Outline
Simplified Models for Interphase Mass Transfer

Interphase mass transfer
- Mass balances at interfaces (phase boundaries, etc)
- Mass transfer coefficients

Film Theory
- gives us insight into defining mass transfer coefficients for a very specific case...

The “Bootstrap Problem”
- given diffusive fluxes, can we find the total fluxes?

Solution procedure - Film Theory

Tuesday, March 20, 12
Interphase Mass Transfer

ChEn 6603
Interface Balance Equations

Generic transport equation (mass-averaged velocity):
\[ \frac{\partial \rho_t \Psi}{\partial t} + \nabla \cdot (\rho_t \Psi \mathbf{v}) + \nabla \cdot \Phi = \zeta \]

Assumes that \( \Psi \) is a continuous function.

Concept: solve the governing equations in each phase, and connect them with an appropriate balance at the interface (boundary condition).

Balance at the interface surface

\[
\int_S (\Phi^q + \rho_t^q \Psi^q (\mathbf{v}^q - \mathbf{u}^I)) \cdot \xi \, dS - \int_S (\Phi^p + \rho_t^p \Psi^p (\mathbf{v}^p - \mathbf{u}^I)) \cdot \xi \, dS = \int_S \zeta^I \, dS
\]

\( \mathbf{u}^I \) Interface velocity

\( \mathbf{v} \) Mass-avg. velocity

\( \Psi \) Quantity we are conserving

\( \Phi \) Non-convective (diffusive) flux

\( \zeta^I \) Interfacial generation of \( \Psi \)

Note that if \( \zeta^I = 0 \)
and \( \mathbf{u}^I = 0 \)
then \( \mathbf{n}_i^p \cdot \xi = \mathbf{n}_i^q \cdot \xi \)

\( \mathbf{u}^I \) may be related to \( \zeta^I \)
(e.g. ablation)
We would need a model for this.
### Interfacial Balance Equations

\[
\int_S \left( \Phi^q + \rho_i^q \Psi^q (v^q - u^I) \right) \cdot \xi \, dS - \int_S \left( \Phi^p - \rho_i^p \Psi^p (v^p - u^I) \right) \cdot \xi \, dS = \int_S \zeta^I \, dS
\]

 Flux of $\Psi$ from $q$ side

 Flux of $\Psi$ from $p$ side

Interfacial generation of $\Psi$

<table>
<thead>
<tr>
<th></th>
<th>Continuity</th>
<th>Momentum</th>
<th>Energy</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi$</td>
<td>1</td>
<td>$v$</td>
<td>$e_0 = u + \frac{1}{2} v \cdot v$</td>
<td>$\omega_i$</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>0</td>
<td>$pI + \tau$</td>
<td>$q + (pI + \tau) \cdot v$</td>
<td>$j_i$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>0</td>
<td>$\sum_{i=1}^n \rho_i f_i$</td>
<td>$\sum_{i=1}^n \rho_i f_i \cdot u_i$</td>
<td>$\sigma_i$</td>
</tr>
<tr>
<td>$\zeta^I$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\sigma^I_i$</td>
</tr>
</tbody>
</table>

#### "Bulk" Governing Equations

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

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

\[
\frac{\partial \rho \omega_i}{\partial t} = -\nabla \cdot (\rho \omega_i v) - \nabla \cdot j_i + s_i
\]

\[
\frac{\partial \rho e_0}{\partial t} = -\nabla \cdot (\rho e_0 v) - \nabla \cdot q - \nabla \cdot (\tau \cdot v) - \nabla \cdot (pv) + \sum_{i=1}^{n_s} f_i \cdot (\rho_i v + j_i)
\]
Mass Transfer Coefficients

Solution Options:

• Resolve the spatial gradients, solve equations as we have thus far, with appropriate interface BCs (flux matching at interface)

• Model the diffusion process at a “larger” scale between interface and “bulk”

Discrete approximation to Fick’s Law for diffusion normal to the interface:

\[(J^p) \approx -c_t^p[D^p](x^p_I) - (x^p_b) \]

Note that if \(L\) is “big” then we may miss important features.

\[
(J^p) \approx c_t^p[D^p](x^p_b) - (x^p_I) \]
\[\Delta x_i^p \equiv x_{ib}^p - x_{II}^p\]
\[\Delta x_q^p \equiv x_{II}^q - x_{ib}^q\]

**Mass transfer coefficient**

• Incorporates “boundary layer” thickness and \(D_{ij}\).

• If \(L\) is “large,” then we are really burying a lot of physics in \(D/L\).

• Is a function of \(J\) itself!

• Must be corrected to account for the fact that we are burying more physics in this description.

• Often used for turbulent boundary layers also (more later)
Comparison w/ Fick’s Law

Fick’s Law
\[(J) = -c_t[D](\nabla x)\]

- Fick’s law can be derived from irreversible thermodynamics.
- \([D]\) are unique (for a given composition and ordering)
- Can describe multicomponent effects (osmotic diffusion, reverse diffusion, diffusion barrier)

M.T. Coeff Approach
\[
(J) = c_t[k_b^\bullet](\Delta x)
\]

- Empirical equation.
- \([k_b^\bullet]\) defined by \((J)\) and \((\Delta x)\). This means that there are \(n-1\) equations defining a matrix with \((n-1)\times(n-1)\) elements. This implies that the \([k_b^\bullet]\) are not unique.
- Can describe multicomponent effects (osmotic diffusion, reverse diffusion, diffusion barrier)
**Binary Mass Transfer Coefficients**

For a binary system, \( k_b > 0 \), and is maximized when \( \Delta x_1 = 1 \) (which also implies \( x_{1b} = 1 \))

\[
J_{1b} = c_t x_{1b} (u_1 - u)
\]

\[
k_b = \frac{J_{1b}}{c_t \Delta x_1}
\]

\[
(k_b) = \lim_{N_1 \to 0} \frac{N_{1b} - x_{1b} N_t}{(x_{1b} - x_{1I})}
\]

\[
k_b^\bullet = k_b \Xi_b
\]

This defines the low-flux MTC

\( k_b \) - maximum velocity (relative to mixture velocity) at which a component can be transferred in a binary system.
Summary & a Path Forward

\[ (J) = c_t [k_b^\bullet] (\Delta x) \quad [k_b^\bullet] = [k_b] [\Xi_b] \]

- MTC Approach is useful when we don’t want to resolve the diffusion path
  - Interfaces, boundary layers, turbulence, etc.
- Formulation is a true multicomponent formulation
  - Can describe osmotic diffusion, reverse diffusion, diffusion barrier.
- Still need to determine how to get \([k_b]\) and \([\Xi_b]\)
  - \([k_b]\) cannot be uniquely determined by \((J)\) and \((\Delta x)\).
  - \([k_b]\) must be corrected ... how do we get \([\Xi_b]\)?
  - We will return to this later:
    - Film theory (turbulent boundary layer theory)
    - Correlations (heat-transfer analogies)
- Can we get the total fluxes from \((J)\)?
  - We will consider this issue soon. But first ... Film Theory!
Film Theory

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Perspective

\[ (J) = c_t [k_b^\bullet] (\Delta x) \quad [k_b^\bullet] = [k_b][\Xi_b] \]

We want to approximate \( J_i \) using \( \Delta x_i \) rather than resolving \( \nabla x_i \).

- Need a way to get \([\Xi_b]\) and \([k_b]\).

- *Film Theory* is one way to get \([\Xi_b]\) and \([k_b]\). It uses an *analytic solution* to the Maxwell-Stefan equations to deduce what \([\Xi_b]\) and \([k_b]\) should be.

To get \( N_i \):

- Could solve governing equations (momentum) & fully resolve everything...
  - This defeats the purpose of using the MTC approach!

- Use the “bootstrap” approach (inject specific knowledge of the problem to get \( N_i \) from \( J_i \)). More soon!
Concepts:

- Mass transfer occurs in a thin "film" or boundary layer. Outside of this, the composition is uniform due to well-mixedness (e.g. turbulence).
- Gradients in the boundary-tangential direction are negligible compared to boundary-normal gradients.

Formulation:

- One-dimensional continuity and species at steady-state w/o reaction:
  \[ \nabla \cdot N_t = 0, \quad \nabla \cdot N_i = 0 \]
  \[ \Downarrow \]
  \[ N_t = \text{const.}, \quad N_i = \text{const.} \]

- Constitutive relations (i.e. expressions for \( J_i \)) given by either GMS or Fick's Law.

- Boundary conditions: known compositions
  \[ x_i = x_{i0} \quad r = r_0 \]
  \[ x_i = x_i\delta \quad r = r_\delta. \]
Assumptions:
- Steady-state
- 1-D
- No reaction
- Isothermal
- Ideal mixtures $[I]=\{I\}$
- “small” pressure gradients
- uniform body forces

Normalized coordinate: \[ \eta \equiv \frac{r - r_0}{\ell} , \quad \ell \equiv r_\delta - r_0 \]

GMS:
\[ \frac{dx_i}{dr} = \sum_{j=1}^{n} \left( \frac{x_iN_j - x_jN_i}{c_tD_{ij}} \right) \]

GMS (n-1 dim) in terms of normalized coordinate.
\[ \frac{dx_i}{d\eta} = \Phi_{ii}x_i + \sum_{j=1 \atop j \neq i}^{n-1} \Phi_{ij}x_j + \phi_i \]
\[ \frac{d(x)}{d\eta} = [\Phi](x) + (\phi) \]

Analytic solution (assuming $N_i$ are all constant)
see T&K Appendix B
\[ (x - x_0) = \exp \left[ [\Phi]\eta - [I] \right] \left[ \exp[\Phi] - [I] \right]^{-1} (x_\delta - x_0) \]

Matrix exponential! \[ \exp[\Phi] \neq [\exp(\Phi_{ij})] \]

Given the total fluxes (to get $\Phi$), we can obtain the compositions analytically!
\[(x - x_0) = \left[ \exp \left( [\Phi] \eta \right) - [I] \right] \left[ \exp[\Phi] - [I] \right]^{-1} (x_\delta - x_0)\]

From the solution, we can calculate the diffusive fluxes and use them to help us determine what the MTCs are for this problem.

**Fick’s Law:** \[(J) = -c_t [D] \frac{d(x)}{dr}\]

\[(J) = -\frac{c_t}{\ell} [D] \frac{d(x)}{d\eta} = c_t [k_b^\bullet](\Delta x)\]

**MTC Formulation:** 
\[(J) = c_t [k_b^\bullet](\Delta x) \quad [k_b^\bullet] = [k_b] [\Xi_b]\]

\[\frac{d(x)}{d\eta} = [\Phi] \left[ \exp[[\Phi] \eta] \right] \left[ \exp[\Phi] - [I] \right]^{-1} (x_\delta - x_0)\]
\[
\frac{d(x)}{d\eta} = [\Phi] \left[ \exp[\Phi] \eta \right] \left[ \exp[\Phi] - [I] \right]^{-1} (x_\delta - x_0)
\]

**At \( \eta = 0 \)**

\[
(J_0) = \frac{c_t}{\ell} [D_0] [\Phi] \left[ \exp[\Phi] - [I] \right]^{-1} (x_0 - x_\delta)
\]

\[
[k_0^\bullet] = \frac{1}{\ell} [D_0] [\Phi] \left[ \exp[\Phi] - [I] \right]^{-1}
\]

**Low-flux limit:**

\[
k_b = \lim_{N_1 \to 0} \frac{N_{1b} - x_{1b} N_t}{(x_{1b} - x_{1I})} = \frac{J_{1b}}{c_t \Delta x_1}
\]

\[
[k_0] = \frac{1}{\ell} [D_0]
\]

**Correction matrix:**

\[
[\Xi_0] = [\Phi] \left[ \exp[\Phi] - [I] \right]^{-1}
\]

**At \( \eta = 1 \)**

\[
(J_\delta) = \frac{c_t}{\ell} [D_\delta] [\Phi] \left[ \exp[\Phi] \right] \left[ \exp[\Phi] - [I] \right]^{-1} (x_0 - x_\delta)
\]

\[
[k_\delta] = \frac{1}{\ell} [D_\delta]
\]

\[
[\Xi_\delta] = [\Phi] \exp[\Phi] \left[ \exp[\Phi] - [I] \right]^{-1} = [\Xi_0] \exp[\Phi]
\]
Re-Cap

We can now easily solve for \((x)\) given \((N)\).

- Assumes \((N)\) is constant.

We can also easily solve for \((J)\) directly given \((N)\).

We must specify:

- \([\Phi]\), which is a function of \((x)\), \((N)\), \(D_{ij}\) and \(\ell\).
- \([k]\), the low-flux MTC matrix.
- \([\Xi]\) - the correction factor matrix.

Coming soon: solution procedure
Calculating $[k]$

\[
[k] = \frac{1}{\ell} [D]
\]

\[
R_{ii} = \frac{x_i}{\kappa_{in}} + \sum_{k=1, k \neq i}^{n} \frac{x_k}{\kappa_{ik}},
\]

\[
R_{ij} = -x_i \left( \frac{1}{\kappa_{ij}} - \frac{1}{\kappa_{in}} \right),
\]

\[
\kappa_{ij} \equiv \frac{D_{ij}}{\ell} \quad \text{Binary low-flux limit MTC}
\]

\[
[k] = [R]^{-1}
\]

\[
[k] = \frac{1}{\ell} [B]^{-1}
\]

**Notes**

- We have a routine to calculate $[B]$ given $(x)$ and $[D]$. We can re-use this to get $[R]$ by passing in $(x)$ and $[\kappa]$.
- Alternatively, just calculate $[B]^{-1}$ and then scale by $\ell$. 

See T&K §8.3.1
Calculating $[\Xi]$ 

Recall what we found for $[\Xi]$ from film theory:

At $r = r_0$ ($\eta = 0$) 
$\Xi_0 = [\Phi] \left[ \exp[\Phi] - [I] \right]^{-1}$

At $r = r_\delta$ ($\eta = 1$) 
$\Xi_\delta = [\Phi] \exp[\Phi] \left[ \exp[\Phi] - [I] \right]^{-1} = [\Xi_0] \exp[\Phi]$ 

recall: $\exp[\Phi]$ is a matrix exponential; $\exp[\Phi] \neq [\exp(\Phi_{ij})]!$  

$[\Xi] = \sum_{i=1}^{n} \hat{\Xi}_i \left\{ \prod_{j=1}^{m} \left[ \Phi - \hat{\Phi}_j [I] \right] \right\}$

$\hat{\Xi}_{i0} = \frac{\hat{\Phi}_i}{\exp \hat{\Phi}_i - 1}$ 
$\hat{\Xi}_{i\delta} = \frac{\hat{\Phi}_i \exp \hat{\Phi}_i}{\exp \hat{\Phi}_i - 1}$

$m$ - number of eigenvalues of $\Phi$

OR, see “expm” function in MATLAB.
Shortcuts...

\[ B_{ii} = \frac{x_i}{D_{in}} + \sum_{j \neq i}^{n} \frac{x_j}{D_{ij}}, \]

\[ B_{ij} = -x_i \left( \frac{1}{D_{ij}} - \frac{1}{D_{in}} \right), \]

\[ \Phi_{ii} = \frac{N_i}{c_t D_{in} / \ell} + \sum_{k=1}^{n} \frac{N_k}{c_t D_{ik} / \ell}, \]

\[ \Phi_{ij} = -N_i \left( \frac{1}{c_t D_{ij} / \ell} - \frac{1}{c_t D_{in} / \ell} \right), \]

\[ R_{ii} = \frac{x_i}{\kappa_{in}} + \sum_{k=1}^{n} \frac{x_k}{\kappa_{ik}}, \]

\[ R_{ij} = -x_i \left( \frac{1}{\kappa_{ij}} - \frac{1}{\kappa_{in}} \right), \quad [k] = [R]^{-1} \]

\[ \kappa_{ij} \equiv \frac{D_{ij}}{\ell} \]

\[ \alpha_i = \frac{\alpha_i}{\beta_{in}} + \sum_{j \neq i}^{n} \frac{\alpha_j}{\beta_{ij}}, \]

\[ \beta_{ij} = D_{ij}, \]

\[ \alpha_i = x_i, \]

\[ \beta_{ij} = D_{ij}, \]

\[ \alpha_i = N_i, \]

\[ \beta_{ij} = \frac{c_t}{\ell} D_{ij}. \]
The “Bootstrap” Problem

Getting $N_i$ from $J_i$ and Physical Insight
The “Bootstrap” Problem

If we know the diffusive fluxes, can we obtain the total fluxes?

\[ J_i \xrightarrow{\text{Bootstrap Problem}} N_i \]

Can be solved for some special cases.

Species Molar Flux:

\[ N_i = J_i + x_i N_t \]

\[ \nu_i N_i = \nu_i J_i + \nu_i x_i N_t \]

\[ \sum_{i=1}^{n} \nu_i N_i = \sum_{i=1}^{n} \nu_i J_i + N_t \sum_{i=1}^{n} \nu_i x_i = 0 \]

General problem formulation:

\[ \sum_{i=1}^{n} \nu_i N_i = 0 \]

\[ N_i = J_i + x_i N_t \]

Remove the \( n^{th} \) diffusive flux:

\[ N_t = - \sum_{k=1}^{n-1} \frac{\nu_k - \nu_n}{\sum_{j=1}^{n} \nu_j x_j \Lambda_k} J_k \]

\[ N_i = \sum_{k=1}^{n-1} \beta_{ik} J_k \]

\[ \beta_{ik} = \delta_{ik} - x_i \Lambda_k \]

If we can get \( \beta_{ik} \) (or \( \Lambda_k \)), we can solve the problem!
Solving the Bootstrap Problem

\[ \sum_{i=1}^{n} \nu_i N_i = 0 \]
\[ N_i = \sum_{k=1}^{n-1} \beta_{ik} J_k \]

\[ \beta_{ik} \equiv \delta_{ik} - x_i \Lambda_k \]
\[ \Lambda_k = (\nu_k - \nu_n) \left( \sum_{j=1}^{n} \nu_j x_j \right)^{-1} \]

**Bootstrap matrix**

Equimolar counterdiffusion: \( N_t = 0 \)

- Isobaric, closed systems...

Stefan Diffusion: \( N_n = 0 \)

One component has a zero flux, \( N_n = 0 \).

- Condensation/evaporation
- Absorption (similar to condensation)

\[ \beta_{ik} = \delta_{ik} \]

\[ \nu_i = 0, \quad \nu_n \neq 0, \quad (N_n = 0) \]

\[ \beta_{ik} = \delta_{ik} + \frac{x_i}{x_n} \]

Flux ratios specified: \( N_i = z_i N_t \)

- Condensation of mixtures (T&K Ch. 15)
- Chemical reaction where the chemistry is fast relative to the diffusion (diffusion-controlled).

\[ N_i = x_i N_t + J_i \]
\[ N_i = x_i \frac{N_i}{z_i} + J_i \]

\[ \sum_{i=1}^{n} N_i \left( 1 - \frac{x_i}{z_i} \right) = \sum_{i=1}^{n} J_i = 0 \]
\[ \sum_{i=1}^{n} \nu_i N_i = 0 \Rightarrow \nu_i = 1 - \frac{x_i}{z_i} \]

\[ \beta_{ik} = \frac{\delta_{ik}}{1 - x_i/z_i} \]
Using the Bootstrap Matrix

\[ N_i = \sum_{k=1}^{n-1} \beta_{ik} J_k \]

Write this in matrix form:

\[ N_t = -(\Lambda)^T(J) \]

\[ (N) = [\beta](J) \]

Use with MTCs:

In the “bulk:”

\[ (J_b) = c_{t,b} [k_b^\bullet] (\Delta x_b) \]
\[ (N_b) = [\beta_b] (J_b) = c_{t,b} [\beta_b] [k_b^\bullet] (\Delta x_b) \]

At the interface:

\[ (J_I) = c_{t,I} [k_I^\bullet] (\Delta x_I) \]
\[ (N_I) = [\beta_I] (J_I) = c_{t,I} [\beta_I] [k_I^\bullet] (\Delta x_I) \]

\[ (N_I) = (N_b) \quad \text{(no reaction in boundary layer)} \]

Binary System

\[ N_1 = c_t \beta_I k_I^\bullet \Delta x_1 = c_t \beta_b k_b^\bullet \Delta x_1 \]
\[ \downarrow \]
\[ \beta_I k_I^\bullet = \beta_b k_b^\bullet = \frac{N_1}{c_t \Delta x_1} \]

Multicomponent System

\[ [\beta_I] [k_I^\bullet] (\Delta x) = [\beta_b] [k_b^\bullet] (\Delta x) \]

Since \([A](x)=[B](x)\) doesn’t imply that \([A]=[B]\), we cannot conclude anything about the relationship between \([\beta_b] [k_b^\bullet]\) and \([\beta_I] [k_I^\bullet]\).
Re-Cap

- **Bootstrap problem**: exists because we don’t want to solve all of the governing equations, but we want to get the total fluxes anyway.

- **Interphase mass transfer**: simplified approach to avoid fully resolving interfaces.
  - Non-uniqueness of MTCs
Film Theory: A “Simple” Solution Procedure

Given \((x_0), (x_\delta), c_t, K_{ij},\)

1. Compute \([k]= [D]/\ell.\)
2. Compute \([\beta]\) from the appropriate expressions given the specific problem.
3. Estimate \((N)= c_t[\beta][k](\Delta x).\) (This does not employ the correction matrix since we don’t yet have \([\Xi]).\)
4. Calculate \([\Phi]\)
5. Calculate \([\Xi]\)
6. Calculate \((J)= c_t[k][\Xi](\Delta x).\)
7. Calculate \((N)= [\beta](J).\)
8. Check for convergence on \((N).\) If not converged, return to step 4.

\[
\Phi_{ii} = \frac{N_i}{c_t D_{in}/\ell} + \sum_{k=1, k \neq i}^{n} \frac{N_k}{c_t D_{ik}/\ell},
\]

\[
\Phi_{ij} = -N_i \left( \frac{1}{c_t D_{ij}/\ell} - \frac{1}{c_t D_{in}/\ell} \right)
\]

Uses successive substitution to converge \((N).\) This could lead to poor convergence (or no convergence) depending on the guess for \((N).\)

Note: we could use “better” ways to iterate \((N)\) to improve convergence.

See Algorithms 8.2 & 8.3 in T&K (pp. 180,182)
Recall we assumed $[\Gamma]=[I]$. What if that is not valid???

**Approach:**

- Repeat original analysis, retaining $[\Gamma]$.
- Write $[D]=[\Gamma][B]^{-1}$.
- We can re-use the original results directly, using $[D]=[\Gamma][B]^{-1}$... (typically also approximate $[\Gamma]$ as constant)
- See also T&K §8.7.2, §8.8.4
Estimation of MTCs \([k]\)

**Motivation:**
- Prior approaches have required knowledge of \(\ell\).
  What if we don’t know this? (often the case)
- Idea: use correlations (dimensionless groups)

**Sherwood number:**
\[
[\text{Sh}] = d[k][D]^{-1}
\]

**Stanton number:**
\[
[\text{St}] = [k]/u
\]

These typically correlate the low-flux MTCs. Still need to apply \([\Xi]\).

- Correlations abound! Be sure that the one you use is appropriate!