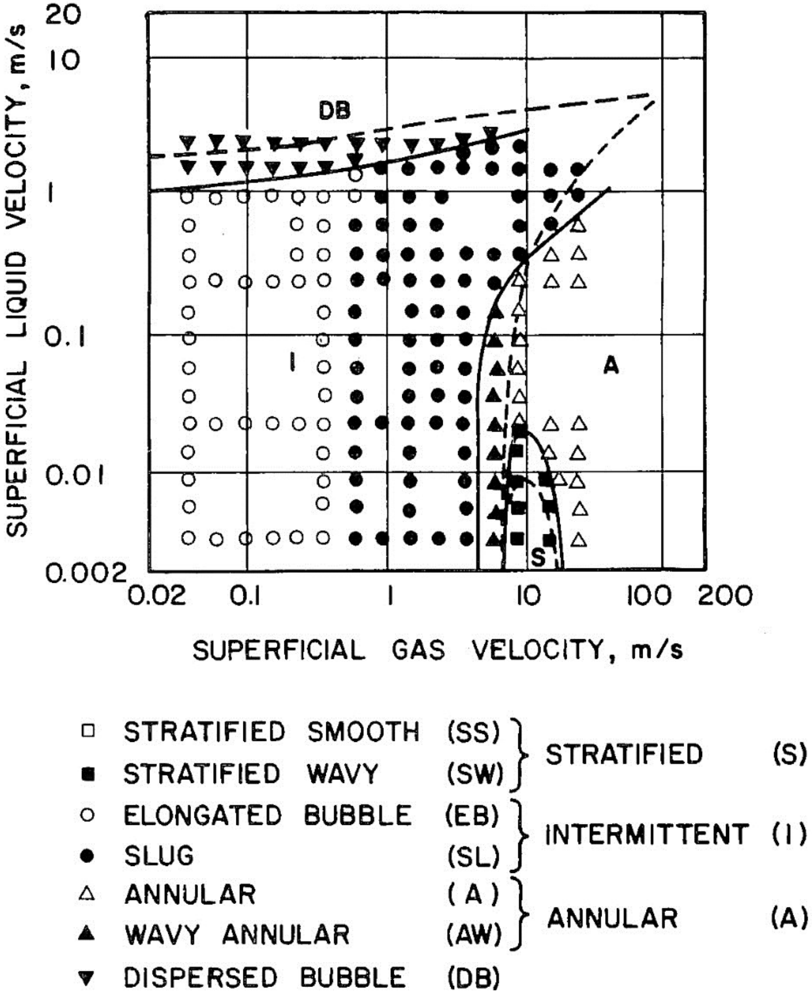
$\Theta = +10°$



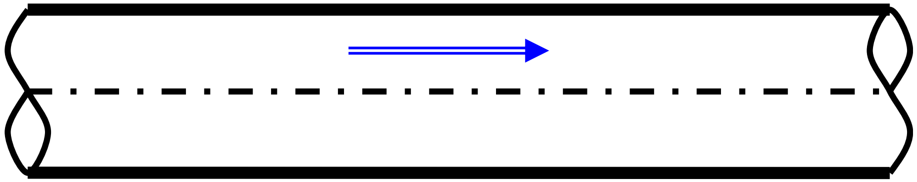
The effect of pipe inclination



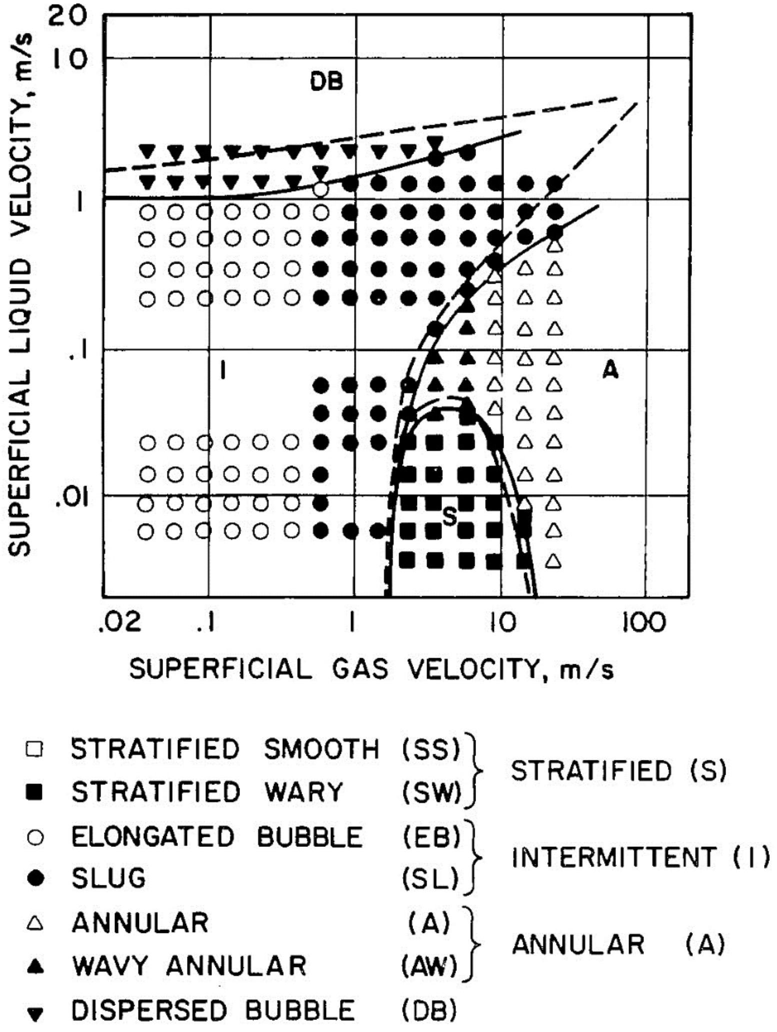
$\Theta = +2°$



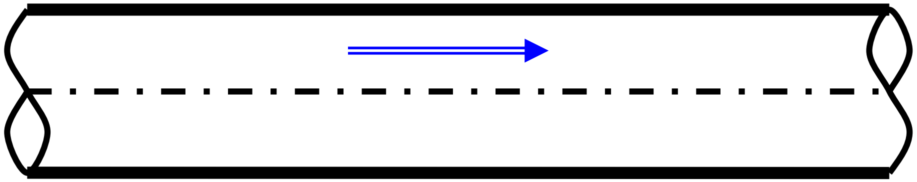
The effect of pipe inclination



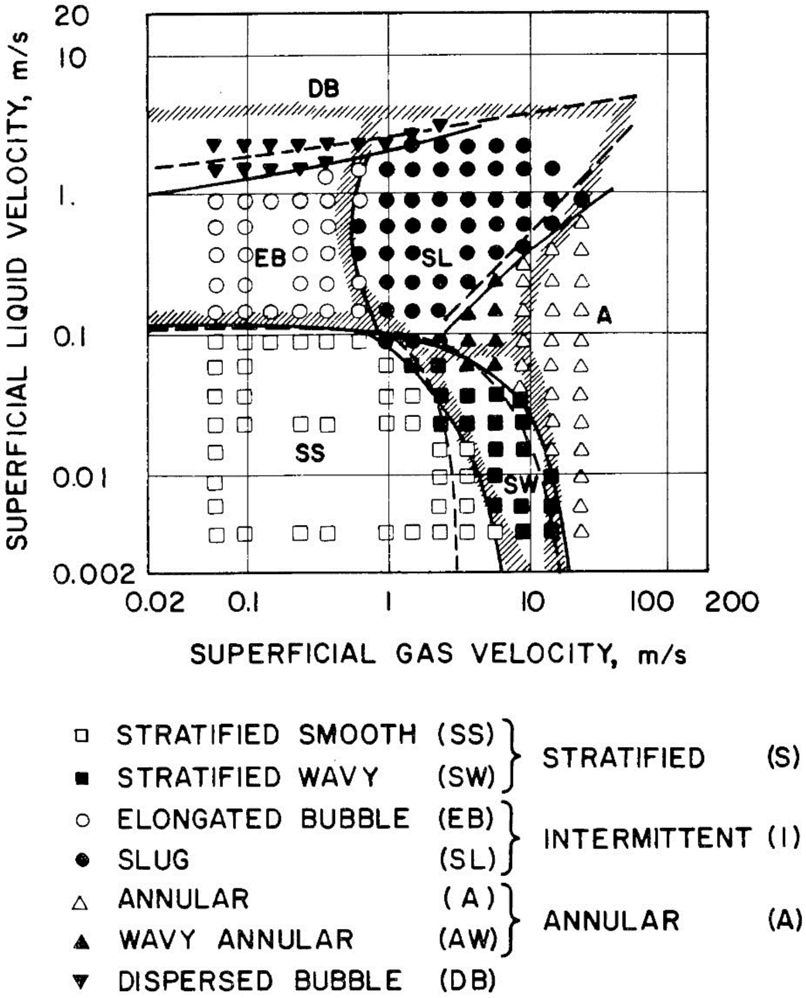
Θ = +0.25°



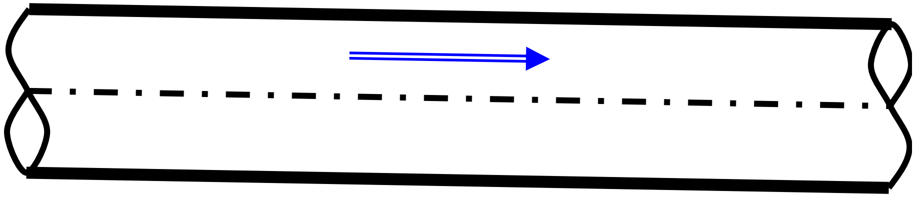
The effect of pipe inclination



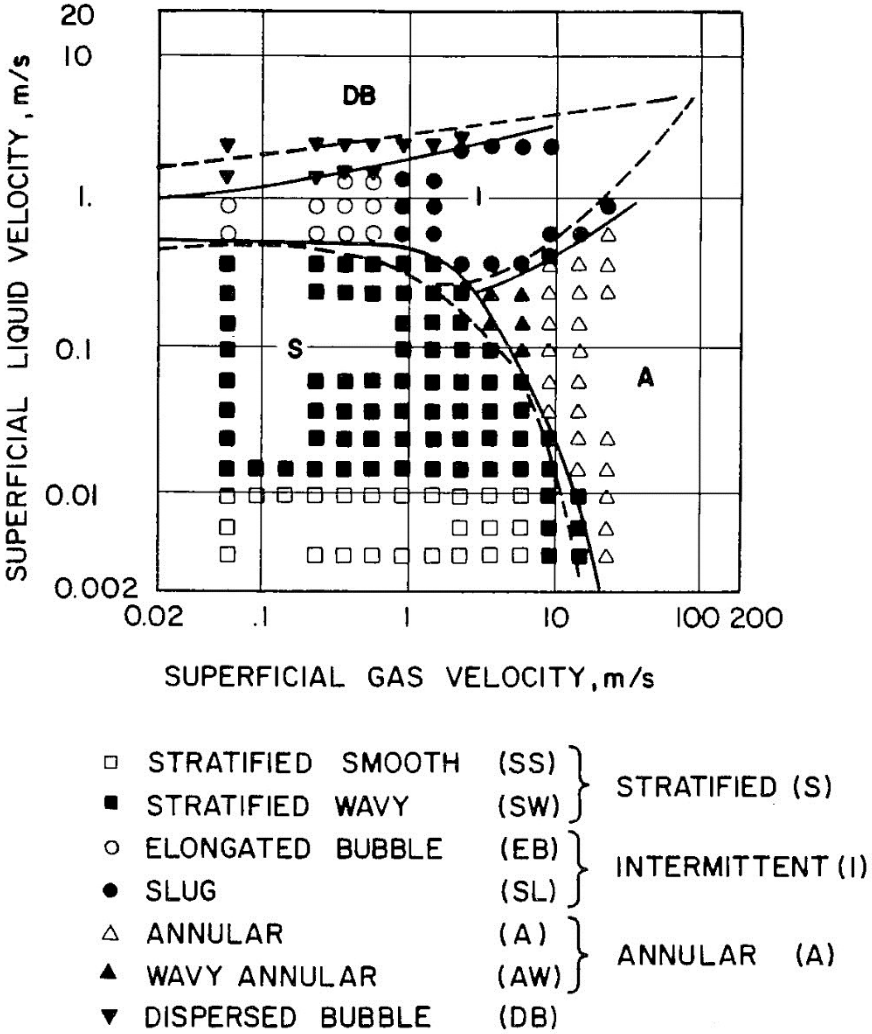
$\Theta = 0^\circ$



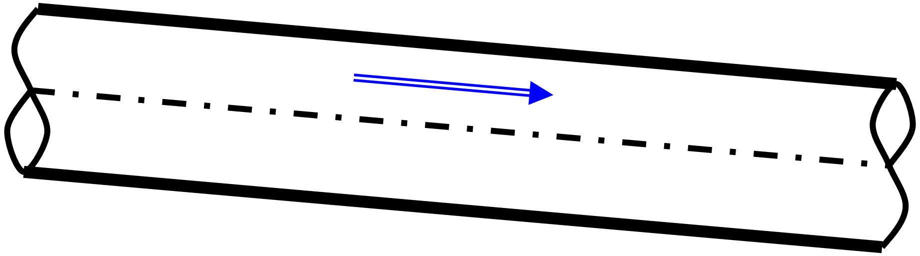
The effect of pipe inclination



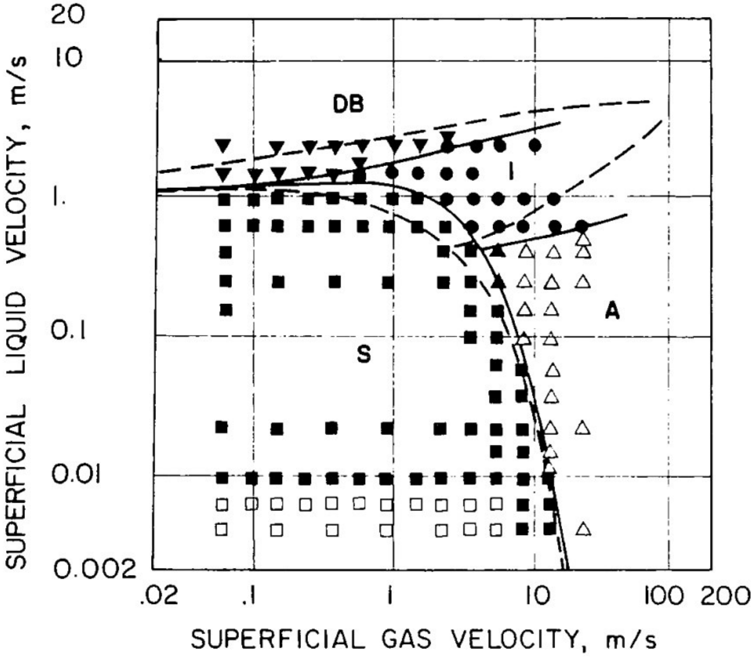
$\Theta = -1°$



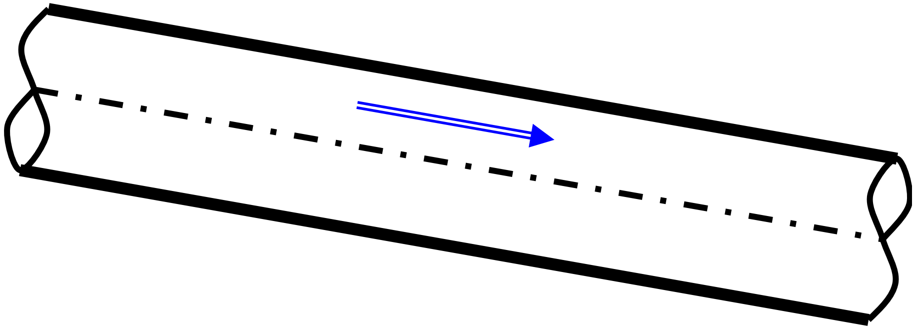
The effect of pipe inclination



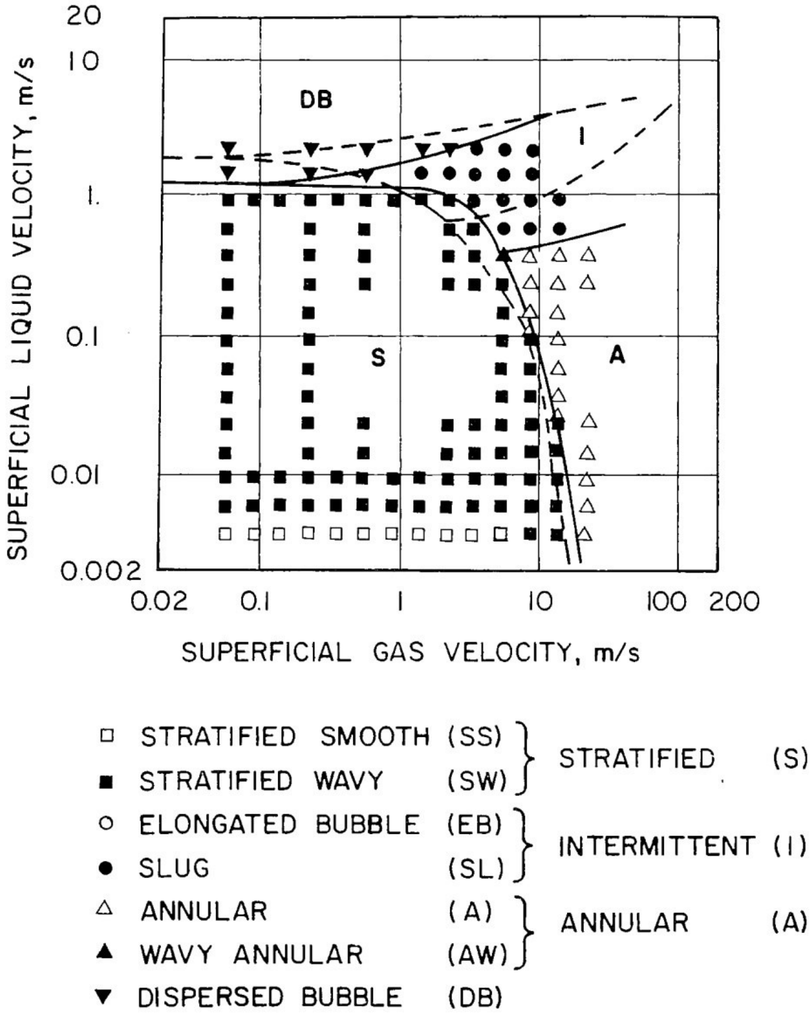
$\Theta = -5°$



The effect of pipe inclination



Θ = − 10°



- Relative flow directions
  - Co-current flow (as shown above)
  - Counter-current flows (one of the mass flow rates is negative): some of the flow patterns exist with opposite flow directions too
- Somewhat analogous flow patterns can be identified in liquid-liquid, liquid-solid and gas-solid systems

- Even more complex flow patterns in three phase pipe flows
- Flow classification is
  - somewhat arbitrary and subjective in pipes
  - hardly possible in 3D containers
- Further points to observe:
  - Heat transfer phenomena
  - Phase transition phenomena

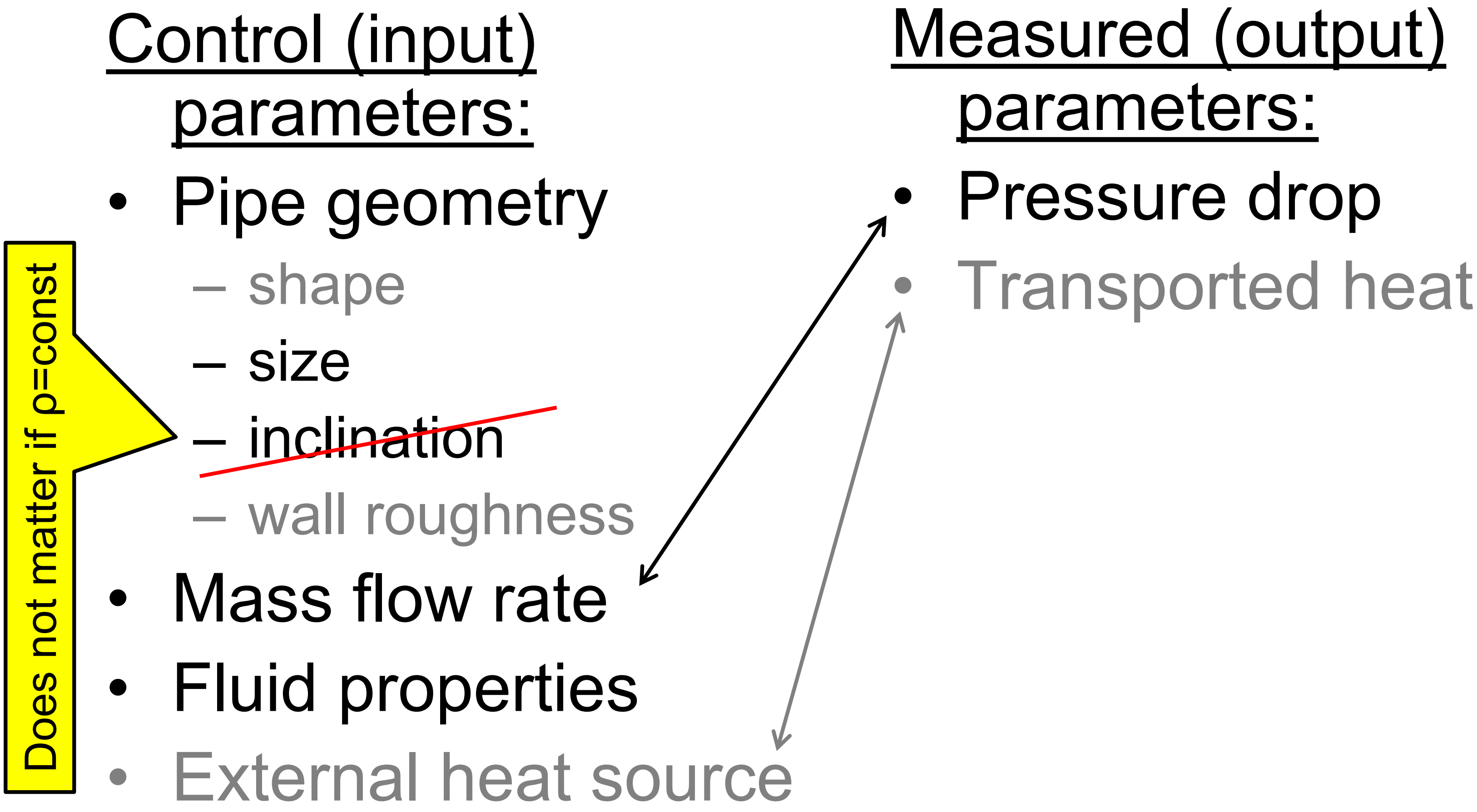
Pipe flow modelling alternatives

- Flow patterns
- Flow regimes
- Flow pattern maps
- Tasks:
  - Model flow region boundaries
  - Model flow behaviour within each flow region

Task:

Create a single fluid model that can correctly reflect fluid behaviour in all flow regimes and thus automatically describes flow pattern transitions

Parameters of one-phase pipe flow



Control (input) parameters:

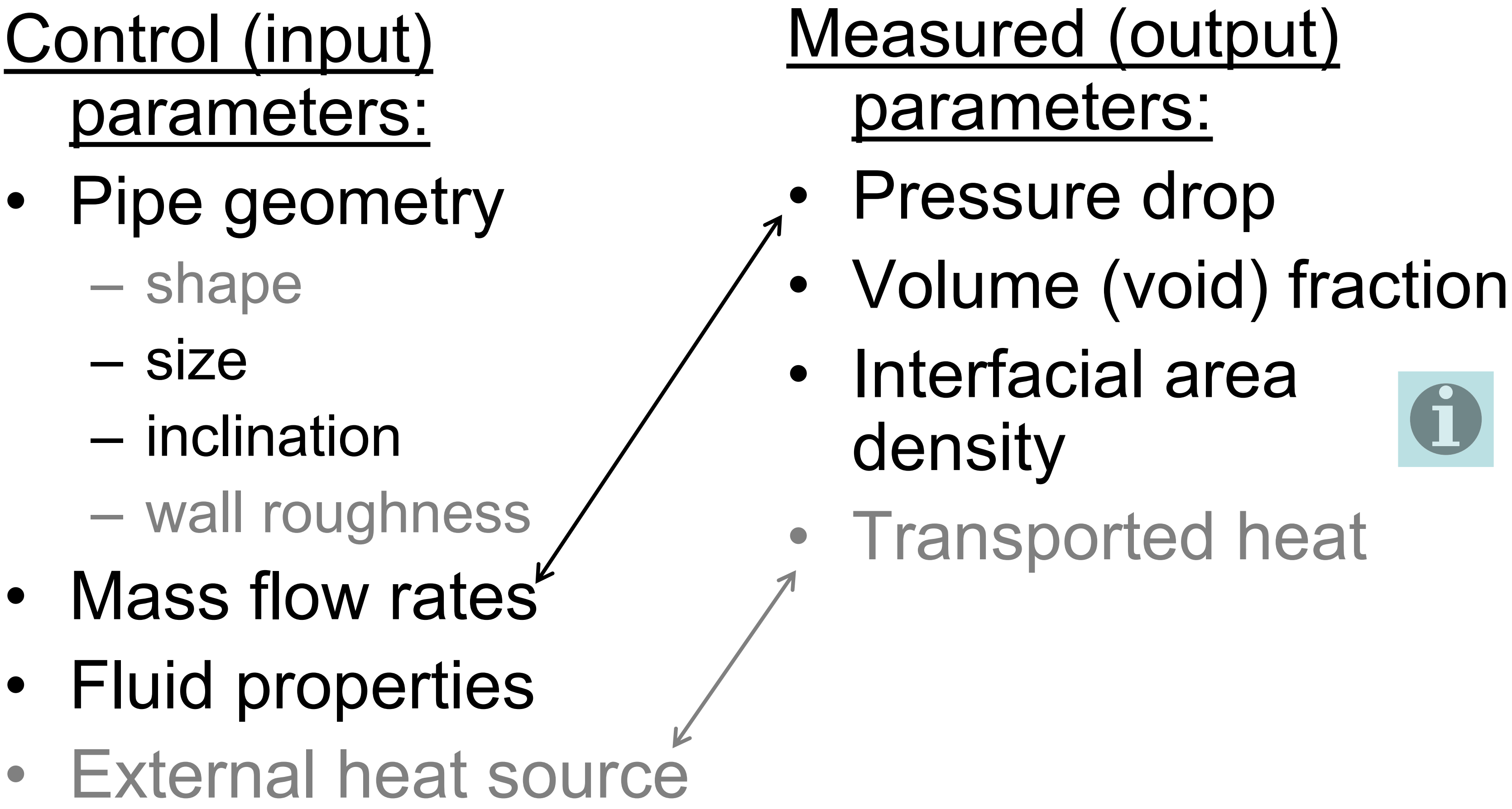
- Pipe geometry
  - shape
  - size
  - ~~inclination~~
  - wall roughness
- Mass flow rate
- Fluid properties
- External heat source

Does not matter if ρ=const

Measured (output) parameters:

- Pressure drop
- Transported heat

Parameters of two-phase pipe flow



<u>Control (input) parameters:</u>

- Pipe geometry
  - shape
  - size
  - inclination
  - wall roughness
- Mass flow rates
- Fluid properties
- External heat source

<u>Measured (output) parameters:</u>

- Pressure drop
- Volume (void) fraction
- Interfacial area density
- Transported heat

Model variables in pipe systems

- Cross sectional integral quantities
  - linear densities
  - flow rates
- Cross sectional average (‘mean`) quantities
  - ‘mean` densities
  - ‘mean` fluxes

Purpose: reduction of independent variables: $(t,x,y,z) \rightarrow (t,x)$

Interfacial (surface) tension

- The origin and interpretation of interfacial/ surface tension (S, σ or γ)
- Interfacial energy:

$$E_{interfacial} = \iint_{interface} \sigma dA \Leftrightarrow \sigma = \frac{E_{interfacial}}{dA} > 0$$

$$dE_{internal} = TdS - pdV + \sigma dA$$

Incomplete without class notes

A gas spontaneously expands.
It is under pressure.

An interface spontaneously shrinks.
It is under tension.

Interfacial area density

- Definition: $\frac{A^{(ij)}}{V_{sample}}$
- If high (e.g. in emulsions), then
  - substantial amount of energy can be stored in the interface
    (interfacial energy density $= \sigma \cdot A^{(ij)} / V_{sample}$)
  - the interface can be treated as a third (extra) phase (being under tension!)

Interfacial area density

- Its importance in chemical engineering: high interfacial energy density increases rate of
  - absorption/desorption,
  - diffusion limited surface reactions,
  - catalytic reactions

Volume fraction

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- Definition:

$$\alpha^{(p)} = \frac{V^{(p)}}{V_{sample}}$$

Volume fractions
in gas—liquid two-phase systems

frequently used alternative notations

- If the volume fraction of the gas phase is used, it is often called <u>void fraction:</u>

$$\varepsilon = \varepsilon_{\mathrm{G}} = \quad \alpha = \alpha^{(\mathrm{g})},\ \ \alpha^{(\ell)} = 1 - \alpha$$

- If the volume fraction of the liquid phase is used, it is often called <u>liquid holdup:</u>

$$h = h_{\mathrm{L}} = \quad \alpha = \alpha^{(\ell)},\ \ \alpha^{(\mathrm{g})} = 1 - \alpha$$

Measurement of volume fraction

Type/definition

- Local (time averaged)

  $$\alpha^{(p)}(x,y,z) = \overline{\alpha^{(p)}(t,x,y,z)}$$

- Chordal averaged
- Cross sectional averaged

  $$\alpha^{(p)}(t,x) = \left\langle \alpha^{(p)}(t,x,y,z) \right\rangle$$

- Volume averaged

  $$\alpha^{(p)}(t;V)$$

Measurement method

- Direct volume/mass measurement
- Optical probe
- Conductivity probe
- Absorption of
  - light
  - X-ray
  - γ-ray
- neutron scattering

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Superficial and phasic velocities

- *Superficial velocity*:

$$\langle u^{(p)} \rangle (t,x) = \frac{\dot{M}^{(p)}(t,x)}{\varrho^{(p)}(t,x) \cdot A(t,x)}$$

- *Phasic* (mean physical) *velocity*:

$$\langle u^{(p)} \rangle^{(p)} (t,x) = \frac{\dot{M}^{(p)}(t,x)}{\varrho^{(p)}(t,x) \cdot A^{(p)}(t,x)}$$

- Relationship:

$$\langle u^{(p)} \rangle (t,x) = \alpha^{(p)}(t,x) \cdot \langle u^{(p)} \rangle^{(p)} (t,x)$$

Incomplete
without class
notes

Balance equations of multiphase pipe flows

- General framework:
  - Mass transport equations
  - Longitudonal momentum transport
  - Energy transport

⚠

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POST-IT NOTES

Usage of thermodynamic relations

Expressing local thermodynamic equilibrium in fluid dynamics:
the use of intensive and extensive state variables

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- Integral forms: intensive and extensive (X)
- Differential forms (PDE’s):
  - fixed control volume (V=const):
    intensive and densities of the extensive ones ($x=X/V$)
  - advected fluid parcel (m=const):
    intensive and specific values of the extensive ones ($x=X/m$)

Notational system for local extensive quantities

- For integral description (in control volumes):
  - extensive quantity: F
- For differential description (local values):
  - density: $\varphi=F/V=\rho\cdot f$
  - specific value $f=F/m$
  - molar value $f=F/n$
  - molecular value $F^{*}=F/N$

Notations to be used (or at least attempted)

- Material derivative of a specific quantity:

$$\frac{Df}{Dt} := \frac{\partial f}{\partial t} + \left(\vec{\mathbf{u}} \cdot \vec{\nabla}\right) f \to D_t f := \partial_t f + \left(\vec{\mathbf{u}} \cdot \vec{\nabla}\right) f$$

Note

Thermodynamical representations

Representation (independent variables)	**TD potential**
entropy and volume (s,1/ρ)	internal energy
temperature and volume (T,1/ρ)	free energy
entropy and pressure (s,p)	enthalpy
temperature and pressure (T,p)	free enthalpy

- All of these are equivalent:
  can be transformed to each other by appropriate formulæ
- Use the one which is most practicable:
  e.g., (s,p) in acoustics: $s = const \Rightarrow \rho(s,p) \rightarrow \rho(p)$.

  We prefer (T,p)

Notations to be used (or at least attempted)

- Phase index (upper):
  - (p) or
  - (s), (ℓ), (g), (v), (f) for solid, liquid, gas , vapour, fluid
- Component index (lower): k
- Coordinate index (lower): i, j or t

Examples: $\boxed{\rho^{(\mathrm{s})},\ c_k^{(p)},\ u_i^{(p)}}$

- Partial differentiation:

$$\boxed{\partial_t,\ \partial_i\,(\partial_1 = \partial_x, \partial_2 = \partial_y, \partial_3 = \partial_z)}$$

Note

Jump of a function

- A point **x** is on a moving interface at *t* (given either implicitly or parametrically).
- The designated normal vector at **x** is **n**.

Then the jump (discontinuity) of a function *f* is:

$$f\left(t,\mathbf{x}+\varepsilon\,\mathbf{n}\right)-f\left(t,\mathbf{x}-\varepsilon\,\mathbf{n}\right)\xrightarrow[\varepsilon\to 0]{}\left[f\left(t,\mathbf{x}\right)\right]$$