Mass transport at the microfluidic scale

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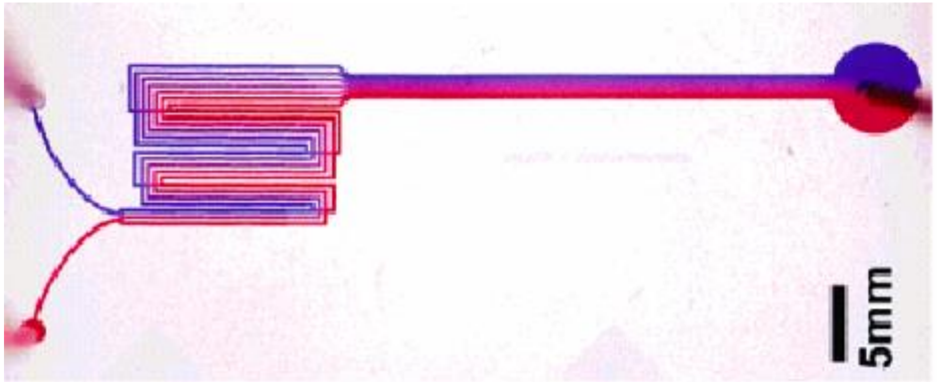
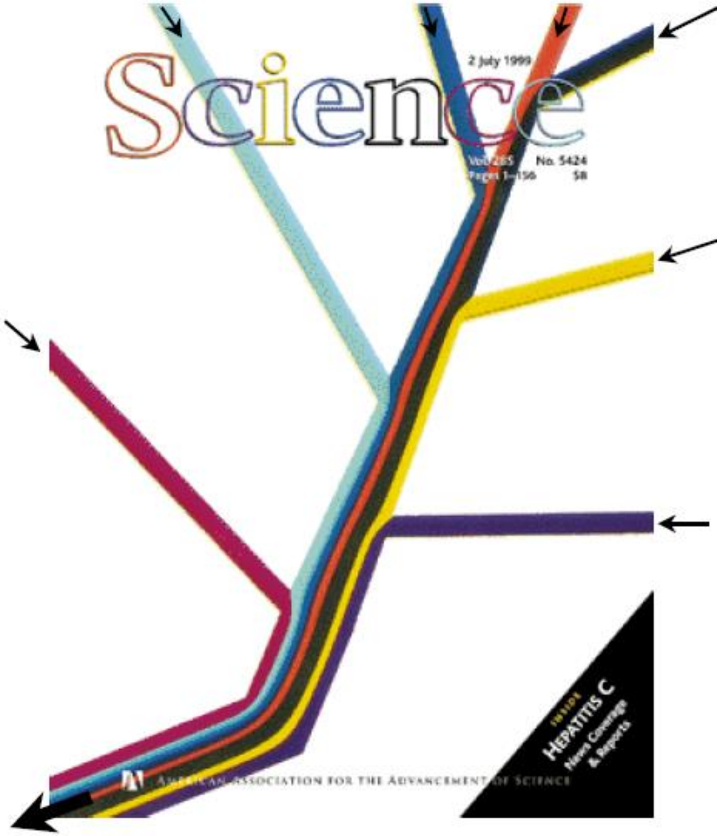
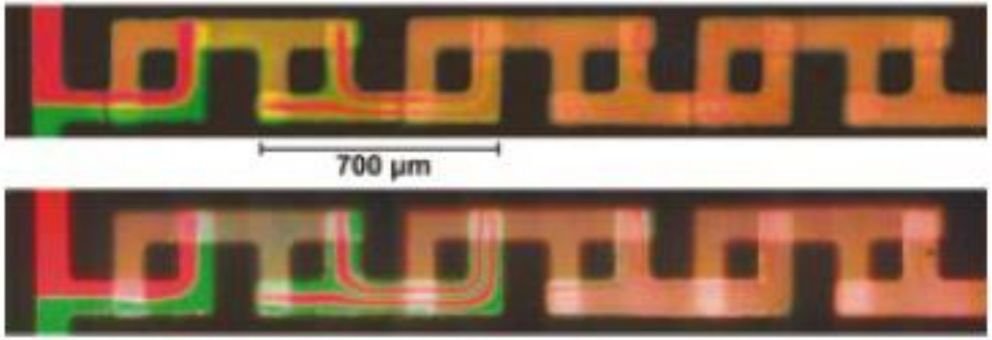


Whitesides *et al.*



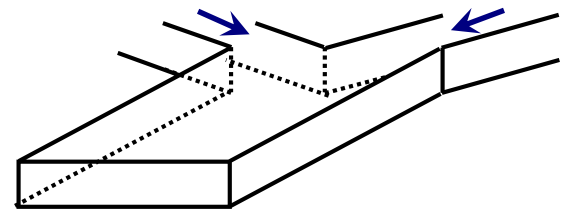
Kenis *et al.* 1999



Chen *et al.* 2004

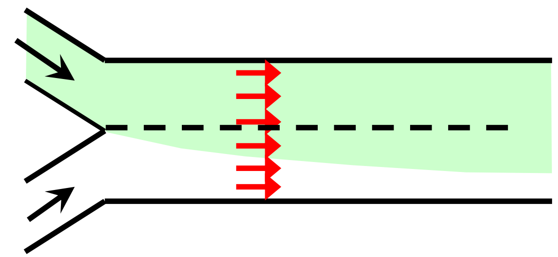
Basics

convection/diffusion, conservation equation



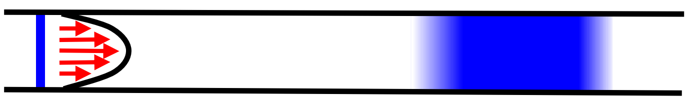
Co-flow

slow mixing, reaction-diffusion



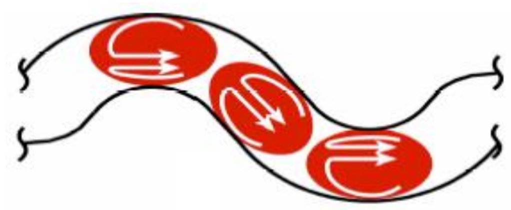
Shear dispersions

Leveque and Taylor-Aris dispersions, role of gravity, application to sensors



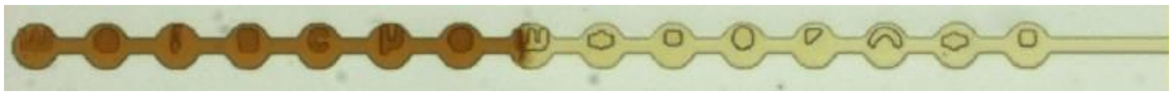
Mixing

small size, chaotic mixers, droplets



Membranes

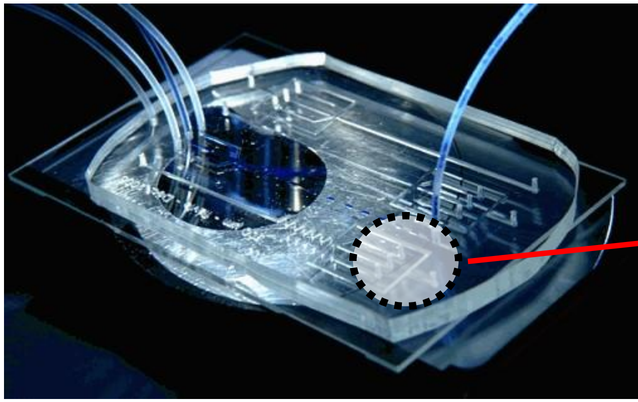
pervaporation



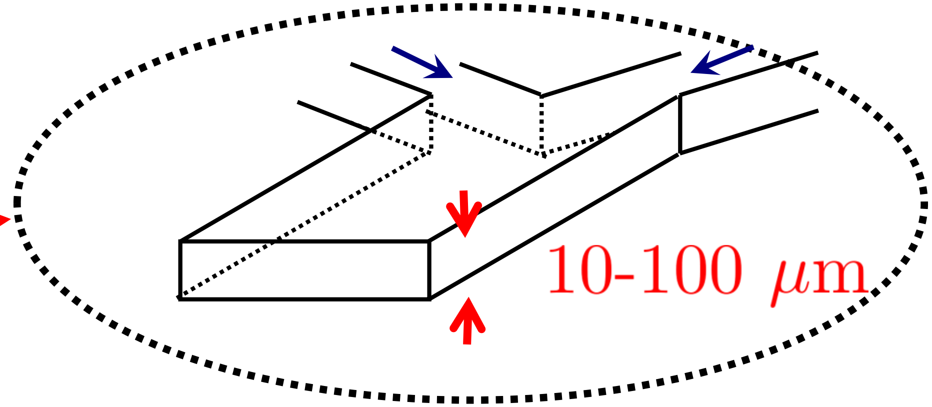
Back to the basics

(see P. Joseph's lecture)

≈ cm

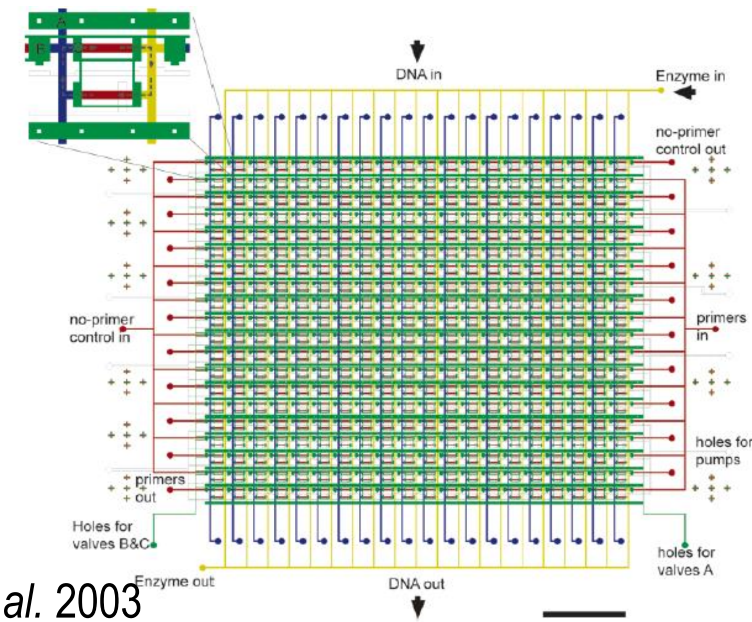


microfluidic scale



from simple geometry.... to complex "lab on chip"

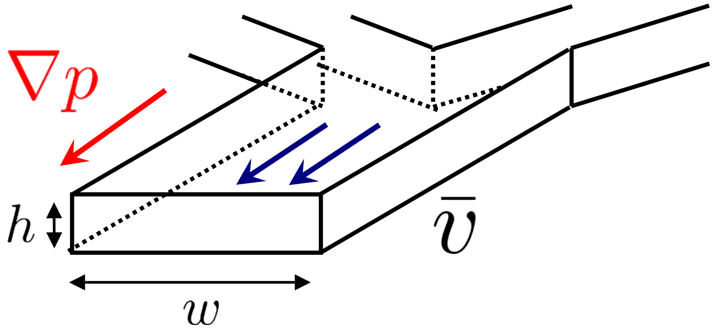
Protron MicroTeknik



Liu *et al.* 2003

Physics of microfluidics

(see M.C. Jullien's lecture)



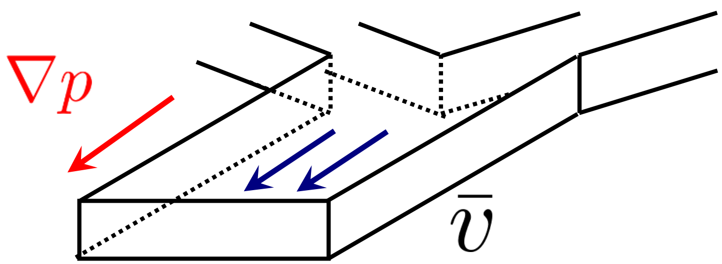
Competion viscous vs. and pressure forces

$$\nabla p = \eta \Delta v$$

+ incompressibility

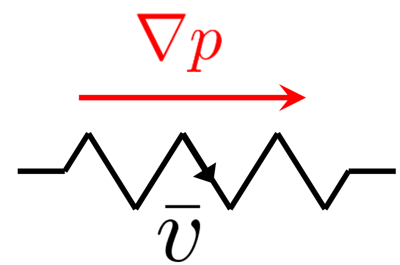
$$\nabla . v = 0$$

analogy with an "electric" circuit



$$\Rightarrow \quad \bar{v} = -\frac{k}{\eta}\nabla p$$

$\Leftrightarrow$



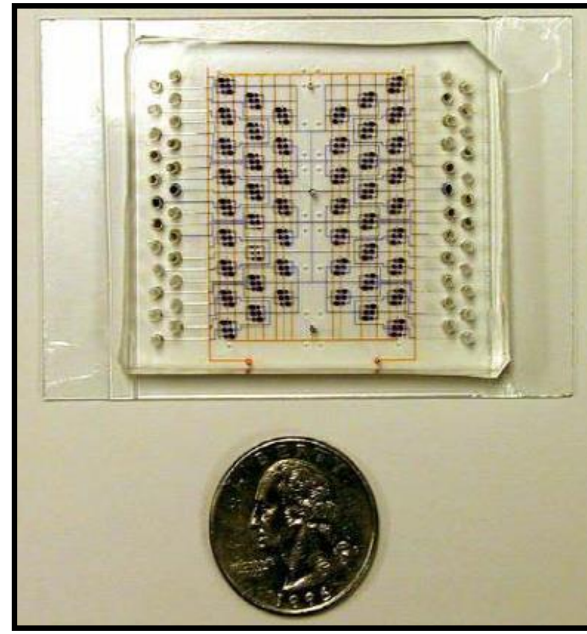
$k/\eta \approx$ "hydrodynamic conductance"

k only depends on geometry

(ex. $k \sim h^2$ for $h \ll w$)

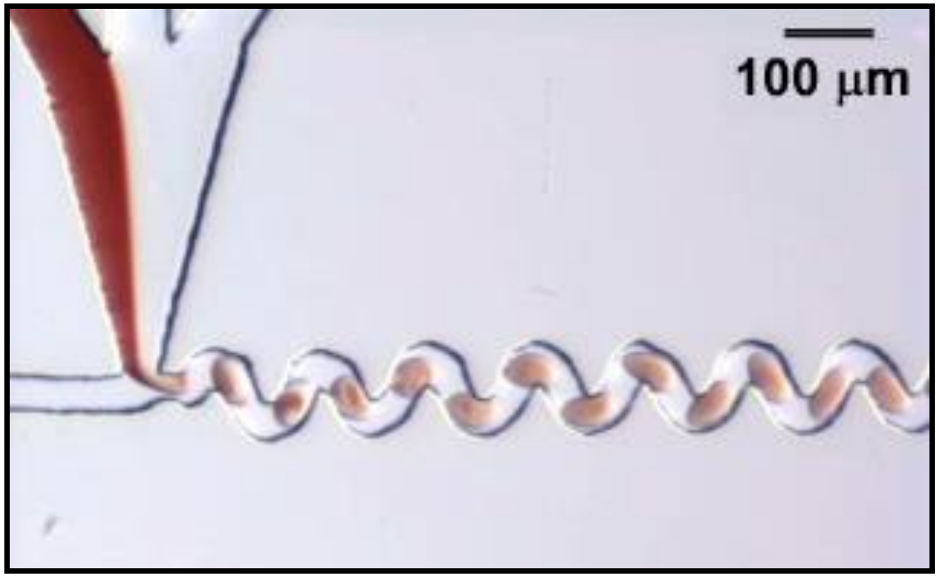
Microfluidics tools are rarely used with pure solvents only

ex. crystallization of proteins



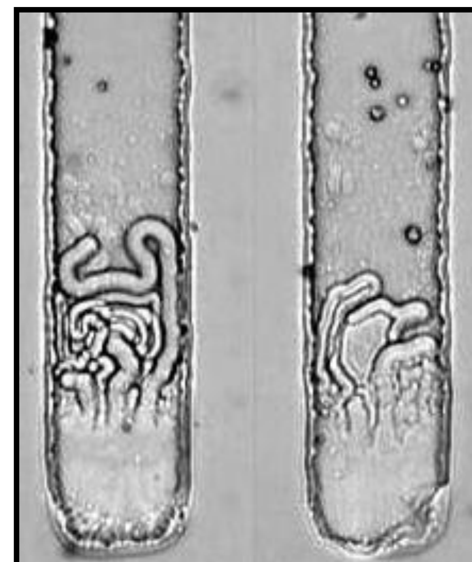
Hansen *et al.*, PNAS 2002

ex. chemistry in droplets



Ismagilov *et al.*

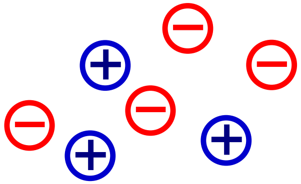
ex. "soft matter"

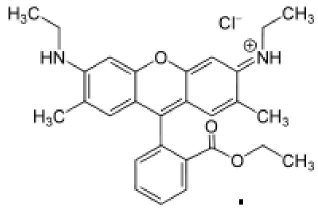


Leng *et al.*

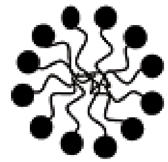
How solutes are transported?

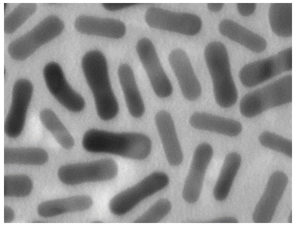
Different kind of solutes...



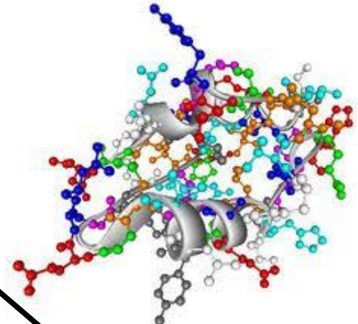


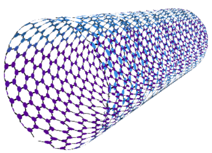
ions and small molecules (1Å - 1 nm)

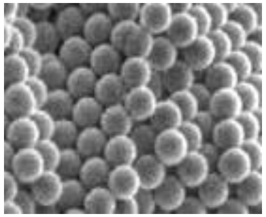




micelles, small proteins, nanoparticles (1-10 nm)







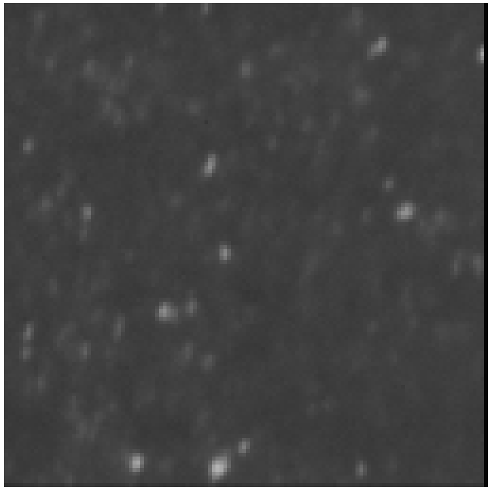
brownian motion

colloids, virus,proteins,....(10 nm - 1 µm)

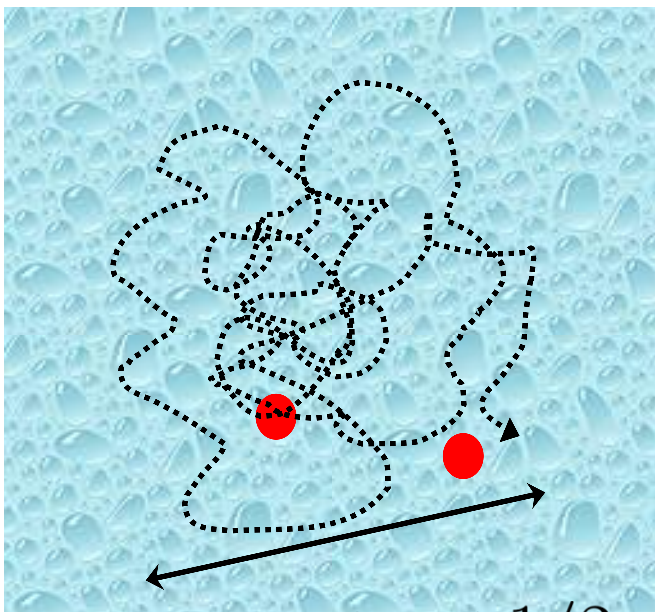
colloidal limit

cells, bacteria, ... (1-10 µm)

Brownian motion: (small) solutes move



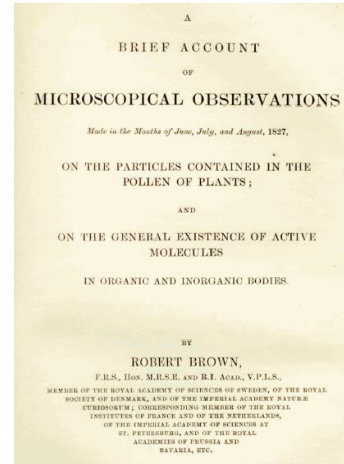
20 nm fluorescent beads in water



random motion due to thermal agitation

$$L \sim (Dt)^{1/2}$$

↑ diffusion coefficient



A

BRIEF ACCOUNT

OF

MICROSCOPICAL OBSERVATIONS

Made in the Months of June, July, and August, 1827,

ON THE PARTICLES CONTAINED IN THE POLLEN OF PLANTS;

AND

ON THE GENERAL EXISTENCE OF ACTIVE MOLECULES

IN ORGANIC AND INORGANIC BODIES.

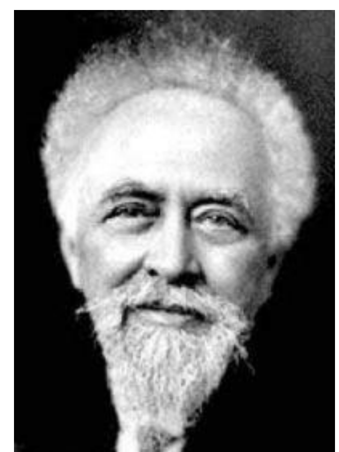
BY

ROBERT BROWN,

F.R.S., HON. M.R.S.E. AND R.I. ACAD., V.P.L.S.,

MEMBER OF THE ROYAL ACADEMY OF SCIENCES OF SWEDEN, OF THE ROYAL SOCIETY OF DENMARK, AND OF THE IMPERIAL ACADEMY NATURÆ CURIOSORUM; CORRESPONDING MEMBER OF THE ROYAL INSTITUTES OF FRANCE AND OF THE NETHERLANDS, OF THE IMPERIAL ACADEMY OF SCIENCES AT ST. PETERSBURG, AND OF THE ROYAL ACADEMIES OF PRUSSIA AND BAVARIA, ETC.

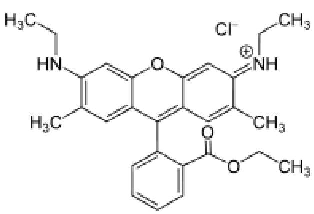
Brown (1827)

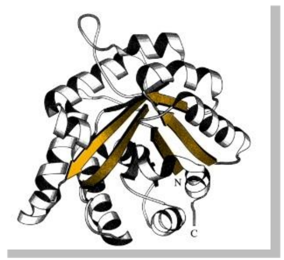
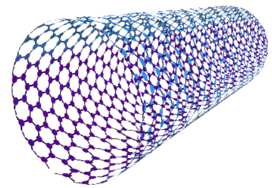
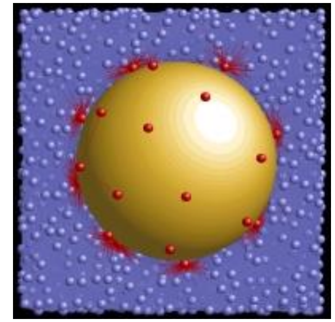


Perrin (1909)

Different values for *D*

$D \approx 10^3\ \mu m^2/s$	$D \approx 40\ \mu m^2/s$	$D \approx 2\ \mu m^2/s$	$D \approx 0.2\ \mu m^2/s$	$D \approx 0.02\ \mu m^2/s$

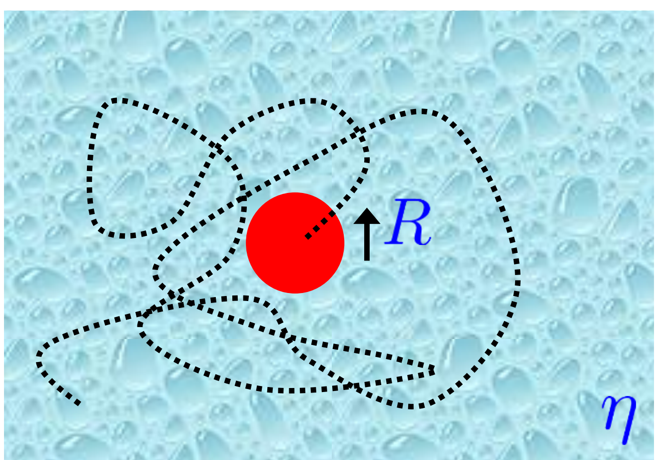



< 1 nm	5 nm	100 nm	1 µm	10 µm

colloidal limit

A simple estimate for *D*



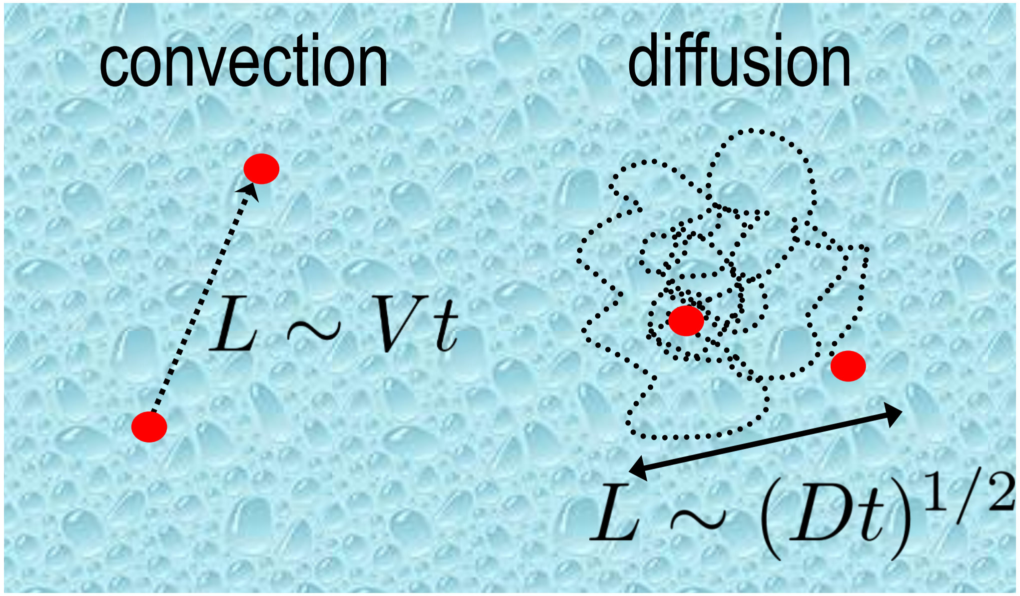
Stokes-Einstein law:

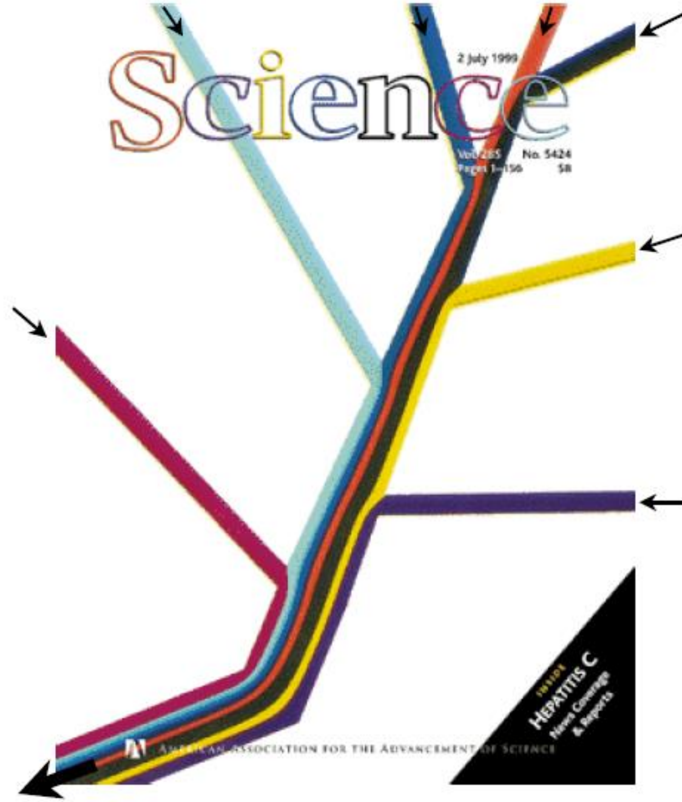
$$D = \frac{k_B T}{6\pi\eta R}$$

"motor" of diffusion

friction forces

Microfluidics: solutes also flow...



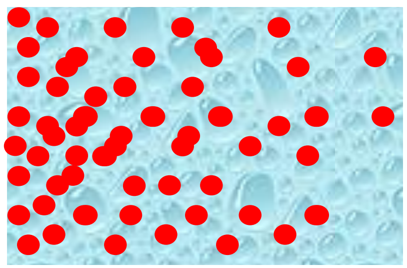


Péclet number $\mathrm{Pe} = \frac{vL}{D}$

Pe = diffusion time / convective time

$L^2/D \qquad L/v$

From "dots" to concentration fields and fluxes



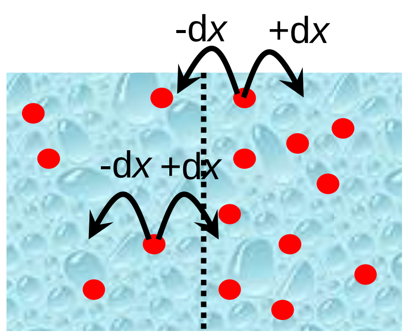
$\Rightarrow$

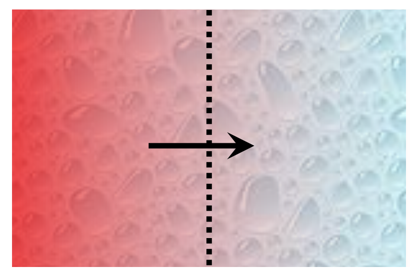
$c(x)$

concentration =

quantity / volume

Browian motion $\Rightarrow$ Fick's law



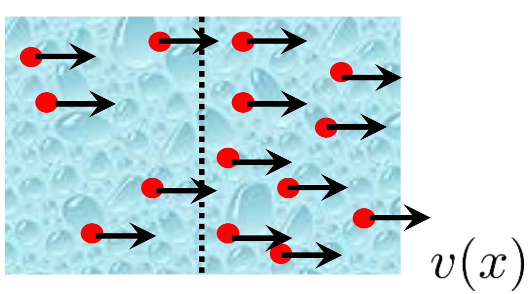


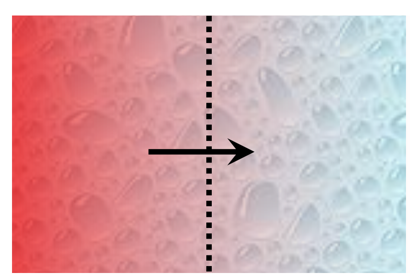
$$j(x) = -D\frac{\partial c(x)}{\partial x}$$

flux =

quantity / time & surface

Flow $\Rightarrow$ convection flux





$$j(x) = c(x)v(x)$$

flux =

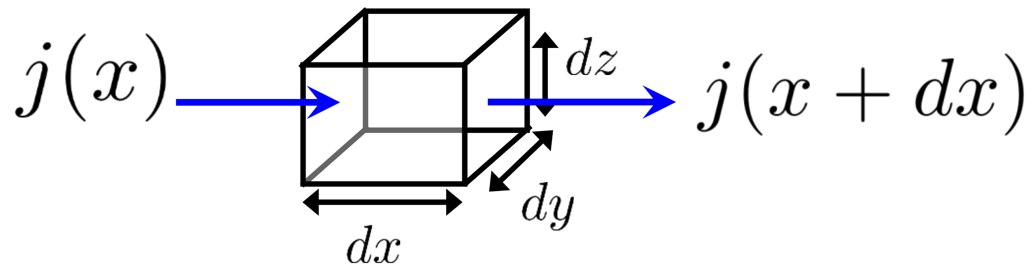
quantity / time & surface

Conservation equation

$c(x,y,z)$ concentration

diffusion/convection flux

$j = -D\nabla c + cv$

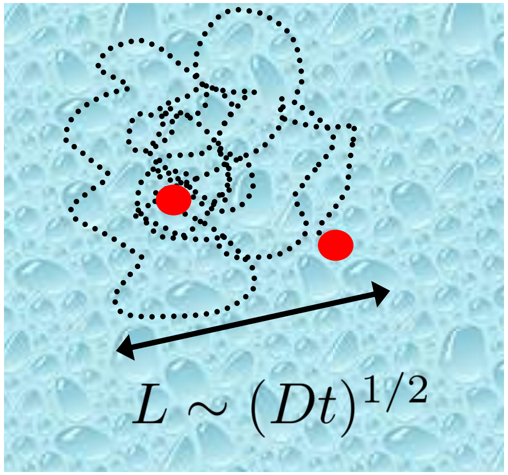


$$\frac{dN}{dt} = -(j(x+dx) - j(x))dydz + \ldots$$

$$\Rightarrow \qquad \frac{\partial c}{\partial t} + \nabla . j = 0$$

$$\Rightarrow \qquad \frac{\partial c}{\partial t} + \underbrace{v.\nabla c}_{\text{convection}} = \underbrace{D\Delta c}_{\text{diffusion}} \underbrace{+R}_{\text{reaction}}$$

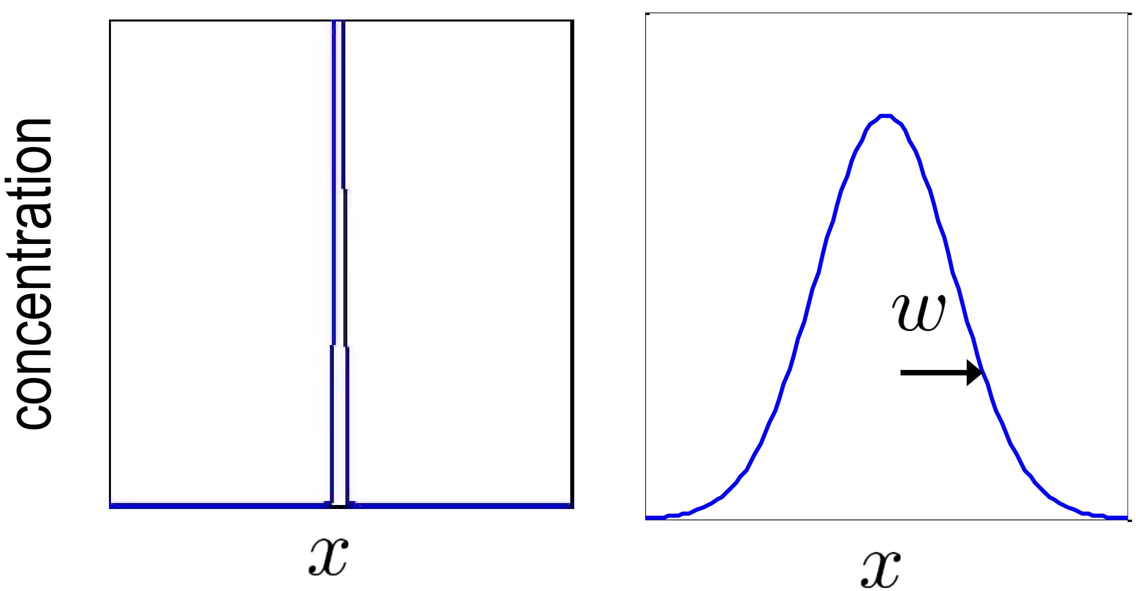
(i) Some "classical" cases: spreading through diffusion



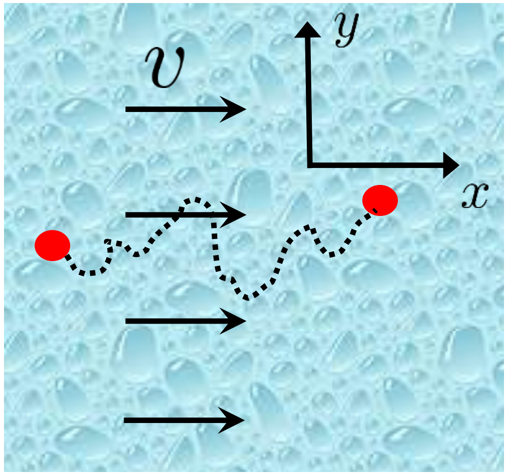
$$\frac{\partial c}{\partial t} = D\Delta c$$

$$c(x, t = 0) = c_0\delta(x)$$

$$c(x, t) = \frac{c_0}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$



$$w \sim \sqrt{Dt}$$

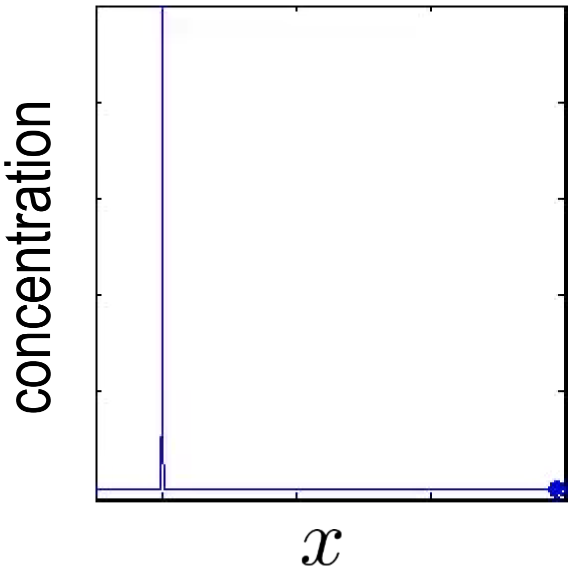


...and with a uniform flow

$$\frac{\partial c}{\partial t} + v.\nabla c = D\Delta c$$

$$c(x, t = 0) = c_0 \delta(x)$$

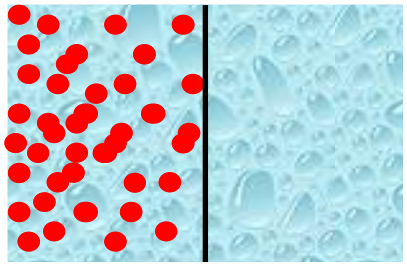
$$c(x,t) = \frac{c_0}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x-vt)^2}{4Dt}\right)$$



$\Rightarrow$ no coupling:

- diffusion & convection along *x*
- diffusion along y

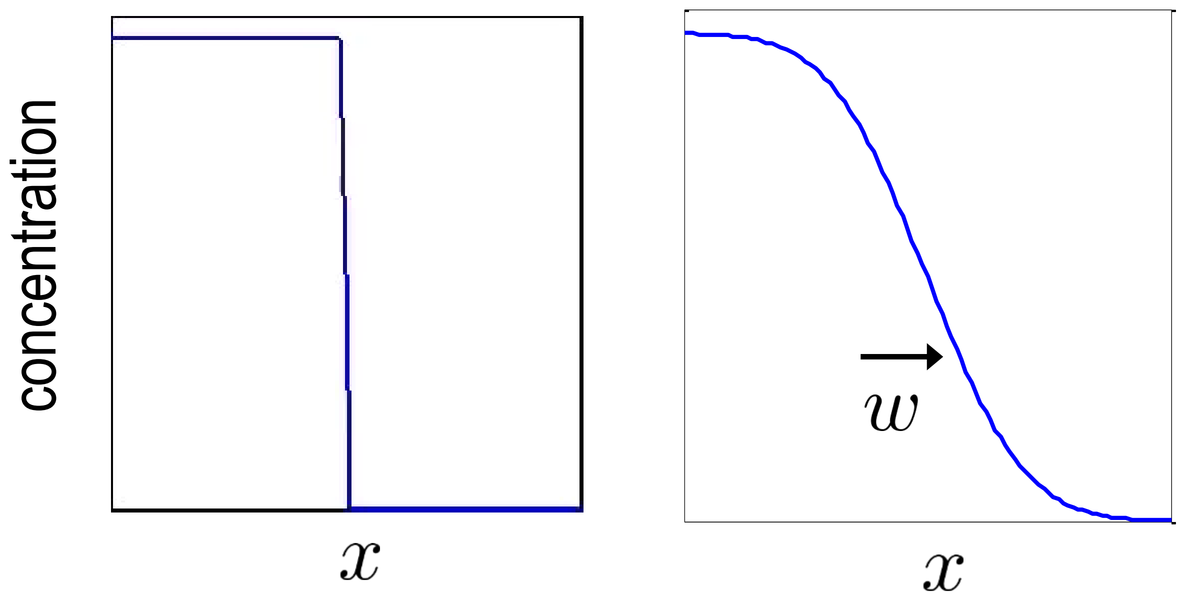
(ii) Some "classical" cases: connecting two reservoirs



$$\frac{\partial c}{\partial t} = D\Delta c$$

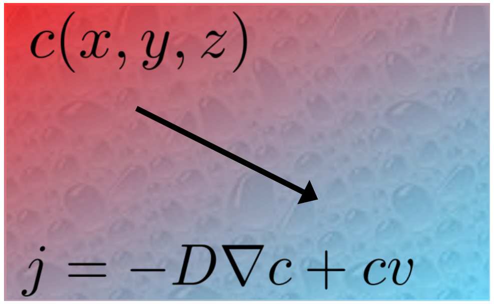
$$c(x, t=0) = c_0 H(x)$$

$$c(x,t) = 1 + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



$$w \sim \sqrt{Dt}$$

Parenthesis: an analogy



$$\partial_t c + \underbrace{v.\nabla c}_{\text{convection}} = \underbrace{D\Delta c}_{\text{diffusion}}$$

$$\mathrm{Pe} = \frac{vL}{D}$$ convection/diffusion

An analogy with the Navier Stokes equation ?

$$\rho(\partial_t + v.\nabla)v = \eta\Delta v - \nabla p$$

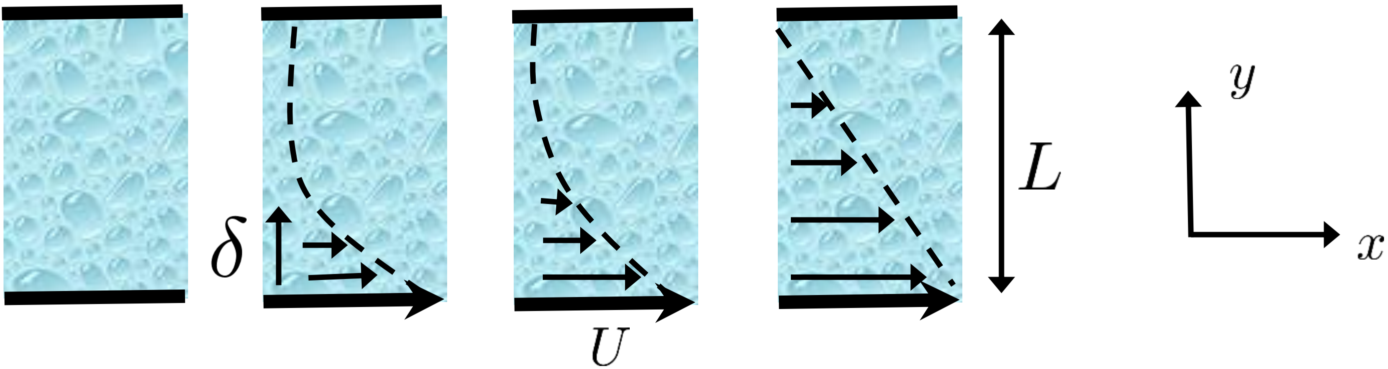
$$\mathrm{Re} = \frac{\rho L v}{\eta} = \frac{vL}{\nu}$$ inertial/viscous effects

$\Rightarrow$ $\nu = \eta/\rho$ is the « diffusion » coefficient of the impulsion

$\Rightarrow$ hydrodynamics = transport of « impulsion »

$\Rightarrow$ $\mathrm{Re} \ll 1$ "diffusion" of impulsion is immediate

Example: start-up of a flow



Navier-Stokes $\rho\partial_t v = \eta\partial_y^2 v$ $\Leftrightarrow$ diffusion equation with $\nu = \eta/\rho$

$\Rightarrow$ « diffusion from a reservoir » $\delta^2 \sim \nu t$

developed profile for $\tau \sim L^2/\nu$

Note: microfluidics ?
water, L = 10 µm, τ = 0.1 ms

multimedia fluid mechanics

The same is true for energy...

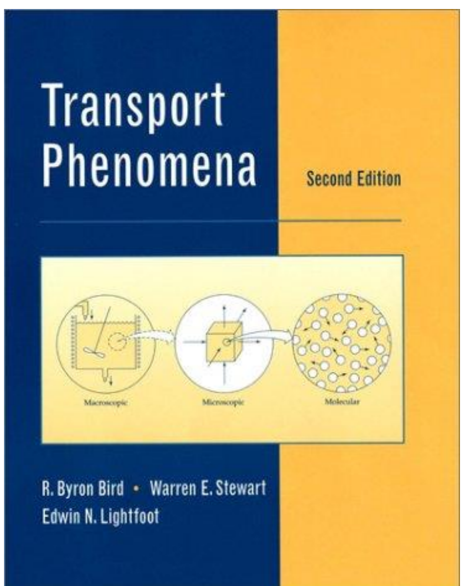
$$\partial_t c + v.\nabla c = D\Delta c$$ mass transport

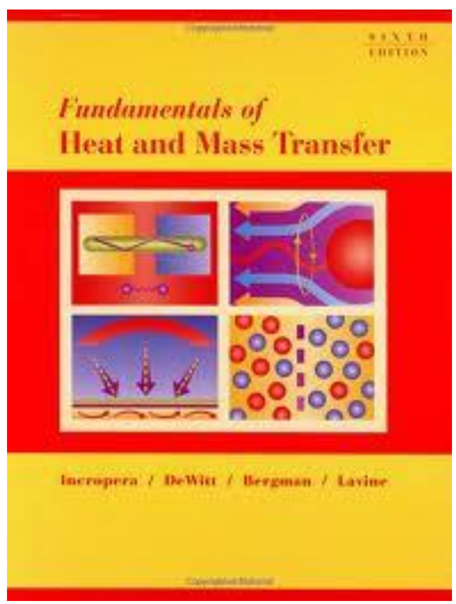
$$\rho(\partial_t + v.\nabla)v = \eta\Delta v - \nabla p$$ hydrodynamics

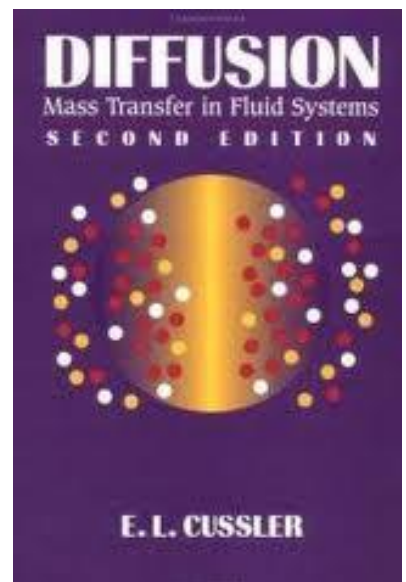
$$\rho C_p(\partial_t + v.\nabla)T = \lambda\Delta T + S$$ thermal transfers

+ coupling terms

Some books:

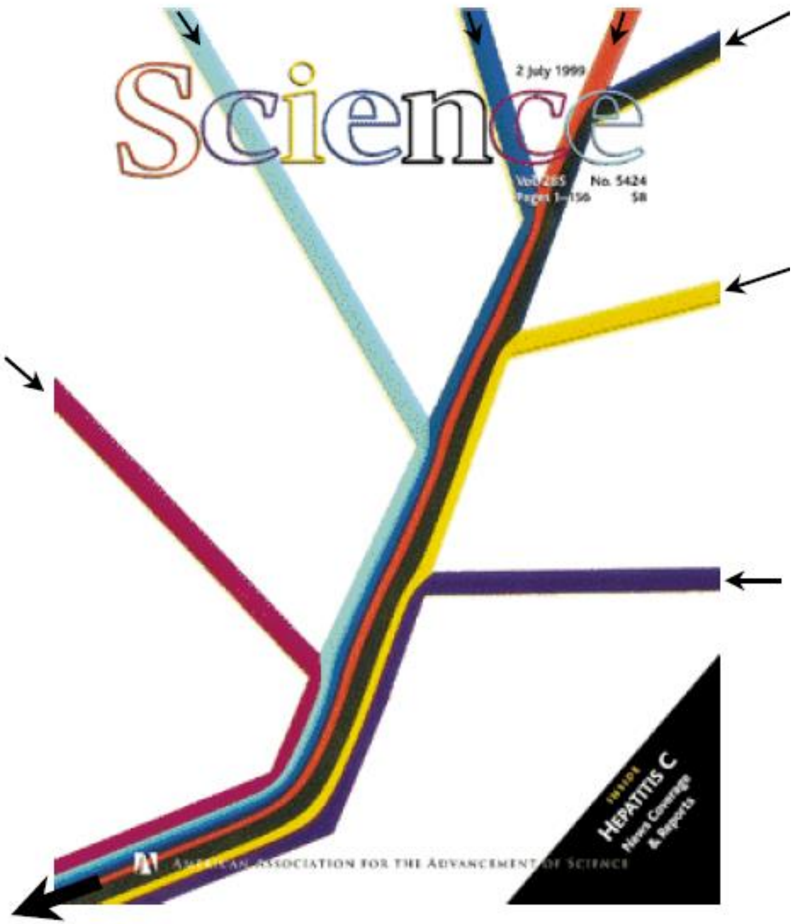


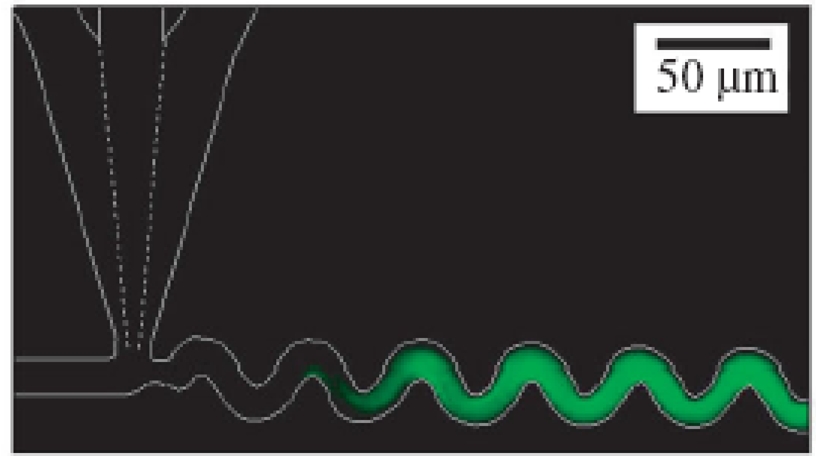


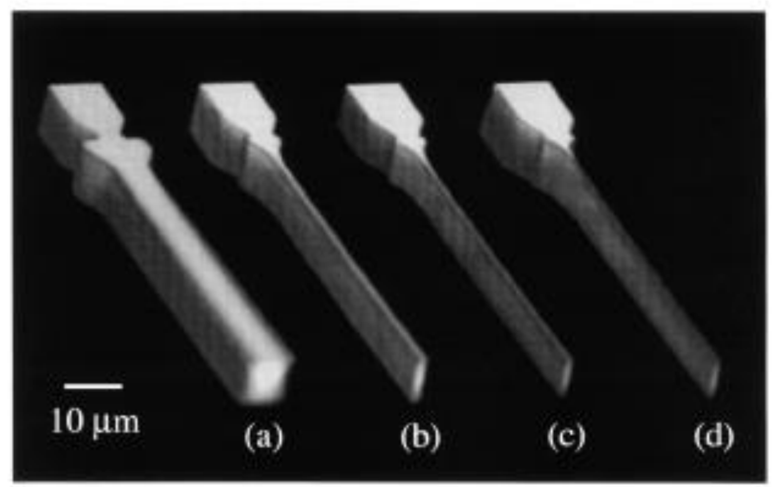


(...)

General remarks on mass transport







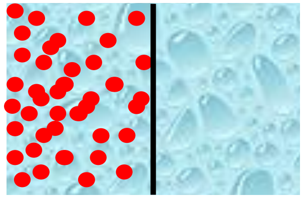
⇒ studies often concern very dilute solutions

Real life is more complex...

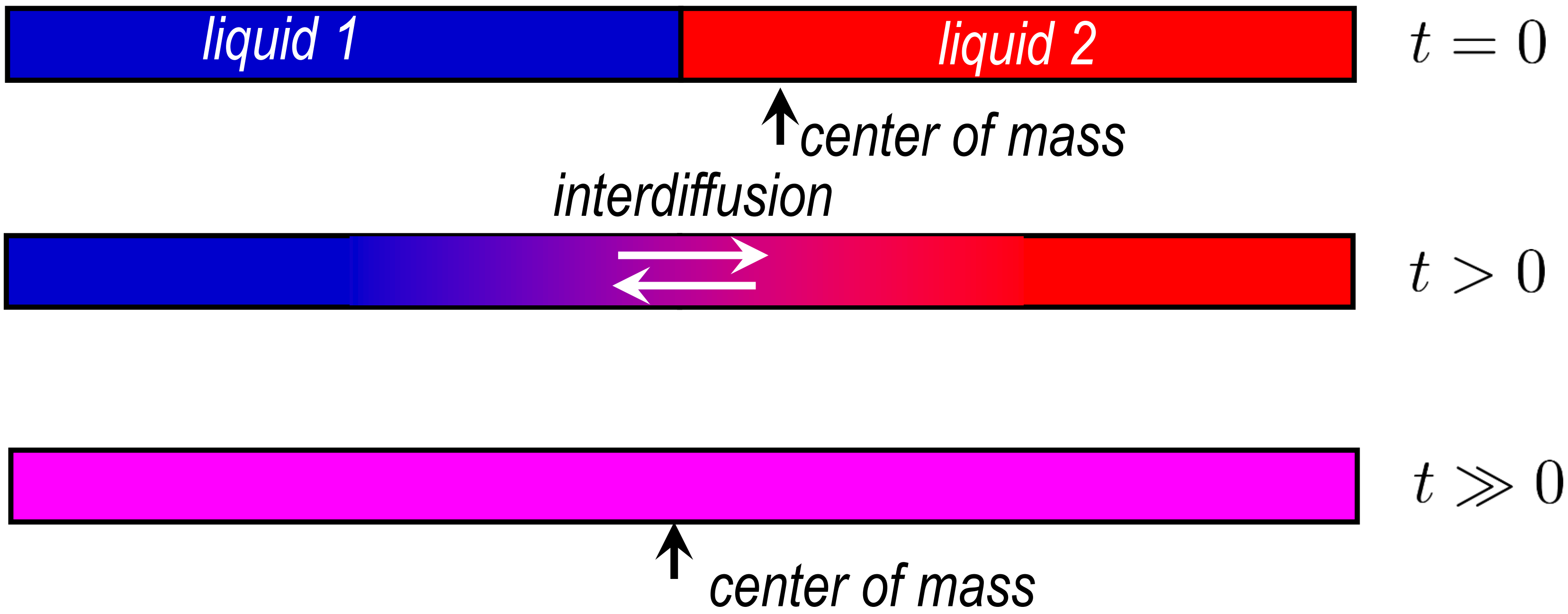
solvants & concentrated solutions

complex fluids

$\Rightarrow$ concentrated systems ? complex fluids ? etc...

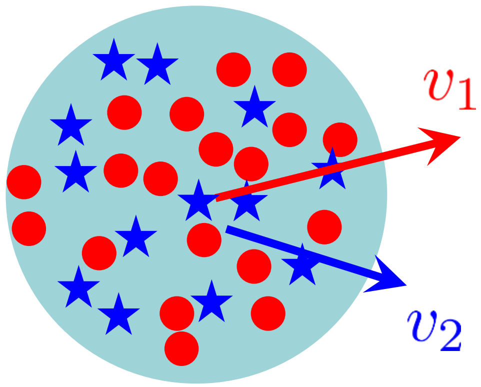


Ex .1: concentrated liquid solutions



diffusion $\Longrightarrow$ convection of mass

$\rightarrow$ reference frame is important



Ex. 1: concentrated solutions

the case of a binary system

Mass-averaged velocity

$$\rho v = \rho_1 v_1 + \rho_2 v_2$$

mass fraction

$$\rho_i = \rho w_i$$

Solute mass conservation

$$\partial_t \rho_i + \nabla(\rho_i v_i) = 0$$

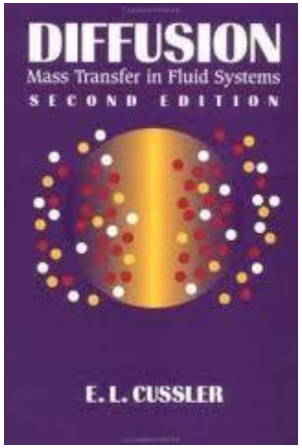
Global mass conservation

$$\partial_t \rho + \nabla(\rho v) = 0$$

General definition of diffusion

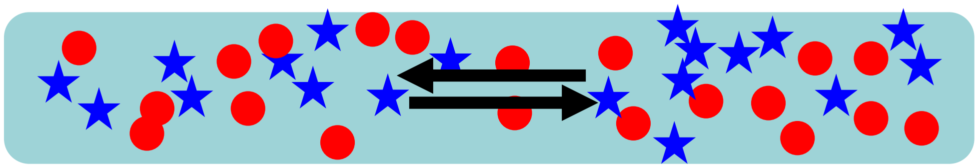
$$\rho_i v_i = \rho_i v - D\rho\nabla w_i$$

$\rightarrow$ importance of the reference frame
(mass/ volume/molar- averaged velocity)



Ex. 2: the case of multicomponent systems

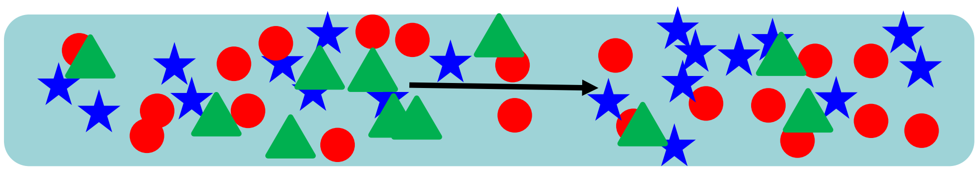
binary system: one diffusion coefficient (interdiffusion)



$$w_1 + w_2 = 1$$

$$-\rho D_i \nabla w_i = -\rho_i (v_i - v) \qquad D_1 = D_2$$

ternary systems: 4 diffusion coefficients



$$\Sigma w_i = 1$$

$$J_1 = (v_1 - v^0)c_1 = -D_{11}\nabla c_1 - D_{12}\nabla c_2$$

$$J_2 = (v_2 - v^0)c_2 = -D_{21}\nabla c_1 - D_{22}\nabla c_2$$

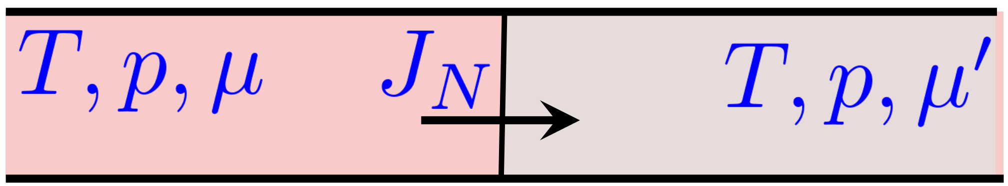
reference frame

possible cross-terms…

Ex. 3: more insights into D

Back to thermodynamics:

flux driven by a difference of a chemical potential



Linear response of irreversible processes

$$J_N = -L_{NN} \nabla \frac{\mu}{T}$$

$$J_N = -\frac{L_{NN}}{T} \frac{\partial \mu}{\partial c} \nabla c$$ Fick's law

$$D = \frac{L_{NN}}{T} \frac{\partial \mu}{\partial c}$$

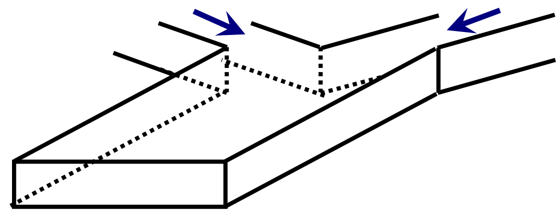
kinetics (→ $\frac{L_{NN}}{T}$) thermodynamics (→ $\frac{\partial \mu}{\partial c}$)

remember for colloids

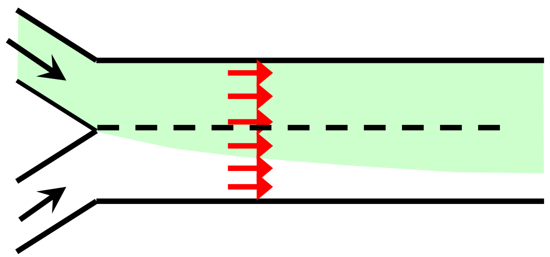
$$D = \frac{k_B T}{6 \pi \eta R}$$

e.g. Pottier, 1997

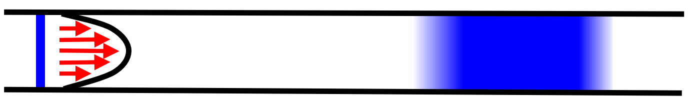
Basics
convection/diffusion, conservation equation



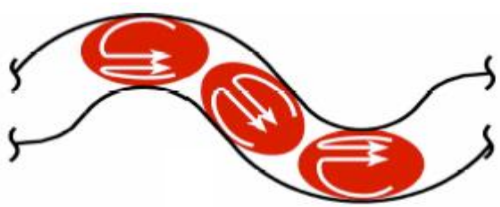
Co-flow
slow mixing, reaction-diffusion



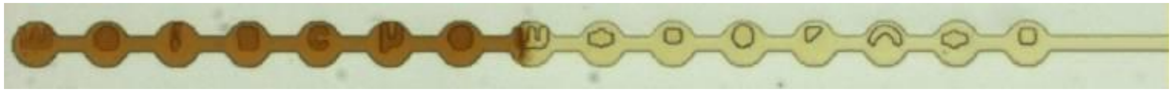
Shear dispersions
Leveque and Taylor-Aris dispersions, role of gravity, application to sensors



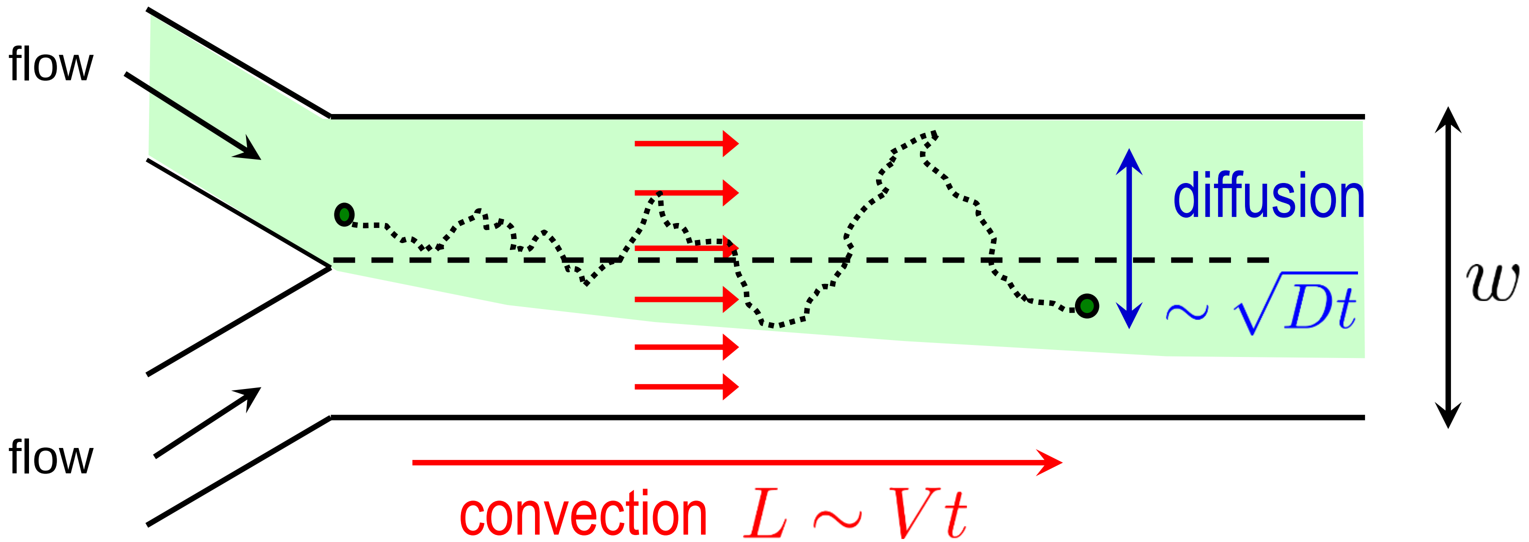
Mixing
small size, chaotic mixers, droplets



Membranes
pervaporation



Back to microfluidics: mixing in a coflow (a simple view)

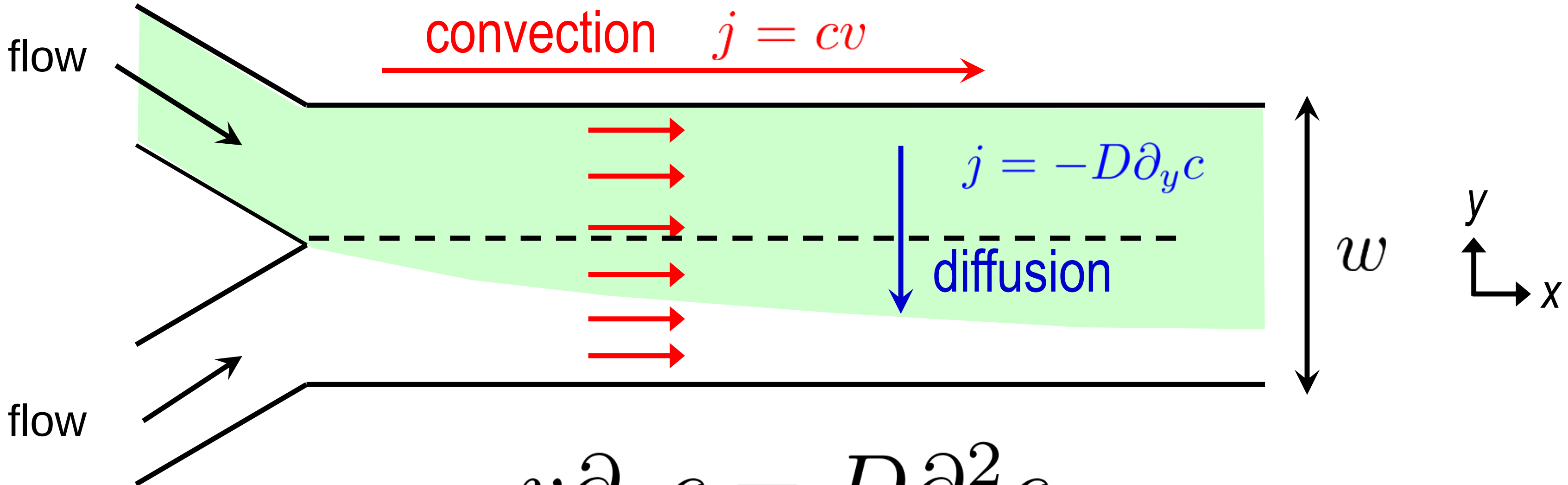


Complete mixing for $\tau \sim w^2/D$ (through diffusion)

Convection during $\tau \sim w^2/D$ $\Rightarrow$ $L \sim vw^2/D = \mathrm{Pe}\,w$

large Péclet $\Rightarrow$ long channels for efficient mixing

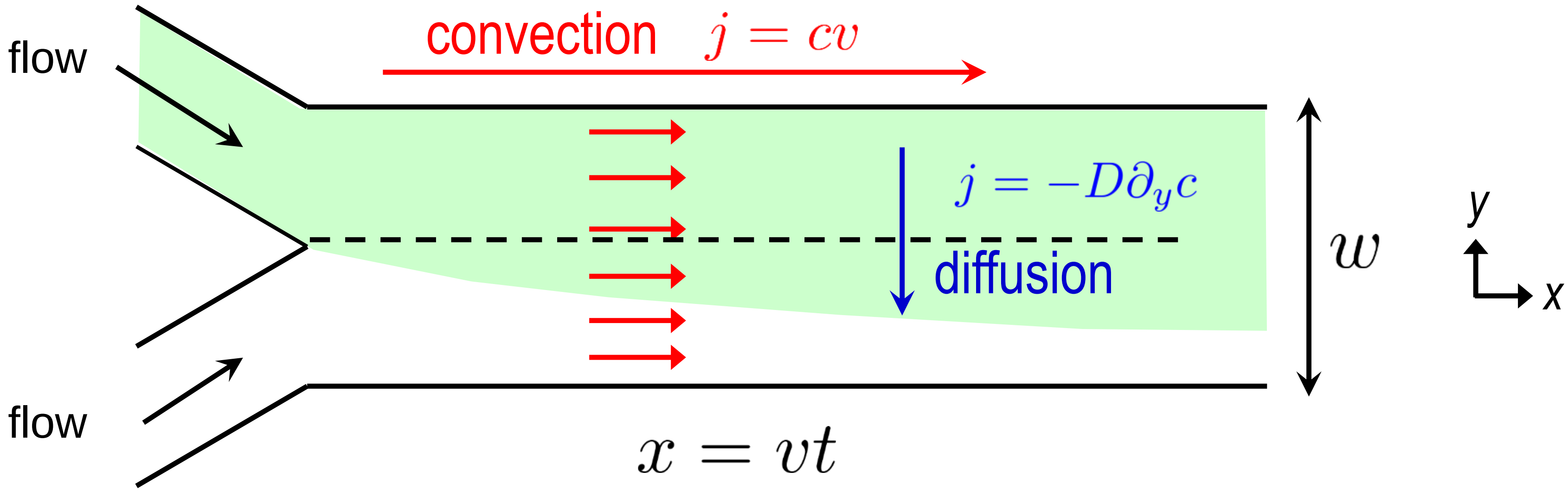
Mixing in a coflow: concentration fields



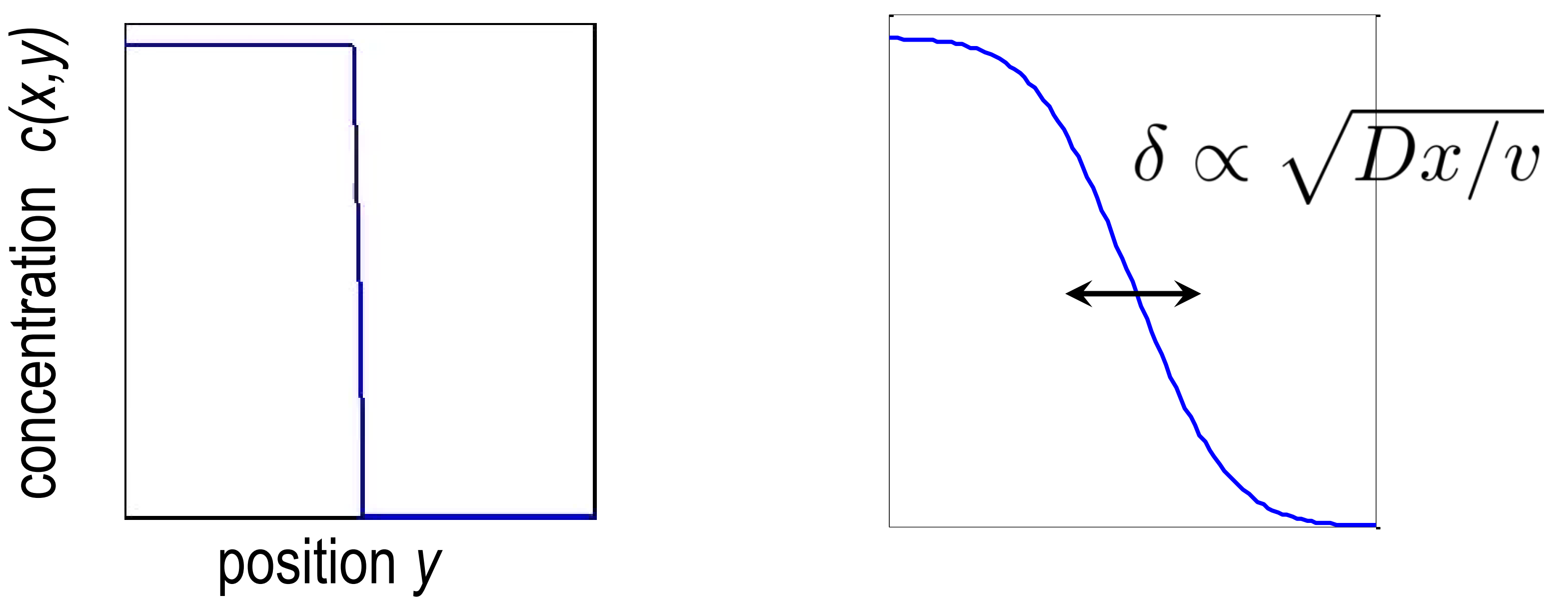
$$\Rightarrow \quad \underbrace{v\partial_x c}_{\text{convection}} = \underbrace{D\partial_y^2 c}_{\text{diffusion}}$$

$\Leftrightarrow \quad \partial_t c = D\partial_y^2 c$ with change of variable $x = vt$

$\Rightarrow$ co-flow is a good tool to investigate *steady kinetics*

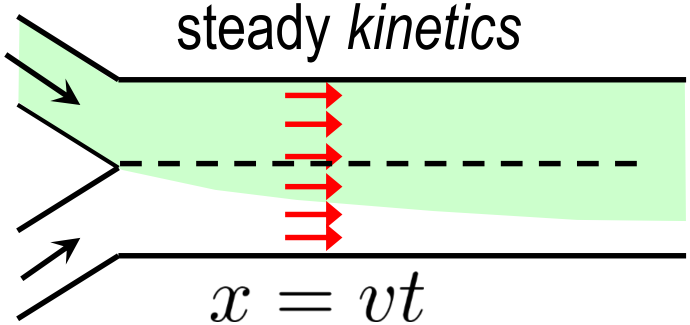


$$\Rightarrow \quad v\partial_x c = D\partial_y^2 c$$

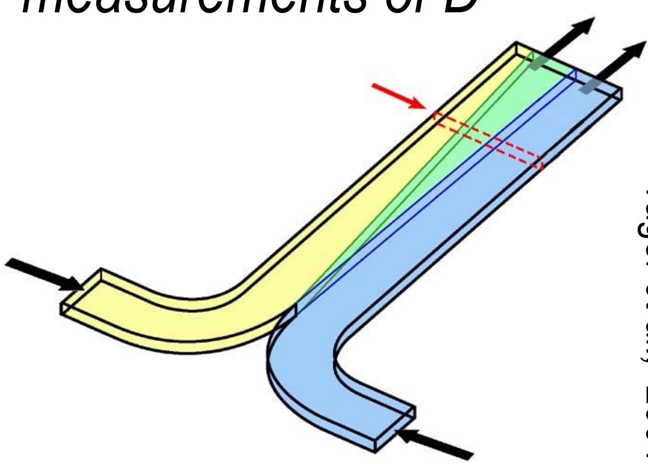


Some applications: data acquisiton

$v \approx$ 10 µm/s - 1 cm/s
w = 100 µm
$\tau = v/w$ = 10 s - 10 ms

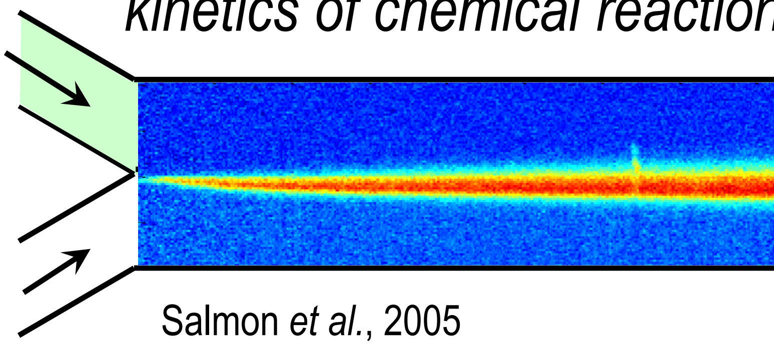


measurements of D



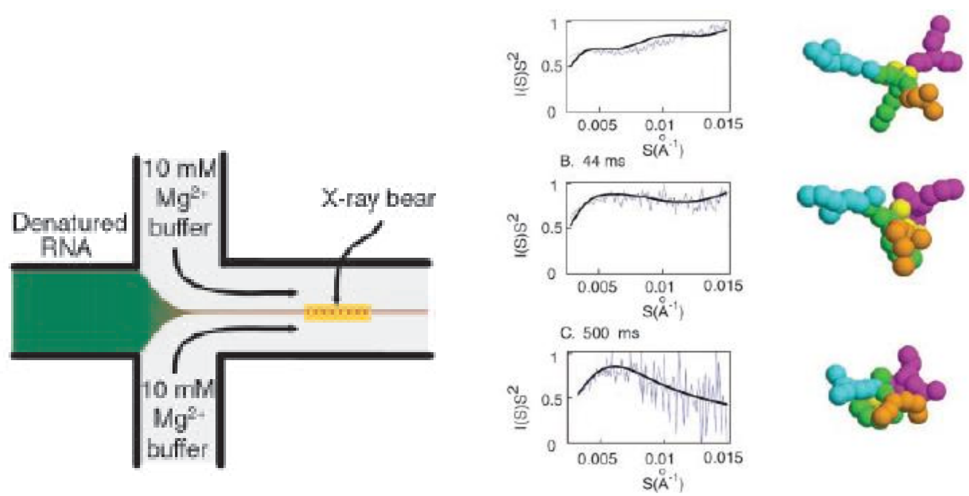
Yager *et al.*, 2001

kinetics of chemical reactions



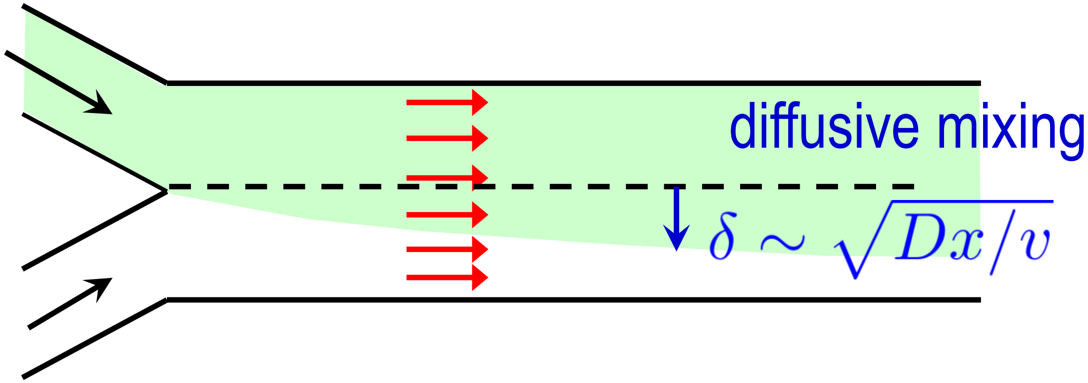
Salmon *et al.*, 2005

kinetics of protein folding



Pollack *et al.*, 2002

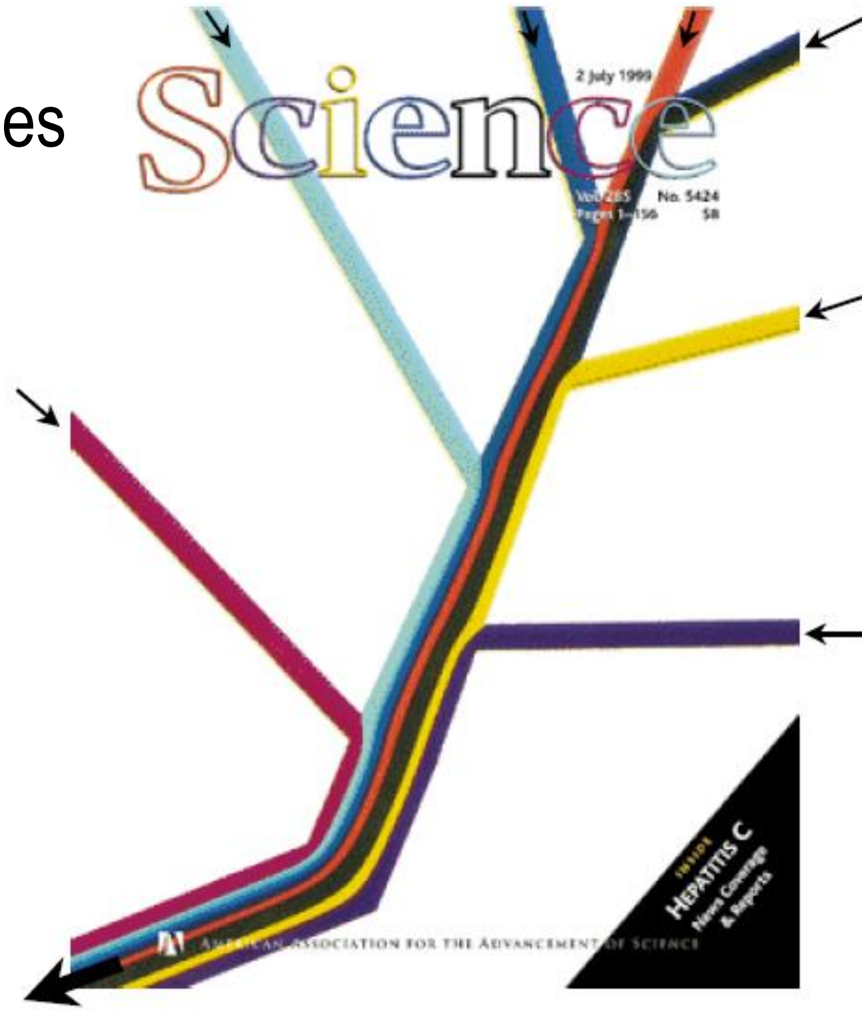
Mixing is slow: some opportunities



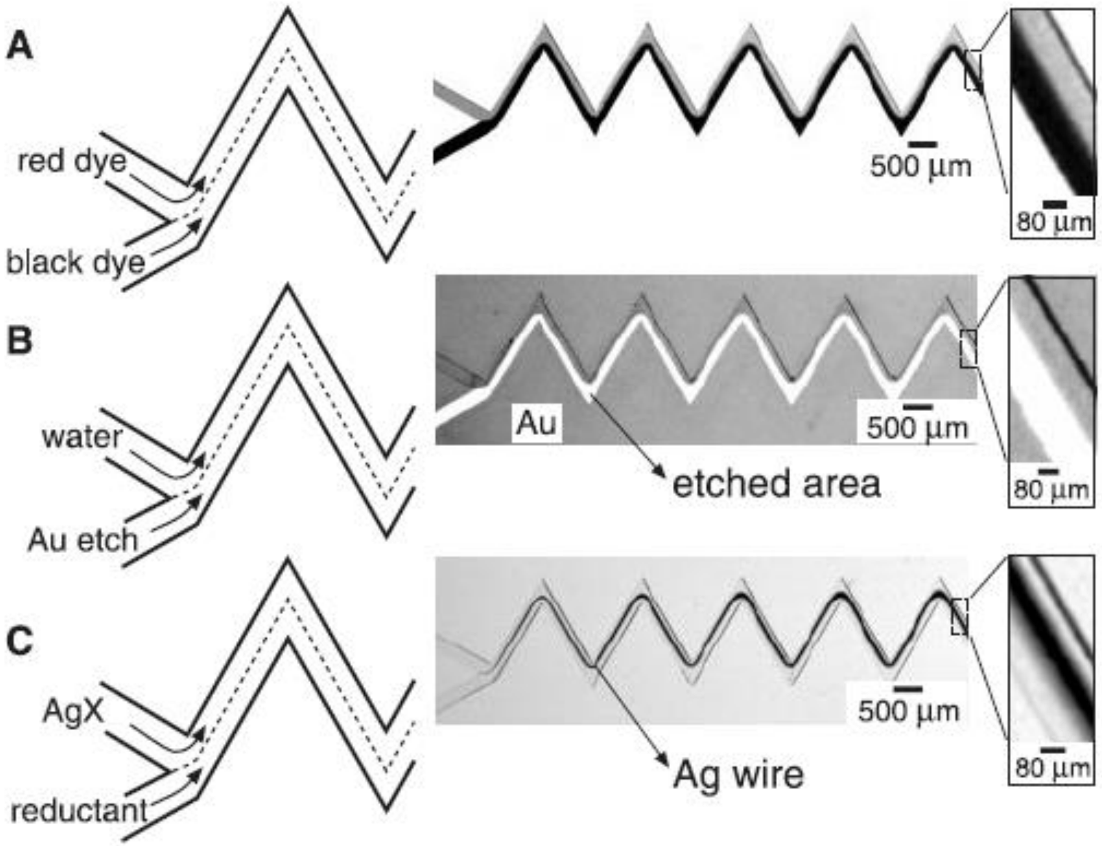
small width of diffusion at high velocities

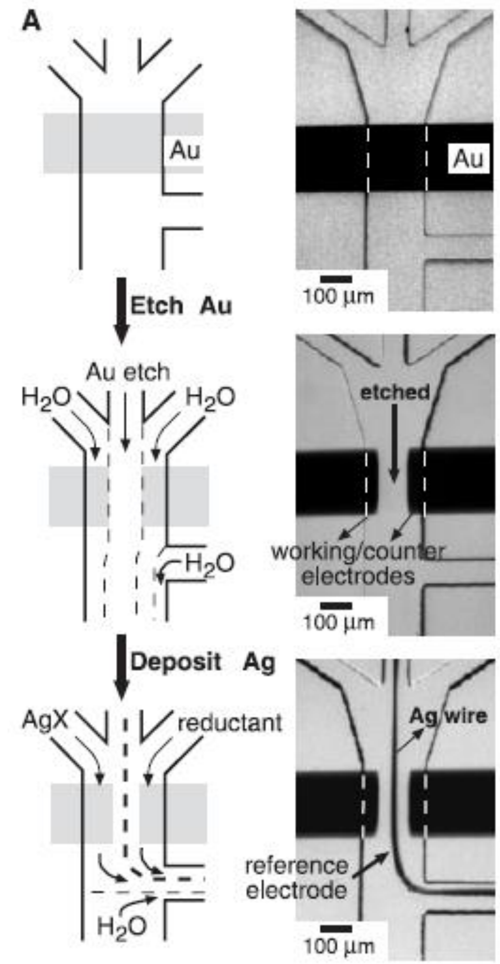
ex: $D = 10^{-10}$ m^2/s, v = 10 cm/s, δ < μm

$\Rightarrow$ possibility to control complex patterns



Mixing is slow: generating microstructures



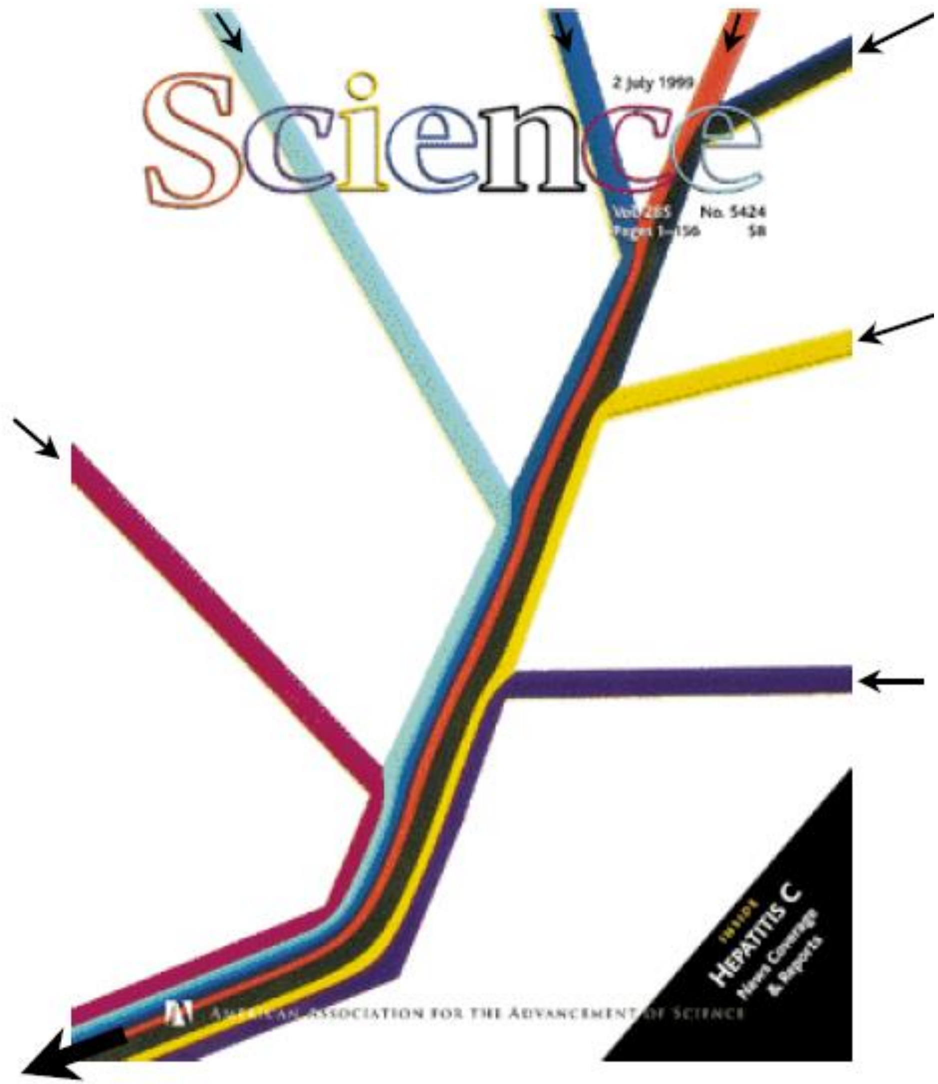


Kenis *et al*., 1999

Mixing with a co-flow ?

1/ molecular dyes $D \approx 10^3$ µm^2/s, $w \approx 100$ µm, v ≈ 1 cm/s

⇒ Pe = 1000, mixing after 10 cm



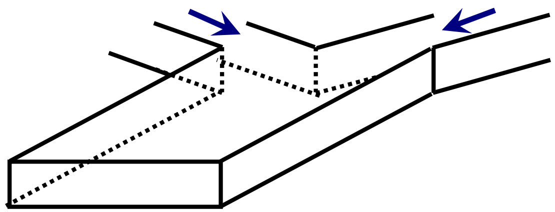
2/ colloidal species, $D \approx 1$ µm^2/s

⇒ Pe = 10^6, mixing after 100 m...

⇒ need for strategies...

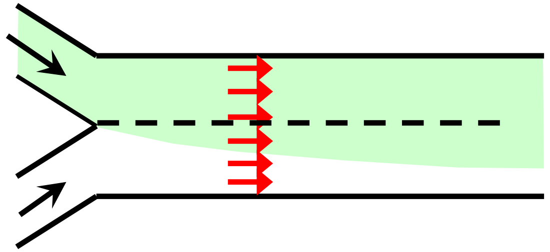
Basics

convection/diffusion, conservation equation



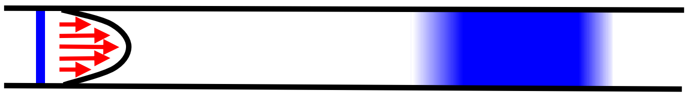
Co-flow

slow mixing, reaction-diffusion



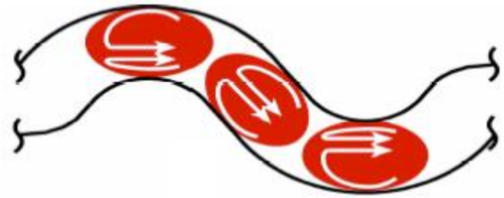
Shear dispersions

Leveque and Taylor-Aris dispersions, role of gravity, application to sensors.



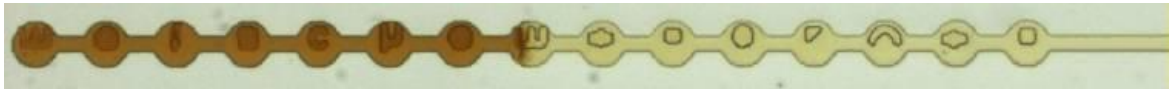
Mixing

small size, chaotic mixers, droplets



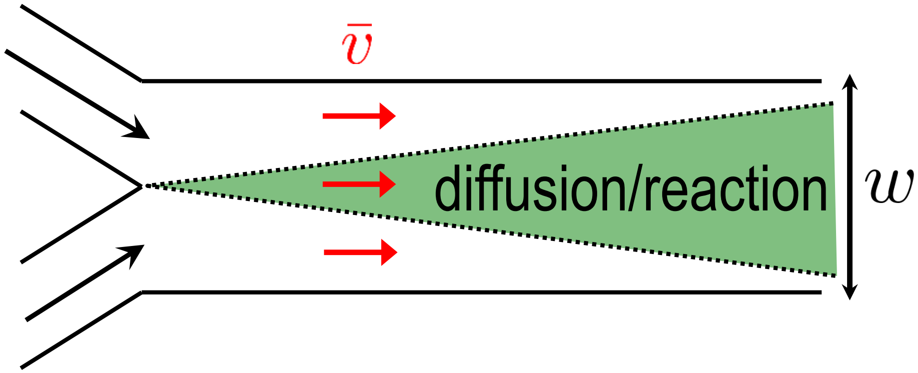
Membranes

pervaporation

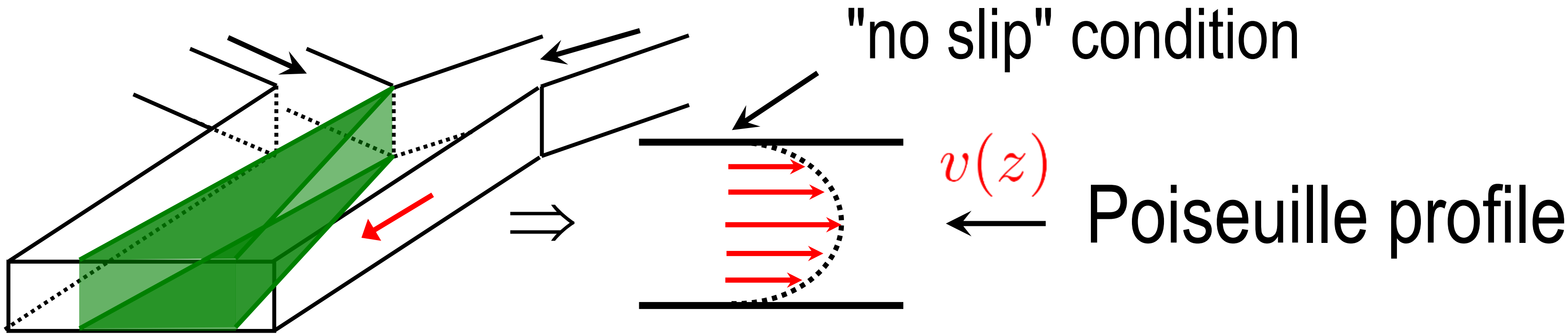


Life is more complex: hydrodynamic dispersion

top view

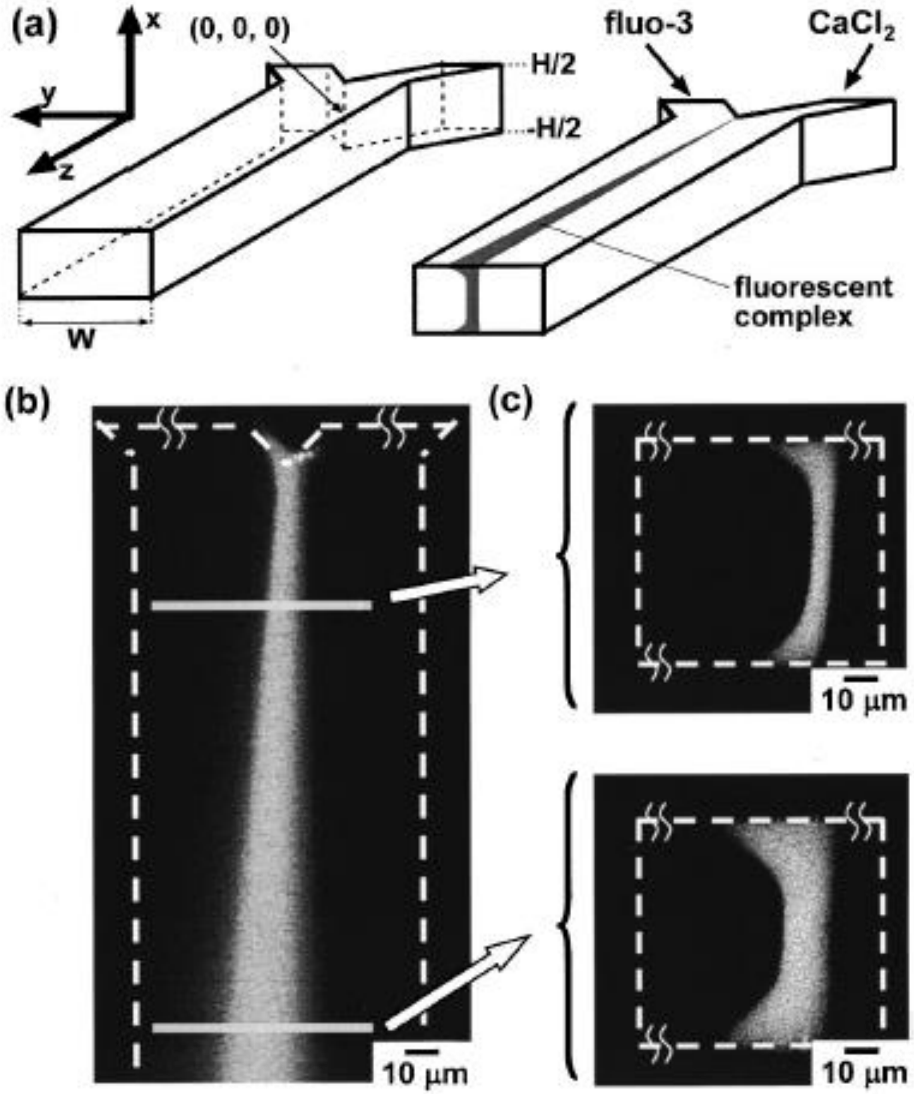


perspective view



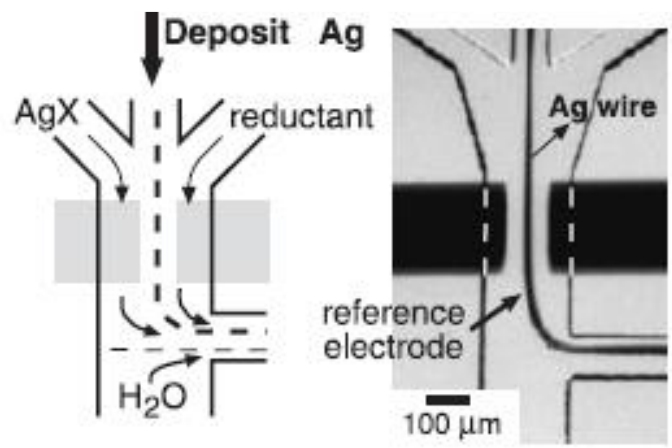
$\Rightarrow$ what about the previous results?

Larger diffuse "width" close to the walls



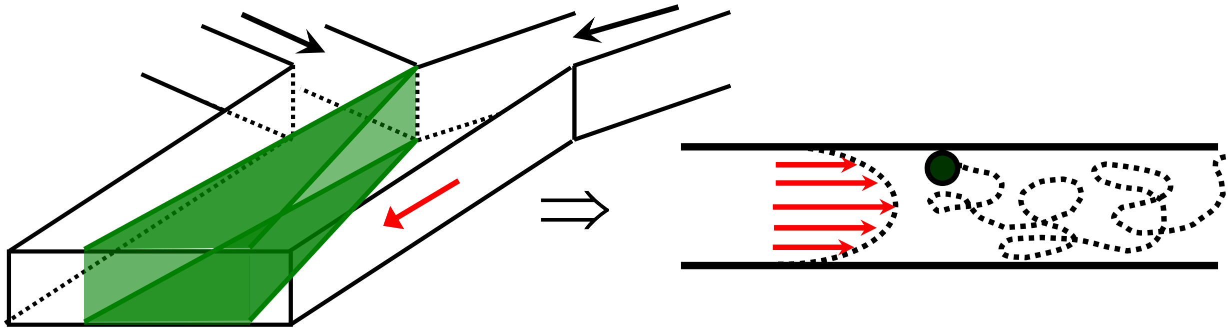
Ismagilov *et al.*, 2000

⇒ a problem to obtain very thin electrodes



Kenis *et al.*, 1999

From 3d to 2d



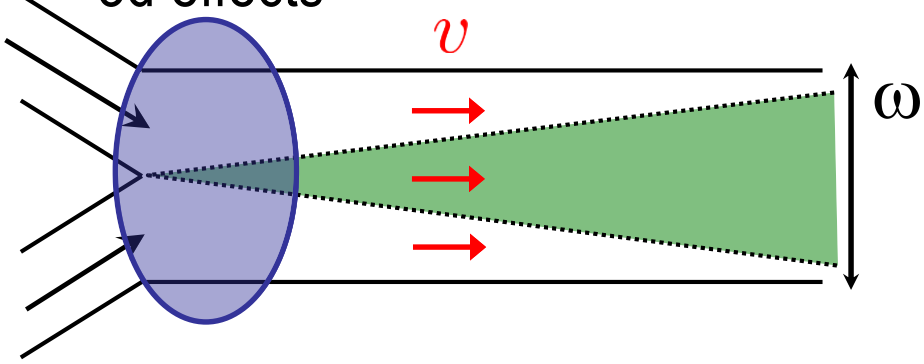
for $t > h^2/D$ i.e. $x > vh^2/D$

$\Rightarrow$ homogeneous concentration gradients (no 3d effects)

ex: h = 10 µm, v = 1 cm/s, D = 10^{-9} m²/s

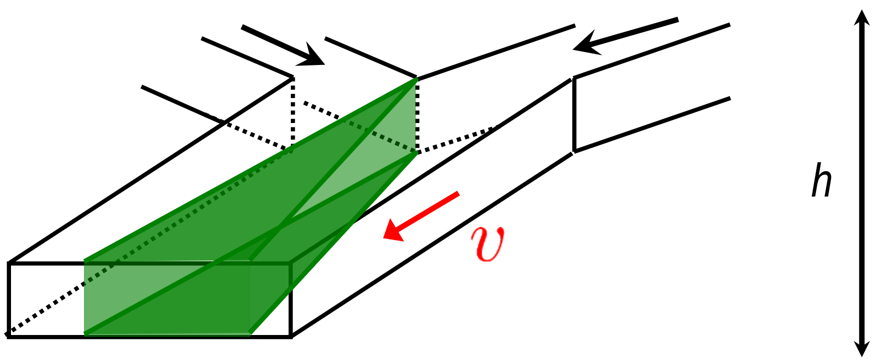
$$vh^2/D = 1 \text{ mm}$$

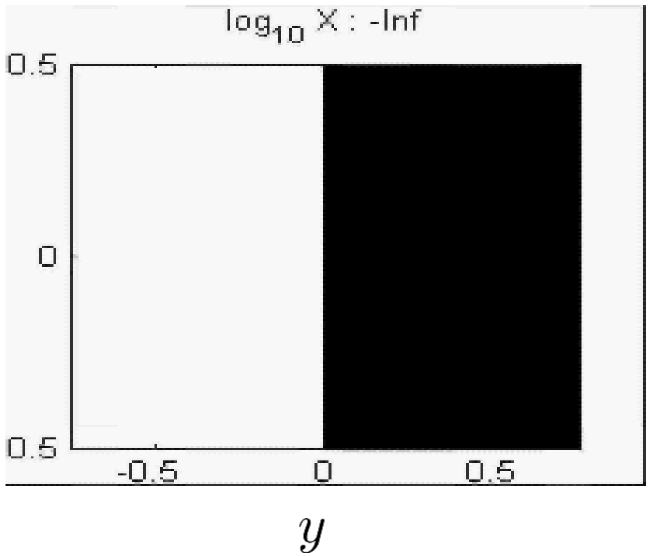
$$h^2/D = 100 \text{ ms}$$



$\Rightarrow$ need to take care of 3d effects for rapid kinetics

3d problem:
transverse hydrodynamic dispersion



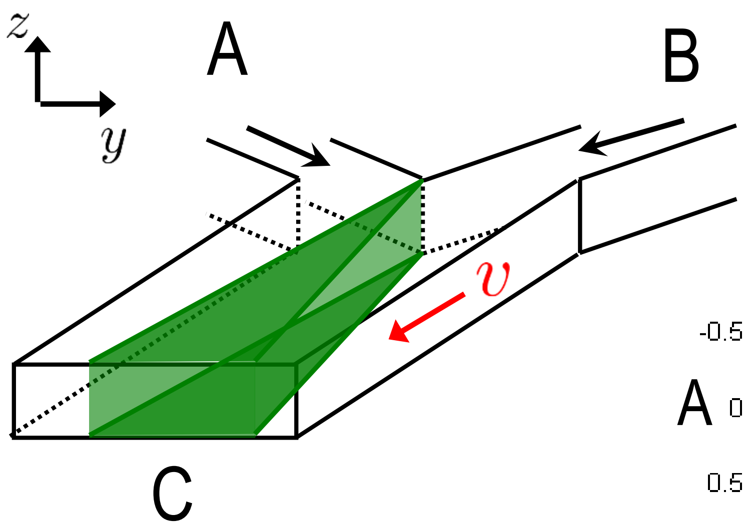


Ismagilov *et al.*, 2000
Salmon *et al.*, 2007

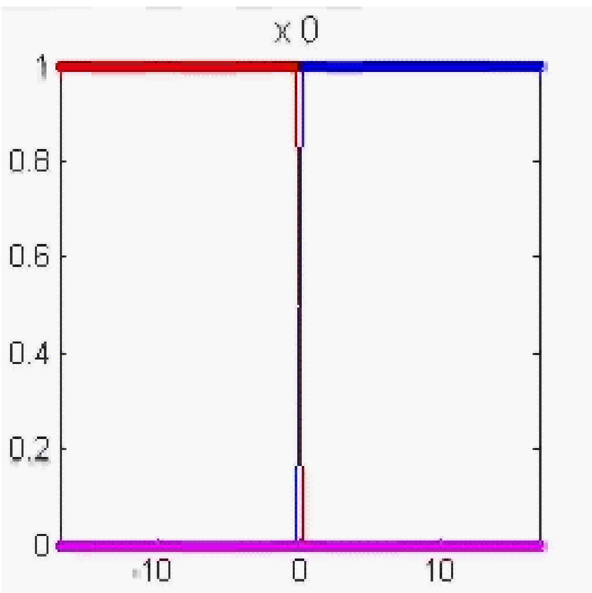
far from to the wall $\delta \sim \sqrt{Dx/v}$

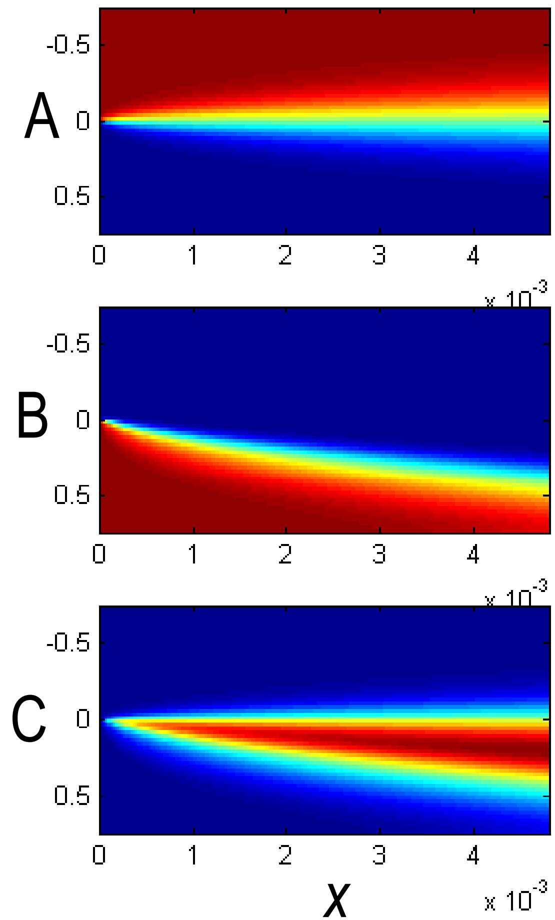
close to the wall $\delta \sim (x/v)^{1/3}$ → "Leveque" dispersion (diffusion in a shear flow)

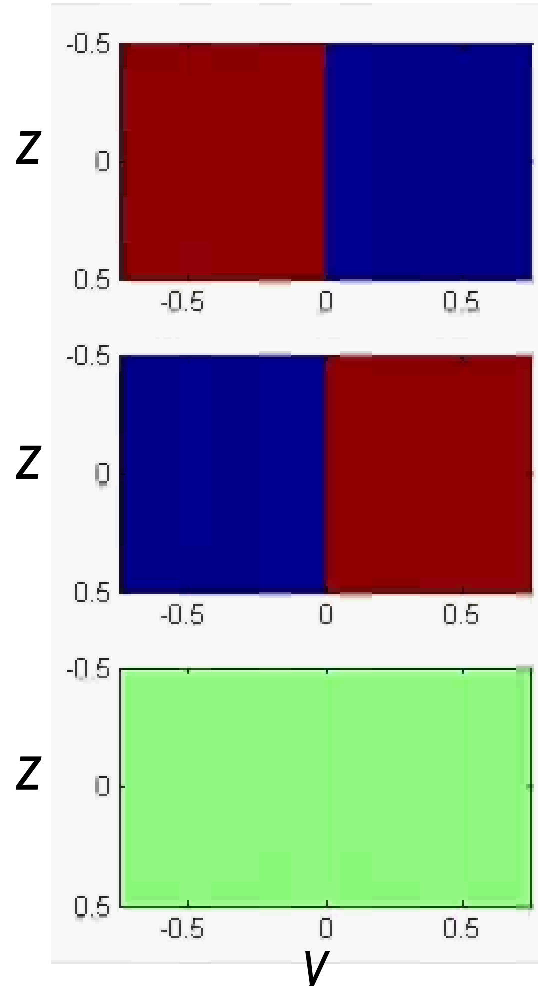
A problem for chemistry?



eg: 2nd order chemical reaction A+B ⇔ C

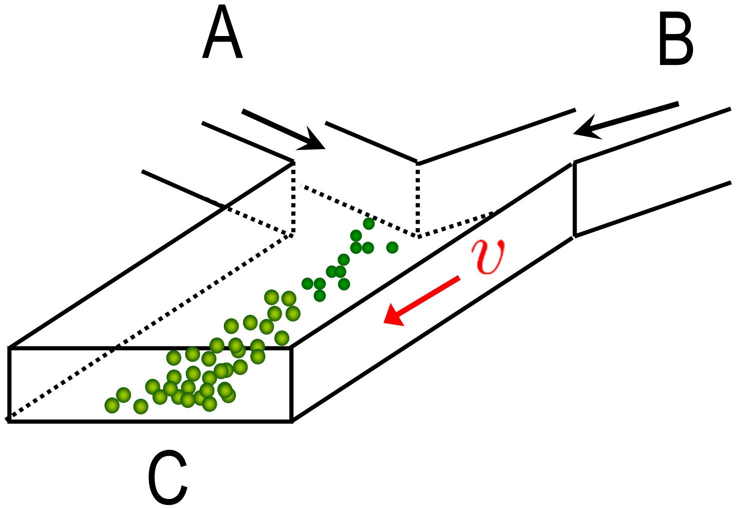


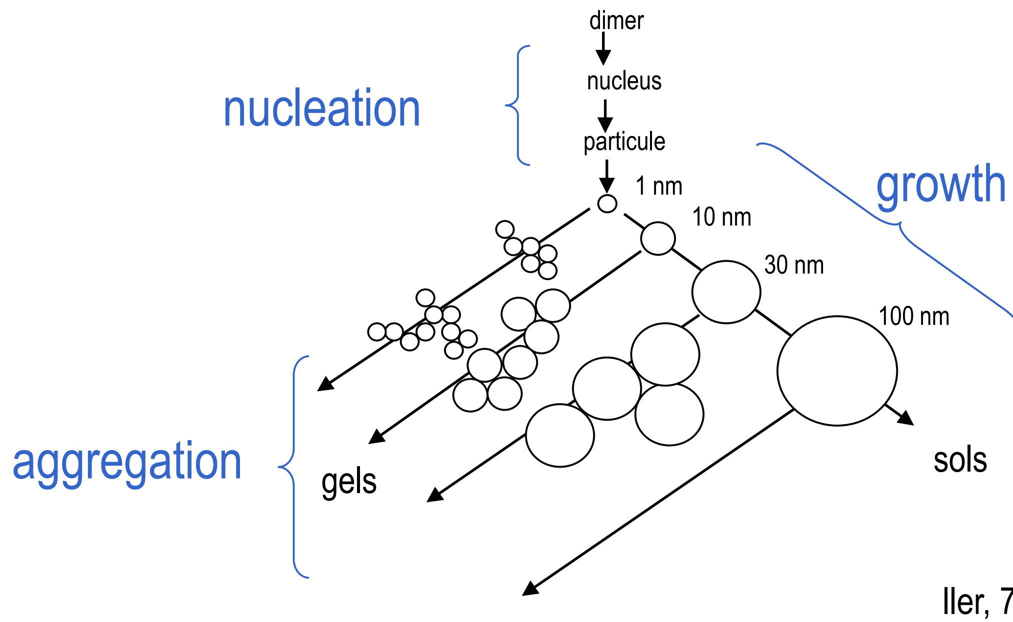


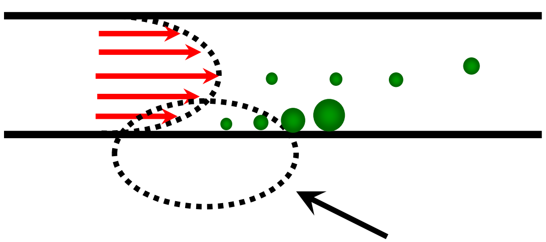


but averaged profiles are not so different from the 2d case...

A problem for chemistry?
yes for complex reactions





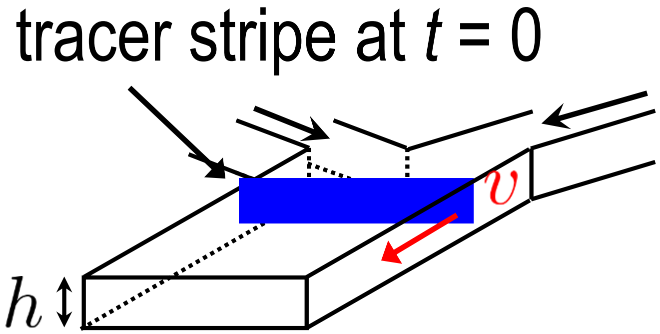


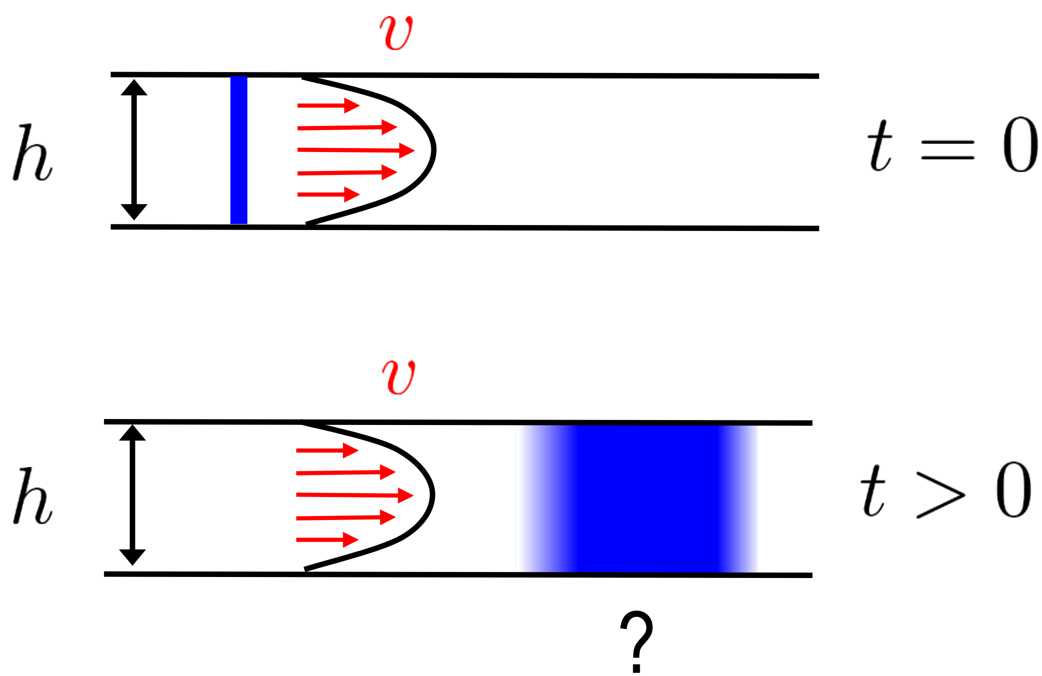
long residence times: bigger & bigger particles
(due to a smaller & smaller diffusivity...)

$\Rightarrow$ clogging & leakages

$\Rightarrow$ need for 3d microfluidics (no walls) or droplets

Another hydrodynamic dispersion: dispersion of residence times

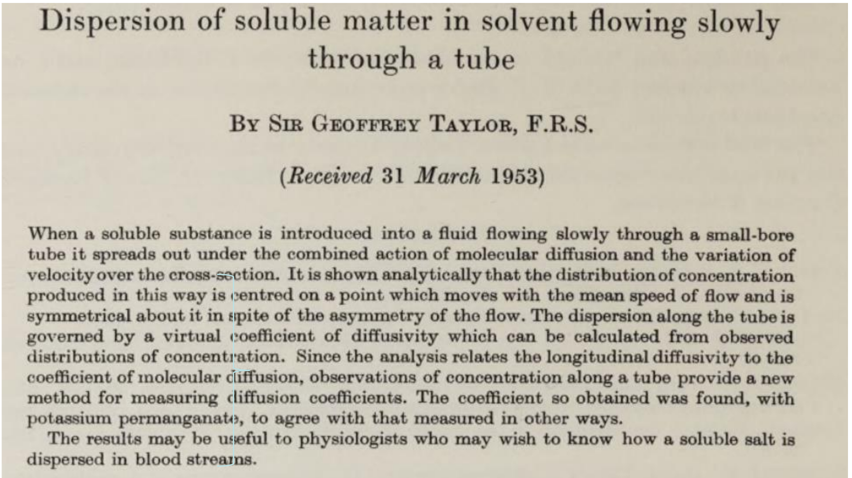




$$\mathrm{Pe} = \frac{vh}{D}$$

⇒ Taylor-Aris dispersion (convection & diffusion)

An old problem…

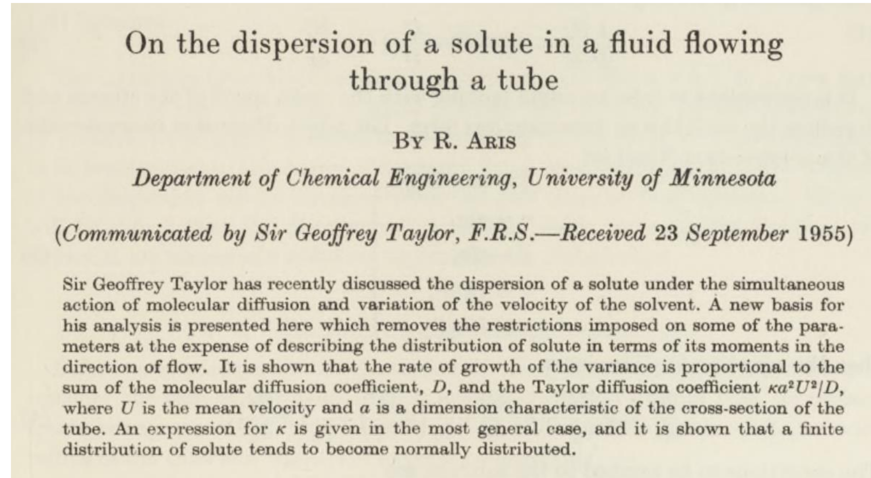

Dispersion of soluble matter in solvent flowing slowly through a tube

By Sir Geoffrey Taylor, F.R.S.

(*Received* 31 *March* 1953)

When a soluble substance is introduced into a fluid flowing slowly through a small-bore tube it spreads out under the combined action of molecular diffusion and the variation of velocity over the cross-section. It is shown analytically that the distribution of concentration produced in this way is centred on a point which moves with the mean speed of flow and is symmetrical about it in spite of the asymmetry of the flow. The dispersion along the tube is governed by a virtual coefficient of diffusivity which can be calculated from observed distributions of concentration. Since the analysis relates the longitudinal diffusivity to the coefficient of molecular diffusion, observations of concentration along a tube provide a new method for measuring diffusion coefficients. The coefficient so obtained was found, with potassium permanganate, to agree with that measured in other ways.

The results may be useful to physiologists who may wish to know how a soluble salt is dispersed in blood streams.


On the dispersion of a solute in a fluid flowing through a tube

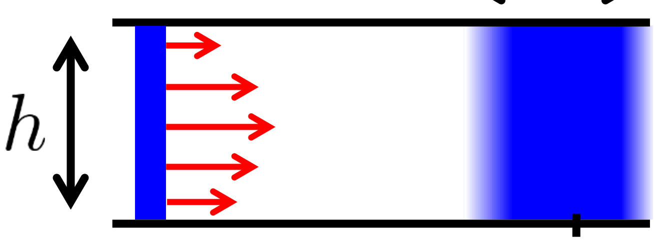
By R. Aris

Department of Chemical Engineering, University of Minnesota

(*Communicated by Sir Geoffrey Taylor, F.R.S.—Received* 23 *September* 1955)

Sir Geoffrey Taylor has recently discussed the dispersion of a solute under the simultaneous action of molecular diffusion and variation of the velocity of the solvent. A new basis for his analysis is presented here which removes the restrictions imposed on some of the parameters at the expense of describing the distribution of solute in terms of its moments in the direction of flow. It is shown that the rate of growth of the variance is proportional to the sum of the molecular diffusion coefficient, D, and the Taylor diffusion coefficient $\kappa a^2U^2/D$, where U is the mean velocity and a is a dimension characteristic of the cross-section of the tube. An expression for κ is given in the most general case, and it is shown that a finite distribution of solute tends to become normally distributed.

$\sim \sqrt{D_{\text{eff}} t}$



$t = 0$ $\qquad$ $t \gg h^2/D$

$$D_{\text{eff}} = D\left(1 + \frac{\text{Pe}^2}{192}\right)$$

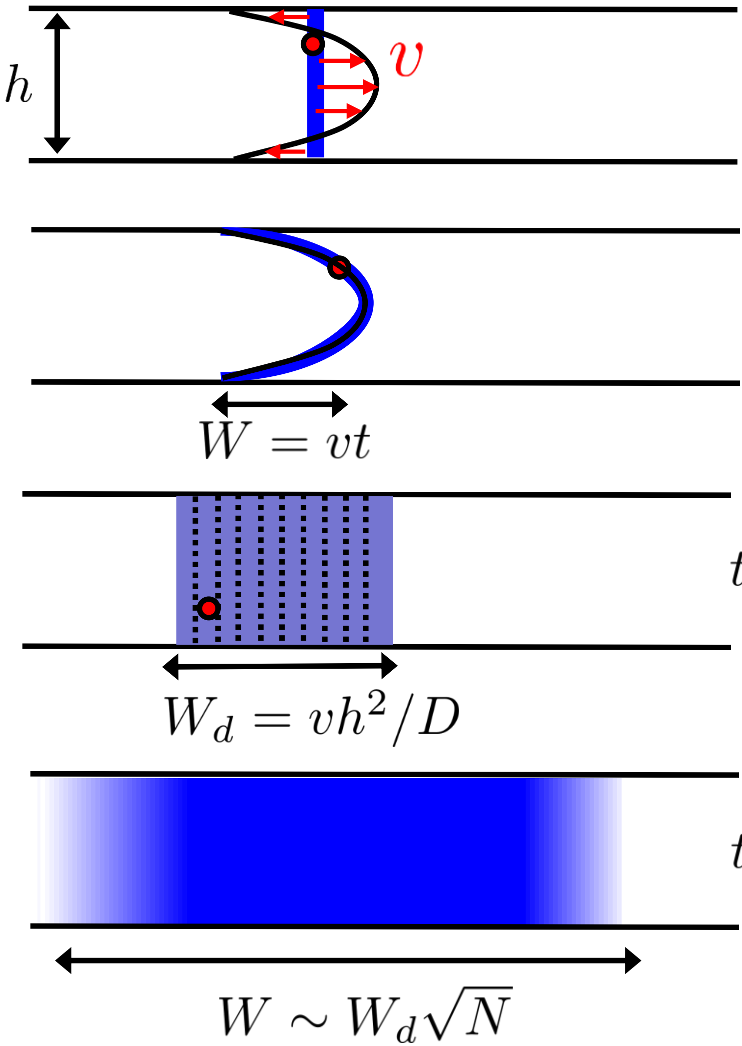
Taylor 1953

Aris 1956

$$\text{Pe} = \frac{vh}{D}$$

Taylor dispersion: a simple view

in the reference frame of the flow



$t = 0$

$t \ll \tau_d = h^2/D$

$t \sim \tau_d = h^2/D$ random step $W_d = vh^2/D$

$t \sim Nh^2/D = N\tau_d$

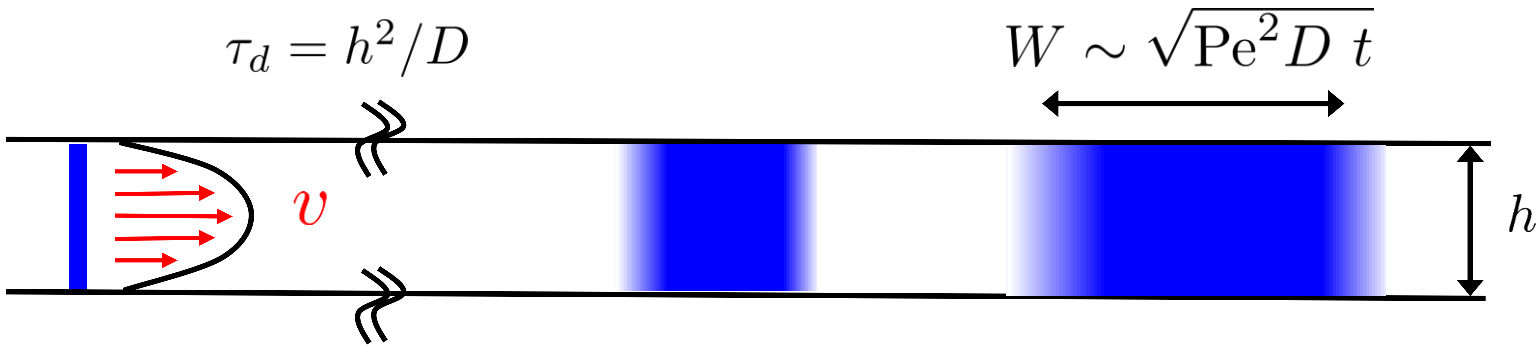
$$\mathrm{Pe} = \frac{vh}{D}$$

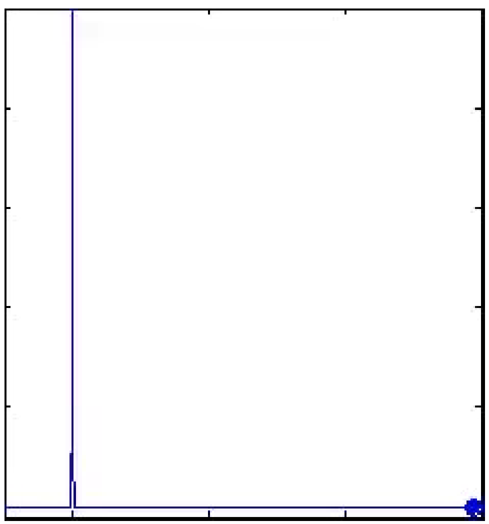
$\Rightarrow$ *effective* diffusion $W \sim W_d\sqrt{N} = \sqrt{\mathrm{Pe}^2 Dt}$

Squires *et al.* 2005

$\mathrm{Pe} = \frac{vh}{D}$

Taylor-Aris dispersion: a simple view



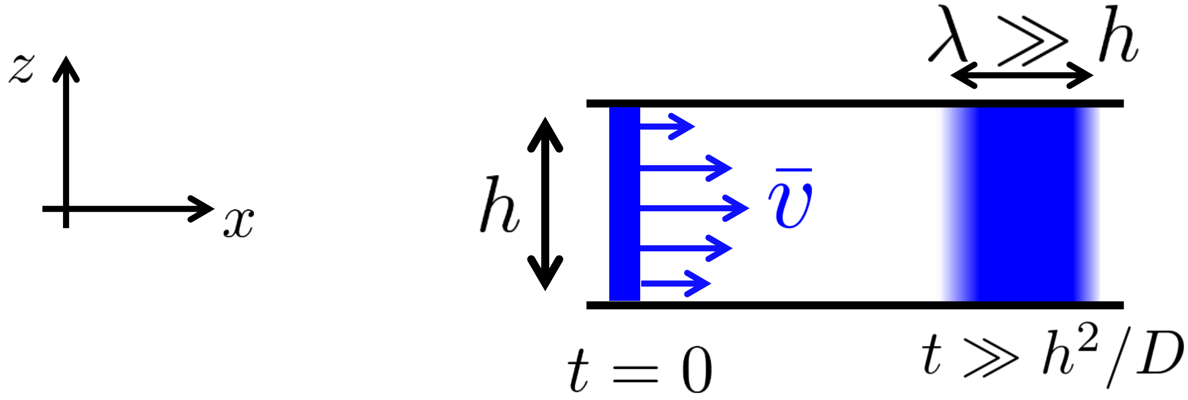


« effective » diffusion coefficient

$$D_{\mathrm{eff}} \sim D(1 + \beta \mathrm{Pe}^2) = D + \beta v^2 h^2 / D$$

$\rightarrow$ large solutes: efficient dispersion

Beyond the scaling, β ?



$$\tilde{z} = z/h$$
$$v(z) = 6\tilde{z}(1-\tilde{z})\bar{v}$$

$$\left.\begin{aligned} &\partial_t c + v(z)\partial_x c = D\Delta c \\ &c_0(x,t) = \tfrac{1}{h}\int_0^h c(x,z,t)\mathrm{d}z \end{aligned}\right\} \partial_t c_0 + < v(z)\partial_x c >= D\partial_x^2 c_0$$

perturbative approach $c(x,t) = c_0(x,t) + c_1(x,z,t)$

$$\rightarrow D\partial_z^2 c_1 \simeq (v(z) - \bar{v})\partial_x c_0$$

$$\rightarrow c_1 \propto \frac{\bar{v}h^2\partial_x c_0}{D}$$

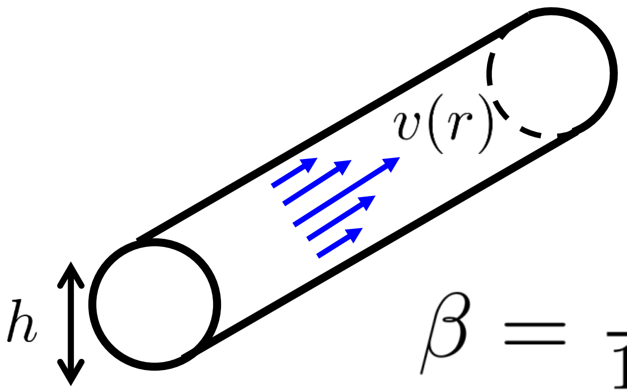
$$\rightarrow \partial_t c_0 + \bar{v}\partial_x c_0 = D(1 + \beta \mathrm{Pe}^2)\partial_x^2 c_0$$

A question of geometry

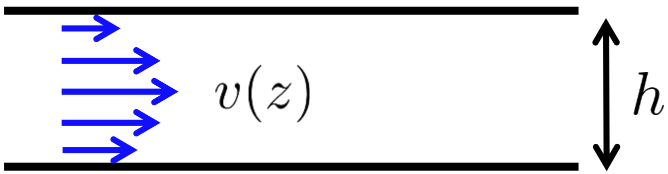
$$\partial_t c_0 + \bar{v}\partial_x c_0 + < v(y,z)\partial_x c_1 > = D\partial_x^2 c_0$$

$$(v(y,z) - \bar{v})\partial_x c_0 = D\Delta_s^2 c_1$$

$$\rightarrow \partial_t c_0 + \bar{v}\partial_x c_0 = D_{\mathrm{eff}}\partial_x^2 c_0 \qquad D_{\mathrm{eff}} = D(1+\beta \mathrm{Pe}^2)$$

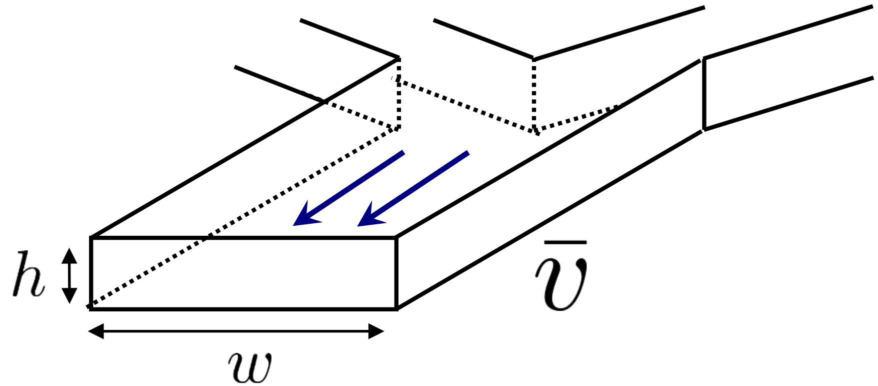


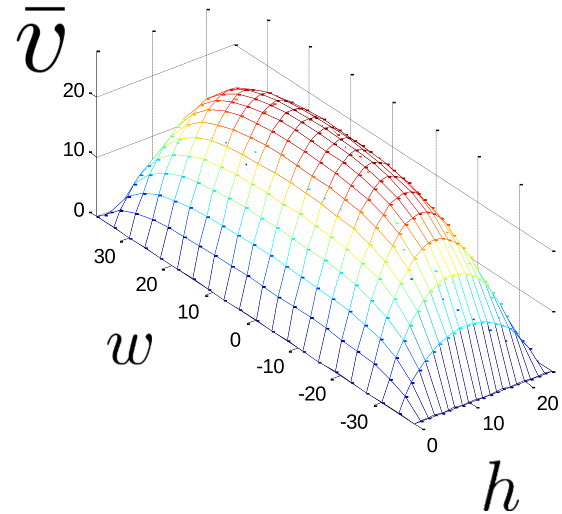
$$\beta = \frac{1}{192}$$



$$\beta = \frac{1}{210}$$

The striking case of rectangular channels

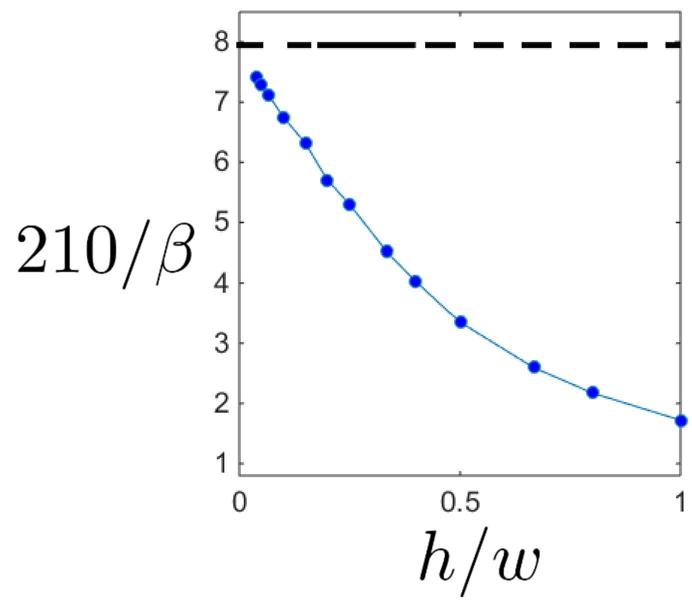




$$D_{\text{eff}} = D(1 + \beta \mathrm{Pe}^2) \qquad \mathrm{Pe} = \frac{vh}{D}$$

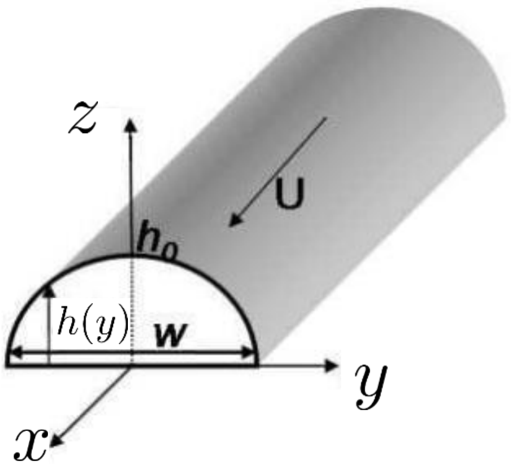
wide channel $h \ll w$

$$\beta \simeq 8/210$$



Doshi *et al.* Chem Eng Science 1978
Chatwin *et al.* J Fluid Mech 1982

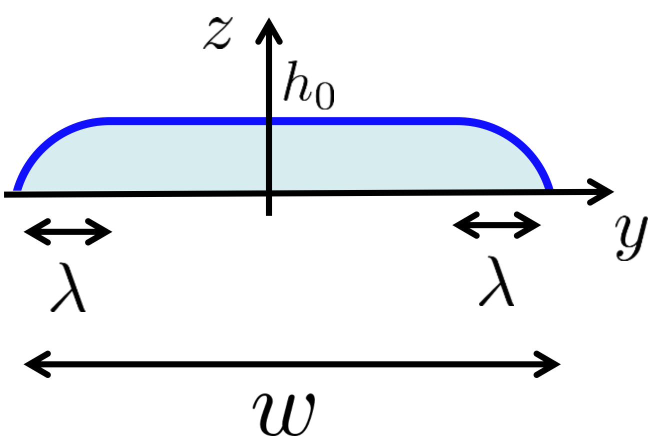
The case of shallow channels



$$h_0 \ll w$$
$$D_{\text{eff}} = D(1 + \beta \text{Pe}_w^2)$$
$$\text{Pe}_w = vw/D$$

the height *h* does not matter

$\rightarrow$ dispersion due to the dispersion of velocities along *y*



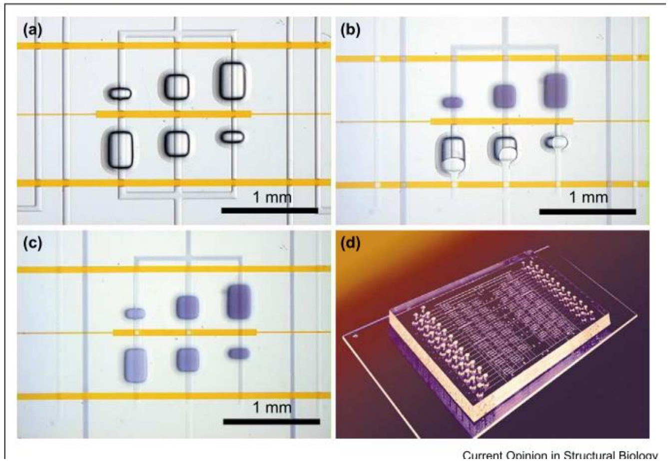
$$\beta\left(\frac{\lambda}{w}\right) = \frac{\lambda^2}{w^2} f\left(\frac{\lambda}{w}\right) \simeq \frac{\lambda^2}{w^2} f$$

$$\rightarrow D_{\text{eff}} \simeq D(1 + \beta' \text{Pe}_\lambda^2)$$

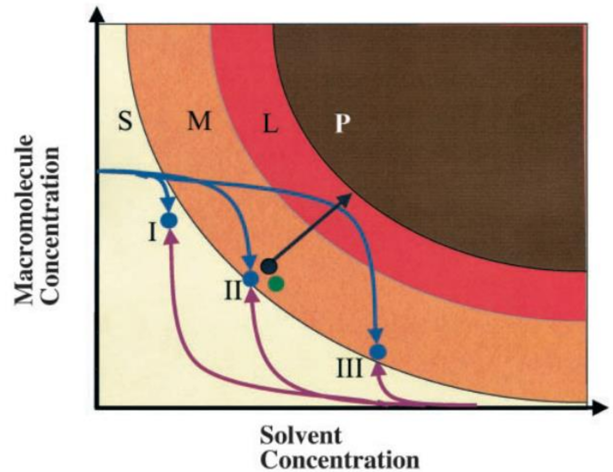
Ajdari *et al.* Anal Chem 2006

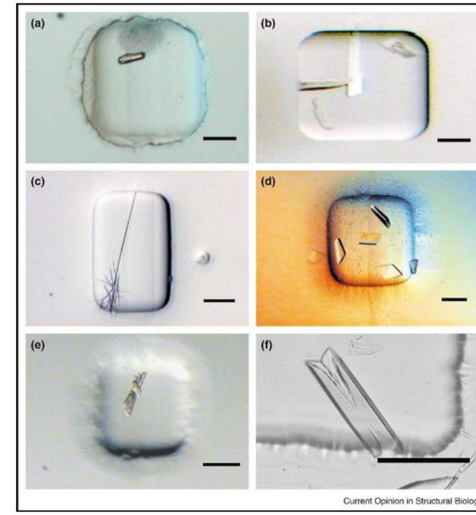
Bontoux *et al.* Lab Chip 2006

Solute diffusion in a box
e.g.: crystallization of proteins

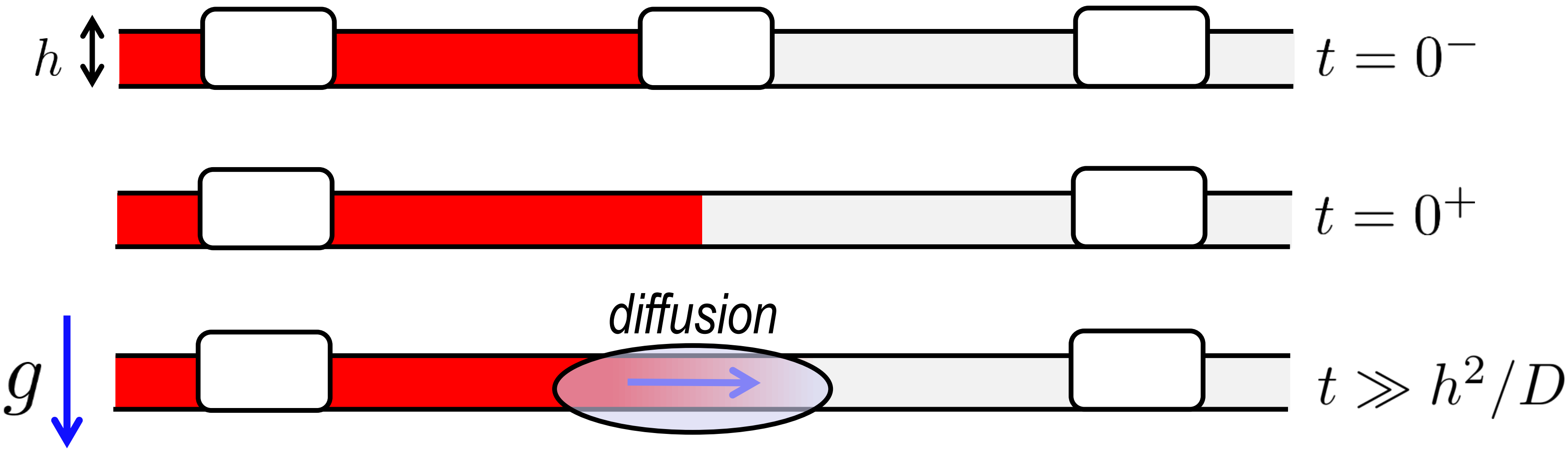


Quake *et al.* 2002



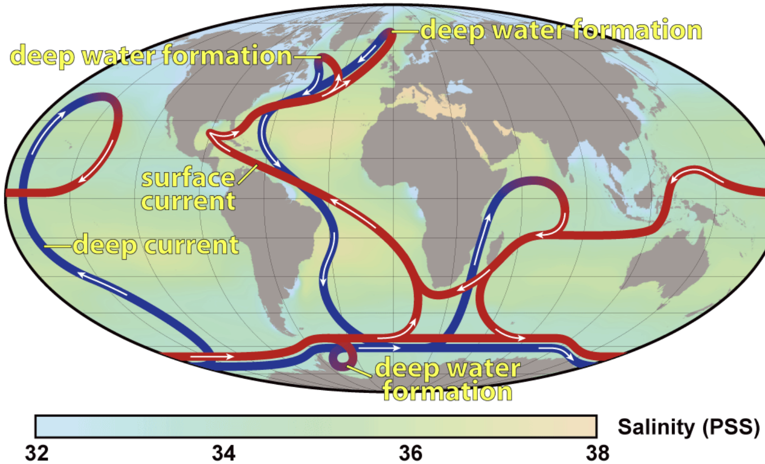


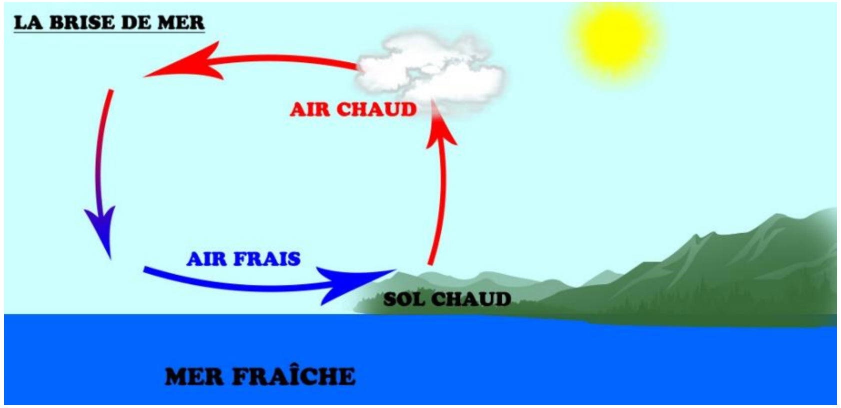
(see P. Joseph's lecture)

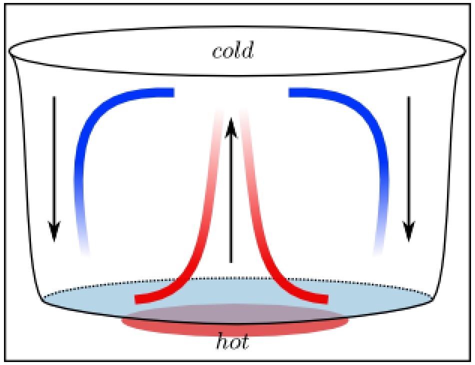


role of buoyancy ?

Buoyancy-driven convection: convection due to density differences





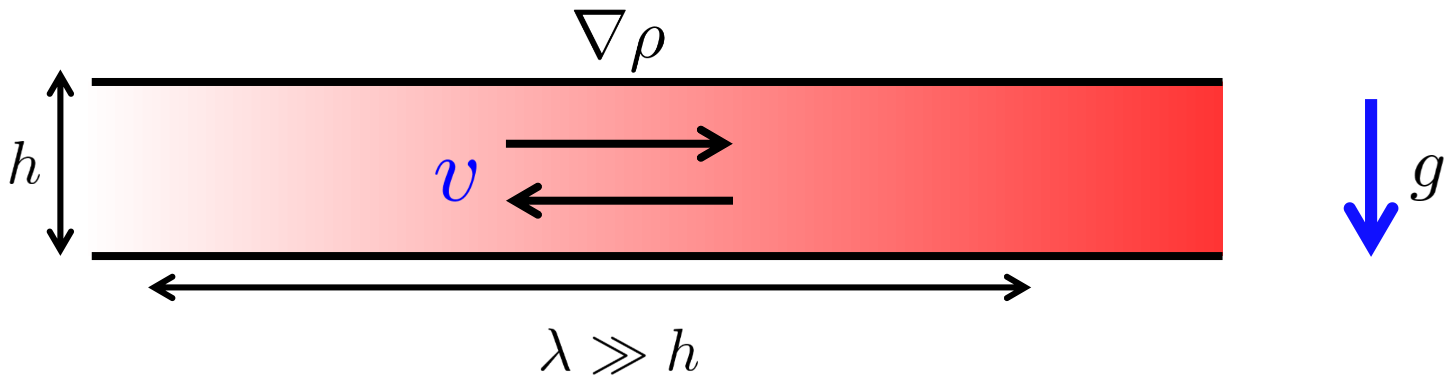


$\nabla\rho$ $\rightarrow$ temperature ∇T and/or concentration gradients ∇C

$\rightarrow$ very common at large scale

images: web

At small scales?
competition with viscous dissipation



gradient of hydrostatic pressure $\nabla p = \nabla \rho g h$

$\longrightarrow$ lubrication flow $v \sim \frac{h^2}{\eta}\nabla p = \frac{gh^3}{\eta}\nabla\rho \sim h^3$

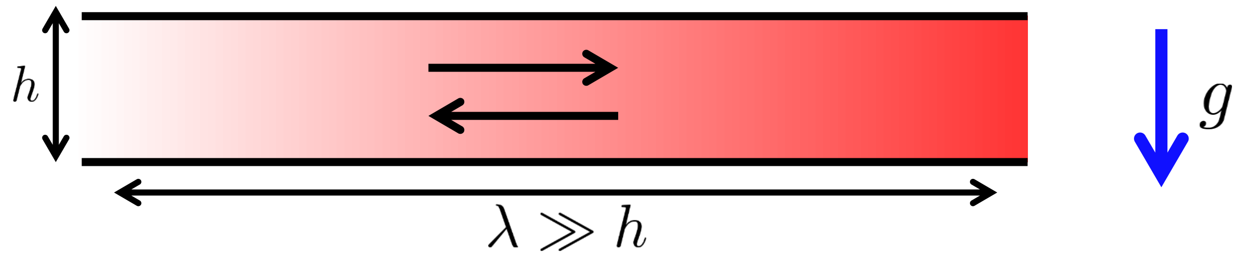
$\longrightarrow$ note: these flows always exist for $\nabla\rho \perp g$

Impact on mass transfer for solutal convection?

$$\rho = \rho_0(1 + \beta c)$$

solutal expansion coefficient

$$\nabla \rho = \rho_0 \beta \nabla c$$



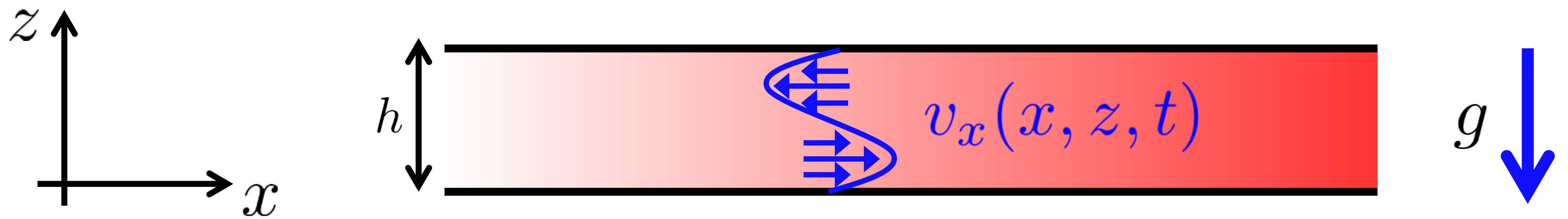
$$v \sim \frac{g\beta h^3}{\nu} \nabla c$$

→ no impact for $\mathrm{Pe} = \frac{vh}{D} \sim \frac{g\beta h^4}{\nu D} \nabla c \ll 1$

→ note: it can have an impact on less mobile species

Squires *et al.* Rev. Mod. Phys. 2005

Beyond the scaling? (i) velocity field



$\rightarrow$ lubrication approximation

$$\nu \frac{\partial v_x}{\partial z} = \frac{1}{\rho_0} \partial_x P$$

$$\frac{\partial P}{\partial z} = -\rho_0 (1 + \beta c) g$$

$$\rightarrow v_x(x, z, t) = \tilde{z}(1 - \tilde{z})(2\tilde{z} - 1) \frac{g \beta h^3}{12 \nu} \frac{\partial c}{\partial x}$$

and for mass transport?

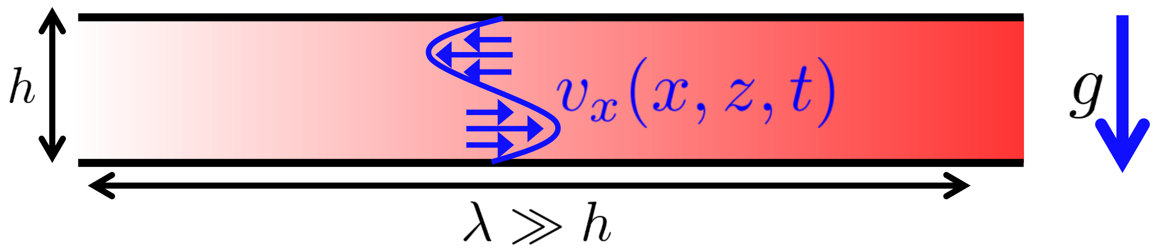
Birikh, J. Appl. Mech. Phys. 1966

(ii) « Taylor-Aris like » perturbative approach

$$c(x,t) = c_0(x,t) + c_1(x,z,t) \qquad \partial_t c + v.\nabla c = D\Delta c$$

$$c_0(x,t) = \frac{1}{h}\int_0^h c(x,z,t)\mathrm{d}z \qquad \partial_t c_0 + \frac{\partial}{\partial x} < v_x(z) c_1 >= D\frac{\partial^2 c_0}{\partial x^2}$$

$$t \gg h^2/D$$



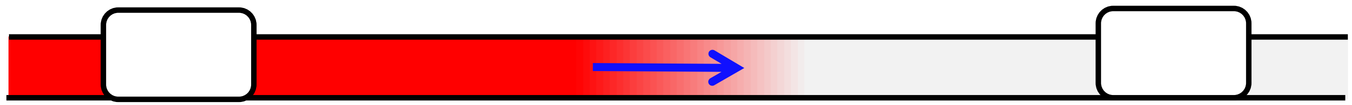
$$\rightarrow v_x(z)\partial_x c_0 \simeq D\frac{\partial^2 c_1}{\partial z^2} \qquad \rightarrow c_1(z) \propto \frac{g\beta h^5}{\nu D}\left(\frac{\partial c_0}{\partial x}\right)^2$$

$$\rightarrow \frac{\partial c_0}{\partial t} = \frac{\partial}{\partial x}\left(D_{\mathrm{eff}}\frac{\partial c_0}{\partial x}\right) \quad D_{\mathrm{eff}} = D\left[1 + \frac{1}{\alpha}\left(\frac{g\beta h^4}{\nu D}\partial_x c_0\right)^2\right]$$

$\rightarrow$ for parallel plates $\quad \alpha = 362880$

Erdogan & Chatwin J Fluid Mech 1967
Young & Jones Phys. Fluids A 1991

Back to diffusion in a box



$t \gg h^2/D$

$$\rightarrow \frac{\partial c_0}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{eff}}\frac{\partial c_0}{\partial x}\right)$$

$$D_{\text{eff}} = D\left[1 + \frac{1}{\alpha}\left(\frac{g\beta h^4}{\nu D}\partial_x c_0\right)^2\right]$$

Dispersion due to gravity negligible for

$$\left(\frac{g\beta h^4}{\nu D}\partial_x c_0\right)^2 \ll \alpha = 362880$$

(parallel plates)

Remember the scaling

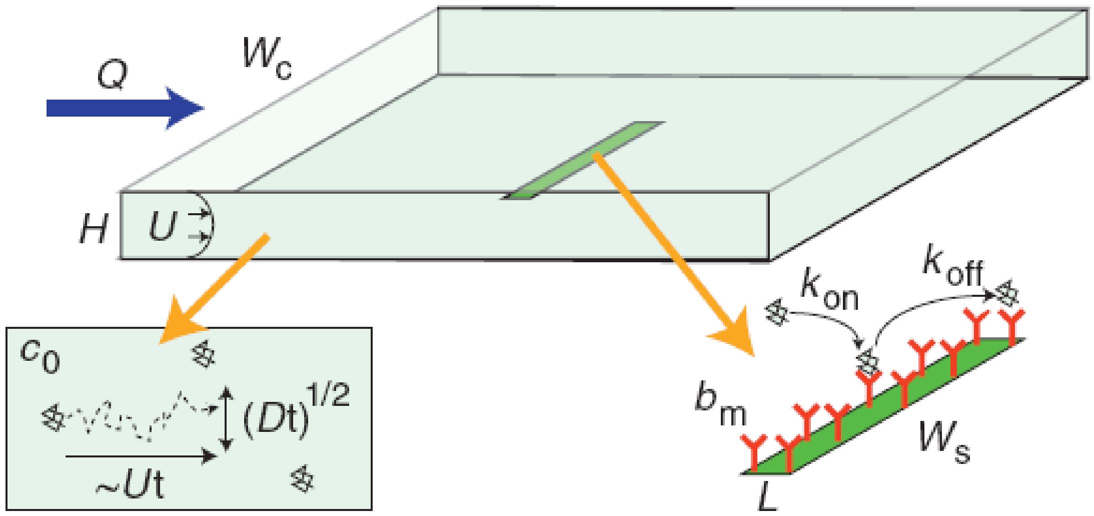
$$\text{Pe} = \frac{vh}{D} \sim \frac{g\beta h^4}{\nu D}\nabla c \ll 1$$

Making it stick: convection, reaction and diffusion in surface-based biosensors

Todd M Squires[1], Robert J Messinger[1] & Scott R Manalis[2]

nature biotechnology

Sensors: *"making it stick"*



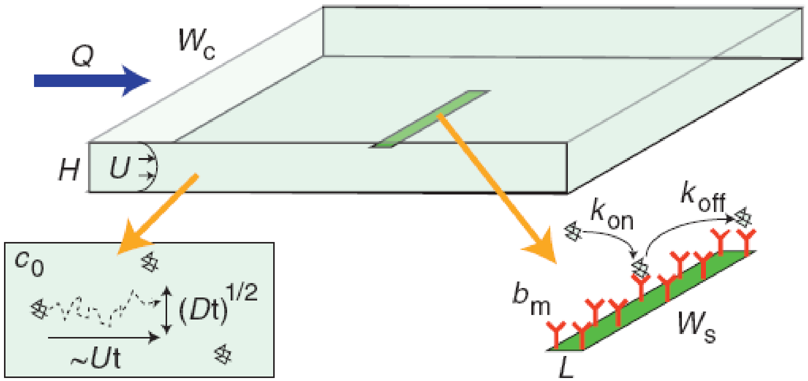
How to improve the efficiency of detection?

⇒ *a priori* a very complex problem (10 parameters !)

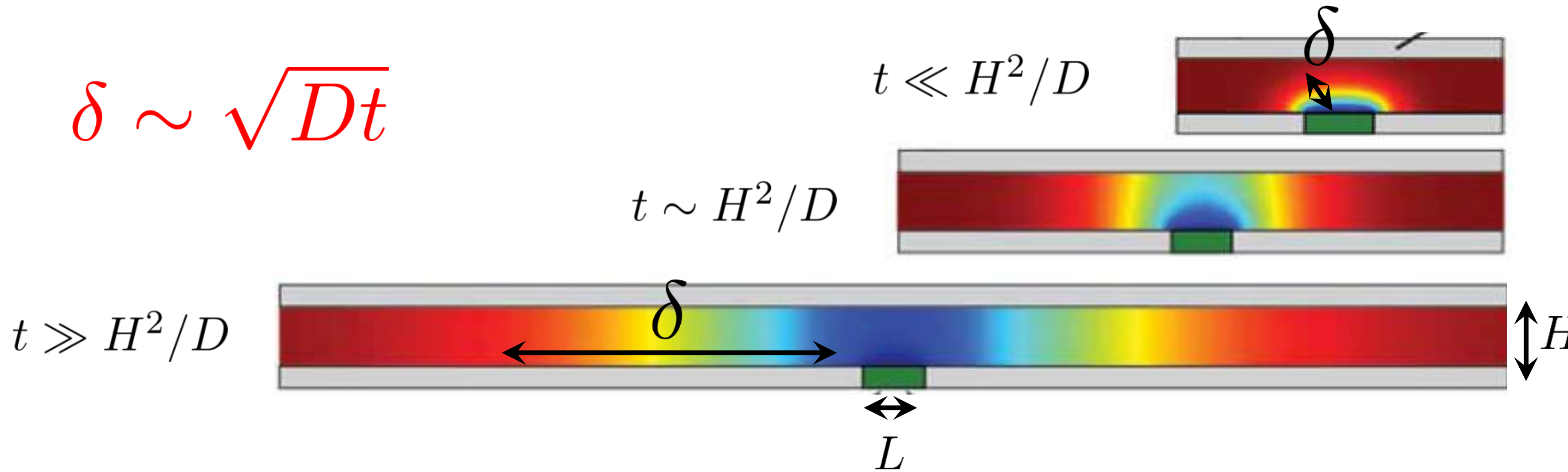
$$(c_0; U; D; k_{on}; k_{off}; H; W_c; W_s; L; b_m)$$

⇒ **scaling arguments for extreme regimes**

(i) No flow and perfect sensor: depletion layer



$$\delta \sim \sqrt{Dt}$$



$\Rightarrow$ no steady state

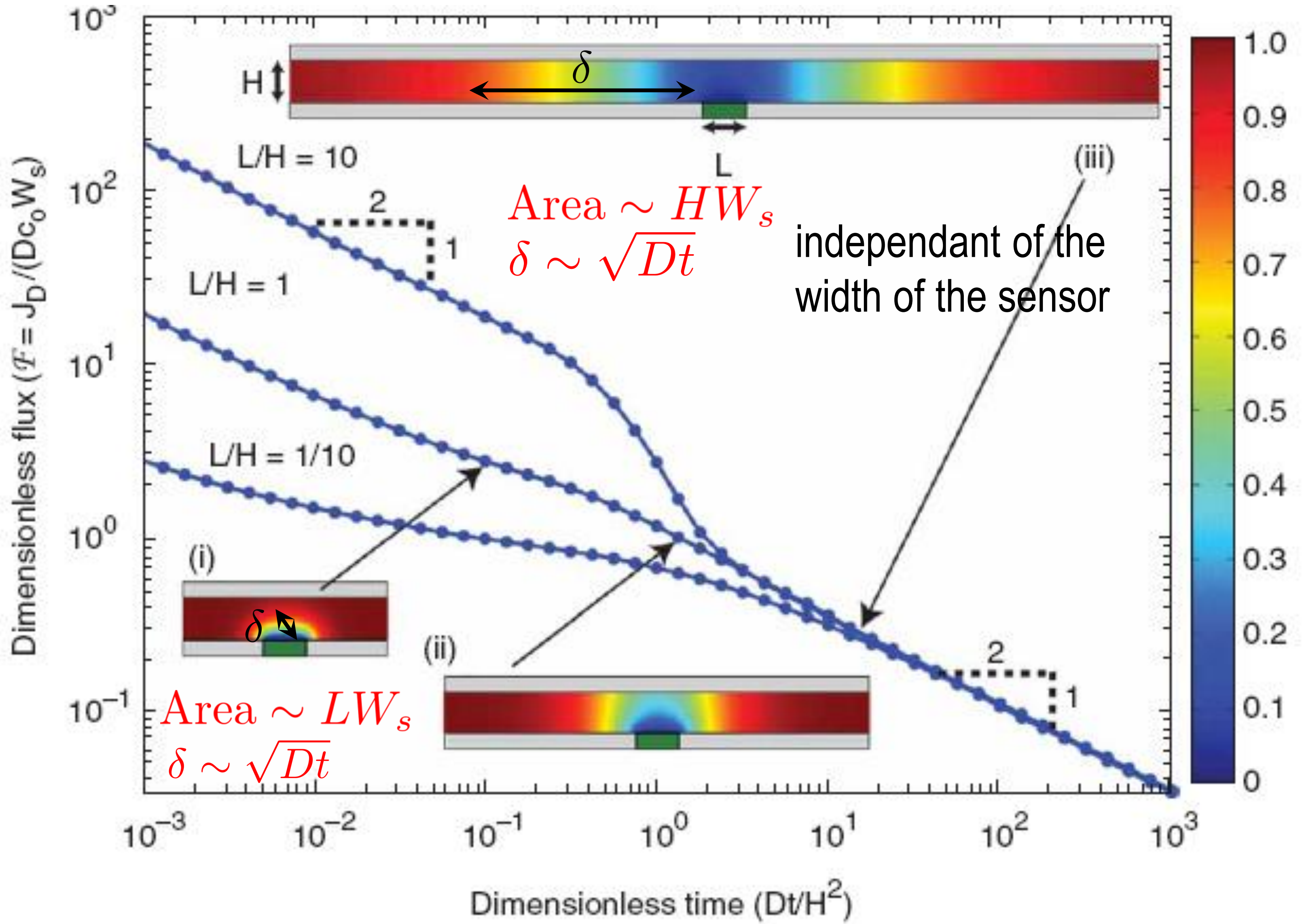
$\Rightarrow$ diffusive flux (#/s/m^2)

$\Rightarrow$ collection rate (#/s)

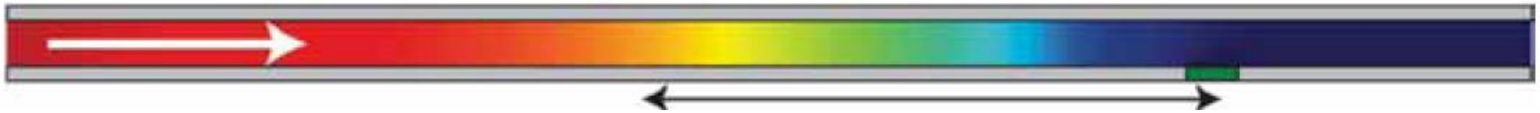
$$j_d = -Dc_0/\delta$$

$$J_d = j_d \times \text{ Area}$$

(i) unitless "diagram"



(ii) "slow" flow (and still a perfect sensor)



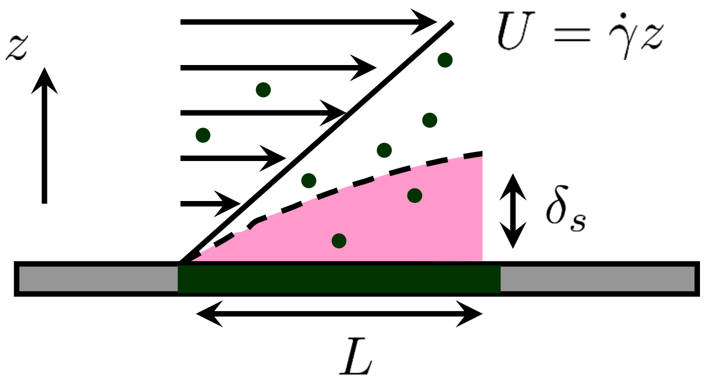
steady depletion layer $J_c \sim J_d \Rightarrow \quad \delta_s = DHW_c/Q$

$\Rightarrow$ full collection rate in this regime

only valid for $\delta_s \gg H$, i.e. $\mathrm{Pe}_H = Q/(DW_c) \ll 1$

(iii) "fast" flow (and still a perfect sensor)

$J_c \sim Q c_0$



transit along the sensor $L/(\dot{\gamma} z)$

diffusion time to the sensor z^2/D

$\Rightarrow$ depletion layer $\delta_s = (DL/\dot{\gamma})^{1/3}$

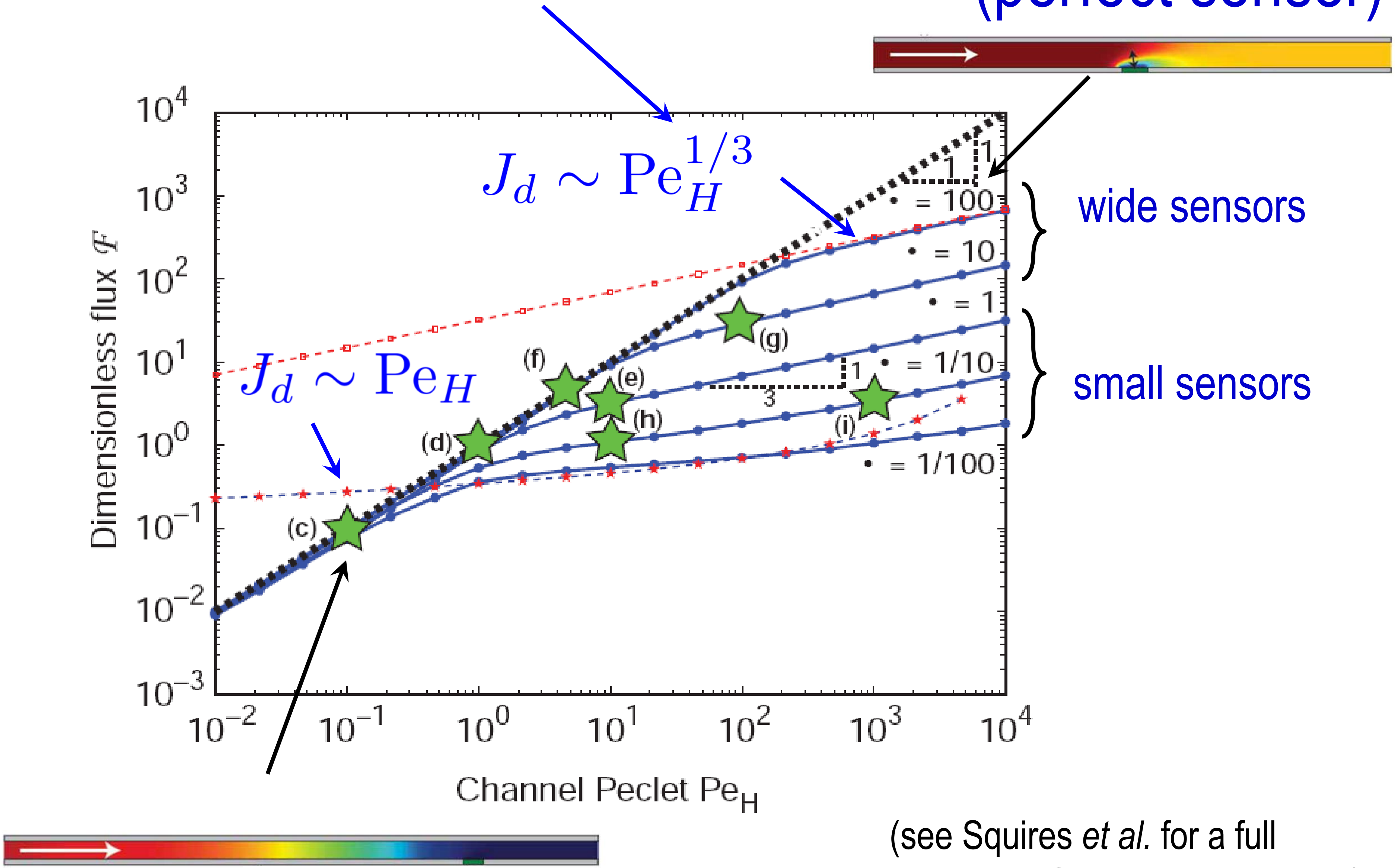
$$\dot{\gamma} \sim \mathrm{Pe}_H$$

$\Rightarrow$ collection rate $J_d \sim D c_0/\delta_s L W_s$

$$J_d \sim \mathrm{Pe}_H^{1/3}$$

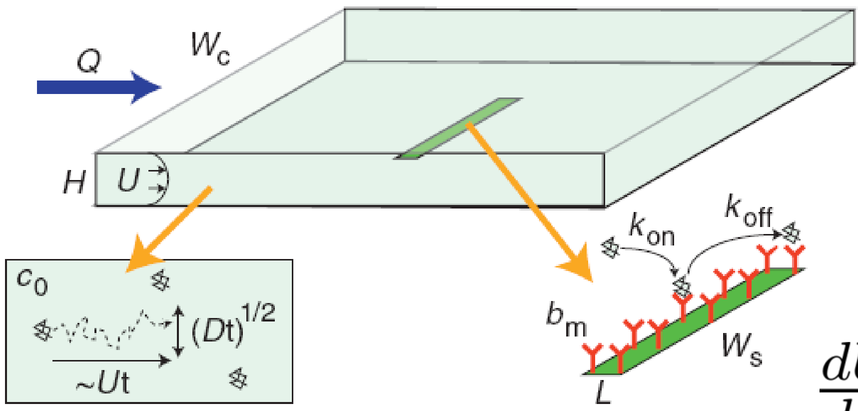
⇒ unitless "diagram" (perfect sensor)

weak dependency



(see Squires *et al.* for a full discussion for the other regimes)

(iv) reaction vs. transport



total concentration of receptors

$$\frac{db}{dt} = k_{\rm on} c_s (b_m - b) - k_{\rm off} b$$

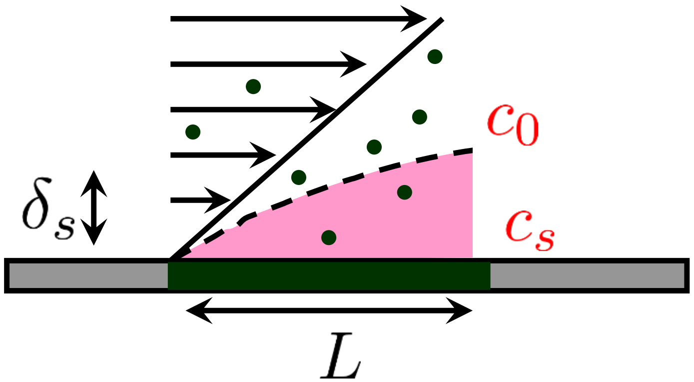
solute concentration close to the sensor

concentration of bounded receptors

for non-saturated sensors $\quad b \ll b_m$

reactive flux $\quad J_r = k_{\rm on} c_s b_m (L W_s)$

(iv) ex: "fast" flow & reaction



reactive flux $J_r = k_{\text{on}} c_s b_m (L W_s)$

diffusive flux $J_d \sim D(c_0 - c_s)/\delta_s (L W_s)$

steady regime: $J_r \sim J_d \;\Rightarrow$

$$c_s = \frac{c_0}{1+\text{Da}}$$

$$\text{Da} = k_{\text{on}} b_m \delta / D$$

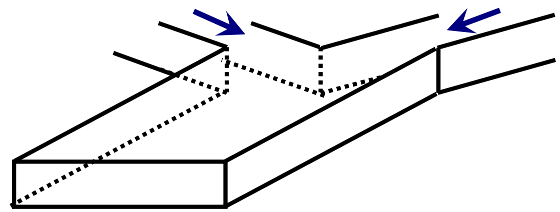
Da (Damkohler) compares reaction rates to transport rate

$\Rightarrow$ Da<1 : reaction limited $\quad c_s \sim c_0$

$\Rightarrow$ Da>1 : mass transport limited $\quad c_s \sim 0$

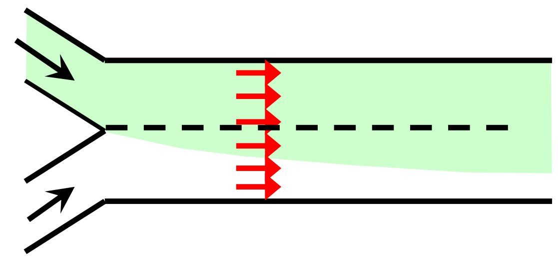
Basics

convection/diffusion, conservation equation



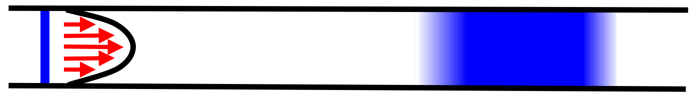
Co-flow

slow mixing, reaction-diffusion



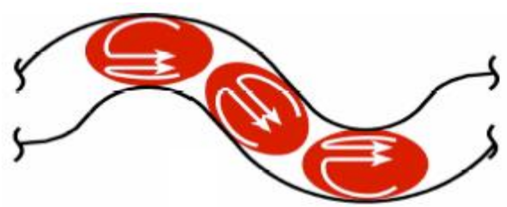
Shear dispersions

Leveque and Taylor-Aris dispersions, role of gravity, application to sensors



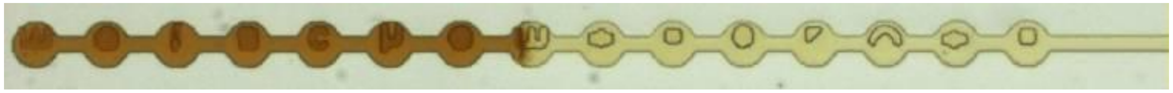
Mixing

small size, chaotic mixers, droplets

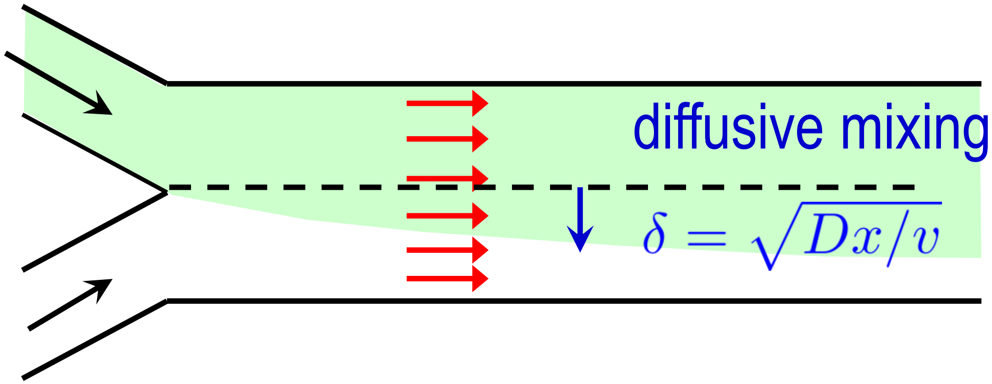


Membranes

pervaporation

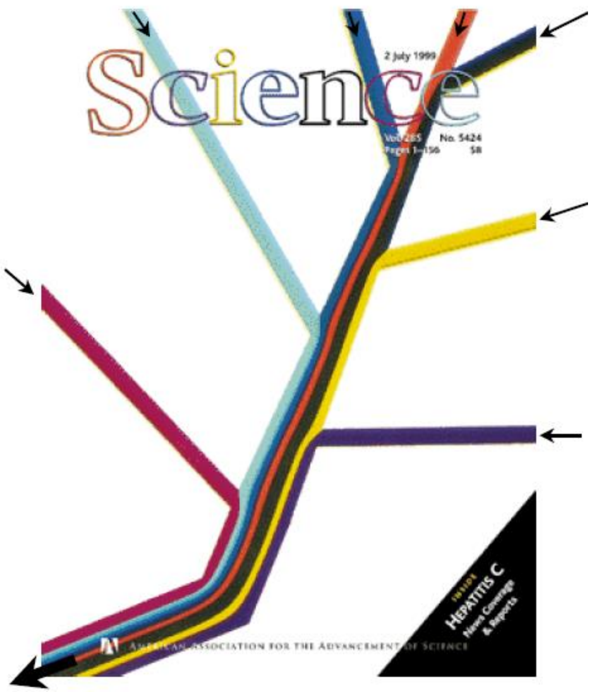


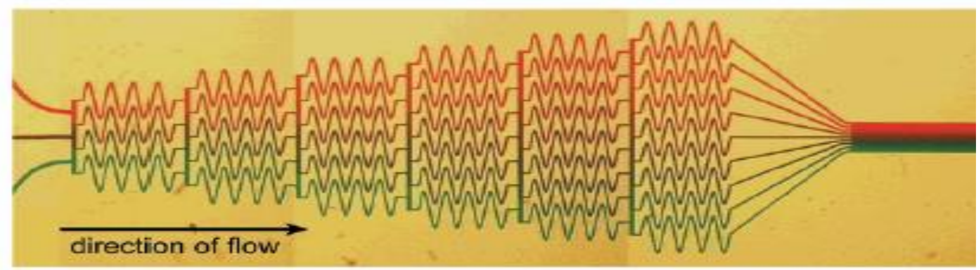
Back to microfluidics: mixing is slow...

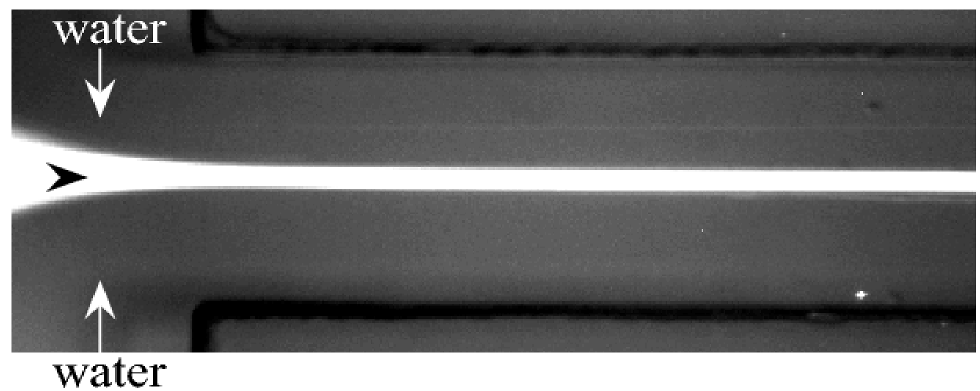


length for efficient mixing

$$L \approx vw^2/D = \mathrm{Pe}\,w$$





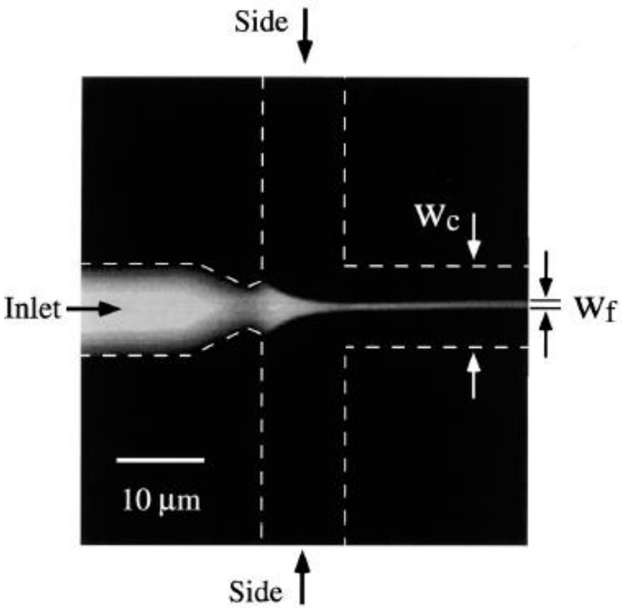


$\Rightarrow$ some strategies for efficient mixing ?

(1) Diminishing the size for a finite velocity)

ex. hydrodynamic focusing

Q_s (water)

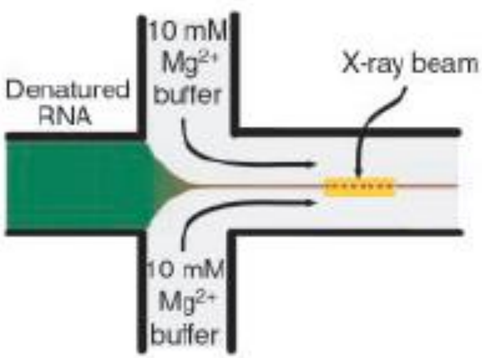


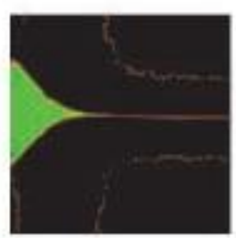
$w_f \approx$ 100 nm - 1 µm

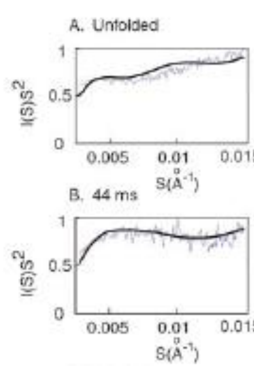
$\tau \sim w_f^2/D \approx$ 10 µs - 1 ms

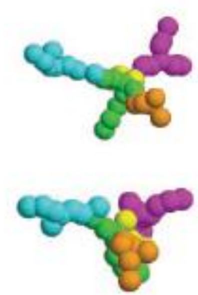
Knight *et al.*, 1998

application fo kinetics of folding of bio-molecules
(first data point at 5 ms !)



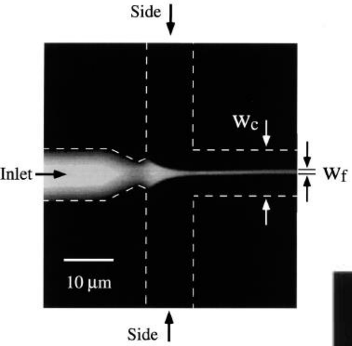




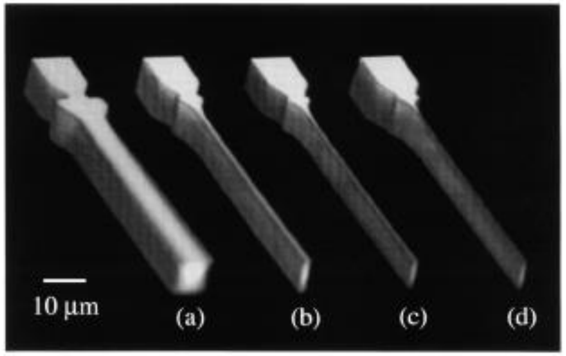


Russel *et al.*, 2002

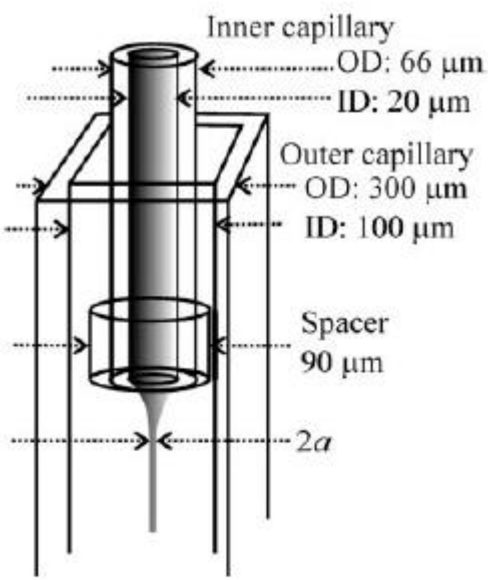
This is always a (complex) 3d problem...



Knight *et al.*, 1998



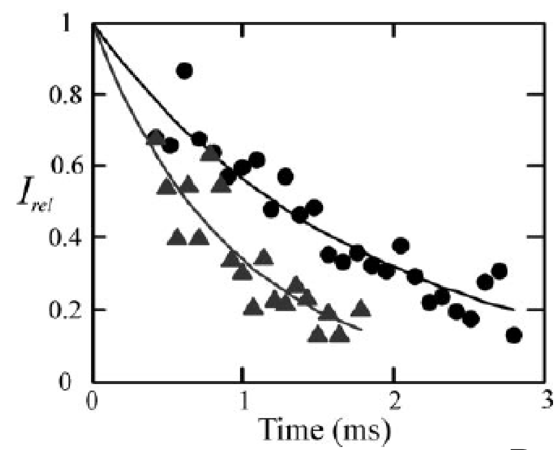
An easy way for hydrodynamic focusing without walls ?



$\Rightarrow$ no walls

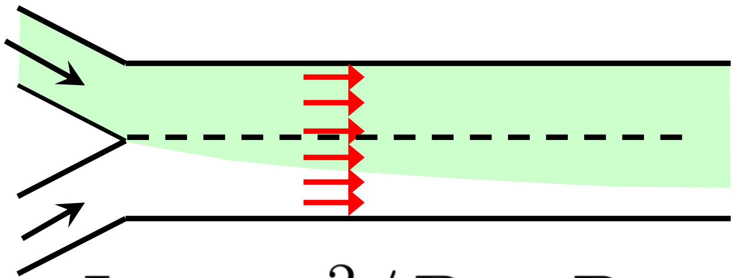
$\Rightarrow$ no dispersion

Kinetics of quenching reaction

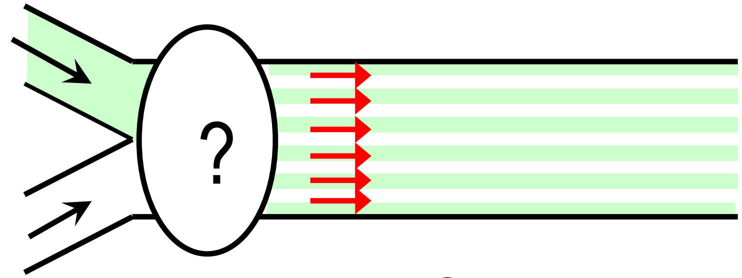


Pabit *et al.* 2002

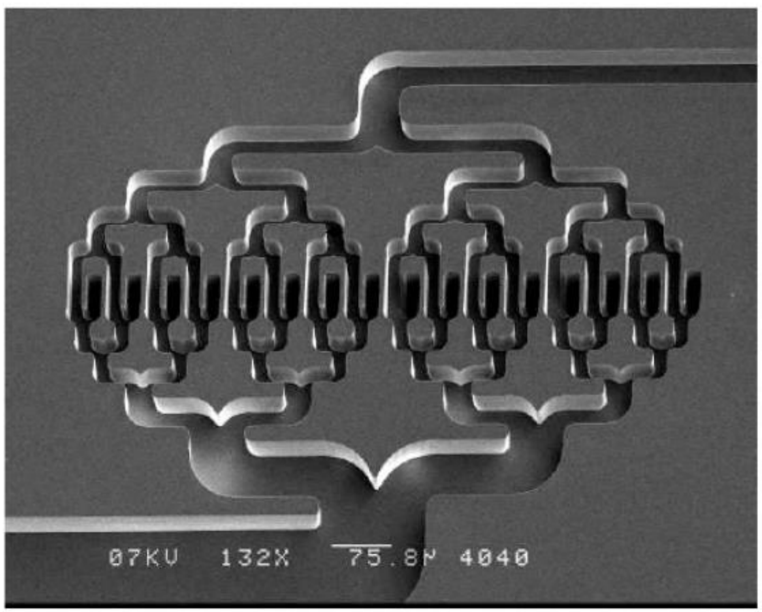
(2) Multilaminating the flow

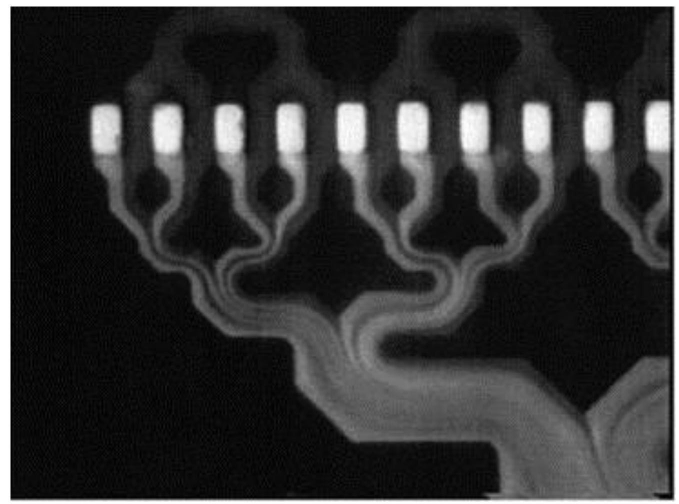


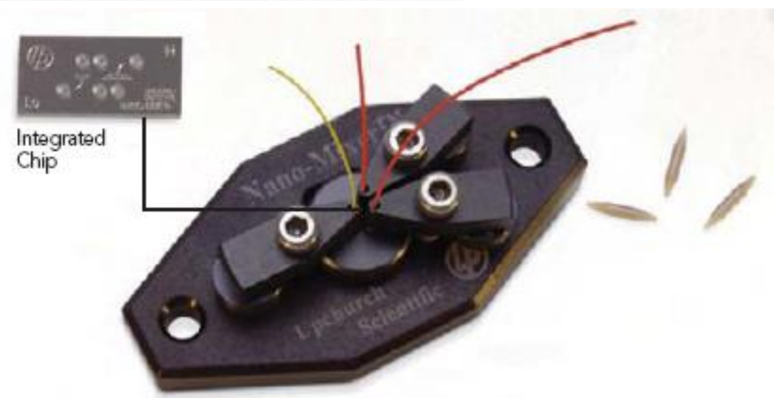
$$L \approx vw^2/D = \mathrm{Pe}w$$



$$L \approx v(w/N)^2/D = \mathrm{Pe}w/N^2$$

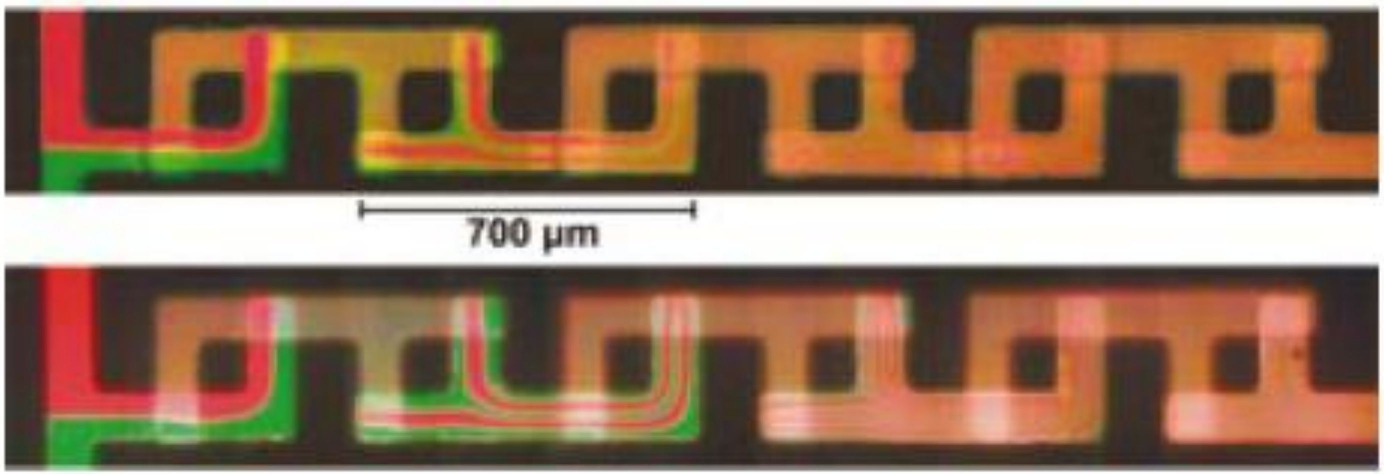






Manz *et al.* 1999

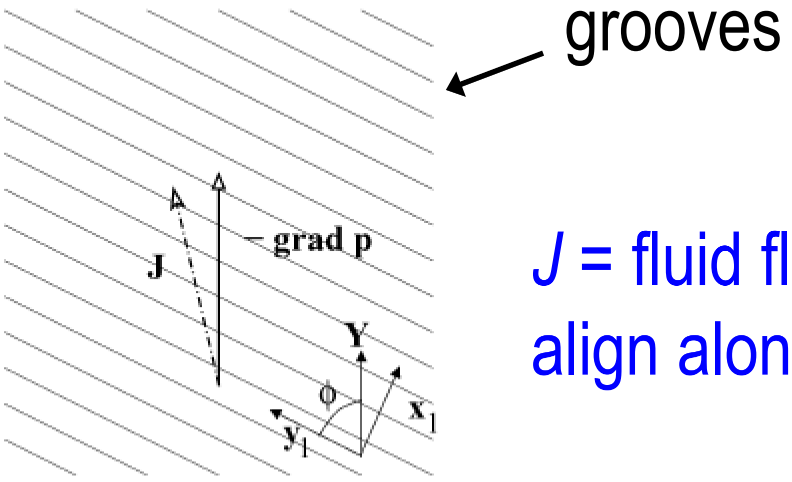
(2) Multilaminating along the flow



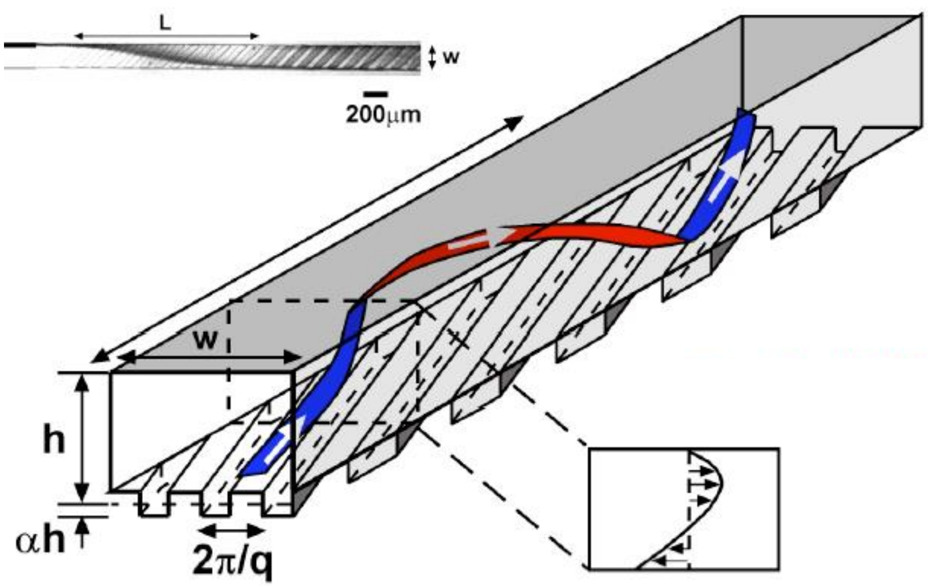
Chen *et al.* 2004

⇒ need for 3d structures

(3) "Grooving" flows: chaotic mixing



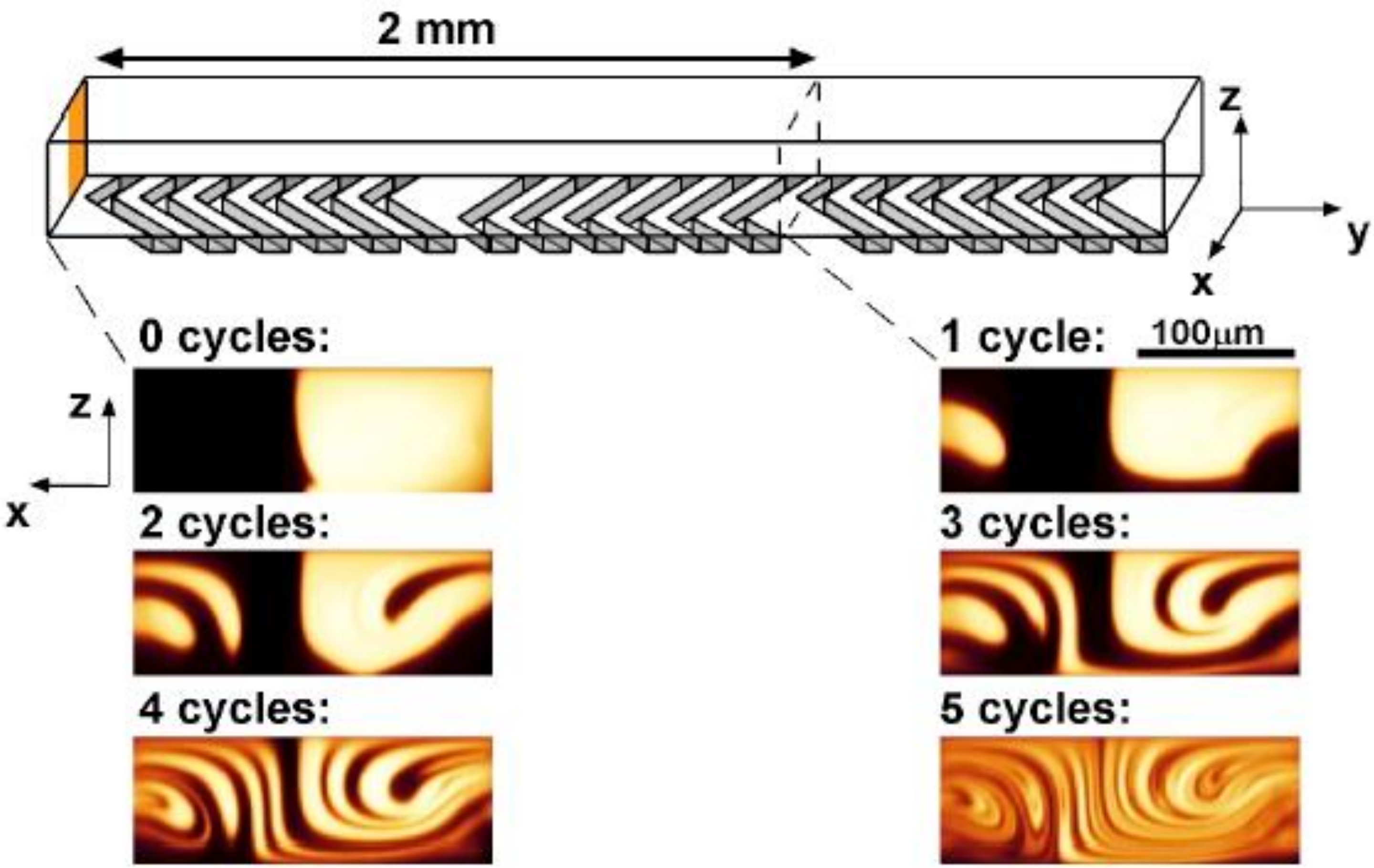
J = fluid flux that that tends to align along the « easy axis »



in a confined channel: helical stream lines !

Stroock *et al.* 2002

(3) "Grooving" flows: chaotic mixing

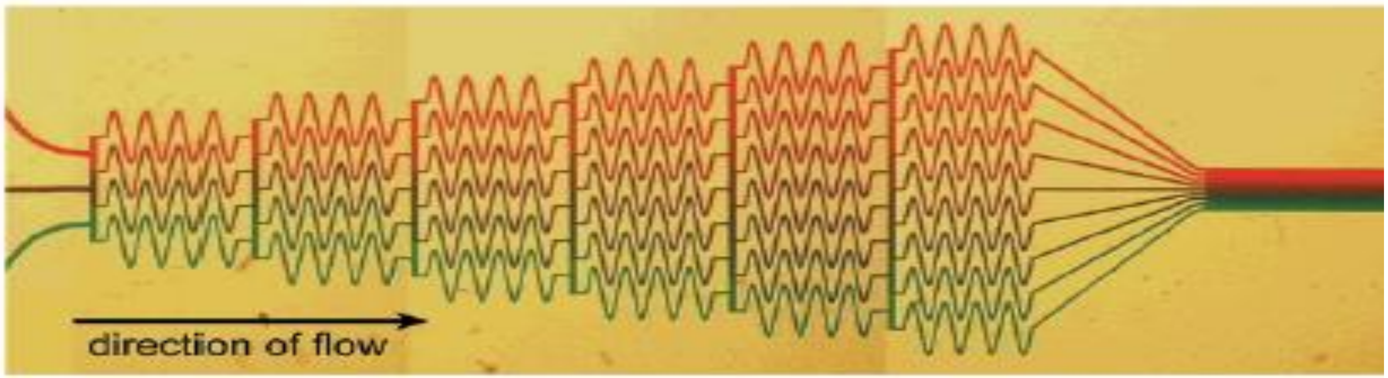


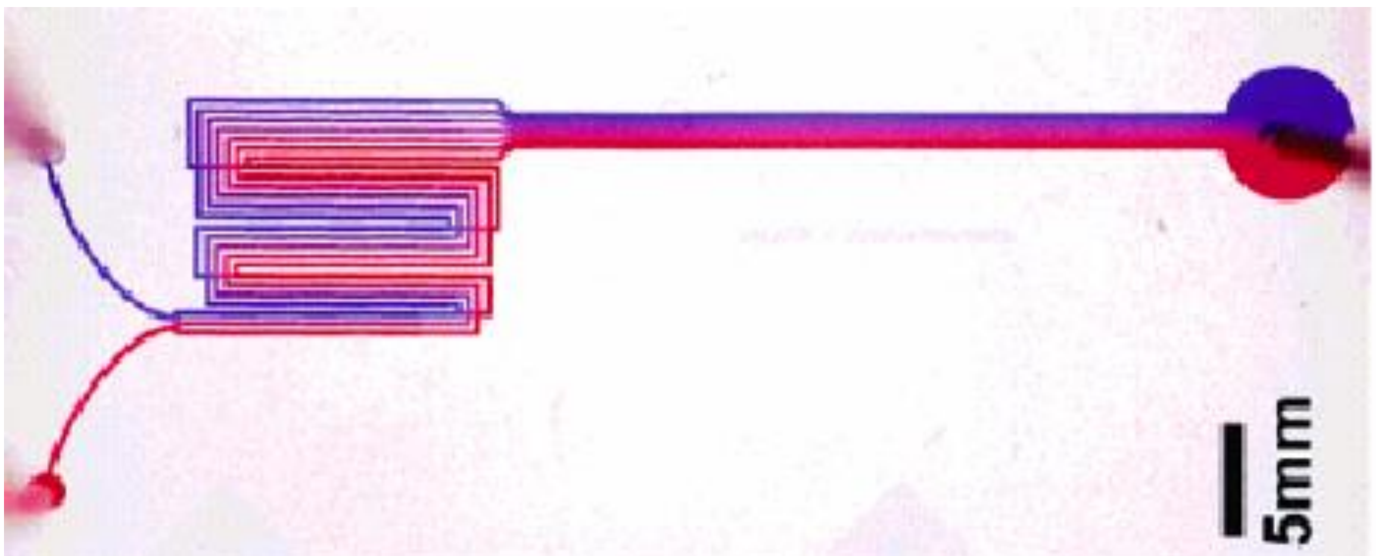
length for efficient mixing $L \sim w \log(\mathrm{Pe})$

$\Rightarrow$ "chaotic mixing" (note: $\mathrm{Re} \sim 0$)

Stroock *et al.* 2002

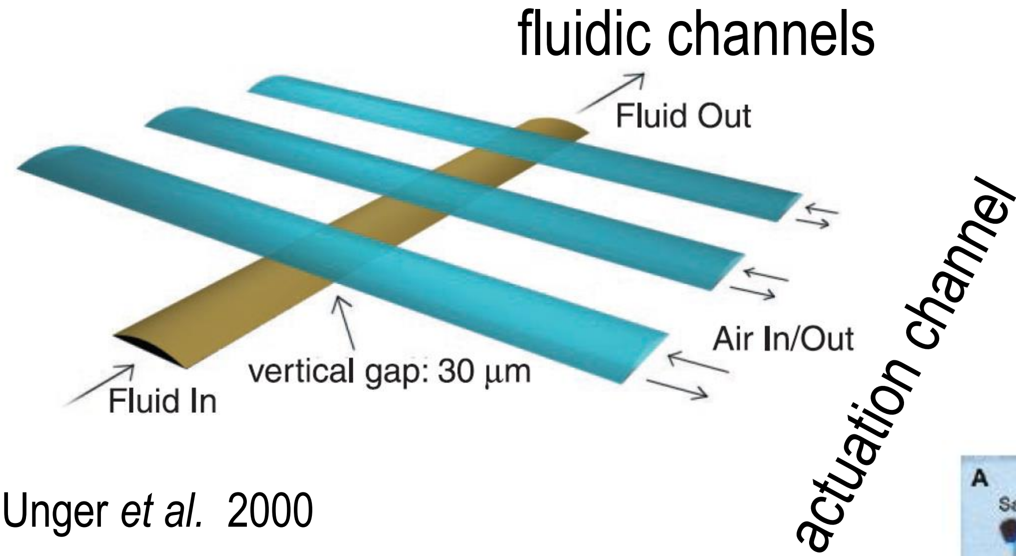
Chaotic mixers help to make compact devices





Whitesides *et al.* 2002

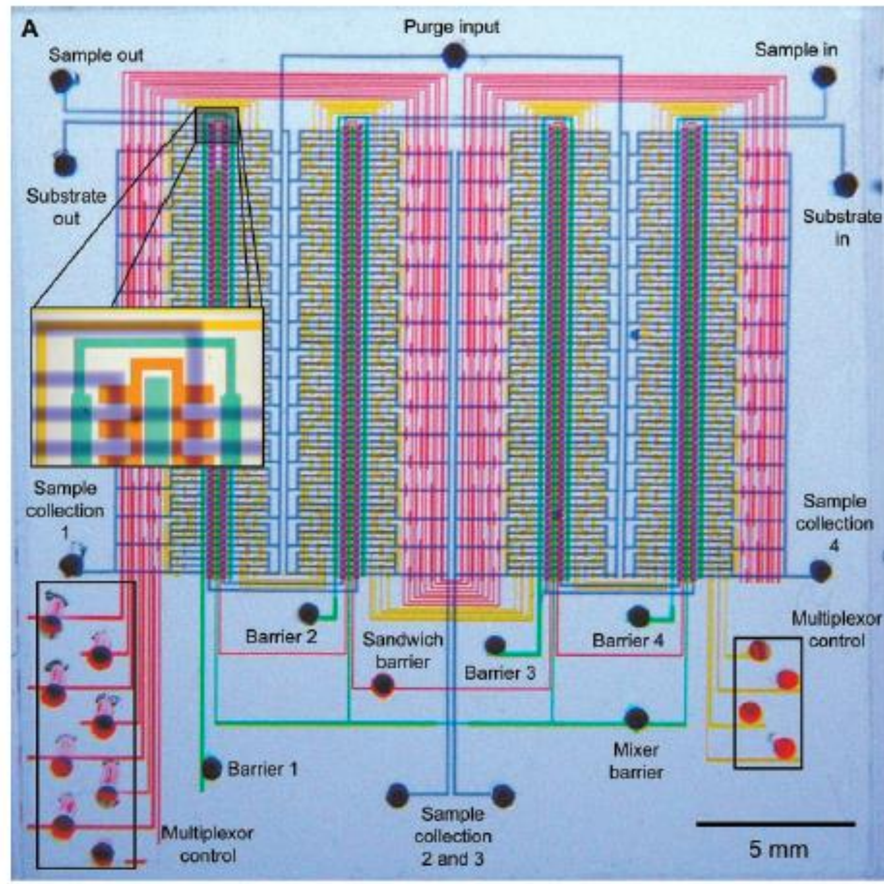
(4) Active mixing: the "rotary" mixer



Unger *et al.* 2000

PDMS is soft ⇒
valves & pumps for a massive integration

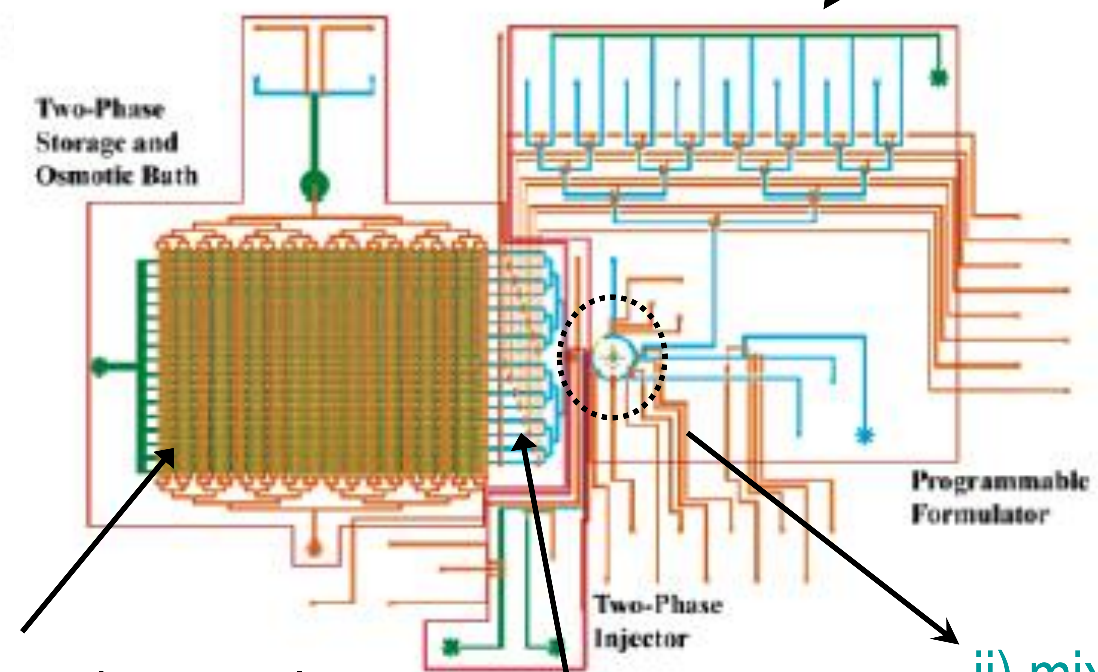
(see P. Joseph's lecture)



Quake *et al.* 2000

Ex: a complete platform for protein crystallization

i) creating mixtures with 64 ≠ reactants



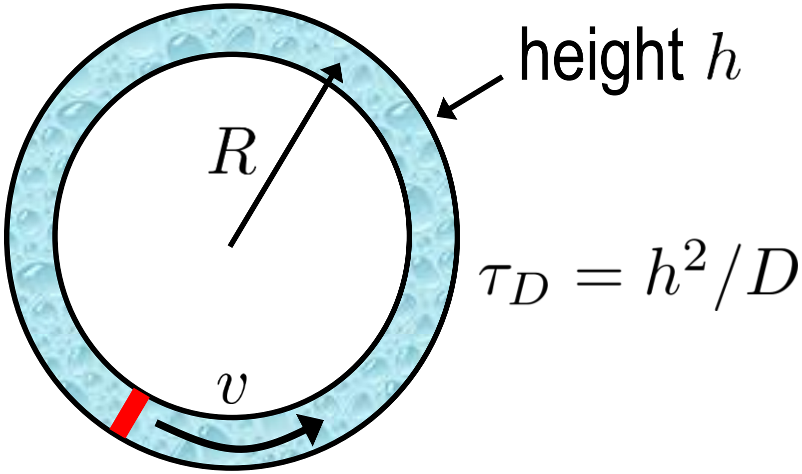
ii) mixing in a nanoliter volume

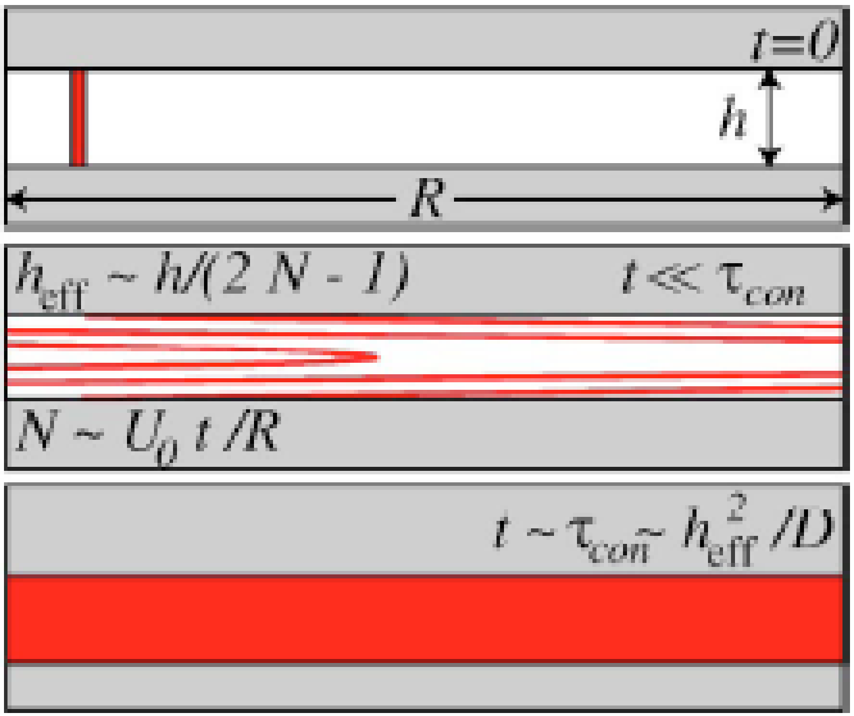
iv) osmotic control

iii) store interesting
mixtures in nL plugs

Lau *et al.* 2007

(4) Active mixing: the "rotary" mixer





Several regimes of mixing

diffusion limited $\quad \mathrm{Pe} = \frac{vh}{D} \ll 1$

$$\tau_1 \sim (2\pi R)^2/D$$

Taylor Aris regime $\quad \tau_d \ll 2\pi R/v$

$$\tau_2 \sim (2\pi R)^2/D_{\mathrm{TA}} \sim \tau_1/\mathrm{Pe}^2$$

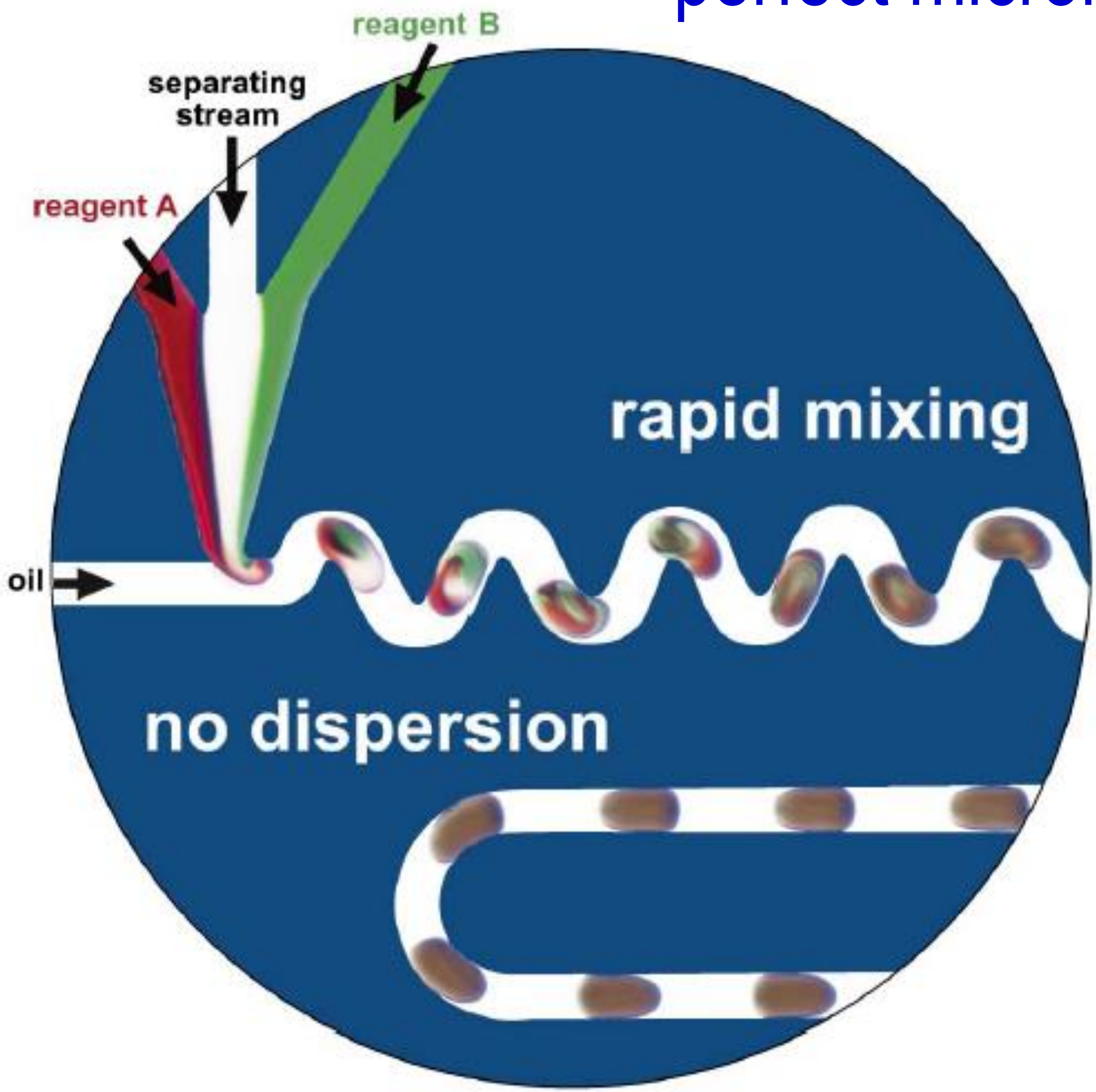
convective stirring regime $\quad \tau_d \gg 2\pi R/v$

$$\tau_3 \sim \tau_1/\mathrm{Pe}^{2/3}$$

$\Rightarrow$ efficient mixing

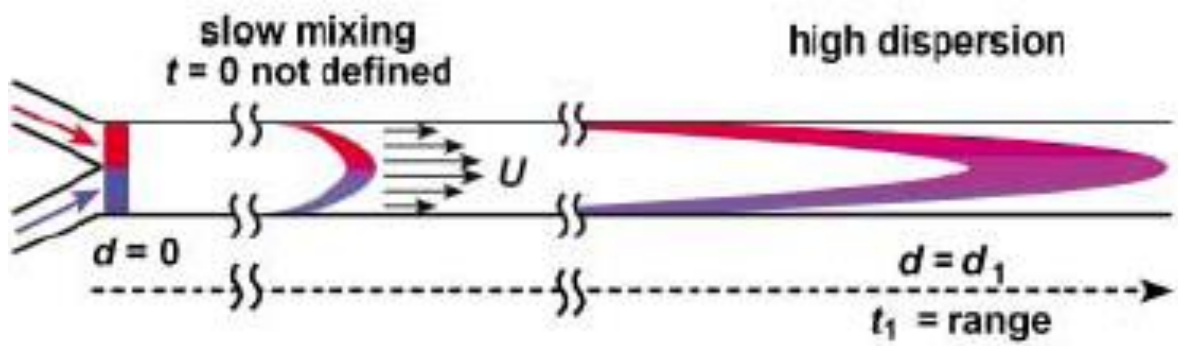
Squires *et al.* 2005

(5) The case of droplets: perfect microreactors ?



Song *et al.* 2003

coflow



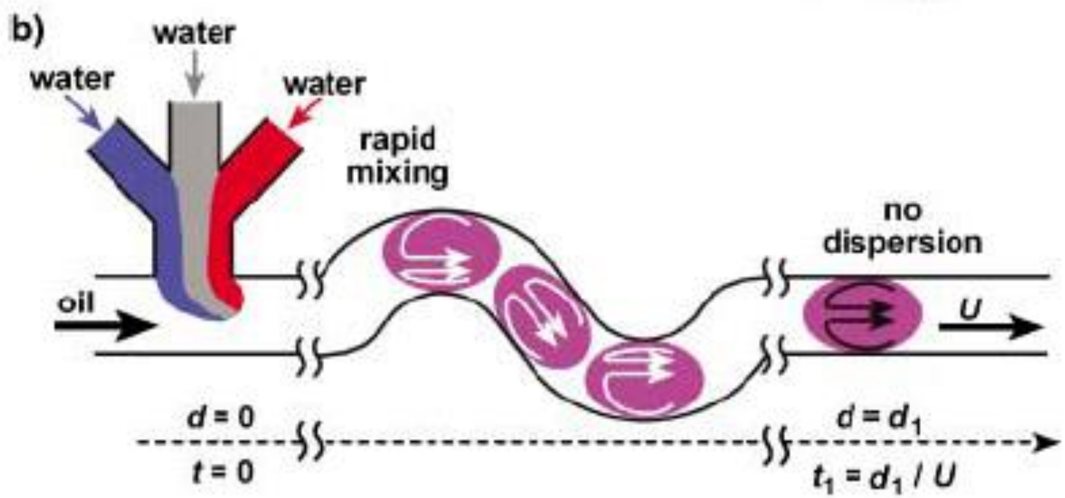
mixing is difficult

$L_n \sim \mathrm{Pe} w$ and $\mathrm{Pe} \gg 1$

hydrodynamic dispersion

dispersion of the residence times

droplets



fast mixing

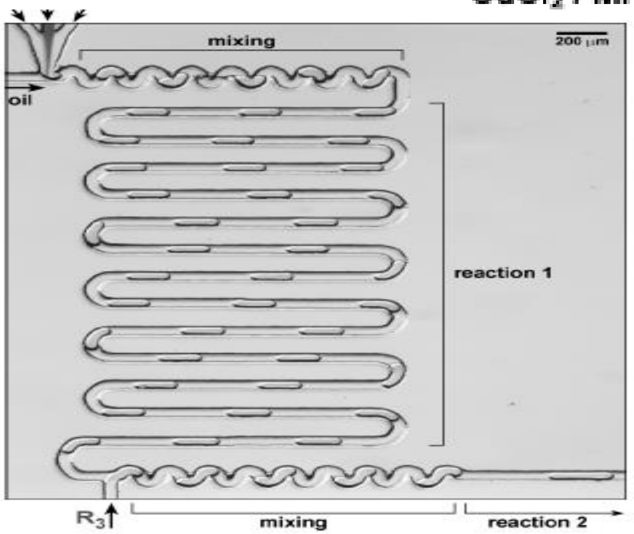
no hydrodynamic dispersion

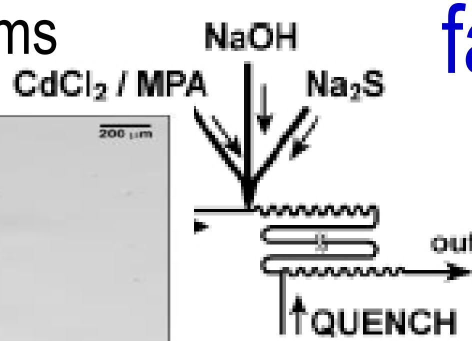
Song *et al.* 2003

Droplets are very well-suited for fast chemical reactions

mixing ≈ 5 ms

75 ms

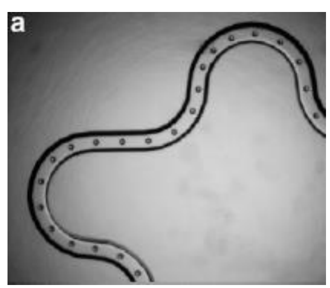


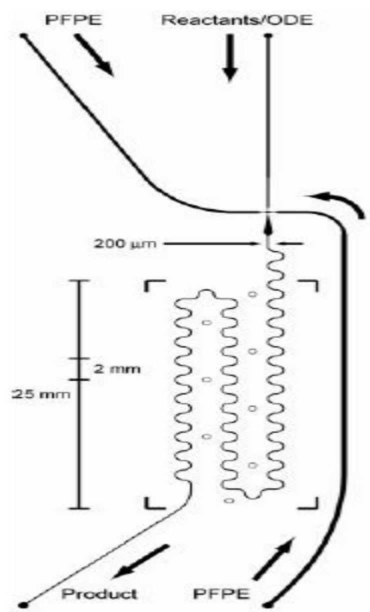


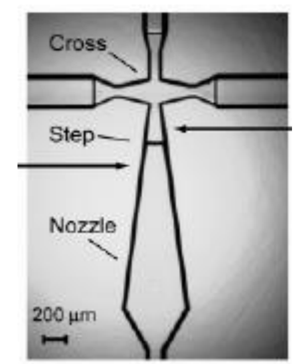
⇒ multistep synthesis of CdS nanoparticles

Shestopalov *et al.* 2004

the same at high temperature:



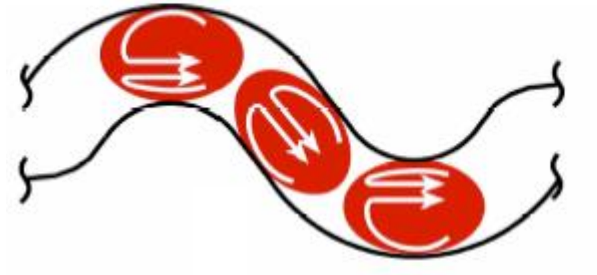


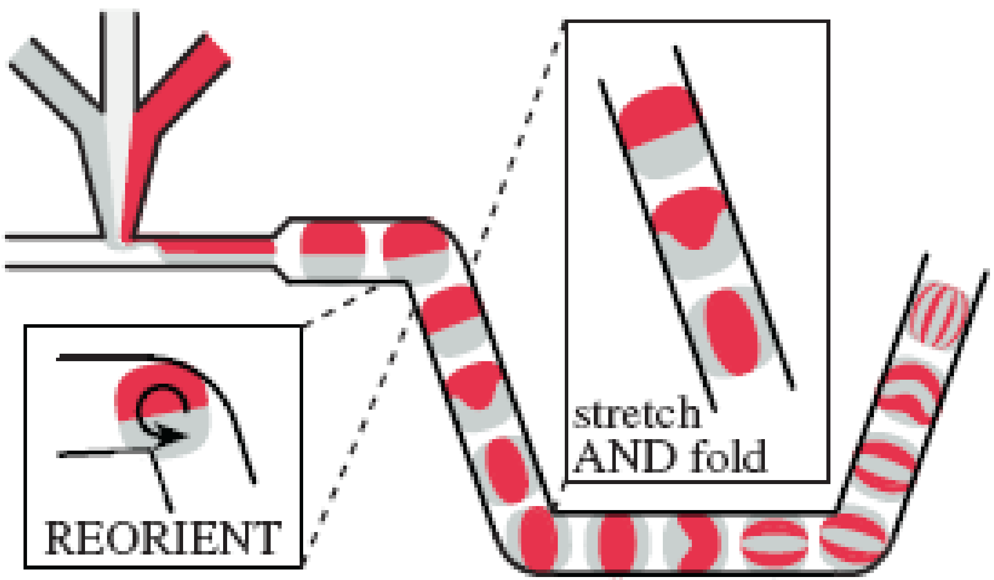


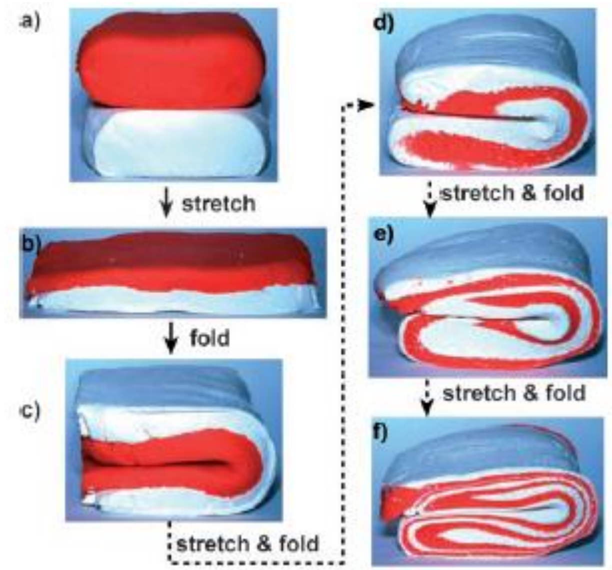
Chan *et al.* 2005

Mixing within droplets ?

Streamlines in windings







chaotic mixing

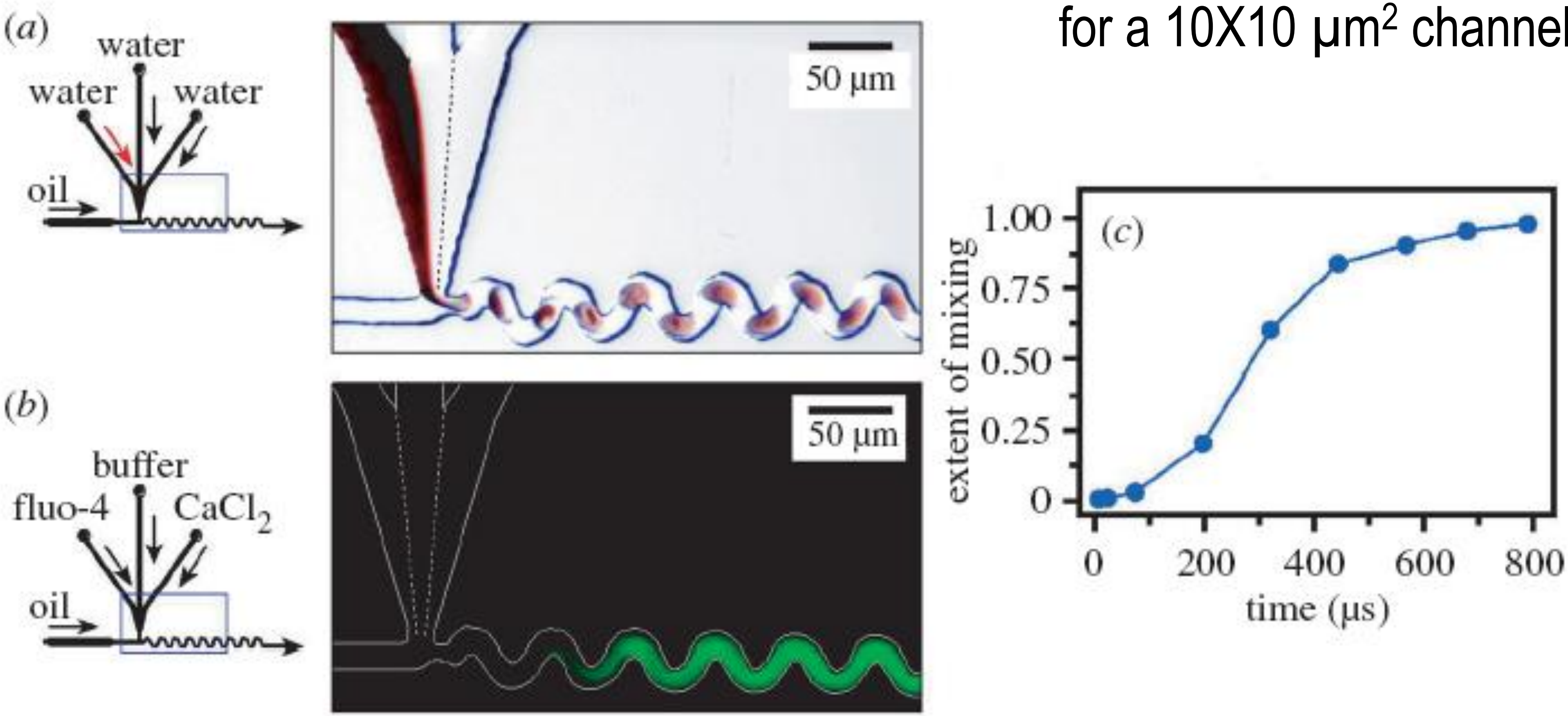
again $\mathrm{Re} \sim 0$

$$L \sim w \log(\mathrm{Pe})$$

Song *et al.* 2003

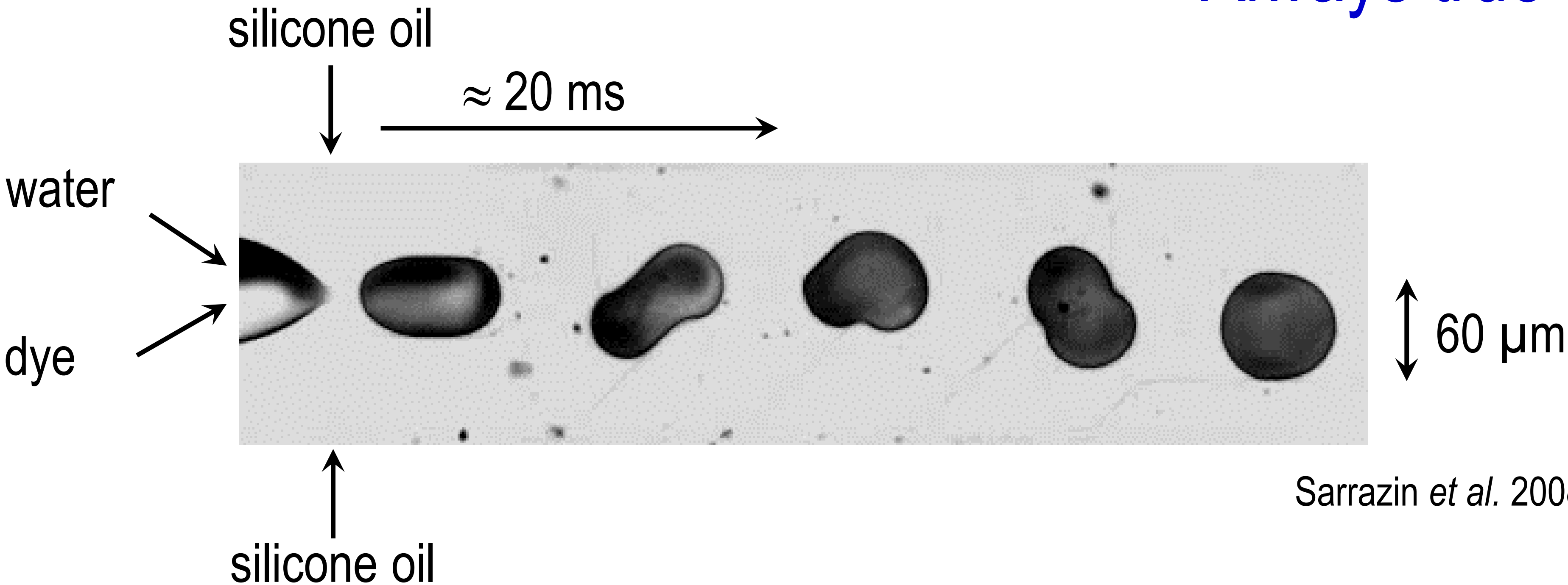
Evidence for a fast mixing

for a 10X10 μm^2 channel

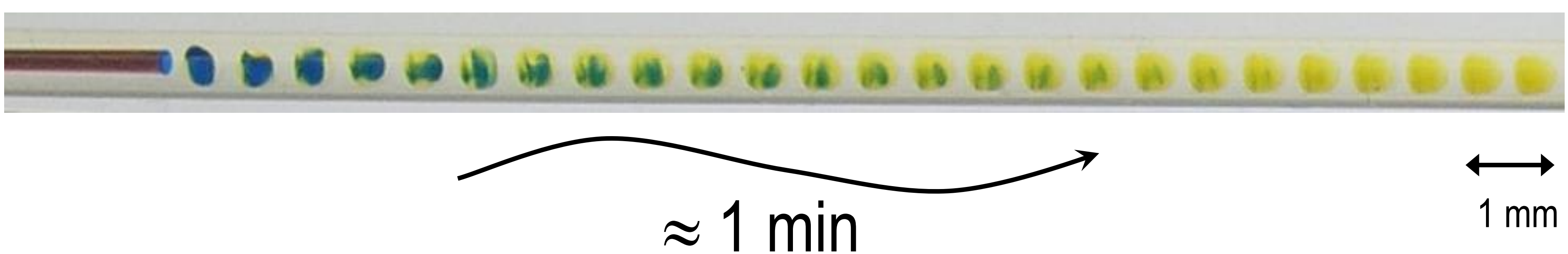


Song *et al.* 2003

Always true ?



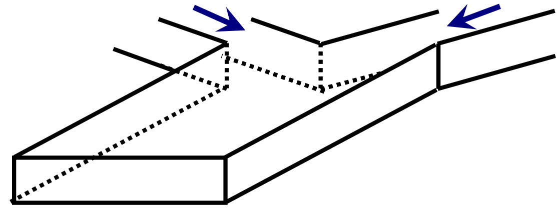
Sarrazin *et al.* 2008



⇒ take care of scale, flow rates, geometry, etc.

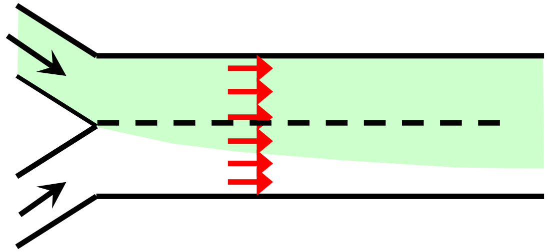
Basics

convection/diffusion, conservation equation



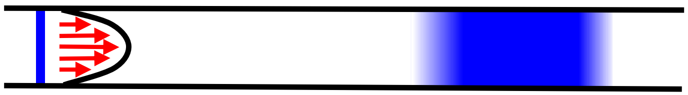
Co-flow

slow mixing, reaction-diffusion



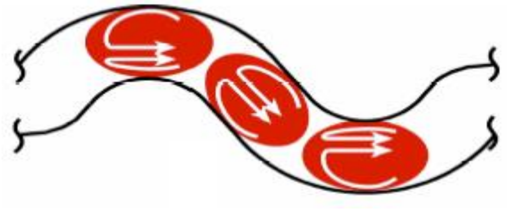
Shear dispersions

Leveque and aylor-Aris dispersions, role of gravity, application to sensors.



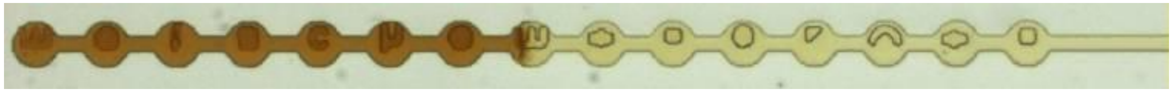
Mixing

small size, chaotic mixers, droplets



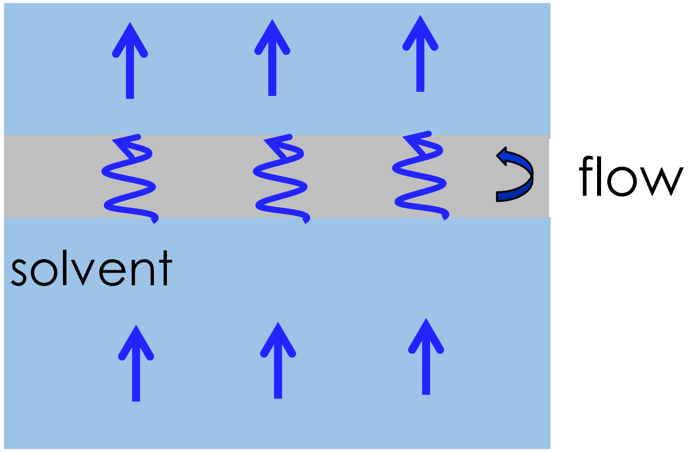
Membranes

pervaporation



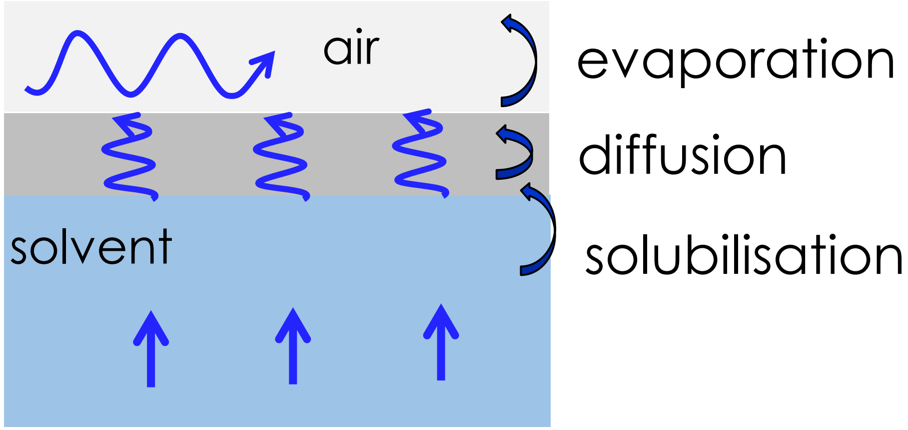
Controlling transport using "membranes"

Ultra-filtration



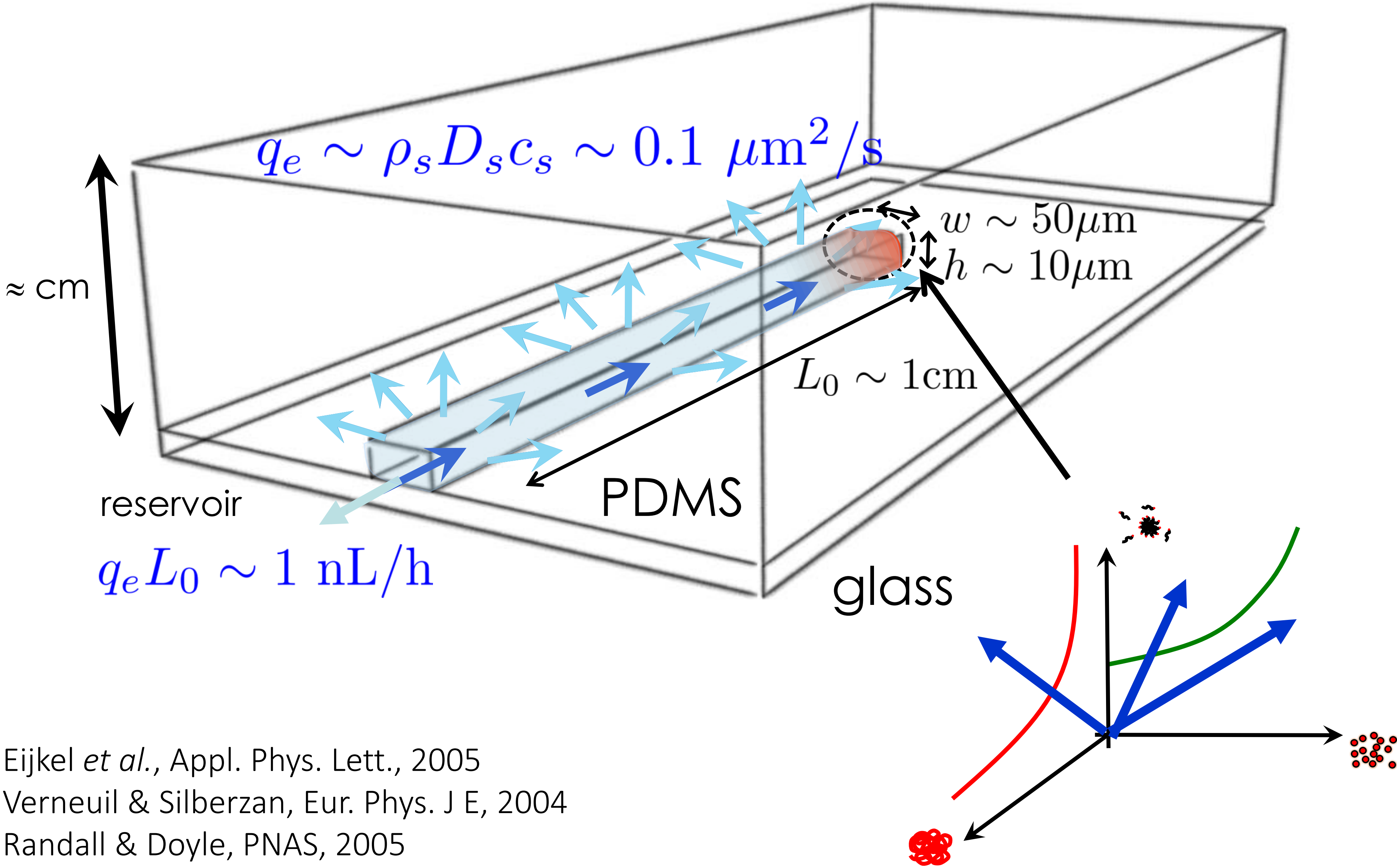
- nanoporous membrane (1-10 nm)
- only solutes below the pore size cross the membrane
- driven by a **pressure difference**

Pervaporation



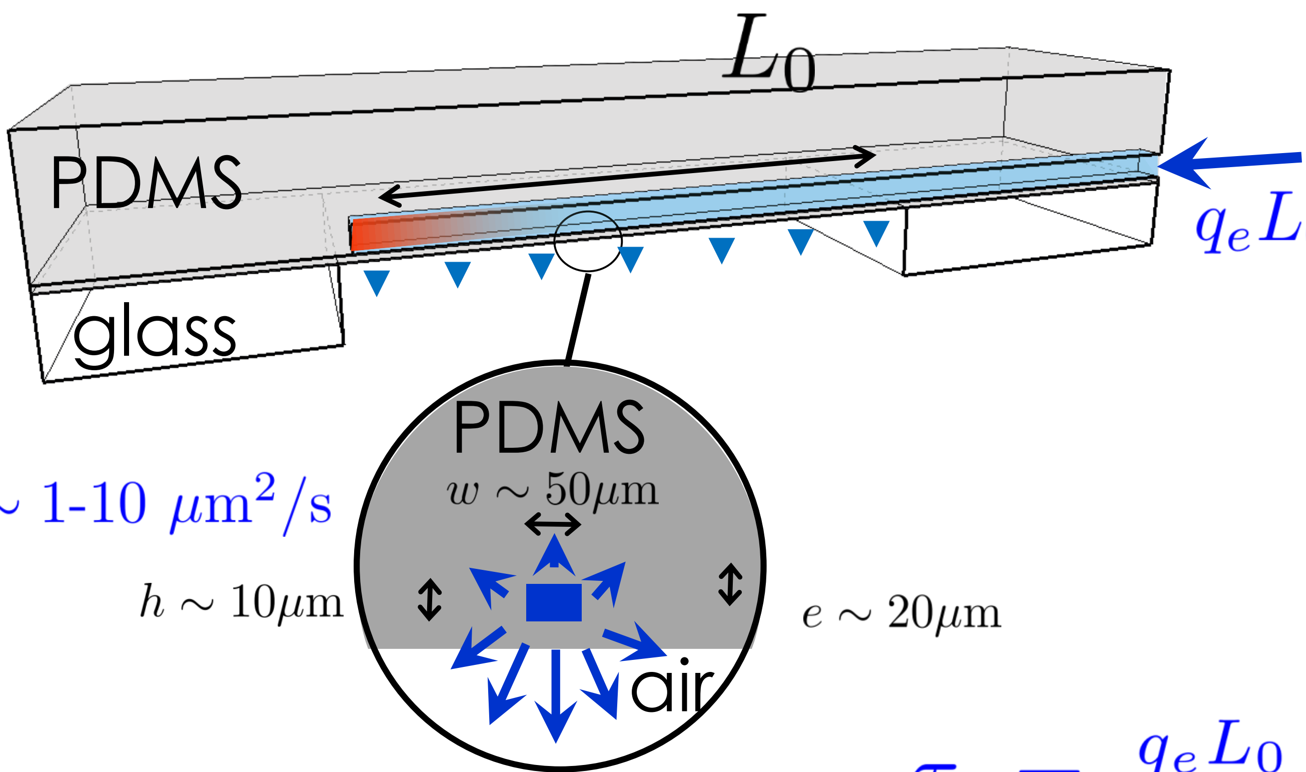
- dense membrane
- only solvents cross the membrane
- driven by a difference of **chemical activity**

PDMS microfluidics:
Water pervaporation through the chip's matrix



Eijkel *et al.*, Appl. Phys. Lett., 2005
Verneuil & Silberzan, Eur. Phys. J E, 2004
Randall & Doyle, PNAS, 2005

Enhanced pervaporation using multilayer soft lithography



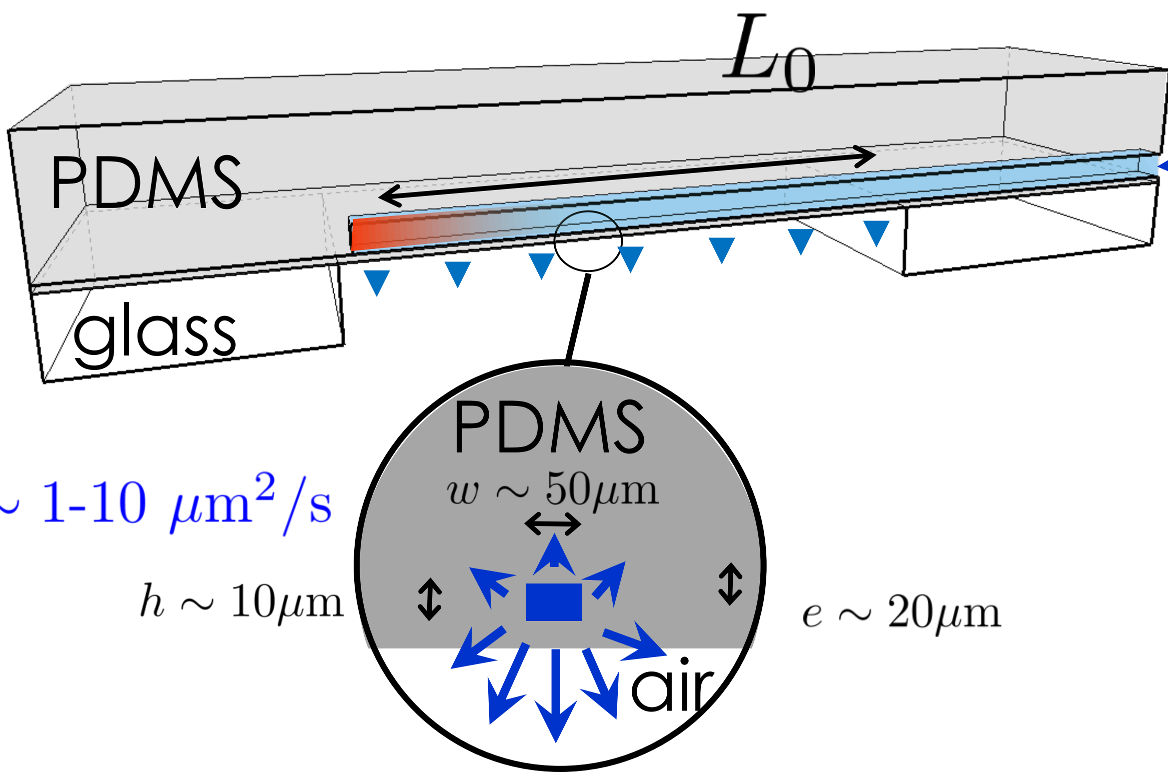
$q_e L_0 \sim$ 10-100 nL/h

$q_e \sim$ 1-10 $\mu m^2/s$

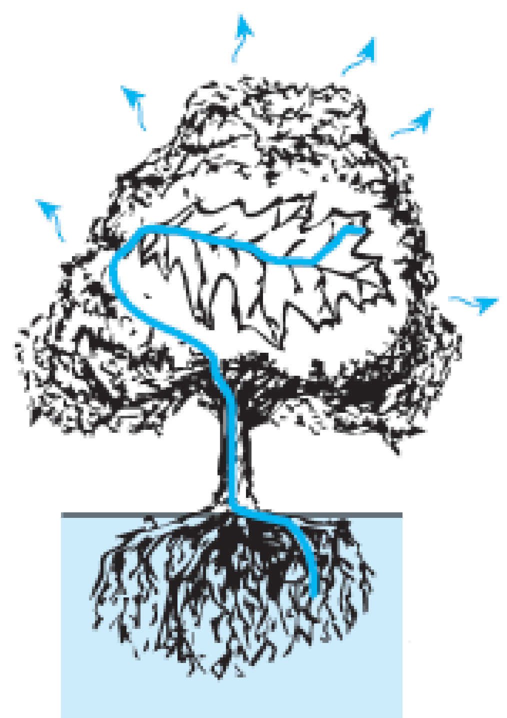
$$\tau_e = \frac{q_e L_0}{h w L_0} \sim \text{100-1000 s}$$

Leng *et al.*, Phys. Rev. Lett., 2006

Enhanced pervaporation using multilayer soft lithography



$q_e \sim$ 1-10 μm^2/s

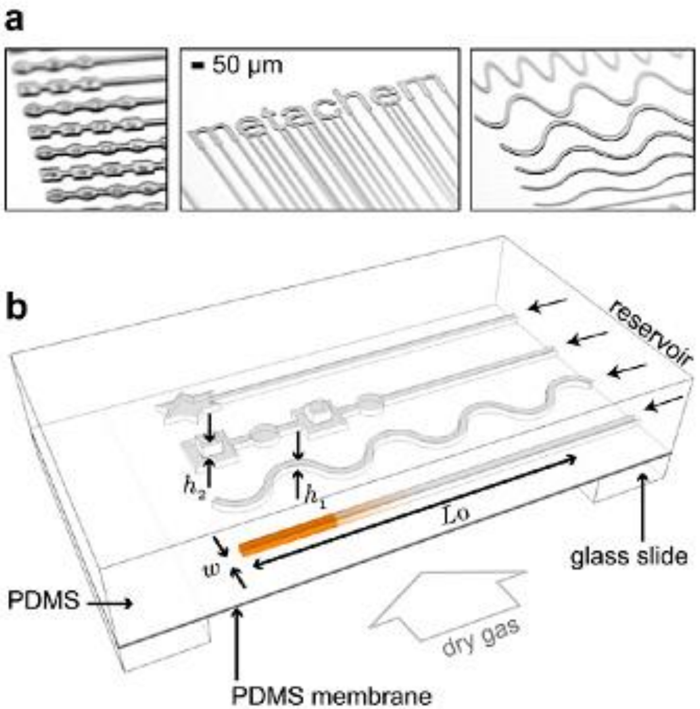


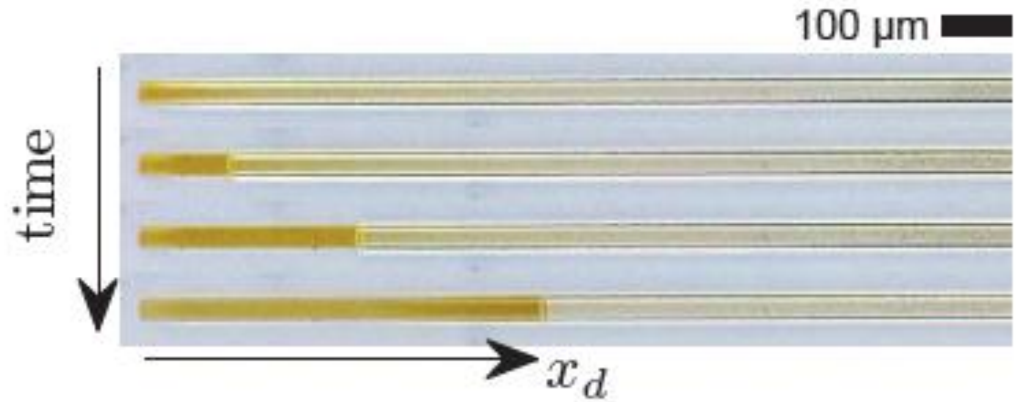
$$\tau_e = \frac{q_e L_0}{h w L_0} \sim 100\text{-}1000 \text{ s}$$

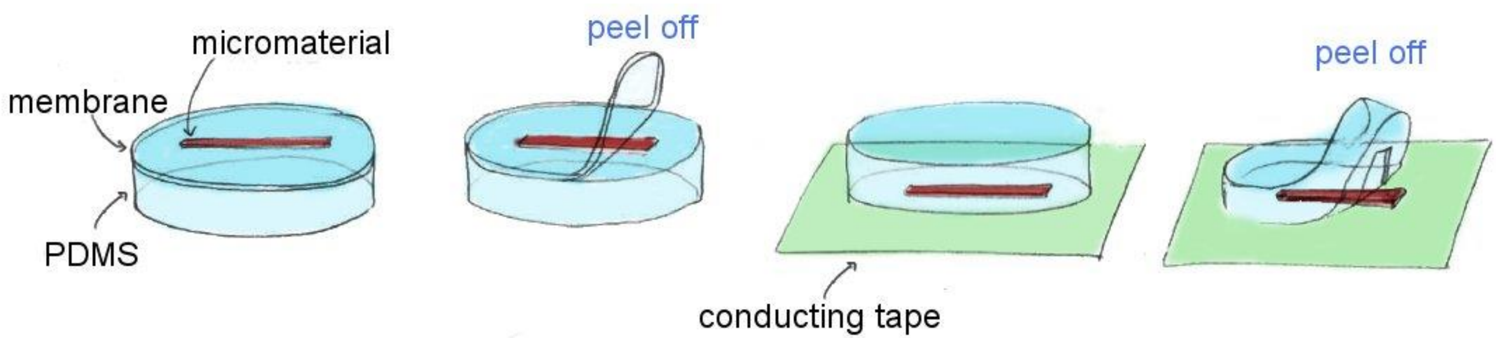
Leng *et al.*, Phys. Rev. Lett., 2006

Wheeler *et al.*, 2008

Application 1: Making micromaterials

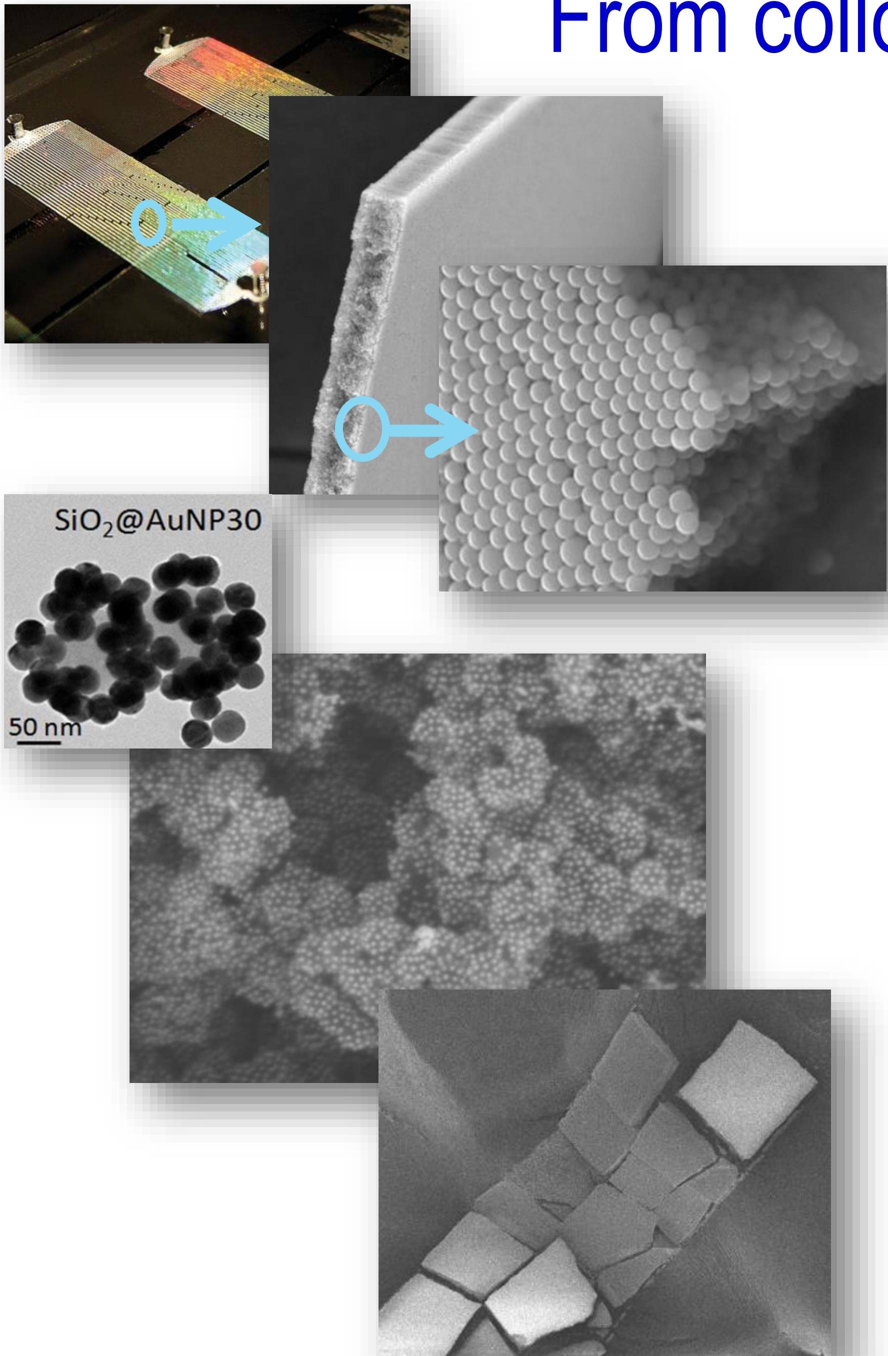


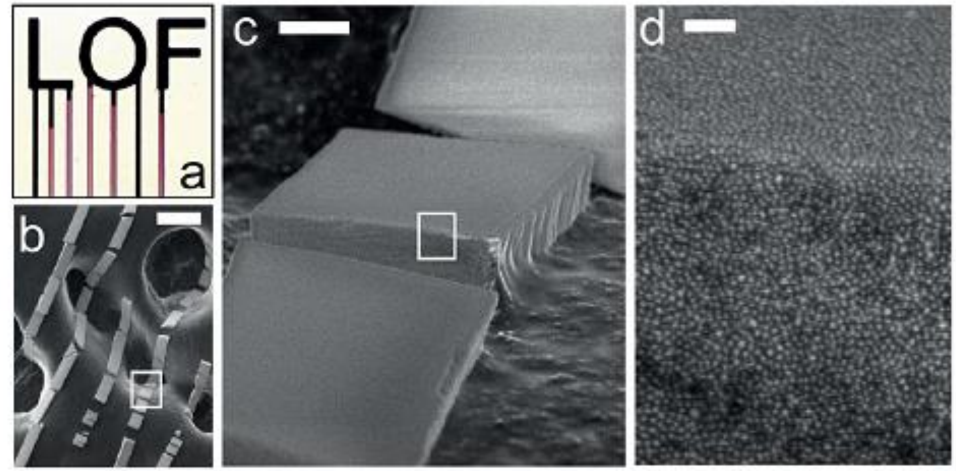




pictures: J. Leng

From colloids & nano (~ 10-100 nm)…

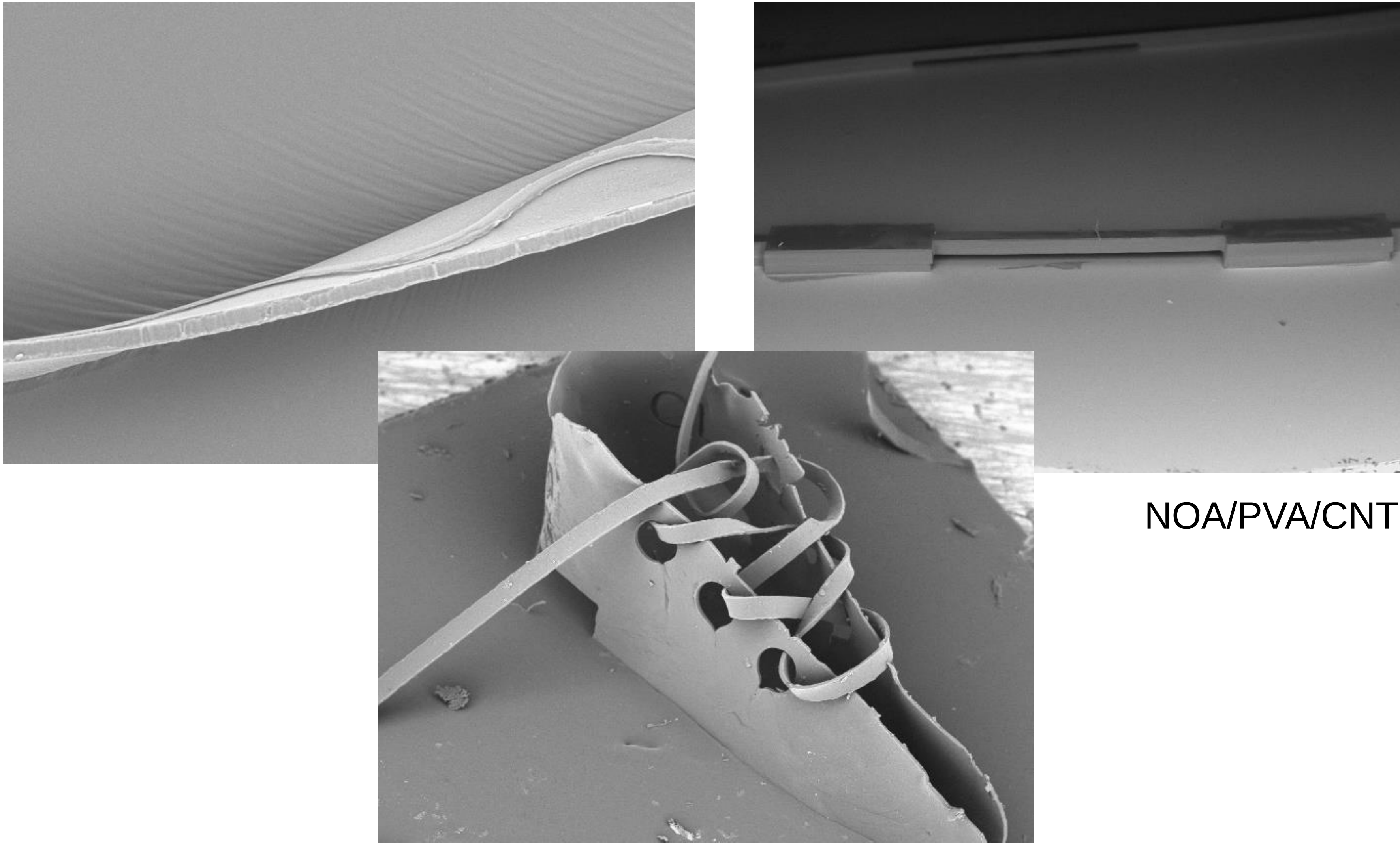




→ optical metamaterials, SERS, …

Merlin *et al.*, Soft Matter, 2012
Angly *et al.*, ACS Nano, 2013
Massé *et al.*, Langmuir, 2013
Baron *et al.*, Opt. Mat. Express, 2013
Gomez-Grana *et al.*, Chem. Mater. 2015
Gomez-Grana *et al.*, Mater. Horizon 2016

…to polymers & composites



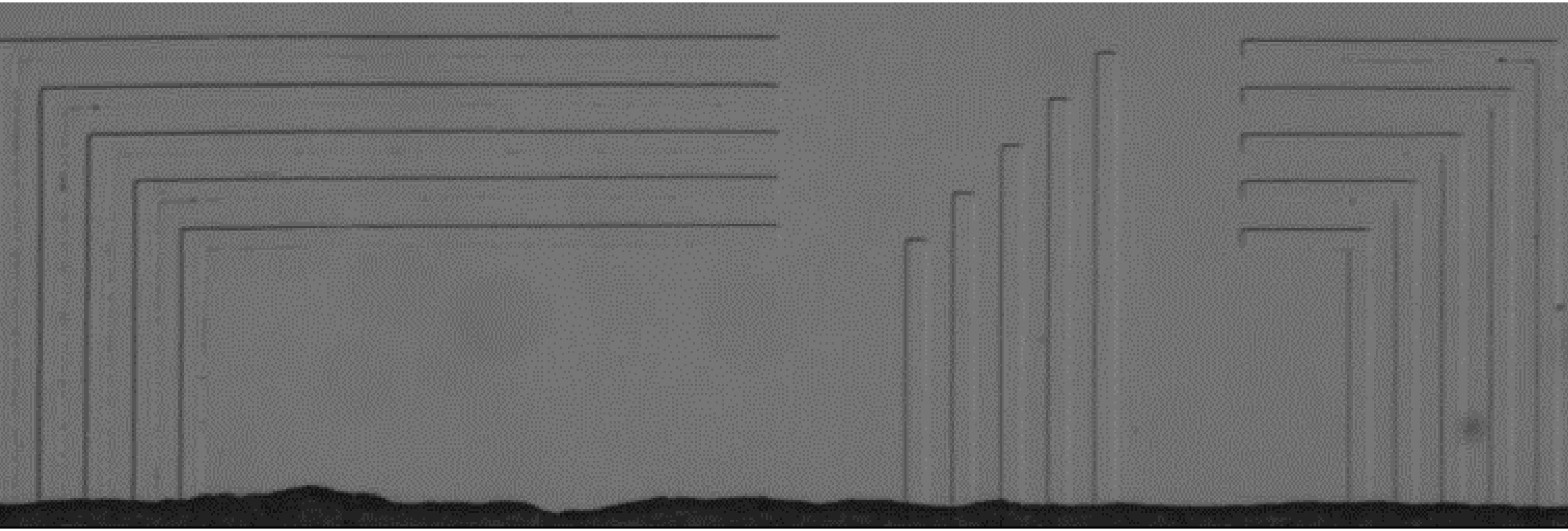
NOA/PVA/CNT

→ organic MEMS, electrodes, …

Yao *et al.* Macromolecules 2015
Laval *et al.* Soft Matter 2016

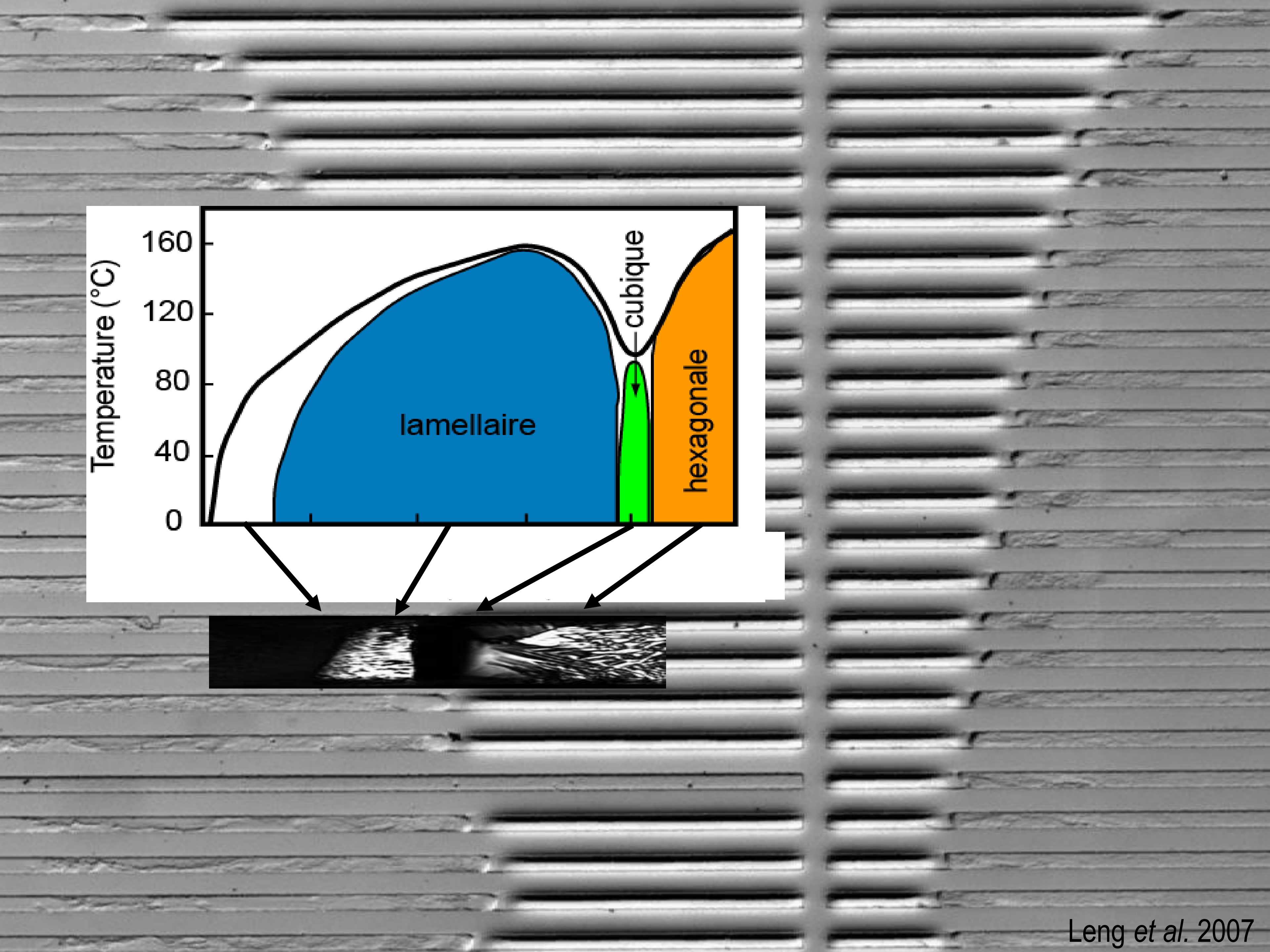
Application 2: Screening phase diagrams

→ e.g. crystallization



Application 2: Screening phase diagrams

→ e.g. surfactants



Leng *et al.* 2007

more informations:

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