“Unsteady” Mass-Transfer Models

ChEn 6603

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Outline

- Context for the discussion
- Solution for transient binary diffusion with constant c_t, N_t.
- Solution for multicomponent diffusion with c_t, N_t.
- Film theory revisited (surface renewal models)
- Transient diffusion in droplets, bubbles

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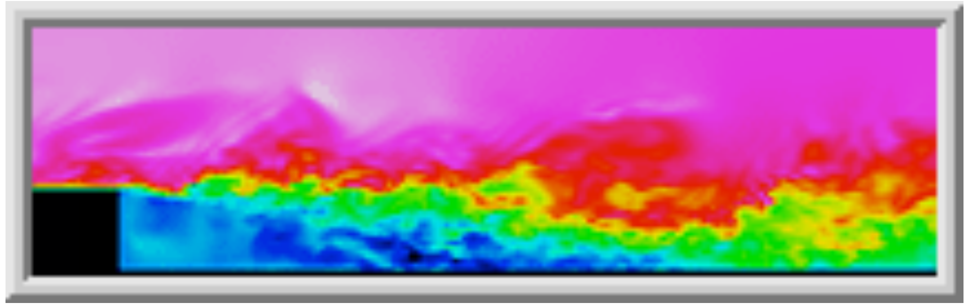
Context

- Film theory - so far we assumed steady state, no reaction in bulk (only potentially at interface)
  - Mass Transfer Coefficients used to simplify problem - don't fully resolve diffusive fluxes.
  - Bootstrap problem solved (via definition of $[\beta]$) to obtain total species fluxes.
- Unsteady cases?
  - What if we want to know the transient concentration profiles?
  - What if we want to consider the effects of transient (perhaps turbulent) mixing near the interface?

Here we consider ***unsteady*** film-theory approaches...



Hung Le and Parviz Moin.
http://www.stanford.edu/group/ctr/gallery/003_2.html

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Solution Options

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + r_i$$

Describes evolution of c_i at all points in space/time, but requires $\mathbf{N}_i$, which may involve solution of the momentum equations...

- Solve the problem numerically
  - Allows us to incorporate "full" description of the physics
    - may be quite complex (particularly if we must solve for a non-trivial velocity profile...)
  - Could also simplify portions (constant $[D]$, c_t, etc.)
  - Can solve this for a variety of BCs, ICs
- Make enough assumptions/simplifications to solve this analytically
  - Different BC/IC may require different form for analytic solution
  - We already did this for effective binary and linearized theory for a few simple problems (2-bulb problem, Loschmidt tube)
    - T&K chapters 5 & 6.
  - Here we show a few more techniques, based on unsteady film theory
    - Don't resolve mass transfer completely - get a coarser description of the diffusive fluxes...

$$\begin{aligned} (J) &= c_t[k^\bullet](\Delta x) \\ (N) &= [\beta](J) \end{aligned}$$

Approximation for diffusive flux (total flux).

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See T&K 9.2

Binary Formulation (1/3)

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + r_i$$

What are the assumptions?

$$c_t \frac{\partial x_i}{\partial t} = -\nabla \cdot \mathbf{N}_i$$

What happened here?

$$c_t \frac{\partial x_i}{\partial t} + \mathbf{N}_t \cdot \nabla x_i = -\nabla \cdot \mathbf{J}_i$$

One-dimensional...

$$c_t \frac{\partial x_i}{\partial t} + N_t \frac{\partial x_i}{\partial z} = -\frac{\partial}{\partial z} J_i$$

$$\frac{\partial x_1}{\partial t} + \frac{N_t}{c_t}\frac{\partial x_1}{\partial z} = D \frac{\partial^2 x_1}{\partial z^2}$$ (binary)

Problem statement:
semi-infinite diffusion

BCs & ICs

$z \geq 0,$	$t = 0,$	$x_i = x_{i\infty}.$	(Initial condition)
$z = 0,$	$t > 0,$	$x_i = x_{i0}.$	(Boundary condition)
$z \to \infty,$	$t > 0,$	$x_i = x_{i\infty}.$	(Boundary condition)

valid for "short" contact times (more later)

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Binary Formulation (2/3)

$$\frac{\partial x_1}{\partial t} + \frac{N_t}{c_t}\frac{\partial x_1}{\partial z} = D\frac{\partial^2 x_1}{\partial z^2}$$

Observation: since x is dimensionless, z, t, D must appear in a dimensionless combination in the solution.

$$\zeta = \frac{z}{\sqrt{4t}}$$

chosen for convenience, ζ^2/D is dimensionless

$$\frac{\partial}{\partial t} = \frac{\mathrm{d}}{\mathrm{d}\zeta}\frac{\partial \zeta}{\partial t} = -\frac{1}{2}\frac{\zeta}{t}\frac{\mathrm{d}}{\mathrm{d}\zeta}$$

$$\frac{\partial}{\partial z} = \frac{\mathrm{d}}{\mathrm{d}\zeta}\frac{\partial \zeta}{\partial z} = \frac{\zeta}{z}\frac{\mathrm{d}}{\mathrm{d}\zeta}$$

$$\frac{\partial^2}{\partial z^2} = \frac{\mathrm{d}^2}{\mathrm{d}\zeta^2}\left(\frac{\partial \zeta}{\partial z}\right)^2 = \frac{\zeta^2}{z^2}\frac{\mathrm{d}}{\mathrm{d}\zeta}$$

$$c_t\left(\frac{-\zeta}{2t}\right)\frac{\mathrm{d}x}{\mathrm{d}\zeta} + N_t\left(\frac{\zeta}{z}\right)\frac{\mathrm{d}x}{\mathrm{d}\zeta} = c_t D_i \frac{\zeta^2}{z^2}\frac{\mathrm{d}^2 x}{\mathrm{d}\zeta^2}$$

$$\left(-2\zeta + \frac{N_t}{c_t}\frac{z}{\zeta}\right)\frac{\mathrm{d}x}{\mathrm{d}\zeta} = D\frac{\mathrm{d}^2 x}{\mathrm{d}\zeta^2}$$

$$D\frac{\mathrm{d}^2 x}{\mathrm{d}\zeta^2} + 2(\zeta - \phi)\frac{\mathrm{d}x}{\mathrm{d}\zeta} = 0$$

$$\phi \equiv \frac{N_t}{c_t}\sqrt{t}$$

$$x_1 = x_{1,0} \qquad \zeta = 0$$

$$x_1 = x_{1,\infty} \qquad \zeta = \infty$$

Solve using order reduction

$$\frac{x_1 - x_{1,0}}{x_{1,\infty} - x_{1,0}} = \frac{1 - \operatorname{erf}\left(\frac{\zeta - \phi}{\sqrt{D}}\right)}{1 + \operatorname{erf}\left(\frac{\phi}{\sqrt{D}}\right)}$$

Note that this is a function of both z and t.

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Binary Formulation (3/3)

$$\frac{x_1 - x_{1,0}}{x_{1,\infty} - x_{1,0}} = \frac{1 - \operatorname{erf}\left(\frac{\zeta - \phi}{\sqrt{D}}\right)}{1 + \operatorname{erf}\left(\frac{\phi}{\sqrt{D}}\right)}$$

Calculate J_1 at z=0,

$$J_{1,0} = c_t \sqrt{\frac{D}{\pi t}} \frac{\exp\left(\frac{-\phi^2}{D}\right)}{1 + \operatorname{erf}\left(\frac{\phi}{\sqrt{D}}\right)} (x_{1,0} - x_{1,\infty})$$

What happens to J_1 as $z \rightarrow \infty$?

Mass Transfer Coefficients (binary system):

Low-flux limit (as $N_t \rightarrow 0$)

$$J_{1,0} = c_t \sqrt{\frac{D}{\pi t}} (x_{1,0} - x_{1,\infty})$$

$$k = \sqrt{\frac{D}{\pi t}} \qquad \Xi = \frac{\exp\left(\frac{-\phi^2}{D}\right)}{1 + \operatorname{erf}\left(\frac{\phi}{\sqrt{D}}\right)}$$

$$\begin{aligned} J_{1,0} &= c_t k \Xi (x_{1,0} - x_{1,\infty}) = c_t k^\bullet (x_{1,0} - x_{1,\infty}) \\ N_{1,0} &= c_t \beta_0 k^\bullet (x_{1,0} - x_{1,\infty}) \end{aligned}$$

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See T&K 9.3.1-9.3.2

Multicomponent System

$$\frac{\partial(x)}{\partial t} + \frac{N_t}{c_t}\frac{\partial(x)}{\partial z} = [D]\frac{\partial^2(x)}{\partial z^2} \qquad \zeta = \frac{z}{\sqrt{4t}} \qquad \phi \equiv \frac{N_t}{c_t}\sqrt{t}$$

This has the analytic solution (see T&K 9.3.1-9.3.2):

$$(x - x_\infty) = \left[[I] - \operatorname{erf}\left[(\zeta - \phi)[D]^{-\frac{1}{2}}\right]\right]\left[[I] + \operatorname{erf}\left[\phi [D]^{-\frac{1}{2}}\right]\right]^{-1}(x_0 - x_\infty)$$

$$(J_0) = \frac{c_t}{\sqrt{\pi t}}[D]^{\frac{1}{2}} \exp\left[\phi [D]^{-\frac{1}{2}}\right]\left[[I] + \operatorname{erf}\left[\phi [D]^{-\frac{1}{2}}\right]\right]^{-1}(x_0 - x_\infty)$$

remember that these are matrix functions!

Low-flux limit (as $N_t \rightarrow 0$) $\quad J_0 = \frac{c_t}{\sqrt{\pi t}}[D]^{\frac{1}{2}}(x_0 - x_\infty)$

$$[k] = (\pi t)^{-\frac{1}{2}}[D]^{\frac{1}{2}} \qquad [\Xi] = \exp\left[\phi [D]^{-\frac{1}{2}}\right]\left[[I] + \operatorname{erf}[\phi [D]^{-\frac{1}{2}}\right]^{-1}$$

$$\begin{aligned}(J_0) &= c_t[k][\Xi](x_0 - x_\infty) = c_t[k^\bullet](x_0 - x_\infty) \\ (N_0) &= c_t[\beta_0][k^\bullet](x_0 - x_\infty)\end{aligned}$$

Possible approaches:

- Solve the transient problem (beware of the "short" time assumption)
- Use this information to formulate other ***steady-state*** models (e.g. **turbulent mixing from bulk to surface**)

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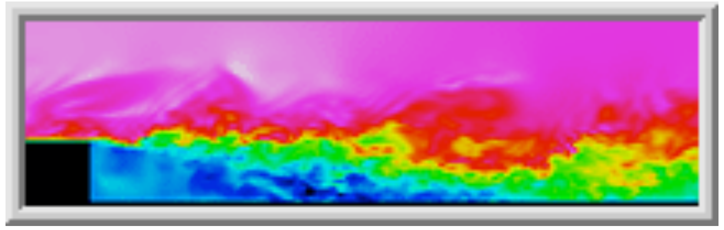
See T&K §9.1

Surface Renewal Models

$$
\begin{aligned}
(J_0) &= c_t[k][\Xi](x_0 - x_\infty) = c_t[k^\bullet](x_0 - x_\infty) \\
(N_0) &= c_t[\beta_0][k^\bullet](x_0 - x_\infty)
\end{aligned}
$$

$$[k] = (\pi t)^{-\frac{1}{2}} [D]^{\frac{1}{2}}$$

(J), (N) are functions of time since $[k]$ is a function of time.



How would we handle this problem?

Idea: develop a model for k that approximates the effects of transients near the surface.

Concept:

"Fresh" fluid from bulk is transported to the interface, where diffusion occurs for some time, t. Then this is transported back to the bulk and replaced by more "fresh" fluid.

Initial & Boundary conditions:

$$
\begin{aligned}
z = 0, &\quad x_i = x_{i0} &\quad t > 0 \\
z \geq 0, &\quad x_i = x_{i\infty} &\quad t = 0 \\
z \to \infty, &\quad x_i = x_{i\infty} &\quad t > 0
\end{aligned}
$$

Assumes that the "bulk" is unaffected by mass transfer ("short" contact times)

Age distribution function, $\psi(t)$, determines how long a fluid parcel is at the interface. (will affect expression for $[k]$)

See T&K §9.1

Surface-Renewal Models

Age distribution function, $\psi(t)$, determines how long a fluid parcel is at the interface. (will affect expression for $[k]$)

$$k_{ij}(t) = \sqrt{\frac{D_{ij}}{\pi t}} \qquad k_{ij} = \int_0^\infty k_{ij}(t)\psi(t)\mathrm{d}t$$

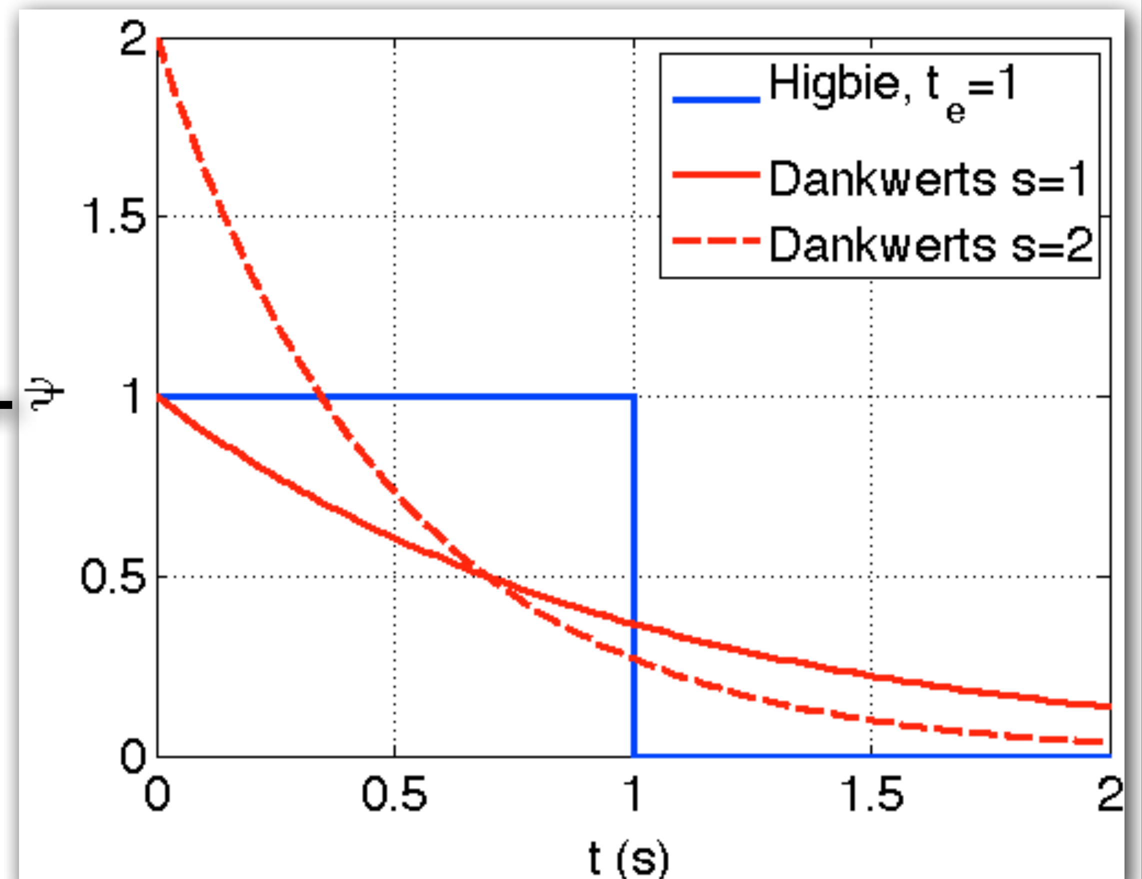
Attempts to model a statistically stationary process (fast mixing, no saturation to bulk) by a steady state $[k]$.

Higbie model (1935)

Assumes that all fluid parcels stay at the interface for a fixed amount of time, t_e.

$$\psi(t) = \begin{cases} 1/t_e & t \le t_e \\ 0 & t > t_e \end{cases} \longrightarrow [k] = \frac{2}{\sqrt{\pi t_e}}[D]^{1/2}$$

Note typo in T&K 9.3.33 (t vs. t_e)



Danckwerts model (1951)

Fluid parcels have a greater chance of being replaced the longer they are at the interface.

$$\psi(t) = s\exp(-st) \longrightarrow [k] = \sqrt{s}[D]^{1/2}$$

s - rate of surface renewal (1/sec) (fraction of surface area replaced by fresh fluid in unit time)

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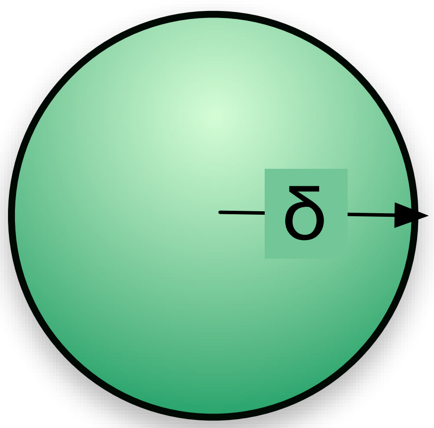
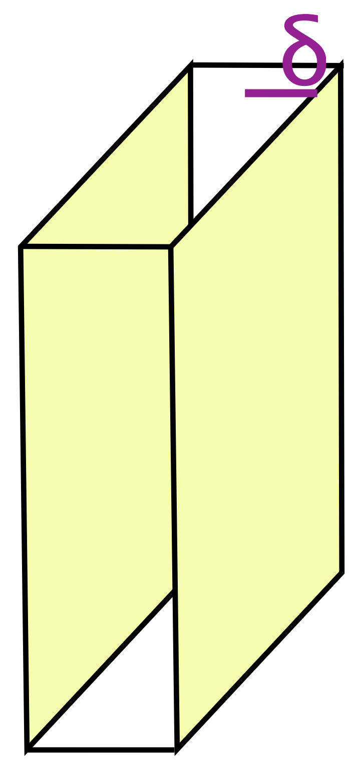
See T&K §9.4

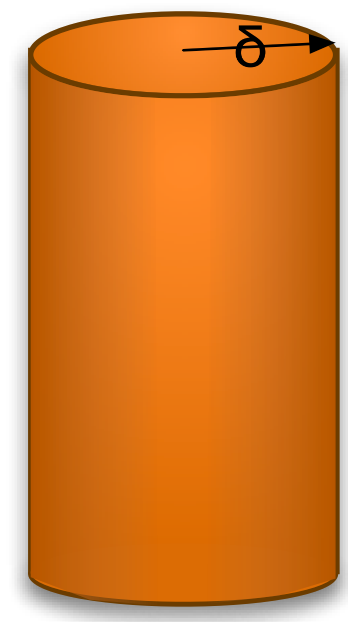
Bubbles, Drops, Jets



Spheres



Channels



Cylinders

$$[\mathrm{Fo}] = \frac{[D]t}{\delta^2}$$

For "small" Fo (Fo«1), we are safe to use surface renewal concepts. What happens at "large" Fo (Fo→1)?

$$\Delta x_i = x_{iI} - \langle x_i \rangle$$

$\langle x_i \rangle$ - "mixing cup" average

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See T&K §9.4

Fractional Approach to EQ

$$(J_0) = c_t[k][\Xi](x_0 - x_\infty) = c_t[k^\bullet](x_0 - x_\infty)$$
$$(N_0) = c_t[\beta_0][k^\bullet](x_0 - x_\infty)$$

x_∞ **is changing!**

(this solution is not valid)

$$F \equiv \frac{(x_{10} - \langle x_1 \rangle)}{(x_{10} - x_{1I})} \quad \text{Binary}$$
$$\Downarrow$$
$$(x_0 - \langle x \rangle) = [F](x_0 - x_I) \quad \text{Multicomponent}$$

x_0 - initial/boundary composition (t=0)

x_I - interface composition (constant in time)

$\langle x \rangle$ - average composition (changing in time), use in place of x_∞.

For a spherical droplet/particle:

$$[F] = \left[[I] - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \tfrac{1}{m^2} \exp\left[-m^2\pi^2 \, \mathrm{Fo}_{\mathrm{ref}} \, [D']\right] \right]$$

$$[D'] = \frac{1}{D_{\mathrm{ref}}}[D] \qquad \mathrm{Fo}_{\mathrm{ref}} \equiv D_{\mathrm{ref}} \frac{t}{r_0^2}$$

note: $\frac{6}{\pi^2} \sum_{m=1}^{\infty} m^{-2} = 1$

$$\mathrm{Sh} \equiv [k] \cdot 2r_0 [D]^{-1}$$

Sherwood number related to ∂F/∂Fo.

$$[\mathrm{Sh}] = \tfrac{2}{3}\pi^2 \left[\sum_{m=1}^{\infty} \exp\left[-m^2\pi^2 \, \mathrm{Fo}_{\mathrm{ref}} \, [D']\right] \right] \left[\sum_{m=1}^{\infty} \tfrac{1}{m^2} \exp\left[-m^2\pi^2 \, \mathrm{Fo}_{\mathrm{ref}} \, [D']\right] \right]^{-1}$$

remember that these are matrix functions!

Limiting cases:

$$\mathrm{Fo}_{\mathrm{ref}} \to \infty \implies \mathrm{Sh} = \tfrac{2}{3}\pi^2 [I] \Rightarrow [k] = \frac{\pi^2}{3r_0}[D]$$

See fig. 9.7 (L'Hopital's rule)

$$\mathrm{Fo}_{\mathrm{ref}} \ll 1 \implies [k] = \frac{2}{\sqrt{\pi t}} [D]^{1/2}$$

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