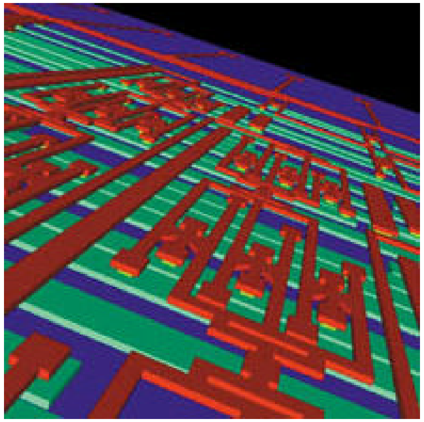
Modeling chemical reactions in immiscible fluids in microchannels

Olga Kuksenok and Anna C. Balazs

University of Pittsburgh, Pittsburgh, PA

• Chemical Reactions in Microchannels: Motivations



www.ercim.org/…/ enw43

❑ Microreactors

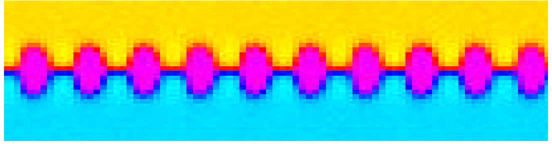
- ☞ Advantages: require nanoliters of substance, faster analysis
- ☞ Use for: drug screenings, advanced material preparation

❑ Challenges

- ☞ Model reactions in immiscible fluids in microchannels
- ☞ Model spatially and temporarily non-uniform reactions
  - ☞ Photosensitive reactions

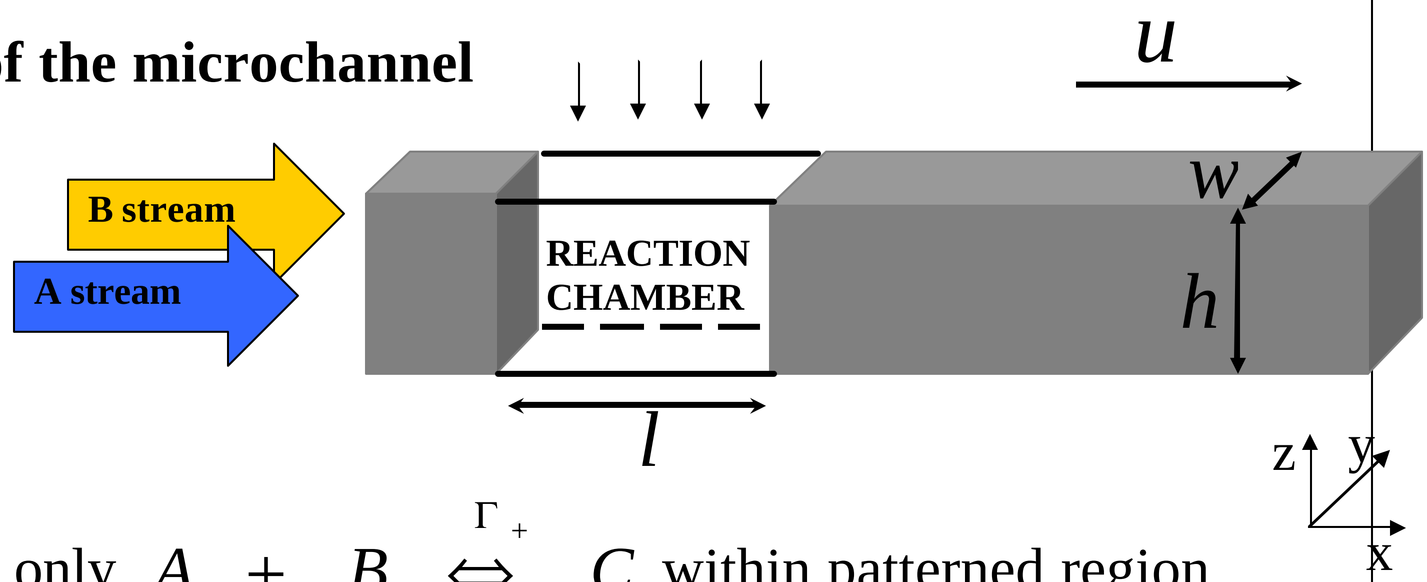
❑ Aim: control dynamics of immiscible fluids in microchannels using photosensitive reactions

- ☞ Create “necklace”of **C** droplets in **AB**



• The Model

- **Schematic of the microchannel**



☞ Reaction only $A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$ within patterned region

- **Two order parameters**

☞ $\varphi = \rho_B - \rho_A$, $y = r_c$; r_i is concentration of *i*-component

☞ $\sum_I r_i = r$

☞ A, B and C are in three-phase coexisting region

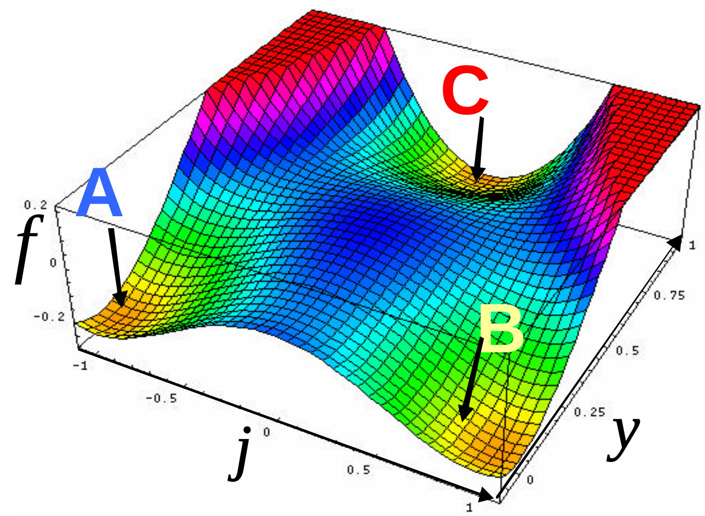
• Ternary Mixtures

❑ Total free energy

$$F(j,y) = \int d\mathbf{r}\left[f(j,y) + k_j(\nabla j)^2 + k_y(\nabla y)^2\right]$$

☞ Local free energy density

$$f(j,y) = -A_{20}j^2 + A_{40}j^4 + A_{02}y^2 - A_{03}y^3 + A_{04}y^4 + A_{22}j^2y^2$$



☞ k_j, k_y define interfacial tensions, s_{AB}, s_{AC}, s_{BC}

☞ $s_{AC} = s_{BC} = s_{AB}$

☞ If $r_c = 0$ reduces to binary phase-separating fluid

• Evolution Equations

❑ **Modified Cahn –Hilliard equations***

$$\frac{\partial j}{\partial t} + \mathbf{u} \cdot \nabla j = M_j \nabla^2 m_j$$

$$\frac{\partial y}{\partial t} + \mathbf{u} \cdot \nabla y = M_y \nabla^2 m_y + \Gamma_+ (r - y + j)(r - y - j) - \Gamma_- y$$

☞ M_j, M_y are mobilities

☞ $m_j = dF/dj, \quad m_y = dF/dy$ are chemical potentials

* *C.Tong at al, J.Phys.Chem B, v106, 2002*

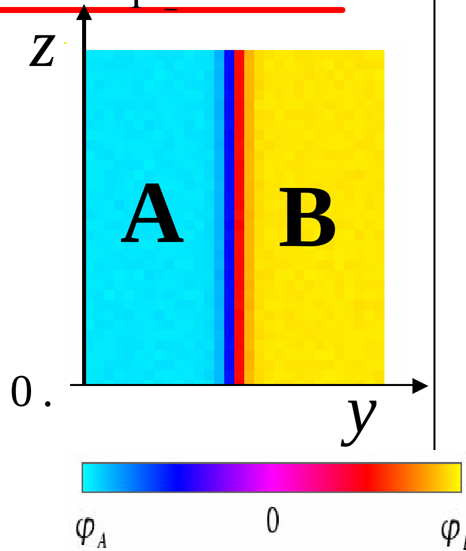
❑ **Navier-Stokes equation:** $0 = H + h \nabla^2 \mathbf{u} - y \nabla m_y - j \nabla m_j$

☞ H is constant pressure gradient along x

☞ Neglect $y \nabla m_y, j \nabla m_j$ (high h)

❑ **To solve use cell dynamic system method**

• *C* Forms in "Reaction Chamber" $A + B \underset{\Gamma_-}{\overset{\Gamma_+}{\Leftrightarrow}} C$

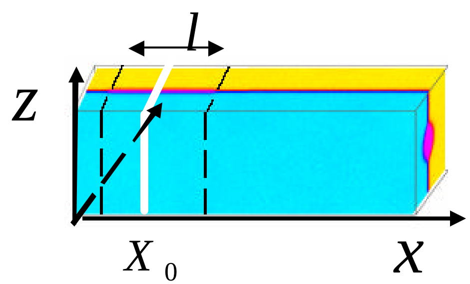


❑ Initial & boundary conditions:

- ☞ At t=0: 2 streams of A & B , no C
- ☞ 2 streams A & B at inlet
- ☞ "Neutral" hard walls:

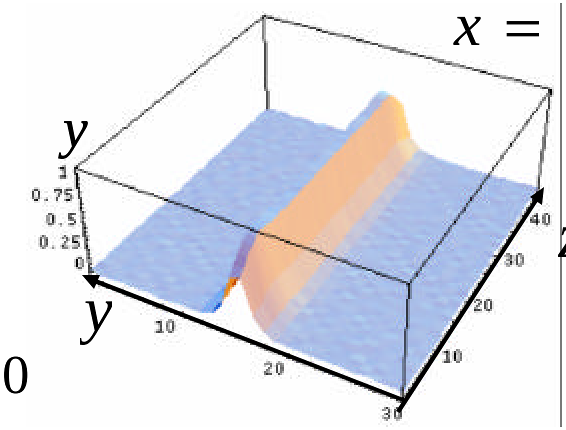
$$\left.\frac{\partial j}{\partial x}\right|_{x=L} = 0, \quad \left.\frac{\partial y}{\partial x}\right|_{x=L} = 0, \quad \left.\frac{\partial m}{\partial n}\right|_{wall} = 0, \quad \left.\frac{\partial m_y}{\partial n}\right|_{wall} = 0.$$

❑ C forms on AB interface in "reaction chamber"

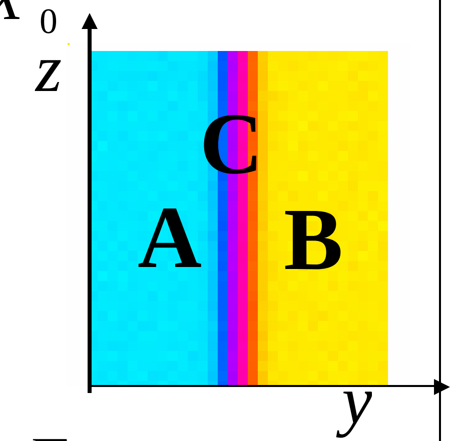


$\Gamma_+ = 0.05, \quad \Gamma_- = 0.00125$

$box\ : 360 \times 30 \times 45;\ l = 50$



$x = X_0$



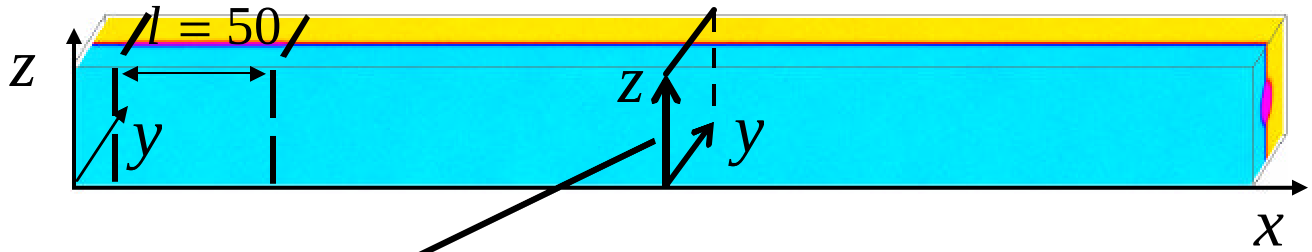
- ☞ Amount of C depends on $\Gamma_+, \ \Gamma_-, s$ $\Gamma_+ \gg \Gamma_-$

• Evolution Within Microchannel $(H = 4 \cdot 10^{-4})$

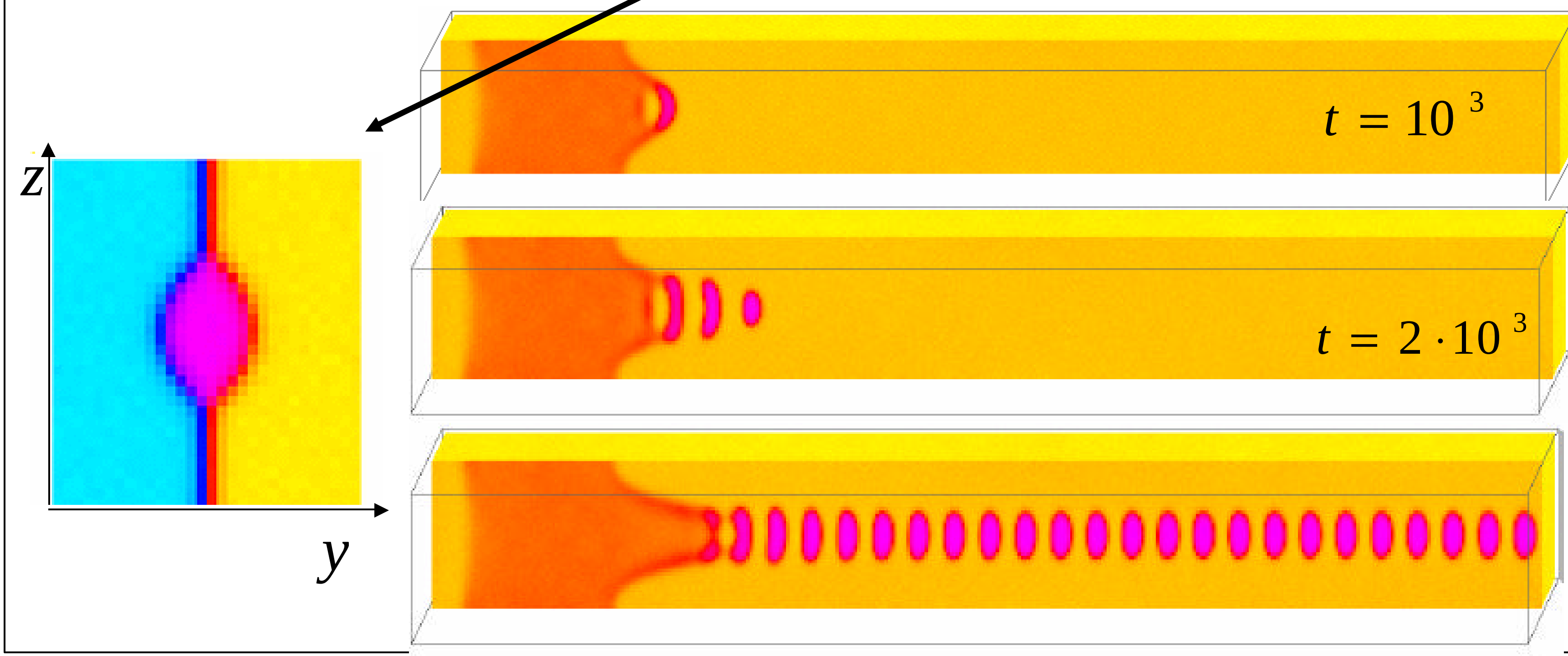
❑ **C layer is created on AB interface in “reaction chamber”**

$\Gamma_+ = 0.05$

$\Gamma_- = 0.00125$



❑ **C is advected along *x* (below A is transparent, y=w/2)**



• Dependence on Imposed Pressure Gradient, *H*

- $H = 2.5 \cdot 10^{-4}$

$\Gamma_{+} = 0.05, \quad \Gamma_{-} = 0.0025$

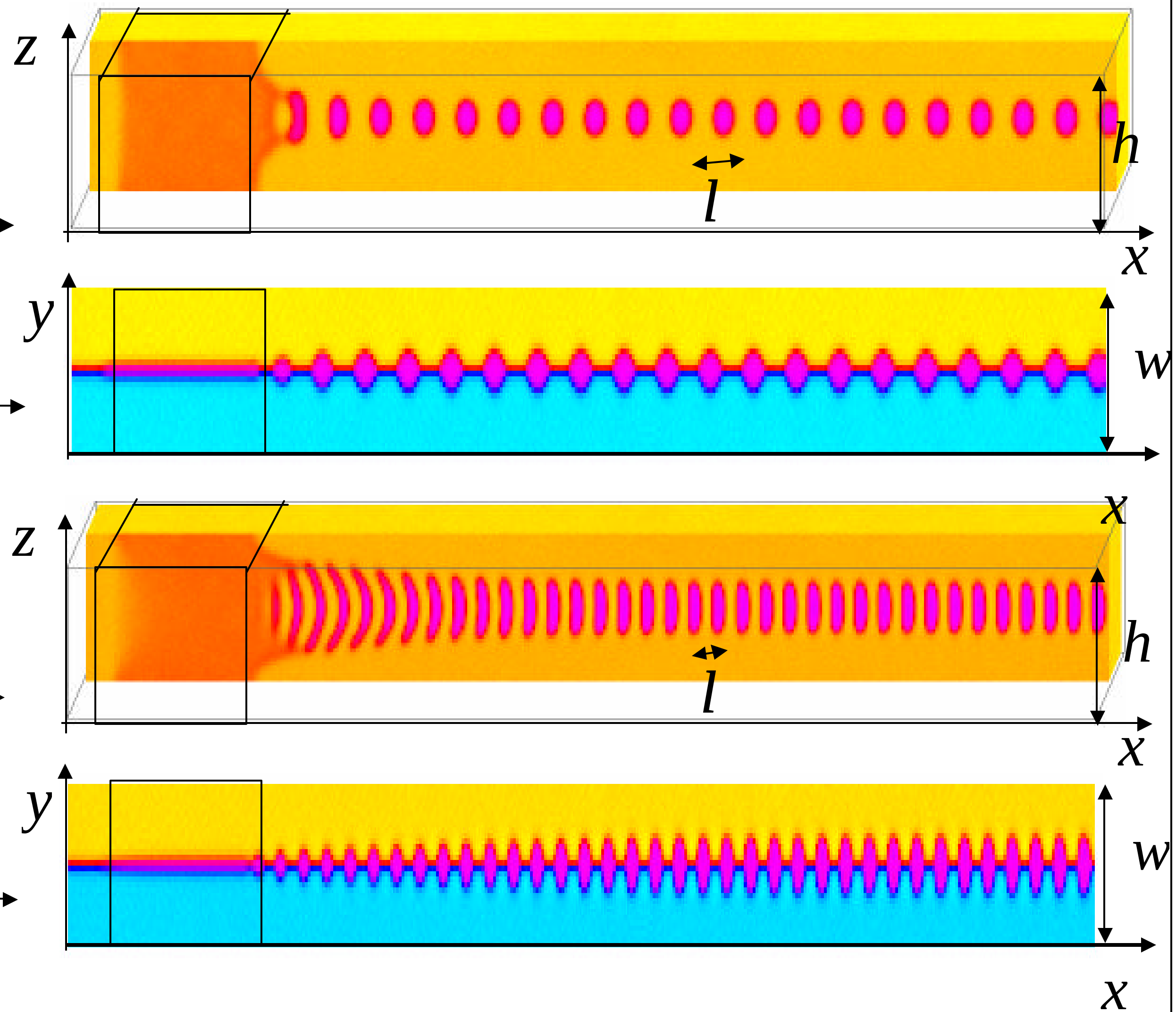
Vertical X-section (y=w/2) →

Horizontal X-section (z=h/2) →

- $H = 8 \cdot 10^{-4}$

Vertical X-section (y=w/2) →

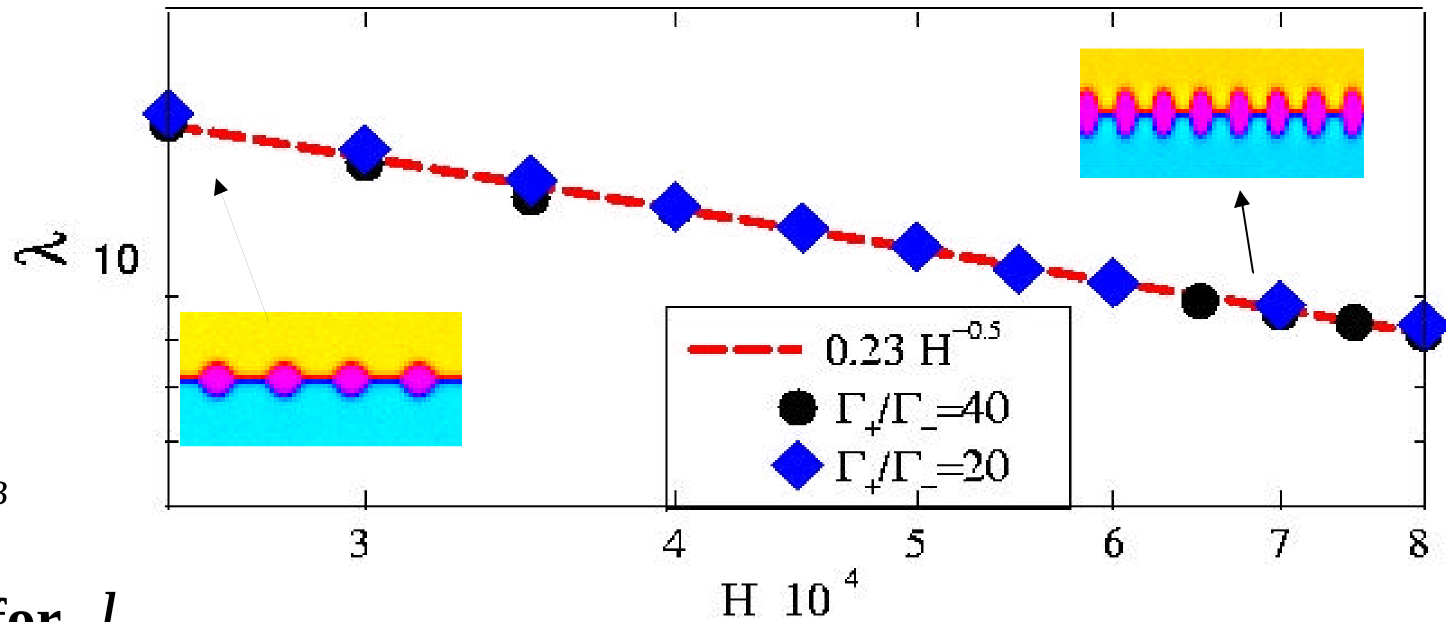
Horizontal X-section (z=h/2) →



- *l* is smaller and droplets are elongated in y & z for higher *H*

• Dependence On Imposed Pressure Gradient, *H*

- **Period in *x*-direction,** l



$\Gamma_+ = 0.05$

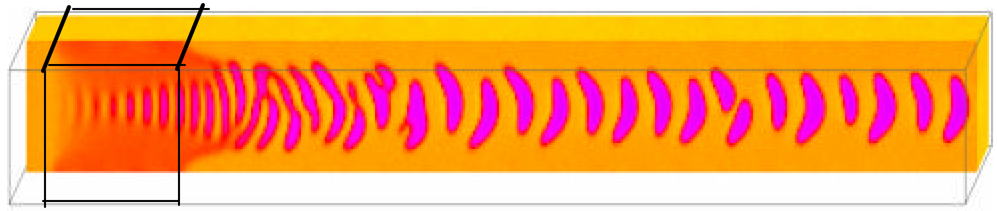
$s_{AC} = s_{AB}$

- **Scaling for** l
  - ☞ Advection time $t_{adv} \sim l \, / \, Hh^2$
  - ☞ Time of *C*-droplet formation $t_{diff} \sim M_y \, l^3 \, / \, s_{AC}$
    - ☞ Period in x: $l \sim \dfrac{1}{h}\sqrt{s_{AC} M_y \, / \, H}$

• Chaotic Pattern Formation

- ❑ **Higher *H***

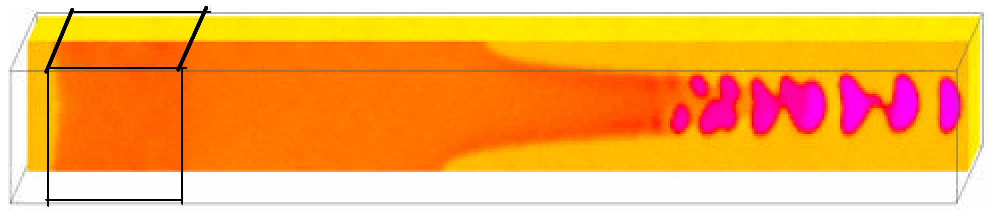
$H = 10^{-3}$



☞ *C*-Layer within reaction chamber is strongly distorted

- ❑ **Lower interfacial tension**

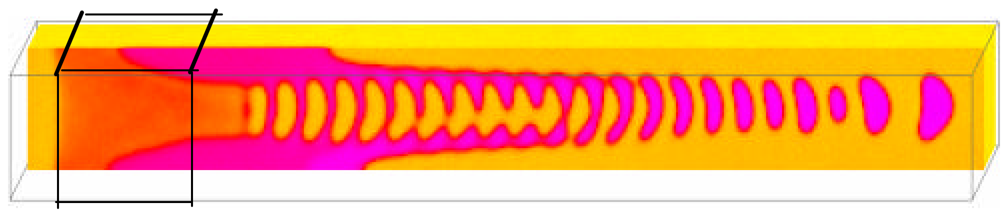
$s_{AC} << s_{AB}$



☞ *C*-Layer is advected longer (droplets do not form)

- ❑ **Higher** Γ_+ **or** $\Gamma_- = 0$

☞ Too much C

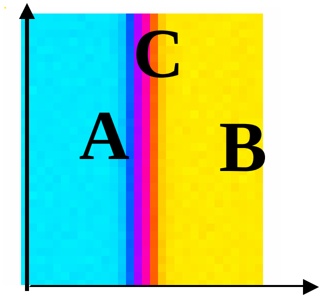


- ❑ **Chaotic patterns are observed for wide range of parameters**

☞ To observe periodic patterns $t_{diff} \approx t_{adv}; \quad l << w.$

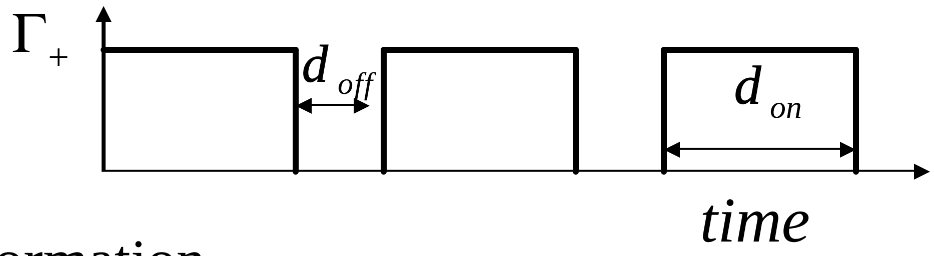
• Time Dependent Reaction Rate Coefficient

- **Light is "continuous"**



  - ☞ Role of "reaction chamber" is equivalent to 3 streams at inlet

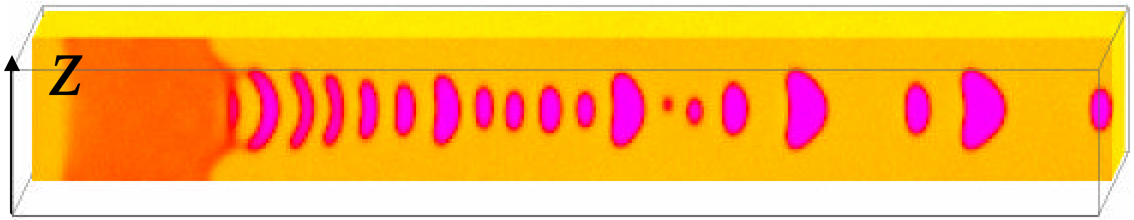
- **Light is "blinking"**



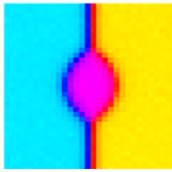
  - ☞ *in-situ* control of pattern formation

$$H = 4 \cdot 10^{-4}$$

$$d_{on} = d_{off} = 10^3$$



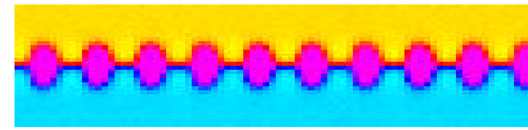
  - ☞ Sequences of droplets of different sizes

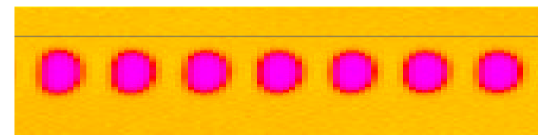


• Conclusions and Future Plans

❑ Pattern formation in ternary systems within microchannels

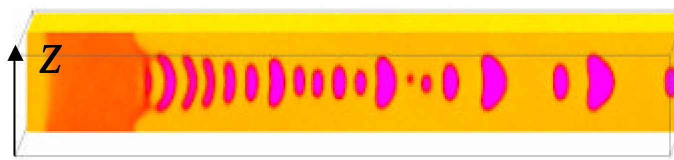
☞ C droplets are formed periodically within A/B streams





❑ Future plans

☞ Time-dependent reaction (light on & off)



☞ *in-situ* control of pattern formation

☞ Surface reactions within "reaction chamber" $\Gamma_+(z)$, $\Gamma_-(z)$

☞ Effect of hydrodynamic interactions