

Multiphase and Reactive Flow Modelling

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Part 1

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Active controls in this slide show

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MODELLING CONCEPTS

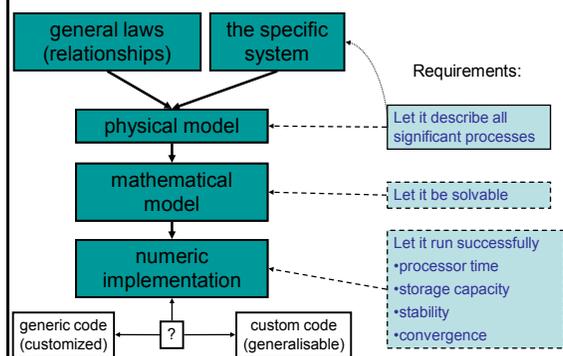


What is modelling?

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



Model layers



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 ← preserves shape
- Liquid
- Gaseous → expands

Condensed states ← preserve volume

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.

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)
 - Thermostatistics: thermal equilibrium (homogenous state)
2. Dynamics
 1. Mechanical dynamics: motion governed by deviation from equilibrium of forces
 2. Thermodynamics 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 $p(t, \vec{r})$, $\vec{u}(t, \vec{r})$ and $T(t, \vec{r})$ ← Primary (direct) field variables
 - Constitutive equations
 - Algebraic equations for $\rho(p, T)$, $\eta(p, T)$, $k(p, T)$, ...
- Boundary conditions ← Secondary (indirect) field variables
 - 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)
- $\rho(p, T), \mu(p, T), k(p, T), \dots$ → 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 latent heat 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!)
 $c_1 = m_1/m, c_2 = m_2/m, \dots, c_k = m_k/m, \dots, \sum_k c_k = \sum_k m_k/m = 1$
- Volume fraction (used in CFD and if volume is conserved upon mixing!)
 $\alpha_1 = V_1/V, \alpha_2 = V_2/V, \dots, \alpha_k = V_k/V, \dots, \sum_k \alpha_k = \sum_k V_k/V = 1$
- Mole fraction (used in case of chemical reactions and diffusion)
 $y_1 = n_1/n, y_2 = n_2/n, \dots, y_k = n_k/n, \dots, \sum_k y_k = \sum_k n_k/n = 1$



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.

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



Material properties in multi-component mixtures

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

For each phase (*p*) one needs to know:

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



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:
 $T^{(1)} = T^{(2)} = \dots = T^{(N)} =: T$
 $p^{(1)} = p^{(2)} = \dots = p^{(N)} =: p \quad 2N \rightarrow \text{only 2 independent unknowns}$
- Mass balance for each component among all phases:

$$\begin{aligned} \mu_1^{(1)}(T, p, c_1^{(1)}, \dots, c_K^{(1)}) &= \mu_1^{(2)}(T, p, c_1^{(2)}, \dots, c_K^{(2)}) = \dots = \mu_1^{(N)}(T, p, c_1^{(N)}, \dots, c_K^{(N)}) \\ \mu_2^{(1)}(T, p, c_1^{(1)}, \dots, c_K^{(1)}) &= \mu_2^{(2)}(T, p, c_1^{(2)}, \dots, c_K^{(2)}) = \dots = \mu_2^{(N)}(T, p, c_1^{(N)}, \dots, c_K^{(N)}) \\ &\vdots \\ \mu_K^{(1)}(T, p, c_1^{(1)}, \dots, c_K^{(1)}) &= \mu_K^{(2)}(T, p, c_1^{(2)}, \dots, c_K^{(2)}) = \dots = \mu_K^{(N)}(T, p, c_1^{(N)}, \dots, c_K^{(N)}) \end{aligned}$$

$K(N-1)$ 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 \rightarrow
 Typically there is at most 1 contiguous gas phase
- Liquids maybe miscible or immiscible \rightarrow
 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)

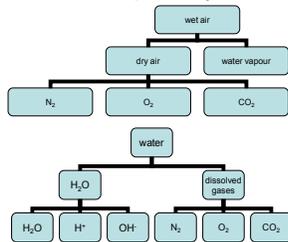


Are components = chemical species?

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

Modelling chemical reactions

conceptual and mathematical analogy for

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

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

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

Mass balance equation

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

By definition:

Component mass balance

For each component:

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

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

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

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

By definition:

The mass transport equations

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

$\sum_k \uparrow$

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

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

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

$\partial_t(c_k \rho) + \vec{\nabla}(c_k \rho \vec{u}) = -\vec{\nabla}(\rho_k \vec{w}_k) = -\vec{\nabla} \cdot \vec{j}_{diff k} \leftarrow \vec{j}_{diff k} := \rho_k \vec{w}_k$

advection diffusion

$c_k [\partial_t \rho + \vec{\nabla}(\rho \vec{u})] + \rho [\partial_t c_k + \vec{u} \cdot \vec{\nabla} c_k] = -\vec{\nabla} \cdot \vec{j}_{diff k}$

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

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

Two ways of resolving redundancy

- Pick exactly K mass transport equations and choose the K primary variables as follows:
 - $k = 1, \dots, K: \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{u}) = -\vec{\nabla} \cdot \vec{j}_{diff k}$
 - $k = 2, \dots, K: D_t c_k = -(1/\rho) \vec{\nabla} \cdot \vec{j}_{diff k}$
- If needed, calculate the remaining secondary variable fields from the algebraic relations:
 - $\rho(t, \vec{x}) = \sum_k \rho_k(t, \vec{x})$
 - $c_k(t, \vec{x}) = \rho_k(t, \vec{x}) / \rho(t, \vec{x})$
 - $c_1(t, \vec{x}) = 1 - \sum_{k=2}^K c_k(t, \vec{x})$
 - $\rho_k(t, \vec{x}) = \rho(t, \vec{x}) \cdot c_k(t, \vec{x})$

Typically, this is the solvent

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

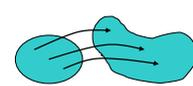
Differential forms in balance equations

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

- equations for the density (φ)
 - general: $\partial_t \varphi + \vec{\nabla} \cdot \vec{j}_F = 0$
 - if $\vec{j}_F = \vec{u} \cdot \varphi$: $\partial_t \varphi + \vec{\nabla}(\vec{u} \cdot \varphi) = 0$
 - if m is conserved: $D_t f \equiv \partial_t f + (\vec{u} \cdot \vec{\nabla}) f = 0$
- equation for the specific value (f)

These forms describe passive advection of F

Passive advection



- Computational advantage: The component transport equations uncouple from the basic fluid dynamical problem and can be solved separately and *a posteriori*
- The concentrations of the fluid particles do not change with time: $D_t c_k \equiv \partial_t c_k + (\vec{u} \cdot \vec{\nabla}) c_k = 0$
- The component densities vary in fixed proportion to the overall density: $\partial_t \rho_k + \vec{\nabla}(\rho_k \vec{u}) = 0$
- The solution requires
 - Lagrangian particle orbits
 - Initial conditions (hyperbolic equations)

Simple diffusion models

- No diffusion → pure advection

i $\vec{j}_{diff,k} = \vec{0}$ $\left\{ \begin{array}{l} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{u}) = 0 \\ D_k c_k = 0 \end{array} \right.$

- Turbulent mixing** → Equimolecular counter-diffusion

$\vec{j}_{diff,k} = -\rho D \vec{\nabla} c_k$ for constant D and $\rho \rightarrow \left\{ \begin{array}{l} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{u}) = D \nabla^2 \rho_k \\ D_k c_k = D \nabla^2 c_k \end{array} \right.$

- Fick's 1st Law

for each solute if $c_k \ll 1$ ($k = 2, \dots, K$)

$\vec{j}_{diff,k} = -\rho D_k \vec{\nabla} c_k$ constant D_k and $\rho \rightarrow \left\{ \begin{array}{l} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{u}) = D_k \nabla^2 \rho_k \\ D_k c_k = D_k \nabla^2 c_k \end{array} \right.$

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

$\vec{j}_{diff} = -\rho D(\nabla c + (k_T/T)\nabla T + (k_p/p)\nabla p)$
 $D \cdot k_T$: 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.)

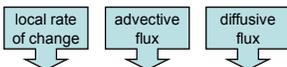
$\vec{j}_{diff,k} = \rho \cdot \sum_{\ell \neq k} \frac{M_\ell}{M} \cdot \frac{\vec{K}_{\ell k} - \vec{K}_{k\ell}}{\det(\mathbf{K})} \cdot \vec{\nabla} y_\ell$
 $\vec{K} = \text{adj}(\mathbf{K})$
 $K_{k\ell} = \frac{y_\ell}{D_{k\ell}} + \frac{M_\ell}{M_k} \cdot \sum_{s \neq k} \frac{y_s}{D_{ks}}$ if $k \neq \ell$
 $K_{kk} = 0$
 $y_k = \frac{M}{M_k} \cdot c_k$: mole fraction
 $M = \sum_k y_k M_k$: mean molar mass
 $D_{k\ell}$: binary diffusion coefficient t
 $D_{k\ell}(T, n_s, M_k, M_\ell) = D_{\ell k}$

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

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

The advection–diffusion equations



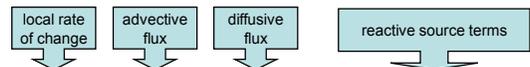
$\partial_t(\rho \cdot c_k) + \vec{\nabla}(\vec{u} \cdot \rho \cdot c_k) = -\vec{\nabla} \cdot \vec{j}_k$
 \Downarrow since m is conserved

$D_k c_k \equiv \partial_t c_k + (\vec{u} \cdot \vec{\nabla}) c_k = -\frac{1}{\rho} \vec{\nabla} \cdot \vec{j}_k$ ← e.g. $D \cdot \nabla^2 c_k$

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



The advection–diffusion–reaction equations



$\partial_t(\rho \cdot c_k) + \vec{\nabla}(\vec{u} \cdot \rho \cdot c_k) = -\vec{\nabla} \cdot \vec{j}_k + (\text{mass production rate density})$
 \Downarrow since m is conserved

$D_k c_k \equiv \partial_t c_k + (\vec{u} \cdot \vec{\nabla}) c_k = -\frac{1}{\rho} \vec{\nabla} \cdot \vec{j}_k + (\text{local specific production rate})$ **i**

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 stochastic processes 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

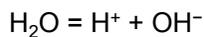


A binary reaction

Stoichiometry

forward reaction

reactant → products



product ← reactants

reverse reaction

$$\forall k : |v_k| = 1$$

Reagents and reaction products	
k	species
1	H ₂ O
2	H ⁺
3	OH ⁻

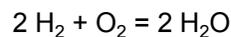


A template reaction

Stoichiometry

forward reaction

reactants → product



products ← reactant

reverse reaction

Reagents and reaction products	
k	species
1	H ₂ O
2	O ₂
3	H ₂



Reaction stoichiometry

Stoichiometric constants

- *forward reaction*:
 $+2 \cdot \text{H}_2\text{O} - 1 \cdot \text{O}_2 - 2 \cdot \text{H}_2 = 0$
 $v_1 = +2, v_2 = -1, v_3 = -2$
- *reverse reaction*:
 $-2 \cdot \text{H}_2\text{O} + 1 \cdot \text{O}_2 + 2 \cdot \text{H}_2 = 0$
 $v_1 = -2, v_2 = +1, v_3 = +2$
- for reactants: $v_k < 0$,
- for reaction products: $v_k > 0$
- for catalysts: $v_k = 0$

$$\sum_k v_k \neq 0$$

Reagents and reaction products	
k	species
1	H ₂ O
2	O ₂
3	H ₂

The number of molecules is not conserved



Reaction stoichiometry

Stoichiometric constants

- *forward reaction*:
 $+2 \cdot \text{H}_2\text{O} - 1 \cdot \text{O}_2 - 2 \cdot \text{H}_2 = 0$
 $v_1 = +2, v_2 = -1, v_3 = -2$
- *reverse reaction*:
 $-2 \cdot \text{H}_2\text{O} + 1 \cdot \text{O}_2 + 2 \cdot \text{H}_2 = 0$
 $v_1 = -2, v_2 = +1, v_3 = +2$
- for reactants: $v_k < 0$,
- for 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 ₂ O
2	O ₂
3	H ₂

BUT: the total mass is conserved



Reactive source terms

Incomplete without class notes

One reaction process: $\forall k: \frac{dn_k}{dt} = v_k \cdot \dot{\xi}$
reaction rate

Several reactions: $\forall k: \frac{dn_k}{dt} = \sum_{[r]} v_{k[r]} \cdot \dot{\xi}_{[r]}$
reaction rate vector

Possible units:

- mol/s, $\rightarrow \forall k: \frac{dn_k}{dt} = M_k \cdot \sum_{[r]} v_{k[r]} \cdot \dot{\xi}_{[r]} = Q_k(t)$
- (mol/m³)/s, $\rightarrow \forall k: \frac{d\rho_k}{dt} = M_k \cdot \sum_{[r]} v_{k[r]} \cdot \dot{\xi}_{[r]}$
- (mol/kg)/s, $\rightarrow \forall k: \frac{dc_k}{dt} = M_k \cdot \sum_{[r]} v_{k[r]} \cdot \dot{\xi}_{[r]}$

reactive source terms

An alternative formulation:

summation over reaction pairs instead of individual reactions

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

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

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

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

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

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

$$\dot{\xi}_{[r]} \propto \left[\prod_i (c_i)^{v_i} \right] \cdot \exp\left(-\frac{E_{act}[r]}{R \cdot T}\right)$$

probability of the simultaneous presence of all reactant molecules

probability of the transition at the prevailing temperature

Typically, v_i are the stoichiometric coefficients of the reactants

Incomplete without class notes

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

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

Flow direction →

Benjamin bubble

Vertical gas-liquid flow patterns

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

Taylor bubble

See videos at www.thermopedia.com/videos

The effect of pipe inclination

$\Theta = +10^\circ$

□	STRATIFIED SMOOTH (SS)	STRATIFIED (S)
■	STRATIFIED WAVY (SW)	STRATIFIED (S)
○	ELONGATED BUBBLE (EB)	INTERMITTENT (I)
●	SLUG (SL)	INTERMITTENT (I)
△	ANNULAR (A)	ANNULAR (A)
▲	WAVY ANNULAR (AW)	ANNULAR (A)
▼	DISPERSED BUBBLE (DB)	

The effect of pipe inclination

$\Theta = +2^\circ$

□	STRATIFIED SMOOTH (SS)	STRATIFIED (S)
■	STRATIFIED WAVY (SW)	STRATIFIED (S)
○	ELONGATED BUBBLE (EB)	INTERMITTENT (I)
●	SLUG (SL)	INTERMITTENT (I)
△	ANNULAR (A)	ANNULAR (A)
▲	WAVY ANNULAR (AW)	ANNULAR (A)
▼	DISPERSED BUBBLE (DB)	

The effect of pipe inclination

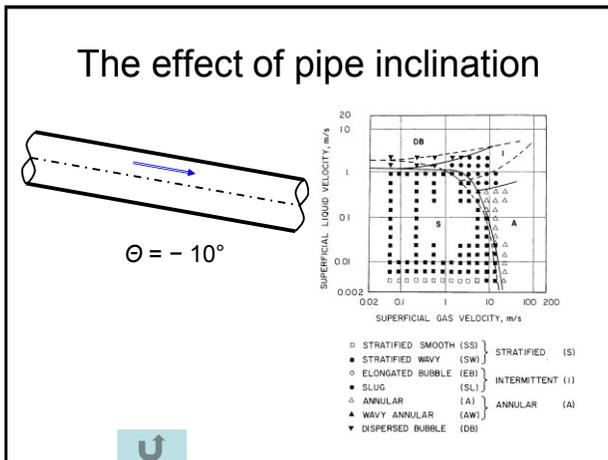
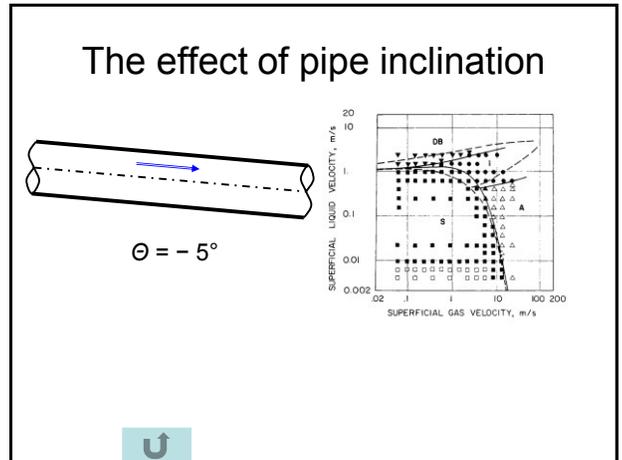
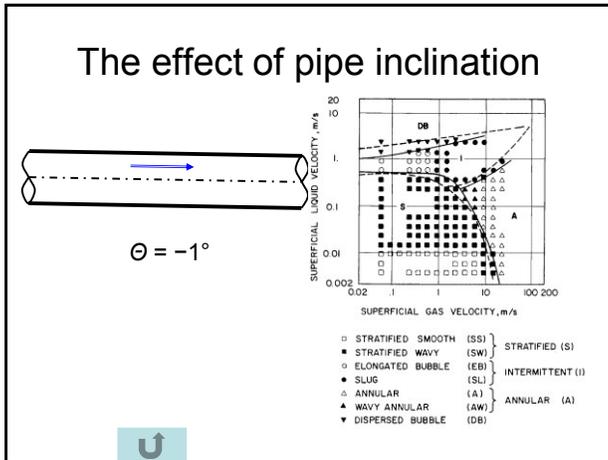
$\Theta = +0.25^\circ$

□	STRATIFIED SMOOTH (SS)	STRATIFIED (S)
■	STRATIFIED WAVY (SW)	STRATIFIED (S)
○	ELONGATED BUBBLE (EB)	INTERMITTENT (I)
●	SLUG (SL)	INTERMITTENT (I)
△	ANNULAR (A)	ANNULAR (A)
▲	WAVY ANNULAR (AW)	ANNULAR (A)
▼	DISPERSED BUBBLE (DB)	

The effect of pipe inclination

$\Theta = 0^\circ$

□	STRATIFIED SMOOTH (SS)	STRATIFIED (S)
■	STRATIFIED WAVY (SW)	STRATIFIED (S)
○	ELONGATED BUBBLE (EB)	INTERMITTENT (I)
●	SLUG (SL)	INTERMITTENT (I)
△	ANNULAR (A)	ANNULAR (A)
▲	WAVY ANNULAR (AW)	ANNULAR (A)
▼	DISPERSED BUBBLE (DB)	



- 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

Measured (output) parameters:

- Pressure drop
- Transported heat

Does not matter if $p = \text{const}$



Parameters of two-phase pipe flow

Control (input) parameters:

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

Measured (output) parameters:

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



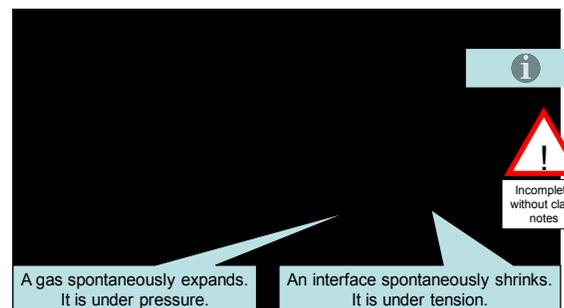
Model variables in pipe systems

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

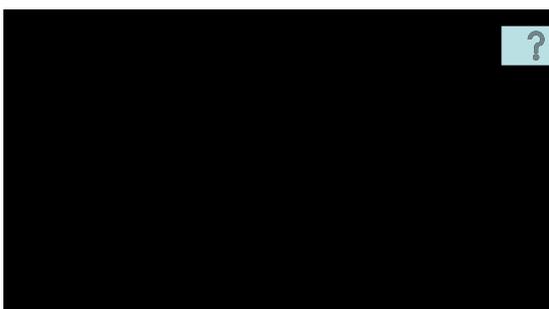
Purpose: reduction of independent variables: $(t, x, y, z) \rightarrow (t, x)$



Interfacial (surface) tension



Interfacial area density



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

- Definition:

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








Volume fractions in gas—liquid two-phase systems

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

$$\varepsilon = \varepsilon_G = \alpha = \alpha^{(g)}, \alpha^{(l)} = 1 - \alpha$$
- If the volume fraction of the liquid phase is used, it is often called liquid holdup:

$$h = h_L = \alpha = \alpha^{(l)}, \alpha^{(g)} = 1 - \alpha$$






Measurement of volume fraction

Type/definition	Measurement method
<ul style="list-style-type: none"> Local (time averaged) $\alpha^{(p)}(x, y, z) = \overline{\alpha^{(p)}(t, x, y, z)}$ Chordal averaged Cross sectional averaged $\alpha^{(p)}(t, x) = \langle \alpha^{(p)}(t, x, y, z) \rangle$ Volume averaged $\alpha^{(p)}(t; V)$ 	<ul style="list-style-type: none"> Direct volume/mass measurement Optical probe Conductivity probe Absorption of <ul style="list-style-type: none"> – light – X-ray – γ-ray neutron scattering






Superficial and phasic velocities

- Superficial velocity*:

$$\langle u^{(p)} \rangle(t, x) = \frac{\dot{M}^{(p)}(t, x)}{\rho^{(p)}(t, x) \cdot A(t, x)}$$
- Phasic (mean physical) velocity*:

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

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






Balance equations of multiphase pipe flows

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








POST-IT NOTES





Usage of thermodynamic relations

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

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



Note



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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 $F^* = F/N$



Note



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Notations to be used (or at least attempted)

- Material derivative of a specific quantity:

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



Note



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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 formulae
- Use the one which is most practicable:
e.g., (s, p) in acoustics: $s = \text{const} \Rightarrow \rho(s, p) \rightarrow \rho(p)$.

We prefer (T, p)



Note



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

- Partial differentiation:

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



Note



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Jump of a function

- A point \mathbf{x} is on a moving interface at t (given either implicitly or parametrically).
 - The designated normal vector at \mathbf{x} is \mathbf{n} .
- Then the jump (discontinuity) of a function f is:

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



Note



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