Diffusion

Consider a two-component fluid or gas, e.g., $N_2 + O_2$ (air)

<u>component 1:</u>

$\rho_1 = \rho c_1$ is the mass density

$c_1 = c$ is the (mass) concentration

<u>component 2:</u>

$\rho_2 = \rho c_2$,

$c_2 = 1 - c$

Total mass density: $\underline{\rho = \rho_1 + \rho_2}$, where $\underline{c_1 + c_2 = 1}$.

Total mass is conserved: $\boxed{\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho v) = 0}$ continuity eq.

In the ideal flow: concentration is in equilibrium and does not change.

$$\Rightarrow \frac{dc}{dt} = 0 \quad \Rightarrow \quad \frac{\partial c}{\partial t} + v \cdot \nabla c = 0 \quad \text{(transport eq.)}$$

Using the continuity eq.: $\boxed{\frac{\partial \rho c}{\partial t} + \operatorname{div}(\rho c v) = 0}$

conservation of component 1 with the <u>flux $\rho c v$</u>.

Diffusion is a nonstationary process: different components flow with different speeds.: $\underbrace{\text{flux}_1}_{\text{flux of comp. 1}} = \underbrace{\rho c v}_{\text{fluid motion}} + \underbrace{i_1}_{\text{flux due to diffusion}}$

For the second component, because of mass conservation:

$$\text{flux}_2 = \rho(1-c)v + i_2 \quad \text{with} \quad \underline{i_1 + i_2 = 0}.$$

The diffusion flux depends (in the first-approximation) on the local gradients of thermodynamic quantities,

$$\underbrace{\nabla c}_{\text{inhomogeneous mixture} \to \text{diffusion}} \qquad \underbrace{\nabla T}_{\text{thermal diffusion}} \qquad \underbrace{\nabla P}_{\text{barodiffusion}}$$

Considering only ∇c, we define $i_1 = -\rho \underbrace{D}_{\text{mass diffusion coefficient}} \nabla c$

<u>Obs</u> In general, $D = D(T, P, c)$ depends on all thermodynamic quantities defining the equilibrium. ~~quantities~~

<u>Resulting eq.</u>

$$\boxed{\frac{\partial \rho c}{\partial t} + \operatorname{div}(\rho c v) = \operatorname{div}(\rho D \nabla c)}$$

If $D \simeq$ const and $\rho \simeq$ const, we obtain

$$\boxed{\frac{\partial c}{\partial t} + \operatorname{div} c v = D \Delta c}$$

Diffusion leads to the increase of entropy (produces heat) $\Rightarrow$ extra terms in the heat transport eq. However, it is usually small and ignored.

Another non-equilibrium process is <u>chemical reaction</u>

$$\mu_A A + \mu_B B \rightarrow \mu_c C \qquad (2H_2 + O_2 \rightarrow 2H_2O)$$

$$\mu_A = 2, \ \mu_B = 1, \ \mu_c = 2.$$

Reaction rate W $\left(\frac{\text{moles}}{s \cdot m^3}\right)$, per unit time and volume.

<u>Obs</u> $W = W(c_A, c_B, T, P)$ depends on concentrations ~~and~~, temperature, etc

Reaction rate leads to mass changes for ~~each~~ reacting components:

$$A: \ -\mu_A M_A W, \quad B: \ -\mu_B M_B W, \quad C: \ +\mu_c M_c W,$$

where M_A, M_B and M_c are molar masses $\left(\frac{kg}{mole}\right)$.

Resulting mass balance equations:

$$\frac{\partial \rho c_A}{\partial t} + \operatorname{div}(\rho c_A v) = \operatorname{div}(\rho D_A \nabla c_A) - \mu_A M_A W$$

$$\frac{\partial \rho c_B}{\partial t} + \operatorname{div}(\rho c_B v) = \operatorname{div}(\rho D_B \nabla c_B) - \mu_B M_B W$$

$$\frac{\partial \rho c_c}{\partial t} + \underbrace{\operatorname{div}(\rho c_B v)}_{\text{advection}} = \underbrace{\operatorname{div}(\rho D_c \nabla c_c)}_{\text{diffusion}} + \underbrace{\mu_c M_c W}_{\text{reaction}}$$

Here $c_A + c_B + c_c = 1$ for three concentrations c_A, c_B, c_c.

<u>Obs</u>: Diffusion terms can have more complicated form ($\sim$ both ∇c_A and ∇c_B)

<u>Obs</u>:
Since total mass is conserved; this provides conditions on diffusion coefficients. Also, $\mu_A M_A + \mu_B M_B = \mu_c M_c$.

$$\left(\text{Adding 3 eqs} \xRightarrow{\text{must be}} \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho v) = 0.\right)$$

<u>Momentum equations</u>: remain the same:

Euler for ideal flow, Navier-Stokes for viscous flow

(no extra terms due to reaction)

<u>Heat equation</u>:

Reaction leads to increase of entropy $\Rightarrow$ heat production

$$(\text{heat of reaction}) = T\,d\mathcal{S} = T\rho\, ds = Q\,dt$$

where $Q = Q(T, P, c_A, c_B \text{ etc.})$ is the reaction heat
(per mole, per units of volume and time)

Often, one takes $Q \simeq$ const.

$Q > 0$ for exothermic reaction (releases heat).

Heat transfer equation: $$T\rho \frac{ds}{dt} = \underbrace{\sigma'_{ij} \frac{\partial v_i}{\partial x_j}}_{\text{viscosity}} + \underbrace{\operatorname{div}(\lambda \nabla T)}_{\text{thermal conduct.}} + \underbrace{QW}_{\text{reaction}}$$

For incompressible flow: $$\frac{\partial T}{\partial t} + v \cdot \nabla T = \underbrace{\frac{\eta}{2\rho c_p}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)^2}_{\text{usually small and neglected}} + \chi \Delta T + \underbrace{q}_{} W$$

$$q = \frac{Q}{\rho c_p}$$

<u>Full system</u>:

Unknown fields: $\underset{\in \mathbb{R}^3}{v}$, $\underbrace{c_1, \dots, c_N}_{N \text{ components}}$, $\underbrace{\rho, T}_{\text{any 2 thermod. variables}}$ $\quad (N+5)$ dependent variables.

Equations: $c_1 + c_2 + \dots + c_N = 1$ (by definition)

Mass balance: $\left.\begin{array}{l} \frac{\partial \rho c_1}{\partial t} + \dots \\ \vdots \\ \frac{\partial \rho c_N}{\partial t} + \dots \end{array}\right\} N$ eq.

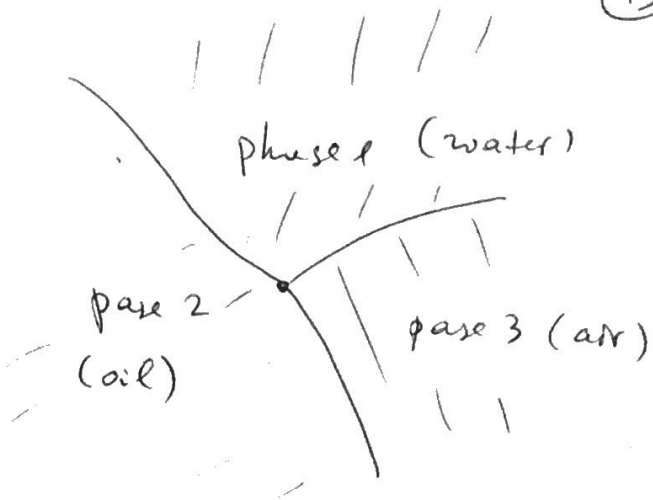
Momentum eq. (3 eq)

Heat eq. (1 eq)

$\Big\}$ $(N+5)$ equations

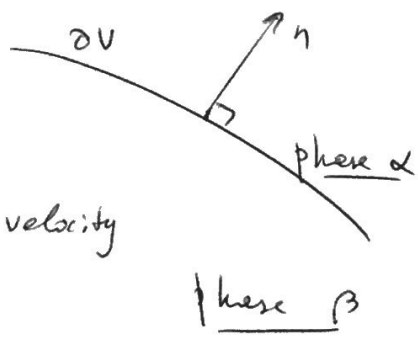
<u>Ok!</u>

Multi-phase flows



Inside the volume of each phase, equations are the same as for a single-phase fluid flow. Difference is at the <u>boundary</u> (<u>interfaces between phases</u>).

Consider an interface between two phases α and β:
Interface conditions at $r \in \partial V$ are:



<u>Mass balance</u>:

ideal flow $\rightarrow (v^\alpha, n) = \underbrace{(v^\beta, n)}_{\text{normal velocity}}$

viscous flow $\rightarrow \underbrace{v^\alpha = v^\beta}_{\text{no-slip}}$

<u>Momentum balance</u>:

ideal flow $\rightarrow p_\alpha = p_\beta$ (pressures are equal)

viscous flow $\rightarrow (-p^\alpha \delta_{ij} + \sigma_{ij}^{\alpha\prime}) n_j = (-p^\beta \delta_{ij} + \sigma_{ij}^{\beta\prime}) n_j$
(equality for the stresses at the interface)

<u>Energy balance</u>: $(\Gamma^{\prime\alpha}, n) = (\Gamma^{\prime\beta}, n)$ dissipative energy fluxes are equal.

For example, neglecting viscosity and keeping therm. conduction:
$(\lambda_\alpha \nabla T_\alpha, n) = (\lambda_\beta \nabla T_\beta, n)$. heat conduction through interface.

<u>Obs</u> Extra effects: surface ~~energy~~ properties (surface tension, adsorption etc.)
reactions and phase transitions $\Rightarrow$ <u>source terms</u> in boundary conditions