TECHNISCHE UNIVERSITÄT DARMSTADT

Modelling, analysis and simulation of transport processes at fluidic interfaces

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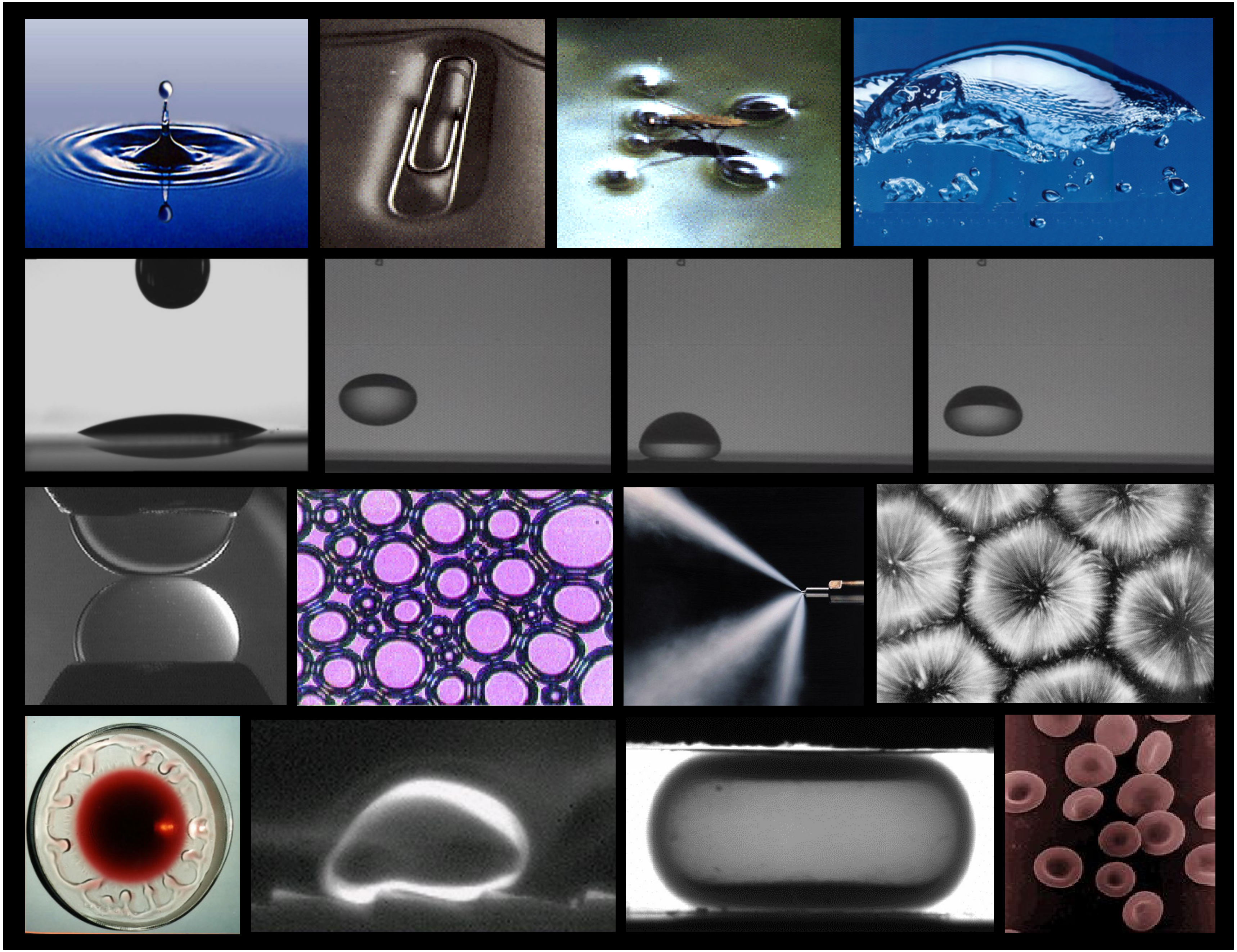
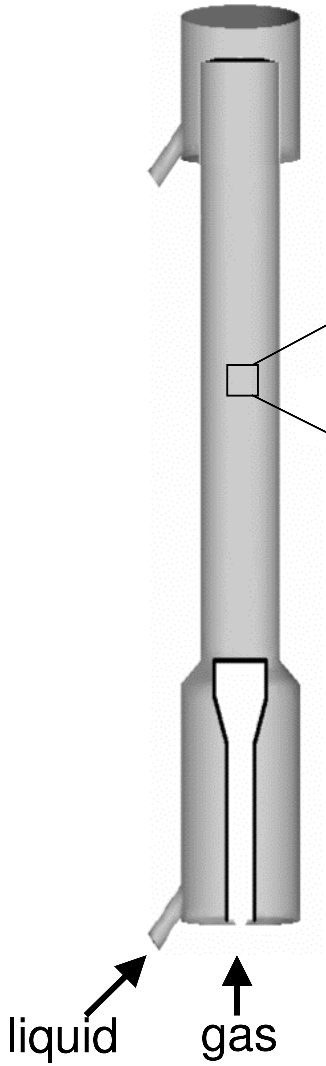


Reactive Gas-Liquid-Processes

Bubble Column



- transport of a chemical component from a gas phase into the ambient liquid phase
- chemical reaction(s) of transfer component with continuous phase chemical species

Bubble Column

multi-scale two-phase process

macro scale

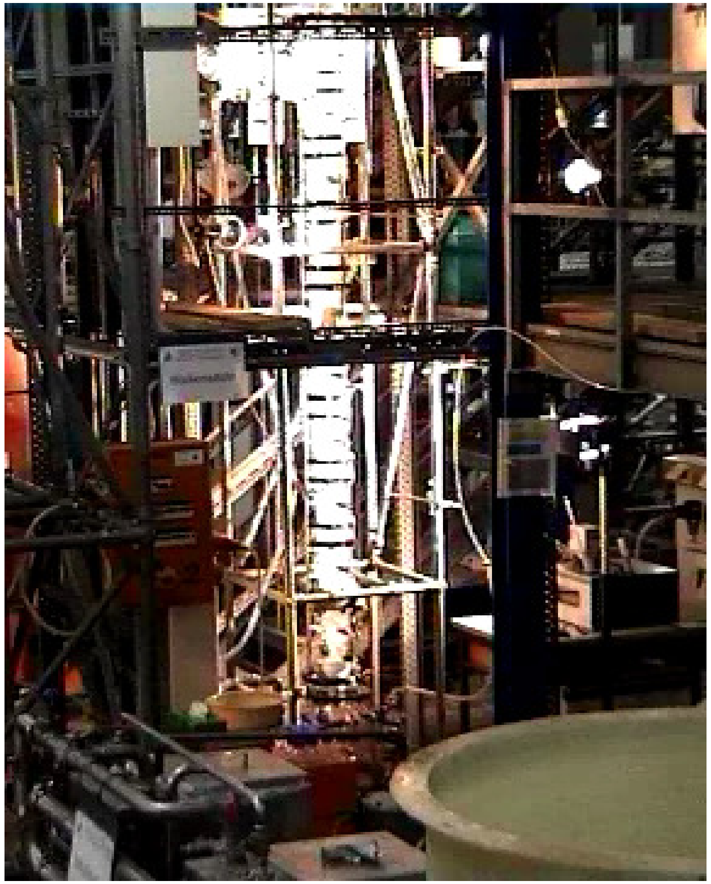
- dispersion (backmixing)
- bubble movement
- convection

meso scale

- coalescence vs. bouncing

micro scale

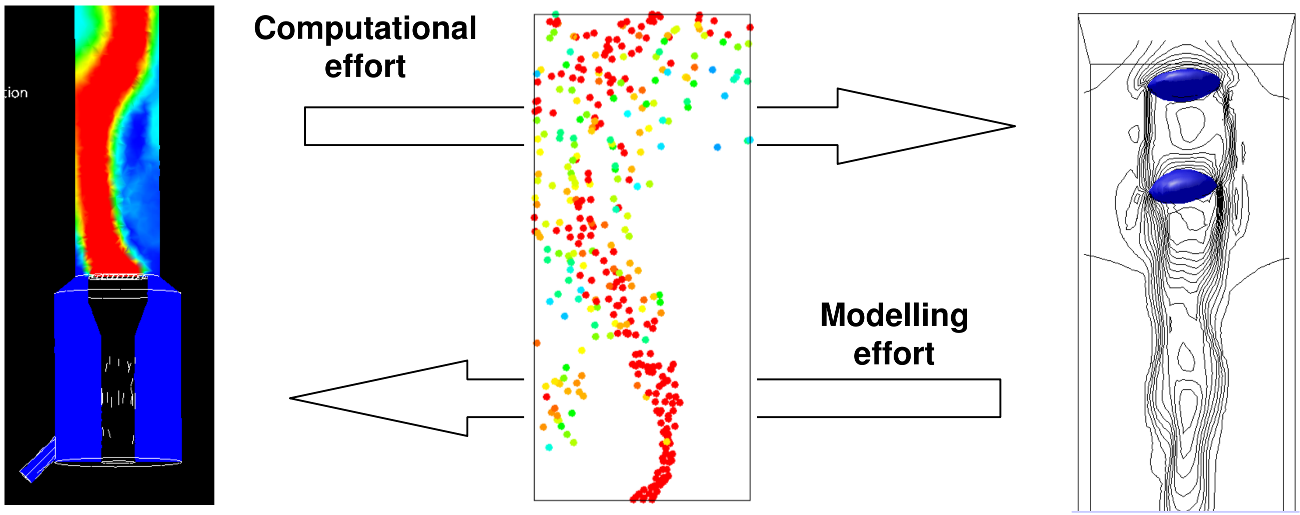
- mass transfer
- diffusion (micro mixing)
- chemical reaction



laboratory bubble column

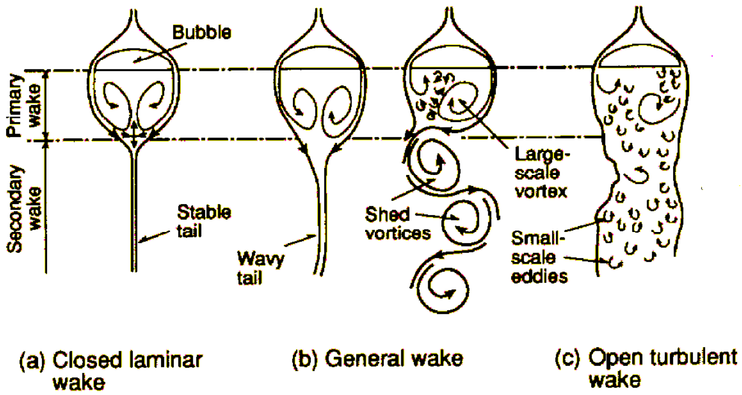
Model Hierarchy

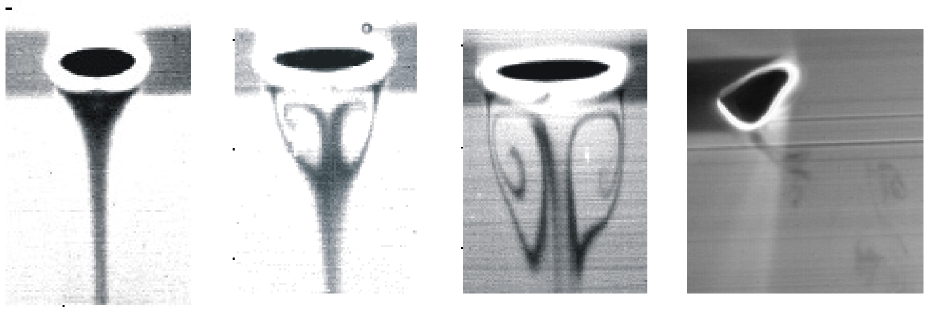
- Multi-scale Modelling



Interpenetrating continua Euler-Euler formulation	Discrete bubble model Euler-Lagrange formulation	Volume of Fluid (VOF), Level Set, Front Tracking
• Two-fluid models (mono-dispersed bubbles) • Multi-fluid model (poly-dispersed bubbles: Coalescence and break-up)	• individual bubble motion • incorporation of additional bubble scale processes possible like heat/mass transport & reaction	• Direct numerical simulation of individual bubble dynamics • Research tool/ yields closures laws • Limited to a few bubbles

Bubble Wake Reactor





Bork, Schlüter, Scheid, Räbiger, IUV, University of Bremen

complex interplay between hydrodynamics, mass transfer, convective and diffusive mass transport and chemical reaction at dynamical interfaces

insufficient knowledge of the underlying ***local*** physico-chemical phenomena

DFG project cluster PAK119

computational bubble dynamics

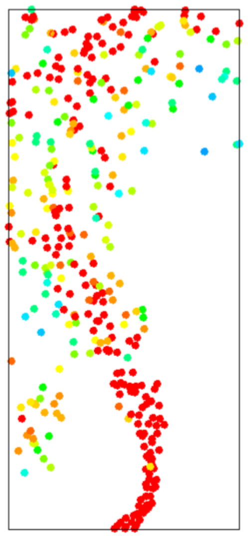
Forces on Bubbles

Equation of motion for single bubbles:

$$\left(\rho_g + a\,\rho_l\right)\frac{d\mathbf{v}_P}{dt} = -\frac{3C_D\rho_l}{4d_B}\,|\,\mathbf{v}_R\,|\,\mathbf{v}_R - C_L\rho_l\mathbf{v}_R \times \operatorname{rot}\mathbf{v}_l + \Delta\rho\,\mathbf{g}$$

Inertial Force | Drag Force | Lift Force | Buoyancy Force

DBM



$\mathbf{v}_P$	particle velocity	a	virtual mass coefficient
$\mathbf{v}_l$	liquid velocity	C_D	drag coefficient
$\mathbf{v}_R$	relative velocity	C_L	lift coefficient

Multi-scale modelling: *Closure laws for C_D, C_L etc. from Direct Numerical Simulations*

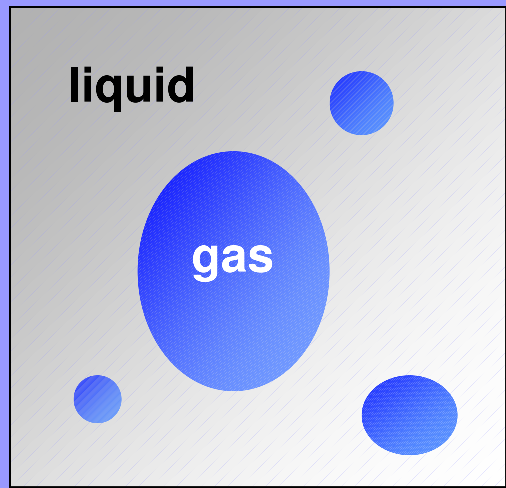
Modeling of Two-Phase Flow

Basis of mathematical model: continuum mechanics

- captures all relevant macroscopic phenomena
- existence of continuous densities of all balanced quantities

Multi-Phase System:

- continuous physical quantities inside the bulk phases
- jump discontinuities at the phase boundaries



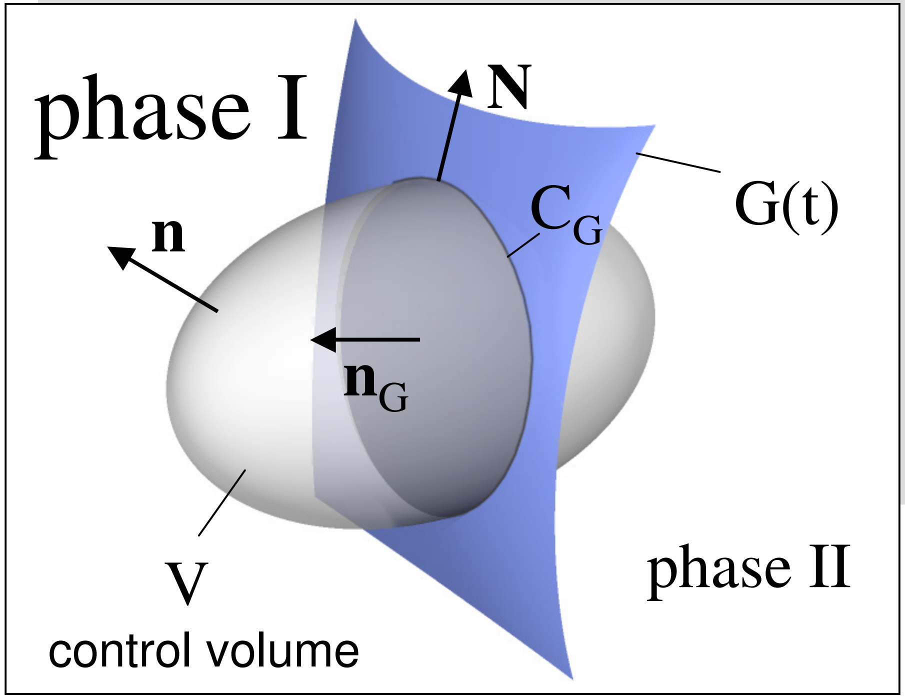
Moving Boundary Problem

shape and distribution of interfaces implicitly determined

Continuum Mechanical Modeling

Balance of an extensive physical quantity with density ϕ

$$\frac{d}{dt}\int_V \rho\phi\, dV = \int_V S\, dV$$	**sources/sinks**
$$-\int_{\partial V} \rho\phi\mathbf{u}\cdot\mathbf{n}\, dA - \int_{\partial V} \mathbf{J}\cdot\mathbf{n}\, dA$$	**convective and molecular flux**
$$+\int_{V\cap G} S_G\, dA$$	**interfacial sources/sinks**
$$-\int_{C_G} \mathbf{J}_G\cdot\mathbf{N}\, dS$$	**interfacial flux**



Local Balances

integral balance equations

local balance equations

$$\partial_t \rho\phi + \nabla\cdot\rho\phi\mathbf{u} + \nabla\cdot\mathbf{J} = S$$

accum. **conv. flux** **mol. flux** **source**

interfacial jump conditions

$$\left[\rho\phi\left(\mathbf{u}-\mathbf{u}_G\right)+\mathbf{J}\right]\cdot\mathbf{n}_G = S_G$$

conv. flux **mol. flux** **source**

jump of a quantity Ψ at the interface:

$$[\Psi](x) := \lim_{h\to 0+} \Psi(x+h\mathbf{n}_G) - \Psi(x-h\mathbf{n}_G)$$

apply to

- *mass* $\phi = 1$
- *momentum* $\phi = \mathbf{u}$
- *energy* $\phi = e + \frac{1}{2}u^2$

Two-Phase Navier-Stokes Eqs

Mathematical model of isothermal incompressible two-phase flow without phase change for *constant* surface tension :

mass

$$\nabla \cdot \mathbf{u} = \mathbf{0} \qquad [\mathbf{u}] = \mathbf{0}$$

momentum

$$\partial_t(\rho_\pm \mathbf{u}) + \nabla \cdot (\rho_\pm \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T} \qquad [-\mathbf{T}] \cdot \mathbf{n} = \sigma\kappa\mathbf{n}$$

phase

$$\partial_t f + \mathbf{u} \cdot \nabla f = 0 \qquad V = \mathbf{u} \cdot \mathbf{n}$$

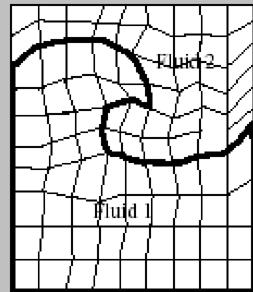
$$\mathbf{T} = -p_\pm \mathbf{I} + \mathbf{S}, \quad \mathbf{S} = \eta_\pm (\nabla \mathbf{u} + \nabla \mathbf{u}^{\mathrm{T}})$$

Principal Approaches

Numerical methods for simulation of two-phase flows

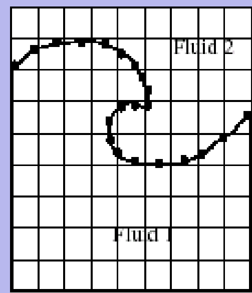
- moving grid methods (Lagrangian)

Each phase represented by a separate grid.
Computational grid advected with the flow.



- fixed grid methods (Eulerian)

Common computational grid for both phases.
Interface is independent of this grid.

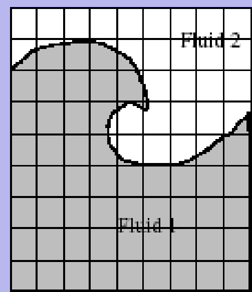


- surface tracking

marker particles / surface grid (front tracking)

- volume tracking

Volume of Fluid (VOF) / Level Set



Volume of Fluid - Method

Phase conservation

$$V = \mathbf{u} \cdot \mathbf{n}$$

$$\partial_t f + \mathbf{u} \cdot \nabla f = 0$$

$f =$ phase indicator function

Volume of Fluid (VOF) - Method

phase I (gas)

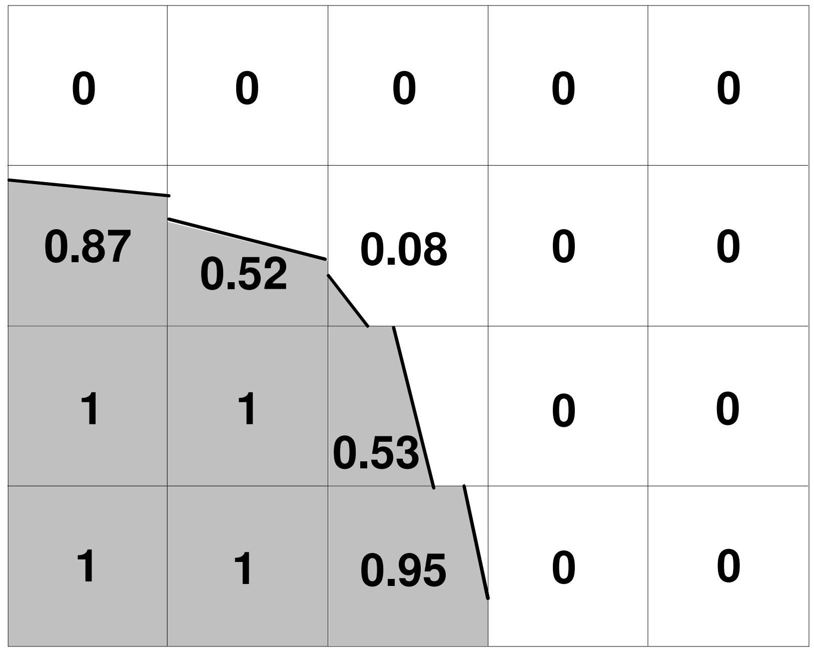
$$f = 0$$

interface

$$0 < f < 1$$

phase II (liquid)

$$f = 1$$



C.W. Hirt, B.D. Nicholls, J. Comput. Phys. 39 (1981).

Volume of Fluid - Method

one-field formulation & incorporation of surface tension

local balance equation	interfacial jump condition
$\partial_t \rho \mathbf{u} + \nabla \cdot \rho \mathbf{u} \otimes \mathbf{u} = \nabla \cdot \mathbf{T} + \rho \mathbf{g}$	$[\rho \mathbf{u} \otimes (\mathbf{u} - \mathbf{u}_G) - \mathbf{T}] \cdot \mathbf{n}_G = \sigma \kappa \mathbf{n}_G$

$\mathbf{T}$: stress tensor, $\mathbf{T} = -p\mathbf{I} + \mathbf{S}$

p: pressure

$\mathbf{S}$: viscous stress tensor

$\mathbf{g}$: body forces

κ: curvature (twice the mean curvature)

σ: surface tension

$\nabla_G \sigma$ surface gradient of σ (vanishes for constant σ)

curvature: $\kappa = -\nabla \cdot \mathbf{n}_G$

interface unit normal: $\mathbf{n}_G = \nabla f / |\nabla f|$

Dirac distribution δ_G w.r.t. interface: $\delta_G = |\nabla f|$

$$\partial_t \rho \mathbf{u} + \nabla \cdot \rho \mathbf{u} \otimes \mathbf{u} = \nabla \cdot \mathbf{T} + \rho \mathbf{g} + \sigma \kappa \nabla f$$

VOF - Code *FS3D*

- Direct Numerical Simulation
  of Navier-Stokes equations
  for two-phase flows

- implicit representation of interface :
  volume tracking,
  fractional volume f of dispersed phase

- additional advection equation for f

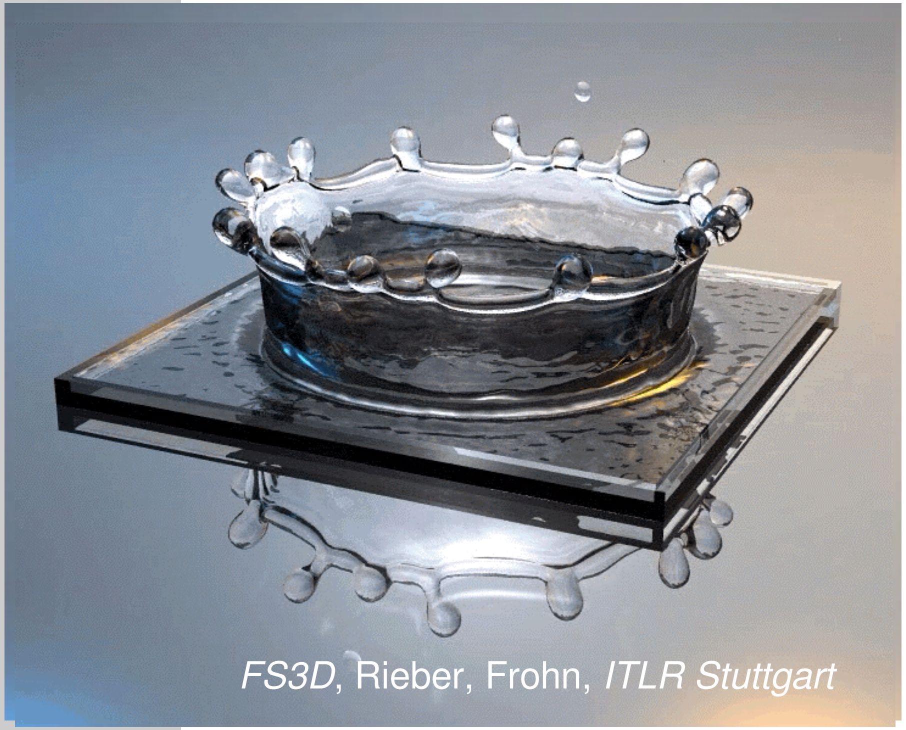
$$\partial_t f + \mathbf{u} \cdot \nabla f = 0$$

- piecewise linear interface reconstruction

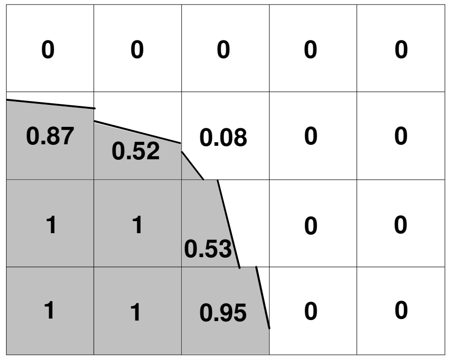
- surface tension: conservative model

- massively parallelized

- well validated for collision of drops



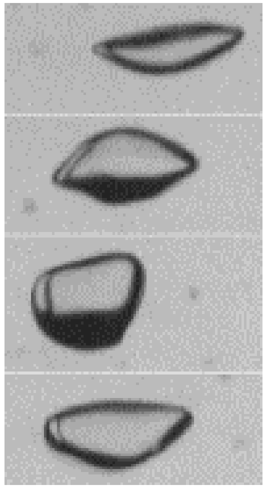
FS3D, Rieber, Frohn, *ITLR Stuttgart*

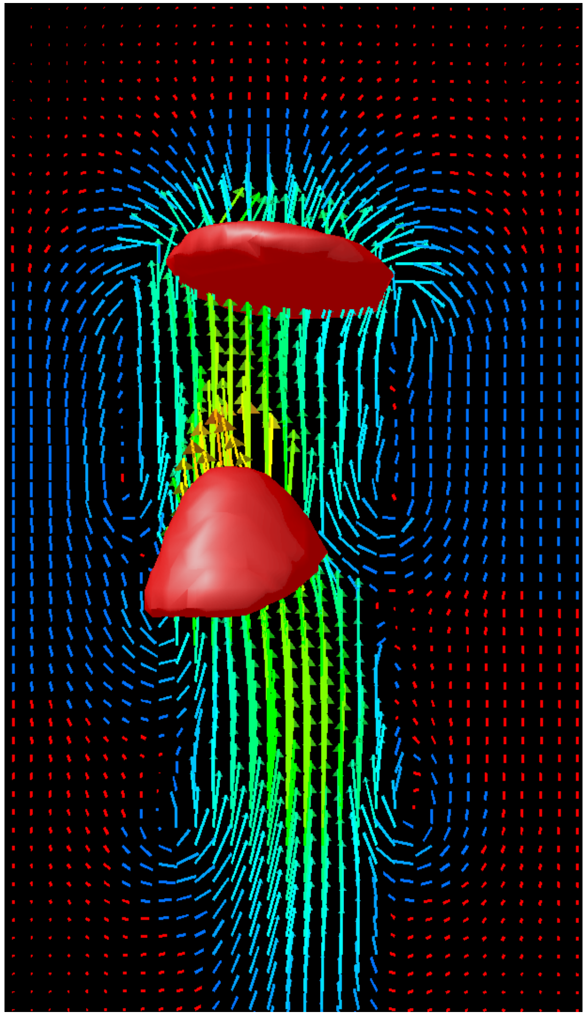


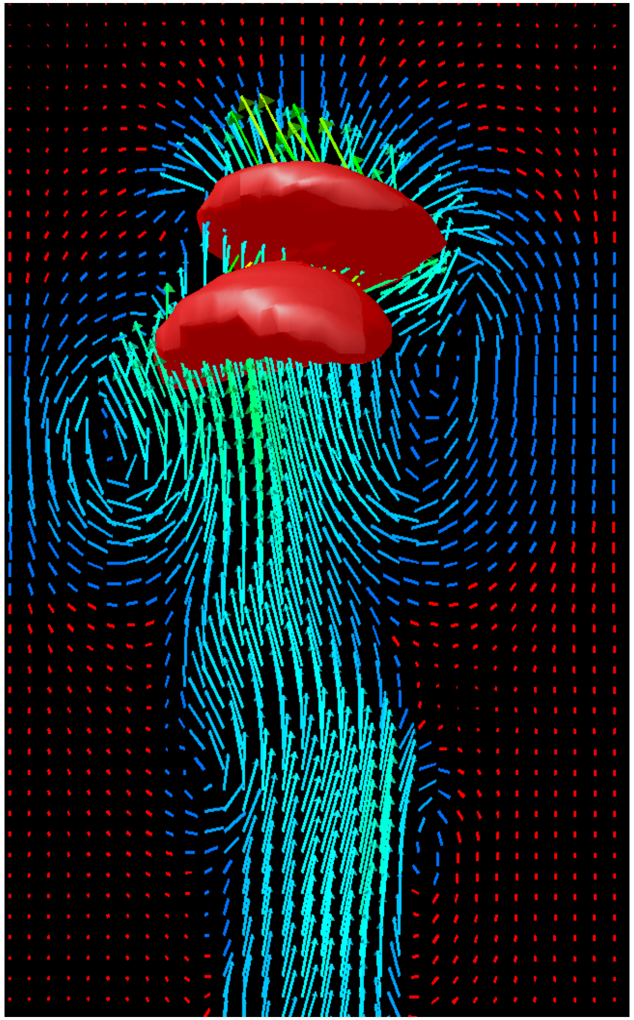
DNS of Air Bubbles in Water

8 mm bubbles, counterflow
initial separation 2,5 d_B

256 x 64 x 64 cells







Terminal Rise Velocity

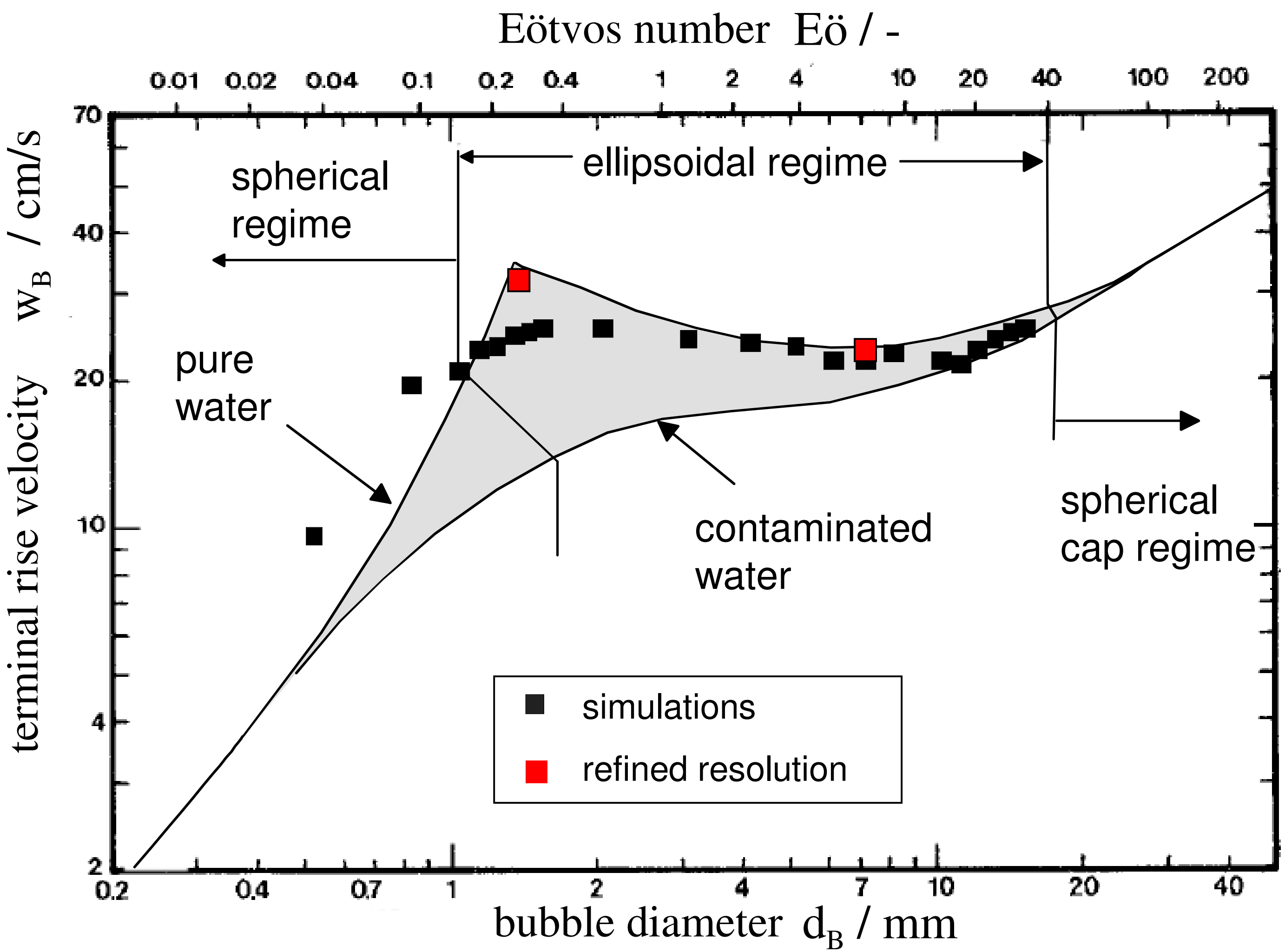
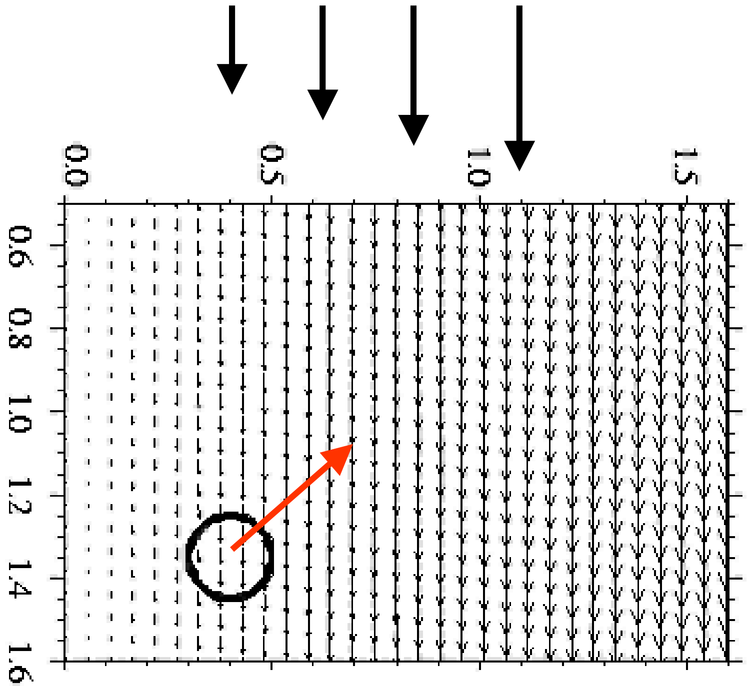


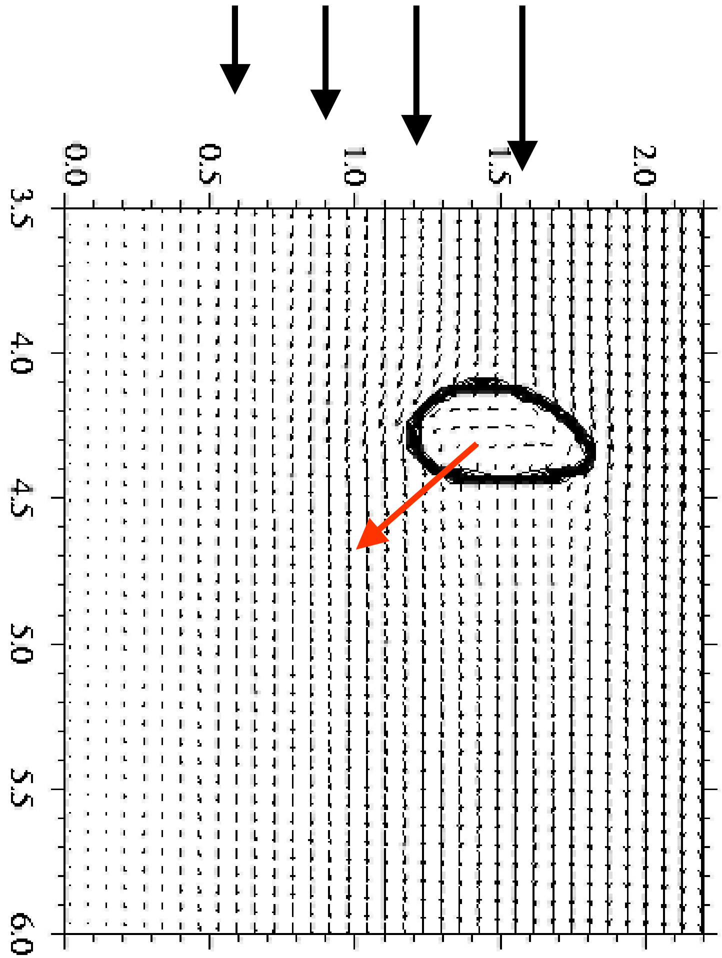
Diagram from Clift, Grace, Weber: *Bubbles, drops and particles*, Academic Press, 1978

Bubbles in Shear Flow



air bubble in water

$d = 2\,mm \qquad \frac{\partial w}{\partial y} = 25\,s^{-1}$

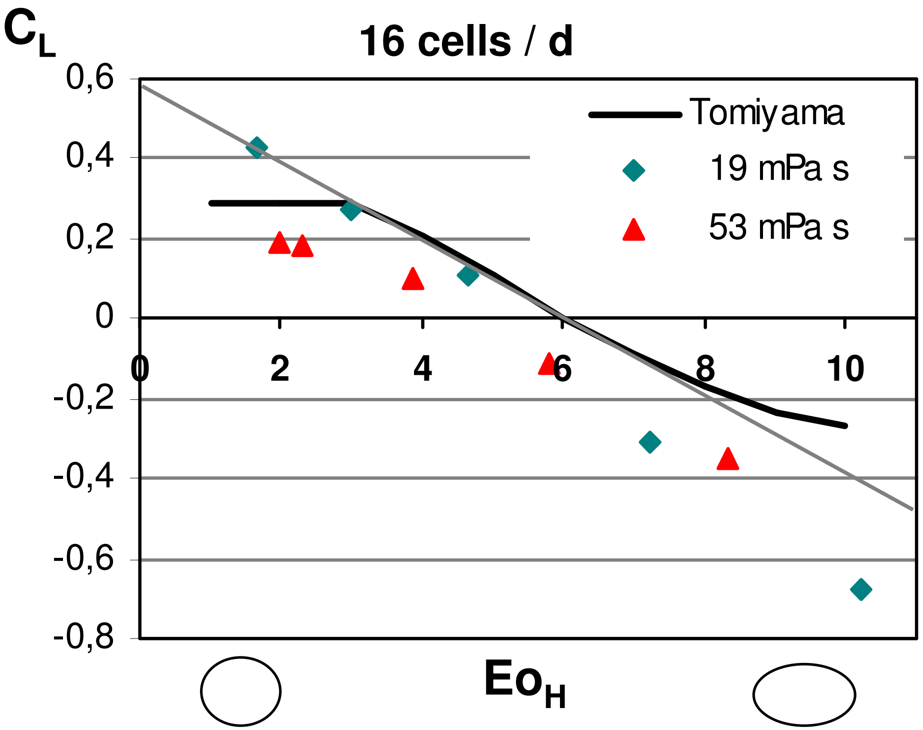


air bubble in water/glycerol

$d = 10\,mm \qquad \frac{\partial w}{\partial y} = 10\,s^{-1}$

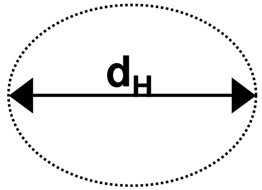
Variation of Bubble Diameter

Bubbles with d = 2.8…5.7 mm in water/glycerol mixtures, 19 and 53 mPa s (cf. Tomiyama et al. 2002)



Tomiyama's experimental result:

$C_L = f\ (Eo_H)$



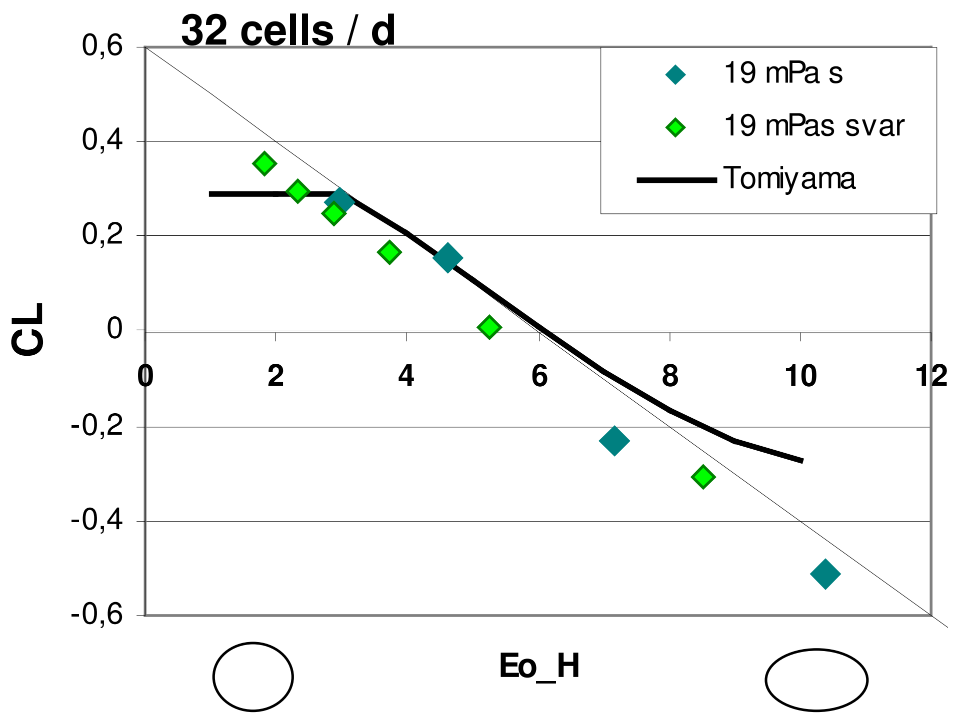
$$Eo_H = \frac{g\,(\rho_l - \rho_g)\,d_H^{\ 2}}{\sigma}$$

Eo = buoyancy / surface tension

Simulated lift coefficients (colored symbols) are below the curve given by Tomiyamas correlation: $C_L = f\ (Eo_H)$

Variation of Surface Tension

Bubbles with d = 3,2 mm in model fluid (μ_l = 53 mPa s; ρ_l= 1200 kg/m³)
Surface tension σ = 15 … 75 mN / m



Variation of σ has an effect on Eo_H *and* on Morton Number Mo

$$\mathrm{Eo_H} = \frac{g\,(\rho_l - \rho_g)\,d_H{}^2}{\sigma}$$

$$\mathrm{Mo} = \frac{g(\rho_l - \rho_g)\mu_l^4}{\rho_l^2 \sigma^3}$$

Here: log Mo = -3.8 … -1.7

Variation of g also effects Eo

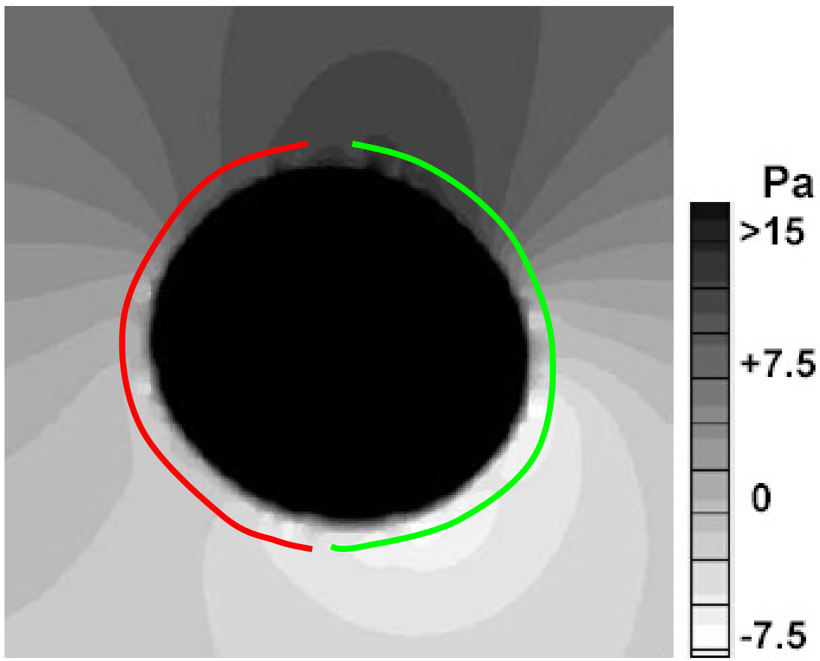
Eo → 0 : C_L = 0.6 (Spheres: Auton)

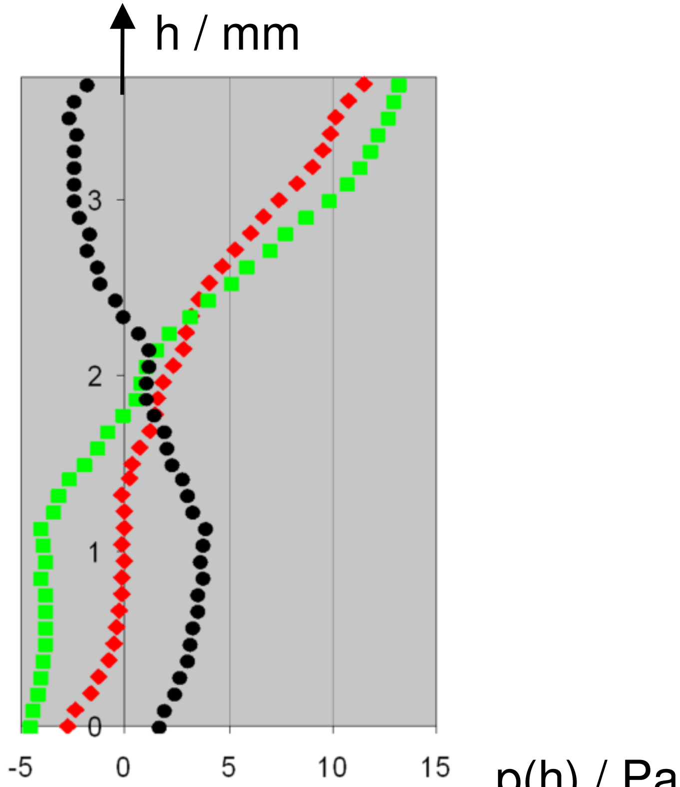
→ *C_L depends on Eo_H, but Morton has little influence*

2D Bubbles in Shear Flow

Small 2D bubble in glycerol (d = 3mm): Dynamic pressure *near* interface

(Numerical smearing of pressure jump:
dynamic pressure can *not* be detected directly at the interface)

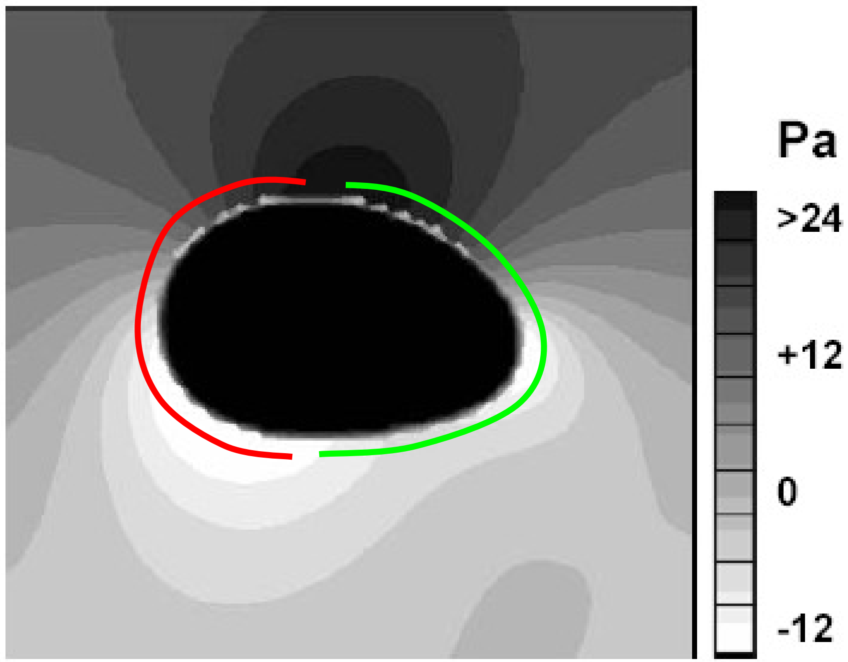




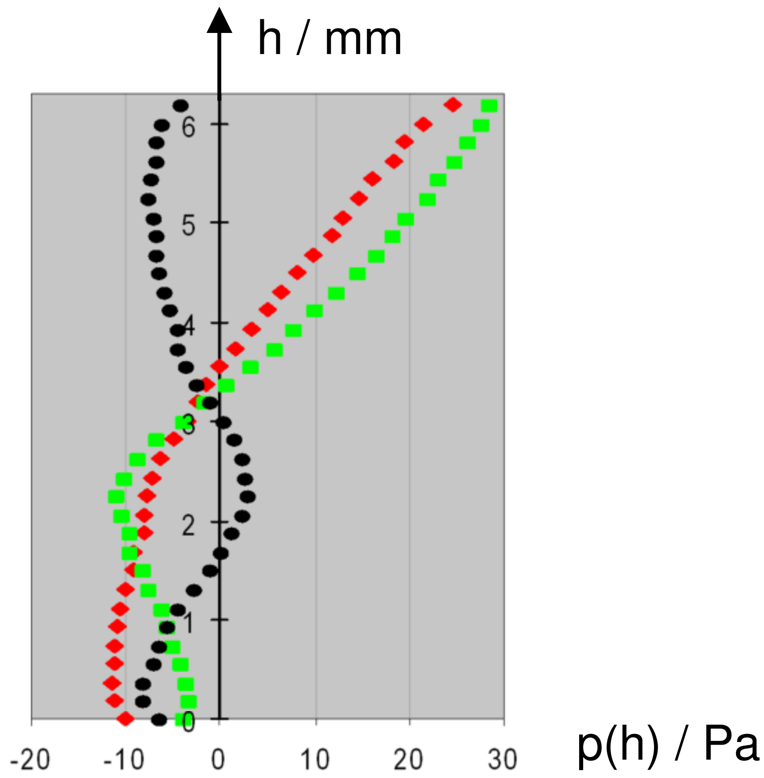
→ *Bubble migrates to the side of the average pressure difference*

2D Bubbles in Shear Flow

Large 2D bubble in glycerol (d =6 mm): Dynamic pressure *near* interface



Distance of control lines to interface: 3 cells

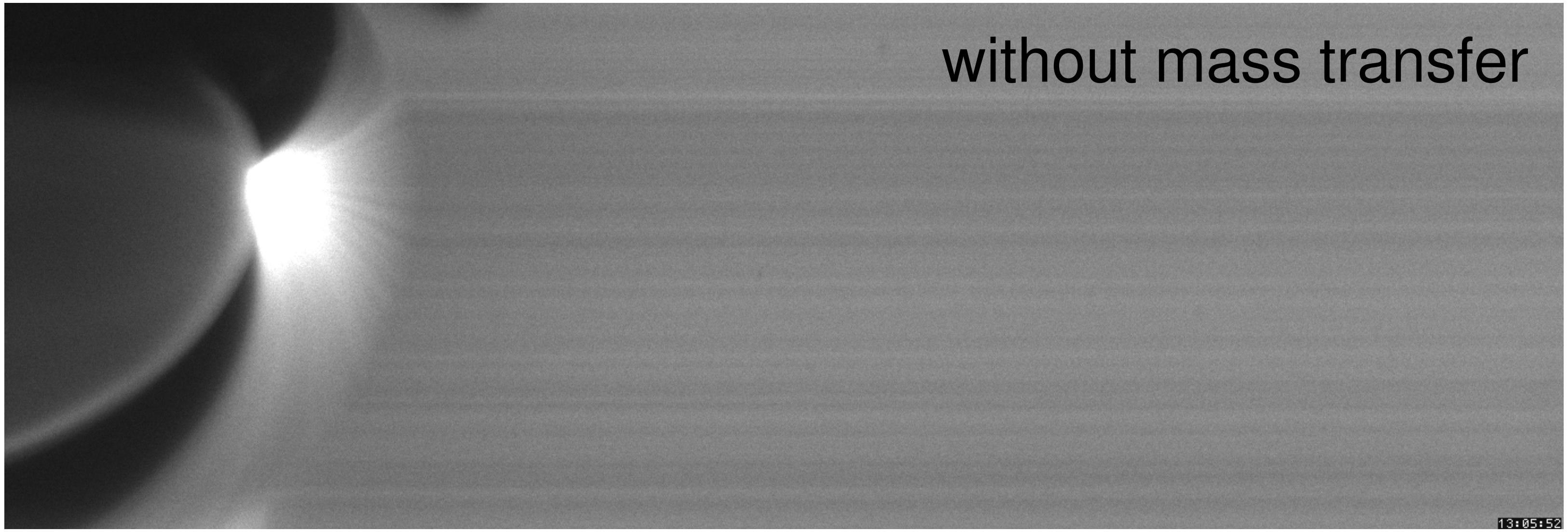


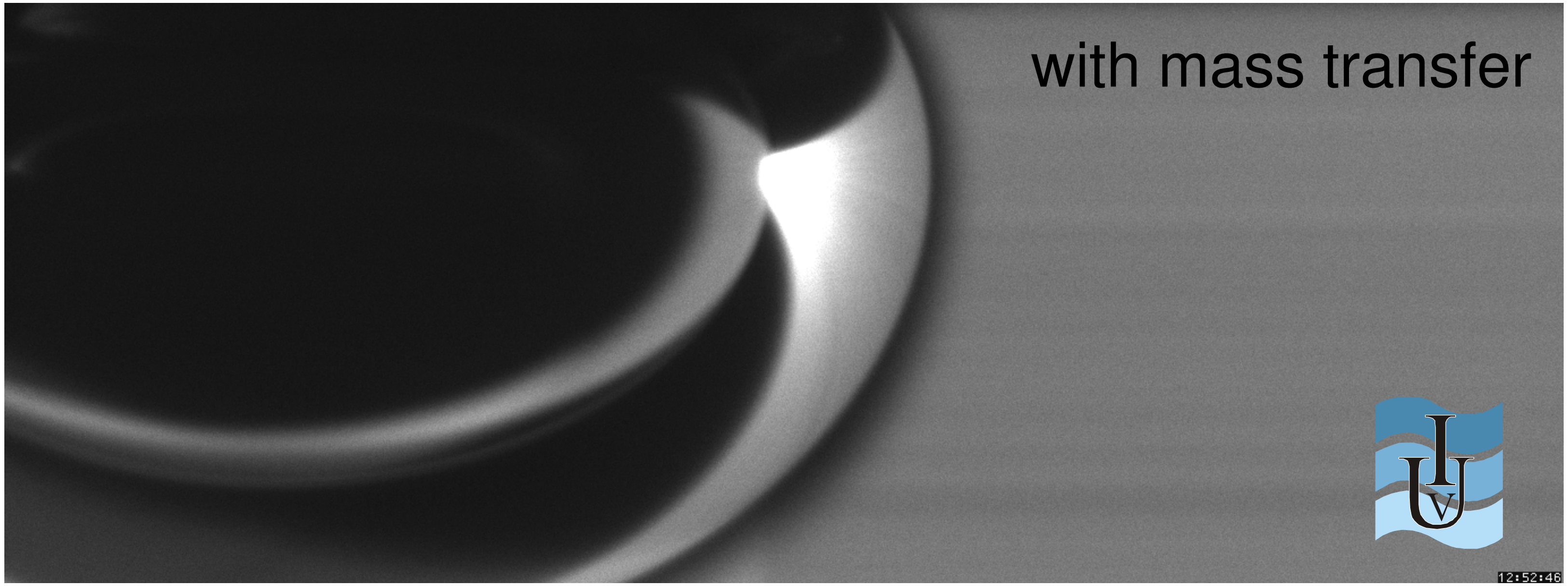
→ *Bubble migrates to the side of the average pressure difference*

not fully understood in 3D!

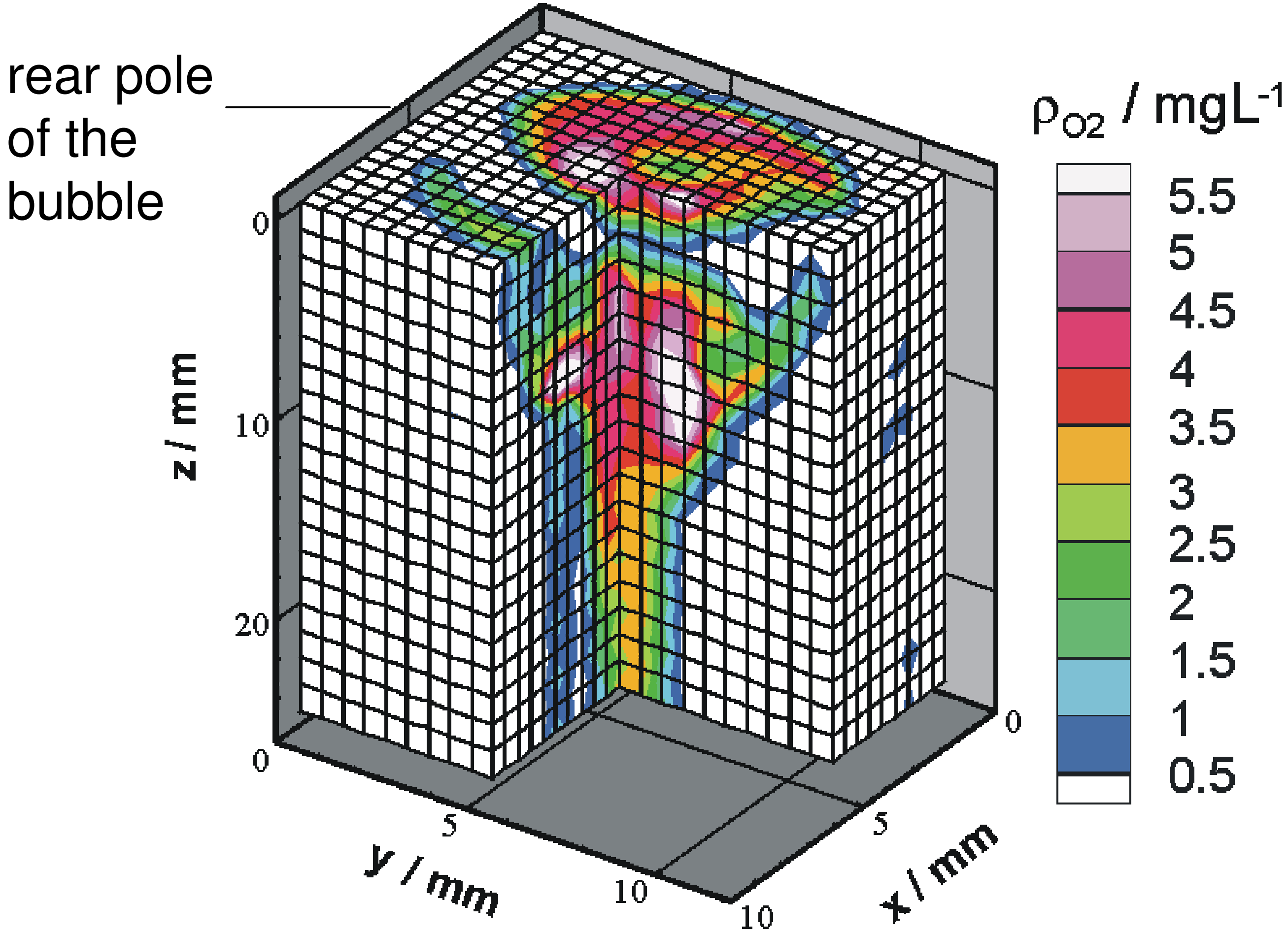
mass transfer across deformable interfaces

LIF-Measurements





Concentration Wake



3D-reconstruction of the concentration wake

Experiments: O. Bork, M. Schlüter, N. Räbiger, IUV, Universität Bremen

Two-Phase Species Equations

species mass balance (dilute case) in terms of molar concentration c_i:

local balance equation	interfacial jump condition
$\partial_t c_i + \nabla \cdot c_i \mathbf{u} + \nabla \cdot \mathbf{J}_i = R_i$	$\left[c_i \left(\mathbf{u} - \mathbf{u}_G \right) + \mathbf{J}_i \right] \cdot \mathbf{n} = 0$

- molecular fluxes according to Fick´s law $\mathbf{J}_i^{\,j} = -D_i^j \nabla c_i^j$ $\quad j = l:$ liquid, $j = g:$ gas
- no phase change $\mathbf{J}_i^{\,l} \cdot \mathbf{n} = \mathbf{J}_i^{\,g} \cdot \mathbf{n}$
- constitutive equation: local thermodynamical equilibrium

<u>continuity of chemical potentials at phase boundaries</u>

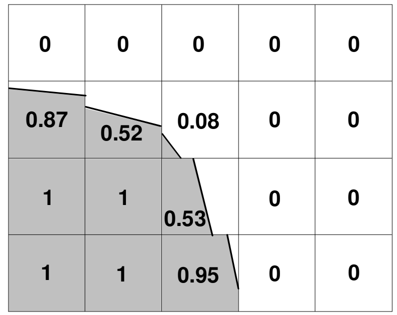
$$\mu_i = \mu_i^0 + RT \ln a_i$$

a_i activity, $a_i = \gamma_i c_i$

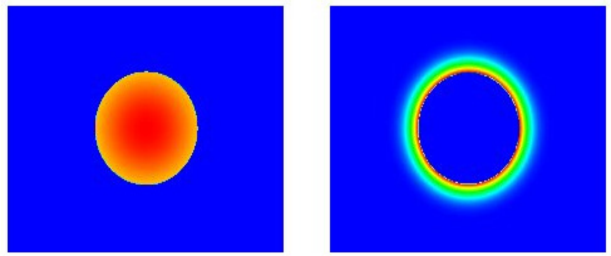
Henry´s law: $\dfrac{c_i^g}{c_i^l} = H_i$

Two-Variable Mass Transfer Approach

- *two* separate variables for *one* species in each phase

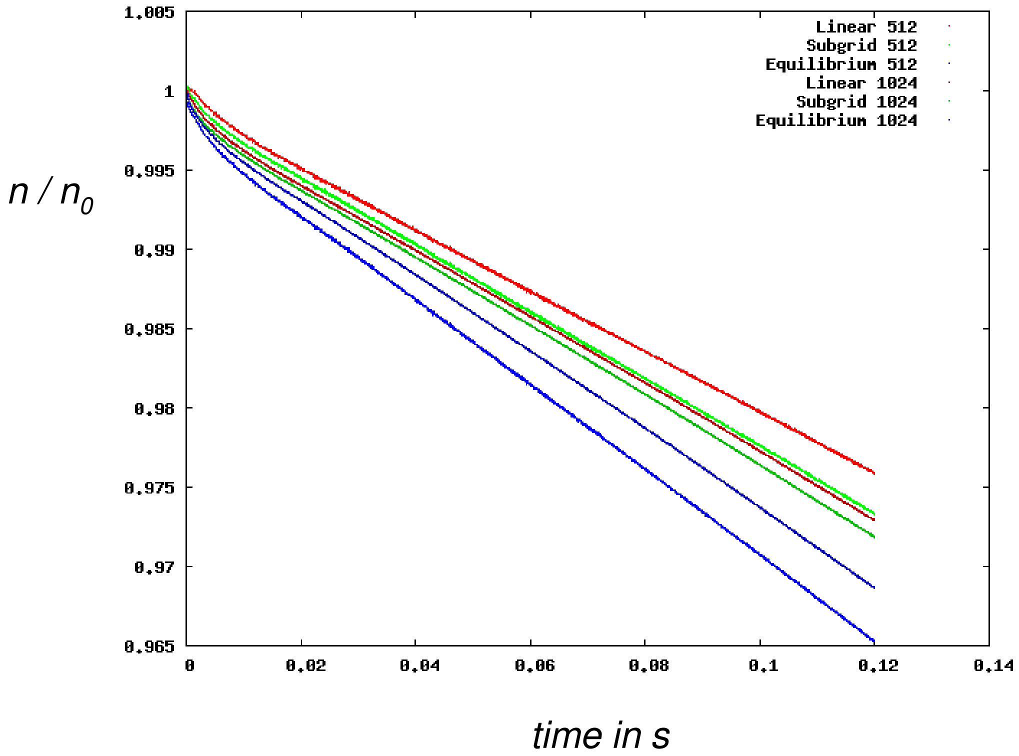


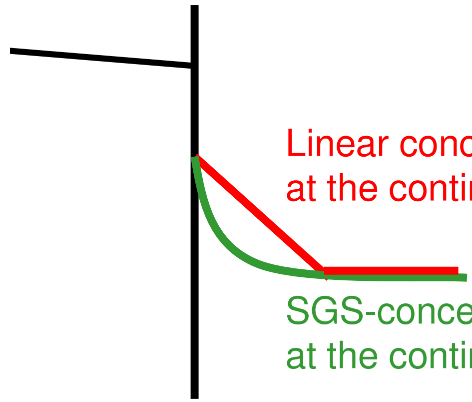
- convective species transport linked to *VOF-transport*
- *no* artificial mass transfer



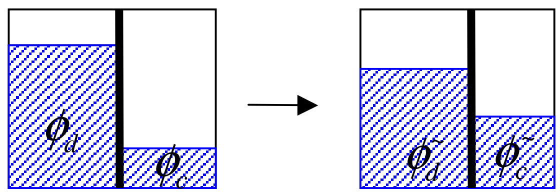
- *mass conservation* for transfer component
- mass transfer computation accounts for concentration gradients at the interface and local thermodynamical equilibrium (Henry's law)

Mass Transfer Source Term

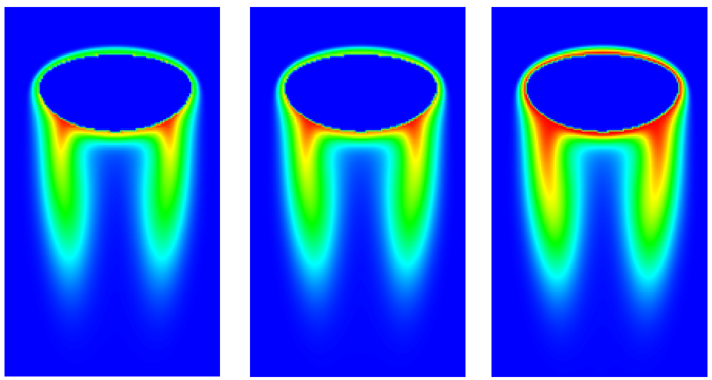




Redistribution of species mass in interfacial cells according thermodynamical equilibrium

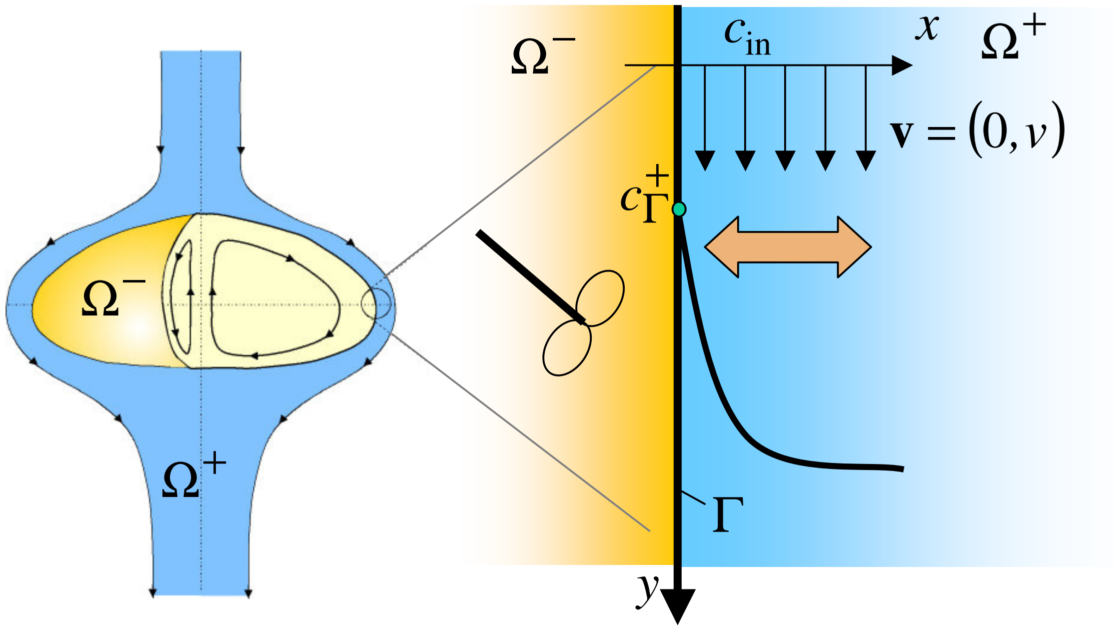


thermodynamical equilibrium



Linear SGS-model Equilibration

Subgrid-Scale Model



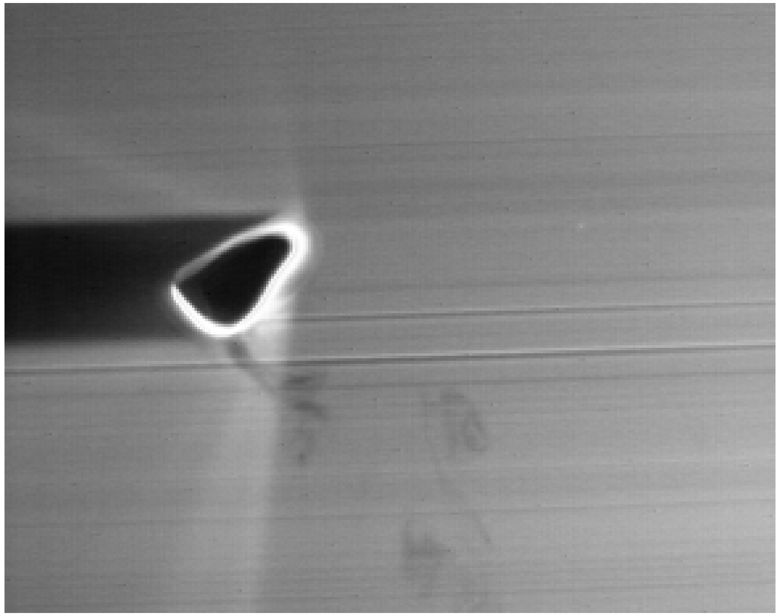
$$\partial_t c + \mathbf{v} \cdot \nabla c = D\,\Delta c$$
$$t > 0,\ x > 0,\ y > 0$$

$$c_{|y=0} = c_{in}$$
$$c_{|x=0} = c_\Gamma^+$$
$$c_{|x=\infty} = 0$$

$$c(x, y) = c_\Gamma^+ \left(1 - \operatorname{erf} x / d(y)\right)$$

Local structure of solutions

Mass Transfer from Single Bubbles



Experiments: O. Bork, M. Schlüter, N. Räbiger,
IUV, Universität Bremen

computed mass transfer coefficients

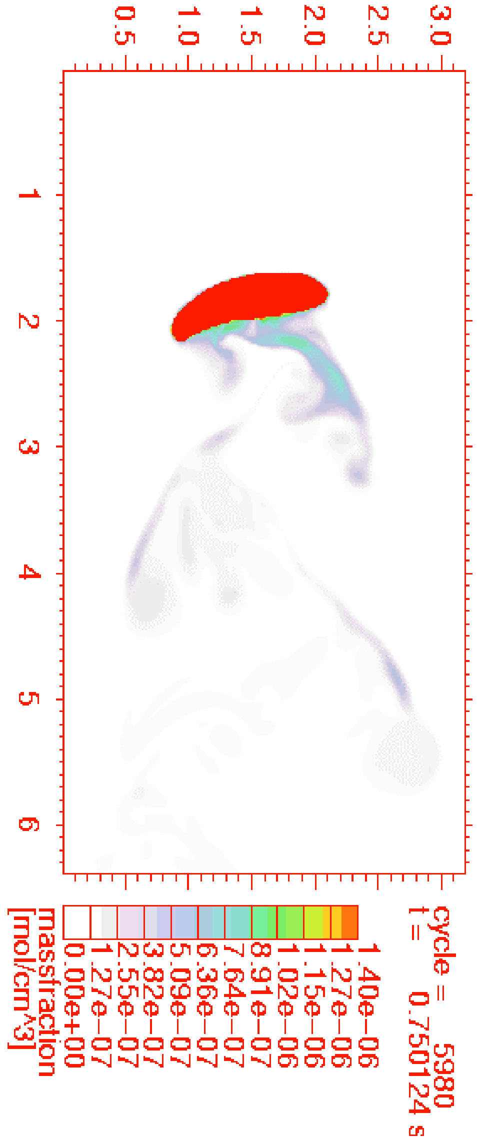
$1.12 \cdot 10^{-4}$ m/s for 4mm bubbles

$1.28 \cdot 10^{-4}$ m/s for 6 or 8mm bubbles

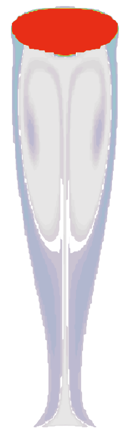
bubble-induced turbulence increases mass transfer

$H = 33$

VOF-Simulation



6,9 mm bubble
25 mPa s
aqueous
CMC-solution

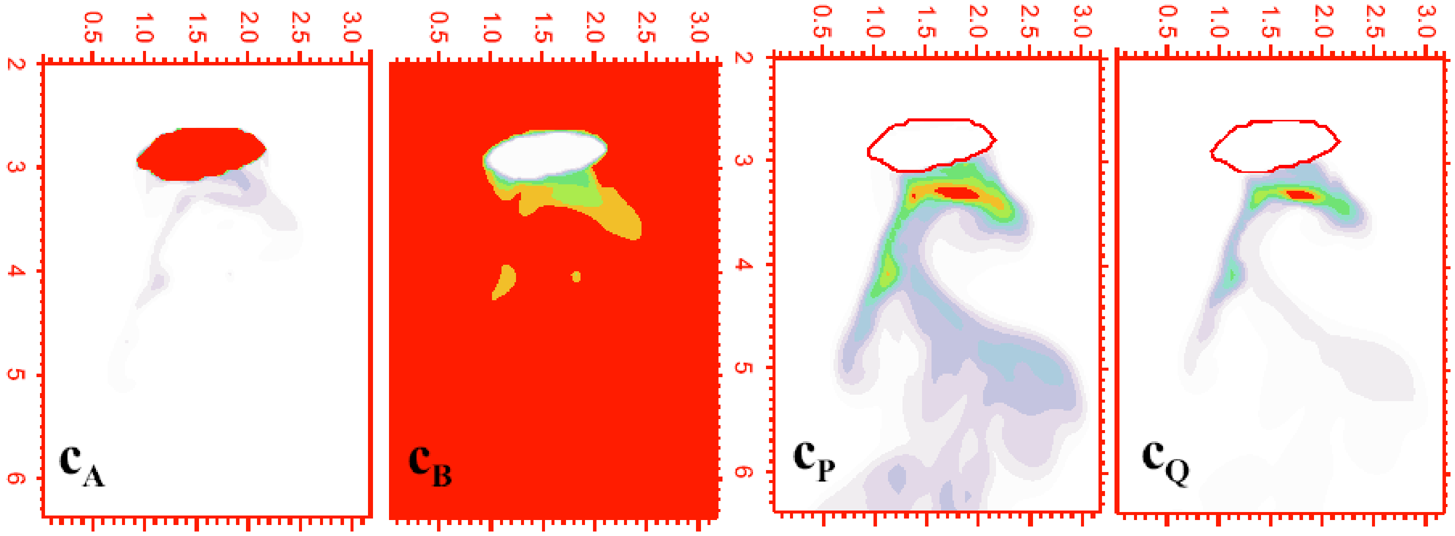


10 mm bubble
25 mPa s
Newtonian
liquid

reactive
mass transfer

Reactive Mass Transfer

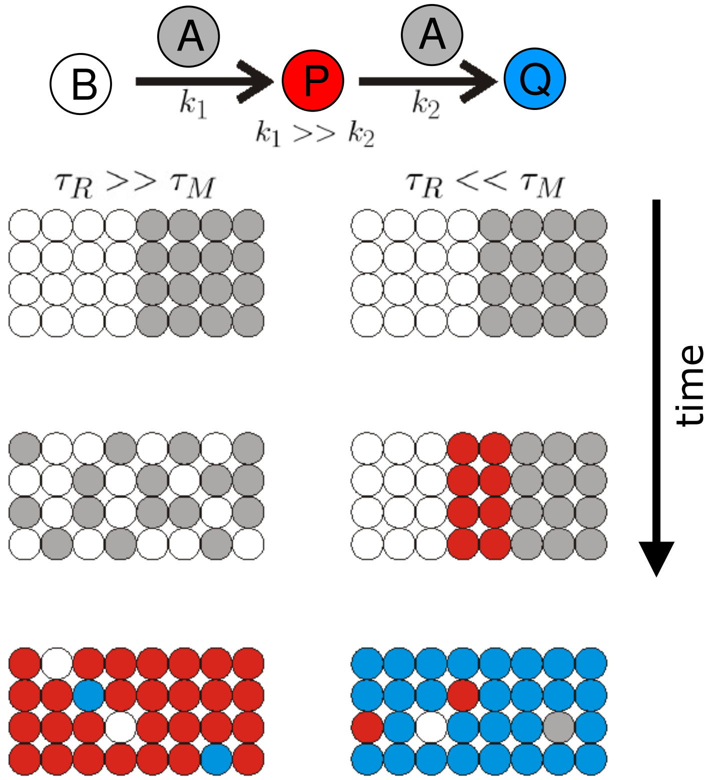
$$A_g \rightarrow A_l \qquad A_l + B \xrightarrow{k_1} P \qquad A_l + P \xrightarrow{k_2} Q$$



3D VOF-simulation

Objectives: Conversion & Selectivity

- Influence of mixing on conversion and selectivity in case of (fast) chemical reactions



Rys et al.

Local Selectivities

Integral selectivity for a pair of competitive, consecutive reactions:

$$\mathrm{A + B \xrightarrow{r_1} P}$$

$$\mathrm{A + P \xrightarrow{r_2} Q}$$

r_1, r_2 reaction laws

$$S_{P,B} = \frac{n_P}{n_B^0 - n_B} = \frac{\int (r_1(c_A, c_B) - r_2(c_A, c_P))dVdt}{\int r_1(c_A, c_B)dVdt}$$

for local analysis: introduction of local selectivities as

$$S_{P,B}^{loc} = \frac{r_1 - r_2}{r_1}$$

$$S_{P,A}^{loc} = \frac{r_1 - r_2}{r_1 + r_2}$$

Local Selectivities

Local selectivities in the wake of a rising bubble in water/CMC-solution
left: 3 mm, right: 6 mm

$$A + B \xrightarrow{r_1} P$$

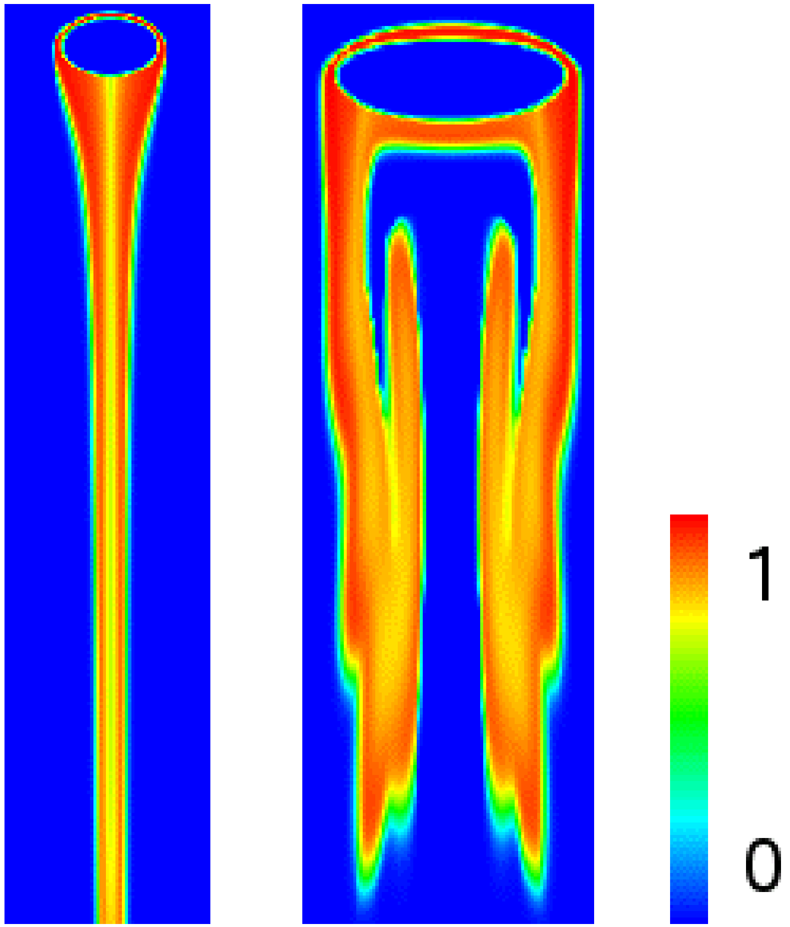
$$A + P \xrightarrow{r_2} Q$$

$$r_1 = k_1 c_A c_B$$

$$r_2 = k_2 c_A c_P$$

$$k_1 : k_2 = 1 : 1$$

requires knowledge of intrinsic kinetics!



1024x128 cells

DFG project cluster PAK119

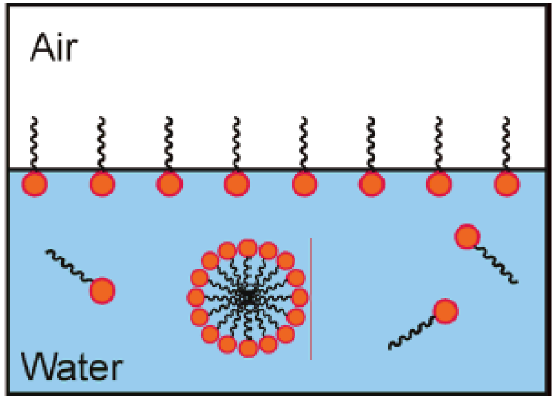
interfacial physico-chemistry

surfactants

Surfactants

<u>sur</u>face <u>act</u>ive <u>age</u><u>nt</u>

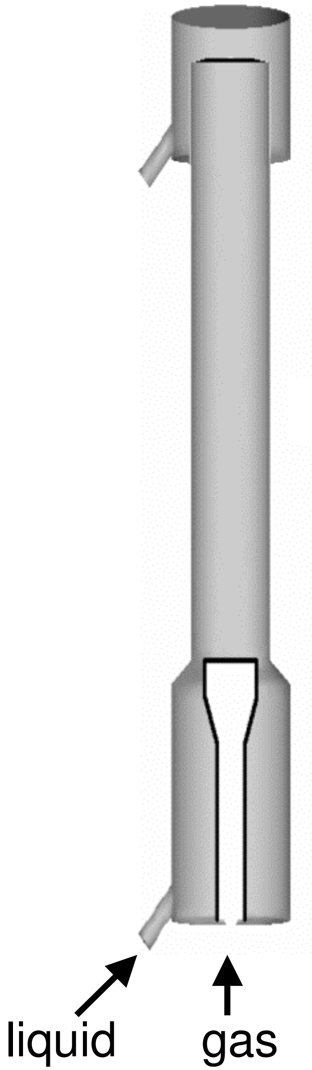
A substance which lowers the surface tension of the medium in which it is dissolved, and/or the interfacial tension with other phases, and, accordingly, is positively adsorbed at the liquid/vapour and/or at other interfaces.

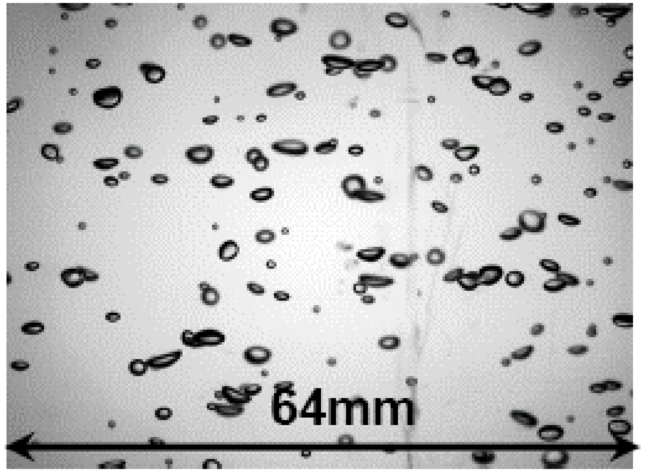


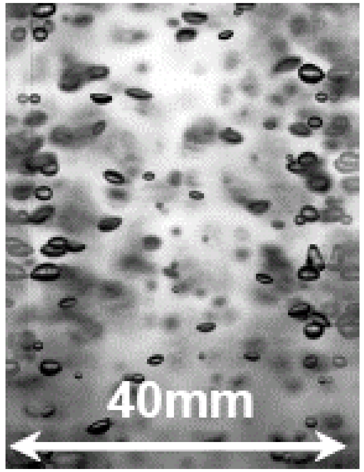
multiphase processes

- emulsions
- foams
- coatings
- polymer blends
- bubbly flows
- free surface flows in μ-g
- respiratory system
- bio-membrane modelling

Influence on Bubble Population



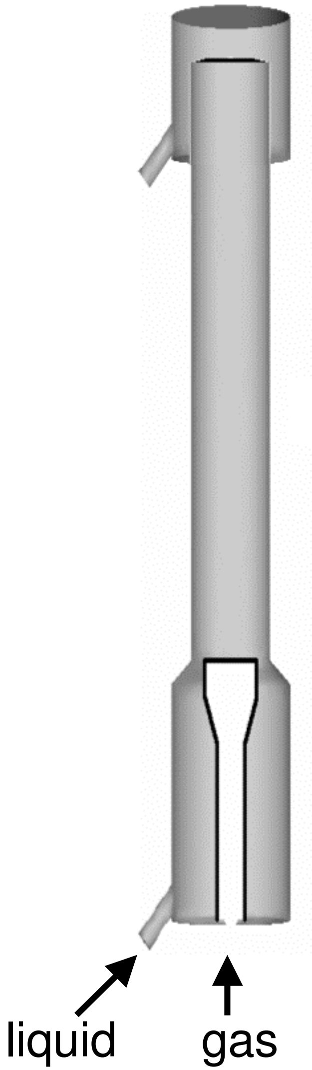


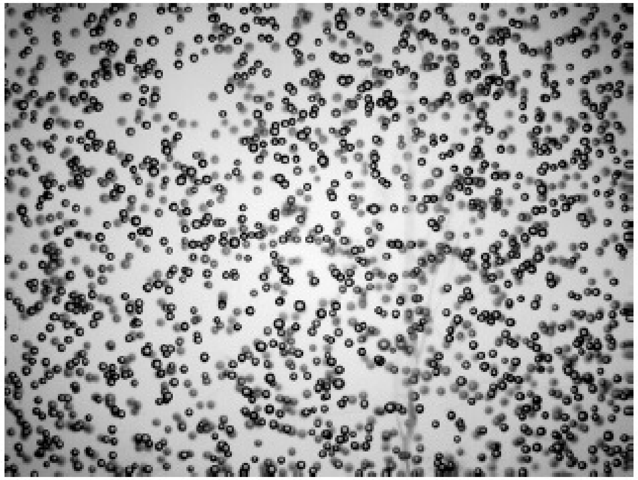


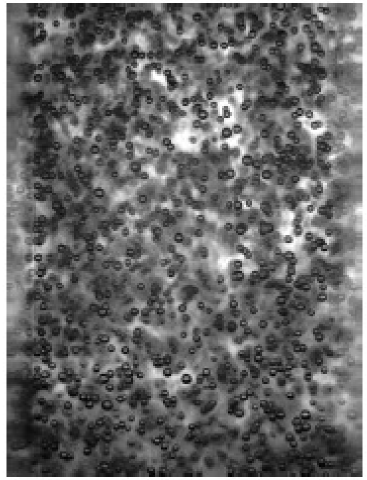
Photographs of bubbly flow
(Re_b=8200, the average void fraction of about 0.6%).
Left; front view, Right; side view.

Experiments: S. Tagaki, Tokyo University

Influence on Bubble Population







Photographs of bubbly flow with 2ppm Triton-X100.
Left; front view, Right; side view.

Experiments: S. Tagaki, Tokyo University

Stagnant Cap Model

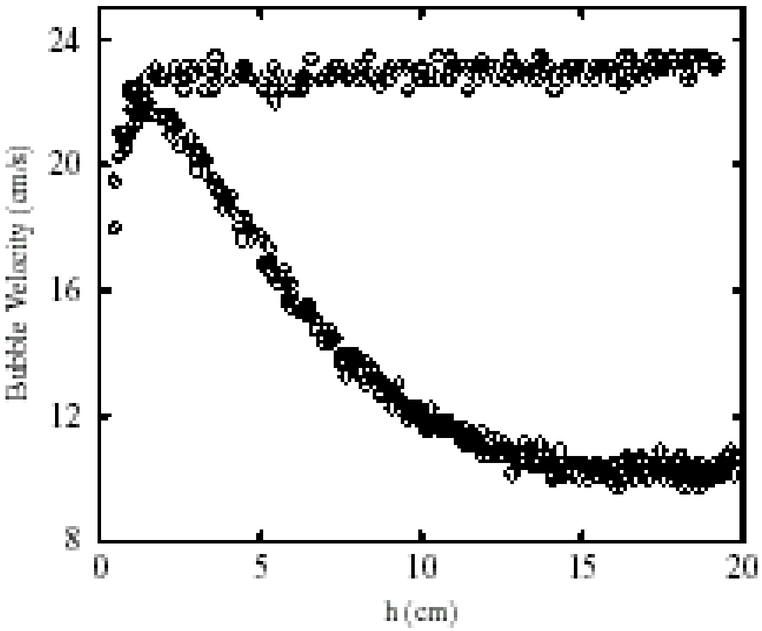
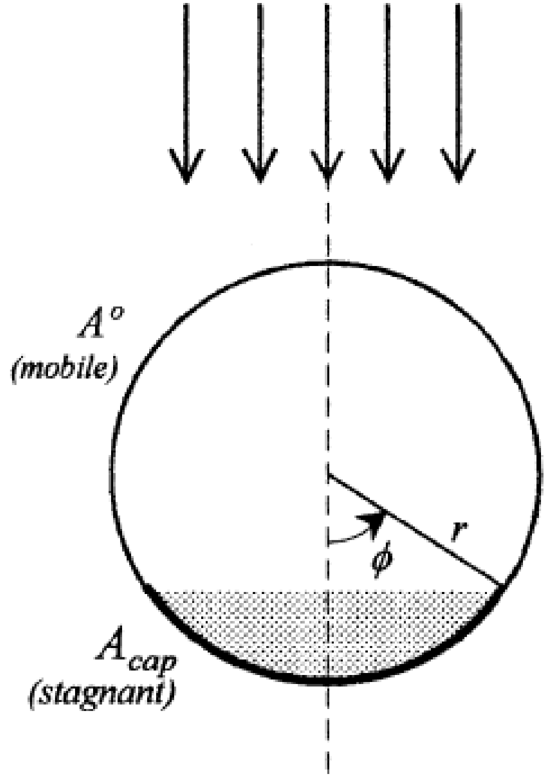


Fig. 2. Evolution of the bubble velocity with h, $R = 0.43$ mm; (∘) pure water, (⋄) BSA solution $c = 10$ mg/l.



stagnant cap model

mathematical modelling

Two-Phase Navier-Stokes Eqs

Mathematical model of isothermal incompressible two-phase flow without phase change for *variable* surface tension :

	bulk	interface
mass	$\nabla \cdot \mathbf{u} = \mathbf{0}$	$[\mathbf{u}] = \mathbf{0}$
momentum	$\partial_t(\rho_\pm \mathbf{u}) + \nabla \cdot (\rho_\pm \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T}$	$[-\mathbf{T}] \cdot \mathbf{n} = \sigma \kappa \mathbf{n}_\Gamma + \nabla_\Gamma \sigma$
		EOS $\sigma = \sigma(c_\Gamma)$
phase	$\partial_t f + \nabla \cdot (f \mathbf{u}) = 0$	$V = \mathbf{u} \cdot \mathbf{n}$

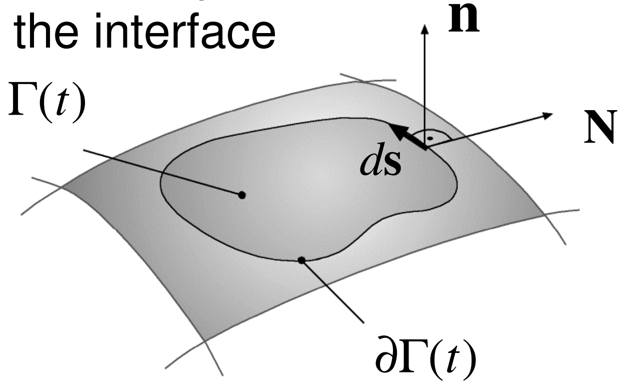
c_Γ area-specific concentration of adsorbed surfactants

Balance of a soluble surfactant

surfactant mass (bulk phase)

$$\partial_t c + \nabla \cdot (c\mathbf{u} + \mathbf{J}) = 0 \quad \text{in } V^+$$

$$c = 0 \quad \text{in } V^-$$



surfactant mass (interface)

$$\Gamma(t) = \Sigma(t) \cap V(t)$$

$$\frac{d}{dt}\int_{\Gamma(t)} c_\Gamma \, dA = -\int_{\partial\Gamma(t)} \mathbf{J}_\Gamma \cdot \mathbf{N} \, d\mathbf{s} + \int_{\Gamma(t)} r(c_\Gamma, c_{|\Gamma}) \, dA$$

Fick's law: $\mathbf{J}_\Gamma = -D_\Gamma \nabla_\Gamma c_\Gamma, \quad D_\Gamma > 0$

ad- & desorption: $r(c_\Gamma, c_{|\Gamma}) = r_{\text{ad}}(c_\Gamma, c_{|\Gamma}) - r_{\text{de}}(c_\Gamma)$

Local Balance Equation

$$\frac{d}{dt}\int_{\Gamma(t)} \psi \, dA = \int_{\Gamma(t)} \left(\frac{D\psi}{Dt} + \psi \nabla_\Gamma \cdot \mathbf{u} \right) dA$$

$$\frac{D\psi}{Dt} = \left[\underbrace{\frac{d}{ds}\psi(t+s, \mathbf{x}(t+s))}_{\text{Lagrangian derivative}} \right]_{s=0} \qquad \dot{\mathbf{x}}(s) = \mathbf{u}(s, \mathbf{x}(s))$$

$$\nabla_\Gamma \cdot \mathbf{u} = \nabla_\Gamma \cdot \mathbf{u}_\Gamma - \kappa_\Gamma V \qquad \kappa_\Gamma = -\nabla \cdot \mathbf{n}$$

sum of principal curvatures

$$\frac{Dc_\Gamma}{Dt} + c_\Gamma \nabla_\Gamma \cdot \mathbf{u}_\Gamma - c_\Gamma \kappa_\Gamma V - D_\Gamma \Delta_\Gamma c_\Gamma = r_{\mathrm{ad}} - r_{\mathrm{de}}$$

Balance Eqs for Soluble Surfactant

mass

$$\nabla \cdot \mathbf{u} = \mathbf{0} \qquad [\mathbf{u}] = \mathbf{0}$$

momentum

$$\partial_t(\rho_\pm \mathbf{u}) + \nabla \cdot (\rho_\pm \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T} \qquad \left[-\mathbf{T}\right] \cdot \mathbf{n} = \sigma \kappa_\Gamma \mathbf{n} + \nabla_\Gamma \sigma$$

phase

$$V = \mathbf{u} \cdot \mathbf{n}$$

surfactant mass (bulk phase)

$$\partial_t c + \nabla \cdot (c\mathbf{u} - D\nabla c) = 0 \quad \text{in } V^+ \qquad c = 0 \quad \text{in } V^-$$

surfactant mass (interface)

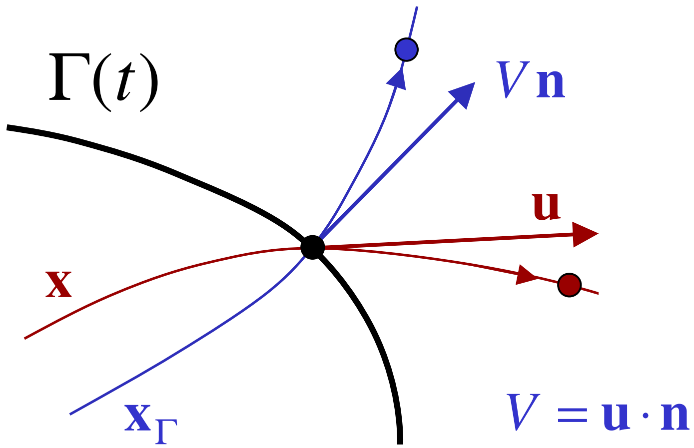
$$\frac{Dc_\Gamma}{Dt} + c_\Gamma \nabla_\Gamma \cdot \mathbf{u}_\Gamma - c_\Gamma \kappa_\Gamma V - D_\Gamma \Delta_\Gamma c_\Gamma = r_{\mathrm{ad}} - r_{\mathrm{de}}$$

Alternative Formulation

$$\dot{\mathbf{x}}_\Gamma(s) = (V\mathbf{n})(s,\mathbf{x}_\Gamma(s)), \quad \mathbf{x}_\Gamma(s) \in \Gamma(t+s)$$

$$\left[\frac{\partial \psi}{\partial t}\right]_{\mathbf{n}} = \left[\frac{d}{ds}\psi(t+s,\mathbf{x}_\Gamma(t+s))\right]_{s=0}$$

normal-path derivative



$$\frac{D\psi}{Dt} = \left[\frac{\partial \psi}{\partial t}\right]_{\mathbf{n}} + \mathbf{u}_\Gamma \cdot \nabla_\Gamma \psi$$

$$\left[\frac{\partial c_\Gamma}{\partial t}\right]_{\mathbf{n}} + \nabla_\Gamma \cdot (c_\Gamma \mathbf{u}_\Gamma) - c_\Gamma \kappa_\Gamma V - D_\Gamma \Delta_\Gamma c_\Gamma = r_{\mathrm{ad}} - r_{\mathrm{de}}$$

The Case of Fast Sorption

additional balance equation at the interface:

$$-D\nabla c \cdot \mathbf{n} = r_{\mathrm{ad}}(c_\Gamma, c_{|\Gamma}) - r_{\mathrm{de}}(c_\Gamma))$$

$$= k\,(r^0_{\mathrm{ad}}(c_\Gamma, c_{|\Gamma}) - r^0_{\mathrm{de}}(c_\Gamma))$$

$k \to \infty$

$$r^0_{\mathrm{ad}}(c_\Gamma, c_{|\Gamma}) = r^0_{\mathrm{de}}(c_\Gamma)$$

quasi-instantaneous sorption:

$$c_\Gamma = g(c_{|\Gamma}), \quad g \nearrow, g(0) = 0,\ g(\infty) = c_\Gamma^\infty$$

e.g.: Langmuir isotherm

$$\frac{c_\Gamma}{c_\Gamma^\infty} = \frac{c_{|\Gamma}}{K + c_{|\Gamma}}$$

Model for Soluble Surfactant

$$\nabla \cdot \mathbf{u} = \mathbf{0} \qquad [\mathbf{u}] = \mathbf{0}$$

$$\partial_t(\rho_\pm \mathbf{u}) + \nabla \cdot (\rho_\pm \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T} \qquad [-\mathbf{T}] \cdot \mathbf{n} = \sigma \kappa_\Gamma \mathbf{n} + \nabla_\Gamma \sigma$$

$$V = \mathbf{u} \cdot \mathbf{n}$$

EOS $\sigma = \sigma(c_\Gamma)$

$$\partial_t c + \nabla \cdot (c\mathbf{u} - D\nabla c) = 0 \quad \text{in } V^- \qquad c = 0 \quad \text{in } V^+$$

$$\left[\frac{\partial c_\Gamma}{\partial t}\right]_{\mathbf{n}} + \nabla_\Gamma \cdot (c_\Gamma \mathbf{u}_\Gamma) - c_\Gamma \kappa_\Gamma V - D_\Gamma \Delta_\Gamma c_\Gamma = -D(\nabla c \cdot \mathbf{n})_{|\Gamma}$$

$$c_\Gamma = g(c_{|\Gamma}), \quad g \text{ increasing}, g(0) = 0, g(\infty) = c_\Gamma^\infty$$

mathematical analysis

Local Existence of Strong Solutions

- vast amount of literature in the Engineering Sciences

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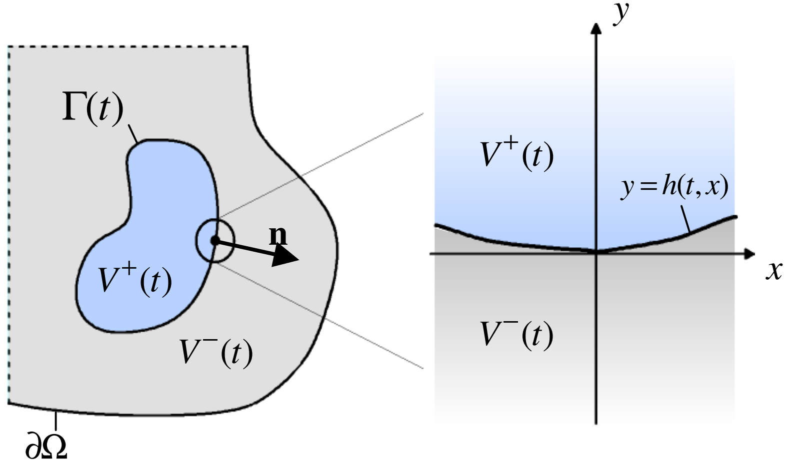
mathematical analysis for the full model:

1. Localization
2. Reduction to halfspace
3. **L_p-max Reg of linearized problem**
4. Fixed-point argument

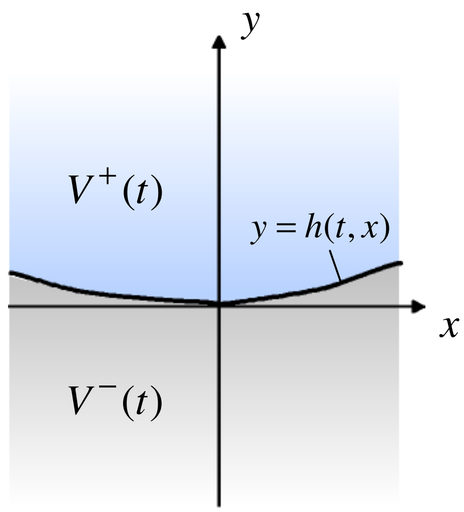


- model problem: *slightly deformed halfspace*

Local Existence of Strong Solutions

Theorem (B., Prüss, Simonett ´05).

- slightly deformed halfspace
- L_p-setting with p > n+3
- g, σ are C^2–functions with σ>0
- natural regularity assumption on intitial data
- compatibility conditions
- small variation of initial surfactant concentration



=> Local-in-time existence and uniqueness

Lyapunov-Functional

Gibbs free energy

$$\Phi(\mathbf{u},c,c_\Gamma,\Gamma)=\frac{1}{2}\int_\Omega \rho\,\|\mathbf{u}\|^2\,dx+\int_{\Omega^+}G(c)\,dx+\int_{\Gamma(t)}G_\Gamma(c_\Gamma)\,dA$$

with

$$G_\Gamma(c_\Gamma)=\sigma(c_\Gamma)+c_\Gamma\mu_\Gamma(c_\Gamma) \qquad \mu_\Gamma(c_\Gamma)=\mu(g^{-1}(c_\Gamma))$$

$G'(c)=\mu(c)$ chemical potential

surface chemical potential

$$\frac{d}{dt}\Phi(\mathbf{u},c,c_\Gamma,\Gamma)=-2\int_\Omega \mu\,\|\mathbf{E}\|^2\,dx-\int_{\Omega^+}G''(c)D\,\|\nabla c\|^2\,dx-\int_{\Gamma(t)}G''_\Gamma(c_\Gamma)D_\Gamma\,\|\nabla c_\Gamma\|^2\,dA$$

Gibbs-Duhem

$$d\sigma=-c_\Gamma\,d\mu \Rightarrow \sigma'(s)=-s\,\mu'_\Gamma(s),\; G''_\Gamma(s)=-\frac{1}{s}\sigma'(s)=\mu'_\Gamma(s)$$

σ decreasing => G_Γ convex; also g increasing => G convex

Mannigfaltigkeit der Equilibria

Implication for equilibria of the systems:

$$2\int_{\Omega} \mu \| \mathbf{E} \|^2 \, dx + \int_{\Omega^+} G''(c) D \| \nabla c \|^2 \, dx + \int_{\Gamma(t)} G''_{\Gamma}(c_{\Gamma}) D_{\Gamma} \| \nabla c_{\Gamma} \|^2 \, dA = 0$$

$$\Rightarrow \qquad \mathbf{u} \equiv 0, \quad c \equiv const, \quad c_{\Gamma} \equiv g(c)$$

$g(\uparrow), \sigma(\downarrow)$

$$\sigma \equiv const, \quad \kappa \equiv const, \quad \Gamma = S_R(\mathbf{x})$$

Theorem (B., Prüss ´09).

- n+2 dimensional manifold of equilibria: spheres of radius R>0, center x in R^n and given surfactant mass
- The energy quality is valid for smooth solutions. The energy functional is a strict Lyapunov functional. Its critical points are the equilibria of the system
- linearization at equilibrium has only λ=0 as eigenvalue with Re λ ≥ 0 and eigenspace for λ=0 corresponds to the spheres of radius R>0, center x in R^n and given surfactant mass

=> Stability of stationary solutions for linearised system if: $g(\uparrow), \sigma(\downarrow)$

numerical simulation

Principal Approach

Numerical solution of the surfactant balance equation based on:

- **the Finite Volume Method**
- **the assumption of fast sorption**

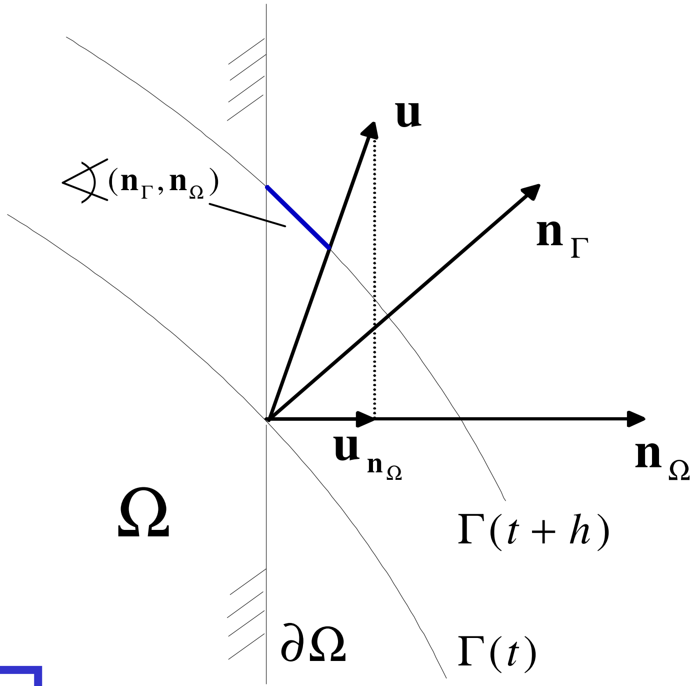
- ***FVM requires extended surface transport theorem***

$$\frac{d}{dt}\int_{\Omega\cap\Gamma(t)} \phi\, dA = \int_{\Omega\cap\Gamma(t)} \left(\frac{D\phi}{Dt} + \phi \nabla_\Gamma \cdot \mathbf{u} \right) dA - \int_{\partial(\Omega\cap\Gamma(t))} \phi \frac{\mathbf{u}\cdot\mathbf{n}_\Omega}{\sqrt{1-(\mathbf{n}_\Gamma\cdot\mathbf{n}_\Omega)^2}}\, ds$$

cf. M.E. Gurtin et al.: A Transport Theorem for Moving Interfaces (1989)

- ***Fast sorption:*** $c_\Gamma = g(c_{|\Gamma})$

no additional scalar needed!



Ω fixed control volume

Numerical Computation

- ***transport steps separately for bulk and interface***

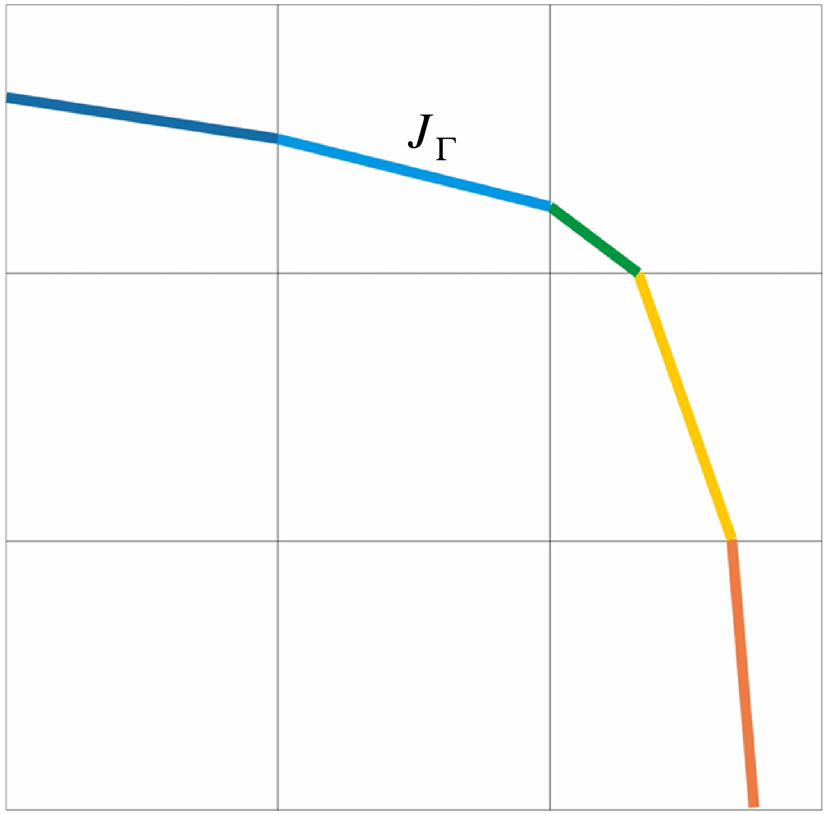
output of time step t^n : discrete values $f^n, \mathbf{u}^n, c^n$ *on the volume grid*

- *transport of bulk quantities:* $f^{n+1}, \mathbf{u}^{n+1}, \tilde{c}^{n+1}$
- *construction of connected interface grid*
- *compute* $\tilde{c}_\Gamma^{n+1}$ *due to equilibrium with* $\tilde{c}^{n+1}$
- *compute interfacial fluxes,*

  changes in interfacial mass,

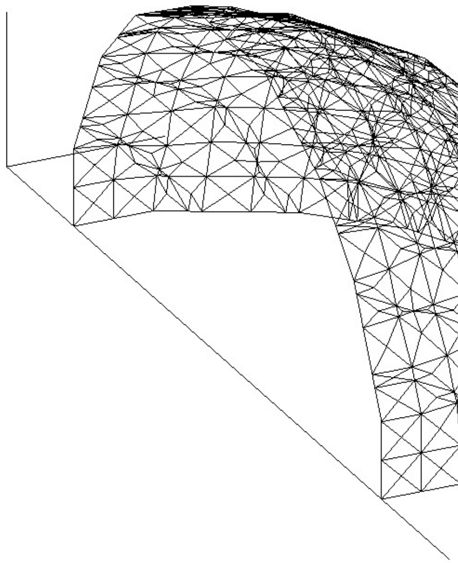
  then n_{tot}^{surf} *in interface carrying cells*
- *mass conservation & equilibrium*

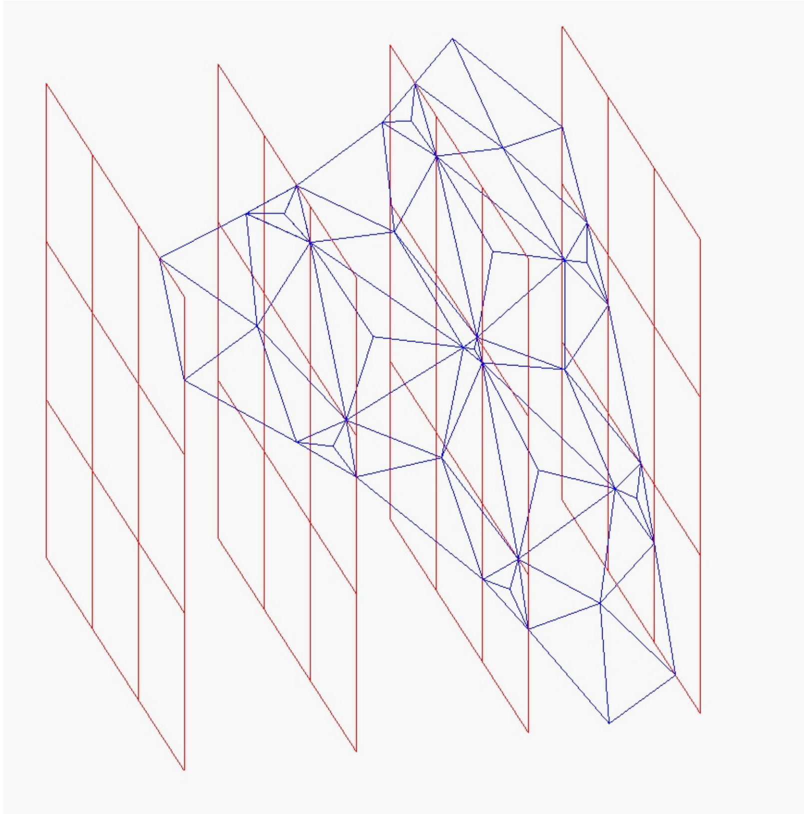
$$\longrightarrow \quad c^{n+1} \quad c_\Gamma^{n+1}$$

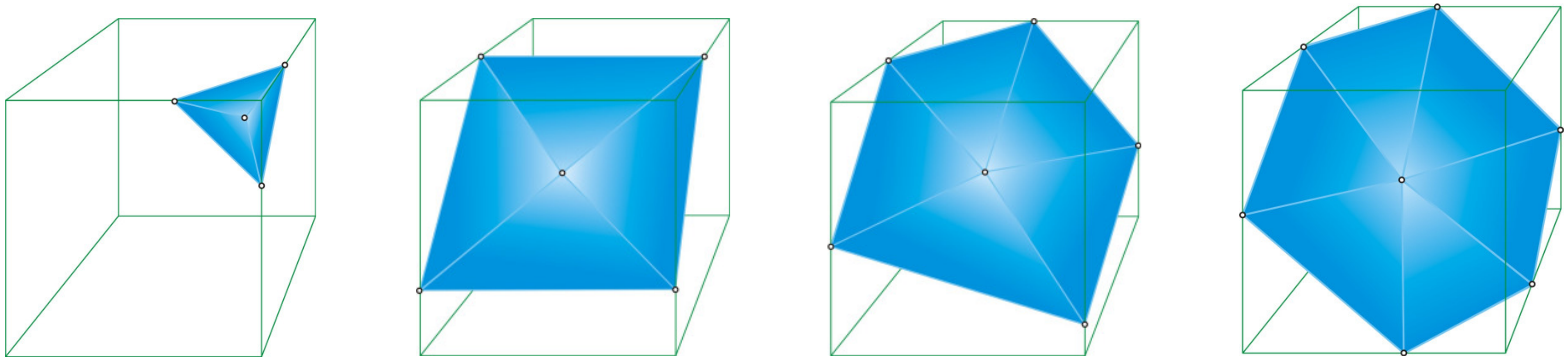


VOF-Iso-Surface

connected interface
approximation in 3D







Surfactant Evolution

Surfactant concentration on the interface

Surfactant: ***Triton X 100***

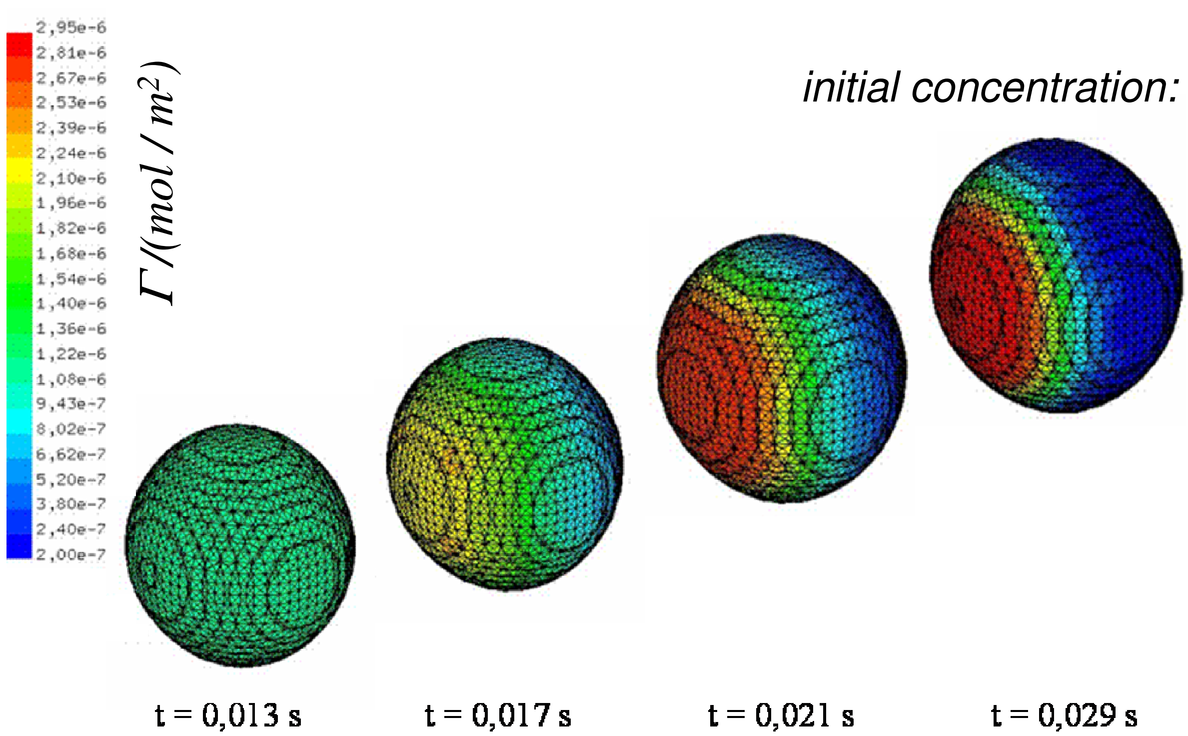
Maximum Concentration: $\Gamma_\infty = 2{,}91 \cdot 10^{-6}\ mol/m^2$

Langmuir-Coefficient: $b = 6{,}63 \cdot 10^{-4}\ mol/m^3$

Diffusion coefficients: $D = 2{,}7 \cdot 10^{-10}\ m^2/s$

$D^\Sigma = 10^{-5}\ m^2/s$

initial concentration: $c_0 = 4{,}443 \cdot 10^{-4}\ mol/m^3$



$\Gamma_{eq}(c_0) = 1{,}17 \cdot 10^{-6}\ mol/m^2$

interfacial rheology

surface viscosities

Two-Phase Navier-Stokes Eqs

Mathematical model of isothermal incompressible two-phase flow without phase change for *variable* surface tension :

	bulk	*interface*
mass	$\nabla \cdot \mathbf{u} = \mathbf{0}$	$[\mathbf{u}] = \mathbf{0}$
momentum	$\partial_t(\rho_\pm \mathbf{u}) + \nabla \cdot (\rho_\pm \mathbf{u} \otimes \mathbf{u}) = \nabla \cdot \mathbf{T}$	$[-\mathbf{T}] \cdot \mathbf{n} = \nabla_\Gamma \cdot \mathbf{T}_\Gamma$
phase	$\partial_t f + \nabla \cdot (f \mathbf{u}) = 0$	$V = \mathbf{u} \cdot \mathbf{n}$

Stress Tensors

bulk

$$\mathbf{T} = -p_{\pm}\mathbf{I} + \mathbf{S}, \quad \mathbf{S} = \eta_{\pm}\,[\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathsf{T}}]$$

interface

<u>without</u> surface viscosity:

$$\mathbf{T}_{\Gamma} = \sigma\mathbf{I}_{\Gamma} \quad \Rightarrow \quad \nabla_{\Gamma}\cdot\mathbf{T}_{\Gamma} = \nabla_{\Gamma}\cdot(-\mathbf{n})\,\mathbf{n}\sigma + \mathbf{I}_{\Gamma}\nabla_{\Gamma}\sigma$$

$$\Rightarrow \quad \nabla_{\Gamma}\cdot\mathbf{T}_{\Gamma} = \sigma\kappa\mathbf{n} + \nabla_{\Gamma}\sigma$$

with $\mathbf{I}_{\Gamma} = \mathbf{I} - \mathbf{n}\otimes\mathbf{n}$ projection onto tangent space

EOS $\sigma = \sigma(c_{\Gamma})$ c_{Γ} area-specific concentration of adsorbed surfactants

Surface Viscosities

Edwards, Brenner, Wasan: *Interfacial Transport Processes and Rheology*, 1991.

$$\mathbf{T}_\Gamma = (\sigma + (\lambda_\Gamma - \eta_\Gamma)\nabla_\Gamma \cdot \mathbf{u})\mathbf{I}_\Gamma + 2\eta_\Gamma \mathbf{D}_\Gamma$$

interfacial shear viscosity η_Γ

$$\mathbf{D}_\Gamma = \frac{1}{2}\mathbf{I}_\Gamma(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathsf{T}})\mathbf{I}_\Gamma \qquad \mathbf{I}_\Gamma = \mathbf{I} - \mathbf{n}\otimes\mathbf{n}$$

interfacial dilatational viscosity λ_Γ

$(\lambda_\Gamma > \eta_\Gamma > 0)$

<u>Boussinesq-Scriven surface fluid</u> (Newtonian surface fluid)

first steps of the analysis: slightly deformed halfspace (B., Prüss ´08)

- linearization at a reference solution $\quad \mathbf{u}^* = (\mathbf{v}, w) \quad \mathbf{E} = (\nabla_{\mathbf{x}'}\mathbf{v} + (\nabla_{\mathbf{x}'}\mathbf{v})^{\mathsf{T}})/2$

$$d = (\sigma + (\lambda_\Gamma - \eta_\Gamma)\,\mathrm{tr}\mathbf{E}) + 2\eta_\Gamma \inf\{\langle \mathbf{E}\zeta, \zeta\rangle : |\zeta| = 1\}$$

- well-posedness of the linearized localized problem if d>0,
  ill-posedness of the linearized localized problem **if d<0**

Note: d<0 can appear at high rates of (local) interface compression!

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Dipl.-Phys. Dominik Weihrich

Deutsche Forschungsgemeinschaft DFG

- PAK119 *Reactive mass transfer from rising gas bubbles*
- EXC236 *Taylor-made fuels from biomass*, IRF2B-7 & IRF3B-6

NEW Priority Research Programm starting 2009/10:

Transport processes at fluidic interfaces

SPP 1506 (Bothe/Reusken)