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a. Measurement Techniques

b. Fundamentals of Biotechnology

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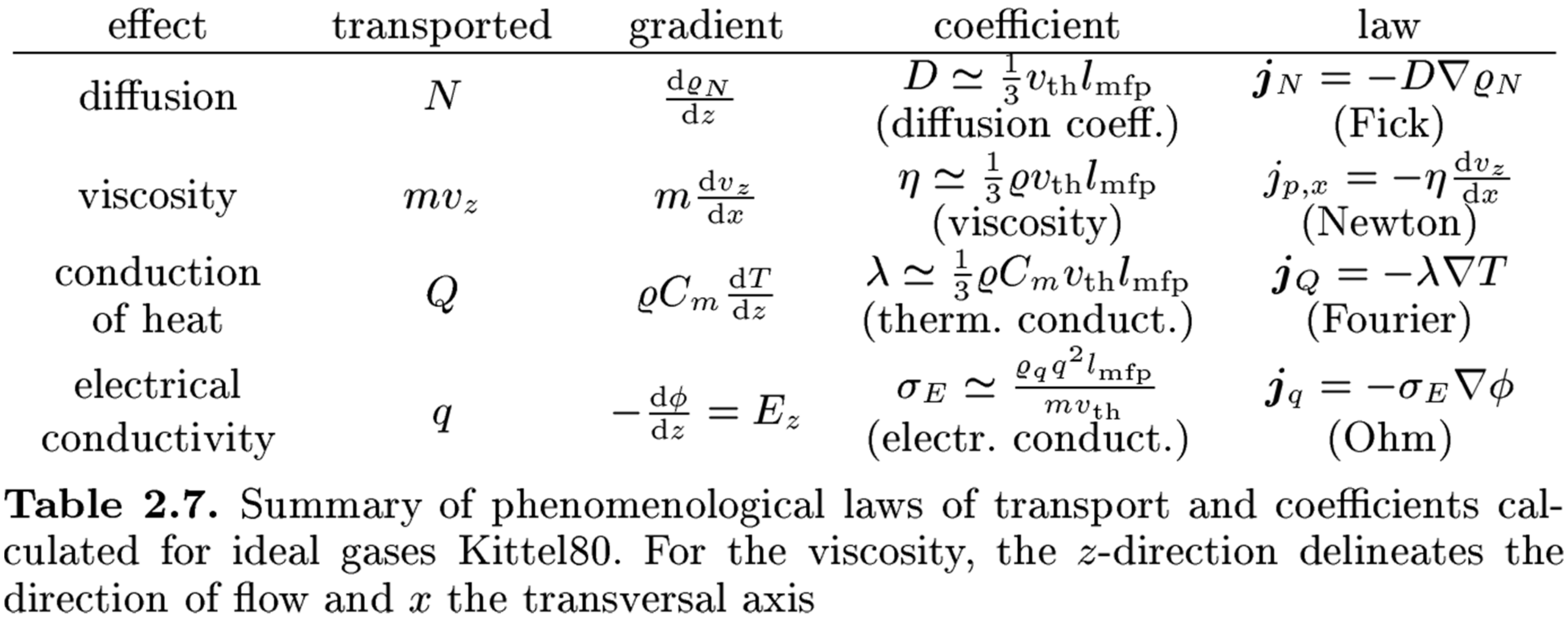
11. Benefits of Miniaturization

- Transport phenomena
  - Well-predictable / reproducible in microstructures
  - Intrinsic driving force
    - No actuation required
    - Processes to large extent controlled by passive structures



effect	transported	gradient	coefficient	law
diffusion	N	$\frac{\mathrm{d}\varrho_N}{\mathrm{d}z}$	$D \simeq \frac{1}{3} v_{\mathrm{th}} l_{\mathrm{mfp}}$ (diffusion coeff.)	$\boldsymbol{j}_N = -D \nabla \varrho_N$ (Fick)
viscosity	$m v_z$	$m \frac{\mathrm{d}v_z}{\mathrm{d}x}$	$\eta \simeq \frac{1}{3} \varrho v_{\mathrm{th}} l_{\mathrm{mfp}}$ (viscosity)	$j_{p,x} = -\eta \frac{\mathrm{d}v_z}{\mathrm{d}x}$ (Newton)
conduction of heat	Q	$\varrho C_m \frac{\mathrm{d}T}{\mathrm{d}z}$	$\lambda \simeq \frac{1}{3} \varrho C_m v_{\mathrm{th}} l_{\mathrm{mfp}}$ (therm. conduct.)	$\boldsymbol{j}_Q = -\lambda \nabla T$ (Fourier)
electrical conductivity	q	$-\frac{\mathrm{d}\phi}{\mathrm{d}z} = E_z$	$\sigma_E \simeq \frac{\varrho_q q^2 l_{\mathrm{mfp}}}{m v_{\mathrm{th}}}$ (electr. conduct.)	$\boldsymbol{j}_q = -\sigma_E \nabla \phi$ (Ohm)

Table 2.7. Summary of phenomenological laws of transport and coefficients calculated for ideal gases Kittel80. For the viscosity, the z-direction delineates the direction of flow and x the transversal axis

11. Benefits of Miniaturization

- Fast diffusion
  - Fick‘s laws

$$j_N = -D \nabla \varrho_N$$

$$\frac{\partial \varrho_N}{\partial t} = D \triangle \varrho_N$$

  - Characteristic diffusion time
    - *D* approx. 10^{-9} m^2 / s for solvated molecules

$$t_D = \frac{\boxed{l^2}}{D}$$

  - Macro: *l* approx. 1 cm = 10^{-2} m
    - *t* approx. **10^5 s**
  - Micro: *l* approx. 100 µm = 10^{-4} m
    - *t* approx. **10 s**

- Brownian motion

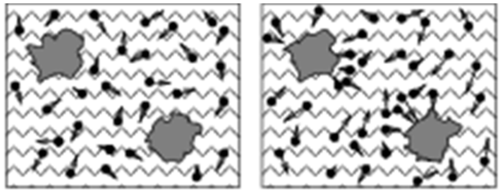


Fig.. Brownian motion resulting from random molecular pressure oscillations leads to wobbling motion of mesoscopic particles that can be observed under a microscope

11. Diffusion Coefficient

Fourier mass number

- Particle diffusion / concentration

$$Fo_m = \frac{Dt}{\boxed{l^2}}$$

solute	solvent	D / 10^{-9} m^2 s^{-1}
I_2	C_6H_{12}	4.05
I_2	CCl_4	3.42
I_2	C_6H_6	2.13
N_2	CCl_4	3.42
O_2	CCl_4	3.82
Ar_2	CCl_4	3.63
H_2O	H_2O (self diffusion)	2.62
dextrose	H_2O	0.67
H^+	H_2O	9.31
Li^+	H_2O	1.03
Na^+	H_2O	1.96
Cl^-	H_2O	2.03
Br^-	H_2O	2.08
I^-	H_2O	2.05

Table 2.8. Diffusion coefficients of molecules and ions in various solvents

11. Benefits of Miniaturization

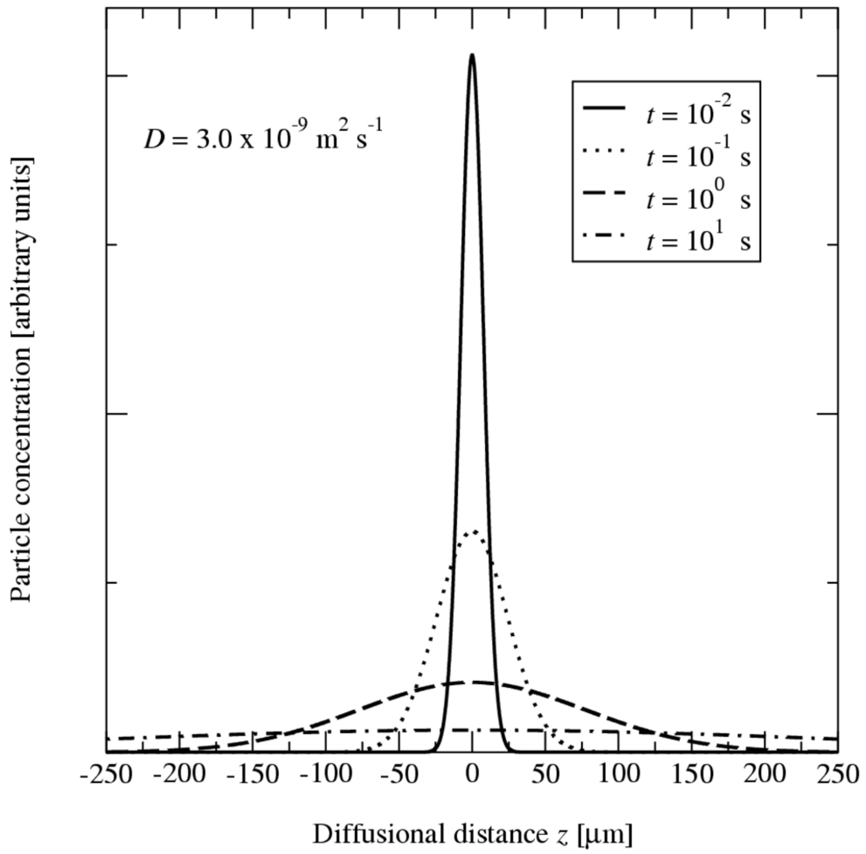


Fig. 0.1. Diffusion of a thin layer of solved molecules centered at $z = 0$ in the surrounding pure solvent at times t for $D = 3.0 \times 10^{-9}\ \mathrm{m}^2\,\mathrm{s}^{-1}$

11. Benefits of Miniaturization

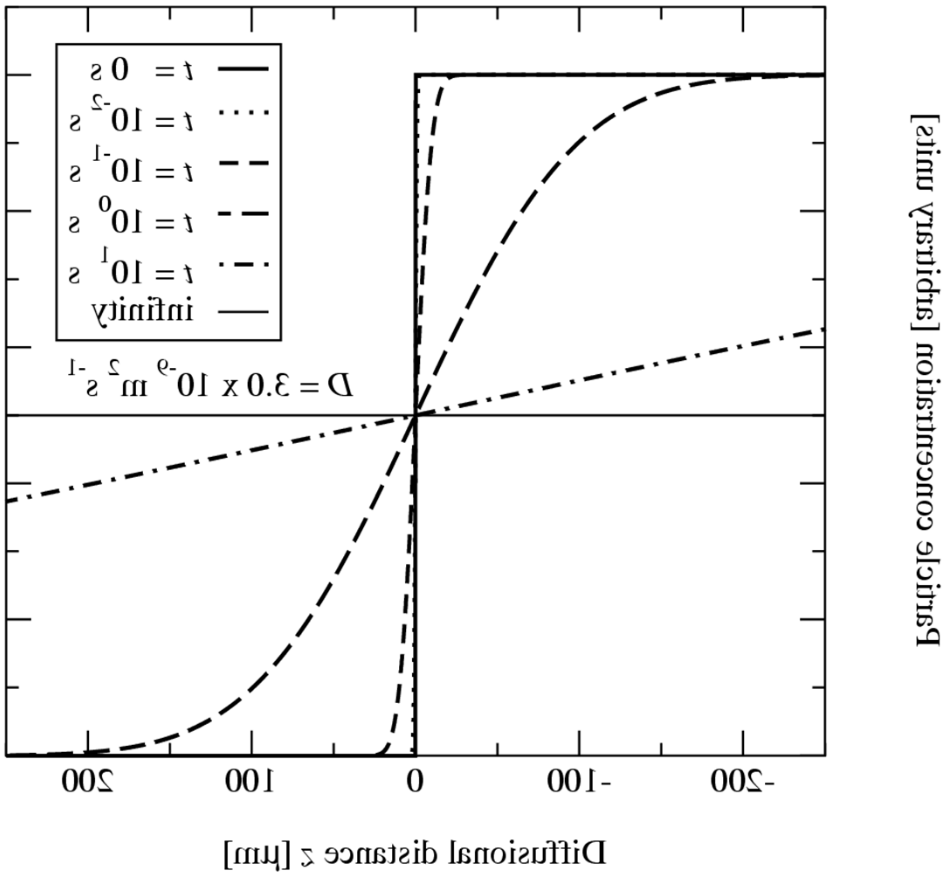


Fig. 0.1. Diffusion of molecules through a permeable wall at $z = 0$ which are initially located at $z < 0$. $D = 3.0 \times 10^{-9}$ m^2 s^{-1} has been assumed. With increasing time, a uniform distribution builds out

11. Benefits of Miniaturization

- Fast heat exchange
  - ➢ Fourier‘s law

$$j_Q = -\lambda \frac{\mathrm{d}T}{\boxed{\mathrm{d}z}}$$

  - ➢ Power associated with heat transport

$$P = j_Q A = \boxed{A}\lambda \frac{\mathrm{d}T}{\boxed{\mathrm{d}z}}$$

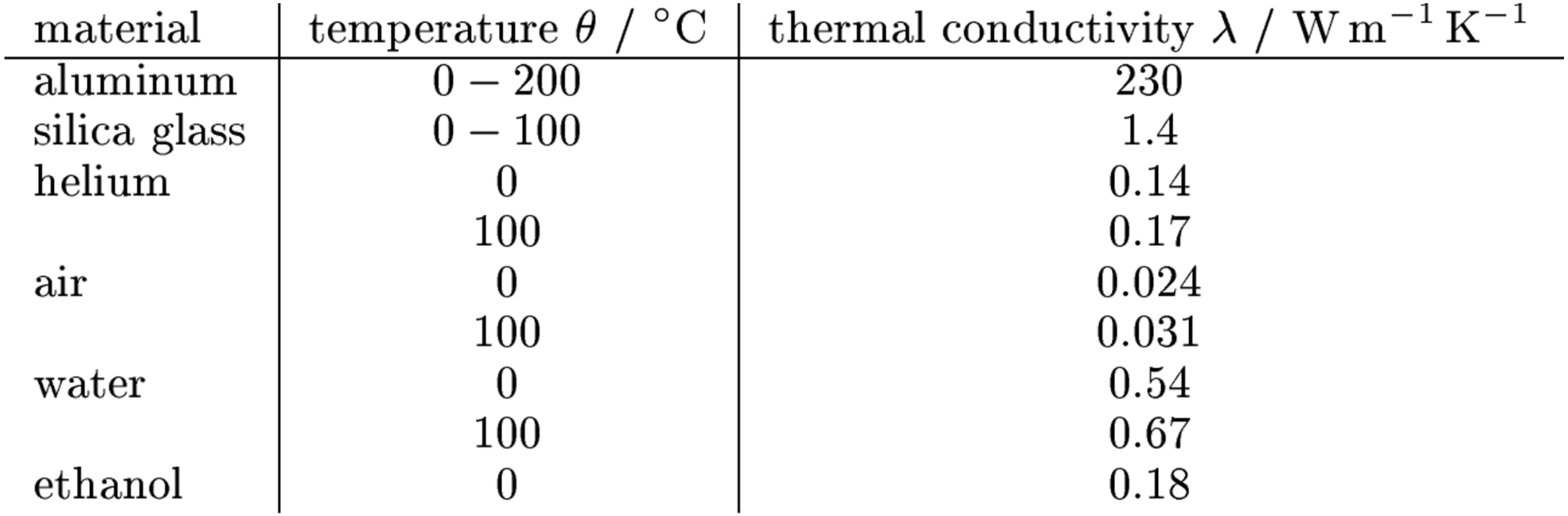
  - ➢ Characteristic time
    - Same scale ~ l^2 as diffusion

$$\tau = \frac{\boxed{d^2}\varrho C_m}{\lambda}$$

  - ➢ Fourier number
    - Heat diffusion / stored heat

$$Fo = \frac{\lambda t}{\boxed{l^2}}$$

11. Thermal Conductivity



material	temperature θ / °C	thermal conductivity λ / $\mathrm{W\,m^{-1}\,K^{-1}}$
aluminum	$0 - 200$	230
silica glass	$0 - 100$	1.4
helium	0	0.14
	100	0.17
air	0	0.024
	100	0.031
water	0	0.54
	100	0.67
ethanol	0	0.18

Table 2.12. Thermal conductivity for solids, liquids and gases

11. Microreactors

1. **Micromixers**
2. Heat Exchangers
3. Chemical Microreactors
4. Splitting of Flow
5. Fuel-Based Power Supplies

11.1. Micromixers

- Mixing of two phases
  - ➢ Liquid – liquid
  - ➢ Liquid – gas
  - ➢ Gas – gas
  - ➢ Particles with fluids (suspensions)
- High accuracy
  - ➢ E.g. Bubble (gas, liquid) sizes
- Mixing of reactants
  - ➢ Key step in chemical process engineering
  - ➢ Fast response times
  - ➢ Low dead volumes

11.1. Mixing of Reactants

- Speed depends on surface-to-volume ratio of interfaces
- Two consecutive processes
- Generation of heterogeneous mixture
  - Time critical step
    - Macroscopic time scales
  - Finely dispersed structure
  - Large surface-to-volume ratio to
  - Enhanced diffusion

$$t_D = \frac{\boxed{l^2}}{D}$$

$$\frac{\partial[\mathrm{AB}]}{\partial t} = k_{\mathrm{AB}}[\mathrm{A}][\mathrm{B}]$$

- Mixing on molecular level
  - Reaction kinetics
  - Fast step, molecular time scales

11.1. Mixing in Macro- and Microdevices

- Macrodevices
  - Fast mixing by turbulences
    - Shaking
    - Stirring

$$Re = \frac{\varrho_\infty v_{\mathrm{char}} l_{\mathrm{char}}}{\eta} = \frac{v_{\mathrm{char}} l_{\mathrm{char}}}{\upsilon}$$

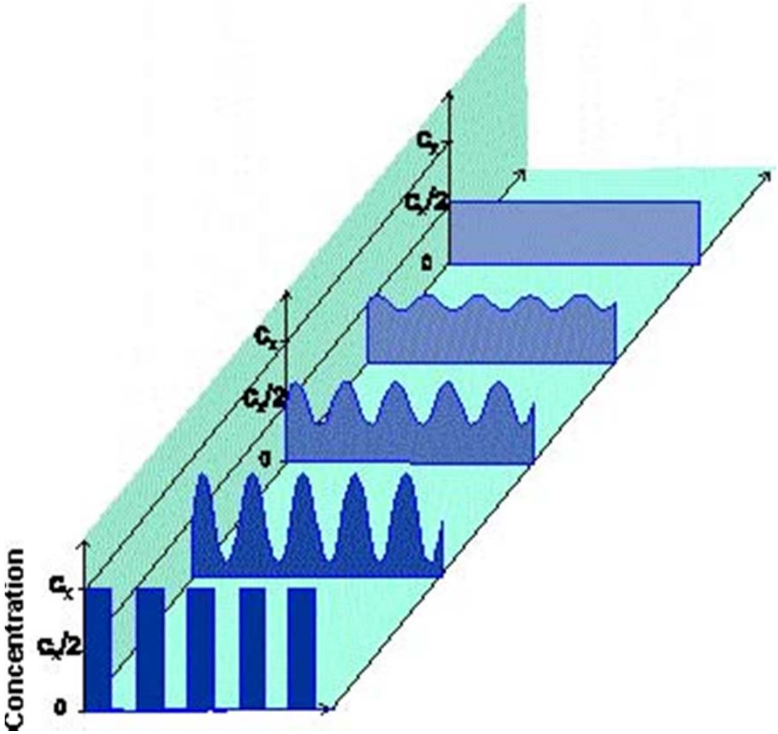
- Microdevices
  - Laminar conditions
  - Turbulences hard to induce
  - Static mixing by diffusion enhanced by passive structures

11.1. Micromixers: Unique Features

- **Ultrafast mixing** as well as **defined slow mixing** by **control over mixing time**
- **Geometrically defined mixing processes** by **control** over **fluid layer thickness**
- **Integrability** of mixing units as parts of **complex assembled systems**
- Generation of **dispersions** with **small particle sizes** and **narrow size distributions**
- Synthesis of **uniform-sized micro-to-nanoscale powder particles**

11.1. Mixing Principles for Miscible and Immiscible Fluids

- **Miscible fluids after contact**
  - Miscible fluids mixed fast by means of **diffusion** due to small thickness of generated **lamellae**



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- **Immiscible fluids after contact**
  - Due to **parabolic flow profile** strong periodical **velocity gradients** generated at **exit** of each channel
  - Velocity gradients lead to **unstable** flow configuration
  - Thin fluid **lamellae** finally **decompose** into **microdroplets** or **microbubbles surrounded** by **continuous phase**

11.1. Multilamination of Layers

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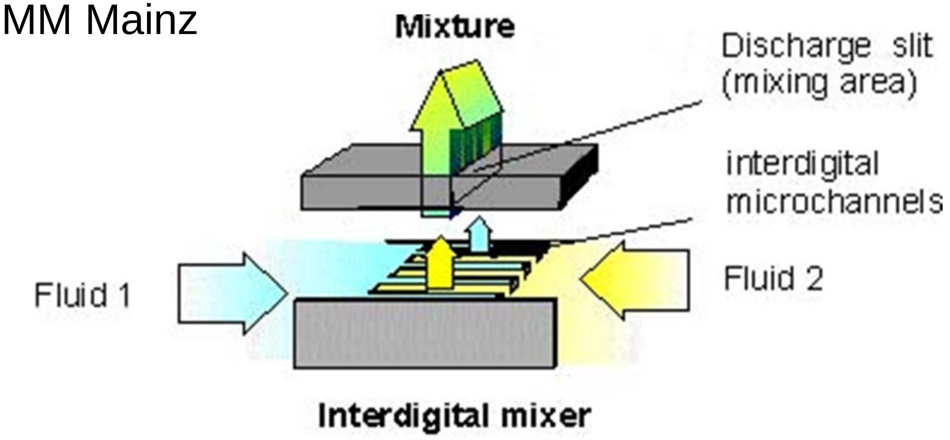
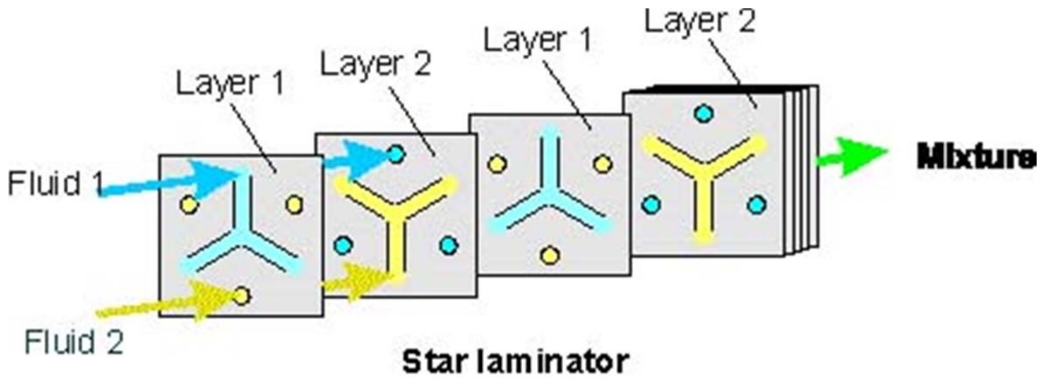


- Fluids to be mixed introduced into mixing element as two **counter-flows**
- Fluids stream into **interdigital** channel configuration
- **Periodical flow configuration** consisting of **lamellae** of two fluids generated by means of **slit-shaped interdigital channels**
- Stratified flow leaves device **perpendicular** to direction of feed flows

11.1. Multi-Lamination of Sheaths



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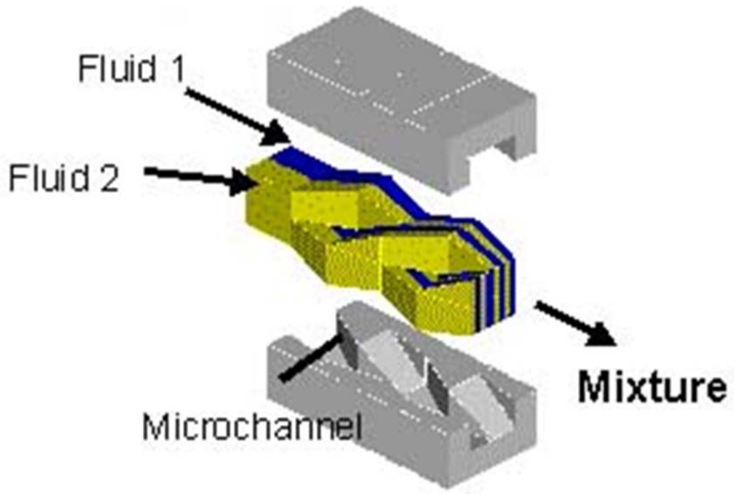
- Fluids to be mixed **introduced** into **boreholes** of mixer
- Fluids entering **single platelets divided into streams**
- From, e.g., **three openings** streams are **guided** through **channel system** to **central position**
- These **streams merge** to **fluid sheaths** of **small thickness**
- **Alternating assembly** of platelets results in **alternating stack of sheaths** of two different fluids
- Mixing performed by **interdiffusion** within this **multi-laminated sheath structure**

11.1. Split and Recombine

- Caterpillar Mixer
    - Fluids to be mixed **introduced** into the device as **two parallel streams**
    - By **special surface shaping** of channel **walls**, referred to as **caterpillar** structure, **each fluid stream split** into **two substreams**
    - **Four** such **substreams recombined** to a **multi-laminated** fluid system
    - Process **repeated** several times



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11.1. Split and Reunify

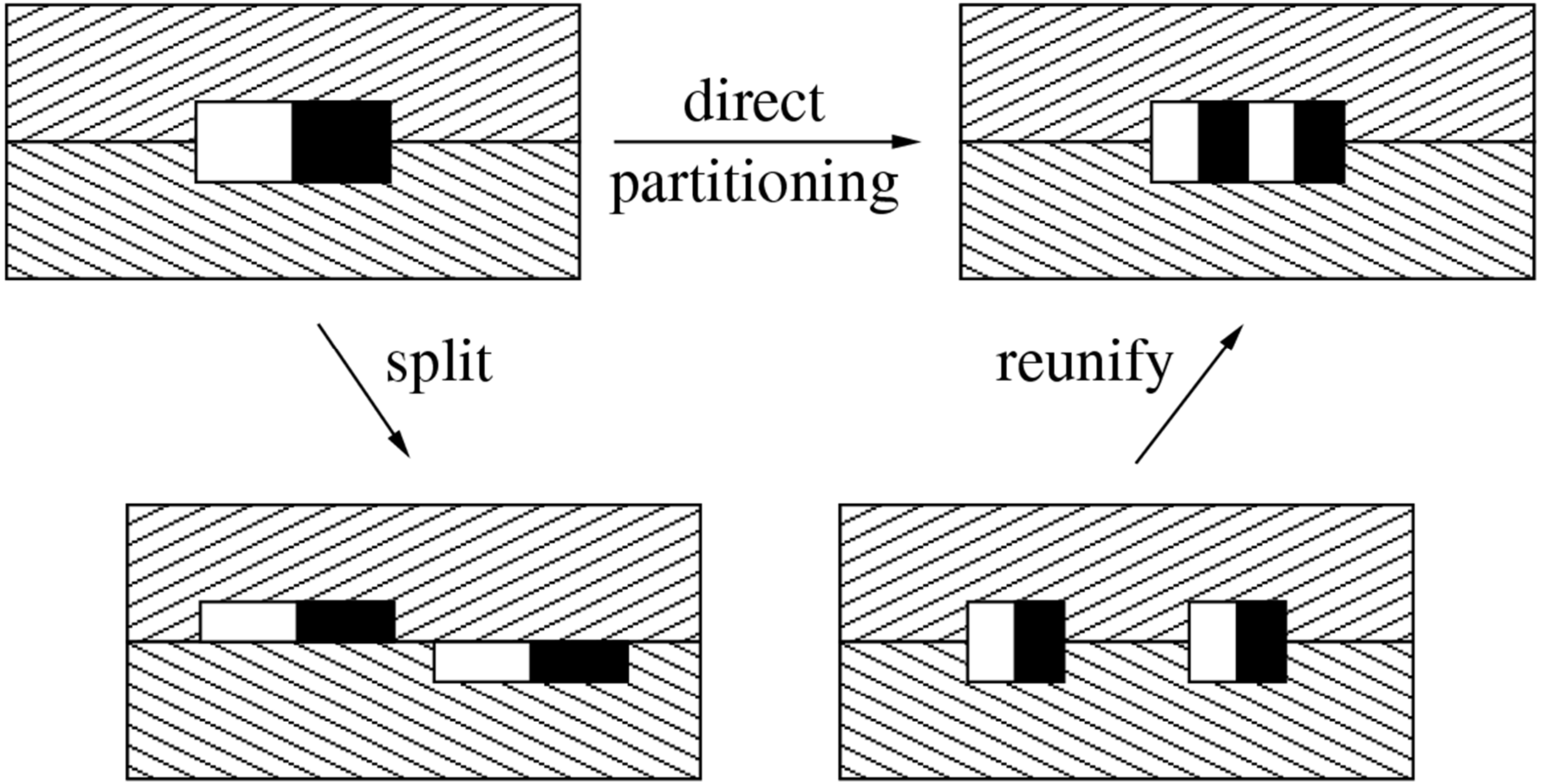


Fig. 11.5. Laminar mixing strategies. Subdivision of the flow by direct splitting generated lamellae of the same width as the channel structure. With the separation–reunification mechanism, the original geometry is generated and can thus be repeated multiple time in the same setup

11.1. Moebius Mixer

- Two vertically stacked flows
- Flow split in horizontal plane
- Each subflow rotated by 90°
- Rejoining of flows
    - Four lamellae

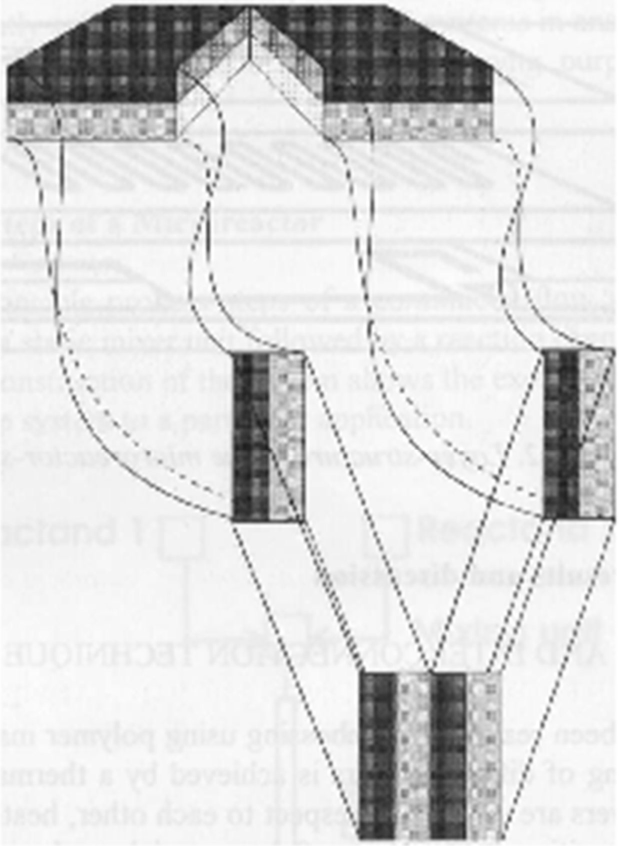


Fig. . "Möbius" principle of a static micromixer (JD: ask Roland for source, IMM?)

11.1. Mixing by Lamination of Flow

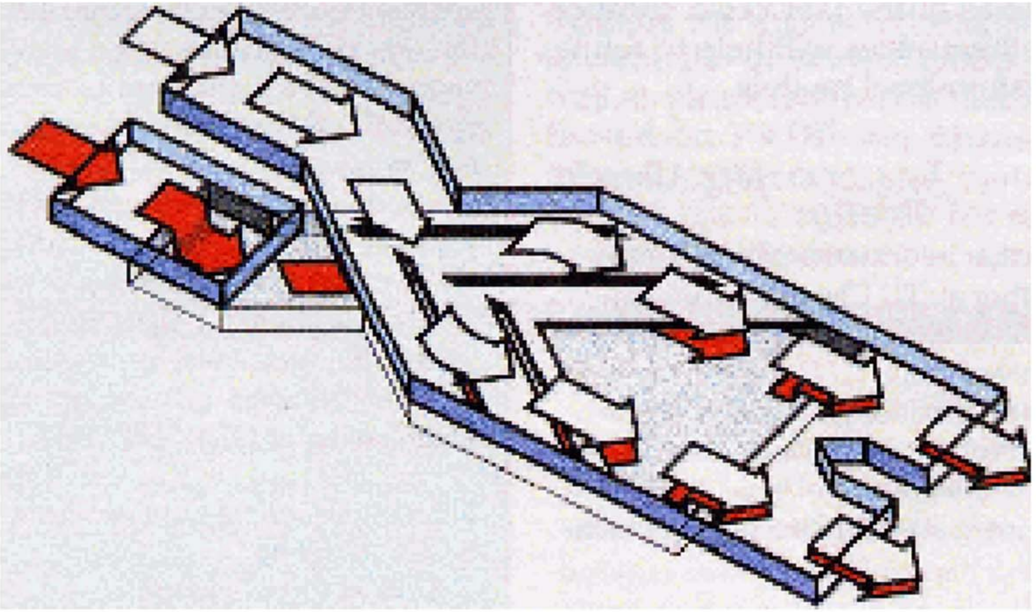


Fig. 11.10. Danfoss lamination mixer. Two broad liquid streams of small height are laminated with a large contact surface to effectuate fast diffusion. In a single-stage alignment, mixing times of 100 – 300 ms are observed, for multiple lamination in repetitive steps mixing times of a few ms are predicted

11.1. Mixing by Lamination of Flow

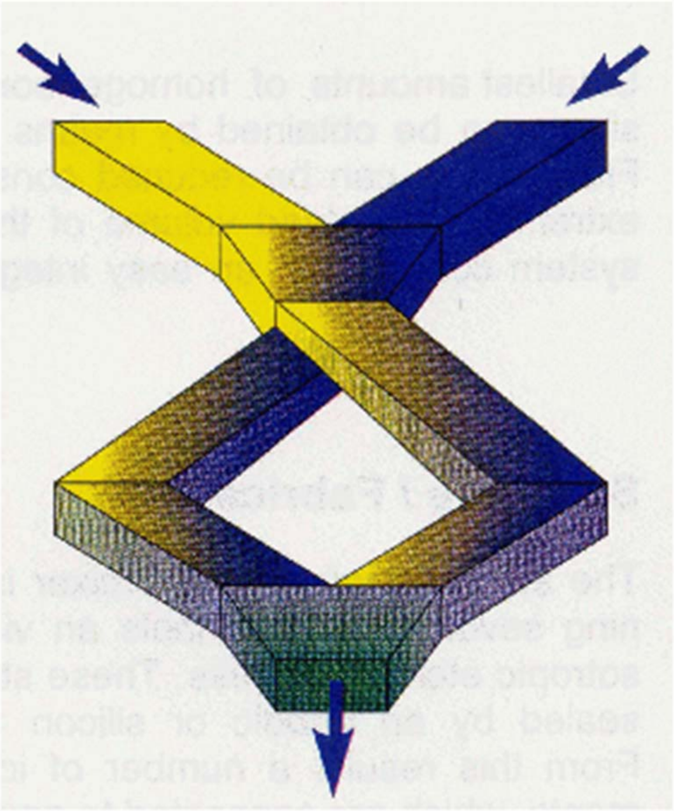


Fig. . Mixing principle developed at TU Illmenau (JD: ask Roland for details)
Illmenau00

11.1. Mixing by Lamination of Flow

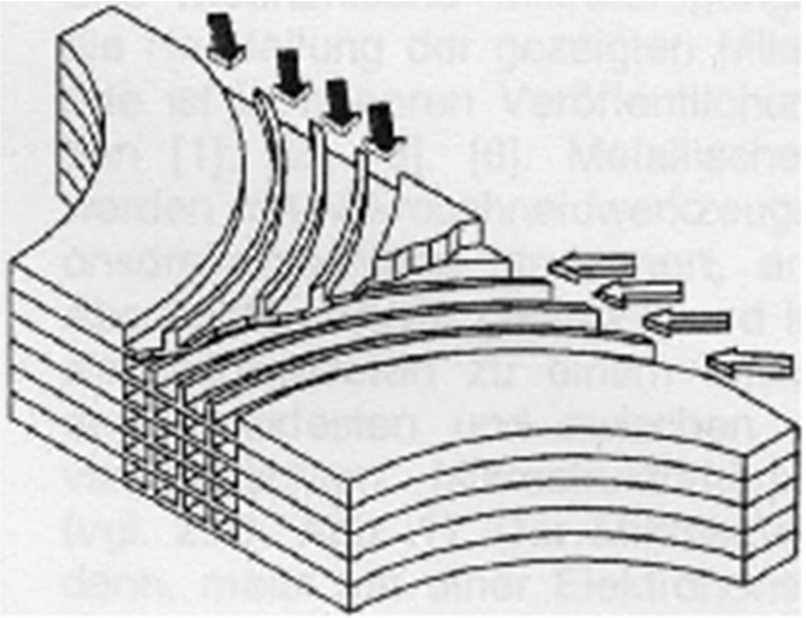


Fig. . Parallel mixer designed at FZ Karlsruhe (JD: ask Roland for details) FZK00

11.1. Mixing by Micro-Plumes

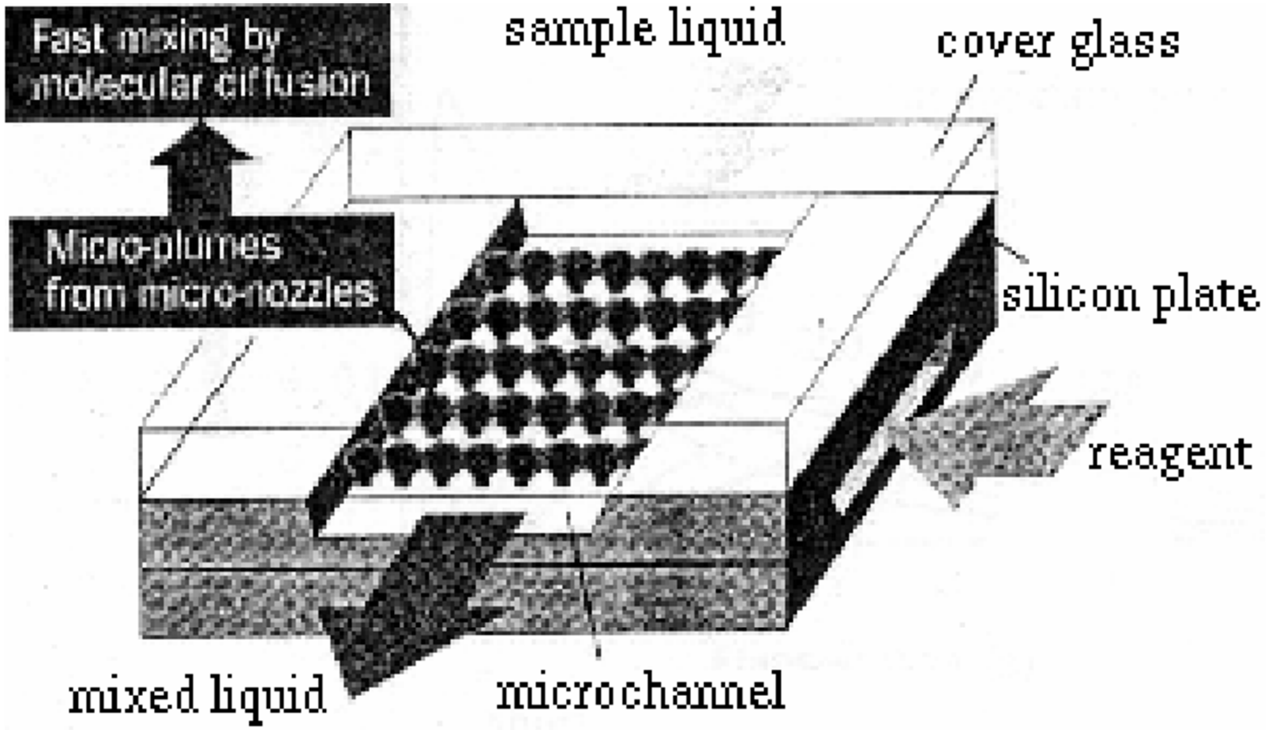


Fig. 11.12. Diffusional mixer. In a crossflow arrangement, reagent plumes enter the sample stream through micronozzles. The high surface-to-volume ratio assures rapid mixing

11.1. Mixing by Micro-Plumes

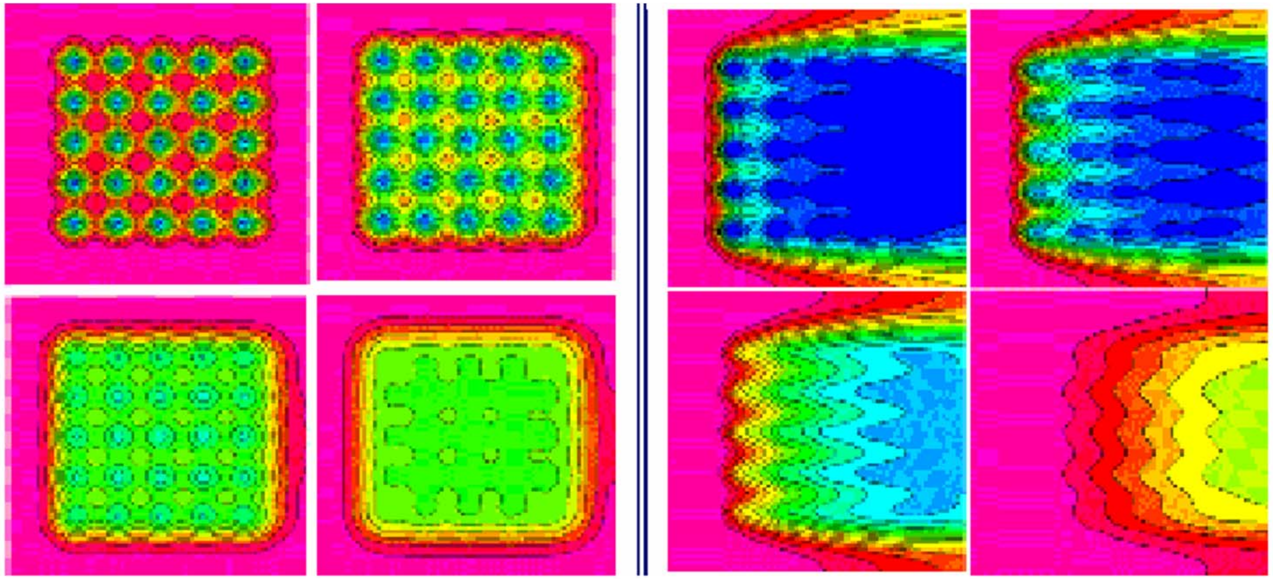


Fig. 11.13. Temporal evolution of mixing by diffusion in the alignment portrayed in Fig. ??. (left) static mixing (right) mixing with the sample liquid flowing from left to right

11.1. Low-Aspect Ratio Mixers

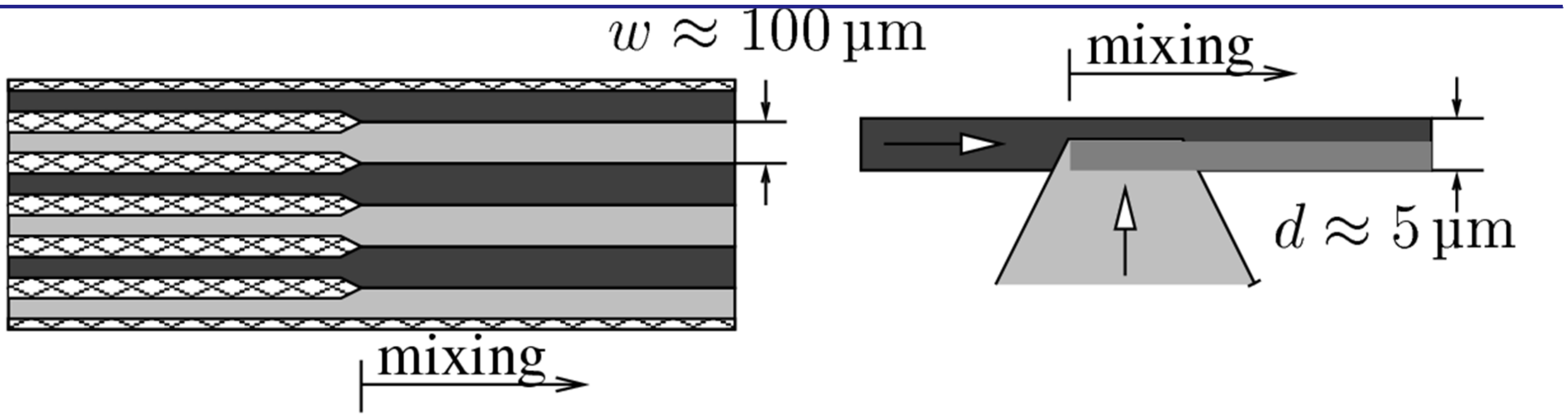


Fig. 11.3. Two mixing strategies for low-aspect-ratio mixers. The two phases can either converge with parallel streamlines in the lateral arrangement (left) or perpendicular to each other in vertical mixing (right)

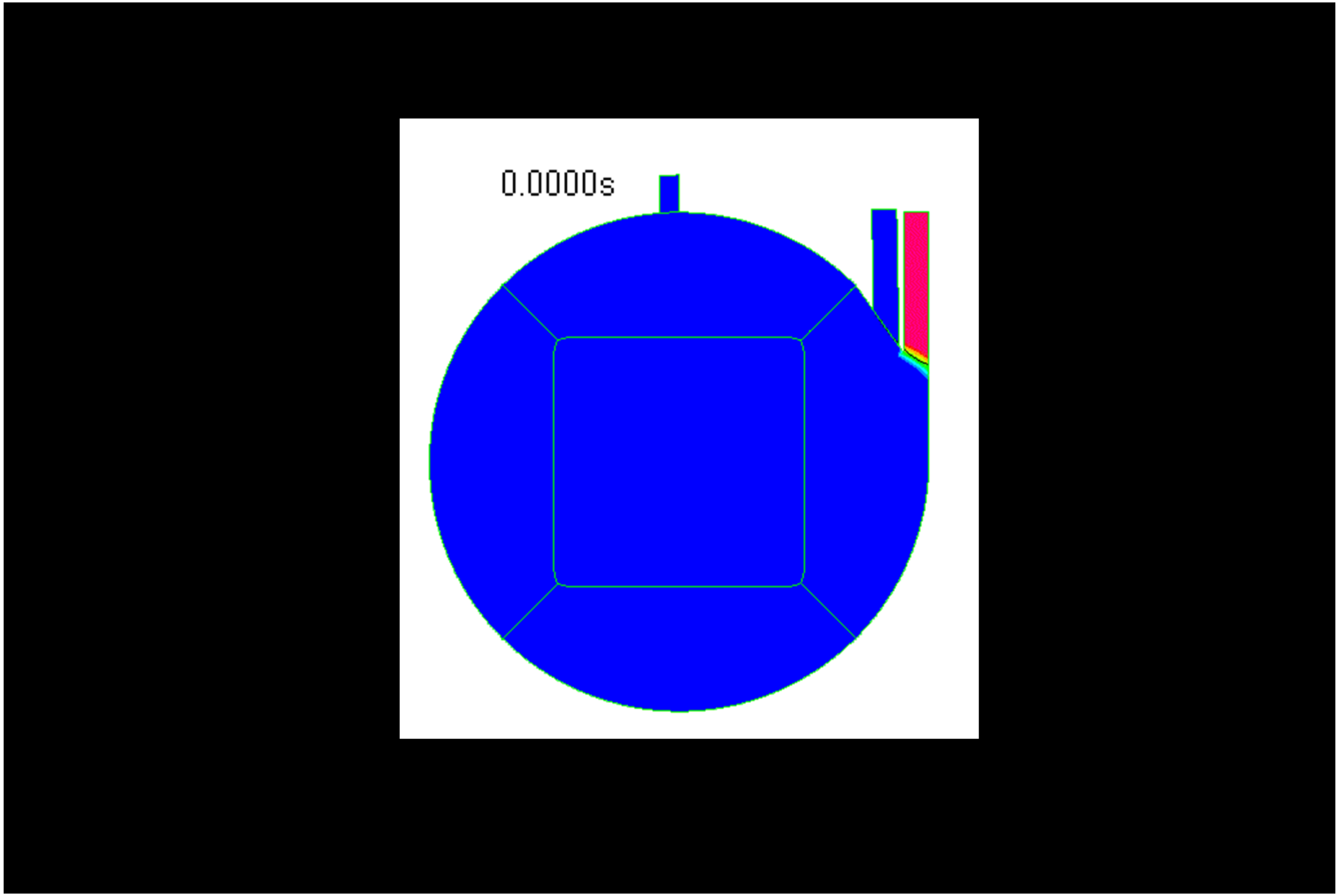
Throughput: function of aspect ratio

$$\boxed{R_{hd} \overset{\mathcal{A}\gg1}{\mapsto} \frac{8\eta l}{\varrho}\frac{1}{N\boxed{\mathcal{A}}w^4}}$$

$$I_V = \frac{\Delta p}{\varrho R_{hd}} \text{ `}=\text{' } \frac{\Delta p w^4}{8\eta l}N\boxed{\mathcal{A}}$$

$$\frac{I_V}{N\mathcal{A}} = 1.25 \times 10^{-7}\,\mathrm{l\,s^{-1}} = 7.5 \times 10^{-6}\,\mathrm{l\,min^{-1}} = 4.5 \times 10^{-4}\,\mathrm{l\,h^{-1}}$$

11.1. Example: Drum Mixer on Bio-Disk



11.1. Mixing by Hydrophobic Barriers

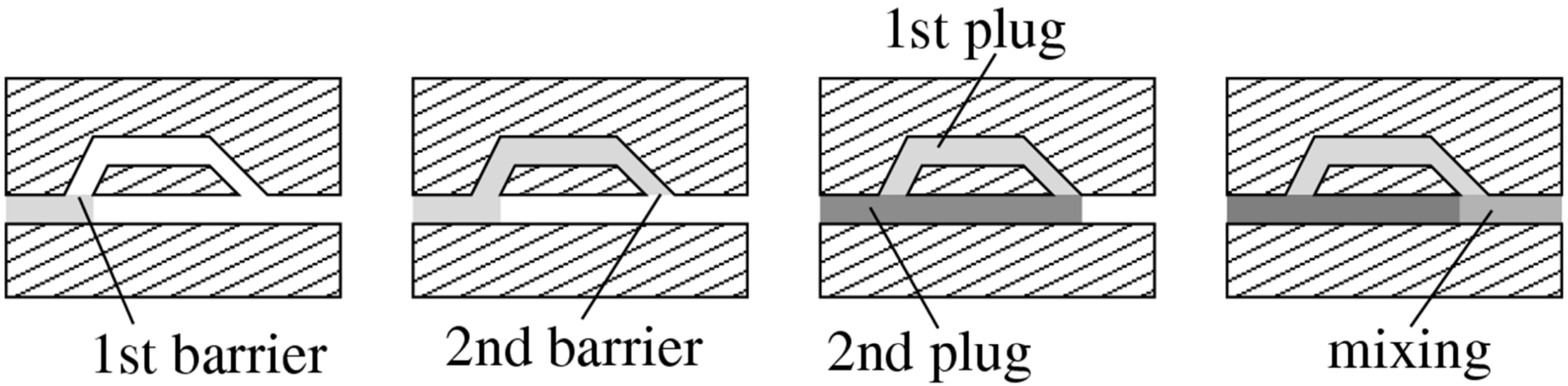


Fig. 11.14. Principle of a hydrophobic bypass mixer/diluter in Fig. **??**. A bypass branches off the main channel. Specially designed capillary breaks at each branch first divert the flow to the bypass where it stops at the end. At enhanced pressure, fluid continues in the main channel and wetting of the bypass meniscus opens the second capillary break to open

11.1. Mixing by Hydrophobic Barriers

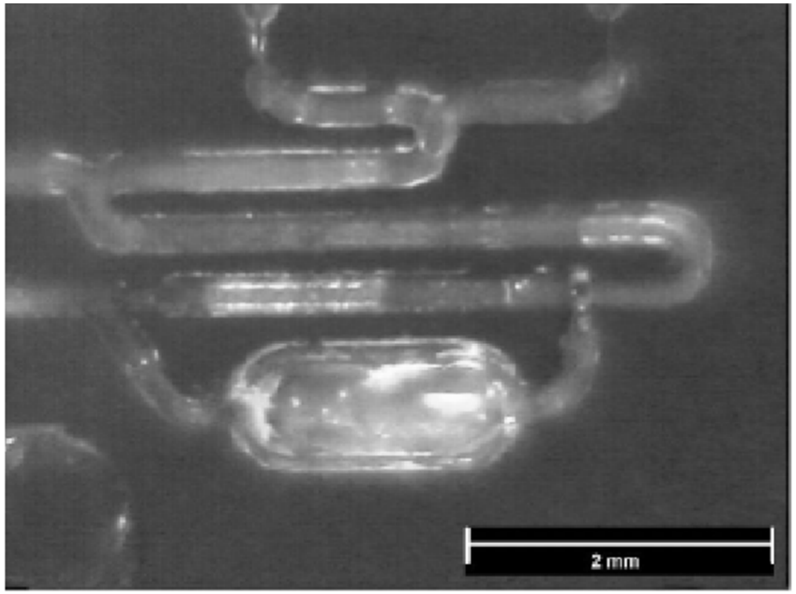


Fig. 11.15. Mixer and diluter based on hydrophobic restrictions

11.1. Coanda-Effect Mixer

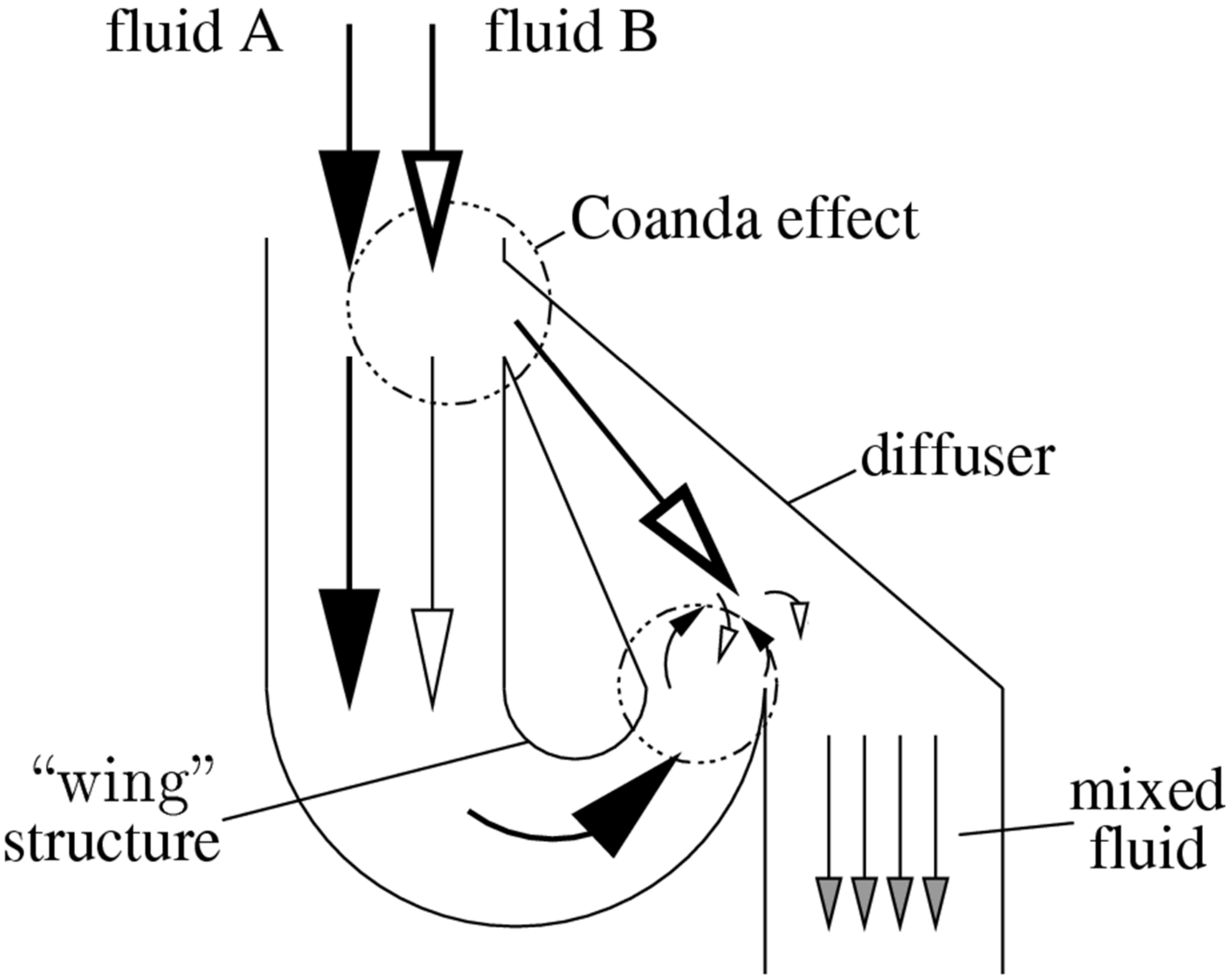
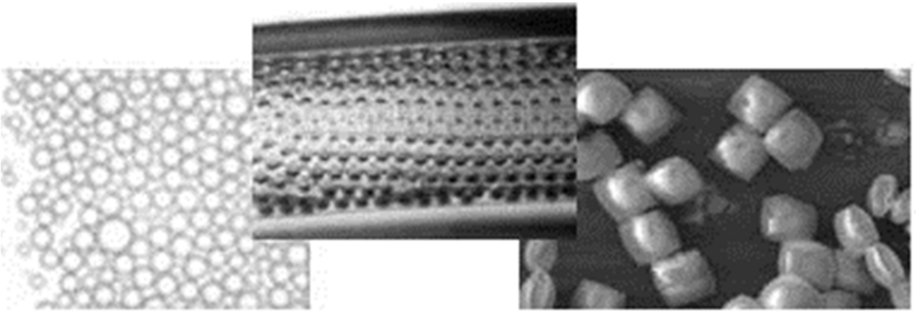


Fig. 11.16. In-plane Coanda mixer

11.1. Dispersions of Immiscible Fluids



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- Liquid / liquid dispersions including emulsions
- Gas / liquid dispersions including foams
- Suspensions of nano-scale particles

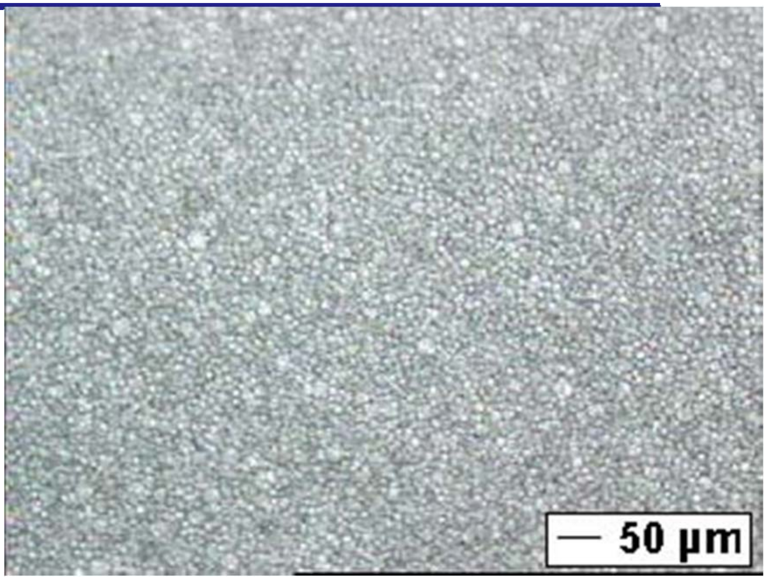
11.1. Mixers for Liquid-Liquid Dispersion

- **Liquid-liquid dispersion including emulsions**

- **Production of small, regularly sized droplets**

- **Droplets of narrow size distribution**

- **Droplets of narrow size distribution**
  - 4 to 50 µm
  - Dependent on operating conditions



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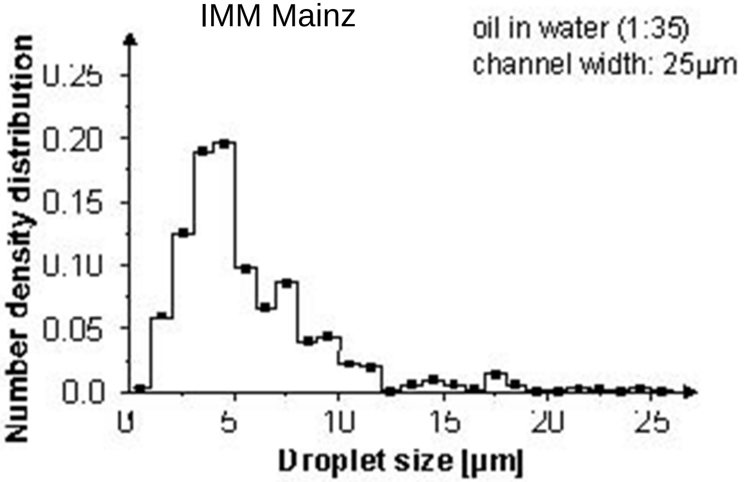
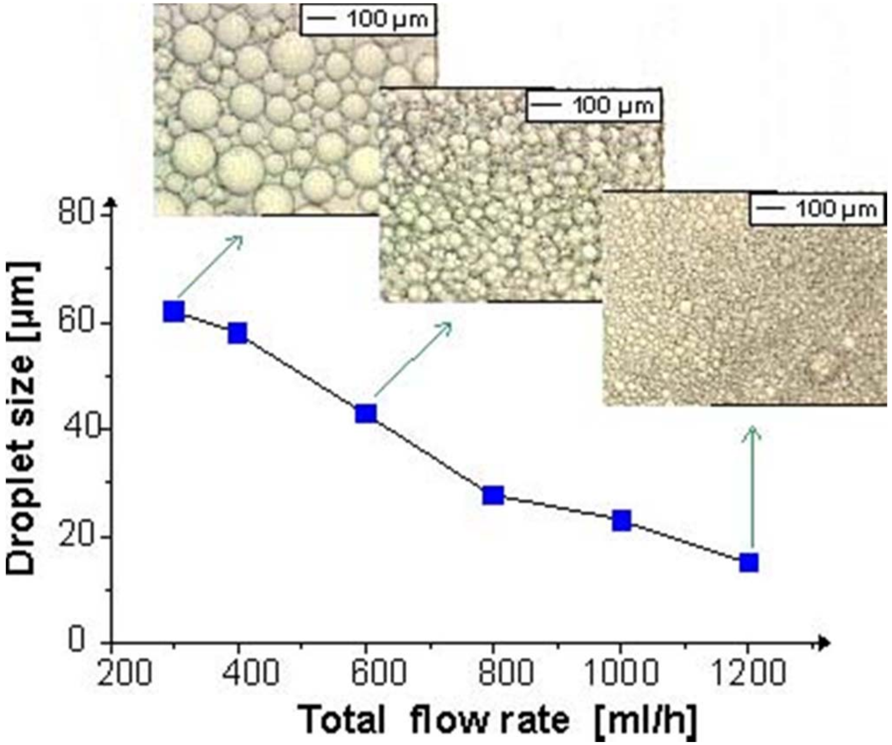


11.1. Mixers for Liquid-Liquid Dispersion

- Critical parameters
  - **Smaller droplets generated at higher volume flows**
  - Smaller droplets generated at higher ratios of flow rates
  - Smaller droplets generated using mixing elements at smaller channel width



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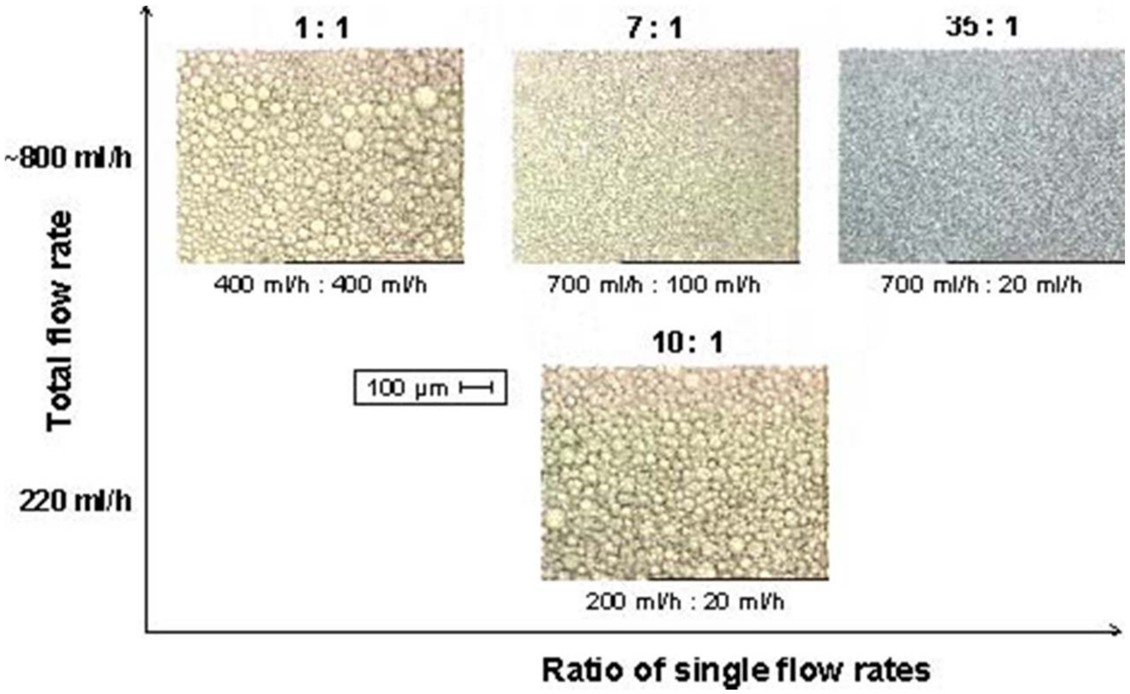
11.1. Mixers for Liquid-Liquid Dispersion

- Critical parameters
  - Smaller droplets generated at higher volume flows
  - **Smaller droplets generated at higher ratios of flow rates**
  - Smaller droplets generated using mixing elements at smaller channel width



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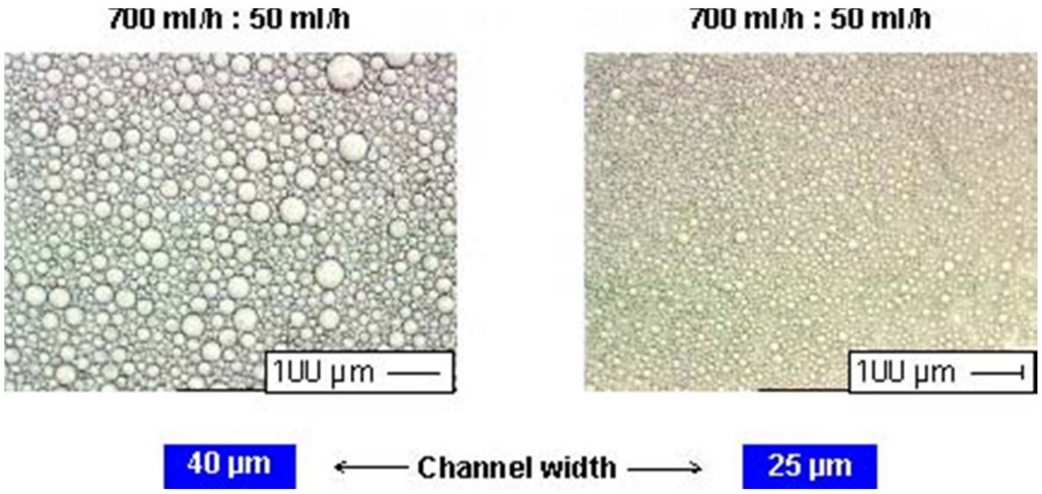
11.1. Mixers for Liquid-Liquid Dispersion

- Critical parameters
  - Smaller droplets are generated at higher volume flows
  - Smaller droplets are generated at higher ratios of flow rates
  - **Smaller droplets generated using mixing elements at smaller channel width**



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11.1. Mixers for Gas-Liquid Dispersions

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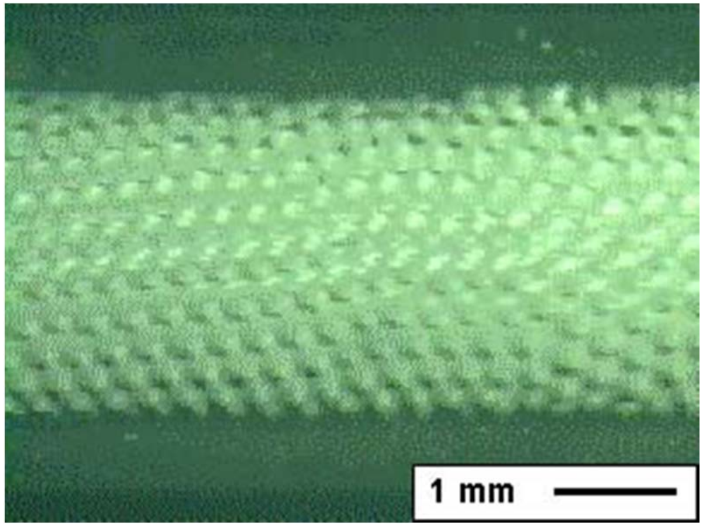
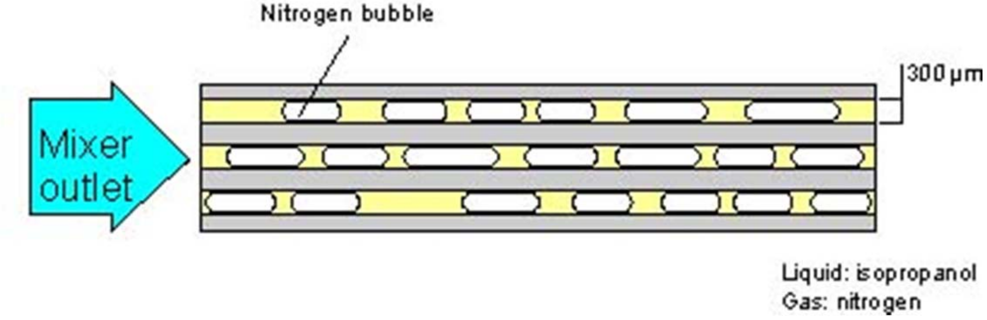


- Production of small, regularly sized bubbles

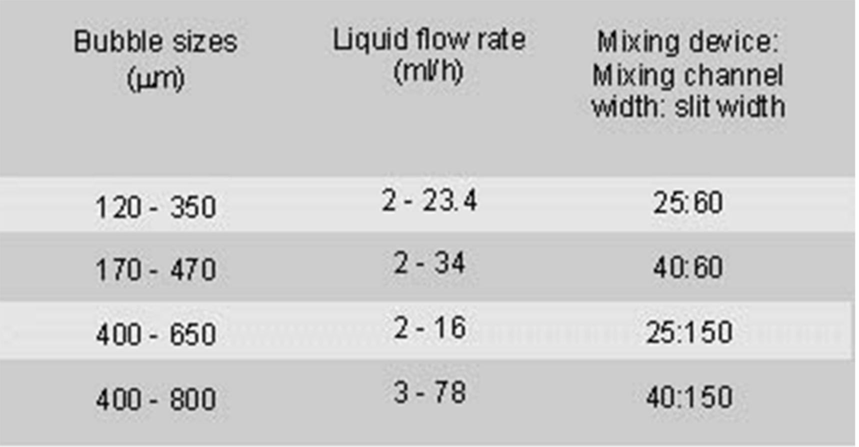
- Under certain operating conditions, production of highly regular bubble trains

- Formation of segmented (slug) and annular flow patterns, when combined with miniaturized residence time channels



11.1. Mixers for Gas-Liquid Dispersions

- **Bubble sizes in model and real systems:**
  - **Diameter**
    - **50 to 500 µm**
  - **Ratio of bubble length to diameter**
    - **1 to 4**
  - **Average bubble size deviation**
    - **Typically 50 µm**



Bubble sizes (µm)	Liquid flow rate (ml/h)	Mixing device: Mixing channel width: slit width
120 - 350	2 - 23.4	25:60
170 - 470	2 - 34	40:60
400 - 650	2 - 16	25:150
400 - 800	3 - 78	40:150

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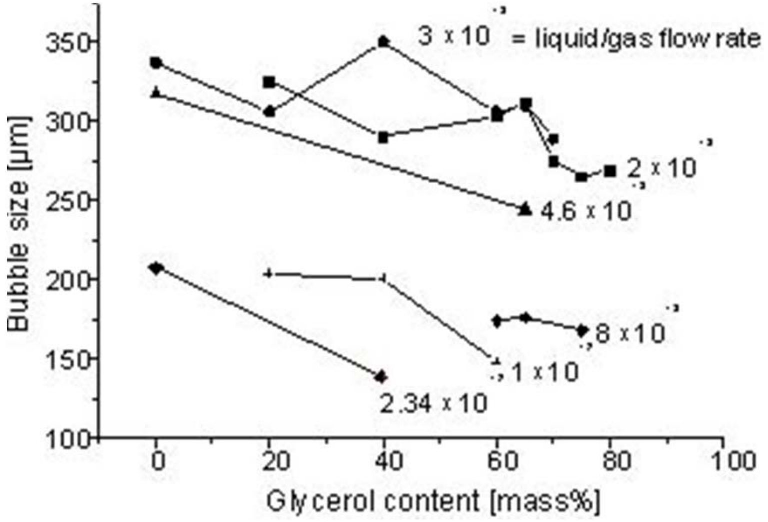
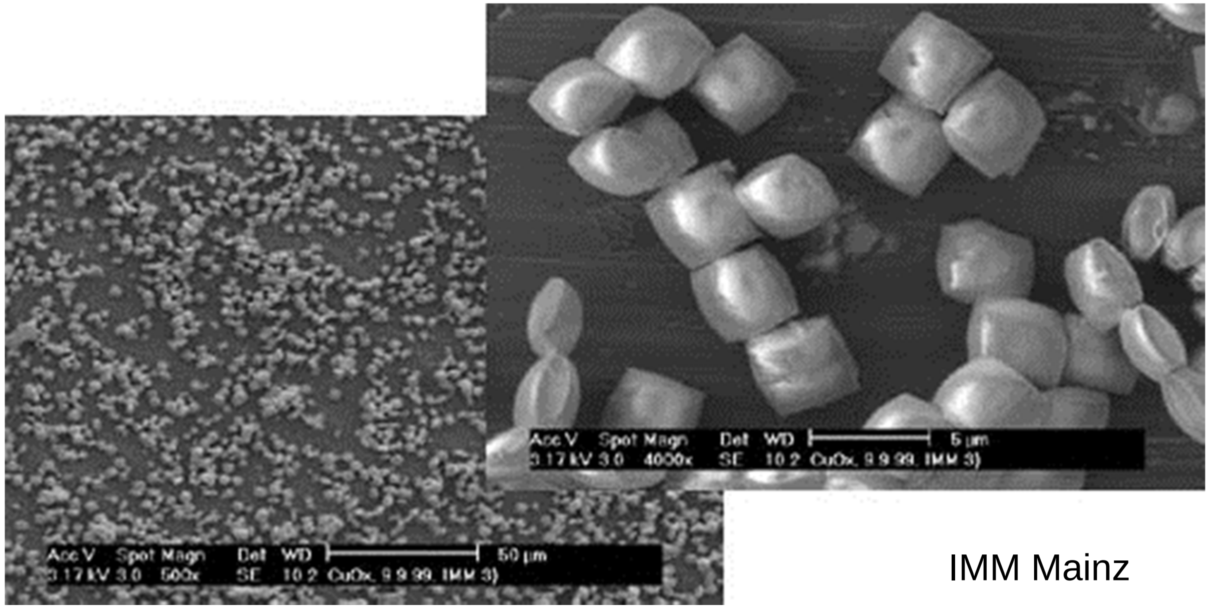


11.1. Mixers for Suspension



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- Production of small micro-scale particles of uniform size
- Model system: precipitation of copper oxalate
  - Particle size: 5 µm

11.1. Active Mixers: Ultrasonic

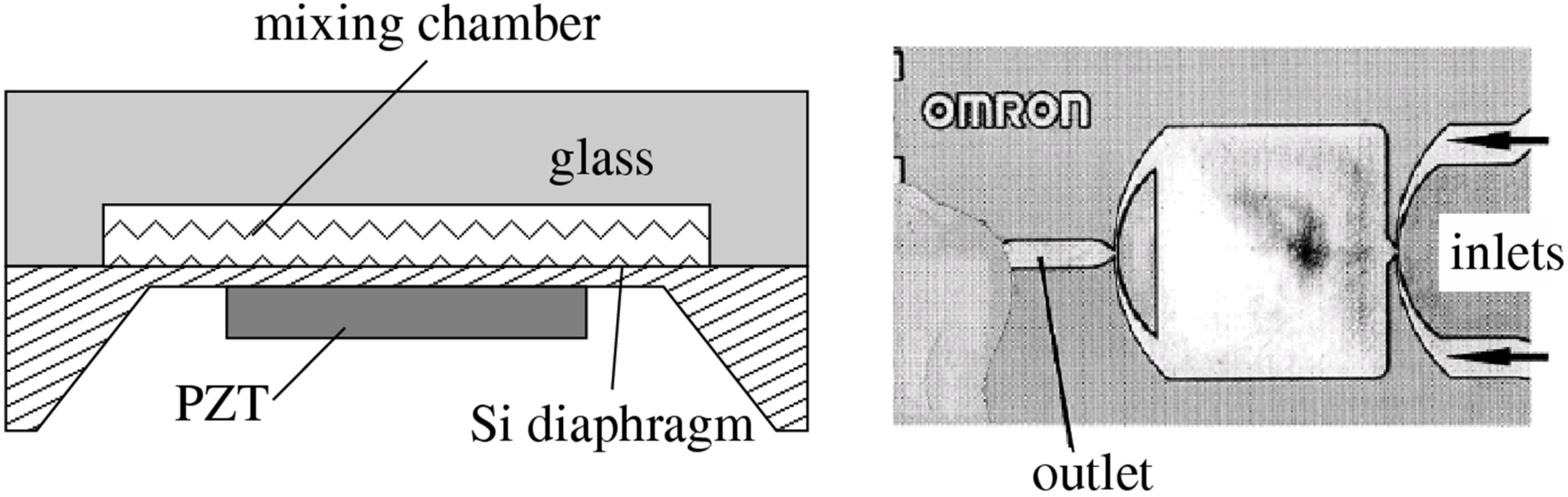


Fig. 11.17. Ultrasonic micromixer. The mixing chamber is structured into a glass substrate which is covered by a PZT-actuated silicon diaphragm

11.1. Active Mixers: Chaotic Advection

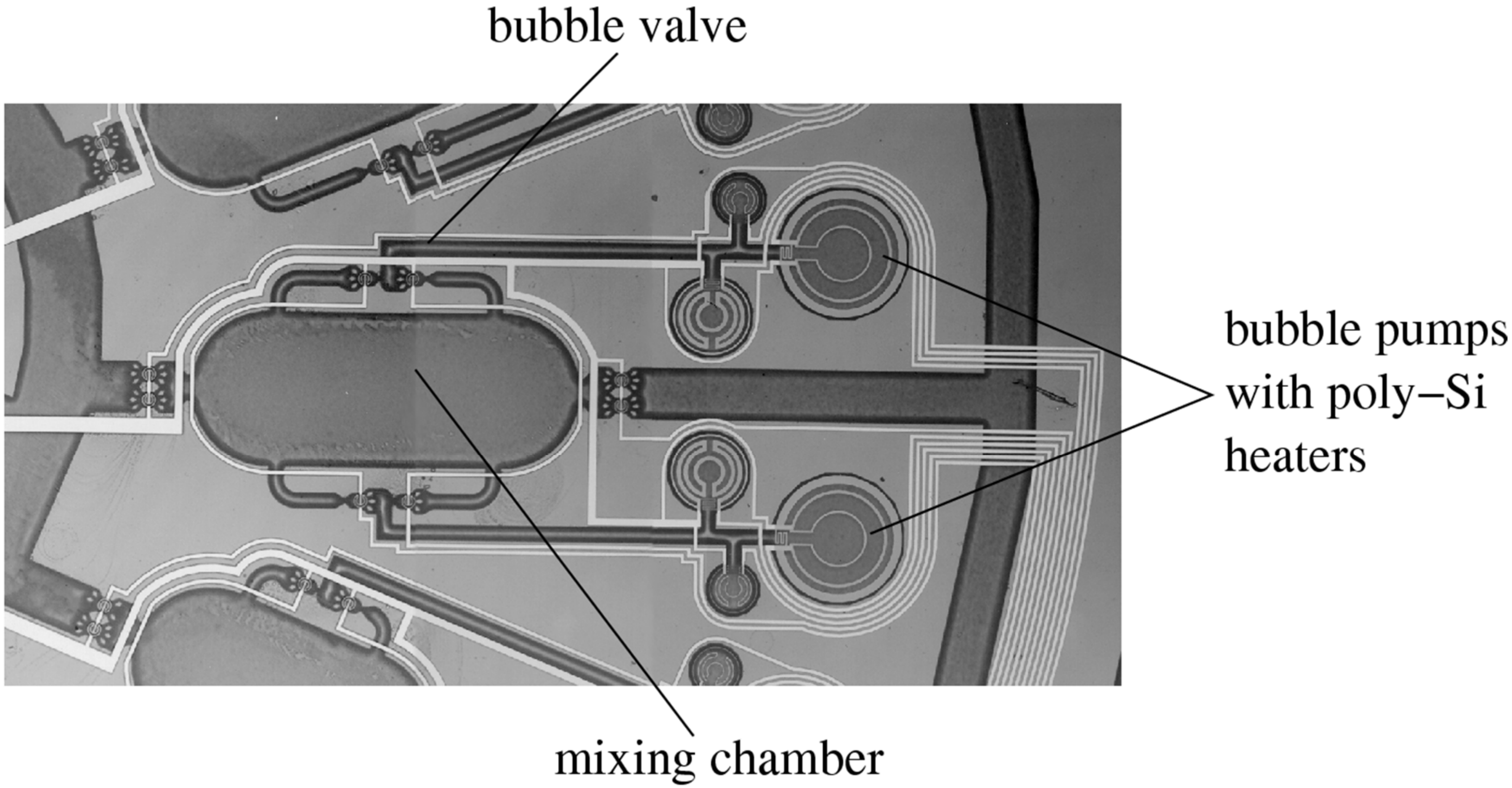


Fig. 11.18. Mixing by chaotic advection in a 2-dimensional source-sink arrangement

11. Microreactors

1. Micromixers
2. **Heat Exchangers**
3. Chemical Microreactors
4. Splitting of Flow
5. Fuel-Based Power Supplies

11.2. Physics of Heat Exchange

- Heat transmission

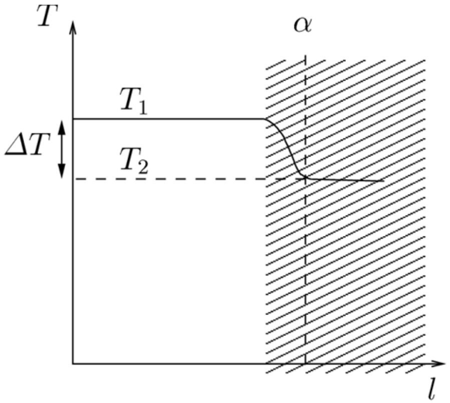


Fig. 0.1. Typical temperature curve for heat transmission between temperatures T_1 and T_2

$$j_Q = h_Q \boxed{\Delta T}$$

$$P = \alpha \boxed{A} \Delta T$$

11.2. Physics of Heat Exchange

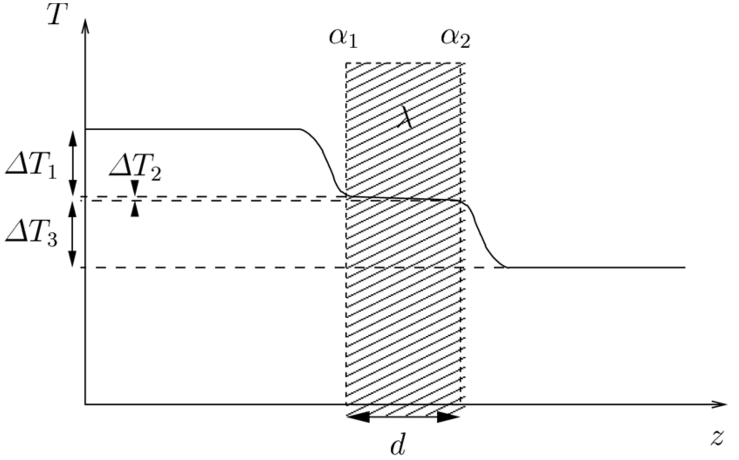


Fig. 0.1. Transition of heat between two vessels at T_1 and T_3 separated by a wall

- Heat transition

$$P = k_Q \boxed{A \Delta T}$$

$$\frac{1}{k_Q} = \frac{1}{\alpha_1} + \frac{\boxed{d}}{\lambda} + \frac{1}{\alpha_2}$$

11.2. Convection and Heat Diffusion

- Convection
  - ➢ Collective transport of macroscopic volumes
    - Buoyancy
    - Pumping

- Peclet number
  - ➢ Ratio convective / diffusive particle transport

$$Pe = ReSc = \frac{vl}{D} = 4\left(\frac{l}{l_D}\right)^2$$

11.2. Convection and Heat Diffusion

- Nußelt number
  - Ratio convective / diffusive heat transport
  - Boundary region: wall / fluid
  - Turbulences enhance heat transport

$$Nu = \frac{Q_{\mathrm{conv}}}{Q_{\mathrm{diff}}}$$

- Note
  - Deviations from macro-theory
  - Turbulence formation in wall layers

$$Nu = \frac{h_Q \boxed{l_{\mathrm{char}}}}{\lambda}$$

11.2. Physics of Heat Exchange

- Newton‘s law of cooling

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{h_Q}{C_m}\boxed{\frac{A}{m}}\Delta T$$

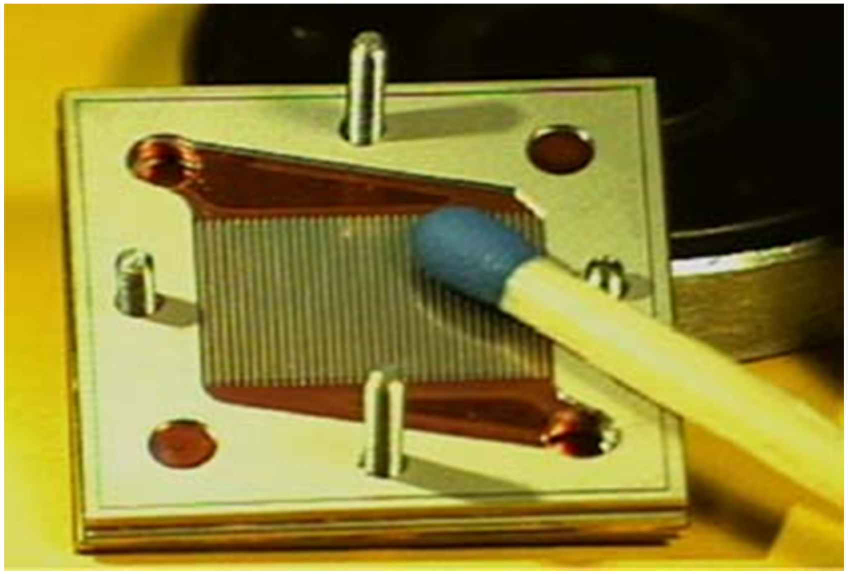
  - ➢ Temperature decay

$$\Delta T = \Delta T_0 \mathrm{e}^{-t/\boxed{\tau}}$$

  - ➢ Characteristic time

$$\tau = \frac{C_m}{h_Q}\boxed{\frac{m}{A}}$$

11.2. Heat Exchangers



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- Mixing and reaction devices often connected to heat transfer systems
- Essential for effective heat management of reaction processes

11.2. Flow Schemes

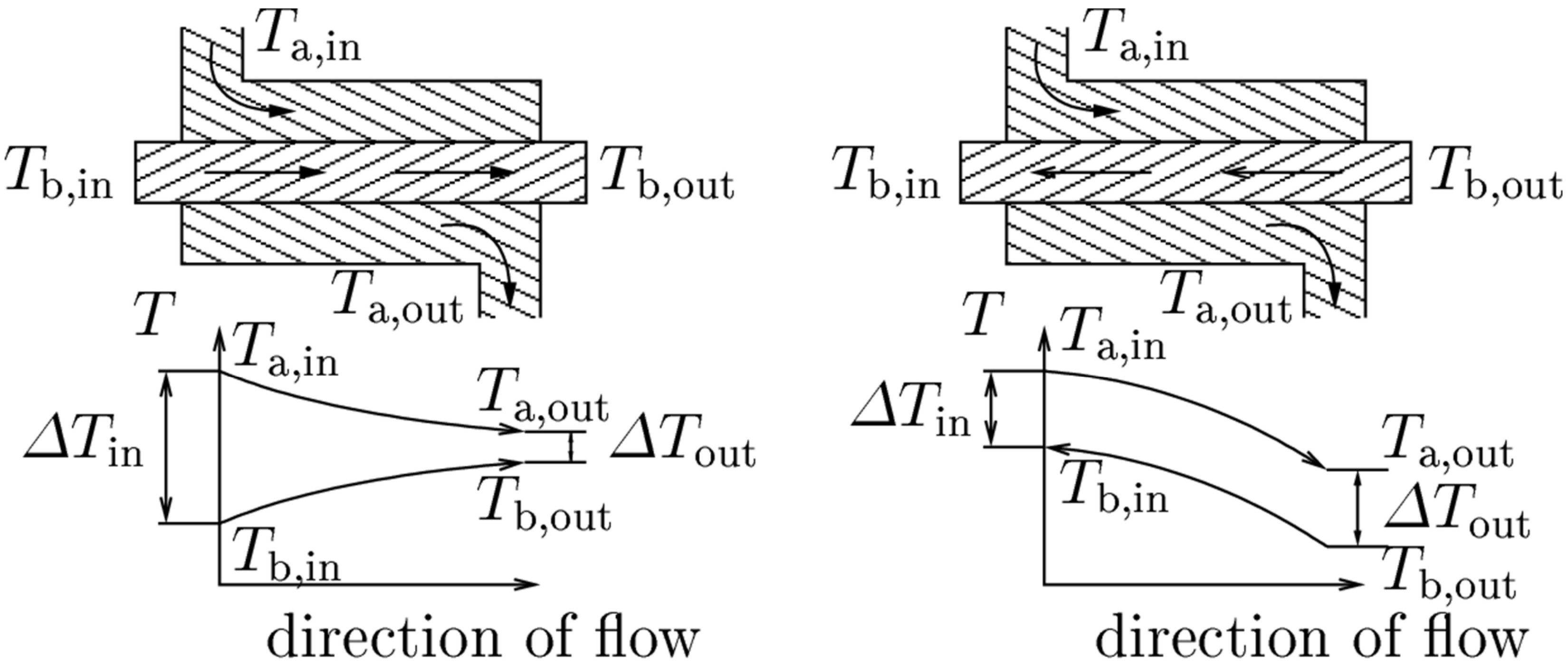

Fig. 11.24. Cocurrent and counter-current flow heat exchangers

11.2. Co-Current Heat Exchanger

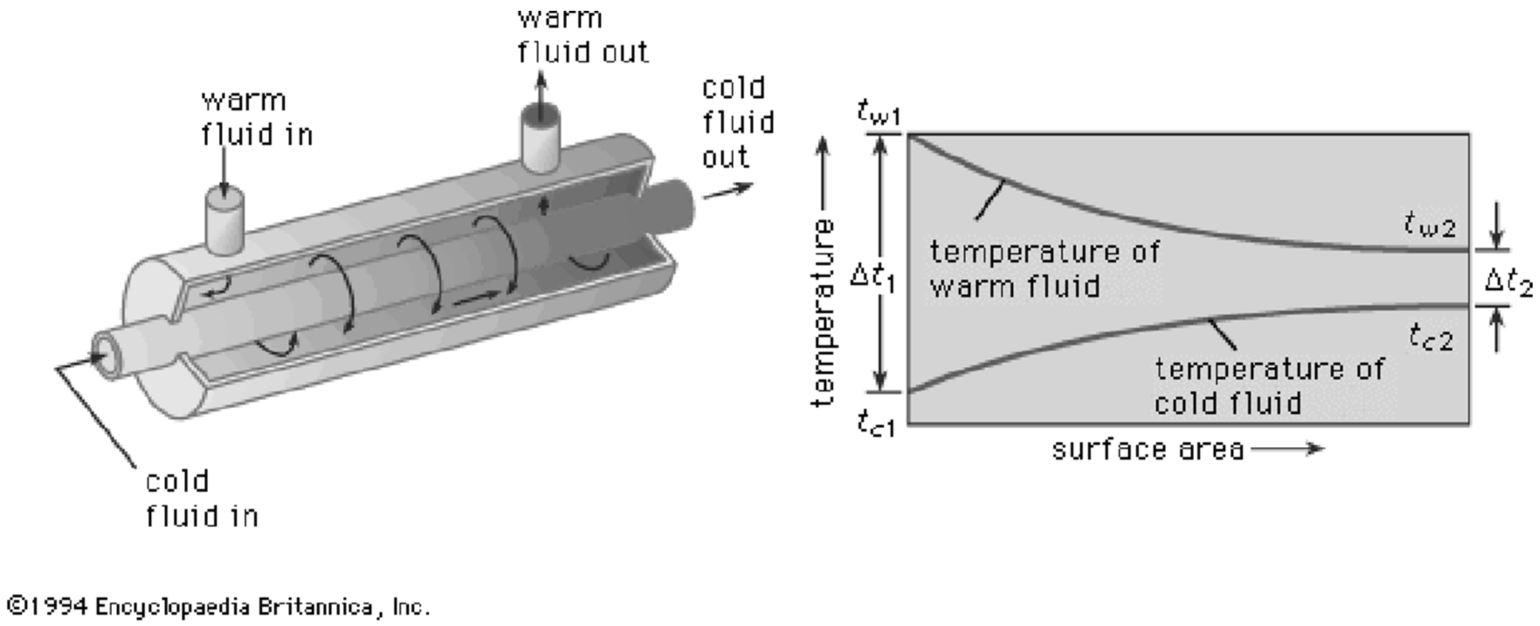

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Fig. 11.25. Principle of a co-current heat exchanger

11.2. Counter-Current Heat Exchanger

- Power of heat transfer

$$\boxed{P = \frac{\mathrm{d}Q}{\mathrm{d}t} = h_{\mathrm{trans}} A \Delta T}$$

  - With

$$\Delta T = \frac{\Delta T_{\mathrm{in}} - \Delta T_{\mathrm{out}}}{\ln(\Delta T_{\mathrm{in}} / \Delta T_{\mathrm{out}})}$$

- Effective surface (cross section)
  - Required to establish given power *P*
  - Measure for efficiency

$$\boxed{A_{\mathrm{counter}} < A_{\mathrm{cross}} < A_{\mathrm{parallel}}}$$

11.2. Crossed-Flow Heat Exchanger

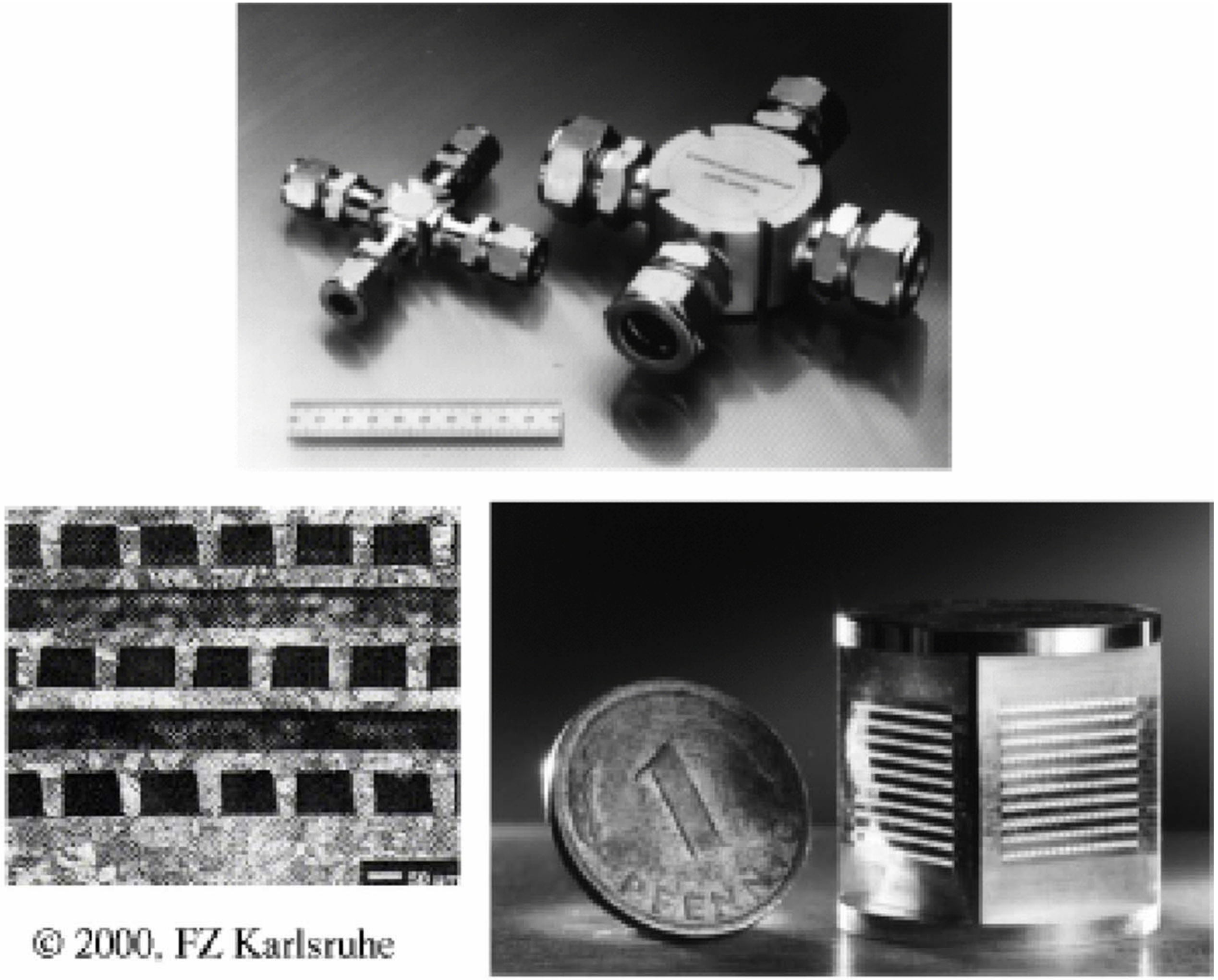

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Fig. 11.26. "Crossed channel" heat exchanger developed at FZK

11. Microreactors

1. Micromixers
2. Heat Exchangers
3. **Chemical Microreactors**
4. Splitting of Flow
5. Fuel-Based Power Supplies

11.3. Introduction

- Production of Chemicals
  - ➢ Contacting of phases
    - Liquid – liquid
    - Gas - gas
    - Gas – liquid
    - Solid – gas
    - Solid – liquid
  - ➢ Contact on molecular level to enable reactions
  - ➢ Controlled mixing of phases
    - E.g. by microfabricated nozzles
- Important parameters
  - Fast mixing
  - Uniform heat distribution

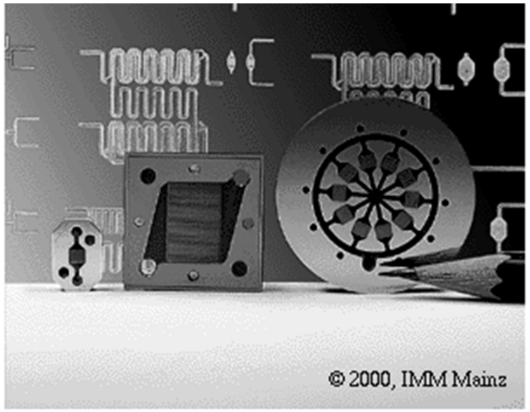

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Fig. . As an example, basic components for microreaction systems in photosensitive glass (FOTURAN) are shown above. Due to its chemical resistance and its biocompatibility glass is an important material for biotechnological applications Ehrfeld98,Lowe99,Ehrfeld00,Ehrfeld00a,IMM00.

11.3. Chemical Microreactors

- Objectives of miniaturization
  - Process intensification
    - Running processes at more aggressive conditions, e.g. higher temperatures
  - Automated gathering of information
    - Generation of comprehensive libraries
  - High-quality chemicals
    - Control of heat management
    - Uniform heat distributions

Fig. . Electrochemical microreactor ELMI IMM00

11.3. Gas-Liquid Reactions

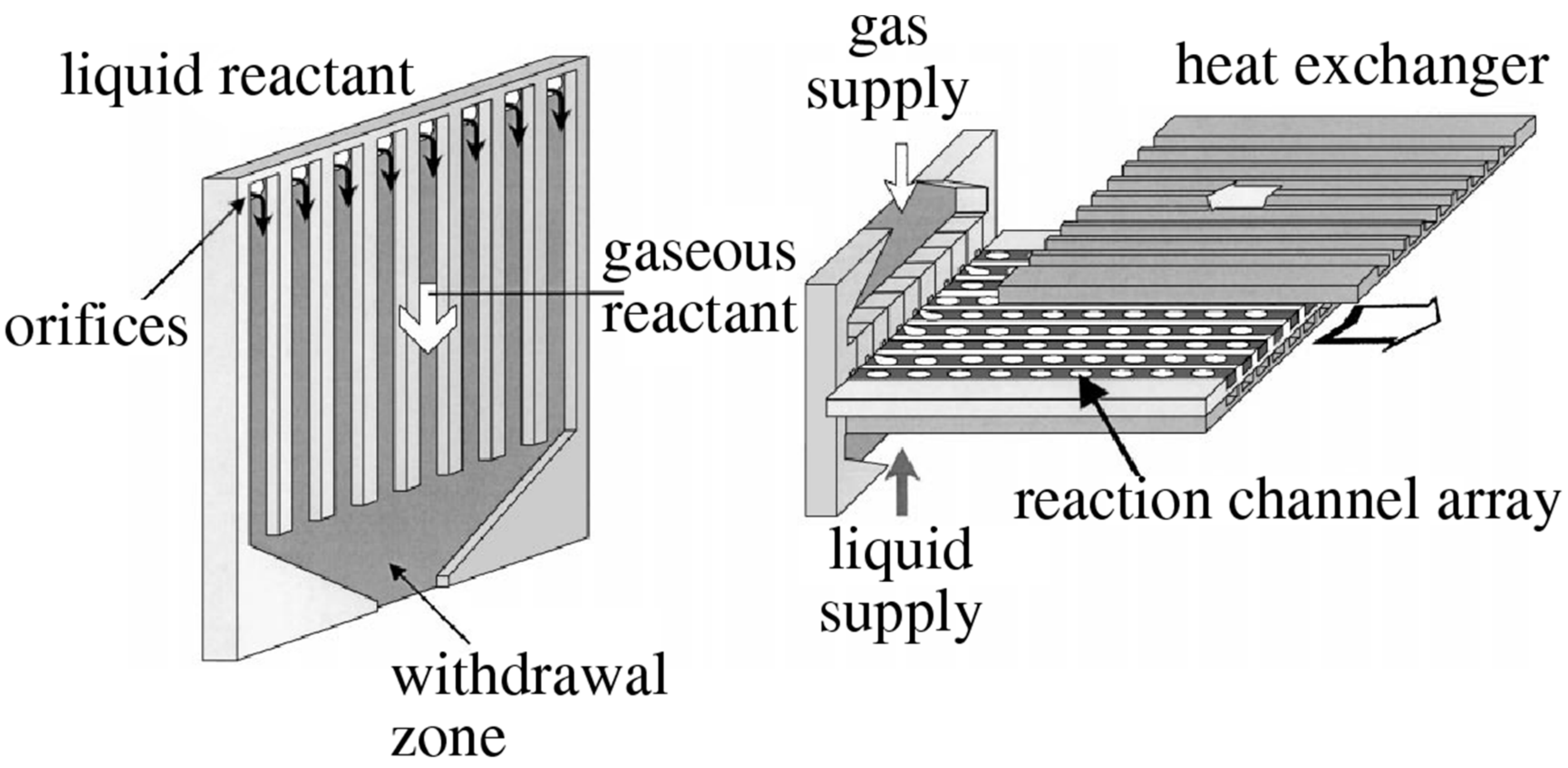

Fig. 11.33. Gas-liquid contactors. In a falling film microreactor (FFMR, left), a liquid is issued through the orifices into an array of channels engraved onto a platelet. Driven downward by gravitation, the resident gas contacts the falling liquid film. The micro bubble column (MBC, right) uses a segmented flow pattern (Fig. **??**) to contact the two phases

11.3. Gas-Liquid Reactions

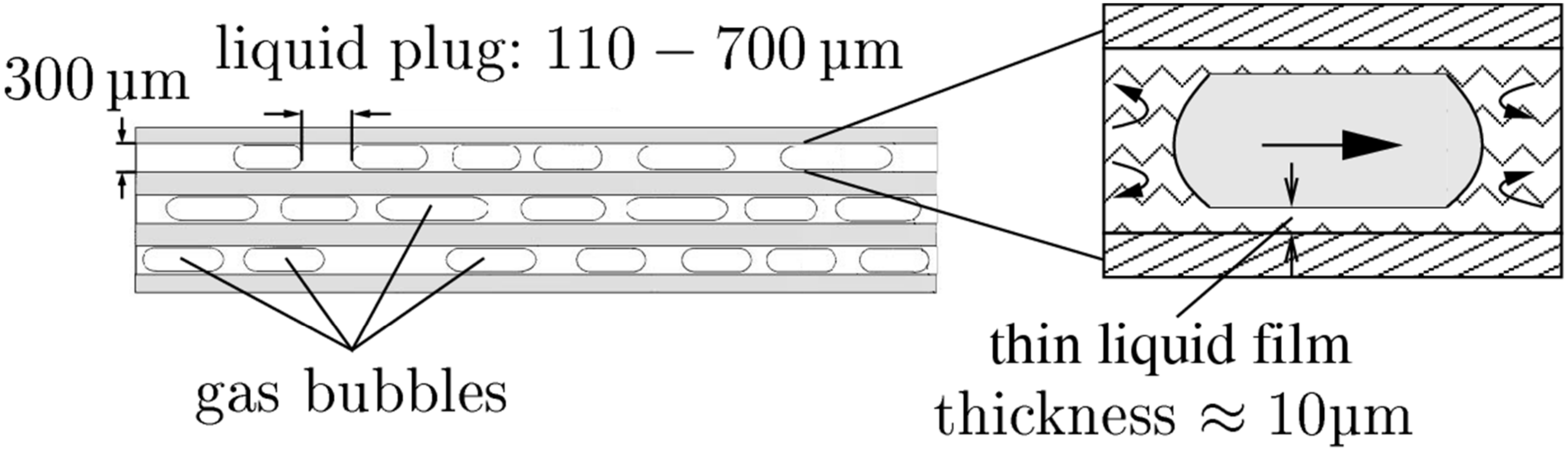

Fig. 11.34. Segmented flow pattern in a micro-bubble column (MBC). Trains of gas bubbles are interspersed by liquid plugs. The two-phase laminar flow pattern displays convection in radial direction similar to the turbulent regime

11.3. Catalytic Gas Reactor

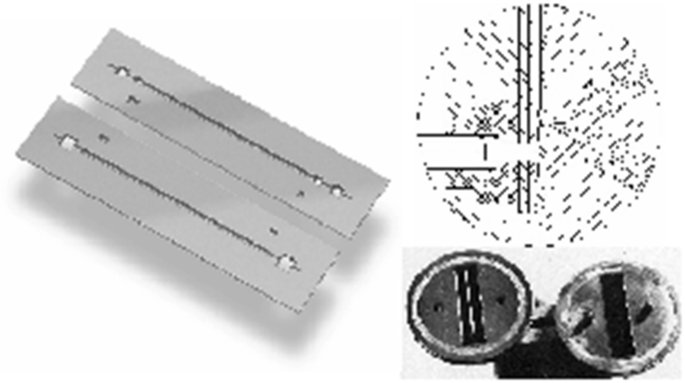

Fig. . Microreactor for catalytic gas reaction developed at HSG–IMIT Veser99,Veser99a,HSG-IMIT00

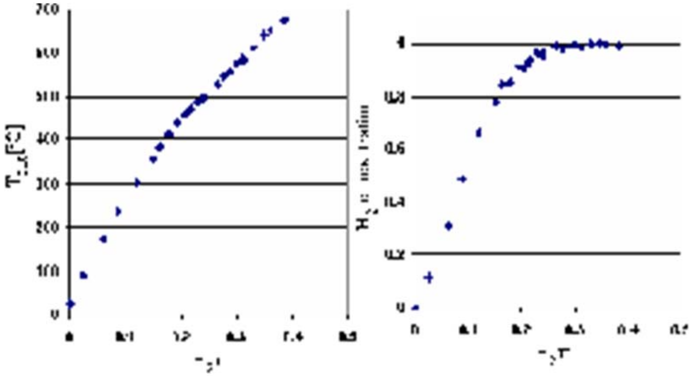

Fig. . Performance of the gas reactor with its output temperature (left) and fraction of H_2O conversion (right) Veser99,Veser99a,HSG-IMIT00 (JD: ask Roland on units "splm" on x-axis)

11. Microreactors

1. Micromixers
2. Heat Exchangers
3. Chemical Microreactors
4. **Splitting of Flow**
5. Fuel-Based Power Supplies

11.4. Throughput

- Usually pressure-driven flow (PDF)
  - EO-pumping strongly depends on
    - Chemical to be transported
    - Interaction between surface and liquid
    - No universal transport mechanisms
  - Law of Hagen-Poisseuille
    - $I_V \sim A^2$

$$I_V = \frac{\pi}{8\eta} \frac{\Delta p}{l} \boxed{r_0^4}$$

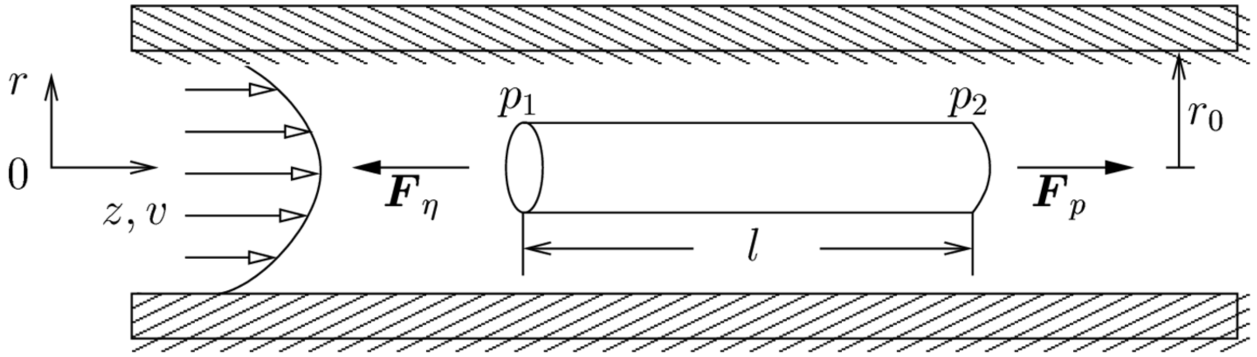

Fig. 0.1. Laminar flow through tube with circular cross section ($F_\eta = F_p$). The auxiliary cylinder is introduced for deriving the analytical solution of the flow profile $v(r)$

11.4. Throughput

- Numbering up
  - Throughput $I_{V,0}$ given
  - N channels
  - Channel radius r
  - $I_{V,0} \sim I_V(r)\, N^2$

$$I_V = \frac{\pi}{8\eta}\frac{\Delta p}{l}\boxed{r_0^4}$$

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11.4. Throughput: Flow Resistance

- Flow resistance
  - Single channel

$$R_{\mathrm{hd}} = \frac{\Delta p}{I_m} \overset{\mathrm{tube}}{=} C_{\mathrm{nc}} \frac{\eta l}{\varrho A^2}$$

  - *N* channels in parallel

$$R_{\mathrm{hd},N} = \frac{R'_{\mathrm{hd}}}{N} = C_{\mathrm{nc}} N \frac{\eta l'}{\varrho A^2}$$

- Ratio of flow resistances

$$\frac{R_{\mathrm{hd}}}{R_{\mathrm{hd},N}} = \frac{l}{l' \boxed{N}}$$

- Throughput

$$\frac{I_m}{I_{m,N}} = \frac{\Delta p R_{\mathrm{hd},N}}{\Delta p' R_{\mathrm{hd}}} = \frac{\Delta p \boxed{N}}{l} \frac{l'}{\Delta p'}$$

11.4. Velocity and Residence Time

- Velocity profile

$$\Delta v_z = v_{\max} - v_z(r)\big|_{r=r_0} = v_{\max} = \frac{\Delta p A}{8\pi\eta l}$$

- Ratio of velocities

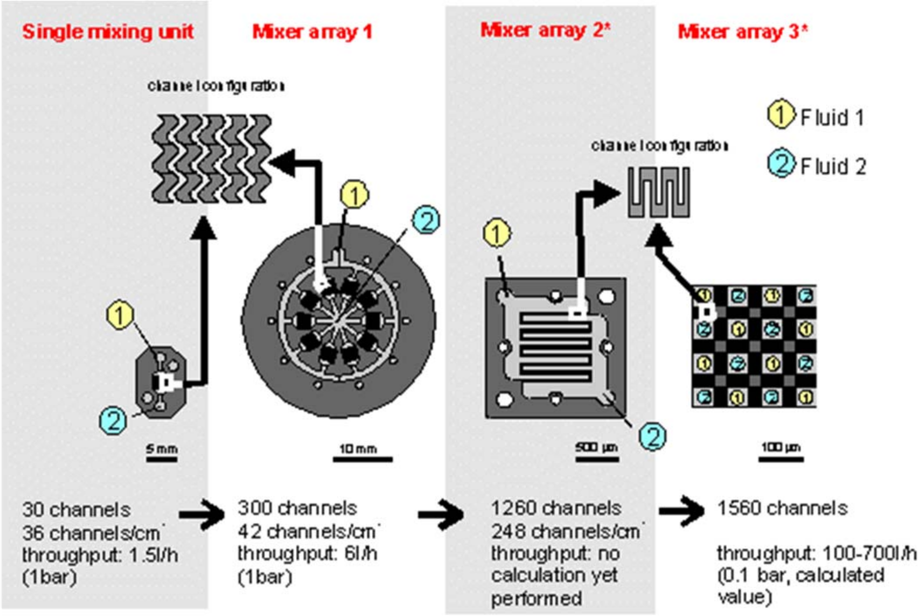
$$\frac{\Delta v_z}{\Delta v_z'} = \frac{\boxed{A}\, l' \Delta p}{\boxed{A'}\, l \Delta p'}$$

- Minimum residence time
  - Center of channel

$$t_l\big|_{r=0} = \frac{l}{v_{\max}} = \frac{4\eta l^2}{\Delta p \boxed{r_0^2}}$$

11.4. Numbering-Up Concepts

- Numbering-up aims at an **increase of throughput** by **parallel operation** of a multitude of mixing units.
- Feeding of these mixing units may be achieved by using a **hierarchic** distribution route, e.g. based on system / platelet / element.
- When numbering up, the **mixing conditions** remain **virtually the same**, because mixing elements are simply added.



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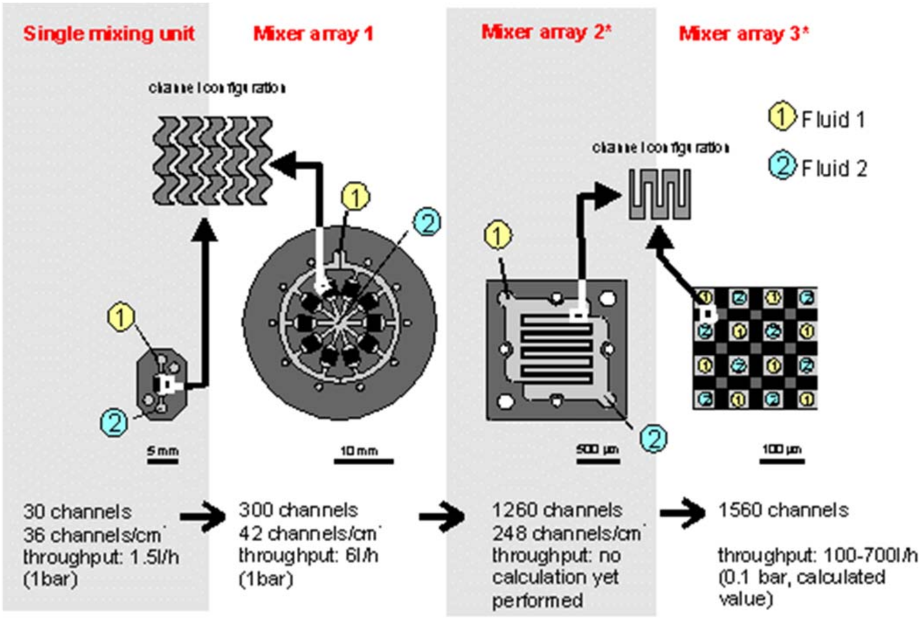
11.4. Numbering-Up Concepts

- Numbering up, hence, is advantageous, because the **step** from **lab-scale processing** to **industrial processing** is **faster** and **more reliable**.
- As demonstrated in <u>industrial case studies</u>, simple combination of several micromixers paves the way to numbering-up.



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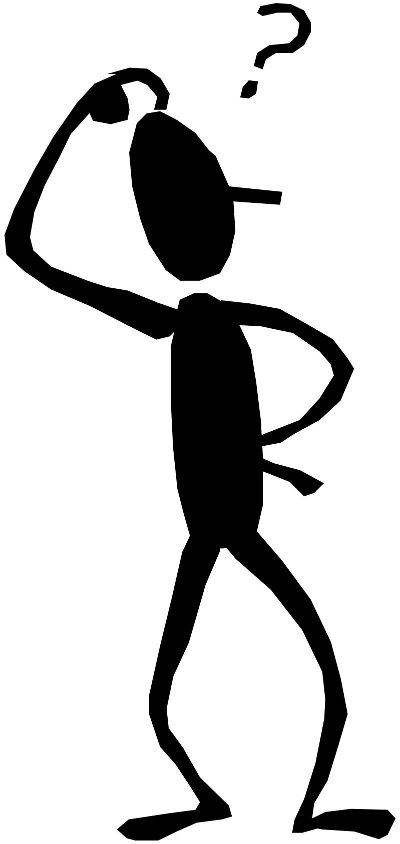
11.4. Numbering-Up: Problem

- Numbering up
  - Source often single stream
- Splitting up
  - Distribution of one source flow to multiple small streams
- Uniformity problem
  - Like electrical resistors in parallel
  - Highest flow rate in channel with smallest flow resistance
- Non-uniformity of resistances
  - Fabrication tolerances
  - Flow patterns in flow splitter
  - Backpressures caused by air pockets
  - ...




CoMix
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Überblick

- Problemstellung
- Systemansatz
  - Zentrifugales Pumpen
  - Hydrodynamisches Mischen
  - Generische Parallelisierung
  - Systemaufbau
- Systemvarianten
  - Coriolis-Mischer
  - Coriolis-Reaktor
  - Rotationslaminator
- Experimentelle Charakterisierung
- Zusammenfassung und Ausblick

Überblick

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Problemstellung: Reaktives Mischen

- Generell
  - ➢ Schnelle, homogene Durchmischung
  - ➢ Hoher Durchsatz
  - ➢ Reaktionsprodukte
    - Ausbeute
    - Selektivität

- Mischen in Mikrostrukturen
  - \+ Gute Prozesskontrolle
    - \+ Thermalisierung
    - \+ Massentransport
  - Mischgeschwindigkeit diffusionsbegrenzt
  - Volumendurchsätze querschnittslimitiert
  - Schnittstellen mit übergeordnetem Makroprozess

- Hier: Reaktives Mischen von mischbaren Flüssigkeiten

Mischsensitive Reaktionen

Warum schnelles Mischen?

- Mehrere (parallelen) chemische Reaktionspfade
- Unterschiedliche Reaktionsraten
  - Konkurrenz zwischen mehreren Reaktionspfaden
  - Langsame Reaktionen: reaktionsraten-begrenzt
  - **Schnelle Reaktionen: mischbegrenzt**

Bei **schnellen Reaktionen** laufen bei **langsamer Durchmischung** daher ungewollte Reaktionspfade unter Bildung von **unerwünschten Nebenprodukten** ab.

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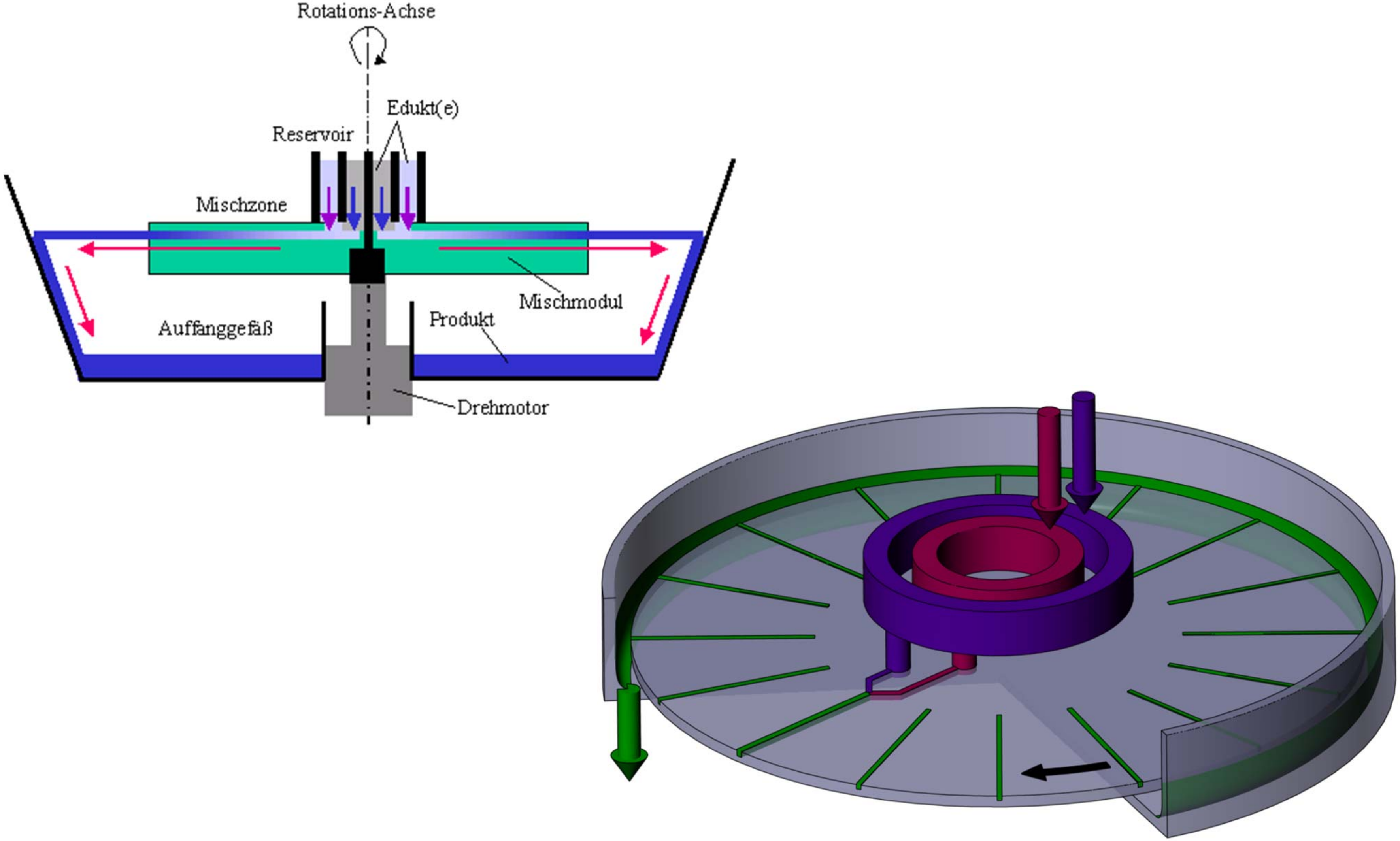
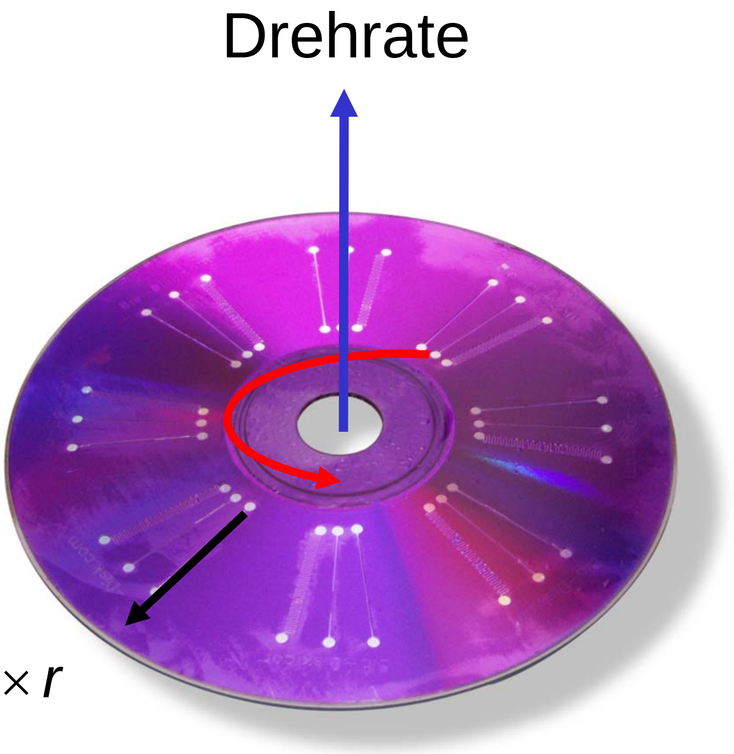
Systemkonzept: Querschnitt & Materialfluss



Neuartiger Systemansatz

- Pumpen
  - Zentrifugalkraft
- Mischen
  - Multi-Lamination an Wand
  - Coriolis-Kraft
    - Querverrührung des Mischkanals
    - Multilamination in Parallelstruktur
- Parallelisierung
  - „Speichenrad“
- Modularer Aufbau
  - Feste Zentrifuge („Player“)
  - Mischmodul als Rotor

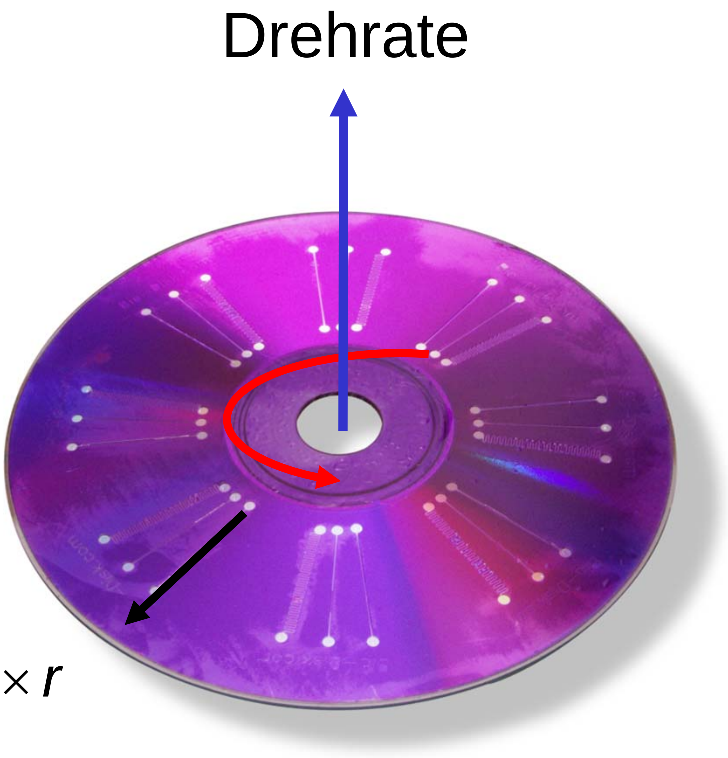
Pumpen: Zentrifugalkraft



$$F_Z = m \cdot \boxed{\omega^2} \times r$$

- Hohe Pumpraten
  - Pumprate proportional zu Quadrat der Drehzahl
  - Volumenkraft
- Sehr robuste Makro-Mikro-Schnittstelle zur Kraftübertragung

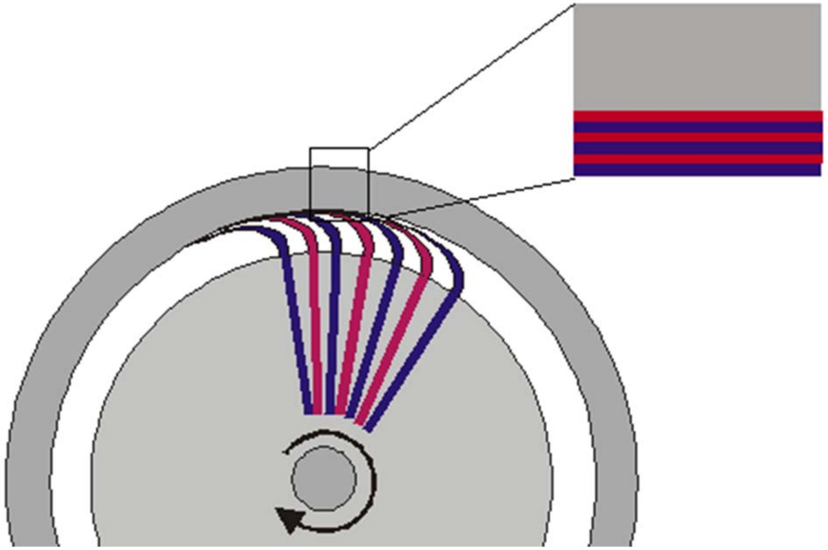
Pumpen: Zentrifugalkraft



$$F_z = m \cdot \boxed{\omega^2} \times r$$

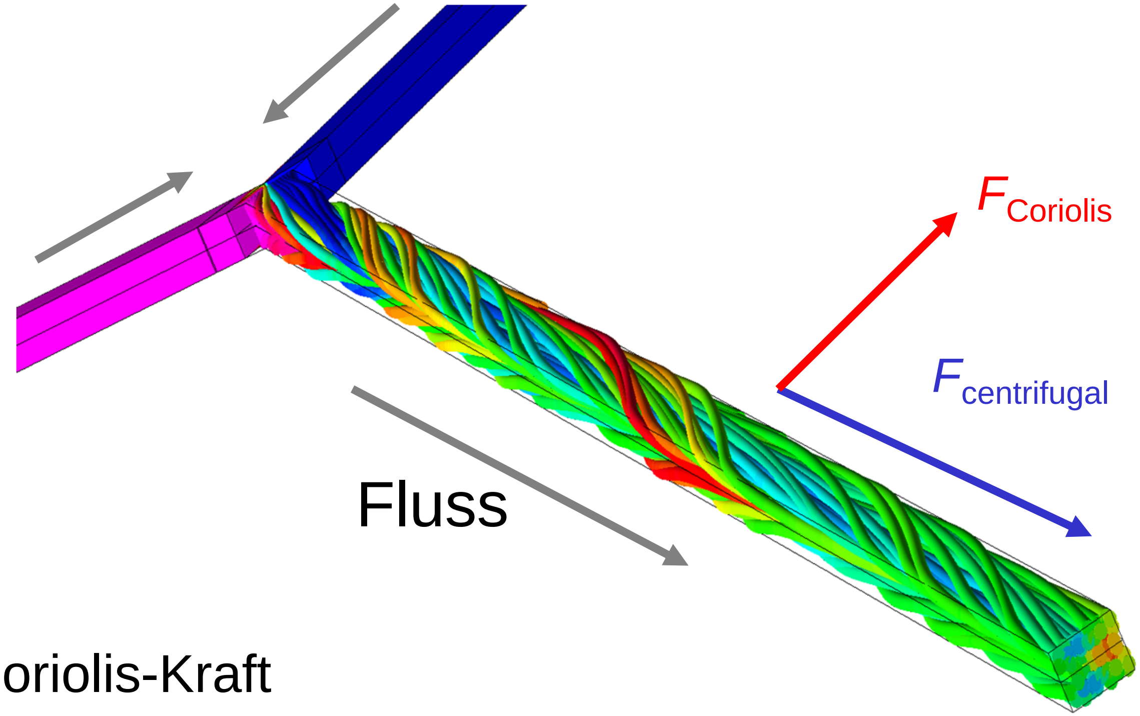
- Drehrate von 100 Hz
  - Beschleunigung: einige 1000 g
  - Äquivalentdruck: ~ 10.000 kPa = 100 bar !

Hydrodynamisches Mischen: Multi-Lamination an Wand



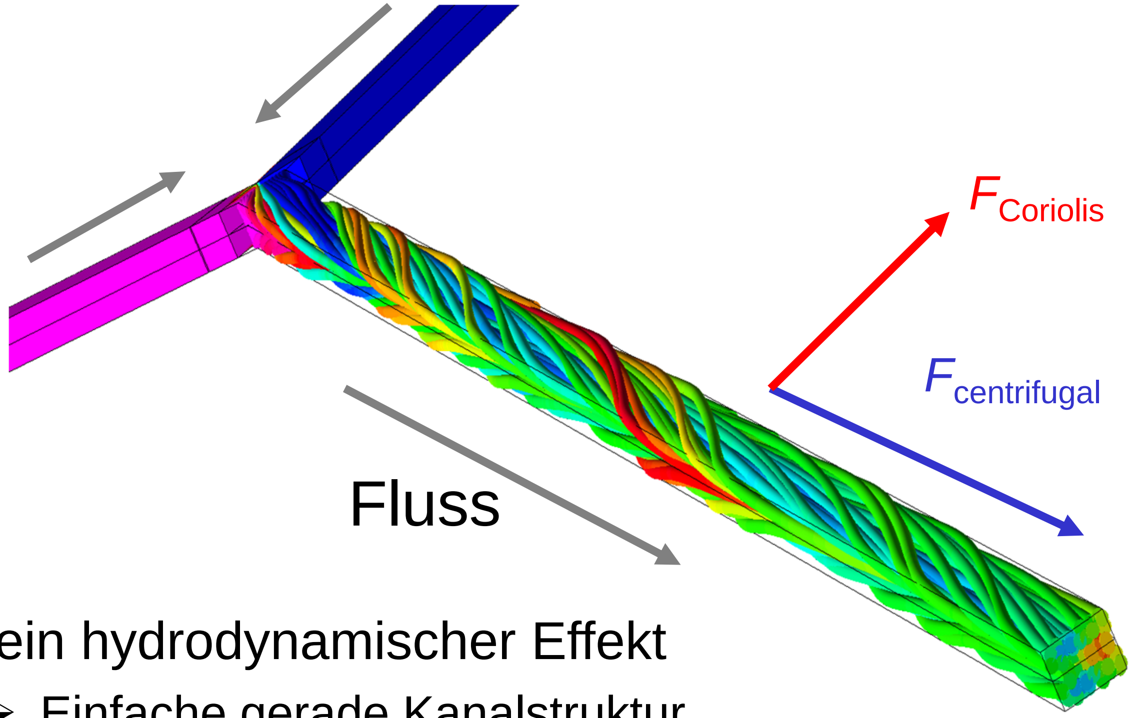
- Rotierendes Mischmodul
- Statische Wand des ortsfesten Auffanggefäßes
- Schichtung (Multi-Lamination) entlang Wand

Hydrodynamisches Mischen: Querverrühren



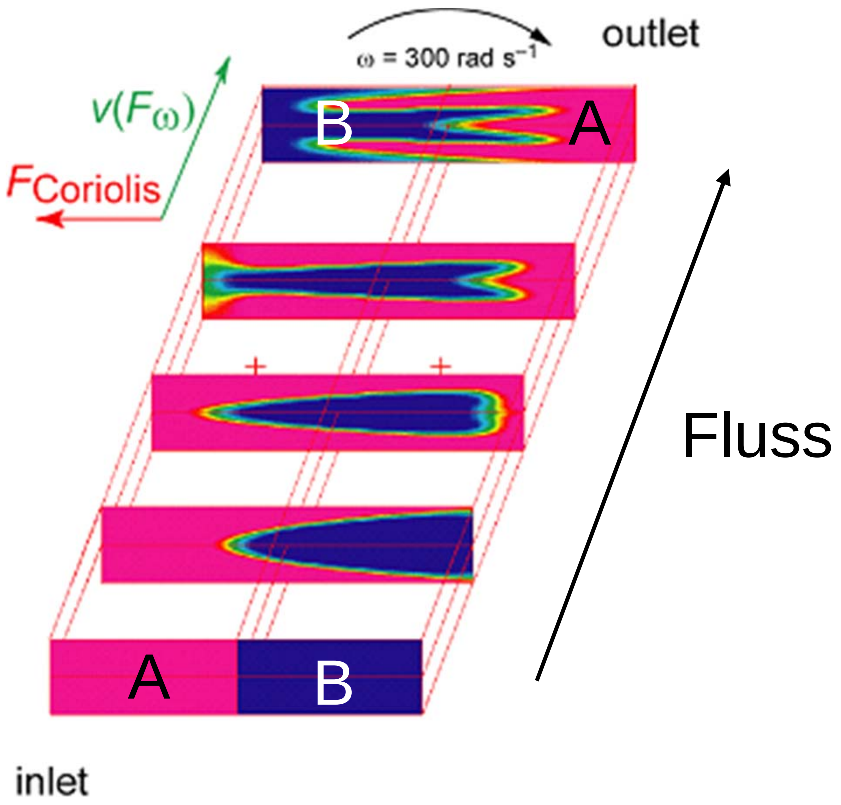
- Coriolis-Kraft
    - Scheinkraft im rotierenden Bezugssystem
    - Senkrecht zur (radialen) Ausbreitungsrichtung
    - Proportional zur Flussgeschwindigkeit

Hydrodynamisches Mischen: Querverrührung



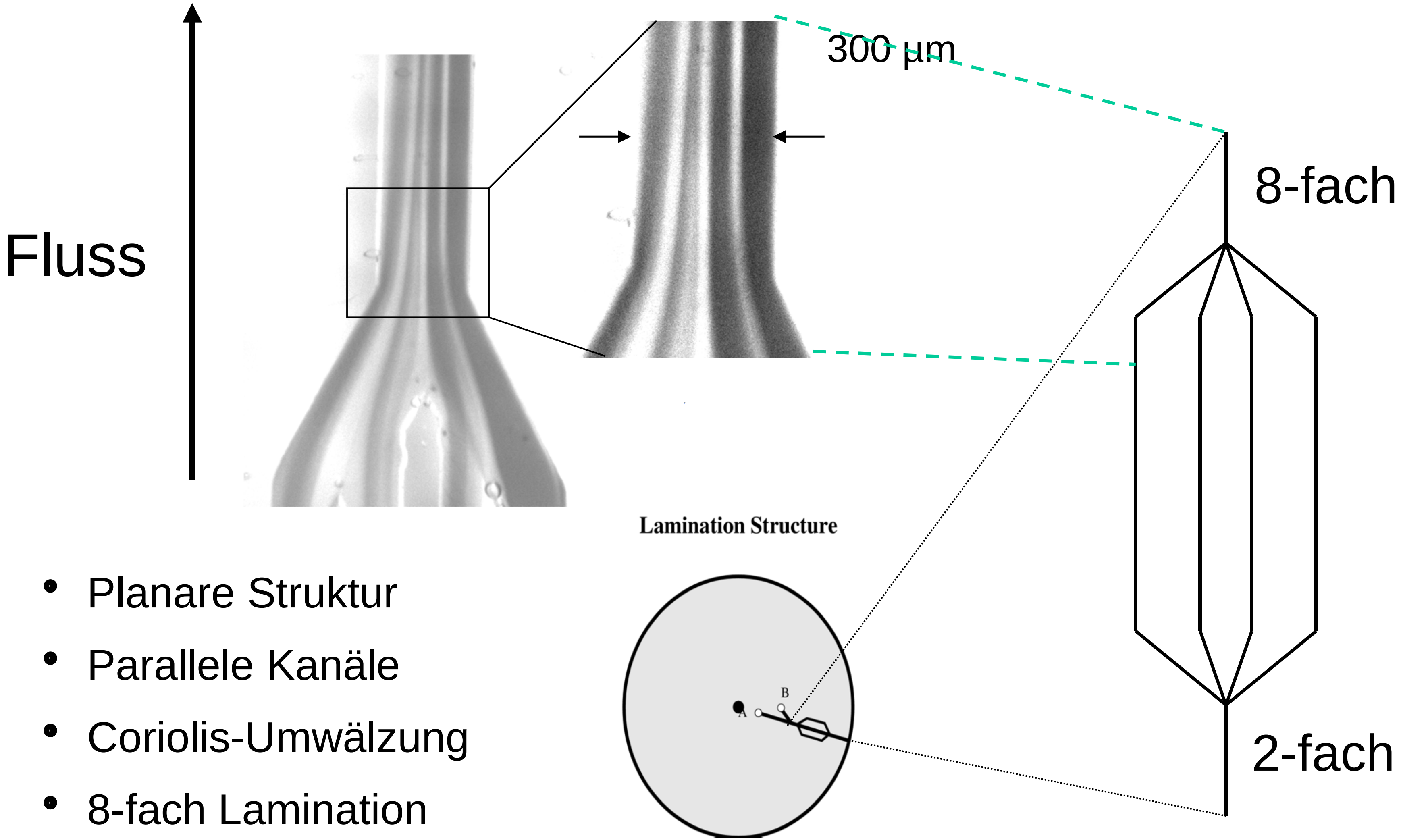
- Rein hydrodynamischer Effekt
  - Einfache gerade Kanalstruktur
  - Keine Strukturierung der Oberfläche notwendig
  - Vergleichsweise große Kanalquerschnitte
  - Dadurch geringer Flusswiderstand

Hydrodynamische Inversion der Schichtung



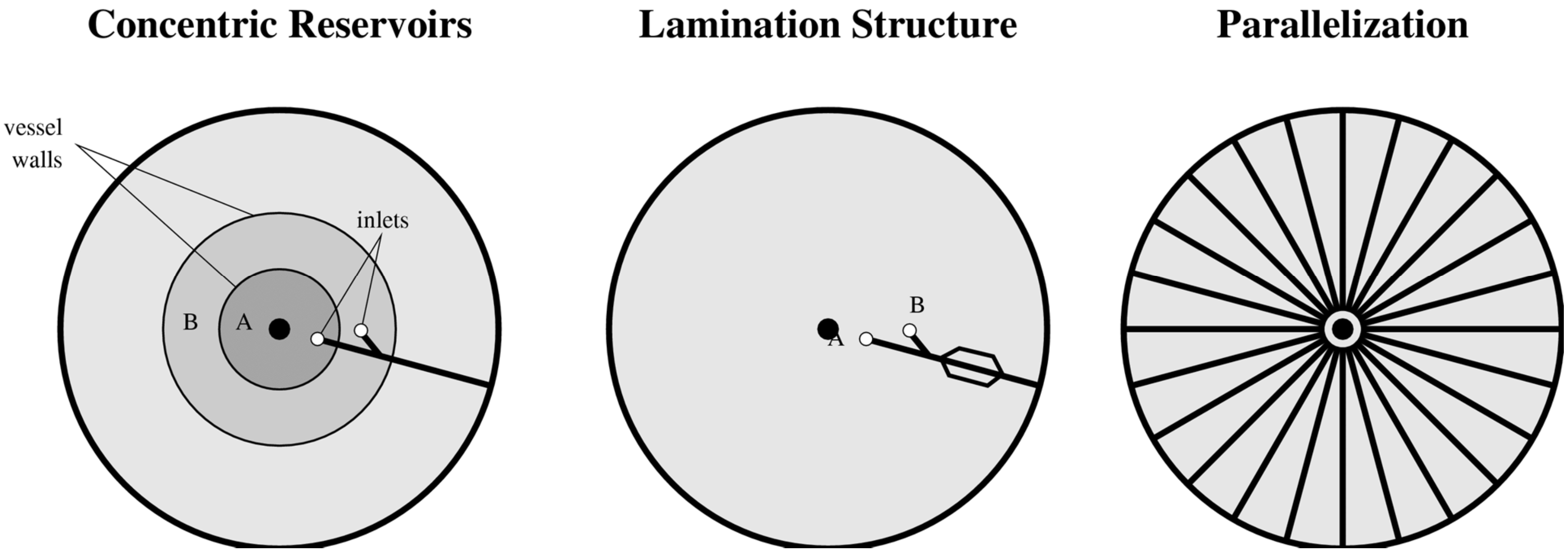
- Einfacher gerader Kanal
- Coriolis-Querkraft im Zentrum maximal
- Rein hydrodynamische Umschichtung von AB zu BA

Hydrodynamischen Mischen: On-Disk Multilamination



- Planare Struktur
- Parallele Kanäle
- Coriolis-Umwälzung
- 8-fach Lamination

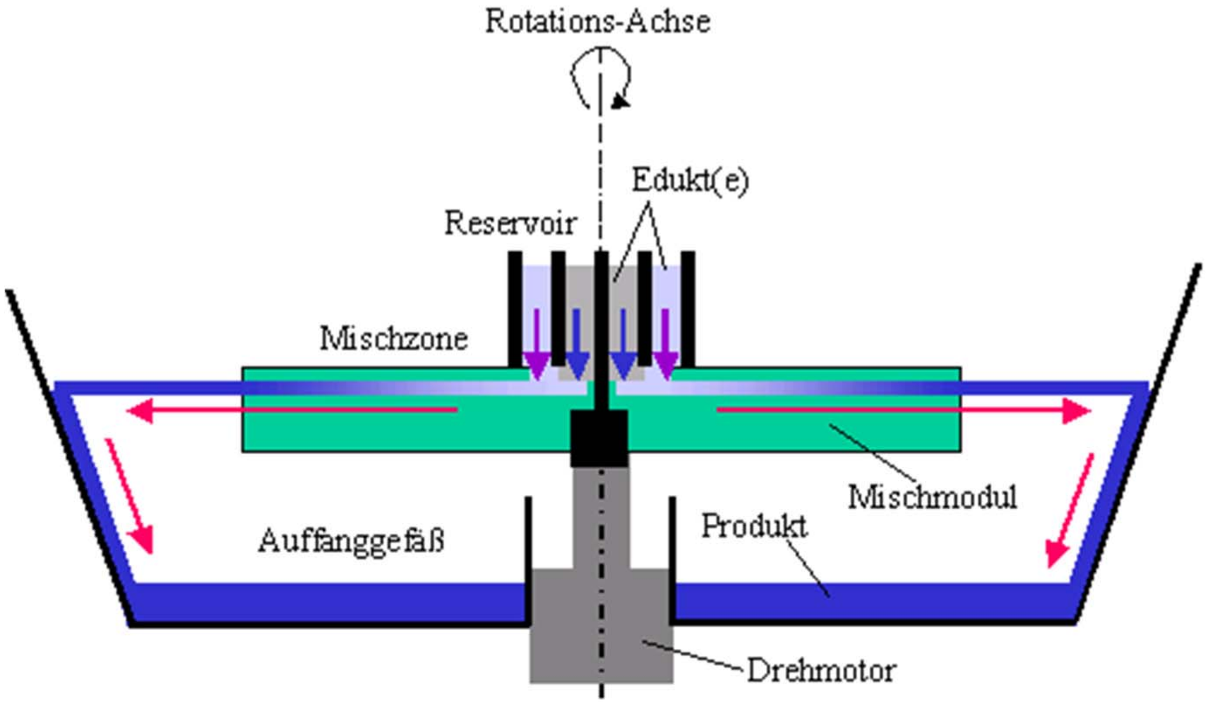
Symmetrie & Parallelisierung


Concentric Reservoirs

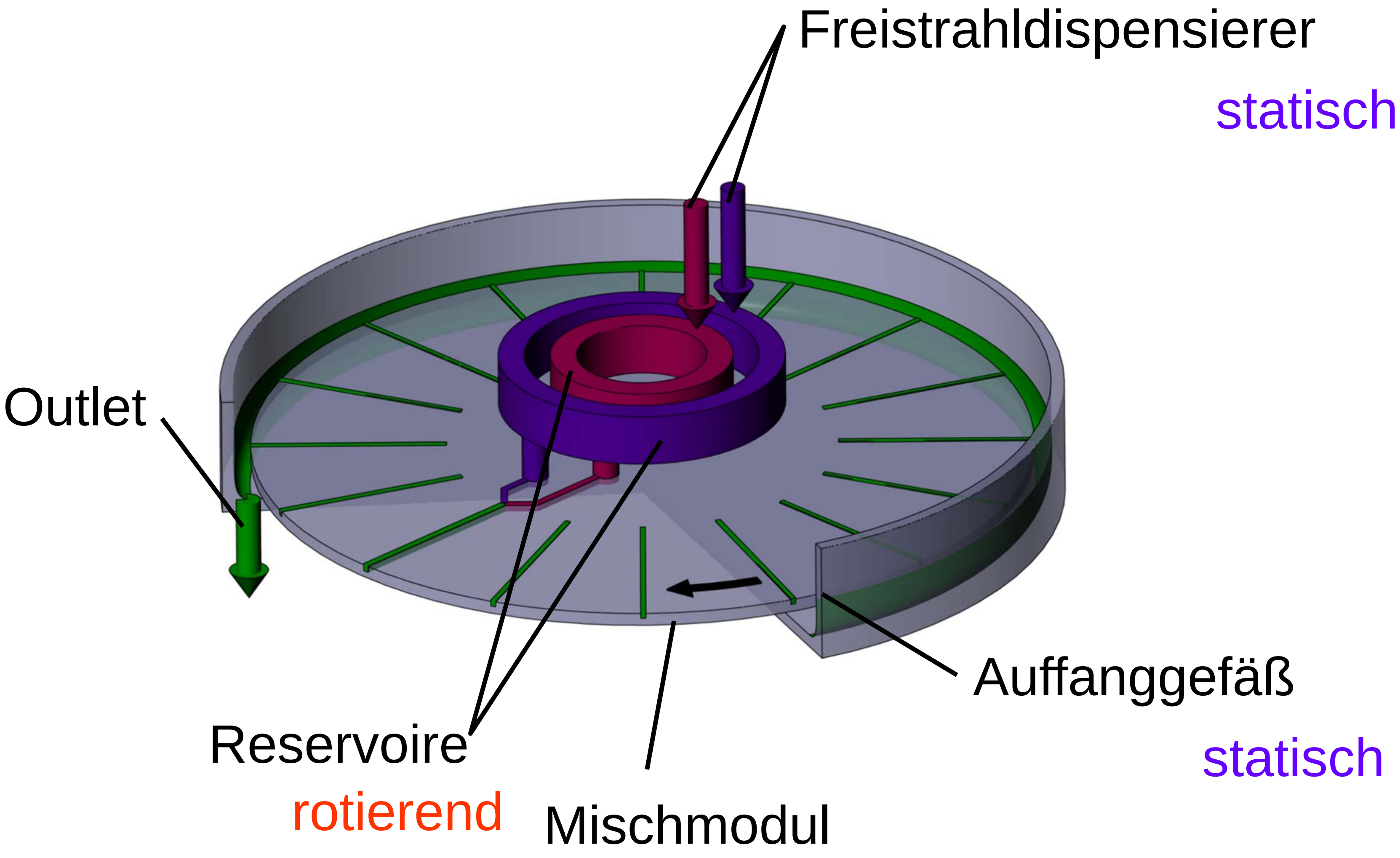
Lamination Structure

Parallelization

Systemkonzept: Schnittstellen & Materialfluss



Systemkonzept



Freistrahldispensierer

statisch

Outlet

Auffanggefäß

statisch

Reservoire

rotierend

Mischmodul

Systemaufbau

- Reservoire
  - Zuführung der Produkte
  - u.U. Aufnahme der Edukte
- Disk als Strukturebene
- Metallträger
- Standardzentrifuge
  - Antrieb
  - Innenwand als Auffanggefäß

Überblick

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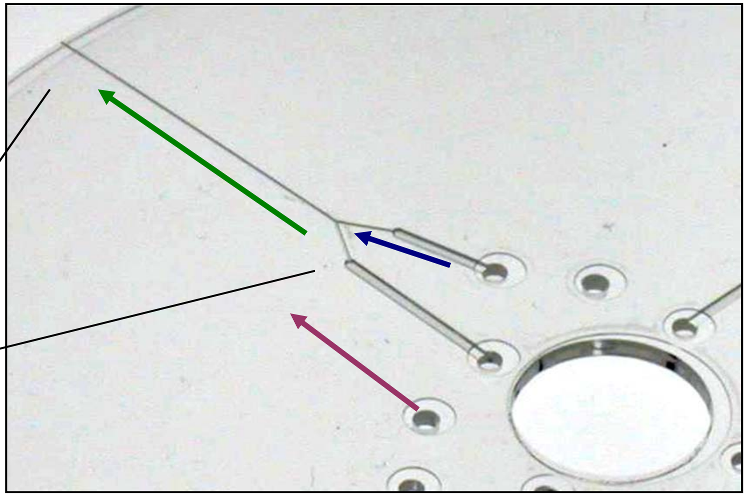
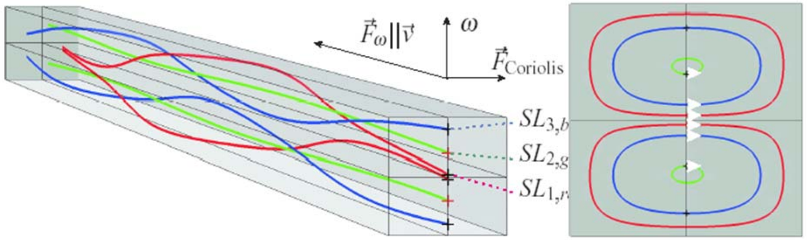
- Zusammenfassung und Ausblick

Systemvariante: Coriolis-Mischer

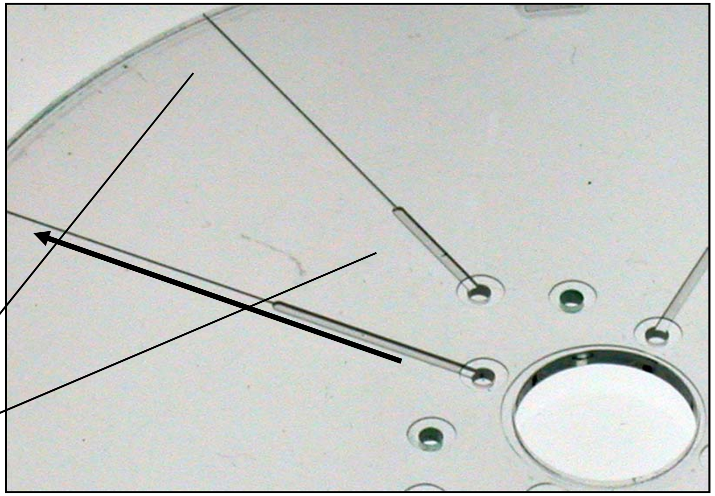
- Zusammenführung **zweier Flüssigkeitsströme** auf Disk
- Coriolis-induziertes Mischen zweier Edukte innerhalb des Mischkanals

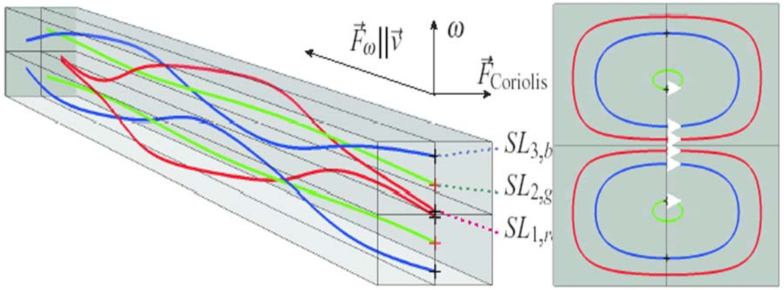




Systemvariante: Katalytischer Coriolis-Reaktor

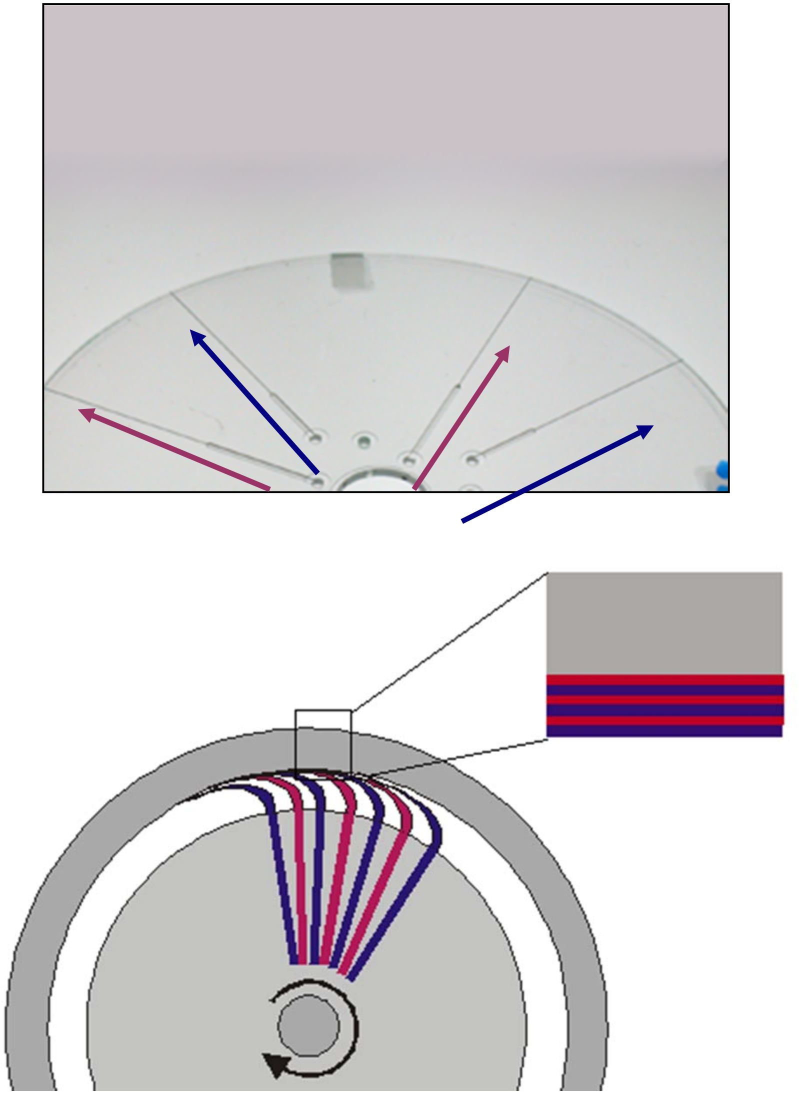
- Einführung eines **Gemisches der Reaktanden**
- Katalytische Oberflächenbeschichtung in gemeinsamem Reaktionskanal
- Coriolis induzierte Stoffumwälzung zwischen Bulk und Kanalwand
  - Verbesserung einer katalytischen Reaktion im Kanal
  - Erhöhung der Reaktionsrate
- Auffangen des Reaktionsproduktes





Systemvariante: Rotationslaminator

- Rotor mit radialen Düsen
- Alternierend Edukt A + B
- Gemisch der Reaktanden
- Scherung der Fluide zwischen Rotor und Wand
  - Dünnere Schichten
  - Vergrößerung der Grenzflächen
- Reaktion im Wandlayer



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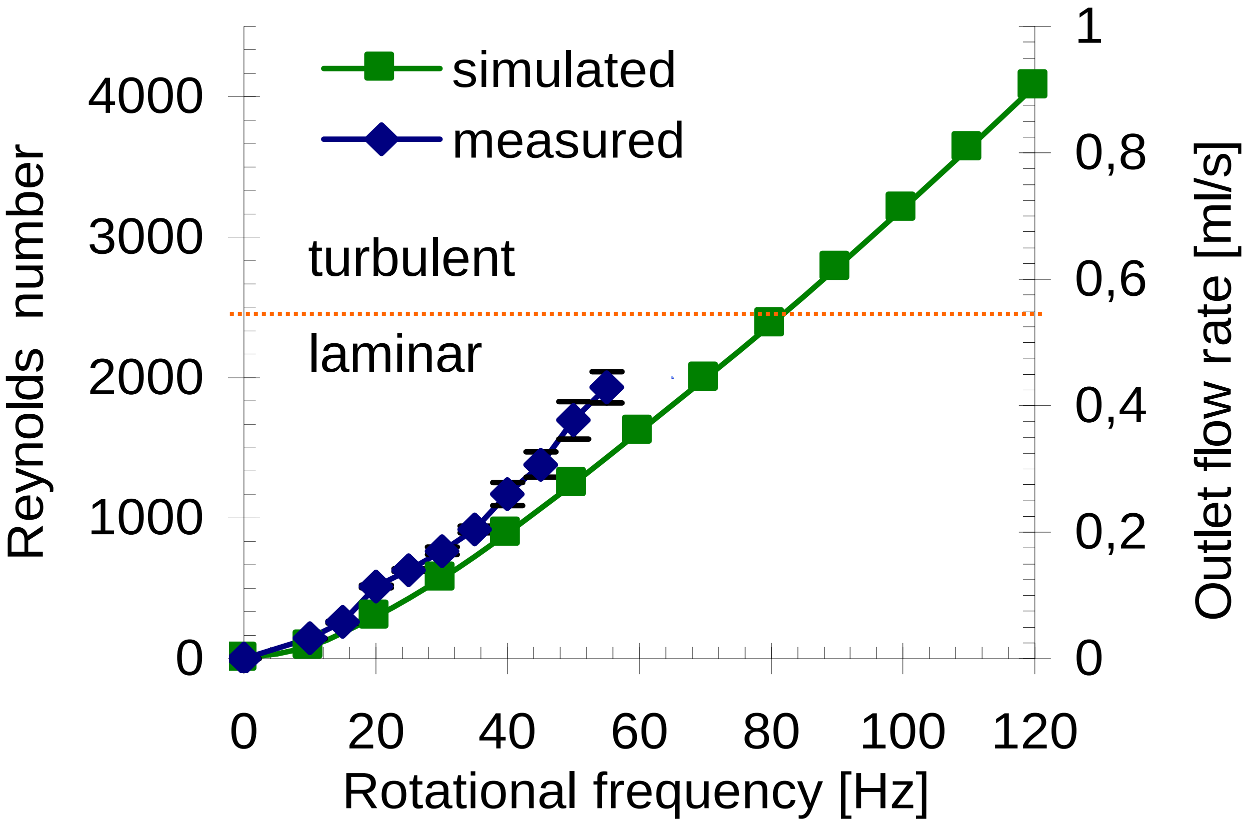
Unmittelbare Projektziele

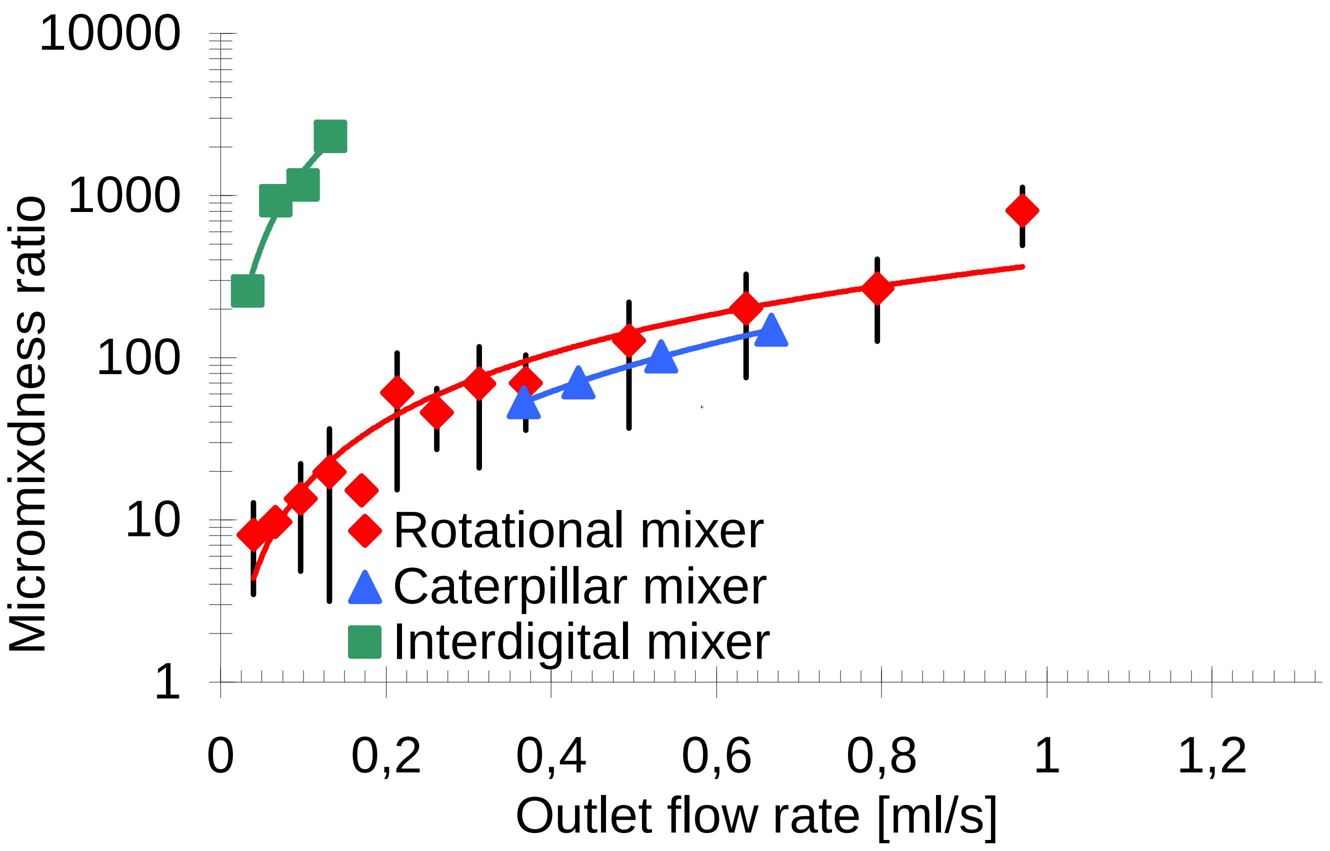
- Demonstrator
  - ➢ Marktforschung
  - ➢ Identifikation geeigneter Modellrektion
    - Misch-(reaktions-)kritisch
    - Schnelle chemische / biochemische / katalytische Synthesen
      - ➢ Flüssigkristalle
      - ➢ Pharmazeutische Wirkstoffe
      - ➢ Insektizide, ...
  - ➢ Identifikation von geeignetem Anlagentyp
    - Multipurpose / kleine Batch-Produktion
    - Kontinuierliche Produktion

- Experimentelle Charakterisierung der Grundperformance
  - ➢ Mischqualität
  - ➢ Durchfluss

Ergebnisse: Durchfluss pro Kanal



Ergebnisse: Mischqualität



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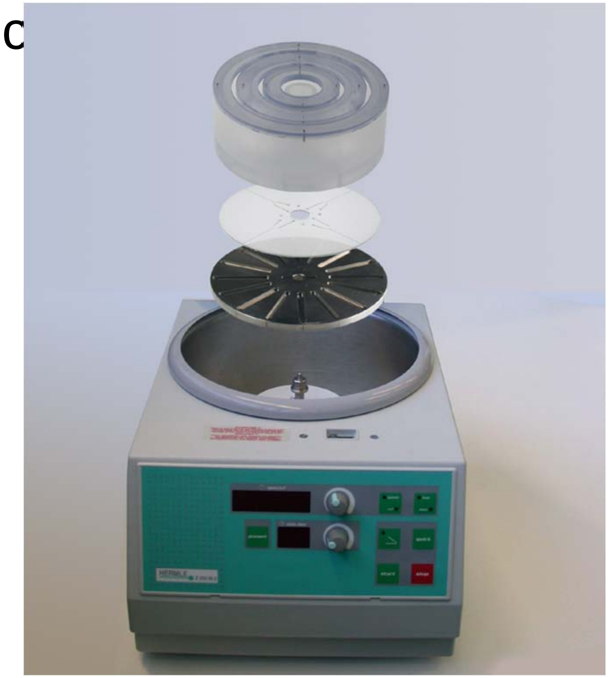
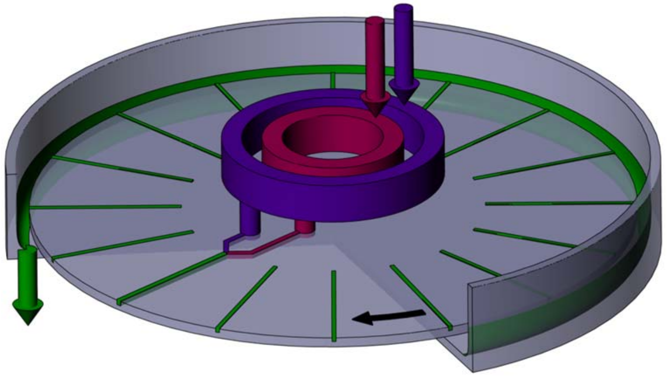
- Systemvarianten
  - Coriolis-Mischer
  - Coriolis-Reaktor
  - Rotationslaminator
- Experimentelle Charakterisierung
- Zusammenfassung und Ausblick

Zusammenfassung

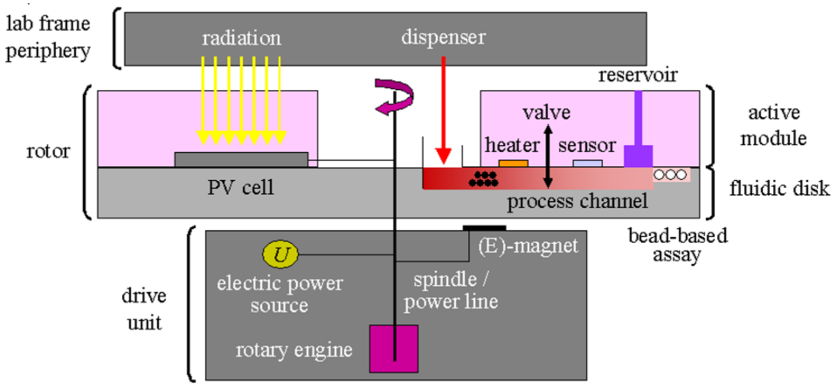
- Neuartige Plattform für reaktives Mikromisc
- Modularer Aufbau
- Pumpen durch Zentrifugalkraft
- Rein hydrodynamische Mischeffekte
  - ➢ Coriolis-Kraft
    - Querverrührung
    - On-Disk Multilamination
  - ➢ Rotationsbewegung
    - Multilamination an Wand
- Experimenteller Charakterisierung
  - ➢ Flussraten
  - ➢ Mischqualität



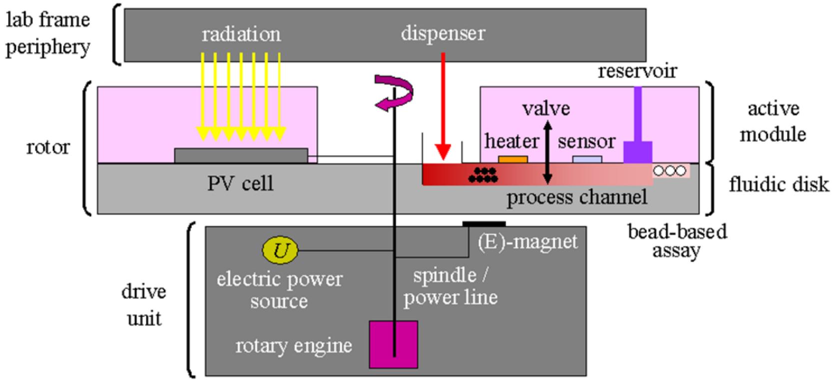


Ausbaustufen für industriellen Einsatz

- Kontinuierliches Zuführen von Edukten
  - Freistrahldispensierer
- Flusskontrolle
  - Anlaufverhalten
  - Abschaltverhalten
  - Differentielle Druckbeaufschlagung der Reservoire
- Online-Prozesskontrolle
  - Flussraten
  - Flussratenverhältnis
  - Temperatur
  - Spektroskopie
- Mischmodul
  - Einweglösung aus Plastik
  - Zentrifugales Spül-Protokoll



Ausbaustufen für industriellen Einsatz



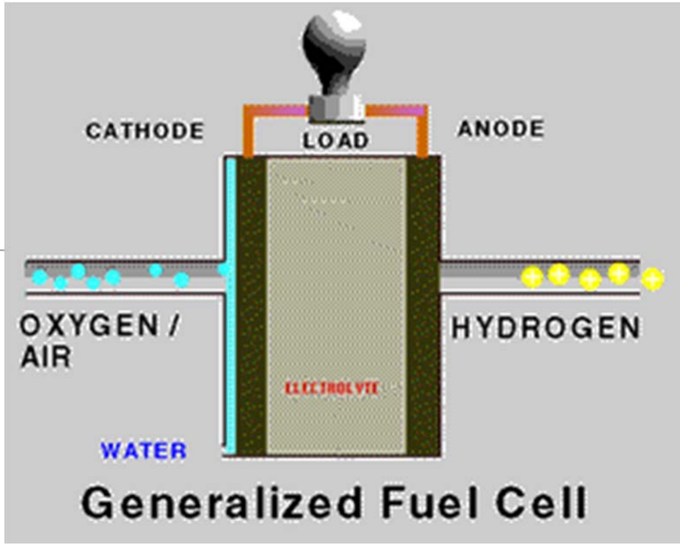
- Heterogene Phasen
  - ➢ Gas-flüssig Reaktionen
  - ➢ Dispersionen
    - Emulsionen
    - Dispersionen, ...
- Schnittstellen mit üblichen industriellen Komponenten
- Integrierbarkeit in übergeordneten Prozess
- Minimierung von Nebenprodukte
  - ➢ Prozessoptimierung
  - ➢ Integrierte / nachgeschaltete Auftrennung
    - Zentrifugal
    - Membran, ...
- Integrierte / nachgeschaltete QC
- Generell
  - ➢ (Reaktives) Mischen nur ein Prozessschritt unter vielen

Vorteile des Zentrifugalmischers

- Hohe Flussraten
  - 0,1 - 1 ml / s pro Kanal
- Generische Parallelisierbarkeit
  - “Speichenrad”
  - Raten von 100 ml / min pro Disk realistisch
- Hohe Mischqualität
- Kontaktfreie Mikro- Makro-Schnittstellen
- Modulares System
  - „Teure“ Komponenten im Makro-Laufwerk
    - Aktorik
    - Drehlager
    - „Standardgerät“
  - Mischmodul (Rotor)
    - Einfach austauschbar
    - Sehr einfache Mikrostrukturen
      - Planar
      - Passiv
      - Keine beweglichen Teile
  - „Mikrotechnik macht nur das, was sie gut kann.“

11. Microreactors

1. Micromixers
2. Heat Exchangers
3. Chemical Microreactors
4. Splitting of Flow
5. **Fuel-Based Power Supplies**



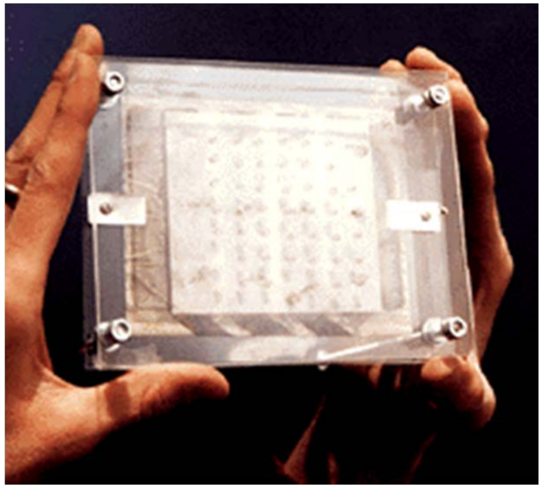
11.5. Micro Fuel Cells

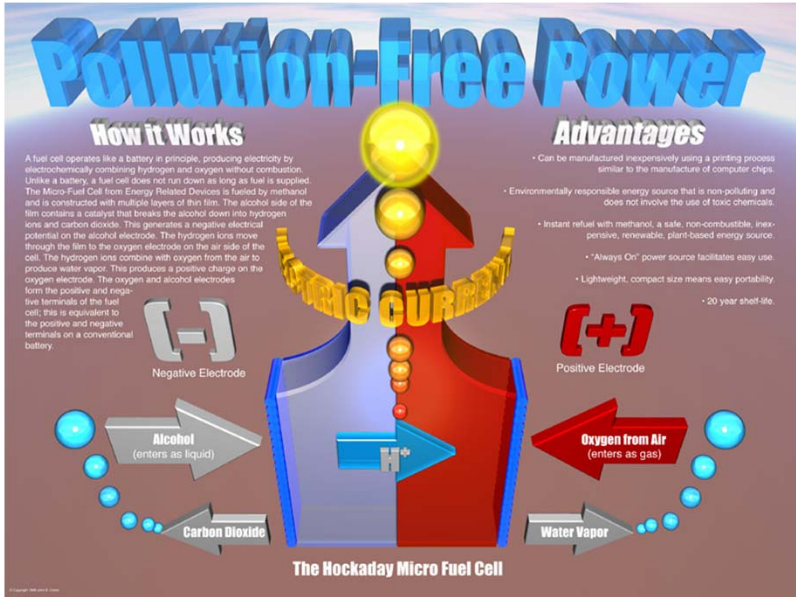
- **A fuel cell operates like a battery in principle, producing electricity by electrochemically combining hydrogen and oxygen without combustion.**
- **Unlike a battery, a fuel cell does not run down as long as fuel is supplied. The Micro Fuel Cell™ from Energy Related Devices is fueled by methanol or ethanol and is constructed with multiple layers of thin films.**
- **The micro-fuel cell is like the cell of any living thing:**
  - ➢ **Input fuel is a hydrocarbon that is broken down catalytically, producing energy and harmless "waste" products of heat, carbon dioxide, and water vapor.**
  - ➢ **The collection and energy distribution scheme of this micro-fuel cell system can be likened to the capillaries and veins in an animal.**

11.5. Micro Fuel Cells

- The alcohol side of the film contains a catalyst that breaks the alcohol down into hydrogen ions and carbon dioxide.
- This generates a negative electrical potential on the alcohol electrode. The hydrogen ions move through the film to the oxygen electrode on the air side of the cell.
- The hydrogen ions combine with oxygen from the air to produce water vapor.
- This produces a positive charge on the oxygen electrode. The oxygen and alcohol electrodes form the positive and negative terminals of the fuel cell; this is equivalent to the positive and negative terminals on a conventional battery.

11.5. Advantages of Fuel Cells





Pollution-Free Power

How it Works

A fuel cell operates like a battery in principle, producing electricity by electrochemically combining hydrogen and oxygen without combustion. Unlike a battery, a fuel cell does not run down as long as fuel is supplied. The Micro-Fuel Cell from Energy Related Devices is fueled by methanol and is constructed with multiple layers of thin film. The alcohol side of the film contains a catalyst that breaks the alcohol down into hydrogen ions and carbon dioxide. This generates a negative electrical potential on the alcohol electrode. The hydrogen ions move through the film to the oxygen electrode on the air side of the cell. The hydrogen ions combine with oxygen from the air to produce water vapor. This produces a positive charge on the oxygen electrode. The oxygen and alcohol electrodes form the positive and negative terminals of the fuel cell; this is equivalent to the positive and negative terminals on a conventional battery.

Advantages

- Can be manufactured inexpensively using a printing process similar to the manufacture of computer chips.
- Environmentally responsible energy source that is non-polluting and does not involve the use of toxic chemicals.
- Instant refuel with methanol, a safe, non-combustible, inexpensive, renewable, plant-based energy source.
- "Always On" power source facilitates easy use.
- Lightweight, compact size means easy portability.
- 20 year shelf-life.

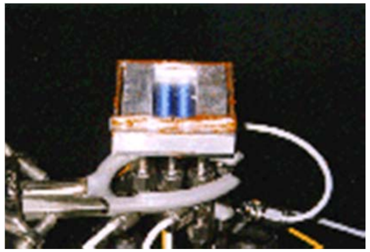
PNNL

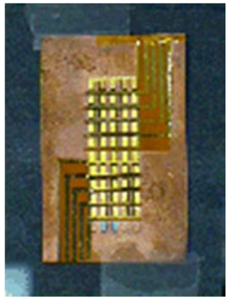
- **Inexpensively manufacturable**
  - **Printing process similar to manufacture of computer chips**
- **Environmentally responsible energy source**
  - **Non-polluting and does not involve use of toxic chemicals**
- **Instant refuel with methanol or ethanol**
  - **Safe, low-flammability, inexpensive, renewable, plant-based energy source**
- **“Always On” power source**
- **Lightweight and compact size**
- **20 year estimated shelf-life**

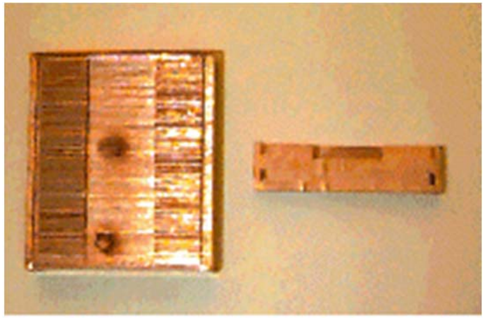
11.5. Microchannel Combustor / Evaporator

- Lightweight and compact sources of electric power and microclimate control
  - **Carry-on power source** for **soldiers**
  - **Thermal energy** could drive **electrical generation** and provide the **heating** or **cooling**
  - **Combustion** of **hydrocarbon fuels** produces **high-density thermal energy**
    - **Energy density (W/kg or W/m^3)** of fuels **factor** of **100 greater** than **most advanced batteries**
  - Current heat generation
    - Power transfer of **25 W / cm^2**
  - **Low air-toxic emissions during operation**
    - **Emissions of both NO$_x$ and CO reduced to below regulatory limits**
  - **Developing an approach to mass production**
    - **Diffusion bonding of laminates for low cost fabrication**

MICRO-CATS Home







PNNL

11.5. Microchannel Reactors for Automotive Fuel Processors

- Microchannel reactors **reduce size** of conventional reactors
  - **Without lowering throughput**
- **Heat and mass transport limitations** slow observed reaction rates in conventional reactors
  - **Minimized** in **microchannel reactors**
- **Distance** between **heat generation** and **removal reduced**
  - Tens of centimeters in conventional reactors
  - Tens of microns in microchannel reactors
- As distance shrinks, corresponding **contribution** of **slow conduction** and **diffusion** to **heat exchange** or **catalyst surface** is **reduced**.
- **Fast heat** and **mass transfer** increases **process efficiency**, enabling **process miniaturization without sacrificing productivity**.

11.5. Microchannel Reactors for Automotive Fuel Processors

MICRO-CATS
Home

- **Fuel processor critical reactor technology** for deployment of **PEM-based fuel cells** for **automotive** applications
- Fuel processor produces **hydrogen rich streams** from **gasoline** or **methanol** in **multi-step process**
  - Fuel vaporizer
  - Primary conversion reactor to produce synthesis gas
  - Water gas shift reactor
  - CO clean-up reactor
- **Conventional** fuel processing technology based on **fixed-bed reactors**
  - **Not scaling** well with **small modular nature** of fuel cells
- Microchannel reactor-based fuel processors
  - **Small**, **efficient**, **modular**, **lightweight** and **potentially inexpensive**
- Based upon our results with other component investigations, we project a complete system volume of less than 9 liters to produce hydrogen at a sufficient rate and quality to produce 50-kW from a PEM fuel cell.

11.5. Fuel Processing

- Conversion of hydrocarbon fuel to molecular hydrogen
- Chain of catalyst-enhanced reactions
  - ➢ Replacing combustion reaction in conventional engine
- Process chain
  - ➢ Reforming reaction
    - Molecular hydrogen
    - Carbon dioxide
    - Carbon monoxide
      - ➢ Detrimental to most types of fuel cells
  - ➢ Removal of carbon monoxide by successive reactions
    - Water-gas shift: reaction with water
    - Selective oxidation: reaction with oxygen
  - ➢ Feeding processed fuel to fuel cell

11.5. Microchannel Reactors for Automotive Fuel Processors