Governing Equations for Multicomponent Systems

ChEn 6603

Outline

- Preliminaries:
  - Derivatives
  - Reynolds' transport theorem (relating Lagrangian and Eulerian)
  - Divergence Theorem
- Governing equations
  - total mass, species mass, momentum, energy
  - weak forms of the governing equations
  - Other forms of the energy equation
    - the temperature equation
- Examples
  - Couette flow - viscous heating
  - Batch reactor

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Derivatives

$\frac{\partial}{\partial t}$ Time-rate of change at a fixed position in space.

$\frac{\mathrm{d}}{\mathrm{d}t}$ Time-rate of change as we move through space with ***arbitrary velocity*** (not necessarily equal to the fluid velocity)

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} \cdot \nabla = \frac{\partial}{\partial t} + \frac{\mathrm{d}x}{\mathrm{d}t}\frac{\partial}{\partial x} + \frac{\mathrm{d}y}{\mathrm{d}t}\frac{\partial}{\partial y} + \frac{\mathrm{d}z}{\mathrm{d}t}\frac{\partial}{\partial z} = \frac{\partial}{\partial t} + \mathbf{u}^a \cdot \nabla$$

$\frac{\mathrm{D}}{\mathrm{D}t}$ Time-rate of change as we move through space at the ***fluid mass-averaged velocity***.

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \mathbf{v} \longrightarrow \frac{\mathrm{d}x}{\mathrm{d}t} = v_x, \quad \frac{\mathrm{d}y}{\mathrm{d}t} = v_y, \quad \frac{\mathrm{d}z}{\mathrm{d}t} = v_z$$

$$\frac{\mathrm{D}}{\mathrm{D}t} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

D/Dt is known as the "material derivative" or "substantial derivative"

Example: $T = \sin(\omega t) + x + 5y \longrightarrow$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \omega\cos(\omega t) + u_x^a + 5u_y^a$$

$$\frac{\mathrm{D}T}{\mathrm{D}t} = \omega\cos(\omega t) + v_x + 5v_y$$

Can you have a steady flow field where d/dt is unsteady?

Lagrangian vs. Eulerian

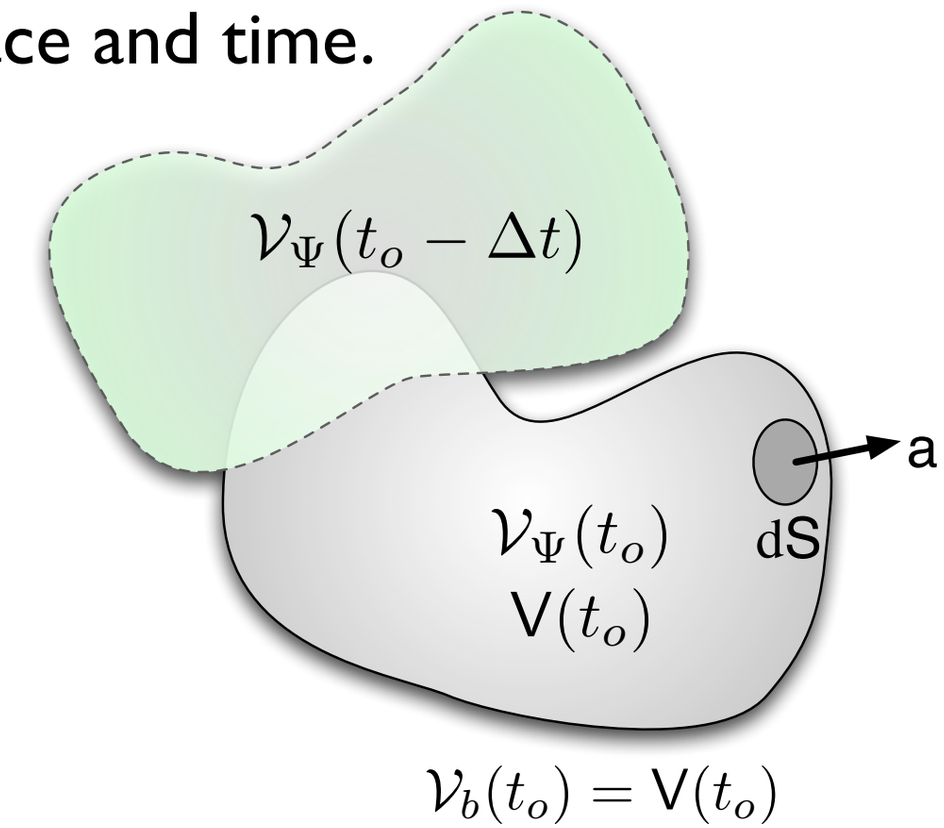
Let Ψ be any field function that is continuous in space and time.

$\mathcal{V}_\Psi(t)$ A Lagrangian volume that defines a ***closed system*** for Ψ

Closed system: $\mathcal{V}_\Psi(t)$ defined by $\mathbf{u}_\Psi$

$\mathsf{V}(t)$ An Eulerian volume defined arbitrarily in space and time.

May have flux through boundaries since it is NOT a closed system!



For a continuous field $\Psi(\mathbf{x},t)$ we relate the Lagrangian and Eulerian descriptions as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_\Psi(t)} \Psi \,\mathrm{dV} = \int_{\mathsf{V}(t)} \frac{\partial \Psi}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \Psi \mathbf{u}_\Psi \cdot \mathbf{a}\,\mathrm{dS}$$

What does each term represent?

Reynolds' Transport Theorem†

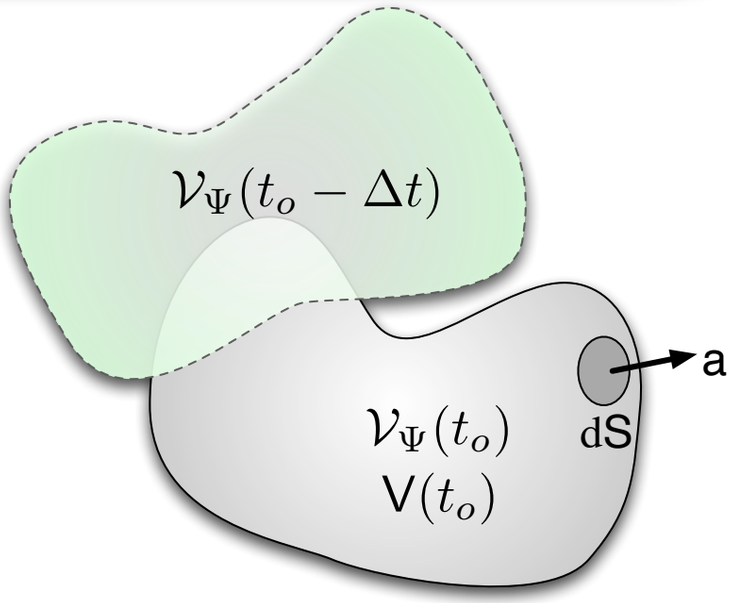
†also known as the Leibniz formula

Intensive & Extensive Properties

B - *extensive* quantity

b - *intensive* quantity (B per unit mass)

ρb - B per unit volume



$$B = \int_{\mathsf{V}} \rho b \, \mathrm{dV}$$

<u>Note</u>: if we use moles rather than mass, we obtain the partial molar properties (also intensive)

<u>Note</u>: if ρ and b are continuous functions then so is ρb.

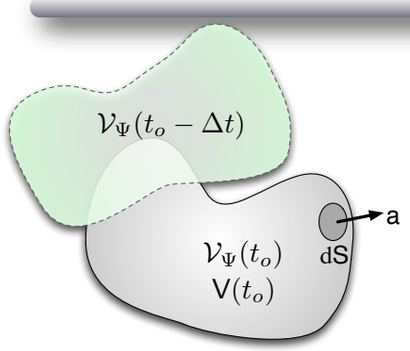
Reynolds' Transport Theorem with $\Psi = \rho b$:

$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathcal{V}_b(t)} \rho b \, \mathrm{dV}}_{\frac{\mathrm{d}B}{\mathrm{d}t}} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t} \, \mathrm{dV} + \int_{\mathsf{S}(t)} \rho b \mathbf{u}_b \cdot \mathbf{a} \, \mathrm{dS}$$

$\rho b \mathbf{u}_b = \mathbf{n}_b$
Mass flux of b

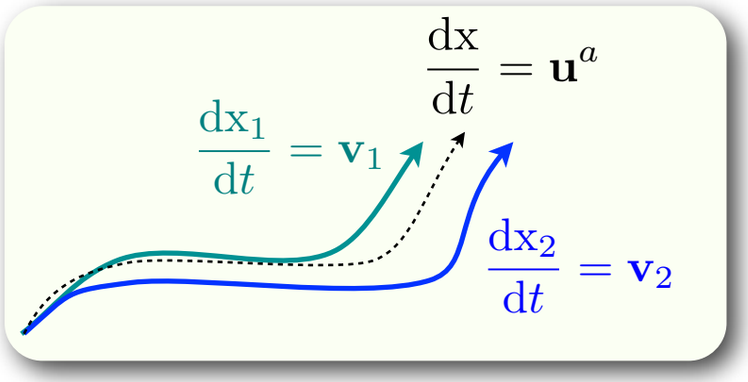
This equation will help us derive balance equations for mass, momentum, energy.

The Lagrangian Volume "Problem"



$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV}}_{\frac{\mathrm{d}B}{\mathrm{d}t}} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_b \cdot \mathbf{a}\,\mathrm{dS}$$

Reynolds' transport theorem



In a multicomponent system, we have many velocities! That means that we have ***different definitions*** of the Lagrangian volume for ***each property*** b!

$$\begin{aligned}\mathbf{n}_b &= \rho b \mathbf{u}_b \\ &= \rho b \mathbf{u}^a + \mathbf{j}_b^a\end{aligned}$$

$\mathbf{j}_b^a$ = mass diffusive flux of b relative to reference velocity $\mathbf{u}^a$.

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV} &= \frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_a(t)} \rho b \,\mathrm{dV} + \int_{\mathcal{S}_a(t)} \mathbf{j}_b^a \cdot \mathbf{a}\,\mathrm{dS} \\ &= \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_b \cdot \mathbf{a}\,\mathrm{dS}\end{aligned}$$

Relates a closed Lagrangian system moving at $\mathbf{u}_b$ to an open Lagrangian system moving at $\mathbf{u}^a$.

Relates a closed Lagrangian system moving at $\mathbf{u}_b$ to an Eulerian system.

The Divergence Theorem

Also called Gauss' theorem, Ostrogradsky's theorem or the Gauss-Ostrogradsky theorem

For any vector field $\mathbf{q}$,

$$\int_{\mathsf{S}(t)} \mathbf{q}\cdot\mathbf{a}\,\mathrm{d}\mathsf{S} = \int_{\mathsf{V}(t)} \nabla\cdot\mathbf{q}\,\mathrm{d}\mathsf{V}$$

This is very useful when moving from macroscopic (integral) balances to differential balances.

Can also be written for scalar & tensor fields:

$$\int_{\mathsf{V}(t)} \nabla\phi\,\mathrm{d}\mathsf{V} = \int_{\mathsf{S}(t)} \phi\mathbf{a}\,\mathrm{d}\mathsf{S}$$

$$\int_{\mathsf{V}(t)} \nabla\cdot\boldsymbol{\tau}\,\mathrm{d}\mathsf{V} = \int_{\mathsf{S}(t)} \boldsymbol{\tau}\cdot\mathbf{a}\,\mathrm{d}\mathsf{S}$$

useful for transforming the momentum equations (p & τ)

Using the divergence theorem, we can rewrite the Reynolds Transport Theorem as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b\,\mathrm{d}\mathsf{V} = \frac{\mathrm{d}B}{\mathrm{d}t} &= \int_{\mathsf{V}(t)} \frac{\partial\rho b}{\partial t}\,\mathrm{d}\mathsf{V} + \int_{\mathsf{S}(t)} \mathbf{n}_b\cdot\mathbf{a}\,\mathrm{d}\mathsf{S} \\ &= \int_{\mathsf{V}(t)} \left(\frac{\partial\rho b}{\partial t} + \nabla\cdot\mathbf{n}_b\right)\mathrm{d}\mathsf{V}\end{aligned}$$

$$\begin{aligned}\mathbf{n}_b &= \rho b\mathbf{u}_b \\ &= \rho b\mathbf{u}^a + \mathbf{j}_b^a\end{aligned}$$

mass flux of b.

Deriving Transport Equations for Intensive Properties

1. Define B and b.

2. Determine $\mathrm{d}B/\mathrm{d}t$ (change in B in a ***closed*** system) This typically comes from some law like Newton's law, thermodynamics laws, *etc.*

   Using a closed system is the most convenient for deriving the equations, but note that each B has a (potentially) different definition for the system.

Lagrangian Form: $$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV} = \frac{\mathrm{d}B}{\mathrm{d}t} = ?$$

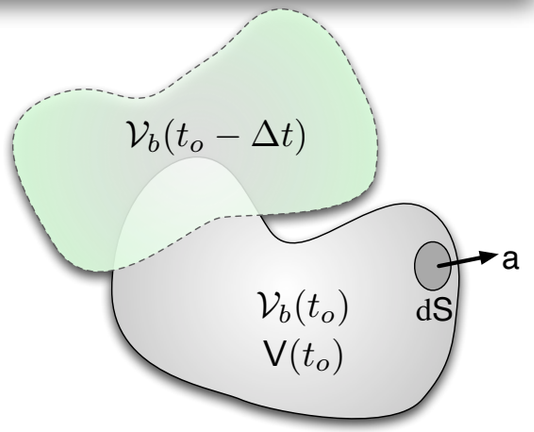
If you need to use an "open" Lagrangian system, see the notes on the Lagrangian volume "Problem".

3. Construct the governing equations in Lagrangian or Eulerian form.

Eulerian Form: $$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV} = \frac{\mathrm{d}B}{\mathrm{d}t}}_{\text{from step 2}} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_b \cdot \mathbf{a}\,\mathrm{dS}$$

Total Mass (Continuity)

Mass: $B = m, \quad b = \dfrac{B}{m} = 1$



Total mass is constant in a closed system $\Rightarrow$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_\rho(t)} \rho \,\mathrm{dV} = \frac{\mathrm{d}m}{\mathrm{d}t} = 0$$

Lagrangian form of the continuity equation.

What defines $\mathcal{V}_\rho(t)$?

Reynolds' transport theorem

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV} = \frac{\mathrm{d}B}{\mathrm{d}t} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_b \cdot \mathbf{a}\,\mathrm{dS}$$

Helps us move between Lagrangian and Eulerian...

Eulerian forms:

$$\begin{aligned}
0 &= \int_{\mathsf{V}(t)} \frac{\partial \rho}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_t \cdot \mathbf{a}\,\mathrm{dS} \\
0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{n}_t \\
0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} \\
0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} + \sum_{i=1}^{n} \nabla \cdot \mathbf{j}_i^u
\end{aligned}$$

You will explore various forms of the continuity equation in your homework...

Lagrangian & Eulerian - A Very Simple Example

What is the density in a piston-cylinder system as a function of time?

- Cylinder stroke: 30 cm
- Head height: $h_0 = 2$ mm

Assumptions:

1. Initial conditions: bottom of cylinder air at STP
2. Adiabatic system
3. Constant composition in space and time.
4. Spatially uniform density
5. $h(t) = h_0 + L/2\ [\ 1+\cos(\Omega t)\ ]$ - this is a simplified description -see http://en.wikipedia.org/wiki/Piston_motion_equations
6. Closed system (no valves)

Eulerian:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{n}_t = -\nabla \cdot (\rho \mathbf{v}) = -\rho \nabla \cdot \mathbf{v}$$

key step! ☆

$$\int_{\mathsf{V}(t)} \frac{\partial \rho}{\partial t}\, \mathrm{dV} = -\rho \int_{\mathsf{V}(t)} \nabla \cdot \mathbf{v}\, \mathrm{dV} = -\rho \int_{\mathsf{S}(t)} \mathbf{v} \cdot \mathbf{a}\, \mathrm{dS}$$

$$\mathsf{V}(t) \frac{\partial \rho}{\partial t} = \rho \pi R^2 v$$

$$\frac{\partial \rho}{\partial t} = \rho \frac{v(t)}{h(t)}$$

Homework: show that these are equivalent.

Lagrangian:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathcal{V}_\rho(t)} \rho\, \mathrm{dV} = \frac{\mathrm{d}m}{\mathrm{d}t} = 0$$

$$m = \rho \mathcal{V} = \rho \pi R^2 h$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \left(\rho \pi R^2 h \right) = 0$$

What level of description do we have of the velocity field in the cylinder? Is it adequate to answer the question?

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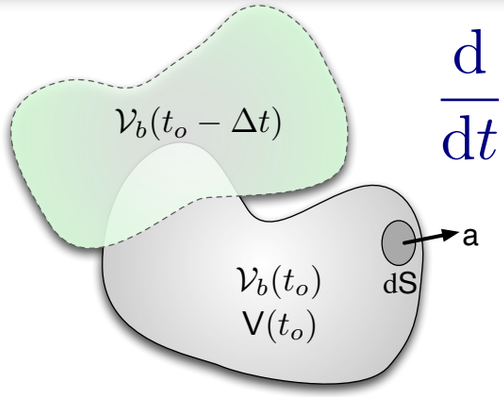
Species Mass

$$B = m_i = m\omega_i$$

$$b = \omega_i$$



$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b \,\mathrm{dV} = \frac{\mathrm{d}B}{\mathrm{d}t} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_b \cdot \mathbf{a}\,\mathrm{dS}$$

In a closed system, the mass of species i changes only due to chemical reaction:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_{\omega_i}(t)} \rho\omega_i \,\mathrm{dV} = \frac{\mathrm{d}m_i}{\mathrm{d}t} = \int_{\mathcal{V}_{\omega_i}(t)} s_i \,\mathrm{dV}$$

Lagrangian form of species conservation.

s_i - mass reaction rate per unit volume.

<u>NOTE</u>: this is for a closed system on species i.
Is this the same system as for species j?

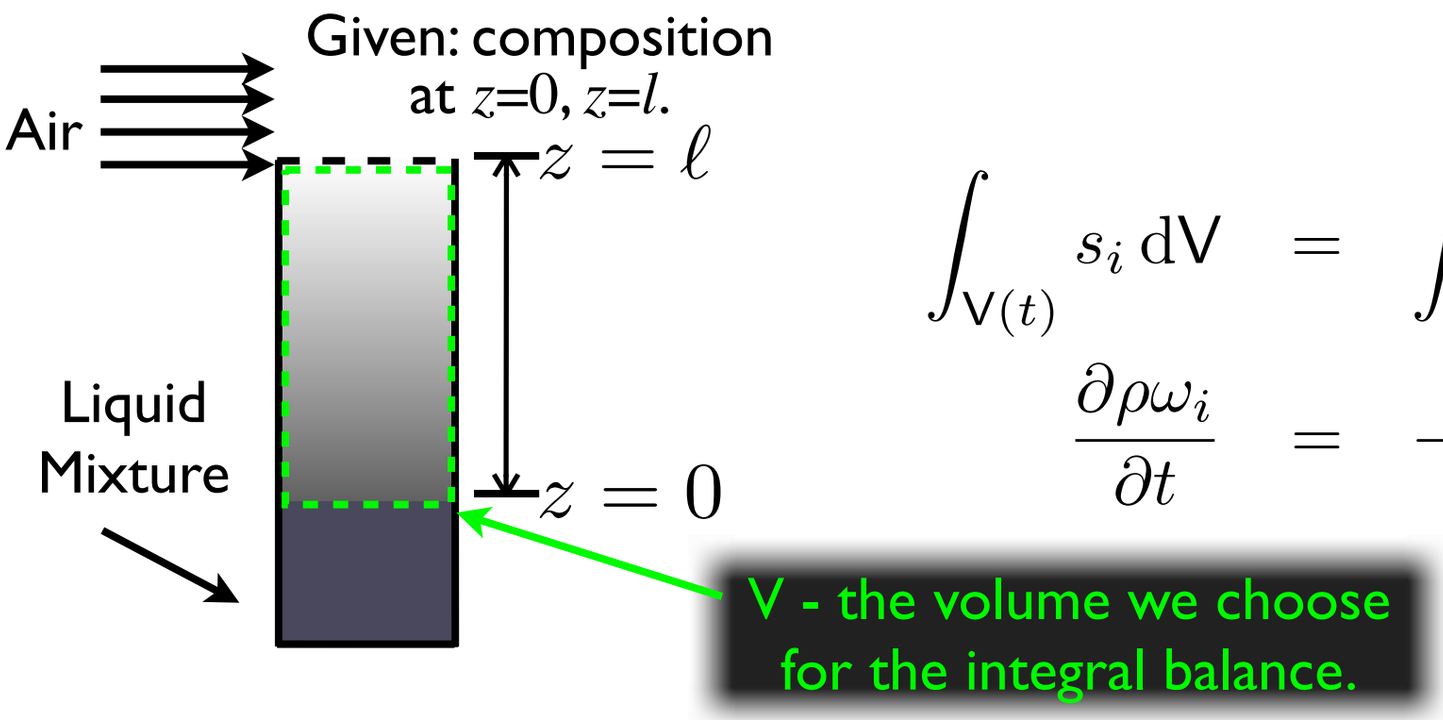
<u>Eulerian forms</u>:

$$\int_{\mathsf{V}(t)} s_i \,\mathrm{dV} = \int_{\mathsf{V}(t)} \frac{\partial \rho\omega_i}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_i \cdot \mathbf{a}\,\mathrm{dS}$$

$$\frac{\partial \rho\omega_i}{\partial t} = -\nabla \cdot \mathbf{n}_i + s_i$$

- Note that fluxes appear in the Eulerian form.
- If the total flux is not readily available, we decompose it into convective and diffusive components, $\mathbf{n}_i = \rho_i \mathbf{v} + \mathbf{j}_i$...
- The total continuity equation is readily obtained by summing the species equations.

Species Balance Example: Stefan Tube



$$\int_{\mathsf{V}(t)} s_i \, \mathrm{dV} = \int_{\mathsf{V}(t)} \frac{\partial \rho \omega_i}{\partial t} \, \mathrm{dV} + \int_{\mathsf{S}(t)} \mathbf{n}_i \cdot \mathbf{a} \, \mathrm{dS}$$

$$\frac{\partial \rho \omega_i}{\partial t} = -\nabla \cdot \mathbf{n}_i + s_i$$

Species balance equations (no reaction):

$$\frac{\partial \rho \omega_i}{\partial t} = \frac{\partial \rho_i}{\partial t} = -\nabla \cdot \mathbf{n}_i,$$

$$\frac{\partial c x_i}{\partial t} = \frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i$$

At steady state (1D),

$$\mathbf{n}_i = \alpha_i$$

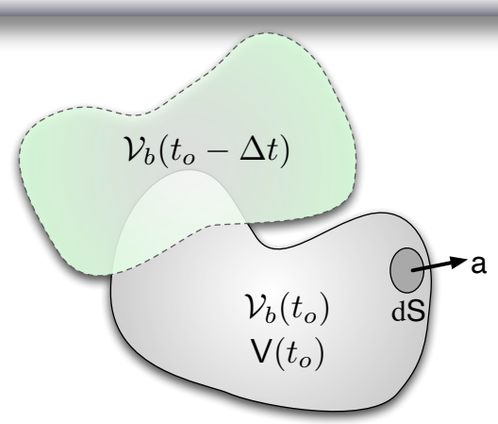
$$\mathbf{N}_i = \beta_i$$

Convection-
diffusion balance...

Momentum - Pure Fluid

$$B = m\mathbf{v}$$

$$b = \frac{m\mathbf{v}}{m} = \mathbf{v}$$



$$\frac{\mathrm{d}B}{\mathrm{d}t} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \rho b \mathbf{u}_b \cdot \mathbf{a}\,\mathrm{dS}$$

Recall, for a pure fluid, there exists a single unique system velocity, $\mathbf{v}$.

Newton's second law of motion: $\frac{\mathrm{d}B}{\mathrm{d}t} = m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \sum \mathbf{F}_{\mathrm{Extenal}}$

$$m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\int_{\mathcal{S}(t)} (\boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a})\,\mathrm{dS} + \int_{\mathcal{V}(t)} \rho\mathbf{f}\,\mathrm{dV}$$

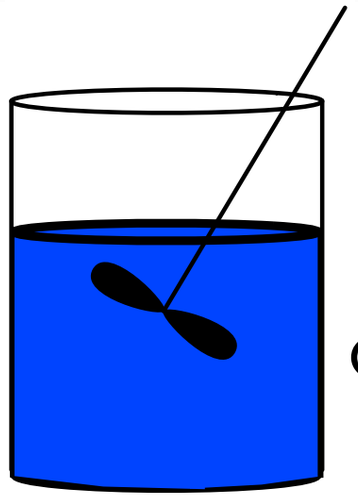
<u>Lagrangian integral form</u> of the momentum equations

$$\int_{\mathsf{V}(t)} \frac{\partial \rho\mathbf{v}}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \rho\mathbf{v}\mathbf{v}\cdot\mathbf{a}\,\mathrm{dS} = -\int_{\mathsf{S}(t)} (\boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a})\,\mathrm{dS} + \int_{\mathsf{V}(t)} \rho\mathbf{f}\,\mathrm{dV}$$

$$\frac{\partial \rho\mathbf{v}}{\partial t} = -\nabla\cdot\rho\mathbf{v}\mathbf{v} - \nabla\cdot\boldsymbol{\tau} - \nabla p + \rho\mathbf{f}$$

<u>Eulerian forms</u>

Momentum Example: Steady Stirred Tank



$$\int_{\mathsf{V}(t)} \frac{\partial \rho \mathbf{v}}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \rho \mathbf{v}\mathbf{v}\cdot\mathbf{a}\,\mathrm{dS} = -\int_{\mathsf{S}(t)} \left(\boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a}\right)\,\mathrm{dS} + \int_{\mathsf{V}(t)} \rho\mathbf{f}\,\mathrm{dV}$$

Choose the liquid-tank & liquid-air interface as the volume over which we will perform the balance.

$$\int_{\mathsf{V}(t)} \frac{\partial \rho \mathbf{v}}{\partial t}\,\mathrm{dV}$$

at steady state this term must be zero

$$\int_{\mathsf{S}(t)} \rho \mathbf{v}\mathbf{v}\cdot\mathbf{a}\,\mathrm{dS}$$

only nonzero if we have flow across the surface (therefore zero for this situation)

$$\int_{\mathsf{S}(t)} \boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a}\,\mathrm{dS}$$

Stresses at the surfaces are nonzero if there are nonzero velocity gradients. What balances this force? What happens if it is not balanced?

$$\int_{\mathsf{V}(t)} \rho\mathbf{f}\,\mathrm{dV}$$

f=g - acceleration due to gravity. How is this force balanced?

Momentum - Multicomponent Mixtures

What velocity *defines* the momentum?

$$\sum_{i=1}^{n} \rho_i \mathbf{u}_i = \rho \sum_{i=1}^{n} \omega_i \mathbf{u}_i = \rho \mathbf{v}$$

species specific momentum (momentum per unit volume for species i)

total specific momentum (total momentum per unit volume)

$$\sum_{i=1}^{n} m_i \mathbf{u}_i = m \sum_{i=1}^{n} \omega_i \mathbf{u}_i = m \mathbf{v}$$

species momentum (momentum for species i)

total momentum

$$B = m\mathbf{v}, \quad b = \frac{B}{m} = \mathbf{v}$$

Velocity is an intensive quantity, momentum per unit mass

What velocity *advects* the momentum?

It seems reasonable that a mass-averaged velocity would advect the mass-averaged velocity (specific momentum)...

Newton's second law of motion: $\frac{\mathrm{d}B}{\mathrm{d}t} = m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \sum \mathbf{F}_{\mathrm{Extenal}}$

Body forces may act differently on different species: $\mathbf{F} = \sum_{i=1}^{n} \rho\omega_i \mathbf{f}_i$

$\mathbf{f}_i$: acceleration on species i.

$$m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\int_{\mathcal{S}_{\rho v}(t)} (\boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a})\,\mathrm{dS} + \int_{\mathcal{V}_{\rho v}(t)} \sum_{i=1}^{n_s} \rho\omega_i \mathbf{f}_i\,\mathrm{dV}$$

Lagrangian integral form of the momentum equation

Reynolds' transport theorem

$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{V}_b(t)} \rho b\,\mathrm{dV}}_{\frac{\mathrm{d}B}{\mathrm{d}t}} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \rho b \mathbf{u}_b \cdot \mathbf{a}\,\mathrm{dS}$$

$$\int_{\mathsf{V}(t)} \frac{\partial \rho\mathbf{v}}{\partial t}\,\mathrm{dV} = -\int_{\mathsf{S}(t)} \rho\mathbf{v}\mathbf{v}\cdot\mathbf{a}\,\mathrm{dS} - \int_{\mathsf{S}(t)} (\boldsymbol{\tau}\cdot\mathbf{a} + p\mathbf{a})\,\mathrm{dS} + \int_{\mathsf{V}(t)} \sum_{i=1}^{n_s} \rho\omega_i\mathbf{f}_i\,\mathrm{dV}$$

$$\frac{\partial \rho\mathbf{v}}{\partial t} = -\nabla\cdot(\rho\mathbf{v}\mathbf{v}) - \nabla\cdot\boldsymbol{\tau} - \nabla p + \sum_{i=1}^{n_s} \rho\omega_i\mathbf{f}_i$$

Eulerian forms

Differences from pure fluid momentum equation:

- body force term includes forces acting on each species
- velocity is a mass-averaged velocity!

Total Internal Energy

$B = E_0 = me_0 \quad b = e_0$

E_0 - *total* internal energy (*kinetic* and *internal* energy)

$$e_0 = \frac{1}{2}\mathbf{v}\cdot\mathbf{v} + e$$
$$= \underbrace{\frac{1}{2}\mathbf{v}\cdot\mathbf{v}}_{\text{specific kinetic energy}} - \underbrace{\frac{p}{\rho}}_{\text{specific internal energy}} + h$$

First law of thermodynamics: $\frac{\mathrm{d}E_0}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} + \frac{\mathrm{d}W}{\mathrm{d}t}$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\int_{\mathcal{S}_{e_0}(t)} \mathbf{q}\cdot\mathbf{a}\,\mathrm{dS}$$

What would $\mathbf{q}$ include?

$$\frac{\mathrm{d}W}{\mathrm{d}t} = ???$$

What is the rate of work done **on** the closed system?

Lagrangian Form:

$$\frac{\mathrm{d}E_0}{\mathrm{d}t} = \int_{\mathcal{V}_{e_0}(t)} \rho e_0\,\mathrm{dV} = -\int_{\mathcal{S}_{e_0}(t)} \underbrace{\boxed{\mathbf{q}}}_{\text{Total heat flux out of the system}}\cdot\mathbf{a}\,\mathrm{dS} - \int_{\mathcal{S}_{e_0}(t)} (\underbrace{\boxed{\boldsymbol{\tau}\cdot\mathbf{v}}}_{\text{Rate of viscous work done on the system}} + \underbrace{\boxed{p\mathbf{v}}}_{\text{Rate of pressure work done on the system}})\cdot\mathbf{a}\,\mathrm{dS} + \int_{\mathcal{V}_{e_0}(t)} \underbrace{\boxed{\sum_{i=1}^{n_s}\mathbf{f}_i\cdot\mathbf{n}_i}}_{\text{Rate of body force work done on the system}}\mathrm{dV}$$

$\mathbf{q}$ - total diffusive heat flux (more later)

$\boldsymbol{\tau}$ - stress tensor

$\mathbf{f}_i$ - body force on species i.

<u>Note</u>: here we have assumed that the mass averaged velocity is the appropriate one...

Total Internal Energy (cont.)

Lagrangian Form:

$$\frac{\mathrm{d}E_0}{\mathrm{d}t} = \int_{\mathcal{V}_{e_0}(t)} \rho e_0 \,\mathrm{dV} = -\int_{\mathcal{S}_{e_0}(t)} \mathbf{q}\cdot\mathbf{a}\,\mathrm{dS} - \int_{\mathcal{S}_{e_0}(t)} (\boldsymbol{\tau}\cdot\mathbf{v} + p\mathbf{v})\cdot\mathbf{a}\,\mathrm{dS} + \int_{\mathcal{V}_{e_0}(t)} \sum_{i=1}^{n_s} \mathbf{f}_i\cdot\mathbf{n}_i\,\mathrm{dV}$$

Reynolds' Transport Theorem: $\displaystyle\int_{\mathcal{V}_b(t)} \rho b\,\mathrm{dV} = \int_{\mathsf{V}(t)} \frac{\partial \rho b}{\partial t}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \rho b \mathbf{u}_b\cdot\mathbf{a}\,\mathrm{dS}$

Eulerian Integral Form:

$$\int_{\mathsf{V}(t)} \underline{\frac{\partial \rho e_0}{\partial t}}\,\mathrm{dV} + \int_{\mathsf{S}(t)} \underline{\rho e_0 \mathbf{v}\cdot\mathbf{a}}\,\mathrm{dS} = -\int_{\mathsf{S}(t)} (\underline{\mathbf{q}} + \underline{\boldsymbol{\tau}\cdot\mathbf{v} + p\mathbf{v}})\cdot\mathbf{a}\,\mathrm{dS} + \int_{\mathsf{V}(t)} \sum_{i=1}^{n_s} \underline{\mathbf{f}_i\cdot\mathbf{n}_i}\,\mathrm{dV}$$

time rate of change of total internal energy in the volume

advective transport of total internal energy across the surfaces

Energy transfer from heat flux

Energy dissipation from viscous and pressure work on the system

work done by body forces due to both advection and diffusion

Eulerian Differential form:

$$\frac{\partial \rho e_0}{\partial t} + \nabla\cdot\rho e_0\mathbf{v} = -\nabla\cdot\mathbf{q} - \nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v} + p\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i\cdot\mathbf{n}_i$$

Recap of Governing Equations

Eulerian Governing Equations in Terms of a Mass-Averaged Velocity

This set of equations is the most frequently used set for many engineering applications.

Continuity: $$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{v}$$

Species mass: $$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \rho_i \mathbf{v} - \nabla \cdot \underline{\mathbf{j}_i} + \underline{s_i}$$

Momentum: $$\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v}\mathbf{v}) - \nabla \cdot \underline{\boldsymbol{\tau}} - \nabla \underline{p} + \sum_{i=1}^{n_s} \rho_i \mathbf{f}_i$$

Total Internal Energy: $$\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot \rho e_0 \mathbf{v} - \nabla \cdot \underline{\mathbf{q}} - \nabla \cdot (\underline{\boldsymbol{\tau}} \cdot \mathbf{v} + \underline{p}\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{n}_i$$

Chemical source terms - requires a chemical mechanism relating T, p, ω_i to s_i.

Diffusive fluxes - require constitutive relationships.

Pressure - requires equation of state.

Thermodynamics: solve for T from ω_i, p and e_0.

$$h = \sum_{i=1}^{n} h_i \omega_i$$

$$h_i = h_i^\circ + \int_{T_i^\circ}^{T} c_{p,i}(T) \mathrm{d}T$$

The "Heat Flux" - a preview

$$\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot \rho e_0 \mathbf{v} - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v} + p\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{n}_i$$

$$\mathbf{q} = \mathbf{q}_{\text{Fourier}} + \mathbf{q}_{\text{Species}} + \mathbf{q}_{\text{Dufour}}$$

- Contributions:
  - Fourier term (due to ∇T)
  - Diffusing species carry energy: $\sum h_i \mathbf{j}_i$
  - Species *gradients* (in absence of species *fluxes*) can move energy!
    - "Dufour Effect" - typically ignored
    - ugly.
  - Radiative heat flux: $\sigma \varepsilon T^4$ (or more complicated)
- More soon...

$$\mathbf{q}_{\text{Fourier}} = -\lambda \nabla T$$

$$\begin{aligned} \mathbf{q}_{\text{Species}} &= \sum_{i=1}^{n} h_i \rho \omega_i (\mathbf{u}_i - \mathbf{v}), \\ &= \sum_{i=1}^{n} h_i \mathbf{j}_i \end{aligned}$$

Mass vs. Molar Equations

- Equations can be written in molar form as well.
  - can be derived using Reynolds' Transport Theorem.
  - Sometimes it is more convenient.
    - ideal gas at constant T, p, no reaction

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{v} \qquad \text{mass form}$$

$$\frac{\partial c_t}{\partial t} = -\nabla \cdot c_t \mathbf{u} + \sum_{i=1}^{n} \frac{s_i}{M_i} \qquad \text{molar form}$$

- Typically when solving the momentum equations, the mass form is used.
  - sometimes the molar form of the species equations are used when momentum is not being solved

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"Weak" Forms of the Governing Equations

The "weak form" of a governing equation is obtained by subtracting the continuity equation.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$$

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho + \rho \nabla \cdot \mathbf{v} = 0 \qquad \frac{\mathrm{D}}{\mathrm{D}t} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} + \rho \nabla \cdot \mathbf{v} = 0$$

<u>Example</u>: species

$$\frac{\partial \rho \omega_i}{\partial t} + \nabla \cdot \rho \omega_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i + s_i$$

"Strong" form or "conservative" form

$$\rho \frac{\partial \omega_i}{\partial t} + \omega_i \frac{\partial \rho}{\partial t} + \rho \mathbf{v} \cdot \nabla \omega_i + \omega_i \nabla \cdot \rho \mathbf{v} =$$

$$\omega_i \left(\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} \right) + \rho \left(\frac{\partial \omega_i}{\partial t} + \mathbf{v} \cdot \nabla \omega_i \right) =$$

substitute continuity

$$\rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t} = -\nabla \cdot \mathbf{j}_i + s_i$$

"Weak" form or "nonconservative" form

Strong & Weak Forms - Summary

	Strong Form	Weak Form
Continuity	$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$	$\frac{\mathrm{D}\rho}{\mathrm{D}t} = -\rho \nabla \cdot \mathbf{v}$
Species	$\frac{\partial \rho \omega_i}{\partial t} + \nabla \cdot \rho \omega_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i + s_i$	$\rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t} = -\nabla \cdot \mathbf{j}_i + s_i$
Momentum	$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla \cdot \boldsymbol{\tau} - \nabla p + \rho \sum_{i=1}^{n} \omega_i \mathbf{f}_i$	$\rho \frac{\mathrm{D}\mathbf{v}}{\mathrm{D}t} = -\nabla \cdot \boldsymbol{\tau} - \nabla p + \rho \sum_{i=1}^{n} \omega_i \mathbf{f}_i$
Total internal energy	$\frac{\partial \rho e_0}{\partial t} + \nabla \cdot (\rho e_0 \mathbf{v}) = -\nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) - \nabla \cdot (p\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{n}_i$	$\rho \frac{\mathrm{D}e_0}{\mathrm{D}t} = -\nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) - \nabla \cdot (p\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{n}_i$

$$\frac{\mathrm{D}}{\mathrm{D}t} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$$

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Forms of the Energy Equation

Total internal energy equation:

$$\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot \rho e_0 \mathbf{v} - \nabla \cdot \mathbf{q} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v} + p\mathbf{v}) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{n}_i$$

Internal energy equation: $e_0 = e + k = e + \frac{1}{2}\mathbf{v} \cdot \mathbf{v}$

subtract kinetic energy equation
from total internal energy equation

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho e \mathbf{v}) = -\tau : \nabla \mathbf{v} - p \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

Enthalpy equation: $h = e + \frac{p}{\rho} \quad \Longrightarrow \quad \frac{\partial \rho h}{\partial t} = \frac{\partial \rho e}{\partial t} + \frac{\partial p}{\partial t}$

$$\frac{\partial \rho h}{\partial t} = \frac{\mathrm{D}p}{\mathrm{D}t} - \nabla \cdot (\rho h \mathbf{v}) - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

Temperature Equation (1/2)

Thermodynamics: choose T, p, ω_i as independent variables.

Then the enthalpy differential is:

$$\mathrm{d}h = \sum_{i=1}^{n} \left(\frac{\partial h}{\partial \omega_i}\right)_{T,p} \mathrm{d}\omega_i + \left(\frac{\partial h}{\partial T}\right)_{\omega_i,p} \mathrm{d}T + \left(\frac{\partial h}{\partial p}\right)_{T,\omega_i} \mathrm{d}p$$

$$h_i \equiv \left(\frac{\partial h}{\partial \omega_i}\right)_{T,p}$$

Species enthalpies

$$c_p = \left(\frac{\partial h}{\partial T}\right)_{\omega_i,p} = \sum_{i=1}^{n} \omega_i c_{p,i}$$

Heat capacity (function of T, ω)

$$\left(\frac{\partial h}{\partial p}\right)_{T,\omega_i} = \hat{V} - T\left(\frac{\partial \hat{V}}{\partial T}\right)_{p,\omega_i} = \hat{V}\left(1 - \alpha T\right)$$

$$\alpha \equiv \frac{1}{\hat{V}}\left(\frac{\partial \hat{V}}{\partial T}\right)_{p,\omega}$$

Coefficient of thermal expansion (from equation of state)

$$\mathrm{d}h = \sum_{i=1}^{n} h_i \mathrm{d}\omega_i + c_p \mathrm{d}T + \hat{V}\left(1 - \alpha T\right)\mathrm{d}p$$

Temperature Equation (2/2)

$$\mathrm{d}h = \sum_{i=1}^{n} h_i \mathrm{d}\omega_i + c_p \mathrm{d}T + \hat{V}\left(1 - \alpha T\right)\mathrm{d}p$$

Solve for $\mathrm{d}T$ and multiply by ρ:

$$\rho c_p \mathrm{d}T = \rho \mathrm{d}h - \left(1 - \alpha T\right)\mathrm{d}p - \sum_{i=1}^{n} h_i \rho \mathrm{d}\omega_i$$

$$\rho \frac{\mathrm{D}h}{\mathrm{D}t} = \frac{\mathrm{D}p}{\mathrm{D}t} - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

$$\rho \frac{\mathrm{D}\omega_i}{\mathrm{D}t} = -\nabla \cdot \mathbf{j}_i + s_i$$

Substitute and simplify...

$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} = \alpha T \frac{\mathrm{D}p}{\mathrm{D}t} - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} h_i \left(\nabla \cdot \mathbf{j}_i - s_i\right) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

Notes:

- For an ideal gas, $\alpha = 1/T$.
- If body forces act equally on species, then $\sum \mathbf{f}_i \cdot \mathbf{j}_i = 0$.
- $\mathbf{q}$ includes the term $\sum h_i \mathbf{j}_i$. The net term is thus $\sum \mathbf{j}_i \cdot \nabla h_i$.

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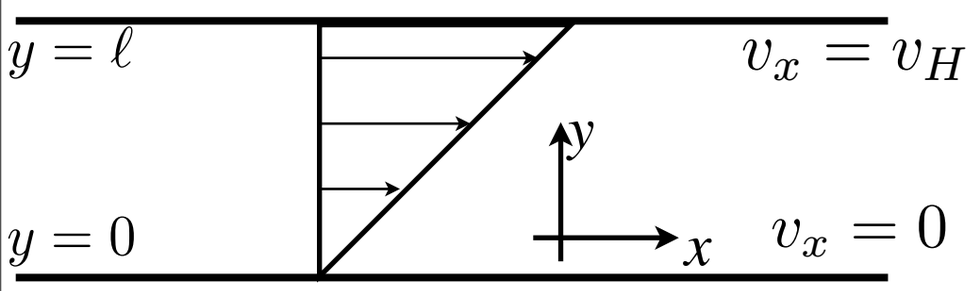
Example: Viscous Heating

Is Couette flow isothermal?



Momentum balance

$$v_y = 0, \quad \frac{\partial v_x}{\partial x} = 0 \quad \frac{\partial v_x}{\partial y} = \gamma$$

$$\frac{\partial \rho v_x}{\partial t} = -\frac{\partial \rho v_x v_x}{\partial x} - \frac{\partial \rho v_x v_y}{\partial y} - \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{xy}}{\partial y} - \frac{\partial p}{\partial x} + \rho g_x$$

$$\frac{\partial \tau_{xy}}{\partial y} = 0 \quad \Rightarrow \tau_{xy} = constant = -\mu \frac{\partial v_x}{\partial y} = -\mu\gamma$$

$$v_x = -\mu\gamma\left(\ell - y\right) + v_H$$

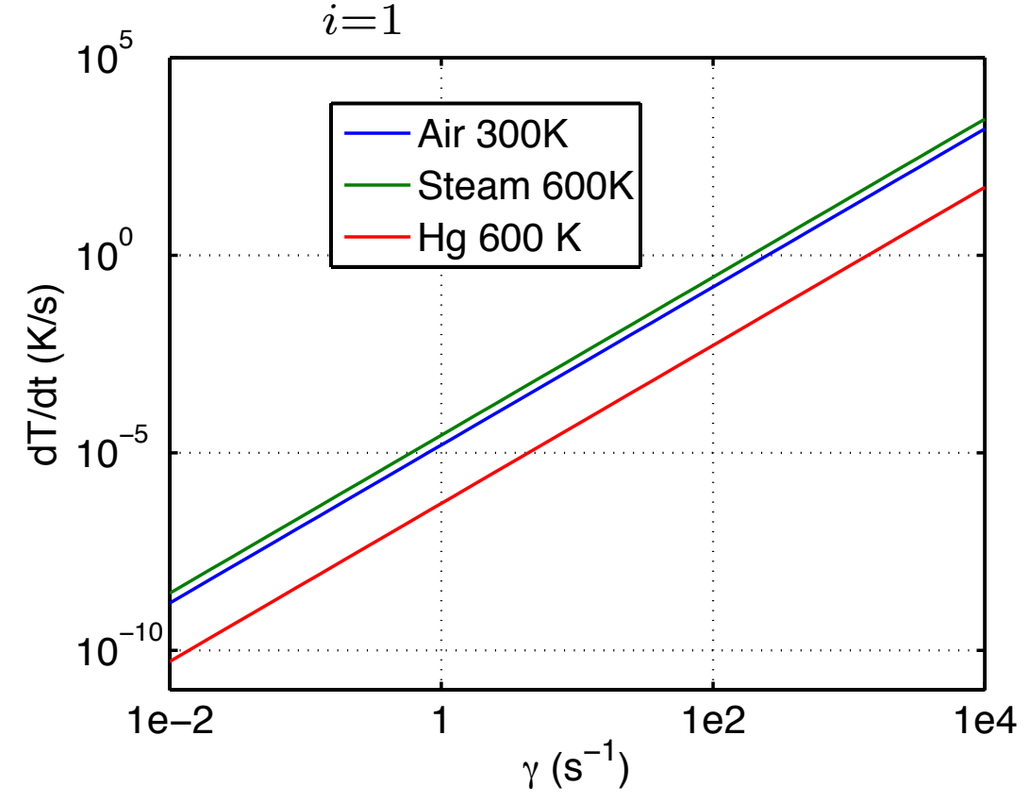
$$\rho c_p \frac{\mathrm{D}T}{\mathrm{D}t} = \alpha T \frac{\mathrm{D}p}{\mathrm{D}t} - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} h_i \left(\nabla \cdot \mathbf{j}_i - s_i\right) + \sum_{i=1}^{n} \mathbf{f}_i \cdot \mathbf{j}_i$$

what happened to the convective terms?

$$\rho c_p \frac{\partial T}{\partial t} = \alpha T \frac{\partial p}{\partial t} - \tau_{xy} \frac{\partial v_x}{\partial y}$$

assume steady pressure field

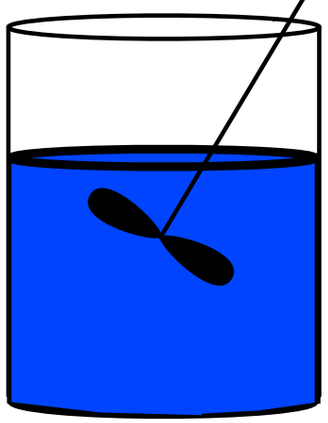
$$\begin{aligned} \frac{\partial T}{\partial t} &= -\frac{\tau_{xy}}{\rho c_p} \frac{\partial v_x}{\partial y}, \\ &= \frac{\mu \gamma^2}{\rho c_p}, \\ &= \frac{\nu}{c_p} \gamma^2 \end{aligned}$$



Are the assumptions valid?

Example: Batch Reactors

Derive the equations describing a well-mixed batch reactor.



Assumptions:

- Well-mixed (no spatial gradients).
- Constant volume.
- Closed system.

$$
\begin{aligned}
\int_{\mathsf{V}(t)} \frac{\partial \rho}{\partial t}\,\mathrm{dV} &= -\int_{\mathsf{S}(t)} \rho \mathbf{v}\cdot\mathbf{a}\,\mathrm{dS} \\
\int_{\mathsf{V}(t)} \frac{\partial \rho\omega_i}{\partial t}\,\mathrm{dV} &= -\int_{\mathsf{S}(t)} \rho\omega_i \mathbf{v}\cdot\mathbf{a}\,\mathrm{dS} + \int_{\mathsf{V}(t)} s_i\,\mathrm{dV} \\
\int_{\mathsf{V}(t)} \frac{\partial \rho\mathbf{v}}{\partial t}\,\mathrm{dV} &= -\int_{\mathsf{S}(t)} (\rho\mathbf{v}\mathbf{v}+\boldsymbol{\tau})\cdot\mathbf{a}\,\mathrm{dS} - \int_{\mathsf{S}(t)} p\mathbf{a}\,\mathrm{dS} - \sum_{i=1}^{n}\int_{\mathsf{V}(t)} \rho_i\mathbf{f}_i\,\mathrm{dV} \\
\int_{\mathsf{V}(t)} \frac{\partial \rho e_0}{\partial t}\,\mathrm{dV} &= -\int_{\mathsf{S}(t)} (\rho e_0\mathbf{v} - \mathbf{q} - \boldsymbol{\tau}\cdot\mathbf{v} + p\mathbf{v})\cdot\mathbf{a}\,\mathrm{dS} + \sum_{i=1}^{n}\int_{\mathsf{V}(t)} \mathbf{f}_i\cdot\mathbf{n}_i\,\mathrm{dV}
\end{aligned}
$$

How do we simplify and solve these equations?