Linearized Theory

CHEN 6603
Motivation

Fick’s Second Law (molar form):
\[
\frac{\partial(x)}{\partial t} + \nabla \cdot u(x) = [D](\nabla^2 x)
\]

Fick’s 2nd law is useful, but is still coupled due to the diffusion coefficient matrix.

- Under some additional assumptions (see equimolar counterdiffusion example), the equations decouple.

We would like to be able to solve transient problems while maintaining the coupling between equations.

- Linearized theory let’s us do this.
Linearized Theory Formulation

Eigenvalue decomposition of $[D]$:

$$[P]^{-1}[D][P] = [\hat{D}]$$

Columns of $[P]$ are the eigenvectors of $[D]$

Diagonal matrix, entries are eigenvalues of $[D]$. 

Fick's 2\textsuperscript{nd} Law:

$$\frac{\partial(x)}{\partial t} = -\nabla \cdot (u(x)) + [D](\nabla^2 x)$$

Assumes $[P]$ is constant!

Decoupled set of equations, since $[\hat{D}]$ is diagonal.

**Approach:**
- Transform the problem
- Solve the transformed problem
- Transform the results back
The equation given in the document is:

\[
\frac{\partial (\hat{x})}{\partial t} = -\nabla \cdot (u(\hat{x})) + [\hat{D}](\nabla^2 \hat{x})
\]

- **\( (\hat{x}) \)**: Pseudo compositions \( \hat{x} = [P]^{-1}(x) \)
- **\([\hat{D}]\)**: Pseudo diffusivity \([P]^{-1}[D][P] = [\hat{D}]\)
- **\([P]\)**: Modal matrix (columns are eigenvalues of \([D]\)).
Diffusion Fluxes

If needed, the diffusive fluxes may be post-processed.

\[
\begin{align*}
(J) &= -c_t [D] (\nabla x), \\
[P]^{-1}(J) &= -c_t [P]^{-1} [D] [P] [P]^{-1} (\nabla x) \\
(\hat{J}) &= -c_t [\hat{D}] (\nabla \hat{x})
\end{align*}
\]

\[
(\hat{J}) = [P]^{-1}(J), \quad (J) = [P](\hat{J})
\]

Notes:

- (J) should be computed using the same approximations that went into the original equation set that was used to obtain (x).
Algorithm

1. Obtain the Fickian diffusion matrix \([D]\) at some representative composition, temperature and pressure.
2. Calculate the modal matrix \([P]\) and its inverse \([P]^{-1}\).
3. Calculate the initial/boundary conditions in pseudo-composition space: \((\hat{x}) = [P]^{-1}(x)\)
4. Calculate the diagonal \([\hat{D}]\) matrix (pseudo-diffusivity matrix) via \([\hat{D}] = [P]^{-1}[D][P]\)
5. Obtain the solution for each species in pseudo-composition space by solving the \((n-1)\) independent PDEs.
6. Convert back to real compositions via the transformation \((x) = [P](\hat{x})\)

**NOTE**: the Matlab “eig” function will calculate the \([P]\) and \([\hat{D}]\) matrices for you!
Re-Cap

- $\hat{D}$ is the same for all reference frames (T&K §3.2.2)
- Assumes that $[D]$ is constant.
- No thermal diffusion (Soret effect)
- Body forces act uniformly on all species (e.g. gravity)
- Negligible pressure gradient (to eliminate pressure gradient from driving force in Fick's law)
- $c_t = \text{constant}$
- Could be solved in mass form as well, with analogous assumptions (may be more restrictive).
Example: 2 Bulb Problem (again)

\[ \frac{d(x^0)}{dt} = \frac{A}{LV_0} \left(1 + \frac{V_0}{V_L}\right) [D] \left((x^\infty) - (x^0)\right) \]

\[ = \beta [D] \left((x^\infty) - (x^0)\right), \]

\[ \beta \equiv \frac{A}{LV_0} \left(1 + \frac{V_0}{V_L}\right) \quad \text{Constant for a given geometry.} \]

Must solve this (coupled) system of ODEs for the change in the composition in bulb 0 in time.

Linearized theory lets us easily solve this system without decoupling the physics.

\[ \frac{d(\hat{x}^0)}{dt} = \beta [\hat{D}] \left((\hat{x}^\infty) - (\hat{x}^0)\right), \]

\[ \frac{\hat{x}^0_i - \hat{x}^\infty_i}{\hat{x}^0_{i,0} - \hat{x}^\infty_i} = \exp \left(-\beta \hat{D}_i(t - t_o)\right) \]