Digital μ-fluidics
The flow of confined bubbles and drops

20-04-2009

Michiel Kreutzer

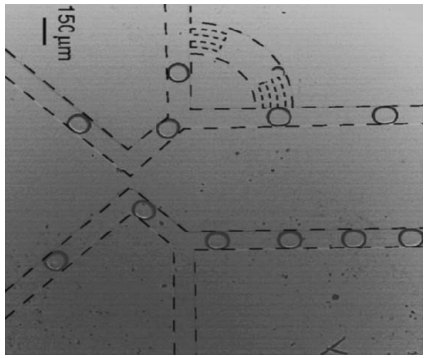
Department of Chemical Engineering

Delft University of Technology

TU Delft

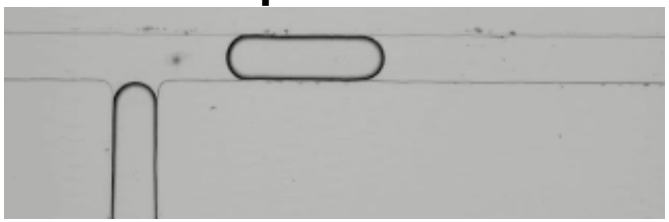
Every drop/bubble is a test tube

Distribute



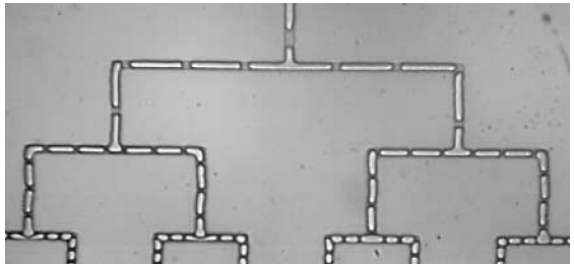
Cristobal *et al.*, App. Phys. Lett. (2006)

Optical valve



Baroud *et al.*, Lab Chip (2007)

Split-up

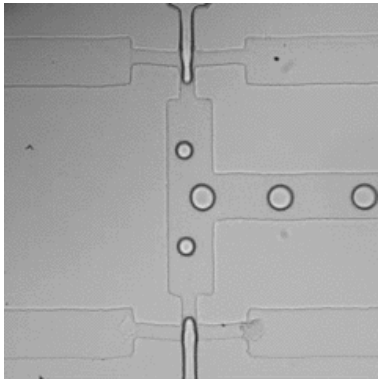


Link *et al.*, Phys. Rev. Lett. (2004)

Synchronize

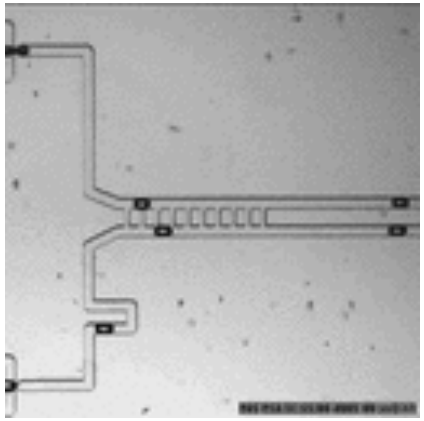
Sort

Merge

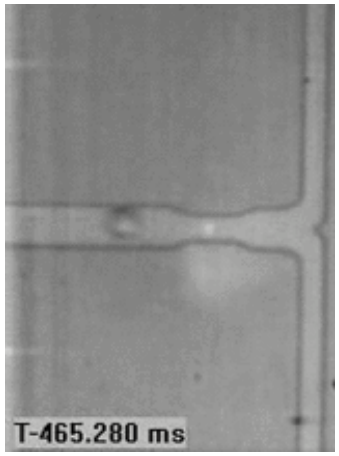


Link *et al.*, Ang. Chem. Int. Ed. (2006)

www.raindancetechnologies.com

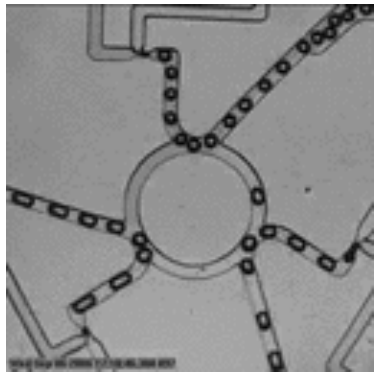


Prakash *et al.*, Science (2007)



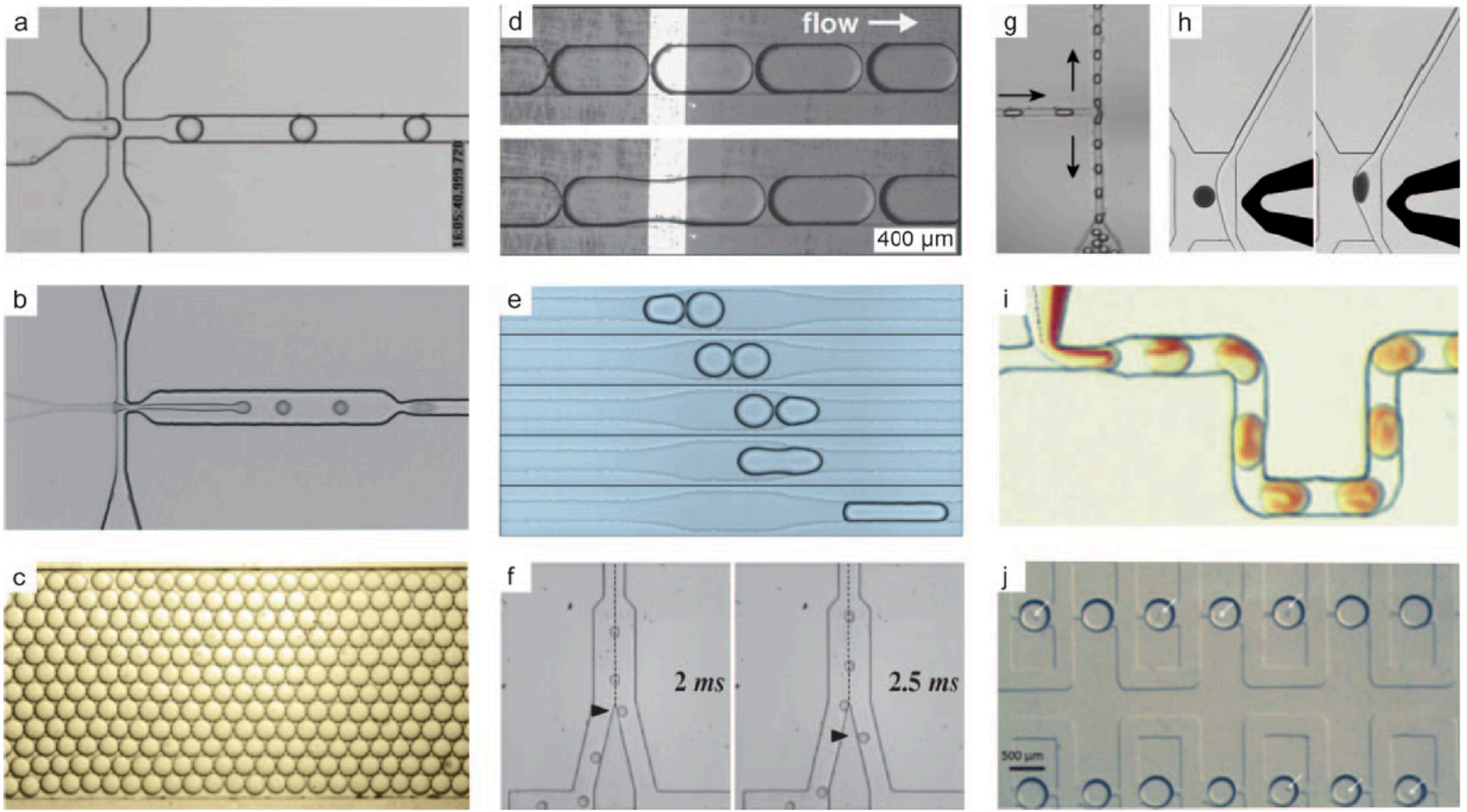
Baroud *et al.*, Lab Chip (2007)

Feedback



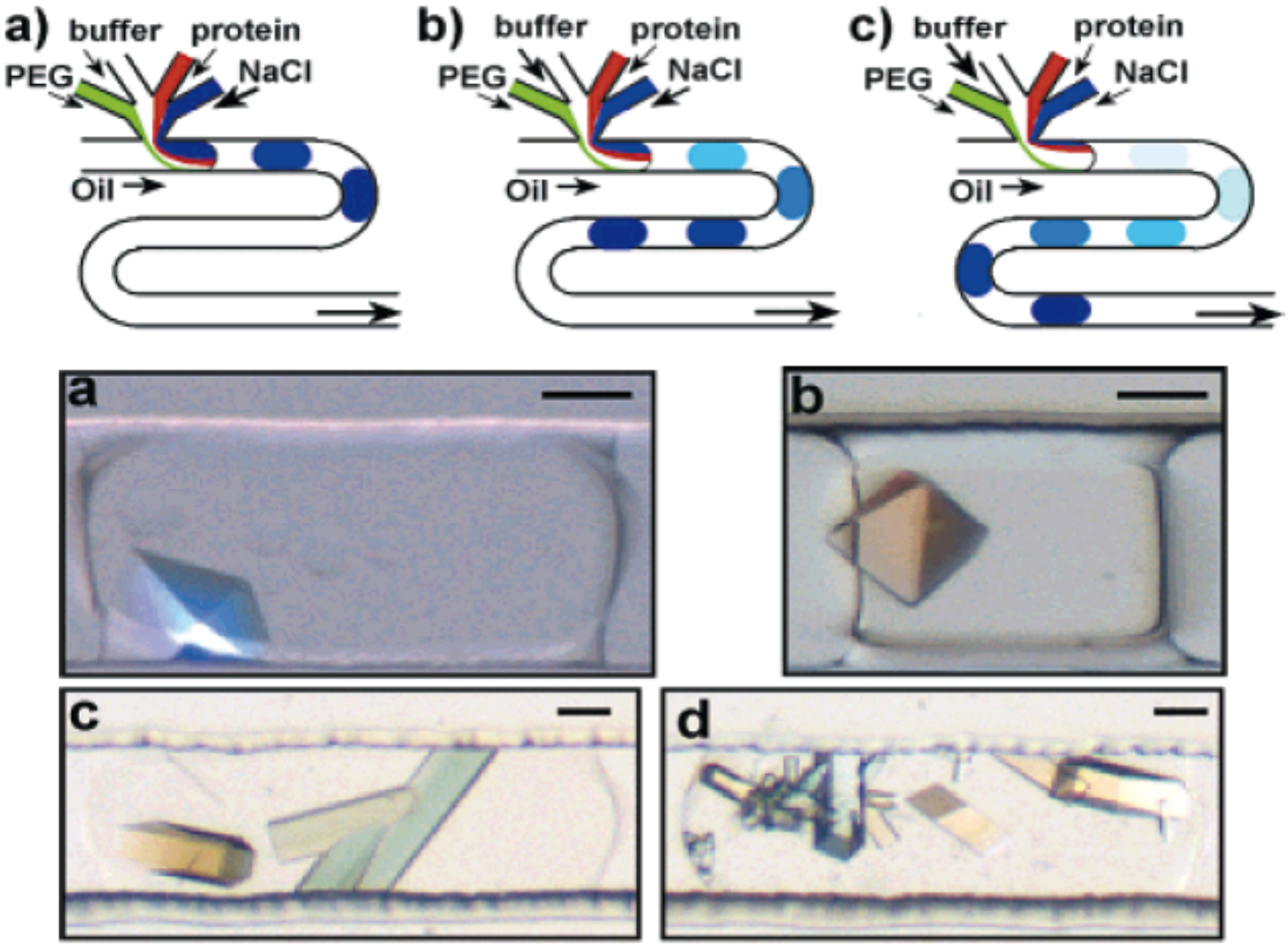
Prakash *et al.*, Science (2007)

Formation, mixing, merging, selection, …



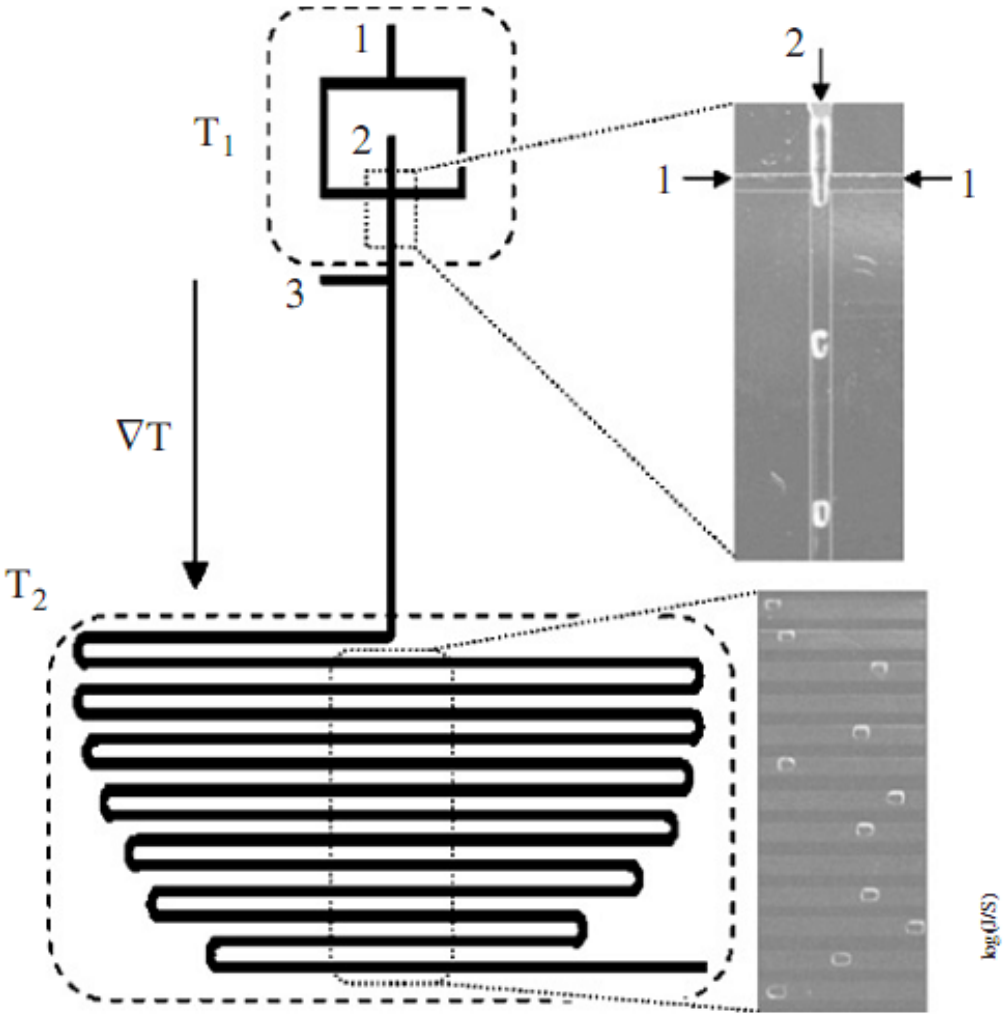
Theberge, *Angew. Chem. Int. Ed.* 49 (2010), 2

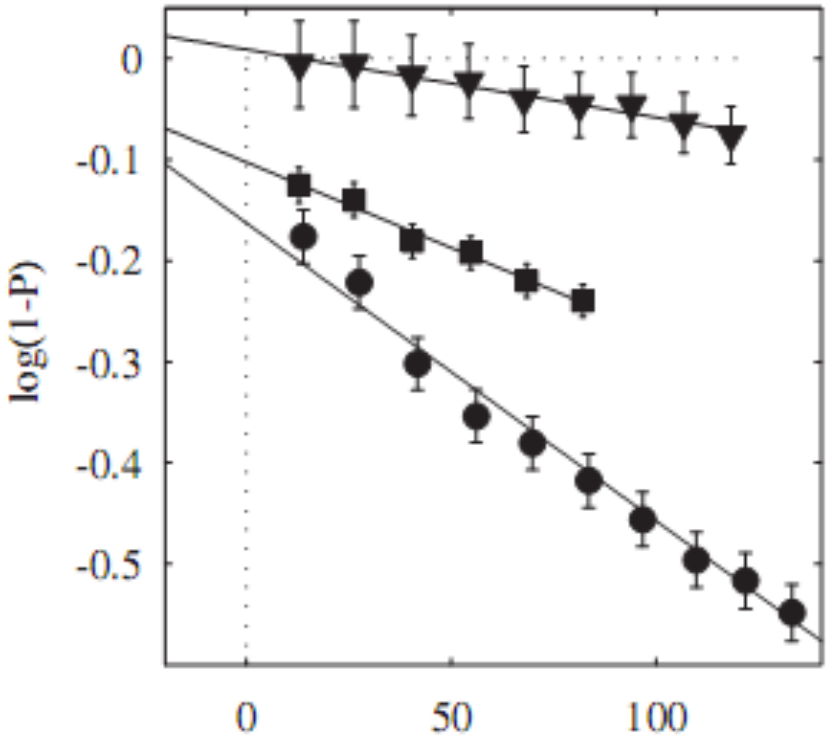
Rapid variations with minimal sample use

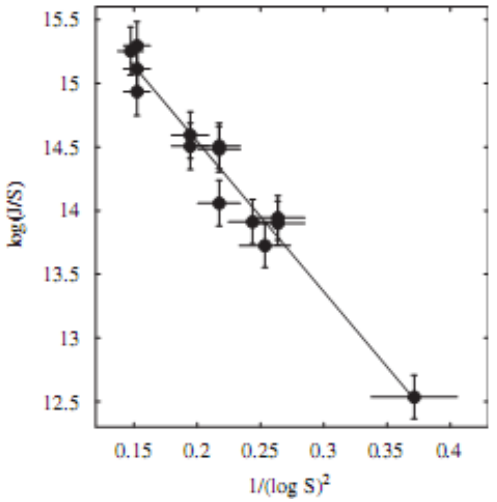


Zheng *JACS* 125 (**2003**), 11170

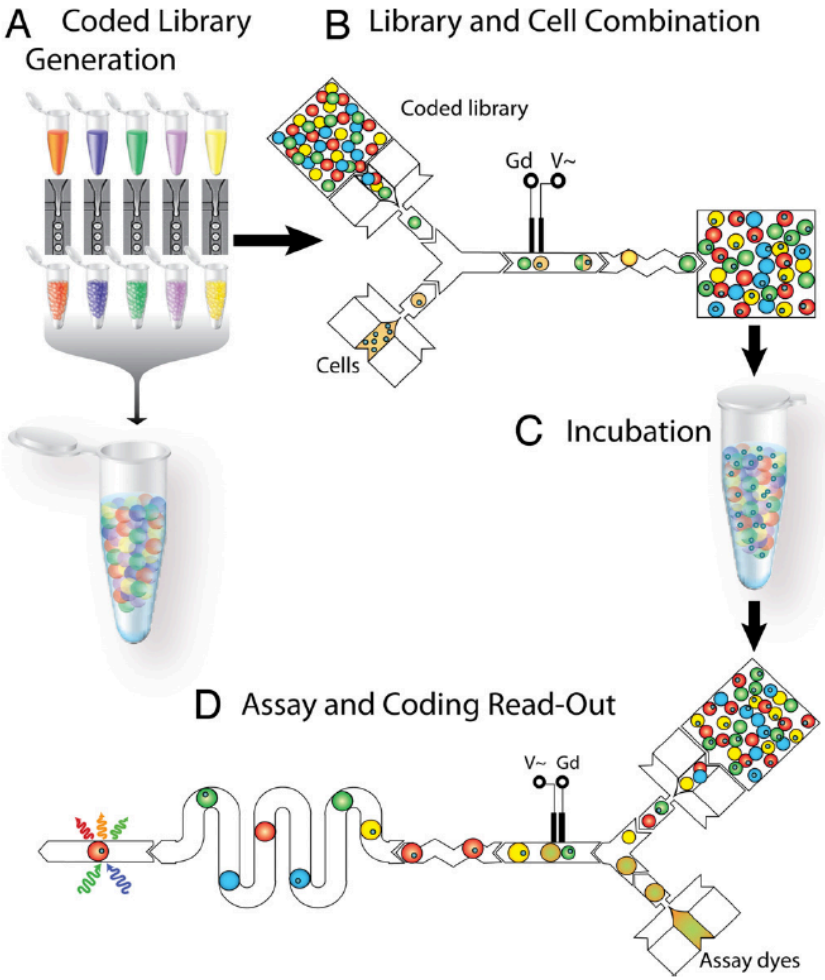
High Throughput Nucleation Statistics

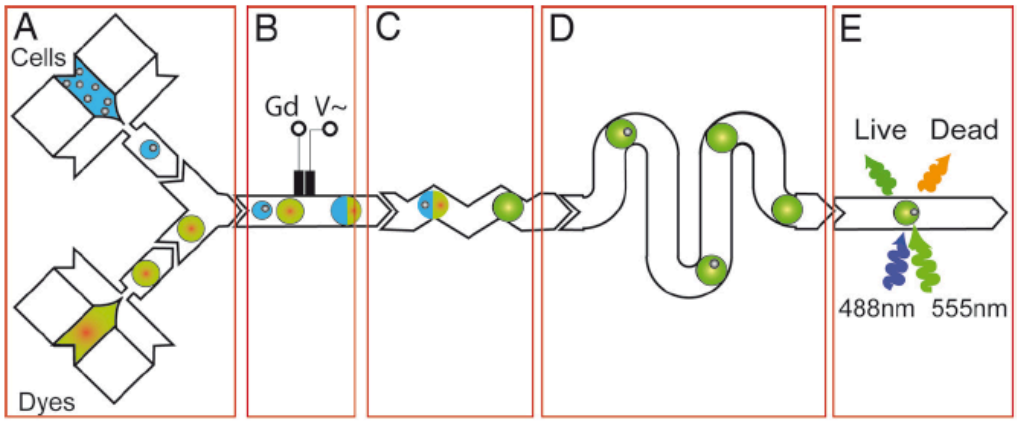


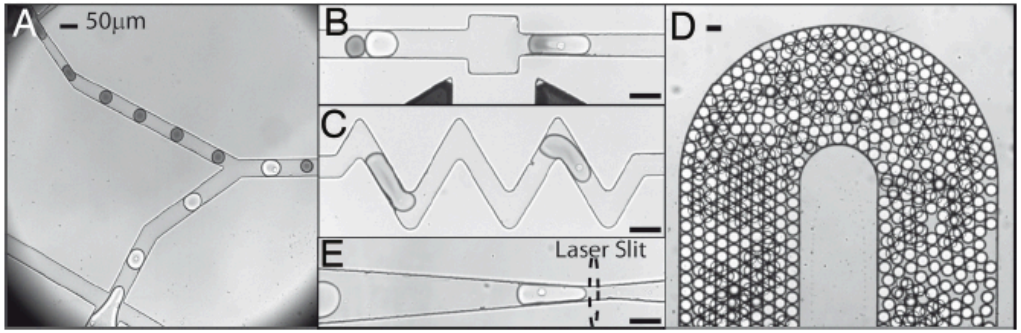




Single cell studies

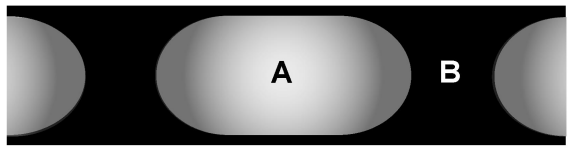






Brouzes, *PNAS* 106 (2009), 14195

Lab-on-a-chip Chemistry



1

A reacts with B

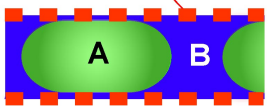
Reaction front

Examples:
- Direct fluorination
- Phase transfer catalysis

2

A reacts with B in the presence of a catalyst Y

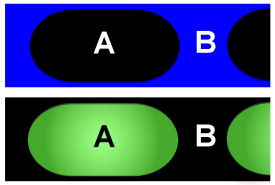
Catalyst Y



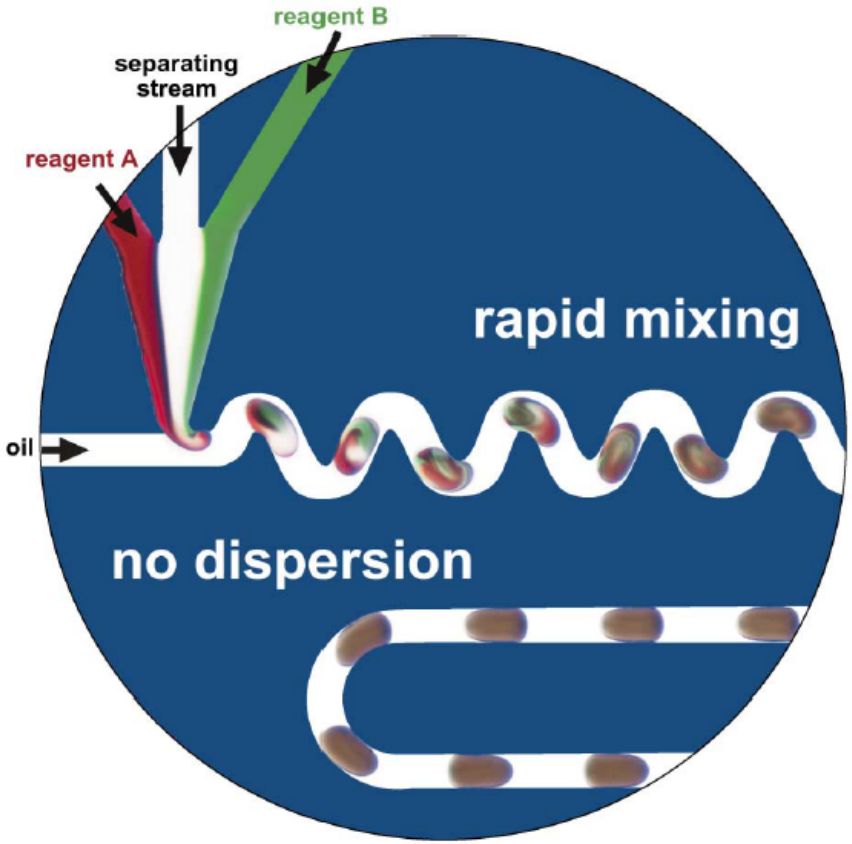
- Hydrogenation
- Oxidation

3

Reaction occurs in A (or B) and B (or A) is a passive 'segmentation tool'



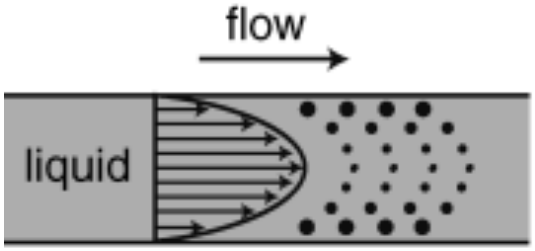
- Liquid-phase reactions
- Particle synthesis



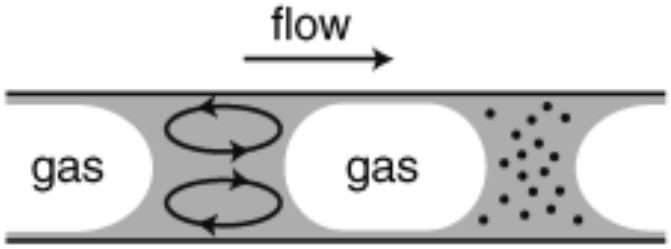
Ismagilov, **2006**

Kreutzer et al., *Chem Eng Sci* 60 (**2005**) 5895
Gunther et al. , *Lab Chip* 6 (**2006**) **1487**

Motivation – Plug Flow & Rapid Mixing

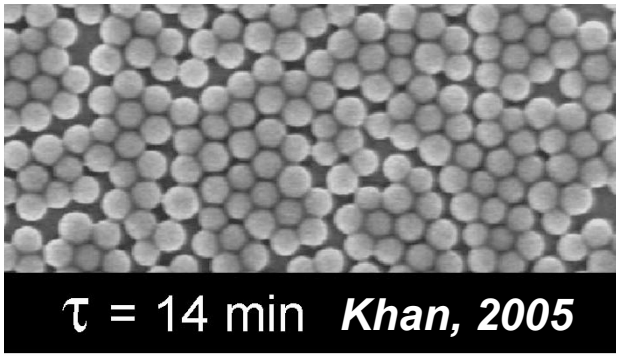


single-phase



segmented

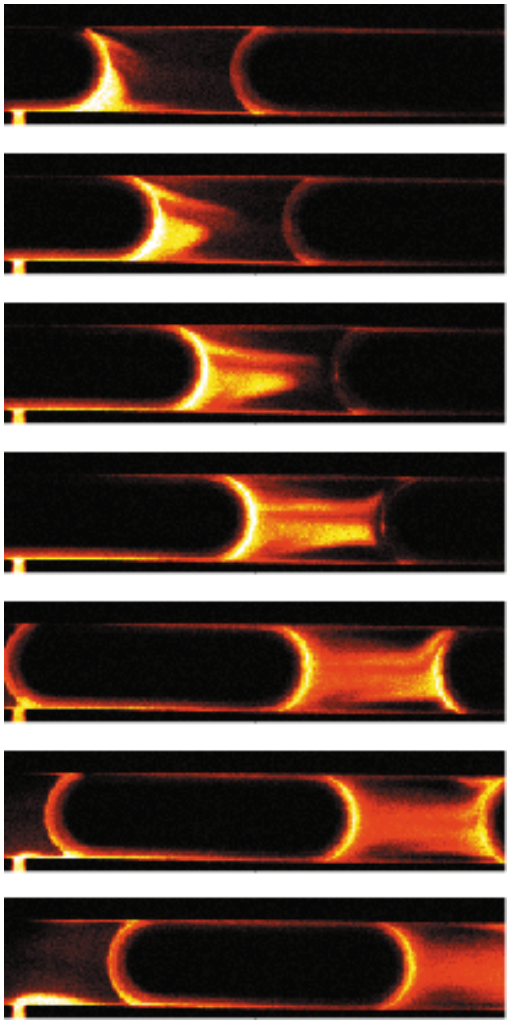
Material Synthesis



Res. Time Distribution = Particle Size Distribution

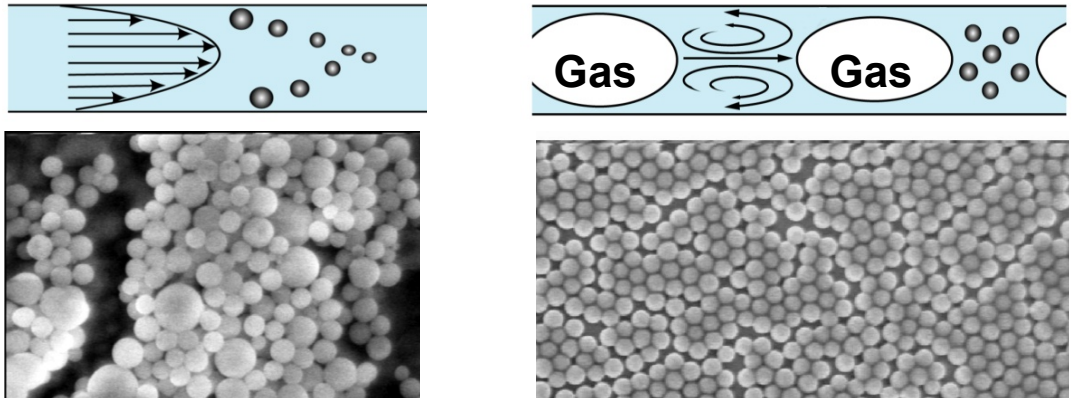
High-Throughput Analytical Chemistry

Karger 2005

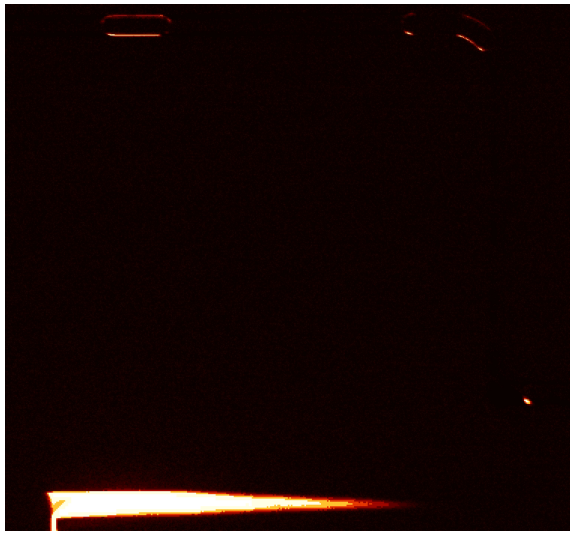


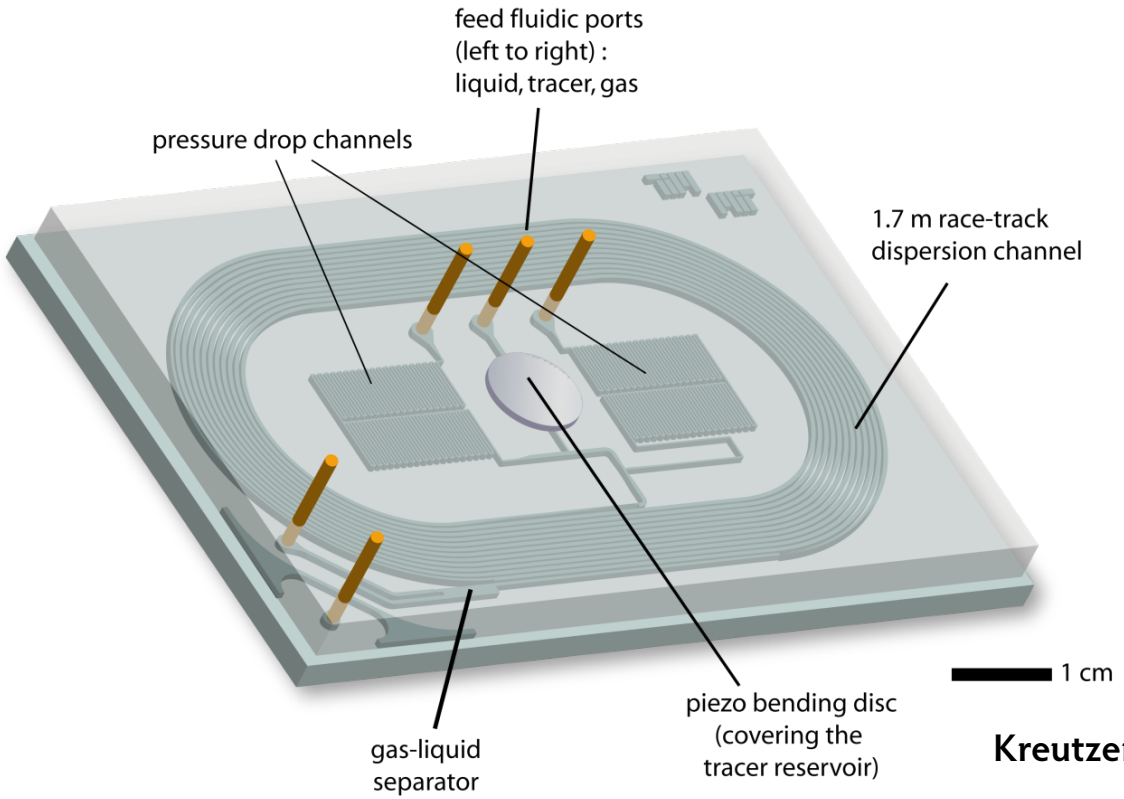
Kreutzer & Guenther, 2005

Residence Time distribution = Particle Size Distribution

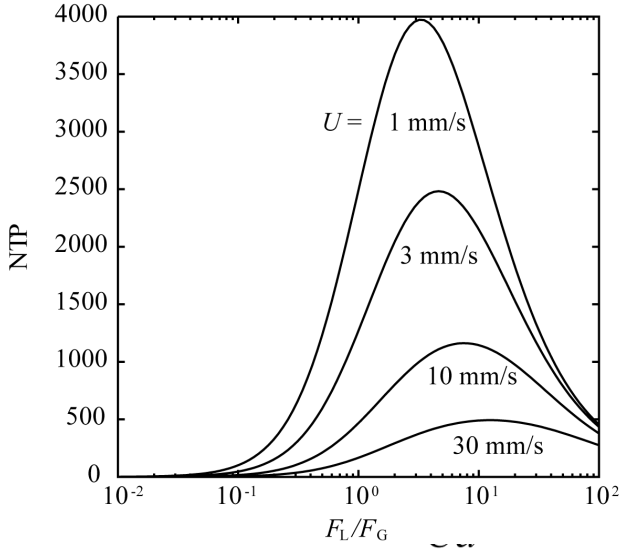


Colloidal Silica. Khan *Langmuir* 2005





Segmentation - Dispersion

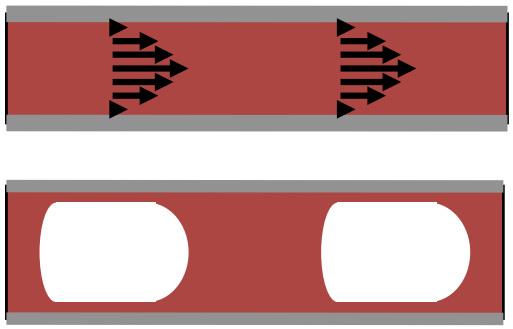


Kreutzer *Anal. Chem.* 2008

TU Delft

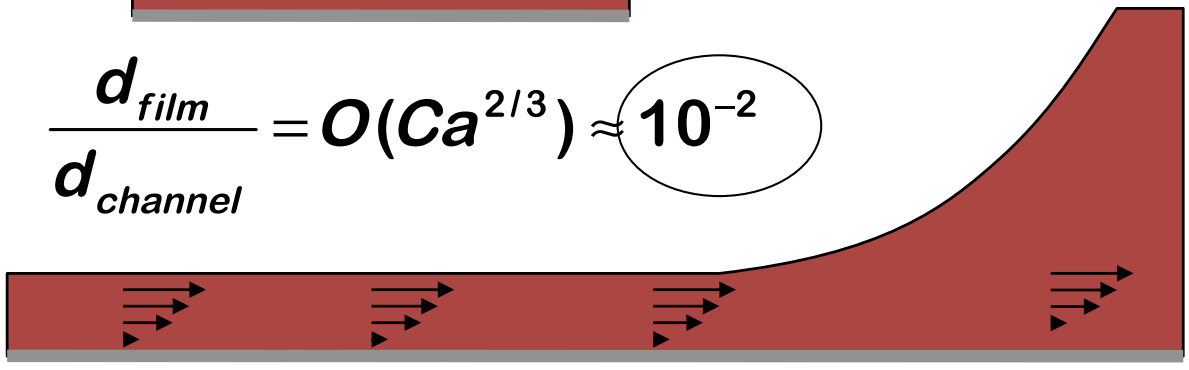
Catalysis: film thickness key parameter

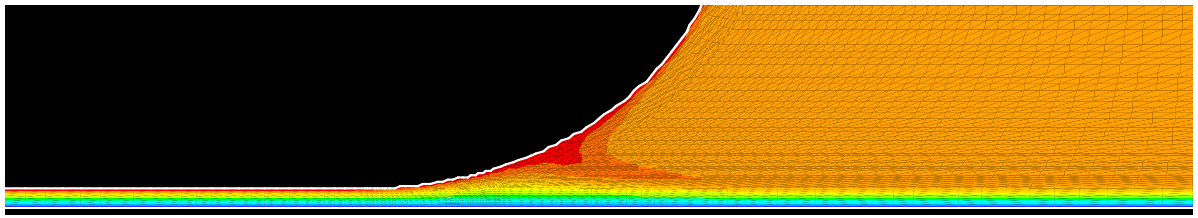
Excellent transport to wall



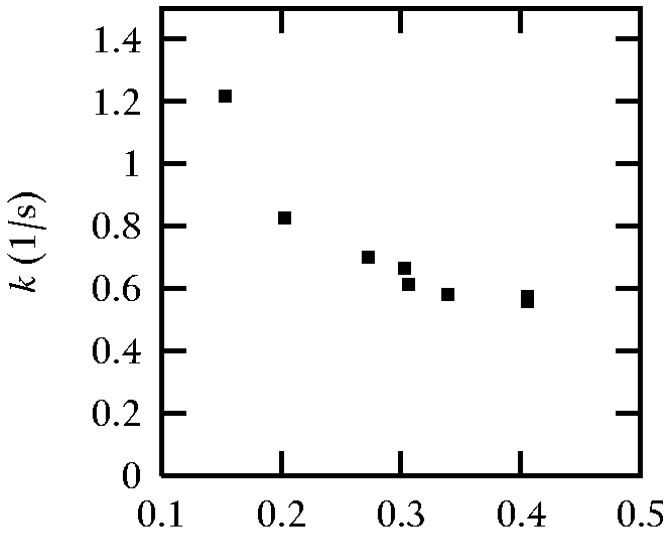
100-fold better mass-xfer

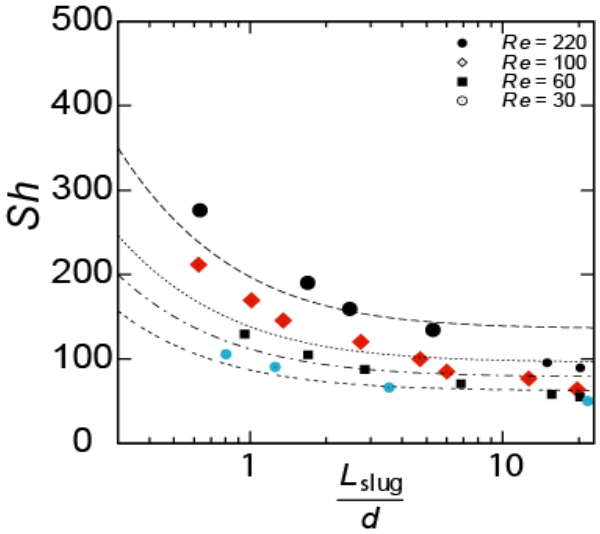
$$\frac{d_{film}}{d_{channel}} = O(Ca^{2/3}) \approx 10^{-2}$$





Full CFD simulation

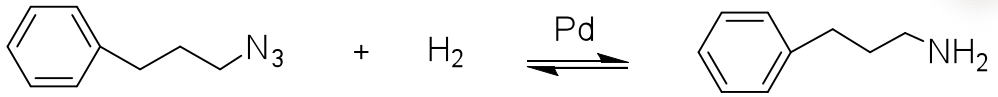




Michiel T. Kreutzer[a,*], Freek Kapteijn[a], Jacob A. Moulijn[a], Johan J. Heiszwolf[b]
Chemical Engineering Science 60 (2005) 5895–5916

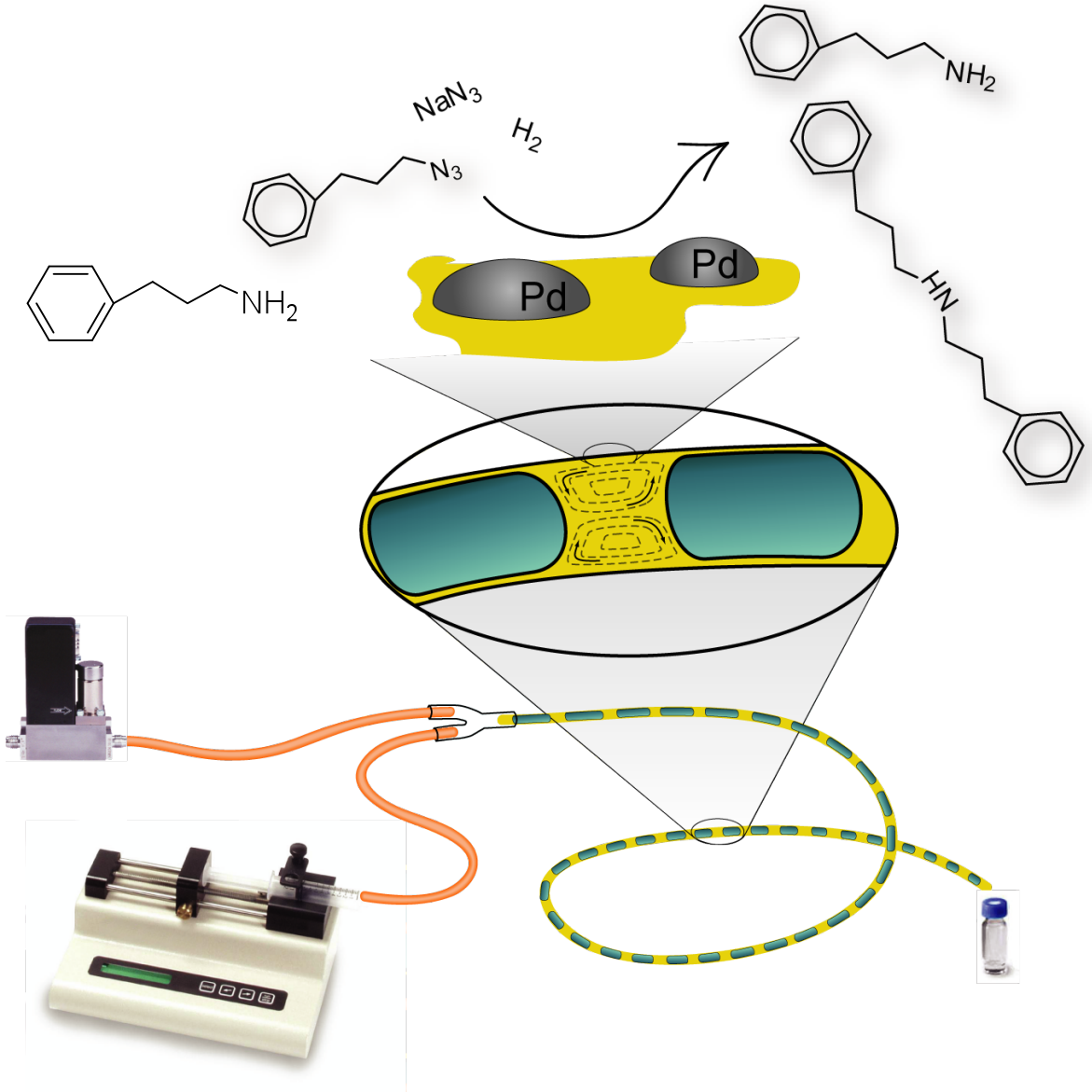
Segmented flow Synthesis

Kinetic tool, Ideal for hazardous chemistry

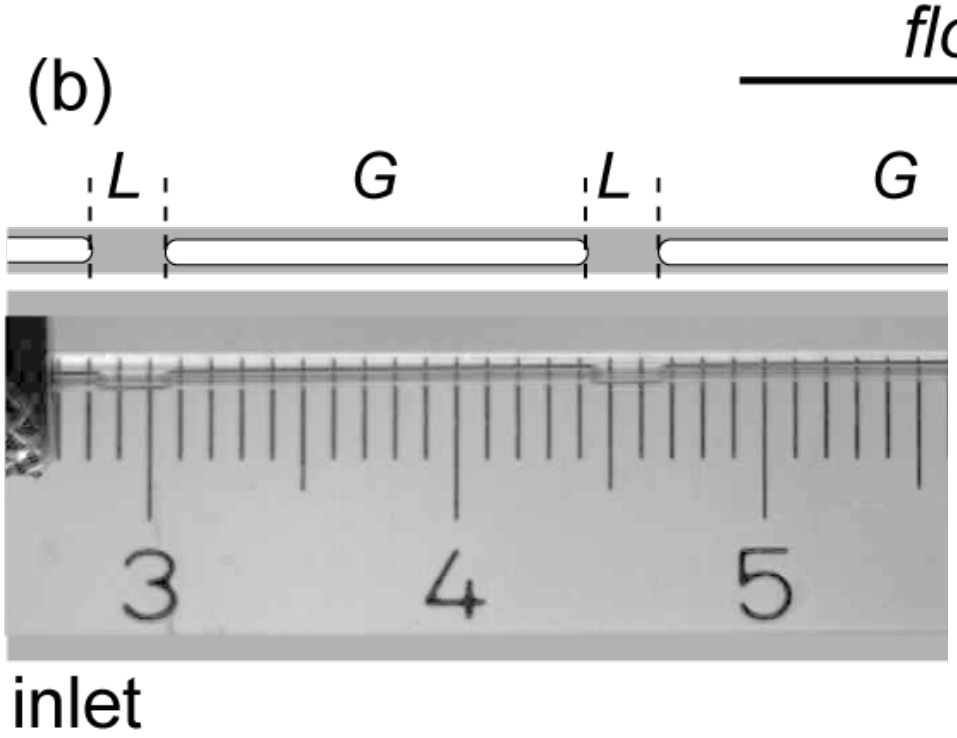


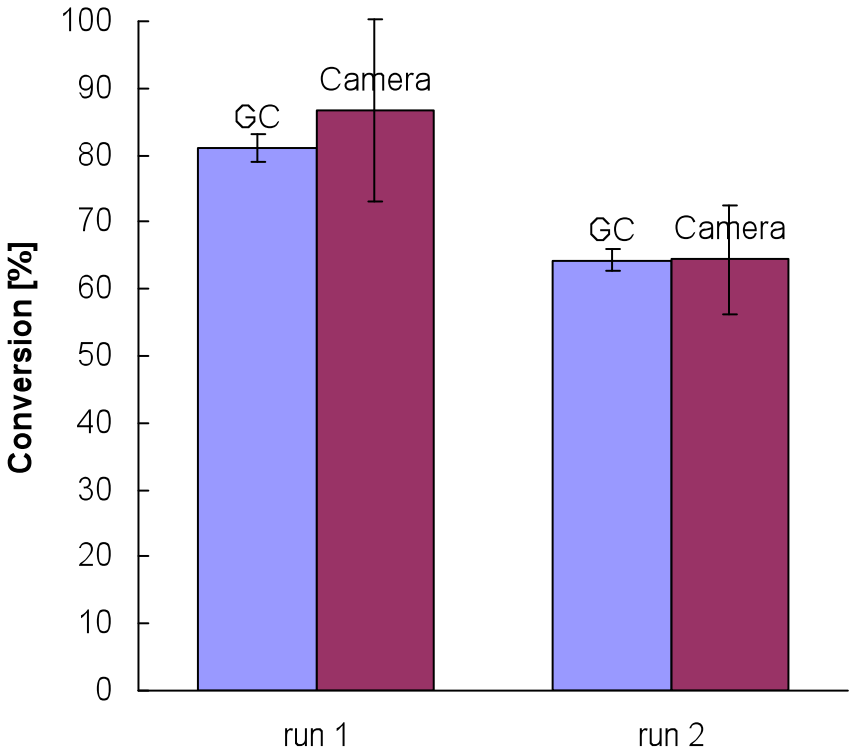
Azide hydrogenation to form amines

Temperature low enough To maintain stereo-specificity



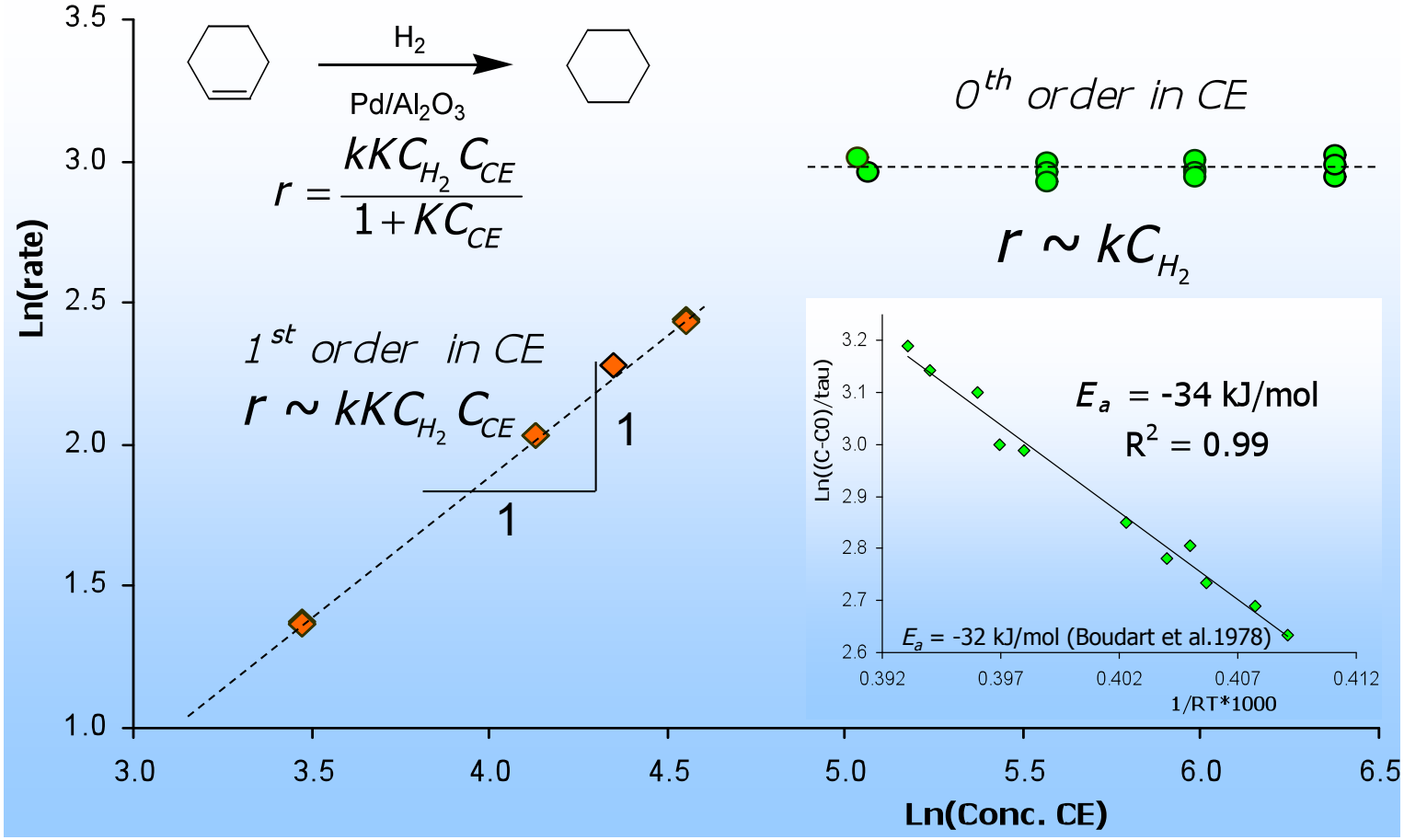
Monitoring conversion is easy





Fast kinetics

Complete kinetics can be measured in a day



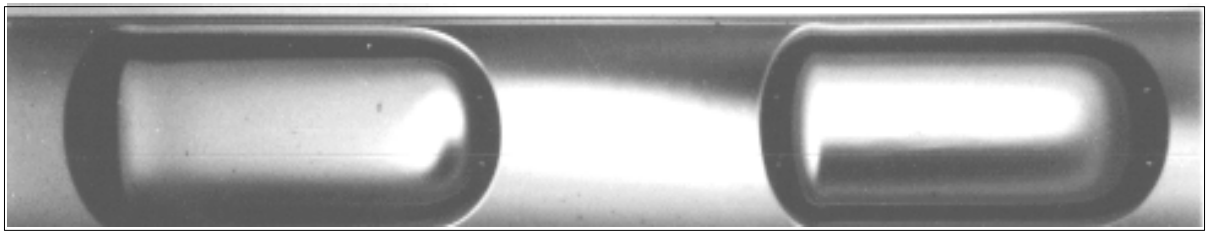
TU Delft

Our basic questions for today

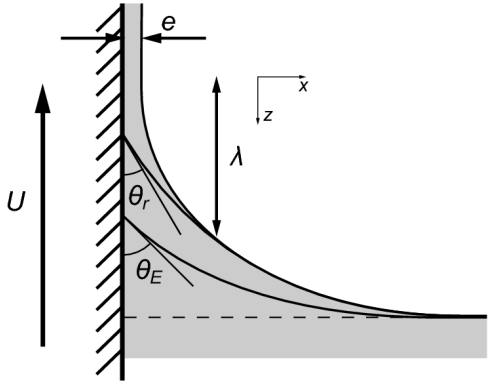
- Simplest case: bubble/droplet in a tube
  - What is the flow resistance? Film thickness?
  - Look at the basic problem of forced wetting (plate, capillary, all the same)
  - Do the full matched-asymptotics that leads to the "BLL 2/3 law"

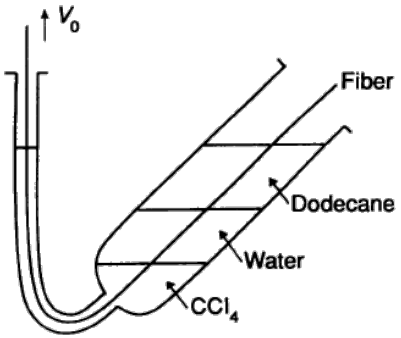
- More complex cases: inertia, marangoni effects?
  - Basic features of the solutions

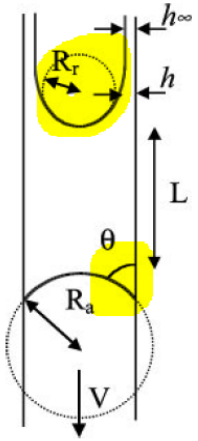
- Channel Shape?



The Bretherton-Landau-Levich problem







Layer on flat plate

coating on a wire

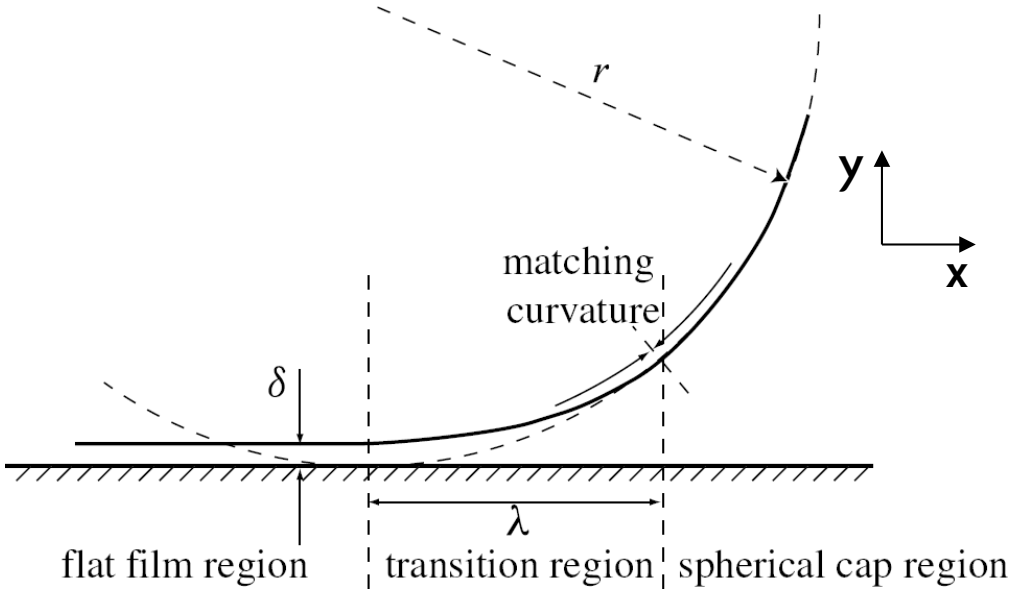
coating in a tube

Characteristics:

- Film deposited, thickness depends on speed
  (so called "2/3-law", thickness scales with $Ca^{2/3}$)
- Both on wetting and non-wetting surfaces
  (the transition to forced wetting is NOT today's topic)

- Matching of film to "outer" solution

Basic setup of the problem - Matching

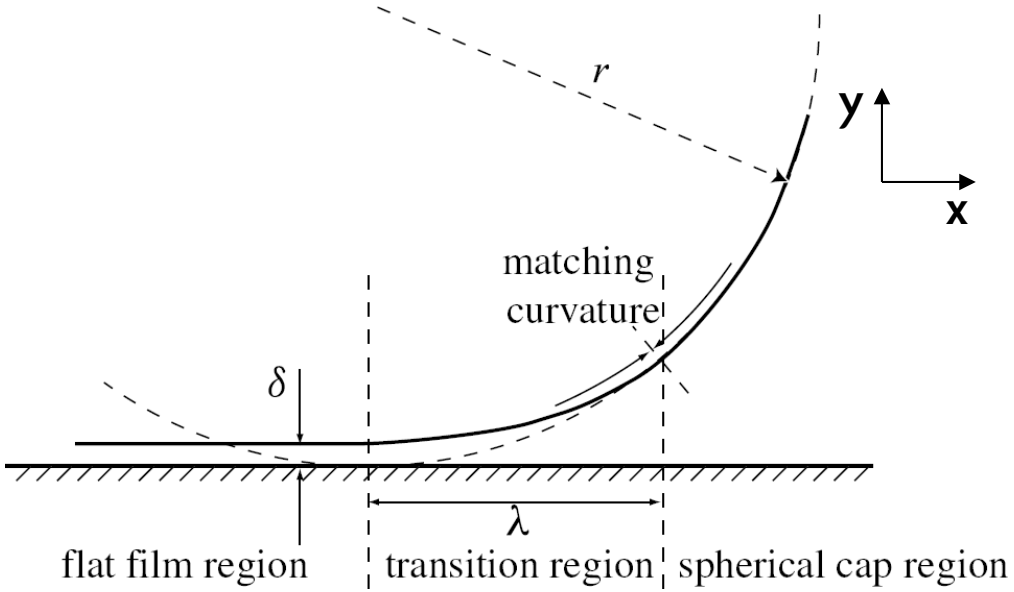


Moving reference frame: bubble stands still: $u(0) = -U, \quad \frac{\partial u}{\partial y}(h) = 0$

Navier Stokes: $\frac{\partial p}{\partial x} = \mu \frac{\partial^2 u}{\partial y^2}$

Continuity $\frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} = 0, \quad with \quad q = \int_0^h u \, dy$

Lubrication thin-film equation



Navier Stokes:

$$u = -U + \frac{\partial p}{\partial x}\left[\frac{y^2}{2\mu} - \frac{yh}{\mu}\right]$$

Laplace pressure

$$\frac{\partial p}{\partial x} \approx \frac{\partial}{\partial x}\left[\gamma \frac{\partial^2 h}{\partial x^2}\right]$$

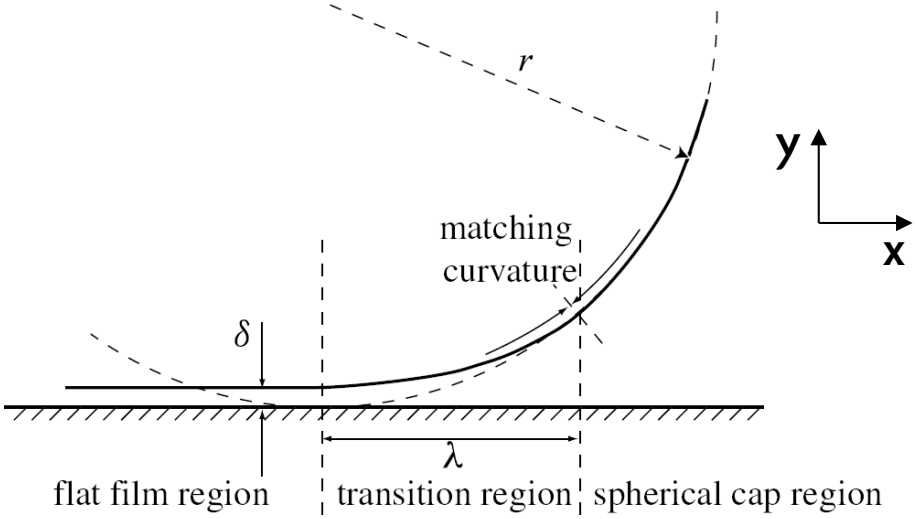
$$q = \int_0^h u\,dy = Uh - \frac{\gamma}{3\mu} h^3 \frac{\partial^3 h}{\partial x^3}$$

Continuity

$$\frac{\partial h}{\partial t} + U\frac{\partial h}{\partial x} - \frac{\gamma}{3\mu}\frac{\partial}{\partial x}\left(h^3 \frac{\partial^3 h}{\partial x^3}\right) = 0$$

Scaling of the transition region: first relation

$$\frac{\partial h}{\partial t} + U\frac{\partial h}{\partial x} - \frac{\gamma}{3\mu}\frac{\partial}{\partial x}\left(h^3\frac{\partial^3 h}{\partial x^3}\right) = 0$$



Bubble stands still, so must be zero , we balance the 2nd and 3rd terms:

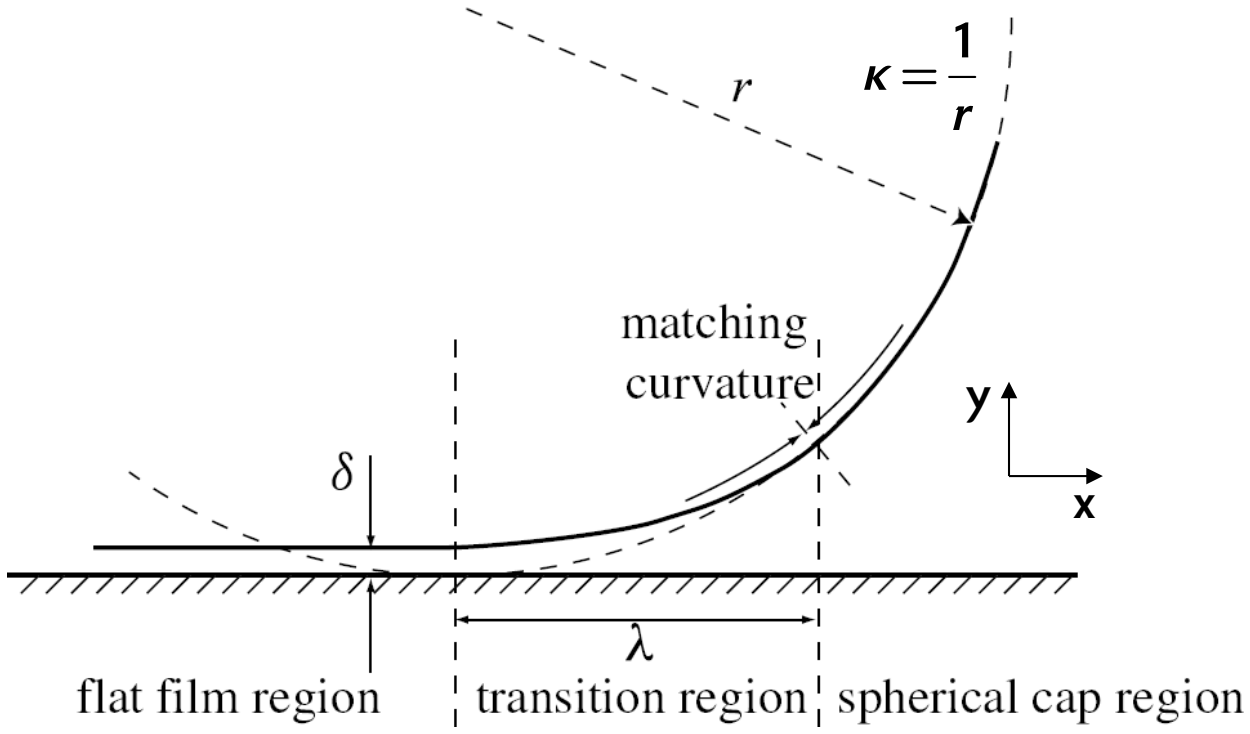
$$\frac{\partial h}{\partial x} \sim \frac{\gamma}{3\mu U}\frac{\partial}{\partial x}\left(h^3\frac{\partial^3 h}{\partial x^3}\right)$$

$$\left.\begin{array}{l} x \sim \lambda \\ h \sim \delta \end{array}\right\} \quad \frac{\delta}{\lambda} \sim \frac{\lambda}{3\mu U}\frac{1}{\lambda}\left(\delta^3\frac{\delta}{\lambda^3}\right) \quad \text{or} \quad Ca^{1/3} \sim \frac{\delta}{\lambda}$$

Matching to outer solution: second scaling relation

First scaling rule

$$Ca^{1/3} \sim \frac{\delta}{\lambda}$$



$$\kappa \sim \frac{\partial^2 h}{\partial x^2} \sim \frac{\delta}{\lambda^2} \qquad \kappa = \frac{1}{r}$$

Second scaling rule

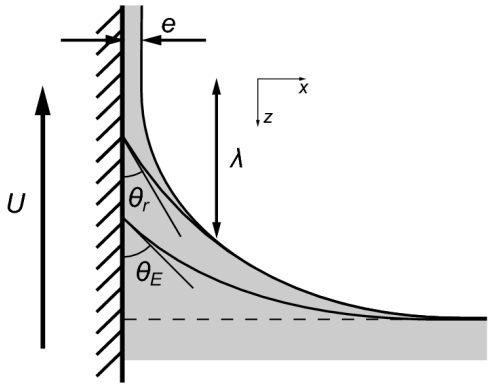
$$\frac{\delta}{\lambda^2} \sim \frac{1}{r}$$

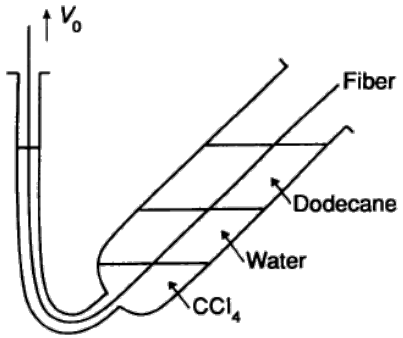
Scaling of the problem

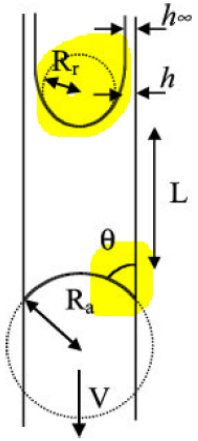
$$\delta \sim r Ca^{2/3}$$

$$\lambda \sim r Ca^{1/3}$$

The Bretherton-Landau-Levich problem





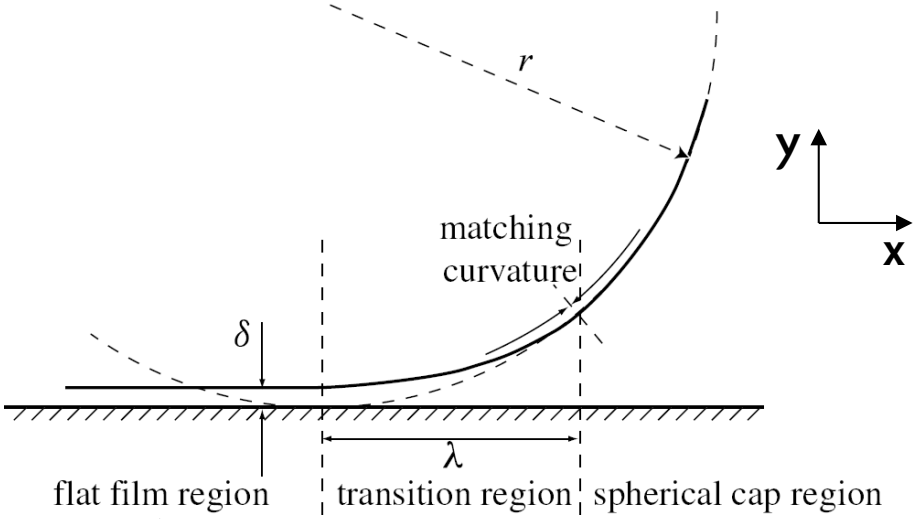


- Clean interface case:
  - 2/3 law experimentally predicted by Morey (1940)
  - Theoretical derivation of 2/3 law for flat plate by Landau-Levich (1942)
  - Theoretical derivation of 2/3 law for capillaries by Bretherton (1961)
- Surfactant case
  - Theoretical derivation by Bretherton (1961)
  - Coating of flat surfaces by Groenveld (1970)
- Additional forces (on top of viscous-capillary)
  - Inertia: Aussilous (2001), Heil (2001), Kreutzer (2005)
  - Gravity & Partial wetting fluids by Snoeijer (2008)

Master equation

Again, using the film evolution equation

$$\frac{\partial h}{\partial t}+\frac{\partial}{\partial x}\left(Uh-\frac{\gamma}{3\mu}h^3\frac{\partial^3 h}{\partial x^3}\right)=0$$



Steady state, so drop the transient term

$$Uh-\frac{\gamma}{3\mu}h^3\frac{\partial^3 h}{\partial x^3}=c \longrightarrow \frac{\partial^3 h}{\partial x^3}=\frac{3\mu U}{\gamma}\frac{h-c}{h^3}$$

In the flat region, $\frac{\partial^3 h}{\partial x^3}=0$

which gives c: $0=\frac{\delta-c}{\delta^3}$,

$$c=\delta$$

$$\eta=\frac{h}{\delta}$$

$$\xi=(3Ca)^{1/3}\frac{x}{\delta}$$

$$\frac{\partial^3 \eta}{\partial \xi^3}=\frac{\eta-1}{\eta^3}$$

Forced Wetting Film Equation

$$\frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3}$$

"exponential range"

$\eta \simeq 1$

$$\frac{\partial^3 \eta}{\partial \xi^3} \simeq \eta - 1$$

which has an analytical solution

$$\eta = 1 + \alpha e^{\xi} + \beta e^{-\xi} \cos\left[\frac{3^{1/2}}{2}\xi\right] + \gamma e^{-\xi} \sin\left[\frac{3^{1/2}}{2}\xi\right]$$

"parabolic range"

$\eta \gg 1$

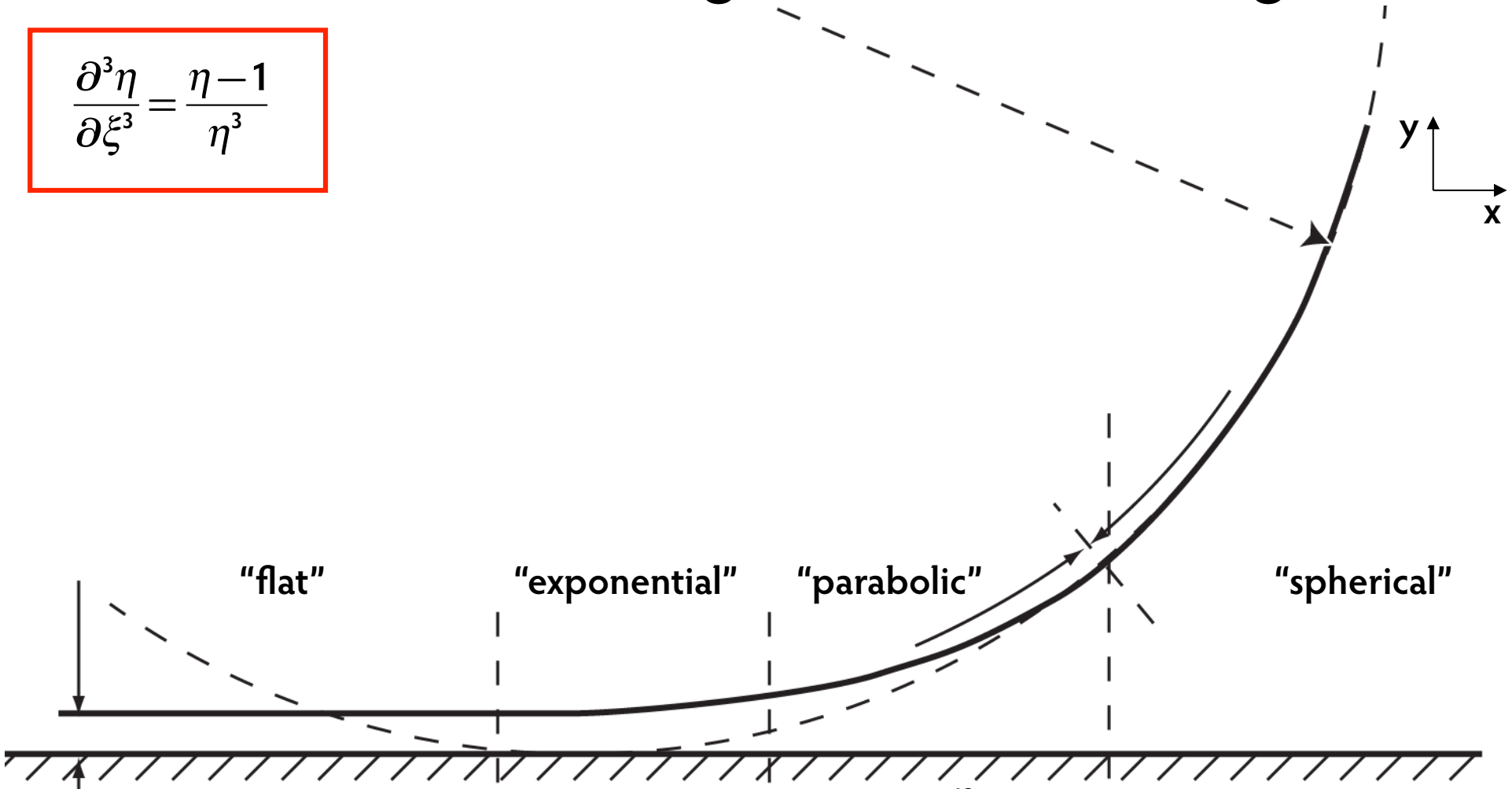
$$\frac{\partial^3 \eta}{\partial \xi^3} \simeq 0$$

which has an analytical solution

$$\eta = \frac{P}{2}\xi^2 + Q\xi + R$$

Four different regions with their scaling

$$\frac{\partial^3\eta}{\partial\xi^3}=\frac{\eta-1}{\eta^3}$$



Set up match of "exp" and "parabolic"

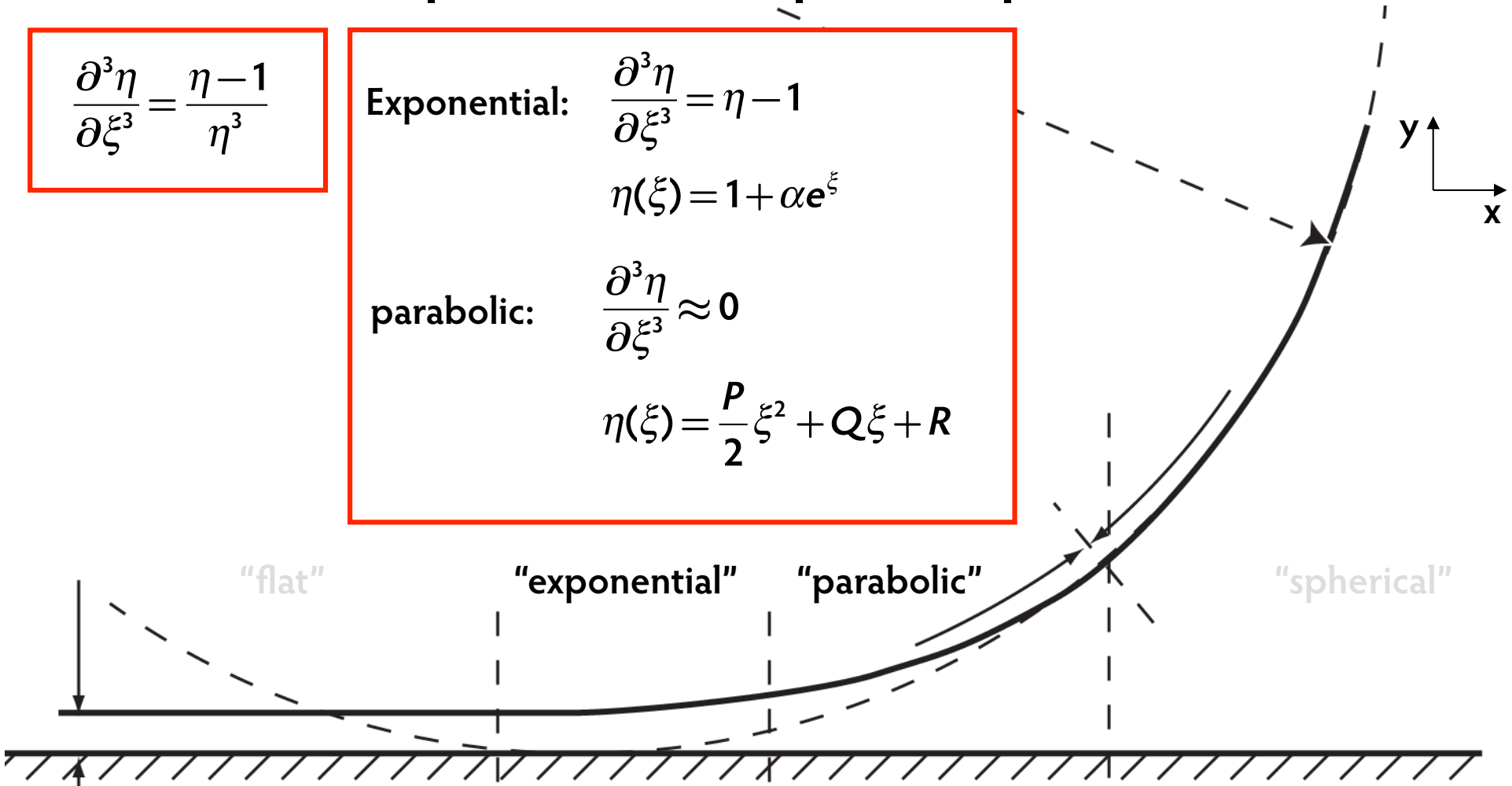
$$\frac{\partial^3\eta}{\partial\xi^3}=\frac{\eta-1}{\eta^3}$$

Exponential: $\frac{\partial^3\eta}{\partial\xi^3}=\eta-1$

$$\eta(\xi)=1+\alpha e^{\xi}$$

parabolic: $\frac{\partial^3\eta}{\partial\xi^3}\approx 0$

$$\eta(\xi)=\frac{P}{2}\xi^2+Q\xi+R$$



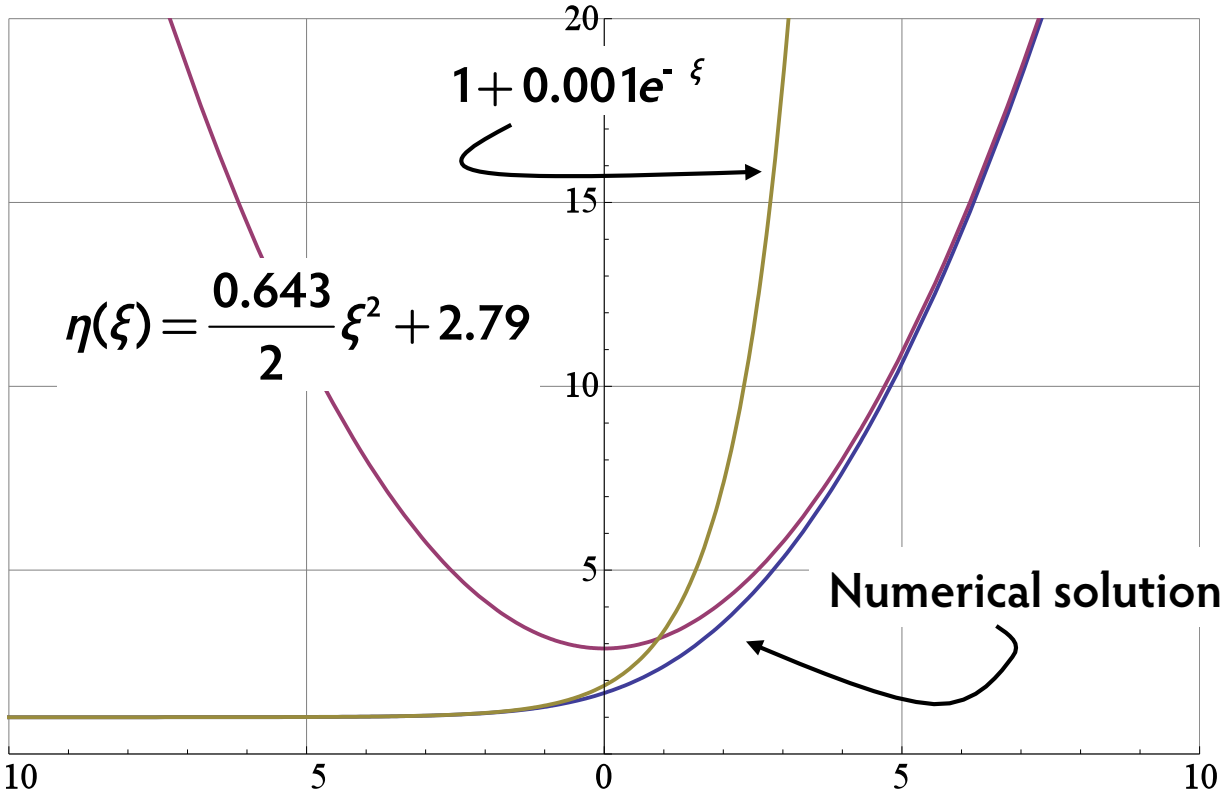
Numerical Shooting

Use exponential for initial conditions:

$$\eta(\xi) = 1 + a e^{-\xi}$$
$$\eta(0) = 1 + a$$
$$\eta'(0) = a$$
$$\eta''(0) = a$$

And integrate full equation with that

$$\frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3}$$



$$\eta(\xi) = \frac{P}{2}\xi^2 + Q\xi + R$$

Move numerical solution to left and right, such that $Q = 0$

Fitting:

$P = 0.643$, $R = 2.79$

$$P = \eta''(\xi)$$
$$Q = \eta'(\xi) - \xi\eta''(\xi)$$
$$R = \eta(\xi) - (\xi^2 + \xi)\eta''(\xi) - \eta'(\xi)$$

Note: MTK gets $a = 0.001$, $P = 0.643$, $Q = 0$, $R = 2.90$ with Mathematica's NDSolve

2/3 law for film thickness

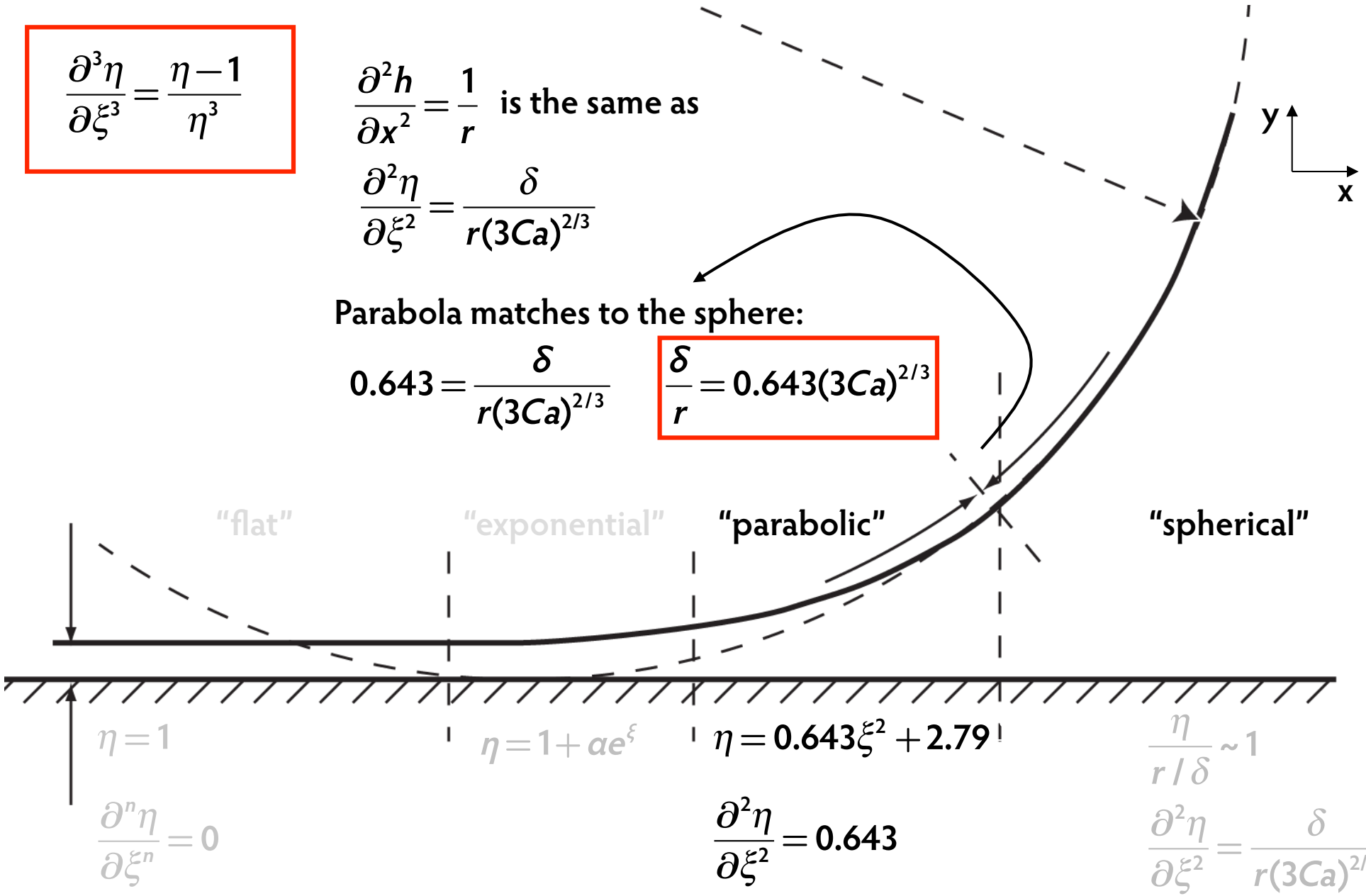
$$\frac{\partial^3 \eta}{\partial \xi^3} = \frac{\eta - 1}{\eta^3}$$

$$\frac{\partial^2 h}{\partial x^2} = \frac{1}{r} \quad \text{is the same as}$$

$$\frac{\partial^2 \eta}{\partial \xi^2} = \frac{\delta}{r(3Ca)^{2/3}}$$

Parabola matches to the sphere:

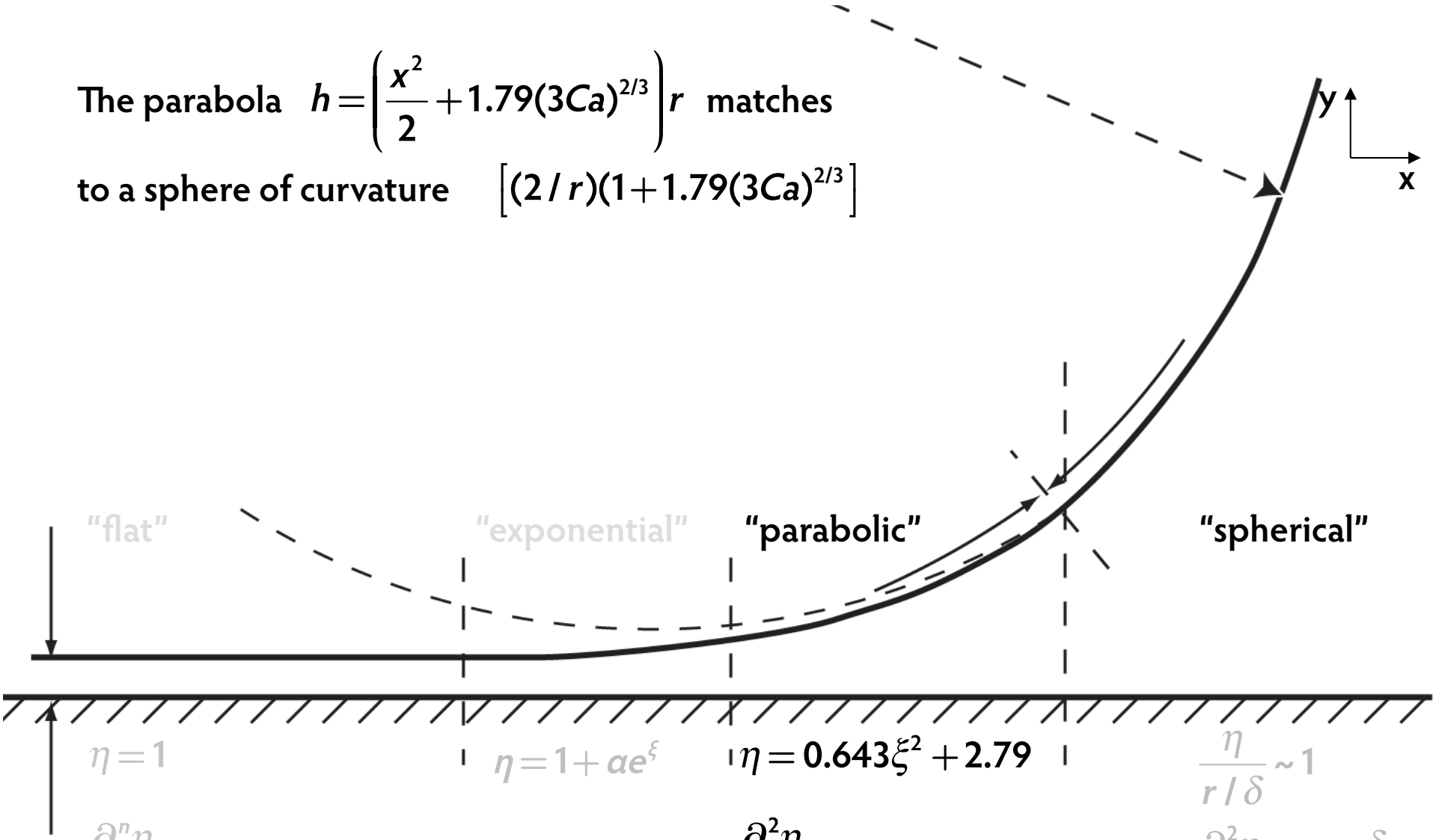
$$0.643 = \frac{\delta}{r(3Ca)^{2/3}} \qquad \frac{\delta}{r} = 0.643(3Ca)^{2/3}$$



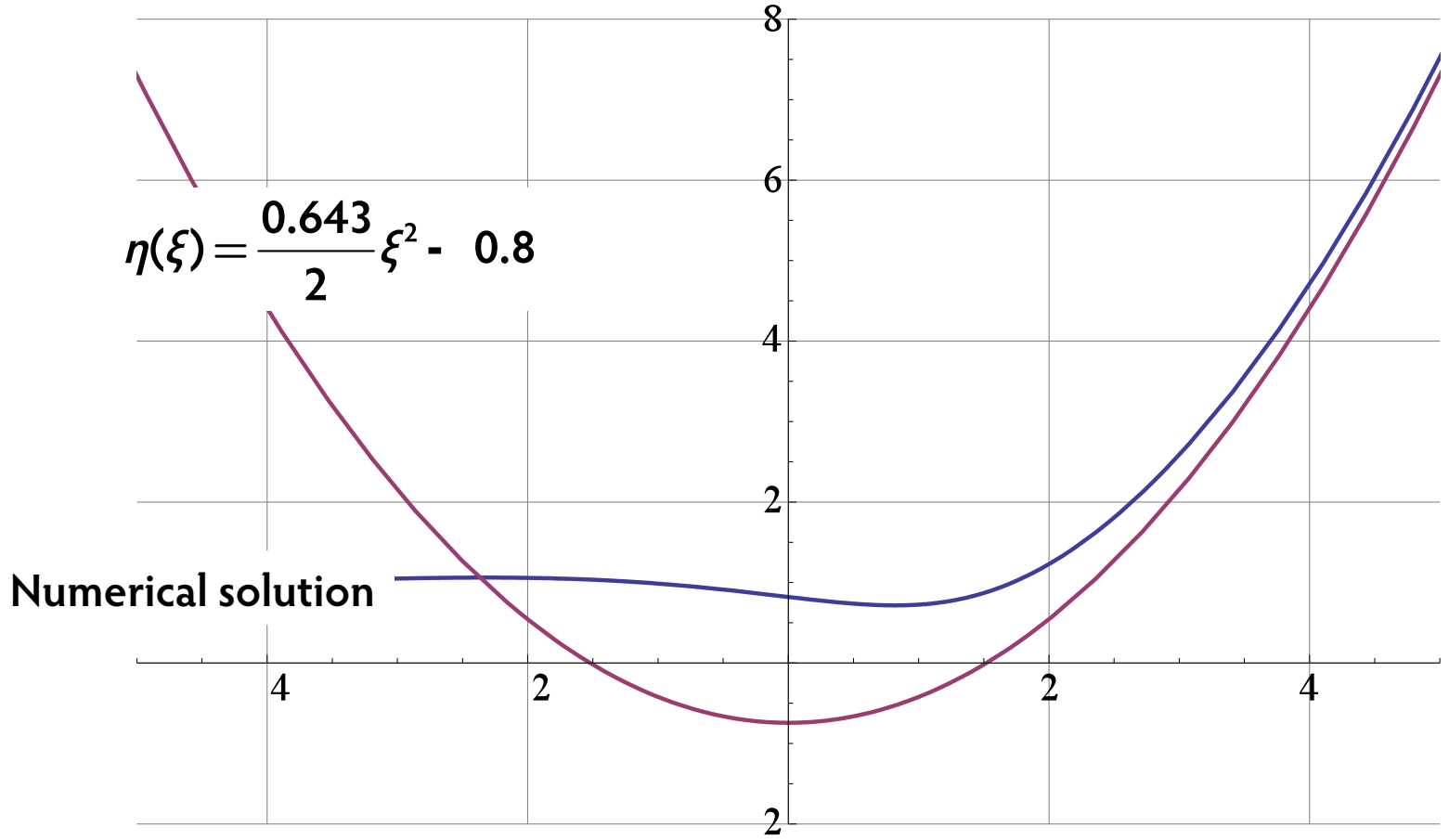
Perturbation of Laplace pressure

The parabola $h = \left(\frac{x^2}{2} + 1.79(3Ca)^{2/3} \right) r$ matches

to a sphere of curvature $\left[(2/r)(1 + 1.79(3Ca)^{2/3}) \right]$



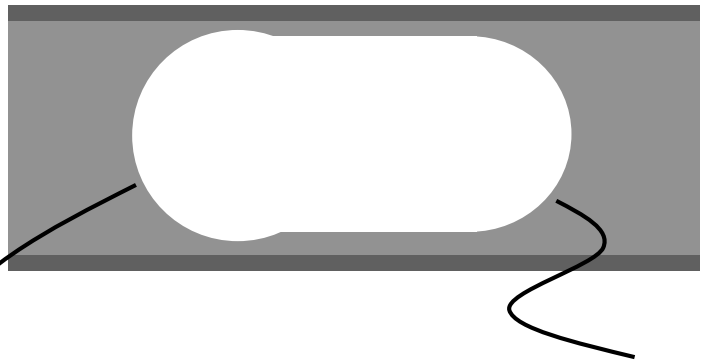
Rear of the bubble



Start numerical solution with exponential function

$$\eta = 1 + \alpha e^{-\xi} \cos\left[\frac{3^{1/2}}{2}\xi\right] + \beta e^{-\xi} \sin\left[\frac{3^{1/2}}{2}\xi\right]$$

Pressure drop over the bubble:



$$\Delta p = [1 + 1.79(3Ca)^{2/3}]\frac{2\gamma}{r}$$

$$\Delta p = [1 - \ 0.46(3Ca)^{2/3}]\frac{2\gamma}{r}$$

$$\Delta p = 4.52(3Ca)^{2/3}\frac{\gamma}{r}$$

Experiments

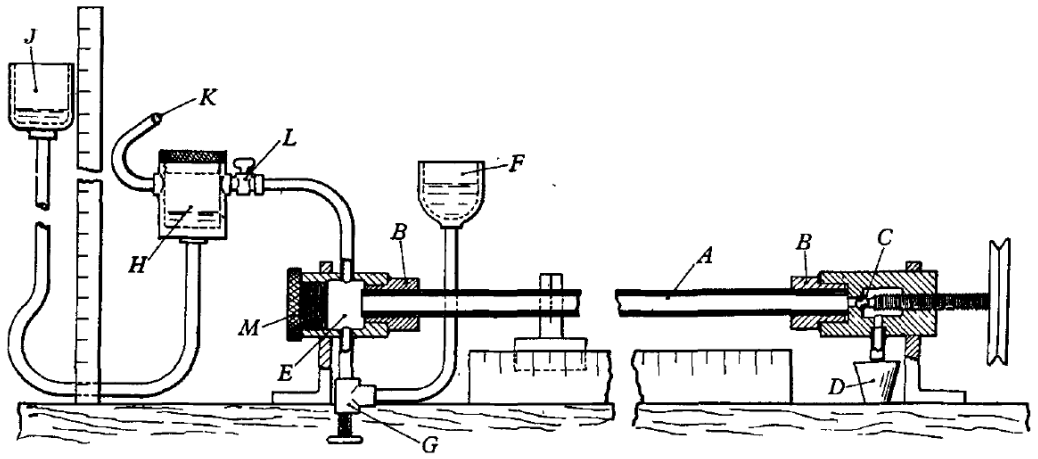
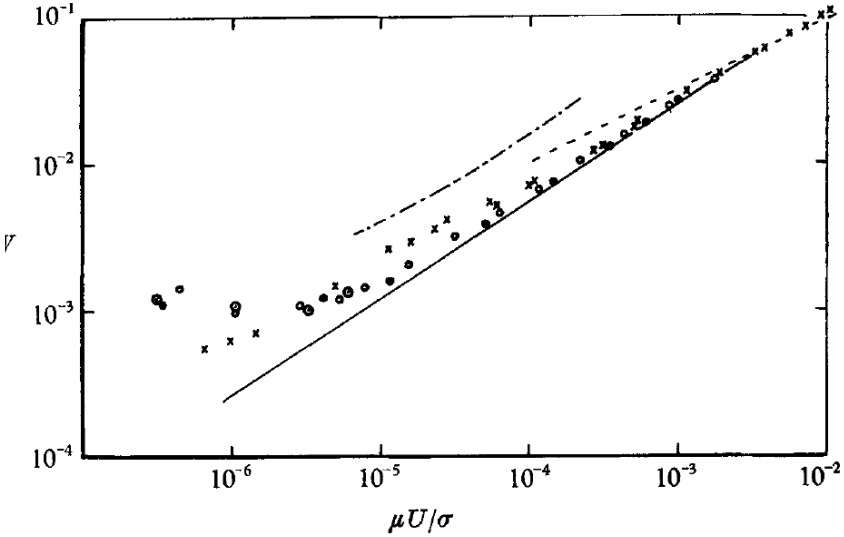
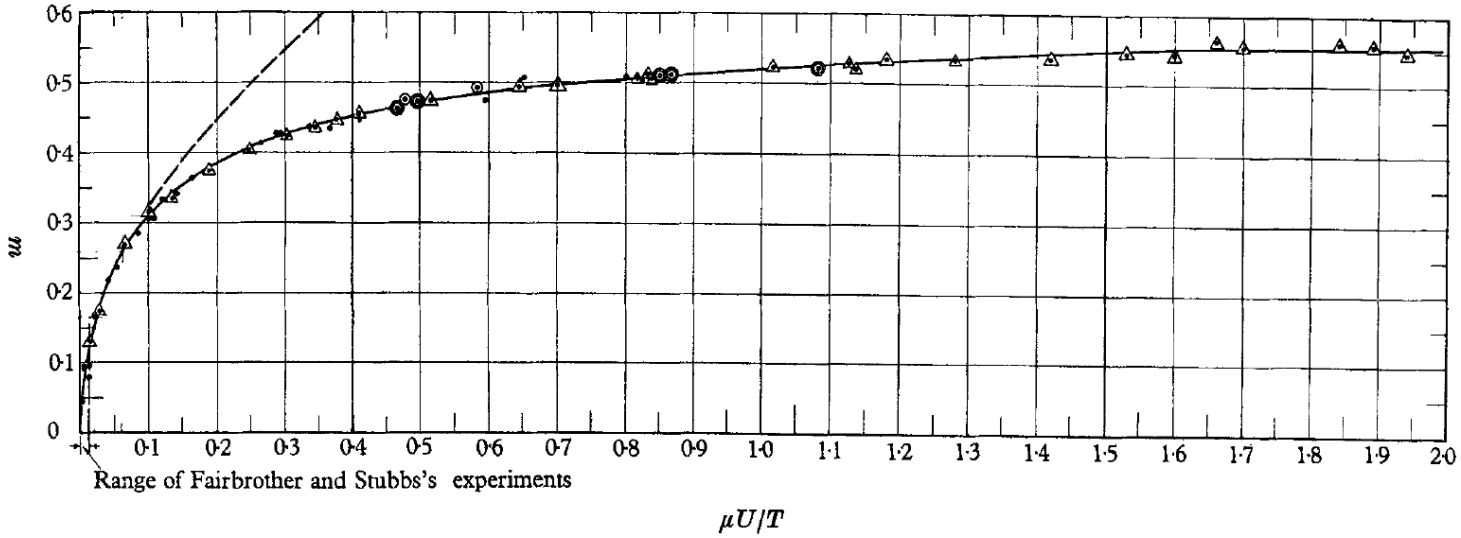


FIGURE 1. Sketch of apparatus.



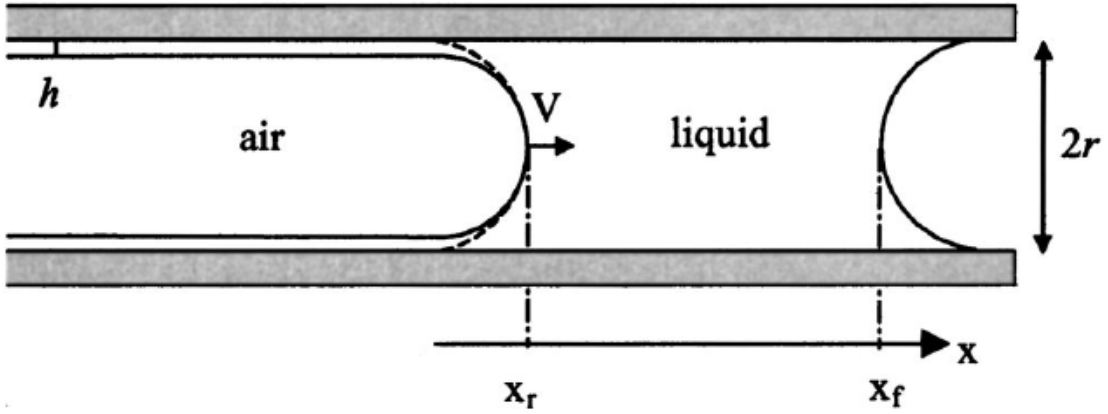


Taylor, *J Fluid Mech* 10 (**1961**), 161
Bretherton, *J Fluid Mech* 10 (**1961**), 166

Why the maximum?

First matching rule

$$Ca^{1/3} \sim \frac{\delta}{\lambda}$$



Second matching rule

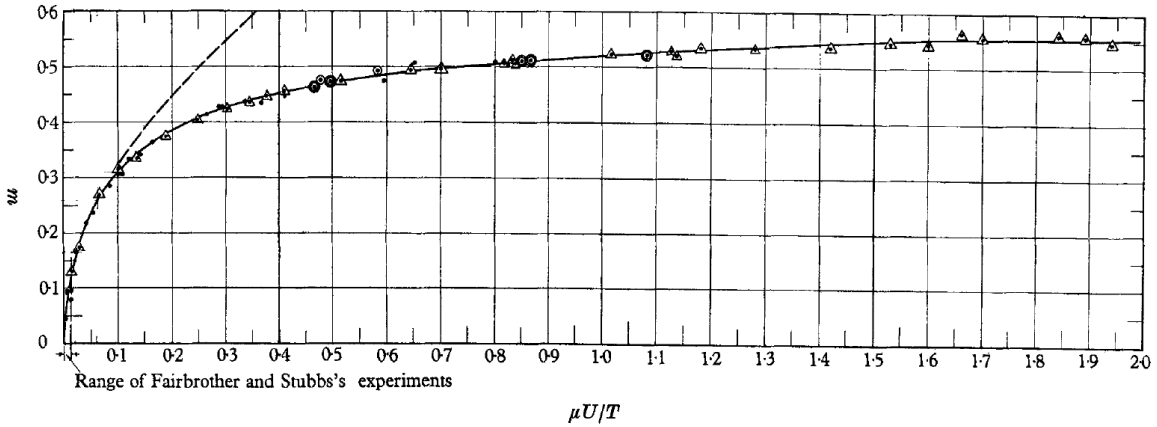
$$\frac{\delta}{\lambda^2} \sim \frac{1}{r - \delta}$$

Thick film decreases radius of curvature!

Scaling of the problem

$$\delta \sim r \frac{Ca^{2/3}}{1 + Ca^{2/3}}$$

$$\lambda \sim r \frac{Ca^{2/3}}{[1 + Ca^{2/3}]^{1/2}}$$

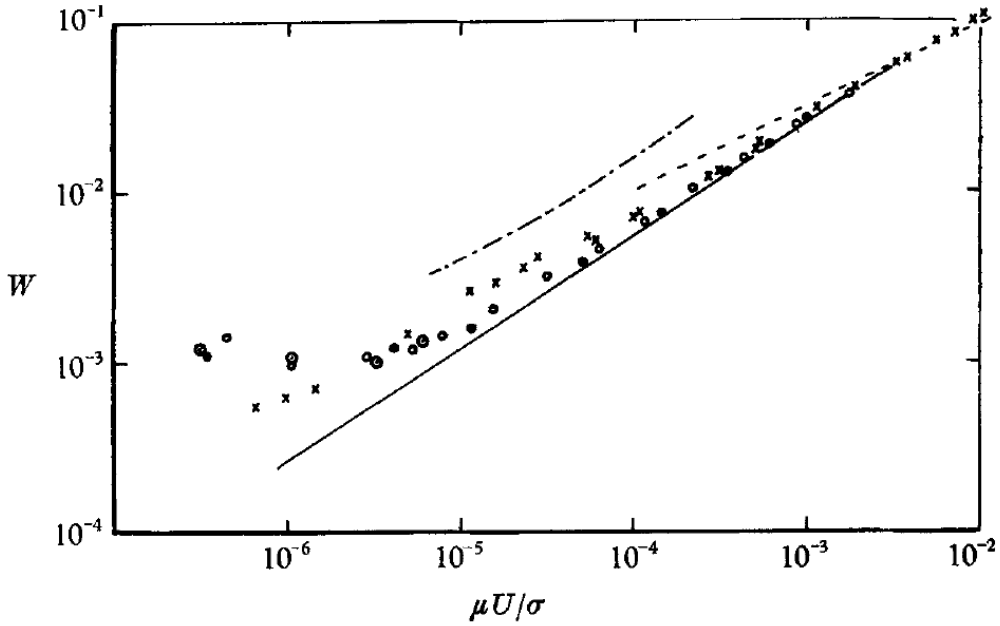


Aussilous, *Phys Fluids* 12 (2000) 2367
Taylor, *J Fluid Mech* 10 (1961), 161

The not-so-simple cases

Marangoni, Inertia, non-round, thick films, …

Marangoni Effects



Moving reference frame: bubble stands still:

$$u(0) = -U, \quad \frac{\partial u}{\partial y}(h) = 0$$

$$u(0) = -U, \quad u(h) = 0$$

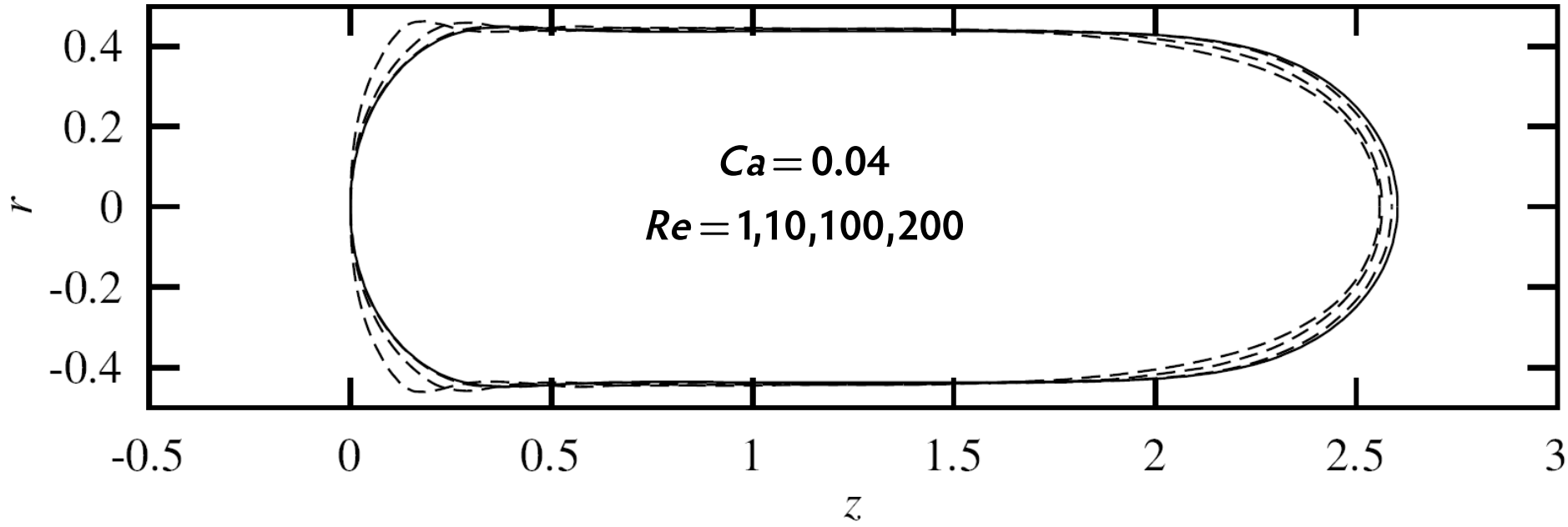
$$\frac{\partial h}{\partial t} + U\frac{\partial h}{\partial x} - \frac{\gamma}{3\mu}\frac{\partial}{\partial x}\left(h^3\frac{\partial^3 h}{\partial x^3}\right) = 0$$

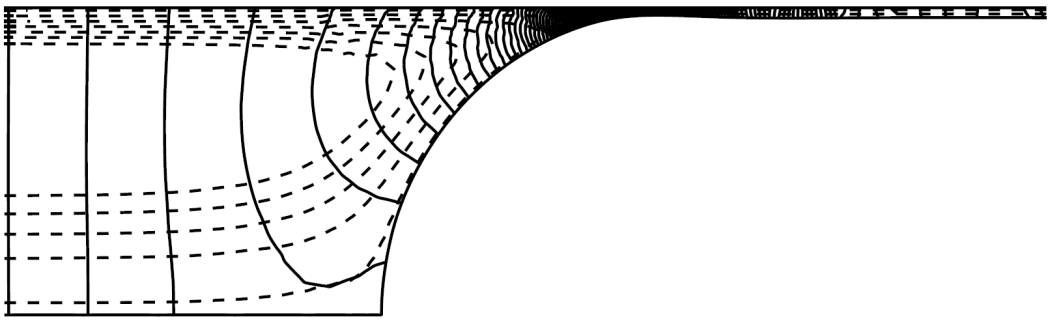
$$\frac{\gamma}{12\mu}$$

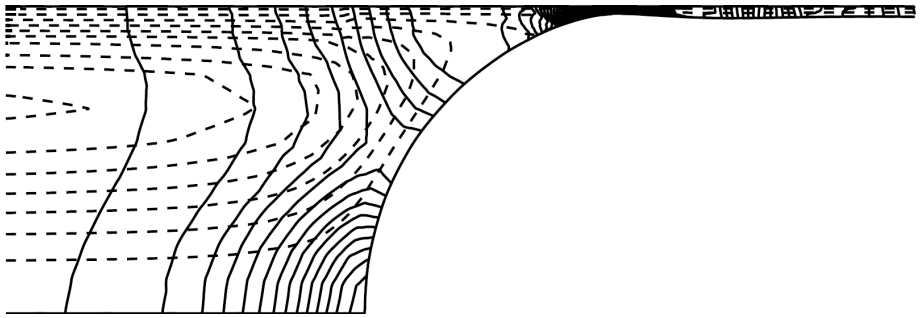
$$\delta = 0.643\, r(3Ca)^{2/3}$$

$$\delta = 0.643\, r(12Ca)^{2/3}$$

Inertia changes bubble shape

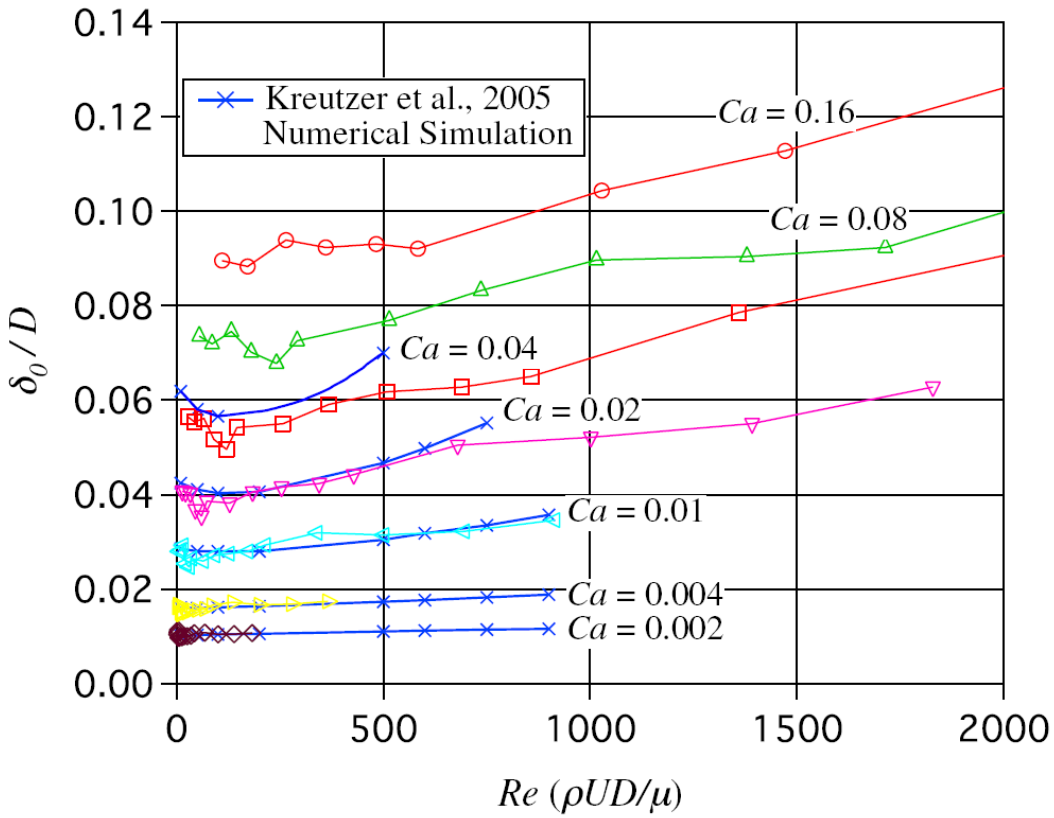






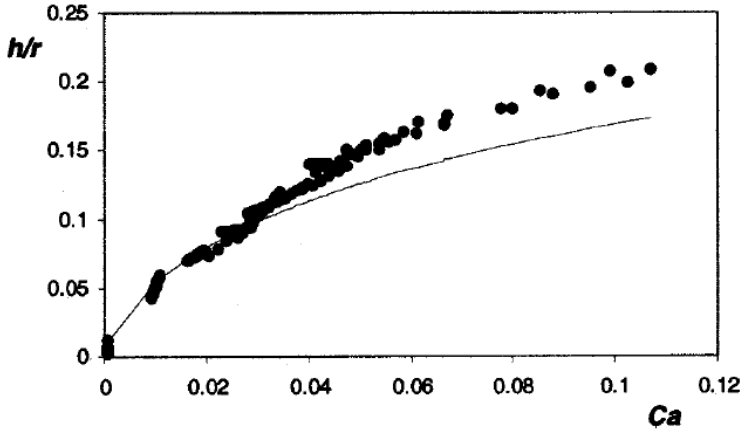
Kreutzer et al, *AIChE J* 51 (2005) 2428

Inertia increases film thickness



$$\delta \sim r \frac{Ca^{2/3}}{1 + Ca^{2/3} - We}$$

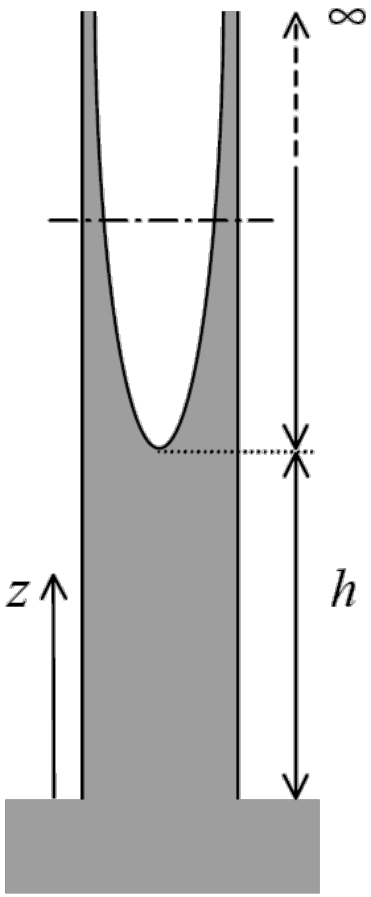
$$We = \frac{\rho U^2 (r - \delta)}{\gamma}$$

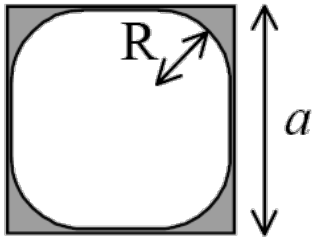


Kreutzer et al, *AIChE J* 51 (2005) 2428
Han and Shikazono, *Int J. Heat Fluid Flow* (2009)

Aussilous, *Phys Fluids* 12 (2000) 2367

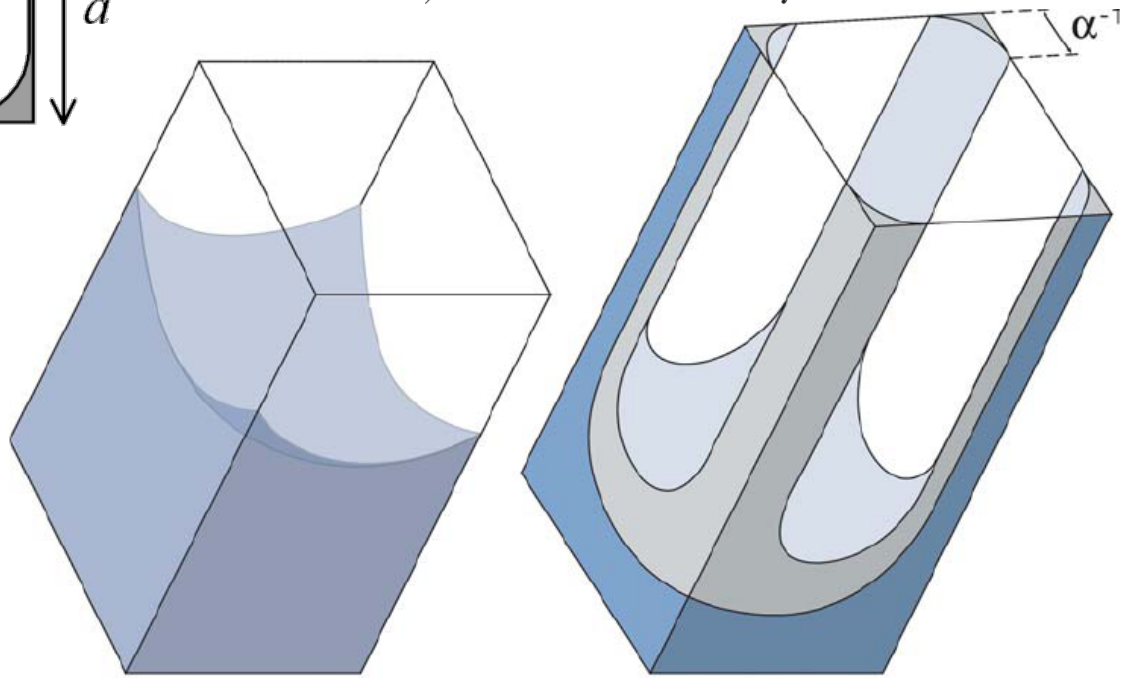
Square Channels





Modeling Shapes and Dynamics of Confined Bubbles

Vladimir S. Ajaev[1] and G.M. Homsy[2]



Annu. Rev. Fluid Mech. 2006. 38:277–307

Rise of Liquids and Bubbles in Angular Capillary Tubes

José Bico and David Quéré[1]

Journal of Colloid and Interface Science **247**, 162–166 (2002)

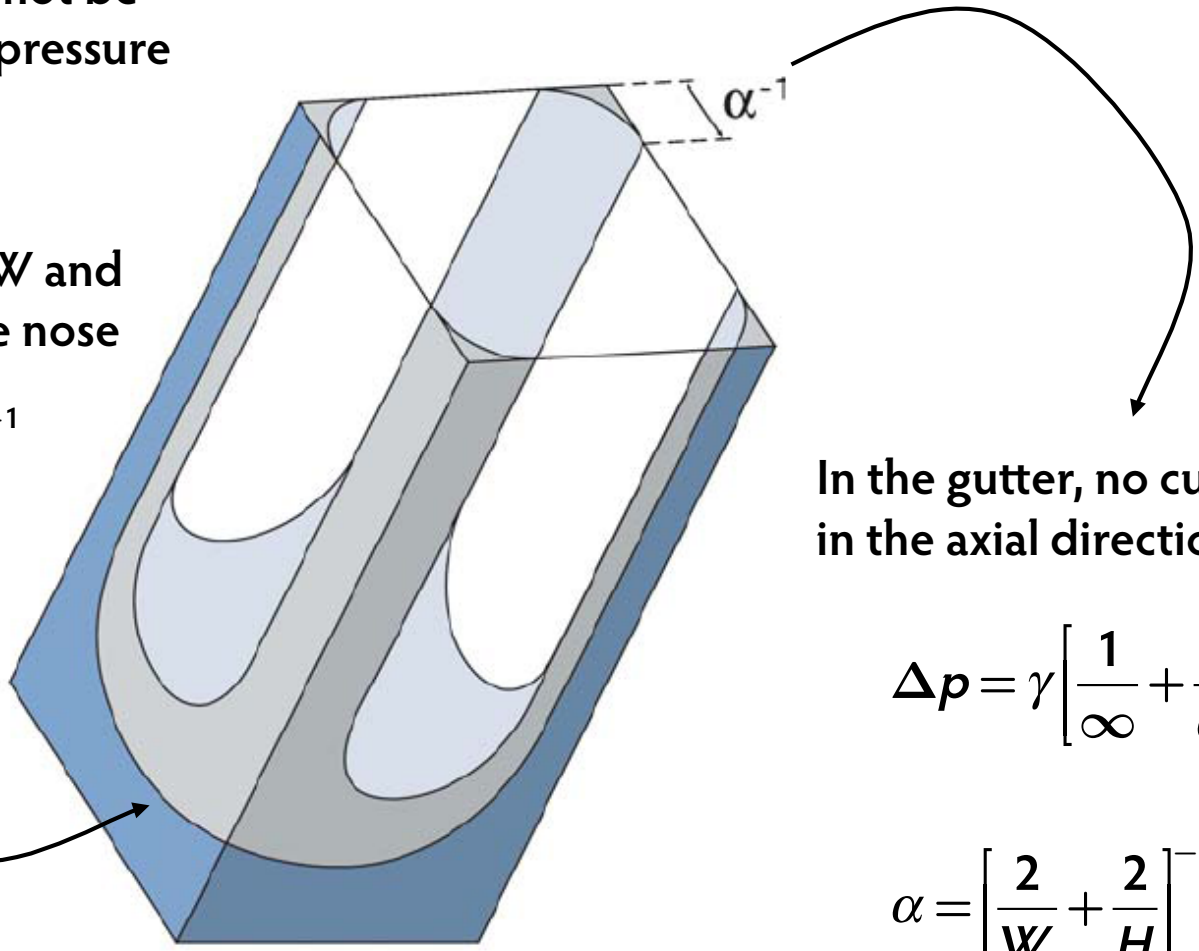
Hydrostatics

Without flow, there cannot be a gradient of (Laplace) pressure

$$\nabla p = 0$$

For a channel of width W and height H, we have at the nose

$$\Delta p = \gamma \left[\frac{2}{H} + \frac{2}{W} \right]^{-1}$$



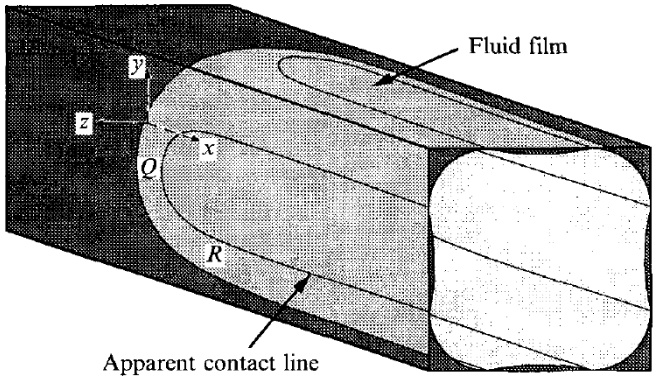
In the gutter, no curvature in the axial direction, so

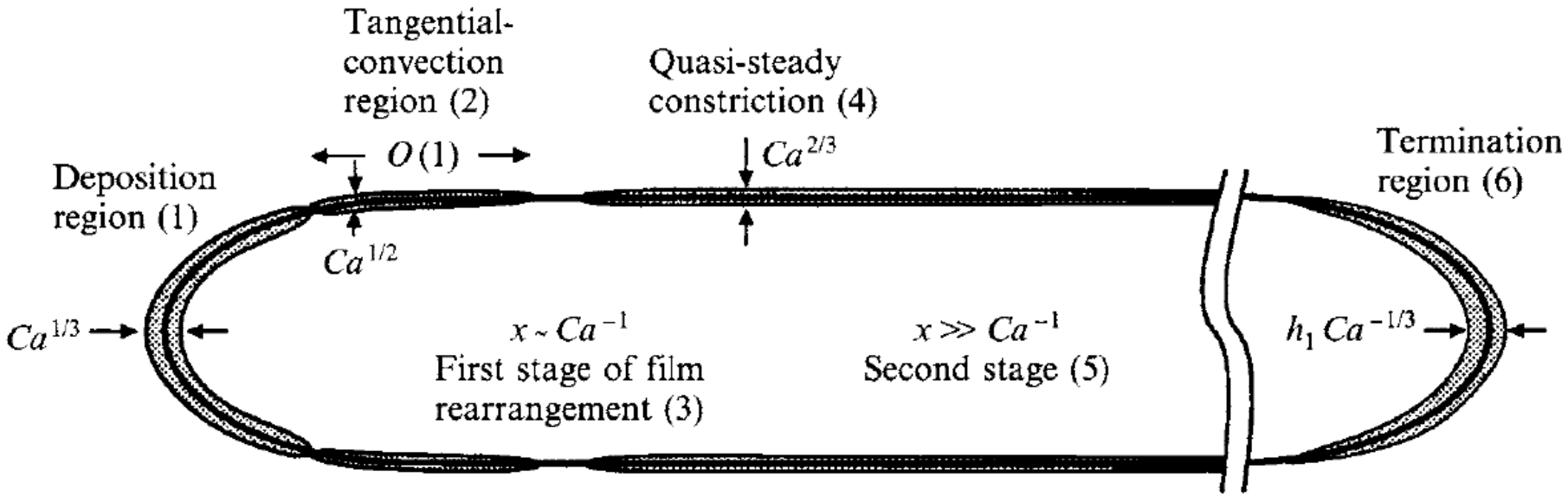
$$\Delta p = \gamma \left[\frac{1}{\infty} + \frac{1}{\alpha} \right]^{-1}$$

$$\alpha = \left[\frac{2}{W} + \frac{2}{H} \right]^{-1}$$

Ajaev & Homsy, *Ann Rev. Fluid Mech* **38** (2006) 277
Wong, Radke & Morris, *J Fluid Mech* 292 (1995) 71

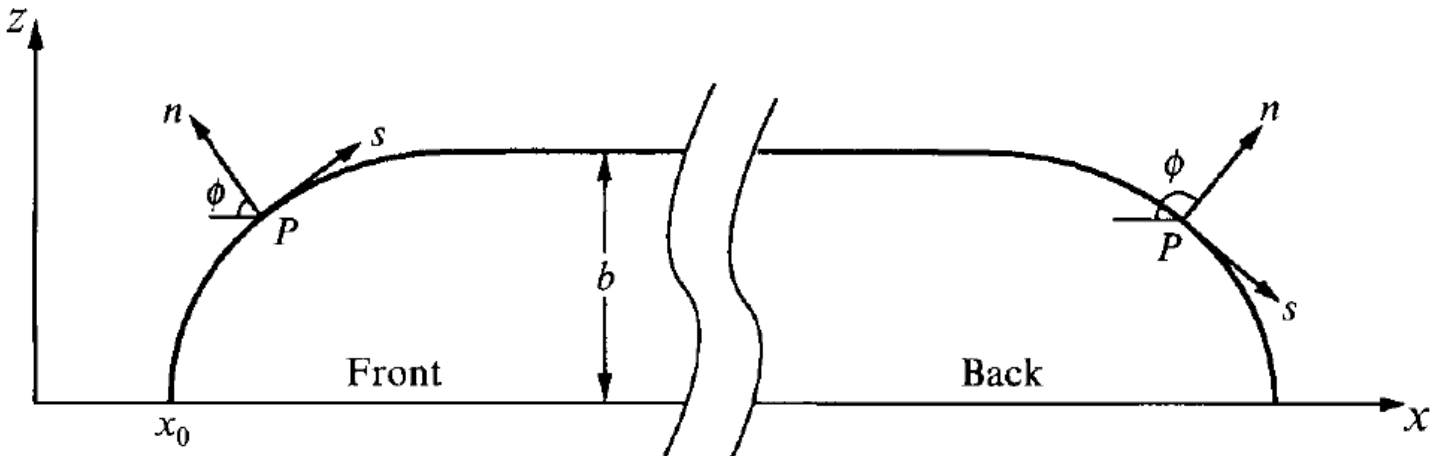
Film Deposition



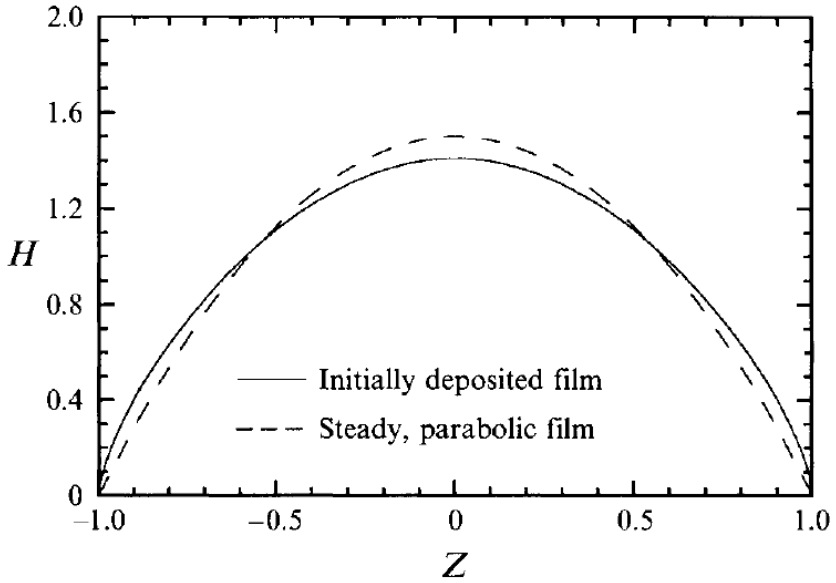


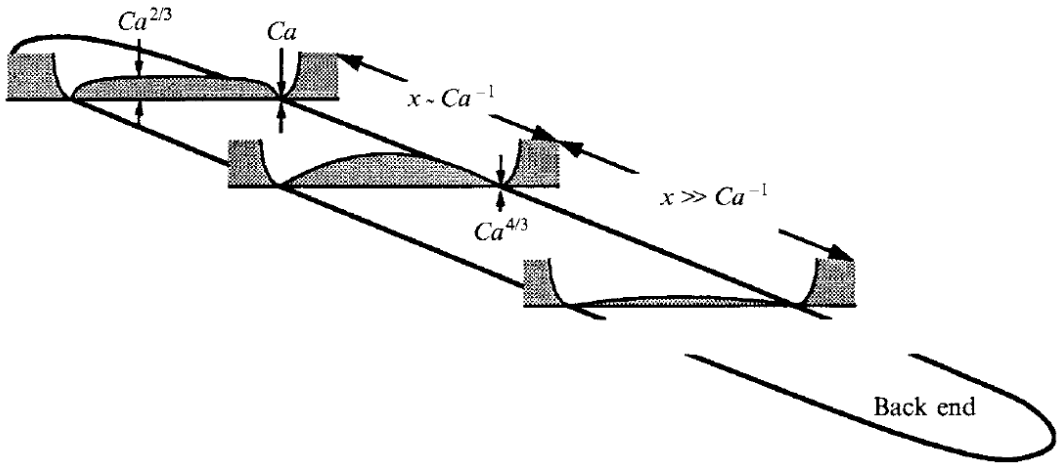
Wong, Radke & Morris, *J Fluid Mech* 292 (1995) 71

The non-uniformity starts at the nose



$$\delta = \frac{0.643}{a}(3Ca\cos\phi)^{2/3}$$





Wong, Radke & Morris, *J Fluid Mech* 292 (1995) 71

What have we learned

- Scaling in flow of long bubbles / droplets in cylindrical tubes
  (basically the same as Landau Levich)

- Marangoni effects increase film thickness and pressure drop by a factor $4^{2/3}$

- There is a maximum film thickness at high Ca
  (this does not happen with a flat plate LL scaling)

- Inertia increases film thickness, numerical solution needed

- Square channels have highly non-uniform films

Further Reading

- Recent reviews

  Ajaev & Homsy, *Ann Rev. Fluid Mech* **38** (2006) 277

  Kreutzer et al., *Chem Eng Sci* 60 (**2005**) 5895

  Gunther et al. , *Lab Chip* 6 (**2006**) **1487**

- Microfluidics: a couple of key papers

  Wong, Radke & Morris, *J Fluid Mech* 292 (1995) 71

  Aussilous, *Phys Fluids* 12 (2000) 2367