Effective Diffusivity Methods

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Motivation

The "problem" - $[D]$ couples the equations.

Potential Solutions:

Linearized Theory:

- Start with Fick's 2nd Law.
- Assume $[D]$ is constant. Then diagonalize $[D]$ using an eigenvector decomposition.
- This maintains the coupling, only assuming constant $[D]$.

$$\begin{aligned} \frac{\partial(x)}{\partial t} + \nabla\cdot\mathbf{u}(x) &= [D](\nabla^2 x) \\ &\Downarrow \\ \frac{\partial(\hat{x})}{\partial t} + \nabla\cdot\mathbf{u}(\hat{x}) &= [\hat{D}](\nabla^2 \hat{x}) \end{aligned}$$

Effective Diffusivity:

- Diagonalize $[D]$: $D_{i,eff}$
- No assumption at this point that $[D]$ is constant, only that it can be diagonalized.
  - Solve equations for c_i or ρ_i (even with reaction).
  - Equations are still coupled unless $D_{i,eff}$ is constant.
- Often, we additionally assume that $[D]$ is constant, no reaction, etc. to start with Fick's 2nd law...

$$\begin{aligned} \mathbf{J}_i &= -c_t D_{i,eff}\nabla x_i \\ \mathbf{j}_i &= -\rho_t D^o_{i,eff}\nabla\omega_i \end{aligned}$$

How do we choose $D_{i,eff}$?

Selection of $D_{i,eff}$

GMS Equations (simplified)

$$\nabla x_i = -\sum_{j=1}^{n} \frac{x_j \mathbf{N}_i - x_i \mathbf{N}_j}{c_t Đ_{ij}}$$

What we want:

$$\begin{aligned} \mathbf{J}_i &= -c_t D_{i,eff} \nabla x_i \\ \nabla x_i &= -\frac{\mathbf{J}_i}{c_t D_{i,eff}}, \\ &= -\frac{\mathbf{N}_i - x_i \mathbf{N}_t}{c_t D_{i,eff}}. \end{aligned}$$

add & subtract $x_i\mathbf{N}_t$.

Substitute for ∇x_i

$$-\sum_{j=1}^{n} \frac{x_j \mathbf{N}_i - x_i \mathbf{N}_j}{c_t Đ_{ij}} = -\frac{\mathbf{N}_i - x_i \mathbf{N}_t}{c_t D_{i,eff}},$$

$$D_{i,eff} = (\mathbf{N}_i - x_i \mathbf{N}_t) \left(\mathbf{N}_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{Đ_{ij}} - x_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\mathbf{N}_j}{Đ_{ij}} \right)^{-1}.$$

<u>NOTE</u>: This is a *molar* diffusion coefficient. We could follow the same approach to get the *mass* diffusion coefficient...

Selection of $D_{i,eff}$

$$D_{i,eff} = (\mathbf{N}_i - x_i \mathbf{N}_t) \left(\mathbf{N}_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{Đ_{ij}} - x_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\mathbf{N}_j}{Đ_{ij}} \right)^{-1}$$

Limiting Cases

- If all binary diffusion coefficients are equal, $Đ_{ij}=Đ$

$$\boxed{D_{i,eff} = Đ_{ij} = Đ}$$

- Component i diffusing through a "stagnant mixture", $\mathbf{N}_{j\neq i}=0$

$$\boxed{D_{i,eff} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{Đ_{ij}}}}$$

Often used even when the $\mathbf{N}_{j\neq i}=0$ assumption is invalid!

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Selection of $D_{i,eff}$ - Dilute Mixtures

$$\begin{aligned}
\text{Effective binary} \quad \mathbf{J}_i &= -c_t D_{i,eff} \nabla x_i \\
\text{Fick's Law} \quad \mathbf{J}_i &= -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j \\
&\Downarrow \\
D_{i,eff} &= \sum_{j=1}^{n-1} D_{ij} \frac{\nabla x_j}{\nabla x_i}
\end{aligned}$$

If component "n" is in large excess, $x_n \to 1, \quad x_{i \neq n} \to 0$

$$\begin{aligned}
B_{ii} &= \frac{x_i}{Đ_{in}} + \sum_{j\neq i}^{n} \frac{x_j}{Đ_{ij}}, \\
B_{ij} &= -x_i \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right)
\end{aligned}
\quad \Longrightarrow \quad
\begin{aligned}
B_{ii} &= \frac{1}{Đ_{in}}, \\
B_{ij} &= 0.
\end{aligned}
\quad \Longrightarrow \quad
\begin{aligned}
[D] &= [\Gamma][B]^{-1}, \\
D_{ij} &= \delta_{ij} Đ_{in} \\
\Aboxed{D_{i,eff} &= Đ_{in}}
\end{aligned}$$

Re-Cap

Not functions of composition!

* Binary Diffusivities are Equal $D_{i,eff} = \text{Đ}_{ij} = \text{Đ}$

* Dilute Mixtures $D_{i,eff} = \text{Đ}_{in}$

Very commonly used (and abused)

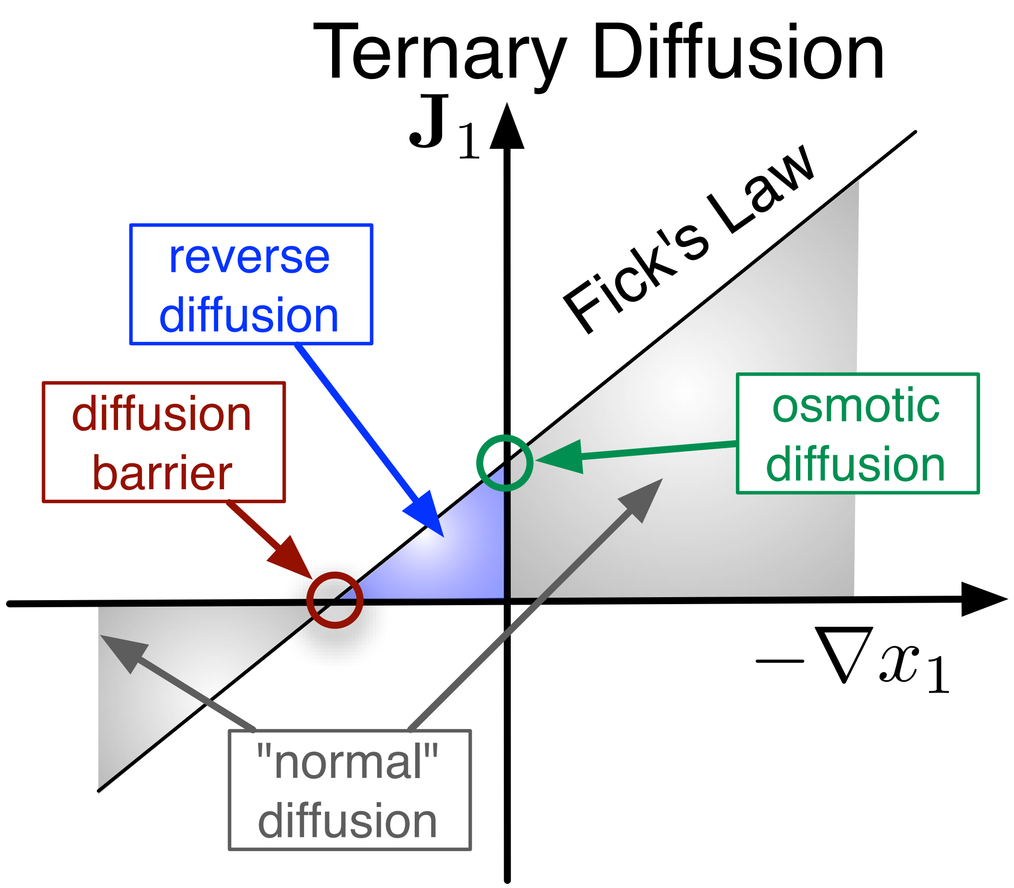
* Diffusion through Stagnant Gases $D_{i,eff} = \dfrac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{\text{Đ}_{ij}}}$

* Other Alternatives

$$
\begin{aligned}
D_{i,eff} &= \frac{1}{B_{ii}} \\
D_{i,eff} &= D_{ii}
\end{aligned}
$$

Behavior of $D_{i,eff}$

Can multicomponent effects be represented by an effective diffusivity approach?



$$\mathbf{J}_i = -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j$$ multicomponent

$$\mathbf{J}_i = -c_t D_{i,eff} \nabla x_i$$ effective diffusivity