CBE 30356 Transport II

- A second class in transport, w/ emphasis on energy & mass transport.

- Text: BS&L Transport Phenomena
- material for this class is available on the class website: lectures, notes, homework, etc.
- daily quizzes should be completed before and after each session! Best of each (2 tries before, 2 after) count, so don't forget!
- We'll focus on energy transport before break, mass transport after, as well as some separations

Let's start!

Readings: Ch 9, sec. 1-5

Fourier's Law of Energy Conduction:

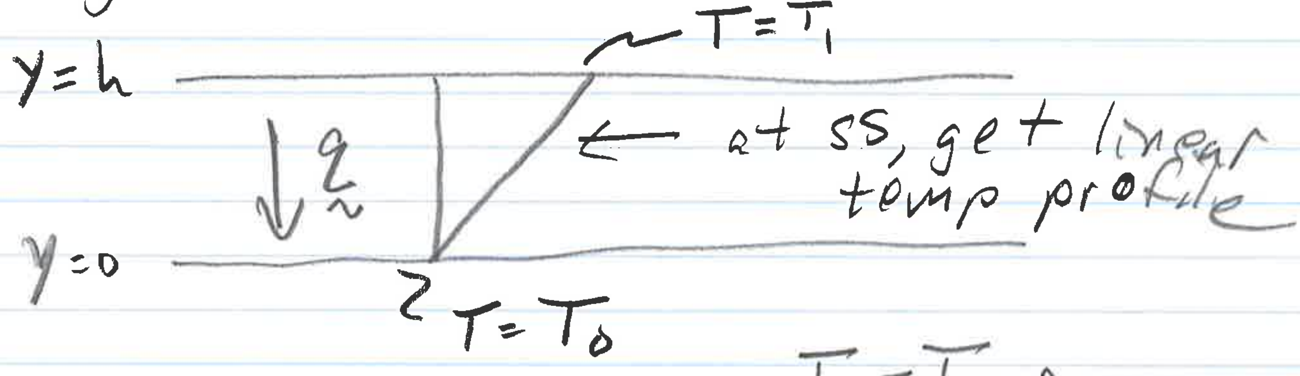
Energy flows from hot to cold!

What is a heat flux $\underset{\sim}{q}$?

$$\underset{\sim}{q} \equiv \frac{\text{Energy}}{\text{Area}\cdot\text{Time}} + \text{direction}$$

it's a vector!

Thought Problem: solid Slab



$$\underset{\sim}{q} \equiv q_y \underset{\sim}{\hat{e}}_y = -k\frac{T_1-T_0}{h}\underset{\sim}{\hat{e}}_y$$

↑ magnitude in y direction

Note parallel w/ plane-Couette flow!

The parallel w/ unidirectional flow is <u>exact</u>

$$\underset{\sim}{q} \equiv \underset{\approx}{\tau} \leftarrow \text{shear stress, mom. flux}$$

energy flux

$$T \equiv u_x \leftarrow \text{velocity}$$

temp

<u>and</u> $k \equiv \mu$

thermal conductivity

dynamic viscosity

$$\underbrace{\underset{\sim}{q} = -k \underset{\sim}{\nabla} T}_{\text{Fourier's Law of ht. cond.}} \equiv \underbrace{\tau_{ij} = \mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)}_{\text{Newton's Law of viscosity}}$$

(Note: BS&L puts a (-) sign in Newton's Law — just makes parallel more obvious)

④

so $\underset{\sim}{q} \equiv (q_x, q_y, q_z)$

$$q_x = -k\frac{\partial T}{\partial x}$$

$$q_y = -k\frac{\partial T}{\partial y}$$

$$q_z = -k\frac{\partial T}{\partial z}$$

Note: This is for isotropic materials

Many materials are anisotropic!

In this case:

$$\underset{\sim}{q} = -\underset{\approx}{k} \cdot \underset{\sim}{\nabla} T \qquad \left(q_i = -k_{ij}\frac{\partial T}{\partial x_j}\right)$$

↳ matrix!

For wood k is 3x higher along the grain than across it!

Now for units!

$$\underset{\substack{\uparrow \\ E/\text{Area}\cdot\text{Time}}}{\underset{\sim}{q}} = -k \underset{\substack{\uparrow \\ 1/L}}{\underset{\sim}{\nabla}} \overset{\text{Temp}}{T} \quad \therefore [k] \equiv \frac{\text{Energy}}{L \cdot \text{Time} \cdot {}^\circ K}$$

Units of energy:

Joules : $\frac{kg\,m^2}{s^2}$ (F · L)

ergs : $\frac{g\,cm^2}{s^2} \equiv 10^{-7}\,J$

cal : $\frac{\text{E to raise 1g}}{\text{water } 1^\circ C} \equiv 4.1868\,J$

(note: food cal ≡ kcal)

BTU : $\frac{\text{E to raise 1lb}}{\text{water } 1^\circ F} \equiv 1.055 \times 10^{3}\,J$

↳ varies a bit dep. on def., still used in nat. gas pricing!

We'll use SI in this class, (mostly) but know how to convert!

$$[K] = \frac{kg\,m^2}{s^2} \cdot \frac{1}{m\,s\,^\circ K}$$

$$= \frac{kg\,m}{s^3\,^\circ K} \equiv \frac{J}{m\,s\,^\circ K}, \text{ etc.}$$

$$\equiv \frac{W}{m\,^\circ K}$$

⑥

What is the <u>magnitude</u> of k?

gases: $k \sim 2 \times 10^{-2} \ \frac{W}{m\,^\circ K}$

liquids: $k \sim 1 \times 10^{-1} \ W/m\,^\circ K$ (organics)

$\sim 6 \times 10^{-1} \ W/m\,^\circ K$ (water!)

solids: messy! (usually sim. to water, except metals!)

Cu: $k \sim 400 \ W/m\,^\circ K$

steel: $k \sim 45 \ W/m\,^\circ K$

Useful to <u>know</u> approx values!

BS&L has several nice tables in sec. 9.1

Ok, so where does thermal conductivity come from? Different mechanisms for dif. materials!

Look at gases: sec. 9.3

In low density gases molecules carry mass momentum & energy with them as they bounce around!

The thermal energy of a monatomic gas (say He) is just $\underset{\text{3 degrees of freedom}}{\frac{3}{2}}\underset{\text{Boltzmann's cst}}{k}T$

$k = 1.38 \times 10^{-23}\ \text{J}/{}^{\circ}\text{K}$

[Note: in these notes k looks a lot like K or K. know from context!

The thermal velocity is $\bar{u} = \sqrt{\frac{8kT}{\pi m}}$ where m is molecular wt.

If molecules have number density n then they cross a plane w/ rate per area of

$$Z = \frac{1}{4} n \bar{u} \quad \left(\frac{\#}{\text{area}\cdot\text{time}}\right)$$

and carry mass, mom & E w/ them!

The net flux depends on the gradient and how far they come from!

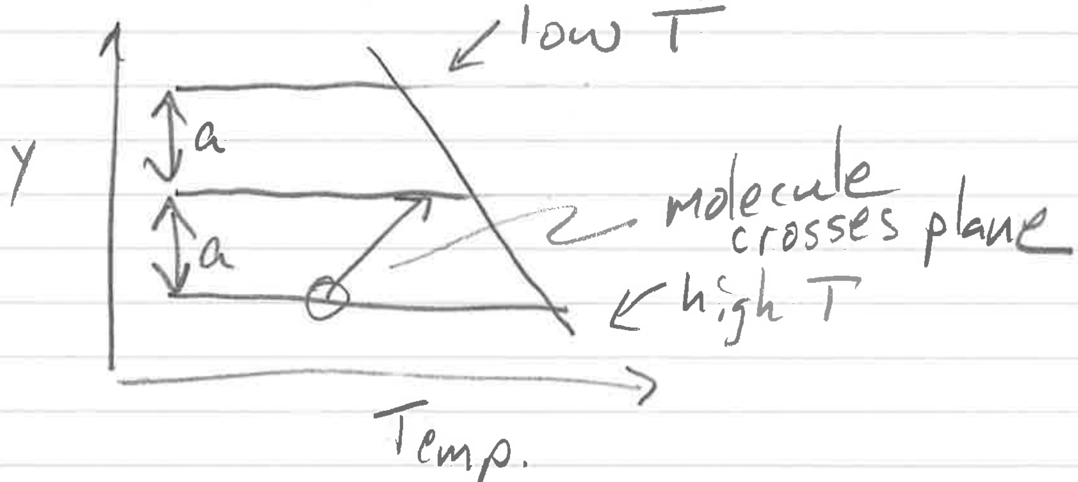
This is determined by mean free path λ between collisions!

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n}$$

$\hookrightarrow$ collision diameter (for hard spheres)

on average, last collision would be a distance $a = \frac{2}{3}\lambda$ from plane

So:



What is the energy flux?

$$q_y = Z\left(\frac{3}{2}KT\Big|_{y-a} - \frac{3}{2}KT\Big|_{y+a}\right)$$

Now $$T\Big|_{y=a} = T\Big|_{y} + a\frac{\partial T}{\partial y} = T\Big|_{y} + \frac{2}{3}\lambda\frac{\partial T}{\partial y}$$

so $$q_y = -\frac{\cancel{3}}{2}K\left(\frac{4}{\cancel{3}}\lambda\frac{\partial T}{\partial y}\right)Z$$

$$= -\underbrace{\left(\frac{1}{2}\, n\, k\, \bar{u}\, \lambda\right)}_{\overset{\|}{K}}\frac{\partial T}{\partial y}$$

$$\therefore\ K = \frac{1}{2} n k \bar{u} \lambda = \frac{\sqrt{mkT/\pi}}{\pi d^2}\,\frac{k}{m}$$

This shows that for gases K is indep. of n - and hence pressure! It's also a weak function of T (e.g., $T^{1/2}$)

While this works pretty well (& shows where k comes from), usually we use the Chapman-Enskog formula

$$K = \frac{25}{32}\,\frac{\sqrt{\pi m k T}}{\pi\sigma^2\Omega_k}\,\hat{C}_V \quad \leftarrow \text{ht cap cst vol}$$

σ is a Lennard-Jones parameter and Ω_κ is a "collision integral"

This works pretty well for monatomic gases. You can find values for σ and Ω_κ in tables E.1 & E.2

For polyatomic gases this is extended by the Eucken formula

$$K = \left(\hat{C}_p + \frac{5}{4}\,\frac{\overset{\text{gas const.}}{R}}{\underset{\text{molecular wt}}{M}}\right)\mu \leftarrow \text{viscosity}$$

where $\mu = \frac{5}{16}\,\frac{\sqrt{\pi m K T}}{\pi \sigma^2 \Omega_\mu}$

from similar arguments. The difference arises because polyatomic gases carry energy via other modes.

The key thing to remember is that (for low density gases)

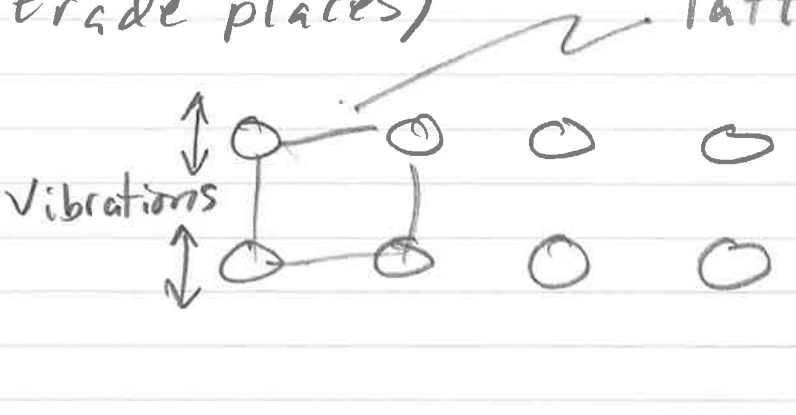
1) κ is indep. of pressure (mostly)
2) is a weak $f^n(T)$ ($\sim T^{1/2}$)
3) is proportional to the viscosity because it is produced by the same mechanism!

What about liquids? Much messier!

A simple model: (sec. 9.4)

Bridgman: energy is transmitted via lattice vibration (molecules don't trade places)

lattice spacing $= \left(\frac{V}{N}\right)^{1/3}$



By analogy w/ low density gases:

$$k \approx \rho \hat{C}_V |\bar{u}_y| \, a$$

speed of sound

$$a \sim \left(\frac{\tilde{V}}{\tilde{N}}\right)^{1/3} \; ; \quad |\bar{u}_y| \sim V_s = \sqrt{\frac{C_p}{C_V}\left(\frac{\partial p}{\partial \rho}\right)_T}$$

$$\hat{C}_V = 3\frac{\kappa}{m} \Big\} \text{ monatomic liquid}$$

$$\approx \sqrt{\frac{\partial p}{\partial \rho}\Big|_T}$$

as $C_p / C_V \approx 1$

so

$$k \approx 3\underbrace{\left(\frac{\rho}{m}\right)}_{\equiv \frac{\tilde{N}}{\tilde{V}}}\left(\frac{\tilde{V}}{\tilde{N}}\right)^{1/3} \kappa V_s$$

a bit smaller ✳

or, empirically, $k \approx 2.80\left(\frac{\tilde{N}}{\tilde{V}}\right)^{2/3} \kappa V_s$

$$\text{where } V_s \approx \sqrt{\frac{\partial p}{\partial \rho}\Big|_T}$$

This shows where k comes from for liquids, but usually you just look it up!

Now for solids: even messier!

Solids are often *porous* *composites*

For *dry* *sand* conduction occurs through grains, grain contacts, and air matrix — because air is a poor conductor, this is slow!

For *wet* sand, water is a better conductor, so conductivity goes up!

For *metals* conduction is via *conduction* *band* *electrons*, so conductivity is *much* higher!

electrical conductivity of copper >> elec. cond. of steel, ∴ so is thermal conductivity!

They are (mostly) proportional...

Now let's look at heat conduction in solids! We need conservation equation. We'll do a simplified derivation (for now)

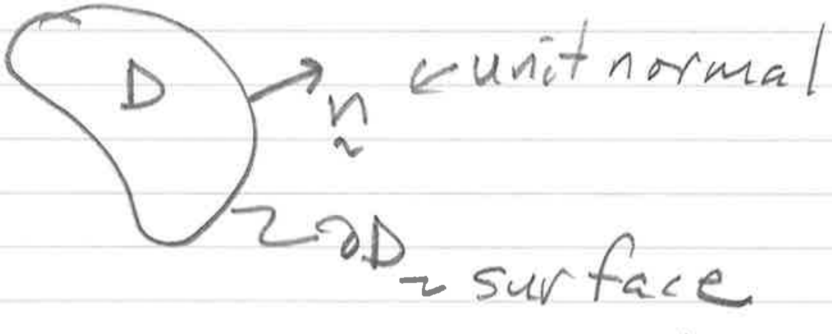
We take $$\frac{\text{thermal energy}}{\text{volume}} = \underbrace{\rho \hat{C}_p}_{\substack{\text{volumetric}\\ \text{ht capacity}}} T$$

conductive ht flux $= \underset{\sim}{q}$

$$\frac{\text{energy source}}{\text{volume}} = \dot{S} \quad (\text{rxn, elec. dissip, etc.})$$

↳ per time, $\frac{\text{watts}}{\text{vol}}$

Take arbitrary control volume D



Energy in D is conserved!

$$\left\{\begin{matrix}\text{accum energy}\\ \text{in } D\end{matrix}\right\} + \left\{\begin{matrix}\text{rate energy}\\ \underline{\underline{\text{out}}} \text{ by cond.}\end{matrix}\right\} = \left\{\text{sources}\right\}$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$\frac{\partial}{\partial t}\int_D \rho \hat{C}_p T \, dV + \int_{\partial D} \underset{\sim}{q} \cdot \underset{\sim}{n} \, dA = \int_D \dot{S} \, dV$$

$$\| $$

$$\int_D \underset{\sim}{\nabla} \cdot \underset{\sim}{q} \, dV \quad \text{by divergence theorem}$$

<u>If</u> $\rho \hat{C}_p$ is constant in time, because D is <u>arbitrary</u> we have the equation valid at every point:

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{q} + \dot{S}$$

Now if $\underset{\sim}{q} = -k \underset{\sim}{\nabla} T$ <u>and</u> k is indep. of position,

$$\underbrace{\rho \hat{C}_p \frac{\partial T}{\partial t}}_{\text{accum of } E} = \underbrace{k \nabla^2 T}_{\text{cond/diffu of } E} + \underbrace{\dot{S}}_{\text{sources of } E}$$

Note parallel w/ unidirectional flow!
- for flow in x-dir. only, x-component of Navier-Stokes equations is:

$$\underbrace{\rho\frac{\partial u_x}{\partial t}}_{\substack{\text{accum of}\\ x\text{-mom}}} = \underbrace{\mu\nabla^2 u_x}_{\substack{\text{dif}^{\underline{n}}\text{ of}\\ x\text{-mom}}} + \underbrace{\left(-\frac{\partial p}{\partial x} + \rho g_x\right)}_{\substack{\text{sources of}\\ x\text{-mom (per vol.)}}}$$

solutions are identical w/ same B.C.'s

plane-Couette flow ≡ cond. through slab

plane-Poiseuille flow ≡ cond. in slab w/ ht. generation

tube-Pois. flow ≡ Cond. in wire w/ ht generation

There are identical parallels w/ mass transfer too!

Solutions depend on B.C.'s — what kinds are there?

- fixed temperature (e.g., $T\big|_{\partial D} = T_0$)
  (equiv. to no-slip condition)
- fixed heat flux (e.g., $\underset{\sim}{q} \cdot \underset{\sim}{n}\big|_{\partial D} = q_0$)
  (equiv. to, say, wall shear stress $\tilde{\tau}_w$)
- mixed B.C. (heat transfer coef.)

$$\underset{\sim}{q} \cdot \underset{\sim}{n}\Big|_{\partial D} = \underset{\substack{\uparrow \\ \text{ht. transf. coef.}}}{h} \left(T\big|_{\partial D} - T_a\right)$$

— we used this BC. for lubricated core-annular flow, actually, but occurs more often in ht transfer

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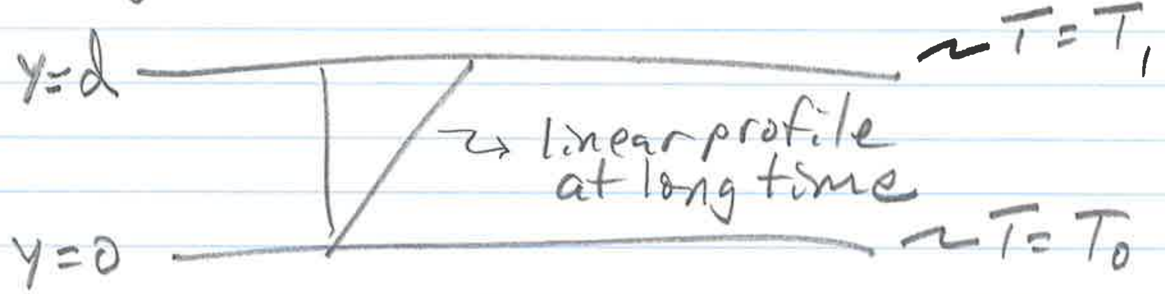
Now let's solve problems! We'll begin w/ SS, then look at start-up transients, Sturm-Liouville theory and boundary layer theory.

First - the simplest problem! Ht Cond. through a slab!



Assume:

1) conduction only in y-direction
2) steady-state
3) no heat sources (inside!)

$$\rho \hat{C}_p \underbrace{\cancel{\frac{\partial T}{\partial t}}}_{0\ (SS)} = k\left(\underbrace{\cancel{\frac{\partial^2 T}{\partial x^2}}}_{0} + \frac{\partial^2 T}{\partial y^2} + \underbrace{\cancel{\frac{\partial^2 T}{\partial z^2}}}_{0}\right) + \underbrace{\cancel{\dot{S}}}_{\text{No source}}$$

<u>So</u> $\frac{\partial^2 T}{\partial y^2} = 0$; $T\big|_{y=0} = T_0$

$T\big|_{y=d} = T_1$

Render dimensionless!

- All dimensionless variables should be of $O(1)$.
- Allow B.C.'s to suggest scaling (often get some from DE too, but not this time!)

$T|_{y=0} = T_0$ ⇒ subtract off ref. temp. T_0

$$\therefore \quad T^* = \frac{T - T_0}{\Delta T_c} \qquad T^*|_{y=0} = 0$$

$$T|_{y=d} = T_1 \qquad \therefore \quad T = T_0 + \Delta T_c T^*$$

$\hookrightarrow y^* = y/d$

$$\therefore \quad \Delta T_c T^*|_{y^*=1} = T_1 - T_0$$

$$T^*|_{y^*=1} = \underbrace{\frac{T_1 - T_0}{\Delta T_c}}_{=1}$$

so $\Delta T_c = T_1 - T_0$

$$\therefore \; \frac{\partial^2 T^*}{\partial y^{*2}} = 0 \; ; \quad T^*\Big|_{y^*=0} = 0 \quad T^*\Big|_{y^*=1} = 1$$

Integ. twice:

$$T^* = \underset{\substack{\downarrow \\ =1 \text{ from other BC!}}}{A}\, y^* + \underset{\substack{\downarrow \\ 0 \text{ since } T^*|_{y^*=0} = 0}}{\cancel{B}}$$

$\therefore \; T^* = y^*$, same as plane-Couette flow!

What is the heat flux at $y = 0$?

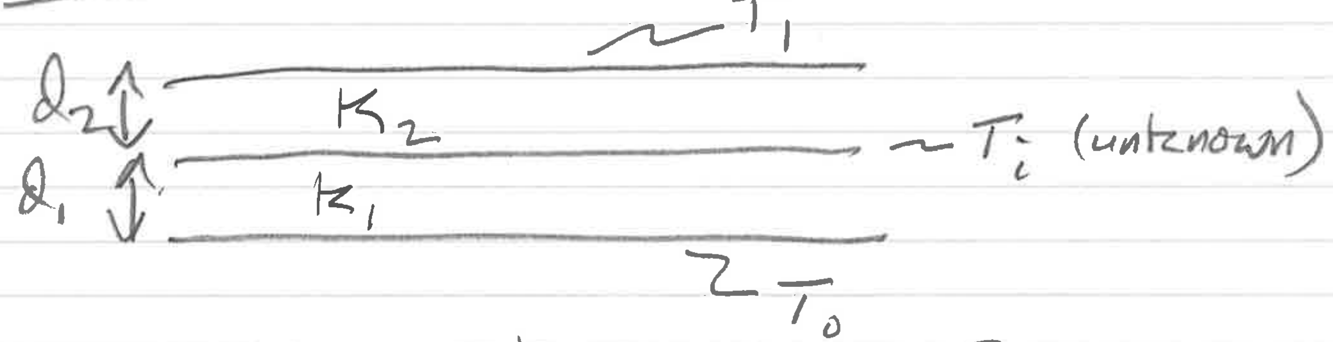
$$q_y\Big|_{y=0} = -k \frac{\partial T}{\partial y}\Big|_{y=0} = -\frac{k(T_1 - T_0)}{l} \underbrace{\frac{\partial T^*}{\partial y^*}\Big|_{y^*=0}}_{=1!}$$

$$\therefore \; q_y = -\frac{k(T_1 - T_0)}{l}$$

Note that in <u>this</u> geometry q_y is <u>constant</u>: the <u>same</u> heat flux through <u>every</u> <u>plane</u>!

Often we have multiple layers w/ different conductivities! (e.g., an insulated wall)

How to solve? Solve in each region and match at interface!



What are the matching conditions?

At the interface T and $\underset{\sim}{q}\cdot\underset{\sim}{n}$ are continuous!

normal ht. flux

For this geometry q_y is just a constant q_0! (but it is unknown)

From the last problem

$$q_0 = -\frac{k_2}{d_2}\left(T_1 - T_i\right) = -\frac{k_1}{d_1}\left(T_i - T_0\right)$$

We can solve these equations to get T_i:

$$T_1 - T_i = \frac{d_2}{d_1}\frac{k_1}{k_2}(T_i - T_0)$$

rearrange:

$$T_i\left(1 + \frac{d_2}{d_1}\frac{k_1}{k_2}\right) = T_1 + T_0\frac{d_2}{d_1}\frac{k_1}{k_2}$$

$$\text{so } T_i = \frac{T_1 + T_0\frac{d_2}{d_1}\frac{k_1}{k_2}}{1 + \frac{d_2}{d_1}\frac{k_1}{k_2}}$$

and the flux:

$$q_0 = \frac{-k_2}{d_2}(T_1 - T_i)$$

$$= \frac{-k_2}{d_2}\left(T_1 - \frac{T_1 + T_0\frac{d_2}{d_1}\frac{k_1}{k_2}}{1 + \frac{d_2}{d_1}\frac{k_1}{k_2}}\right)$$

$$= \frac{-k_2/d_2}{1 + \frac{d_2}{d_1}\frac{k_1}{k_2}}\left(\cancel{T_1} + T_1\frac{d_2}{d_1}\frac{k_1}{k_2} - \cancel{T_1} - T_0\frac{d_2}{d_1}\frac{k_1}{k_2}\right)$$

$$= \frac{-(T_1 - T_0)\,k_1/d_1}{1 + \frac{d_2}{d_1}\frac{k_1}{k_2}}$$

$$= \frac{-(T_1 - T_0)}{d_1/k_1 + d_2/k_2}$$

very simple!

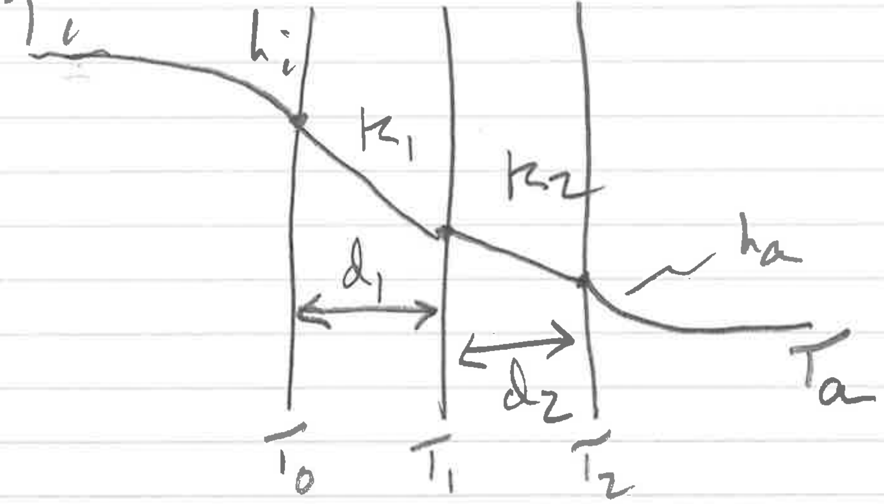
This suggests an analogy w/ electrical circuits:

$$\text{Resistance} \sim \frac{d \leftarrow \text{thickness}}{k \leftarrow \text{conductivity}}$$

current $\sim q$; voltage $\sim T$

for resistors in series, total resistance is the sum of resistance of each layer!

We can use this to solve a much messier problem: two layers w/ internal & external heat transfer coefficient!



By definition $q = h_i(T_i - T_0)$ (inside)

So the resistance of this layer is $\frac{1}{h_i}$!

So:
$$q = \frac{-(T_i - T_a)}{\underset{\overset{\nearrow}{\text{inside}}}{\frac{1}{h_i}} + \underset{\overset{\uparrow}{\text{layer 1}}}{\frac{\delta_1}{K_1}} + \underset{\overset{\uparrow}{\text{layer 2}}}{\frac{\delta_2}{K_2}} + \underset{\overset{\uparrow}{\text{outside}}}{\frac{1}{h_a}}}$$

The quantity $U \equiv \dfrac{1}{\underset{\longrightarrow \text{sum over all layers}}{\sum} \frac{1}{h}}$

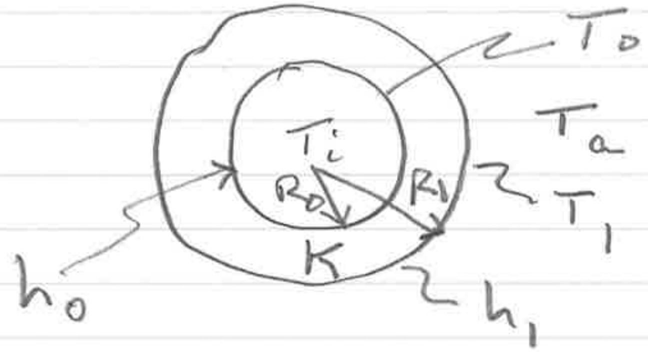
is called the overall ht. transfer coefficient.

The total flux is

$$q = U \Delta T$$

and heat loss is $Q = q\overset{\substack{\text{area of wall}\\ \downarrow}}{A} = UA\Delta T$

While insulating walls is important, often we want to insulate pipes! We can use the same approach:



Say we have hot water in a pipe w/ radius R_0, temp T_i

We have a heat transfer coeff. h_0 s.t. $q_r\Big|_{r=R_0} = h_0(T_i - T_0)$

We have an external ht transfer coeff. h_1 s.t.

$$q_r\Big|_{r=R_1} = h_1(T_1 - T_a)$$

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We don't know T_0 or T_1!

We need to solve for the temp. dist. in the insulation!

In cyl. coord:

$$k \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) = 0$$

$$\therefore \quad r \frac{\partial T}{\partial r} = A \qquad \text{(cst. of integ)}$$

$$\therefore \quad T = A \ln r + B$$

Now $T\Big|_{r=R_0} = T_0 \; ; \; T\Big|_{r=R_1} = T_1$

$$\therefore \quad T = T_0 + (T_1 - T_0)\frac{\ln r/R_0}{\ln R_1/R_0}$$

We need the flux at R_0:

$$q_r\Big|_{r=R_0} = -k\frac{\partial T}{\partial r}\Big|_{R_0} = k\frac{(T_0 - T_1)}{R_0 \ln(R_1/R_0)}$$

The total heat transfer through each cylinder is <u>constant</u>!

Thus:

$$Q = 2\pi R_0 L \, q_r \Big|_{r=R_0} = 2\pi \cancel{R_0} L \, k \frac{(T_0 - T_1)}{\cancel{R_0} \ln\left(R_1/R_0\right)}$$

we <u>also</u> have

$$\left.\begin{aligned} Q &= 2\pi R_0 L h_0 (T_i - T_0) \\ &= 2\pi R_1 L h_1 (T_1 - T_a) \end{aligned}\right\} \text{other layers!}$$

Rearranging:

$$\left.\begin{aligned} \frac{Q}{2\pi L} \frac{1}{h_0 R_0} &= T_i - T_0 \\ \frac{Q}{2\pi L} \frac{\ln(R_1/R_0)}{k} &= T_0 - T_1 \\ \frac{Q}{2\pi L} \frac{1}{h_1 R_1} &= T_1 - T_a \end{aligned}\right) \text{add these up!}$$

$$\frac{Q}{2\pi L}\left[\frac{1}{h_0 R_0} + \frac{\ln(R_1/R_0)}{k} + \frac{1}{h_1 R_1}\right] = T_i - T_a$$

$$\text{or } Q = \frac{2\pi L (T_i - T_a)}{\frac{1}{h_0 R_0} + \frac{\ln(R_1/R_0)}{k} + \frac{1}{h_1 R_1}}$$

This has the curious feature that if K is too large (bad insulation) then increasing R_1 will increase Q!

Let's look at this:

$$\frac{\partial Q}{\partial R_1} = \frac{-Q}{\frac{1}{h_0 R_0} + \frac{\ln(R_1/R_0)}{K} + \frac{1}{h_1 R_1}} \left(\frac{1}{R_1 K} - \frac{1}{h_1 R_1^2} \right)$$

This is positive if

$$\frac{1}{R_1 K} - \frac{1}{h_1 R_1^2} < 0$$

or $$\frac{h_1 R_1}{K} < 1$$

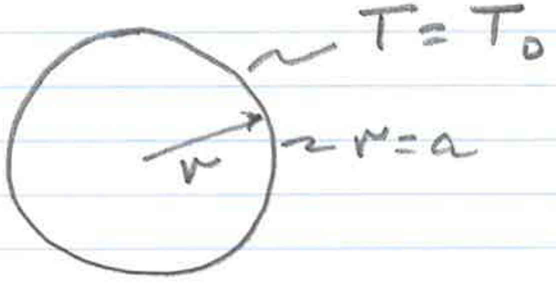
or $$R_1 < \frac{K}{h_1}$$

Now $R_1 > R_0$ so this can only occur if $R_0 < \frac{K}{h_1}$

or $K > h_1 R_0$

If K is less than $h_1 R_0$, Q always decreases!

Now let's look at conduction w/ an energy source: electrical dissip.!



$$\dot{S} \equiv cst \qquad \left(\text{for a wire, } \frac{\overset{\text{power}}{\overset{\downarrow}{I^2R}}}{\underbrace{\pi a^2 L}_{\text{volume}}}\right)$$

This (for DC) is uniform in the wire!

$$\therefore \rho \hat{C}_p \frac{\partial T}{\partial t} = k \nabla^2 T + \dot{S}$$

- Assume SS $\therefore \frac{\partial T}{\partial t} = 0$
- Dif$^{\underline{n}}$ (conduction) only in radial direction

* - Choose coord system in which boundary has a convenient rep.!

$\therefore$ cyl. coords!

All equations of change, operators, etc. are in Appendix B! know where it is!!

$$\nabla^2 = \underset{\substack{\nearrow \\ \sim \frac{T}{a^2}}}{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \theta^2} + \underset{\substack{\nearrow \\ \sim \frac{T}{L^2}}}{\frac{\partial^2 T}{\partial z^2}}$$

If $a \ll L$ then conduction in z direction is negligible (for this problem)

So:

$$0 = k\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \dot{S}$$

$$T\Big|_{r=a} = T_0 \qquad T\Big|_{r=0} = \underline{\text{finite}} \quad (\underline{\text{not}}\ \text{singular})$$

Let's render dimensionless:

$$T^* = \frac{T - T_0}{\Delta T_c} \qquad r^* = r/a \quad \Bigg) \text{ suggested by BC's}$$

What's ΔT_c?

Plug into D.E.:

$$0 = \frac{k\,\Delta T_c}{a^2}\,\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right) + \dot{S}$$

Divide out:

$$0 = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right) + \underset{1}{\underset{\shortparallel}{\left[\frac{\dot{S}a^2}{k\,\Delta T_c}\right]}}$$

$$\therefore\ \Delta T_c = \frac{\dot{S}a^2}{k}\ !$$

$$\text{so}\quad \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right) = -1$$

Integrate (mult by r^* first):

$$r^*\frac{\partial T^*}{\partial r^*} = -\frac{1}{2}r^{*2} + A$$

Divide by r^* & integ again:

$$T^* = -\frac{1}{4}r^{*2} + A\ln r^* + B$$

$$T^*\Big|_{r^*=0} = \text{finite, so } A = 0$$

(note- not true for a hollow pipe!)

$$T^*\Big|_{r^*=1} = 0 \quad \therefore \; B = \frac{1}{4}$$

and $T^* = \frac{1}{4}\left(1 - r^{*2}\right)$

or $T = T_0 + \frac{\dot{S}a^2}{k}\frac{1}{4}\left(1 - \frac{r^2}{a^2}\right)$

This is identical to Poiseuille flow!

What is the energy flux at r=a?

$$q\Big|_{r=a} = -k\frac{\partial T}{\partial r}\Big|_{r=a} = -k\frac{\Delta T_c}{a}\frac{\partial T^*}{\partial r^*}\Big|_{r^*=1}$$

Now $\frac{\partial T^*}{\partial r^*}\Big|_{r^*=1} = -\frac{1}{2}$! (nice $O(1)$ #)

$$\therefore \; q\Big|_{r=a} = -\frac{\cancel{k}}{\cancel{a}}\frac{\dot{S}a^{\cancel{2}}}{\cancel{k}}\left(-\frac{1}{2}\right) = \frac{1}{2}\dot{S}a$$

indep. of k - as it has to be!

We can get it from an energy balance without knowing T!

$$q_r\Big|_{r=a} \cdot \underbrace{2\pi a L}_{\text{surface area}} = \dot{S}\, \underbrace{\pi a^2 L}_{\text{volume}}$$

$$\therefore \; q_r\Big|_{r=a} = \frac{1}{2}\dot{S} a$$

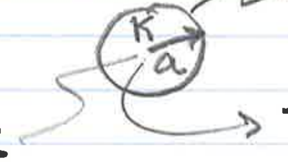
The same relation was found between the wall shear stress and pressure gradient for Poiseuille flow!

This problem is done w/ shell balances in section 10.2

We can look at a similar problem in the spherical coord system: a spherical pellet of radioactive material in a solid matrix at const. temp. at infinity: related to nuclear waste storage, for example!

$T|_{r\to\infty} = T_\infty$

$T|_{r=a} = T_s$ (unknown)



$T|_{r=0} = T_0$ (also unknown)

$\dot{S}$ energy $\frac{\text{source}}{\text{volume}}$

We want to calculate the temp. at the center T_0!

We solve this inside and outside the sphere!

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = K\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 T}{\partial\phi^2}\right] + \dot{S}$$

we're at SS, and all θ & ϕ derivatives are zero (symmetry), so:

$$0 = k \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r} \right) + \dot{S}$$

Outside the sphere:

$$k \equiv k_\infty , \quad \dot{S} = 0$$

$$T\Big|_{r=a} = T_s \text{ (unknown)}$$

$$T\Big|_{r\to\infty} = T_\infty$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right) = 0 \; !$$

$$\therefore \; r^2 \frac{\partial T}{\partial r} = A$$

$$\frac{\partial T}{\partial r} = \frac{A}{r^2}$$

$$T = -\frac{A}{r} + B$$

From BC's $T = T_\infty + (T_s - T_\infty)\frac{a}{r}$

What is the heat flux?

$$q_r\Big|_{r=a} = -k_\infty \frac{\partial T}{\partial r}\Big|_{r=a}$$

$$= +k_\infty (T_s - T_\infty)\frac{a}{r^2}\Big|_{r=a}$$

$$= \frac{k_\infty}{a}(T_s - T_\infty)$$

so we have a heat transfer coef

$$h \equiv \frac{k_\infty}{a}$$

for external heat transfer!

Now for the inside:

$$k\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) = -\dot{S}$$

$$r^2\frac{\partial T}{\partial r} = -\frac{\dot{S}}{k}\frac{1}{3}r^3 + A$$

$$\frac{\partial T}{\partial r} = -\frac{\dot{S}}{k}\frac{1}{3}r + \cancel{\frac{A}{r^2}}$$

0 since $T\big|_{r=0}$ is finite!

$$\therefore T = -\frac{\dot{S}}{k}\frac{1}{6}r^2 + B$$

Now $T\big|_{r=a} = T_s$

$$\therefore T_s = \frac{-\dot{S}}{k}\frac{1}{6}a^2 + B$$

$$B = T_s + \frac{\dot{S}}{k}\frac{1}{6}a^2$$

and $T\big|_{r=0} = B$!

We still need T_s to finish!

We need to match heat flux at the surface!

$$q_r\Big|_{r=a} = -k\frac{\partial T}{\partial r}\Big|_{r=a} = (-\cancel{k})\left(-\frac{\dot{S}}{\cancel{k}}\frac{1}{3}a\right)$$

$$= \frac{1}{3}a\dot{S} = \frac{k_\infty}{a}\left(T_s - T_\infty\right)$$

Note that we could also have gotten $q_r\big|_{r=a}$ from an energy balance!

$$\underbrace{4\pi a^2}_{\text{surf. area}} q_r\Big|_{r=a} = \underbrace{\frac{4}{3}\pi a^3}_{\text{volume}}\dot{S}$$

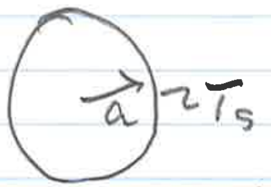
Anyway,

$$T_S = T_\infty + \frac{1}{3}\frac{a^2\dot{S}}{k_\infty}$$

and so

$$T\Big|_{r=0} \equiv T_0 = T_\infty + \underbrace{\frac{1}{3}\frac{a^2\dot{S}}{k_\infty}}_{\text{temp increase from far away}} + \underbrace{\frac{1}{6}\frac{a^2\dot{S}}{k}}_{\text{temp inc. from surface}}$$

Interestingly, this <u>doesn't</u> work for exterior temp variation for a cylinder:



T_∞ at $r \to \infty$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = 0$$

$$\therefore \quad T = A\ln r + B$$

$$\text{or} \quad T - T_s = A\ln r/a$$

The problem is that this blows up at $r \to \infty$! No solution!

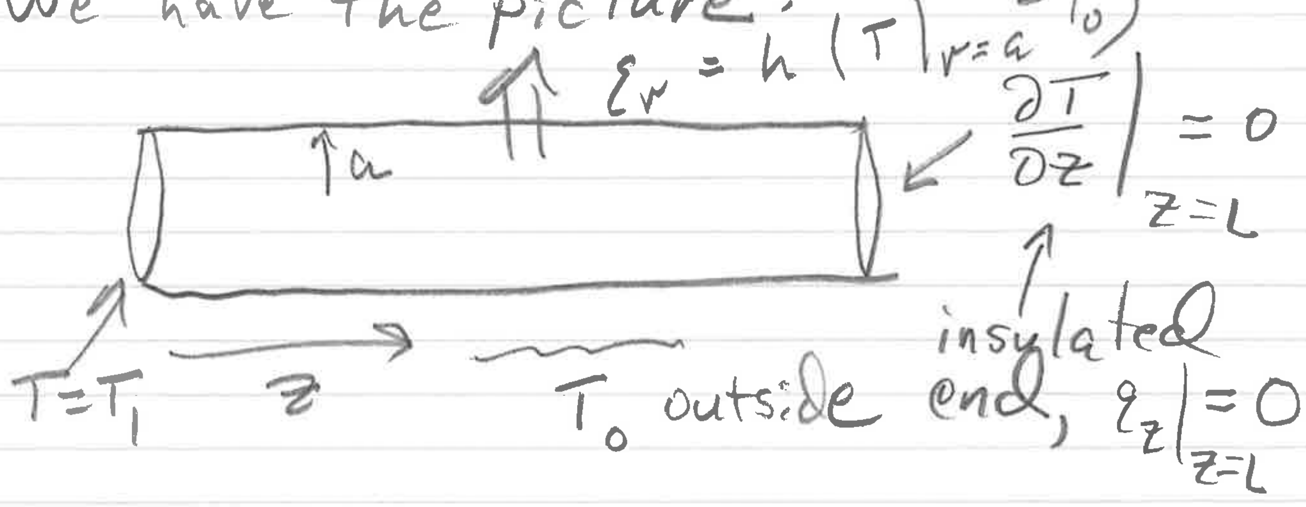
OK, now for a bit trickier problem: the cooling fin (section 10.7). We have a <u>rod</u> of length L & radius a heated at one end! All along the length we lose heat (usually via convection). We <u>model</u> this with a heat transfer coef.:

$$q_r\Big|_{r=a} = h\left(T\Big|_{r=a} - T_0\right)$$

Both q_r <u>and</u> T vary w/ z!

What is the equation for T?

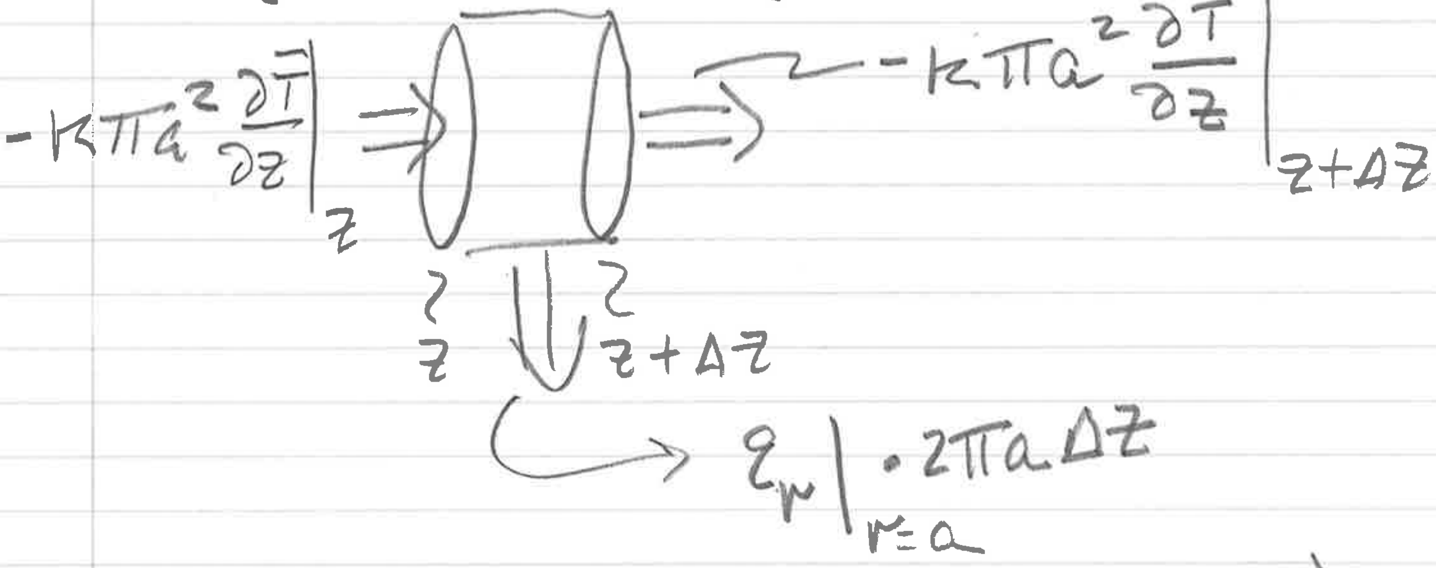
We have the picture:



We can get the equation from <u>shell</u> <u>balances</u>

Suppose we have some <u>area</u> <u>avg</u> temp. $\bar{T} \equiv \frac{1}{\pi a^2}\int_0^a T\, 2\pi r\, dr$

Along the rod we get:



$$= 2\pi a \Delta z\, h\left(T\big|_{r=a} - T_0\right)$$

Thus we get the balance:

$$0 = -k\pi a^2\left(\frac{\partial \bar{T}}{\partial z}\Big|_{z+\Delta z} - \frac{\partial \bar{T}}{\partial z}\Big|_{z}\right) + 2\pi a h \Delta z\left(T\big|_{r=a} - T_0\right)$$

Divide by Δz and take limit $\Delta z \to 0$

$$-\kappa \pi a^2 \frac{\partial^2 \bar{T}}{\partial z^2} + 2\pi a h \left(T\big|_{r=a} - T_0\right) = 0$$

Let's render dimensionless.

At $z=0$, $T=T_1$ (hot end)

From DE, ref. temp. is T_0

$$\therefore \quad T^* = \frac{T-T_0}{T_1-T_0}, \quad r^* = r/a, \quad z^* = \frac{z}{L}$$

$$\therefore \quad \frac{\partial^2 \bar{T}^*}{\partial z^{*2}} - \left[\frac{2hL^2}{\kappa a}\right] T^*\Big|_{r^*=1} = 0$$

$$T^*\Big|_{z^*=0} = 1 \qquad \frac{\partial \bar{T}^*}{\partial z^*}\Big|_{z^*=1} = 0$$

To close, we make the approx. that $\bar{T}^* \approx T^*\big|_{r^*=1}$ – negligible radial temp. gradients!

This works provided $a/L \ll 1$

We can get the <u>same</u> equation by averaging the ht transfer equation over the rod!

$$\rho\hat{C}_p \underbrace{\cancel{\frac{\partial T}{\partial t}}}_{0\ (SS)} = k\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right]$$

Recall $\bar{T} \equiv \frac{1}{\pi a^2}\int_0^a T\,2\pi r\,dr$

∴ mult by $2\pi r$, integ. over r, divide by πa^2

$$\frac{\rho\hat{C}_p}{\pi a^2}\frac{\partial}{\partial t}\int_0^a T\,2\pi r\,dr = \frac{k}{\pi a^2}\int_0^a \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)2\pi r\,dr$$

$$+\frac{k}{\pi a^2}\frac{\partial^2}{\partial z^2}\int_0^a T\,2\pi r\,dr$$

$$\rho\hat{C}_p\frac{\partial \bar{T}}{\partial t} = \frac{k}{\pi a^2}\left(r\frac{\partial T}{\partial r}\right)\Bigg|_0^a 2\pi + k\frac{\partial^2 \bar{T}}{\partial z^2}$$

Now $\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0$ (symmetry, finite T, etc.)

<u>and</u> $\left.q\right|_{r=a} = -k\left.\frac{\partial T}{\partial r}\right|_{r=a} = h\left(\left.T\right|_{r=a} - T_0\right)$

So $k \frac{\partial T}{\partial r}\Big|_{r=a} = -h\left(T\Big|_{r=a} - T_0\right)$

or, plugging back in:

$$\rho \hat{C}_p \frac{\partial \bar{T}}{\partial t} = -\frac{2h}{a}\left(T\Big|_{r=a} - T_0\right) + k\frac{\partial^2 \bar{T}}{\partial z^2}$$

At SS $\frac{\partial \bar{T}}{\partial t} = 0$

$$\therefore \frac{\partial^2 \bar{T}^*}{\partial z^{*2}} - \left(\frac{2hL^2}{ak}\right) T^*\Big|_{r^*=1} = 0$$

as before!

Again, we take $T^*\Big|_{r^*=1} \approx \bar{T}^*$ by neglecting radial variations!

So how do we solve this? This is a constant coef. ODE! The solutions are exponentials. For this one, the solution is more easily expressed as hyperbolics!

Let $\lambda^2 \equiv \frac{2hL^2}{ak}$

$\therefore \frac{\partial^2 \bar{T}^*}{\partial z^{*2}} = \lambda^2 \bar{T}^*$ (neglecting radial var.!)

$\therefore \bar{T}^* = A\cosh\lambda z^* + B\sinh\lambda z^*$

$\bar{T}^*\big|_{z^*=0} = 1 \quad \therefore A = 1$

$\frac{\partial \bar{T}^*}{\partial z^*}\Big|_{z^*=1} = 0 = \lambda\sinh\lambda + B\lambda\cosh\lambda$

$\therefore B = -\frac{\sinh\lambda}{\cosh\lambda}$

and $\bar{T}^* = \cosh\lambda z^* - \frac{\sinh\lambda}{\cosh\lambda}\sinh\lambda z^*$

We are <u>most</u> <u>interested</u> in the heat loss at $z=0$ (base of fin/rod)

$$Q = \underbrace{-k\frac{\partial \bar{T}}{\partial z}}_{\bar{q}_z}\Big|_{z=0} \cdot \underbrace{\pi a^2}_{\text{area}} = -k\underbrace{\frac{\pi a^2 (T_1 - T_0)}{L}}_{\text{scaling}}\frac{\partial \bar{T}^*}{\partial z^*}\Big|_{z^*=0}$$

Now from sol'n:

$$\left.\frac{\partial \bar{T}^*}{\partial z^*}\right|_{z^*=0} = \underbrace{\lambda \sinh \lambda z^*\Big|_{z^*=0}}_{=0\,!} - \lambda \frac{\sinh\lambda}{\cosh\lambda} \underbrace{\cosh\lambda z^*\Big|_{z^*=0}}_{=1}$$

$$= -\lambda \frac{\sinh\lambda}{\cosh\lambda}$$

$$\therefore \; Q = \underline{\frac{k\pi a^2 (T_1 - T_0)}{L}} \left(\frac{2hL^2}{ak}\right)^{1/2} \frac{\sinh\lambda}{\cosh\lambda}$$

This is a little messy, but it has 2 useful asymptotic limits depending on

$$\lambda \equiv \left(\frac{2hL^2}{ak}\right)^{1/2} \equiv \frac{L}{\left(\frac{ak}{2h}\right)^{1/2}}$$

which is a dimensionless rod length!

First, if $\lambda \ll 1$ then $\frac{\sinh\lambda}{\cosh\lambda} \approx \lambda$

$$\therefore \; Q = \frac{\cancel{k}\pi a^2 (T_1 - T_0)}{\cancel{L}} \left(\frac{2hL^{\cancel{2}}}{a\cancel{k}}\right)$$

$$= h(2\pi a L)(T_1 - T_0)$$

which is the heat loss you get if the entire surface is at T_1!

The limit $\lambda >> 1$ yields $\frac{\sinh\lambda}{\cosh\lambda} \approx 1$

$$\therefore\ Q = \frac{k\pi a^2(T_1-T_0)}{\cancel{L}}\left(\frac{2h\cancel{L^2}}{ak}\right)^{1/2}$$

$$= (T_1-T_0)\left(2\pi^2 a^3 h k\right)^{1/2}$$

which is indep. of L! This is because the rod cools off over a lengthscale $\left(\frac{ak}{2h}\right)^{1/2}$ & does so exponentially! Thus, only the length of $O\left(\left(\frac{ak}{2h}\right)^{1/2}\right)$ contributes to the cooling at the base!

You could use this to optimize your design!

over and over we have made use of the heat transfer coefficient h:

$$\underset{\underset{\frac{E}{\text{area}}\cdot\text{time}}{\uparrow}}{q} = \underset{\underset{\frac{E}{\text{area}\cdot\text{time}\cdot{}^\circ\text{K}}}{\uparrow}}{h} \; \Delta T \leftarrow \text{appropriate } \Delta T \text{ (varies w/ application)}$$

For a slab of thickness d

$$h = \frac{k}{d}$$

For external ht transfer from a sphere (w/ no convection)

$$h = \frac{K}{a} \leftarrow \text{radius}$$

For an annulus (pipe insulation)

$$h = \frac{K}{R_0 \ln(R_1/R_0)} \qquad \text{(based on area of inner } (R_0) \text{ surf)}$$

- this has the limiting value $\frac{K}{\Delta R}$ for $\frac{\Delta R}{R_0} \ll 1$

- Note: no sol'n as $R_1/R_0 \to \infty$

What about *convection*? for a cylinder (such as our rod) h arises from air (or water) blowing past!

layer over which heat transfer takes place!

If we think of this (boundary layer) region as insulation of thickness δ, then:

$$h = \frac{K}{\delta}$$

What is δ?? Fluid blows past over a time $t \sim D/U$

Energy *diffuses* a length

$$\delta \sim (\alpha t)^{1/2}$$

α → thermal diffusivity $\frac{K}{\rho c_p}$

over this time!

Thus: $$h \sim \frac{K}{(\alpha t)^{1/2}} \sim \frac{K}{\left(\frac{\alpha D}{U}\right)^{1/2}}$$

$$\equiv \frac{K}{D} \underbrace{\left(\frac{UD}{\nu}\right)^{1/2}}_{Re} \underbrace{\left(\frac{\nu}{\alpha}\right)^{1/2}}_{Pr}$$

where $\nu \equiv$ mom dif. (kinematic viscosity)

In fact, correlations based on exp't get pretty close to this!

from Whittaker (e.g., sec. 14-4)

$$h = \frac{K}{D}\left(0.4\,Re^{1/2} + 0.06\,Re^{2/3}\right) Pr^{0.4} \underbrace{\left(\frac{\mu_\infty}{\mu_0}\right)^{1/4}}_{\text{correction due to visc. variation w/T}}$$

Many other correlations exist for different geometries. We will look at this and other correlations (& sources!) again and again!

It is useful to look at heat transfer in terms of <u>dimensionless numbers</u>. There are <u>many</u>, but so far we've looked at the Biot number:

$$Bi = \frac{ha}{K} \begin{array}{l} \leftarrow \text{external ht transfer coef} \\ \leftarrow \text{material length scale} \\ \leftarrow \text{material thermal cond} \end{array}$$

$$\equiv \frac{h}{K/a} \begin{array}{l} \leftarrow \text{external ht transf. coef} \\ \leftarrow \text{internal ht transf coef} \end{array}$$

so if $Bi \gg 1$ we are dominated by <u>internal</u> resistance

if $Bi \ll 1$ we are dominated by <u>external</u> resistance.

For general shapes $a \sim \frac{V}{A} \begin{array}{l} \leftarrow \text{vol} \\ \leftarrow \text{surf area} \end{array}$

(e.g., for a sphere $\frac{V}{A} \sim \frac{1}{3}a$

cylinder $\frac{V}{A} \sim \frac{1}{2}a$

slab $\frac{V}{A} \sim a$ (half width)

The <u>second</u> (and most important!) group is the Nusselt number - which looks the same!

$$Nu = \frac{hD}{K}$$

ht trans. coef. → h

D ← diameter (or length scale)

K ← external conductivity

$$Nu = \frac{h}{K/D}$$

h ← actual ht transf. coef.

K/D ← expected ht transf coef. if pure conduction

For our sphere in a solid, $h = \frac{K}{a}$

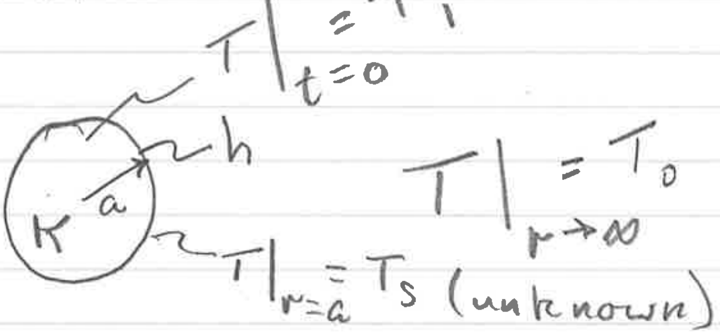
$$\therefore \underline{Nu = 2} \quad \text{(pure conduction limit)}$$

If we have <u>convection</u>, from Whittaker

$$\frac{hD}{K} \equiv Nu = 2 + \left(0.4 Re^{1/2} + 0.06 Re^{2/3}\right) Pr^{0.4} \left(\frac{\mu_\infty}{\mu_0}\right)^{1/4}$$

e.g., <u>same</u> as for a cylinder, but w/ conduction limit added in!

To see how this works, let's look at a classic problem: Quenching of a hot sphere!



$$q_r\Big|_{r=a} = h\left(T\Big|_{r=a} - T_0\right)$$

$$\text{where } \frac{h\overset{2a}{D}}{K_{ext}} = Nu \quad \text{(either 2, or from correlation...)}$$

Ok, we have the PDE:

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = K \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T}{\partial r}\right)$$

$$\text{and } T\Big|_{t=0} = T_1, \quad T\Big|_{r=0} = \text{finite}$$

$$-K\frac{\partial T}{\partial r}\Big|_{r=a} = q_r\Big|_{r=a} = h\left(T\Big|_{r=a} - T_0\right)$$

Let's render dimensionless!

$r^* = r/a$, $T^* = \dfrac{T - T_0}{T_1 - T_0}$ (from BC & IC)

$t^* = t/t_c$ (to be determined!)

Recall $\alpha \equiv \dfrac{k}{\rho \hat{C}_p}$ (thermal diffusivity)

$$\therefore \underbrace{\frac{\rho \hat{C}_p}{t_c}} \frac{\partial T^*}{\partial t^*} = \frac{k}{a^2} \frac{1}{r^{*2}} \frac{\partial}{\partial r^*}\left(r^{*2} \frac{\partial T^*}{\partial r^*}\right)$$

divide out

$$\therefore \frac{\partial T^*}{\partial t^*} = \left[\frac{t_c \alpha}{a^2}\right] \frac{1}{r^{*2}} \frac{\partial}{\partial r^*}\left(r^{*2} \frac{\partial T^*}{\partial r^*}\right)$$

$\left[\dfrac{t_c \alpha}{a^2}\right] = 1$ so $t_c = a^2/\alpha$ - dif^n time!

And we have BC's:

$T^*\Big|_{t^*=0} = 1$ $T^*\Big|_{r^*=0} =$ finite

$$-\frac{k}{a} \frac{\partial T^*}{\partial r^*}\Big|_{r^*=1} = h T^*\Big|_{r^*=1}$$

or $\dfrac{\partial T^*}{\partial r^*}\Big|_{r^*=1} = -\underbrace{\dfrac{ha}{k}}_{\to \text{Biot \#!}} T^*\Big|_{r^*=1}$

It's <u>easiest</u> to look at 2 limits,

Bi >> 1 ⇒ internal resistance

Bi << 1 ⇒ external resistance

We do the <u>latter</u> first!

This is similar to the cooling fin: we want to look at the <u>average temp</u>

$$\bar{T} = \frac{1}{\underbrace{\frac{4}{3}\pi a^3}_{\text{vol of sphere}}} \int_0^a T \underbrace{4\pi r^2 dr}_{dV}$$

$$\therefore \bar{T}^* = 3\int_0^1 T^* r^{*2} dr^*$$

To get the equation for $\bar{T}^*$, multiply PDE by $3r^{*2}dr^*$ and integrate!

$$\frac{\partial}{\partial t^*}\left[3\int_0^1 T^* r^{*2} dr^*\right] = 3\int_0^1 \cancel{\frac{1}{r^{*2}}} \frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial T^*}{\partial r^*}\right)\cancel{r^{*2}} dr^*$$

cancels!

$$= 3\, r^{*2}\frac{\partial T^*}{\partial r^*}\bigg|_0^1 = 3\frac{\partial T^*}{\partial r^*}\bigg|_{r^*=1}$$

Now $\left.\frac{\partial T^*}{\partial r^*}\right|_{r^*=1} = -Bi\,T^*\Big|_{r^*=1}$ from BC

So: $\frac{\partial \bar{T}^*}{\partial t^*} = -3Bi\,T^*\Big|_{r^*=1}$

<u>If</u> $Bi \ll 1$ then $T^*\Big|_{r^*=1} \approx \bar{T}^*$ (no internal resistance)

$\therefore \frac{\partial \bar{T}^*}{\partial t^*} \approx -3Bi\,\bar{T}^*, \quad \bar{T}^*\Big|_{t^*=0} = 1$

and $\bar{T}^* = e^{-3Bi\,t^*}$ $\qquad t^* \equiv \frac{\alpha t}{a^2}$

sometimes called Fourier #

so $$\frac{\bar{T} - T_0}{T_1 - T_0} \approx e^{-3\frac{ah}{\cancel{k}}\frac{\frac{\cancel{k}}{\rho C_p}t}{a^2}} = e^{-\frac{3ht}{\rho C_p a}}$$

We can rewrite this!

$A \equiv 4\pi a^2 \qquad V \equiv \frac{4}{3}\pi a^3$

$\therefore \frac{A}{V} = \frac{3}{a}$

and

$$\frac{\bar{T} - T_0}{T_1 - T_0} \approx e^{-\frac{Aht}{\rho \hat{C}_p V}}$$

which is good for <u>any</u> shape (provided $Bi \ll 1$ <u>and</u> h is constant)!

This is called the <u>Lumped Capacitance Model</u>

Now for the $Bi \to \infty$ limit!

$$T^*\Big|_{r^*=1} = -\frac{1}{Bi}\frac{\partial T^*}{\partial r^*}\Big|_{r^*=1} \approx 0 \,!$$

w/ $$\frac{\partial T^*}{\partial t^*} = \frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial T^*}{\partial r^*}\right)$$

$$T^*\Big|_{t^*=0} = 1 \,, \quad T^*\Big|_{r^*=0} = \text{finite}$$

How do we solve? Use <u>separation of variables</u>

This only works for linear homogeneous PDE's w/ homogeneous B.C.'s - but that's a lot of transport problems!

Key ref: Boyce & DiPrima, Ch 10&11
(this was your text, mine was '77 3rd ed...)

Ok, let $T^* = \underset{\substack{\uparrow \\ \text{only } f^n(r)}}{F(r^*)}\,\underset{\substack{\uparrow \\ \text{only } f^n(t)}}{G(t^*)}$

Plug in:

$$F\frac{\partial G}{\partial t^*} = G\frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial F}{\partial r^*}\right)$$

Divide by FG, let ′ denote deriv:

$$\underbrace{\frac{G'}{G}}_{f^n(t)} = \underbrace{\frac{1}{r^{*2}F}\left(r^{*2}F'\right)'}_{f^n(r^*)} = \underbrace{-\sigma^2}_{\text{constant!}}$$

Look at G:

$$\frac{\partial G}{\partial t^*} = -\sigma^2 G$$

so $G = e^{-\sigma^2 t^*}$ (exponential decay, why choose $\underline{\underline{-\sigma^2}}$)

Now for F:

$$\left(r^{*2} F'\right)' + \sigma^2 r^{*2} F = 0$$

$F(0) =$ finite, $F(1) = 0$

We can solve this via a $\underline{\underline{\text{trick}}}$!

Let $F = \frac{H}{r^*}$

so: $F' = -\frac{H}{r^{*2}} + \frac{H'}{r^*}$

$$r^{*2} F' = -H + r^* H'$$

$$\left(r^* F'\right)' = \cancel{-H'} + \cancel{H'} + r^* H''$$

so plugging in:

$$r^* H'' + \sigma^2 r^* H = 0$$

or $$H'' + \sigma^2 H = 0$$

$$H(0) = r^* F(r^*)\Big|_{r^*=0} = 0$$

$$H(1) = r^* F(r^*)\Big|_{r^*=1} = 0$$

The solutions are just sines & cosines!

$$H = C_1 \sin \sigma r^* + C_2 \cos \sigma r^*$$

$H(0) = 0 \therefore C_2 = 0$

$H(1) = 0 \therefore \underline{\underline{\sigma = n\pi}} \quad n = 1, 2, 3 \ldots$

e.g., the eigenvalues!

So: $$T^* = \sum_{n=1}^{\infty} A_n e^{-n^2\pi^2 z^*} \frac{\sin n\pi r^*}{n\pi r^*}$$

$\nearrow$ chosen so that $F_n(0) = 1$ (can absorb into A_n)

It turns out (via orthogonality) that
↳ get to in a bit

$$A_n = 2(-1)^{n-1} \quad \text{w/ } A_1 = 2$$

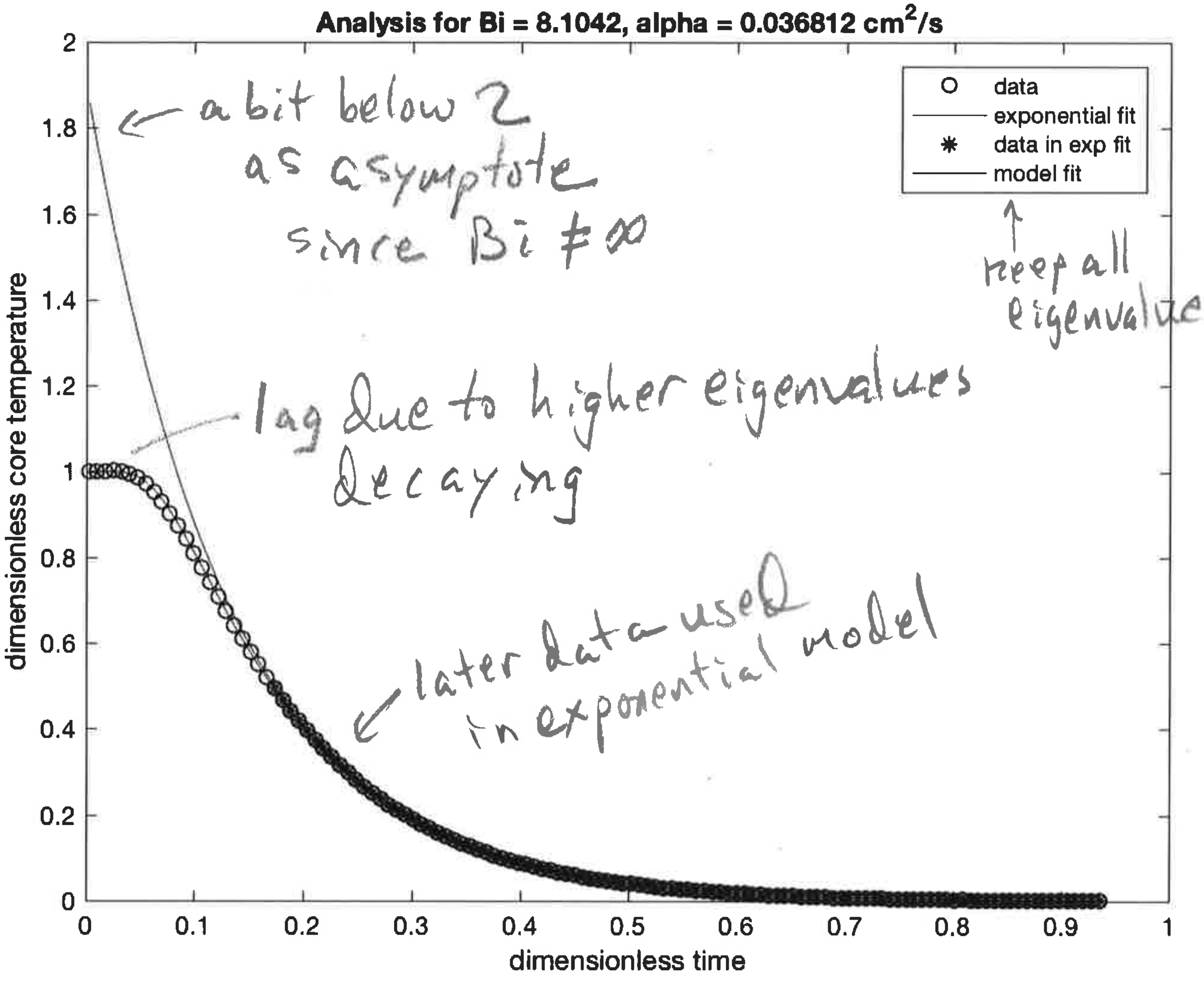
So $$T^*\Big|_{Bi\to\infty} = \sum_{n=1}^{\infty} 2(-1)^{n-1} e^{-n^2\pi^2 t^*} \frac{\sin n\pi r^*}{n\pi r^*}$$

Note that the higher eigenvalues decay away really fast! Thus, after a short time

$$T^* \approx 2e^{-\pi^2 t^*} \frac{\sin \pi r^*}{\pi r^*}$$

So you can use an exponential fit of, say, $T^*\big|_{r^*=0}$ at later times to measure α! This is done in UG lab.

Bi isn't infinite (but $\gg 1$)



a bit below 2 as asymptote since $Bi \neq \infty$

keep all eigenvalues

lag due to higher eigenvalues decaying

later data used in exponential model

Data from UG lab exp't, Steel sphere

Separation of variables problems (when it works!) lead to Sturm-Liouville Boundary Value problems. These are discussed in ch 11 of Boyce & Diprima - here will just state theorem (they prove it)

For a problem of the form:

$$[p(x)y']' - q(x)y + \lambda w(x)y = 0$$

on interval $0 < x < 1$

w/ homogeneous B.C.'s:

$$a_1 y(0) + a_2 y'(0) = 0$$

$$b_1 y(1) + b_2 y'(1) = 0$$

and p, p', q & w are continuous functions of x on $[0,1]$ and $p(x) > 0$ and $w(x) > 0$ on $[0,1]$

(this condition can be relaxed for singular SL problems...)

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Then:

1) all eigenvalues λ & corresp. eigenfunctions are real (not complex)

2) All eigenvalues are simple: one-to-one correspondence w/ eigenfunctions. and may be ordered by mag. w/ $\lambda_n \to \infty$ as $n \to \infty$

3) Orthogonality: if ϕ_i, ϕ_j are eigenfunctions corresp. to λ_i, λ_j then $\int_0^1 \phi_i(x)\,\phi_j(x)\,\omega(x)\,dx = 0$ if $i \neq j$

weight $f^{\underline{n}}$!

4) The set of eigenfunctions is complete (you can represent any function over $[0,1]$ by a linear combination of the $\phi_i(x)$ - very useful!)

Let's apply this to our quenching problem!

We had:

$$(r^2F')' + \sigma^2 r^2 F = 0$$

$F(0) = \text{finite}$ $F(1) = 0$

↳ actually, $F'(0) = 0$ by symmetry

So: $P(r) \equiv r^2$ $w(r) \equiv r^2$ $q(r) = 0$

$\lambda \equiv \sigma^2$

$$\left.\begin{array}{l} a_1 = 0,\ a_2 = 1 \\ b_1 = 1,\ b_2 = 0 \end{array}\right\} \text{for B.C.'s}$$

Since $P(0) = 0$ (not pos.) it's a singular SL problem, but still works!

The key result is orthogonality, which we need to get our coef.

we had $\phi_n \equiv \frac{\sin n\pi r}{n\pi r}$, $\lambda \equiv n^2\pi^2$

and $T^* = \sum_{n=1}^{\infty} A_n e^{-n^2\pi^2 t^*} \frac{\sin n\pi r}{n\pi r}$

Now $T^*\Big|_{t^*=0} = \sum_{n=1}^{\infty} A_n \frac{\sin n\pi r}{n\pi r} = \underline{\underline{1}}$ (IC)

we get the A_n via orthogonality!

Multiply by $\frac{\sin m\pi r}{m\pi r}\ \underset{\uparrow \atop \text{weight f}^{\underline{n}}}{r^2}$ & integrate!

$$\therefore \sum_{n=1}^{\infty} A_n \int_0^1 \frac{\sin n\pi r}{n\pi r}\,\frac{\sin m\pi r}{m\pi r}\, r^2\, dr$$

$$= \int_0^1 (1)\, \frac{\sin m\pi r}{m\pi r}\, r^2\, dr$$

by orthogonality, LHS is <u>zero</u> unless $n = m$!

So $A_n \int_0^1 \frac{\sin^2 n\pi r}{n^2\pi^2}\, dr^* = \int_0^1 \frac{\sin n\pi r^*}{n\pi}\, r^*\, dr^*$

$$A_n = \frac{\int_0^1 \frac{\sin n\pi r^*}{n\pi} r^* \, dr^*}{\int_0^1 \frac{\sin^2 n\pi r^*}{n^2\pi^2} \, dr^*}$$

$$= 2\int_0^1 n\pi r \sin n\pi r \, dr$$

$$= 2\left(\frac{\sin n\pi}{n\pi} - \cos(n\pi)\right)$$

$$= 2(-1)^{n-1}$$

and we get

$$T^* = \sum_{n=1}^{\infty} 2(-1)^{n-1} e^{-n^2\pi^2 t^*} \frac{\sin n\pi r^*}{n\pi r^*}$$

Now in general we would get

$$T^* = T^*_\infty + \sum_{n=1}^{\infty} A_n e^{-\lambda_n t^*} \phi_n(x^*)$$

where
$$A_n = \frac{\int_0^1 \left(T^*\big|_{t=0} - \vec{T}^*_\infty\big|_{t^*=0}\right)\phi_n(x) w(x) \, dx}{\int_0^1 \phi_n^2(x^*) w(x^*) \, dx^*}$$

The solution to a wide variety of separation of variable solutions are provided in Carslaw & Jaeger conduction of heat in solids. If you can't get an analytic solution, numerical solutions are easy to get.

How to Solve!

1) Problem must be linear - if not, it won't work (but you may be able to linearize it even then)

2) Obtain the asymptotic solution at long times : this may not be constant, depending on BC's!

3) Subtract off this asymptotic solution at long times to render DE & BC's homogeneous (but not the IC!)

4) Use separation of variables to get a S-L eigenvalue problem

5) Determine the lead eigenvalue as this tells you how fast your asymptotic solution becomes valid!

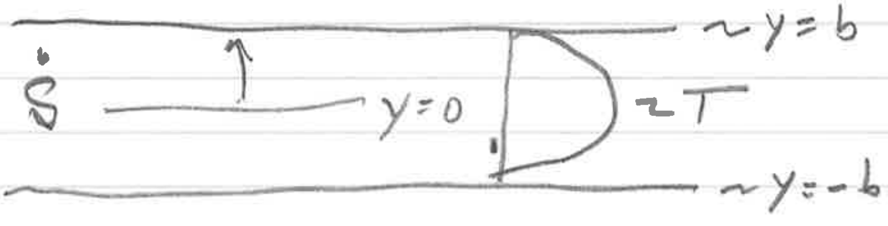
6) Determine lead eigenfunction & (via orthogonality) the lead coef. This is the last bit to decay away!

7) Get all the rest - if you need them!

For most problems, order of importance:

1) asymptotic solution (what's left at the end)
2) lead eigenvalue (how fast things go away)
3) lead eigenf$^{\underline{n}}$ & coef (last correction to decay)
4) everything else

Let's apply this: slab with heat generation.



$$T\Big|_{t=0} = T_0 \qquad T\Big|_{y=\pm b} = T_0$$

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial y^2} + \dot{S}$$

1) Render Dimensionless:

$$y^* = y/b \qquad t^* = t/t_c \qquad T^* = \frac{T - T_0}{\Delta T_c}$$

$$\therefore\ T^*\Big|_{t^*=0} = T^*\Big|_{y^*=\pm 1} = 0$$

Now for DE:

$$\frac{\rho \hat{C}_p \Delta T_c}{t_c} \frac{\partial T^*}{\partial t^*} = \frac{k \Delta T_c}{b^2} \frac{\partial^2 T^*}{\partial y^{*2}} + \dot{S}$$

Divide out by $\dot{S}$ (has to be there!)

$$\underbrace{\left[\frac{\rho \hat{C}_p \Delta T_c}{t_c \dot{S}}\right]}_{=1} \frac{\partial T^*}{\partial t^*} = \underbrace{\left[\frac{k \Delta T_c}{\dot{S} b^2}\right]}_{=1} \frac{\partial^2 T^*}{\partial y^{*2}} + 1$$

$$\therefore\ \Delta T_c = \frac{\dot{S} b^2}{k}$$

$$\therefore\ t_c = \frac{\rho \hat{C}_p \Delta T_c}{\dot{S}} = \frac{b^2 \rho \hat{C}_p}{k} = \frac{b^2}{\alpha}\ !$$

So $$\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}} + 1$$

$$T^*\Big|_{t^*=0} = 0 \qquad T^*\Big|_{y^*=\pm 1} = 0$$

2) Ok, at long times the $T^*\big|_{y^*=\pm 1} = 0$ BC means we would be at S.S.

$$\therefore \quad \cancelto{0}{\frac{\partial T_\infty^*}{\partial t^*}} = \frac{\partial^2 T_\infty^*}{\partial y^{*2}} + 1$$

$$\text{so} \quad T_\infty^* = -\frac{1}{2} y^{*2} + A y^* + B$$

Let's use the symmetry condition

$$\left.\frac{\partial T^*}{\partial y^*}\right|_{y^*=0} = 0 \qquad \therefore \; A = 0$$

and if $T_\infty^*\big|_{y^*=1} = 0$ we have $B = \frac{1}{2}$

$$\text{so} \quad T_\infty^* = \frac{1}{2}\left(1 - y^{*2}\right)$$

3) Subtract off T_∞^*

Let $T_d^* = T^* - T_\infty^*$

$$\therefore \quad T^* = T_d^* + T_\infty^*$$

Plug into DE:

$$\frac{\partial T_d^*}{\partial t^*} + \underbrace{\cancel{\frac{\partial T_\infty^*}{\partial t^*}}}_{0} = \frac{\partial^2 T_d^*}{\partial y^{*2}} + \underbrace{\left[\frac{\partial^2 T_\infty^*}{\partial y^{*2}} + 1\right]}_{\overset{\shortparallel}{0}}$$

(removes source!)

$$\therefore \frac{\partial T_d^*}{\partial t^*} = \frac{\partial^2 T_d^*}{\partial y^{*2}}$$

$$T_d^*\Big|_{t^*=0} = -T_\infty^*\Big|_{t^*=0} = -\frac{1}{2}(1-y^{*2})$$

$$T_d^*\Big|_{y^*=1} = 0 \quad , \quad \frac{\partial T_d^*}{\partial y^*}\Big|_{y^*=0} = 0 \quad \text{(sym)}$$

d) Use separation of variables:

$$T_d^* = G(t^*)F(y^*)$$

$$\therefore \quad FG' = GF''$$

or $$\frac{G'}{G} = \frac{F''}{F} = -\sigma^2$$

so $G = e^{-\sigma^2 t^*}$

$F'' + \sigma^2 F = 0 \qquad F'(0) = F(1) = 0$

5) solve SL problem (this one's easy!)

$$F = A \sin \sigma y^* + B \cos \sigma y^*$$

$$F'(0) = 0 \quad \therefore \quad A = 0$$

$$F(1) = 0 \quad \therefore \quad \cos \sigma = 0$$

$$\therefore \quad \sigma = \left(n - \tfrac{1}{2}\right)\pi \qquad n = 1, 2, 3 \ldots$$

so the lead eigenvalue is $\frac{\pi}{2}$

and the solution decays as:

$$e^{-\left(\frac{\pi}{2}\right)^2 t^*} = e^{-\frac{\pi^2}{4} \frac{\alpha t}{b^2}}$$

Note that the second term decays nine times faster!

6) Get the lead coefficient via orthogonality:

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$$T_Q^* = \sum_{n=1}^{\infty} B_n e^{-\sigma_n^2 t^*} \cos \sigma_n y^*$$

where $B_n = \dfrac{\int_0^1 -T_\infty^*\big|_{t^*=0} \cos \sigma_n y^*}{\int_0^1 \cos^2 \sigma_n y^* dy^*}$

Now $\int_0^1 \cos^2 \sigma_n y^* dy^* = \frac{1}{2}$ (avg. of $\cos^2$ or $\sin^2$)

$$\therefore B_n = 2\int_0^1 -\tfrac{1}{2}(1-y^{*2}) \cos\left[(n-\tfrac{1}{2})\pi y^*\right] dy^*$$

$$= \frac{8\left(\pi(2n-1)\sin(n\pi) + 2\cos(n\pi)\right)}{\pi^3(2n-1)^3}$$

from wolfram alpha...

now $\sin(n\pi) = \underline{0}$ and $\cos(n\pi) = (-1)^n$

$$\therefore B_n = \frac{16(-1)^n}{\pi^3(2n-1)^3}$$

w/ $B_1 = -\dfrac{16}{\pi^3} = -0.516...$

Note that B_2 is 27x smaller and decays 9x faster!

7) Put it together:

$$T^* \approx \frac{1}{2}(1-y^{*2}) - \frac{16}{\pi^3} e^{-\frac{\pi^2 t^*}{4}} \cos\frac{\pi y^*}{2}$$

+ small terms...

This is identical to start-up flow in a channel!

What is the wall heat flux?

$$q_r\Big|_{y=b} = -k\frac{\partial T}{\partial y}\Big|_{y=b} = -k\frac{\frac{\dot{S}b^2}{k}}{b}\frac{\partial T^*}{\partial y^*}\Big|_{y^*=1}$$

$$= -\dot{S}b\frac{\partial T^*}{\partial y^*}\Big|_{y^*=1}$$

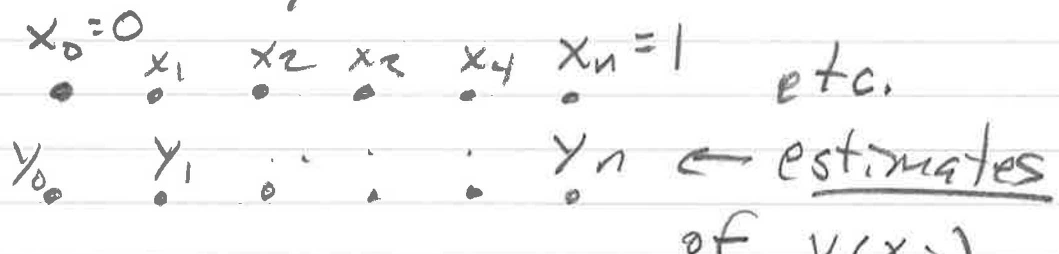
$$\approx \dot{S}b\left(1 - \frac{8}{\pi^2}e^{-\frac{\pi^2 t^*}{4}} + \cdots\right)$$

Many other things could be calculated!

Many linear heat (&mass!) transfer probs admit SL solutions - but it may not be possible to solve analytically! We still want the answer (in particular the lead eigenvalue) — so we have to get it numerically!

We get this via matrix methods

- Suppose we have a standard SL problem on $x \in [0, 1]$
- Discretize domain into $n+1$ nodes
- evaluate y at each x!



To get the equation for the y_i we use a center dif formula.

$$y'\Big|_{x_i} \approx \frac{y_{i+1} - y_{i-1}}{2\,\Delta x}$$

error is $O(\Delta x^2 y''')$

→ numerical approx in Ch 8 of B&D

The second derivative is similar:

$$y''\Big|_{x_i} \approx \frac{\dfrac{y_{i+1}-y_i}{\Delta x} - \dfrac{y_i - y_{i-1}}{\Delta x}}{\Delta x} = \frac{y_{i+1} - 2y_i + y_{i-1}}{\Delta x^2}$$

center dif est of y' at $x_i + \frac{\Delta x}{2}$, etc.

This is also second order

Suppose we have the problem

$$y'' + \lambda y = 0$$

Let's discretize y:

$$\underset{\sim}{y} = \begin{bmatrix} y_0 \\ \vdots \\ y_n \end{bmatrix}$$

we need to generate a matrix representing y'':

$$\underset{\sim}{y''} = \underset{\approx}{A}\,\underset{\sim}{y}$$

$$\underset{\approx}{A}\,\underset{\sim}{y} = \left[\begin{array}{cccccccc} & & & & & & & \\ \frac{1}{\Delta x^2} & -\frac{2}{\Delta x^2} & \frac{1}{\Delta x^2} & 0 & \cdots & 0 & & \\ 0 & \frac{1}{\Delta x^2} & -\frac{2}{\Delta x^2} & \frac{1}{\Delta x^2} & 0 & \cdots & 0 & \\ & & & & & & & \\ & & & & & \frac{1}{\Delta x^2} & -\frac{2}{\Delta x^2} & \frac{1}{\Delta x^2} \\ & & & & & & & \end{array}\right] \begin{array}{l} \leftarrow \text{replace w/ BC at } x=0 \\ \\ \\ \\ \\ \leftarrow \text{replace w/ BC at } x=1 \end{array}$$

This is a tri-diagonal matrix!

What about the BC's?

say $y'(0) = 0$ $\quad y(1) = 0$

BC at $y = 1$ would just be

$y_n = 0$ <u>or</u>

$\underset{\sim}{A}_n = [0 \; 0 \; 0 \cdots \; 1]$ (last row)

Derivative is more complex

We <u>could</u> use

$$y'(0) \approx \frac{y_1 - y_0}{\Delta x}$$

but this is less accurate! It's a center dif. approx at $x = \frac{\Delta x}{2}$!

We can fix this by subtracting $\frac{\Delta x}{2} y''$

i.e. $$y'\Big|_{x=0} \approx \frac{y_1 - y_0}{\Delta x} - \frac{\Delta x}{2} \frac{y_2 - 2y_1 + y_0}{\Delta x^2}$$

$$= \frac{-\frac{1}{2} y_2 + 2y_1 - \frac{3}{2} y_0}{\Delta x}$$

Which makes the first row of $\underset{\sim}{A}$:

$$\left[-\frac{3}{2}\frac{1}{\Delta x}, \frac{2}{\Delta x}, \frac{-1}{2\Delta x}, 0 \;\ldots\ldots\; 0 \right]$$

So how do we apply this to a SL problem?

We have:

$$\left(p(x) y'\right)' - q(x) y + \lambda\, \omega(x)\, y = 0$$

So $$\left(p(x) y'\right)'\Big|_{x_i} = \frac{p\left(x_i + \frac{\Delta x}{2}\right) \frac{y_{i+1} - y_i}{\Delta x} - p\left(x_i - \frac{\Delta x}{2}\right) \frac{y_i - y_{i-1}}{\Delta x}}{\Delta x}$$

and it is easy to construct the matrix $\underset{\approx}{A}$:

$$\underset{\approx}{A}\,\underset{\sim}{y} + \lambda\, \underset{\approx}{\omega}(x)\, \underset{\sim}{y} = 0$$

where $\underset{\approx}{\omega}(x)$ is a diagonal matrix of the weights $\omega(\underset{\sim}{x})$

we replace the first and last rows w/ BC's and we get a standard eigenvalue problem!

The eigenvalues are just the λ_i, the eigenvectors are the finite dif rep. of the eigenfunctions

This is implemented in the Matlab function slsolve.m

```
function [lambda,eigenvec]=slsolve(varargin)
%This function solves the Sturm-Liouville eigenvalue problem given by:
%
%  [p(x) y']' - q(x) y + lambda w(x) y = 0
%
% subject to the boundary conditions:
%
%  bc(1) y(0) + bc(2) y'(0) = 0
%
%  bc(3) y(1) + bc(4) y'(1) = 0
%
% over the domain 0< x <1.
%
% The function is called by the command:
%
% [lambda,eigenvec]=slsolve('pfun','qfun','wfun',bc,n);
%
% The function call requires that you provide the function names (or
% handles if you are using the anonymous function utility) for the
% functions p, q, and w.  These functions must be able to handle an array
% of values.  You also provide the boundary coefficients in the array bc.
% In addition, you may specify the degree of discretization n.  Its default
% value is 50.  The matrices which are generated are of size (n+1,n+1).
% The function returns the eigenvalues in the array lambda (sorted by size
% in ascending order) and the matrix eigenvec which contains the
% corresponding eigenfunctions.  The eigenfunctions are all normalized by
% their maximum value over the domain 0<x<1.
%
% A last note on error:  The code uses second order derivative
% approximations, so the error in the eigenvalues and eigenvectors will be
% of O(1/n^2).  In general, the first few eigenvalues will be reliable, but
% the accuracy will deteriorate as you look at the higher eigenvalues, with
% the last few being meaningless.

p=varargin{1};
q=varargin{2};
w=varargin{3};
bc=varargin{4};

if nargin<5;n=50;else;n=varargin{5};end

h=1/n; %set discretization
x=[0:h:1]'; %this is the array of x values

%Now we set up the arrays used in making the matrix A:
pp=zeros(1,n+1);
pm=zeros(1,n+1);
ww=zeros(1,n+1);
qq=zeros(1,n+1);
for i=2:n
 pp(i)=feval(p,x(i)+h/2);
 pm(i)=feval(p,x(i)-h/2);
 ww(i)=feval(w,x(i));
 qq(i)=feval(q,x(i));
end

%The matrix W is easy:
weight=-diag(ww);
```

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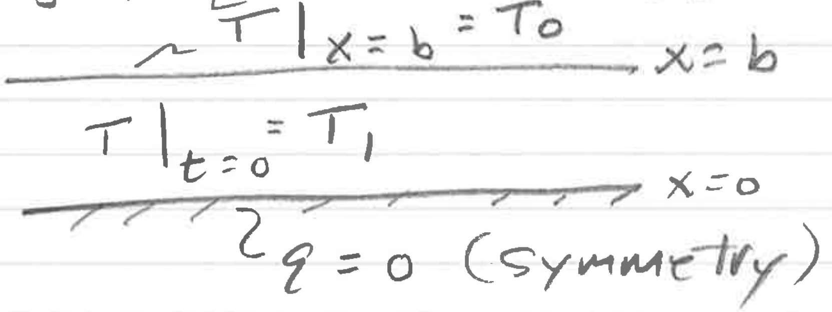
```
%The matrix A is a bit more complex.  First we do
%the main diagonal:
a=diag(-pp-pm-qq*h^2);
%and then the super and sub diagonals:
a=a+diag(pp(1:n),1);
a=a+diag(pm(2:n+1),-1);

%Finally, we divide by h^2:
a=a/h^2;

%And now for the boundary conditions.  First at the left edge:
a(1,1)=bc(1)-bc(2)*1.5/h;
a(1,2)=bc(2)*2/h;
a(1,3)=-bc(2)/2/h;

%and at the right edge:
a(n+1,n+1)=bc(3)+bc(4)*1.5/h;
a(n+1,n)=-bc(4)*2/h;
a(n+1,n-1)=bc(4)/2/h;

%Now we are ready to calculate the eigenvalues:
[v,d]=eig(a,weight);

%The number of eigenvalues and vectors will be less
%than the size of A and W, thus:
evals=diag(d);
i=find(isfinite(evals)); %The matlab 7 form of finite!
evals=evals(i);
evecs=v(:,i);

%Now we sort the eigenvalues and eigenvectors according
%to the size of the eigenvalues:
[~,i]=sort(abs(real(evals)));
lambda=evals(i);
evecs=evecs(:,i);

%and finally, we normalize the eigenvectors by their
%maximum value.
eigenvec=zeros(size(evecs));
for j=1:length(lambda)
 eigenvec(:,j)=evecs(:,j)/norm(evecs(:,j),inf)/sign(evecs(2,j));
end
```

OK, let's implement this for a problem where we know the answer!

Let's just quench a slab!



$$\rho \hat{C}_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2}$$

Render Dimensionless!

Want homogeneous BC's, so subtract asymptotic solution $T_\infty = T_o$

$$\therefore \quad T^* = \frac{T - T_o}{T_1 - T_o} \qquad x^* = \frac{x}{b}$$

and from PDE $\quad t^* = \frac{t}{b^2} \frac{k}{\rho C_p} \equiv \frac{\alpha t}{b^2}$

So: $\quad \frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial x^{*2}} \qquad T^*\Big|_{t^*=0} = 1, \; T^*\Big|_{x^*=0} = 0$

$T^*\Big|_{t^*=0} = 1$ (inhomogeneous IC)

OK, use sep. of variables:

$$T^* = G(t^*)\, F(x^*)$$

$$\frac{G'}{G} = \frac{F''}{F} = -\lambda \quad (\text{or} -\sigma^2)$$

$$\therefore G = e^{-\lambda t^*}$$

$$\left.\begin{array}{l} F'' + \lambda F = 0 \\ F(1) = 0 \quad F'(0) = 0 \end{array}\right\} \text{SL problem!}$$

solution is one we've seen before!

$$F = A\cos\sqrt{\lambda}\, x^* + B\sin\sqrt{\lambda}\, x^*$$

$$F'(0) = 0 \quad \therefore B = 0$$

$$F(1) = 0 \quad \therefore \sqrt{\lambda_n} = \left(n - \tfrac{1}{2}\right)\pi$$

and

$$T^* = \sum_{n=1}^{\infty} A_n e^{-\lambda_n t^*} \cos\sqrt{\lambda_n}\, x^*$$

where, from orthogonality,

$$A_n = \frac{\int_0^1 (1)\cos\sqrt{\lambda_n}\, x^* \, dx^*}{\int_0^1 \cos^2\sqrt{\lambda_n}\, x^* \, dx^*} = \frac{-2(-1)^n}{\left(n - \frac{1}{2}\right)\pi}$$

Contents

- Sturm-Liouville Example Problem
- Comparison of Eigenvalues
- First Five Eigenfunctions
- Calculation of the Coefficients
- Comparison of Decaying Solution

Sturm-Liouville Example Problem

We examine the numerical solution to the Sturm-Liouville problem of a slab of half-width 1 being quenched. Initially the temperature is 1 and at t = 0 the surface at x = 1 is lowered to zero. We use the symmetry condition at the centerline. Thus:

```
p = @(x) ones(size(x));
q = @(x) zeros(size(x));
w = @(x) ones(size(x));
bc = [0,1,1,0];

n = 100; %The number of points we would like (the number of intervals)

[lambda, eigenvecs] = slsolve(p,q,w,bc,n);

% And that's it!
```

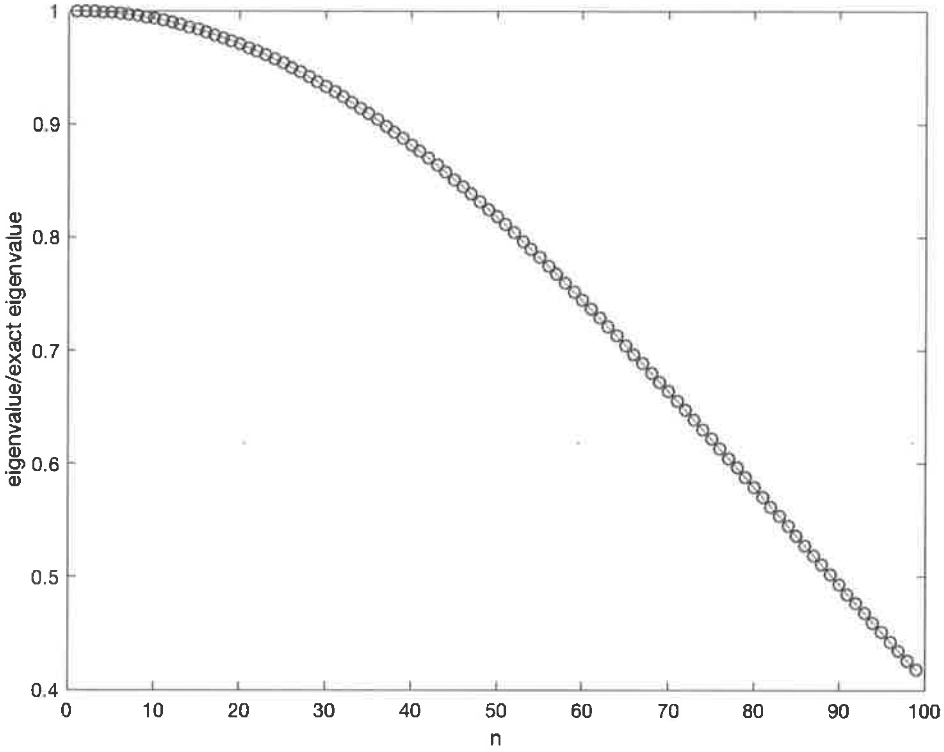
Comparison of Eigenvalues

We have the exact eigenvalues ((n-1/2)*pi)^2. We can compare them graphically and numerically. We find that the first 11 eigenvalues match to within 1%, but then the deviation gets larger. The highest eigenvalues are off by a factor of two or so. This is generically the case: the eigenvalues (and eigenfunctions) are sensitive to the degree of discretization as each higher eigenfunction has one more zero crossing, and you lose numerical accuracy! These higher eigenvalues would decay away very quickly, however.

```
figure(1)
neigenvec=length(lambda);
exactlambda = (([1:neigenvec]'-.5)*pi).^2;
eratio = lambda./exactlambda;
plot([1:neigenvec],eratio,'o-')
xlabel('n')
ylabel('eigenvalue/exact eigenvalue')
grid on

first20ratios = eratio(1:20)
```

```
first20ratios =

    1.0000
    0.9998
    0.9995
    0.9991
    0.9984
    0.9977
    0.9967
    0.9956
    0.9944
    0.9930
    0.9915
```

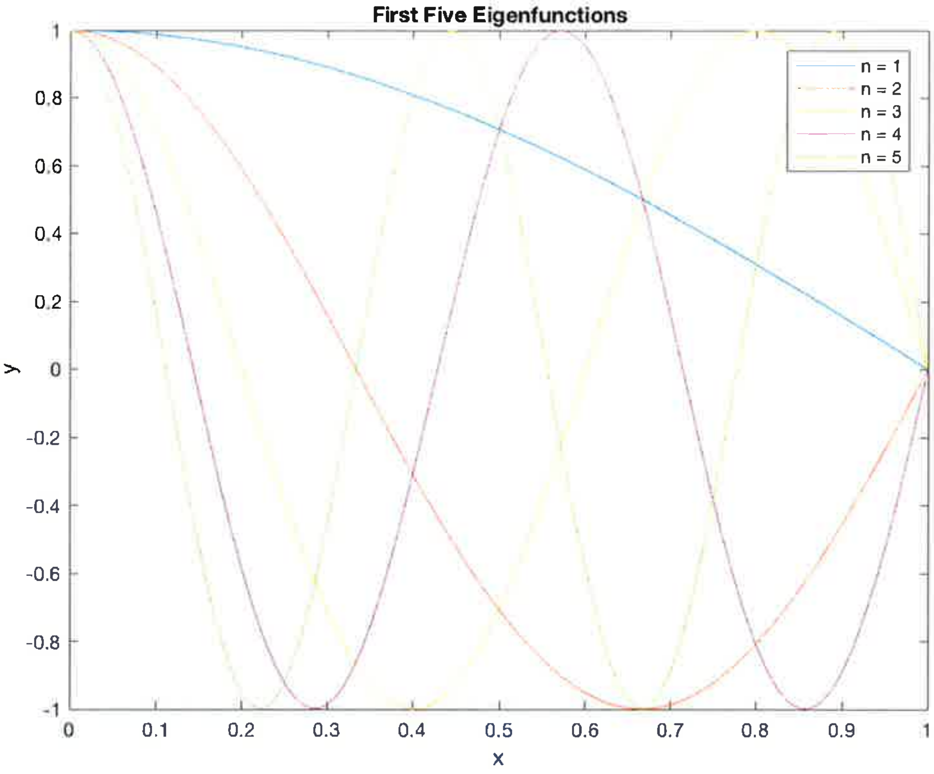
```
0.9898
0.9879
0.9859
0.9837
0.9814
0.9789
0.9763
0.9735
0.9706
```



First Five Eigenfunctions

We plot up the first five eigenfunctions. You will note that the eigenfunctions have a number of zero crossings that increase by one each time.

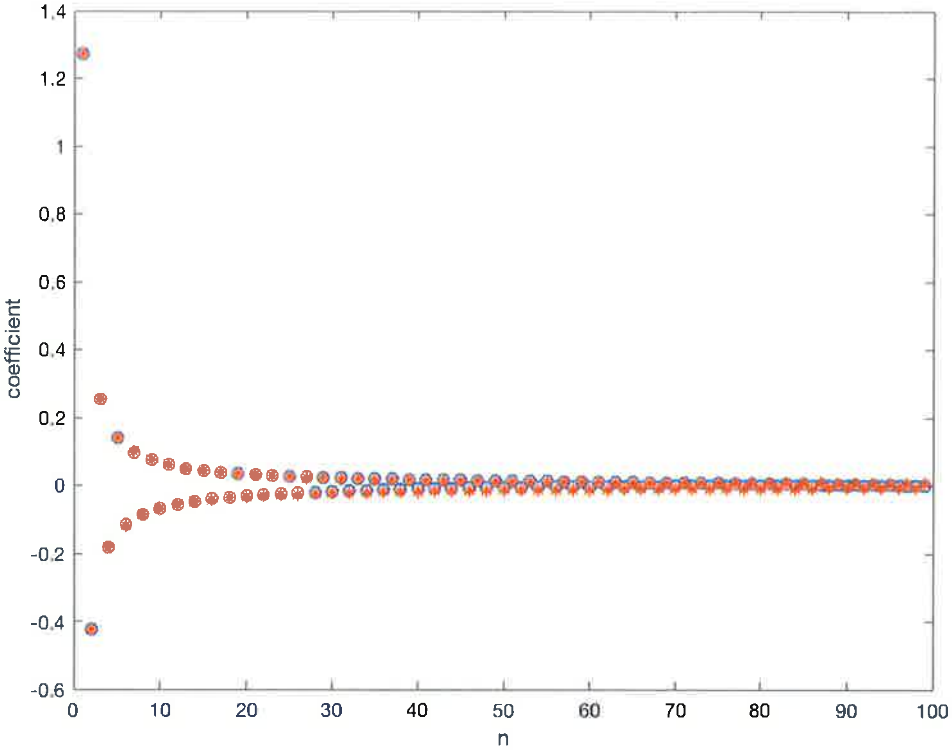
```
x = [0:1/n:1]';
figure(2)
plot(x,eigenvecs(:,1:5))
xlabel('x')
ylabel('y')
title('First Five Eigenfunctions')
legend('n = 1','n = 2','n = 3','n = 4','n = 5')
grid on
```



Calculation of the Coefficients

We make use of orthogonality to calculate the coefficients. We can use the trapezoidal rule to do the integration. Comparison with the exact solution shows that the first coefficients are very good, but after awhile the values are a little random. These coefficients are very small, however.

```
weights = ones(1,n+1);
weights(1) = 0.5;
weights(n+1) = 0.5;
weights=weights/n;

tinit = ones(n+1,1); %The initial temperature

a = zeros(length(lambda),1);

for i = 1:length(lambda)
    numerator = weights*(w(x).*tinit.*eigenvecs(:,i));
    denominator = weights*(w(x).*eigenvecs(:,i).^2);
    a(i) = numerator/denominator;
end

aexact = -2*(-1).^[1:neigenvec]'./([1:neigenvec]'-.5)/pi;

figure(3)
plot([1:neigenvec]',a,'o',[1:neigenvec]',aexact,'*')
xlabel('n')
ylabel('coefficient')
grid on
```

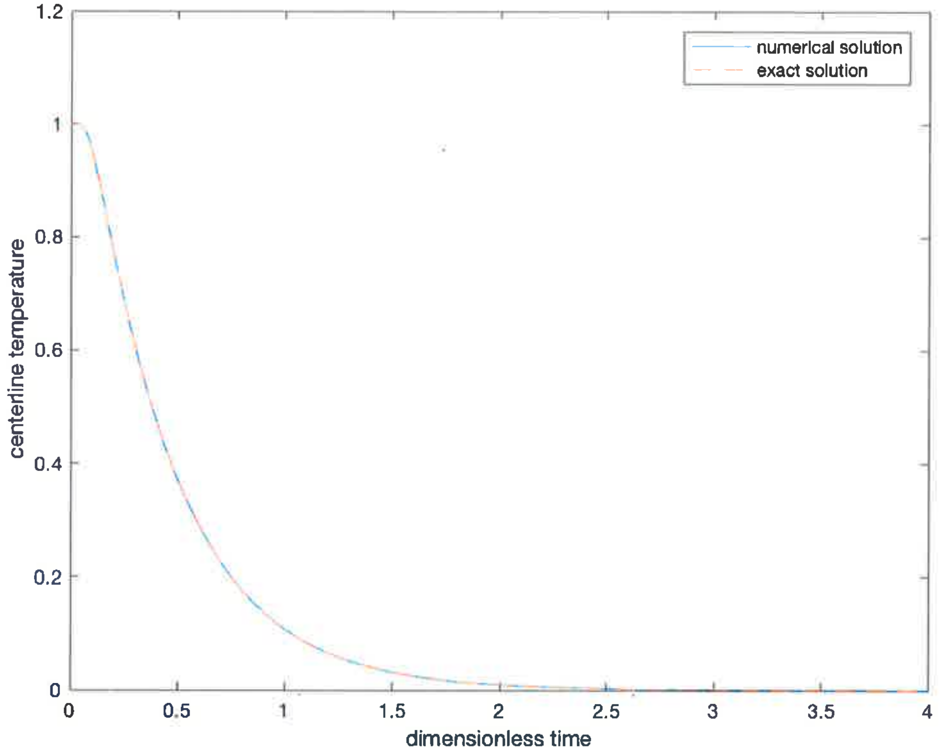


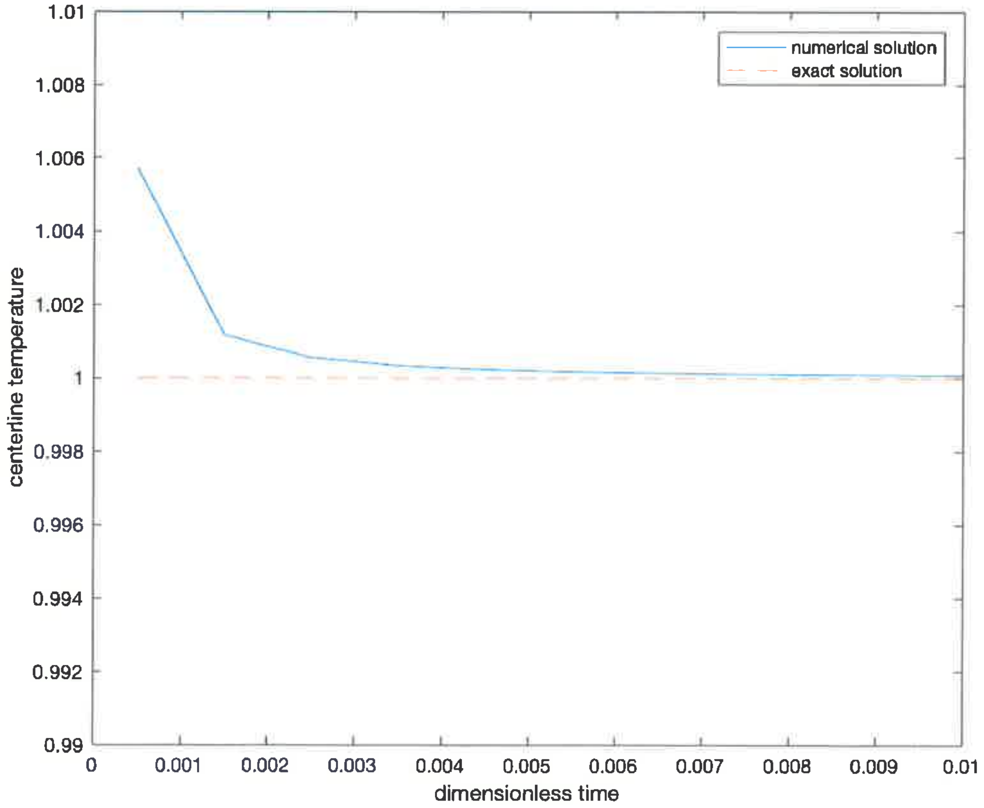
Comparison of Decaying Solution

Here we calculate the temperature at the centerline as a function of time. We have both the exact solution as well as our numerical one. We plot this up for a dimensionless time of 4. The match is pretty much perfect except exactly at t = 0. This error occurs because of the problems with all of the higher eigenvalues and eigenfunctions - which decay away almost instantly. This related to the classic Gibbs ringing phenomenon, which is well known in signal processing. We avoid this by starting our time series at a value slightly greater than zero.

```
t = [0.0005:.001:4];
cltemps = zeros(size(t));
cltempexact = zeros(size(t));

for i = 1:length(t)
    nrange = [1:1000]; %We use lots of eigenvalues for the exact expression
    cltempexact(i) = sum(-2*(-1).^nrange./(nrange-.5)/pi.*exp(-t(i)*(nrange-.5).^2*pi^2));

    %And now for the numerical value:
    cltemps(i) = sum(a.*exp(-lambda*t(i)).*eigenvecs(1,:)');
end

figure(4)
plot(t,cltemps,t,cltempexact,'--')
xlabel('dimensionless time')
ylabel('centerline temperature')
legend('numerical solution','exact solution')
grid on

figure(5)
plot(t,cltemps,t,cltempexact,'--')
xlabel('dimensionless time')
ylabel('centerline temperature')
legend('numerical solution','exact solution')
```

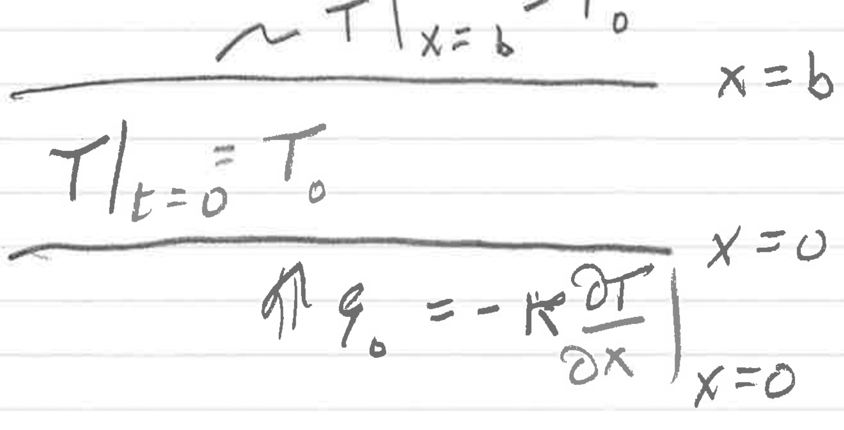
```
axis([0 1e-2 .99 1.01])
grid on
```





That problem had an *analytic solution* which was *easy* to get! We need numerics for *nastier* problems!

Suppose we are *heating* our slab w/ some flux q_0 at $x=0$. (still no problem!) **And** we have a gradient in the heat capacity and conductivity! This happens if you have, say, a gradient in composition for a composite: pretty common! *Now* we need numerics!



Let's take:

$$\rho C_p = (\rho C_p)_0 \,(1 + c_1 x)$$

$$k = k_0 \,(1 + c_2 x)$$

What is our PDE?

Recall $\quad \rho \hat{C}_p \dfrac{\partial T}{\partial t} = - \underset{\sim}{\nabla} \cdot \underset{\sim}{q}$

and $\quad \underset{\sim}{q} = - k \underset{\sim}{\nabla} T$

Since k isn't constant we have to leave it in the middle of the operator!

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x} \right)$$

Ok, let's scale!

Clearly, $\quad x^* = \dfrac{x}{b} \quad , \quad T^* = \dfrac{T - T_0}{\Delta T_c}$

$$t^* = \frac{t}{t_c}$$

From BC at $x=0$:

$$-\frac{k_0 \Delta T_c}{b}\left(1+\frac{C_2}{b}x^*\right)\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0} = q_0$$

$$\therefore \ \Delta T_c = \frac{q_0 b}{k_0}$$

and $$\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0} = -1$$

Finally, from PDE:

$$\frac{\Delta T_c}{t_c}(\rho C_p)_0\left(1+\frac{C_1}{b}x^*\right)\frac{\partial T^*}{\partial t^*} = \frac{k_0 \Delta T_c}{b^2}\frac{\partial}{\partial x^*}\left(\left(1+\frac{C_2}{b}x^*\right)\frac{\partial T^*}{\partial x^*}\right)$$

Dividing out gives:

$$t_c = \frac{(\rho C_p)_0 b^2}{k_0} \quad \text{or} \quad t^* = \frac{\alpha_0 t}{b^2}$$

where $\alpha_0 \equiv \frac{k_0}{(\rho C_p)_0}$ (ref diffusivity)

w/ PDE

$$\left(1+C_1^* x^*\right)\frac{\partial T^*}{\partial t^*} = \frac{\partial}{\partial x^*}\left(\left(1+C_2^* x^*\right)\frac{\partial T^*}{\partial x^*}\right)$$

$C_1^* \equiv C_1/b \qquad C_2 \equiv \frac{C_2}{b}$

To get an SL problem we must subtract off T_∞^* to remove inhomogeneous BC at $x^* = 0$!

At S.S.:

$$0 = \frac{\partial}{\partial x^*}\left((1 + c_2^* x^*) \frac{\partial T_\infty^*}{\partial x^*} \right)$$

$$\left.\frac{\partial T_\infty^*}{\partial x^*}\right|_{x^*=0} = -1 \qquad \left. T_\infty^* \right|_{x^*=1} = 0$$

Integrating:

$$(1 + c_2^* x^*) \frac{\partial T_\infty^*}{\partial x^*} = cst = A$$

but $\left.\frac{\partial T_\infty^*}{\partial x^*}\right|_{x^*=0} \simeq -1$ so $A = -1$

$$\therefore \frac{\partial T_\infty^*}{\partial x^*} = \frac{-1}{1 + c_2^* x^*}$$

$$\therefore\ T_\infty^* = -\frac{1}{C_2^*}\ln\left(1+C_2x^*\right) + B$$

$$T_\infty^*\Big|_{x^*=1} = 0 \quad \therefore\ B = \frac{1}{C_2^*}\ln\left(1+C_2^*\right)$$

$$\text{or } T_\infty^* = \frac{1}{C_2^*}\ln\left(\frac{1+C_2^*}{1+C_2^*x^*}\right)$$

$$\text{Now } T^* = T_\infty^* + T_d^*$$

$$\therefore\ \left(1+C_1^*x^*\right)\frac{\partial T_d^*}{\partial t^*} = \frac{\partial}{\partial x^*}\left(\left(1+C_2^*x^*\right)\frac{\partial T_d^*}{\partial x^*}\right)$$

$$\frac{\partial T_d^*}{\partial x^*}\Big|_{x^*=0} = \underline{\underline{0}} \qquad T_d^*\Big|_{x^*=1} = 0$$

$$\left(T_d^* + T_\infty^*\right)\Big|_{t^*=0} = 0$$

$$\therefore\ T_d^*\Big|_{t^*=0} = -T_\infty^* = -\frac{1}{C_2^*}\ln\left(\frac{1+C_2^*}{1+C_2^*x^*}\right)$$

Let $T_d^* = G(t^*)\,F(x^*)$

$$\therefore \; (1+c_1x^*)G'F = G\left((1+c_2^*x^*)F'\right)'$$

Divide by $(1+c_1x^*)FG$:

$$\frac{G'}{G} = \frac{\left((1+c_2^*x^*)F'\right)'}{(1+c_1x^*)F} = -\lambda$$

$$\therefore \; G = e^{-\lambda t^*}$$

$$\left((1+c_2^*x^*)F'\right)' + \lambda(1+c_1x^*)F = 0$$

$$F'(0) = 0 \qquad F(1) = 0$$

and $$T_d^* = \sum_{n=1}^{\infty} A_n e^{-\lambda_n t^*} F_n(x^*)$$

where $$A_n = \frac{\int_0^1 -T_\infty^* F_n(x^*)(1+c_1x^*)\,dx^*}{\int_0^1 F_n^2(x^*)(1+c_1x^*)\,dx^*}$$

Let's solve!

Contents

- Sturm-Liouville Example: Varying Heat Capacity and Conductivity
- Eigenvalues, Eigenvectors, and Coefficients
- Temperature of the Lower Wall
- Temperature Profile at Various Times

Sturm-Liouville Example: Varying Heat Capacity and Conductivity

We examine the numerical solution to the Sturm-Liouville problem of a slab of width 1 undergoing a uniform heat flux at the bottom, and a fixed temperature at the top. The conductivity k and the heat capacity are linear functions of position. The dimensionless Sturm-Liouville problem for the decaying solution is:

((1+c2*x)*y')' + lambda*(1+c1*x)*y = 0

y'(0) = 0; y(1) = 0

The asymptotic solution at long times is the logarithm:

Tinf = (1/c2)*log((1+c2)./(1+c2*x))

Thus, the initial value for the Sturm-Liouville expansion is just the negative of this function.

Solving the problem we get:

```
c1 = 2;
c2 = -.7;

p = @(x) (1 + c2*x);
q = @(x) zeros(size(x));
w = @(x) (1 + c1*x);
bc = [0,1,1,0];

n = 100; %The number of points we would like (the number of intervals)

[lambda, eigenvecs] = slsolve(p,q,w,bc,n);

Tinf = @(x) (1/c2)*log((1+c2)./(1+c2*x))

% And that's it!
```

```
Tinf =

  function_handle with value:

    @(x)(1/c2)*log((1+c2)./(1+c2*x))
```

Eigenvalues, Eigenvectors, and Coefficients

We are interested in the lead eigenvalues, coefficients, and eigenvectors. We just look at the first five:

```
firsteigenvecs = lambda(1:5)
```

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```
% And we calculate the coefficients using the Trapezoidal Rule:

x = [0:1/n:1]';

% The Trapezoidal Rule weights:
weights = ones(1,n+1);
weights(1) = 0.5;
weights(n+1) = 0.5;
weights=weights/n;

a = zeros(length(lambda),1);

for i = 1:length(lambda)
    numerator = -weights*(w(x).*Tinf(x).*eigenvecs(:,i));
    denominator = weights*(w(x).*eigenvecs(:,i).^2);
    a(i) = numerator/denominator;
end

firstcoefficients = a(1:5)

% And we plot the first five eigenfunctions:
figure(1)
plot(x,eigenvecs(:,1:5))
xlabel('x')
ylabel('y')
title('First Five Eigenfunctions')
legend('n = 1','n = 2','n = 3','n = 4','n = 5')
grid on
```

```
firsteigenvecs =

    0.6849
    6.5141
   18.0404
   35.2805
   58.2210


firstcoefficients =

   -1.3832
   -0.1558
   -0.0577
   -0.0298
   -0.0182
```

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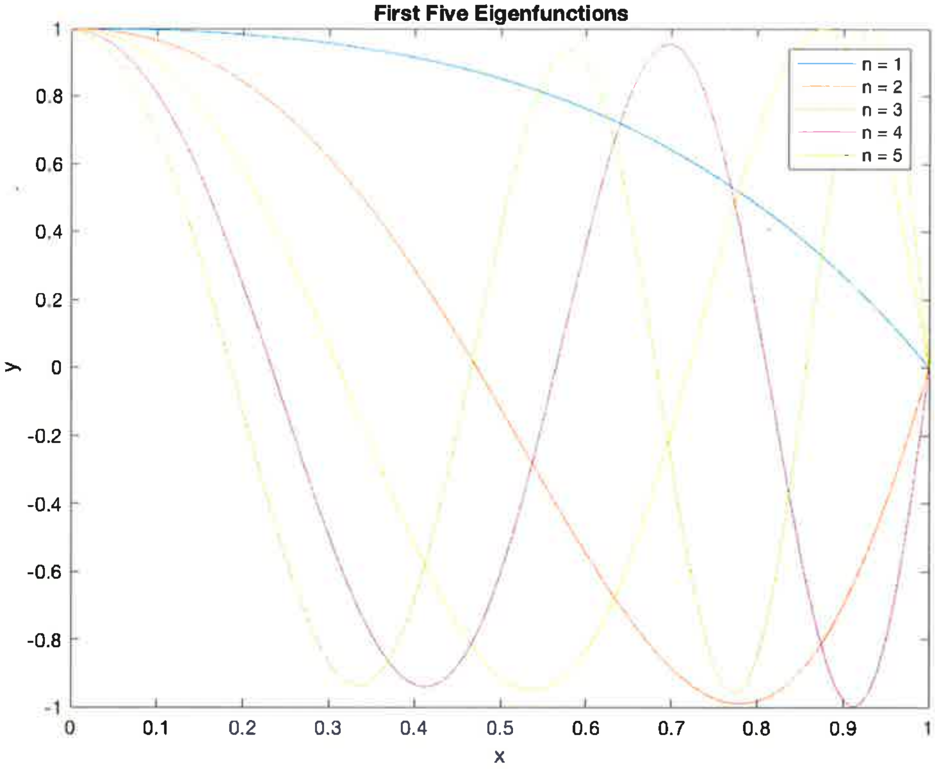


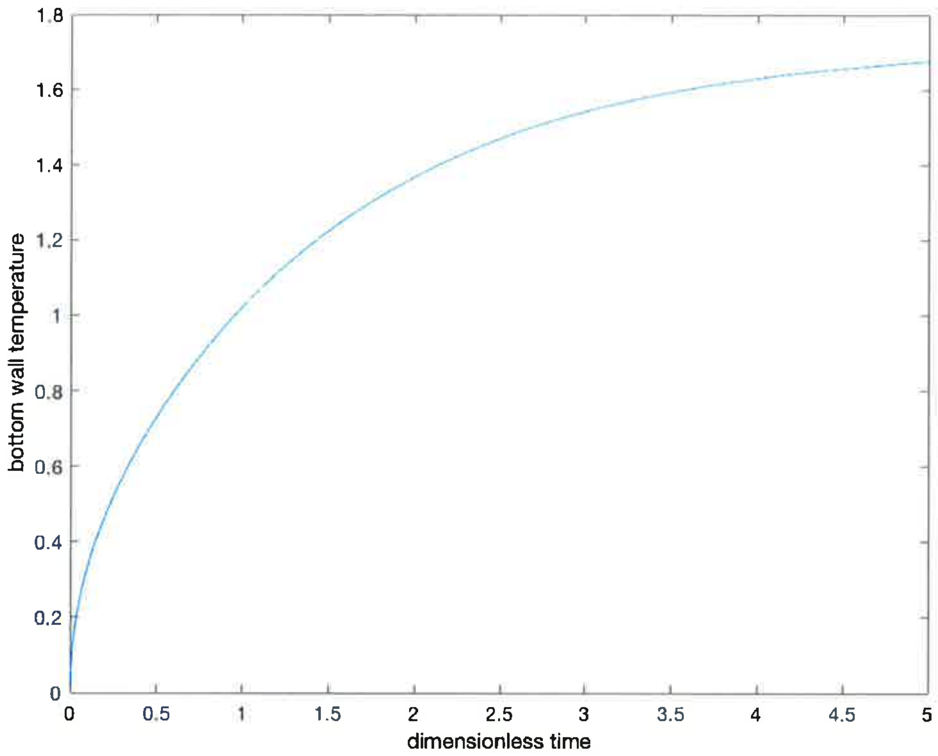
Temperature of the Lower Wall

We wanted the temperature of the lower wall. This will be Tinf + Tdecaying evaluated at x = 0. So:

```
t = [0.0005:.001:5];
tbottom = zeros(size(t)); %We initialize the array

for i = 1:length(t)
    tbottom(i) = log(1+c2)/c2 + sum(a.*exp(-lambda*t(i)).*eigenvecs(1,:)');
end

figure(2)
plot(t,tbottom)
xlabel('dimensionless time')
ylabel('bottom wall temperature')
grid on
```



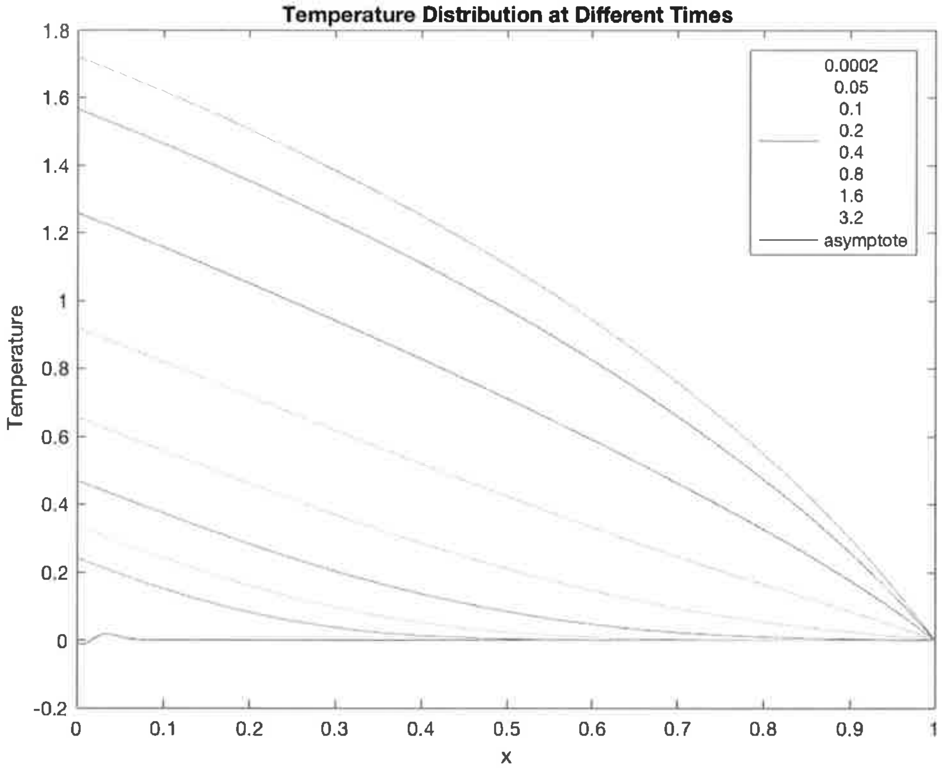
Temperature Profile at Various Times

We can also plot up the temperature distribution for specific times. You will note the issue near the origin at very short times. This is known as the Gibbs ringing phenomenon and is well known in signal processing.

```
tplot = [0.0002,.05,.1,.2,.4,.8,1.6,3.2]';

tprofile = zeros(length(x),length(tplot));
for j = 1:length(tplot)
    for i=1:length(x)
        tprofile(i,j) = log((1+c2)/(1+c2*x(i)))/c2 + sum(a.*exp(-lambda*tplot(j)).*eigenvecs(i,:)');
    end
end
figure(3)
plot(x,tprofile,x,Tinf(x))
legend(num2str(tplot),'asymptote')
xlabel('x')
ylabel('Temperature')
title('Temperature Distribution at Different Times')
grid on
```

100



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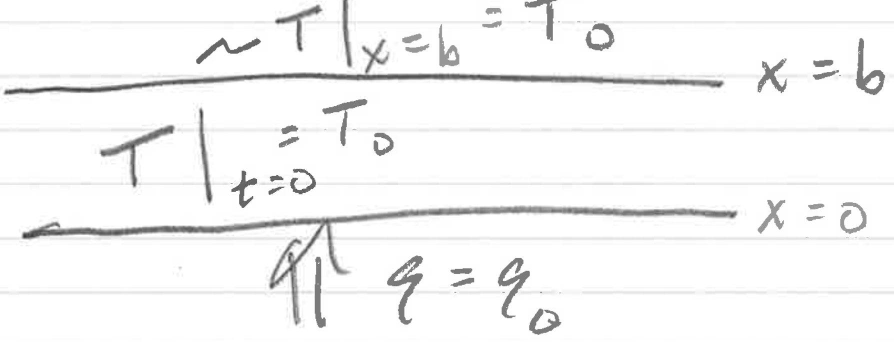
For linear problems which admit separation of variables solutions, SL works great - either analytic (if possible) or numeric if not. But non-linear problems won't work!

Suppose k is a $f^{\underline{n}}(T)$ (and thus x & t too!). The equation won't separate, you can't "subtract off asymptotic solution", etc.

Usually solve these numerically! Dozens of methods have been developed, but for parabolic PDE the simplest is finite differences / marching solution!

Let's examine the slab again:



<u>but</u> $\quad k = \underset{\uparrow \text{ref } k}{k_0}\left(1 + c\left(T - \underset{\uparrow \text{ref temp.}}{T_0}\right)\right)$

Thus:

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_0\left(1 + c(T - T_0)\right)\frac{\partial T}{\partial x}\right)$$

w/ B.C.: $\quad T|_{x=b} = T_0 \quad T|_{t=0} = T_0$

$$q_0 = -k_0\left(1 + c(T - T_0)\right)\frac{\partial T}{\partial x}\bigg|_{x=0}$$

This is <u>non-linear</u> in dependent variable!

First, we scale!

From BC: $\quad x^* = \frac{x}{b} \quad T^* = \frac{T - T_0}{\Delta T_c}$

$$q_0 = -k_0\left(1 + c\,\Delta T_c\, T^*\right)\frac{\Delta T_c}{b}\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0}$$

so $\Delta T_c = \frac{q_0 b}{k_0}$ and define $c^* = c\,\Delta T_c$

From the PDE: $t^* = \frac{k_0 t}{\rho C_p b^2} \equiv \frac{\alpha_0 t}{b^2}$

as usual!

So:

$$\frac{\partial T^*}{\partial t^*} = \frac{\partial}{\partial x^*}\left((1 + c^* T^*)\frac{\partial T^*}{\partial x^*}\right)$$

$$(1 + c^* T^*)\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0} = -1 \quad T^*\bigg|_{x^*=1} = T^*\bigg|_{t^*=0} = 0$$

We want the asymptotic sol'n!

$$\frac{\partial}{\partial x^*}\left((1 + c^* T_\infty^*)\frac{\partial T_\infty^*}{\partial x^*}\right) = 0$$

Integrate:

$$(1 + c^* T_\infty^*)\frac{\partial T_\infty^*}{\partial x^*} = cst = -1$$

from BC at $x^* = 0$!

Even though it's non-linear, we can still solve it:

$$(1 + c^* T_\infty^*)\frac{\partial T_\infty^*}{\partial x^*} \equiv \frac{1}{2c^*}\frac{\partial}{\partial x^*}(1 + c^* T_\infty^*)^2 = -1$$

Now we can integrate!

$$\frac{1}{2c^*}\left(1+c^*T_\infty^*\right)^2 = -x^* + B$$

Now $T_\infty^*\Big|_{x^*=1} = 0$

$$\therefore \quad \frac{1}{2c^*} = -1 + B \quad \therefore \quad B = 1 + \frac{1}{2c^*}$$

So

$$\frac{1}{2c^*}\left(1+c^*T_\infty^*\right)^2 = 1 - x^* + \frac{1}{2c^*}$$

$$\left(1+c^*T_\infty^*\right)^2 = 1 + 2c^*(1-x^*)$$

$$\text{so } T_\infty^* = \frac{1}{c^*}\left[\left(1+2c^*(1-x^*)\right)^{1/2} - 1\right]$$

This looks strange, but as $c^* \to 0$ it is just $T_\infty^*\Big|_{c^*\to 0} = \underline{1 - x^*}$

(linear profile for constant k)

Now we solve for the transient!

we discretize our domain:

$$\underset{\sim}{x} = \begin{bmatrix} 0 \\ \vdots \\ 1 \end{bmatrix} \qquad \underset{\sim}{T}^* = \begin{bmatrix} T_0^* \\ \vdots \\ T_n^* \end{bmatrix}$$

we thus have at the $i^{\underline{th}}$ node:

$$\frac{\partial T_i^*}{\partial t^*} = \left[\frac{\partial}{\partial x^*}\left((1+cT^*)\frac{\partial T^*}{\partial x^*}\right)\right]_i$$

Which we get by finite differences!

Between $i+1$ & i:

$$\left((1+c^*T^*)\frac{\partial T^*}{\partial x^*}\right)\Bigg|_{i+\frac{1}{2}} \approx \left(1+c^*\overset{\substack{\text{avg value}\\ \downarrow\ \text{for k}}}{\frac{(T_{i+1}^*+T_i)}{2}}\right)\frac{T_{i+1}-T_i}{\Delta x}$$

& equiv. expression for deriv. at $i-\frac{1}{2}$

So $$\frac{\partial T_i^*}{\partial t^*} \cong \left[\left(1+c^*\frac{(T_{i+1}^*+T_i^*)}{2}\right)\frac{T_{i+1}^*-T_i^*}{\Delta x} - \left(1+c^*\frac{(T_i^*+T_{i-1}^*)}{2}\right)\frac{T_i^*-T_{i-1}^*}{\Delta x}\right]\frac{1}{\Delta x}$$

and we <u>march</u> <u>forward</u> in time!

$$T_i^*\Big|_{t^*+\Delta t^*} \approx T_i^*\Big|_{t^*} + \Delta t\,\frac{\partial T_i^*}{\partial t^*}$$

This <u>forward</u> <u>difference</u> approach has stability issues! We have the Neumann condition:

$$\Delta t < \frac{1}{2}\frac{\Delta x^2}{\alpha}$$

for diffusion equations!

If Δt is <u>just</u> too large, it blows up!

This equation is good for <u>interior</u> <u>nodes</u> (not $i=0, n$)

on the edges we use BC's!

At the upper wall $T^*=0$

$\therefore\ T_n^* = 0$ at all times!

The BC at $x^*=0$ is more complex:

$$\left(1 + c^*T^*\right)\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0} = -1$$

Now $$\frac{\partial T^*}{\partial x^*}\bigg|_{x^*=0} \approx \frac{T_1^* - T_0^*}{\Delta x} - \frac{\Delta x}{2}\,\frac{T_2^* - 2T_1^* + T_0^*}{\Delta x}$$

$$= \frac{1}{\Delta x}\left(-\frac{1}{2}T_2^* + 2T_1^* - \frac{3}{2}T_0^*\right)$$

so $$\frac{(1 + CT^*)}{\Delta x}\left(-\frac{1}{2}T_2^* + 2T_1^* - \frac{3}{2}T_0^*\right) = -1$$

or $$T_0^* = \frac{4}{3}T_1^* - \frac{1}{3}T_2^* + \frac{2}{3}\,\frac{\Delta x}{1 + CT^*}$$

we'd like to eval. the last at $x^*=0$ -
but then it's non-linear!

Instead $$T^*\Big|_{x^*=0} \approx T_1^* - \Delta x\,\frac{T_2 - T_1}{\Delta x} = 2T_1^* - T_2^*$$

Thus in our scheme we update the temp. at $x^* = 0$:

$$T_0^* \approx \frac{4}{3} T_1^* - \frac{1}{3} T_2^* + \frac{2}{3} \frac{\Delta x}{1 + C^* (2T_1^* - T_2^*)}$$

we start our array with $T^* = 0$ and update in time!

Contents

- Finite Difference Marching Solution: Temperature Dependent Conductivity
- Plot of Bottom Temperature

Finite Difference Marching Solution: Temperature Dependent Conductivity

In this script we demonstrate the simplest of the techniques for numerical solutions to non-linear parabolic PDEs: the finite difference approach. We solve the example problem of a heated slab of width 1 with a temperature dependent conductivity. We use a simple explicit forward difference in time and a second order finite difference in space. We take the conductivity to be k = k0*(1+c*(T-T0)).

```
c = 2;

% The analytic solution to the asymptotic temperature is just:
Tinf = @(x) ((1+2*c*(1-x)).^.5-1)/c

% We discretize the domain in space:
n = 50;
dx = 1/n;
x = [0:dx:1]'; %Note: there are n+1 elements

T = zeros(size(x)); %The initial condition

dt = .49/(c+1)/n^2; %The time discretization we need to avoid instability for c>0

t = 0;

tkeep = [0:dt:2]; %The times we want to evaluate the bottom temperature at
Tbottomkeep = zeros(size(tkeep)); %We initialize that array

pt = [2:n]'; %These are the indices of the interior points.

for i = 2:length(tkeep)
    right = (1+c*(T(pt+1)+T(pt))/2).*(T(pt+1)-T(pt))/dx;
    left = (1+c*(T(pt)+T(pt-1))/2).*(T(pt)-T(pt-1))/dx;
    dTdt = (right-left)/dx;
    T(pt) = T(pt)+dTdt*dt;

    % and the boundary conditions:
    T(n+1) = 0;
    T(1) = 4/3*T(2) -T(3)/3 + 2/3*dx/(1+c*(2*T(2)-T(3)));

    Tbottomkeep(i) = T(1);

    % We add a little graphics (comment out for speed!)
    if i/200==floor(i/200) % We plot up every 200th iteration
    figure(1)
    plot(x,T,x,Tinf(x))
    xlabel('x')
    ylabel('T')
    legend(['t = ',num2str(tkeep(i))],'asymptote')
    title('Temperature Distribution for non-linear conductivity')
    drawnow
    end
end
```

```
Tinf =
```

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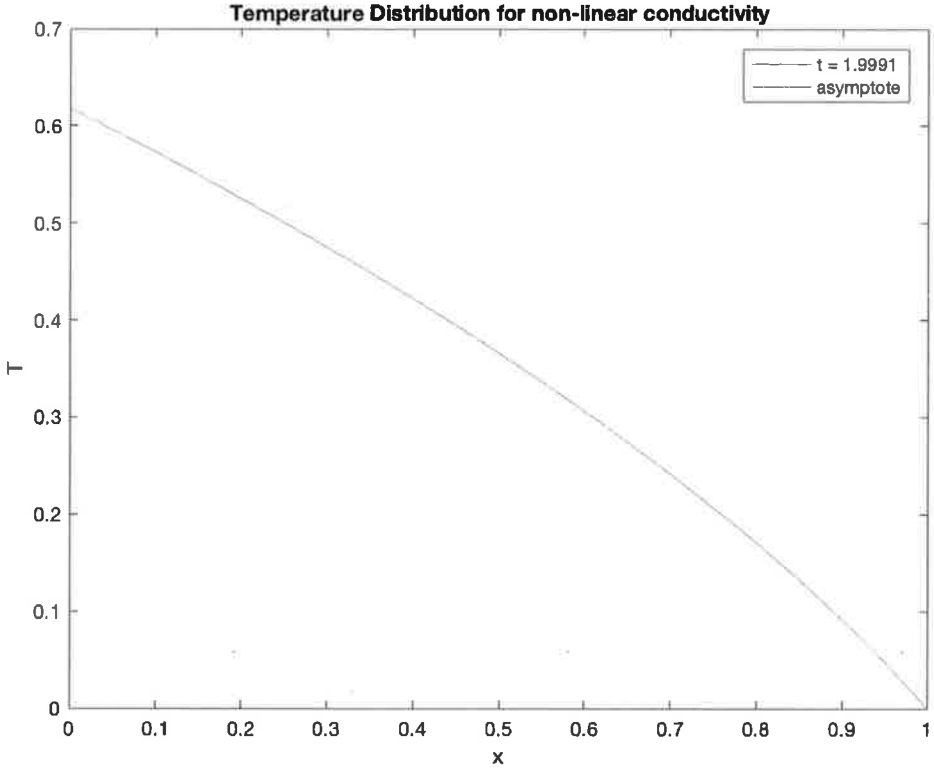
```
function_handle with value:

  @(x)((1+2*c*(1-x)).^.5-1)/c
```



Plot of Bottom Temperature

We can plot up the bottom temperature vs. time. We could have kept some of the intermediate temperature profiles as well, but not all of them! Because of the Neumann condition we have to use a very small discretization in time: way too much data!

```
figure(2)
plot(tkeep,Tbottomkeep)
xlabel('time')
ylabel('Temperature at x = 0')
grid on
```

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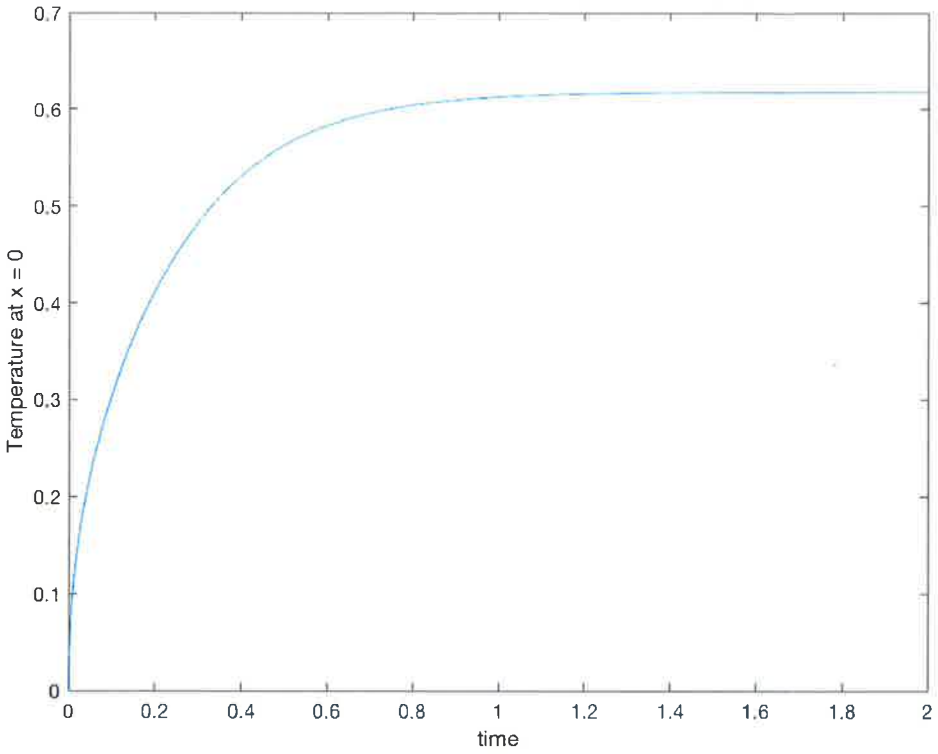

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There are many methods & canned PDE solvers on all computational platforms!

In Matlab these are in the Partial Differential Equation Toolbox - search on this plus "Documentation" in a browser to get the tutorial.

If it's a simple problem, directly coding a finite difference algorithm is probably easiest - if it's a harder problem/more complicated system, learn and use a canned solver

Upshot: If you can write down equation, you can solve it!

Partial Differential Equation Toolbox

Solve partial differential equations using finite element analysis

Partial Differential Equation Toolbox™ provides functions for solving structural mechanics, heat transfer, and general partial differential equations (PDEs) using finite element analysis.

You can perform linear static analysis to compute deformation, stress, and strain. For modeling structural dynamics and vibration, the toolbox provides a direct time integration solver. You can analyze a component's structural characteristics by performing modal analysis to find natural frequencies and mode shapes. You can model conduction-dominant heat transfer problems to calculate temperature distributions, heat fluxes, and heat flow rates through surfaces. You can also solve standard problems such as diffusion, electrostatics, and magnetostatics, as well as custom PDEs.

Partial Differential Equation Toolbox lets you import 2D and 3D geometries from STL or mesh data. You can automatically generate meshes with triangular and tetrahedral elements. You can solve PDEs by using the finite element method, and postprocess results to explore and analyze them.

Release Notes

PDF Documentation

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Solve linear static, transient, modal analysis, and frequency response problems

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Solve conduction-dominant heat transfer problems with convection and radiation occurring at boundaries

Electromagnetics

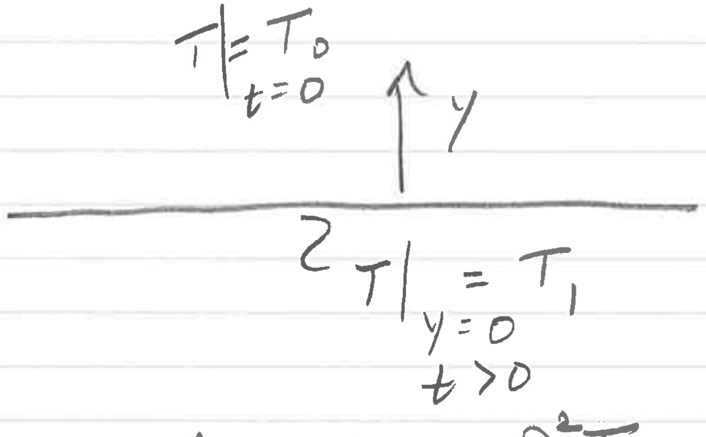
Solve problems that model electric and magnetic fields

General PDEs

Solve general linear and nonlinear PDEs for stationary, time-dependent, and eigenvalue problems

So far we've (mostly) looked at bounded domains (slab, sphere, rod, etc.) — What about semi-infinite domains? These problems are <u>usually</u> <u>length scale deficient</u> and admit boundary layer / self-similar solutions!

The <u>classic</u> problem is ex. 12.1-1 in BS&L (we'll solve a different way)



Now $\rho \hat{C}_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial y^2}$

Let's render dimensionless!

From B.C., $T^* \doteq \frac{T - T_0}{T_1 - T_0}$

$\therefore T^*\big|_{t=0} = 0 \qquad T^*\big|_{y^*=0,\, t^*>0} = 1$

Let's take $t^* = t/t_c$, $y^* = y/\delta$

So: $$\rho \hat{C}_p \frac{\Delta T_c}{t_c}\frac{\partial T^*}{\partial t^*} = \frac{k \Delta T_c}{\delta^2}\frac{\partial^2 T^*}{\partial y^{*2}}$$

Divide out:

$$\underbrace{\left[\frac{\delta^2}{t_c \underbrace{\left(k/\rho \hat{C}_p\right)}_{= \alpha}}\right]}_{= 1}\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

so $\dfrac{\delta^2}{\alpha t_c} = 1$ or $\dfrac{\delta}{(\alpha t_c)^{1/2}} = 1$

But we're done! What's t_c??

We get the *dimensionless* *problem*

$$\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}} \; ; \; T^*\Big|_{t^*=0} = 0$$

$$T^*\Big|_{y^* \to \infty} = 0 \qquad T^*\Big|_{\substack{y^* = 0 \\ t^* > 0}} = 1$$

but *never* specified t_c!

This means that the solution is self-similar: T^* is *not* a $f^{\underline{n}}$

of y & t independently, but instead is a function of a similarity variable which is a combination of y & t!

We can turn our PDE into an ODE!

A more general way of getting self-similar solutions is via Morgan's Theorem:

1) If a well posed problem (e.g., DE, BC's, location of BC's) is invariant to a one parameter group of continuous transformations then the number of independent variables may be reduced by one.

2) Reduction is accomplished by choosing as new dependent

and independent variables combinations which are invariant under the transformation.

What does this mean? Simplest approach is via simple affine stretching / scaling!

We have:

$$\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}} \qquad T^*\Big|_{t^*=0} = 0$$

$$T^*\Big|_{y^*\to\infty} = 0$$

$$T^*\Big|_{y^*=0} = 1$$

Let's stretch (scale) T^*, y^*, t^*

Let $T^* = A\bar{T}$, $t^* = B\bar{t}$, $y^* = C\bar{y}$

where A, B, C are parameters (our group!)

Plug into PDE:

$$\frac{A}{B}\frac{\partial \bar{T}}{\partial \bar{t}} = \frac{A}{C^2}\frac{\partial^2 \bar{T}}{\partial \bar{y}^2}$$

Divide through

$$\therefore \frac{\partial \bar{T}}{\partial \bar{t}} = \left[\frac{B}{C^2}\right]\frac{\partial^2 \bar{T}}{\partial \bar{y}^2}$$

So DE will be invariant if $\frac{B}{C^2} = 1$!

Now for BC's:

$$A\bar{T}\Big|_{B\bar{t}=0} = 0 \Rightarrow \bar{T}\Big|_{\bar{t}=0} = 0 \quad \text{(no restriction)}$$

$$A\bar{T}\Big|_{C\bar{y}\to\infty} = 0 \Rightarrow \bar{T}\Big|_{\bar{y}\to\frac{\infty}{C}\equiv\infty} = 0 \quad \text{(also no restr.)}$$

finally

$$A\bar{T}\Big|_{C\bar{y}=0} = 1 \Rightarrow \bar{T}\Big|_{\bar{y}=0} = \underbrace{\left[\frac{1}{A}\right]}_{\text{\rotatebox{90}{=}}\ 1}$$

So if $A = 1$ and $\frac{B}{C^2} = 1$

our problem is invariant!

Now for the second part: the transf.

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New dep. variable invariant under transf: since $A = 1$, $T^* = f$ (boring - no change here!)

New indep variable:

$$\frac{B}{C^2} = 1 \quad \text{so} \quad \frac{t^*}{y^{*2}} \ \underline{\underline{\text{is}}} \ \text{invariant}$$

$$\text{e.g.} \left(\frac{B}{C^2}\right)\frac{\bar{t}}{\bar{y}^2} = \frac{\bar{t}}{\bar{y}^2}$$

$$\therefore \quad \eta = \frac{t^*}{y^{*2}}$$ would work as a new indep. variable!

$$\text{e.g.} \quad T^* = f(\eta) \quad \eta = \left(\frac{t^*}{y^{*2}}\right)$$

This works but very very badly!!

Instead use canonical form!

Put all the complexity in the indep. variable whose highest deriv. in PDE is the lowest!

we have a 2nd deriv. w.r.t. y^* but only 1st deriv w.r.t. t^* ∴ put complexity in t^*!

Recall $\frac{B}{C^2} = 1$

so $\frac{C}{B^{1/2}} = 1$ is the same!

∴ $\eta = \frac{y^*}{t^{*1/2}}$ is in canonical form

∴ $T^* = f(\eta) \quad \eta = \frac{y^*}{t^{*1/2}}$

(note: BSL uses $\frac{y^*}{2t^{*1/2}}$ – no sig. to factor of 2!)

Now to get the new ODE!

$$\frac{\partial T^*}{\partial y^*} = \frac{\partial f}{\partial y^*} = \frac{df}{d\eta}\frac{\partial \eta}{\partial y^*} = f' \frac{1}{t^{*1/2}}$$

$$\frac{\partial^2 T^*}{\partial y^{*2}} = \frac{\partial}{\partial y^*}\left(\frac{\partial T^*}{\partial y^*}\right) = f'' \frac{1}{t^*}$$

These are easy because of canonical form!

Now for t^*: harder!

$$\frac{\partial T^*}{\partial t^*} = \frac{df}{d\zeta}\frac{\partial \zeta}{\partial t^*}$$

but $\displaystyle \frac{\partial \zeta}{\partial t^*} = \frac{\partial}{\partial t^*}\left(\frac{y^*}{t^{*1/2}}\right) = -\frac{1}{2}\frac{y^*}{t^{*3/2}} = -\frac{1}{2}\frac{\zeta}{t^*}$

In <u>general</u> if $\displaystyle \zeta = \frac{y^*}{t^{*n}}$

<u>then</u> $\displaystyle \frac{\partial \zeta}{\partial t^*} = -n\frac{\zeta}{t^*}$ – very convenient!

So:
$$-\frac{1}{2}\frac{\zeta}{t^*}f' = \frac{1}{t^*}f''$$

or $f'' = -\frac{1}{2}\zeta f'$

w/ BC's $f(0) = 1$, $f(\infty) = 0$

$$\nearrow \quad \swarrow y^* \to \infty$$

$$\underbrace{\frac{y^*}{t^*} \to \infty \leftarrow t^* \to 0}_{\text{collapses BC \& IC!}}$$

How do we solve? This one's pretty easy!

Divide by f':

$$\underbrace{\frac{1}{f'}\frac{df'}{d\zeta}}_{\hookrightarrow\, = \frac{d\ln f'}{d\zeta}} = -\frac{1}{2}\zeta$$

Now integrate!

$$\therefore \quad \ln f' = -\frac{1}{4}\zeta^2 + cst$$

or $$f' = f'(0)\, e^{-\frac{1}{4}\zeta^2}$$

$\hookrightarrow$ unknown - but yields the heat flux!

$$f = 1 + \int_0^\zeta f'(0)\, e^{-\frac{1}{4}\zeta^2}\, d\zeta$$

↑ applied BC at $\zeta = 0$ to get constant

Now we have $f(\infty) = 0$

$$\therefore \quad 0 = 1 + \int_0^\infty f'(0)\, e^{-\frac{1}{4}\zeta^2}\, d\zeta$$

or $$f'(0) = -\frac{1}{\int_0^\infty e^{-\frac{1}{4}\zeta^2}\, d\zeta}$$

which yields

$$f(\eta) = 1 - \frac{\int_0^{\eta} e^{-\frac{1}{4}\eta^2} d\eta}{\int_0^{\infty} e^{-\frac{1}{4}\eta^2} d\eta}$$

Now these integrals are related to the <u>error function</u> erf(x)

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

Thus after a little algebra:

$$T^* = 1 - \operatorname{erf}\left(\frac{\eta}{2}\right) \equiv \operatorname{erfc}\left(\eta/2\right)$$

complementary error function

or $$\frac{T - T_0}{T_1 - T_0} = 1 - \operatorname{erf}\left(\frac{y}{\sqrt{4\alpha t}}\right)$$

which is the eq'n 12.1-8 in BS&L...

What does this mean? There is a <u>penetration</u> <u>depth</u> that goes as $y \sim (\alpha t)^{1/2}$ over which the temp. varies! Note that for a finite slab (of thickness b) you can regard it as infinite if $b/\delta \gg 1$ as for short times the energy doesn't diffuse to the other wall (yet).

There's another way to solve this - which is useful if you don't know error functions! Set it up as a system of 1st order ODE's & solve via the shooting method!

$$f'' = -\frac{1}{2}\eta f', \quad f(0) = 1 \quad f(\infty) = 0$$

So:

$$\text{let } \underset{\sim}{f} \equiv \begin{Bmatrix} f \\ f' \end{Bmatrix} \equiv \begin{Bmatrix} f_1 \\ f_2 \end{Bmatrix}$$

$$\therefore \frac{d}{d\eta}\begin{Bmatrix} f_1 \\ f_2 \end{Bmatrix} = \begin{Bmatrix} f_2 \\ -\frac{1}{2}\eta f_2 \end{Bmatrix}$$

Thus we have:

$f_1(0) = 1$ (BC)

$f_2(0) = ?? = x$ (unknown)

Adjust x until $f_1(\infty) = 0$!

We actually don't have to go out very far!

This is done numerically on the next page - very simple to do!

Note that this also works for non-linear problems (like the Blasius eq'n) for which there is no analytical solution!

Contents

- Heated Semi infinite slab: comparison of numerical solution to exact
- Plotting things up
- Conclusion

Heated Semi infinite slab: comparison of numerical solution to exact

In this case we use the shooting method to compare the numerical solution for this problem to the exact error function solution. We use the function miss.m to get the degree to which we miss our boundary condition at infinity. Because the solution decreases exponentially as exp(-0.5 eta^2) we just go out to a value of 10.

The miss program is:

function out = miss(x) % This function takes in a guess for the derivative of the temperature at % y = 0 for an impulsively heated semi-infinite domain.

fdot = @(eta,f) [f(2), -0.5*eta*f(2)]; %The differential equation

f0 = [1,x]; %The initial value

[etaout fout] = ode45(fdot,[0 10],f0);

out = fout(end,1);

```
x = -1; % Our initial guess

x = fzero('miss',x) % Our solution!
```

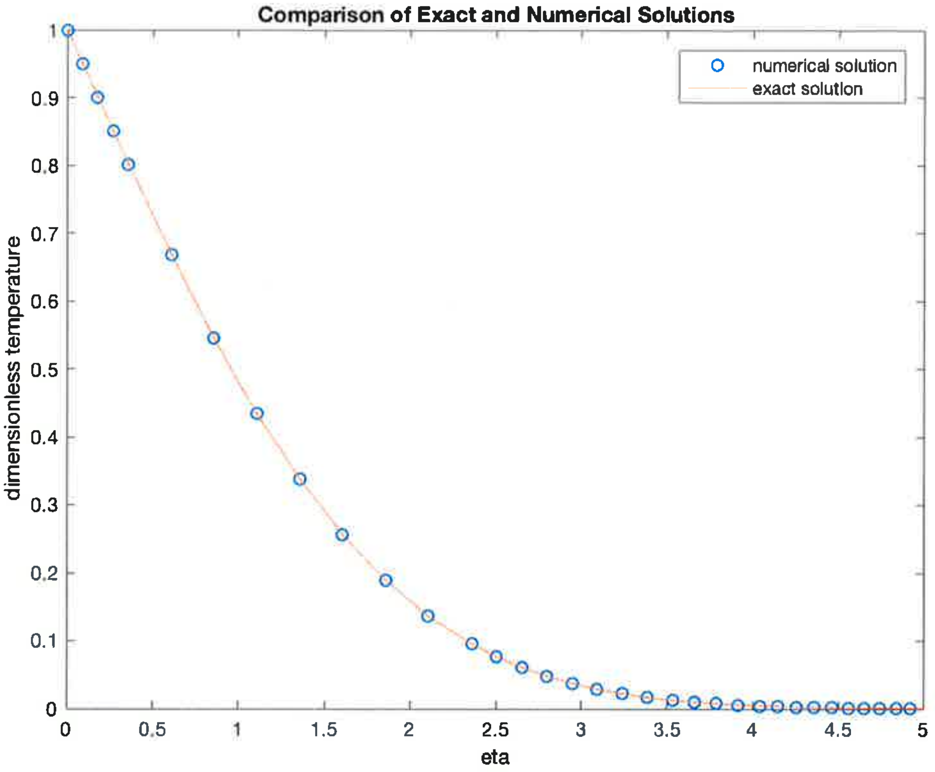
```
x =

   -0.5642
```

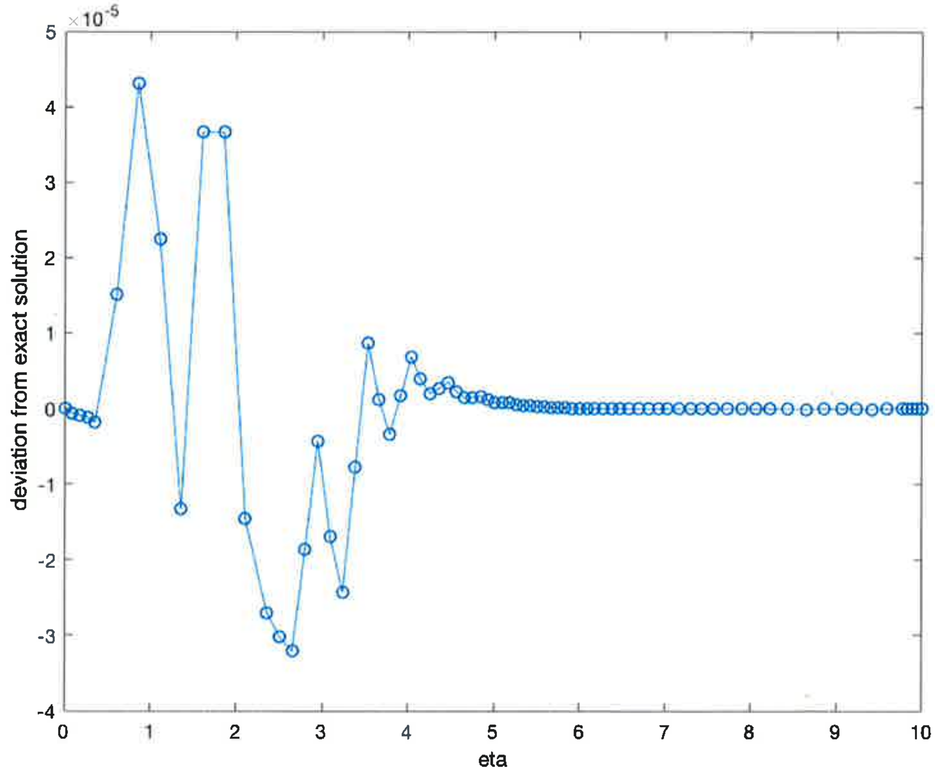
Plotting things up

We just cut and paste from the miss.m routine to get the profile:

```
fdot = @(eta,f) [f(2); -0.5*eta*f(2)]; %The differential equation

f0 = [1,x]; %The initial value

[etaout fout] = ode45(fdot,[0 10],f0);

fexact = 1 - erf(etaout/2); %The exact solution

figure(1)
plot(etaout,fout(:,1),'o',etaout,fexact)
legend('numerical solution','exact solution')
xlabel('eta')
ylabel('dimensionless temperature')
title('Comparison of Exact and Numerical Solutions')
axis([0 5 0 1])
```

```
% We can also plot up the deviation:
figure(2)
plot(etaout,fout(:,1)-fexact,'o-')
xlabel('eta')
ylabel('deviation from exact solution')
```





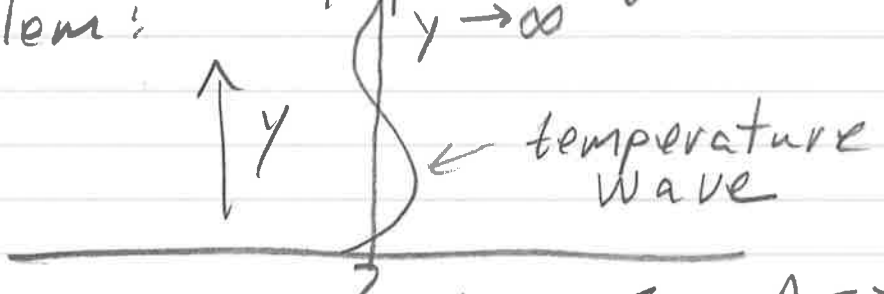
Conclusion

The deviation between the numerical and exact solutions is less than 5e-5 for all eta. This could be further reduced if you set a tighter tolerance for fzero (the root finder) or ode45 (the integrator), but it illustrates the ease of solving this sort of problem numerically.

Another example of semi-infinite domains is found in periodic heating. This is what determines how deep you have to bury pipes to avoid freezing, or to set foundations to avoid melting permafrost for the Alaska pipeline! It's covered in example 12.1-3 of BS&L, but again we'll look at it (abit) differently.

The problem:

$$T\Big|_{y\to\infty} = T_0$$



$$T\Big|_{y=0} = T_0 + A\sin\omega t$$

We have the PDE (as usual):

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = k\frac{\partial^2 T}{\partial y^2}$$

w/ BC's : $T\big|_{y\to\infty} = T_0$

$$T\big|_{y=0} = T_0 + A\sin\omega t$$

where ω is the angular frequency of the oscillation!

Let's scale:

$$T^* = \frac{T-T_0}{\Delta T_c}, \quad t^* = \frac{t}{t_c}, \quad y^* = y/\delta$$

From BC:

$$T^*\Delta T_c + \cancel{T_0} = \cancel{T_0}\ A\sin\left[(\omega t_c)t^*\right]$$

or $$T^* = \underset{\overset{\shortparallel}{1}}{\left[\frac{A}{\Delta T_c}\right]}\sin\left(\underset{\overset{\shortparallel}{1}}{[\omega t_c]}\,t^*\right)$$

So $\Delta T_c = A$, $t_c = \frac{1}{\omega}$, no surprise!

Now for PDE

$$\frac{\Delta T_c\, \rho\hat{C}_p}{t_c}\frac{\partial T^*}{\partial t^*} = \frac{k\,\Delta T_c}{\delta^2}\frac{\partial^2 T^*}{\partial y^{*2}}$$

Divide out:

$$\frac{\partial T^*}{\partial t^*} = \underset{\overset{\shortparallel}{1}}{\left[\frac{\alpha t_c}{\delta^2}\right]} \frac{\partial^2 T^*}{\partial y^{*2}}$$

so $\delta = (\alpha t_c)^{1/2} = \left(\frac{\alpha}{\omega}\right)^{1/2}$

which is the penetration depth – the length scale of our diffusing wave!

So:

$$\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

$$T^*\Big|_{y^* \to \infty} = 0 \qquad T^*\Big|_{y^*=0} = \sin t^*$$

For periodic problems we are only interested in the asymptotic sol'n – but that's also periodic!

We can't take $T^* = \sin t^* f(y^*)$

because the phase will shift w/ depth due to the diffusion time!

Instead, because the problem is linear, we solve via analytic continuation onto the complex plane!

Remember the Euler formula?

$$e^{it^*} = \cos t^* + i \sin t^*$$

Let's let our BC become:

$$\hat{T}\Big|_{y^*=0} = e^{it^*} = \cos t^* + i \sin t^*$$

In this way $T^* = \mathrm{Im}\{\hat{T}\}$

(the real part would be the temp. dist. driven by $\cos t^*$!)

So:
$$\frac{\partial \hat{T}}{\partial t^*} = \frac{\partial^2 \hat{T}}{\partial y^{*2}}, \quad \hat{T}\Big|_{y^*\to\infty} = 0$$

$$\hat{T}\Big|_{y^*=0} = e^{it^*}$$

Now we take $\hat{T} = f(y^*) e^{it^*}$

So $f(0) = 1$, $f(\infty) = 0$

Plug into PDE:

$$\frac{\partial^2 \hat{T}}{\partial y^{*2}} = e^{it^*} f''$$

$$\frac{\partial \hat{T}}{\partial t^*} = i e^{it^*} f$$

So eq'n for f is simple!

$$f'' \cancel{e^{it^*}} = i f \cancel{e^{it^*}}$$

w/ $f(0) = 1$, $f(\infty) = 0$

The solutions are just exponentials:

$$f = c_1 e^{\sqrt{i}\, y^*} + c_2 e^{-\sqrt{i}\, y^*}$$

we want decaying sol'n, so $c_1 = 0$

and $c_2 = 1$!

Thus: $\hat{T} = e^{-\sqrt{i}\,y^*} e^{i t^*}$

ok, what's $\sqrt{i}$?

$$\sqrt{i} = \frac{1+i}{\sqrt{2}}$$

e.g. $\left(\frac{1+i}{\sqrt{2}}\right)^2 = \frac{1}{2}\left(\cancel{1} + 2i + \underset{-\cancel{1}}{\underset{\shortparallel}{i^2}}\right) = i$

So $\hat{T} = e^{-\frac{y^*}{\sqrt{2}}} e^{i(t^* - y^*/\sqrt{2})}$

$$= e^{-\frac{y^*}{\sqrt{2}}}\left(\cos\left(t^* - y^*/\sqrt{2}\right) + i\sin\left(t^* - y^*/\sqrt{2}\right)\right)$$

The imaginary part is:

$$T^* = \mathrm{Im}\{\hat{T}\} = e^{-y^*/\sqrt{2}} \sin\left(t^* - y^*/\sqrt{2}\right)$$

What does this mean?

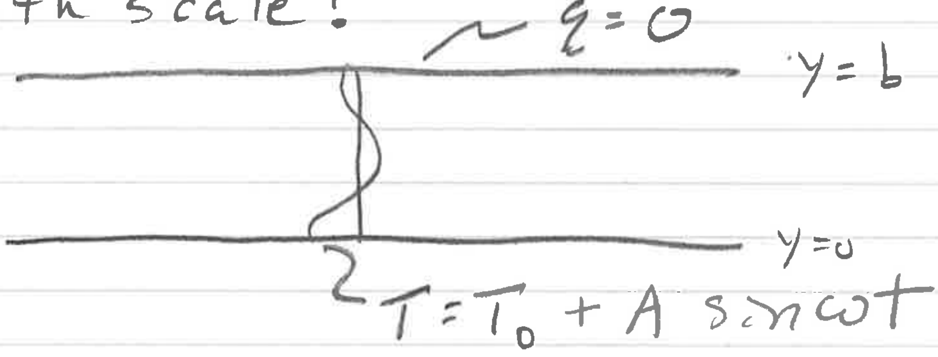
The amplitude of the wave decreases exponentially: $e^{-y^*/\sqrt{2}} = e^{-\frac{y}{\sqrt{2\alpha/\omega}}}$

So a <u>higher</u> <u>frequency</u> means a <u>shorter</u> penetration depth!

The other bit is the phase lag: when $y^*/\sqrt{2} = \pi$ your temp. will be 180° out of phase w/ the surface! (But the <u>mag</u> will be $e^{-\pi}$ - pretty small!)

This technique is <u>very</u> useful for many <u>linear</u> <u>periodic</u> problems!

What happens if the slab is <u>finite</u>? Now we get <u>another</u> length scale!



We have the same eq^n, but we will scale differently!

Let $y^* = y/b$, $t^* = t/t_c$,

$T^* = \frac{T - T_0}{A}$ ← forced by BC

So: $$\left[\frac{b^2}{\alpha t_c}\right] \frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

$$T^*\Big|_{y^*=0} = \sin([\omega t_c]\, t^*)$$

$$\frac{\partial T^*}{\partial y^*}\Big|_{y^*=1} = 0 \quad \text{(no flux)}$$

How do we pick t_c? Usually for periodic problems we still use $t_c = 1/\omega$

So: $$\left(\frac{\omega b^2}{\alpha}\right) \frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

$$T^*\Big|_{y^*=0} = \sin t^* \qquad \frac{\partial T^*}{\partial y^*}\Big|_{y^*=1} = 0$$

Let's define $\beta^2 \equiv \frac{\omega b^2}{\alpha}$

so $\beta = \frac{b}{\left(\frac{\alpha}{\omega}\right)^{1/2}}$ is a ratio of our two length scales!

This is known as the Womersley number (usually used in fluid mechanics)

if $\beta >> 1$ you are at high frequency and our solution is the same as an unbounded system!

if $\beta << 1$ you are at low frequency and you just have a pseudo-steady temperature!

Let's solve for $\beta \sim O(1)$:

Use analytic continuation again!

$$\hat{T}\Big|_{y^*=0} = e^{it^*}$$

As before, let $\hat{T} = e^{it^*} f(y^*)$

$\therefore \; i\beta^2 f = f'' \quad f(0) = 1 \;\; f'(1) = 0$

Now our solutions are hyperbolics!

$$f = c_1 \sinh \sqrt{i}\,\beta y^* + c_2 \cosh \sqrt{i}\,\beta y^*$$

$f(0) = 1$ so $c_2 = 1$

$$f'(1) = 0 = c_1 \sqrt{i}\,\beta \cosh \sqrt{i}\,\beta + \sqrt{i}\,\beta \sinh \sqrt{i}\,\beta$$

$$\therefore \; c_1 = -\frac{\sinh \sqrt{i}\,\beta}{\cosh \sqrt{i}\,\beta}$$

So $$\hat{T} = e^{it^*}\left(\cosh \sqrt{i}\,\beta y^* - \frac{\sinh \sqrt{i}\,\beta}{\cosh \sqrt{i}\,\beta} \sinh \sqrt{i}\,\beta y^* \right)$$

and $T^* = \operatorname{Im}\{\hat{T}\}$

At $y^*=1$ we get:

$$\hat{T}\Big|_{y^*=1} = e^{it^*}\left(\cosh\sqrt{i}\beta - \frac{\sinh^2\sqrt{i}\beta}{\cosh\sqrt{i}\beta}\right)$$

$$= e^{it^*}\left(\cosh\sqrt{i}\beta - \frac{\cosh^2\sqrt{i}\beta - 1}{\cosh\sqrt{i}\beta}\right)$$

$$= \frac{e^{it^*}}{\cosh\sqrt{i}\beta}$$

and $T^*\Big|_{y^*=1} = Im\left\{\frac{e^{it^*}}{\cosh\sqrt{i}\beta}\right\}$

The amplitude of $T^*\Big|_{y^*=1}$ is just

$$\left|\frac{1}{\cosh\sqrt{i}\beta}\right|$$

These sorts of complex things are easy to plot up in Matlab, which handles $i \equiv \sqrt{-1}$ just fine! Most functions in Matlab can take complex arguments.

Contents

- Temperature Distribution in a Finite Slab with Periodic Heating
- Plot of Upper Surface Amplitude as a Function of Beta
- Conclusion

Temperature Distribution in a Finite Slab with Periodic Heating

In this script we plot up the temperature distribution in a finite thickness slab where we have oscillatory heating at the bottom and an insulation condition at the top. We start by plotting the temperature distribution at a number of times:

```
i = (-1)^.5; %just in case i was used as an index elsewhere!
beta = 4;

% We require t to be a column vector and y to be a row vector.

T = @(t,y) imag(exp(i*t)*(cosh(i^.5*beta*y)-sinh(i^.5*beta)/cosh(i^.5*beta)*sinh(i^.5*beta*y)))

t = [0,pi/2,pi,3*pi/2,2*pi]';

y = [0:.01:1];

figure(1)
plot(y,T(t,y))
grid on
xlabel('y')
ylabel('T')
legend(num2str(t))
title(['Plot of Temperature Distribution for beta = ',num2str(beta),' at different times'])
```

```
T =

  function_handle with value:

    @(t,y)imag(exp(i*t)*(cosh(i^.5*beta*y)-sinh(i^.5*beta)/cosh(i^.5*beta)*sinh(i^.5*beta*y)))
```

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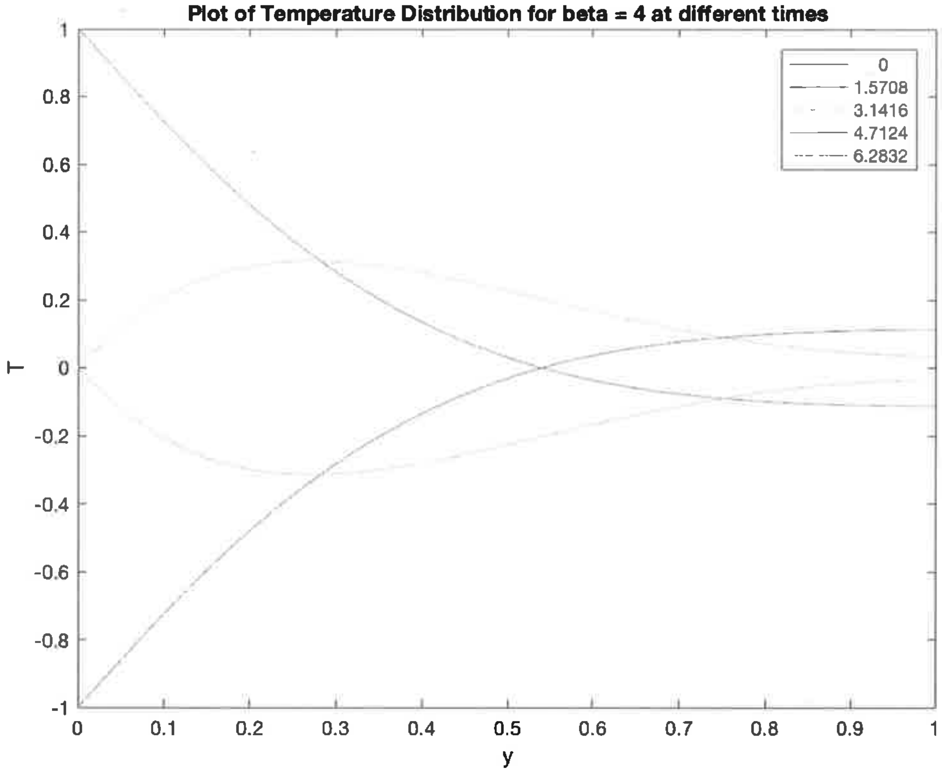


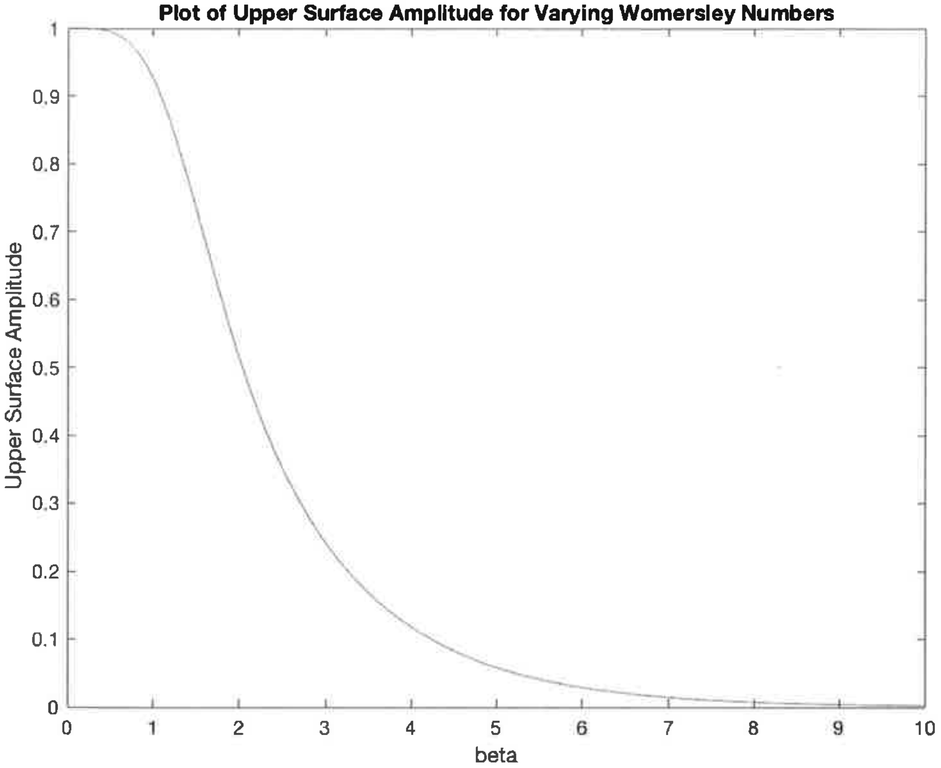
Plot of Upper Surface Amplitude as a Function of Beta

We can also plot up the amplitude of the temperature variation of the upper surface as a function of beta.

```
beta = [0:.01:10];

Tamp = abs(1.0./cosh(i^.5*beta));

figure(2)
plot(beta,Tamp)
xlabel('beta')
ylabel('Upper Surface Amplitude')
title('Plot of Upper Surface Amplitude for Varying Womersley Numbers')
```



Conclusion

As can be seen, for small values of the Womersley number the oscillations at the upper surface are the same as the lower: the whole slab is at a uniform, time varying temperature. For large Womersley number, however, the amplitude of the oscillations at the upper surface decreases exponentially.

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So far we have focused on ht transfer in solids, but we need to consider fluids too! The necessary eq'ns are derived in ch 11 of BS&L.

Key is that total energy is conserved!

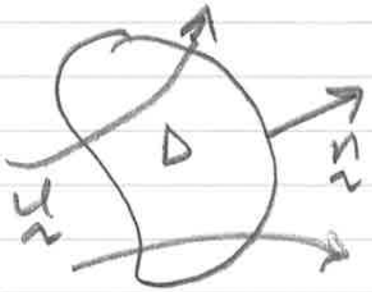
Let $\hat{U}$ be the internal energy per unit mass.

Then $\rho\hat{U}$ is internal energy/vol

Likewise $\frac{1}{2}\rho u^2$ is the KE/vol of the fluid

So $\left(\frac{1}{2}\rho u^2 + \rho\hat{U}\right)$ is the total energy/volume!

Now let's draw a control volume



$$\left\{\begin{matrix}\text{accum of } E\\ \text{in } D\end{matrix}\right\} + \left\{\begin{matrix}E\ \underline{\text{out}}\text{ by}\\ \text{convection}\end{matrix}\right\} + \left\{\begin{matrix}E\text{ out by}\\ \text{conduction}\end{matrix}\right\} = \left\{\text{sources}\right\}$$

$$\left\{\begin{matrix}\text{accum of } E\\ \text{in } D\end{matrix}\right\} \equiv \frac{\partial}{\partial t}\int_D \left(\tfrac{1}{2}\rho u^2 + \rho \hat{U}\right) dV$$

$$\left\{\begin{matrix}E\ \underline{\text{out}}\text{ by}\\ \text{convection}\end{matrix}\right\} \equiv \int_{\partial D} \left(\tfrac{1}{2}\rho u^2 + \rho \hat{U}\right) \underbrace{\underset{\sim}{u} \cdot \underset{\sim}{n}}_{\text{vol flux } \underline{\text{normal}} \text{ to } \partial D}\, dA$$

$$\left\{\begin{matrix}E\text{ out by}\\ \text{conduction}\end{matrix}\right\} = \int_{\partial D} \underset{\sim}{q} \cdot \underset{\sim}{n}\, dA$$

What are the sources?

This is total energy (including KE) so it includes forces as well as thermal sources:

$$\int_{\partial D} - \underset{\sim}{u}\, p \cdot \underset{\sim}{n}\, dA \quad \text{(pressure forces)}$$

shear forces (use dif. sign convention

$$+ \int_{\partial D} \underset{\sim}{u} \cdot \underset{\approx}{\tau} \cdot \underset{\sim}{n}\, dA \quad \text{(viscous forces)}$$

$$+ \int_{D} \rho \underset{\sim}{g} \cdot \underset{\sim}{u}\, dV \quad \text{(gravity forces)}$$

$$+ \int_{D} \dot{S}\, dV \quad \left(\begin{array}{l}\text{thermal sources like} \\ \text{rxn, dissip, etc.}\end{array}\right)$$

To get an eq'n at a point in the fluid, apply divergence theorem to surface integrals to convert to vol. integrals. Since D is arb. eq'n is valid at every point in flow!

So we get eq'n 11.1-7:

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho u^2+\rho\hat{U}\right)+\underset{\sim}{\nabla}\cdot\left[\left(\frac{1}{2}\rho u^2+\rho\hat{U}\right)\underset{\sim}{u}\right]$$

$$= -\underset{\sim}{\nabla}\cdot\underset{\sim}{q} \quad -\underset{\sim}{\nabla}\cdot(p\underset{\sim}{u}) + \underset{\sim}{\nabla}\cdot(\underset{\approx}{\tau}\cdot\underset{\sim}{u})$$

$$+ \rho(\underset{\sim}{u}\cdot\underset{\sim}{g}) + \dot{S}$$

we want toget rid of KE term & just have it involve internal energy we subtract off the mechanical energy balance (from F=ma) used last term!

You thus get eq. 11.2-1:

$$\frac{\partial}{\partial t}(\rho\hat{U}) + \underset{\sim}{\nabla}\cdot(\rho\hat{U}\underset{\sim}{u}) = -\underset{\sim}{\nabla}\cdot\underset{\sim}{q}$$

$$\underset{\underset{\text{reversible conversion of mech E to thermal Energy (pressurework)}}{\uparrow}}{-p(\underset{\sim}{\nabla}\cdot\underset{\sim}{u})} \quad + \underset{\underset{\text{Irreversible conversion (viscous dissipation)}}{\uparrow}}{\underset{\approx}{\tau}:\underset{\sim}{\nabla}\underset{\sim}{u}} \quad + \dot{S}$$

so $-p(\underset{\sim}{\nabla}\cdot\underset{\sim}{u})$ => if you compress a gas it gets hot!
(pos or neg!)

$\tau : \underset{\sim}{\nabla}\underset{\sim}{u}$ => viscous heating due to shear - always positive (but usually small - not always!)

From Thermo we can relate $\hat{U}$ to T & P

This yields eq'n 11.2-5:

$$\rho\hat{C}_p\left(\frac{\partial T}{\partial t} + \underset{\sim}{u}\cdot\underset{\sim}{\nabla}T\right) = -\underset{\sim}{\nabla}\cdot q + \underset{\approx}{\tau}:\underset{\sim}{\nabla}\underset{\sim}{u} - \left(\frac{\partial \ln\rho}{\partial \ln T}\right)\frac{DP}{Dt} + \dot{S}$$

Note: $\frac{DP}{Dt} \equiv \frac{\partial P}{\partial t} + \underset{\sim}{u}\cdot\underset{\sim}{\nabla}P$

(material Derivative, Lagrangian perspective)

For a fluid at constant pressure (usual case), neglecting viscous dissip. as it is usually small, we get (w/ Fourier's Law, const. k):

eq'n 11.2-8:

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} T \right) = k \nabla^2 T + \dot{S}$$

This is the eq'n we will use - but if you work w/ compressible gases (e.g., gas turbines!) you would use a different form! Table 11.4-1 has lots of versions for different applications!

So: let's review $\frac{DT}{Dt} \equiv \frac{\partial T}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} T$

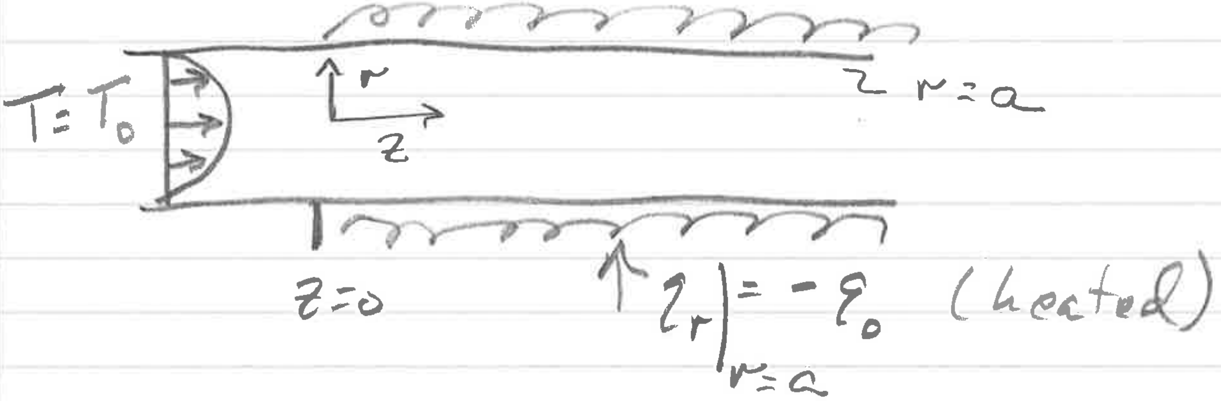
This is material derivative: there are 2 ways a fluid element can change temp. (1) $\frac{\partial T}{\partial t}$ = time deriv

(2) $\underset{\sim}{u} \cdot \underset{\sim}{\nabla} T$ ≡ convected in direction of temp. gradient!

Material derivative has both pieces!

OK, let's apply this!

Probably *the* classic problem in convective transport is the Graetz (or Nusselt-Graetz) problem: laminar flow through a heated pipe!



We want to calculate the heat transfer coefficient:

$$q_0 = h\left(T\big|_{r=a} - T_b\right)$$

T_b is the *bulk* or cup-mixing temperature ⇒ what you would get for the temp. in a cup holding the fluid coming out of the pipe!

$$T_b \equiv \frac{\int_0^a T\, u_z\, 2\pi r\, dr}{\int_0^a u_z\, 2\pi r\, dr}$$

This is <u>much</u> more useful than the area avg $\overline{T}$ or centerline T!

What are the equations governing this problem? <u>Assume</u> incompressible flow w/ constant properties!

CE: $\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$

NS: $\rho\left(\frac{\partial \underset{\sim}{u}}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} \underset{\sim}{u}\right) = -\underset{\sim}{\nabla} p + \mu \nabla^2 \underset{\sim}{u} + \rho \underset{\sim}{g}$

Energy: $\rho \hat{C}_p\left(\frac{\partial T}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} T\right) = k \nabla^2 T + \mu \underset{\nearrow}{\phi_v}$

$\left(\underset{\approx}{\tau} : \underset{\sim}{\nabla} \underset{\sim}{u}\right)$

Viscous Dissip.

How do we solve?

1) choose coord system in which bdy has convenient rep! ⟹ cyl. coord!

2) Get rid of terms that are zero

3) scale the rest to further simplify!

Start with C.E. & velocity profile!

$\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$

$\therefore \quad \frac{1}{r}\frac{\partial (r u_r)}{\partial r} + \frac{1}{r}\frac{\partial u_\theta}{\partial \theta} + \frac{\partial u_z}{\partial z} = 0$

Assume unidirectional flow!

$\therefore \quad u_r = u_\theta = 0$ and $\frac{\partial u_z}{\partial z} = 0$!

This is valid for fully developed flow! otherwise (if $\frac{\partial u_z}{\partial z} \neq 0$) then $u_r \neq 0$!

Now for z-component of NS eq'ns:

$$\rho\left(\frac{\partial u_z}{\partial t} + u_r\frac{\partial u_z}{\partial r} + \frac{u_\theta}{r}\frac{\partial u_z}{\partial \theta} + u_z\frac{\partial u_z}{\partial z}\right)$$

$$= -\frac{\partial P}{\partial z} + \mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 u_z}{\partial \theta^2} + \frac{\partial^2 u_z}{\partial z^2}\right] + \rho g_z$$

Ok, assume uni*directional* flow in z dir., also axisymmetric.

We can *ignore* ρg_z term as it is the *difference* from *hydrostatics* that drives flow $\left(-\frac{\partial P}{\partial z} + \rho g_z\right) \equiv -\frac{\partial \mathcal{P}}{\partial z}$ (augmented pressure!)

since from CE $\frac{\partial u_z}{\partial z} = 0 \therefore \frac{\partial^2 u_z}{\partial z^2} = 0$!

We're left with:

$$\rho\cancel{\frac{\partial u_z}{\partial t}} = -\frac{\partial P}{\partial z} + \mu\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right)\right]$$

Assume SS too!

In general we impose a flow rate or avg. vel U which yields the pressure gradient!

Anyway, we get Poiseuille flow:

$$u_z = 2U\left(1 - \frac{r^2}{a^2}\right)$$

e.g., CL velocity is twice average! (geometry specific: this is for circular tube only!)

This yields $\frac{\partial P}{\partial z} = -\frac{8\mu U}{a^2}$

with flow rate $Q = U\pi a^2$

Ok, now for energy!

$$\rho\hat{C}_p\left(\frac{\partial T}{\partial t} + u_r\frac{\partial T}{\partial r} + \frac{u_\theta}{r}\frac{\partial T}{\partial \theta} + u_z\frac{\partial T}{\partial z}\right)$$

$$= k\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2}\right]$$

$$+ \mu\phi_v$$

Again, assume SS, so $\underline{\dfrac{\partial T}{\partial t} = 0}$

unidirectional flow ∴ $u_r = u_\theta = 0$

axi-symmetric so $\dfrac{\partial^2 T}{\partial \theta^2} = 0$

$$\therefore \rho \hat{C}_p \, 2U\left(1 - \frac{r^2}{a^2}\right)\frac{\partial T}{\partial z} = k\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right] + \mu\left(\frac{\partial u_z}{\partial r}\right)^2$$

↳ viscous dissip.

Ok, now for BC's:

$$T\Big|_{z \to -\infty} = T_0 \qquad \frac{\partial T}{\partial r}\Big|_{r=0} = 0 \quad \text{(finite)}$$

$$-k\frac{\partial T}{\partial r}\Big|_{\substack{r=a \\ z>0}} = -q_0 \quad \text{(heating)}$$

So let's scale this!

Let $r^* = r/a$, $z^* = \dfrac{z}{z_c}$, $T^* = \dfrac{T - T_0}{\Delta T_c}$

Look at inhomogeneous BC:

$$-k\frac{\Delta T_c}{a}\frac{\partial T^*}{\partial r^*}\bigg|_{\substack{r^*=1\\ z^*>0}} = -q_0$$

$$\therefore \quad \Delta T_c = \frac{q_0 a}{k}$$

and $$\frac{\partial T^*}{\partial r^*}\bigg|_{\substack{r^*=1\\ z^*>0}} = 1$$

And for DE:

$$\frac{\rho\hat{C}_p U \Delta T_c}{z_c}\, 2(1-r^{*2})\frac{\partial T^*}{\partial z^*} = k\frac{\Delta T_c}{a^2}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right)$$

$$+\, k\frac{\Delta T_c}{z_c^2}\frac{\partial^2 T^*}{\partial z^{*2}} + \mu\left(\frac{4Ur}{a^2}\right)^2$$

$$\hookrightarrow \left(\frac{16\mu U^2}{a^2}\right) r^{*2}$$

OK - next divide by scaling of important term!

Heating from wall, so radial cond. has to matter!

Divide by $\dfrac{k\Delta T_c}{a^2}$

So:

$$\left[\frac{\rho \hat{C}_p U a^2}{k Z_c}\right] 2\left(1-r^{*2}\right)\frac{\partial T^*}{\partial z^*}$$

$$= \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right) + \left[\frac{a^2}{Z_c^2}\right]\frac{\partial^2 T^*}{\partial z^{*2}}$$

$$+ \left[\frac{16\mu U^2}{k\Delta T_c}\right] r^{*2}$$

Choose Z_c so that we balance axial convection w/ radial conduction!

$$\therefore Z_c = \frac{\rho \hat{C}_p a^2}{k} U \equiv \underbrace{\left(\frac{a^2}{\alpha}\right)}_{\text{dif}^{\underline{n}}\text{ time}} U$$

∴ Z_c is the distance fluid is convected down the tube during radial dif$^{\underline{n}}$ t!

So we are left w/ two groups.

Look at $\dfrac{a^2}{Z_c^2} = \dfrac{a^2}{\left(\frac{a^2}{\alpha}U\right)^2} = \left(\dfrac{\alpha}{Ua}\right)^2 = \left[\dfrac{\nu}{Ua}\,\dfrac{\alpha}{\nu}\right]^2$

$$= \left(\frac{1}{Re}\frac{1}{Pr}\right)^2$$

normally Re is D, not a!

In general, $RePr >> 1$!!

Say, water in a 2 cm dia pipe
at slow speed of 10 cm/s

$$\frac{Ua}{\nu} = \frac{(10)(1)}{0.01} = 1000!$$

$$Pr \cong 7 \quad (20°C)$$

$$\therefore \frac{\alpha}{Ua} = \frac{1}{7000} \qquad \left(\frac{\alpha}{Ua}\right)^2 = \underline{2\times 10^{-8}}!$$

That is why you neglect thermal cond$^{\underline{n}}$ in direction of motion!
It's small!

Ok, what about viscous dissipation?

$$\frac{16\mu U^2}{k\Delta T_c} = \frac{16\mu U^2}{q_0 a} \approx \frac{(16)(0.01)(10)^2}{(10^3)(1)} = 0.016$$

e.g., $1\ W/m^2 = 1000\ erg/s\,cm^2$

This is actually high - usually q_0 is bigger!

Except for specific cases, if you are heating things, viscous dissipation is negligible!

So: $$2(1-r^{*2})\frac{\partial T^*}{\partial z^*} = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right)$$

$$T^*\Big|_{z^*=0} = 0 \qquad \frac{\partial T^*}{\partial r^*}\Big|_{r^*=1} = 1 \qquad \frac{\partial T^*}{\partial r^*}\Big|_{r^*=0} = 0 \text{ (Axis)}$$

We want the asymptotic solution!

It gets hotter w/ z^*, so expect

$$T^*_\infty = z^* f_1(r^*) + f_2(r^*)$$

$$\therefore \quad \frac{1}{r^*}\left(r^* f_1'\right)' = 0 \qquad f_1'(0) = 0 \quad \underline{\underline{f_1'(1) = 0}}$$

This just yields $f_1 = c$ (cst!)

Now for f_2:

$$\frac{1}{r^*}\left(r^* f_2'\right)' = 2(1-r^{*2})f_1; \quad f_2'(0) = 0, \; \underline{f_2'(1) = 1}$$

$$\uparrow$$

Except for specific cases, if you are heating things, viscous dissipation is negligible!

So: $$2(1-r^{*2})\frac{\partial T^*}{\partial z^*} = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T^*}{\partial r^*}\right)$$

$$T^*\Big|_{z^*=0} = 0 \qquad \frac{\partial T^*}{\partial r^*}\Big|_{r^*=1} = 1 \qquad \frac{\partial T^*}{\partial r^*}\Big|_{r^*=0} = 0 \text{ (Axis)}$$

We want the asymptotic solution!

It gets hotter w/ z^*, so expect

$$T_\infty^* = z^* f_1(r^*) + f_2(r^*)$$

$$\therefore \frac{1}{r^*}\left(r^* f_1'\right)' = 0 \qquad f_1'(0)=0 \quad \underline{\underline{f_1'(1)=0}}$$

This just yields $f_1 = c$ (cst!)

Now for f_2:

$$\frac{1}{r^*}\left(r^* f_2'\right)' = 2(1-r^{*2})f_1; \quad f_2'(0)=0, \ \underset{\uparrow}{\underline{f_2'(1)=1}}$$

f_1 is a constant, so we just integrate:

$$(r^* f_2') = c \int 2(1-r^{*2}) r^* dr^*$$
$$= \left(r^{*2} - \frac{1}{2} r^{*4}\right) c + c_2$$

divide:

$$f_2' = c\left(r^* - \frac{1}{2} r^{*3}\right) + \underset{\swarrow\; 0}{\cancel{\frac{c_2}{r^*}}}$$

but $f_2'(1) = 1$

$\therefore\ c = 2!$

so $f_2' = 2r^* - r^{*3}$

$$f_2 = r^{*2} - \frac{1}{4} r^{*4} + c_3$$

We require that the flow average temp at $z^* = 0$ vanishes!

$$\int_0^1 f_2\, 2(1-r^{*2}) 2r^* dr^* = 0$$

so $c_3 + \int_0^1 \left(r^{*2} - \frac{1}{4} r^{*4}\right) 4(1-r^{*2}) r^* dr^* = 0$

$= c_3 + \frac{7}{24}$ so $c_3 = -\frac{7}{24}$

$\therefore T_\infty = 2z^* + r^{*2} - \frac{1}{4}r^{*4} - \frac{7}{24}$

We can define the heat transfer coefficient:

$$h_\infty = \frac{q_0}{T|_{r=a} - T_b} = \frac{k}{a}\frac{1}{T^*|_{r=1} - T_b^*}$$

but $T_b^* = 2z^*$! (get from an energy balance)

$$T^*|_{r^*=1} = 2z^* + 1 - \frac{1}{4} - \frac{7}{24} = \frac{11}{24}$$

so $h_\infty = \frac{k}{a}\frac{24}{11}$ (note: $Nu = \frac{hD}{k} = \frac{48}{11}$)

How long does it take to get there?

Let $T^* = T_\infty^* + T_d^*$

$$2(1-r^{*2})\frac{\partial T_d^*}{\partial z^*} = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial T_d^*}{\partial r^*}\right)$$

$$\left.\frac{\partial T_d^*}{\partial r^*}\right|_{r^*=0,1} = 0 \qquad T_d^*\Big|_{z^*=0} = -T_\infty^*\Big|_{z^*=0}$$

Solve via sep. of variables:

$$T_d^* = G(z^*)\,F(r^*)$$

$$\therefore \quad \frac{G'}{G} = \frac{(r^* F')'}{2r^*(1-r^{*2})F} = -\sigma^2$$

$$F'(0) = F'(1) = 0$$

This has to be solved numerically, but it's easy to do!

$p(x) \equiv r^*$

$q(x) \equiv 0$

$w(x) \equiv 2r^*(1-r^{*2})$

and $-T_\infty^*\Big|_{z^*=0} = -\left(r^{*2} - \frac{1}{4}r^{*4} - \frac{7}{24}\right)$

From the numerical solution,

$\sigma_1^2 \approx 12.8$

so it decays pretty fast!

The numerical distance goes as $z^* \cdot U\frac{a^2}{\alpha}$ which may be fairly large! (for RePr >> 1)

Contents

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- Eigenvalues, Eigenvectors, and Coefficients
- Temperature of the Cylinder Wall
- Temperature Profile at Various Times
- Heat Transfer Coefficient
- Conclusion

The Nusselt-Graetz Problem: Constant Heat Flux at the Wall

We solve the Sturm-Liouville problem for constant heat flux at the wall for laminar flow through a circular tube.

The eigenvalue problem for the decaying solution is

((x*y')' + lambda*2*r*(1-r^2)*y = 0

y'(0) = 0; y'(1) = 0

The asymptotic solution at large z is:

Tinf = 2*z + r.^2 - r.^4/4 - 7/24

Thus, the initial value for the Sturm-Liouville expansion is just the negative of this function.

Solving the problem we get:

```
p = @(x) x;
q = @(x) zeros(size(x));
w = @(x) 2*x.*(1-x.^2);
bc = [0,1,0,1];

n = 100; %The number of points we would like (the number of intervals)

[lambda, eigenvecs] = slsolve(p,q,w,bc,n);

Tinf = @(z,r) 2*z + r.^2 - r.^4/4 - 7/24

% And that's it!
```

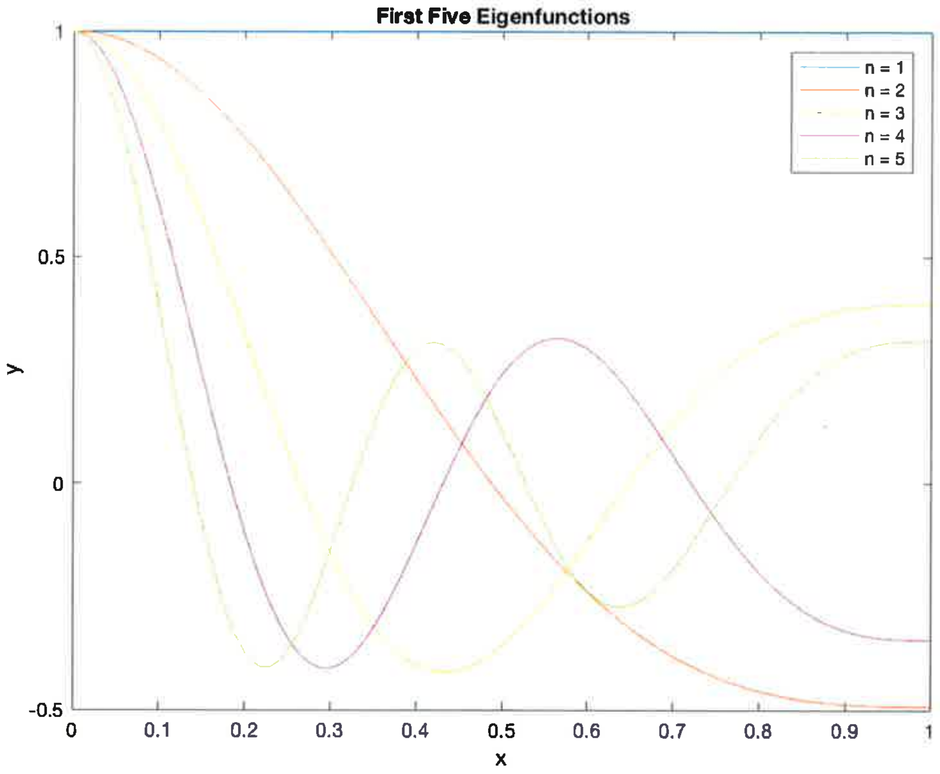
```
Tinf =

  function_handle with value:

    @(z,r)2*z+r.^2-r.^4/4-7/24
```

Eigenvalues, Eigenvectors, and Coefficients

We are interested in the lead eigenvalues, coefficients, and eigenvectors. We just look at the first five:

```
firsteigenvecs = lambda(1:5)

% And we calculate the coefficients using the Trapezoidal Rule:

r = [0:1/n:1]';

% The Trapezoidal Rule weights:
weights = ones(1,n+1);
weights(1) = 0.5;
weights(n+1) = 0.5;
weights=weights/n;

a = zeros(length(lambda),1);

for i = 1:length(lambda)
    numerator = -weights*(w(r).*Tinf(0,r).*eigenvecs(:,i));
    denominator = weights*(w(r).*eigenvecs(:,i).^2);
    a(i) = numerator/denominator;
end

firstcoefficients = a(1:5)

% And we plot the first five eigenfunctions:
figure(1)
plot(r,eigenvecs(:,1:5))
xlabel('x')
ylabel('y')
title('First Five Eigenfunctions')
legend('n = 1','n = 2','n = 3','n = 4','n = 5')
grid on
```

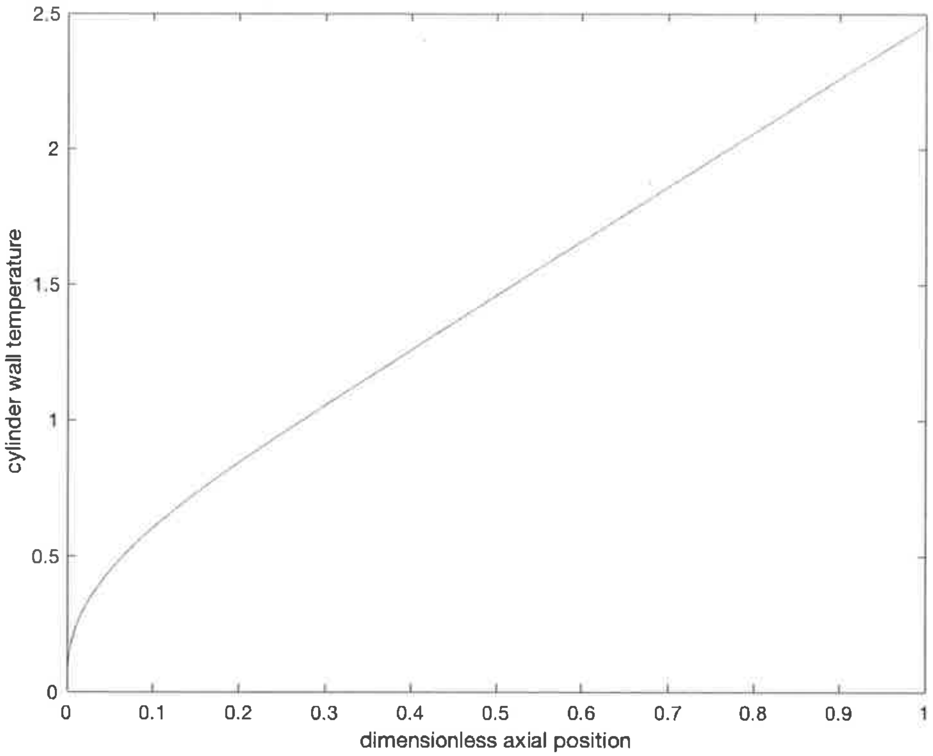
```
firsteigenvecs =

    0.0000
   12.8321
   41.8881
   86.9418
  147.9090


firstcoefficients =

    0.0000
    0.4035
   -0.1749
    0.1049
   -0.0728
```



Temperature of the Cylinder Wall

We want the temperature at the outer radius, necessary for obtaining the heat transfer coefficient:

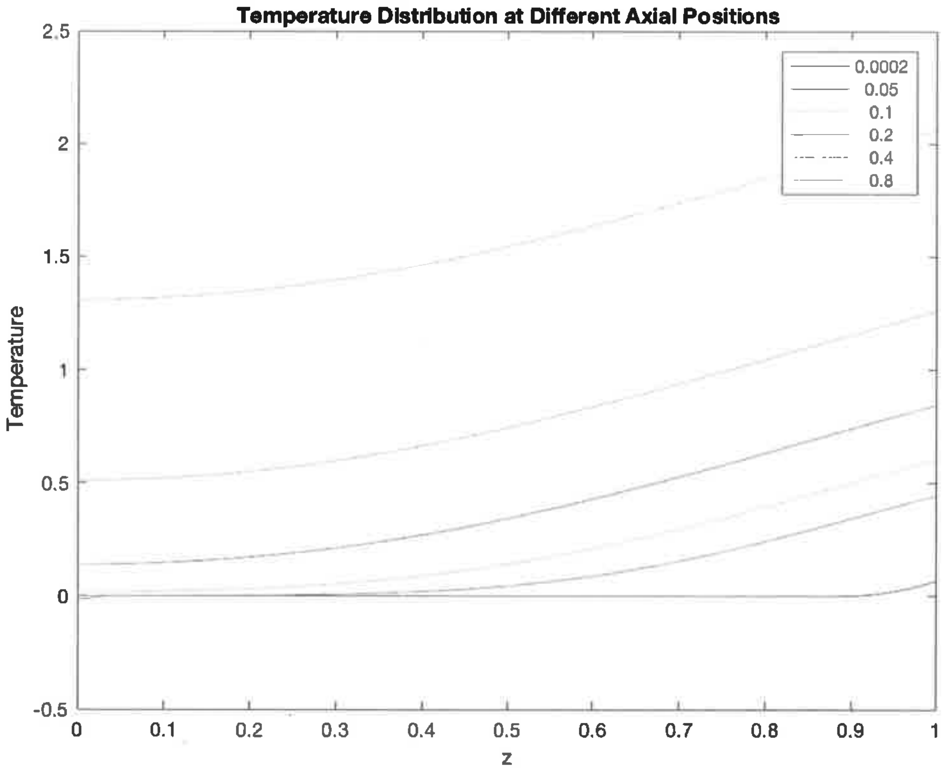
```
z = [0.0005:.001:1];
twall = zeros(size(z)); %We initialize the array

for i = 1:length(z)
    twall(i) = Tinf(z(i),1) + sum(a.*exp(-lambda*z(i)).*eigenvecs(end,:)');
end

figure(2)
plot(z,twall)
xlabel('dimensionless axial position')
ylabel('cylinder wall temperature')
grid on
```



Temperature Profile at Various Times

We can also plot up the temperature distribution for specific z locations. You will note the issue near the origin at very small z. This is known as the Gibbs ringing phenomenon and is well known in signal processing.

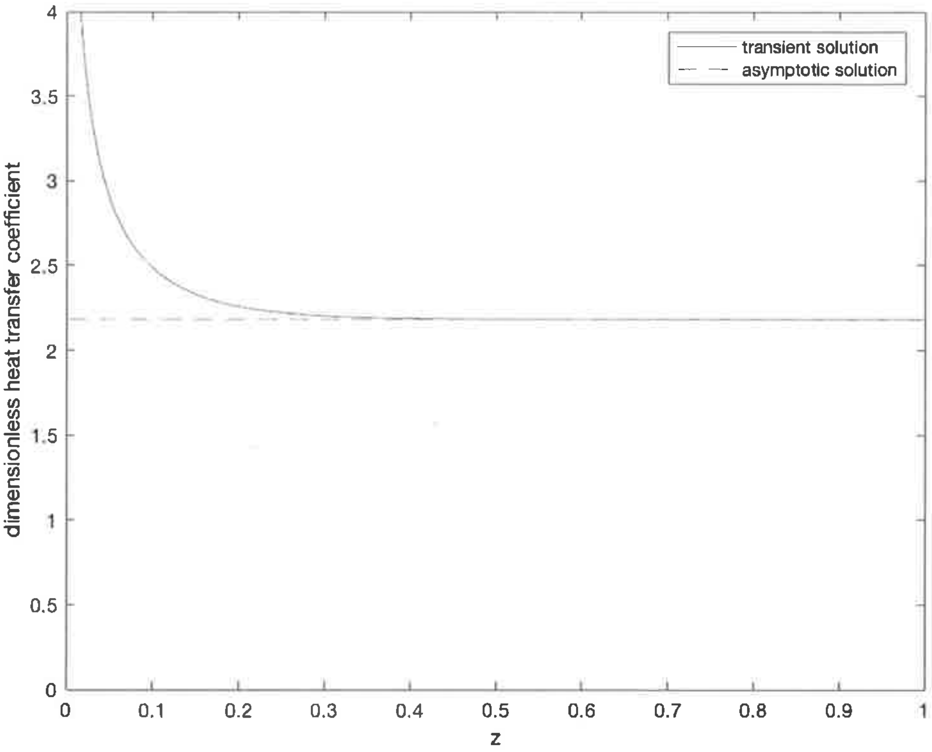
```
zplot = [0.0002,.05,.1,.2,.4,.8]';

tprofile = zeros(length(r),length(zplot));
for j = 1:length(zplot)
    for i=1:length(r)
        tprofile(i,j) = Tinf(zplot(j),r(i)) + sum(a.*exp(-lambda*zplot(j)).*eigenvecs(i,:)');
    end
end
figure(3)
plot(r,tprofile)
legend(num2str(zplot))
xlabel('z')
ylabel('Temperature')
title('Temperature Distribution at Different Axial Positions')
grid on
```



Heat Transfer Coefficient

Finally, we are interested in how the heat transfer coefficient varies with axial position. The dimensionless value is just the inverse of twall - Tb(z), where Tb(z) is just 2*z. So:

```
h = 1./(twall - 2*z);

figure(4)
plot(z,h,z,24/11*ones(size(z)),'--')
axis([0,1,0,4])
xlabel('z')
ylabel('dimensionless heat transfer coefficient')
legend('transient solution','asymptotic solution')
grid on
```



Conclusion

The initial heat transfer coefficient is larger than the asymptotic value due to the small thickness of the developing boundary layer. After a short distance, however, the asymptotic result is reached. The zero initial eigenvalue is the result of a zero derivative condition at both r = 0 and r = 1, however the coefficient for it is likewise zero, removed via the energy balance enforced on the asymptotic solution.

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From our calculations we found that the Nusselt number Nu is a function of dimensionless distance down the pipe. This is the local Nu and our $z^* = \frac{z}{U\frac{a^2}{\alpha}}$

It's usually written in terms of diameter $D = 2a$, thus:

$$\frac{h_{loc}D}{k} = Nu_{loc} = \frac{48}{11} + f^n\left(\frac{z}{UD^2/\alpha}\right)$$

This ratio is $1/Gz$, Graetz #

$$Gz = \frac{UD^2}{\alpha z} = \underset{\overset{\uparrow}{Re}}{\left(\frac{UD}{\nu}\right)}\underset{\overset{\uparrow}{Pr}}{\left(\frac{\nu}{\alpha}\right)}\left(\frac{D}{z}\right)$$

The solution is valid as $Gz \rightarrow 0$, but actually is good way before! Let's look at some numbers.

The lead eigenfunction decays exponentially as $e^{-4\lambda_1 \frac{\alpha z}{UD^2}}$ where $\lambda_1 = 12.8$

So the term is small when

$$z > \frac{1}{50} \frac{UD^2}{\alpha}$$

Suppose we have water flowing through a 1 cm ID tube at 10 cm/s. This yields

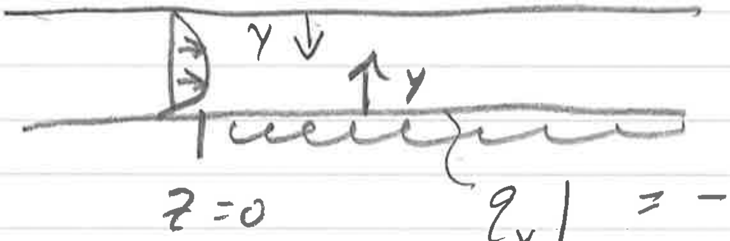
$Re = \frac{(10)(1)}{(0.01)} = 1000$ so it's laminar

$Pr = \nu/\alpha = 7$, so $\frac{UD^2}{\alpha} = 7000$ cm $= 70$m!

Thus, even though λ_1 is large, you are still in the entrance region for over 1m!

For short tubes we can look at the entrance region using boundary layer analysis!

we define a coord $y \equiv a - r$
(e.g., distance from wall)



$$q_y\Big|_{y=0} = -k\frac{\partial T}{\partial y}\Big|_{y=0} = q_0$$

Let the characteristic thickness of BL be $\delta << a$

Recall $u_z = 2U\left(1 - r^2/a^2\right)$

Now $r = a - y$

$$\therefore\ u_z = 2U\left(1 - \frac{(a-y)^2}{a^2}\right)$$

$$= 2U\left(\cancel{1} - \cancel{1} + 2\,y/a - \cancel{y^2/a^2}\right)$$

small

$$\therefore\ u_z \cong \frac{4U}{a}\,y \quad \text{or} \quad \frac{8U}{D}\,y$$

shear rate at wall

Let $\dot{\gamma} \equiv \dfrac{8U}{D}$

Provided $\delta/a << 1$ we can approximate our equation w/ Cartesian coords – the "flat earth limit"!

$$\rho \hat{C}_p \dot{\gamma} y \frac{\partial T}{\partial z} = \kappa \frac{\partial^2 T}{\partial y^2}$$

$$T\Big|_{y\to\infty} = T_0 \quad T\Big|_{z=0} = T_0 \quad -\kappa \frac{\partial T}{\partial y}\Big|_{y=0} = q_0$$

Because $\delta/a \ll 1$ (for small z!)

we have $T_b \simeq T_0$ (most of tube is unheated)

Thus $$h \simeq \frac{q_0}{T\big|_{y=0} - T_0}$$

Let's scale:

$$T^* = \frac{T - T_0}{\Delta T_c} \qquad y^* = y/\delta \qquad z^* = z/z_c$$

Plug in:

$$\frac{\rho \hat{C}_p \dot{\gamma} \Delta T_c}{z_c} y^* \frac{\partial T^*}{\partial z^*} = \frac{\kappa \Delta T_c}{\delta^2} \frac{\partial^2 T^*}{\partial y^{*2}}$$

so:

$$\left[\frac{\delta^3 \dot{\gamma}}{\alpha \, z_c}\right] y^* \frac{\partial T^*}{\partial z^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

Thus $\delta = \left(\frac{\alpha z_c}{\dot{\gamma}} \right)^{1/3}$

And from the BC:

$$-\frac{\Delta T_c}{\delta} k \left. \frac{\partial T^*}{\partial y^*} \right|_{y^*=0} = q_0$$

or $$\left. \frac{\partial T^*}{\partial y^*} \right|_{y^*=0} = -\underset{\overset{\shortparallel}{1}}{\left[\frac{q_0 \delta}{k \Delta T_c} \right]}$$

so $$\Delta T_c = \frac{q_0 \delta}{k} = \frac{q_0}{k} \left(\frac{\alpha z_c}{\dot{\gamma}} \right)^{1/3}$$

Thus: $$y^* \frac{\partial T^*}{\partial z^*} = \frac{\partial^2 T^*}{\partial y^{*2}}$$

$$\left. T^* \right|_{y^* \to \infty} = \left. T^* \right|_{z^*=0} = 0 \; ; \; \left. \frac{\partial T^*}{\partial y^*} \right|_{y^*=0} = -1$$

Note: $$h \equiv \frac{q_0}{\left. T \right|_{y=0} - T_0} = \frac{q_0}{\Delta T_c} \frac{1}{\left. T^* \right|_{y^*=0}}$$

$$= \frac{k}{\left(\frac{\alpha z_c}{\dot{\gamma}} \right)^{1/3}} \frac{1}{\left. T^* \right|_{y^*=0}}$$

We can use this to get the local Nu in the entrance region:

$$Nu_{loc} = \frac{hD}{k} = \frac{D}{\cancel{k}} \cancel{k} \left(\frac{8U}{D \alpha z_c} \right)^{1/3} \frac{1}{T^*|_{y^*=0}}$$

$$= 2 \left(\frac{UD}{\alpha} \frac{D}{z_c} \right)^{1/3} \frac{1}{T^*|_{y^*=0}}$$

$$= 2 \left(Gz_c \right)^{1/3} \frac{1}{T^*|_{y^*=0}}$$

where $Gz_c = Re\, Pr \frac{D}{z_c}$

Now we need $T^*|_{y^*=0}$!

z_c disappeared from dimensionless eq'n, so we are length scale deficient

Affine stretching would yield the same thing!

Let $T^* = A\bar{T}$, $z^* = B\bar{z}$, $y^* = c\bar{y}$

$$\therefore \frac{AC}{B} \bar{y} \frac{\partial \bar{T}}{\partial \bar{z}} = \frac{A}{c^2} \frac{\partial^2 \bar{T}}{\partial \bar{y}^2}$$

Divide out:

$$\frac{C^3}{B}\,\bar{y}\,\frac{\partial \bar{T}}{\partial \bar{z}} = \frac{\partial^2 \bar{T}}{\partial \bar{y}^2}$$

and from BC. : $\frac{A}{C}\frac{\partial \bar{T}}{\partial \bar{y}}\Big|_{\bar{y}=0} = -1$

so $\frac{A}{C} = 1 \quad \frac{C^3}{B} = 1$

or in <u>canonical</u> <u>form</u>

$$\frac{C}{B^{1/3}} = 1 \qquad \therefore \quad \zeta = \frac{y^*}{z^{*\,1/3}}$$

$$\frac{A}{B^{1/3}} = 1 \qquad \therefore \quad \frac{T^*}{z^{*\,1/3}} = f(\zeta)$$

So we <u>know</u> $T^*\Big|_{y^*=0} = z^{*\,1/3} f(0)$

and thus

$$Nu_{loc} = \frac{2}{f(0)}\left(\frac{UD}{\alpha}\,\frac{D}{z}\right)^{1/3}$$

Now we just need $f(0)$!

We take deriv. to get transformed ODE:

$$\frac{\partial T^*}{\partial y^*} = f' \quad \therefore \quad f'(0) = -1 \quad (\text{BC})$$

$$\frac{\partial^2 T^*}{\partial y^{*2}} = \frac{1}{z^{*1/3}} f''$$

$$\frac{\partial T^*}{\partial z^*} = \frac{\partial}{\partial z^*}\left(z^{*1/3} f(\zeta)\right) = \frac{1}{3} z^{*-2/3} f + z^{*1/3} f'\left(-\frac{1}{3}\frac{\zeta}{z^*}\right)$$

$$= \frac{1}{3} z^{*-2/3}\left(f - \zeta f'\right)$$

So:

$$\frac{1}{3} y^* z^{*-2/3}\left(f - \zeta f'\right) = z^{*-1/3} f''$$

or $\quad f'' = \frac{1}{3}\zeta\left(f - \zeta f'\right)$

w/ BC's $f'(0) = -1$, $f(\infty) = 0$

You can solve analytically, but its easier to get numerically!

Let $\underset{\sim}{f} \equiv \begin{bmatrix} f \\ f' \end{bmatrix} = \begin{bmatrix} f_1 \\ f_2 \end{bmatrix}$

$\therefore \underset{\sim}{f}' = \begin{bmatrix} f_2 \\ \frac{1}{3}\eta(f_1 - 3f_2) \end{bmatrix}$

w/ $\underset{\sim}{f}(0) = \begin{bmatrix} x \\ -1 \end{bmatrix}$ where x is our shooting param!

we find $x = 1.5363$,

thus $Nu_{loc} = 1.3018\left(\frac{UD}{\alpha}\frac{D}{z}\right)^{1/3}$

which matches table 14.2-1:

$$Nu_{loc} = \frac{2\,\Gamma(2/3)}{9^{1/3}}\left(\frac{UD}{\alpha}\frac{D}{z}\right)^{1/3}$$

to our precision of integration

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Contents

- Nusselt-Graetz Entrance Region Problem
- Conclusion:

Nusselt-Graetz Entrance Region Problem

In this problem we look at the boundary layer solution for the Nusselt-Graetz problem for short tubes in the entrance region. We use the constant wall heat flux boundary condition. The transformed ODE is:

f'' = 1/3 * eta * (f - eta * f')

f'(0) = -1; f(inf) = 0

We want the temperature at the wall f(0), which is our unknown shooting parameter. We solve the differential equation in the function miss4.m given below:

function out = miss4(x) % This function takes in a guess for the unknown wall temperature for the % constant heat flux entrance length problem and returns the temperature % far away.

fdot = @(eta,f) [f(2); 1/3*eta*(f(1) - eta*f(2))];

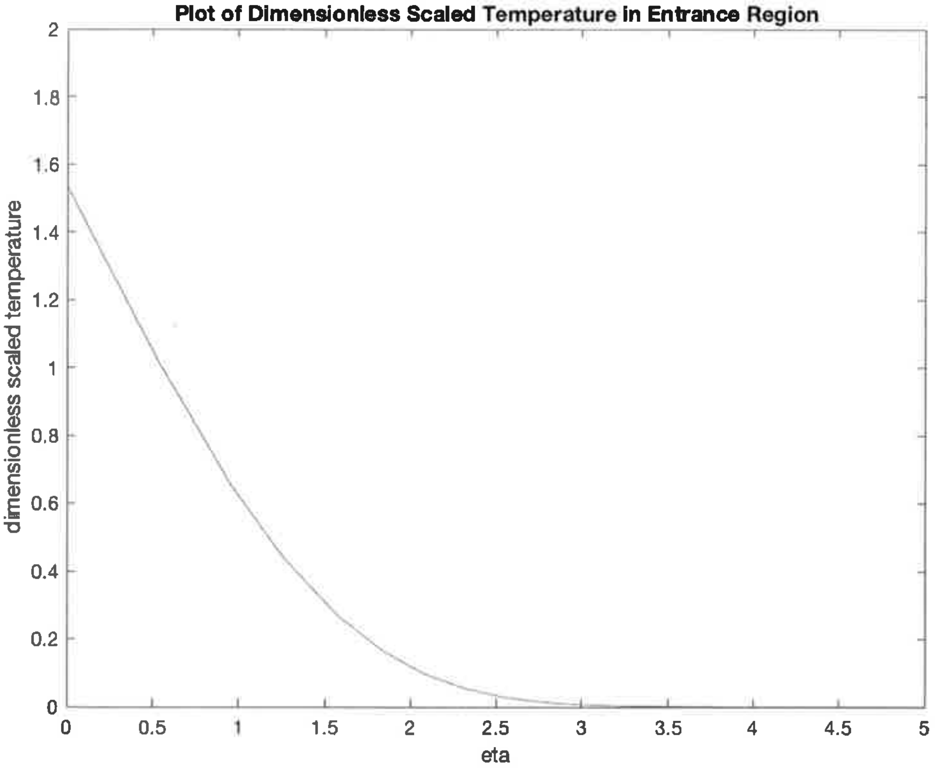
f0 = [x,-1];

[etaout fout] = ode23(fdot,[0,10],f0);

out = fout(end,1);

```
x = fzero('miss4',1)

% We can plot it up too:
fdot = @(eta,f) [f(2); 1/3*eta*(f(1) - eta*f(2))];

f0 = [x,-1];

[etaout fout] = ode23(fdot,[0,10],f0);

figure(1)
plot(etaout,fout(:,1))
xlabel('eta')
ylabel('dimensionless scaled temperature')
title('Plot of Dimensionless Scaled Temperature in Entrance Region')
axis([0 5 0 2])
grid on
```

```
x =

    1.5363
```



Conclusion:

The boundary layer solution converges quite fast, so a limit of 10 is more than adequate. The dimensionless wall temperature is f(0) = 1.5363, a nicely O(1) result.

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It's interesting to see where the entrance region Nu_{loc} crosses the asymptotic $Nu_{loc} = \frac{48}{11}$

This occurs at:

$$\frac{48}{11} = 1.3018 \left(\frac{UD}{\alpha} \frac{D}{z} \right)^{1/3}$$

$$\text{or} \quad z = 0.0266 \frac{UD^2}{\alpha}$$

which is about what would be expected from the lead eigenvalue. These results are plotted below.

Next week we'll see what you do with h: heat exchangers!

Contents

- Comparison of Local Nusselt Number Calculations
- Conclusion

Comparison of Local Nusselt Number Calculations

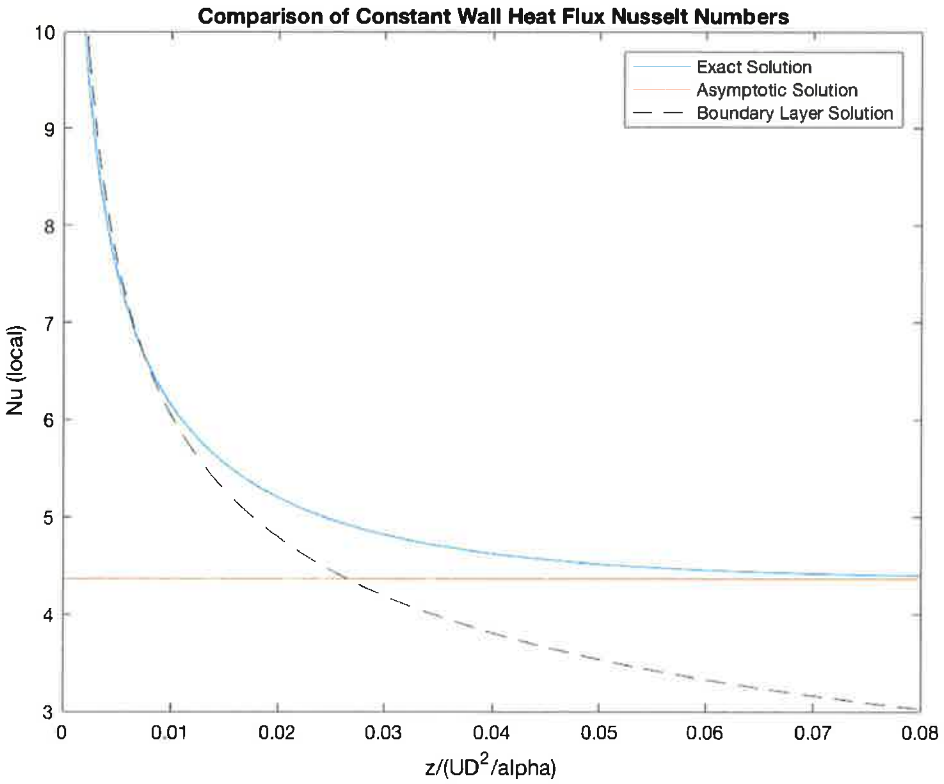
In this script (which must be run after the nusseltgraetz.m script) compares the asymptotic 48/11 solution, the Sturm-Liouville solution, and the thermal boundary layer solution for the local Nusselt number for the constant wall heat flux problem. We convert z and h to the conventional scalings Nu = hD/k and z* = z/(UD^2/alpha).

```
zstar = z/4;

Nu = 2*h;

NuBL = 2*gamma(2/3)/9^(1/3)./zstar.^(1/3);

figure(1)
plot(zstar,Nu,zstar,48/11*ones(size(zstar)),zstar,NuBL,'--k')
xlabel('z/(UD^2/alpha)')
ylabel('Nu (local)')
legend('Exact Solution','Asymptotic Solution','Boundary Layer Solution')
title('Comparison of Constant Wall Heat Flux Nusselt Numbers')
axis([0 .08 3 10])
grid on
```



Conclusion

Examination of the graph indicates that the boundary layer solution is good up to a dimensionless value of about 0.01 while the asymptotic solution is approached at a dimensionless value of 0.05.

We have often discussed analogy between mass, mom. & E transfer - this is particularly useful in understanding heat exchangers. These usually operate under turbulent conditions as eddies are far more efficient at mixing up fluids than is diffusion! Most resistance to transport is in a narrow layer at the walls.

Let's compare momentum & energy transport along a flat plate (or inside wall of a tube in the "flat earth limit"!).

x-mom:

$$\rho \underset{\sim}{u} \cdot \underset{\sim}{\nabla} u_x = -\frac{\partial P}{\partial x} + \mu \nabla^2 u_x$$

and the energy eq'n:

$$\rho \hat{C}_p \underset{\sim}{u} \cdot \underset{\sim}{\nabla} T = k \nabla^2 T$$

In the boundary layer $\frac{\partial P}{\partial x}$ is usually small - certainly for the Blasius problem where its zero!

Ifff $\frac{\mu}{\rho} \equiv \frac{k}{\rho \hat{C}_p}$ (e.g., $Pr = 1$)

we get the dimensionless temp. & u_x profiles are identical (for same BC's)

This means: $u_x|_{y=0} = 0$ (no-slip)

$$\frac{\partial}{\partial y}\left(\frac{u_x}{u_\infty}\right)\bigg|_{y=0} = \frac{\partial}{\partial y}\left(\frac{T - T_s}{T_\infty - T_s}\right)\bigg|_{y=0}$$

Now $h \equiv \frac{q}{\Delta T} = k \frac{\partial}{\partial y}\left(\frac{T - T_s}{T_\infty - T_s}\right)\bigg|_{y=0}$

$$\therefore h = +k \frac{\partial}{\partial y}\left(\frac{u_x}{u_\infty}\right)\bigg|_{y=0}$$

but $\tau_w = \mu \left.\frac{du_x}{\partial y}\right|_{y=0}$

so $h = k \frac{\tau_w}{\mu U_\infty}$ for $Pr = 1$!

Recall from last term we had the Fanning Friction Factor f_f

$$f_f \equiv \frac{\tau_w}{\frac{1}{2}\rho U_\infty^2} \begin{array}{l} \leftarrow \text{wall shear stress} \\ \leftarrow KE/\text{vol of fluid} \end{array}$$

so: $h = k \frac{\frac{1}{2}\rho U_\infty^{\cancel{2}} f_f}{\mu \cancel{U_\infty}}$

but $Pr = 1$ (assumed!)

$$\therefore \mu = \frac{k}{\hat{C}_p} Pr = \frac{k}{\hat{C}_p}$$

so $h = \frac{1}{2}(\rho U_\infty \hat{C}_p) f_f$

We can <u>define</u> the Stanton # St:

$$St \equiv \frac{h}{\rho U_\infty \hat{C}_p} \equiv \frac{Nu}{Re\,Pr}$$

Thus, we get $St = \frac{f_f}{2}$

which is the Reynolds Analogy

good (only) for $Pr = 1$!

What is St?? $\equiv \frac{\text{heat flux}}{\text{convective flux}}$

For liquids (other than metals!) $Pr > 1$ (usually $\gg 1$!). This means that $\alpha < \nu$ and energy transport is less efficient. This yields the Colburn Analogy

$$St \cong \frac{f_f}{2} Pr^{-2/3}$$

or $j_H \equiv St\, Pr^{2/3} = \frac{1}{2} f_f$

$\hookrightarrow$ Colburn "j factor"

there's an equivalent j_D for mass transfer w/ $Sc = \nu/D$ rather than Pr!

This is fine for laminar BL flow, but we can do a little better for turbulent boundary layers! If we apply Prandtl Mixing Length theory (discussed last term) to this, we get the Prandtl Analogy:

$$St = \frac{h}{\rho U_\infty \hat{C}_p} = \frac{f_f/2}{1 + 5\sqrt{f_f/2}\,(Pr - 1)}$$

A further improvement by von Karman included the buffer region & led to the von Karman Analogy:

$$St = \frac{h}{\rho U_\infty \hat{C}_p} = \frac{f_f/2}{1 + 5\sqrt{f_f/2}\left\{Pr - 1 + \ln\left(1 + \frac{5}{6}(Pr - 1)\right)\right\}}$$

All reduce to the Reynolds Analogy for $Pr \approx 1$.

What's f_f ??

for turbulent flow in a pipe:

$$\frac{1}{\sqrt{f_f}} = 4.0 \log_{10}\left\{Re\sqrt{f_f}\right\} - 0.40$$

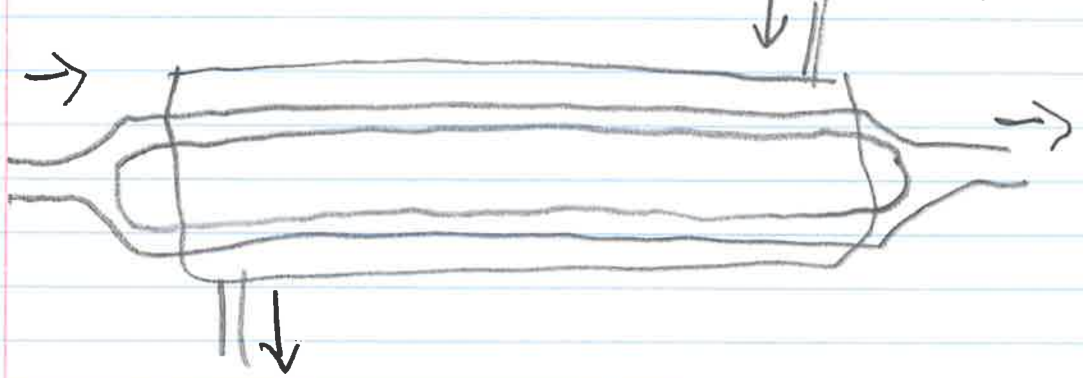
for $Re > 3000$

from Prandtl mixing length theory & exp't!

For $3000 < Re < 10^5$ we have the <u>useful</u> <u>correlation</u>

$$f_f \approx \frac{0.0791}{Re^{1/4}}$$

Let's apply this! Suppose we have a shell & tube heat exchanger:



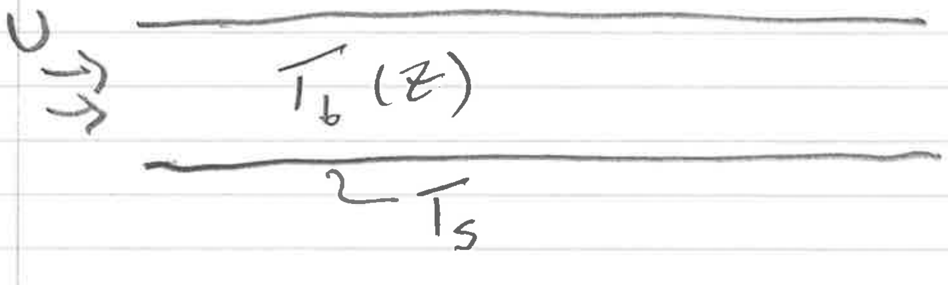
Let's make this even simpler: We feed shell side w/ condensing steam! This gives extremely high heat transfer to the pipes, so that the wall temperature is essentially constant!

Our overall heat transfer coef. is thus (resistances in series!):

$$h_{eff} = \left(\frac{1}{h_{internal}} + \frac{1}{h_{wall}} + \frac{1}{h_{ext}} \right)^{-1}$$

if walls are copper and $h_{ext} \sim \infty$, we get $h_{eff} \approx h_{internal} = h$

What is our temperature profile?



So $\rho \hat{C}_p U \frac{\pi D^2}{4} \frac{\partial T_b}{\partial z} = h \pi D \left(T_s - T_b\right)$

$\therefore \frac{1}{T_s - T_b} \frac{\partial T_b}{\partial z} = \frac{4h}{\rho \hat{C}_p U D} = 4 \frac{St}{D}$

$\therefore -\frac{\partial \ln(T_s - T_b)}{\partial z} = 4 \frac{St}{D}$

$\therefore \ln\left(T_s - T_b\right) = -4 \frac{St}{D} z + cst$

or $T_b = T_s - \left(T_s - T_{b_0}\right) e^{-4 St \frac{z}{D}}$

At $z = L$

$$T_b\Big|_{z=L} = T_s - \left(T_s - T_{b_0}\right) e^{-4 St \frac{L}{D}}$$

$\hookrightarrow$ outlet temperature!

Let's pick some numbers:

Take $T_s = 100°C$, $T_{b_0} = 20°C$

and working fluid is water

Say that $U = 2\ m/s = 200\ cm/s$

and $D = 2\ cm$ ID, $L = 1\ m$

This yields a flow rate $= U\frac{\pi D^2}{4} = 0.63\ l/s$

We need some properties. Let's evaluate at the average of T_s & $T_b = 60^\circ C$

So: $\nu = 0.47\ cs$, $\rho = 0.99\ g/cm^3$

$\hat{C}_p = 4.18\ \frac{J}{g\ ^\circ K}$, $\alpha = 0.0016\ cm^2/s$

$\therefore\ Pr = \nu/\alpha = 3.14$; $\rho\hat{C}_p = 4.14\ \frac{J}{cm^3\ ^\circ K}$

$$Re = \frac{(200)(2)}{(0.0047)} = 8.51 \times 10^4$$

$$\therefore\ f_f \approx \frac{0.0791}{Re^{1/4}} = 0.0046$$

What's St? $T_b\big|_{z=L}$? $\Rightarrow L/D = 50$

Reynolds Analogy:

$$St = f_f/2 = 0.0023 \Rightarrow T_{b_L} = 49.5^\circ C$$

Colburn Analogy:

$$St = \frac{f_f}{2} Pr^{-2/3} = 1.07 \times 10^{-3} \; ; \; T_{b_L} = 35.5°C$$

Prandtl Analogy:

$$St = 1.52 \times 10^{-3} \; ; \; T_{b_L} = 41.0°C$$

von Karman Analogy:

$$St = 1.31 \times 10^{-3} \; ; \; T_{b_L} = 38.4°C$$

Because Colburn analogy is close to the von Karman analogy, and is much simpler, it is usually used...

For these conditions the flow was turbulent. What if it were laminar?

If it were fully developed (it's not) we would have (for this BC) $Nu = \frac{hD}{k} = 3.66$

Recall $St = \frac{h}{\rho \hat{C}_p U} = \frac{hD}{k} \frac{k}{\rho \hat{C}_p U D} = \frac{Nu}{Re\,Pr}$

So *if* the thermal profile was fully developed (e.g. a really long tube) and it were (magically) laminar,

$$St_{laminar} = \frac{3.66}{(8.51\times10^{4})(3.14)} = 1.4\times10^{-5}$$

This is two orders of mag. below the turbulent result!

For a shorter laminar pipe we could use the boundary layer analysis or the Mills correlation:

$$Nu = \frac{hD}{k} = 3.66 + \frac{0.065\, RePr \frac{D}{L}}{1+0.04\left(RePr\frac{D}{L}\right)^{2/3}}$$

which smoothly goes from the developed value of 3.66 to the Seider-Tate correlation obtained by integrating our BL result over the pipe length.

Even for this, $Nu = 30.4$ (a *lot* higher as our profile is still developing!) *but*

$$St = \frac{Nu}{RePr} = 1.1 \times 10^{-4},$$

still an order of mag. lower!

This is why you *really* *really* want your heat exchangers to be *turbulent*! It's *much* more efficient!

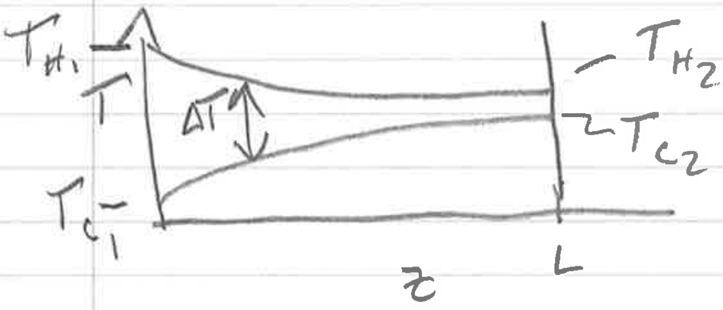
To finish, let's look at a classic problem: the *double pipe heat exchanger*

Two concentric cylinders, one carrying the cold stream, one the hot!

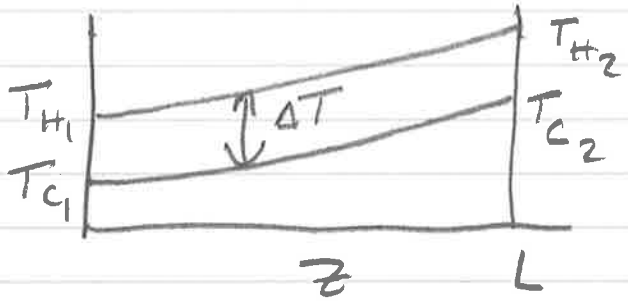
This can be operated in co-current (same direction of flow) or counter-current (opposite directions).

In general:

co-current:



Counter-current



Note that for co-current the leaving cold temp T_{C_2} < the leaving hot temp T_{H_2}

For counter-current you can have leaving cold T_{C_2} > leaving hot T_{H_1} & it is more efficient

We have a differential area $dA \equiv \pi D\, dz$ where D is a ref diameter (usually inner pipe)

We also have an overall heat transfer coef:

$$U = \left[\frac{1}{h_{inner}} + \frac{1}{h_{wall}} + \frac{1}{h_{outer}} \right]^{-1}$$

→ **Not** velocity, but usual symbol!

We can _define_ some $dq = U \Delta T \, dA$ as the differential heat transfer along the tube.

Finally, we define a _capacity_ for heat for each stream:

$$C_H \equiv \underbrace{\dot{M}_H}_{\text{mass flow}} \hat{C}_{pH} \leftarrow \text{heat capacity}$$

$$C_c \equiv \dot{M}_c \hat{C}_{pc} \quad \text{for cold stream.}$$

From an energy balance:

$$dq = C_c \, dT_c = C_H \, dT_H$$

Thus $d\Delta T \equiv d(T_H - T_c)$

$$= \frac{dq}{C_H} - \frac{dq}{C_c} = dq\left(\frac{1}{C_H} - \frac{1}{C_c}\right) = \frac{dq}{C_H}\left(1 - \frac{C_H}{C_c}\right)$$

We also have the <u>overall</u> energy balance:

$$C_H\left(T_{H_2} - T_{H_1}\right) = C_c\left(T_{c_2} - T_{c_1}\right) = Q$$

Thus $\dfrac{C_H}{C_c} = \dfrac{T_{c_2} - T_{c_1}}{T_{H_2} - T_{H_1}}$

Plug this into the relation for $d\Delta T$:

$$d\Delta T = \frac{dq}{C_H}\left(1 - \frac{T_{c_2} - T_{c_1}}{T_{H_2} - T_{H_1}}\right) = \frac{dq}{C_H(T_{H_2} - T_{H_1})}\left(\Delta T_2 - \Delta T_1\right)$$

so $d\Delta T = \dfrac{dq}{Q}\left(\Delta T_2 - \Delta T_1\right)$

Now $dq = U\,\Delta T\,dA$

so $\dfrac{d\Delta T}{\Delta T} = \dfrac{U\,dA}{Q}\left(\Delta T_2 - \Delta T_1\right)$

or $\dfrac{d\ln\Delta T}{dA} = \dfrac{U}{Q}\left(\Delta T_2 - \Delta T_1\right)$

If U is constant (not bad for turbulent flow as development region is very short!)

Then:

$$\ln \Delta T_2 = \ln \Delta T_1 + \frac{UA}{Q}\left(\Delta T_2 - \Delta T_1\right)$$

or, rearranging,

$$Q = UA \, \frac{\Delta T_2 - \Delta T_1}{\ln \frac{\Delta T_2}{\Delta T_1}}$$

This is known as the log mean temperature difference ΔT_{lm}

Note that if $\Delta T_2 = \Delta T_1$ this just reduces to ΔT. It gets things right (or better) if ΔT is changing!

So we have the overall balances:

$$T_{H_2} - T_{H_1} = \frac{Q}{C_H}$$

$$T_{C_2} - T_{C_1} = \frac{Q}{C_C}$$

and

$$Q = UA \frac{\Delta T_2 - \Delta T_1}{\ln \frac{\Delta T_2}{\Delta T_1}}$$

So if you know the entering hot & cold temperatures, U, C_H, C_C & A you can calculate the exit temps.

If you specify, say, some other combination you can get the rest!

This works for both cocurrent & counter-current exchangers!

There are many other designs, but w/ approp. correlations they can be analyzed in the same way!

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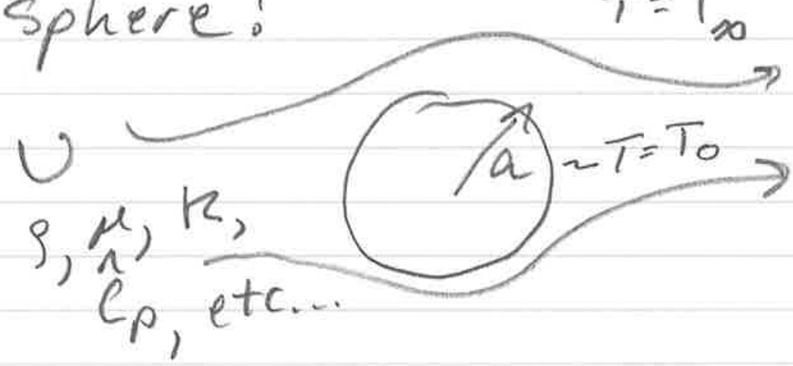
We've discussed convective heat transfer for internal flows - but what about external flows?

The classic example is flow past a sphere!



What is the Nusselt # $\equiv \frac{hD}{k}$?

At S.S., we have:

$$\rho \hat{C}_p \underset{\sim}{u} \cdot \underset{\sim}{\nabla} T = k \nabla^2 T$$

$$T\Big|_{r=a} = T_0 \qquad T\Big|_{r\to\infty} = T_\infty$$

Let's scale:

$$\underset{\sim}{u}^* = \frac{\underset{\sim}{u}}{U}, \qquad T^* = \frac{T - T_\infty}{T_0 - T_\infty}$$

$$\underset{\sim}{x}^* = \frac{\underset{\sim}{x}}{a} \quad (\text{e.g., } r^* = r/a)$$

$$\therefore \left(\frac{Ua}{\alpha}\right) \underset{\sim}{u}^* \cdot \underset{\sim}{\nabla}^* T^* = \nabla^{*2} T^*$$

$$T^*\Big|_{r^*=1} = 1 \qquad T^*\Big|_{r^*\to\infty} = 0$$

where $\frac{Ua}{\alpha} \equiv \frac{1}{2}\frac{UD}{\alpha} = \frac{1}{2} Re\,Pr \equiv \frac{1}{2} Pe$ $\quad \hookrightarrow \frac{UD}{\nu}$

Now if $Pe \underline{= 0}$ we have the pure conduction result!

$$\underline{T^* = \frac{1}{r^*}}$$

What's the heat flux?

$$q_r\Big|_{r=a} = -k\frac{\partial T}{\partial r}\Big|_{r=a} = -\frac{k}{a}(T_0 - T_\infty)\frac{\partial T^*}{\partial r^*}\Big|_{r^*=a}$$

Thus $h = \frac{k}{a}\left(-\frac{\partial T^*}{\partial r^*}\Big|_{r^*=a}\right)$

and $Nu = \frac{hD}{k} = 2\left(-\frac{\partial T^*}{\partial r^*}\Big|_{r^*=a}\right)$

but for pure conduction $T^* = \frac{1}{r^*}$

$\therefore Nu = 2$!

You get a similar result for finite shapes (not infinite cylinders, etc., due to Stokes Paradox analog), just the number is a bit different!

OK, now for convection: this depends on the velocity profile in a complex way! If $Re \ll 1$ (really small sphere!) and you have

$$Re \ll RePr \ll 1$$

then Taylor & Acrivos showed

$$Nu = 2 + \frac{1}{2} Pe + O(Pe^2 \ln Pe)$$

via singular perturbation expansion — a really advanced technique!

For higher Re the problem isn't tractable at all!

Instead, let's use correlations & reasoning!

Recall $Nu = \frac{hD}{k}$ and $h \sim \frac{k}{\delta}$ where δ is the distance over which diffusion of E takes place!

We have the geometry:

Fluid flows past our object in time D/U. During this time energy diffuses a distance of $\delta \sim O((\alpha t_c)^{1/2}) \sim O((\alpha \frac{D}{U})^{1/2})$ from a Lagrangian (fluid element) sense!

Thus, $Nu = \frac{hD}{k} \sim \frac{D}{k} \frac{k}{(\frac{\alpha D}{U})^{1/2}}$

$= \left(\frac{UD}{\alpha}\right)^{1/2} \sim (Re\,Pr)^{1/2}$

So we expect $Nu \sim Re^{1/2} Pr^{1/2}$

What are the results of correlations?

We have the Whittaker Correlation:

$$Nu = 2 + \left(0.4 Re^{1/2} + 0.06 Re^{2/3}\right) Pr^{0.4} \left(\frac{\mu_\infty}{\mu_0}\right)^{1/4}$$

where the extra term accounts for an added effect of turbulence.

The viscosity ratio accounts for the effect of temp. inside the boundary layer (very small for gases).

This correlation is good for

$$3.5 < Re < 7.6 \times 10^4 \; ; \; 0.71 < Pr < 380$$

$$\text{and} \quad 1.0 < \mu_\infty/\mu_0 < 3.2$$

You should always check to see if you are in the right range!

What about other shapes?

For a horizontal cylinder there is no conduction limit, and Whittaker proposed the same correlation but without the "2".

For a general shape,

$$Nu \approx \underset{\nearrow \text{ pure cond. limit}}{Nu\Big|_{Re=0}} + 0.6\, Re^{1/2} Pr^{1/3}$$

as a reasonable estimate.

Many correlations are available, but they yield similar results!

For forced convection along a flat plate we would just use the Colburn Analogy for Nu – for laminar flow $f_f = 0.664 \left(\frac{Ux}{\nu}\right)^{-1/2}$ from solution to the Blasius problem.

Thus $Nu_x = 0.332\, Re_x^{1/2}\, Pr^{1/3}$

This is the <u>local</u> Nusselt # defined as $Nu_x \equiv \frac{h_{loc}\, x}{k}$; $Re_x \equiv \frac{U x}{\nu}$

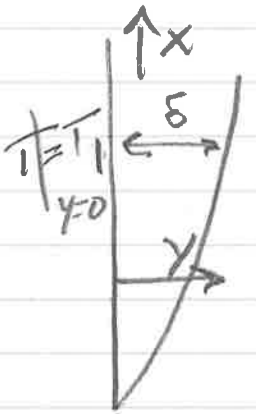
Note that because we don't have a length scale <u>perpendicular</u> to the flow (like D!) we define it in terms of x - distance down the plate!

In <u>all</u> <u>other</u> <u>cases</u> use the <u>transverse</u> length (e.g. pipe <u>diameter</u>)

Ok - convection is usually the strongest source of heat transfer - but what if we don't <u>force</u> it? You get "free" or "natural" convection! This arises from <u>gravity</u> and the change in density w/ temperature!

This means we have to solve both momentum & energy simultaneously!

Let's look at a vertical heated plate:



$$T\Big|_{y\to\infty} = T_0$$

The key is that density is a decreasing function of temperature (usually!).

$$\rho = \rho_0 \left(1 - \beta (T - T_0) \right).$$

where $\beta = \frac{-1}{\rho} \frac{\partial \rho}{\partial T}$ is the coef. of thermal expansion!

For an ideal gas $\beta = \frac{1}{T} \leftarrow {}^\circ K$!

For water it's $\sim 2.2 \times 10^{-4}$ at 22°C and increases to $\sim 5 \times 10^{-4}$ 1/°C at 50°C

Changes are small, but they matter!

Let's write down the eq'ns:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \quad \text{(incompressible)}$$

x-momentum:

$$\rho\left(u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y}\right) = -\frac{\partial P}{\partial x} + \mu\left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2}\right) + \rho g_x$$

Energy:

$$\rho \hat{C}_p\left(u_x \frac{\partial T}{\partial x} + u_y \frac{\partial T}{\partial y}\right) = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right)$$

The buoyancy term becomes:

$$\rho g_x = -\rho_0 g\left(1 - \beta(T - T_0)\right)$$

Far from the plate $T = T_0$ and there is no flow. Thus we get hydrostatics:

$$\left.-\frac{\partial P}{\partial x}\right|_{y\to\infty} - \rho_0 g = 0$$

As we saw last term, the <u>pressure distribution</u> outside the <u>boundary</u>

layer is impressed on the boundary layer! In other words, by scaling the y-momentum equations you find you can't have a pressure differential over a thin $(O(\delta))$ region!

Thus at the plate:

$$-\frac{\partial P}{\partial x} + \rho g_x \equiv \rho_0 \beta (T - T_0)$$

This is the Bousinesq approximation: the only material property that varies w/ temperature is density, and that just in the buoyancy term!

So:

$$\rho\left(u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y}\right) = \mu\left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2}\right) + \rho_0 \beta (T - T_0)$$

Ok, let's scale!

$u_x^* = u_x / U_c$, $u_y^* = u_y / V_c$ $\qquad T^* = \dfrac{T - T_0}{\underbrace{T_1 - T_0}_{\to \Delta T}}$

$x^* = \dfrac{x}{\underbrace{H}_{\to \text{plate height}}}$ $\qquad y^* = y/\delta$

We start w/ CE:

$$\frac{U_c}{H}\frac{\partial u_x^*}{\partial x^*} + \frac{V_c}{\delta}\frac{\partial u_y^*}{\partial y^*} = 0$$

$$\therefore \underbrace{\left[\frac{\delta}{V_c}\frac{U_c}{H}\right]}_{=1}\frac{\partial u_x^*}{\partial x^*} + \frac{\partial u_y^*}{\partial y^*} = 0$$

or $V_c = \dfrac{\delta}{H} U_c$ as usual...

Now for energy:

same scale!

$$\rho \hat{C}_p \frac{U_c \Delta T}{H}\left(u_x^* \frac{\partial T^*}{\partial x^*} + u_y^* \frac{\partial T^*}{\partial y^*}\right)$$

$$= \frac{k\,\Delta T}{\delta^2}\left(\frac{\delta^2}{H^2}\frac{\partial^2 T^*}{\partial x^{*2}} + \frac{\partial^2 T^*}{\partial y^{*2}}\right)$$

Divide out:

$$\underbrace{\left[\frac{\delta^2 U_c}{\alpha H}\right]}_{\substack{\| \\ 1}}\left(u_x^*\frac{\partial T^*}{\partial x^*}+u_y^*\frac{\partial T^*}{\partial y^*}\right) = \frac{\delta^2}{H^2}\frac{\partial^2 T^*}{\partial x^{*2}}+\frac{\partial^2 T^*}{\partial y^{*2}}$$

$$\therefore\ \delta = \left(\frac{\alpha H}{U_c}\right)^{1/2} \equiv \left(\underbrace{\alpha}_{\text{thermal diffusivity}}\ \underbrace{\frac{H}{U_c}}_{\text{time to flow up plate}}\right)^{1/2}$$

and we take $\frac{\delta}{H} << 1$ (thin BL)

so we ignore dif^n in <u>direction</u> of motion!

Now for the x-mom eq'n:

$$\rho\frac{U_c^2}{H}\left(u_x^*\frac{\partial u_x^*}{\partial x^*}+u_y^*\frac{\partial u_x^*}{\partial y^*}\right)=\frac{\mu U_c}{\delta^2}\left(\frac{\partial^2 u_x^*}{\partial y^{*2}}+\underbrace{\cancel{\frac{\delta^2}{H^2}}}_{\text{small}}\frac{\partial^2 u_x^*}{\partial x^{*2}}\right)+\rho_0\beta g\Delta T\, T^*$$

Let's divide by $\frac{\mu U_c}{\delta^2}$

$$\left[\frac{\delta^2 U_c}{\nu H}\right]\left(u_x^* \frac{\partial u_x^*}{\partial x^*} + u_y^* \frac{\partial u_x^*}{\partial y^*}\right) = \frac{\partial^2 u_x^*}{\partial y^{*2}}$$

$$+ \frac{\delta^2}{H^2}\frac{\partial^2 u_x^*}{\partial x^{*2}} + \left[\frac{\delta^2 \rho_o \beta g \Delta T}{\mu U_c}\right] T^*$$

$\equiv \frac{1}{Pr}$ as δ was scaled in E eq'n

$$\left[\frac{\delta^2 \rho_o \beta g \Delta T}{\mu U_c}\right] = 1$$

$$U_c = \frac{\alpha H}{\delta^2}$$

$$\therefore \quad \frac{\delta^4 \rho_o \beta g \Delta T}{\mu \alpha H} = 1 \qquad \left(\text{take } \nu \equiv \frac{\mu}{\rho_o}\right)$$

$$\therefore \quad \delta = \left(\frac{\nu \alpha H}{\beta g \Delta T}\right)^{1/4}$$

This is what we need!

$$q_y = -k \left.\frac{\partial T}{\partial y}\right|_{y=0} = -\frac{k \Delta T}{\delta} \left.\frac{\partial T^*}{\partial y^*}\right|_{y^*=0}$$

so $q_y \sim k\Delta T \left(\frac{\beta g \Delta T}{\nu \alpha H}\right)^{1/4}$

or $h = \frac{q_y}{\Delta T} = \frac{k}{H}\left(\frac{\beta g \Delta T H^3}{\nu \alpha}\right)^{1/4} \times \left.\frac{-\partial T^*}{\partial y^*}\right|_{y^*=0}$

The quantity $\frac{\beta g \Delta T H^3}{\nu \alpha} \equiv$ Rayleigh #

$Ra = Gr\,Pr$

↳ Grashoff #, closely related!

$\therefore\ Nu_H \sim Ra^{1/4}$

So:

$$\frac{\partial u_x^*}{\partial x^*} + \frac{\partial u_y^*}{\partial y^*} = 0 \qquad (CE)$$

$$u_x^* \frac{\partial T^*}{\partial x^*} + u_y^* \frac{\partial T^*}{\partial y^*} = \frac{\partial^2 T^*}{\partial y^*} \qquad (E)$$

$$\frac{1}{Pr}\left(u_x^* \frac{\partial u_x^*}{\partial x^*} + u_y^* \frac{\partial u_x^*}{\partial y^*}\right) = \frac{\partial^2 u_x^*}{\partial y^{*2}} + T^*$$

w/ BC's: $\left. T^*\right|_{y^*=0} = 1 \quad \left. T^*\right|_{y^*\to\infty} = 0$

$\left. u_x^*\right|_{y^*=0} = \left. u_y^*\right|_{y^*=0} = 0 \quad \left. u_x^*\right|_{y^*\to\infty} = 0$

Note that H disappeared – but we didn't specify it! That means that the profile is self-similar! We can turn PDE's into ODE's!

Because the x-mom eq'n is non-linear you have to solve it numerically as a set of 5 coupled 1st order ODEs.

It will also be a (weak) function of Pr – you can't get rid of it.

Numerical solution shows that

$$Nu \equiv \frac{h_m H}{k} = C\, Ra^{1/4}$$

mean over whole plate

where $C = 0.518$ for air ($Pr = 0.73$)

and $C = 0.670$ for $Pr \to \infty$

What about other shapes? The scaling & mechanism is the same!

For a sphere we have the Churchill correlation:

$$Nu = \frac{hD}{k} = \underset{\substack{\uparrow \\ \text{conduction}}}{2} + \frac{0.589\, Ra^{1/4}}{\left(1 + (0.492/Pr)^{9/16}\right)^{4/9}}$$

where $Ra = \dfrac{\beta g \Delta T D^3}{\nu \alpha}$

Similar results have been obtained for many shapes. The most common are tabulated in 14.6-1 of BS&L

Correlations have been developed for combinations of free & forced convection, turbulence, etc.

Remember: $h \sim \dfrac{k}{\delta}$ where δ is some appropriate length scale!

So far we've looked at <u>conductive</u> & convective transport - now we look at <u>radiation</u>

This is <u>Energy</u> transmission via electromagnetic radiation, propagating w/ velocity $c \equiv 3 \times 10^{10}$ cm/s across space, even in a vacuum!

Sometimes this is the <u>largest</u> source of energy transport!

What is electromagnetic radiation?

When a molecule is heated it moves into a <u>higher</u> <u>energy</u> <u>excited</u> <u>state</u>.

low temps, just rotation

higher temps, vibration

plasma temps = ionization

Transition is accomplished by thermal interaction <u>or</u> by absorption of radiation.

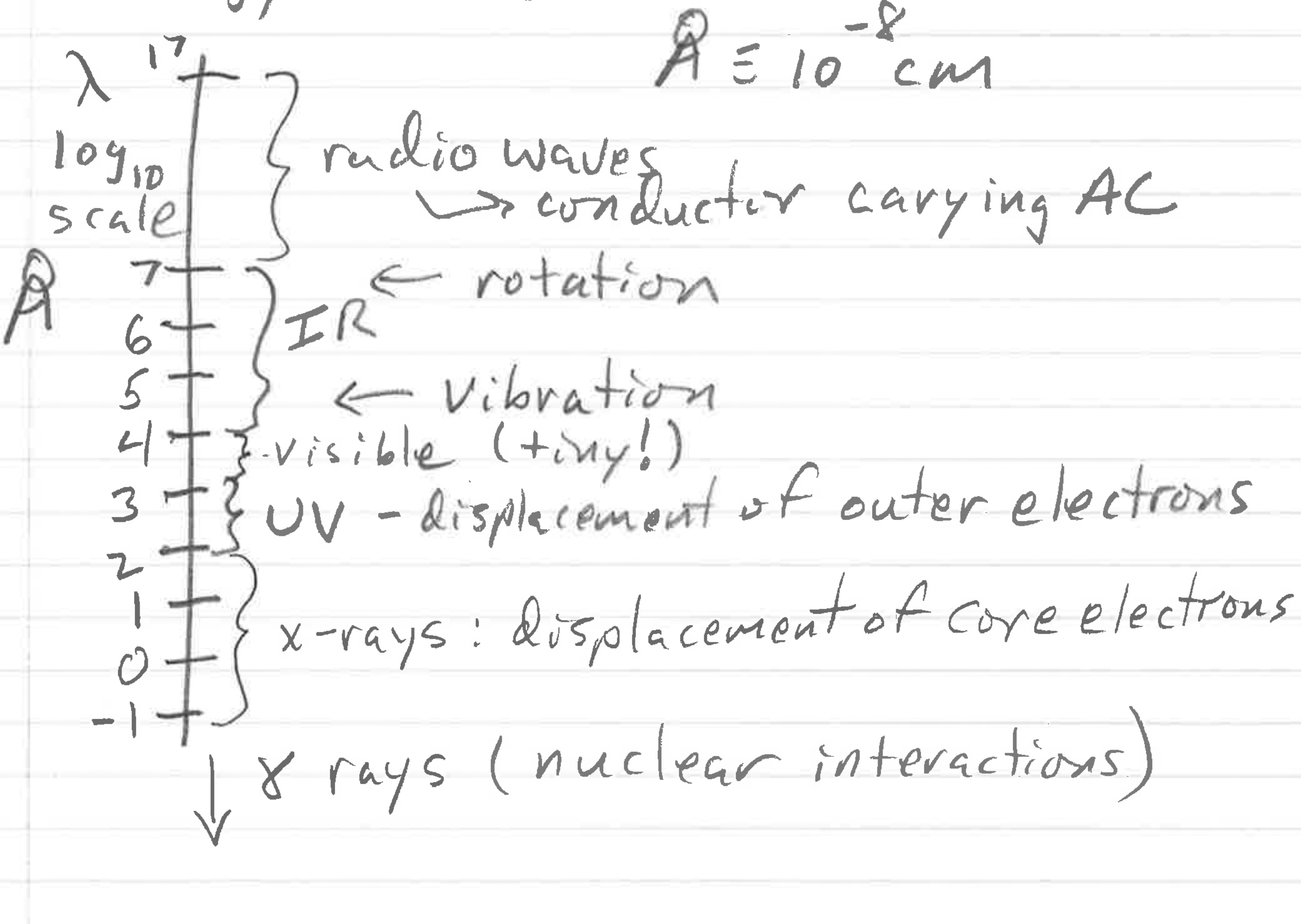
Transition to lower energy state is by thermal interaction or emission of radiation

Radiation is quantized: A transition of energy ΔE emits a photon of energy

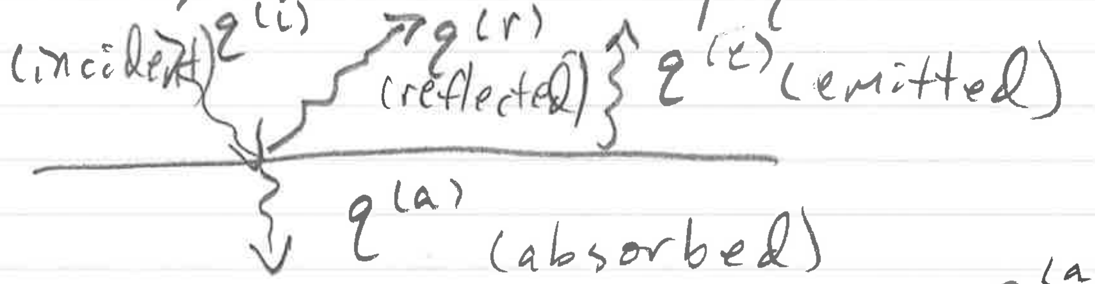
$\Delta E = h\nu$ ← frequency of radiation
↳ plank's constant

The wavelength of radiation is $\lambda = c/\nu$

There is a continuous spectrum of ΔE Energy levels!



To examine the heat flux from radiation, consider an opaque solid:



we *define* absorptivity $a \equiv \frac{q^{(a)}}{q^{(i)}}$

the absorptivity *is* a $f^{\underline{n}}$(angle) *and* ν.

By definition $a \leq 1$ for all ν

We have an ideal gray body:

$a_\nu < 1$ *but* indep of ν

If $a_\nu = 1$ then it is a *black body* which absorbs *all* incident radiation.

A black body *emits* the largest flux of thermal radiation at all frequencies!

We can define an emissivity e:

$$e \equiv \frac{q^{(e)}}{q_b^{(e)}} \quad \& \quad e_\nu \equiv \frac{q_\nu^{(e)}\,d\nu}{q_{b\nu}^{(e)}\,d\nu}$$

$\nwarrow$ blackbody

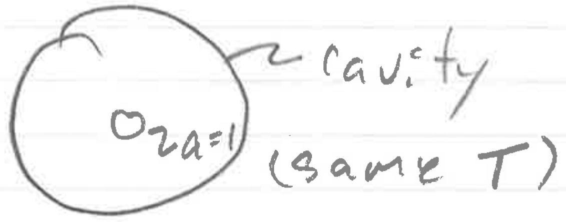
$\hookrightarrow$ at frequency ν

Now we prove that $e \equiv a$!

Suppose we have an evacuated cavity w/ isothermal walls. At equilibrium there is no net exchange of energy between the cavity (filled w/ radiation) and the walls. Thus, the energy distribution of the cavity radiation is a function of T alone - wall composition doesn't matter!

It is also isotropic and unpolarized.

OK, now put a black body in the cavity at the same temp.



The black body absorbs the cavity radiation: $q_b^{(a)} = q^{(cav)} \equiv q_b^{(e)}$

and has to emit the same!

∴ Cavity radiation ≡ black body radiation.

If you put a gray body in you get

$$q^{(a)} \equiv a\, q_b^{(e)} = \underset{\uparrow}{e}\, q_b^{(e)}$$

because no change in T!

∴ $a = e$

and at all ν, $a_\nu = e_\nu$

emissivity ≡ absorptivity

This is known as Kirchoff's Law

Ok, how does $q_b^{(e)}$ depend on temperature?

Let's look at cavity radiation.
Consider it as a gas madeup of
photons w/ energy $h\nu$ and momentum
$h\nu/c$. Because it is isotropic
the energy density is:

$$u^{(r)} = \frac{4}{c} \varrho_b^{(e)} \qquad (\text{energy}/\text{volume})$$

The momentum of the photons exerts
a pressure on the walls

$$p^{(r)} = \frac{1}{3} u^{(r)}$$

(This pressure is what drives light sails
in space!)

The internal energy of our gas is

$$U = V u^{(r)}$$

From thermo:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Thus:

$$u^{(r)} = \frac{T}{3}\frac{\partial u^{(r)}}{\partial T} - \frac{u^{(r)}}{3}$$

or $\frac{\partial \ln u^{(r)}}{\partial \ln T} = 4$ so $\underbrace{u^{(r)} = bT^4}_{\to \text{ some const.}}$

Thus, $q_b^{(e)} = \sigma T^4$ (Stefan-Boltzmann Law)

$$\sigma = 5.67 \times 10^{-8} \frac{W}{m^2\,{}^{\circ}K^4}$$

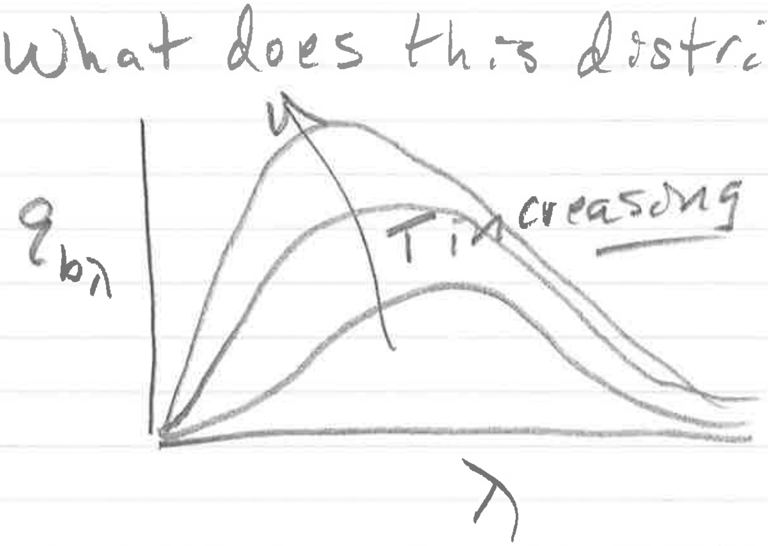
You get the <u>same thing</u> from quantum theory! If photons obey Bose-Einstein statistics then you get Plank's Distribution Law:

$$q_{b\lambda}^{(e)} = \frac{2\pi c^2 h}{\lambda^5}\frac{1}{e^{ch/\lambda kT} - 1}$$

Which, integrated over λ yields:

$$q_b^{(e)} = \underbrace{\left(\frac{2}{15}\frac{\pi^5 k^4}{c^2 h^3}\right)}_{\to\ \sigma} T^4$$

What does this distribution look like?

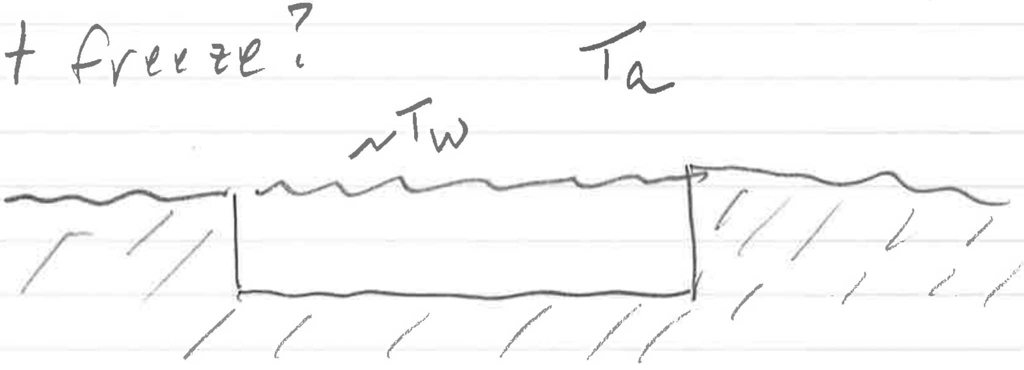


the *max* in $q_{b\lambda}$ shifts to *shorter* wavelengths (higher ν) w/ inc. T

For the *sun* the max is visible (green)

Ok, now let's solve a problem! (ex16.5-3)

Suppose you put a pan of water out in the desert at night (insulating its bottom!). At what *air* temp. will it freeze?



For dry still air you have a balance between natural convection to the surface & thermal radiation away!

$$\therefore\ q = h(T_a - T_w) = e\sigma T_w^4 - e\sigma T^4$$

but $T \approx 0$

clear dry night is transparent (night sky!) to thermal radiation & space is cold

Ignore back radiation!

What's h? For a horizontal plane it's roughly $h = 1.3\,(T_a - T_w)^{1/4}$ where h is in $\frac{W}{m^2\,°K}$ and T is °C (or °K)

so: $1.3(T_a - T_w)^{5/4} = e\sigma T_w^4$

i.e. $$T_a = T_w + \left(\frac{e\sigma T_w^4}{1.3}\right)^{4/5}$$

Now at freezing $T_w = 273°K$

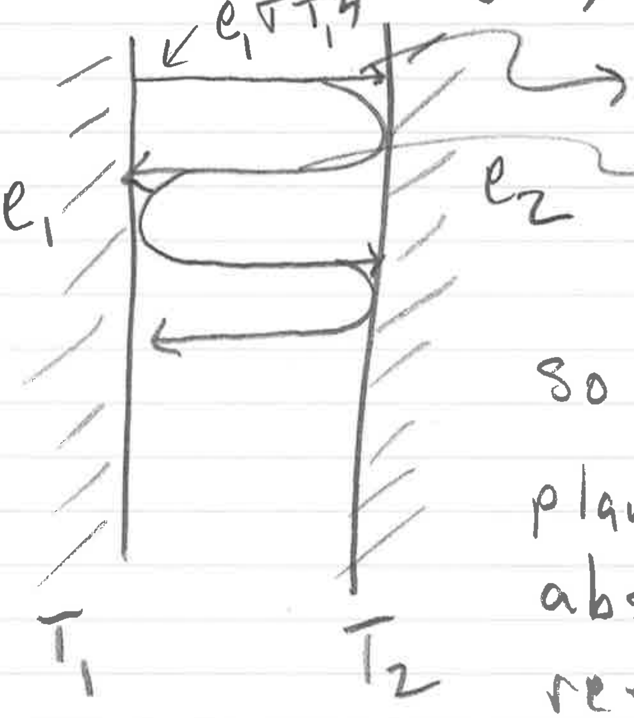
and $e \approx 0.95$ (black body at thermal λ)
↳ close, anyway!

$$\therefore T_a \cong T_w + \left(\frac{0.95\,(5.67\times10^{-8})(273)^{4}}{1.3}\right)^{\overset{\boxed{223}}{4/5}}$$

$$= T_w + 78\,°K \equiv 78\,°C!$$

This is <u>unrealistic</u> because you would get gain through your insulation, but it does show why the desert is cold at night (and why clouds keep it warmer!)

OK, how about energy exchange between <u>two</u> gray planes?



absorbed $= e_1 e_2 \sigma T_1^4$

reflected back $= e_1 \sigma T_1^4 (1-e_2)$

So energy <u>emitted</u> by plane 1 gets both absorbed by (2) <u>and</u> reflected back to (1)

Thus, the energy transmitted from (1) to (2) is:

$$e_1 e_2 \sigma T_1^4 \sum_{i=0}^{\infty} (1-e_1)^i (1-e_2)^i$$

$$= \frac{e_1 e_2 \sigma T_1^4}{1 - (1-e_1)(1-e_2)} = \frac{\sigma T_1^4}{\frac{1}{e_1} + \frac{1}{e_2} - 1}$$

↳ summing series!

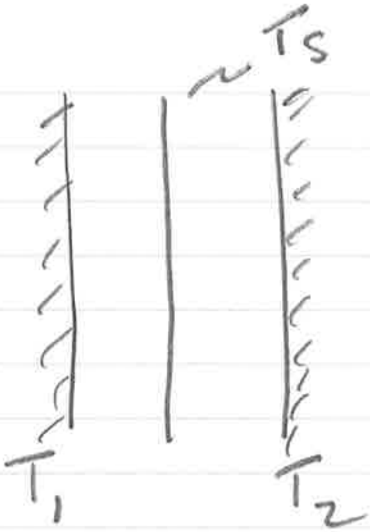
The energy from (2) to (1) is the same!

$$= \frac{\sigma T_2^4}{\frac{1}{e_1} + \frac{1}{e_2} - 1}$$

∴ <u>Net</u> flux is $\mathcal{E}_{12} = \dfrac{\sigma(T_1^4 - T_2^4)}{\left(\frac{1}{e_1} + \frac{1}{e_2} - 1\right)}$

We can use this to see the effect of a <u>radiation</u> <u>shield</u>.

Put a thin sheet w/ low e between two surfaces!



Now $q_{1s} = \dfrac{\sigma\left(T_1^4 - T_s^4\right)}{\frac{1}{e_1} + \frac{1}{e_s} - 1}$

and $q_{s2} \equiv \underset{\text{at SS}}{q_{1s}} = \dfrac{\sigma\left(T_s^4 - T_2^4\right)}{\frac{1}{e_2} + \frac{1}{e_s} - 1}$

∴ solve for T_s and get:

$$q_{12}^{(w/s)} = \frac{\sigma\left(T_1^4 - T_2^4\right)}{\left(\frac{1}{e_1} + \frac{1}{e_s} - 1\right) + \left(\frac{1}{e_2} + \frac{1}{e_s} - 1\right)}$$

If $e_1 = e_2 = e$

$$q_{12}^{(w/s)} = \frac{1}{2}\,\frac{\sigma\left(T_1^4 - T_2^4\right)}{\left(\frac{1}{e} + \frac{1}{e_s} - 1\right)}$$

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so the ratio of w/s & without is:

$$\frac{\mathcal{E}_{12}^{(w/s)}}{\mathcal{E}_{12}} = \frac{1}{2}\frac{\left(\frac{2}{e}-1\right)}{\left(\frac{1}{e}+\frac{1}{e_s}-1\right)}$$

even if $e_s = e_1$ we have a factor of 2 improvement, and it is still reducing energy transp. if $e_s = 1$! (but a lot better if $e_s << 1$!)

You get a further reduction w/ multiple layers! In general, however, you would have conduction in the air between that limits the effect.

To finish off, let's look at spectral effects: What happens if two sources are at dif. T and e_ν is a function of ν?

This is *exactly* the greenhouse effect!

The *sun* is a black body at 5800°K and $q_\lambda\big|_{max}$ is $\lambda \sim 0.5\mu m$

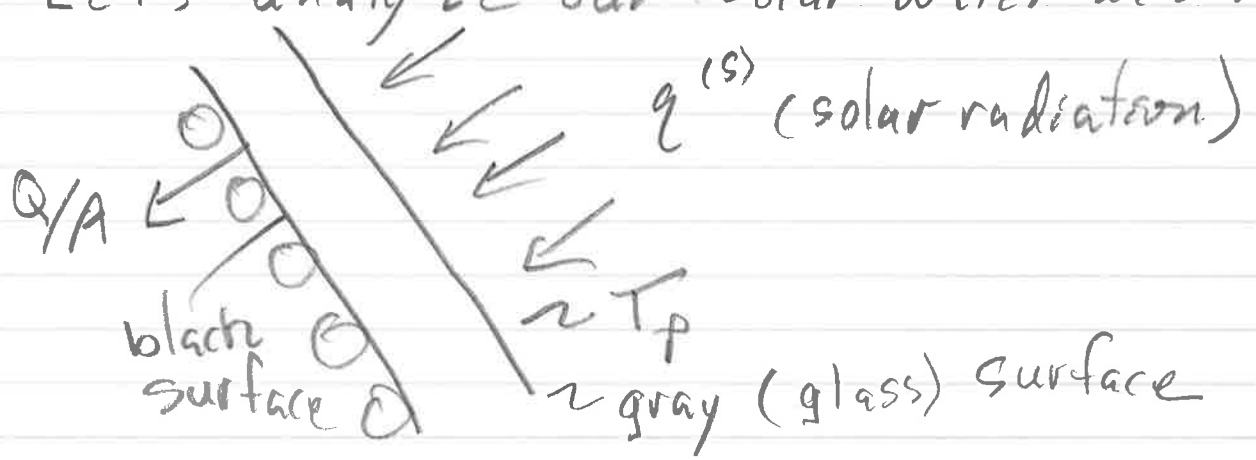
$>99\%$ of total E is for $\lambda < 4\mu m$

For a body at 300°K $\lambda_{max} \cong 10\mu m$ and $>99\%$ of total E is $\lambda > 4\mu m$!

We can *maximize* (thermal) solar gain if we cover our absorber w/ a sheet of glass!

glass is *transparent* to short wavelengths and a *black body* to long!

Let's analyze our solar water heater!



Ok, let's say we are <u>boiling</u> water!

$\therefore\ T_c = 373\,^\circ K$

we have air at 300°K blowing over our glass plate w/ velocity of 10mph, thus

$h_s \cong 20\ \frac{W}{m^2\,^\circ K}$ (approx external h)

we have <u>natural</u> <u>convection</u> between the collector & glass plate, take $h_i \approx 2\ \frac{W}{m^2\,^\circ K}$

we have an incident solar flux of

$$q^{(s)} = 1350\ \frac{W}{m^2}$$

we can do an energy balance on the plate!

$$0 = \overset{\text{abs. from collector}}{e\sigma T_c^4} - \overset{\text{emit both sides}}{2e\sigma T_p^4} + \overset{\text{radiation from surroundings}}{e\sigma T_a^4}$$

$$- \underset{\text{losses to atmosphere}}{h_s (T_p - T_a)} + \underset{\text{gain from collector}}{h_i (T_c - T_p)}$$

<u>If</u> we take $e = 1$ then

$$T_p = 323\,^\circ K$$

What is the energy gain of our collector?

reflectivity of top plate

$$\frac{\dot{Q}}{A} = q^{(s)} + e\sigma T_p^4 - \underset{\swarrow}{(1-\rho)}\sigma T_c^4 - h_i(T_c - T_p)$$

(say $\rho = 1-e$)

So if $e = 1$ then $\frac{\dot{Q}}{A} = 770$ W/m²
(about half incident $q^{(s)}$)

We can do better w/ low emissivity coatings! A "low e" Fe_2O_3 glass is commercially available.

Ideally $t = 1$ for $0 < \lambda < 2.5\,\mu m$
and $e = a = 0.25$ for $\lambda > 2.5\,\mu m$
$(t = 0)$

Plugging this in yields $T_p = 312$°K
and $Q/A = 1090$ W/m²

If $e = 0$ (perfect) then $T_p = 307$°K
and $\dot{Q}/A = 1220$ W/m² !

Now let's look at Mass Transport

This is very closely related to energy transport, and most problems are identical w/ identical solutions!

There are differences, and we'll focus on these!

Key differences:

Fick's law: diffusive mass transfer is due to gradients in either mass fraction (liquids) or mole fraction (gases). Diffusion can lead to convection since mass is moving! This is primarily important in gases.

In liquids the diffusivity is very small rel. to α & ν. Thus it matters only on small length scales.

otherwise it's dominated by the fluid motion!

ok, let's define things! we need parallel definitions for mass & molar basis:

Mass	Molar
mass conc.: ρ_i	molar conc.: c_i
$\rho_i = \frac{\text{mass of species } i \text{ in}}{\text{volume } V}$	$c_i \equiv \frac{\text{moles of species } i \text{ in}}{\text{volume } V}$

connection: $c_i \equiv \rho_i / M_i \leftarrow$ mol wt. of i

mass fraction ω_i	mole fraction x_i
$\omega_i \equiv \frac{\text{mass of } (i) \text{ in } V}{\text{total mass in } V}$	$x_i \equiv \frac{\text{moles of } (i) \text{ in } V}{\text{total moles in } V}$
$= \frac{\rho_i}{\sum_i \rho_i} = \frac{\rho_i}{\underbrace{\rho}_{\text{total density}}}$	$\equiv \frac{c_i}{\sum_i c_i} = \frac{c_i}{\underbrace{c}_{\text{molar density}}}$

For an ideal gas c is fixed by the ideal gas law (moles occupy same space)

Now for velocities

Let $\underset{\sim}{u}_i$ be the velocity of species i in a mixture!

We can define two average velocities:

Mass	Molar
Mass avg. vel. $\underset{\sim}{u}$:	mol avg vel. $\underset{\sim}{u}^+$
$\underset{\sim}{u} \equiv \dfrac{\sum \rho_i \underset{\sim}{u}_i}{\sum \rho_i}$	$\underset{\sim}{u}^+ = \dfrac{\sum c_i u_i}{\sum c_i} \equiv \sum x_i \underset{\sim}{u}_i$
$\equiv \sum \omega_i u_i$	
$\rho \underset{\sim}{u}$: total mass flux in mixture!	$c \underset{\sim}{u}^+$: total molar flux in a mixture!

↑

used in conservation of momentum!

Diffusion velocity is the difference between species velocity & avg velocity!

Mass	Molar
$\underset{\sim}{u}_i - \underset{\sim}{u} \equiv$ vel. of (i) <u>relative</u> to avg!	$u_i - \underset{\sim}{u}^+ \equiv$ molar diffusive velocity

We can also define <u>fluxes</u>

Mass	Molar
$\underset{\sim}{n}_i \equiv \rho_i \underset{\sim}{u}_i$	$\underset{\sim}{N}_i \equiv c_i u_i^+$
mass flux of (i)	molar flux of (i)

And the <u>relative</u> <u>fluxes</u>

Mass	Molar
$\underset{\sim}{j}_i = \rho_i(\underset{\sim}{u}_i - \underset{\sim}{u})$	$\underset{\sim}{J}_i = c_i(\underset{\sim}{u}_i - \underset{\sim}{u}^+)$
where $\sum \underset{\sim}{j}_i = \sum \rho_i \underset{\sim}{u}_i - \rho \underset{\sim}{u} = \underline{0}$	$\sum \underset{\sim}{J}_i = \sum c_i \underset{\sim}{u}_i - c \underset{\sim}{u}^+ = \underline{0}$
so $\underset{\sim}{n}_i = \rho_i \underset{\sim}{u} + \underset{\sim}{j}_i$	$\underset{\sim}{N}_i = c_i \underset{\sim}{u}^+ + \underset{\sim}{J}_i$

Now we relate the relative flux to concentration gradients via Fick's Law!

For a binary system (A&B)

$$\underset{\sim}{j}_A = -\rho \mathscr{D}_{AB} \underset{\sim}{\nabla} \omega_A$$

or $$\underset{\sim}{J}_A = -c \mathscr{D}_{AB} \underset{\sim}{\nabla} x_A$$

This yields the total flux

Mass: $\rho \underset{\sim}{u} \equiv \underset{\sim}{n}_A + \underset{\sim}{n}_B$ (binary!)

$$\therefore \underset{\sim}{n}_A = \rho_A \underset{\sim}{u} + \underset{\sim}{j}_A$$

$$\equiv \omega_A(\underset{\sim}{n}_A + \underset{\sim}{n}_B) - \rho \mathscr{D}_{AB} \underset{\sim}{\nabla} \omega_A$$

Molar:

$$\underset{\sim}{N}_A = x_A(\underset{\sim}{N}_A + \underset{\sim}{N}_B) - c \mathscr{D}_{AB} \underset{\sim}{\nabla} x_A$$

↑

this is why diffusion of A leads to convection unless $x_A \ll 1$

OK, what is $\mathcal{D}_{AB}$?

First, $\mathcal{D}_{AB} = \mathcal{D}_{BA}$

but it may be composition dependent!

What is $\mathcal{D}_{AB}$ in a gas? It is similar to both α & ν since transport is via the same mechanism!

For a low density gas

$$\mathcal{D}_{AB} \sim T^{3/2} p^{-1}$$ and is a very weak function of x_A, x_B

We have the analogy to $Pr = \nu/\alpha$:

Schmidt ~~#~~ $Sc = \nu/\mathcal{D}_{AB}$

This is $O(1)$ for gases!

Sometimes people use the Lewis # $Le \equiv \frac{\alpha}{\mathcal{D}_{AB}} = \frac{Sc}{Pr}$

This is also $O(1)$ for gases.

BS&L gives empirical correlations for $\mathcal{D}_{AB}$

Ok, now for liquids.

$\mathcal{D}_{AB}$ is very composition dependent but usually one species is dilute!

This suggests we use a hydrodynamic approach! The Nernst-Einstein eq'n:

$$\mathcal{D}_{AB} = \underset{\substack{\uparrow \\ \text{thermal energy} \\ \text{of molecule}}}{KT} \left.\frac{u_A}{F_A}\right\} \begin{array}{l}\text{mobility of} \\ \text{molecule A in} \\ \text{fluid!}\end{array}$$

$K \equiv$ Boltzmann's constant!

Suppose we have a Colloidal Particle (a really really small sphere...)

We have Stokes Law!

$$F_A = 6\pi \overset{\text{viscosity}}{\overset{\swarrow}{\mu}} \underset{\substack{\uparrow \\ \text{radius}}}{a} U_A$$

This yields the Stokes-Einstein Def.

$$\mathcal{D}_{AB} = \frac{KT}{6\pi \underset{\substack{\uparrow \\ \text{viscosity of "B"}}}{\mu_B}\, a_A} \leftarrow \text{radius of "A"}$$

Usually this is used for particles $1\mu m$ dia. or smaller.

It also works for large macromolecules (e.g., polymers, coiled DNA, proteins) in solution where "a" is radius of gyration

For small molecules you get slip at the surface. The 6π factor for a solid sphere becomes 4π for a bubble!

For a liquid you estimate a from the molecules/volume $\hat{N}/\tilde{V}$

If you have a cubic lattice

$$2a \approx \left(\frac{\hat{V}}{\tilde{N}}\right)^{1/3}$$

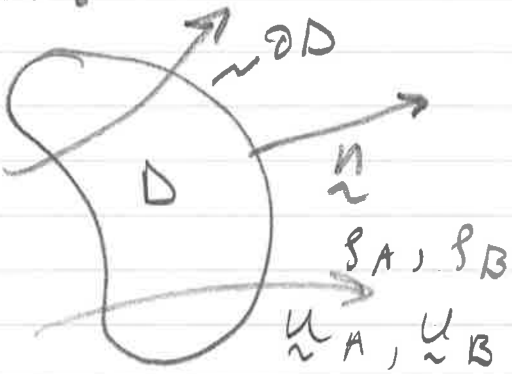
so for self-diffusion

$$\mathcal{D}_{AA} = \frac{1}{2\pi}\frac{KT}{\mu_A}\left(\frac{\tilde{N}}{\hat{V}_A}\right)^{1/3}$$

which is good for non-polar liquids.

What about solids? This is much smaller and is highly material dependent! Where it matters: diffusion of gases through membranes! It's the basis of solid membrane separation techniques, and much of the work some of your classmates are doing right now!

OK, we need to develop conservation equations!



What is a conservation eq'n for species A?

$$\left\{\begin{matrix}\text{accum of } A\\ \text{in } D\end{matrix}\right\} + \left\{\begin{matrix}A \text{ traveling } \underline{\text{out}}\\ \text{through } \partial D\end{matrix}\right\} = \left\{\begin{matrix}\text{source}\\ \text{of } A\end{matrix}\right\}$$

$$\therefore \int_D \frac{\partial \rho_A}{\partial t}\,dV + \int_{\partial D} \underbrace{\rho_A \underset{\sim}{u}_A}_{\overset{\parallel}{\underset{\sim}{n}_A}} \cdot \underset{\sim}{n}\,dA = \int_D \underset{\overset{\uparrow}{\text{rate of prod. of } A}}{r_A}\,dV$$

$$\therefore \frac{\partial \rho_A}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{n}_A + r_A$$

similarly,

$$\frac{\partial \rho_B}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{n}_B + r_B$$

We can add these up!

$$\frac{\partial(\rho_A+\rho_B)}{\partial t} = -\underset{\sim}{\nabla}\cdot(\underset{\sim}{n}_A+\underset{\sim}{n}_B) + (r_A + r_B)$$

Now on a mass basis $r_A = -r_B$!

likewise $\underset{\sim}{n}_A + \underset{\sim}{n}_B \equiv \rho\underset{\sim}{u}$

and $\rho = \rho_A + \rho_B$

$\therefore$ we get the C.E.: $\dfrac{\partial\rho}{\partial t} = -\underset{\sim}{\nabla}\cdot(\rho\underset{\sim}{u})$

Now recall $\underset{\sim}{n}_A = \rho_A\underset{\sim}{u} + \underset{\sim}{j}_A$

$$= \omega_A\rho\underset{\sim}{u} - \rho\mathcal{D}_{AB}\underset{\sim}{\nabla}\omega_A$$

$$\therefore \frac{\partial\rho_A}{\partial t} + \underset{\sim}{\nabla}\cdot(\rho_A\underset{\sim}{u}) = \underset{\sim}{\nabla}\cdot(\rho\mathcal{D}_{AB}\underset{\sim}{\nabla}\omega_A) + r_A$$

If ρ & $\mathcal{D}_{AB}$ are constant, $\underset{\sim}{\nabla}\cdot\underset{\sim}{u} = 0$

and:

$$\underbrace{\frac{\partial\rho_A}{\partial t}}_{\text{accum of A}} + \underbrace{\underset{\sim}{u}\cdot\underset{\sim}{\nabla}\rho_A}_{\text{conv. of A}} = \underbrace{\mathcal{D}_{AB}\nabla^2\rho_A}_{\text{Diffn of A}} + \underbrace{r_A}_{\text{prod. of A}}$$

On a <u>molar</u> <u>basis</u> we get, similarly,

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_A = R_A$$

<u>and</u>

$$\frac{\partial c_B}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_B = R_B$$

w/

$$\frac{\partial c}{\partial t} + \underset{\sim}{\nabla} \cdot (c\, \underset{\sim}{u}^{+}) = \underbrace{R_A + R_B}_{\underline{\underline{\text{Not}}}\text{ necessarily zero!}}$$

(say A → 2B!)

This yields:

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{\nabla} \cdot (c_A \underset{\sim}{u}^{+}) = \underset{\sim}{\nabla} \cdot (c\, \mathcal{D}_{AB} \underset{\sim}{\nabla} x_A) + R_A$$

or, if c is constant (gases)

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{u}^{+} \cdot \underset{\sim}{\nabla} c_A = \mathcal{D}_{AB} \nabla^2 c_A + (x_B R_A - x_A R_B)$$

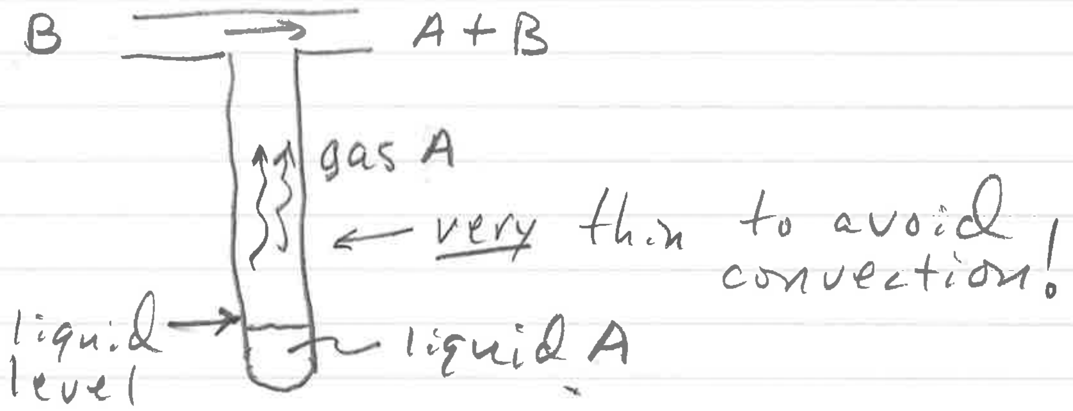
The <u>last</u> term arises because for constant c,

$$\underset{\sim}{\nabla} \cdot \underset{\sim}{u}^{+} = R_A + R_B$$

Note: if $R_B = -R_A$, $x_B R_A - x_A R_B = R_A$!

Now we use this to solve mass transfer problems!

Classic example: the Stefan Tube



Developed in 1874 to measure gas phase diffusivities

Key idea: at $z = 0$ the evaporating liquid is at equilibrium w/ molar concentration x_{A_1}. It diffuses out the tube & is swept away by gas B. As it evaporates the liquid level drops very slowly! You would measure this change and use it to calculate $\mathcal{D}_{AB}$!

We have the equation for $\underset{\sim}{N}_A$:

$$\underset{\sim}{N}_A = x_A\left(\underset{\sim}{N}_A + \underset{\sim}{N}_B\right) - c\mathcal{D}_{AB}\underset{\sim}{\nabla} x_A$$

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{\nabla}\cdot\underset{\sim}{N}_A = R_A$$

w/ similar eq'n for B.

We only need to worry about flux in z-direction. We have no rxn ($R_A = 0$). We assume pseudo-steady state! The molar conc. in the liquid is 10^3 higher than the gas, so this is good!

This yields:

$$\frac{\partial N_{Az}}{\partial z} = 0 \quad ; \quad \frac{\partial N_{Bz}}{\partial z} = 0$$

$\therefore N_{Az} = cst \; ; \; N_{Bz} = cst$!

We further assume B doesn't dissolve in liquid A!

$\therefore N_{Bz}\Big|_{z=0} = 0$ so $N_{Bz} = 0$ everywhere!

So:
$$N_{Az} = x_A\left(N_{Az} + \cancelto{0}{N_{Bz}}\right) - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

and $N_{Az} = N_{A_0}$ (constant)

Thus $$-c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z} = (1 - x_A)N_{A0}$$

with B.C.'s $x_A\big|_{z=0} = x_{A_0}$, $x_A\big|_{z=h} = x_{A_1} = 0$

(usually take $x_{A_1} = 0$ for "clean" B)

Let's render dimensionless

$$x_A^* = \frac{x_A}{x_{A_0}} \qquad z^* = \frac{z}{h} \qquad N_{A_0}^* = \frac{N_{A_0}}{N_{A_c}}$$

$$\therefore\ -c\mathcal{D}_{AB}\frac{x_{A_0}}{h}\frac{\partial x_A^*}{\partial z^*} = \left(1 - x_{A_0}x_A^*\right)N_{A_0}^*N_{A_c}$$

Divide out:

$$-\underset{\overset{\shortparallel}{1}}{\left[\frac{c\mathcal{D}_{AB}x_{A_0}}{h\,N_{A_c}}\right]}\frac{\partial x_A^*}{\partial z^*} = \left(1 - x_{A_0}x_A^*\right)N_{A_0}^*$$

$$\therefore\ N_{A_c} = \frac{c\mathcal{D}_{AB}x_{A_0}}{h}$$

This is the characteristic magnitude of the molar flux

So:
$$\frac{\partial x_A^*}{\partial z^*} = -\left(1 - x_{A_0} x_A^*\right) N_{A_0}^*$$

$$x_A^*\Big|_{z^*=0} = 1 \qquad x_A^*\Big|_{z^*=1} = 0$$

Let's look at the dilute limit $x_{A_0} \ll 1$

In this case,
$$\frac{\partial x_A^*}{\partial z^*} \cong -N_{A_0}^*$$

$$x_A^* = -N_{A_0}^* z^* + C_1$$

but $x_A^*\Big|_{z^*=0} = 1 \quad \therefore \; C_1 = 1$

and since $x_A^*\Big|_{z^*=1} = 0$, $N_{A_0}^* = 1$!

So $x_A^* = 1 - z^*$

Which is identical to SS cond. in a slab!

In this limit:

$$N_{Az} = N_{A_L} = \frac{c\mathcal{D}_{AB}x_{A_0}}{h}$$

so if you measure N_{Az} by looking at the liquid level and <u>know</u> x_{A_0}, you get $\mathcal{D}_{AB}$!

Ok, what if x_{A_0} <u>isn't</u> small??

we have:

$$\frac{\partial x_A^*}{\partial z^*} = -\left(1 - x_{A_0}x_A^*\right)N_{A_0}^*$$

Divide:

$$\frac{1}{1 - x_{A_0}x_A^*}\frac{\partial x_A^*}{\partial z^*} = -N_{A_0}^*$$

$$\frac{1}{x_{A_0}}\frac{\partial \ln(1-x_{A_0}x_A^*)}{\partial z^*} = N_{A_0}^*$$

$$\therefore \ln\left(1 - x_{A_0}x_A^*\right) = x_{A_0}N_{A_0}^*z^* + C_1$$

$$x_A^*\Big|_{z^*=0} = 1$$

$$\therefore \ln\left(1 - x_{A_0}\right) = C_1$$

so $$\ln\left(\frac{1 - x_{A_0}x_A^*}{1 - x_{A_0}}\right) = x_{A_0}N_{A_0}^* z^*$$

but at $z^* = 1$ $x_A^* = 0$

$$\therefore \quad \ln\left(\frac{1}{1 - x_{A_0}}\right) = x_{A_0}N_{A_0}^*$$

so $$N_{A_0}^* = \frac{-\ln(1 - x_{A_0})}{x_{A_0}} \geq 1$$

and the flux is increased by this factor due to the convection arising from diffusion!

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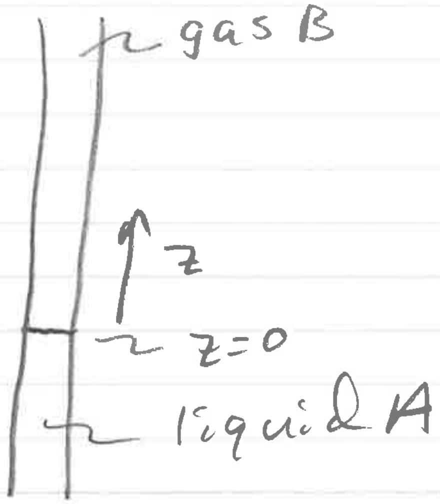
ok, what if we look at the transient problem?



We have a long tube filled w/ gas B & dip it into liquid A so that the liquid level is kept at $z = 0$

Again,

$$\frac{\partial c_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = 0 \; ; \; \frac{\partial c_B}{\partial t} + \frac{\partial N_{Bz}}{\partial z} = 0$$

Let's add these!

$$\underset{''}{\frac{\partial (c_A + c_B)}{\partial t}} + \frac{\partial}{\partial z}\left(N_{Az} + N_{Bz}\right) = 0$$

$\frac{\partial c}{\partial t} = 0$ because c is constant for our gas!

$N_{Bz}|_{z=0} = 0$

$$\therefore \; N_{Az} + N_{Bz} = N_{A_0} \neq f^n(z)!$$

but both N_{Az} & N_{Bz} will be $f^n(z,t)$ - just the sum is only a $f^n(t)$

$$\text{So} \quad N_{Az} = x_A\left(N_{Az} + N_{Bz}\right) - c\,\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

At $z = 0$ $N_{Bz} = 0$, $N_{Az} = N_{A_0}$ $(f^n(t))$

$$\therefore \; N_{A_0} = x_{A_0} N_{A_0} - c\,\mathcal{D}_{AB}\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$$

$$\text{So} \quad N_{A_0} = \frac{-c\,\mathcal{D}_{AB}}{1 - x_{A_0}}\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$$

$$\therefore\ N_{Az} = \underbrace{x_A \left(-\frac{c\mathcal{D}_{AB}}{1-x_{A_0}}\right)\frac{\partial x_A}{\partial z}\bigg|_{z=0}}_{\text{extra term due to convection}} - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

$$\text{so } \frac{\partial c_A}{\partial t} \equiv c\frac{\partial x_A}{\partial t} = -\frac{\partial N_{Az}}{\partial z}$$

$$\therefore\ \underbrace{\frac{\partial x_A}{\partial t}}_{\text{accum}} = \underbrace{\mathcal{D}_{AB}\frac{\partial^2 x_A}{\partial z^2}}_{\text{dif}^{\underline{n}}} + \underbrace{\frac{\mathcal{D}_{AB}}{1-x_{A_0}}\frac{\partial x_A}{\partial z}\bigg|_{z=0}\frac{\partial x_A}{\partial z}}_{\text{convection \underline{from} diffusion}}$$

BC's are $x_A\big|_{z=0} = x_{A_0}$, $x_A\big|_{t=0} = 0$, $x_A\big|_{z\to\infty} = 0$

Let's scale: $x_A^* = \dfrac{x_A}{x_{A_0}}$ (from BC)

$t^* = t/t_c \qquad z^* = z/z_c$

$$\therefore\ \frac{x_{A_0}}{t_c}\frac{\partial x_A^*}{\partial t^*} = \frac{\mathcal{D}_{AB}x_{A_0}}{z_c^2}\frac{\partial^2 x_A^*}{\partial z^{*2}}$$

$$+ \frac{\mathcal{D}_{AB}x_{A_0}}{z_c^2}\frac{x_{A_0}}{1-x_{A_0}}\frac{\partial x_A^*}{\partial z^*}\bigg|_{z^*=0}\frac{\partial x_A^*}{\partial z^*}$$

Divide out:

$$\left[\frac{z_c^2}{\mathcal{D}_{AB} t_c}\right] \frac{\partial x_A^*}{\partial t^*} = \frac{\partial^2 x_A^*}{\partial z^{*2}} + \frac{x_{A_0}}{1-x_{A_0}} \left.\frac{\partial x_A^*}{\partial z^*}\right|_{z^*=0} \frac{\partial x_A^*}{\partial z^*}$$

$\parallel$

$1 \quad \therefore \quad \dfrac{z_c}{(\mathcal{D}_{AB} t_c)^{1/2}} = 1 \quad$ or $\quad z_c = (\mathcal{D}_{AB} t_c)^{1/2}$

B.C.'s $\quad \left. x_A^* \right|_{z^*=0} = 1 \qquad \left. x_A^* \right|_{t^*=0} = \left. x_A^* \right|_{z^* \to \infty} = 0$

Note that t_c disappeared – but we never specified it! That means that our problem is self-similar!

∴ from scaling (or affine stretching!)

$$x_A^* = f(\eta) \; ; \quad \eta = \frac{z^*}{t^{*1/2}}$$

Getting the transformed ODE isn't too bad:

$$\frac{\partial x_A^*}{\partial z^*} = t^{*-1/2} f' \qquad \frac{\partial^2 x_A^*}{\partial z^{*2}} = t^{*-1} f''$$

$$\frac{\partial x_A^*}{\partial t^*} = -\frac{1}{2}\frac{\zeta}{t^*} f'$$

$$\therefore -\frac{1}{2}\frac{\zeta}{t^*} f' = \frac{1}{t^*} f'' + \frac{x_{A_0}}{1-x_{A_0}} f'(0) f' \frac{1}{t^*}$$

so $$f'' = -\frac{1}{2}\zeta f' - \frac{x_{A_0}}{1-x_{A_0}} f'(0) f'$$

$$= -\left(\frac{1}{2}\zeta + \frac{x_{A_0}}{1-x_{A_0}} f'(0)\right) f'$$

$$f(0) = 1, \quad f(\infty) = 0$$

It's probably easier to solve numerically, but the analytic solution is:

$$f = \frac{1 - \operatorname{erf}\left(\frac{1}{2}\zeta + \frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}{1 - \operatorname{erf}\left(\frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}$$

where $$f'(0) = \frac{e^{-\left(\frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}}{1 - \operatorname{erf}\left(\frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}$$

which is an implicit expression for $f'(0)$

This is useful for measuring $\mathcal{D}_{AB}$ for volatile materials. Note that if $x_{A_0} << 1$ (dilute), then we get

$$\frac{\partial x_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 x_A}{\partial z^2}$$

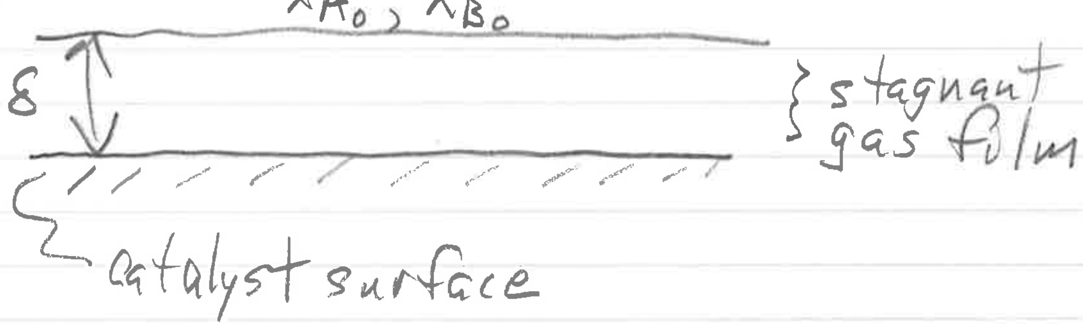
and (from heat transfer problem!)

$$\frac{x_A}{x_{A_0}} = 1 - \operatorname{erf}\left(\tfrac{1}{2}\zeta\right)$$

A key difference between mass & energy transfer is the possibility of chemical rxn: turning one species into another! This leads to all sorts of possibilities!

If a rxn is heterogeneous (e.g. on a catalyst surface) then it appears in the BC's. If it is homogeneous (e.g., occurs per volume in a fluid) then it is a source or sink in the DE.

Let's look at heterogeneous rxn's first!



Let's look at case where $2A \rightarrow B$ (dimerization rxn) in the gas phase

So 2 molecules of A diffuse to surface & form one molecule of B. This yields a net convection towards the catalyst!

We have balances:

$$\underbrace{\cancel{\frac{\partial C_A}{\partial t}}}_{0} + \frac{\partial N_{Az}}{\partial z} = \underbrace{\cancel{R_A}}_{0} \qquad \Bigg| \qquad \underbrace{\cancel{\frac{\partial C_B}{\partial t}}}_{SS} + \frac{\partial N_{Bz}}{\partial z} = \underbrace{\cancel{R_B}}_{0\,!!}$$

(at surface, not in bulk)

So $N_{Az} = cst = N_{Az}\big|_{z=0}$

$N_{Bz} = cst = N_{Bz}\big|_{z=0}$

From Stoichiometry $N_{Az} = -2N_{Bz}$

$\therefore N_{Az} + N_{Bz} = -N_{Bz} = \frac{1}{2}N_{Az}$

and $N_{Az} = x_A(N_{Az} + N_{Bz}) - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$

so:
$$N_{Az} = cst = \frac{-c\mathcal{D}_{AB}}{1-\frac{x_A}{2}} \frac{dx_A}{dz}$$

Solving:
$$N_{Az} = +2c\mathcal{D}_{AB} \frac{d\ln\left(1-\frac{x_A}{2}\right)}{dz}$$

$$\therefore \frac{z}{2c\mathcal{D}_{AB}} N_{Az} = \ln\left(1-\frac{x_A}{2}\right) + C_1$$

At $z = \delta$ $x_A = x_{A_0}$ (conc. at film edge)

$$\therefore \frac{\delta}{2c\mathcal{D}_{AB}} N_{Az} = \ln\left(1-\frac{x_{A_0}}{2}\right) + C_1$$

so
$$\frac{z-\delta}{2c\mathcal{D}_{AB}} N_{Az} = \ln\left(\frac{1-x_A/2}{1-x_{A0}/2}\right)$$

To finish, we need the rxn rate at the surface!

If we have instantaneous rxn, then

$$x_A\Big|_{z=0} = 0$$

Thus:

$$\frac{0-\delta}{2c\mathcal{D}_{AB}} N_{Az} = \ln\left(\frac{1}{1-x_{A0}/2}\right)$$

or $$N_{Az} = -\frac{2c\mathcal{D}_{AB}}{\delta}\ln\left(\frac{1}{1-x_{A0}/2}\right)$$

If $x_{A0}/2 \ll 1$ then we get

$$N_{Az} \cong -\frac{2c\mathcal{D}_{AB}}{\delta}\frac{x_{A0}}{2} = -\frac{c_A}{\delta}\mathcal{D}_{AB}$$

This is equivalent to a simple shear flow $\left(\tau_w = \frac{U}{\delta}\mu\right)$
or ht cond. in a slab $\left(q = -k\frac{\Delta T}{\delta}\right)$

More often, we have a limited rxn rate! Suppose it is 1st order:

$$N_{Az}\Big|_{z=0} = -k_1 c_A\Big|_{z=0} = -k_1 c\, x_A\Big|_{z=0}$$

so $$\frac{-\delta}{2c\mathcal{D}_{AB}} N_{Az} = \ln\left(\frac{1 - x_A/2\big|_{z=0}}{1 - x_{A0}/2}\right)$$

$$= \frac{k_1\delta}{2\mathcal{D}_{AB}} x_A\big|_{z=0}$$

which yields a transcendental eq'n for $x_A\big|_{z=0}$

Going the other way, $x_A\big|_{z=0} = \frac{-N_{Az}}{k_1 c}$

$$\therefore \quad \frac{-\delta N_{Az}}{2c\mathcal{D}_{AB}} = \ln\left(\frac{1 + \frac{1}{2}\frac{N_{Az}}{k_1 c}}{1 - x_{A0}/2}\right)$$

Note: $N_{Az} < 0$ as flux is towards surface

If k_1 is large then $x_A\big|_{z=0}$ is small and expanding the log term yields:

$$N_{Az} \approx \frac{-2c\mathcal{D}_{AB}/\delta}{1 + \frac{\mathcal{D}_{AB}}{k_1\delta}} \ln\left(\frac{1}{1 - x_{A0}/2}\right)$$

The ratio $\frac{k_1\delta}{\mathcal{D}_{AB}}$ is known as the second Damkohler # Da^{II}

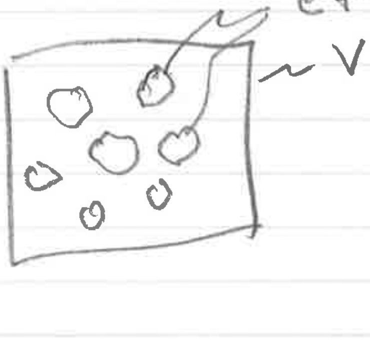
This is the ratio of rxn rate/dif$^{\underline{n}}$ rate and is important in diffusion limited reactions!

For 2nd order reactions ($N_{Az} = -k_2 C_A^2\big|_{z=0}$) we would get equivalent expressions (just a bit messier!)

Although heterogeneous catalysis occurs at surfaces, a catalyst pellet is usually modeled as an effective porous medium/homogeneous rxn!

The idea is that you have a volume which has some surface per volume

a :



$$\frac{\text{effective surface area}}{\text{Volume}} \equiv a$$

Suppose we have a 1st order rxn

A → B w/ rate $k_1 a c_A$

Then this is a homogeneous 1st order rxn over both solid & pores!

If A → B then we have equi-molar counter diffusion: diffusion does not lead to convection!

Let $N_{A_r} = -\mathcal{D}_A \frac{\partial c_A}{\partial r}$

↳ "effective" diffusivity

In general, $\mathcal{D}_A \approx \frac{\varepsilon \mathcal{D}_{AB}}{\lambda} \leftarrow \text{tortuosity}$

void fraction ↗

but it may be quite different! If the pores are smaller than the mean free path, you get Knudsen diffusion instead of $\mathcal{D}_{AB}$!

In a spherical geometry (usual model for a catalyst pellet):

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{A_r}\right) = R_A = -k_1 a C_A$$

or, w/ Fick's law:

$$\mathcal{D}_A \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_A}{\partial r}\right) = k_1 a C_A$$

We have BC at $r = R$: $C_A \Big|_{r=R} = C_{A_0}$

Let's render dimensionless:

$$r^* = r/R, \quad C_A^* = C_A / C_{A_0}$$

$$\therefore \quad \frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial C_A^*}{\partial r^*}\right) = \frac{k_1 a R^2}{\mathcal{D}_A} C_A^*$$

Let's let $\frac{k_1 a R^2}{\mathcal{D}_A} \equiv \phi^2$

or $\phi = \left(\frac{k_1 a}{\mathcal{D}_A}\right)^{1/2} R \equiv$ Thiele Modulus

Ernest Thiele was a famous ChE for Standard Oil, later an ND prof. for 10 years.

So: $$\frac{1}{r^{*2}}\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial C_A^*}{\partial r^*}\right) = \phi^2 C_A^*$$

$$C_A^*\Big|_{r^*=0} = \text{finite}, \quad C_A^*\Big|_{r^*=1} = 1$$

we can solve this via the substitution

$$C_A^* = \frac{f(r^*)}{r^*}$$

$$\therefore \frac{\partial C_A^*}{\partial r^*} = \frac{1}{r^*} f' - \frac{1}{r^{*2}} f$$

$$r^{*2}\frac{\partial C_A^*}{\partial r^*} = r^* f' - f$$

$$\frac{\partial}{\partial r^*}\left(r^{*2}\frac{\partial C_A^*}{\partial r^*}\right) = \cancel{f'} + r^* f'' - \cancel{f'}$$

So plugging in yields:

$$f'' = \phi^2 f \quad ; \quad f(0) = 0, \quad f(1) = 1$$

The solution is just:

$$f = A\sinh\phi r^* + \underset{0}{\cancel{B}}\cosh\phi r^*$$

and w/ $f(1)=1$: $f = \frac{\sinh\phi r^*}{\sinh\phi}$

$$\therefore\ C_A^* = \frac{1}{r^*}\frac{\sinh\phi r^*}{\sinh\phi}$$

we need $N_{A_r}\Big|_{r=R}$ as this is the overall rxn rate (or × $4\pi R^2$)

$$\therefore\ W_{AR} = 4\pi R^2 N_A\Big|_{r=R} = -4\pi R^2 \mathcal{D}_A \frac{\partial C_A}{\partial r}\Big|_{r=R}$$

$$= -4\pi R\,\mathcal{D}_A C_{A_0}\frac{\partial C_A^*}{\partial r^*}\Big|_{r^*=1}$$

$$= 4\pi R\,\mathcal{D}_A C_{A_0}\left(1-\phi\coth\phi\right)$$

Now if all the surface was exposed to the catalyst (no diffⁿ limitation) we would get $W_{AR_0} = \left(\frac{4}{3}\pi R^3\right) a\left(-k_1 C_{A_0}\right)$

The ratio of these is Thiele's effectiveness factor $\eta = \frac{W_{AR}}{W_{AR_0}}$

$$\eta = \frac{3}{\phi^2}(\phi \coth \phi - 1)$$

For slow reaction $\phi << 1$

Then $\coth \phi \approx \frac{1}{\phi}\left(1 + \frac{1}{3}\phi^2 - \frac{1}{45}\phi^4 + \dots\right)$

$$\therefore \eta = 1 - \frac{1}{15}\phi^2$$

For $\phi >> 1$ (fast rxn)

$$\eta \approx \frac{3}{\phi}$$

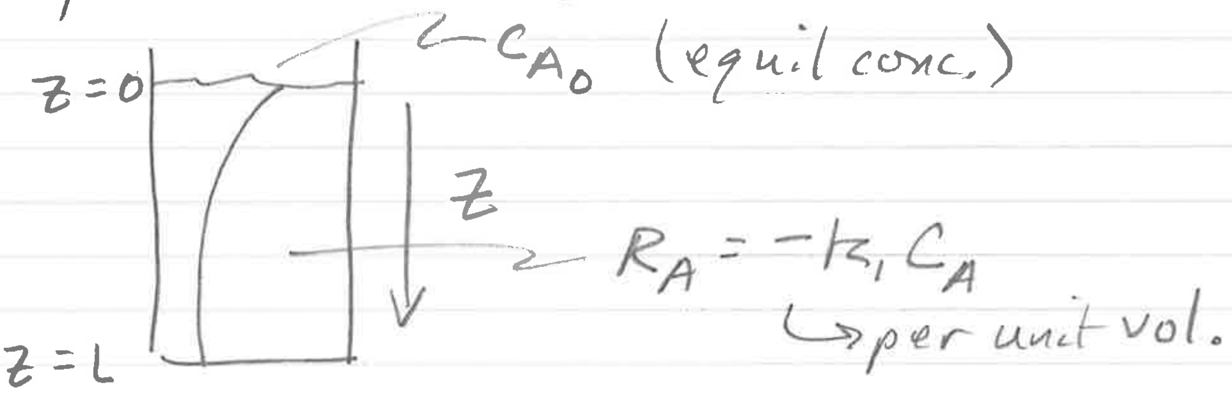
for a general shape

$$|W_{AR}| \cong V_p a k_1 C_{A_0} \eta_A$$

where $\eta_A = \frac{1}{3\Lambda^2}(3\Lambda \coth 3\Lambda - 1)$

and $\Lambda = \left(\frac{k_1 a}{\mathcal{D}_A}\right)\left(\frac{V_p}{S_p}\right) \leftarrow = R/3$ for sphere

A classic problem of homogeneous reaction in liquids is gas absorption. Say you are absorbing a gas like CO_2. To increase the capacity of the liquid for the gas you have a compound which reacts with it!



(large excess of absorbing compound, so 1st order rxn is reasonable)

So:
$$\frac{\partial C_A}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_A = R_A = -k_1 C_A$$

At steady state $\frac{dN_{Az}}{dz} = -k_1 C_A$

We have:
$$N_{Az} = \underset{\text{small}}{\cancel{x_A}}\left(N_{Az} + \underbrace{N_{Bz}}_{\text{stagnant}}\right) - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

In general, convection from diffusion in liquids is negligible!

$$\therefore \; N_{Az} = -\mathcal{D}_{AB}\frac{\partial C_A}{\partial z} \qquad (\text{take } C \equiv \text{cst})$$

So

$$\mathcal{D}_{AB}\frac{\partial^2 C_A}{\partial z^2} = K_1 C_A$$

$$C_A\Big|_{z=0} = C_{A_0} \qquad \mathcal{D}_{AB}\frac{\partial C_A}{\partial z}\Big|_{z=L} = 0$$

↪ no flux B.C.

Let's scale

$$C_A^* = C_A / C_{A_0} \qquad z^* = \frac{z}{L}$$

$$\therefore \; \frac{\partial^2 C_A^*}{\partial z^{*2}} = \underbrace{\left[\frac{K_1 L^2}{\mathcal{D}_{AB}}\right]}_{\parallel \; b_1^2} C_A^*$$

So we get a dimensionless parameter:

$$b_1 = \frac{L}{\left(\frac{\mathcal{D}_{AB}}{K_1}\right)^{1/2}} \equiv \text{Hatta } \#$$

This is the ratio of the film depth L to diffusion length during rxn time $1/k_1$ (k_1 has units $1/T$)

$$\therefore \quad \frac{d^2 C_A^*}{dz^{*2}} = b_1^2 C_A^* \; ; \quad C_A^*\Big|_{z^*=0} = 1 \; , \quad \frac{\partial C_A^*}{\partial z^*}\Big|_{z^*=1} = 0$$

Solution is hyperbolics!

$$C_A^* = A \sinh b_1 z^* + B \cosh b_1 z^*$$

$$C_A^*\Big|_{z^*=0} = B = 1$$

$$\frac{\partial C_A^*}{\partial z^*}\Big|_{z^*=1} = 0 = A b_1 \cosh b_1 + b_1 \sinh b_1$$

$$\therefore \quad A = -\tanh b_1$$

so $C_A^* = \cosh b_1 z^* - \tanh b_1 \sinh b_1 z^*$

We are interested in the total rxn rate. This is just the flux at $z^*=0$!

$$N_{Az}\Big|_{z=0} = -\mathcal{D}_{AB}\frac{\partial c_A}{\partial z}\Big|_{z=0} = -\frac{\mathcal{D}_{AB}c_{A_0}}{L}\frac{\partial c_A^*}{\partial z^*}\Big|_{z^*=0}$$

Now:

$$\frac{\partial c_A^*}{\partial z^*}\Big|_{z^*=0} = \Big[b_1\sinh b_1 z^* - b_1\tanh b_1 \cosh b_1 z^*\Big]_{z^*=0}$$

$$= -b_1\tanh b_1$$

so $$N_{Az}\Big|_{z=0} = \frac{\mathcal{D}_{AB}c_{A_0}}{L} b_1 \tanh b_1$$

There are <u>two</u> interesting limits!

If $b_1 << 1$ then $\tanh b_1 \approx b_1$

and $$N_{Az}\Big|_{z=0} \cong \frac{\mathcal{D}_{AB}c_{A_0}}{L} b_1^2 = c_{A_0} k_1 L$$

This corresponds to the <u>whole</u> <u>film</u> being at $c_A = c_{A_0}$ – <u>no</u> Diff$^{\underline{n}}$ limitation!

The other limit is more interesting:

$b_1 >> 1$

Here $\tanh b_1 \approx 1$, so:

$$N_{Az}\Big|_{z=0} = \frac{\mathcal{D}_{AB} C_{A0}}{L} \left(\frac{k_1}{\mathcal{D}_{AB}}\right)^{1/2} L$$

$$= C_{A0} \left(\mathcal{D}_{AB} k_1\right)^{1/2}$$

so the reaction rate is independent of L!

This makes sense: the rxn is fast enough that all A is consumed over distance of $O\left(\left(\frac{\mathcal{D}_{AB}}{k_1}\right)^{1/2}\right)$ and it doesn't make it to the bottom!

The transient problem is also relevant:

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 c_A}{\partial z^2} - k_1 c_A$$

Let's scale: $c_A^* = c_A / c_{A0}$, $z^* = z/L$, $t^* = t/t_c$:

$$\frac{c_{A0}}{t_c} \frac{\partial c_A^*}{\partial t^*} = \frac{\mathcal{D}_{AB} c_{A0}}{L^2} \frac{\partial^2 c_A^*}{\partial z^{*2}} - k_1 c_{A0} c_A^*$$

so:

$$\underset{\overset{\shortparallel}{1}}{\left(\frac{L^2}{\mathcal{D}_{AB}t_c}\right)}\frac{\partial c_A^*}{\partial t^*} = \frac{\partial^2 c_A^*}{\partial z^{*2}} - b_1^2 c_A^*$$

so $t_c = L^2/\mathcal{D}_{AB}$

Note that we <u>could</u> have taken $t_c = 1/K_1$, would get a b_1^2 mult. the transient term in this case.

ok, we have:

$$\frac{\partial c_A^*}{\partial t^*} = \frac{\partial^2 c_A^*}{\partial z^{*2}} - b_1^2 c_A^*$$

$$c_A^*\Big|_{t^*=0} = 0 \qquad c_A^*\Big|_{z^*=0} = 1 \qquad \frac{\partial c_A^*}{\partial z^*}\Big|_{z^*=1} = 0$$

This problem is <u>linear</u> so we will use separation of variables again!

<u>First</u> we subtract off the asymp. solution!!

$$c_{A\infty}^* = \cosh b_1 z^* - \tanh b_1 \sinh b_1 z^*$$

So we let:

$$C_A^* = C_{A_\infty}^* + C_{Ad}^*$$

$$\therefore \frac{\partial C_{Ad}^*}{\partial t^*} = \frac{\partial^2 C_{Ad}^*}{\partial z^{*2}} - b_1^2 C_{Ad}^*$$

$$C_{Ad}^*\Big|_{t^*=0} = -C_{A_\infty}^* \, ; \quad C_{Ad}^*\Big|_{z^*=0} = 0 \, , \quad \frac{\partial C_{Ad}^*}{\partial z^*}\Big|_{z^*=1} = 0$$

This 1st order decay has a very curious solution:

$$C_A^* = e^{-b_1^2 t^*} f(z^*, t^*)$$

$$\text{so } \frac{\partial C_A^*}{\partial t^*} = -b_1^2 C_A^* + e^{-b_1^2 t^*} \frac{\partial f}{\partial t^*}$$

$$\text{and } \frac{\partial^2 C_A^*}{\partial z^{*2}} = \frac{\partial^2 f}{\partial z^{*2}} e^{-b_1^2 t^*}$$

$$\therefore \frac{\partial f}{\partial t^*} = \frac{\partial^2 f}{\partial z^{*2}} \, ; \quad f\Big|_{z^*=0} = 0 \, , \quad \frac{\partial f}{\partial z^*}\Big|_{z^*=1} = 0$$

$$f\Big|_{t^*=0} = -C_{A_\infty}^*$$

Why does this work? We have homogeneous BC's - molecules of A are just leaking away (or not) at the boundaries. The reaction is also 1st order - each molecule's fate doesn't depend on the local concentration. Thus, it's much like radioactive decay: the concentration is decreasing exponentially in time!

The solution for f is exactly what we've done before:

$$f = G(t^*) F(z^*)$$

$$\frac{G'}{G} = \frac{F''}{F} = -\sigma^2$$

$$G = e^{-\sigma^2 t^*}, \quad F = A \sin \sigma z^* + B \cos \sigma z^*$$

$$F(0) = \underline{0} \quad \therefore \quad B = 0$$

$$F'(1) = 0 \quad \therefore \quad \sigma_n = (n - \tfrac{1}{2})\pi$$

So:

$$c^*_{Ad} = e^{-b_1^2 t^*} \sum_{n=1}^{\infty} A_n e^{-\sigma_n^2 t^*} \sin \sigma_n z^*$$

where $\sigma_n = \underline{(n - \tfrac{1}{2})}\pi$

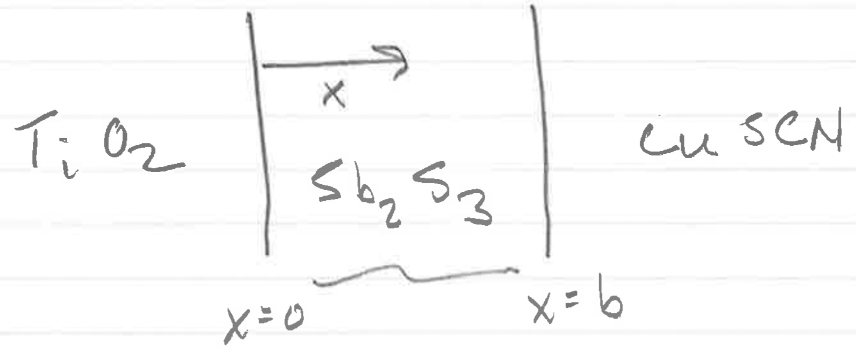
$\underline{\text{and}}$ $$A_n = \frac{\int_0^1 -c^*_{A0} \sin \sigma_n z^* \, dz^*}{\underset{\frac{1}{2} =}{} \int_0^1 \sin^2 \sigma_n z^* \, dz^*}$$

So the solution approaches S.S. as

$$\underline{e^{-(b_1^2 + \sigma_1^2)t^*}}$$

A bit faster than just the lead eigenvalue alone!

A nearly identical problem was encountered in the Kamat lab in their study of Sb_2S_3 solar cells. Such a thin film solar cell looks like:



Illumination of the Antimony sulfide layer produces "holes" which diffuse to the Copper thiocyanate layer. They have some resistance crossing (e.g., a mass transfer coef.) and also decay over a time scale τ. You want to collect the holes, so you want a high diffusivity, a high mass transfer rate & a low recombination rate. The Kamat group could measure the decay rate independently but needed to tease apart diffusional and interfacial transfer limitations.

The hole concentration in the Sb_2S_3 layer (the <u>total</u> could be measured) was governed by:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \frac{c}{\tau}$$ ← decay time (homogeneous recombination)

$$c\Big|_{t=0} = c_0 e^{-\alpha x}$$ ← α: absorbance decay length scale

$$\frac{\partial c}{\partial x}\Big|_{x=0} = 0$$ (nothing goes through TiO_2 layer)

$$-D\frac{\partial c}{\partial x}\Big|_{x=b} = k\, c\Big|_{x=b}$$ ↑ k: mass transfer coef. at CuSCN interface

Let's render dimensionless!

$$x^* = \frac{x}{b} \qquad c^* = c/c_0 \qquad t^* = \frac{Dt}{b^2}$$

$$\therefore \quad \frac{\partial c^*}{\partial t^*} = \frac{\partial^2 c^*}{\partial x^{*2}} - \lambda c^*$$ λ → Hatta squared

$$c^*\Big|_{t^*=0} = e^{-\alpha b x^*}$$ αb → dimensionless absorbance profile

BC's: $$\frac{\partial c^*}{\partial x^*}\Big|_{x^*=0} = 0 \qquad \frac{\partial c^*}{\partial x^*}\Big|_{x^*=1} = -\left[\frac{\kappa b}{D}\right] c^*\Big|_{x^*=1}$$

where $\frac{\kappa b}{D} \equiv$ Biot # for mass transfer!

The problem already has homogeneous BC's, so we remove exponential decay and use sep. of variables!

$$c^* = e^{-\lambda t^*} f(x^*, t^*)$$

$$\therefore \quad \frac{\partial f}{\partial t} = \frac{\partial^2 f}{\partial x^{*2}} \qquad f\Big|_{t^*=0} = e^{-\alpha b x^*}$$

$$\frac{\partial f}{\partial x^*}\Big|_{x^*=0} = 0 \qquad \frac{\partial f^*}{\partial x^*}\Big|_{x^*=1} = -Bi\, f\Big|_{x^*=1}$$

Let $f = G(t^*)\,F(x^*)$

$$\therefore \quad \frac{G'}{G} = \frac{F''}{F} = -\sigma^2$$

$$G = e^{-\sigma^2 t^*} \qquad F'' + \sigma^2 F = 0$$

$$F'(0) = 0 \qquad F'(1) = -Bi\,F(1)$$

Solutions are just sines & cos!

$$F = A \sin \sigma x^* + B \cos \sigma x^*$$

$$F'(0) = 0 \quad \therefore \; A = 0$$

$$F'(1) = -\cancel{B}\,\sigma \sin \sigma = -\cancel{B}\,Bi \cos \sigma$$

$$\text{so} \qquad \sigma \tan \sigma = Bi$$

determines eigenvalues!

$$\text{so} \quad c^* = e^{-\lambda t^*} \sum_{n=1}^{\infty} B_n e^{-\sigma_n^2 t^*} \cos \sigma_n x^*$$

$$\text{where} \quad B_n = \frac{\int_0^1 e^{-\kappa b x^*} \cos \sigma_n x^* \, dx^*}{\int_0^1 \cos^2 \sigma_n x^* \, dx^*}$$

We need the <u>total</u> hole amount:

$$\int_0^1 c^* dx^* = e^{-\lambda t^*} \sum_{n=1}^{\infty} \frac{B_n}{\sigma_n} e^{-\sigma_n^2 t^*} \sin \sigma_n$$

Jeff Christians used measurements of this decay rate to get <u>both</u> K & D by fitting different thicknesses of Sb_2S_3

Rate limiting interfacial hole transfer in Sb_2S_3 solid-state solar cells†

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Jeffrey A. Christians,‡ David T. Leighton, Jr. and Prashant V. Kamat‡§*

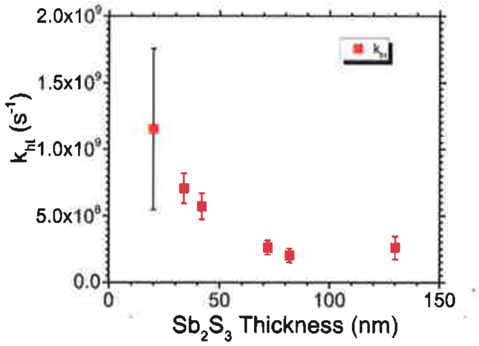


Fig. 5 Trace showing how the estimated hole transfer rate calculated decreases with increasing Sb_2S_3 film thickness. Error bars represent the error in k_{ht} as calculated from the error of the fitting parameters as shown in Table 1.

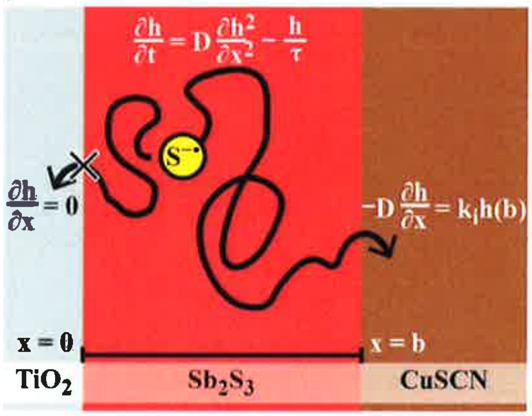


Fig. 6 (A) Scheme showing the TiO_2–Sb_2S_3–CuSCN system modeled using Fick's second law of diffusion with appropriate boundary conditions.

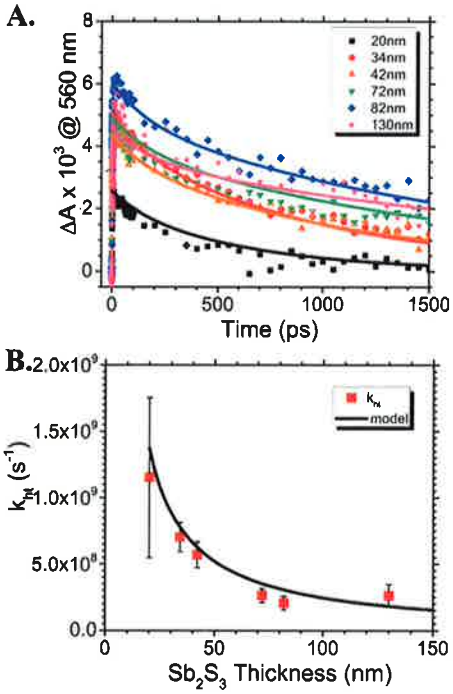
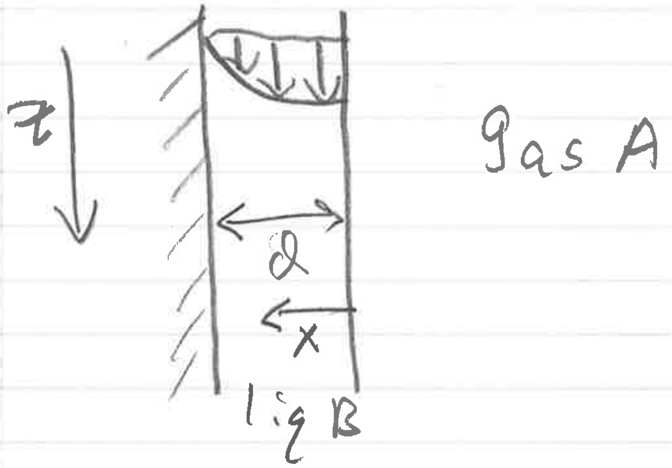


Fig. 7 (A) Plots of transient absorption decay model fit to experimental time resolved transient kinetic data at 560 nm. (B) Plot of modeled & experimentally calculated hole transfer rate *vs.* Sb_2S_3 film thickness.

A key problem in processing is the absorbtion or desorption of a gas from a falling liquid film:



We assume that diffusion doesn't affect the velocity profile of the liquid.

What's the velocity profile? Assume a laminar falling film

Let's solve this!

For constant properties:

$$\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$$

$$\rho\left(\frac{\partial \underset{\sim}{u}}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} \underset{\sim}{u}\right) = -\underset{\sim}{\nabla} p + \mu \nabla^2 \underset{\sim}{u} + \rho \underset{\sim}{g}$$

First look at C.E.:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0$$

No variation in y (into paper)

Assume that u_x is small (due to diffusion!)

$$\therefore \quad \frac{\partial u_z}{\partial z} = 0 \quad \text{(uni-directional flow)}$$

z-mom:

$$\rho\left(\frac{\partial u_z}{\partial t} + u_x\frac{\partial u_z}{\partial x} + u_y\frac{\partial u_z}{\partial y} + u_z\frac{\partial u_z}{\partial z}\right) = -\frac{\partial P}{\partial z} + \mu\left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2}\right) + \rho g_z$$

SS: $\frac{\partial u_z}{\partial t} = 0$

only $u_z \neq 0$ but $\frac{\partial u_z}{\partial z} = 0$ from CE so all convective terms vanish!

$\frac{\partial u_z}{\partial z} = 0$ so $\frac{\partial^2 u_z}{\partial z^2} = 0$ too!

No variation in y direction!

$$\therefore \quad 0 = -\frac{\partial p}{\partial z} + \mu \frac{\partial^2 u_z}{\partial x^2} + \rho g_z$$

Now recall that it is the deviation from hydrostatics that drives the flow!

In this case $\frac{\partial p}{\partial z} = 0$ and $g_z \equiv g$

$$\therefore \quad 0 = \mu \frac{\partial^2 u_z}{\partial x^2} + \rho g$$

We have B.C.'s $\mu \frac{\partial u_z}{\partial x}\Big|_{x=0} = 0$ (no shear stress at interface)

and $u_z\Big|_{x=\delta} = 0$ (no slip at wall)

So: $u_z^* = \frac{u_z}{U_c}$ $x^* = x/\delta$

$$\therefore \quad \mu \frac{U_c}{\delta^2} \frac{\partial^2 u_z^*}{\partial x^{*2}} = -\rho g$$

$$\therefore \frac{\partial^2 u_z^*}{\partial x^{*2}} = -\underset{\underset{1}{\shortparallel}}{\left[\frac{\rho g d^2}{\mu U_c}\right]}$$

so $U_c = \dfrac{\rho g d^2}{\mu}$

and $u_z^* = -\frac{1}{2} x^{*2} + A x^* + B$

$$\left.\frac{\partial u_z^*}{\partial x^*}\right|_{x^*=0} = 0 \quad \therefore \quad A = 0$$

$$\left. u_z^* \right|_{x^*=1} = 0 \quad \therefore \quad -\frac{1}{2} + 0 + B = 0$$

so $B = +\frac{1}{2}$

and $u_z^* = -\frac{1}{2} x^{*2} + \frac{1}{2} = \frac{1}{2}(1 - x^{*2})$

w/ $\left. u_z^* \right|_{x^*=0} = \frac{1}{2}$ (velocity at interface)

we also have the average velocity $\bar{u}_z^*$

$$\bar{u}_z^* = \int_0^1 u_z^* \, dx^* = \frac{1}{2}\left(1 - \frac{1}{3}\right) = \frac{1}{3}$$

which is also useful.

ok, now for mass transfer!

we have:

$$\underbrace{\cancel{\frac{\partial c_A}{\partial t}}}_{SS} + \underset{\sim}{\nabla} \cdot \underset{\sim}{N_A} = \underbrace{\cancel{R_A}}_{\text{No rxn}}$$

$$\therefore \quad \frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Az}}{\partial z} = 0$$

Now $N_{Az} = x_A (N_{Az} + N_{Bz}) - c\,\mathcal{D}_{AB} \frac{\partial x_A}{\partial z}$

$$= c_A (x_A u_{Az} + x_B u_{Bz}) - c\,\mathcal{D}_{AB} \frac{\partial x_A}{\partial z}$$

we take $u_{Az} = u_{Bz} = u_z$! (dif^{n} is much too small to affect velocity in z direction!)

If $c \approx cst$ then:

$$N_{Az} = c_A u_z - \underbrace{\cancel{\mathcal{D}_{AB} \frac{\partial c_A}{\partial z}}}_{\text{Also small!}}$$

Now $N_{Ax} = x_A (N_{Ax} + N_{Bx}) - c\,\mathcal{D}_{AB} \frac{\partial x_A}{\partial x}$

$$\cong c_A (x_A u_{Ax} + x_B u_{Bx}) - \mathcal{D}_{AB} \frac{\partial c_A}{\partial x}$$

If there is no net flow in x-dir, and $x_A << 1$ then

$$N_{Ax} \approx -\mathcal{D}_{AB}\frac{\partial c_A}{\partial x}$$

so since $\underset{\sim}{\nabla}\cdot\underset{\sim}{N}_A = 0$ we get

$$\frac{\partial}{\partial z}(u_z c_A) - \frac{\partial}{\partial x}\left(\mathcal{D}_{AB}\frac{\partial c_A}{\partial x}\right) = 0$$

if $\mathcal{D}_{AB}$ is constant and since $\frac{\partial u_z}{\partial z} = 0$ we get

$$u_z\frac{\partial c_A}{\partial z} = \mathcal{D}_{AB}\frac{\partial^2 c_A}{\partial x^2}$$

This is just a specific example of the convective diffusion equation usually used for liquids:

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{u}\cdot\underset{\sim}{\nabla} c_A = \mathcal{D}_{AB}\nabla^2 c_A + R_A$$

Note the similarity w/ energy:

$$\frac{\partial T}{\partial t} + \underset{\sim}{u}\cdot\underset{\sim}{\nabla} T = \alpha\nabla^2 T + \frac{\dot{S}}{\rho\hat{C}_p}$$

These equations are identical and w/ the same B.C's have identical solutions!

Ok, for this problem we have

$$\frac{3}{2}\bar{U}\left(1-\frac{x^2}{\ell^2}\right)\frac{\partial C_A}{\partial z} = \mathcal{D}_{AB}\frac{\partial^2 C_A}{\partial x^2}$$

where $\bar{U} = \frac{1}{3}U_c = \frac{1}{3}\frac{\rho g \ell^2}{\mu}$

$$C_A\Big|_{x=0} = C_{A_0} \qquad \frac{\partial C_A}{\partial x}\Big|_{x=\ell} = 0 \quad \text{(impermeable)}$$

Let's scale

$$x^* = \frac{x}{\ell}\,, \qquad z^* = z/z_c\,, \qquad C_A^* = \frac{C_{A_0}-C_A}{C_{A_0}}$$

choose so that $C_A^* \to 0$ as $z^* \to \infty$

$$\therefore \quad \frac{3}{2}\frac{\bar{U}\,C_{A_0}}{z_c}\left(1-x^{*2}\right)\frac{\partial C_A^*}{\partial z^*} = \frac{\mathcal{D}_{AB}C_{A_0}}{\ell^2}\frac{\partial^2 C_A^*}{\partial x^{*2}}$$

Or dividing:

$$\frac{3}{2}\left(1-x^{*2}\right)\frac{\partial C_A^*}{\partial z^*} = \underbrace{\left[\frac{z_c\,\mathcal{D}_{AB}}{\bar{U}\,\ell^2}\right]}_{=1}\frac{\partial^2 C_A^*}{\partial x^{*2}}$$

So $$z_c = \frac{\bar{U}\, d^2}{D_{AB}} \equiv \underbrace{\bar{U}}_{\text{average velocity}} \underbrace{\left(\frac{d^2}{D_{AB}}\right)}_{\text{diff}^n\text{ time}}$$

and $$\frac{3}{2}(1 - x^{*2})\frac{\partial C_A^*}{\partial z^*} = \frac{\partial^2 C_A^*}{\partial x^{*2}}$$

w/ BC's: $C_A^*\big|_{x^*=0} = 0$ $\quad \frac{\partial C_A^*}{\partial x^*}\Big|_{x^*=1} = 0$

Solve via sep. variables:

$$C_A^* = G(z^*)F(x^*)$$

$$\therefore \frac{G'}{G} = \frac{F''}{\frac{3}{2}(1-x^{*2})F} = -\sigma^2$$

$$G = e^{-\sigma^2 z^*}$$

$$\begin{cases} F'' + \frac{3}{2}(1-x^{*2})F\sigma^2 = 0 \\ F(0) = 0 \quad F'(1) = 0 \end{cases}$$

→ SL problem w/ weight fⁿ $= \frac{3}{2}(1-x^{*2})$

So $$C_A^* = \sum_{n=1}^{\infty} A_n e^{-\sigma_n^2 z^*} F_n(x^*)$$

Because of wt fn, there is no analytical solution. If $\frac{3}{2}(1-x^{*2})$ is replaced by 1 (e.g., avg. value) then:

$$F = A\sin\sigma x^* + B\cos\sigma x^*$$

$F(0)=0 \therefore B=0$

$F'(1)=0 \therefore \sigma_n = (n-\frac{1}{2})\pi$

and

$$C_A^* \cong \sum_{n=1}^{\infty} A_n e^{-\sigma_n^2 z^*} \sin\sigma_n x^*$$

where A_n would be determined from the IC via orthogonality!

Just as in heat transfer we want to define a mass transfer coefficient!

$$N_{Ax}\Big|_{x=0} = -k_M\left(C_A\Big|_{x=0} - (C_A)_{bulk}\right)$$

where $(C_A)_{bulk} = \dfrac{\int_0^d u_z C_A \, dx}{\int_0^d u_z \, dx}$

Now $N_{Ax}\Big|_{x=0} = -\mathcal{D}_{AB} \dfrac{\partial C_A}{\partial x}\Big|_{x=0}$

so since $C_A\Big|_{x=0} = C_{A_0}$ we get

$$\frac{k_m d}{\mathcal{D}_{AB}} = \frac{-1}{(C_A^*)_{bulk}} \frac{\partial C_A^*}{\partial x^*}\Big|_{x^*=0}$$

If $z^* >> 1$ we are dominated by the lead eigenvalue!

$$\therefore \frac{k_m d}{\mathcal{D}_{AB}} \approx \frac{\sigma_1}{\int_0^1 \sin\sigma_1 x^* dx^*} = \sigma_1^2 = \frac{\pi^2}{4}$$

A similar result is obtained for the parabolic profile numerically.

The problem is that this takes a huge distance to reach the asymptote!

How far? Look at some numbers:

Suppose we have $d = 1mm$ (very thin) w/ water ($\nu \equiv \mu/\rho = 0.01\ cm^2/s$)

Now suppose we have a typical small molecule diffusing in water, $D \sim 10^{-5}\ cm^2/s$

we get
$$z_c = \frac{\bar{U} d^2}{D_{AB}} = \frac{1}{3}\frac{d^2}{D_{AB}}\ \frac{g d^2}{\nu}$$
$$= \frac{1}{3}\frac{g d^4}{D_{AB}\nu} = \frac{1}{3}\frac{(980)(0.1)^4}{(10^{-5})(0.01)} = 3.3\ km!!$$

For any reasonable length we don't reach the asymptote! Only the surface matters unless d was $\sim 100\mu m$ or less! (note that approach to SS is governed by the decay of the second eigenvalue $\left(\frac{3\pi}{2}\right)^2$)

Still, we now turn to the thin boundary layer problem!

Just as in heat transfer, we have:

$$\frac{3}{2}\bar{U}\left(1-\frac{x^2}{d^2}\right)\frac{\partial C_A}{\partial z} = \mathcal{D}_{AB}\frac{\partial^2 C_A}{\partial x^2}$$

We are looking for a <u>thin</u> layer of $O(\delta/d \ll 1)$. So:

$$x^* = x/\delta, \quad z^* = z/z_c \qquad C_A^* = \frac{C_A}{C_{A_0}}$$

So: $$\frac{3}{2}\bar{U}\left(1-\frac{\delta^2}{d^2}x^{*2}\right)\frac{C_{A_0}}{z_c}\frac{\partial C_A^*}{\partial z^*} = \frac{\mathcal{D}_{AB}C_{A_0}}{\delta^2}\frac{\partial^2 C_A^*}{\partial x^{*2}}$$

small!

$$\therefore \underbrace{\left[\frac{\frac{3}{2}\bar{U}\delta^2}{\mathcal{D}_{AB}z_c}\right]}_{=1}\frac{\partial C_A^*}{\partial z^*} = \frac{\partial^2 C_A^*}{\partial x^{*2}}$$

$$\therefore \delta = \left(\frac{\mathcal{D}_{AB}z_c}{\frac{3}{2}\bar{U}}\right)^{1/2}$$ – diffusion length!

BC's: $C_A^*\Big|_{x^*=0} = 1, \quad \frac{\partial C_A^*}{\partial x^*}\Big|_{x^*\to d/\delta=\infty} = 0$

$C_A^*\Big|_{z^*=0} = 0$ (clean at start - but really only the <u>difference</u> matters!)

This is <u>identical</u> to unsteady heating of a slab (or equiv. convection prob!)

We <u>know</u> the answer!

$$C_A^* = f(\eta), \quad \eta = \frac{x^*}{z^{*1/2}}$$ (from <u>scaling</u> or <u>stretching</u>)

So: $$\frac{\partial C_A^*}{\partial x^*} = f' \frac{\partial \eta}{\partial x^*} = \frac{1}{z^{*1/2}} f'$$

$$\frac{\partial^2 C_A^*}{\partial x^{*2}} = \frac{1}{z^*} f''$$

$$\frac{\partial C_A^*}{\partial z^*} = f' \left(-\frac{1}{2} \frac{\eta}{z^*} \right)$$

$$\therefore \quad f'' = -\frac{1}{2} \eta f'$$

$$f(0) = 1, \quad f'(\infty) = 0$$

Solving: $$\frac{1}{f'} f'' \equiv \frac{d \ln f'}{d\eta} = -\frac{1}{2}\eta$$

$$f' = c_1 e^{-\eta^2/4}$$

$$f = 1 + c_1 \int_0^\eta e^{-\eta^2/4} d\eta$$

Now $f(\infty) = 0$ ($f'(\infty)$ too...)

$$\therefore \quad C_1 = \frac{-1}{\int_0^\infty e^{-\eta^2/4}\,d\eta} = -\frac{1}{\sqrt{\pi}} = f'(0)!$$

We want to get the mass transfer coefficient:

$$N_{A_x} = -k_{m_{loc}}\left(C_{A_0} - (C_A)_b\right) = -\mathcal{D}_{AB}\left.\frac{\partial C_A}{\partial x}\right|_{x=0}$$

Now $\underline{\underline{(C_A)_b = 0}}$ (BL is <u>thin</u>)

$$\therefore \quad k_{m_{loc}} = -\frac{\mathcal{D}_{AB}}{\delta}\left.\frac{\partial C_A^*}{\partial x^*}\right|_{x^*=0}$$

$$= +\frac{\mathcal{D}_{AB}}{\delta}\frac{1}{z^{*1/2}}\frac{1}{\sqrt{\pi}}$$

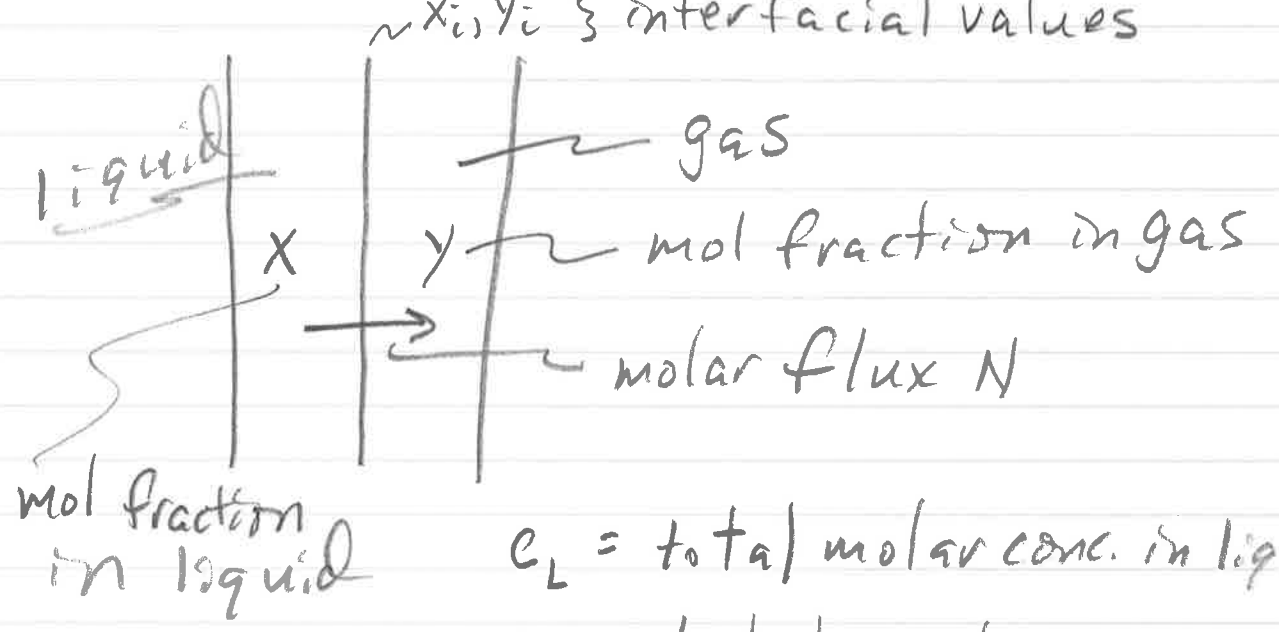
$$= \frac{\mathcal{D}_{AB}}{\left(\frac{\mathcal{D}_{AB}\,z}{\frac{3}{2}\bar{U}}\right)^{1/2}}\frac{1}{\sqrt{\pi}} = \frac{\left(\frac{3}{2}\bar{U}\mathcal{D}_{AB}\right)^{1/2}}{z^{1/2}}\frac{1}{\sqrt{\pi}}$$

We want the <u>average</u> k_m over some height H:

$$\bar{k}_m = \frac{1}{H}\int_0^H k_{m_{loc}}\,dz = \frac{2}{\sqrt{\pi}}\left(\frac{\frac{3}{2}\bar{U}\mathcal{D}_{AB}}{H}\right)^{1/2}$$

In general, we would do gas-liquid contacting in a packed column. It's filled with packing rings, saddles, lot's of shapes that give you a large surface area for mass transfer. The liquid side mass transfer coef. k_L will scale like that above, but (because the flow pattern is very complex) is given by correlation for different shapes.

In the last lecture we looked at the mass transfer coef. for a liquid film K_m (or k_L). This was for a gas A absorbing *into* a liquid, so there was *no gas phase* resistance. In general there's *both* (but liquid is *usually* larger!) and we want an *overall mass transfer* coef. (analogous to overall heat transfer coef!). Let's look at this:



c_L = total molar conc. in liquid

c_G = total molar conc. in gas

Just as the heat flux is the same on both sides of an interface, so is the molar flux!

Let $N = K_L C_L (x - x_i) = K_g C_g (y_i - y)$

$$\therefore \frac{N}{K_L C_L} = x - x_i \; ; \quad \frac{N}{K_g C_g} = y_i - y$$

We have the equilibrium Henry's Law equilibrium relation at the interface:

$$y_i = m x_i \qquad \text{(dilute sol'n)}$$

$$\therefore \frac{N}{K_g C_g m} = x_i - y/m$$

Adding these up yields:

$$N\left(\frac{1}{K_L C_L} + \frac{1}{m K_g C_g} \right) = x - \frac{y}{m}$$

$$\text{So} \quad N = \frac{x - y/m}{\frac{1}{K_L C_L} + \frac{1}{m K_g C_g}}$$

So the molar flux depends on the difference between the bulk liquid concentration and the liquid concentration that would be in equilibrium with the gas concentration. The overall (liquid side) mass transfer coef. is obtained by adding resistances in each side, w/ gas side adjusted by Henry's law constant.

This works on a mass basis too!

In a packed tower - like a catalyst pellet - you have some area/vol a of interface.

We can define an overall liquid mass transfer coef: $K_L^o a$

$$K_L^0 a = \frac{1}{\frac{1}{K_L a} + \frac{1}{H K_g a}}$$

$K_L^0 a$ has units 1/Time

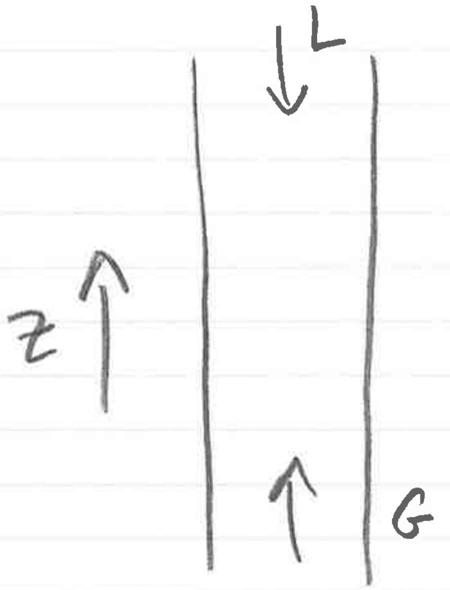
and H is the Henry's Law constant (adjusted for gas & liquid total molar conc.)

Now in general:

$$K_L^0 a = K_L a \left(\frac{1}{1 + \frac{K_L}{H K_g}} \right)$$

For many cases $\frac{H K_g}{K_L} >> 1$ so we are liquid phase limited. This has the advantage that gas phase mass transfer is less important in tower design.

Ok, how do we use all this? Let's look at designing a tower to strip out a pollutant (VOC) from water:



c_L = liquid conc. of pollutant

C_G = gas conc. of pollutant

$L \equiv$ superficial liquid flow rate (Vol/Area·Time)

$G \equiv$ superficial gas flow

$K_L^o a \equiv$ overall liquid mass transfer coef (units 1/T)

We have the mass (or molar) balance:

$$L \frac{dc_L}{dz} = K_L^o a \left(c_L - c_L^* \right)$$

where $c_L^* \equiv \frac{C_G}{H}$ (conc. in eq. w/ C_G)

so just like heat exchanger:

$$\frac{L}{K_L^o a} \frac{dc_L}{c_L - c_L^*} = dz$$

So

$$Z_T = \frac{L}{K_L^0 a} \int_{(C_L)_{in}}^{(C_L)_{out}} \frac{dC_L}{C_L - C_L^*}$$

where $(C_L)_{out}$ is the conc. at the bottom and $(C_L)_{in}$ is the conc. at the top.

This is usually written as:

$$Z_T = \underset{\substack{\uparrow \\ \text{ht of a transfer unit} \\ \text{based on liquid phase}}}{H_{ox}} N_{ox} \leftarrow \text{number of transfer units based on liquid phase}$$

where $N_{ox} = \int_{(C_L)_{in}}^{(C_L)_{out}} \frac{dC_L}{C_L - C_L^*}$

$$\equiv \int_{x_{in}}^{x_{out}} \frac{dx}{x - x^*}$$ based on mole fractions (same thing)

$H_{ox} \equiv \frac{L}{K_L^0 a} \equiv$ ht of a transfer unit.

Now we need to determine the NTU $\equiv N_{0x}$

We need a mass (or mole) balance:

$$\underbrace{\left(C_G - (C_G)_{in}\right)G}_{\text{rate mass (or moles) are gained from } z \text{ to bottom}} = \underbrace{\left(C_L - (C_L)_{out}\right)L}_{\text{rate mass (or moles) are lost to liquid from } z \text{ to bottom}}$$

Now $C_L^* = \frac{C_G}{H} \leftarrow$ Henry's law

$$\therefore\; C_L^* = \frac{(C_G)_{in} G}{H} + \left(C_L - (C_L)_{out}\right)\frac{L}{H}$$

We shall take $(C_G)_{in} = 0$ (clean gas) as it makes things a little simpler

We also <u>define</u> a stripping factor

$$R \equiv \frac{HG}{L}$$

This is the <u>capacity</u> of the gas stream to absorb our pollutant. If $R < 1$ you <u>can't</u> get it all out even for an infinite Z_T!

So: $C_L^* = \dfrac{C_L - (C_L)_{out}}{R}$

$$\therefore\ N_{ox} = \int_{(C_L)_{in}}^{(C_L)_{out}} \frac{dC_L}{C_L - \dfrac{(C_L - (C_L)_{out})}{R}}$$

$$= \frac{R}{R-1} \ln\left[\frac{\left((C_L)_{in}/(C_L)_{out}\right)(R-1)+1}{R}\right]$$

if $R \neq 1$

and $\left[(C_L)_{in}/(C_L)_{out}\right] - 1$ if $R = 1$

So to size a tower for some desired separation (e.g., you know $(C_L)_{in}/(C_L)_{out}$), you need to know your gas & liquid flow rates and Henry's law constant to get R and N_{ox}, then estimate $H_{ox} \equiv \dfrac{L}{K_L^0 a}$ to get the tower height!

This made a number of assumptions:

1) Gas enters "clean" (e.g. $(C_G)_{in} = 0$) - usually good for this application.

2) H (or m) is <u>constant</u>: This requires a constant temperature in your tower. (You <u>also</u> assume it's valid!)

3) There's no <u>mixing</u> in your tower (plug flow for both phases) and that it's <u>uniform</u>)

4) $K_L^0 a$ is <u>constant</u>.

These are actually the sorts of approx. we made for a double-pipe heat exch, but they were more robust there!

Now let's turn to <u>correlations</u> for $k_L a$ and $k_G a$, necessary to get $K_L^0 a$

In the last lecture we showed that there were two limits.

If the film depth approaches equilibrium then $k_L \sim \mathcal{D}_{AB}$ - but this almost never happens! Instead we use penetration theory

$$k_L \sim \frac{\mathcal{D}_{AB}}{(\mathcal{D}_{AB} t_c)^{1/2}}$$ where t_c is a contact time. For our falling film this was H/U.

There are a number of correlations based on experimental measurements. These can get pretty complicated!

A sophisticated one is the Onda correlation. Suppose we have some total area/vol. of our packing a_t. Not all of this is wetted. The wetted area a_w is given by:

$$\frac{a_w}{a_t} = 1 - \exp\left[-1.45\left(\sigma_c/\sigma_L\right)^{0.75} \times (Re_L)^{0.1}(Fr)^{-0.05}(We_L)^{0.2}\right]$$

The ratio σ_c / σ_L is the ratio of the packing surface tension to the liquid surface tension - basically a measure of wettability. Re_L is the liquid phase Reynolds number $\left(\frac{\rho_L L}{a_t \mu_L} \right)$ (recall a_t has units of 1/length). Fr_L is the Froude = $\left(\frac{L^2 a_t}{g} \right)$, the ratio of inertia/gravity. We_L is the Weber number = $\left(\frac{L^2 \rho_L}{\sigma_L a_t} \right)$ which is inertia / surface tension.

So as L increases (more liquid) the wetted area approaches the total area. The key correlation is that for k_L: we have the Sherwood number:

$$Sh = \frac{k_L}{a\, D_L}$$

units 1/length! $\nearrow$ a

$D_L \rightarrow$ liquid side dif.

so: $$Sh = 0.0051 \left(\frac{\mu_L a_t^3}{\rho_L^2 g} \right)^{-1/3} (Re_L)^{2/3} (Sc_L)^{1/2} (a_t d_p)^{0.4}$$

where $\frac{\mu_L a_t^3}{\rho_L^2 g}$ ≡ Galileo number, which is a 1/Reynolds number for a falling film,

Sc_L ≡ Schmidt # = $\frac{\nu_L}{D_L} \leftarrow \frac{\mu_L}{\rho_L}$

d_p ≡ nominal packing size

so $a_t d_p$ ≡ shape factor

This would yield

$$K_L = 0.0051 \left(\frac{\mu_L g}{\rho_L} \right)^{1/3} Re^{2/3} \, Sc^{\overset{\text{note neg}}{\downarrow} -1/2} (a_t d_p)^{0.4}$$

so $k_L \sim D_L^{1/2}$

For the gas phase:

$$K_G = c \, a_t D_G \underbrace{\left(\frac{G \rho_G}{a_t \mu_G} \right)^{0.7}}_{\uparrow \, Re_G} \underbrace{\left(\frac{\mu_G}{\rho_G D_G} \right)^{1/3}}_{\uparrow \, Sc_G} (a_t d_p)^{-2}$$

The constant $c = 2.0$ if $d_p < 15\,mm$ and $= 5.23$ otherwise.

The key thing to note is that $k_G \sim D_G^{2/3}$, a different dependence than the liquid side.

Finally, you calculate the overall coefficient:

$$\overset{o}{K}_L a \equiv \overset{o}{K}_L a_w = a_w \left[\frac{1}{k_L} + \frac{1}{Hk_G}\right]^{-1}$$

A note on Henry's law constants: These are given in different ways: either a molar basis (e.g. $y = mx$) or a volume basis, or a mass basis.

$$\text{Our } H = \frac{(C_A)_{Gas}}{(C_A)_{liquid}} = \frac{\text{total molar conc gas} * y}{\text{total molar conc. liq.} * x}$$

$$= \frac{\rho_{gas}/M_{gas}}{\rho_{liq}/M_{liq}} \cdot m$$

This gets it into a volume basis which is necessary for calculating $R = \frac{HG}{L}$ if G and L are superficial velocities (vol/area·time) which is easier to work with. Any form works - you just have to be consistent and check!

If you ever have to design a stripper for VOCs, read through the award winning thesis of Staudinger - it's a remarkably clear discussion of the problem! It's linked into today's notes.

Nowadays industry is moving towards structured packings as they have lower resistance. A recent review (2021) of correlations for these is provided by Flagiello, et al., also linked in.

Now that we've looked at interfacial transport, let's look at problems in convective diffusion which are functions of both space and time. A classic phenomenon in this area is Taylor (or Taylor-Aris) Dispersion. This is the mechanism which leads to peak broadening in a GC, among many examples!

If diffusion is so slow, why do you get peak broadening? It's because diffusion is so slow!!

Taylor dispersion is the combination of shear (or anything which causes different molecules of the same species to move w/ different velocities coupled with the slow interchange between different velocities due to slow diffusion.

This means that the Taylor dispersivity is inversely proportional to the (small) molecular diffusivity. That's why it's so big!

To understand this phenomenon, we start with a much simpler problem: transient diffusion from an initial point distribution (no shear!)

So: $$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad c\Big|_{t=0} = \underset{\substack{\uparrow \\ \text{total amount} \\ \text{of solute}}}{I}\,\delta(x)$$

$$c\Big|_{x\to\pm\infty} = 0$$

Solute is conserved, so $\int_{-\infty}^{\infty} c\,dx = I$

at all times!

$\delta(x)$ is known as the Dirac δ f$^{\underline{n}}$

$\delta(x) = 0$ if $x \neq 0$

$$\int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

(e.g., a GC peak w/ zero width)

We want to get $c(x,t)$!

Let's scale:

$$c^* = \frac{c}{c_c}, \quad x^* = \frac{x}{x_c}, \quad t^* = t/t_c$$

So:
$$\frac{\partial c^*}{\partial t^*} = \underbrace{\left[\frac{D t_c}{x_c^2}\right]}_{1} \frac{\partial^2 c^*}{\partial x^{*2}}$$

$$\text{so } \frac{x_c}{(D t_c)^{1/2}} = 1$$

and
$$\int_{-\infty}^{\infty} [c_c x_c]\, c^* dx^* = I$$

$$\therefore \int_{-\infty}^{\infty} c^* dx^* = \left[\frac{I}{c_c x_c}\right] = 1$$

$$\text{so } c_c = \frac{I}{x_c} = \frac{I}{(D t_c)^{1/2}}$$

Because our problem is *dimensionless* and we never specified t_c, it will be self-similar! From scaling (in canonical form!):

$$c^* t^{*1/2} = f(\eta) \qquad \eta = \frac{x^*}{t^{*1/2}}$$

Let's solve! $c^* = t^{*-1/2} f$

$$\therefore \frac{\partial^2 c^*}{\partial x^{*2}} = t^{*-3/2} f''$$

$$\frac{\partial c^*}{\partial t^*} = -\frac{1}{2} t^{*-3/2} f - \frac{1}{2} \frac{\eta}{t^*} t^{*-1/2} f'$$

$$= -\frac{1}{2} t^{*-3/2} (f + \eta f')$$

So: $f'' = -\frac{1}{2}(f + \eta f')$

$$f\Big|_{\eta = \pm\infty} = 0 \qquad \int_{-\infty}^{\infty} f \, d\eta = 1$$

The *trick* to solving is:

$$f + \eta f' \equiv (\eta f)'$$

$$\therefore \quad f'' = -\tfrac{1}{2}(\zeta f)'$$

so

$$f' = -\tfrac{1}{2}\zeta f + \cancelto{0}{cst} \quad \text{as } f\big|_{\zeta=\pm\infty} = 0$$

$$\therefore \quad \frac{f'}{f} = \frac{\partial \ln f}{\partial \zeta} = -\frac{1}{2}\zeta$$

so

$$f = c_1 e^{-\frac{1}{4}\zeta^2}$$

Now

$$\int_{-\infty}^{\infty} f\, d\zeta = 1 = c_1 \int_{-\infty}^{\infty} e^{-\frac{1}{4}\zeta^2} d\zeta = c_1\sqrt{4\pi}$$

So:

$$f = \frac{1}{\sqrt{4\pi}} e^{-\frac{1}{4}\zeta^2}$$

and

$$c = \frac{I}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

This is exactly the Gaussian (Normal) Distribution from statistics!

The mean location of the solute molecules is:

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x \; c(x,t)\, dx}{\int_{-\infty}^{\infty} c(x,t)\, dx}$$

This is the *first* *moment* of the distribution $\equiv m_1$

For *this* problem, $m_1 = 0$ by symmetry!

We can define the *second* *moment*

$$m_2 \equiv \frac{\int_{-\infty}^{\infty} x^2 \, c(x,t)\, dx}{\int_{-\infty}^{\infty} c(x,t)\, dx}$$

and the (closely related) *variance*:

$$\sigma^2 \equiv \frac{\int_{-\infty}^{\infty} (x-\bar{x})^2 \, c(x,t)\, dx}{\int_{-\infty}^{\infty} c(x,t)\, dx}$$

$$= m_2 - m_1^2$$

For *this* problem:

$$m_1 = 0 \quad , \quad m_2 = \int_{-\infty}^{\infty} \frac{x^2}{\sqrt{4\pi D t}}\, e^{-\frac{x^2}{4Dt}}\, dx$$

$$= \underline{2Dt}$$

so $\sigma^2 \equiv 2Dt$: The variance of the distribution grows *linearly* w/ a rate $2D$!

You can *measure* the Stokes-Einstein diffusivity of a colloidal particle by watching it move w/ Brownian motion and plotting the *variance* of location vs. time. The slope vs. t is just $2D$!

OK, how do we use this? If we calculate the rate of growth of the variance of our concentration distribution in a shear flow, it's just $2K$ ← Taylor Dispersivity!

Let's look at the simplest problem:

TA Dispersion in Channel Flow (plane-Poiseuille flow):

$$u \doteq u_x = \frac{3}{2} U \left(1 - y^2/b^2\right)$$

Now $\dfrac{\partial c}{\partial t} + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} c = D \nabla^2 c$

so: $\dfrac{\partial c}{\partial t} + u \dfrac{\partial c}{\partial x} = D \left(\dfrac{\partial^2 c}{\partial x^2} + \dfrac{\partial^2 c}{\partial y^2} \right)$

$\left.\dfrac{\partial c}{\partial y}\right|_{y=0} = 0$ (sym.) $\quad \left.\dfrac{\partial c}{\partial y}\right|_{y=\pm b} = 0$ (no flux)

and: $\displaystyle\int_0^b \int_{-\infty}^{\infty} c \, dx \, dy = I$ (total amount)

$\hookrightarrow$ just use top half of channel (sym)

We'll leave the IC alone for a bit!

Let's scale

$$y^* = y/b \qquad u^* = \frac{u}{U} = \frac{3}{2}\left(1 - y^{*2}\right)$$

$$x^* = \frac{x}{x_c} \qquad c^* = \frac{c}{C_c} \qquad t^* = t/t_c$$

So:

$$\frac{C_c}{t_c}\frac{\partial c^*}{\partial t^*} + \frac{UC_c}{x_c}u^*\frac{\partial c^*}{\partial x^*} = \frac{DC_c}{b^2}\frac{\partial^2 c^*}{\partial y^{*2}} + \frac{DC_c}{x_c^2}\frac{\partial^2 c^*}{\partial x^{*2}}$$

We anticipate that the key mechanisms are diffusion in the y-dir & convection in the x-dir, with diffusion in the x-dir small

$$\therefore \underset{\substack{\| \\ 1}}{\left[\frac{b^2}{Dt_c}\right]}\frac{\partial c^*}{\partial t^*} + \underset{\substack{\| \\ 1}}{\left[\frac{Ub^2}{Dx_c}\right]}u^*\frac{\partial c^*}{\partial x^*} = \frac{\partial^2 c^*}{\partial y^{*2}} + \frac{b^2}{x_c^2}\frac{\partial^2 c^*}{\partial x^{*2}}$$

so $t_c = b^2/D$ (diffⁿ time!)

$x_c = U\dfrac{b^2}{D} \equiv Ut_c$ (convection length in difⁿ time!)

So:

$$\frac{\partial c^*}{\partial t^*} + u^* \frac{\partial c^*}{\partial x^*} = \frac{\partial^2 c^*}{\partial y^{*2}} + \left(\frac{D}{Ub}\right)^2 \frac{\partial^2 c^*}{\partial x^{*2}}$$

and the integral condition:

$$\int_0^1 \int_{-\infty}^{\infty} c^* dx^* dy^* = \left[\frac{I}{c_c x_c b}\right] = 1$$

where we just use the top half.

We have $\left.\frac{\partial c^*}{\partial y^*}\right|_{y^*=0,1} = 0$

We will use the method of moments approach of Aris. We define:

$$c_p^* = \int_{-\infty}^{\infty} x^{*^p} c^* dx^*$$

$$m_p^* = \int_0^1 c_p^* dy^* \quad \text{(the p'th moment)}$$

Recall we need to figure out the

<u>rate</u> of gr<u>owth</u> of the va<u>riance</u> to get K!

$$\sigma_x^2 \equiv \frac{\int_{-\infty}^{\infty}\int_0^b (x-\bar{x})^2 c \, dy \, dx}{\int_{-\infty}^{\infty}\int_0^b c \, dy \, dx}$$

where $\bar{x} = \dfrac{\int_{-\infty}^{\infty}\int_0^b x \, c \, dy \, dx}{\int_{-\infty}^{\infty}\int_0^b c \, dy \, dx}$

<u>and</u> $\dfrac{d \sigma_x^2}{dt} = \underline{2K}$

Scaling: $\bar{x}^* = \dfrac{\bar{x}}{x_c}$ <u>and</u> $\bar{x}^* = m_1^*$ by definition!

Likewise, $\sigma_x^2 = \left(\dfrac{Ub^2}{D}\right)^2 (m_2^* - m_1^{*2})$

So $$2\kappa = \frac{d\sigma_x^2}{dt} = \left(\frac{Ub^2}{D}\right)\left(\frac{D}{b^2}\right)\frac{d}{dt^*}\left(m_2^* - m_1^{*2}\right)$$

or $$\frac{\kappa}{D} = \frac{1}{2}\left(\frac{Ub}{D}\right)^2\left(\frac{dm_2^*}{dt^*} - 2\,m_1^*\frac{dm_1^*}{dt^*}\right)$$

So to get κ/D we need:

$$\frac{dm_1^*}{dt^*}\ ;\ m_1^*\ ;\ \frac{dm_2^*}{dt^*}$$

To get these moments we multiply the equation by x^{*p} and integrate!

We had:

$$\frac{\partial c^*}{\partial t^*} + u^*\frac{\partial c^*}{\partial x^*} = \left(\frac{D}{Ub}\right)^2\frac{\partial^2 c^*}{\partial x^{*2}} + \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$\text{w/ } \left.\frac{\partial c^*}{\partial y^*}\right|_{y^*=0,1} = 0$$

mult by x^{*p} & integrate over x^*!

$$\frac{\partial c_p^*}{\partial t^*} + \int_{-\infty}^{\infty} x^{*p} u^* \frac{\partial c^*}{\partial x^*}\,dx^* = \left(\frac{D}{Ub}\right)^2\int_{-\infty}^{\infty} x^{*p}\frac{\partial^2 c^*}{\partial x^{*2}}\,dx^* + \frac{\partial^2 c_p^*}{\partial y^{*2}}$$

where $C_p^* \equiv \int_{-\infty}^{\infty} x^{*p} c^* \, dx^*$

The two integrals are integrated by parts:

$$\int_{-\infty}^{\infty} x^{*p} u^* \frac{\partial c^*}{\partial x^*} dx^* = x^{*p} u^* c^* \Big|_{-\infty}^{\infty} - p \int_{-\infty}^{\infty} x^{*p-1} u^* c^* dx^*$$

Now $c^* \Big|_{x^* = \pm\infty} = 0$ (far away from peak!)

$$\therefore \int_{-\infty}^{\infty} x^{*p} u^* \frac{\partial c^*}{\partial x^*} dx^* = -p u^* C_{p-1}^*$$

Similarly (doing it twice):

$$\int_{-\infty}^{\infty} x^{*p} \frac{\partial^2 c^*}{\partial x^{*2}} dx^* = p(p-1) C_{p-2}^*$$

So:

$$\frac{\partial C_p^*}{\partial t^*} = p u^* C_{p-1}^* + p(p-1)\left(\frac{D}{Ub}\right)^2 C_{p-2}^* + \frac{\partial^2 C_p^*}{\partial y^{*2}}$$

$$\text{and} \quad \frac{\partial C_p^*}{\partial y^*}\Big|_{y^* = 0,1} = 0$$

Integrating again yields m_p^*:

$$\frac{\partial m_p^*}{\partial t^*} = p\int_0^1 u^* c_{p-1}^* \, dy^* + \left(\frac{D}{Ub}\right)^2 p(p-1)\, m_{p-2}^*$$

where the integral $\int_0^1 \frac{\partial^2 c_p^*}{\partial y^{*2}} dy^* = 0$ from BC's.

We thus have the sequence of problems!

$p=0$ $\quad \frac{\partial m_0^*}{\partial t^*} = 0 \qquad$ constant, so $m_0^* = 1$

$$\frac{\partial c_0^*}{\partial t^*} = \frac{\partial^2 c_0^*}{\partial y^{*2}}, \quad \left.\frac{\partial c_0^*}{\partial y^*}\right|_{y^*=0,1} = 0, \quad \int_0^1 c_0^* \, dy^* = 1$$

This also has the solution $c_0^* = 1$

Interpretation: Solute is conserved and the solute is uniformly distributed in the y-direction!

$p = 1$:

$$\frac{d m_1^*}{d t^*} = \int_0^1 u^* c_0^* \, dy^*$$

$$\frac{\partial c_1^*}{\partial t^*} = u^* c_0^* + \frac{\partial^2 c_1^*}{\partial y^{*2}}$$

w/ BC's $\left.\frac{\partial c_1^*}{\partial y^*}\right|_{0,1} = 0$, $\int_0^1 c_1^* \, dy^* = m_1^*$

and for $p = 2$:

$$\frac{d m_2^*}{d t^*} = 2 \int_0^1 u^* c_1^* \, dy^* + 2 \left(\frac{D}{Ub} \right)^2 m_0^*$$

which is all we need - c_2^* would be messy to get, but we don't need it!

So:

$m_0^* = 1$ (total amount of solute is conserved)

$c_0^* = 1$ (uniform distribution in y-dir)

P = 1:

$$\frac{\partial m_1^*}{\partial t^*} = \int_0^1 u^* \cdot (1)\, dy^* = 1$$

$\hookrightarrow$ u^* chosen to have avg. value = 1

We need an initial condition. We shall take the average x position of the solute at t = 0 to be zero

so $m_1^* = t^*$ (or $\langle u^* \rangle t^*$)

Now for the only hard part!

$$\frac{\partial c_1^*}{\partial t^*} = u^* + \frac{\partial^2 c_1^*}{\partial y^{*2}} \; ; \; \left.\frac{\partial c_1^*}{\partial y^*}\right|_{y^*=0,1} = 0$$

$$\int_0^1 c_1^* \, dy^* = m_1^* = t^* \quad (\text{or } \langle u^* \rangle t^*)$$

We seek a solution of the form

$$c_1^* = m_1^* + f(y^*)$$

So we get the equation:

$$\langle u^* \rangle = u^* + f''$$

or $f'' = \langle u^* \rangle - u^*$ } f is driven by deviation from avg. velocity

$$f'(0) = 0 , \quad f'(1) = 0$$

$$\int_0^1 f \, dy^* = 0$$

So: $f'' = \overset{\langle u^* \rangle}{1} - \overset{u^*}{\frac{3}{2}(1 - y^{*2})}$

$$= \frac{3}{2} y^{*2} - \frac{1}{2}$$

$f' = \frac{1}{2} y^{*3} - \frac{1}{2} y^* + \underset{0}{c}$ since $f'(0) = 0$

(note that $f'(1) = 0$ is automatically satisfied!)

$\therefore f = \frac{1}{8} y^{*4} - \frac{1}{4} y^{*2} + c$

Integrating: $\int_0^1 f \, dy^* = \frac{1}{40} - \frac{1}{12} + c = 0$

$$\therefore c = \frac{7}{120}$$

and $f = \frac{1}{8} y^{*4} - \frac{1}{4} y^{*2} + \frac{7}{120}$

So $c_1^* = m_1^* + f(y^*)$

Now for $p = 2$:

$$\frac{\partial m_2^*}{\partial t^*} = 2\int_0^1 u^* c_1^* \, dy^* + 2\left(\frac{D}{Ub}\right)^2 m_0^*$$

$$= 2m_1^* + 2\left(\frac{D}{Ub}\right)^2 m_0^* + 2\int_0^1 u^* f \, dy^*$$

But $\frac{K}{D} = \frac{1}{2}\left(\frac{Ub}{D}\right)^2\left(\frac{\partial m_2^*}{\partial t^*} - 2m_1^* \underbrace{\frac{\partial m_1^*}{\partial t^*}}_{=1}\right)$

So $\frac{K}{D} = \overset{\text{molecular dif.}}{1} + \left(\frac{Ub}{D}\right)^2 \int_0^1 u^* f \, dy^*$

since $\int_0^1 f \, dy^* = 0$ we get:

$$\frac{K}{D} = 1 + \left(\frac{Ub}{D}\right)^2 \int_0^1 (u^* - \langle u^* \rangle) f \, dy^*$$

$$= 1 + \frac{2}{105}\left(\frac{Ub}{D}\right)^2$$

For a tube you get

$\frac{K}{D} = 1 + \frac{1}{48}\left(\frac{Ua}{D}\right)^2$, almost the same

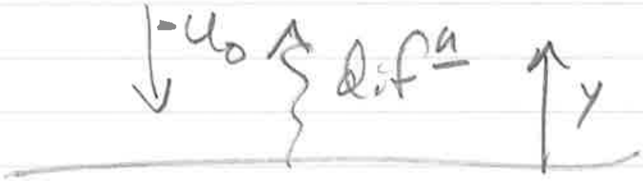
So what does this mean?

- The coefficient $\frac{2}{105}$ is small, but $\left(\frac{Ub}{D}\right)^2$ is usually huge, so Taylor disp. dominates solute spread in the flow direction.
- It scales as $\langle (u^* - \langle u^* \rangle)^2 \rangle$ so it is the difference between local and avg. velocities that drives it!
- It scales as $K \sim Ub\left(\frac{Ub}{D}\right)$ so it is cut off by diffusion - molecules sample different streamlines and (eventually) move with the average.
- The TA limit is reached only after molecules have a chance to diffuse across the channel: the transient is a SL eigenvalue problem.

A nice example of convective diffusion as applied to separations is Field Flow Fractionation (FFF). There are many subtypes of this, but the key is that they use a field (electric, gravity, magnetic, convection, etc.) to force a solute to one wall of a flow cell (usually channel or tube). This field force is balanced by diffusion yielding an equilibrium conc. distribution. This distribution combines with the shear flow in the flow cell to get separation!

To understand this, we need to know what a concentration polarization layer is.

Suppose, either due to convection through a porous membrane, or electric field, or gravity we have a solute velocity $-u_0$ toward an accumulating wall



We have the convective diffusion eq'n:

$$-u_0 \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$$

at steady state.

The flux at the wall is $-u_0 c\Big|_{y=0} - D\frac{\partial c}{\partial y}\Big|_{y=0} = 0$ as the solute doesn't penetrate!

The conc. as $y \to \infty = 0$

Let's scale:

$$c^* = \frac{c}{c_0} \qquad y^* = y/y_c$$

$$-\frac{u_0 C_0}{y_c}\frac{\partial c^*}{\partial y^*} = \frac{D C_0}{y_c^2}\frac{\partial^2 c^*}{\partial y^{*2}}$$

or $$-\underset{\substack{\shortparallel \\ 1}}{\left[\frac{y_c u_0}{D}\right]}\frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

$\therefore\ y_c = D/u_0$ which is the length scale of the concentration polarization layer.

We determine C_0 from the integral balance:

$$I = \int_0^\infty c\,dy$$

$$\therefore\quad C_0 = \frac{I}{y_c} = \frac{I}{(D/u_0)}$$

so low D or high u_0 yields high concentrations at the wall.

The solution is just:

$$c^* = e^{-y^*}$$

OK, how can we use this for sep.?

We *induce* a tangential flow!

Let $u_x = \dot{\gamma} y$ (simple shear)

So the *average solute velocity* is

$$\frac{\int_0^\infty u_x \, c \, dy}{\int_0^\infty c \, dy} = \dot{\gamma} y_c \int_0^\infty y^* e^{-y^*} dy^*$$

where $\int_0^\infty y^* e^{-y^*} dy^* = \underbrace{-y^* e^{-y^*}\Big|_0^\infty}_{=0} + \int_0^\infty e^{-y^*} dy^* = \underline{1}$

So the *average* solute velocity is

$$\langle u_x \rangle = \dot{\gamma} \frac{D}{U_0}$$

This would separate, say, nanoparticles by size through the Stokes-Einstein Diffusivity:

$$D = \frac{kT}{6\pi\mu a}$$

Alternatively if u_0 is different for different species (say, you had an electric field and different electrophoretic mobility, or a gravitational field and different sedimentation velocities) you would also separate.

To achieve separation you need the peak width to be smaller than the difference in elution time. The peak width is governed by Taylor dispersion! Let's look at this:

$$\frac{\partial c}{\partial t} + \dot{\gamma} y \frac{\partial c}{\partial x} - u_0 \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \qquad (x\text{-dif is very small!})$$

Let's scale:

$$t^* = t/t_c \,, \quad x^* = x/x_c \,, \quad y^* = y/y_c \,, \quad c^* = c/c_0$$

So:

$$\frac{c_0}{t_c} \frac{\partial c^*}{\partial t^*} + \frac{\dot{\gamma} y_c c_0}{x_c} y^* \frac{\partial c^*}{\partial x^*} - \frac{u_0 c_0}{y_c} \frac{\partial c^*}{\partial y^*} = \frac{D c_0}{y_c^2} \frac{\partial^2 c^*}{\partial y^{*2}}$$

Dividing by y-dif^n:

$$\underset{\substack{\parallel\\1}}{\left[\frac{y_c^2}{D t_c}\right]}\frac{\partial c^*}{\partial t^*} + \underset{\substack{\parallel\\1}}{\left[\frac{\dot{\gamma} y_c^3}{D x_c}\right]} y^*\frac{\partial c^*}{\partial x^*} - \underset{\substack{\parallel\\1}}{\left[\frac{u_0 y_c}{D}\right]}\frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

so $y_c = \frac{D}{u_0}$ as before

$x_c = \frac{\dot{\gamma} y_c^3}{D} = \frac{\dot{\gamma} D^2}{u_0^3}$ char. length in separation direction

$t_c = \frac{y_c^2}{D} = \frac{D}{u_0^2}$ char. timescale to reach TA limit.

and $\int_{-\infty}^{\infty}\int_0^{\infty} c \, dy \, dx = I$ (total amount)

$\therefore \quad c_0 = \frac{I}{y_c x_c}$

so $\int_{-\infty}^{\infty}\int_0^{\infty} c^* \, dy^* \, dx^* = 1$

and we have the BCs:

$$c^*\Big|_{y^*\to\infty} = 0 \quad , \quad c^*\Big|_{y^*=0} + \frac{\partial c^*}{\partial y^*}\Big|_{y^*=0} = 0$$

(no flux at wall)

From scaling alone we expect the Taylor Dispersivity κ to scale as:

$$\frac{\kappa}{D} \sim \frac{x_c^2}{D t_c} = \frac{(\dot{\gamma} y_c t_c)^2}{D t_c} = \frac{\dot{\gamma}^2 y_c^2 t_c}{D} = \frac{\dot{\gamma}^2 y_c^4}{D^2}$$

but $y_c = \frac{D}{u_0}$

$$\therefore \frac{\kappa}{D} \sim \frac{\dot{\gamma}^2 D^2}{u_0^4}$$

How do we get the constant? We can use the method of moments again!

$$\frac{\partial c^*}{\partial t^*} + y^* \frac{\partial c^*}{\partial x^*} - \frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

We define:

$$c_p^* = \int_{-\infty}^{\infty} x^{*p} c^* \, dx^*$$

$$m_p^* = \int_0^{\infty} c_p^* \, dy^*$$

and $$\frac{\kappa}{D} = 1 + \frac{\dot{\gamma}^2 D^2}{u_0^4} \left(\frac{dm_2^*}{dt^*} - 2m_1^* \frac{dm_1^*}{dt^*} \right)$$

After a fair amount of algebra, we get:

$$m_0^* = 1$$

$$c_0^* = e^{-y^*}$$

$$m_1^* = t^*$$

$$c_1^* = t^* e^{-y^*} + f(y^*)$$

where:

$$f(y^*) = e^{-y^*}\left(1 - y^* + \frac{1}{2} y^{*2} - \frac{1}{6} y^{*3}\right)$$

and

$$\frac{K}{D} = 1 + 2\,\frac{\dot{\gamma}^2 D^2}{u_0^4}$$

Ok, now that we have the solute velocity and dispersivity, what do we do with it? For chromatography it is usual to calculate the NTP: number of theoretical plates. This is the square of the ratio of elution time to peak SD (in time domain) or column length to peak SD in spatial domain.

we had the average velocity:

$$\langle u_x \rangle = \dot{\gamma} \frac{D}{u_0}$$

so if our plate length is L then our elution time is $t = \frac{L}{\langle u_x \rangle} = \frac{L u_0}{\dot{\gamma} D}$

our peak SD is just $(2Kt)^{1/2}$

so the ratio is:

$$NTP = \left[\frac{L}{(2Kt)^{1/2}} \right]^2 = \frac{L^2}{4 \, \frac{\dot{\gamma}^2 D^3}{u_0^4} \, \frac{L u_0}{\dot{\gamma} D}}$$

$$= \frac{1}{2} \, \frac{u_0^3 L}{\dot{\gamma} D^2}$$

of course, as $D/u_0 \to 0$ the solute moves <u>very</u> slowly!

In a practical FFF device you <u>don't</u> have a simple shear, instead you have plane-Poiseuille flow! For a channel of height h this yields:

$u_x = 6U\frac{y}{h}\left(1-\frac{y}{h}\right)$ where U is the average velocity. Near the wall (where the solute is - $\frac{D}{u_0 h} \ll 1$ for efficient separations) the shear rate is just

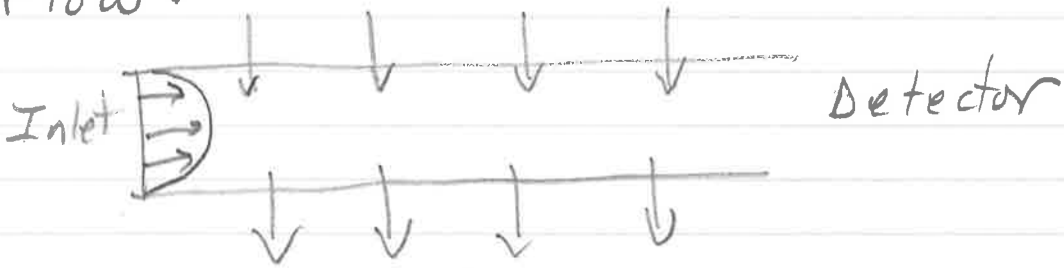
$$\dot{\gamma} = 6\frac{U}{h}$$

we can obtain a retention ratio

$$\frac{\langle u_x \rangle}{U} = 6\frac{D}{u_0 h}$$

In general this is in the range of [0.02, 0.1]

The first cross-flow FFF device had a channel w/ two porous walls for the cross flow:



This was pretty hard to make work. A better idea was proposed by Giddings

(Synonymous w/ *most* FFF techniques) of asymmetric flow field flow frac. (AF4 for short). Basically, it just replaced the *top* wall w/ glass! The lower (accumulating) wall was membrane supported on a glass frit:

This means that the y direction velocity (and x too) isn't uniform!

By continuity:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0$$

Now u_x is *still* a parabola, but it's leaking out!

$$\therefore \quad u_x = \left(U_0 - u_0 \frac{x}{h}\right) 6 \frac{y}{h}\left(1 - \frac{y}{h}\right)$$

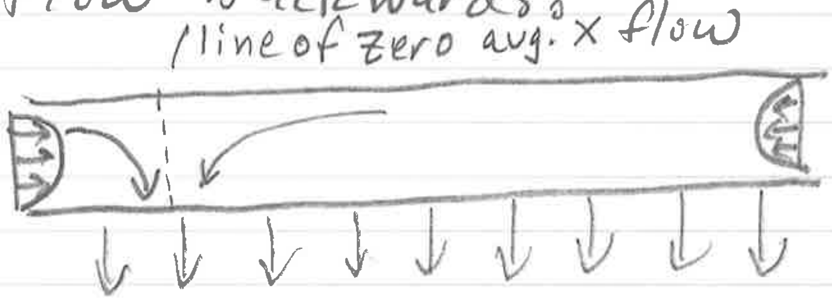
by a mass balance.

Plugging in we get for u_y:

$$\frac{\partial u_y}{\partial y} = -\frac{\partial u_x}{\partial x} = +\frac{u_0}{h}\, 6\, \frac{y}{h}\left(1 - \frac{y}{h}\right)$$

$$\text{so} \quad u_y = -u_0\left(1 - 3\frac{y^2}{h^2} + 2\, {y^3}/{h^3}\right)$$

Now because there is no flow through the top wall, you <u>have</u> to concentrate the solute at the lower wall prior to separation. In addition, you need to <u>focus</u> your solute slug (reduce initial width). This is done by running your outflow backwards!



By adjusting the two flows you <u>control</u> where the solute starts!

The AF4 techniques separates based on diffusivity! Suppose we have two species w/ dif. D_1 & D_2

At the outlet L they would be separated (on average) by $\Delta L = L\left(1 - \frac{D_2}{D_1}\right)$ we require this to be greater than twice the σ of the peaks (generally 4x for good resolution).

So:
$$\frac{L\left(1 - D_2/D_1\right)}{\left(2K \frac{L u_0}{\dot{\gamma} D_1}\right)^{1/2}} \gg 2$$

but $K = 2 \frac{\dot{\gamma}^2 D^3}{u_0^4}$ for simple shear

$$\therefore \left(\frac{1}{2} \frac{L u_0^3}{\dot{\gamma} D^2}\right)^{1/2} \left(1 - D_2/D_1\right) \gg 2$$

$$\text{or} \quad (NTP)^{1/2} \left(1 - D_2/D_1\right) \gg 2$$

for separation! Plugging in values allows you to design an efficient separation!

In these calculations we have ignored the decrease in x velocity with x. Since u_0 (cross flow) is produced by U_0 they are all related! In fact, for some u_0 there is a lower bound on U (or upper bound on L) s.t.:

$$U_0 > u_0 \frac{L}{h}$$

This means, since $\dot{\gamma} = 6 \frac{U_0}{h} \left(1 - \frac{u_0 x}{U_0 h} \right)$

they are all related. If we define

$L^* = \frac{u_0 L}{U_0 h}$ and plug this in, we get

$$\frac{L u_0^3}{\dot{\gamma} D^2} = \frac{1}{6} \frac{L^*}{1 - L^* \frac{x}{L}} \frac{u_0^2 h^2}{D^2}$$

So we require

$$\left[\frac{1}{12} \left(\frac{L^*}{1 - L^* \frac{x}{L}} \right) \right]^{1/2} \frac{u_0 h}{D} \left(1 - \frac{D_2}{D_1} \right) \gg 2$$

↳ $\hat{\sim} \frac{1}{5}$ for typical values

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Properties of an Asymmetrical Flow Field-Flow Fractionation Channel Having One Permeable Wall

Karl-Gustav Wahlund and J. Calvin Giddings
Anal. Chem. 1987, 59, 1332-1339

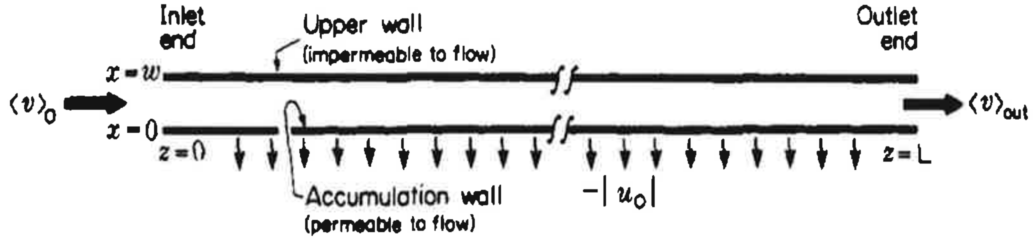


Figure 1. Schematic illustration of asymmetrical channel for flow field-flow fractionation. Flow velocities at designated locations are shown as $\langle v \rangle_0$, $\langle v \rangle_{out}$, and u_0 where the first two are the longitudinal flow velocities at the inlet and outlet ends, respectively, and u_0 is the crossflow velocity at the accumulation wall.

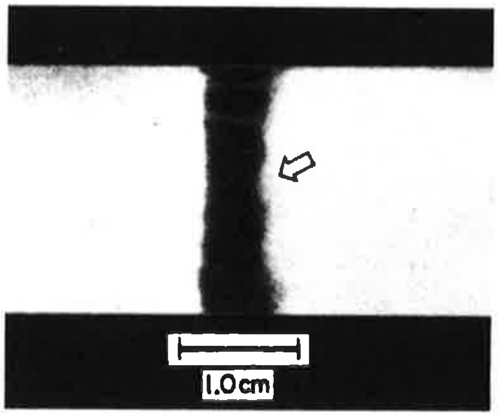


Figure 9. Photograph of focused sample of cytochrome *c* using opposing flow relaxation. The focusing point was at $z' = 22.5$ cm anc the cross flowrate ($\dot{V}_{in}' + \dot{V}_{out}$) was 6.2 mL/min.

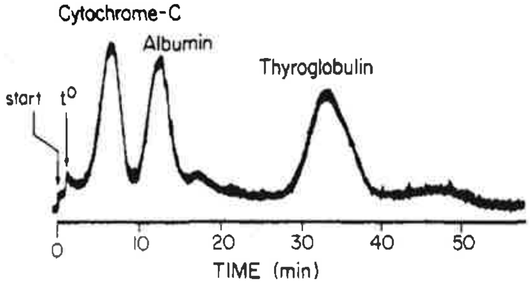
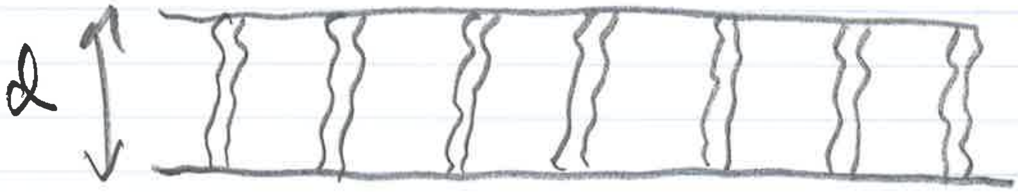


Figure 10. Separation of cytochrome *c*, albumin, and thyroglobulin in an asymmetrical system using opposing flow relaxation with $z' = 4.0$ cm, relaxation/focusing time (preceding "start") = 23 min (τ(95%) = 10 min), and cross flowrate = 3.1 mL/min. Flowrates during elution are $\dot{V}_{out} = 1.69$ mL/min and $\dot{V}_c = 3.24$ mL/min. Retention ratios were 0.20, 0.10, and 0.04, which gave diffusion coefficients of 1.2×10^{-6}, 6.0×10^{-7}, and 2.3×10^{-7} cm^2/s, respectively.

In FFF concentration polarization is good: it's what leads to separation! In filtration it's bad because it reduces the permeate flux through the membrane. Let's look at this!

What is a membrane? Simplistically, it is a solid layer with pores:



ε ≡ open area

a ≡ pore radius

ℓ ≡ membrane thickness

Λ ≡ tortuosity

Pores are usually small, so inertial effects are negligible.

We can approximate the flow through a single pore w/ Poiseuille's Law:

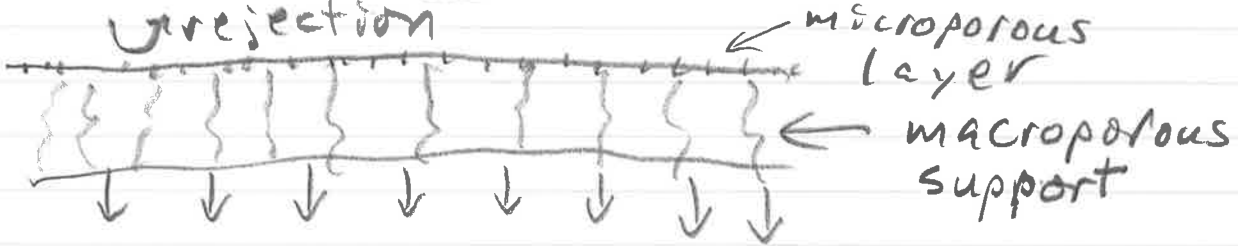
$$Q_{pore} = \frac{1}{8} \underset{\text{pressure drop}}{\Delta P} \, \frac{\pi a^4 \leftarrow \text{pore radius}}{\underset{\text{fluid viscosity}}{\mu} \underbrace{\lambda d}_{\text{effective length}}}$$

We have n pores/area $= \frac{\varepsilon}{\pi a^2}$

$\therefore$ trans-membrane flux $= u_0 = n Q_{pore} = \frac{\Delta P}{\mu}\left(\frac{\varepsilon a^2}{8 \lambda d}\right)$

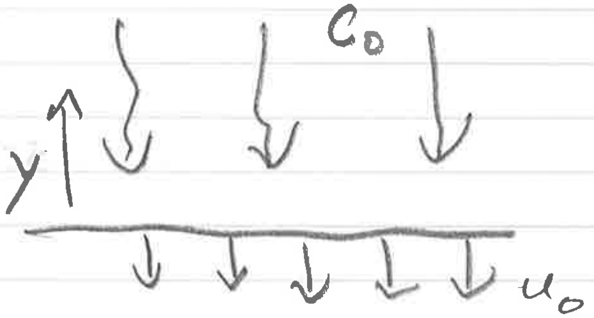
the quantity $K_H = \frac{\varepsilon a^2}{8 \lambda d}$ is the <u>hydraulic</u> <u>permeability</u> of the membrane! For <u>track</u> <u>etched</u> membranes (nuclepore) where pores are circular & straight this works (w/ $\lambda = 1$). For more complicated membranes it is just a <u>scaling</u> and K_H is determined empirically.

Because of the strong dep. on pore size, for rejecting small species you want to use asymmetric membranes:



Most of the hydrodynamic resistance is in the thin microporous layer.

ok, so what happens in dead end filtration:



we have one-D diffusion:

$$\frac{\partial c}{\partial t} - u_0 \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$$

$$c\Big|_{y\to\infty} = c_0 \qquad u_0 c\Big|_{y=0} + D\frac{\partial c}{\partial y}\Big|_{y=0} = 0$$

Let's scale:

$$c^* = c/c_0 \,, \quad y^* = y/y_c \,, \quad t^* = t/t_c$$

$$\therefore \frac{c_0}{t_c}\frac{\partial c^*}{\partial t^*} - \frac{u_0 c_0}{y_c}\frac{\partial c^*}{\partial y^*} = D\frac{C_0}{y_c^2}\frac{\partial^2 c^*}{\partial y^{*2}}$$

$$\text{So } \underset{\overset{\shortparallel}{1}}{\left[\frac{y_c^2}{D t_c}\right]}\frac{\partial c^*}{\partial t^*} - \underset{\overset{\shortparallel}{1}}{\left[\frac{u_0 y_c}{D}\right]}\frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$\text{So } y_c = D/u_0 \,, \quad t_c = \frac{y_c^2}{D} = \frac{D}{u_0^2}$$

$$\therefore \frac{\partial c^*}{\partial t^*} - \frac{\partial c^*}{\partial y^*} = \frac{\partial^2 c^*}{\partial y^{*2}}$$

$$c^*\Big|_{y^*\to\infty} = 1 \qquad c^*\Big|_{y^*=0} + \frac{\partial c^*}{\partial y^*}\Big|_{y^*=0} = 0$$

Ignoring the IC, this has the solution:

$$c^* = 1 + t^* e^{-y^*} + (1-y^*)e^{-y^*}$$

The problem is that the conc. at the membrane grows linearly in time! This has three primary effects:

1) For dilute small molecules (e.g., salt) you will have more unwanted solute flux (e.g., the rejection ratio of, say, Li^+/K^+ will go down due to buildup of K^+)

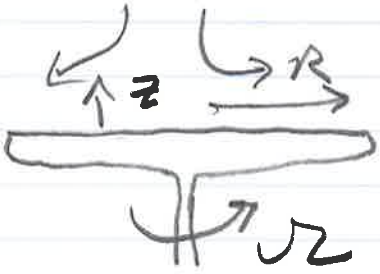
2) For more conc. small molecules you will increase the osmotic pressure

$$\Pi = \underset{\substack{\uparrow\\ \text{van't Hoff Index}\\ (\text{dissociated ions/mol})}}{i}\ \overset{\leftarrow \text{molar conc}}{C}\ \underset{\text{Ideal gas const}}{R}\ T \leftarrow \text{temp in } {}^\circ K$$

This reduces the permeate flux by effectively reducing the driving force (e.g., $u_0 = K_H(\Delta P - \Pi)$)

3) For larger species you may exceed the solubility limit, or simply build up a cake layer! This would plug the holes, or otherwise reduce K_H. How do we control the buildup? Introduce a cross-flow! This would sweep away the concentration polarization layer and permit steady operation!

A classic approach used for study of membranes is a rotating filter:



The rotation introduces a centrifugal force which causes fluid to sweep the membrane surface. The reason why this works so well is the mass transfer BL is uniform over the whole surface. Let's look at this!

First, we need the velocity profile! we have an axi-sym. problem: no θ variation!

$\therefore$ CE:

$$\frac{1}{r}\frac{\partial}{\partial r}(r u_r) + \frac{\partial u_z}{\partial z} = 0$$

θ mom:

$$\rho\left(u_r \frac{\partial u_\theta}{\partial r} + u_z \frac{\partial u_\theta}{\partial z} + \frac{u_r u_\theta}{r}\right)$$

$$= \mu\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r u_\theta)\right) + \frac{\partial^2 u_\theta}{\partial z^2}\right]$$

r-mom:

$$\rho\left(u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} - \frac{u_\theta^2}{r}\right)$$

$$= -\frac{\partial P}{\partial r} + \mu\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}(r u_r)\right) + \frac{\partial^2 u_r}{\partial z^2}\right]$$

We have BCs:

$u_\theta \big|_{z=0} = \Omega r$ (rotation)

$u_\theta \big|_{z \to \infty} = 0$

$u_r \big|_{z=0,\infty} = 0$

$u_z \big|_{z=0} = -u_0$ (permeate flux!)

We are interested in the boundary layer limit. We anticipate that $z_c << R$! Recall that in this limit the pressure gradient outside the BL is impressed on the BL. Thus,

$$\frac{\partial P}{\partial r} = 0$$

Let's scale this!

From BC $u_\theta^* = \frac{u_\theta}{\Omega R}$, $r^* = r/R$

we take $u_r^* = u_r / U_{rc}$, $u_z^* = u_z / U_{zc}$

$z^* = z / z_c$

From the CE:

$$\frac{U_{rc}}{R}\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^* u_r^*\right) + \frac{U_{zc}}{z_c}\frac{\partial u_z^*}{\partial z^*} = 0$$

$$\therefore \quad U_{zc} = \frac{z_c}{R} U_{rc}$$

θ mom:

$$\rho \frac{U_{rc}\,\Omega R}{R}\left(u_r^*\frac{\partial u_\theta^*}{\partial r^*} + u_z^*\frac{\partial u_\theta^*}{\partial z^*} + \frac{u_r^* u_\theta^*}{r^*}\right)$$

$$= \mu \frac{\Omega R}{z_c^2}\left(\frac{\partial^2 u_\theta^*}{\partial z^{*2}} + \underbrace{\frac{z_c^2}{R^2}}_{\text{small}}\frac{\partial}{\partial r^*}\left(\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^* u_\theta^*\right)\right)\right)$$

So $\dfrac{U_{rc} z_c^2}{\nu R} = 1$

r mom:

$$\rho \frac{U_{rc}^2}{R}\left(u_r^*\frac{\partial u_r^*}{\partial r^*} + u_z^*\frac{\partial u_r^*}{\partial z^*}\right) - \rho \Omega^2 R \frac{u_\theta^{*2}}{r^*}$$

$$= \mu \frac{U_{rc}}{z_c^2}\left[\frac{\partial^2 u_r^*}{\partial z^{*2}} + \underbrace{\frac{z_c^2}{R^2}}_{\text{small}}\frac{\partial}{\partial r^*}\left(\frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^* u_r^*\right)\right)\right]$$

so: $\frac{U_{rc} Z_c^2}{\nu R} = 1$ (as before)

and $\frac{\Omega^2 R Z_c^2}{U_{rc}\nu} = 1$ (balancing centrifugal force w/ dif^{n} of radial mom in z-dir)

This has the solution:

$$U_{rc} = \Omega R \quad ; \quad Z_c = \left(\frac{\nu}{\Omega}\right)^{1/2}$$

and $U_{zc} = \Omega\left(\frac{\nu}{\Omega}\right)^{1/2}$

We have the dimensionless eq'ns:

$$\frac{\partial u_z^*}{\partial z^*} = -\frac{1}{r^*}\frac{\partial}{\partial r^*}(r^* u_r^*)$$

$$\frac{\partial^2 u_\theta^*}{\partial z^{*2}} = u_r^*\frac{\partial u_\theta^*}{\partial r^*} + u_z^*\frac{\partial u_\theta^*}{\partial z^*} + \frac{u_r^* u_\theta^*}{r^*}$$

$$\frac{\partial^2 u_r^*}{\partial z^{*2}} = u_r^*\frac{\partial u_r^*}{\partial r^*} + u_z^*\frac{\partial u_r^*}{\partial z^*} - \frac{u_\theta^{*2}}{r^*}$$

w/ BC's $u_\theta^*\big|_{z^*=0} = r^*$, $u_z^*\big|_{z^*=0} = -\frac{u_0}{(\Omega\nu)^{1/2}} = -u_0^*$

and $u_\theta^*\big|_{z^*\to\infty} = u_r^*\big|_{z^*=0,\infty} = 0$

ok, now for the concentration:

$$u_r \frac{\partial c}{\partial r} + u_z \frac{\partial c}{\partial z} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^2}\right]$$

or, w/ $c^* = c/c_0$:

$$u_r^* \frac{\partial c^*}{\partial r^*} + u_z^* \frac{\partial c^*}{\partial z^*} = \frac{D}{\nu} \frac{\partial^2 c^*}{\partial z^{*2}}$$

$\hookrightarrow 1/Sc$

Recall for liquids $Sc \gg 1$

BC's : $c^*\Big|_{z^* \to \infty} = 1$

and at $z=0$: $-u_0 c\Big|_{z=0} - D\frac{\partial c}{\partial z}\Big|_{z=0} = 0$

(this is for complete rejection - if some solute gets through, it would be equal to the solute flux)

This yields $u_0^* c^*\Big|_{z^*=0} + \frac{1}{Sc}\frac{\partial c^*}{\partial z^*}\Big|_{z^*=0} = 0$

These equations are non-linear, <u>but</u> they admit a <u>similarity</u> <u>solution</u>!

$u_\theta^* = r^* f(z^*)$

$u_r^* = r^* g(z^*)$

$u_z^* = h(z^*)$

<u>and</u> $c^* = f^n(z^*)$ alone!

So:

$$f'' = fg + hf' + fg \equiv 2fg + hf'$$

$$g'' = g^2 + hg' - f^2$$

$$h' = -2g$$

w/ $f(0) = 1$, $f(\infty) = 0$

$g(0) = g(\infty) = 0$

$h(0) = -u_0^*$

and $c^{*''} = Sc\, h c^{*'}$

$c^*(\infty) = 1 \qquad c^{*'}(0) + Sc\, u_0^* c^*(0) = 0$

So our dimensionless conc. at $z=0$ is a function of $u_0^* = \frac{u_0}{(\Omega\nu)^{1/2}}$ and Sc. We can solve these for arbitrary u_0^* and Sc, but since $Sc \gg 1$ we can get at the scaling another way. We want to remove the concentration polarization layer via radial convection. If our polarization layer is thin, the excess concentration needs to balance the inward flux:

$$\underbrace{(2\pi R)}_{\text{circumference}} \underbrace{\frac{(\Omega R)}{\left(\frac{\nu}{\Omega}\right)^{1/2}} g'(0)}_{\substack{\text{shear rate at}\\ \text{membrane}}} \underbrace{\left(\frac{D}{u_0}\right)^2}_{\substack{\text{length scale}\\ \text{of polarization}\\ \text{layer}}} \overbrace{\left(c^*\Big|_{z^*=0} - 1\right)}^{\text{excess conc.}} = \underbrace{u_0 \pi R^2}_{\substack{\text{flux in}\\ \text{from outside}}}$$

$$\therefore\ c^*\Big|_{z^*=0} - 1 \sim \frac{1}{2g'(0)}\left(\frac{\nu^2}{D^2}\right)\frac{u_0^3}{(\Omega\nu)^{3/2}}$$

$$= \frac{1}{2g'(0)} \; Sc^2 \; u_0^{*3}$$

Let's see how this works! In the Bruening lab they are using a track etched membrane (30 nm pores) to separate Li^+ and K^+. They get great selectivity (RR 150) at 1000 RPM rotation, but at 100 RPM it drops to 2! (K^+ gets through) The hydraulic permeability is 22.5 LMH (liters/m^2, hr at 1 bar) and the ΔP is about 6 bar. The radius $R = 1.45$ cm, and the diffusivity of K^+ in solution is about 1.8×10^{-5} cm^2/s. So:

$$u_0 = (6\text{ bar})\left(22.5 \times \frac{1000}{10^4} \frac{1}{3600}\right) = 0.0038 \text{ cm/s}$$

$$(\Omega \nu)^{1/2} = \left(1000 \times \frac{2\pi}{60} \times 0.01\right)^{1/2} = 1.02 \text{ cm/s}$$

so $u_0^* = 0.0038$ at 1000 RPM

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$$Sc = \frac{\nu}{\Delta} = \frac{0.01}{1.8\times10^{-5}} = 555$$

$$\therefore\ Sc^2 u_0^{*3} = 0.016$$

A numerical solution shows $g'(0) \sim \frac{1}{2}$ (not exact), so from scaling

$$c^*\Big|_{z^*=0} \sim 1 + 0.016 \quad \text{at this rotation rate.}$$

At 100 RPM, however, $(\Omega\nu)^{1/2} \sim 0.32$ cm/s and thus:

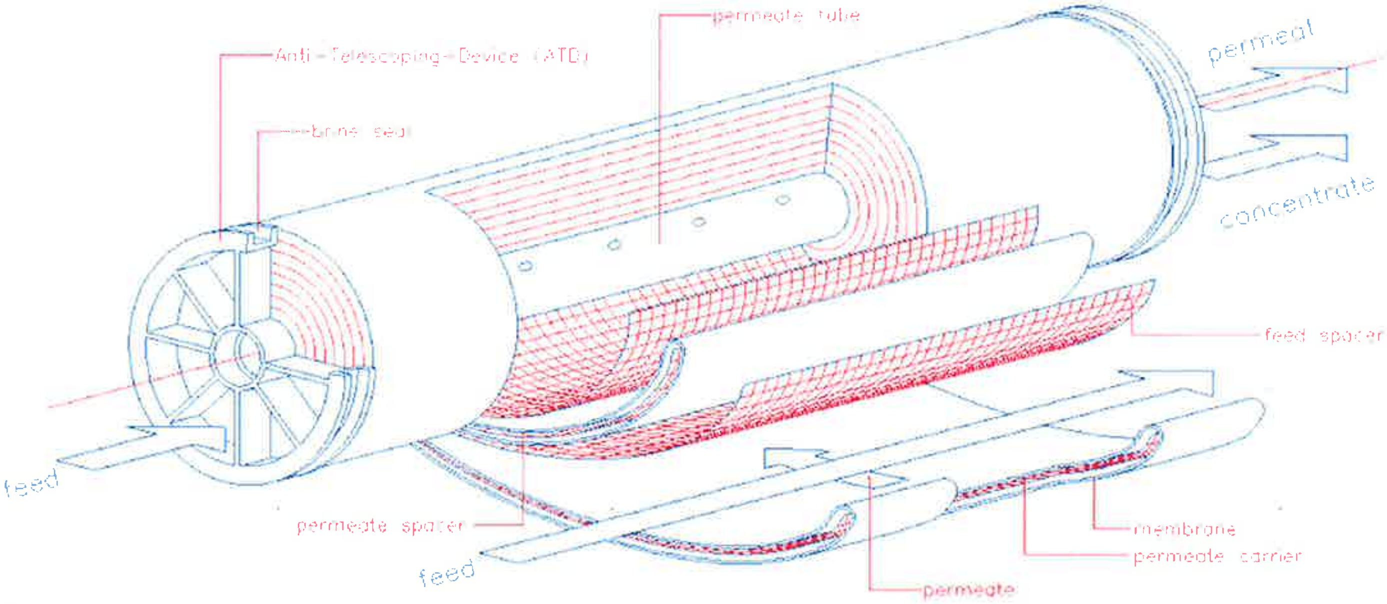
$$c^*\Big|_{z^*=0} \sim 1 + 0.5$$

so we are starting to see buildup of K^+

The rotatong membrane considered on the last lecture was particularly useful for the study of a small membrane sample, for larger scale systems two other geometries are much more useful: spiral wound and hollow fiber modules. Let's look at these!

An industrially important membrane application is seawater desalinization using spiral wound RO (reverse osmosis) membranes. These allow water to pass, but reject ~99.8% of the salt, yielding drinkable water! The active membrane is a polyamide layer on a porous backing. A blown up view of an SWRO is below:

FUNCTIONAL SCHEME OF A SPIRAL WOUND MODULE



(from Unisol Global)

The R/O membrane forms a sealed pouch or envelope around a permeate spacer (porous mesh) and the open end is sealed to the permeate tube. These pouches are separated by the feed spacer (another porous mesh about 1mm thick) and coiled up. The brine goes throug axially, and the permeate goes in the θ direction, winding up in the tube.

Water is a pretty inexpensive (of vital) fluid, so costs of a desalinization unit are critical. For SWRO this is capital cost and recurring costs. The latter is membrane replacement due to fouling and energy.

Let's look at energy costs!

This is all on pumping! For a 100% efficient pump, the energy cost is:

$$\frac{E}{\text{time}} = \underset{\substack{\uparrow \\ \text{vol flow} \\ \text{rate}}}{Q} \; \underset{\substack{\uparrow \\ \text{pressure} \\ \text{applied}}}{\Delta P}$$

The problem is that the pressure necessary must exceed the osmotic pressure of seawater at the concentrated exit to get anything out! $\Delta P_{osm}\Big|_{\text{seawater}} = 27$ atm!

Concentration polarization and flow losses make the energy cost higher!

Suppose we have a membrane w/ hydraulic permeability k_H. Our <u>local</u> flux is $j_w = k_H(\Delta P - \Pi_m)$

where $\Pi_m \equiv i\, c_m R T$

↳ conc. at membrane

2.0 for dossoc. salt.

In general $\Pi_m = \Pi e^{(j_w/k_m)}$

↳ osmotic pressure in feed layer

mass transf. coef to membrane

where $k_m = \frac{D}{\delta}$ → BL thickness

You need to use empirical data to get k_m

Π changes along the length too!

From a mass balance:

$$\Pi = \Pi_F \frac{Q_F}{Q_F - \int_0^z j_w \frac{A}{L}\, dz}$$

where L is the length of the module and A is the total area. Π_F, Q_F are the feed osm. pressure and flow rate.

ΔP is reduced w/ z due to pressure losses flowing through the 1mm thick feed spacer mesh.

If you have all these parameters you can predict performance - but what is the best you can do? (No losses! No polarization!)

We can define a minimum specific energy consumption.

Suppose we have a feed flow rate Q_F and permeate flow rate Q_P. We have a recovery ratio $RR = Q_P/Q_F$.

What is the optimal choice for RR?

our $SEC = \frac{Q_F(P_F - P_p)}{Q_p} \approx \frac{Q_F P_F}{Q_p} = \frac{P_F}{RR}$

where P_p is usually ~ 0 (in guage)

Now our pressure at the feed must be greater than the osmotic pressure at the exit

$$\pi\Big|_{z=L} = \pi_F \frac{Q_F}{Q_F - Q_p} = \pi_F \frac{1}{1-RR}$$

So $SEC = \frac{\pi_F}{RR(1-RR)}$

This has a minimum when $RR = \frac{1}{2}$ (half is filtered).

For salt water the best you could do is ~ $4\pi_F$ (ignoring recovery - later...)

Now $\pi_F = 27$ atm so it takes ~ 4 × 2.7 MJ to obtain 1 m^3 permeate. 1 kwhr = 3.6 MJ

so this is $\frac{4 \times 2.7}{3.6} = 3$ kwhr / 1 m^3

You always have losses, so the number goes up from this – but you can also recover some energy from the brine coming off at high pressure. In fact, if you get complete recovery, your energy cost goes to $SEC = \frac{\pi_F}{1-RR}$ and the optimum shifts to lower RR.

Current systems are as low as 2.5 kWh/m^3 so you are close to optimum: increasing K_H doesn't save you much! Lots of tradeoffs: higher K_H means more flux/area – so lower capital costs. But higher flux means more conc. polarization and more rapid fouling!

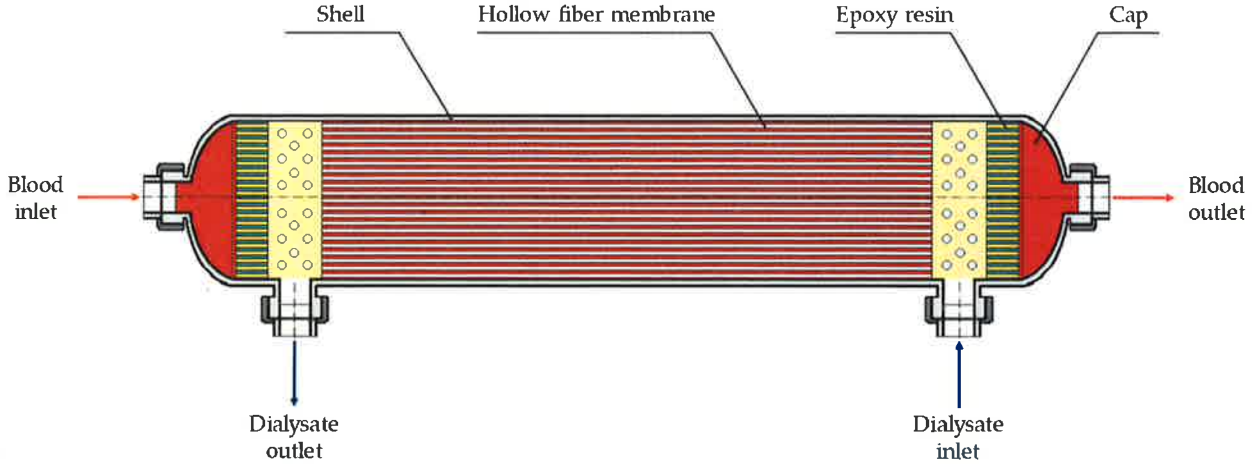
Main area for improvement: cheaper, more selective membranes with comparable K_H!

While increasing membrane performance can't do much on energy consumption, other methods such as staging (so not all the feed is at the final pressure) does help some. Still, the absolute minimum is 0.75 kwhr/m^3 (no losses anywhere, total recovery of ΔP, etc.) and current systems get within ~3x of this.

Improving K_H does have a large impact on waste water treatment because Π_F is far lower and so other losses are more significant! Other applications such as metal ion separations are also significant. (These aren't RO membranes, but use other mechanisms). An active area of research!

Another critical application of cross-flow filtration is hemodialysis: the use of hollow fiber membranes to remove undesired waste products from blood. This procedure is done nearly 1 M times per year in the US!

Your kidneys are remarkable active filters, removing urea & other compounds you don't want from the blood, maintaining salt & fluid balance, & even pumping glucose (which gets through the filters) back into the blood! It processes about 180 l/day of fluid! If it fails you have renal failure which requires (until a transplant is available) dialysis 3 times / wk for 3-4 hours each using a hollow fiber membrane



From: Performance Comparison of Alternative Hollow-Fiber Modules for Hemodialysis by Means of a CFD-Based Model, Nunzio Cancilla, et al., Membranes 2022

Blood is drawn from a patient, injected w/ heparin to prevent clotting, and pumped through the *tube* side of a hollow fiber bundle. The Dialysate flows through the *shell* side. Unlike R/O membranes, the fibers are permeable to ions & *small molecules*. Water moves across due to both hydrostatic *and* osmotic pressure.

You *need* to remove water – but not too much! (or too little)

The exact composition of the dialysate (and the patient's blood pressure) must be matched *throughout* the process.

Ok, so what does the *mass transfer process* look like? A *lot* like a shell & tube heat exchanger!

We have a mass transfer coef. for the *lumen* (k_ℓ), the membrane (K_m) and the shell (k_s). The *overall* transfer coef. is:

$$\frac{1}{k^0} = \left(\frac{1}{k_\ell} + \frac{1}{k_m} + \frac{1}{k_s}\right)^{-1}$$

(add resistances)

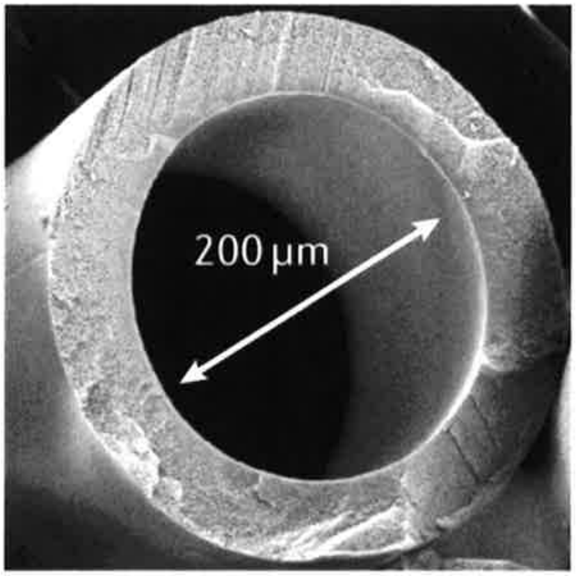
Orogmally the resistance of the membrane was very high (low flux cellulose acetate membranes). Now hemodialysis is moving toward *high flux* low resistance membranes. This does interesting things: because of pressure drop in the lumen the direction of flow can be reversed at the distal end: convection into the lumen. This can be useful, but requires careful control of pressure differential.

What is a typical hollow fiber system? Bundle of ~15K fibers, 200μm ID asymmetric membrane, ~20 cm long.

Total flow is ~300 ml/min

Human blood vol ~5l, so ~17 min for exchange (but regard person as CSTR - only a small fraction is processed on each pass). ~10 x volume filtered in each session.

Polyethersulfone
Wall thickness 30 μm



Haemodialysis membranes
Claudio Ronco & William R. Clark
Nature Reviews Nephrology volume 14, pages 394–410 (2018)

It is interesting to look at some parameters:

$U = \frac{Q}{A} = 1\ \mathrm{cm/s}$ in each fiber

$$Re = \frac{UD}{\nu} = \frac{(1)(0.02\,\mathrm{cm})}{0.05\ \mathrm{cm^2/s}} = 0.4 \ll 1$$

$\hookrightarrow$ viscosity of blood

$$\dot{\gamma}\big|_{wall} = \frac{1\ \mathrm{cm/s}}{0.01\,\mathrm{cm}} \times 4 = 400\ \mathrm{s^{-1}}$$

this is less than the critical shear rate for cell lysis of $\sim 1000\ \mathrm{s^{-1}}$

$$\Delta P = L \mu\, 8 \frac{U}{a} \approx 800\ \mathrm{dynes/cm^2} = 80\ \mathrm{Pa}$$

For whole blood, diffusion is actually dominated by shear-induced dispersion.

This is the dispersion caused by the motion of the RBC's in the shear flow. This is characterized by $\dot{\gamma} a^2$
↳RBC radius ~ 4 μm

for $\dot{\gamma} = 400\ s^{-1}$ this is $\sim 6 \times 10^{-5}\ cm^2/s$, much greater than the molecular dif. of proteins or large molecules. It's comparable to the diffusivity of small molecules.

For small molecules resistance to mass transfer is dominated by transport in the blood, but for larger molecules it is diffusion through the membrane. Thus, exact choice of membrane material and dialysate (and operating conditions) needs to be optimized for each patient – a tough problem!

In many systems from charged membrane separations to electrokinetic flows, the behavior of <u>ions</u> <u>in aqueous media</u> plays a crucial role. There are a number of elective courses avail. dedicated to this topic - here we will just look at some of the basics.

The starting point is Maxwell's Equations for the electric field in a vacuum:

$$\varepsilon_0 \underset{\sim}{\nabla} \cdot \underset{\sim}{E} = \rho^{(e)} \quad ; \quad \underset{\sim}{\nabla} \times \underset{\sim}{E} = 0$$

$\rho^{(e)} \equiv$ electric charge/volume

$\varepsilon_0 \equiv$ permittivity of the vacuum

$\underset{\sim}{E}$ is the electric field vector

If we apply this to a spherical volume containing total charge Q

we get $\underset{\sim}{E} = \frac{Q}{4\pi\varepsilon_0 r^3}\underset{\sim}{r}$

so the electric field (like gravity!) goes as $\frac{1}{r^2}$. If you have two charges Q_1 & Q_2 sep. by $\underset{\sim}{r}_{12}$ the force is:

$$\underset{\sim}{F}_{12} = \underset{\sim}{E}_1 Q_2 = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_{12}^3}\underset{\sim}{r}_{12}$$

Now because $\underset{\sim}{\nabla} \times \underset{\sim}{E} = 0$ (irrotational) it must be represented as the gradient of a scalar (potential)

$$\underset{\sim}{E} = -\underset{\sim}{\nabla}\psi$$

Plugging this into Maxwell's eq'n we get: $\varepsilon_0 \nabla^2 \psi = -\rho^{(e)}$

So around an isolated charge Q:

$$\psi = \frac{Q}{4\pi\varepsilon_0} r^{-1}$$

If you have a sphere of radius a and Charge Q, the surface potential ψ_s is just $\psi_s = \dfrac{Q}{4\pi\varepsilon_0 a}$.

This was for a vacuum. In a dielectric medium the capacitance $(4\pi\varepsilon_0 a)$ increases due to polarization. This is due to orientation of permanent dipoles and deformation of electron clouds.

We define a polarization vector $\underset{\sim}{P}$ s.t.

$$\underset{\sim}{P} = \underset{\overset{\uparrow}{\frac{\text{dipoles}}{\text{vol}}}}{N}\ \overset{\swarrow\ \text{charge separated to produce dipole}}{Q}\ \underset{\sim}{d} \leftarrow \text{distance \& orientation of separation}$$

For a linear dielectric

$$\underset{\sim}{P} = N \underset{\hookrightarrow \text{polarizability of mat'l (units } L^3)}{\alpha} \varepsilon_0 \underset{\sim}{E}$$

The product $N\alpha$ is the electric susceptibility of the material $\chi \equiv N\alpha$

If we have a non-zero divergence of $\underset{\sim}{P}$ we get an effective charge! This is known as the polarization charge density $\rho^{(P)}$: $\underset{\sim}{\nabla} \cdot \underset{\sim}{P} = -\rho^{(P)}$

combining this with the total charge density we get:

$$\varepsilon_0 \underset{\sim}{\nabla} \cdot \underset{\sim}{E} = \rho^{(e)}$$

$$\varepsilon_0 \underset{\sim}{\nabla} \cdot \chi \underset{\sim}{E} = -\rho^{(P)}$$

$$\therefore \varepsilon_0 \underset{\sim}{\nabla} (1+\chi) \underset{\sim}{E} = \rho^{(e)} - \rho^{(P)} \equiv \rho^{(f)}$$

where $\rho^{(f)}$ is the free charge density

Now if there are no free charges, then

$$\varepsilon_0 \underset{\sim}{\nabla} \cdot (1+\chi) \underset{\sim}{E} = 0$$

If we put a charged sphere in our dielectric there will be an effective polarizatom charge at the surface which reduces the potential & electric field. Putting this together you get

$$Q = 4\pi\varepsilon_0 \underbrace{(1+\chi)}_{\substack{\shortparallel \\ \varepsilon\text{ : dielectric constant} \\ \text{of the material}}} a\,\psi_s$$

What does this do?

1) For a given ψ_s (surface potential, voltage) it increases the charge (capacitance). That's why capacitors have high ε!

2) For a given charge it reduces ψ_s and the electric field. This reduces the force between two charges by a factor of ε too!

All this was for dielectrics w/ no free charge (e.g., no ions). In aqueous solutions ions respond to the electric field to produce a non-uniform dist!

In an aqueous system, surfaces tend to acquire a charge! While this can be due to a different affinity for electrons or ionizable species it is often due to ionizable species that are bound to the surface: a sialic acid group on the surface of an RBC will ionize, leaving a bound negative charge. Proteins are usually amphoteric where amine groups will protonate (yielding + charge) or COOH groups will ionize (yielding − charge) depending on the pH!

At a charged surface in an electrolyte the counter ion will be attracted by the electric field, but will also diffuse away. This leads to the "diffuse layer". we need to model this!

At equilibrium,

$$\varepsilon \varepsilon_0 \nabla^2 \psi = -\rho^{(f)}$$

For a particular ion κ the <u>force</u> on the ion balances the gradient in the chemical potential:

$$\underset{\substack{\uparrow\\ \text{Boltzmann's}\\ \text{const.}}}{\kappa}\,\underset{\substack{\uparrow\\ {}^{\circ}K}}{T}\,\underset{\sim}{\nabla} \ln \underset{\substack{\uparrow\\ \#\text{ density}\\ \text{of } k^{th}\\ \text{ion}}}{n}^{\kappa} + \underset{\substack{\uparrow\\ \text{electron}\\ \text{charge}}}{e}\,\overset{\substack{\text{charge (sign) of } k^{th}\text{ ion}\\ \downarrow}}{z}^{\kappa}\,\underset{\substack{\sim\\ \hookrightarrow \underset{\sim}{E}\text{ (elec. field)}}}{\underset{\sim}{\nabla}\psi} = 0$$

If we integrate this we get Boltzmann distribution:

$$n^{\kappa} = n_b^{\kappa} e^{-\left(\frac{e z^{\kappa} \psi}{\kappa T}\right)}$$

where n_b^{κ} is the concentration where $\psi = 0$

Now in your electrolyte you have at *least* two types of ions! The *free charge density* is the excess charge from the mixture. Thus:

$$\rho^{(f)} = \sum_{1}^{N} e z^{K} n^{K}$$

Putting this together, you get the Poisson-Boltzmann eq'n:

$$\varepsilon \varepsilon_0 \nabla^2 \psi = - e \sum_{1}^{N} z^{K} n_b^{K} e^{-\left(\frac{e z^{K} \psi}{kT}\right)}$$

This equation has the B.C. at the surface $-\varepsilon \varepsilon_0 \underset{\sim}{\nabla} \psi \cdot \underset{\sim}{n} = q$

where q is the surface charge density which is driving the non-uniform ion distribution.

Suppose we have a *flat* interface and a z-z electrolyte (e.g., Na^{+} Cl^{-})

our balance becomes:

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2ez}{\varepsilon \varepsilon_0} n_b \sinh(ez\psi/kT)$$

If $ez\psi/kT \ll 1$ (small potentials)

we get the Debye - Hückel approx:

$$\frac{d^2 \psi}{\partial x^2} = \underbrace{\left(\frac{2e^2 z^2 n_b}{\varepsilon \varepsilon_0 kT}\right)}_{\text{units of } \frac{1}{L^2}} \psi$$

we can use this to define a Debye decay length (or double layer thickness)

$$K^{-1} \equiv \left(\frac{\varepsilon \varepsilon_0 kT}{2e^2 z^2 n_b}\right)^{1/2}$$

This is the length scale of the cloud of counter ions near a charged surface! It is also the most important part of this lecture! The key is the relationship between κ^{-1} and, say, pore radii. If you have a pore w/ fixed surface charges whose diameter is less than κ^{-1} then the surface charge modifies the ion distribution across the pore and you can get selective ion transport! If κ^{-1} is smaller than the pore diameter, the pore is unaffected (mostly) by the surface charge!

So how big is it?

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 kT}{2 e^2 z^2 n_b} \right)^{1/2}$$

Water: $\varepsilon = 80$ (dimensionless)

$T = 298°K$

$$\varepsilon_0 = 8.854 \times 10^{-12}\ \underset{\hookrightarrow \text{Farad}}{F}/m$$

$z = 1$ (e.g., NaCl)

$k = 1.381 \times 10^{-23}\ m^2\,kg/s^2\,°K$

ok, now for n_b: this is the salt concentration. Say we have a 0.01M solution of NaCl:

$$n_b = 0.01\ \frac{\text{moles}}{l} \times 1000\ \frac{l}{m^3} \times 6.022 \times 10^{23}$$

(oh - and $e = 1.602 \times 10^{-19}$ Coulombs)

So for these numbers:

$$\kappa^{-1} = 3.07 \times 10^{-9}\ m \quad = 3\ nm$$

As an example, Prof Bruening's Li^+/K^+ separation w/ 15 nm radius pores works <u>fine</u> at 2×10^{-4} M ionic strength, but <u>fails</u> at 0.2M ionic strength. At 2×10^{-4} M (0.2mM) $\kappa^{-1} = 22$ nm, greater than the pore radius. At 0.2M

$\kappa^{-1} = 0.7\,\text{nm}$, much less than the pore radius!

It is interesting that there is an <u>exact</u> solution to the potential <u>without</u> linearizing. If we define $\Psi \equiv \frac{ez\psi}{kT}$ (e.g., normalized) we get:

$$\Psi = 2\ln\left(\frac{1 + e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}{1 - e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}\right)$$

and $q = 2\left(2\varepsilon\varepsilon_0 kTn_b\right)^{1/2}\sinh\left(\frac{1}{2}\Psi_s\right)$

Now if Ψ_s is <u>small</u>, we get the linearized result. If $\Psi_s \gg 1$, however,

$$\Psi \sim 4\tanh\left(\frac{1}{4}\Psi_s\right)e^{-\kappa x}$$

away from the surface. Since $\tanh\left(\frac{1}{4}\Psi_s\right) \to 1$ at large Ψ_s, the potential and electric field away from the surface behave as if there is a saturation potential $\Psi_s = 4$ no matter how large the charge is!

All this is for a flat plate. If we have a colloidal particle it's usually a sphere of radius a! The behavior depends on κa - the ratio of the radius to the Debye length. If $\kappa a \ll 1$ (say, a nano particle in a dilute electrolyte) then the force between two charged spheres is:

$$F \approx 2\pi \varepsilon \varepsilon_0 \left(\frac{kT}{ze}\right)^2 \kappa a \Psi_s \frac{e^{-\kappa h}}{1+e^{-\kappa h}}$$

where h is the separation distance

If $\kappa a \gg 1$ (usual case)

$$F \approx 32\pi \varepsilon \varepsilon_0 \left(\frac{kT}{ze}\right)^2 \kappa a \left[\tanh\left(\tfrac{1}{4}\Psi_s\right)\right]^2 e^{-\kappa h}$$

The *rapid* decrease (exponential) w/ κh means that decreasing κ^{-1} (e.g., increasing κ) *reduces* the force. Since κ^{-1} goes as $1/n_b^{1/2}$, *increasing* *salt* concentration *reduces* electrostatic repulsion! That means *adding* *salt* to a colloidal suspension usually leads to aggregation as attractive short-range van der Waals forces take over!

Next lecture we'll look at what happens in an imposed electric field: electroosmosis & electrophoresis!

Because of the net free charge in the diffuse layer, if you apply a tangential electric field you get motion! This is called electroosmosis and is very useful in μfluidic systems.

First, what is the free charge density $\rho^{(f)}$? Recall that we had the Boltzmann distribution:

$$n^K = n_b^K \, e^{-\left(\frac{e z^K \psi}{kT}\right)}$$

we defined $\Psi \equiv \dfrac{e z \psi}{kT}$

$$\text{so} \quad n^K = n_b^K \, e^{-\Psi\left(\frac{z^K}{z}\right)}$$

+1 or -1 dep. on + or - charge

That's because, say, positive ions are attracted to a negative surface & neg. ions are repelled!

Suppose we have a z-z electrolyte where the bulk concentration of each is n_b

(They have to be the same for electro-neutrality). The net free charge is:

$$\rho^{(f)} = e\sum n^k z^k = e n_b z\Big(\underset{\substack{\uparrow\\ \text{pos. ions}}}{e^{-\Psi}} - \underset{\substack{\uparrow\\ \text{neg. ions}}}{e^{+\Psi}}\Big)$$

For 1-1 electrolytes, $z=1$

We also had, for some surface potential Ψ_s:

$$\Psi = 2\ln\left(\frac{1+e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}{1-e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}\right)$$

so $$e^{-\Psi} \equiv \left(\frac{1-e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}{1+e^{-\kappa x}\tanh\left(\frac{1}{4}\Psi_s\right)}\right)^2$$

and e^{Ψ} is just the inverse.

It is convenient (but not necessary!) to work w/ the low Ψ_s limit:

$$\Psi \approx \Psi_s e^{-\kappa x}$$

and so $$\rho^{(f)} = -2 e n_b z \sinh(\Psi)$$

$$\approx -2 e n_b z \Psi_s e^{-\kappa x}$$

If we recall that $\kappa^{-1} = \left(\frac{\varepsilon\varepsilon_0 kT}{2e^2z^2n_b}\right)^{1/2}$

we can recast this as:

$$\rho^{(f)} \approx -\varepsilon\varepsilon_0 \kappa^2 \psi_s e^{-\kappa x}$$

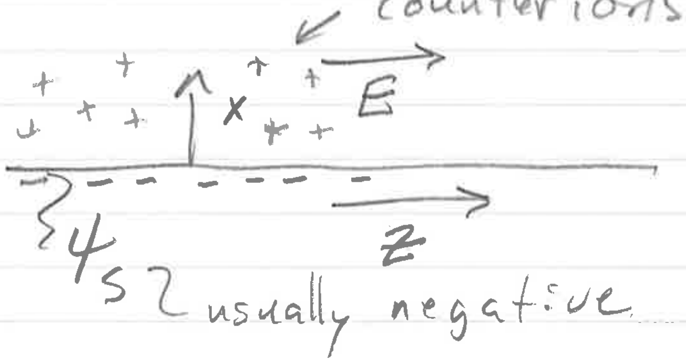
or, as usually written,

$$\rho^{(f)} = -\varepsilon\varepsilon_0 \kappa^2 \zeta e^{-\kappa x}$$

↳ known as the __zeta potential__

The ζ zeta potential is known as the potential at the __shearing surface__, but for small Ψ_s it is just ψ_s - for __large__ potentials there is a "bound" Stern layer of counter-ions that have __low mobility__.

OK, now we apply a __tangential field__ E.



There is a force per volume on the fluid:

$$0 = \mu \frac{\partial^2 u_z}{\partial x^2} + \rho^{(f)} E$$

so: $$\frac{\partial^2 u_z}{\partial x^2} = -\frac{\rho^{(f)} E}{\mu} = \frac{\varepsilon \varepsilon_0 K^2 \zeta}{\mu} e^{-Kx} E$$

Let's scale:

$$x^* = Kx \qquad u_z^* = \frac{u_z}{U_c}$$

$$\therefore \cancel{K^2} U_c \frac{\partial^2 u_z^*}{\partial x^{*2}} = E \frac{\varepsilon \varepsilon_0 \cancel{K^2}}{\mu} \zeta e^{-x^*}$$

$$\therefore U_c = \left(\frac{\varepsilon \varepsilon_0 \zeta}{\mu}\right) E$$

and $$\frac{\partial^2 u_z^*}{\partial x^{*2}} = e^{-x^*}$$

Integrating once:

$$\frac{\partial u_z^*}{\partial x^*} = -e^{-x^*} + C_1$$

At infinity the stress is zero, so $C_1 = 0$

Integrating again:

$$u_z^* = e^{-x^*} + C_2$$

but $u_z^*\big|_{x^*=0} = \underline{\underline{0}}$ (no-slip) $\therefore C_2 = -1$

So $u_z^* = e^{-x^*} - 1$

Far away (but remember how short κ^{-1} is!)

$$\underline{u_z^* = -1}$$

So our electroosmotic velocity is just $-U_0$!

The quantity $\frac{\varepsilon\varepsilon_0 \zeta}{\mu}$ is the electroosmotic mobility. Note that this is independent of n_b! It only depends on ζ and fluid properties!

why? If n_b increases, so does $\rho^{(f)}$ but since κ^{-1} decreases viscous drag (which goes as κ^2) cancels this out!

So what is $\mu_{eo} \equiv \frac{\varepsilon \varepsilon_0 \zeta}{\mu}$ $\equiv$ electroosmotic mobility?

We can plug in some numbers!

Say $\zeta = 100\,mV$ (typical value)

$\mu = 10^{-3}$ Pa·s (or 1 cp) and $\varepsilon = 80$ (water)

This yields:

$$\mu_{eo} = 7.08 \times 10^{-8} \frac{m/s}{V/m}$$

The more usual units are:

$$\mu_{eo} = 7.08 \frac{\mu m/s}{V/cm}$$

as microfluidic channels are pretty short!

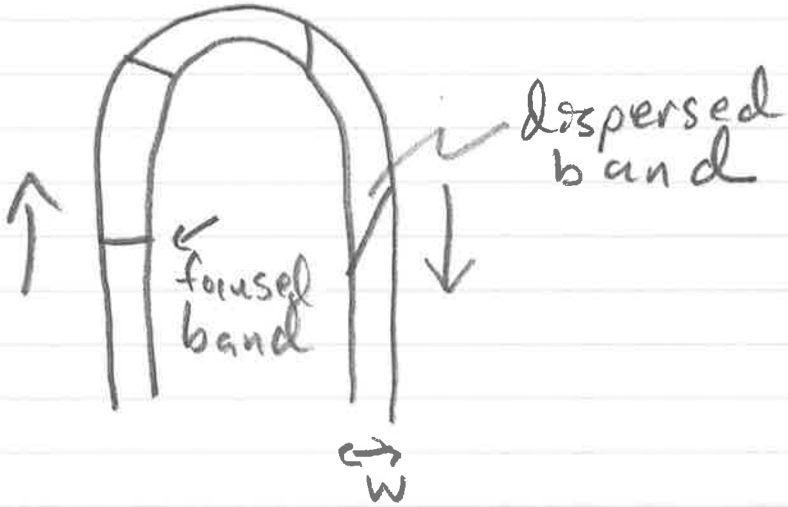
This is a good approx provided Ψ_s isn't too big. For larger values, just integrate the exact solution numerically!

EO velocities are small, but they are very useful for driving fluid through thin channels! For pressure driven flow

The velocity goes as depth^2. That means that for, say, 50μm deep channels you need a large ΔP! For EO the velocity is indep of depth.

Another advantage – there's no shear as you get plug flow – essentially slip at the walls! For a straight channel there's no dispersion!

Now for disadvantage: For a large aspect ratio channel curves are huge sources of dispersion due to the "race track effect":



The explanation is simple: The inside of the 180° bend is πW shorter than the outside. This means a higher electric field and a shorter distance. A focused band smears out by $2\pi W$ after every bend, which really adds up on a serpentine channel (needed for length). Modifications to the width profile can reduce this, but it's still a problem!

Another issue is the generation of the electric field. To get any field beyond κ^{-1} thickness (really short) you have to have a current! That means an electrode reaction at each end! This is usually producing electrolysis, acid & base (pH change) and bubbles –

all of which cause trouble!

A last disadvantage: If you have a slug of mixed solutes, the electric field will separate them. This can be undesirable, but is actually the basis of capillary electrophoresis, our next topic!

Suppose we have a particle of radius a and surface charge Q. If $\kappa a \ll 1$ (e.g. really small particle or a low n_b) then the diffuse layer is spread out! If we apply an electric field E_∞ then the force is just $E_\infty Q$. This is balanced by Stokes Law drag:

$$E_\infty Q = 6\pi\mu a U$$

The electrophoretic mobility of the particle is :

$$\mu_{ep} = \frac{Q}{6\pi\mu a} \; ; \; u = \mu_{ep} E_\infty$$

For a thin double layer $\kappa a >> 1$ and we have a more complicated result. Essentially, you get EO flow at the surface of the particle (in the double layer) and the particle moves in the opposite direction of this!

we get :

$$u = \frac{Q}{4\pi\mu a} \frac{1}{\kappa a} E_\infty$$

or, in terms of the ζ potential :

$$u = \frac{\varepsilon \varepsilon_0 \zeta}{\mu} E_\infty$$

which is indep of a as $\frac{Q}{4\pi a^2}$ is the charge density

Because of this, mobilities in an electric field are used to *measure* the ζ potential of colloids.

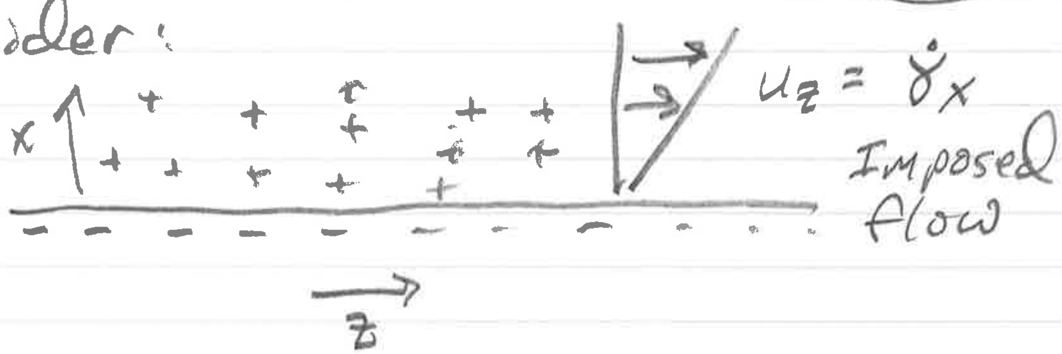
So how is this used in capillary electrophoresis? A mixture of analytes (pos or neg charge!) are drawn through the capillary by *electroosmosis*: The EO velocity needs to be *higher* than the neg. vel of opposite charge species. Species w/ different charge *or* size move w/ dif. velocities and separate into bands for detection at the end of the capillary.

A key is initial focusing of the band at injection using stacking: If you suspend the analyte in a low conc. buffer at the entrance it will *focus* at the lead edge due to a higher electric field in the initial slug (low conductivity = high field for same current).

Other tricks are things like isoelectric focusing: The charge on a protein depends on the pH. If you put it in an axial pH gradient it will focus at its isoelectric point (pH of neutral charge) and be convected along w/ the EO velocity. Many other variations have also been developed!

Another way the diffuse layer, EO and electrophoresis can combine is if you also have a shear flow in the absence of an imposed electric field. This leads to a streaming potential.

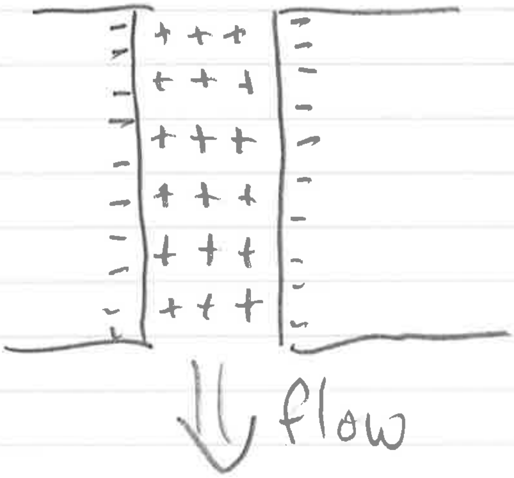
Consider:



If there's no electric field the positive counter ions are swept along with the shear flow. This net current will (like a VandeGraaf generator) lead to a charge buildup! The current scales as $$\underbrace{(\kappa^{-1}\dot{\gamma})}_{\text{char velocity}}\underbrace{\kappa^{-1}}_{\text{length}}\cdot\underset{\uparrow\ \text{extension into paper}}{w}\cdot\underset{\nwarrow\ \text{avg. free charge}}{\rho^{(f)}}$$

Since it goes as $(\kappa^{-1})^2$ it is most important for large κ^{-1} (low ion conc. in the bulk) and is quite a problem in pumping gasoline! Ground your pipes to avoid sparks!

This is also important for charged pores in membranes.



If the pore radius is comparable to κ^{-1} pressure driven flow leads to a net convection of counter ions across the membrane. By overall electro neutrality this leads to a membrane polarization and EO flow back the other way!

Polarization can also occur if a membrane is permeable to some ions but not others – diffusion alone can lead to a Donnan potential – which is how your nerves work! Electrokinetics is a huge subject! This is just an introduction!