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
Derivatives

\[ \frac{\partial}{\partial t} \]

Time-rate of change at a fixed position in space.

\[ \frac{d}{dt} \]

Time-rate of change as we move through space with \textit{arbitrary velocity} (not necessarily equal to the fluid velocity)

\[
\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{dx}{dt} \cdot \nabla = \frac{\partial}{\partial t} + \frac{dx}{dt} \frac{\partial}{\partial x} + \frac{dy}{dt} \frac{\partial}{\partial y} + \frac{dz}{dt} \frac{\partial}{\partial z} = \frac{\partial}{\partial t} + \mathbf{u}^a \cdot \nabla
\]

\[ \frac{D}{Dt} \]

Time-rate of change as we move through space at the \textit{fluid mass-averaged velocity}.

\[
\frac{dx}{dt} = \mathbf{v} \quad \Rightarrow \quad \frac{dx}{dt} = v_x, \quad \frac{dy}{dt} = v_y, \quad \frac{dz}{dt} = v_z
\]

\[ \frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \]

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

\[
\frac{dT}{dt} = \omega \cos(\omega t) + u_x^a + 5u_y^a
\]

\[ \frac{DT}{Dt} = \omega \cos(\omega t) + v_x + 5v_y \]

Can you have a steady flow field where \( d/dt \) is unsteady?
For a continuous field $\Psi(x,t)$ we relate the Lagrangian and Eulerian descriptions as

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

**Reynolds’ Transport Theorem**

Where $\mathcal{V}_\Psi(t)$ is a Lagrangian volume that defines a *closed system* for $\Psi$, and $\mathcal{V}(t)$ is an Eulerian volume defined arbitrarily in space and time. May have flux through boundaries since it is NOT a closed system!
Intensive & Extensive Properties

*B* - extensive quantity

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

\( \rho b \) - *B* per unit volume

\[
B = \int_V \rho b \, dV
\]

**Note:** if we use moles rather than mass, we obtain the partial molar properties (also intensive)

**Note:** if \( \rho \) and \( b \) are continuous functions then so is \( \rho b \).

Reynolds’ Transport Theorem with \( \Psi = \rho b \):

\[
\frac{d}{dt} \int_{V_b(t)} \rho b \, dV = \int_{V(t)} \frac{\partial \rho b}{\partial t} \, dV + \int_{S(t)} \rho b \mathbf{u}_b \cdot \mathbf{a} \, dS
\]

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

\[ \rho b \mathbf{u}_b = \mathbf{n}_b \]

Mass flux of *b*
The Lagrangian Volume “Problem”

\[
\frac{d}{dt} \int_{\mathcal{V}_b(t)} \rho_b \, dV = \int_{\mathcal{V}(t)} \frac{\partial \rho_b}{\partial t} \, dV + \int_{S(t)} n_b \cdot a \, dS
\]

Reynolds' transport theorem

In a multicomponent system, we have many velocities! That means that we have \textbf{different definitions} of the Lagrangian volume for each property \( b \)!

\[
\begin{align*}
\frac{dx_1}{dt} &= v_1 \\
\frac{dx_2}{dt} &= v_2 \\
\frac{dx}{dt} &= u^a
\end{align*}
\]

\[
\begin{align*}
n_b &= \rho_b u_b \\
&= \rho_b u^a + j_b^a
\end{align*}
\]

\( j_b^a \) = mass diffusive flux of \( b \) relative to reference velocity \( u^a \).

Relates a closed Lagrangian system moving at \( u_b \) to an open Lagrangian system moving at \( u^a \).

Relates a closed Lagrangian system moving at \( u_b \) to an Eulerian system.
The Divergence Theorem

Also called Gauss’ theorem, Ostrogradsky’s theorem or the Gauss-Ostrogradsky theorem.

For any vector field \( \mathbf{q} \),

\[
\int_{S(t)} \mathbf{q} \cdot a \, dS = \int_{V(t)} \nabla \cdot \mathbf{q} \, dV
\]

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

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

\[
\frac{d}{dt} \int_{V_b(t)} \rho b \, dV = \frac{dB}{dt} = \int_{V(t)} \frac{\partial \rho b}{\partial t} \, dV + \int_{S(t)} \mathbf{n}_b \cdot a \, dS
\]

\[
= \int_{V(t)} \left( \frac{\partial \rho b}{\partial t} + \nabla \cdot \mathbf{n}_b \right) \, dV
\]

\[
\mathbf{n}_b = \rho b \mathbf{u}_b = \rho b \mathbf{u}^a + \mathbf{j}^a
\]

mass flux of \( b \).
1. Define $B$ and $b$.

2. Determine $dB/dt$ (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:  \[ \frac{d}{dt} \int_{V_b(t)} \rho_b \, dV = \frac{dB}{dt} = ? \]

   Eulerian Form:  \[ \frac{d}{dt} \int_{V_b(t)} \rho_b \, dV = \frac{dB}{dt} = \int_{V(t)} \frac{\partial \rho_b}{\partial t} \, dV + \int_{S(t)} n_b \cdot a \, dS \]

   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.
Total Mass (Continuity)

Mass: \( B = m, \quad b = \frac{B}{m} = 1 \)

Total mass is constant in a closed system \( \Rightarrow \)
\[
\frac{d}{dt} \int_{V(t)} \rho \, dV = \frac{dm}{dt} = 0
\]

What defines \( V_\rho(t) \)?

Reynolds’ transport theorem
\[
\frac{d}{dt} \int_{V_b(t)} \rho b \, dV = \frac{dB}{dt} = \int_{V(t)} \frac{\partial \rho b}{\partial t} \, dV + \int_{S(t)} \mathbf{n}_b \cdot \mathbf{a} \, dS
\]

Eulerian forms:
\[
0 = \int_{V(t)} \frac{\partial \rho}{\partial t} \, dV + \int_{S(t)} \mathbf{n}_t \cdot \mathbf{a} \, dS
\]
\[
0 = \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{n}_t
\]
\[
0 = \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v}
\]
\[
0 = \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} + \sum_{i=1}^{n} \nabla \cdot \mathbf{j}_i^u
\]

Lagrangian form of the continuity equation.

Helps us move between Lagrangian and Eulerian...

You will explore various forms of the continuity equation in your homework...
What is the density in a piston-cylinder system as a function of time?

**Assumptions:**

1. Cylinder stroke: 30 cm
2. Head height: $h_0 = 2$ mm
3. Initial conditions: bottom of cylinder air at STP
4. Adiabatic system
5. Constant composition in space and time.
6. Spatially uniform density
7. $h(t) = h_0 + L/2 \left[ 1+\cos(\Omega t) \right]$ - this is a simplified description - see [http://en.wikipedia.org/wiki/Piston_motion_equations](http://en.wikipedia.org/wiki/Piston_motion_equations)
8. Closed system (no valves)

**Eulerian:**

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

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

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

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

**Lagrangian:**

$$\frac{d}{dt} \int_{V_{\rho}(t)} \rho \, dV = \frac{dm}{dt} = 0$$

$$m = \rho V = \rho \pi R^2 h$$

$$\frac{dm}{dt} = \frac{d}{dt} \left( \rho \pi R^2 h \right) = 0$$

*Homework: show that these are equivalent.*

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

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

$$B = m_i = m \omega_i$$

$$b = \omega_i$$

$Lagrangian$ form of species conservation.

$$\frac{d}{dt} \int_{V_{\omega_i}(t)} \rho \omega_i \, dV = \frac{d}{dt} \int_{V(t)} m_i \, dV = \int_{S(t)} \frac{\partial \rho_i}{\partial t} \, dV + \int_{S(t)} n_i \cdot a \, dS$$

**NOTE:** this is for a closed system on species $i$. Is this the same system as for species $j$?

**Eulerian forms:**

$$\int_{V(t)} s_i \, dV = \int_{V(t)} \frac{\partial \rho_i}{\partial t} \, dV + \int_{S(t)} n_i \cdot a \, dS$$

$$\frac{\partial \rho_i}{\partial t} = - \nabla \cdot n_i + s_i$$

- Note that fluxes appear in the Eulerian form.
- If the total flux is not readily available, we decompose it into convective and diffusive components, $n_i = \rho_i v + j_i$...
- The total continuity equation is readily obtained by summing the species equations.
Species Balance Example: Stefan Tube

Given: composition at $z=0, z=l$.

Air

Liquid Mixture

At steady state (1D),

\[
\begin{align*}
\frac{\partial \rho \omega_i}{\partial t} &= \frac{\partial \rho_i}{\partial t} = -\nabla \cdot \mathbf{n}_i, \\
\frac{\partial c x_i}{\partial t} &= \frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i
\end{align*}
\]

Species balance equations (no reaction):

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

$V$ - the volume we choose for the integral balance.

$\mathbf{n}_i = \alpha_i$

$\mathbf{N}_i = \beta_i$

Convection-diffusion balance...
Momentum - Pure Fluid

\[ B = m \mathbf{v} \]
\[ b = \frac{m \mathbf{v}}{m} = \mathbf{v} \]

Newton’s second law of motion:
\[ \frac{dB}{dt} = m \frac{dv}{dt} = \sum F_{\text{External}} \]

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

Lagrangian integral form of the momentum equations:
\[ \int_{V(t)} \frac{\partial \rho \mathbf{v}}{\partial t} \, dV + \int_{S(t)} \rho \mathbf{v} \cdot \mathbf{a} \, dS = - \int_{S(t)} (\mathbf{\tau} \cdot \mathbf{a} + p \mathbf{a}) \, dS + \int_{V(t)} \rho \mathbf{f} \, dV \]

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

Eulerian forms
Momentum Example: Stirred Tank

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

Choose liquid as the volume over which we will perform the balance.

\[
\int_{V(t)} \frac{\partial \rho \mathbf{v}}{\partial t} \, dV
\]

at steady state this term must be zero

\[
\int_{S(t)} \rho \mathbf{v} \cdot \mathbf{a} \, dS
\]

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

\[
\int_{S(t)} \mathbf{\tau} \cdot \mathbf{a} + p \mathbf{a} \, dS
\]

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

\[
\int_{V(t)} \rho \mathbf{f} \, dV
\]

\( \mathbf{f} = g \) - acceleration due to gravity. How is this force balanced?
**Momentum in a Mixture**

**What velocity defines the momentum?**

\[
\sum_{i=1}^{n} \rho_i u_i = \rho \sum_{i=1}^{n} \omega_i u_i = \rho \mathbf{v}
\]

- **species specific momentum**
  (momentum per unit volume for species \(i\))

\[
\sum_{i=1}^{n} \rho_i u_i = \rho \sum_{i=1}^{n} \omega_i u_i = \rho \mathbf{v}
\]

\[
\sum_{i=1}^{n} m_i u_i = m \sum_{i=1}^{n} \omega_i u_i = m \mathbf{v}
\]

- **total specific momentum**
  (momentum per unit volume)

- **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:
\[
\frac{dB}{dt} = m \frac{dv}{dt} = \sum F_{\text{External}}
\]

Body forces may act differently on different species:
\[
F = \sum_{i=1}^{n} \rho \omega_i f_i
\]

\( f_i \): acceleration on species \( i \).

Differences from pure fluid momentum equation:

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

\[ B = E_0 = m e_0 \quad b = e_0 \quad E_0 - \text{total internal energy (kinetic and internal energy)} \]

\[ e_0 = \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + e \]

First law of thermodynamics:

\[ \frac{dE_0}{dt} = \frac{dQ}{dt} + \frac{dW}{dt} \]

\[ \frac{dQ}{dt} = - \int_{S_{e_0}(t)} \mathbf{q} \cdot \mathbf{a} \, dS \quad \text{What would } \mathbf{q} \text{ include?} \]

\[ \frac{dW}{dt} = ??? \quad \text{What is the rate of work done on the closed system?} \]

\[ \frac{dE_0}{dt} = \int_{V_{e_0}(t)} \rho e_0 \, dV = - \int_{S_{e_0}(t)} \mathbf{q} \cdot \mathbf{a} \, dS - \int_{S_{e_0}(t)} (\mathbf{\tau} \cdot \mathbf{v} + \rho \mathbf{v}) \cdot \mathbf{a} \, dS + \int_{V_{e_0}(t)} \sum_{i=1}^{n_s} \mathbf{f}_i \cdot \mathbf{n}_i \, dV \]

\[ \mathbf{q} - \text{total diffusive heat flux (more later)} \]

\[ \mathbf{\tau} - \text{stress tensor} \]

\[ \mathbf{f}_i - \text{body force on species } i. \]

Note: here we have assumed that the mass averaged velocity is the appropriate one...
Total Internal Energy (cont.)

Lagrangian Form:

\[
\frac{dE_0}{dt} = \int_{V_{e_0}(t)} \rho e_0 \, dV = - \int_{S_{e_0}(t)} q \cdot a \, dS - \int_{S_{e_0}(t)} (\tau \cdot v + pv) \cdot a \, dS + \int_{V_{e_0}(t)} \sum_{i=1}^{n_s} f_i \cdot n_i \, dV
\]

Reynolds’ Transport Theorem:

\[
\int_{V_b(t)} \rho b \, dV = \int_{V(t)} \frac{\partial \rho b}{\partial t} \, dV + \int_{S(t)} \rho b u_b \cdot a \, dS
\]

Eulerian Integral Form:

\[
\int_{V(t)} \frac{\partial \rho e_0}{\partial t} \, dV + \int_{S(t)} \rho e_0 v \cdot a \, dS = - \int_{S(t)} (q + \tau \cdot v + pv) \cdot a \, dS + \int_{V(t)} \sum_{i=1}^{n_s} f_i \cdot n_i \, dV
\]

Eulerian Differential form:

\[
\frac{\partial \rho e_0}{\partial t} + \nabla \cdot \rho e_0 v = -\nabla \cdot q - \nabla \cdot (\tau \cdot v + pv) + \sum_{i=1}^{n} f_i \cdot n_i
\]

- 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

Wednesday, January 26, 2011
### Recap of Governing Equations

**Continuity:**

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})
\]

**Species mass:**

\[
\frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}) - \nabla \cdot \mathbf{j}_i + s_i
\]

**Momentum:**

\[
\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) - \nabla \mathbf{p} + \sum_{i=1}^{\text{n}_s} \rho_i \mathbf{f}_i
\]

**Total Internal Energy:**

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

#### Chemical source terms
- Requires a chemical mechanism relating \( T, p, \omega_i \) to \( s_i \).

#### Diffusive fluxes
- Require constitutive relationships.

#### Pressure
- Requires an equation of state.

**Thermodynamics:** solve for \( T \) from \( \omega_i, p \) and \( e_0 \).

\[
h = \sum_{i=1}^{\text{n}} h_i \omega_i
\]

\[
h_i = h_i^\circ + \int_{T_i^\circ}^{T} c_{p,i}(T) \, dT
\]
The “Heat Flux” - a preview

\[
\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot \rho e_0 \mathbf{v} - \nabla \cdot \mathbf{q} - \nabla \cdot (\mathbf{\tau} \cdot \mathbf{v} + p \mathbf{v}) + \sum_{i=1}^{n} f_i \cdot n_i
\]

Contributions:

• Fourier term (due to $\nabla T$)

• Diffusing species carry energy: $\sum h_i j_i$

• 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...
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

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

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

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
"Weak" Forms of the Governing Equations

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

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

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

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

Example: 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

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

"Weak" form or "nonconservative" form

$$\rho \frac{\text{D} \omega_i}{\text{D}t} = -\nabla \cdot \mathbf{j}_i + s_i$$
### Strong & Weak Forms - Summary

<table>
<thead>
<tr>
<th></th>
<th>Strong Form</th>
<th>Weak Form</th>
</tr>
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<tbody>
<tr>
<td><strong>Continuity</strong></td>
<td>$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$</td>
<td>$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v}$</td>
</tr>
<tr>
<td><strong>Species</strong></td>
<td>$\frac{\partial \rho \omega_i}{\partial t} + \nabla \cdot \rho \omega_i \mathbf{v} = -\nabla \cdot \mathbf{j}_i + s_i$</td>
<td>$\rho \frac{D\omega_i}{Dt} = -\nabla \cdot \mathbf{j}_i + s_i$</td>
</tr>
<tr>
<td><strong>Momentum</strong></td>
<td>$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla \cdot \mathbf{\tau} - \nabla \cdot \mathbf{p} + \rho \sum_{i=1}^{n} \omega_i \mathbf{f}_i$</td>
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</tr>
<tr>
<td><strong>Total internal energy</strong></td>
<td>$\frac{\partial \rho e_0}{\partial t} + \nabla \cdot (\rho e_0 \mathbf{v}) = -\nabla \cdot \mathbf{q} - \nabla \cdot (\mathbf{\tau} \cdot \mathbf{v})$</td>
<td>$</td>
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</tr>
</tbody>
</table>

\[ \frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \]
Forms of the Energy Equation

Total internal energy equation:

\[
\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot (\rho e_0 \mathbf{v}) - \nabla \cdot \mathbf{q} - \nabla \cdot (\mathbf{\tau} \cdot \mathbf{v} + p \mathbf{v}) + \sum_{i=1}^{n} f_i \cdot n_i
\]

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

\[
\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho e \mathbf{v}) = -\mathbf{\tau} : \nabla \mathbf{v} - p \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} f_i \cdot j_i
\]

Enthalpy equation:

\[
h = e + \frac{p}{\rho} \quad \Rightarrow \quad \frac{\partial \rho h}{\partial t} = \frac{\partial \rho e}{\partial t} + \frac{\partial p}{\partial t}
\]

\[
\frac{\partial \rho h}{\partial t} = \frac{\partial \rho}{\partial t} \frac{Dp}{Dt} - \nabla \cdot (\rho h \mathbf{v}) - \mathbf{\tau} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} f_i \cdot j_i
\]
Temperature Equation (1/2)

Thermodynamics: choose $T, p, \omega_i$ as independent variables.

Then the enthalpy differential is:

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

$$
\begin{align*}
    h_i &\equiv \left( \frac{\partial h}{\partial \omega_i} \right)_{T,p} \\
    c_p &\equiv \left( \frac{\partial h}{\partial T} \right)_{\omega_i,p} = \sum_{i=1}^{n} \omega_i c_{p,i}
\end{align*}
$$

Species enthalpies

Heat capacity (function of $T, \omega$)

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

Coefficient of thermal expansion

( from equation of state)

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

Then:

$$
\frac{dh}{dh} = \sum_{i=1}^{n} h_i d\omega_i + c_p dT + \hat{V} (1 - \alpha T) dp
$$
Temperature Equation (2/2)

\[ dh = \sum_{i=1}^{n} h_i d\omega_i + c_p dT + \hat{V} (1 - \alpha T) dp \]

Solve for \(dT\) and multiply by \(\rho\):

\[ \rho c_p dT = \rho dh - (1 - \alpha T) dp - \sum_{i=1}^{n} h_i \rho d\omega_i \]

\[ \frac{Dh}{Dt} = \frac{Dp}{Dt} - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} f_i \cdot j_i \]

\[ \frac{D\omega_i}{Dt} = -\nabla \cdot j_i + s_i \]

Substitute and simplify...

\[ \rho c_p \frac{DT}{Dt} = \alpha T \frac{Dp}{Dt} - \tau : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} + \sum_{i=1}^{n} h_i (\nabla \cdot j_i - s_i) + \sum_{i=1}^{n} f_i \cdot j_i \]

Notes:

- For an ideal gas, \(\alpha = I/T\).
- If body forces act equally on species, then \(\sum f_i j_i = 0\).
- \(q\) includes the term \(\sum h_i j_i\). The net term is thus \(\sum j_i \cdot \nabla h_i\).
Example: Viscous Heating

Is Couette flow isothermal?

\[ y = \ell \quad v_x = v_H \]
\[ y = 0 \quad v_x = 0 \]

Momentum balance

\[ v_y = 0, \quad \frac{\partial v_x}{\partial x} = 0 \quad \frac{\partial v_x}{\partial y} = \gamma \]
\[ \frac{\partial \rho v_x}{\partial t} - \frac{\partial \rho v_x v_y}{\partial x} = \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{xy}}{\partial y} - \frac{\partial p}{\partial x} + \rho g_x \]
\[ \frac{\partial \tau_{xy}}{\partial y} = 0 \quad \Rightarrow \tau_{xy} = \text{constant} = -\mu \frac{\partial v_x}{\partial y} = -\mu \gamma \]
\[ v_x = -\mu \gamma (\ell - y) + v_H \]

Assume steady pressure field. What happened to the convective terms?

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

\[ \frac{\partial T}{\partial t} = -\frac{\tau_{xy} \partial v_x}{\rho c_p \partial y}, \]
\[ = \frac{\mu \gamma^2}{\rho c_p}, \]
\[ = \frac{\nu \gamma^2}{c_p} \]

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.

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

How do we simplify and solve these equations?