Multiphase and Reactive Flow Modelling

BMEGEÁT(MW17|MG27)

Part 1

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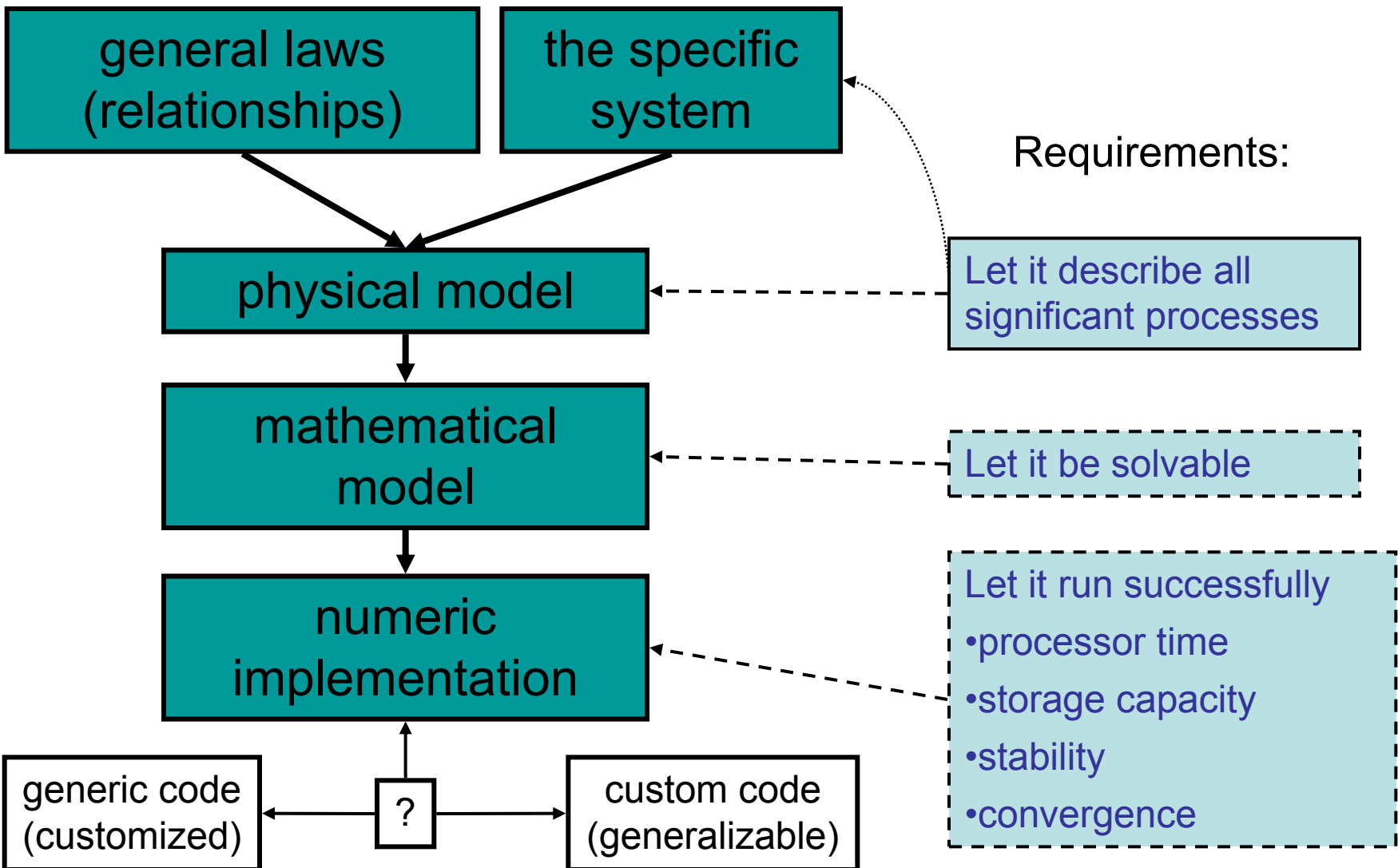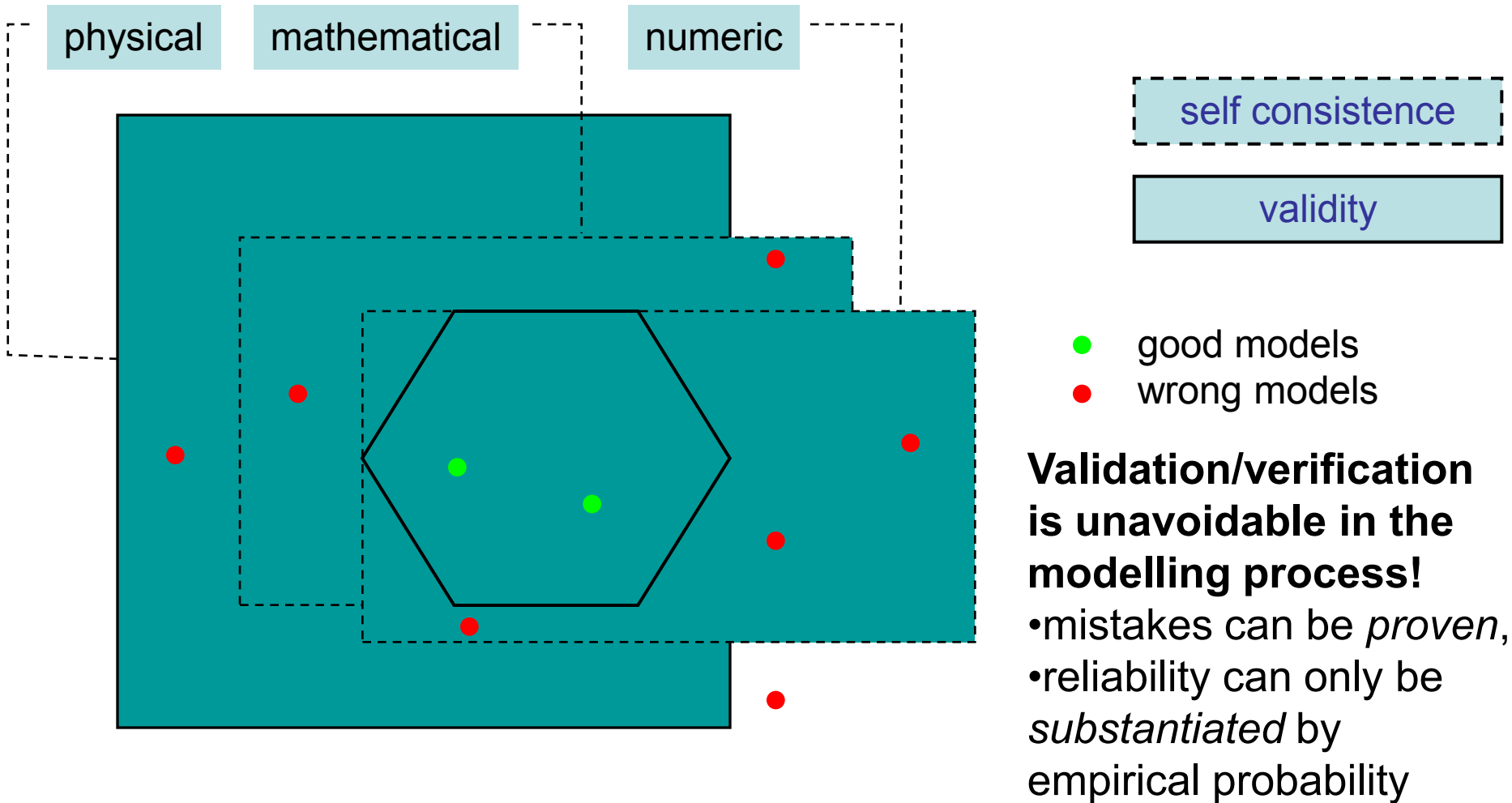Faculty of Civil Engineering

Contents

What is modelling?

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

Model layers

general laws (relationships)

the specific system

Requirements:

physical model

Let it describe all significant processes

mathematical model

Let it be solvable

numeric implementation

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

generic code (customized)

?

custom code (generalizable)

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

Basic notions and terminology

Ordinary phases:

preserve volume

Condensed phases

– Solid ← preserves shape

– Liquid   Fluid phases

expands → – Gaseous   deform

There also exist extraordinary phases, like plastics 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.

Modelled features:

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

Mass point model

Rigid body model

The simplest continuum model

Even more complex models

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 $\; p(t,\vec{\mathbf{r}}),\; \vec{\mathbf{u}}(t,\vec{\mathbf{r}}) \text{ and } T(t,\vec{\mathbf{r}})$ ← Primary (direct) field variables

  - Constitutive equations

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

- Boundary conditions   Secondary (indirect) field variables

  On explicitly or implicitly specified surfaces

- Initial conditions

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

Incomplete without class notes

- 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 ($x=X/m$)

Thermodynamical representations

Representation (independent variables)	TD potential
entropy and volume $(s, 1/\rho)$	internal energy
temperature and volume $(T, 1/\rho)$	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)

Note

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
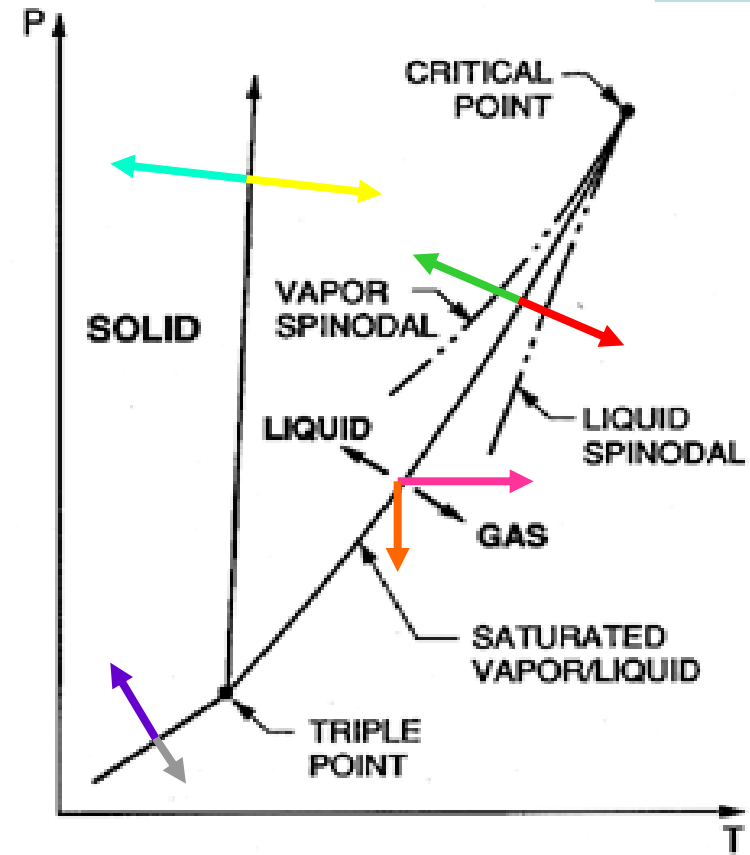## in case of a single compound

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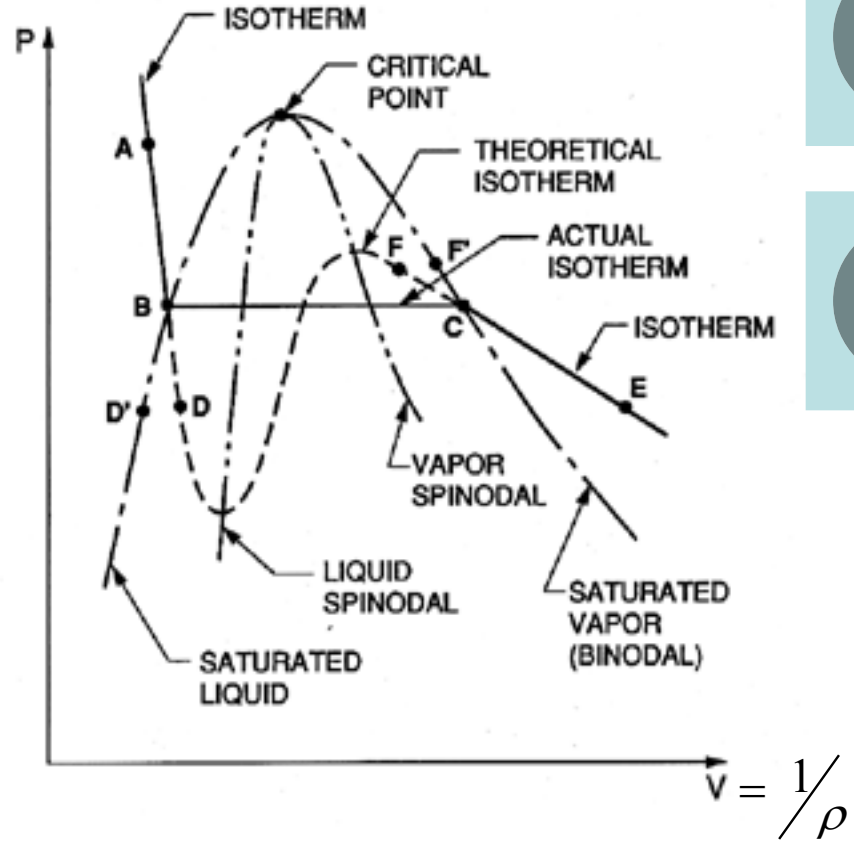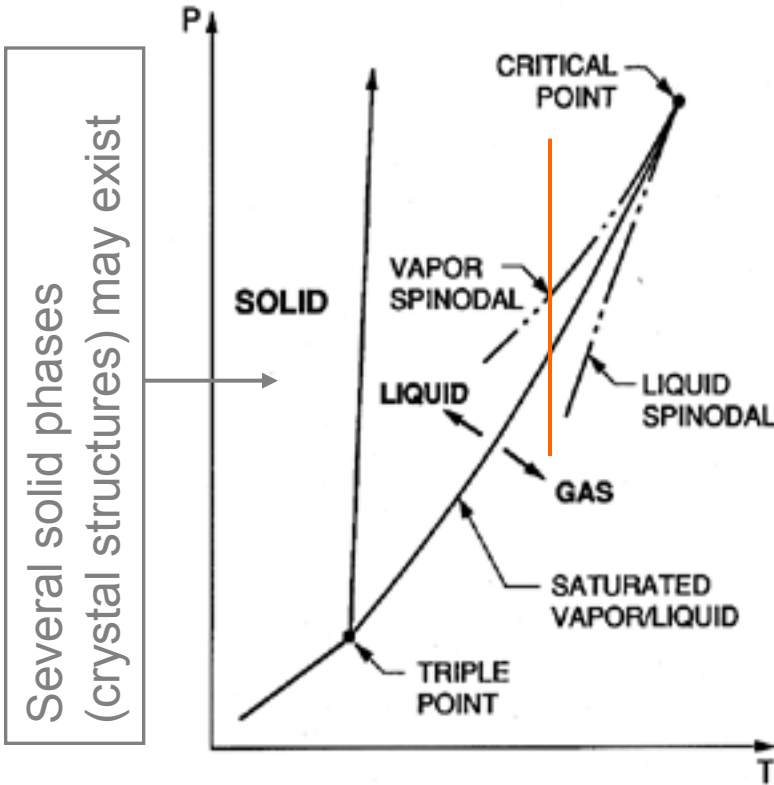 - Liquefaction
  - Solidification
- Sublimation
- Freezing
- Melting

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 <u>explicit</u> 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!)
$$c_1 = m_1/m, \quad c_2 = m_2/m, \dots \quad c_k = m_k/m, \dots \quad \sum_k c_k = \sum_k m_k/m = 1$$

– Volume fraction (used in CFD and if volume is conserved upon mixing!)
$$\alpha_1 = V_1/V, \quad \alpha_2 = V_2/V, \dots \quad \alpha_k = V_k/V, \dots \quad \sum_k \alpha_k = \sum_k V_k/V = 1$$

– Mole fraction (used in case of chemical reactions and diffusion)
$$y_1 = n_1/n, \quad y_2 = n_2/n, \dots \quad y_k = n_k/n, \dots \quad \sum_k y_k = \sum_k n_k/n = 1$$

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.

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

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

- Partial differentiation:

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

Note

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

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:

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

    $p^{(1)} = p^{(2)} = \ldots = p^{(N)} =: p$ $2N \rightarrow$ 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*:

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

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. <u>Surface tension</u> (gas-liquid interface)
2. <u>Interfacial tension</u> (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.

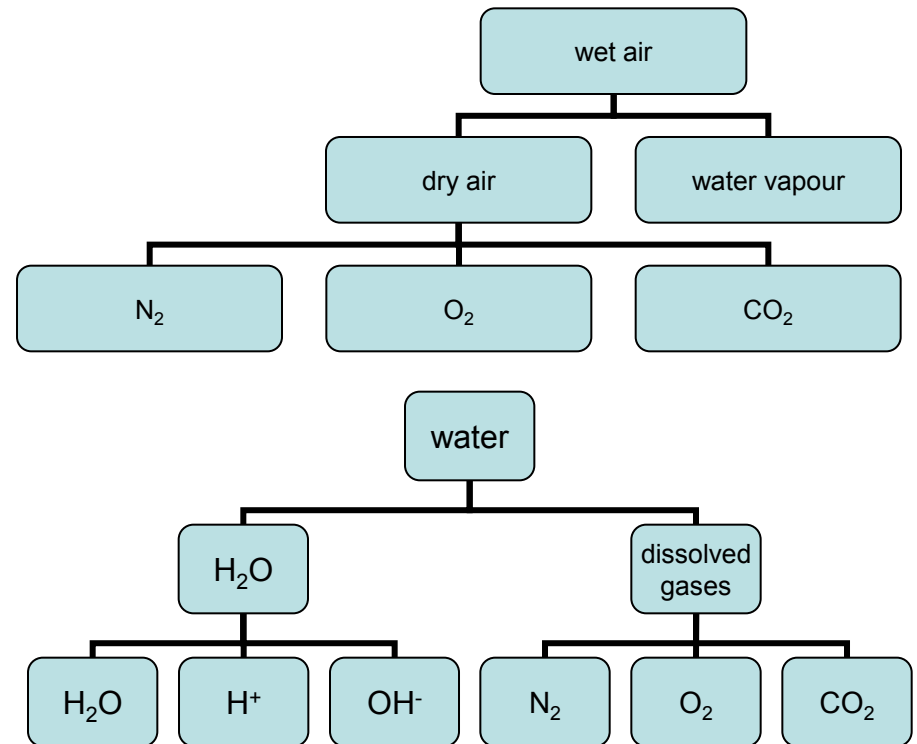(Local deviation from total TD equilibrium is typical)

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

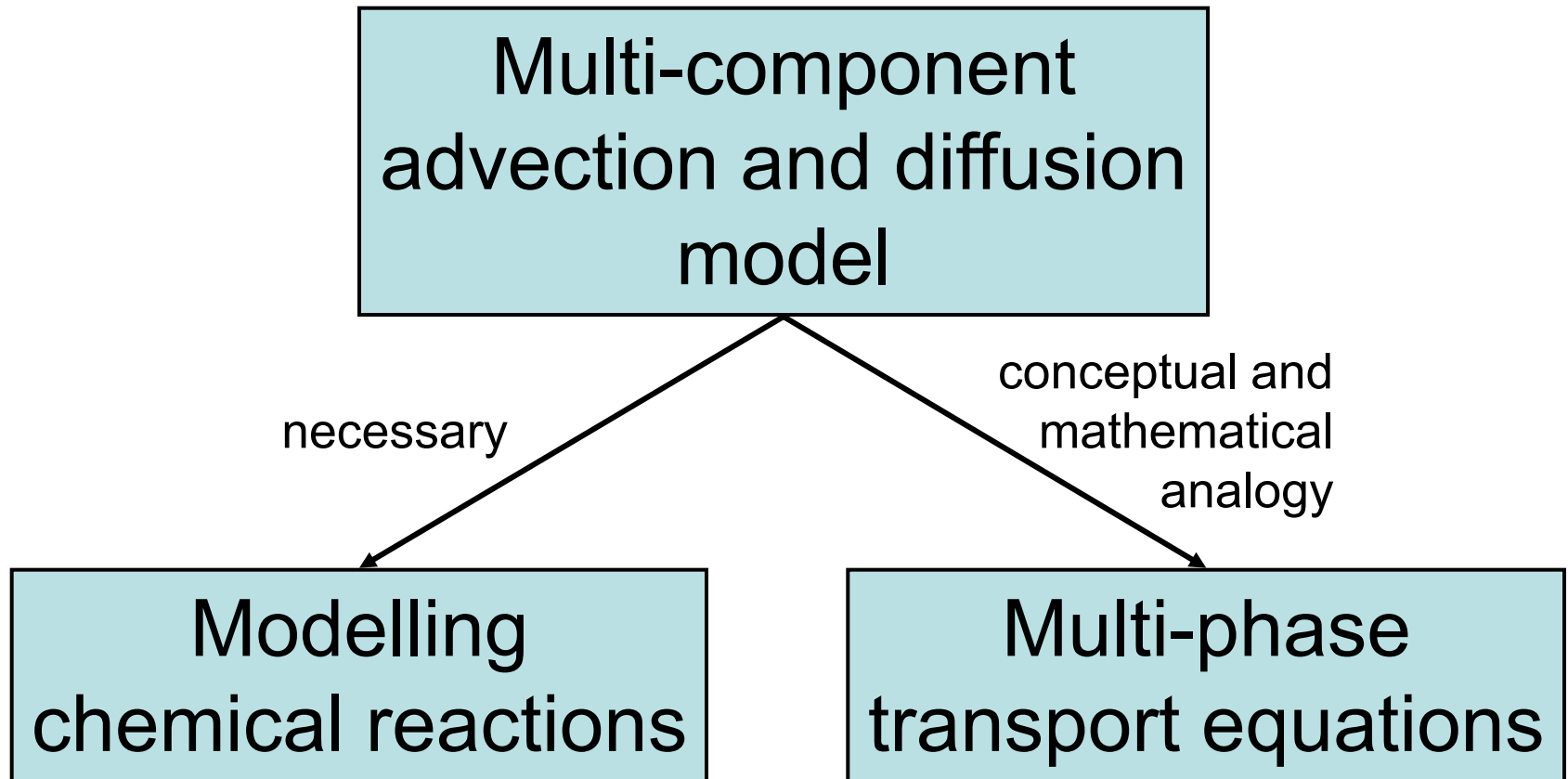 - The grouping can be refined in the course of the modelling

Example: components in an air-water two phase system

Multi-component transport

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

Multi-component advection and diffusion model

necessary

conceptual and mathematical analogy

Modelling chemical reactions

Multi-phase transport equations

Multi-component transport
Outline

- Balance equations

- Mass balance — equation of continuity

- Component balance

- Advection

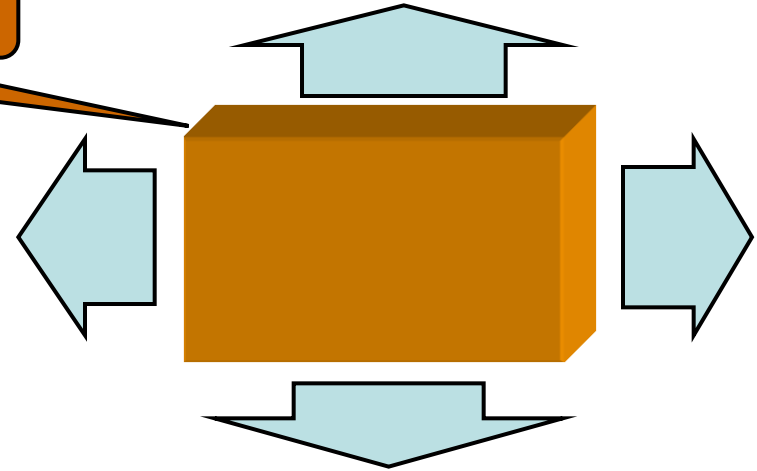- Molecular diffusion

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

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: $\dfrac{dm}{dt} = -J(t) + Q(t)$

Mass balance equation

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

By definition:

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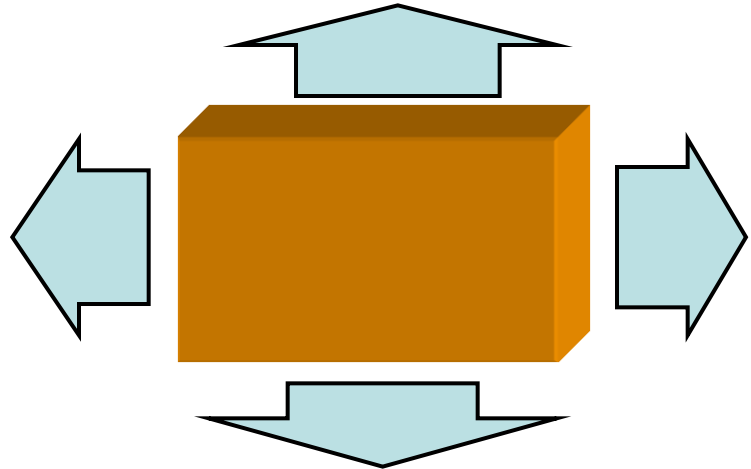
Component mass balance

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

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

These are also conservation laws

Mass balance equations $\quad \updownarrow \qquad \updownarrow \qquad \updownarrow$

By definition:

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

The mass transport equations

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

$$\sum_k \Uparrow$$

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

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

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

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

$$\Updownarrow$$

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

advection   **diffusion**

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

$$\forall k: D_t c_k = \partial_t c_k + \vec{\mathbf{u}}\vec{\nabla}c_k = -\frac{1}{\rho}\vec{\nabla}\vec{\mathbf{j}}_{\mathrm{diff}\,k} \qquad \sum_k \vec{\mathbf{j}}_{\mathrm{diff}\,k} = \sum_k \rho_k \vec{\mathbf{w}}_k = \vec{\mathbf{0}}$$

Notations to be used (or at least attempted)

- Material derivative of a specific quantity:

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

Note

Two ways of resolving redundancy

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

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

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

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

$$\rho\left(t,\vec{\mathbf{x}}\right) = \sum_k \rho_k\left(t,\vec{\mathbf{x}}\right) \qquad c_1\left(t,\vec{\mathbf{x}}\right) = 1 - \sum_{k=2}^{K} c_k\left(t,\vec{\mathbf{x}}\right)$$

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

Typically, this is the solvent

For a binary mixture:
$$c_2\left(t,\vec{\mathbf{x}}\right) =: c\left(t,\vec{\mathbf{x}}\right)$$
$$c_1\left(t,\vec{\mathbf{x}}\right) = 1 - c\left(t,\vec{\mathbf{x}}\right)$$

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

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

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

  – only convective flux
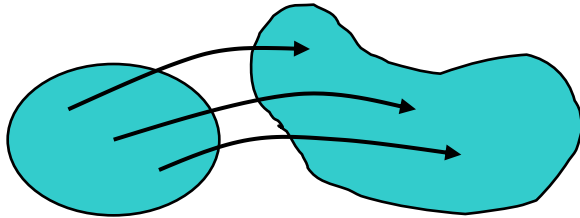
  $$\partial_t \varphi + \vec{\nabla}(\vec{\mathbf{u}} \cdot \varphi) = 0$$

  $$\Downarrow \text{if } m \text{ is conserved}$$

- equation for the specific value (f)

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

These forms describe <u>passive advection</u> 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>

  $$\vec{\mathbf{j}}_{\text{diff } k} = \vec{\mathbf{0}}$$

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

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

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

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

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

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

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

Turbulent mixing

Fick's 2nd Law:
$$\partial_t c_k = D_k \nabla^2 c_k$$

Further diffusion models

Thermodiffusion and/or barodiffusion

Occur(s) at

- high concentrations
- high T and/or p gradients

For a binary mixture:

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

$D \cdot k_T$: coefficient of thermodiffusion

$D \cdot k_p$: coefficient of barodiffusion

Analogous cross effects appear in the heat conduction equation

Further diffusion models

Nonlinear diffusion model

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.)

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

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

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

$$K_{kk} = 0$$

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

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

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

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

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

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

The advection–diffusion equations

local rate of change	advective flux	diffusive flux
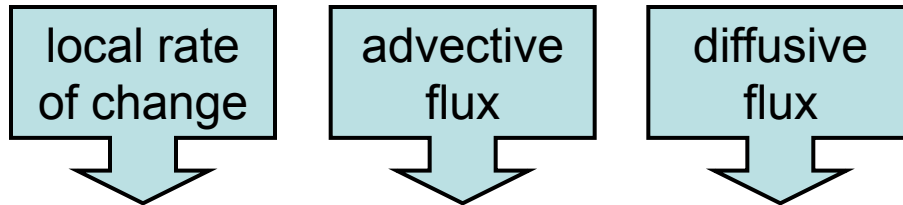
$$\partial_t\left(\rho\cdot c_k\right)+\vec{\nabla}\left(\vec{\mathbf{u}}\cdot\rho\cdot c_k\right)=-\vec{\nabla}\cdot\vec{\mathbf{j}}_k$$
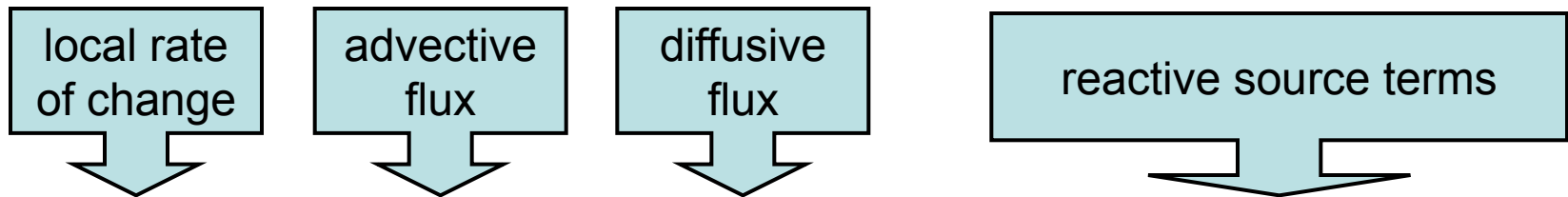
$\updownarrow$ since m is conserved

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

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

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

$\Updownarrow$ since m is conserved

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

The component masses are *not conserved* quantities

Reaction modelling OUTLINE

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

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

Energetics

forward reaction: $\Delta E>0$ energy released → *exothermic*

reverse reaction: $\Delta E<0$ energy consumed → *endothermic*

A binary reaction
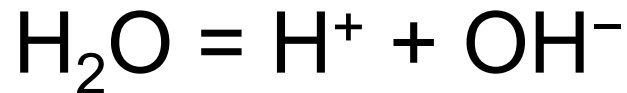
Stoichiometry

forward reaction

reactant → products

$H_2O = H^+ + OH^-$

product ← reactants

reverse reaction

$$\forall k : \left| \nu_k \right| = 1$$

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

A template reaction

Stoichiometry

forward reaction

reactants $\rightarrow$ product

2 H_2 + O_2 = 2 H_2O

products $\leftarrow$ reactant

reverse reaction

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

Reaction stoichiometry

Stoichiometric constants

- *forward reaction:*

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

  $v_1 = +2, \ v_2 = -1, \ v_3 = -2$

- *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*: $v_k = 0$

$$\sum_k v_k \neq 0$$

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

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

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*: $v_k = 0$

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

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

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

Reactive source terms

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

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

probability of the simultaneous presence of all reactant molecules

probability of the transition at the prevailing temperature

!

Incomplete without class notes

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 $F^* = F/N$