Mass Transport in liquids

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Outline

- Chemical potential
- Species conservation including convection
- H-filter design & eigenfunction expansion
- Taylor dispersion, the microfluidicist's enemy
- Mixing

Chemical potential

- It comes from thermodynamics
- Chemical potential gradients are the driving force for the movement of molecules
- It is the electron Fermi level in semiconductors
- At equilibrium, there are no gradients in μ

$$\mu = \left(\frac{\partial W}{\partial N} \right) \bigg|_{T,V}$$

For an ideal solution:

$$\mu_i(x) = \mu_i^0 + k_B T \ln \frac{c_i(x)}{c_i^0}$$

Chemical potential

- We can derive Fick's first law from the chemical potential
- First, note that there are two concentration units
- Relate flux to velocity
- Then relate the velocity to a force *f*, using a mobility *M*
- Then the force to a potential ($\mathcal{P}$) gradient

$$c_i = N_A C_i$$

$$\left[\frac{\#}{m^3}\right] = \left[\frac{\#}{mol}\right]\left[\frac{mol}{m^3}\right]$$

$$J_i = c_i U_i = N_A C_i U_i$$

$$U_i = Mf = -M\frac{\partial \mathcal{P}}{\partial x}$$

$$U = \mu_n E = \frac{\mu_n}{q_e}(q_e E) = -\frac{\mu_n}{q_e}(\nabla q_e \phi)$$

U [m/s]; μ_n [m²/V-s]; $\frac{\mu_n}{q_e}$ [s/kg]; E [V/m]; $q_e E$ [N]

Chemical potential

- Finally, find flux due to a chemical potential gradient

$$\mu_i(x) = \mu_i^0 + k_B T \ln \frac{c_i(x)}{c_i^0}$$

- Can relate diffusivity to mobility

$$J_i = -c_i M \frac{\partial \mu_i}{\partial x} = -c_i M k_B T \frac{\partial}{\partial x}\left(\ln \frac{c_i(x)}{c_i^0} \right)$$

$$J_i = -c_i M k_B T \frac{\partial}{\partial x}\left(\ln c_i(x) - \ln c_i^0 \right)$$

$$J_i = -M k_B T c_i \frac{\partial}{\partial x}\left(\ln c_i(x) \right)$$

$$J_i = -M k_B T c_i \frac{1}{c_i} \frac{\partial c_i}{\partial x}$$

$$J_i = -M k_B T \frac{\partial c_i}{\partial x} = -D \frac{\partial c_i}{\partial x}$$

$$k_B T = \frac{D}{M}$$

Einstein Relation

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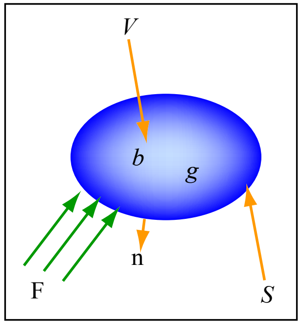
Species conservation equation

- One more conservation equation…
- Flux now includes convection and diffusion
- Incompressible flow



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$$\frac{d}{dt}\int b\,dV = -\int \mathbf{F}\cdot\mathbf{n}\,dS + \int g\,dV$$

$$\frac{\partial b}{\partial t} = -\nabla\cdot\mathbf{F} + g$$

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot \mathrm{J}_i + R_{Vi}$$

convection

$$\mathrm{J}_i = -D_i\nabla c_i + c_i\mathbf{U}_\mathbf{i}$$

diffusion

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot\left(-D_i\nabla c_i + c_i\mathbf{U}_\mathbf{i}\right) + R_{Vi}$$

$$\frac{\partial c_i}{\partial t} = D_i\nabla^2 c_i - c_i\nabla\cdot\mathbf{U}_\mathbf{i} - \mathbf{U}_\mathbf{i}\cdot\nabla c_i + R_{Vi}$$

$$\frac{\partial c_i}{\partial t} + \mathbf{U}_\mathbf{i}\cdot\nabla c_i = D_i\nabla^2 c_i + R_{Vi}$$

$$\frac{Dc_i}{Dt} = D_i\nabla^2 c_i + R_{Vi}$$

Convection-Diffusion Equation

Convective term

- We have seen this equation before

$$\frac{\partial c_i}{\partial t} + \mathbf{U_i} \cdot \nabla c_i = D_i \nabla^2 c_i + R_{Vi}$$

- We can compare the convective to diffusive flux terms, and get a Peclet number again
  - Now for diffusive vs. convective mass transport

$$\frac{convection}{diffusion} \sim \frac{\mathbf{U_i} \cdot \nabla c_i}{D_i \nabla^2 c_i} \sim \frac{U \, {}^{c}\!/_{L}}{D \, {}^{c}\!/_{L^2}} \sim \frac{LU}{D}$$

- For BSA (66 kDA) in microscale flows, L~100 μm, U~1 mm/s, D~7x10^{-11} m^2/s

$$Pe = \frac{LU}{D} = \frac{\left(10^{-4}\,m\right)\left(10^{-3}\,m/s\right)}{7 \cdot 10^{-11}\, m^2\!/_{s}} \sim 10^3$$

- Convection *is* important because molecular diffusivity is 10^7 times slower than heat diffusivity and 10^5 times slower than momentum diffusivity

D_{heat} ~10^{-4} m^2/s for water

$D_{momentum}$ ~10^{-6} m^2/s for water

Diffusivities

- How can we get diffusivities for different objects?
- Use mobility due to Stokes drag
- Result is Stokes-Einstein relation
- Larger particles have smaller diffusivity
- Often used to get an effective radius (R_h) for a species

$$D = Mk_BT = \frac{U_i}{f} k_BT$$

$$f = 6\pi\eta R U_i \Rightarrow \frac{U_i}{f} = \frac{1}{6\pi\eta R}$$

$$\boxed{D = Mk_BT = \frac{k_BT}{6\pi\eta R}}$$

R=45 nm

R_h=44.8 nm

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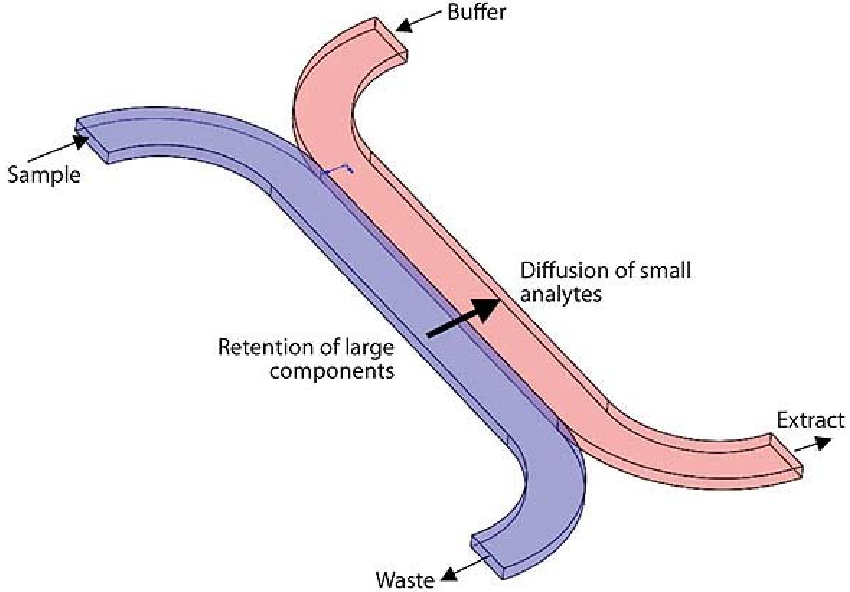
H-filter

- What are the minimum diffusivity differences that we can separate?
- How to choose channel width, length, flowrate



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H-filter

- First, let's try a quick and dirty diffusion calculation
- Assume 1-D diffusion across width of channel
- Ignore convection effects along length of channel
- No generation terms
- Result suggests that separation will go as $\sqrt{D}$

$$\frac{\partial c_i}{\partial t} + \mathbf{U_i} \cdot \nabla c_i = D_i \nabla^2 c_i + R_{Vi}$$

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}$$

$$\frac{c_i}{\tau} \sim D_i \frac{c_i}{\delta^2}$$

$$\delta \sim \sqrt{D_i \tau}$$

$$\delta \sim \sqrt{D_i \frac{L}{U}}$$

H-filter

> **Can we do better?**

> **Yes, using eigenfunction analysis**

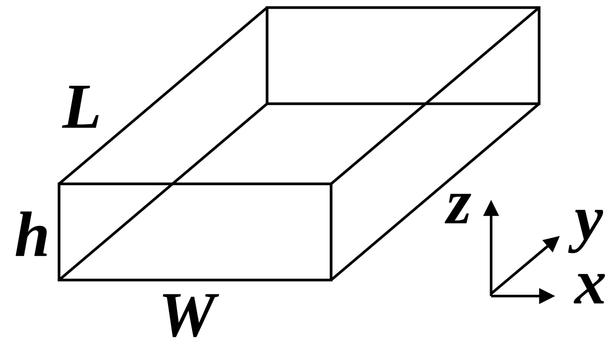
> **Assumptions**

- **Ignore convection**
- **No generation**
- **No concentration gradients along channel height or length**
  - » **1-D diffusion**
- **One dilute component in solvent**

$$\frac{\partial c_i}{\partial t} + \mathbf{U}_i \cdot \nabla c_i = D_i \nabla^2 c_i + R_{Vi}$$

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i$$

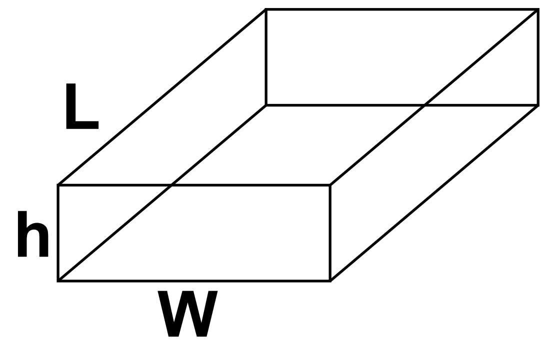
$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$



H-filter

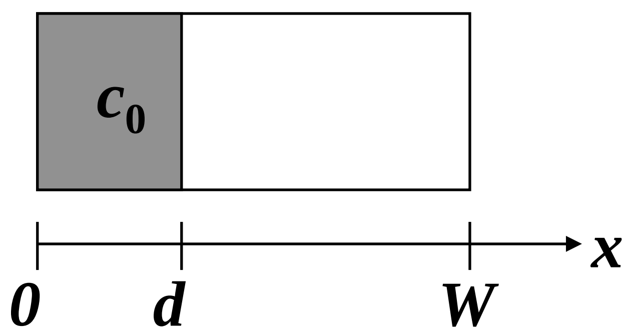
> Initial condition

- **Solute initially fills part of channel**



> Boundary condition

- **No solute flux through walls**



Initial condition:

$$c(x,0) = \begin{cases} c_0 & \text{for } 0 < x < d \\ 0 & \text{for } d < x < W \end{cases}$$

Boundary condition:

$$\left.\frac{\partial c}{\partial x}\right|_{x=0,W} = 0 \quad \text{for all } t$$

H-filter

- First, separate variables
- Time response is exponential
- Spatial eigenfunctions are sinusoids
- Must include DC term in series

$$\frac{\partial Y}{\partial t} = -\alpha Y \Rightarrow Y = e^{-\alpha t}$$

$$D\frac{d^2\hat{C}}{dx^2} = -\alpha\hat{C}$$

$$\hat{C}(x) = a_0 + \sum_{n=1}^{\infty}\left(A_n\sqrt{\frac{2}{W}}\sin k_n x + B_n\sqrt{\frac{2}{W}}\cos k_n x \right)$$

$$k_n^2 = {\alpha_n}/{D}$$

$$\frac{\partial c}{\partial t} = D\ \frac{\partial^2 c}{\partial x^2}$$

$$c(x,t) = \hat{C}(x)Y(t)$$

H-filter

- Sine does not meet BCs
- Cosine does

$$\hat{C}(x) = a_0 + \sum_{n=1}^{\infty}\left(A_n\sqrt{\frac{2}{W}}\sin k_n x + B_n\sqrt{\frac{2}{W}}\cos k_n x \right)$$

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = \left.\frac{d\hat{C}}{dx}\right|_{x=0} = 0$$

$$0 = \sum_{n=1}^{\infty}\left(A_n k_n\sqrt{\frac{2}{W}}\cos k_n 0 - B_n k_n\sqrt{\frac{2}{W}}\sin k_n 0 \right)$$

$$\Rightarrow A_n = 0$$

$$\left.\frac{\partial c}{\partial x}\right|_{x=W} = \left.\frac{d\hat{C}}{dx}\right|_{x=W} = 0$$

$$0 = \sum_{n=1}^{\infty} -B_n k_n\sqrt{\frac{2}{W}}\sin k_n W$$

$$\Rightarrow k_n = \frac{n\pi}{W} \quad \text{for } n = 1, 2, 3, \ldots$$

H-filter

> **Finally, use eigenfunction expansion to meet initial concentration profile**

$$c(x,t) = a_0 + \sum_{n=1}^{\infty} B_n \sqrt{\frac{2}{W}} \cos k_n x \cdot e^{-\alpha_n t}$$

↓ **t=0**

$$c(x,0) = a_0 + \sum_{n=1}^{\infty} B_n \sqrt{\frac{2}{W}} \cos k_n x = \begin{cases} c_0 & \text{for } 0 < x < d \\ 0 & \text{for } d < x < W \end{cases}$$

↓ **multiply both sides by eigenfctn & integrate**

$$\int_0^W c(x,0)\sqrt{\frac{2}{W}} \cos k_m x dx = \int_0^W a_0 \sqrt{\frac{2}{W}} \cos k_m x dx + \sum_{n=1}^{\infty} \int_0^W B_n \sqrt{\frac{2}{W}} \cos k_n x \sqrt{\frac{2}{W}} \cos k_m x dx$$

↓ **extract coefficient**

$$B_n = \int_0^W c(x,0)\sqrt{\frac{2}{W}} \cos\left(k_n x\right) dx$$

H-filter

- Get coefficients and DC term

$$B_n = \int_0^W c(x,0)\sqrt{\frac{2}{W}}\cos\left(k_n x\right)dx$$

$$B_n = \sqrt{\frac{2}{W}}\left[\int_0^d c_0\cos\left(k_n x\right)dx + \int_d^W 0\cos\left(k_n x\right)dx\right]$$

$$B_n = \sqrt{\frac{2}{W}}\frac{c_0}{k_n}\sin\left(k_n x\right)\Big|_0^d$$

$$\boxed{B_n = \sqrt{\frac{2}{W}}\frac{c_0}{k_n}\sin\left(k_n d\right) \qquad \text{for } n = 1,2,3,\ldots}$$

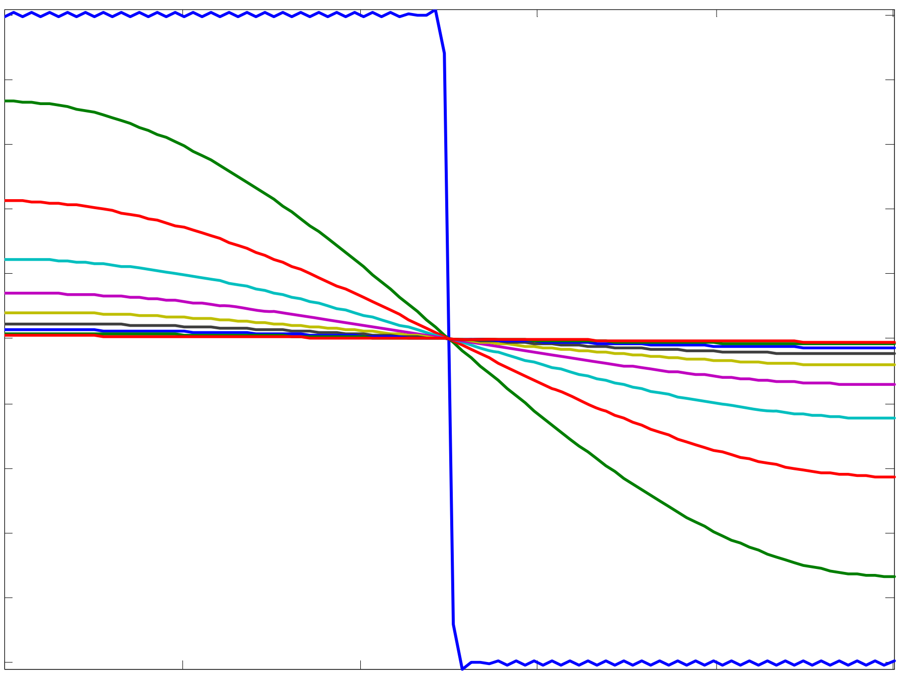
$$a_0 = \frac{1}{W}\int_0^W c(x,0)dx = \boxed{\frac{c_0 d}{W}}$$

H-filter

- Can plot time evolution for d=W/2
- Lowest-order mode (n=1) is dominant

$$c(x,t) = \sum_{n=1}^{\infty} \frac{2c_0}{n\pi} \sin\left(\frac{n\pi d}{W}\right) \cos\left(\frac{n\pi x}{W}\right) \cdot e^{-\alpha_n t} + \frac{c_0 d}{W}$$

$$\alpha_n = \left(\frac{n\pi}{W}\right)^2 D$$



H-filter

- **What we'd like to know is how separation scales with *D*, *t*, etc.**
- **We can determine the concentration of solute in output channel**
- **Solve for case of *d*=*W/2***

$$c_{out} = \frac{1}{W-d}\int_{d}^{W} c(x,t)\,dx$$

$$c_{out} = \frac{2}{W}\int_{W/2}^{W} c(x,t)\,dx$$

$$c(x,t) = \sum_{n=1}^{\infty} \frac{2c_0}{n\pi}\sin\left(\frac{n\pi}{2}\right)\cos\left(\frac{n\pi x}{W}\right)\cdot e^{-\alpha_n t} + \frac{c_0}{2}$$

$$c(x,t) = \sum_{n\ odd} \frac{2c_0}{n\pi}(-1)^{n+1/2}\cos\left(\frac{n\pi x}{W}\right)\cdot e^{-\alpha_n t} + \frac{c_0}{2}$$

H-filter

> **Only focus on 1st mode**
- **Simplifies math**
- **Is dominant mode**

> **First mode has error at t=0**
- **Need other terms to meet I.C.**

$$c(x,t) \approx \frac{2c_0}{\pi}\cos\left(\frac{\pi x}{W}\right)\cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt} + \frac{c_0}{2}$$

$$c_{out} = \frac{2}{W}\int_{W/2}^{W}\left(\frac{2c_0}{\pi}\cos\left(\frac{\pi x}{W}\right)\cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt} + \frac{c_0}{2}\right)dx$$

$$c_{out} = \frac{2}{W}\left[\frac{2c_0 W}{\pi^2}\sin\left(\frac{\pi x}{W}\right)\Bigg|_{W/2}^{W}\cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt} + \frac{c_0 W}{4}\right]$$

$$c_{out} = \frac{2}{W}\left[\frac{-2c_0 W}{\pi^2}\cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt} + \frac{c_0 W}{4}\right]$$

$$\boxed{c_{out} = \frac{c_0}{2}\left[1 - \frac{8}{\pi^2}\cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt}\right]}$$

H-filter

- Can also look at all modes at short time
- Result is that increases as √Dt for short times

$$c(x,t)=\sum_{n=1}^{\infty}\frac{2c_0}{n\pi}\sin\left(\frac{n\pi}{2}\right)\cos\left(\frac{n\pi x}{W}\right)\cdot e^{-\alpha_n t}+\frac{c_0}{2}$$

↓ **Take average over output channel**

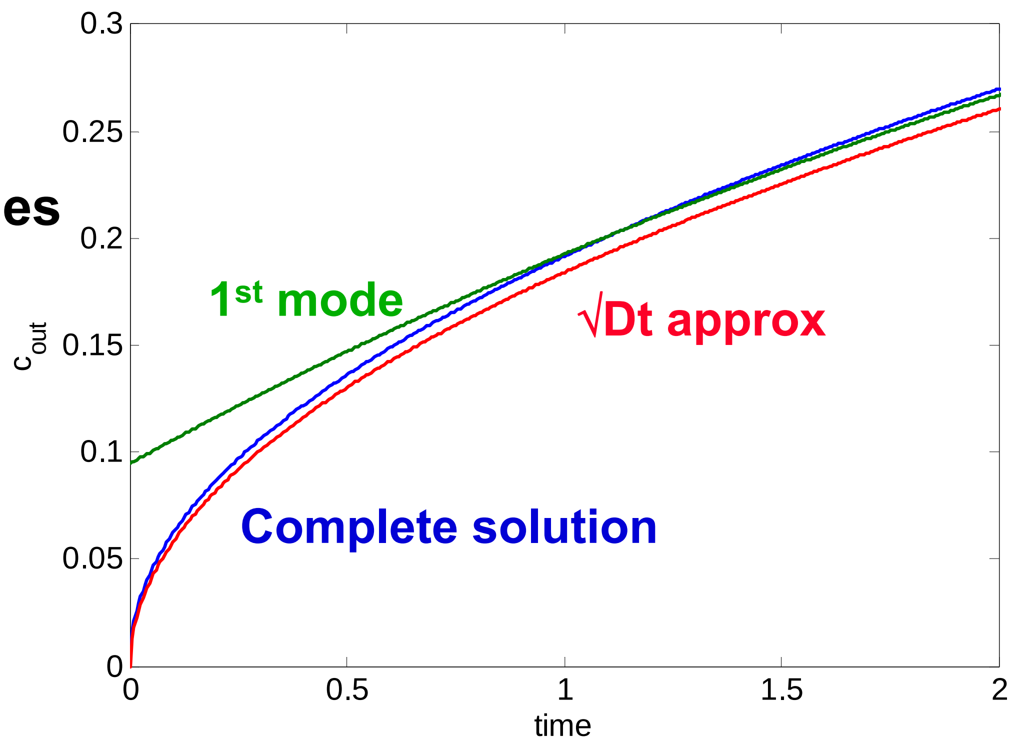
$$c_{out}=\frac{c_0}{2}-\frac{4c_0}{\pi^2}\sum_{n\ odd}\frac{1}{n^2}e^{-\alpha_n t}$$

↓ **?**

$$c_{out}\approx 1.1\sqrt{\frac{Dt}{W^2}}$$

H-filter design implications

- Since c_{out} scales with both D and t, $c_{out,1}/c_{out,2}$ will be independent of time *at short times*
- If D_1>>D_2, then increasing time and decreasing W helps
  - Minimum W is set by
    - » Pressure drop increases
    - » Clogging and bubbles



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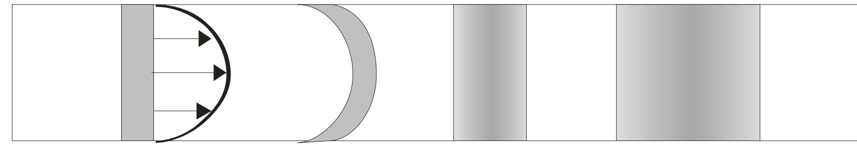
Taylor dispersion

- Was ignoring convection OK?
  - Not really
- One can solve the 1-D convection-diffusion problem
- This is called Taylor Dispersion
  - Axial convection + transverse diffusion
- The result is that the plug spreads out faster than from simple diffusion
- The apparent diffusivity is K
- EOF does NOT suffer from Taylor dispersion
  - Uniform flow field



$$K_i = D_i + \frac{U^2 h^2}{210 D_i} = D_i\left(1 + \frac{Pe^2}{210}\right)$$

Parallel-plate flow channel

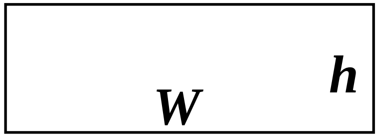
$$K_i = D_i + \frac{U^2 h^2}{210 D_i} f\left(\frac{h}{W}\right)$$

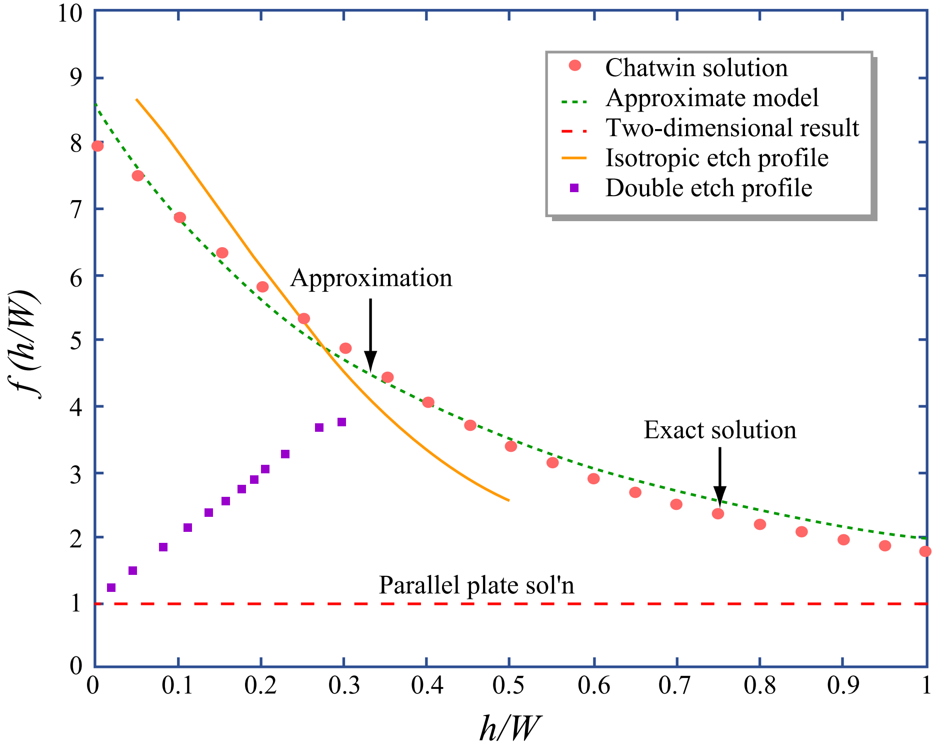
Rectangular flow channel

Taylor dispersion

- **Can determine K_i for rectangular channels**
- **As $h/W \rightarrow 0$, $f(h/W) \rightarrow$ ~7.95 NOT 1**
  - **Because of 2-D profile at wall**
- **This implies that for a given h, bigger h/W is better → area small**
- **But this means a smaller channel cross-section and higher U, therefore possibly more dispersion**

$$f\left(\frac{h}{W}\right) \approx \frac{W}{h}\frac{8.5hW}{h^2 + 2.4hW + W^2}$$





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Convection, diffusion, and mixing

- **We can use convection for good as well as evil**
- **At steady state, fluid mixing time turns into distance**
- **Short distances from inlet, two fluids appear not to mix**

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Mixing

- Mixing is driven by diffusion
- Macroscale mixing uses turbulence (e.g., stirring) to reduce length for diffusive mixing
- In liquid microfluidics, there is no turbulence to decrease mixing lengths

THEREFORE,

- Microfluidic mixing is EASY
- Microfluidic mixing is HARD
- Mixing length scales with Pe

$$L \sim U\frac{W^2}{D} \sim Pe \cdot W$$

$$\tau \approx 2.5\ \text{s} \quad \text{for a 50 } \mu\text{m channel } (D = 10^{-5}\ \text{cm}^2/\text{s})$$

$$\tau \approx 40\ \text{s} \quad \text{for a 200 } \mu\text{m channel } (D = 10^{-5}\ \text{cm}^2/\text{s})$$

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Cover of *Science* 285, no. 5425 (July 2, 1999): 1-156.

Mixing

- How does one define mixing?
- No universal definition
- One definition:
  - When concentration profile is uniform to within 1% (or 5%)
- For our rectangular channel, concentration difference is biggest between *x=0* and *x=W*

$$\Delta c_{\max} = c(0,t) - c(W,t)$$

$$= \sum_{n=1}^{\infty} \frac{2c_0}{n\pi} \sin\left(\frac{n\pi d}{W}\right)\left[1-(-1)^n\right] \cdot e^{-\alpha_n t}$$

$$= \sum_{n\ \mathrm{odd}} \frac{4c_0}{n\pi} \sin\left(\frac{n\pi d}{W}\right) \cdot e^{-\alpha_n t}$$

$$\Delta c_{\max} \approx \frac{4c_0}{\pi} \sin\left(\frac{\pi d}{W}\right) \cdot e^{-\left(\frac{\pi}{W}\right)^2 Dt}$$

$$\frac{\Delta c_{\max}}{c_0\, d/W} = 0.01$$

$$c(x,t) = \sum_{n=1}^{\infty} \frac{2c_0}{n\pi} \sin\left(\frac{n\pi d}{W}\right) \cos\left(\frac{n\pi x}{W}\right) \cdot e^{-\alpha_n t} + \frac{c_0 d}{W}$$

$$\alpha_n = \left(\frac{n\pi}{W}\right)^2 D$$

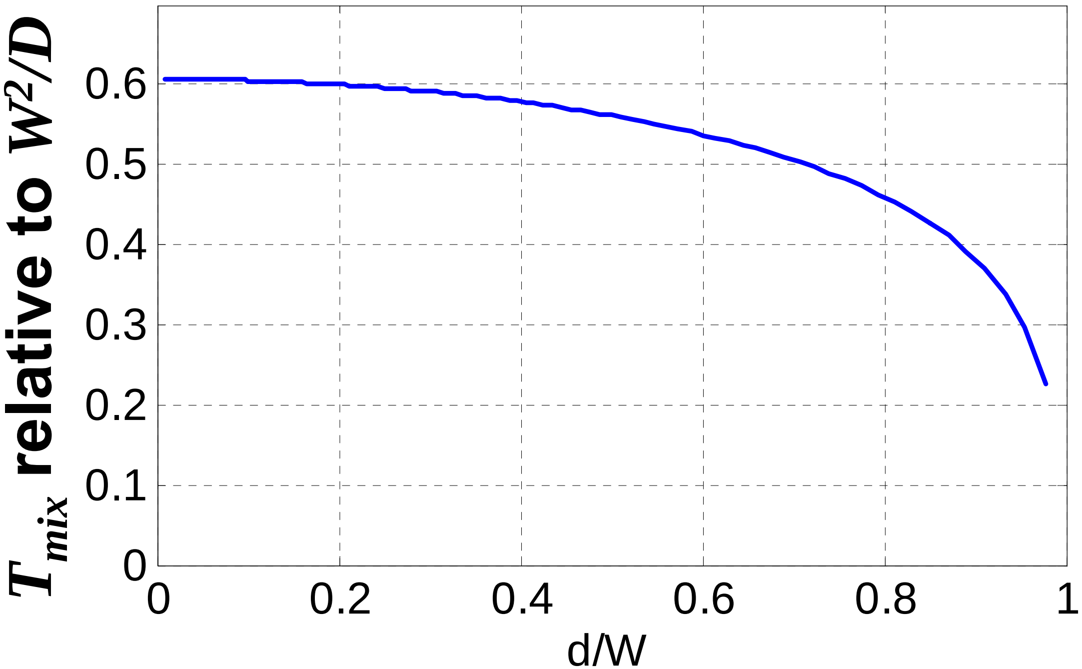
$$T_{mix} = \left(\frac{W^2}{D}\right) \frac{1}{\pi^2} \ln\left[\frac{400}{\pi} \frac{W}{d} \sin\left(\frac{\pi d}{W}\right)\right]$$

Mixing

> **Mixing time scales as expected for semi-infinite diffusion**

$$T_{mix} = \left(\frac{W^2}{D}\right)\frac{1}{\pi^2}\ln\left[\frac{400}{\pi}\frac{W}{d}\sin\left(\frac{\pi d}{W}\right)\right]$$

$$T_{mix} \approx 0.5\left(\frac{W^2}{D}\right)$$



Mixing

- At the microscale various approaches exist for reducing diffusion lengths
  - Depends on how fast you need to mix
- Approaches trade off fabrication complexity, generality, mixing time, etc.
- All find ways to laminate two fluids

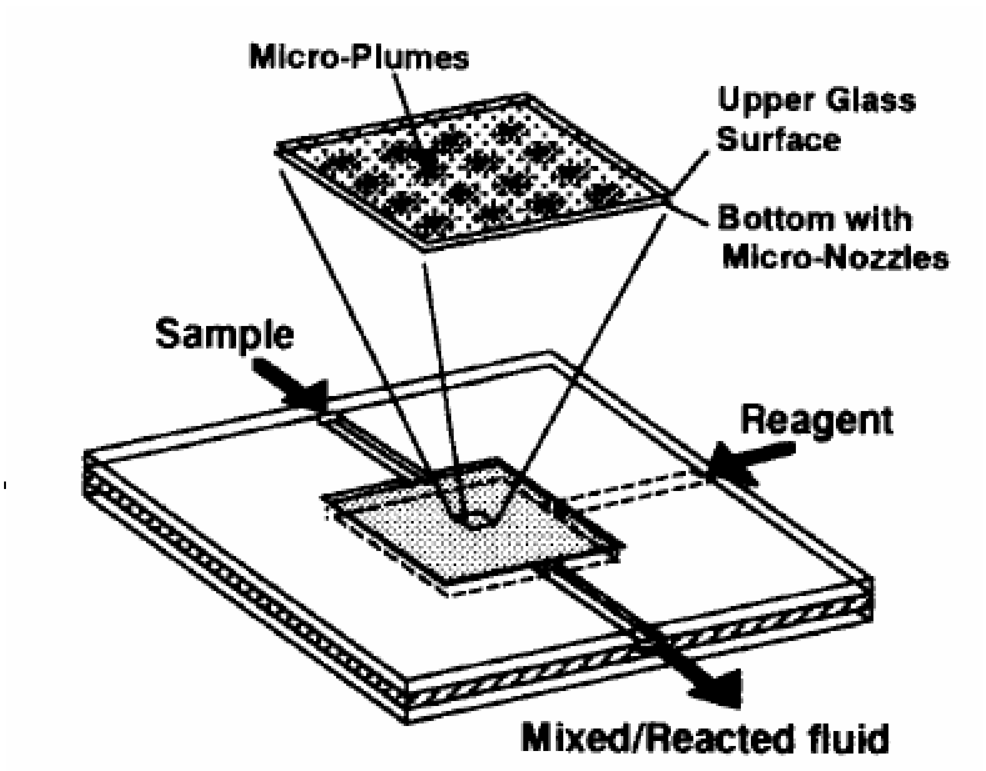


Figure 2 on p. 249 in Miyake, R., T. S. J. Lammerink, M. Elwenspoek, and J. H. J. Fluitman. "Micro-Mixer with Fast Diffusion." In *Micro Electro Mechanical Systems, 1993, MEMS '93: An Investigation of Micro Structures, Sensors, Actuators, Machines and Systems, February 7-10, 1993*. New York, NY: Institute of Electrical and Electronics Engineers, 1993, pp. 248-253. ISBN: 9780780309579. © 1993 IEEE.

Mixing

- 3-D split and recombine lamination
- Complicated fab
- Typical of early designs that focused on Si

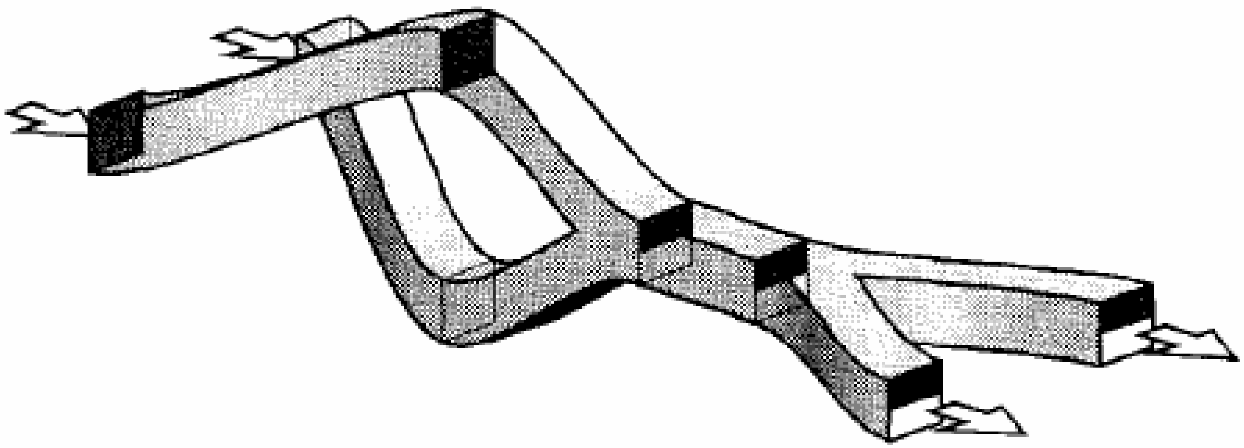


Figure 1 on p. 442 in Branebjerg, J., P. Gravesen, J. P. Krog, and C. R. Nielsen, C.R. "Fast Mixing by Lamination." In *Micro Electro Mechanical Systems, 1996, MEMS '96: An Investigation of Micro Structures, Sensors, Actuators, Machines and Systems, February 11-15, 1996*. New York, NY: Institute of Electrical and Electronics Engineers, 1996, pp. 441-446. ISBN: 9780780329850. © 1996 IEEE.

Mixing

- **Laminate in one level of channels by moving complexity from fab to packaging**

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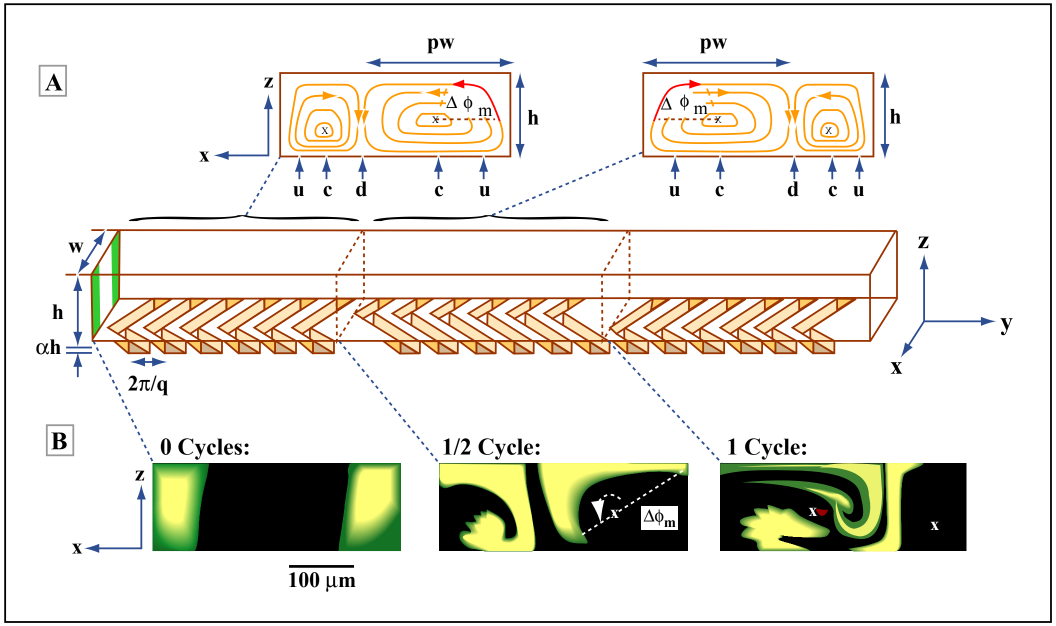
Figures 2 and 4 on pp. 266-267 in Jackman, R. J., T. M. Floyd, R. Ghodssi, M. A. Schmidt, and K. F. Jensen. "Microfluidic Systems with On-line UV Detection Fabricated in Photodefinable Epoxy." *Journal of Micromechanics and Microengineering* 11, no. 3 (May 2001): 263-269.

Passive chaotic micromixer

- Fairly simple to make
- Uses simple pressure-driven flow
- Anisotropic boundary induces anisotropic flow
- Stroock *et al.*, Science 295(2002):647



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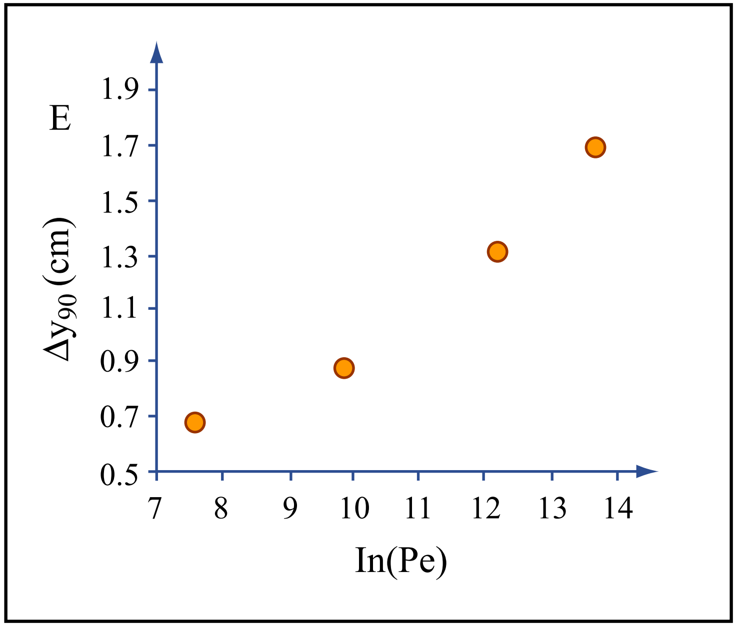
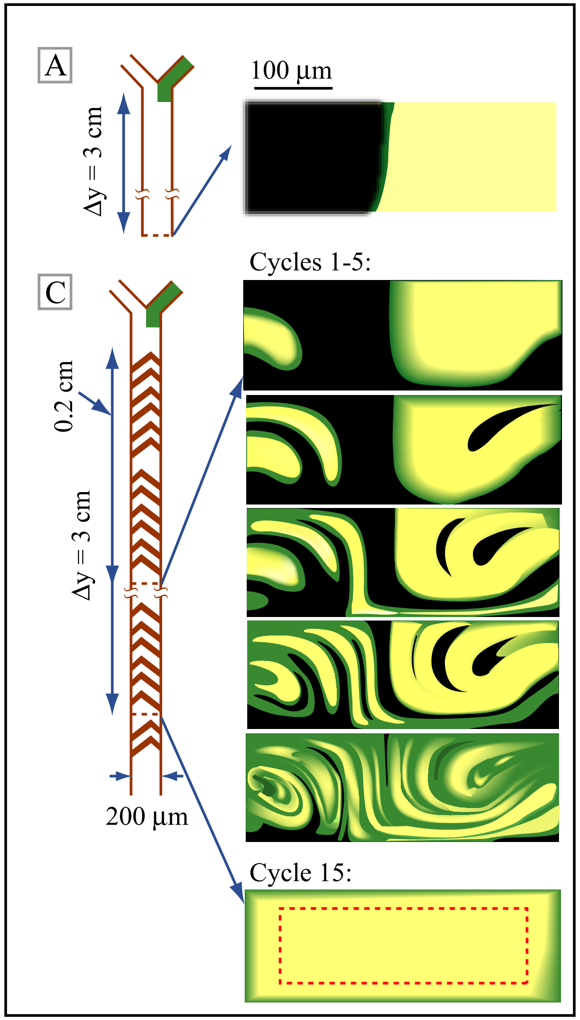
Passive chaotic micromixer

> **Mixing length scales with ln(Pe)**
> - **Rather than Pe in pure diffusive mixing**





Images by MIT OpenCourseWare. Adapted from Figure 3 on p. 649 in Stroock, A. D., S. K. W. Dertinger, A. Ajdari, I. Mezic, H. A. Stone, and G. M. Whitesides. "Chaotic Mixer for Microchannels." *Science* New Series, 295, no. 5555 (January 25, 2002): 647-651.

More info

- **Microfluidic flow**
  - ***Viscous fluid flow*, F. White**
  - ***Low Reynolds Number Hydrodynamic*, Happel & Brenner**
  - **Gravesen et al., "Microfluidics, A Review", JMME 3(1993) 168**
    - **Includes lumped resistances for turns, constrictions, etc.**
  - **"Life at Low Reynolds Number", E.M. Purcell**
    - ***http://brodylab.eng.uci.edu/%7Ejpbrody/reynolds/lowpurcell.html***
  - **Stone et al., Ann. Rev. Fluid Mech., 36(2004) 381.**
- **Transport**
  - ***Analysis of Transport Phenomena,* W. Deen**
  - ***Transport Phenomena,* Bird, Stewart & Lightfoot**
- **Taylor Dispersion**
  - **Dutta & Leighton, Anal. Chem., 73(2001), 504**
  - **Chatwin & Sullivan, J. Fluid Mech., 120(1982), 347**