The Maxwell-Stefan Equations

ChEn 6603

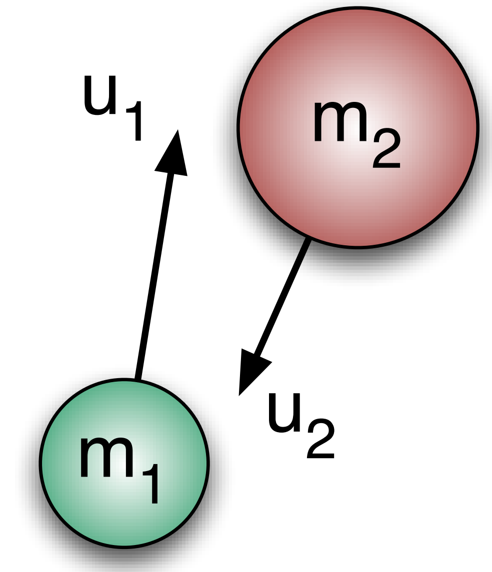
Outline

- Diffusion in "ideal," binary systems
  - Particle dynamics
  - Maxwell-Stefan equations
  - Fick's Law
- Diffusion in "ideal" multicomponent systems
  - Example: Stefan tube
  - Matrix form of the Maxwell-Stefan equations
  - Fick's Law for multicomponent systems
  - Reference velocities again

Particle Dynamics

Conservation of momentum:

$$m_1(\mathbf{u}_1 - \mathbf{u}_{f1}) + m_2(\mathbf{u}_2 - \mathbf{u}_{f2}) = 0$$



Conservation of kinetic energy (elastic collision):

$$m_1(\mathbf{u}_1^2 - \mathbf{u}_{f1}^2) + m_2(\mathbf{u}_2^2 - \mathbf{u}_{f2}^2) = 0$$

For molecules, inelastic collisions are known by another name ... what is it?

Solve for final particle velocities:

$$\mathbf{u}_{f1} = \frac{\mathbf{u}_1(m_1 - m_2) + 2m_2\mathbf{u}_2}{m_1 + m_2},$$

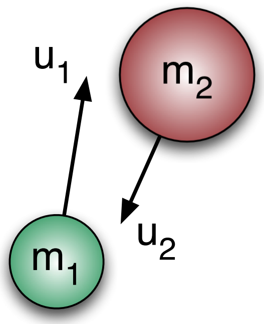
$$\mathbf{u}_{f2} = \frac{\mathbf{u}_2(m_2 - m_1) + 2m_1\mathbf{u}_1}{m_1 + m_2}$$

Momentum exchanged in a collision:

$$\begin{aligned} m_1(\mathbf{u}_1 - \mathbf{u}_{f1}) &= m_1\mathbf{u}_1 - \frac{m_1}{m_1+m_2}\left(\mathbf{u}_1(m_1 - m_2) + 2m_2\mathbf{u}_2\right), \\ &= \frac{2m_1m_2(\mathbf{u}_1 - \mathbf{u}_2)}{m_1+m_2}. \end{aligned}$$

Sum of forces acting on particles of type "1" per unit volume ∝ Rate of change of momentum of particles of type "1" per unit volume ∝ Momentum exchanged per collision between "1" and "2" × Rate of 1-2 collisions per unit volume

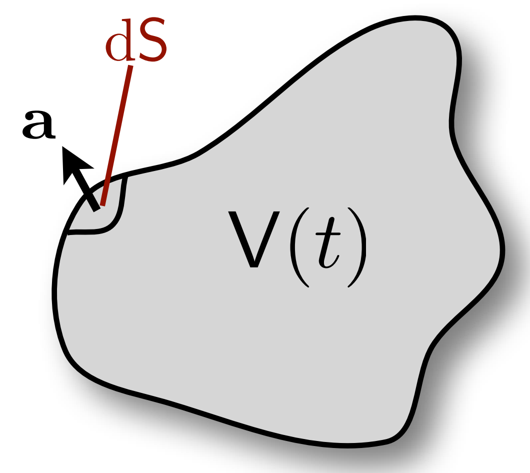
$\mathbf{u}_1 - \mathbf{u}_2$ $x_1 x_2$



Sum of forces acting on particles of type "1" per unit volume $\propto$ Momentum exchanged per collision between "1" and "2" $\times$ Rate of 1-2 collisions per unit volume

Assume:

- System pressure is constant
- Collisions are purely elastic (kinetic energy is conserved in collisions)
- No shear stress (negligible velocity gradients)



$$-\int_{S(t)} x_1 p\, \mathbf{a}\, dS = -\int_{V(t)} \nabla(p x_1)\, dV$$
$$= -\int_{V(t)} p \nabla x_1\, dV$$

Why the (-) sign?

So our force (momentum) balance becomes:

$$-p\nabla x_1 \propto x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2),$$
$$= f_{12}\, x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)$$

f_{12}: drag coefficient for drag that particle "1" feels as a result of interactions with particles of type "2"

Define a "binary diffusion coefficient" as $\mathcal{D}_{12} = \dfrac{p}{f_{12}}$

What is the binary diffusivity a function of?

$$\nabla x_1 = -\frac{x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)}{\mathcal{D}_{12}}$$

Maxwell-Stefan Equations for a binary, ideal mixture.

What about ∇x_2?

diffusion driving force for species 1

drag force on species 1 (resisting diffusion)

Fick's Law - Binary Ideal System

$$\nabla x_1 = -\frac{x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)}{Đ_{12}}$$

Maxwell-Stefan equations for a binary, ideal system at constant pressure.

$$\begin{aligned} \nabla x_1 &= -\frac{x_2 \mathbf{N}_1 - x_1 \mathbf{N}_2}{c_t Đ_{12}} \\ &= -\frac{x_2 \mathbf{J}_1 - x_1 \mathbf{J}_2}{c_t Đ_{12}} \end{aligned}$$

can you show this?

$$\nabla x_1 = -\frac{\mathbf{J}_1}{c_t Đ_{12}}$$

$$\mathbf{J}_1 = -c_t Đ_{12} \nabla x_1$$

Fick's law for a binary, ideal system at constant pressure

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Re-Cap

- $Đ_{12}$ can be interpreted as an inverse drag coefficient.
- $Đ_{12} = Đ_{21}$ (symmetric due to momentum conservation)
- $Đ_{12}$ depends on the characteristics of species 1 and 2 (molecule shapes, etc.), but not on their relative compositions.
- $Đ_{12}$ may depend on temperature and pressure.
- We call $Đ_{12}$ the "Maxwell-Stefan" diffusivity or "Binary" diffusivity.
- There are no "1-1" interactions here - $Đ_{11}$ is not defined.

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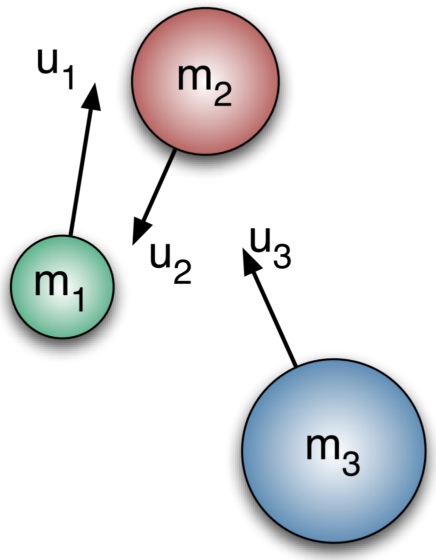
Multicomponent Systems



Binary system: $\nabla x_1 = -\frac{x_1 x_2(\mathbf{u}_1 - \mathbf{u}_2)}{Đ_{12}}$

Ternary system: must consider 1-2, 1-3, and 2-3 interactions.

$$\nabla x_1 = -\frac{x_1 x_2(\mathbf{u}_1 - \mathbf{u}_2)}{Đ_{12}} - \frac{x_1 x_3(\mathbf{u}_1 - \mathbf{u}_3)}{Đ_{13}}$$

$$\nabla x_2 = -\frac{x_1 x_2(\mathbf{u}_2 - \mathbf{u}_1)}{Đ_{12}} - \frac{x_2 x_3(\mathbf{u}_2 - \mathbf{u}_3)}{Đ_{23}}$$

Multicomponent system: must consider *i*-*j* interactions.

$$\nabla x_i = -\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j(\mathbf{u}_i - \mathbf{u}_j)}{Đ_{ij}} \quad \xrightarrow{\text{in general...}} \quad \mathbf{d}_i = -\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j(\mathbf{u}_i - \mathbf{u}_j)}{Đ_{ij}}$$

What about $i=j$?

Recall: $\mathbf{N}_i = x_i c \mathbf{u}_i \quad \mathbf{J}_i = \mathbf{N}_i - x_i c \mathbf{u}$

$\mathbf{d}_i = \nabla x_i$

(so far)

$$\begin{aligned} \mathbf{d}_i &= -\sum_{j \neq i}^{n} \frac{x_j \mathbf{N}_i - x_i \mathbf{N}_j}{c Đ_{ij}}, \\ &= -\sum_{j \neq i}^{n} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c Đ_{ij}} \end{aligned}$$

Assumptions:

- Constant Pressure
- Ideal mixture (elastic collisions)
  - Conservation of translational energy.
  - Where else could the energy go?

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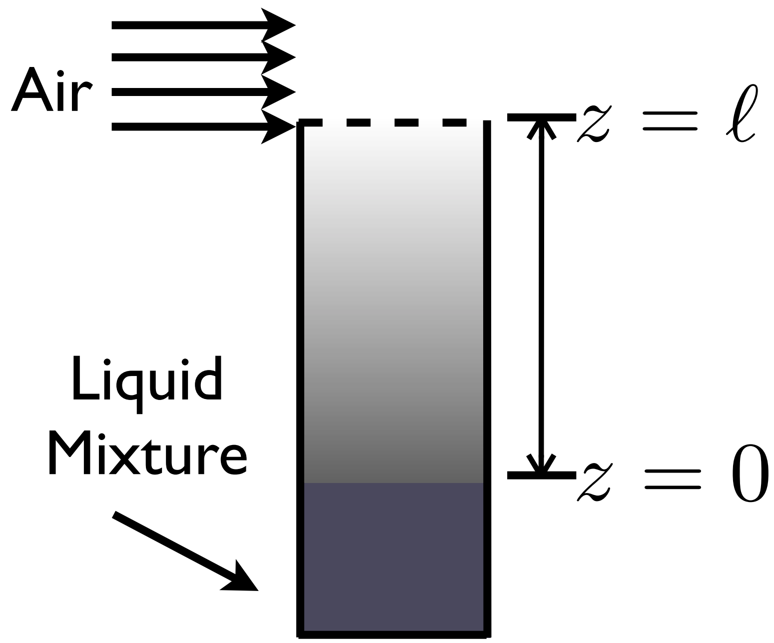
T&K Example 2.1.1

Example: Stefan Tube



Given: $Đ_{ij}$, $x_i(z=0)$, $x_i(z=\ell)$,

$\ell = 0.238$ m, $T = 328.5$ K

Find $x_i(z)$

Acetone (1), Methanol (2), Air (3)

$x_1(z=0)=0.319$, $x_2(z=0)=0.528$

$$
\begin{aligned}
Đ_{12} &= 8.48 \quad \mathrm{mm}^2/\mathrm{s} \\
Đ_{13} &= 13.72 \quad \mathrm{mm}^2/\mathrm{s} \\
Đ_{23} &= 19.91 \quad \mathrm{mm}^2/\mathrm{s}
\end{aligned}
$$

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),

$$
\begin{aligned}
\mathbf{n}_i &= \alpha_i \\
\mathbf{N}_i &= \beta_i
\end{aligned}
$$

Convection-diffusion balance...

From the Maxwell-Stefan equations:

$$
\frac{\mathrm{d}x_i}{\mathrm{d}z} = -\sum_{j \neq i}^{n} \frac{x_j N_i - x_i N_j}{c_t Đ_{ij}}
$$

A semi-analytic solution

Maxwell-Stefan Equations

$$\frac{\mathrm{d}x_i}{\mathrm{d}z} = -\sum_{j \neq i}^{n} \frac{x_j N_i - x_i N_j}{c_t Đ_{ij}}$$

Normalized coordinate: $\eta \equiv \frac{z}{\ell}$, $\quad \frac{\mathrm{d}}{\mathrm{d}z} = \frac{\mathrm{d}}{\mathrm{d}\eta}\frac{\mathrm{d}\eta}{\mathrm{d}z} = \frac{1}{\ell}\frac{\mathrm{d}}{\mathrm{d}\eta}$

$$\frac{1}{\ell}\frac{\mathrm{d}x_i}{\mathrm{d}\eta} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t Đ_{ij}},$$

We need to eliminate x_n from the equation so that we have unknowns $x_1 \ldots x_{n-1}$.

$$= x_i \sum_{j \neq i}^{n} \frac{N_j}{c_t Đ_{ij}} - \frac{x_n N_i}{c_t Đ_{in}} - \sum_{j \neq i}^{n-1} \frac{x_j N_i}{c_t Đ_{ij}}$$

Eliminate x_n by substituting: $x_n = 1 - \sum_{j=1}^{n-1} x_j = 1 - x_i - \sum_{j \neq i}^{n-1} x_j$

$$\frac{1}{\ell}\frac{\mathrm{d}x_i}{\mathrm{d}\eta} = x_i \sum_{j \neq i}^{n} \frac{N_j}{c_t Đ_{ij}} - \frac{N_i}{c_t Đ_{in}} \left(1 - x_i - \sum_{j \neq 1}^{n-1} x_j \right) - \sum_{j \neq i}^{n-1} \frac{x_j N_i}{c_t Đ_{ij}},$$

rearrange a bit, collecting terms on x_i, x_j.

$$= x_i \left(\frac{N_i}{c_t Đ_{in}} + \sum_{j \neq i}^{n} \frac{N_j}{c_t Đ_{ij}} \right) - \frac{N_i}{c_t Đ_{in}} + \sum_{j \neq i}^{n-1} \left(\frac{N_i}{c_t Đ_{in}} - \frac{N_i}{c_t Đ_{ij}} \right) x_j,$$

move ℓ over.

$$\frac{\mathrm{d}x_i}{\mathrm{d}\eta} = = \underbrace{\left(\frac{N_i}{c_t Đ_{in}/\ell} + \sum_{j \neq i}^{n} \frac{N_j}{c_t Đ_{ij}/\ell} \right)}_{\Phi_{ii}} x_i + \sum_{j \neq i}^{n-1} \underbrace{\left(\frac{N_i}{c_t Đ_{in}/\ell} - \frac{N_i}{c_t Đ_{ij}/\ell} \right)}_{\Phi_{ij}} x_j - \underbrace{\frac{N_i}{c_t Đ_{in}/\ell}}_{\phi_i}$$

almost there...

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$$\frac{\mathrm{d}x_i}{\mathrm{d}\eta} = \underbrace{\left(\frac{N_i}{c_t Đ_{in}/\ell} + \sum_{j\neq i}^{n} \frac{N_j}{c_t Đ_{ij}/\ell} \right)}_{\Phi_{ii}} x_i + \sum_{j\neq i}^{n-1} \underbrace{\left(\frac{N_i}{c_t Đ_{in}/\ell} - \frac{N_i}{c_t Đ_{ij}/\ell} \right)}_{\Phi_{ij}} x_j \underbrace{- \frac{N_i}{c_t Đ_{in}/\ell}}_{\phi_i}$$

$$\frac{\mathrm{d}(x)}{\mathrm{d}\eta} = [\Phi](x) + (\phi)$$

A system of linear ODEs with constant coefficients (c_t, N_j are constant)

$$\Phi_{ii} = \frac{N_i}{c_t Đ_{in}/\ell} + \sum_{k\neq i}^{n} \frac{N_k}{c_t Đ_{ik}/\ell},$$

$$\Phi_{ij} = N_i \left(\frac{1}{c_t Đ_{in}/\ell} - \frac{1}{c_t Đ_{ij}/\ell} \right),$$

$$\phi_i = -\frac{N_i}{c_t Đ_{in}/\ell}$$

Analytic solution (assuming N_i are all constant)

see T&K §8.3 and Appendix B

$$(x) = \Big[\exp\left[[\Phi]\eta\right]\Big](x_0) + \Big[[\exp\left[[\Phi]\eta\right]] - [I]\Big]\Big[\Phi\Big]^{-1}(\phi)$$

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

In Matlab, use "expm"

Note: if we had not eliminated the "n^{th}" equation, we could not form the inverses required here.

Algorithm:

1. Guess N_i
2. Calculate $[\Phi]$, (ϕ)
3. Calculate (x) at $\eta=1$ ($z=\ell$)
4. If (x_ℓ) matches the known boundary condition, we are done. Otherwise return to step 1.

Note: we could also solve the equations numerically in step 3 and eliminate step 2 (work straight from the original Maxwell-Stefan equations)

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Later in the course, we will show another way of getting N_i.

Matrix Form of Maxwell-Stefan Equations

$$\mathbf{d}_i = -\sum_{j\neq i}^{n} \frac{x_j \mathbf{N}_i - x_i \mathbf{N}_j}{c Đ_{ij}},$$
$$= -\sum_{j\neq i}^{n} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c Đ_{ij}}$$

$$\sum_{i=1}^{n} \mathbf{d}_i = 0$$

Easily shown for the case we have addressed thus far, $\mathbf{d}_i = \nabla x_i$.

Only n-1 of these equations are independent.

For a binary system, we have:

$$\nabla x_1 = -\frac{x_2 \mathbf{N}_1 - x_1 \mathbf{N}_2}{c_t Đ_{12}},$$
$$\nabla x_2 = -\frac{x_1 \mathbf{N}_2 - x_2 \mathbf{N}_1}{c_t Đ_{21}}$$

Show that these sum to zero.

Eliminate $\mathbf{J}_n$ from the set of n equations $\Rightarrow$ n-1 equations.

$$\mathbf{J}_n = -\sum_{j=1}^{n-1} \mathbf{J}_j = -\mathbf{J}_i - \sum_{\substack{j=1\\ j\neq i}}^{n-1} \mathbf{J}_j$$

$$\mathbf{d}_i = -\sum_{j\neq i}^{n} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c_t Đ_{ij}},$$

Split the summation into individual terms. Recall that we don't have a $Đ_{ii}$ term!

$$c_t \mathbf{d}_i = -\mathbf{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} + x_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\mathbf{J}_j}{Đ_{ij}},$$

Isolate the n^{th} diffusive flux.

$$= -\mathbf{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} + x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\mathbf{J}_j}{Đ_{ij}} + x_i \frac{\mathbf{J}_n}{Đ_{in}},$$

eliminated the n^{th} diffusive flux

$$= -\mathbf{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} + x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\mathbf{J}_j}{Đ_{ij}} - \frac{x_i}{Đ_{in}} \left(\mathbf{J}_i + \sum_{\substack{j=1\\ j\neq i}}^{n-1} \mathbf{J}_j \right),$$

Gather $\mathbf{J}_i$ and $\mathbf{J}_j$ terms

$$= -\mathbf{J}_i \left(\frac{x_i}{Đ_{in}} + \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} \right) + x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right) \mathbf{J}_j$$

Define diagonal and off-diagonal matrix entries.

$$= -B_{ii} \mathbf{J}_i - \sum_{j\neq i}^{n-1} B_{ij} \mathbf{J}_j$$

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$$
\begin{aligned}
c_t \mathbf{d}_i &= -\mathbf{J}_i \left(\frac{x_i}{Đ_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{Đ_{ij}} \right) + x_i \sum_{\substack{j=1 \\ j \neq i}}^{n-1} \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right) \mathbf{J}_j, \\
&= -B_{ii} \mathbf{J}_i - \sum_{j \neq i}^{n-1} B_{ij} \mathbf{J}_j
\end{aligned}
$$

n-1 dimensional form of the Maxwell-Stefan equations

n-1 dimensional matrix form:

$$
c_t(\mathbf{d}) = -[B](\mathbf{J})
$$

$$
\begin{aligned}
B_{ii} &= \frac{x_i}{Đ_{in}} + \sum_{j \neq i}^{n} \frac{x_j}{Đ_{ij}}, \\
B_{ij} &= -x_i \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right)
\end{aligned}
$$

$$
c_t \begin{pmatrix} \mathbf{d}_1 \\ \mathbf{d}_2 \\ \vdots \\ \mathbf{d}_{n-1} \end{pmatrix} = - \begin{bmatrix} B_{1,1} & B_{1,2} & \cdots & B_{1,n-1} \\ B_{2,1} & B_{2,2} & \cdots & B_{2,n-1} \\ \vdots & \vdots & \ddots & \vdots \\ B_{n-1,1} & B_{n-1,2} & \cdots & B_{n-1,n-1} \end{bmatrix} \begin{pmatrix} \mathbf{J}_1 \\ \mathbf{J}_2 \\ \vdots \\ \mathbf{J}_{n-1} \end{pmatrix}
$$

Note: we can write this in n-dimensional form, but then $[B]^{-1}$ cannot be formed.

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T&K §3.2

Fick's Law

Maxwell-Stefan Equations (matrix form)

$$c_t(\mathbf{d}) = -[B](\mathbf{J})$$

Fick's Law (matrix form)

$$(\mathbf{J}) = -c_t[B]^{-1}(\mathbf{d}) = -c_t[D](\nabla x)$$

so far, $\mathbf{d}_i = \nabla x_i$.

Some Observations:

- For an ideal gas mixture, the $Đ_{ij}$ are largely independent of composition (but are functions of T and p), while the D_{ij} are complicated functions of composition.
- The Fickian diffusion coefficients (D_{ij}) may be *negative*, while $Đ_{ij} \geq 0$.
- The binary diffusivity matrix is symmetric ($Đ_{ij} = Đ_{ji}$) but the Fickian diffusivity matrix is not symmetric ($D_{ij} \neq D_{ji}$).
- Note that $Đ_{ii}$ never enter in to any expression, and have no physical meaning. However, the Fickian D_{ii} enter directly into the expression for the fluxes, and represent the proportionality constant between the driving force and the diffusion flux for the i^{th} component.
- $Đ_{ij}$ are independent of reference frame. D_{ij} is for a molar-averaged velocity reference frame.

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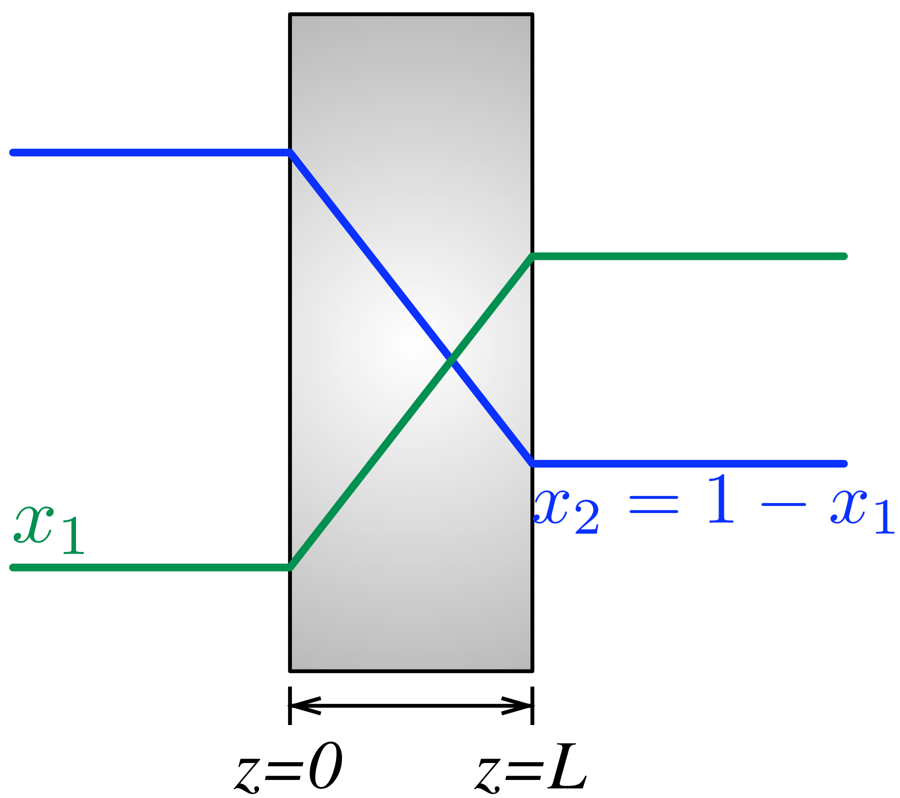
T&K §3.2

Binary/Ternary Comparison

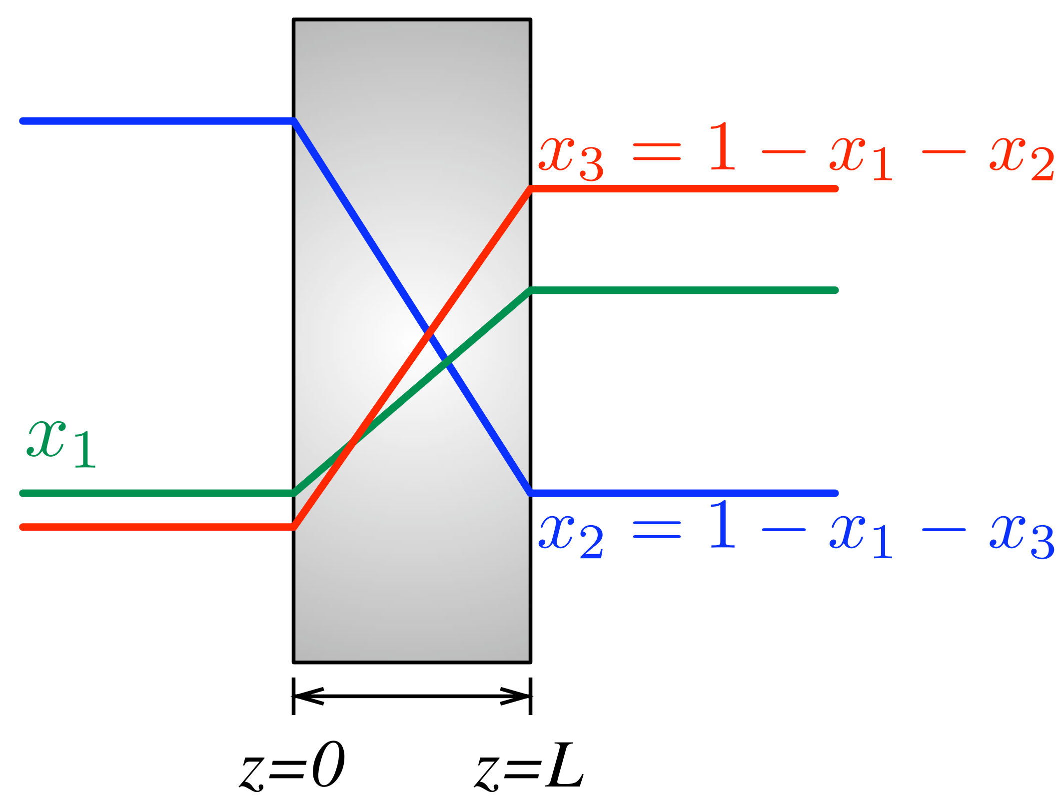
$$\sum_{i=1}^{n} x_i = 1 \quad \Rightarrow \quad \sum_{i=1}^{n} \nabla x_i = 0$$

Binary Diffusion



$$\nabla x_2 = -\nabla x_1$$

Ternary Diffusion

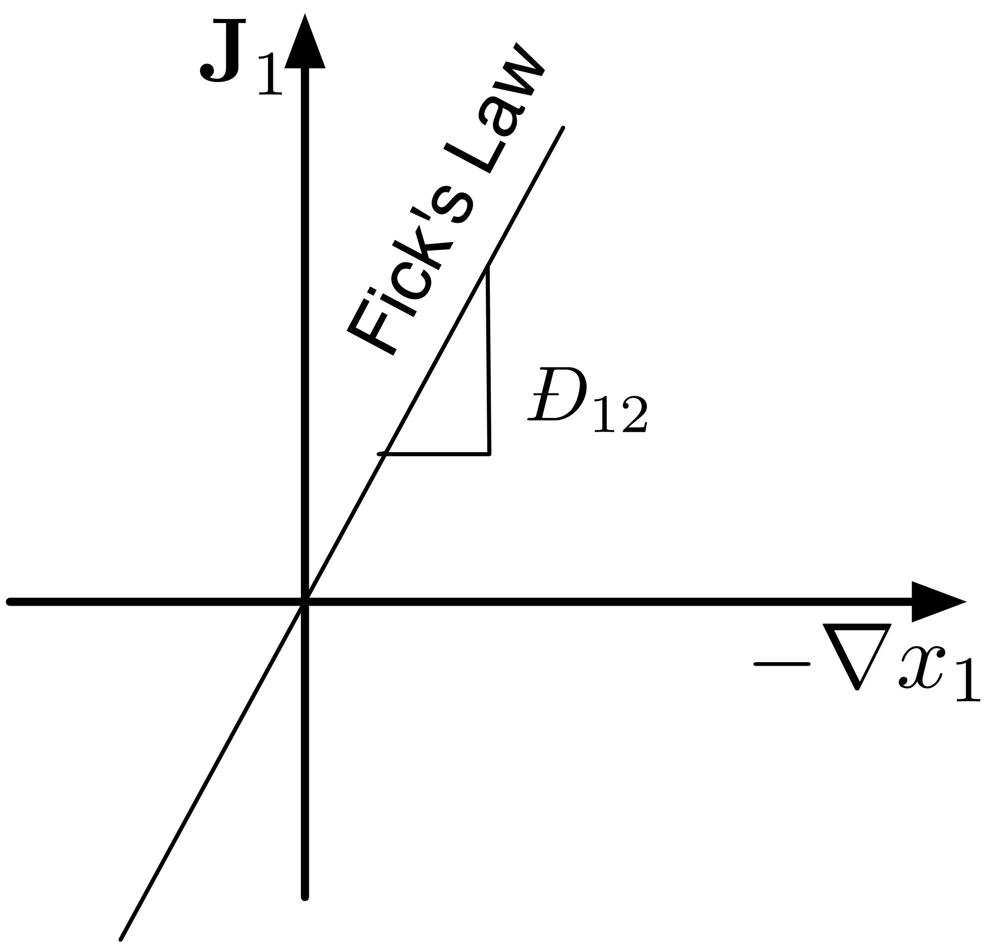


$$\nabla x_1 = -\nabla x_2 - \nabla x_3$$

Diffusion Regimes

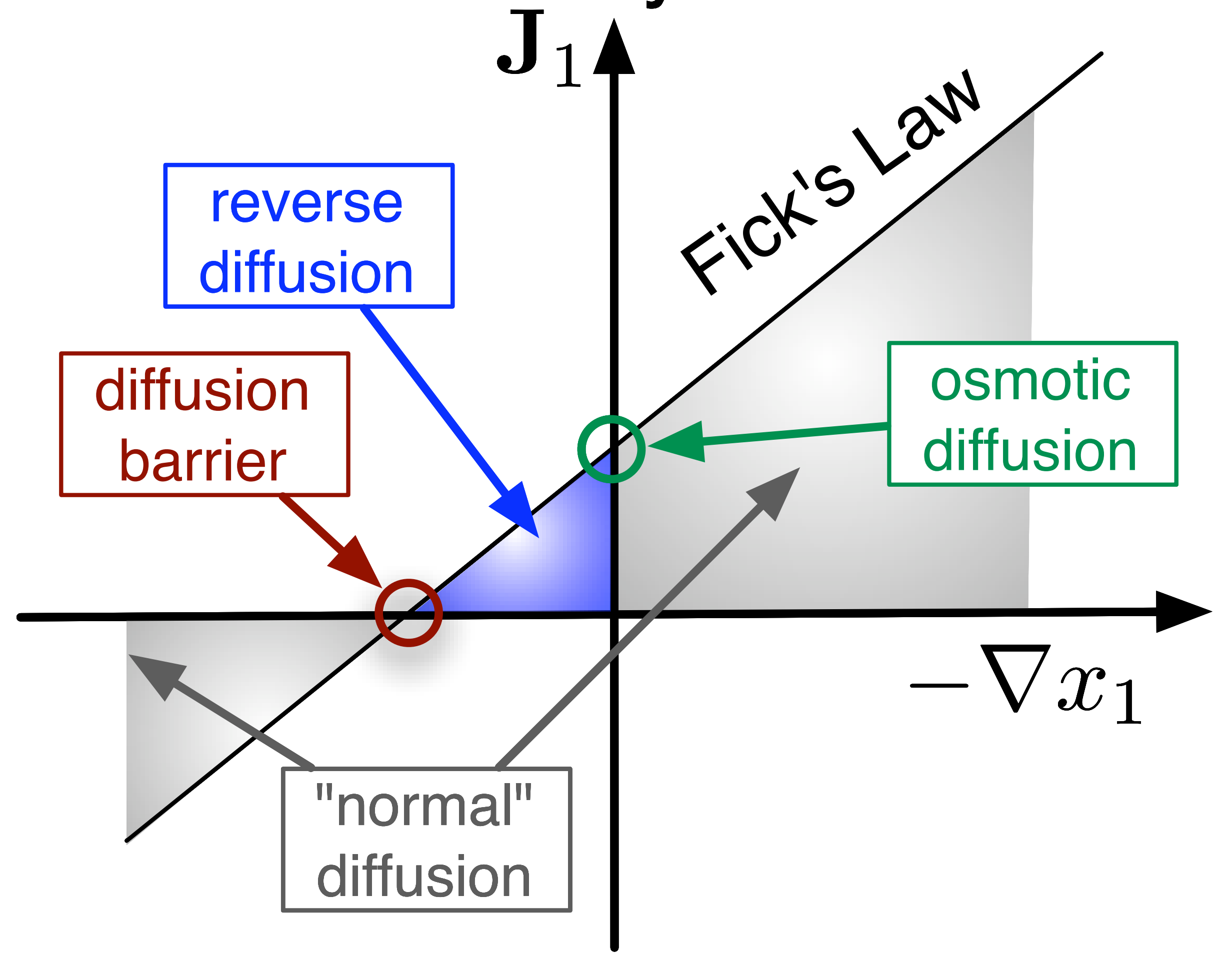
$$(J) = -c_t [D](\nabla x)$$

Binary Diffusion



$$\mathbf{J}_1 = -c_t D \nabla x_1$$

Ternary Diffusion

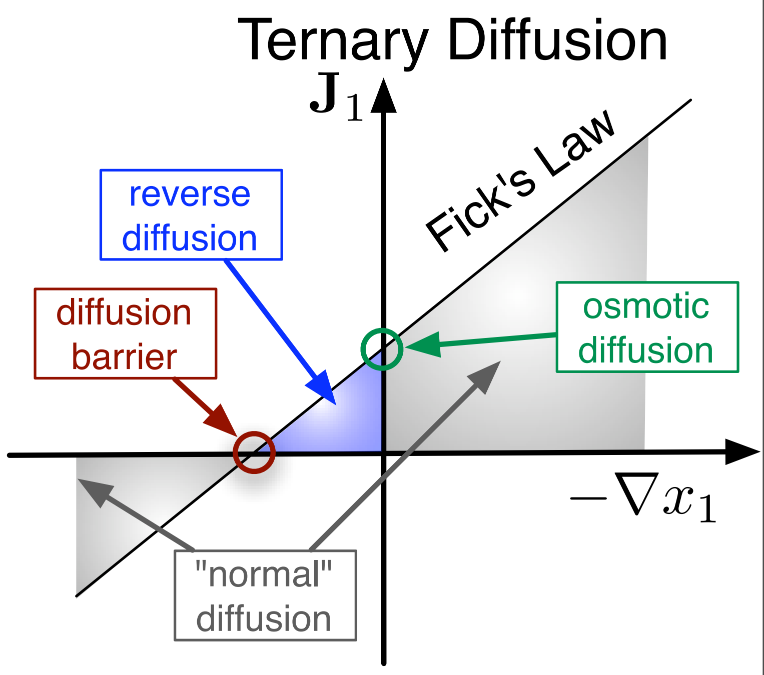


$$\begin{aligned} \mathbf{J}_1 &= -c_t D_{11} \nabla x_1 - c_t D_{12} \nabla x_2, \\ \mathbf{J}_2 &= -c_t D_{21} \nabla x_1 - c_t D_{22} \nabla x_2. \end{aligned}$$

Multicomponent Effects

$$(\mathbf{J}) = -c_t [B]^{-1} (\mathbf{d})$$

$$\begin{pmatrix} \mathbf{J}_1 \\ \mathbf{J}_2 \\ \vdots \\ \mathbf{J}_{n-1} \end{pmatrix} = -c_t \begin{bmatrix} D_{1,1} & D_{1,2} & \cdots & D_{1,n-1} \\ D_{2,1} & D_{2,2} & \cdots & D_{2,n-1} \\ \vdots & \vdots & \ddots & \vdots \\ D_{n-1,1} & D_{n-1,2} & \cdots & D_{n-1,n-1} \end{bmatrix} \begin{pmatrix} \mathbf{d}_1 \\ \mathbf{d}_2 \\ \vdots \\ \mathbf{d}_{n-1} \end{pmatrix}$$



For multicomponent effects to be important, $D_{ij}\nabla x_j$ must be significant compared to $D_{ii}\nabla x_i$.

$$\left| \frac{D_{ij}\nabla x_j}{D_{ii}\nabla x_i} \right| \sim \mathcal{O}(1)$$

$$|D_{ij}/D_{ii}| \sim \mathcal{O}(1)$$

$$\nabla x_j \neq 0$$

Fick's Law & Reference Velocities

How do we write Fick's law in other reference frames?

$(\mathbf{J}) = -c[D](\nabla x)$ Molar diffusive flux relative to a molar-averaged velocity.

$(\mathbf{j}) = -\rho_t[D^\circ](\nabla \omega)$ Mass diffusive flux relative to a mass-averaged velocity.

$(\mathbf{J}^V) = -[D^V](\nabla c)$ Molar diffusive flux relative to a volume-averaged velocity.

Option 1: Start with GMS equations and write them for the desired diffusive flux and driving force. Then invert to find the appropriate definition for $[D]$.

Option 2: Given $[D]$, define an appropriate transformation to obtain $[D^\circ]$ or $[D^V]$.

$$
\begin{aligned}
[D^\circ] &= [B^{uo}]^{-1}[\omega][x]^{-1}[D][x][\omega]^{-1}[B^{uo}] \\
&= [B^{ou}][\omega][x]^{-1}[D][x][\omega]^{-1}[B^{ou}]^{-1}
\end{aligned}
$$

$$
\begin{aligned}
B_{ik}^{uo} &= \delta_{ik} - \omega_i \left(\frac{x_k}{\omega_k} - \frac{x_n}{\omega_n} \right) \\
B_{ik}^{ou} &= \delta_{ik} - \omega_i \left(1 - \frac{\omega_n x_k}{x_n \omega_k} \right)
\end{aligned}
$$

$$
\begin{aligned}
[D^V] &= [B^{Vu}][D][B^{Vu}]^{-1} \\
&= [B^{Vu}][D][B^{uV}]
\end{aligned}
$$

$$
\begin{aligned}
B_{ik}^{Vu} &= \delta_{ik} - \frac{x_i}{\bar{V}_t} (\bar{V}_k - \bar{V}_n) \\
B_{ik}^{uV} &= \delta_{ik} - x_i \left(1 - \frac{\bar{V}_k}{\bar{V}_n} \right)
\end{aligned}
$$

T&K Example 3.2.1

Given $[D^V]$ for the system acetone (1), benzene (2), and methanol (3), calculate $[D]$.

$$(\mathbf{J}) = -c[D](\nabla x) \qquad (\mathbf{j}) = -\rho_t[D^\circ](\nabla \omega) \qquad (\mathbf{J}^V) = -[D^V](\nabla c)$$

$$\begin{aligned}[D^V] &= [B^{Vu}][D][B^{Vu}]^{-1} \\ &= [B^{Vu}][D][B^{uV}]\end{aligned}$$

$$\begin{aligned}\bar{V}_1 &= 74.1 \times 10^{-6}\,\frac{\text{m}^3}{\text{mol}} \\ \bar{V}_2 &= 89.4 \times 10^{-6}\,\frac{\text{m}^3}{\text{mol}} \\ \bar{V}_3 &= 40.7 \times 10^{-6}\,\frac{\text{m}^3}{\text{mol}}\end{aligned}$$

Diffusivities in units of 10^{-9} m^2/s

x_1	x_2	D^V_{11}	D^V_{12}	D^V_{21}	D^V_{22}
0.350	0.302	3.819	0.420	-0.561	2.133
0.766	0.114	4.440	0.721	-0.834	2.680
0.533	0.790	4.472	0.962	-0.480	2.569
0.400	0.500	4.434	1.866	-0.816	1.668
0.299	0.150	3.192	0.277	-0.191	2.368
0.206	0.548	3.513	0.665	-0.602	1.948
0.102	0.795	3.502	1.204	-1.130	1.124
0.120	0.132	3.115	0.138	-0.227	2.235
0.150	0.298	3.050	0.150	-0.269	2.250

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