EPFL

Process Intensification and Green Chemistry

Microreactors

EPFL
Master of Science in Chemical Engineering and Biotechnology
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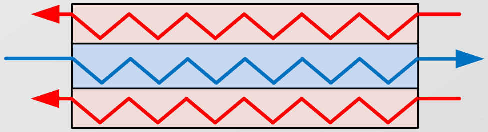
Outlook

- Overview of microreactors
  - Applications
  - Pros & cons
  - Materials of construction
  - Key dimensionless numbers
- Passive micromixers
  - Parallel lamination
    - T and Y mixers: flow regimes, mixing mechanism
    - Multilamination mixers: mixing mechanism, examples
  - Serial lamination
    - Mixing mechanism
    - Examples
  - Chaotic mixers
    - Mixing mechanism
    - Examples
  - Segmented flow
    - Flow regimes
    - Taylor flow
    - Mass transfer
    - Mixing
  - Active micromixers
    - Overview
    - Pressure-induced disturbance
    - Electrokinetic instability
  - Commercial microreactors

1. Overview of microreactors

Microreactors

- Miniaturized systems referred to as
  - Microstructured devices
  - Microstructured reactors
  - Microreactors
  - Micromixers
- Three-dimensional structures with internal dimensions in the sub-millimeter range
- Usually sandwich-like structures consisting of integrated layers with micro-machined channels



- Some function of layers include: mixing, catalytic reaction, heat exchange, separation

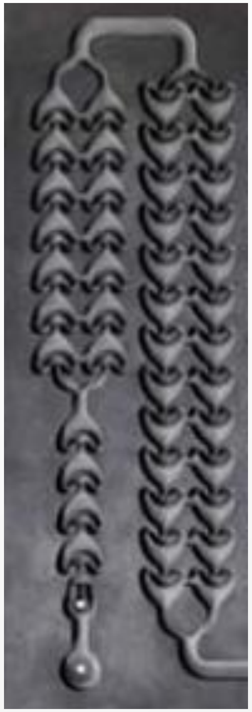
Classification of micromixers

Passive	Active

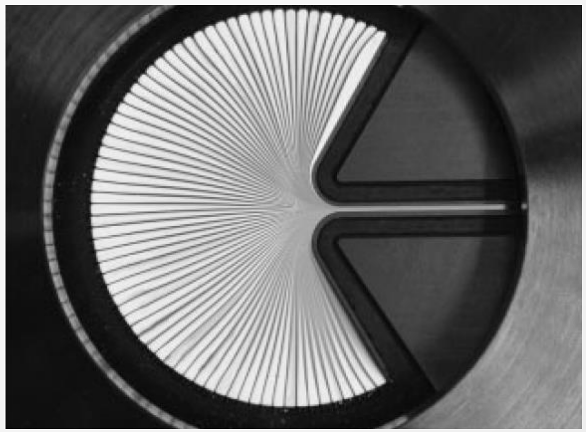
• Lamination
  • Parallel
  • Serial
• Injection
• Chaotic advection
• Droplet
	• Pressure disturbance
	• Electrohydrodynamic
	• Dielectrophoretic
	• Electrokinetic
	• Magneto hydrodynamic
	• Accoustic
	• Thermal

Nam-Trung Nguyen and Zhigang Wu 2005 J. Micromech. Microeng. 15

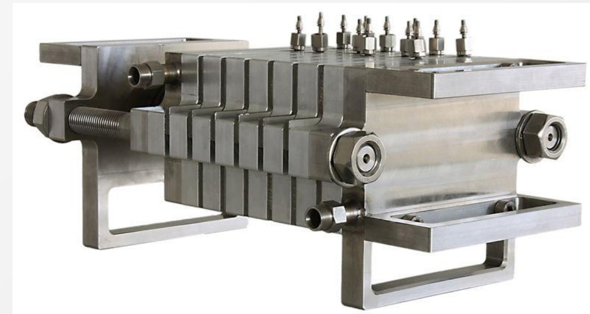
Pictures of a few micro- (or milli-) reactors



Corning

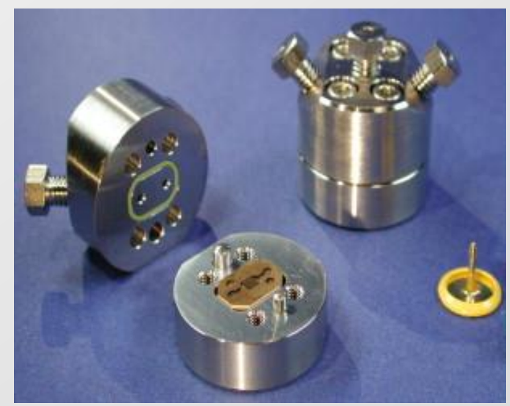


SuperFocus



Lonza FlowPlate®

Little Things Factory



IMM mainz

Optional

Some institutes and companies active in the field of microprocess engineering

Microreactors activities	Company / institute
Microreactor design and fabrication **Process development**	Fraunhofer ICT-IMM Mainz Forschungszentrum Karlsruhe GmbH Ehrfeld Mikrotechnik BTS Microinnova Engineering GmbH
Microreactor design and fabrication **Development of laboratory systems**	Mikroglas GmbH, Mikronit Microfluidics Little Things Factory, Syrris
Engineering services	Bayer Technology Services Alfa laval
Development of Microreactor materials	Corning
Microreactor process development **Demonstration of industrial production**	Merck, SK Chemicals, Ampac Fine Chemicals, Phoenix Chemicals, Clariant, DSM, Lonza, Sigma-Aldrich

Ranges of application of microreactors

- Gas-phase reactions
- Gas-liquid reactions
- Liquid phase reactions
- Liquid-liquid reactions
- Heterogeneous catalysis (e.g. wall-coating with catalyst)

Ranges of application of microreactors

- Fast, mixing-sensitive reactions
  - ⇨Maximize selectivity
- Fast exothermic reactions
  - ⇨Fast heat removal, avoid hot-spot, increased safety in case of large adiabatic temperature rise and hazardous product decomposition
- Hazardous (e.g., toxic or explosive) reactants, intermediate or products
  - ⇨Lower inventory of hazardous substances, minimizing impact in case of accidental release

Some examples of applications of microreactors

- Nitrations
- Hydrogenations
- Polymerizations
- Oxidations (e.g. hydrogen peroxide, air, oxygen)
- Halogenations
- Reactions with diazomethane
- Phosgene generation
- Nanoparticles

Advantages of microreactors

- Advantages come from their small dimensions
  - ⇨ Increase in rates of transport processes
  - ⇨ Increase in interfacial area (surface-to-volume ratio)
- High heat transfer rates
  - ○ Small channel dimensions → high surface/volume ratio $\frac{A}{V}$
    - up to $50000\,\frac{m^2}{m^3}$ vs $<\ 100\,\frac{m^2}{m^3}$ for conventional lab/production equipment
  - ○ High overall heat transfer coefficient U
    - up to $10000\,\frac{W}{m^2K}$ vs $< 2000\ \frac{W}{m^2K}$ for conventional heat exchangers
  - ⇨ Overall specific rate of heat transfer $\dot{q} = U\frac{A}{V}\Delta T$ is 2-3 orders of magnitude higher than in conventional equipment

Advantages of microreactors

- High mass transfer rates for multiphasic systems
  - Fluid/fluid interfacial area (a) up to $3 \cdot 10^4 \frac{m^2}{m^3}$ vs $\sim 100 \frac{m^2}{m^3}$ for conventional equipment (e.g. bubble-columns)
- Low mixing times
  - Milliseconds or even less can be attained vs ~1 s in conventional devices
- Small holdup
  - Reduce inventory of hazardous reaction mixture (toxicity, thermal instability)→enhanced process safety
- Residence time distribution near to plug flow
  - Required to maximize selectivity for many reaction types
- Access to novel operating windows
  - High p/T/c to accelerate reactions, increase gas solubility, shift equilibria, avoid solvent evaporations, minimize or avoid use of solvent, obtain single-phase process,...

Advantages of microreactors

- Numbering-up (or scaling-out) instead of scaling up
  - Increase number of parallel operating units
  - Simple and fast (no redesign, no pilot plant experiments)
  - Shorter time to market
  - Quickly adapt production to market demand
- Often a combination of numbering up and scaleup is used to contain the costs

Disadvantages of microreactors

- Inline measurement / monitoring is challenging (small scale and high rate)
    - (temperature, concentration, …)
- Solids handling
    - Solid reactants, catalysts or by-products may lead to clogging
- Life and robustness
    - Limited industrial experience with long term operation available (corrosion, scaling, performance,…)
- Scale-up and numbering up
    - Numbering-up (parallelization) → proportional cost increase, which may oppose benefits of intensification
    - Scaling up to the right characteristic size of the process avoids the later problem but generic design rules/methodologies are still missing

Materials of construction

Some pros/cons of typical materials used

- **Silicon**
  - ✓ Available, inexpensive, inert, usable in wide temperature range, high-precision fabrication: micromachining experience from IC (Integrated Circuits) and MEMS (Micro-Electro-Mechanical Systems)
  - ✗ Expensive fabrication, clean-room required, not safe at high P/T (connections to inlet/outlet ports)
- **Metals**
  - ✓ No clean-room needed, durable materials, well-established fabrication techniques (Micromachining, wet chemical etching, selective laser melting,…), robust, good mechanical resistance, good heat conduction
- **Glass**
  - ✓ Cheap, transparent, corrosion-proof, withstands relatively high-pressure, electro-osmotic flow possible
  - ✗ Bad heat exchange, delicate, difficult to create high aspect-ratio structures

Materials of construction

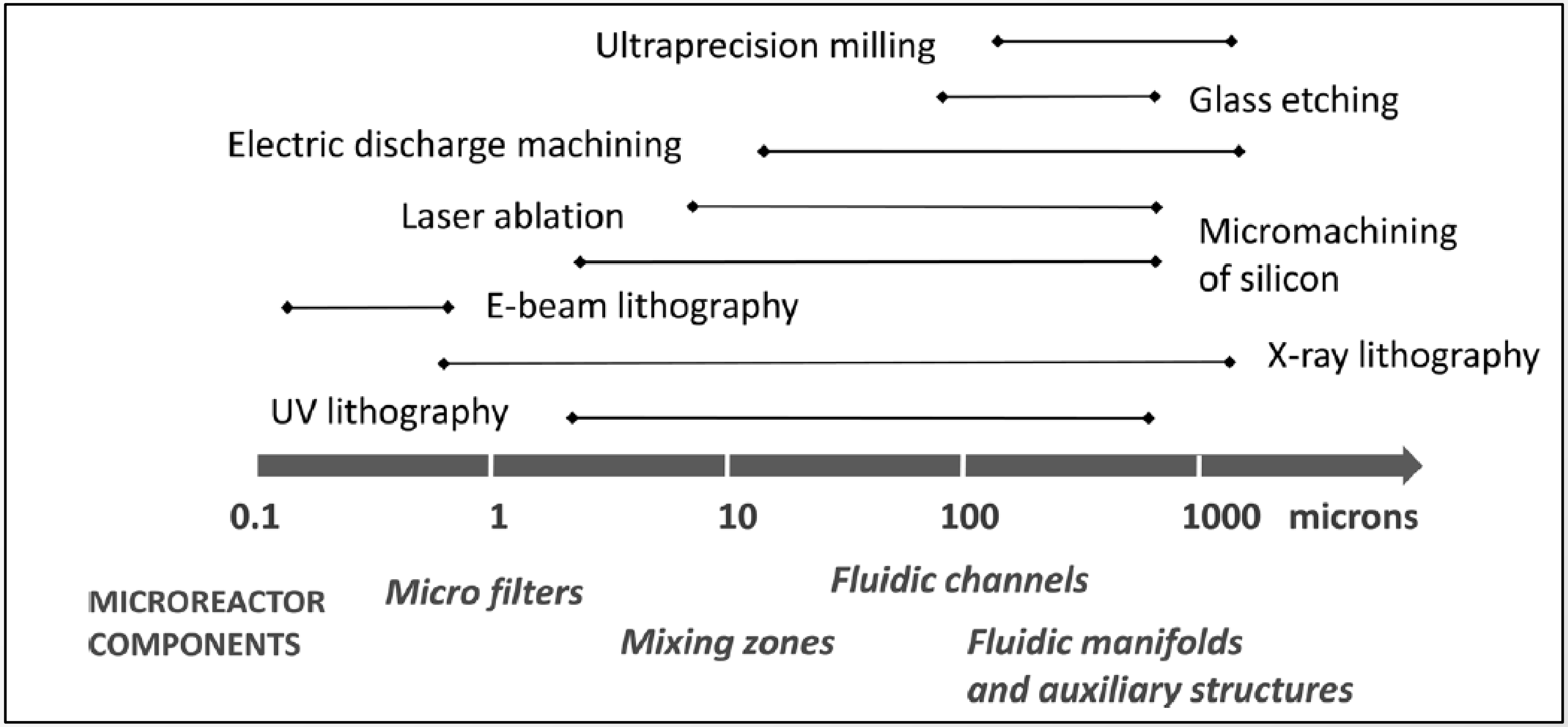
Some pros/cons of typical materials used

- **Silicon carbide**
  - ✓ High thermal conductivity
  - ✘ Brittleness
- **Plastics**
  - ✓ Low cost, various fabrication techniques, fast prototyping cycle, tunable properties, disposable microreactors available, PDMS (polydimethylsiloxane) transparent >280 nm, PFA also transparent
  - ✘ Thermal stability, chemical compatibility

Materials of construction
Some selection criteria

- Operating conditions
  - Pressure, temperature
- Physical properties of the reaction mixture
  - pH, viscosity, phase, reactivity
- Cost
- Ability of mass production
- Ease of fabrication

Fabrication techniques

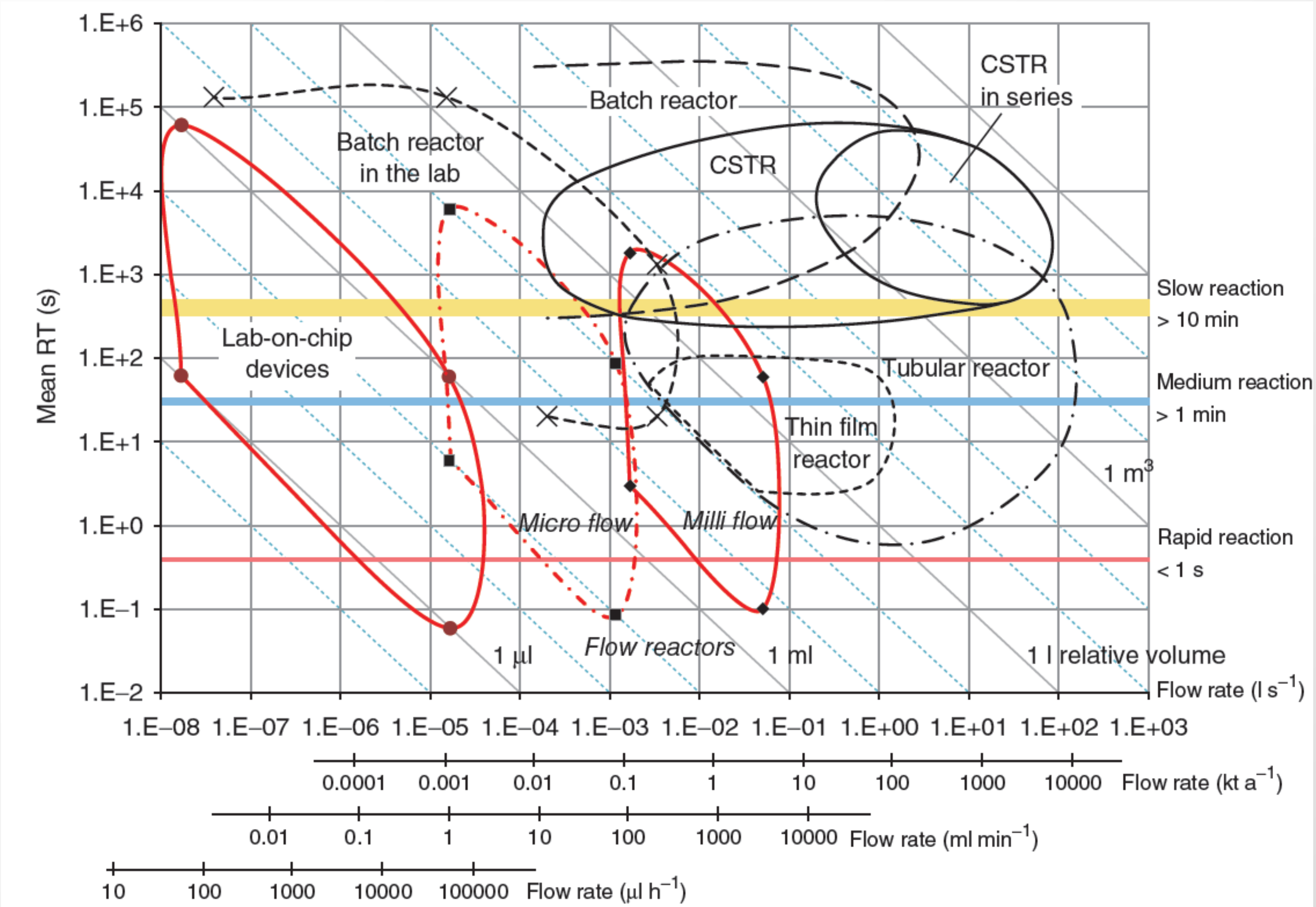


Accuracy of manufacturing techniques

Ehrfeld, W., Hessel, V. and Löwe, H. (2000) Microreactors (New Technology for Modern Chemistry), Wiley-VCH Verlag, Weinheim.

Mapping of chemical reactors

Flowrate / mean residence time



Hessel, V., Kralisch, D. and N. Kockmann. Novel Process Windows, Chapter 12, 2015. Wiley.

Key dimensionless numbers
Reynolds and Peclet numbers

Hydraulic diameter

$$Re = \frac{\text{momentum}}{\text{viscous friction}} = \frac{u\, d_h}{\nu}$$

Small d_h ⇨ laminar regime (Re<~2300) occurs in most micromixers

Mixing path, not reactor length!

$$Pe = \frac{\text{convective transport}}{\text{diffusive transport}} = \frac{u\, L}{D}$$

Decrease diffusion path to decrease *Pe*

Key dimensionless numbers

Strouhal number

Frequency of the perturbation $(\mathrm{p}, \vec{E}, etc)$

$$Str = \frac{\text{residence time}}{\text{period of disturbance}} = \frac{f\ d_h}{u}$$

Used for active micromixers

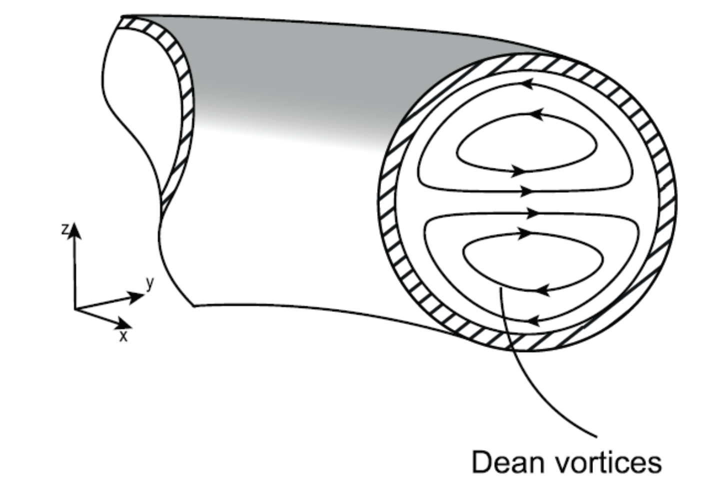
Key dimensionless numbers
Dean number (curved channels)

- Appearance of secondary flow (Dean vortices) for flow in curved pipes
- Characterized by Dean number

$$\boldsymbol{De} = \frac{\sqrt{0.5(\text{inertial forces} \times \text{centripetal forces})}}{\text{viscous forces}} = \boldsymbol{Re}\sqrt{\frac{\boldsymbol{r}}{\boldsymbol{r_c}}}$$

Radius of curvature

- Critical Dean number De_{cr}~150
- $De < De_{cr}$: 1 pair of counter-rotating vortices
- $De > De_{cr}$: 2 additional vortices at outer-channel wall



2. Passive micromixers

2.1. Introduction

Passive micromixers

- Mixing mechanism based on
  - Molecular diffusion
    - Slow but can be accelerated by **reducing the thickness of the fluid lamellae**
  - Chaotic advection
    - Complicated fluid trajectories generated by modulation of the flow system: **splitting, stretching, folding, breaking up a laminar flow**
    - Introduction of a secondary flow
    - Efficient mixing of fluids even at high *Sc* and low *Re*

Passive micromixers

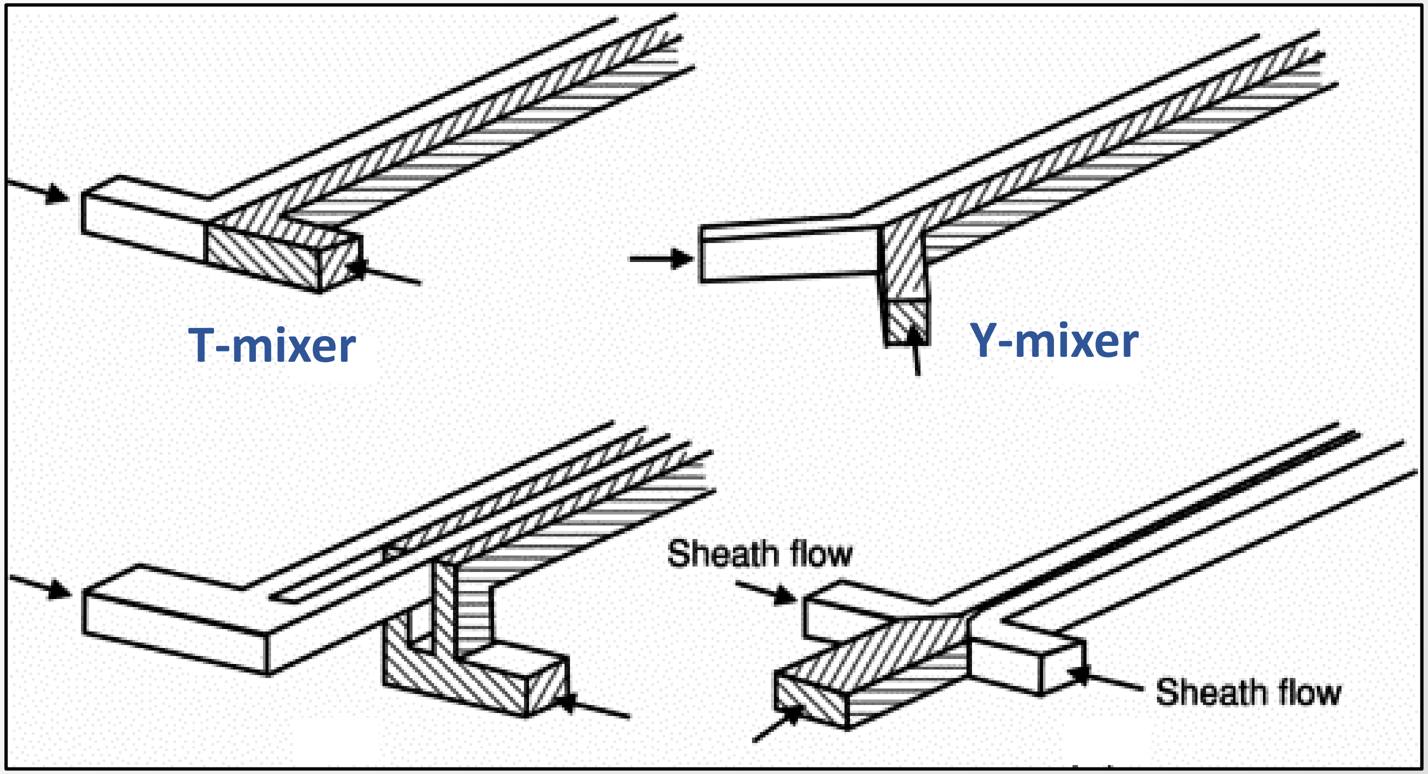
- Energy is only required to generate the flow
- No additional external energy required
- Simpler structures (compared to active mixers)
- No external actuators required
- Robust, stable operation
- Easy to integrate into the process

2. Passive micromixers

2.2. Parallel lamination mixers

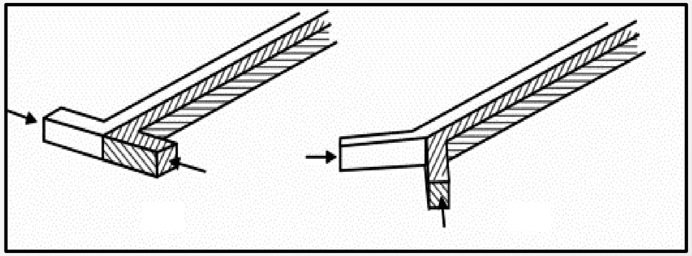
Passive micromixers:
Parallel lamination mixers

Some examples



Parallel lamination principle | **Hydraulic focusing**

Passive micromixers:
Single channel parallel lamination mixers



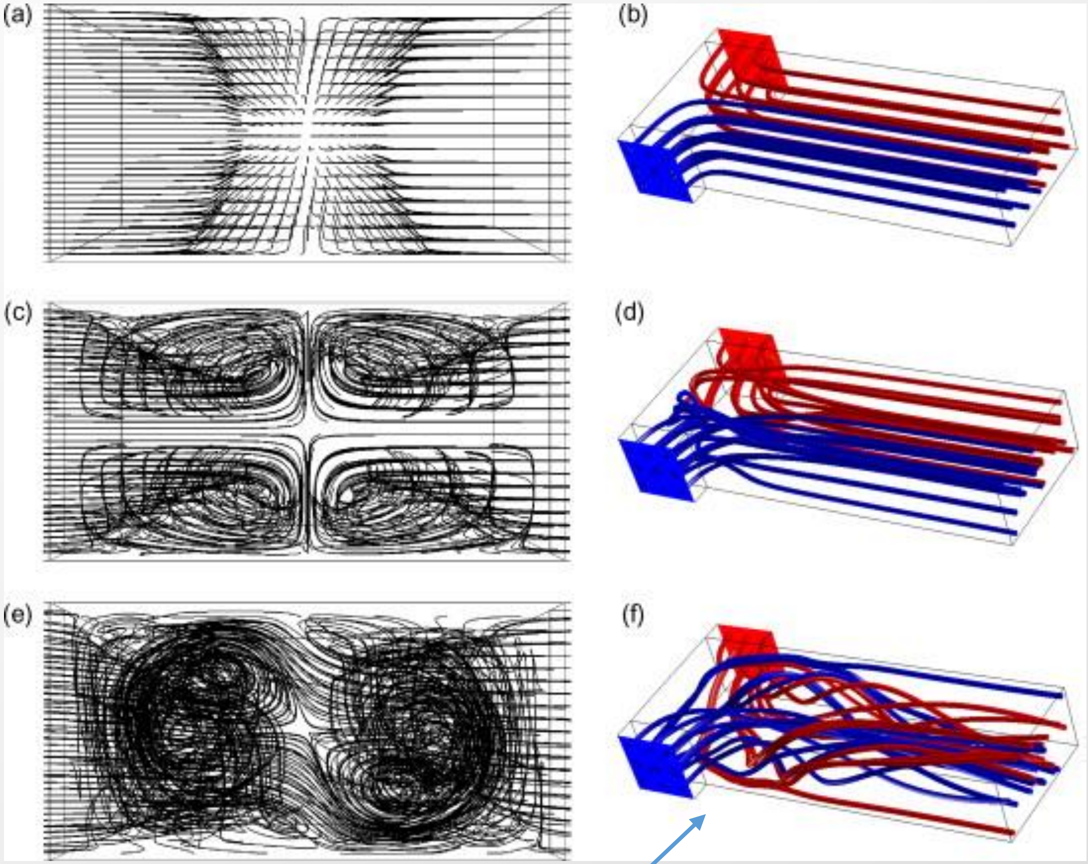
- Simplest forms: T and Y shaped mixers
  - Single channel mixers
  - Rather slow mixing at low Re (stratified flow, diffusion-dependent, low interfacial area)→ long channels required to achieve complete mixing
  - Increase Re → vortex formation → streams get entangled (engulfment flow regime) → accelerated mixing
  - Obstacles and roughening of walls can be used to generate vortices → promotes advection, thus mixing

Flow regimes in T-mixers

Re=12
Stratified flow

Re=80
Vortex flow

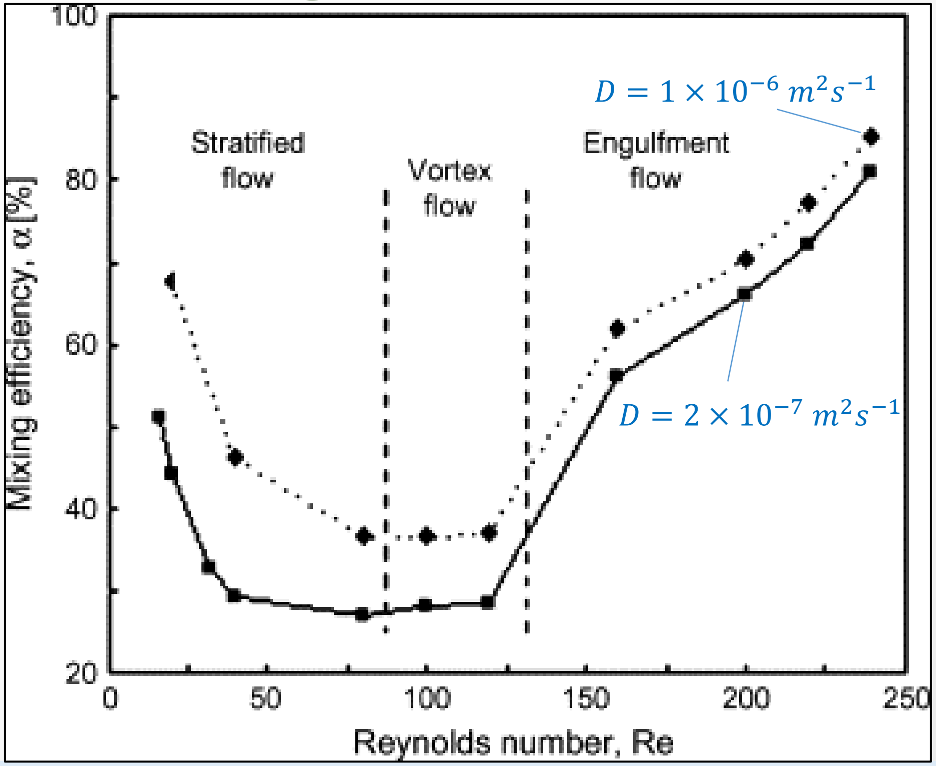
Re=240
Engulfment flow



Engulfment: swirling of fluid drags fluid from the middle to the top and bottom sides of the mixer → mixing improvement

Soleymani et al., Chemical Engineering Journal 135S (2008) S219–S228

Flow regimes in T-mixers



$$\alpha = 1 - \sqrt{\frac{\sigma^2}{\sigma_{max}^2}}$$

$$\sigma^2 = \frac{1}{n}\sum_{i=1}^{n}(c_i - \bar{c})^2$$

Soleymani et al., Chemical Engineering Journal 135S (2008) S219–S228

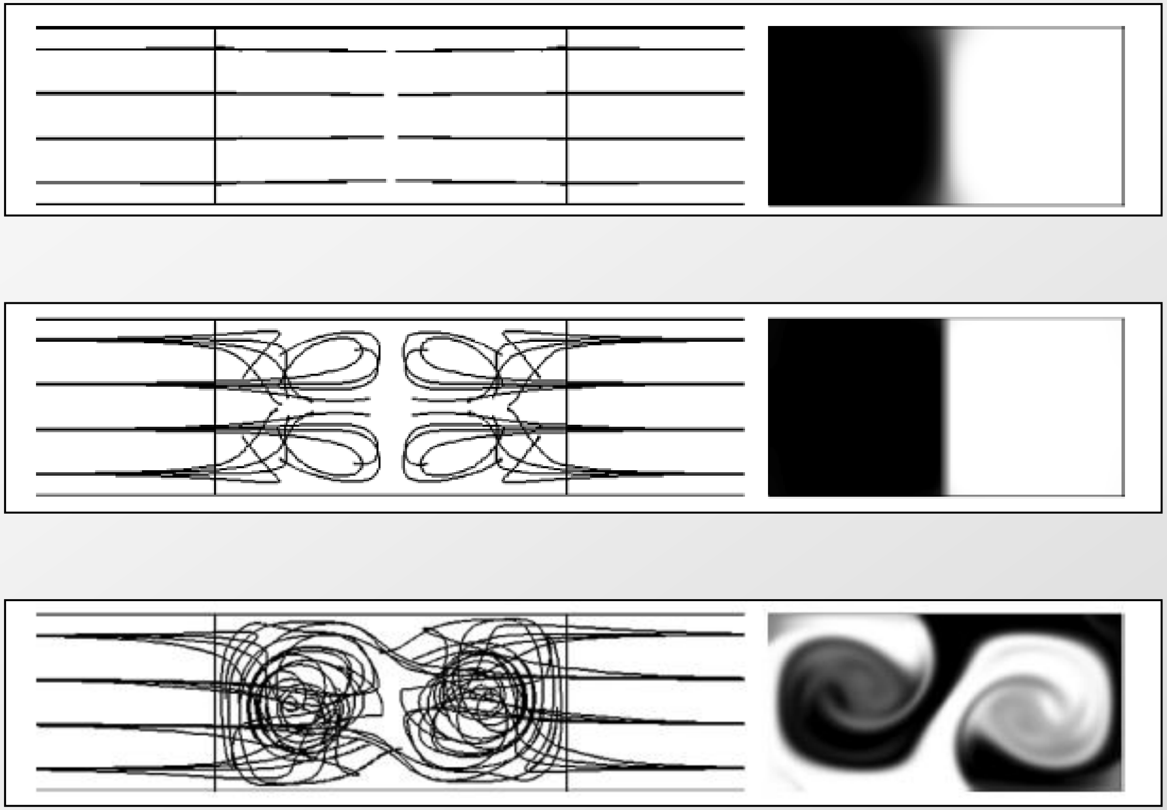
- **Low Re**: laminar, stratified flow → mixing only by diffusion
- Increased Re in stratified and vortex regimes: lower efficiency due to decreased residence time
- **Moderate Re**: increase in mixing efficiency due to convective mass transfer (vorticity).
- **Higher Re**, complex convection-dominated mixing mechanisms; axial symmetry breaks up. Vorticity → increase in contact area → decrease in mixing distance → faster mixing

Flow in T-mixer

Re=1
Stratified flow

Re=100
Vortex flow

Re=200
Engulfment flow



Dreher et al., Heat Transfer Engineering, 30(1–2):91–100, 2009

Passive micromixers

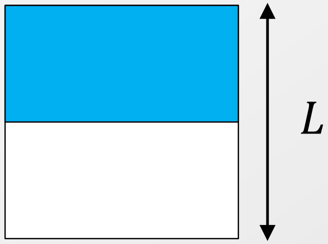
Parallel lamination mixers: multilamination mixers

- Multilamination: generate a decrease (abrupt or progressive) in hydraulic diameter in order to decrease diffusion path → decrease in mixing time
- Two types:
    - Bifurcation type feeds
        - Alternate arrangements of feeds. Sequential splitting and combination
    - Hydrodynamic focusing
        - Focusing of multilaminated feed using a geometric constraint (reduction in flow path dimensions)

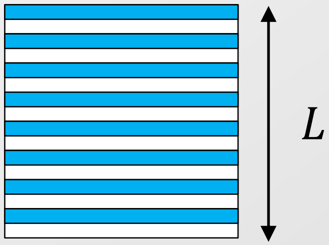
Multilamination mixers

Mixing time reduction by lamination:

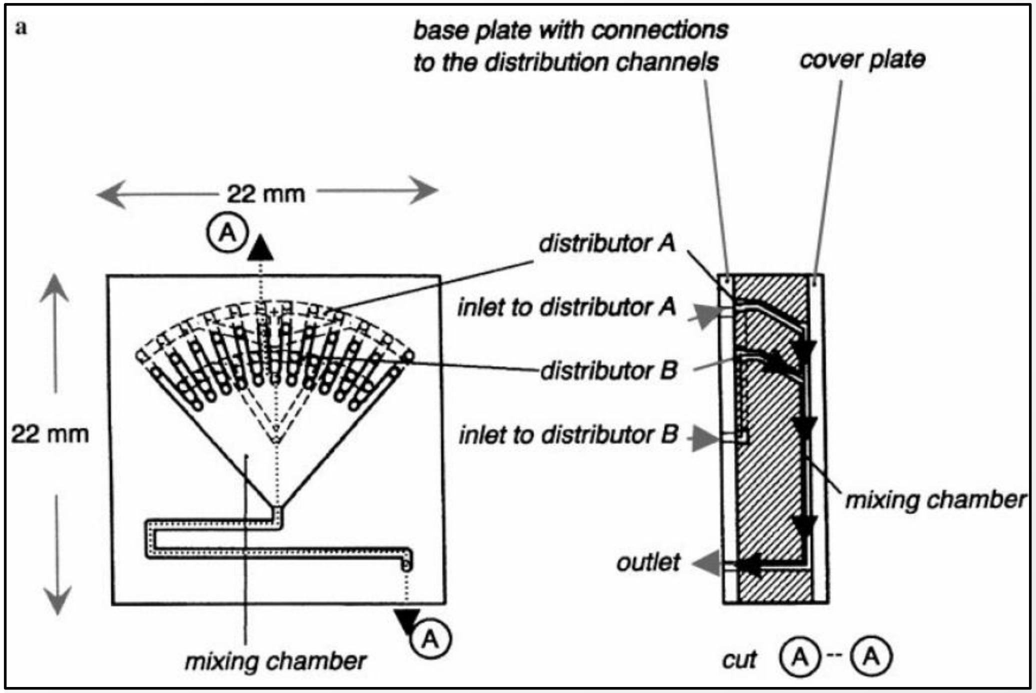
<u>One layer</u>: $t_{mx} \propto \frac{L^2}{D}$

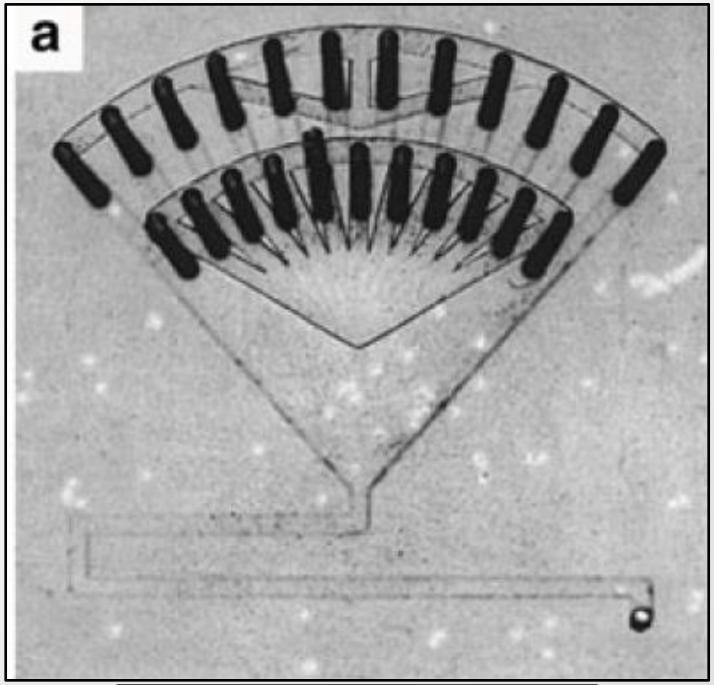


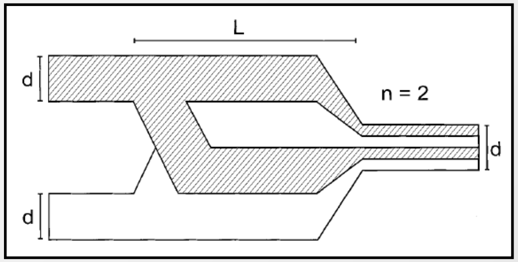
<u>n layers</u>: $t_{mx} \propto \frac{L^2}{\boldsymbol{n^2} D}$

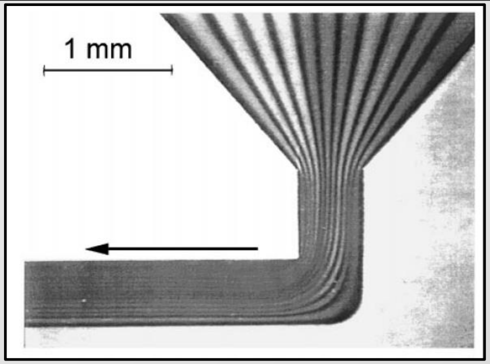


Example of bifurcation-type multilamination micromixer







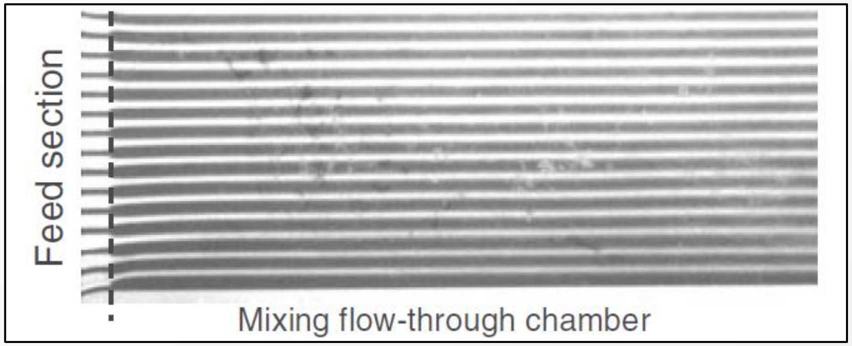


Erbacher et al., Mikrochim. Acta 131, 19-24 (1999)

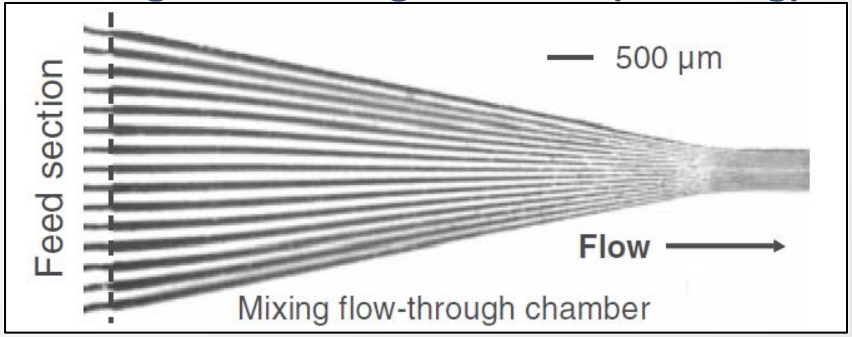
Passive micromixers

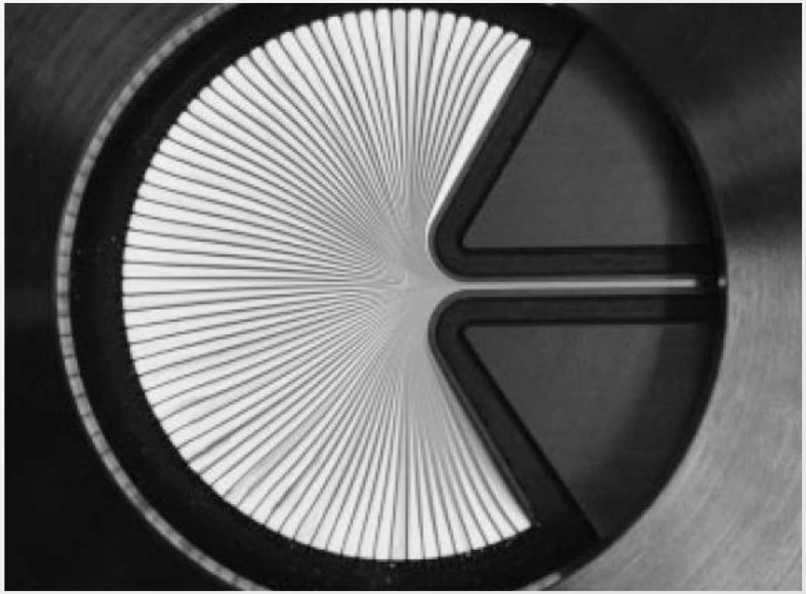
Parallel lamination mixers: multilamination mixers

Rectangular interdigital mixer (no focusing)



Triangular interdigital mixer (focusing)





SuperFocus micromixer

SuperFocus:

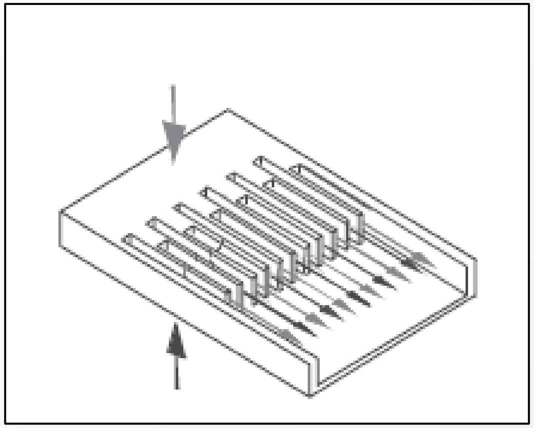
- 138 nozzles
- 4 μm lamellae
- 350l/h (10 bar)
- $t_{mx}(95\%) = 4\ ms$

Lob et al., Chem. Eng. Technol., 27, 340–345 (2004).

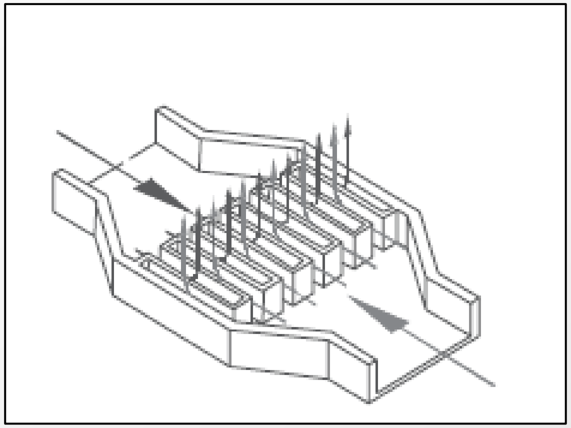
Passive micromixers

Parallel lamination mixers: multilamination mixers

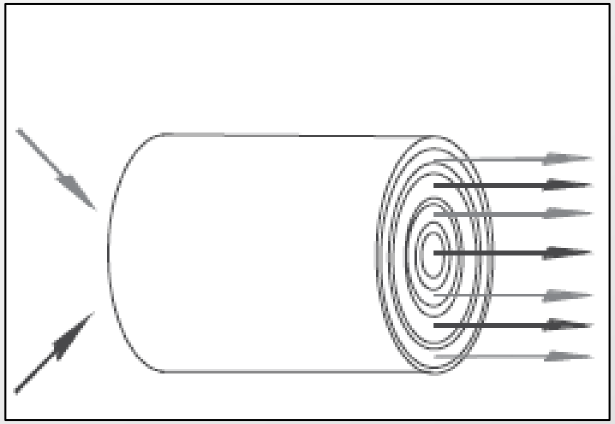
Interdigital mixers



Parallel flow multichannel array



Counter-flow multichannel array



Multi-nozzle system

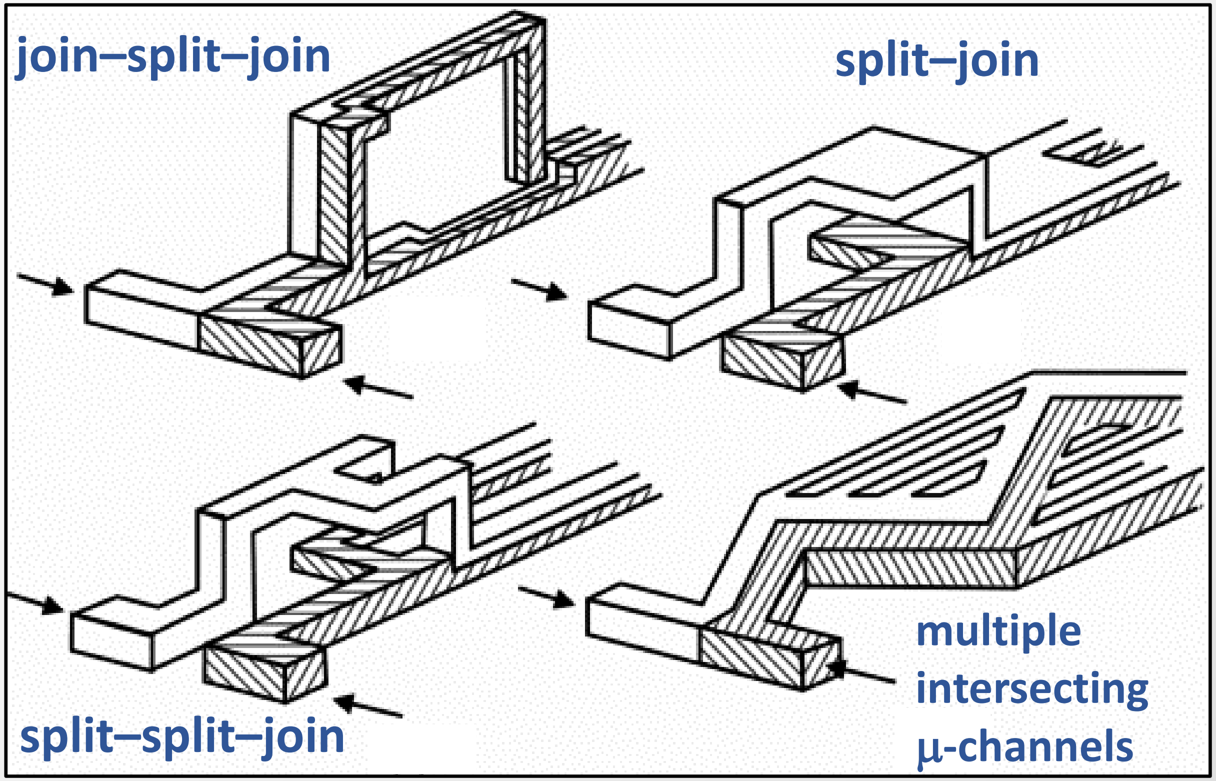
2. Passive micromixers

2.3. Serial lamination mixers

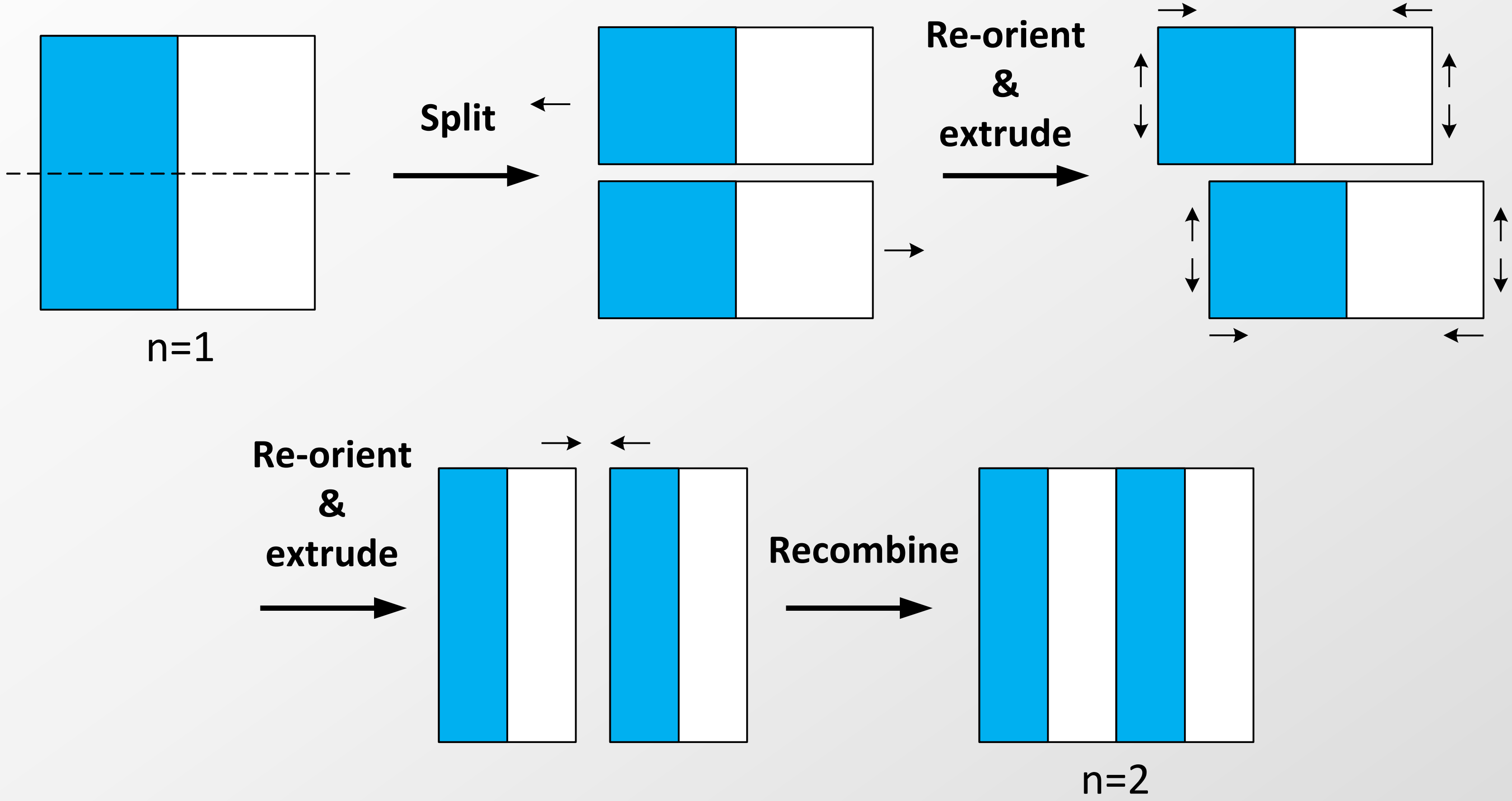
Passive micromixers
Serial lamination mixers

Also called **sequential lamination** or **split-and-recombine** (**SAR**) micromixers

Some examples

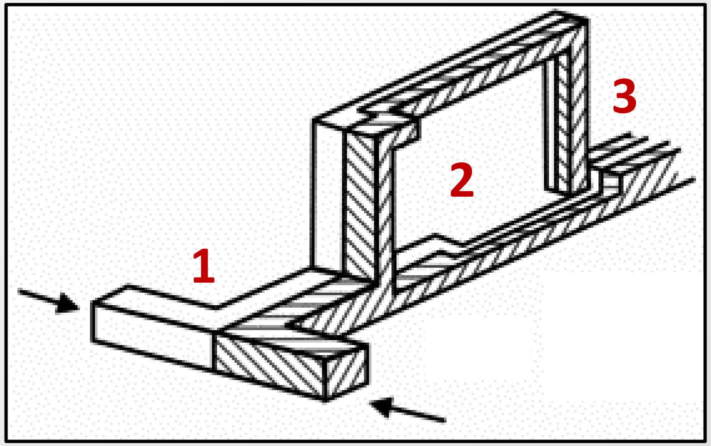


Serial lamination mechanism



Serial lamination principle

1. Inlet streams joined horizontally
2. Twisted vertically and elongated
3. Joined again



For n stages:

- 2^n laminated liquid layers
- 2^{n-1} reduction in diffusion distance
- 4^{n-1} reduction in mixing time

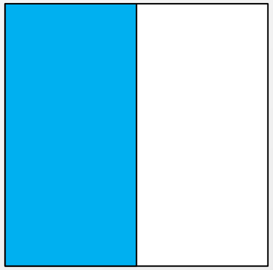
(next slide)

$$t_{mx} \propto \frac{L^2}{D}$$

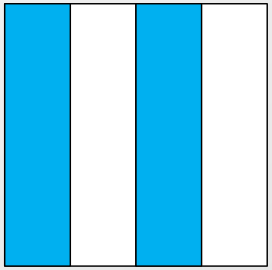
$$\frac{t_{mx,1}}{t_{mx,n}} = 4^{n-1}$$

Serial lamination principle

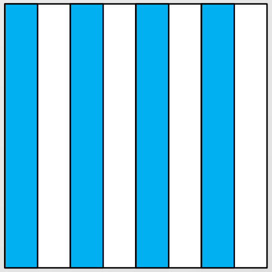
n (steps)	m (layers)	L	t_{mx}	L/L_0	$t_{mx}/t_{mx,0}$
1	2	L_0	$\frac{L_0^2}{D}$	1	1
2	4	$\frac{L_0}{2}$	$\frac{L_0^2}{4D}$	$\frac{1}{2}$	$\frac{1}{4}$
3	8	$\frac{L_0}{4}$	$\frac{L_0^2}{16D}$	$\frac{1}{4}$	$\frac{1}{16}$
n	$\boldsymbol{2^n}$	$\frac{L_0}{2^{n-1}}$	$\frac{L_0^2}{4^{n-1}D}$	$\boldsymbol{\frac{1}{2^{n-1}}}$	$\boldsymbol{\frac{1}{4^{n-1}}}$



n=1

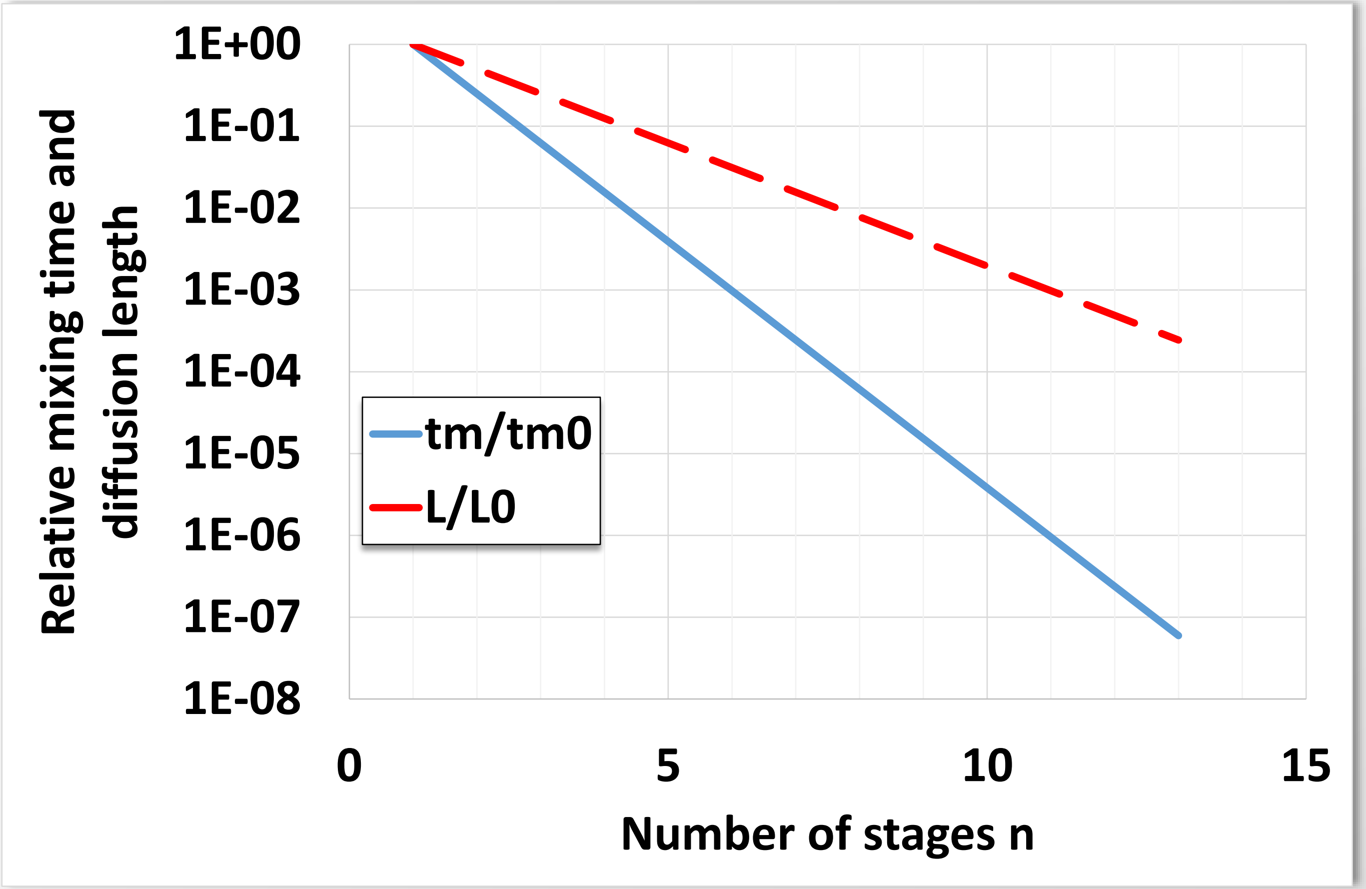


n=2



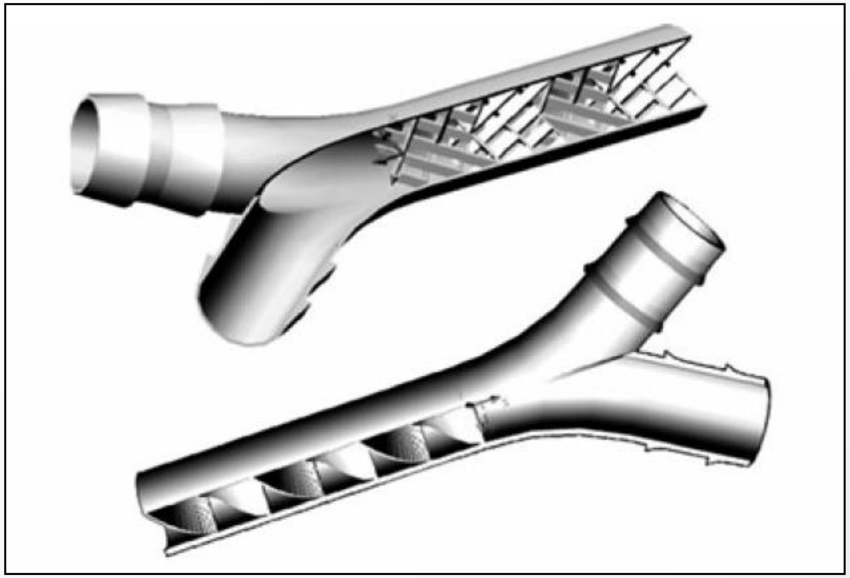
n=3

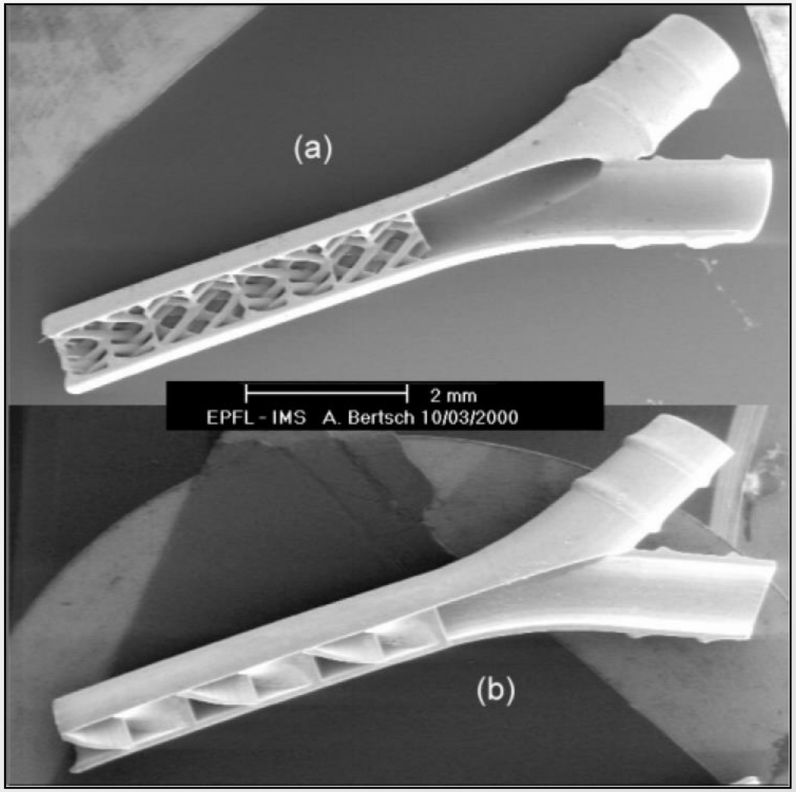
Serial lamination: diffusion path length and mixing time vs step number



Examples of serial lamination mixers

Miniaturized static mixers





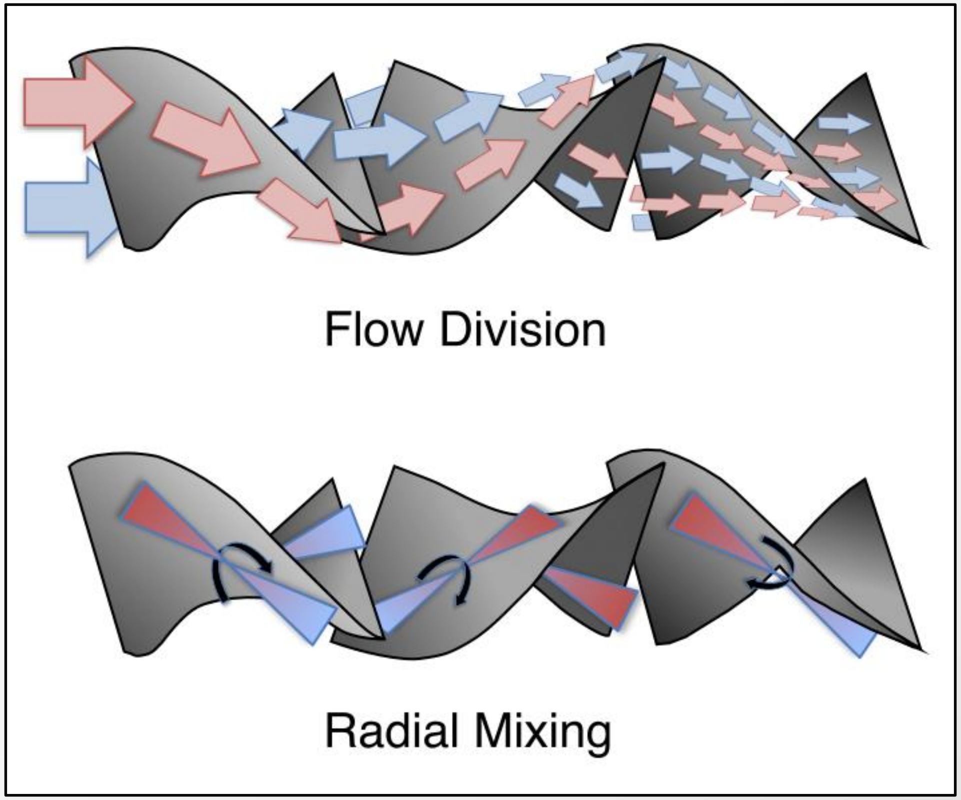
Miniaturized static mixers

(a) Split-rearrange-combine (Sulzer SMX type)
(b) Stretch-fold (Kenics®-type)

Bertsch et al., Lab on a Chip, 2001, **1**, 56–60

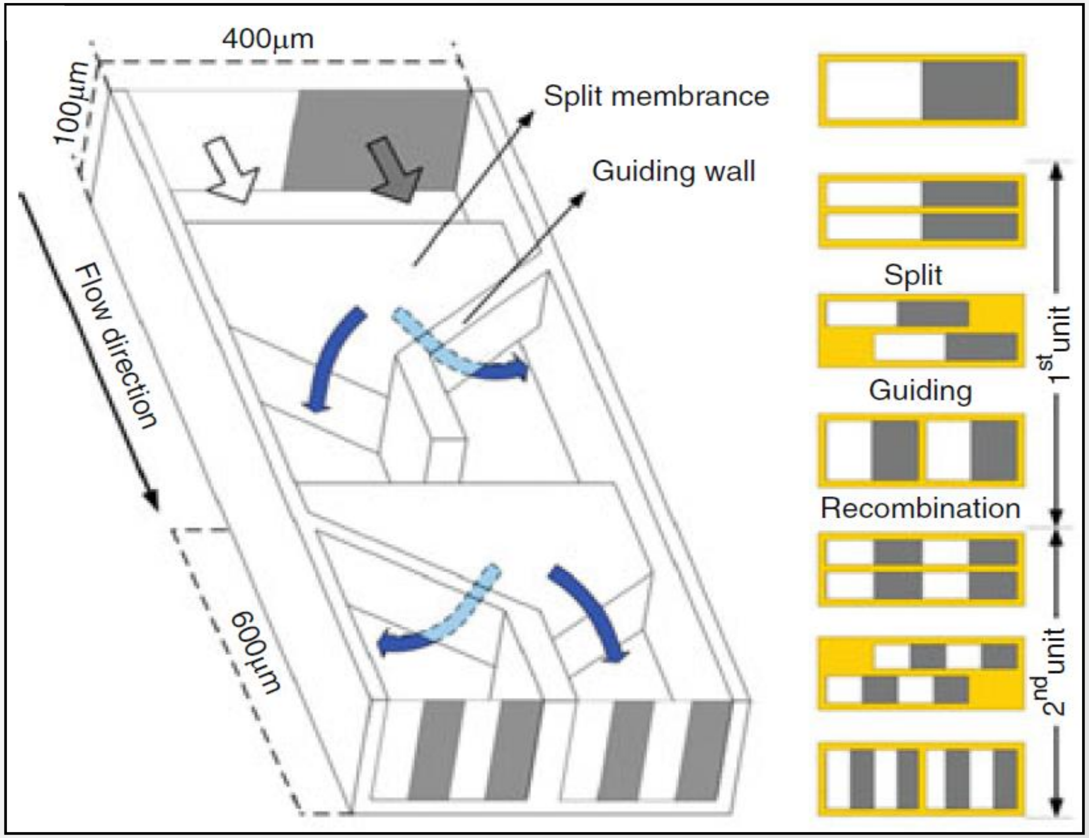
Kenics and Sulzer static mixers

Kenics



Sulzer

Split and recombine example



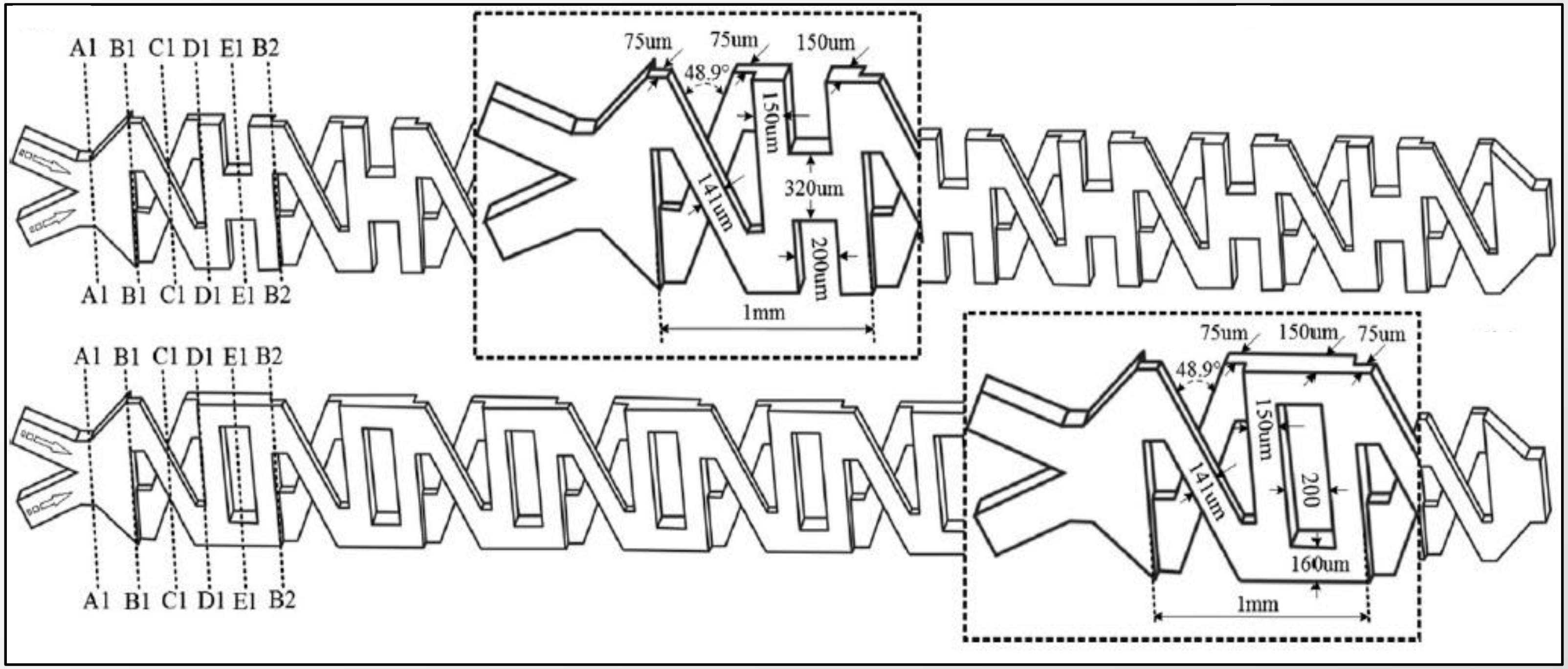
Capretto et al., Top Curr Chem (2011) 304: 27–68

Examples of serial lamination mixers
XH and XO micromixers

- 3D micromixers, effective even at low Re
- 2D mixers need longer mixing lengths at low Re (no vortices)

XH:

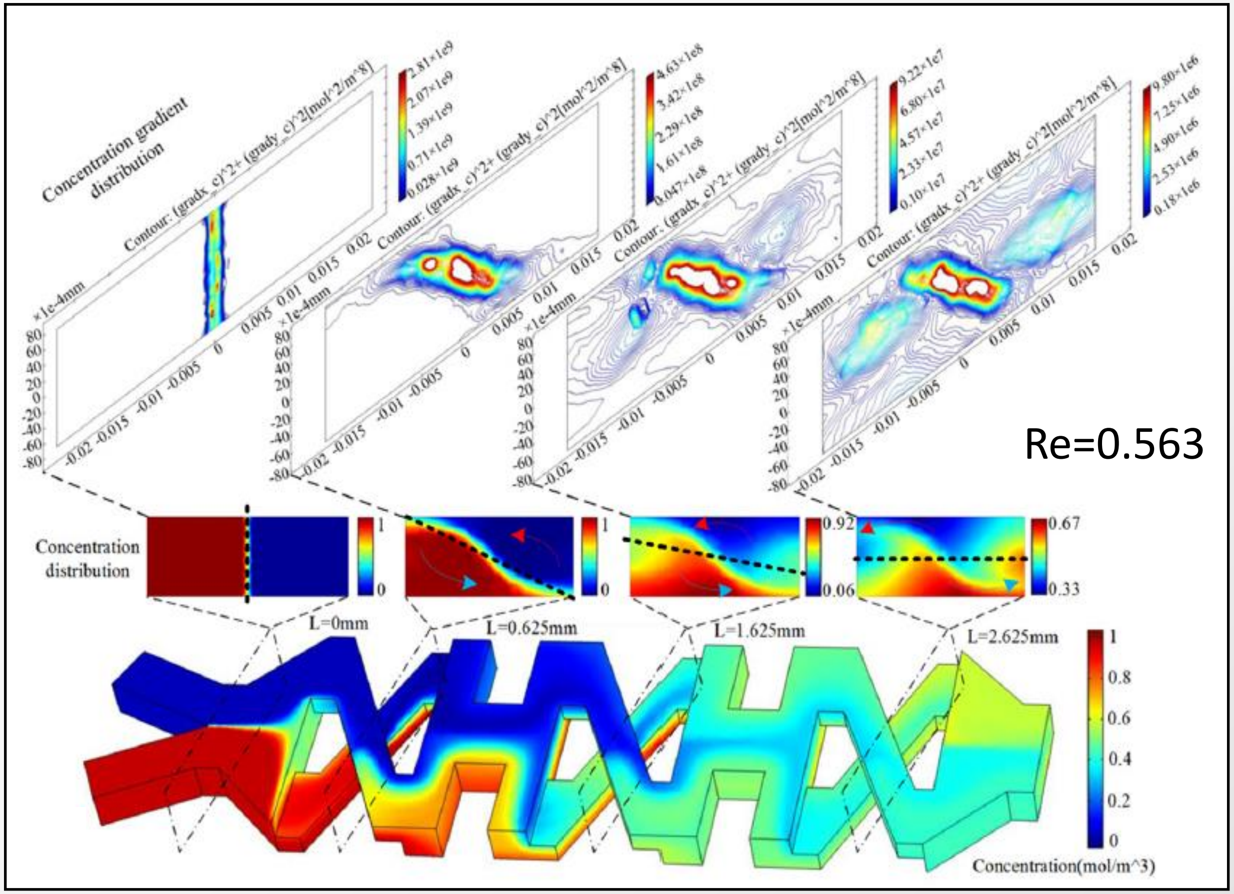
XO:



Feng et al., Biomicrofluidics 7, 054121 (2013)

Optional

Examples of serial lamination mixers
XH mixer



Re: 0.3 – 60
σ_s: $88 - 92\%$
L: 10.2 mm

Feng et al., Biomicrofluidics 7, 054121 (2013)

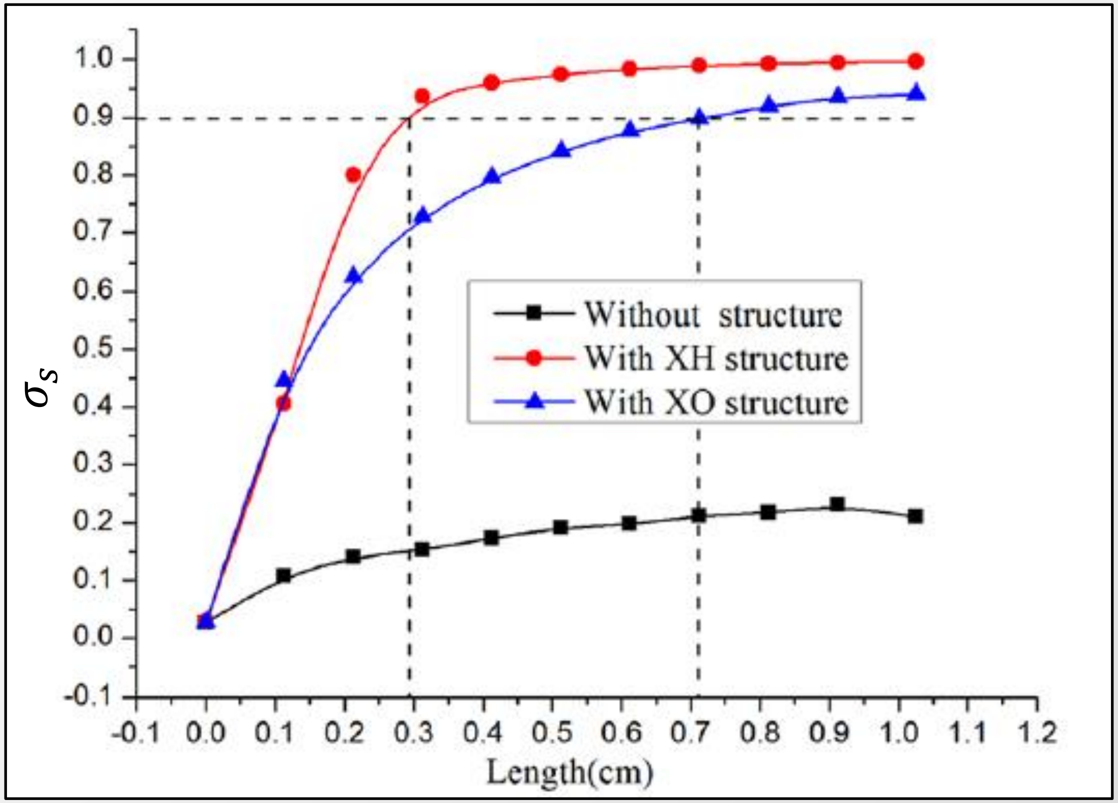
Optional

Examples of serial lamination mixers

XH and XO mixers

Mixing performance:

$$\sigma_s = 1 - \sqrt{\frac{\sigma^2}{\sigma_{max}^2}}$$



$$\sigma^2 = \frac{1}{n}\sum_{i=1}^{n}(c_i - c_\infty)^2$$

c_∞: perfect mixing

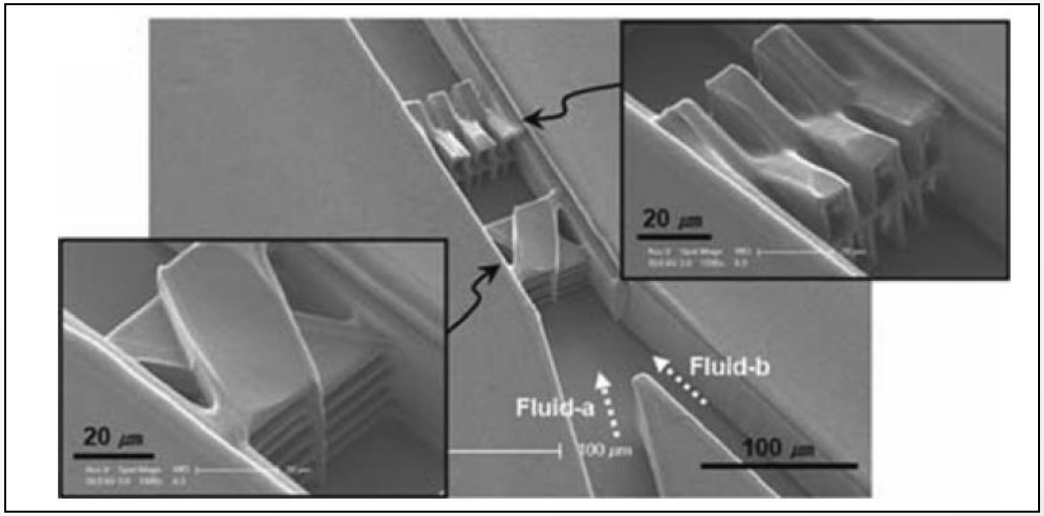
$\sigma_s = 0$ (no mixing)

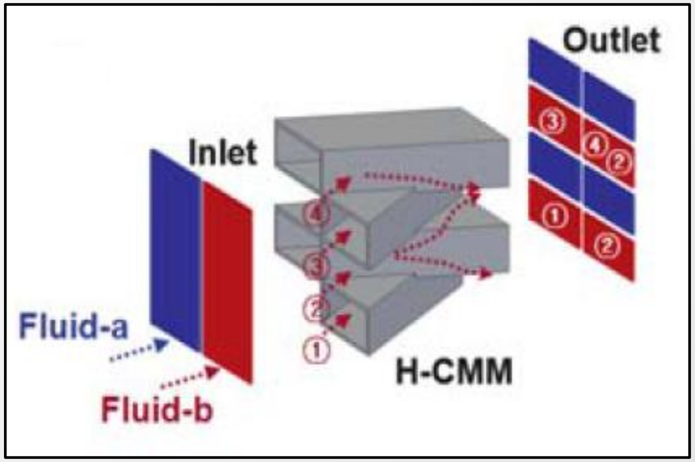
$\sigma_s = 1$ (perfect mixing)

σ_{max}: max. stand. deviation (no mixing at inlet)

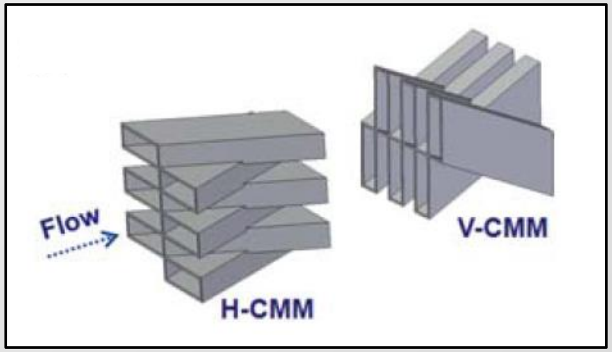
Feng et al., Biomicrofluidics 7, 054121 (2013)

Examples of serial lamination mixers
H-CMM and V-CMM





- Layered crossing tubes that effectively realign the fluid
- Requires less stages than conventional SAR
  - More interfaces created in each stage
  - Fluid momentum gained after H-CMM (Horizontal crossing manifold micromixer)
    - ✓ Inside tubes: left and right
    - ✓ Outside tubes: up and down
  - ✓ H-CMM combination with V-CMM is efficient

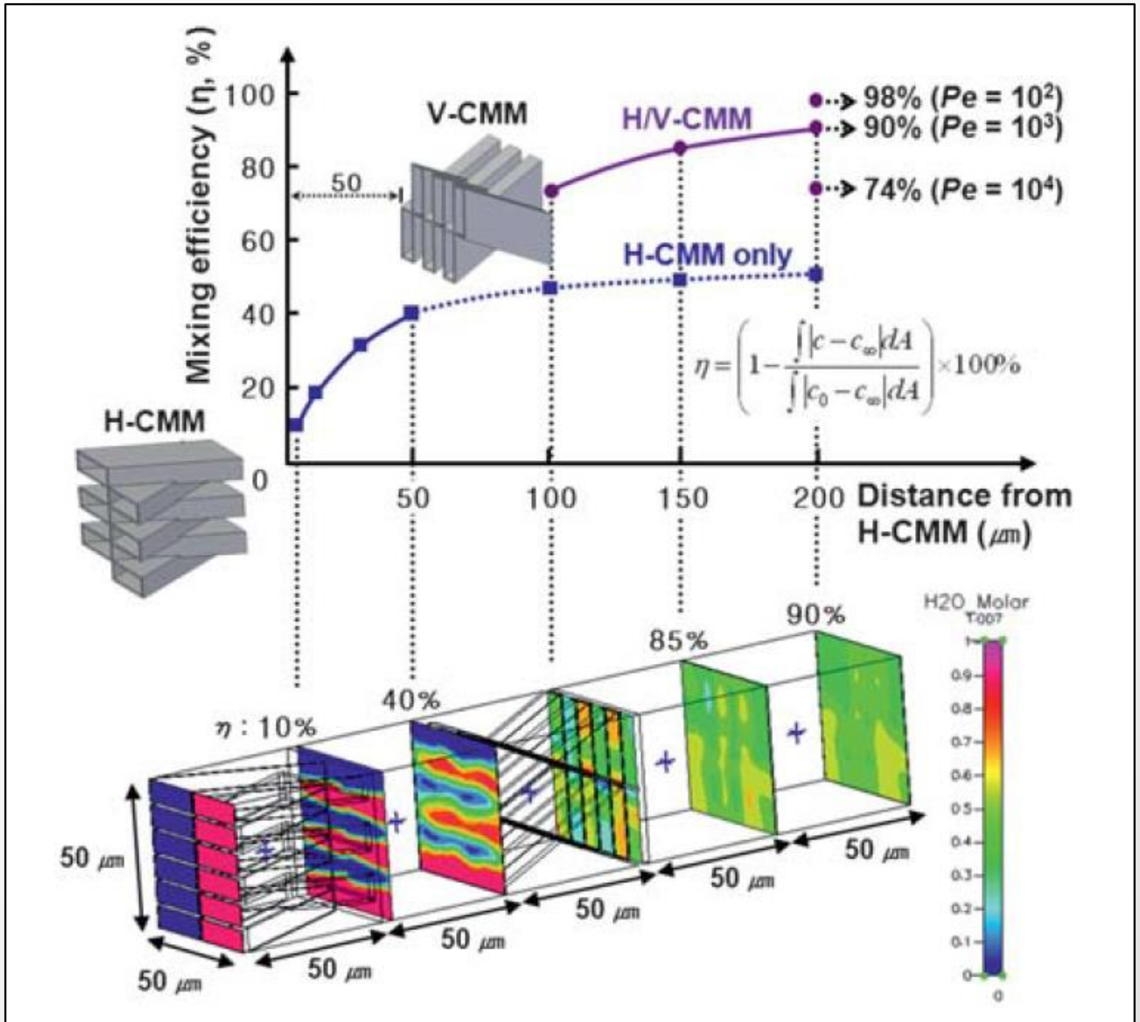


Optional

Lim et al., Lab Chip, 2011, 11, 100–103

Examples of serial lamination mixers

H-CMM and V-CMM



High mixing efficiency in only 5 channel widths (250 μm)

Lim et al., Lab Chip, 2011, 11, 100–103

Optional

2. Passive micromixers

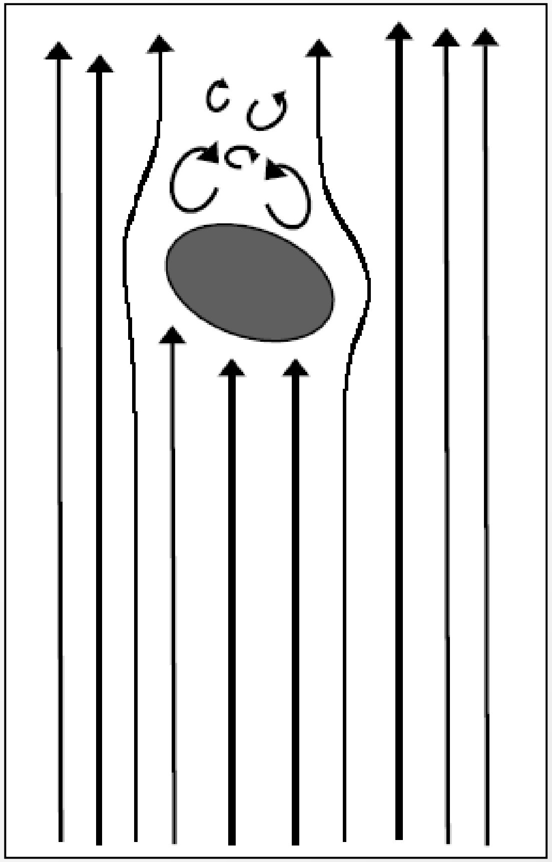
2.4. Chaotic mixers

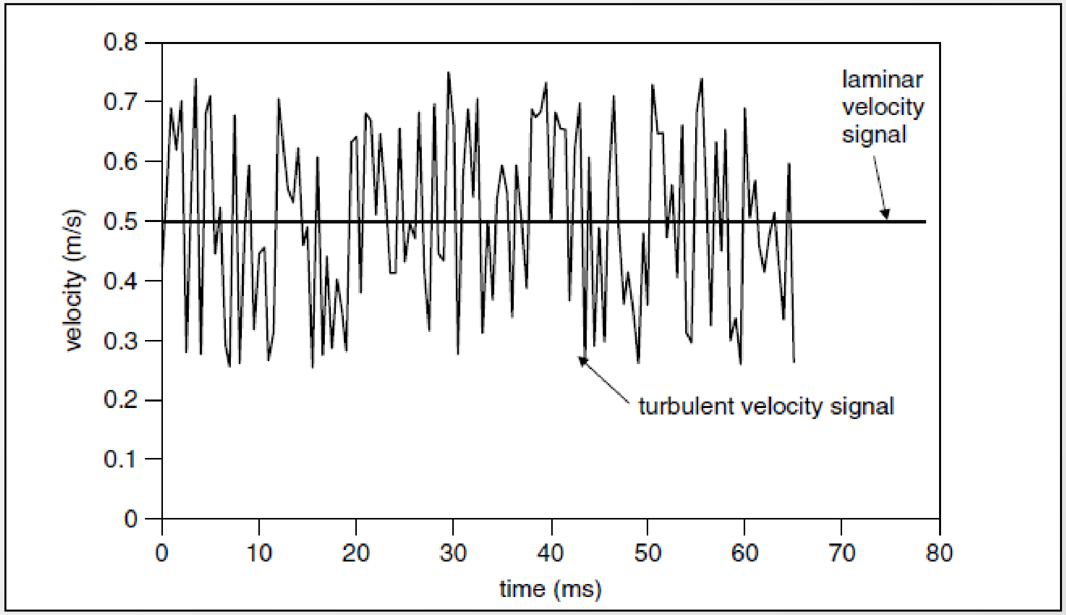
Chaotic mixers

- Chaotic advection
  - Complicated fluid trajectories generated by modulation of the flow system: **splitting, stretching, folding, breaking up a laminar flow**
  - Introduction of a secondary flow (e.g. Dean vortices in curves channels)

✓ Efficient mixing of fluids even at high *Pr* and *Sc* and at low *Re*

Chaotic advection



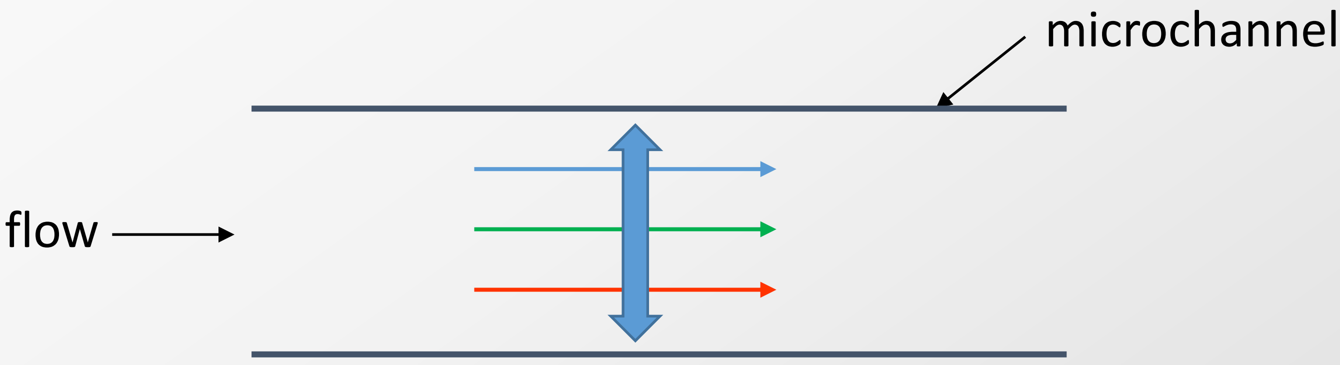


Local velocity fluctuations in turbulent flow

Eddy formations behind obstacle (wake)

Diffusion and chaotic advection

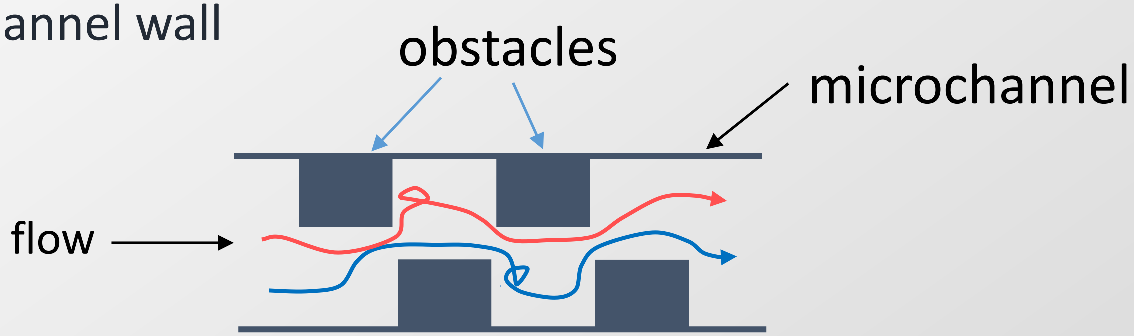
- Advection at low *Re* (laminar regime) is parallel to flow
  - ⇨ Slow mixing process by diffusion



Mixing of parallel streams only by diffusion

Chaotic advection

- Chaotic advection: introduction of <u>transversal</u> flow components between mixing species
- Create eddy-based flow patterns with high specific interfaces
- Advection faster than diffusion even on microscale
  - ➢ Widely used to design micromixers
- Principle: splitting, stretching, folding & breaking of flow by modifying the channel geometry
- Example: obstacles on channel wall

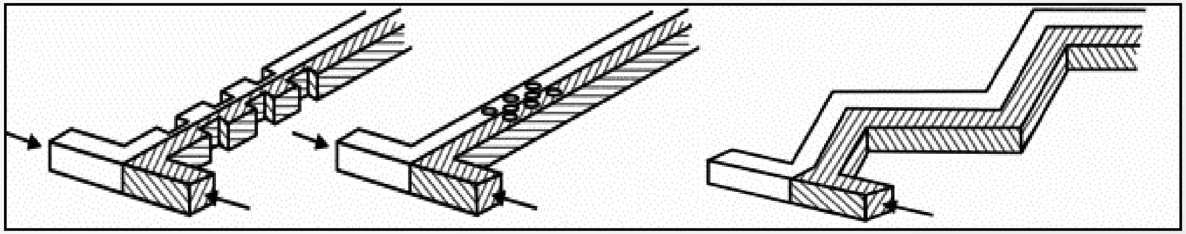


Transversal velocity components generated by obstacles
⇨ Mixing occurs by diffusion <u>and advection</u>

Chaotic mixers

- Geometry of mixer imposes spatial periodicity:

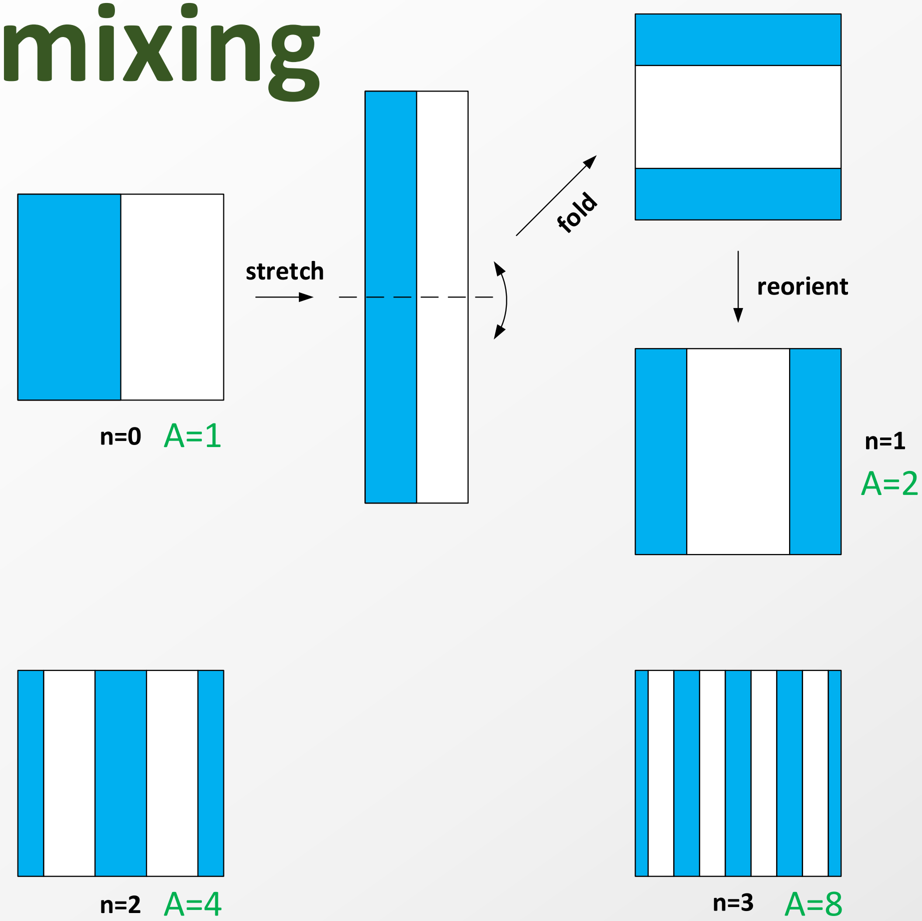
Examples of chaotic micromixers

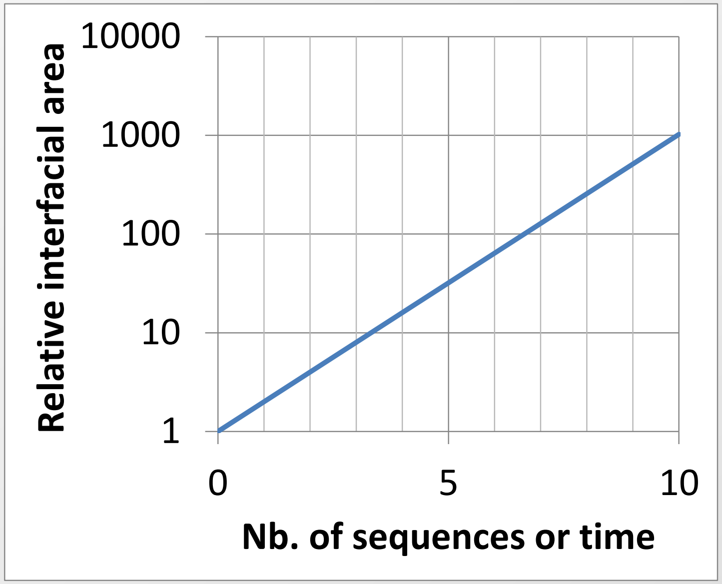


obstacles on wall **obstacles in channel** **zig-zag-shaped channel**

- Fluid elements stretched and reoriented (an additional motion compared to strictly laminar flow) due to repeated change in direction of flow field
- As a result, an exponential rate of stretching is observed (as opposed to simply linear in non-chaotic flow)
- Reorientation leads to folding of material area exponentially
- Segregation of the system also decreases exponentially

Stretching and folding in chaotic mixing



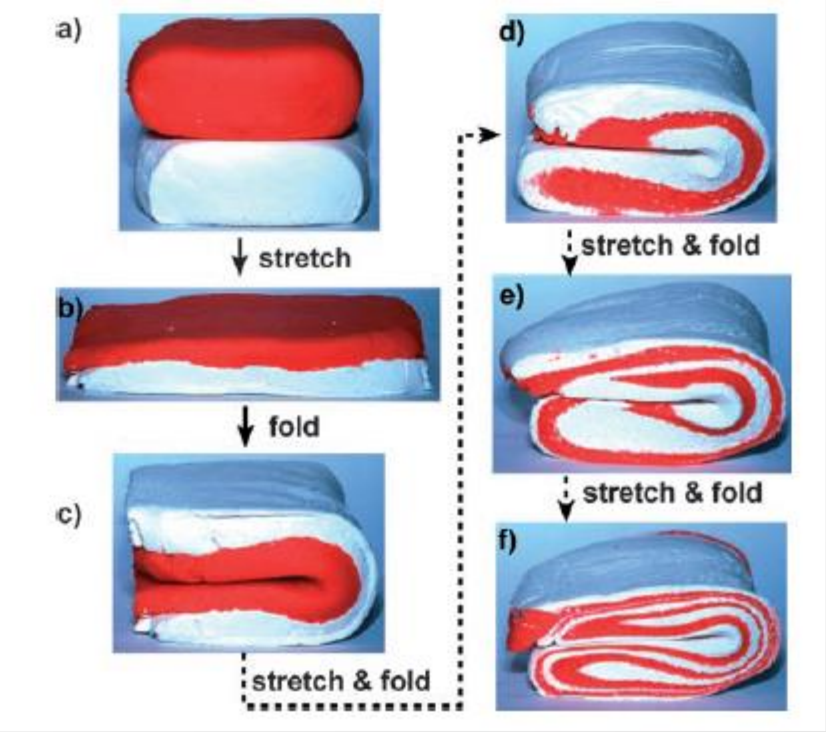


$$\frac{A}{A_0} = 2^n = e^{(\ln(2)\cdot n)} = e^{(0.693n)}$$

- One sequence: fluid element stretched to twice its length, folded and reoriented
- Equal time for each sequence

→ Interfacial area grows exponentially with time

Mixing of two reagents by chaotic advection



Ismagilov et al., Angew. Chem. Int. Ed. 2006, 45, 7336 – 7356

Chaotic mixers

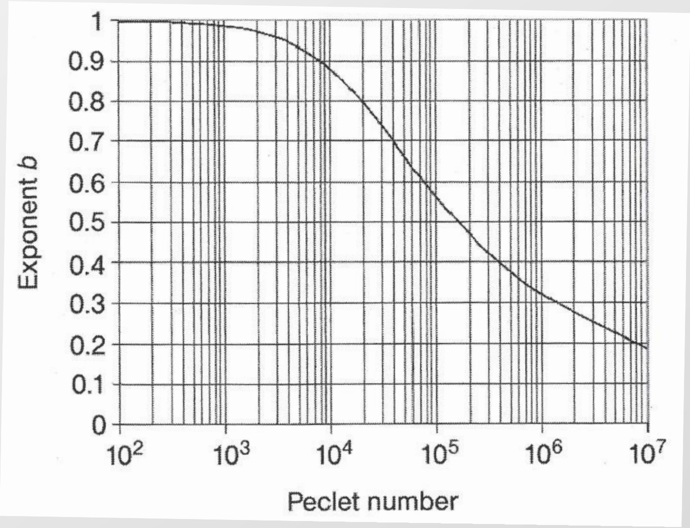
- Characteristic time for chaotic mixing

$$t_{chaotic} \sim \frac{d^2}{\nu}\frac{1}{Re}Pe^b$$

$$Pe < 1 \rightarrow b = 1$$

$$Pe \gg 1 \rightarrow b = 0$$

- $b = 0.5$ for a large range of unidirectional flows in periodic domains

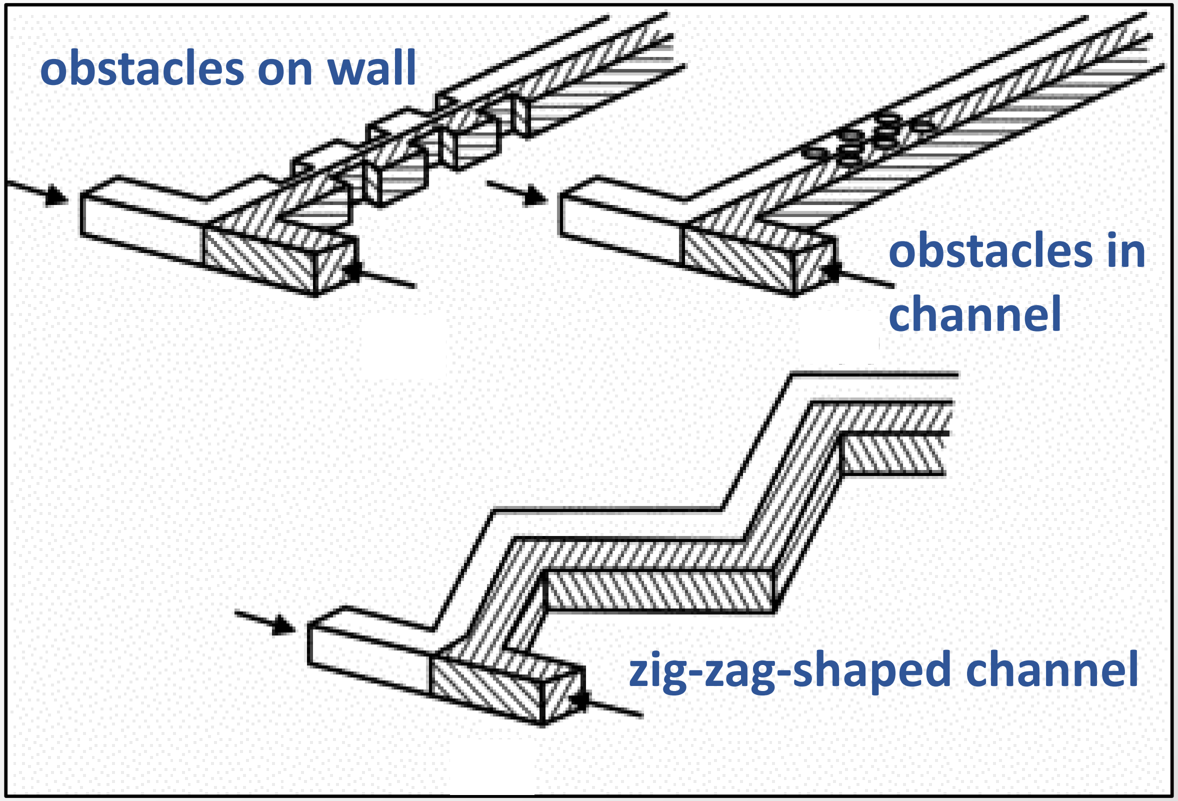


Optional

Critical Reynolds number

- Below the critical Reynolds number (Re_{cr}), no eddies are formed, and mixing occurs solely by diffusion
- Re_{cr} is a function of the mixer geometry
- For obstacles on wall, obstacles in channel and zigzag geometries, $Re_{cr} \cong 100$
- Intermediate Re_{cr} (10-100) are observed for C-shapes, L-shapes and twisted microchannels
- Lower Re_{cr} (<10) are obtained for slanted ribs and staggered herringbone types

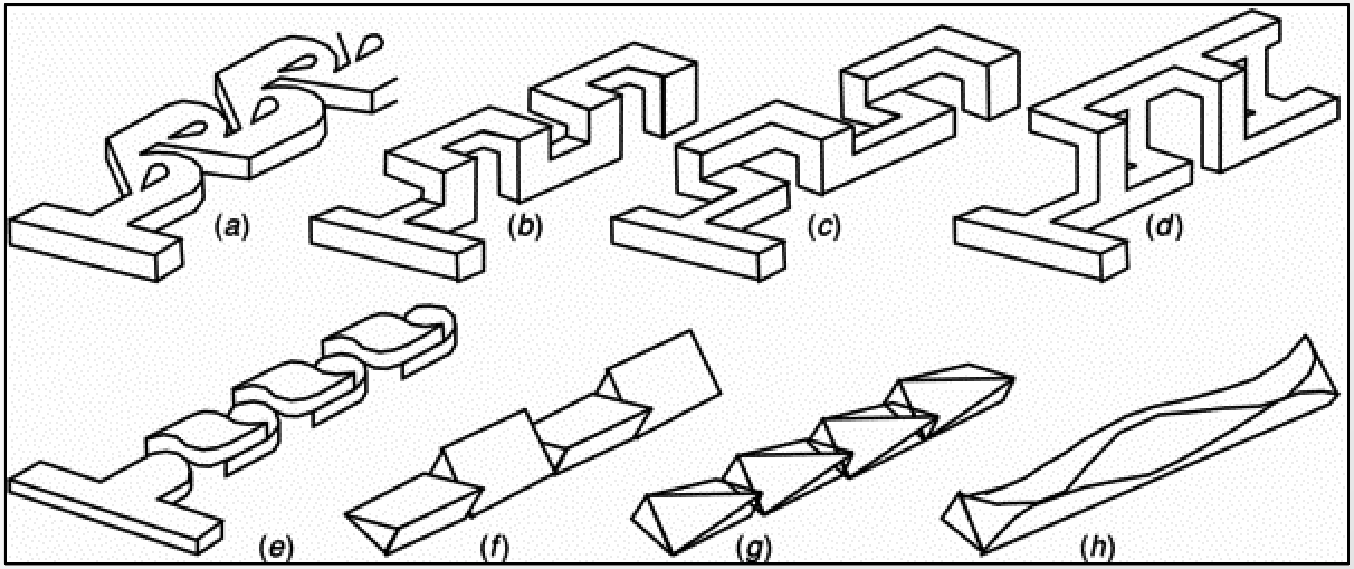
Planar (2D) designs for mixing with chaotic advection at high Re



$$Re_{cr} \cong 100$$

Micromixer designs for chaotic advection at intermediate Re

$$10 < Re_{cr} < 100$$

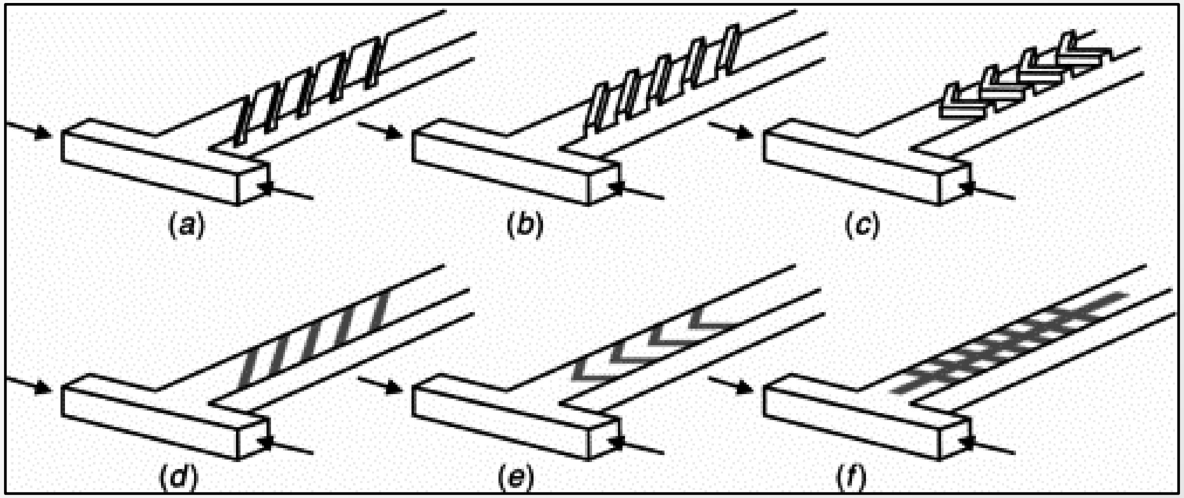


(a) modified Tesla structure
(b) C-shape
(c) L-shape
(d) connected out-of-plane L-shapes

(e) twisted microchannel
(f), (g), (h) other designs of twisted channels

Optional

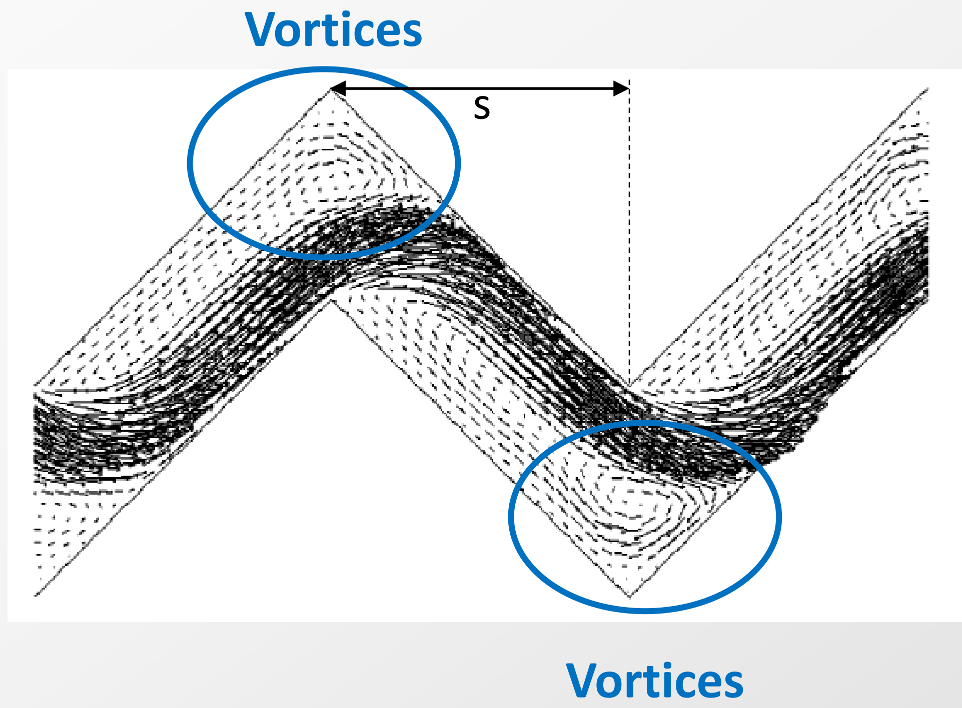
Micromixer designs for chaotic advection at low Reynolds numbers



$Re_{cr} < 10$

(a) slanted ribs
(*b*) slanted grooves
(*c*) staggered-herringbone grooves
(*d*)–(*f*) patterns for surface modification with electrokinetic flows

Example of chaotic mixers
The zigzag channel micromixer



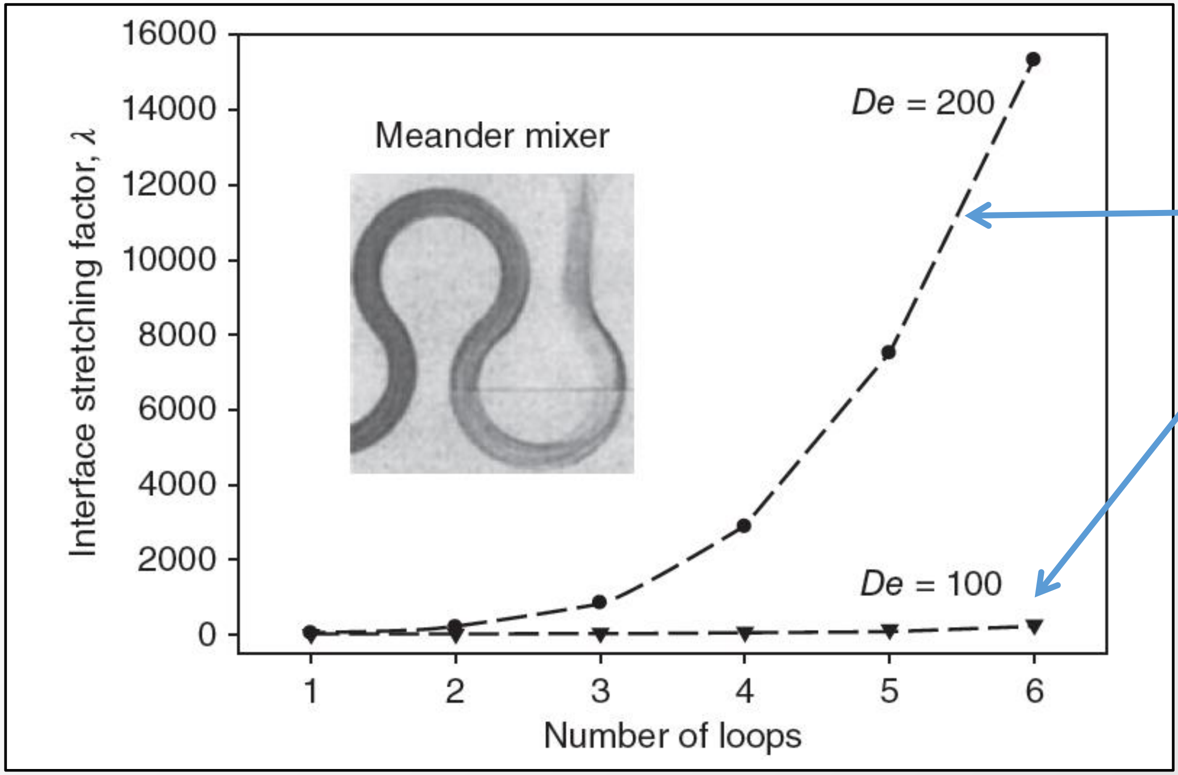
Flow →

Re =267
s = 400 μm

- Generation of transversal flow component
- $Re_{cr} \cong 80$

Mengeaud et al., Anal. Chem. 2002, 74, 4279-4286

Example of chaotic mixers
The Meander micromixer



De=200: exponential stretching

De=100: no stretching

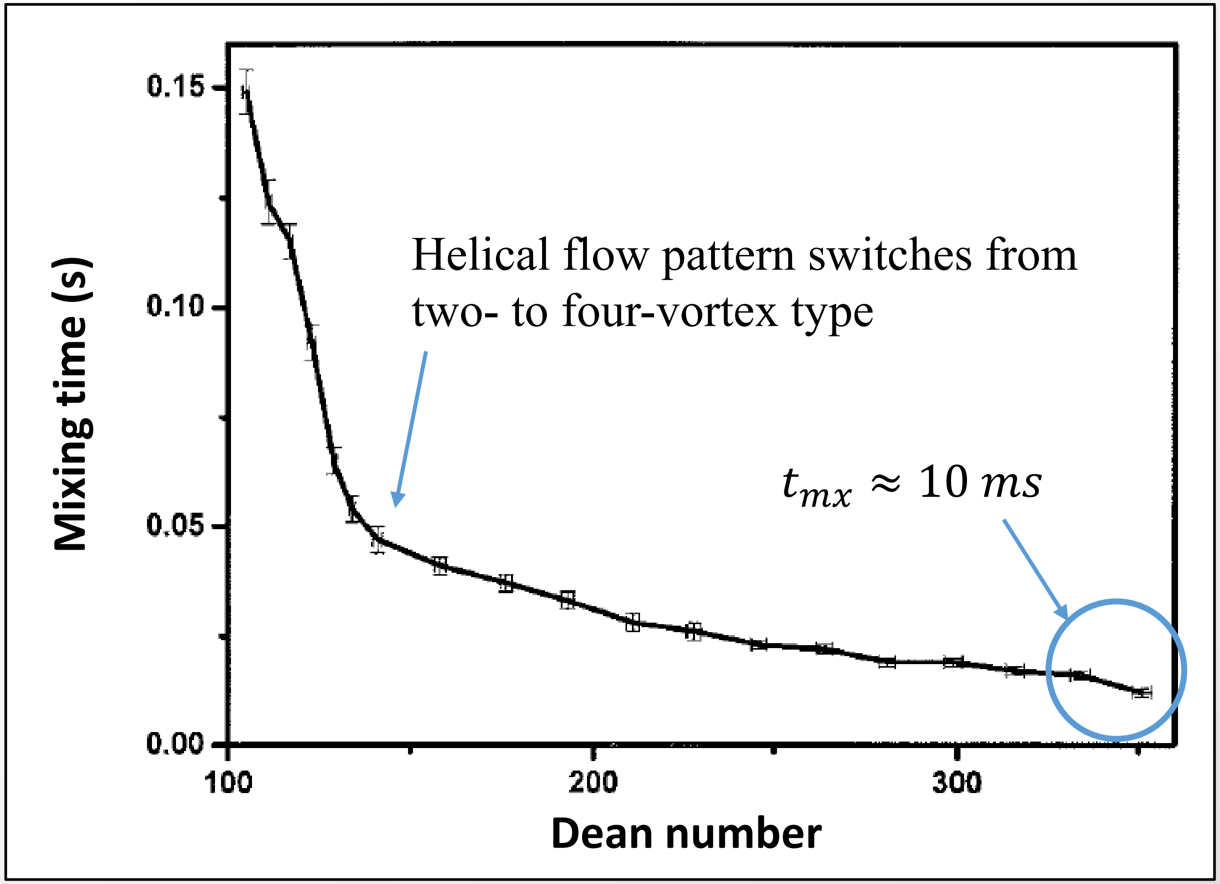
Interface stretching factor:

$$\lambda = \frac{Interface\ length}{Initial\ interface\ length}$$

Interface stretching factor in meander mixer as a function of number of loops and Dean number

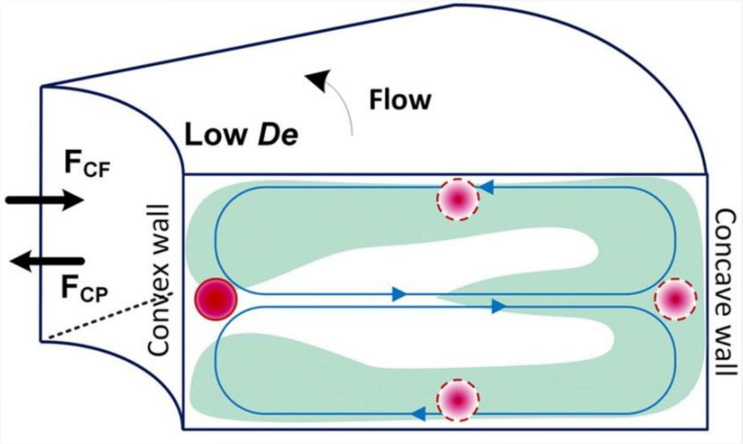
Jiang et al, AIChE J., 50 (9), 2297-2305 (2004).

Example of chaotic mixers
The Meander micromixer

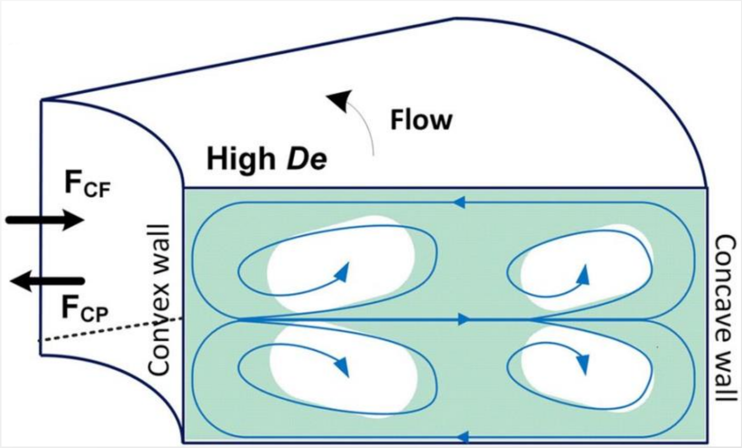


Jiang et al, AIChE J., 50 (9), 2297-2305 (2004).

Dean vortices



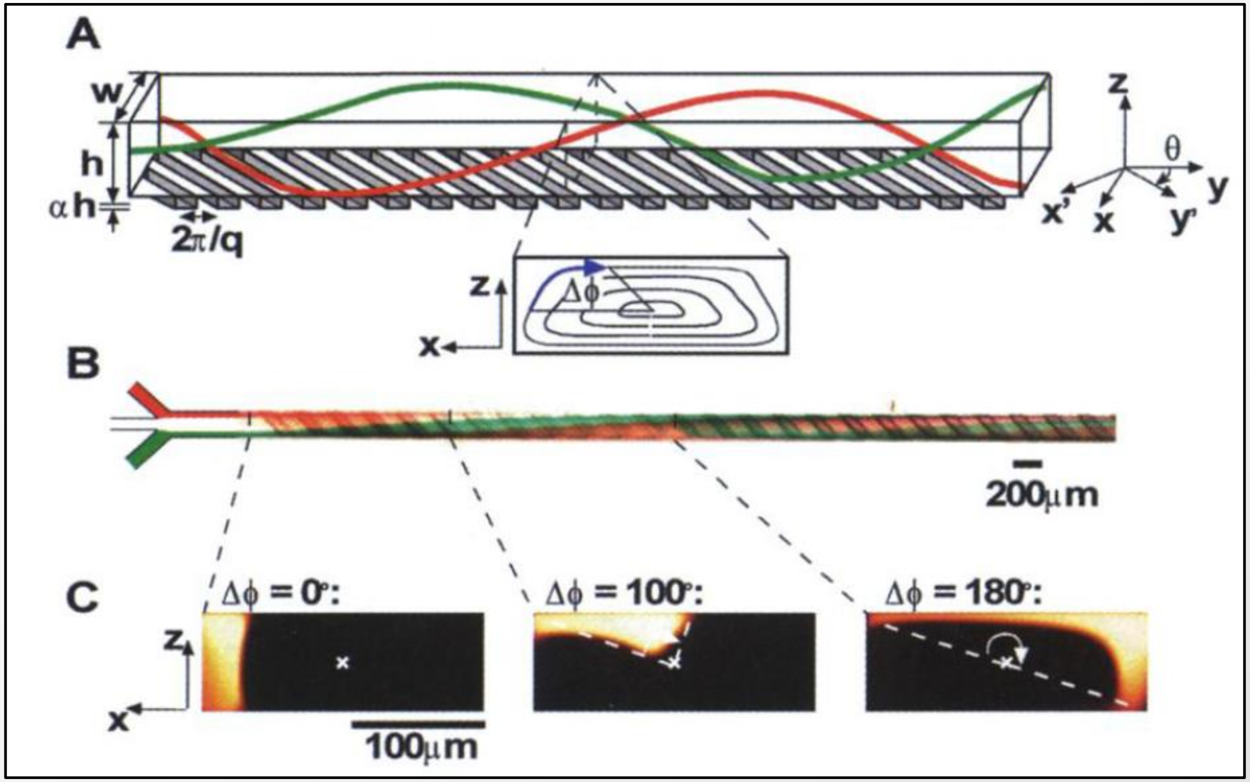
Two counter-rotating vortices in a curved rectangular channel at low De caused by the effect of centrifugal (F_{CF}) and centripetal (F_{CP}) forces on the parabolic velocity profile



Flow behavior at high De causing the formation of multiple vortices

Nivedita, N. et al. Dean Flow Dynamics in Low-Aspect Ratio Spiral Microchannels. Sci. Rep. 7 (2017), 44072

Example of chaotic mixers
The staggered herringbone mixer (SHM)



- 3D twisting flow in channel with obliquely oriented ridges on one wall

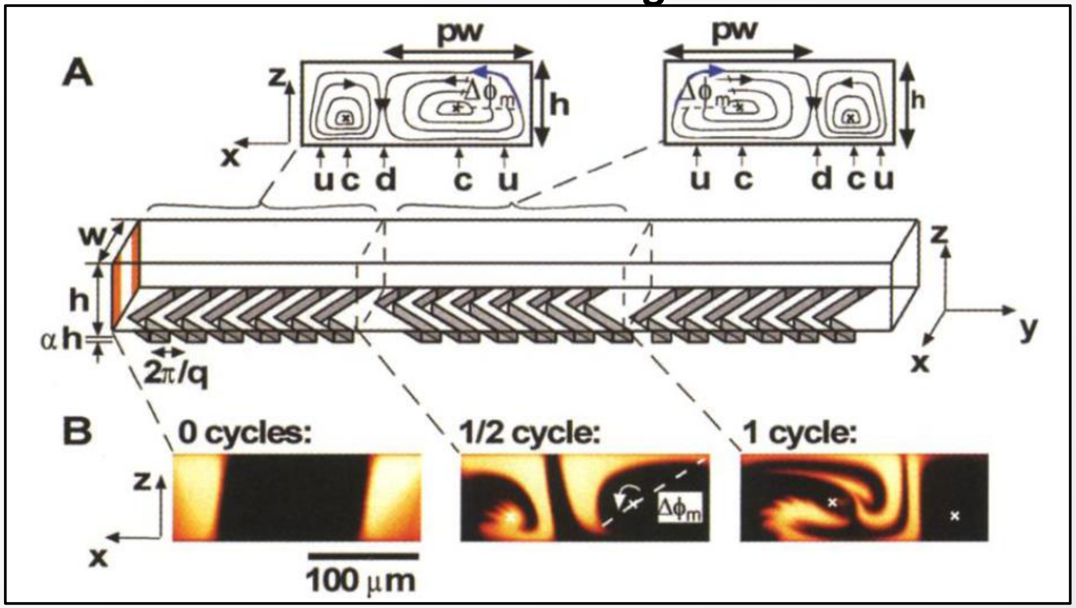
⇨ Transverse flow component generated

Stroocke et al., Science (2002) 295, 647-651

Example of chaotic mixers

The staggered herringbone mixer (SHM)

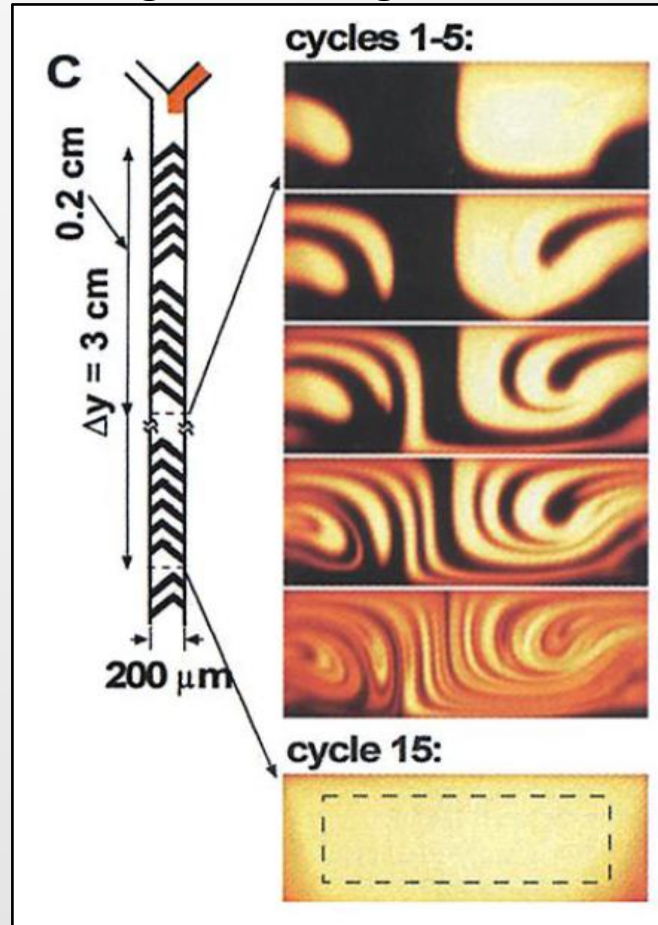
Initial formation and folding of the lamellae



Grooves shape vary as a function of axial position in the channel

- Easily-fabricated structures on channel floor
- Transverse flow generated, making it possible to induce chaotic flow generated at low Re
- High performance at Re<10

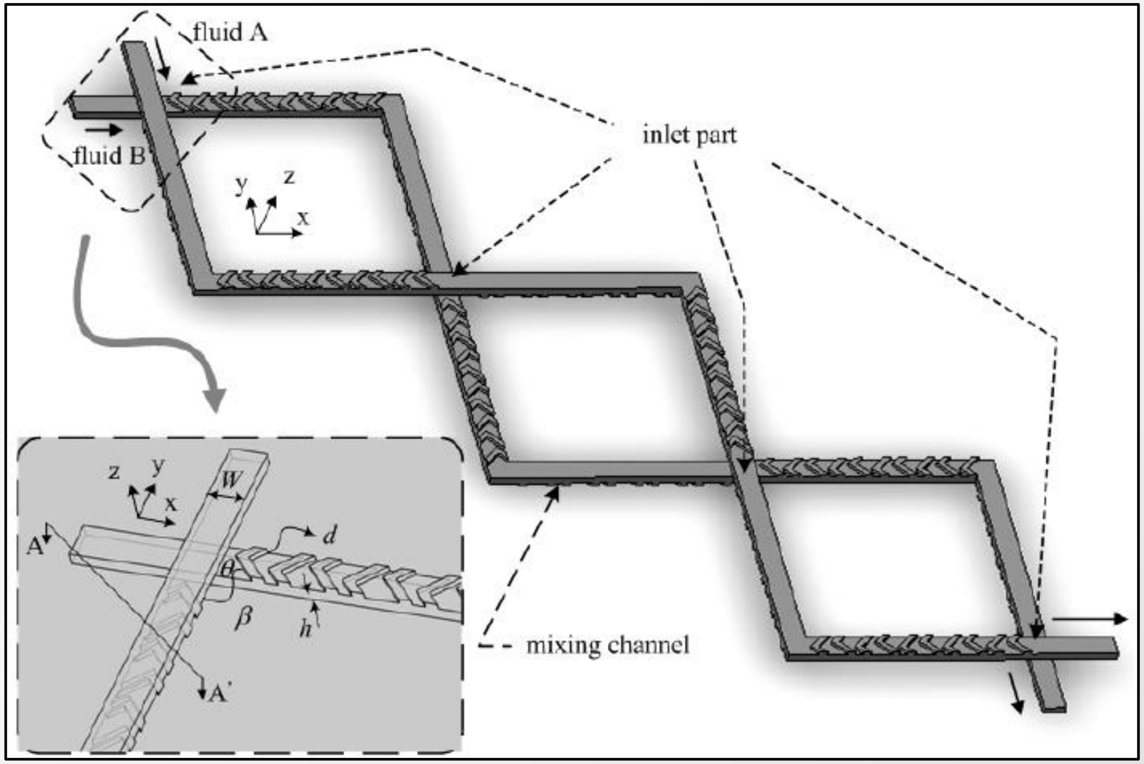
Thinning and folding of the lamellae



Stroocke et al., Science (2002) 295, 647-651

Example of chaotic mixers

The overlapping crisscross micromixer (OCM)



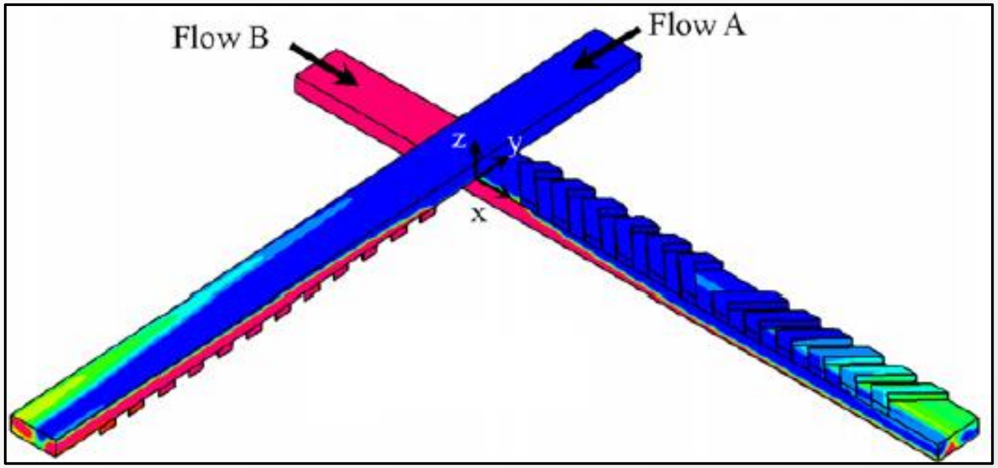
- Combined grooved surface and SAR features
- 46% better mixing than SHM due to cross flow at the intersection of the two channels and vertical tumbling of the flow.

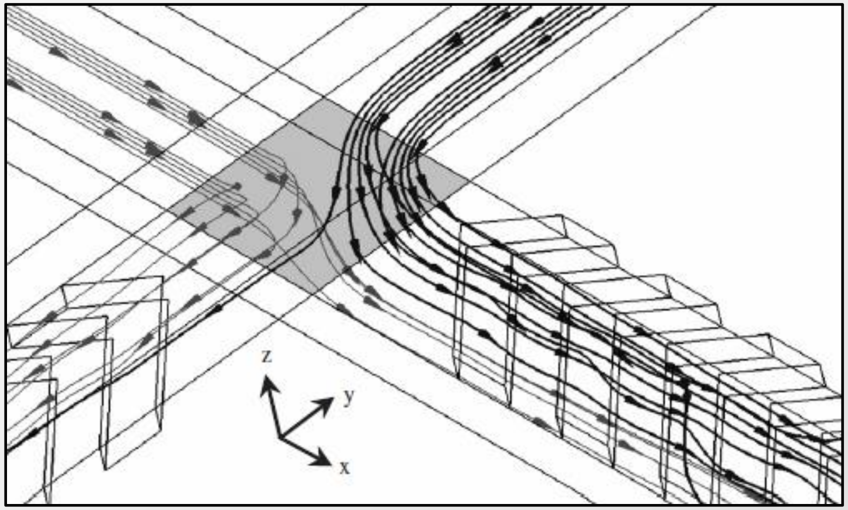
Wang et al., Chemical Engineering Science 62 (2007) 711 – 720

Optional

Example of chaotic mixers

The overlapping crisscross micromixer (OCM)



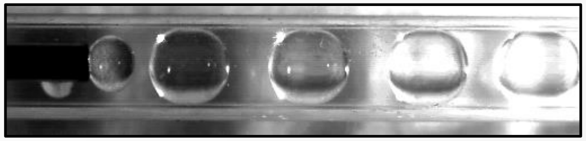


Wang et al., Chemical Engineering Science 62 (2007) 711 – 720

Optional

2. Passive micromixers
2.5. Segmented flow in micromixers

Segmented flow (Taylor flow)



Example of Taylor flow (L/L system)

- Under certain flow conditions (low flowrates of the two immiscible phases), both phases (L/L or G/L) flow through the channel as (1) regular sized liquid "slugs" and (2) liquid "plugs" (or droplets) or gas bubbles

⇨ Reaction mixture flows as segments separated from each other by gas bubbles or another immiscible liquid

- Various denominations of this flow regime: Slug flow, plug flow, Taylor flow, segmented flow

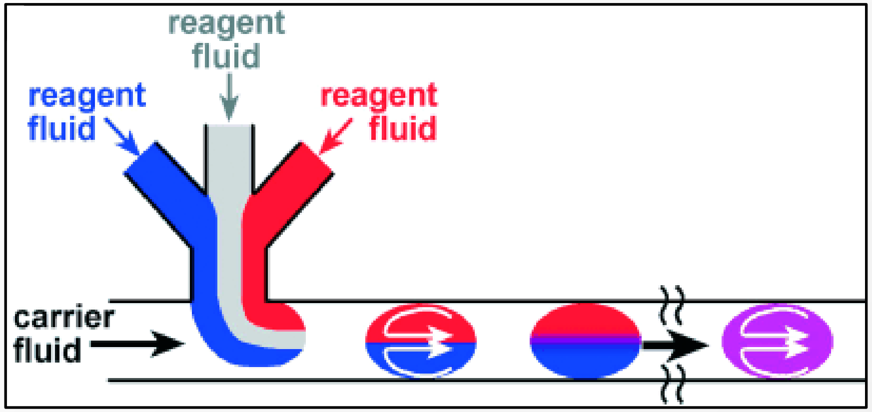
Advantages of segmented-flow microreactors

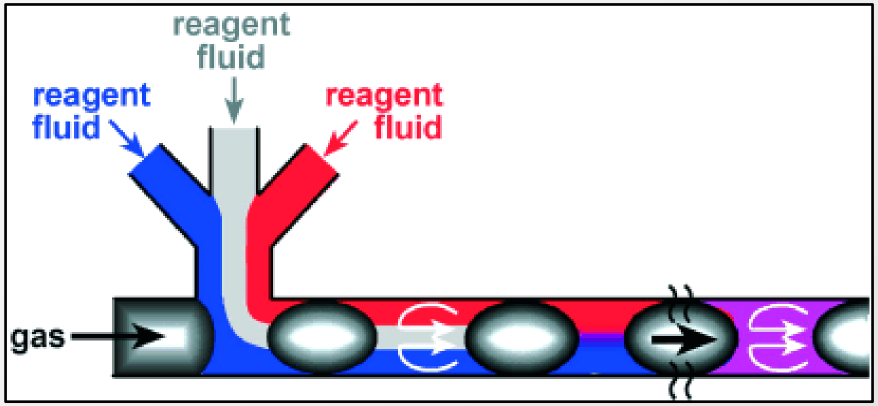
- Stability
- Ability to provide well-defined high specific interfacial area
- Recirculation within the liquid slugs improves heat and mass transfer from liquid to wall and interfacial mass transfer from gas or liquid to liquid
- Enhanced radial mixing → reduced axial dispersion
- Radial mixing can further be enhanced using meandering channels

Advantages of segmented-flow microreactors

- Miniaturization of reactions by compartmentalizing reactions in droplets of very small volumes ($10^{-15} - 10^{-6}$ liters)
- Compartmentalization in droplets provides
  - ✓Rapid mixing of reagents ($t_{mx} < 10^{-3} s$)
  - ✓Tight control of the timing of reactions on timescales from milliseconds to days
  - ✓Control of interfacial properties
  - ✓Ability to synthesize and transport solid reagents and products
  - ✓High-throughput screening
  - ✓Handling of very small amounts of reagents

Running a chemical reaction in a plug or a slug



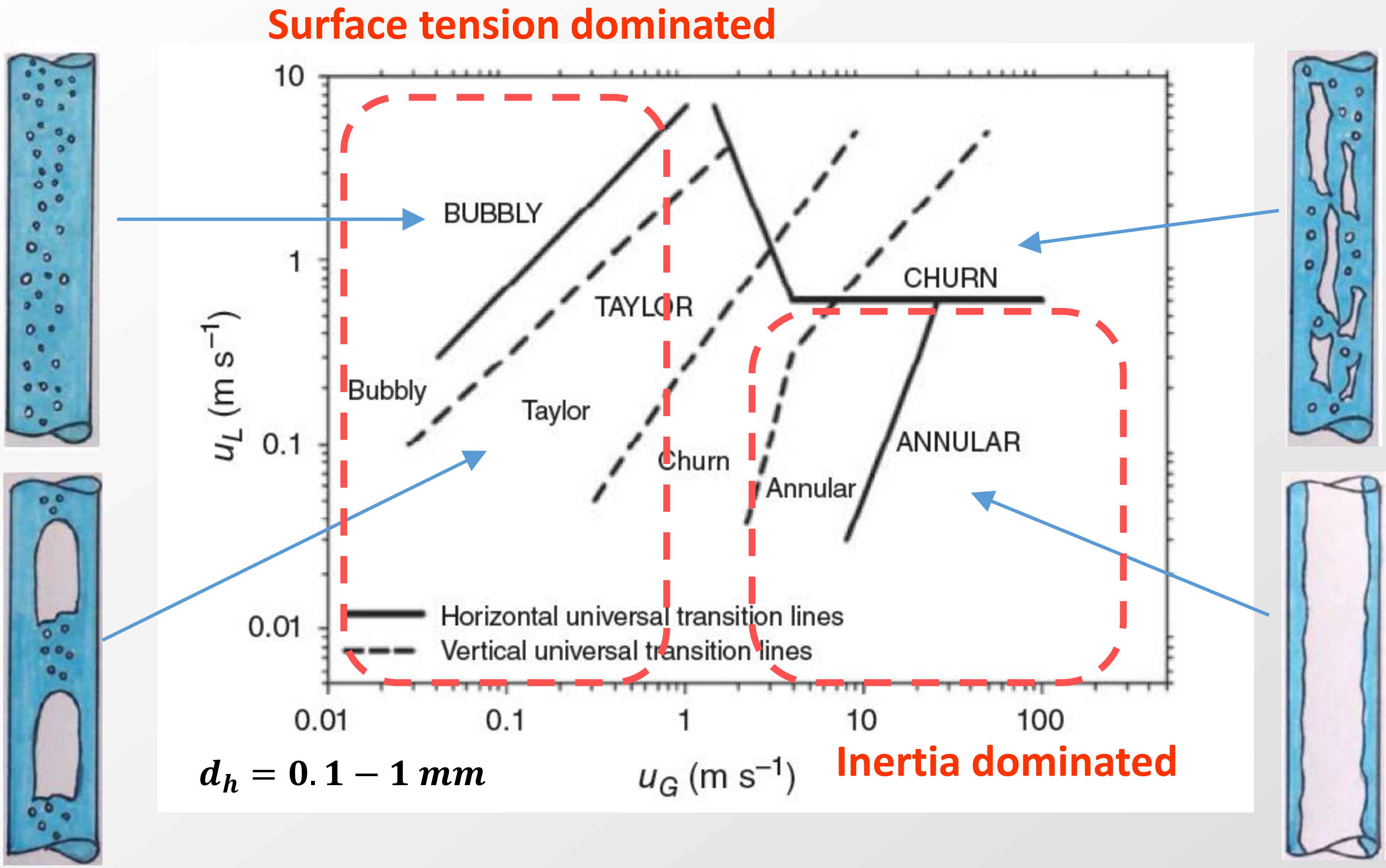


- Discrete **liquid plugs** surrounded by continuous phase (e.g., fluorocarbon-based carrier fluid).
- Reactions occur in dispersed phase.
- Microchannel walls surface properties adjusted so that they are preferentially wetted by the continuous phase.

- **Aqueous slugs** separated by immiscible phase (e.g. discrete gas bubbles).
- Reactions occur in continuous phase (i.e. within the slugs).

Song et al., Angew. Chem. Int. Ed., 45, 7336–7356 (2006).

Flow regimes for gas-liquid systems

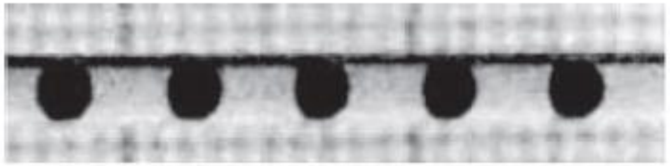


Shao et al., Chem. Eng. Sci. (2009), 64 (11), 2749–2761

Flow regimes for gas-liquid systems

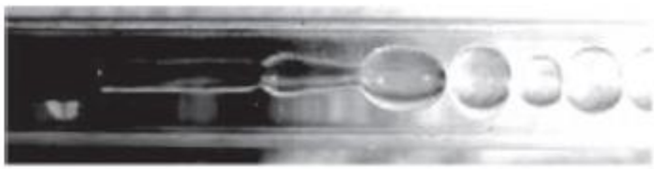
- Low gas and liquid velocity
  - **Taylor** (slug) flow: regular sized bubbles (with larger effective diameter than channel diameter) and liquid slugs.
- High liquid/gas velocity ratio
  - **Bubbly** flow: bubbles smaller than channel diameter
- High gas/liquid velocity ratio
  - **Annular** flow: central core of gas fills the channel, thin film of liquid at channel wall
- High liquid and gas velocities
  - **Churn** flow: bubbles ripped from gas core into the liquid film

Flow regimes for liquid-liquid systems



Drop

Slug



Slug-drop

Deformed interface

Annular

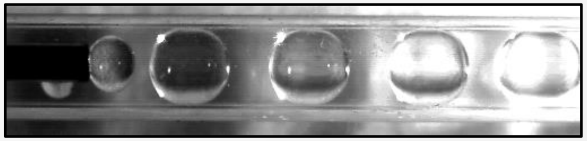
Parallel

Slug-dispersed

Dispersed

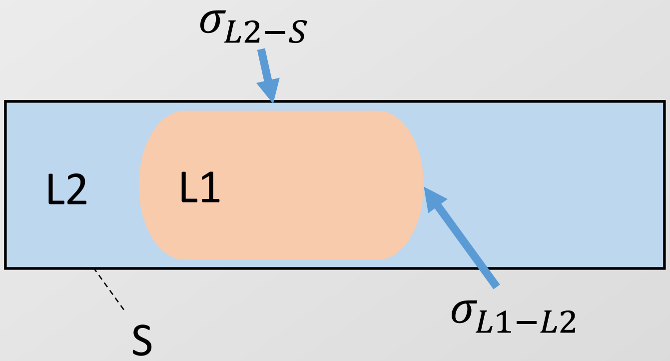
Optional

Conditions for slug flow (L/L)

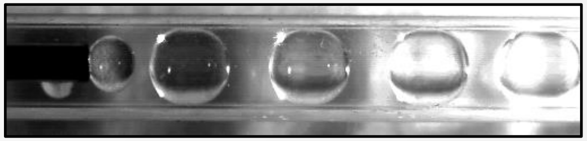


- One liquid L2 is the continuous phase while the other liquid L1 forms slugs (droplets) longer than the diameter of the microchannel
- The surface tension between one of the liquids and the wall material (S) is higher than the interfacial tension between two liquids ($\sigma_{L1-S} > \sigma_{L1-L2}$)
- The high surface tension phase flows in the form of enclosed slugs
- The other phase flows as a continuous phase forming a thin wall film of a few micrometers in size

$$dG = +\sigma dA$$



Conditions for slug flow (L/L)



- The surface tension at the liquid–liquid interface σ_{L1-L2} must be sufficiently high in order to avoid the destruction of slugs by the shear
- Slug flow occurs at relatively low and ~ equal flow rates of both liquids where interfacial forces dominate
- This is a commonly observed stable flow regime in microchannels
- Surface-tension dominated domain (slug-flow) in capillaries*:

Optional:

$$\frac{Re_D d_h}{\varepsilon_D} < 0.1\ (m);\ Re_D = \frac{u_D d_h}{\nu_D};\ \varepsilon_D = \frac{\dot{V}_D}{\dot{V}_D + \dot{V}_C}$$

D = dispersed
C = continuous

*Kashid, M. and Kiwi-Minsker, L. (2011) Chem. Eng. Process., **50** (10), 972–978*

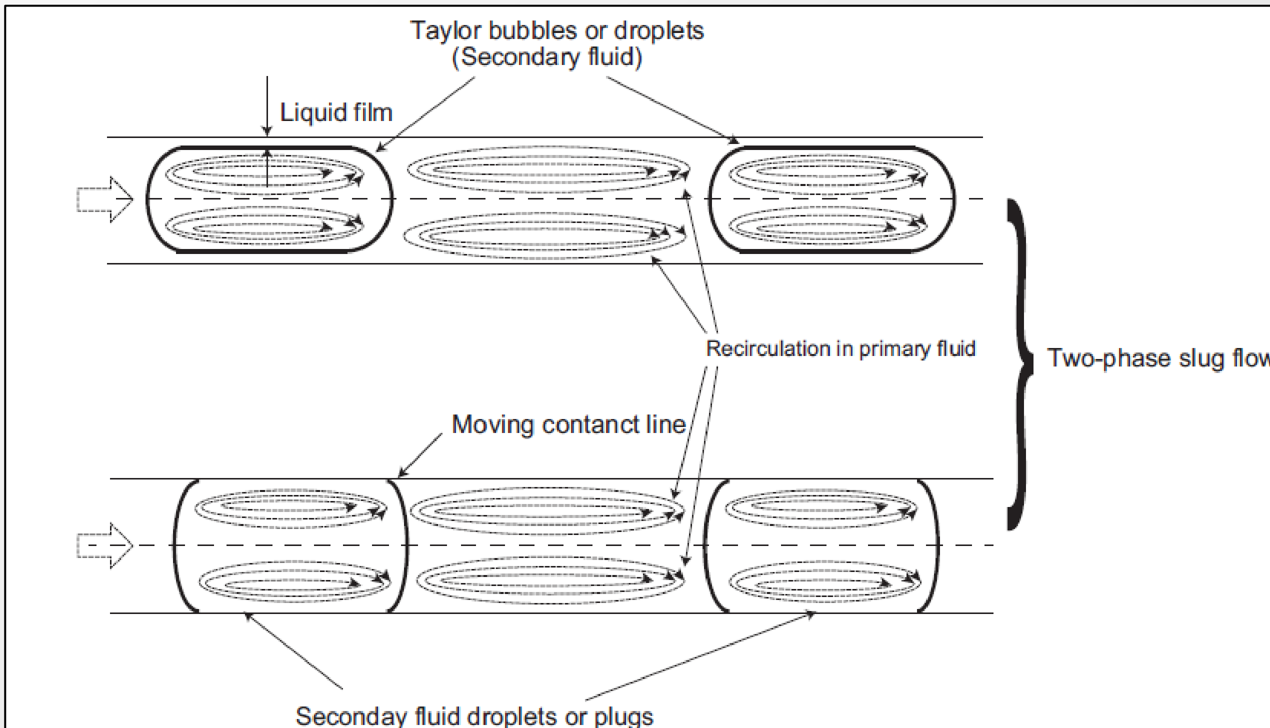
Segmented flow

Effect of capillary number on film thickness

- Fluid droplets can flow without creating a thin film at low capillary numbers (Ca) by sliding along the channel wall due to the **weak shear forces which cannot overcome the adhesion forces**
- Capillary number: $Ca = \frac{Viscous\ force}{Surface\ tension\ force} = \frac{\mu_{L1} \cdot u}{\sigma_{L1-L2}}$

Taylor flow with liquid film (high Ca)

Sliding slug flow without a liquid film (low Ca)

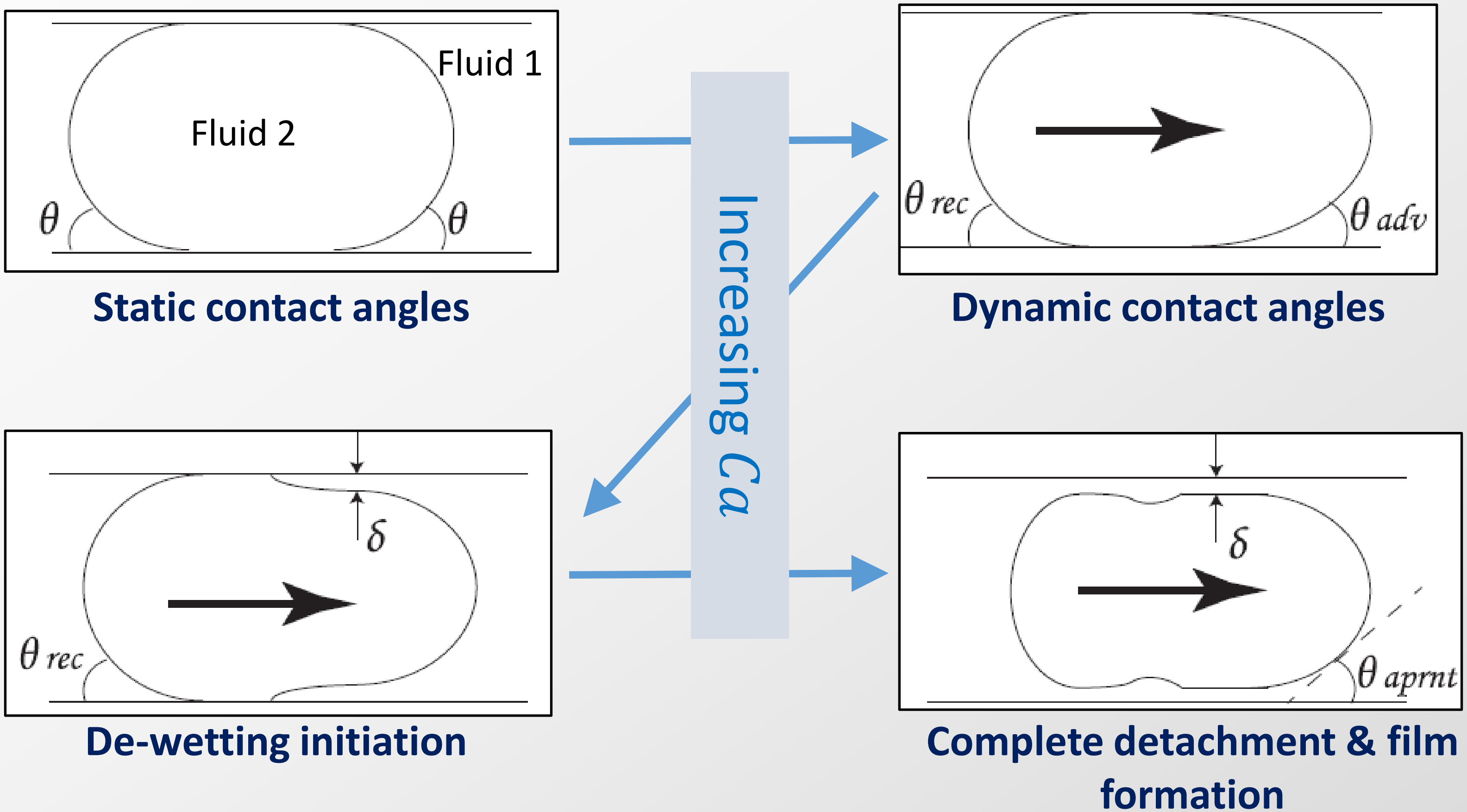


Bandara et al., Chemical Engineering Science 126 (2015) 283–295

Segmented flow

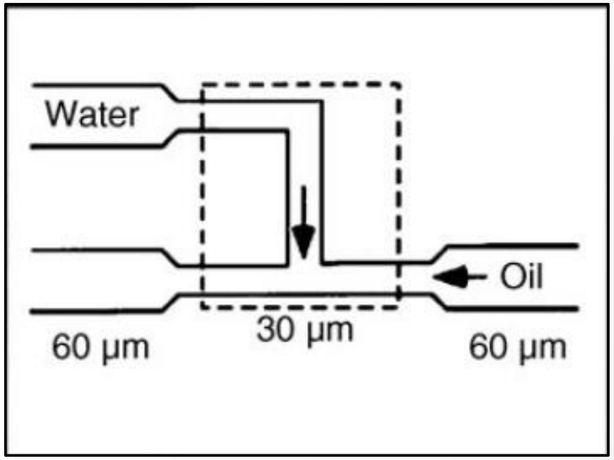
Effect of capillary number on film thickness

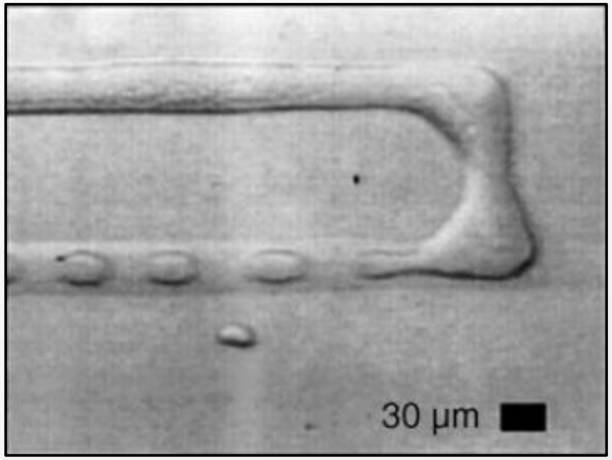
$$\text{Capillary number: } Ca = \frac{\text{Viscous force}}{\text{Surface tension force}} = \frac{\mu_{L1} \cdot u}{\sigma_{L1-L2}}$$



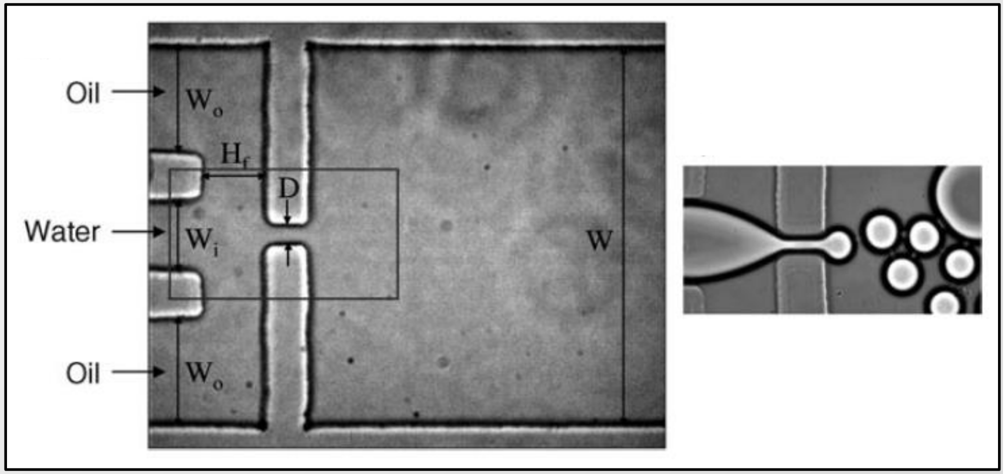
Bandara et al., Chemical Engineering Science 126 (2015) 283–295

L/L segmented flow: generation of droplets





Formation of droplets within T-junction.

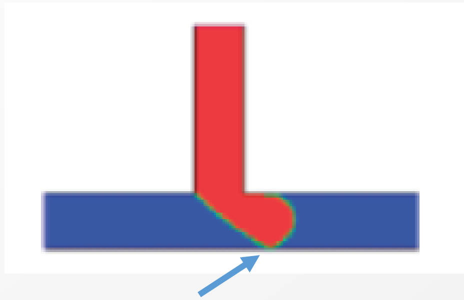


Optional

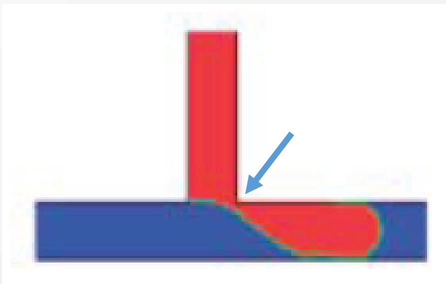
Formation of droplets by flow-focusing

Segmented flow: bubble generation mechanism
Generating a slug (Taylor) flow (gas-liquid system)

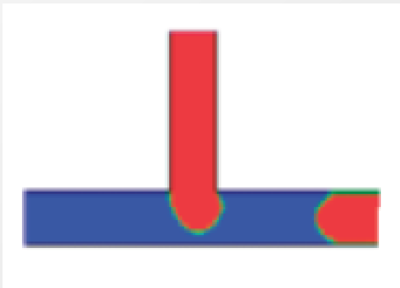
1. Bubble penetration & growth



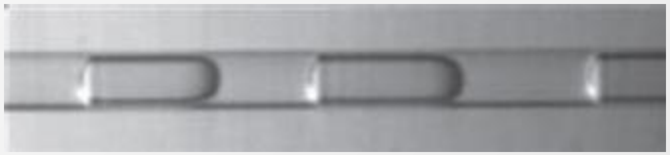
2. Dispersed phase almost blocks passage → pressure increase upstream & increased velocity of continuous through passage

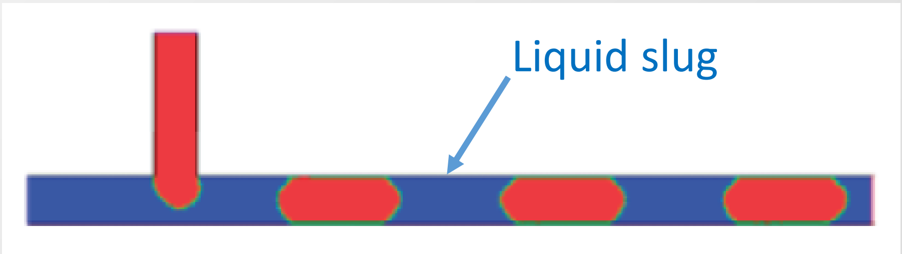


3. Shear+ Δp: bubble elongates grows → slug formed



4. Neck gets squeezed further, slug separates





Process of bubble penetration & separation from the dispersed phase → production of well-defined slug flow.

Optional

Gas-liquid mass transfer in microchannels vs conventional equipment

Type of contactor	$k_L \times 10^5$ (m s^{-1})	a (m^2 m^{-3})	$k_L a$ (s^{-1})
Bubble columns	10–40	50–600	0.005–0.24
Couette–Taylor flow reactor	9–20	200–1200	0.03–0.21
Impinging jet absorbers	29–66	90–2050	0.025–1.22
Packed columns, concurrent	4–60	10–1700	0.0004–1.02
Packed columns, countercurrent	4–20	10–350	0.0004–0.07
Spray column	12–19	75–170	0.015–0.022
Static mixers	100–450	100–1000	0.1–2.5
Stirred tank	0.3–80	100–2000	0.03–0.4
Tube reactors, horizontal, and coiled	10–100	50–700	0.005–0.7
Tube reactors, vertical	20–50	100–2000	0.02–1
Gas–liquid microchannel	40–160	3400–9000	0.3–21

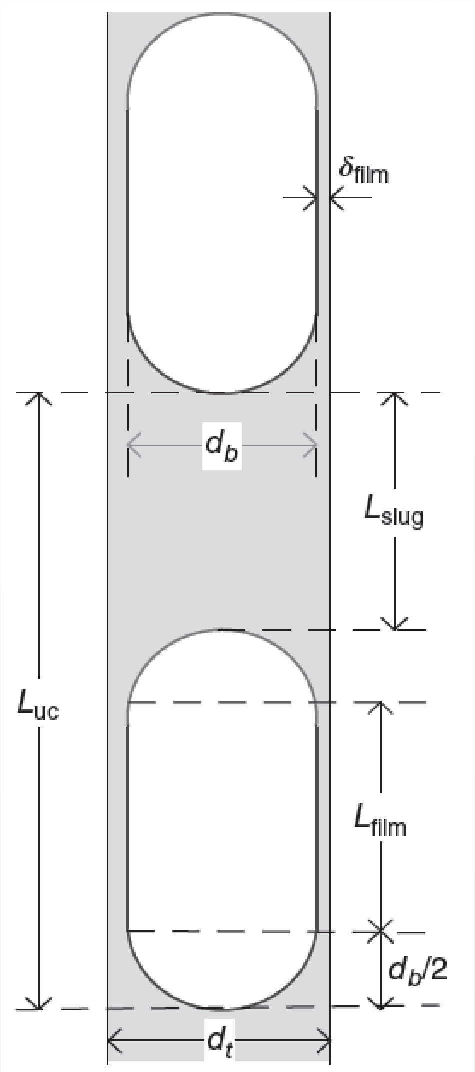
Two orders of magnitude faster mass transfer compared to most conventional technologies

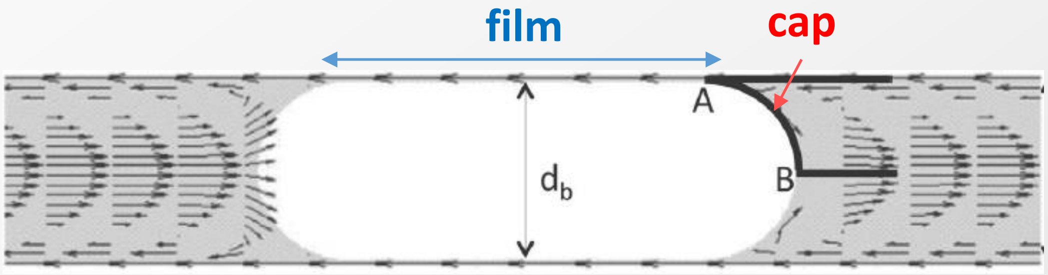
Liquid-liquid mass transfer in microchannels vs conventional equipment

Contactor	a ($m^2\ m^{-3}$)	$k_{ov}a$ (s^{-1})
Agitated contactor [57]	32–311	0.048–0.083
Packed bed column (Pall/Raschig ring, Intalox saddles) [58]	80–450	0.0034–0.005
RTL extractor (Graesser raining bucket) [59]	90–140	0.0006–0.0013
Air operated two impinging jet reactors [60]	350–900	0.075
Two impinging jets reactor [61]	1000–3400	0.28
Capillary microchannel (ID = 0.5–1 mm)	830–3200	0.88–1.67

Two orders of magnitude faster mass transfer compared to most conventional technologies

Model for mass transfer in slug flow





$$k_L = 2\sqrt{\frac{D}{\pi\,\tau_C}}$$

Penetration theory = Higbie model, τ_C=contact time

$$k_L a = k_{L,cap} a_{cap} + k_{L,film} a_{film}$$

$$k_L a = 2\sqrt{\frac{2 D_m u_b}{\pi^2 d_t}} \frac{4}{L_{UC}} + 2\sqrt{\frac{D_m}{\pi\,\tau_{c,film}}} \frac{4\varepsilon_G}{d_t}$$

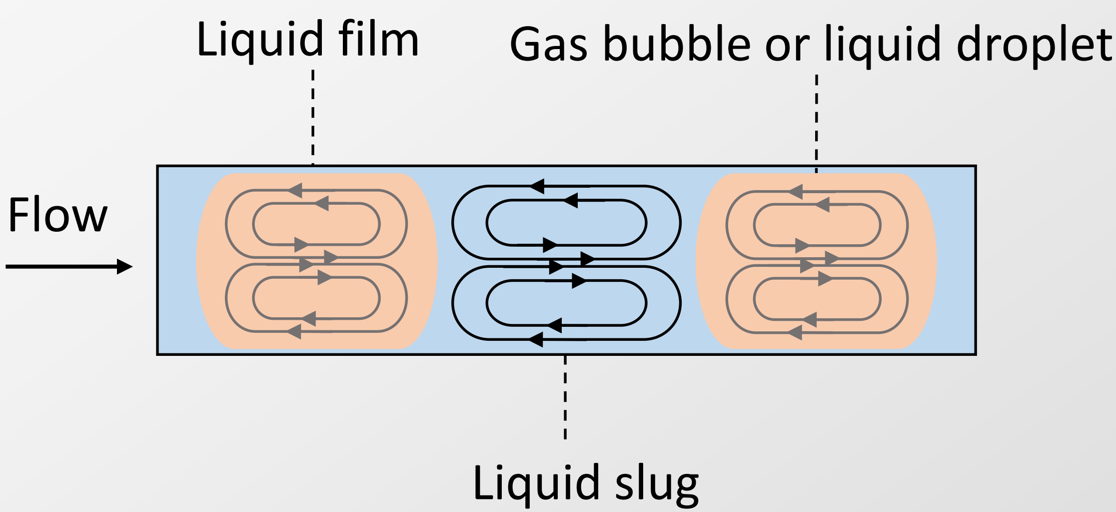
$$\tau_{c,film} = \frac{L_b}{u_b}$$

(Higbie model)

Optional

Mass transfer in slug flow
(gas-liquid or liquid-liquid)

- Mass transfer significantly faster for segmented flow *vs* single-phase flow
- Sherwood number increases due to:
  - ✓Internal flow circulation within liquid slugs
  - ✓Constant fluid layer renewal at wall / bubble interface



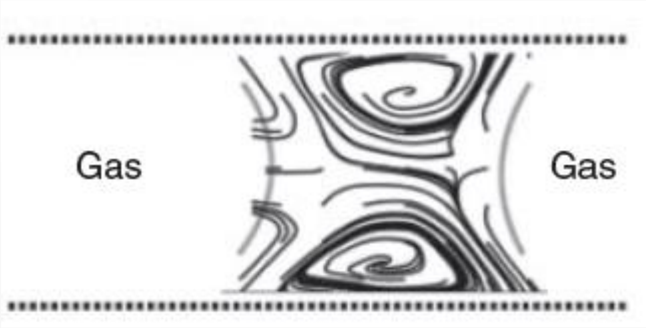
Power input requirement in microchannels vs conventional equipment

Contactor type	Power input, (kJ m^{-3}) of liquid
Agitated extraction column	0.5–190
Mixer-settler	150–250
Rotating disk impinging streams contactor	175–250
Impinging streams	280
Impinging stream extractor	35–1500
Centrifugal extractor	850–2600
Liquid–liquid slug flow	0.2–20

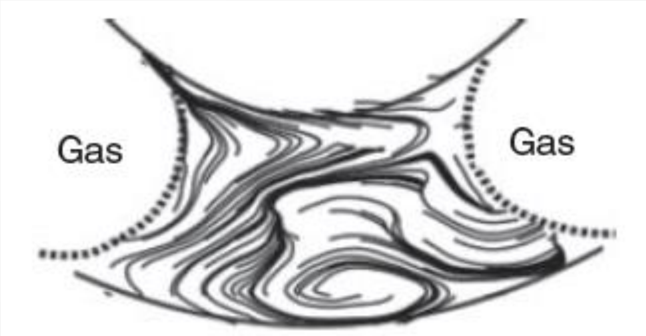
Significantly lower power requirement compared to most conventional technologies

Taylor flow (gas-liquid system)

Increase of radial mixing through channel curvature (meandering channels)



Internal circulation patterns
Straight channel

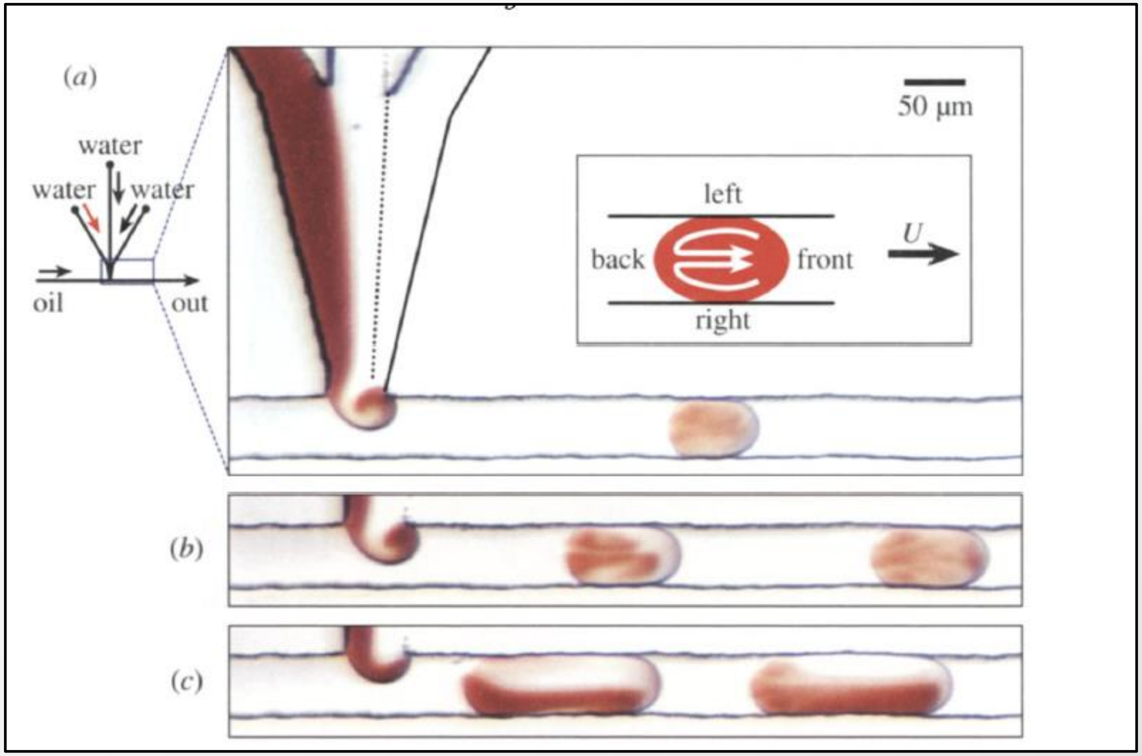


Internal circulation patterns
Meandering channel

Increased radial mixing → narrower RTD, increased heat and mass transfer rates

Mixing in segmented flow

Internal circulation patterns in straight microfluidic channels



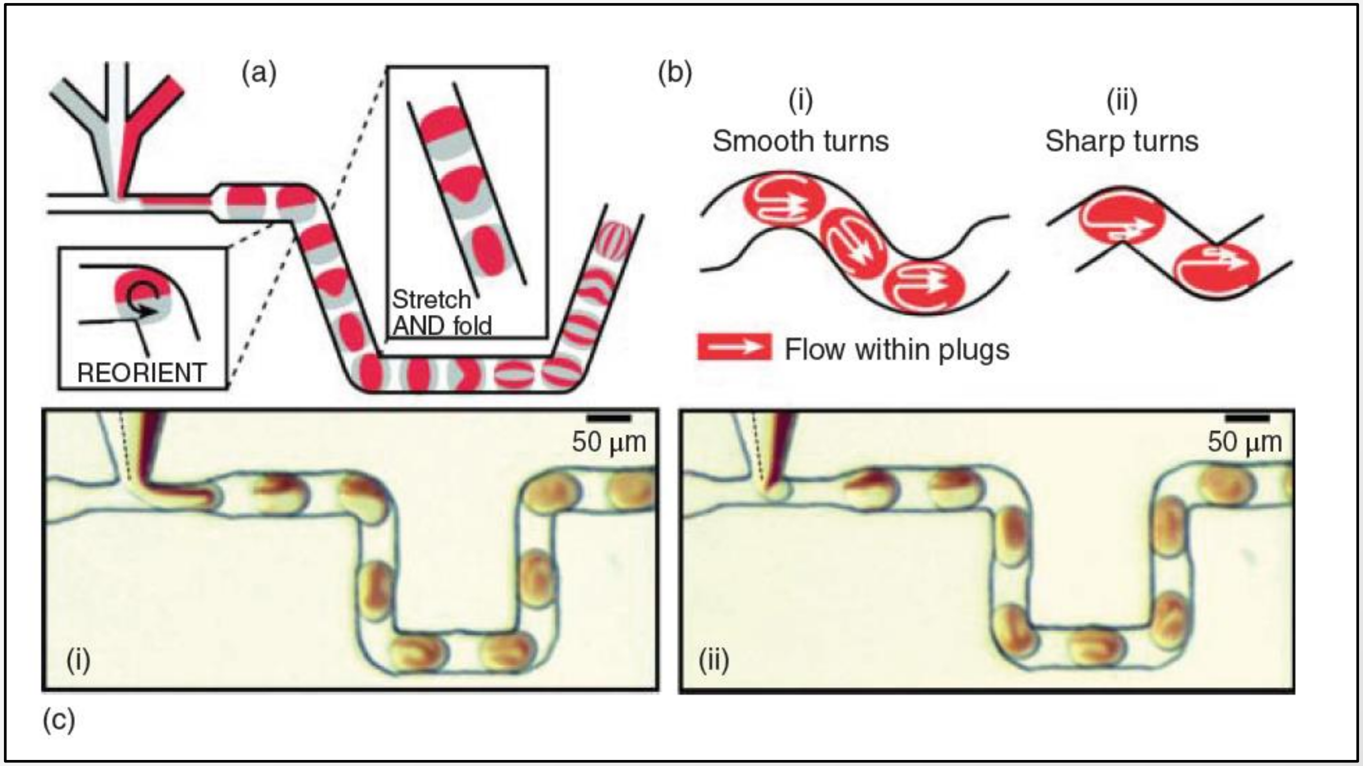
Water fractions
(a) 0.14
(b) 0.3
(c) 0.6

Formation of two vortices in each half of a plug

Bringer et al., Phil. Trans. R. Soc. Lond. A (2004) 362

Mixing in segmented flow

Chaotic advection in winding microfluidic channels

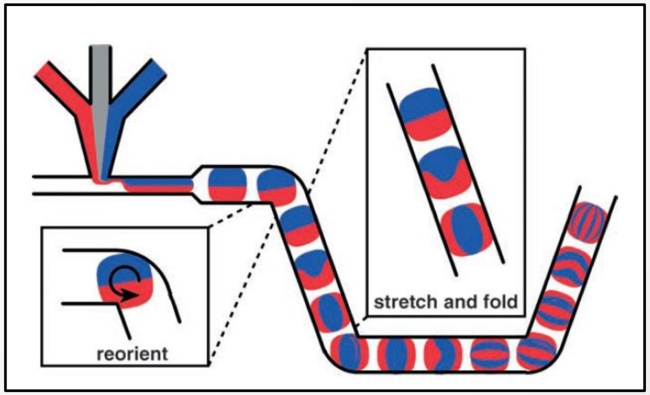


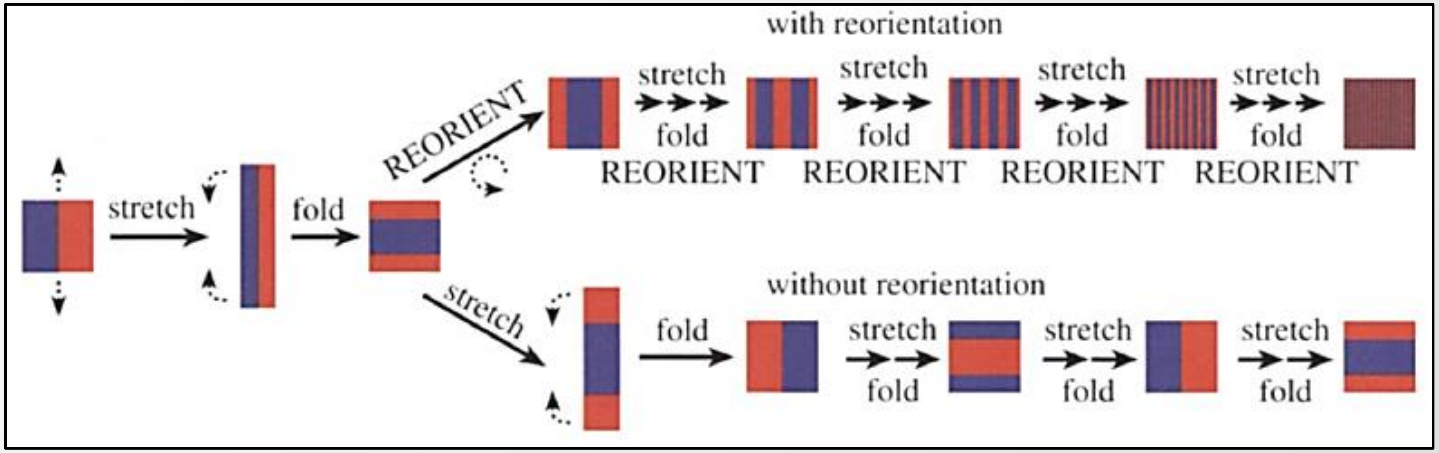
- Straight channels: stretch and fold only → no decrease in striation thickness
- Winding channels: stretch, fold <u>and</u> reorient (Baker's transformation) → decrease in striation thickness

Bringer et al., Phil. Trans. R. Soc. Lond. A (2004) 362

Mixing in segmented flow

Chaotic advection in winding microfluidic channels

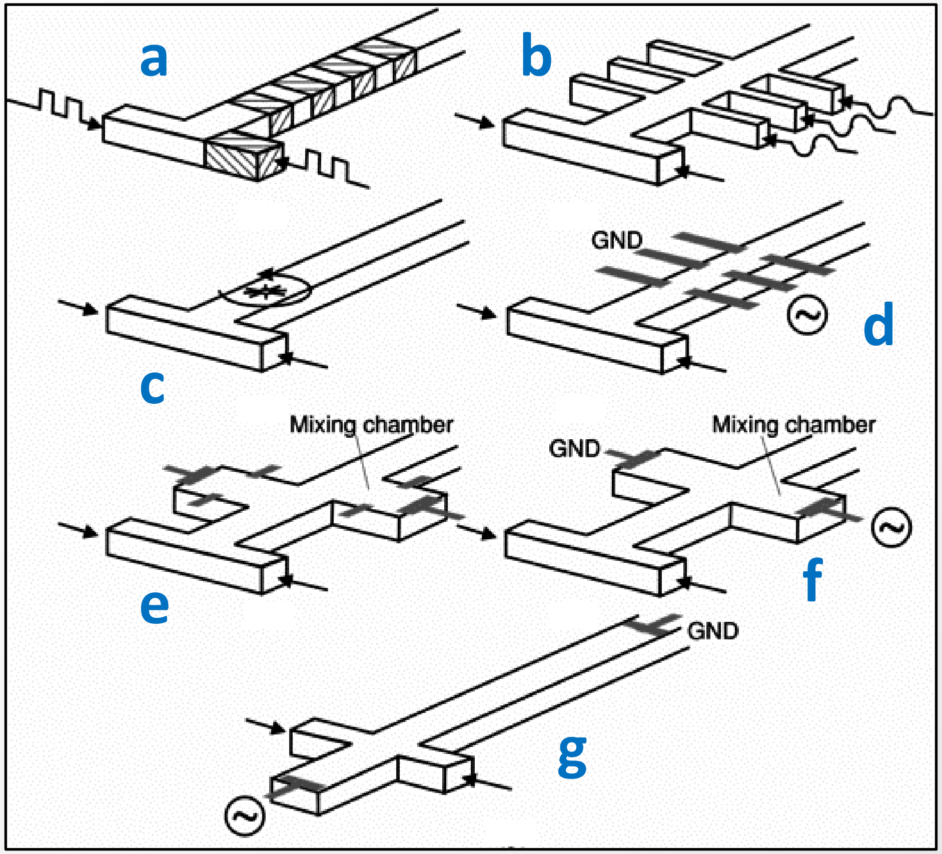




- Top: fluid element undergoing stretching, folding <u>and</u> reorientation (Baker's transformation)
- Bottom: fluid element undergoing stretching and folding only → no decrease in striation thickness

3. Active micromixers

Some active micromixers



(a) Serial segmentation

(b) Pressure disturbance along the mixing channel

(c) Integrated microstirrer in the mixing channel

(d) Electrohydrodynamic disturbance

(e) Dielectrophoretic disturbance

(f) Electrokinetic disturbance in the mixing chamber

(g) Electrokinetic disturbance in the mixing channel

Optional

Active micromixers

- Can provide fast mixing at very low Re
- Need for external power source
- Complex/costly fabrication processes
- Some techniques include
    - Pressure disturbance
    - Electrokinetic
    - Accoustic
    - Electrohydrodynamic
    - Dielectrophoretic
    - Magneto hydrodynamic
    - Thermal

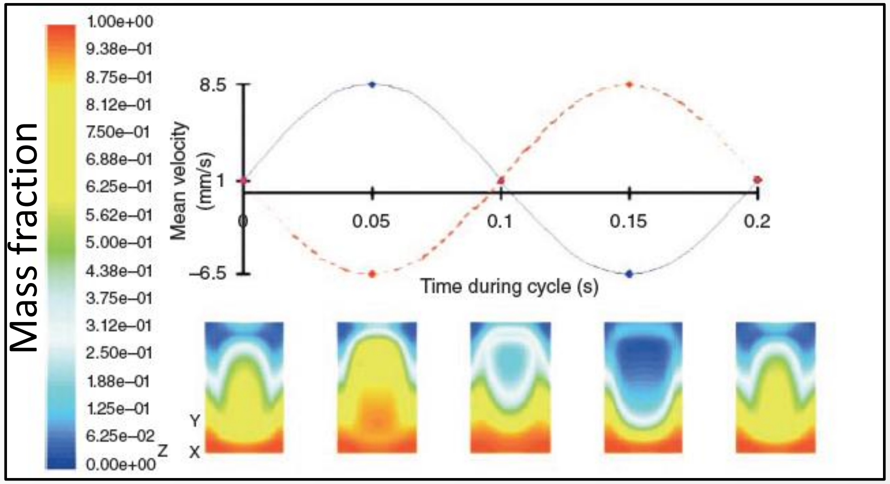
Active micromixers

- Pressure disturbance
- Electrokinetic

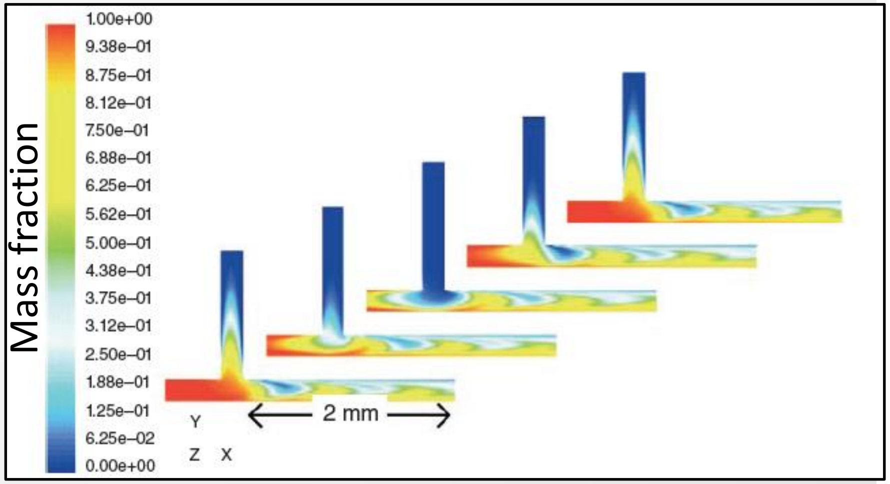
Pressure-induced disturbances

- Chaotic advection generated by superimposing a pulsating flow at channel inlet(s)
- Mixing efficiency influenced by periodicity and number of pulsating streams
- Best results obtained for two pulsed inlet flows having a phase difference of 180° (same amplitude and frequency)
- Mixing enhanced by:
    - Bending of the fluid interface along the channel cross section.
    - Stretching and folding in the direction of the flow.

Pressure-induced disturbances

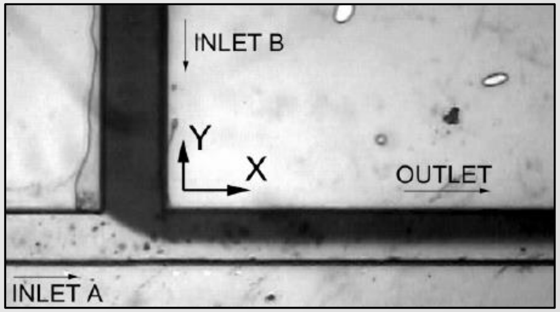


Y-Z plane



X-Y plane

- Periodic forcing at very low Re (0.3) using simple geometry (T-mixer)
- Best results (best mixing) occur when both inlets are pulsed out of phase.

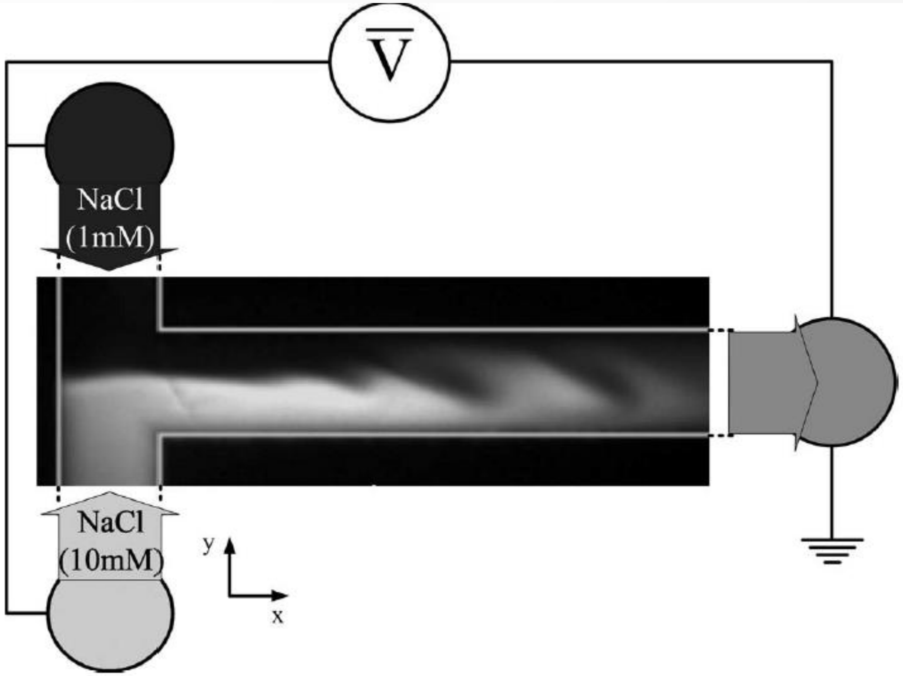


Glasgow and Aubry, Lab Chip, 2003, 3, 114–120

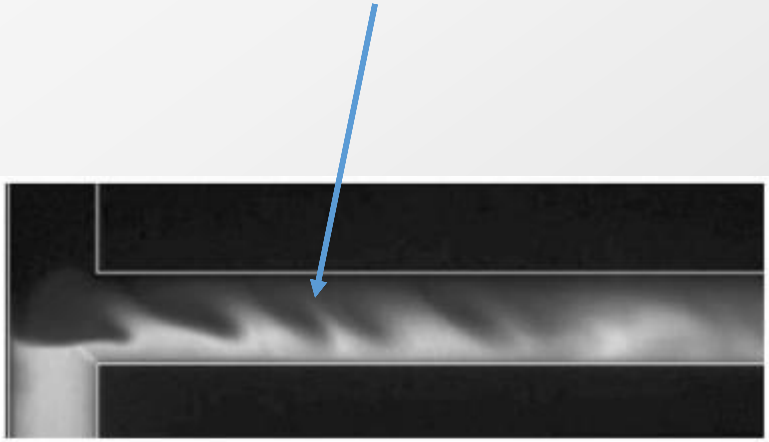
Electrokinetic instability

- Sinusoidal oscillation of the electric field
- Rapid stretching and folding leading to efficient mixing even at low Re (<1)

Electrokinetic instability

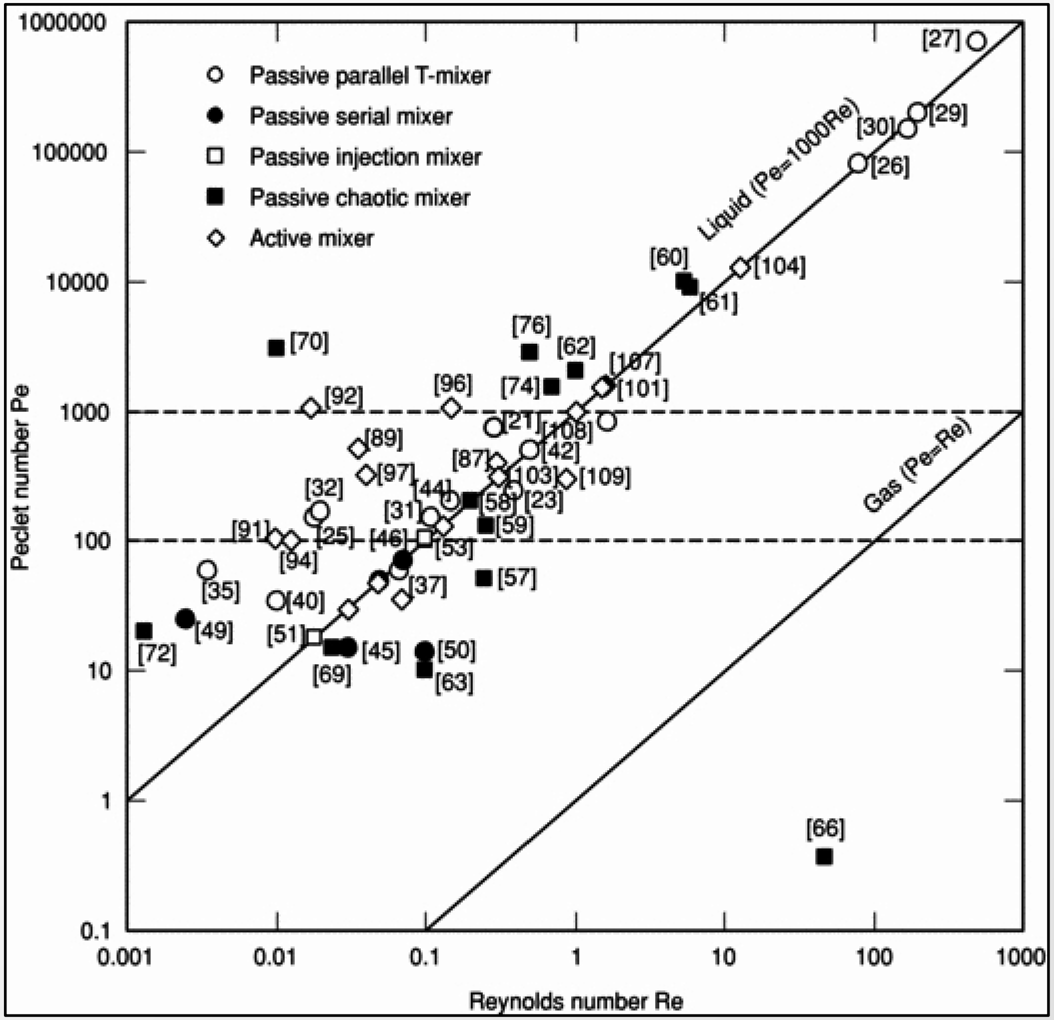


An interfacial wave is generated



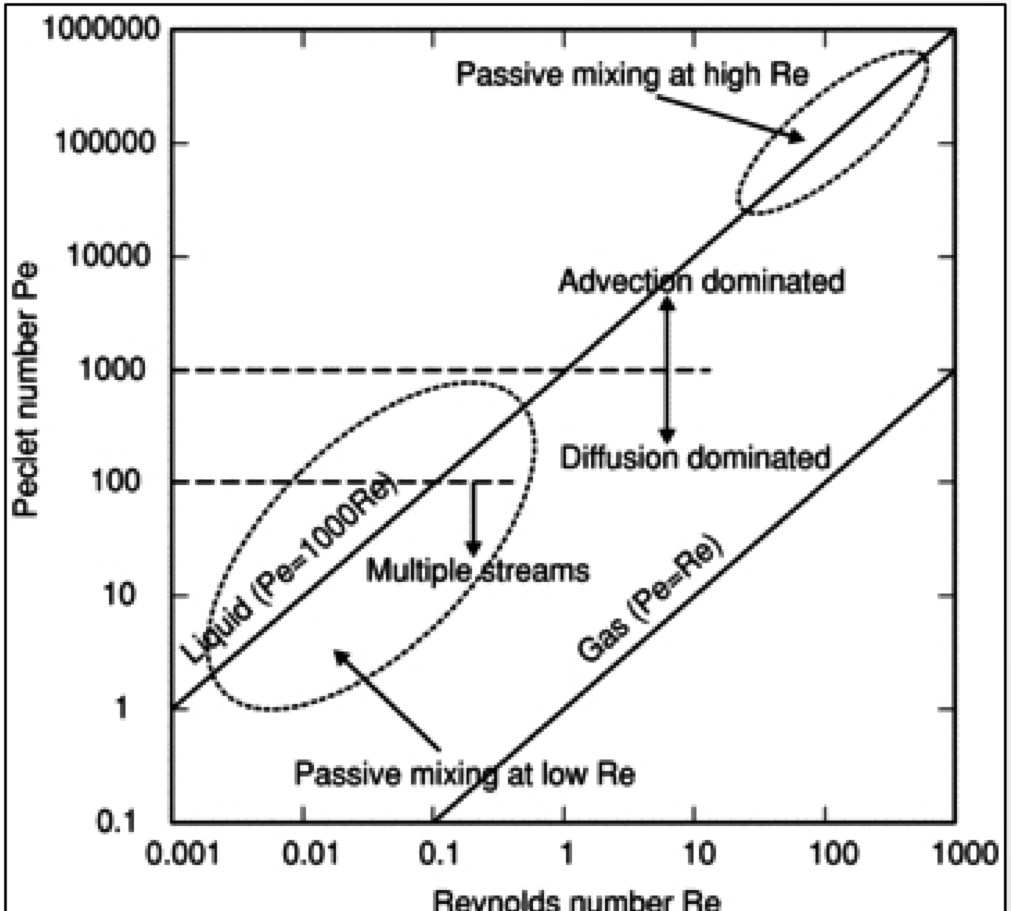
Park et al., Physics of fluids ***17****, 118101 2005*

Typical operation ranges of micromixers



Optional

Peclet-Reynolds diagram



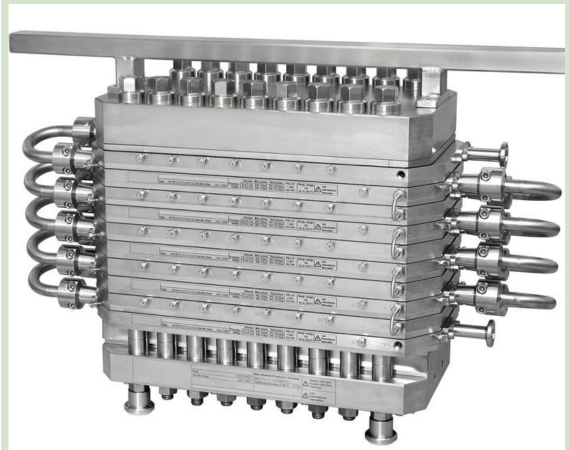
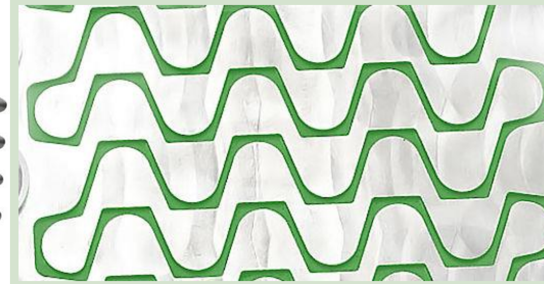
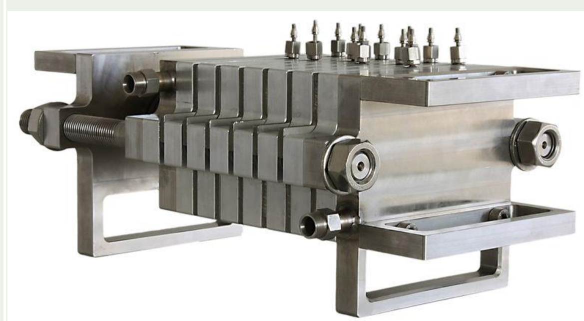
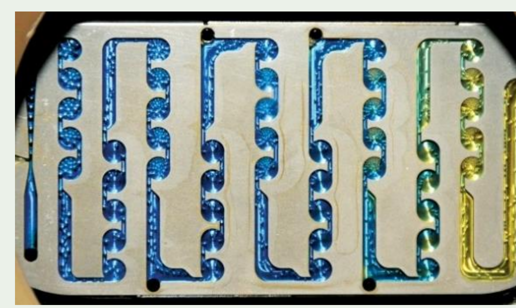
- Passive micromixers: low Re and low Pe or high Re in the transition regime
- Passive mixers based on chaotic advection and active mixers: around characteristic lines for liquids and gases for a wide range of Re
- Passive lamination micromixers with multiple streams: small Pe ($Pe < 100$).
- In the range of ($Pe < 1000$), the mixer can be considered as diffusion based

Optional

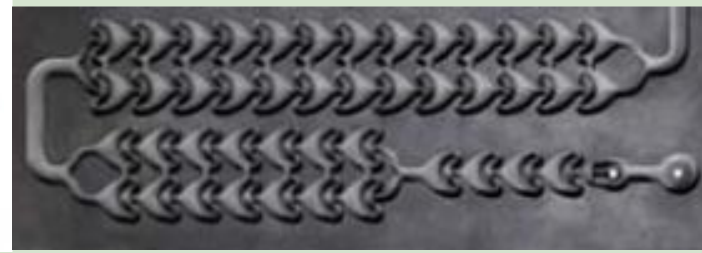
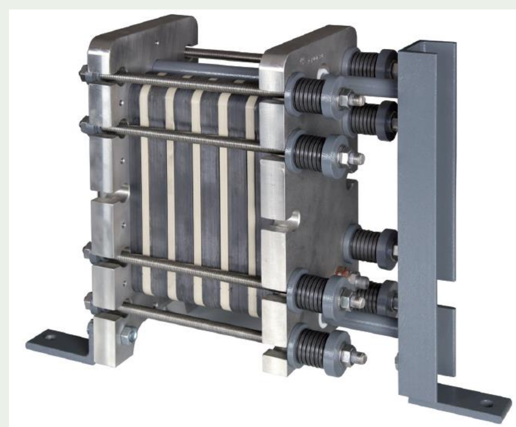
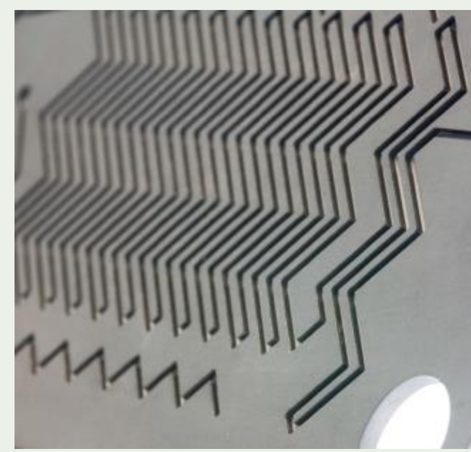
6. Commercial microreactors

6.1. Introduction

Some industrial systems

Reactor	Specifications	Assembly / channel shape
Alfa Laval (Ehrfeld AG)	SS, Hastelloy 0.3 – 1000 l/h →20 bar -60 – 200°C 0.8 – 180 mm^2	 
Lonza FlowPlate® (Ehrfeld AG)	Hastelloy 0.06 – 20 l/h →100 bar -55 – 200°C 0.1 – 20 mm^2 SZ and TG type channels	 

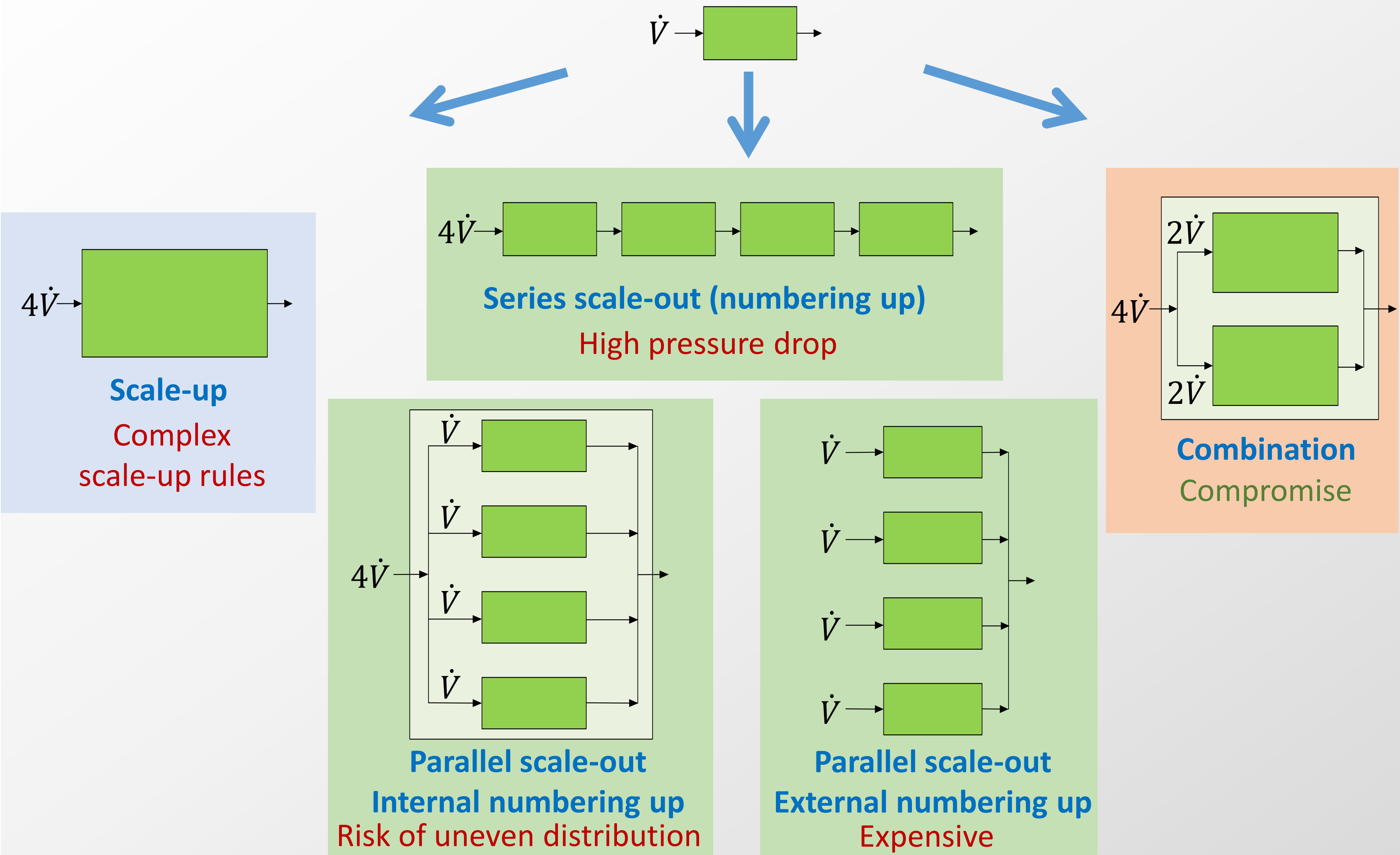
Some industrial systems

Reactor	Specifications	Assembly / channel shape
Corning	Glass, SiC 0.15 – 500 l/h →18 bar -60 – 200°C Heart-shaped channels	  
Chemtrix	Glass, SiC 0.01 – 400 l/h →25 bar -30 – 200°C Zigzag channels	 

Scaleup / equipment choice

- Mastered ('linear') scaleup from lab to plant in the aforementioned industrial systems (~1 → ~1000 l/h)
- Channel size is adjusted for scaleup
  - ✓Heat and mass transfer characteristics, as well as mixing time and RTD are maintained upon scaleup
  - ✓Note that the external numbering-up strategy is not used in the latter examples of industrial systems!
  - ✓In general, millichannels, not microchannels
- Some criterial for equipment selection:
  - ✓Modularity, heat and mass transfer characteristics, scaleup, pressure resistance, pressure drop, flow visualization, opening/cleaning, residence time range, cost

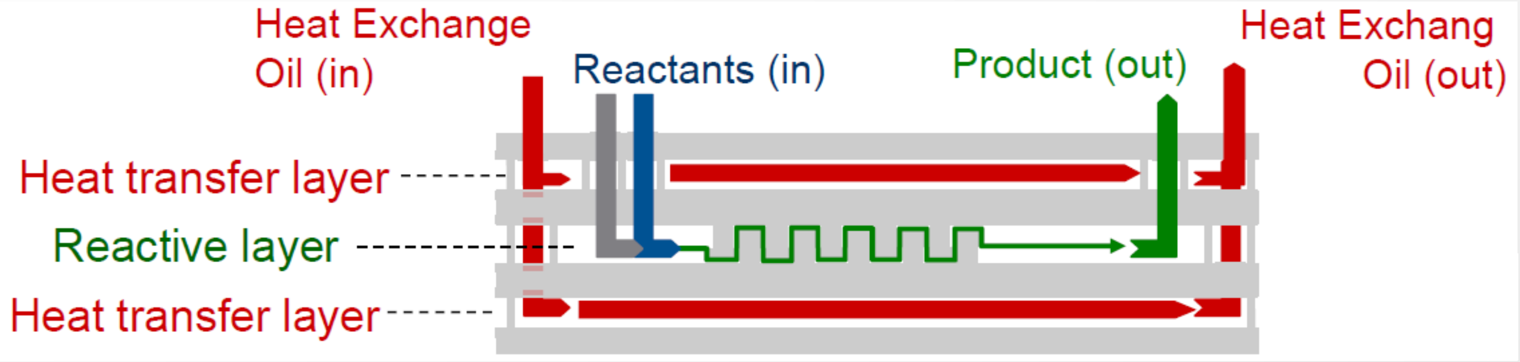
Scale-up strategies

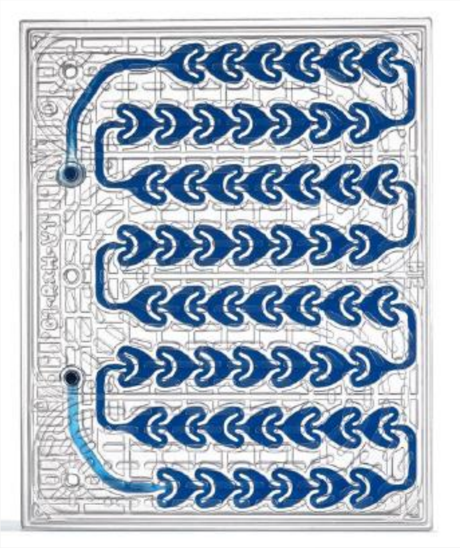


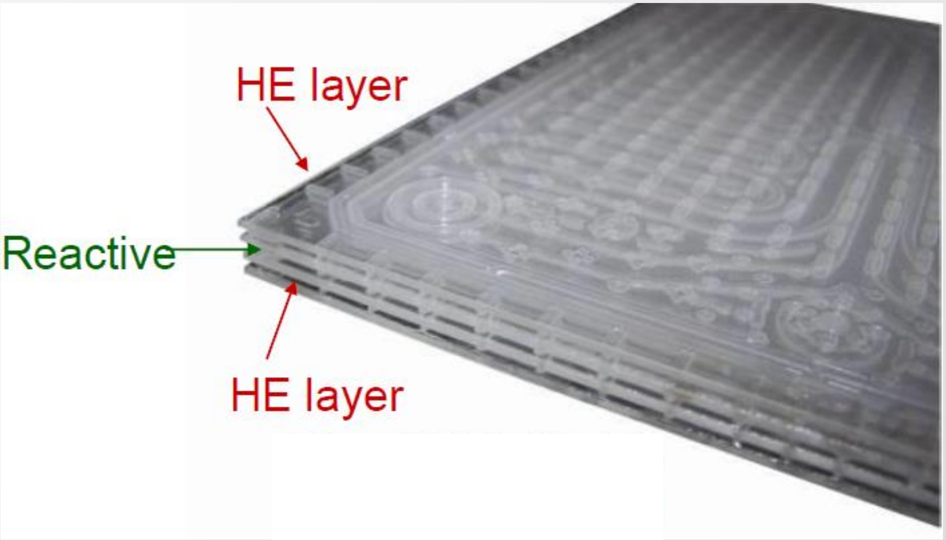
6. Commercial microreactors

6.2. Example: Corning reactors

Example: Corning Advanced Flow Reactor







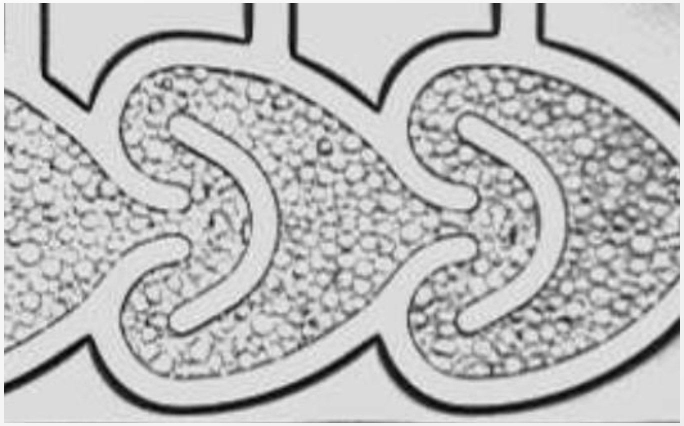
Reproduced with permission from Corning

Corning reactor specifics

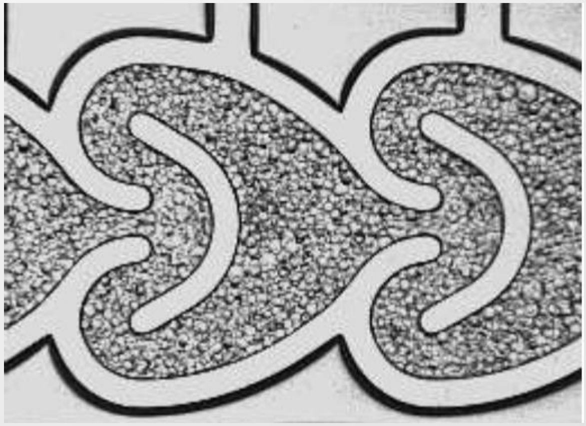
- Sandwich-type structure
- Heart-shaped channels
  - Good for immiscible fluid systems (L/L, L/G)
- Glass or ceramic (SiC)
  - Glass: photoreactions feasible
- Flowrate range 0.15 – 500 l/h
- Pressure up to 18 bar
- Temperature range -60 to +200°C
- Millimeter-sized
- $U_V \cong 10^6\ Wm^{-3}$
- $a \cong 2500\ m^{-1}$

Liquid / liquid dispersion
Toluene / water

Flow direction →



20 g/min toluene-20g/min water

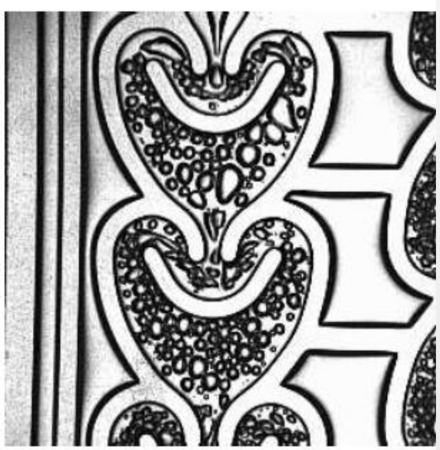


40 g/min toluene-40g/min water

Periodic merging and break-up of droplets/bubbles → constant interface renewal

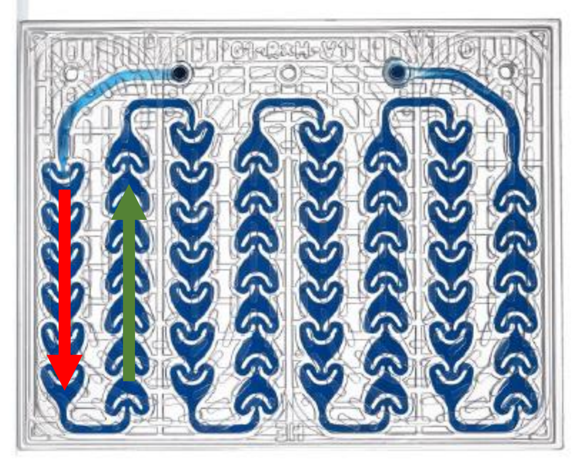
Gas / liquid systems

Nitrogen / water

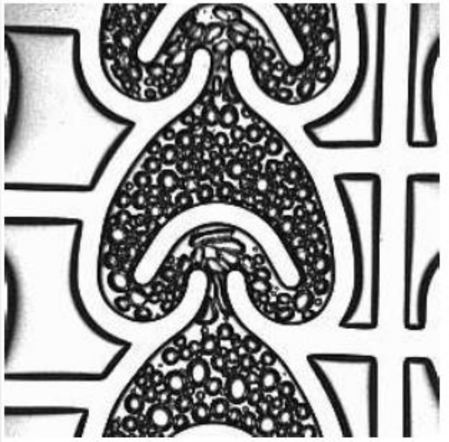


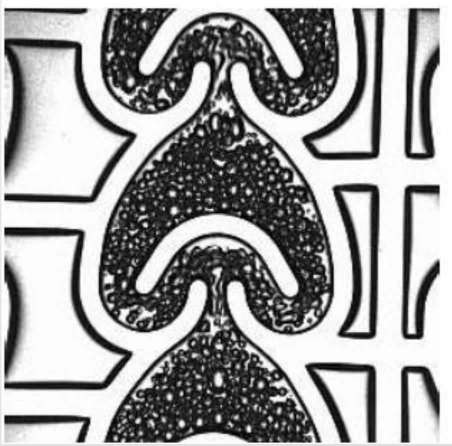
Flow direction

$$L = 50\,ml \cdot min^{-1}$$
$$G = 100\,ml \cdot min^{-1}$$



$$L = 100\,ml \cdot min^{-1}$$
$$G = 200\,ml \cdot min^{-1}$$

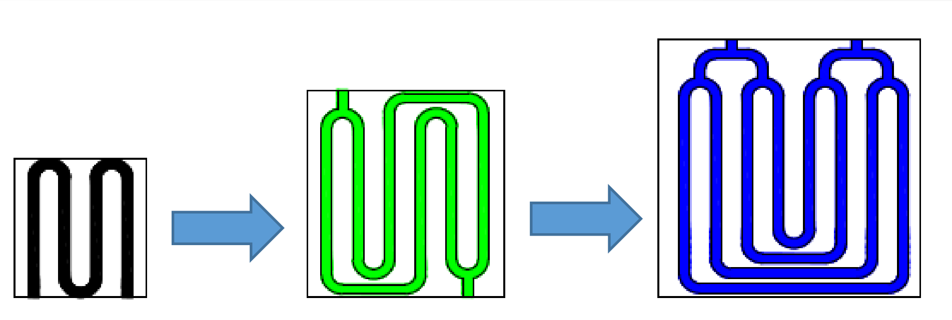




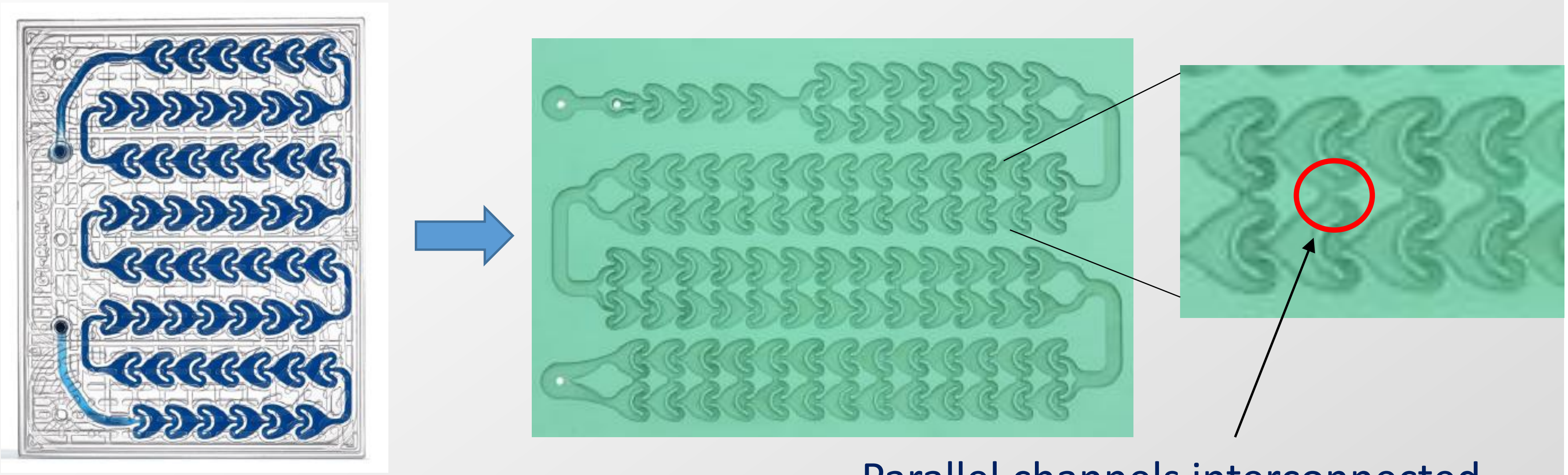
Flow direction

Hybrid scaleup approach

Internal numbering up



Conventional internal numbering up
→ high risk of uneven distribution



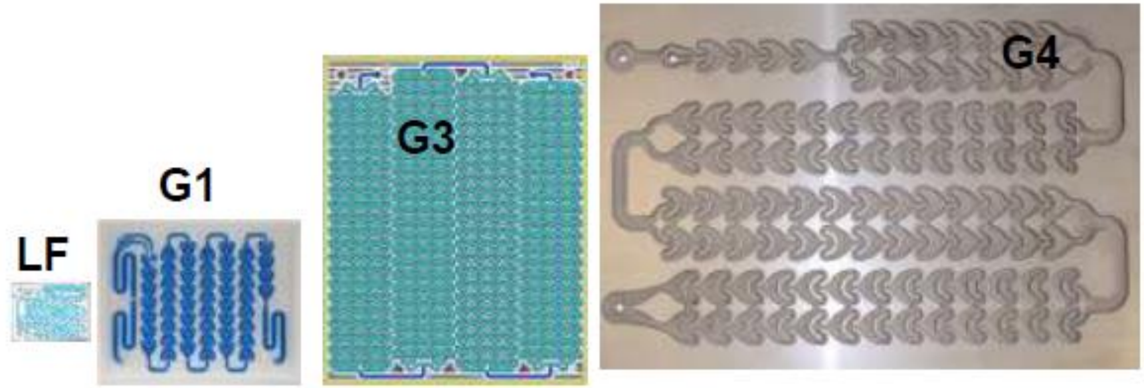
Parallel channels interconnected
to minimize uneven distribution

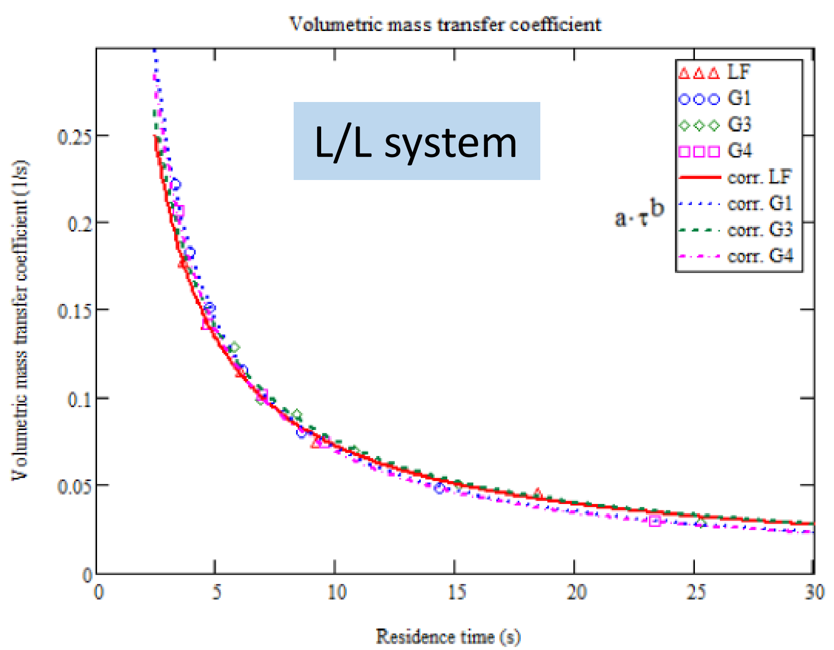
Hybrid scaleup approach
Increase channel height upon scaleup

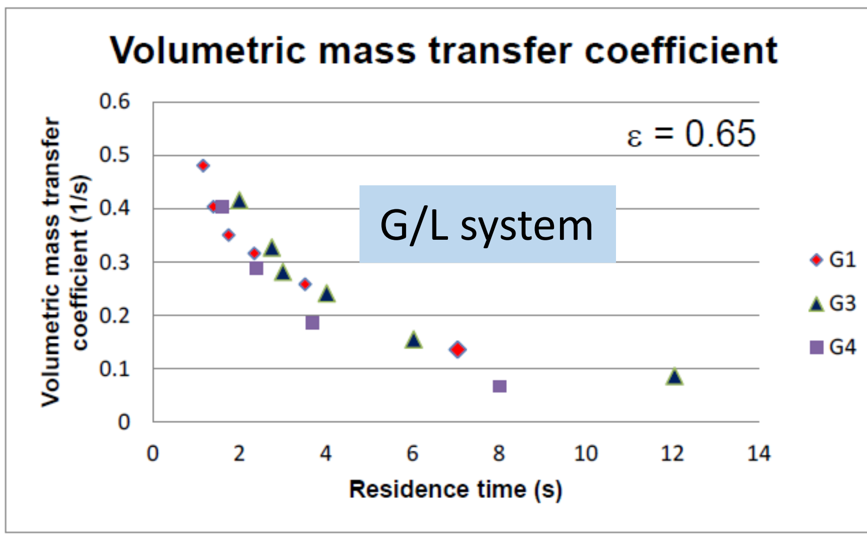
Height 1 mm, volume 8 ml

Height 5 mm, volume 240 ml

Scalability







Equal $k_L \cdot a$ at equal residence time ⇨ 'linear' scaleup

Mass transfer capability

L/L system

Type	V, mm^3	k_L-a @ 5 s RT, s^{-1}	Throughput (ml/min)
T square[1]	48.23	0.07	0.6
T trapezoidal[1]	48.23	0.07	0.6
Y rectangular[1]	82.95	0.05	1
Concentric[1]	394.08	0.053	4.7
Caterpillar[1]	23.67	0.035	0.3
LF	**633**	**0.135**	**7.5**
G 1	**$7.5 \cdot 10^3$**	**0.146**	**90**
G 3	**$55 \cdot 10^3$**	**0.14**	**650**
G 4	**$250 \cdot 10^3$**	**0.14**	**3000**

$k_L \cdot a$ higher than in conventional microreactors

Mass transfer capability

G/L system

Contacting equipment	Volumetric mass transfer coefficient, $k_L a$ (s^{-1})
Plate column[1]	0.01–0.05
Packed column[1]	0.005–0.02
Gas bubble column[1]	0.005–0.01
Stirred bubble absorber[1]	0.02–0.2
Spray column[1]	0.0007–0.015
Jet (loop)[1]	0.1–3.0
Multi-stage ELALR[1]	0.01–0.05
Microchannel[2]: V = 25 μL Q_G = 15 – 375 mL/min Q_L = 2.5 – 30 mL/min	0.3-21
Corning® G1: V = 8 mL Q_G = 20 – 600 mL/min Q_L = 20 – 130 mL/min	**0.08-0.55**
Corning® G4 V = 250 mL Q_G = 3000 – 30000 mL/min Q_L = 600 – 3000 mL/min	**0.045-0.65**

$k_L \cdot a$ higher than in conventional equipment