

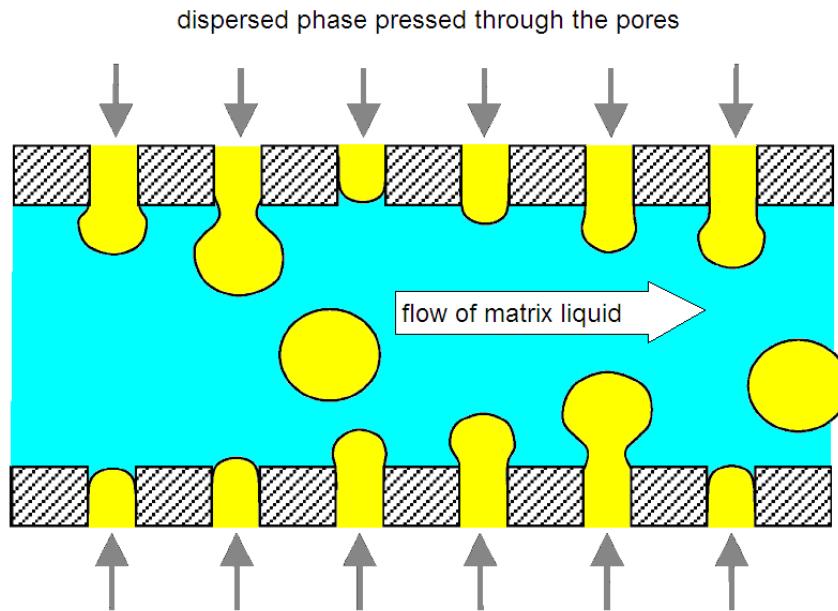
# Single Drop/Bubble Experiments to Study the Dynamics of Liquid Interfaces

A. Javadi, N. Mucic, J.Y. Won, M. Born, J. Krägel and R. Miller

*MPI Colloids and Interfaces, Potsdam,  
Germany*

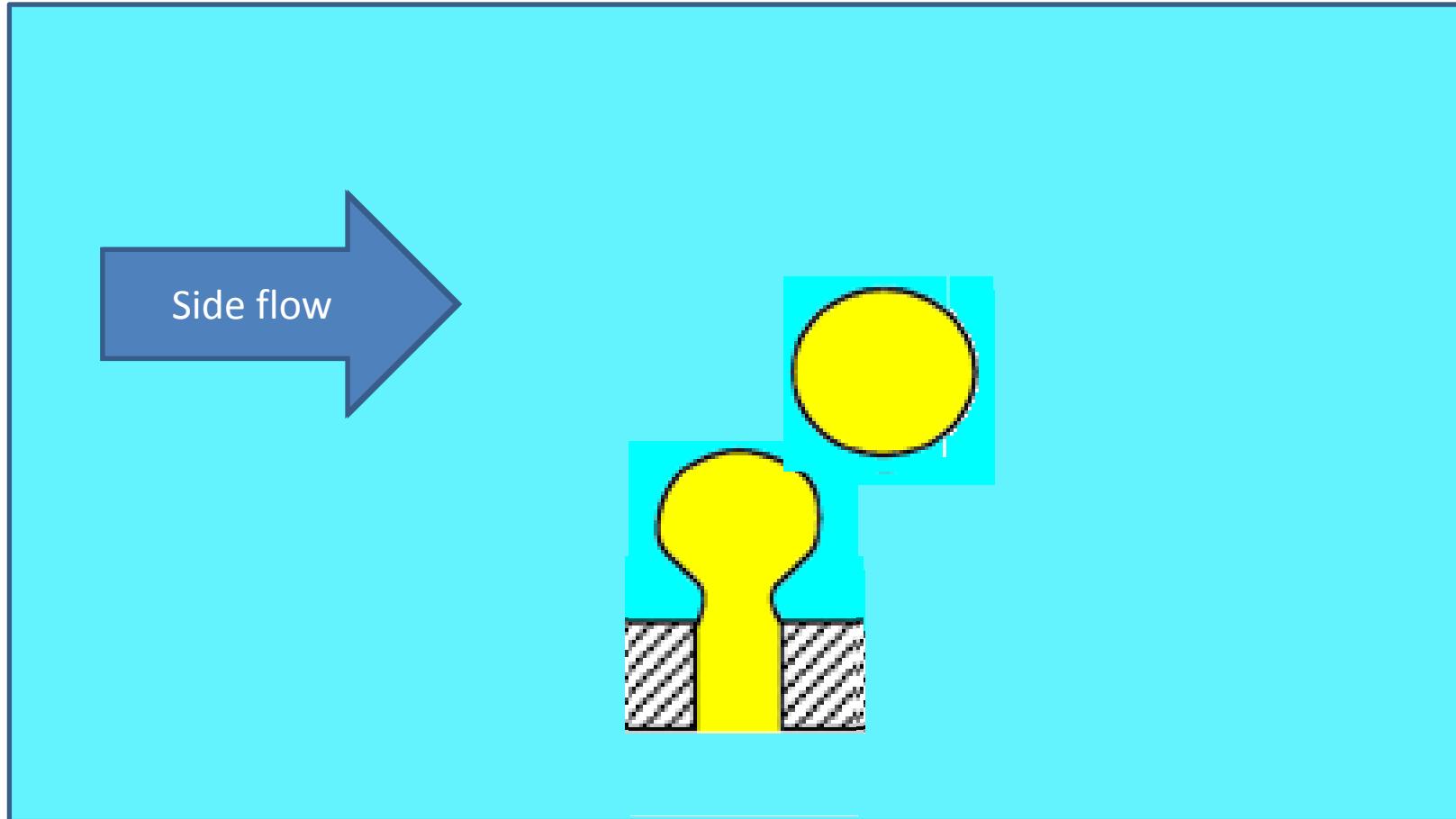
# Motivation

Why is knowledge on the dynamics of liquid interfaces essential?



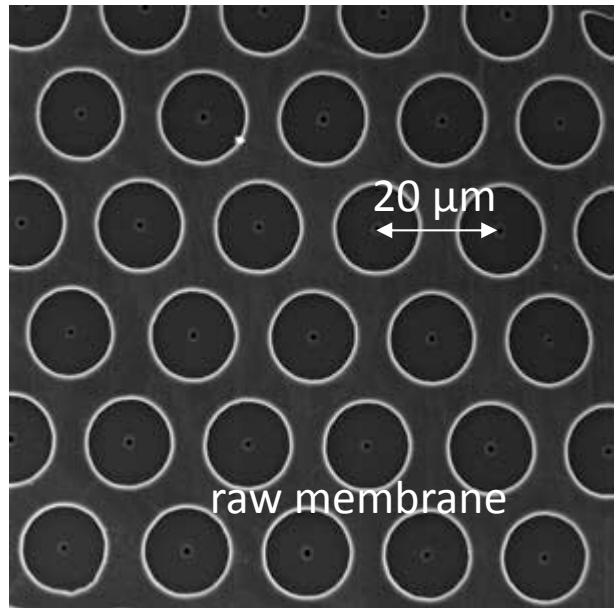
Membrane emulsification is a modern technology to produce emulsions of a narrow droplet size distribution. Also monodispers foams are produced by such a methodology using rotating membranes.

# Membrane Emulsification



# Motivation

Why is knowledge on the dynamics of liquid interfaces essential?

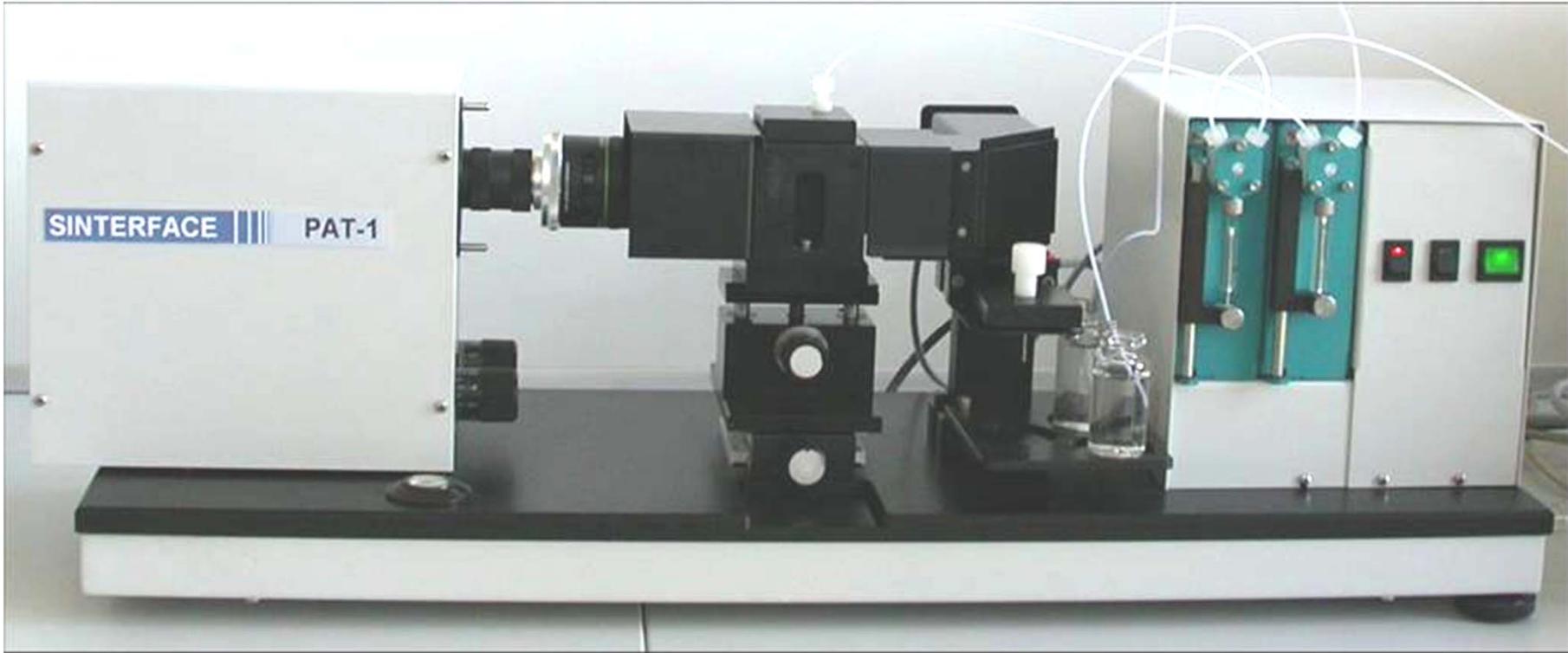


Erich Windhab, ETH Zurich (DE 10307568 A1)



Also monodisperse foams are produced by a membrane technology using rotating membranes.

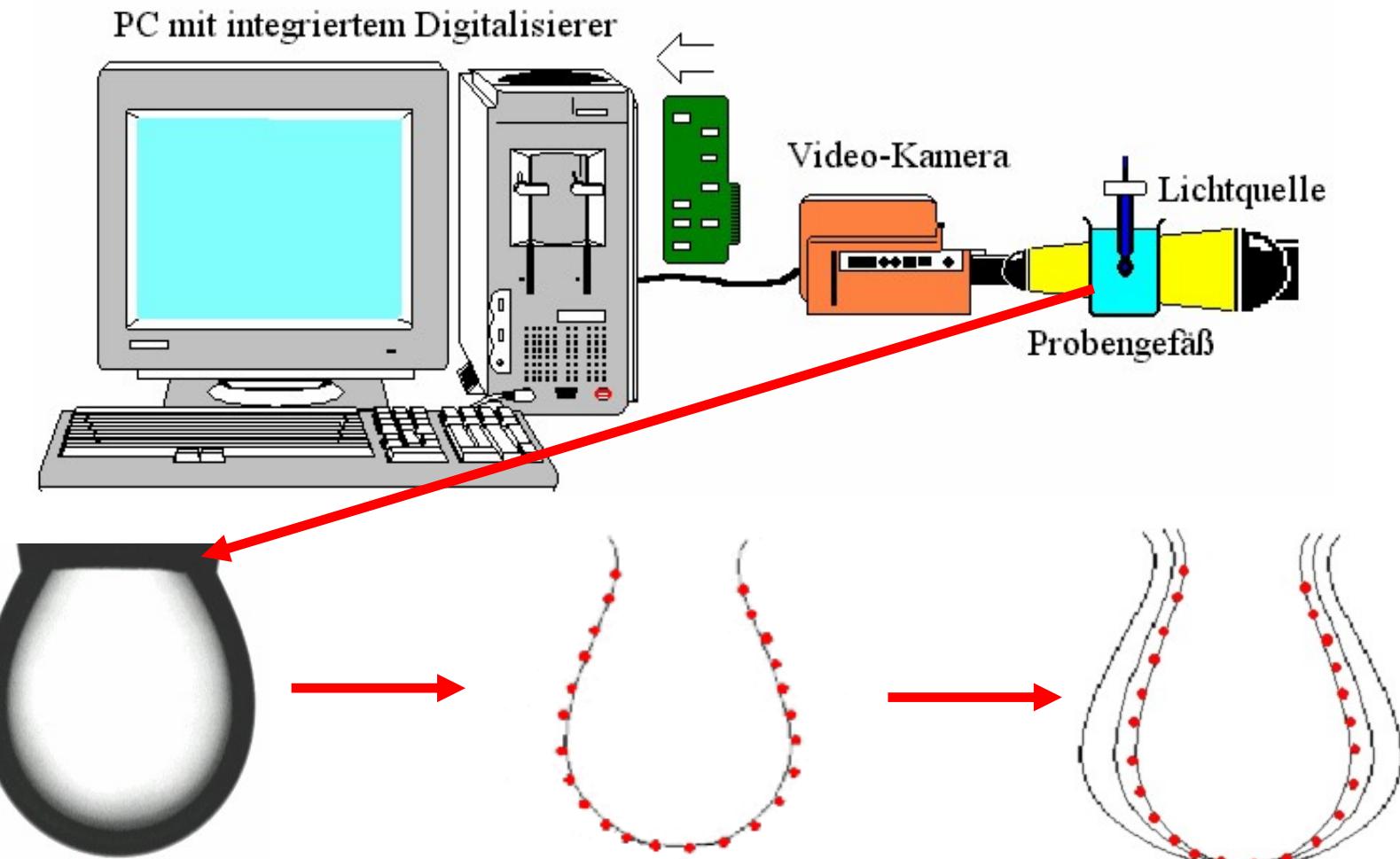
## Drop Profile Tensiometry



*Drop and Bubble Profile Tensiometer PAT1 of SINTERFACE Technologies, Berlin*

Drop and bubble profile analysis is the most versatile method and the working horse in many interfacial laboratories.

# Drop Profile Tensiometry



*The coordinates of the drop profiles are determined from a video image.*

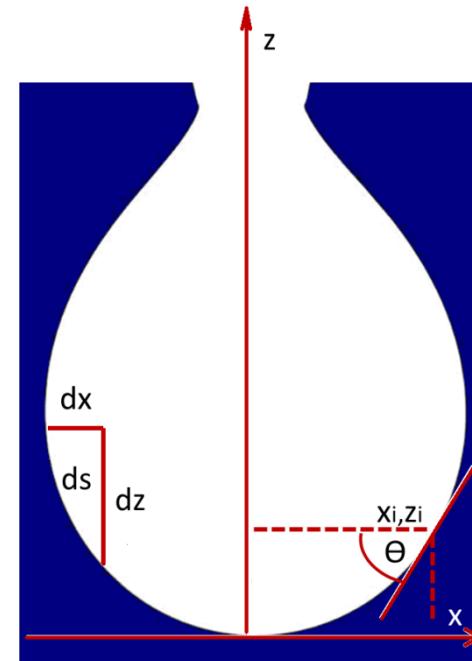
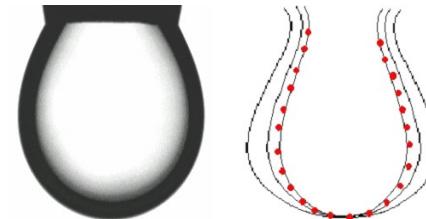
# Drop Profile Tensiometry

## Gauss Laplace Equation

$$\frac{dx}{ds} = \cos \theta$$

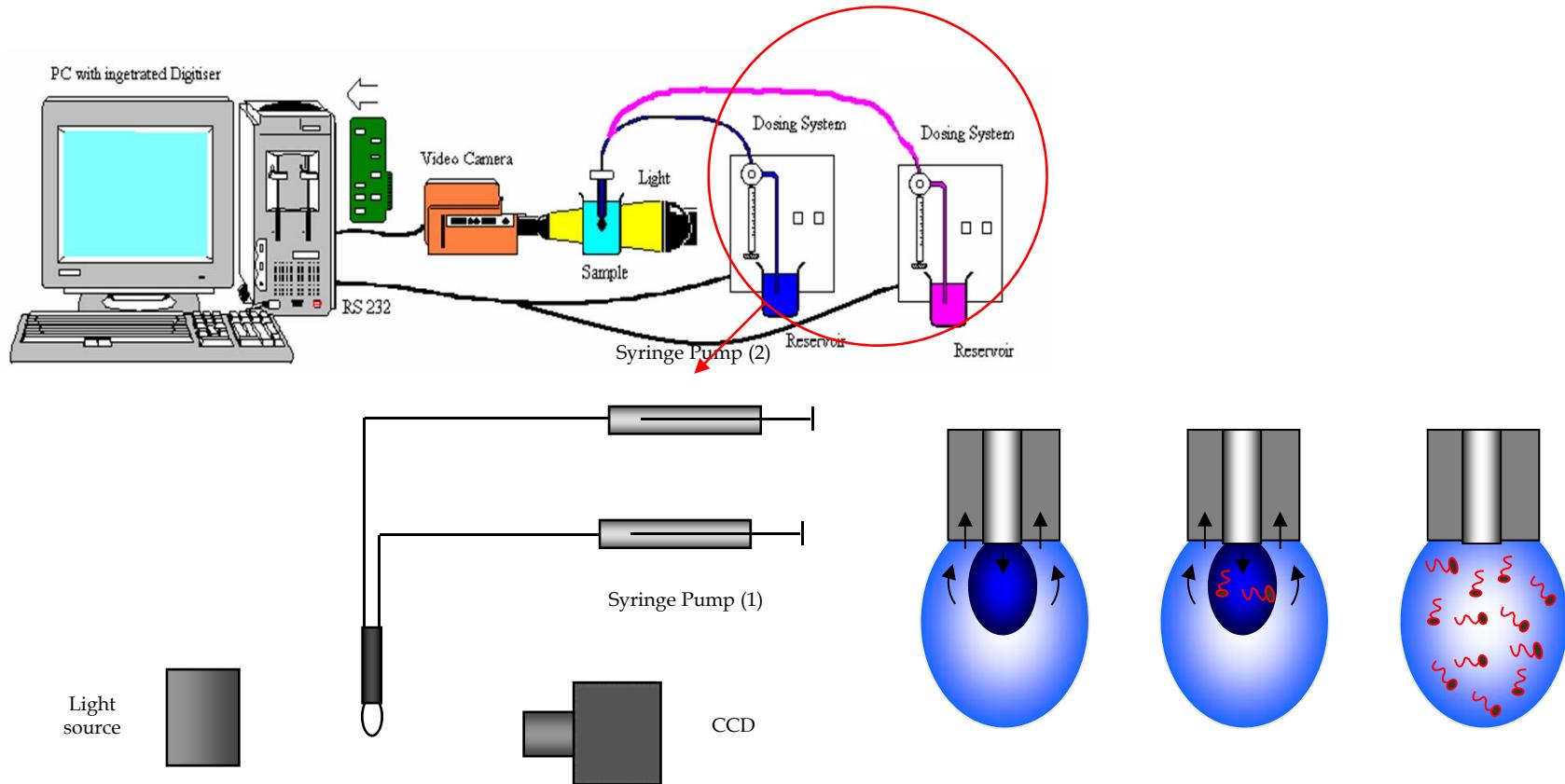
$$\frac{dz}{ds} = \sin \theta$$

$$\frac{d\theta}{ds} = \frac{2}{R_0} - \frac{\Delta\rho g z}{\gamma} - \frac{\sin \theta}{x}$$



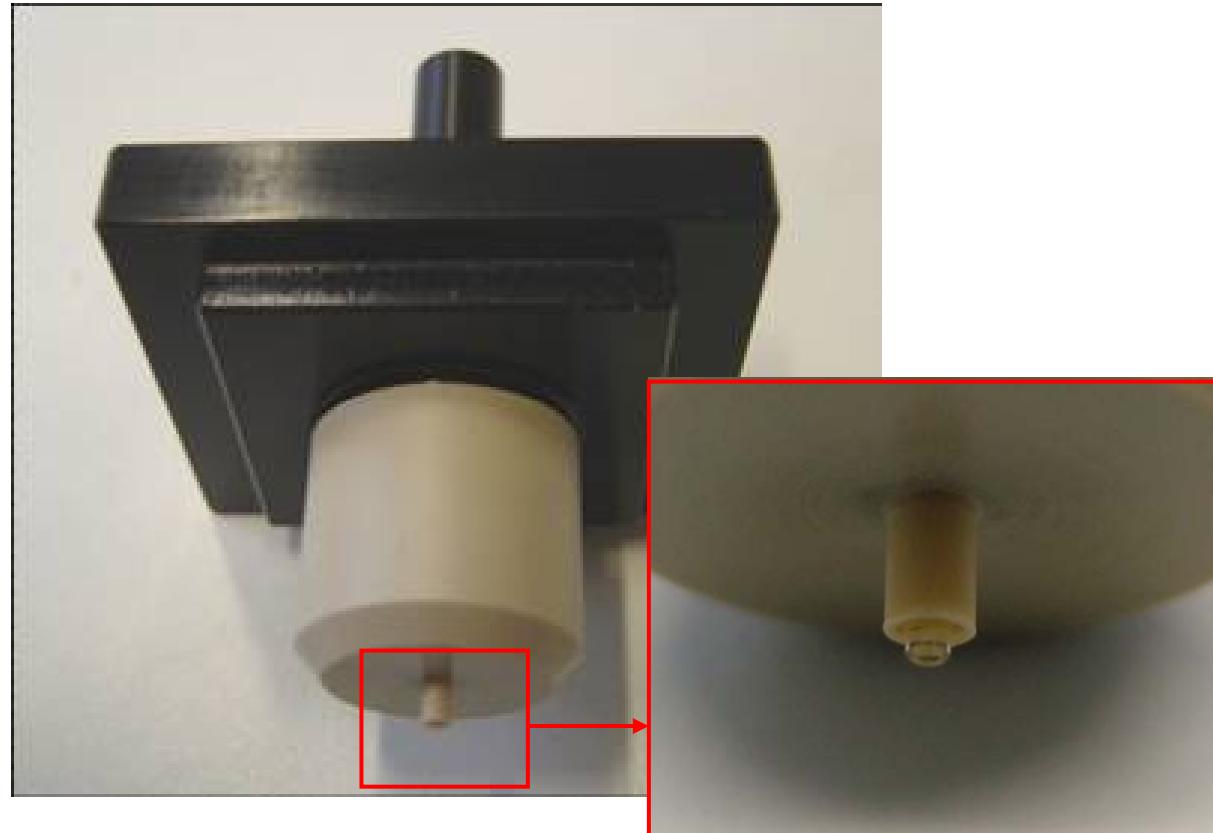
The experimental coordinates are then compared with the „theoretical shape“ of a drop calculated from the Gauss Laplace Equation. The “best fit” provides the interfacial tension value  $\gamma$ .

# Drop profile Analysis Tensiometry PAT-1 with coaxial capillary and double dosing system

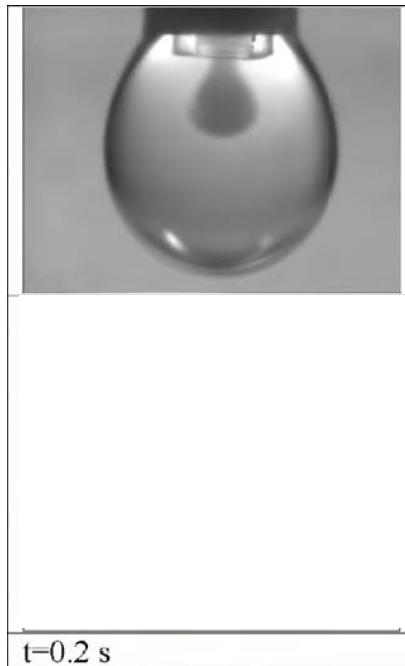


Wege, H. A.; Holgado-Terriza, J. A.; Neumann, A. W.; Cabrerozo-Vilchez, M. A. *Colloids Surf. A* 1999, 156, 509.  
Ferri, J. K.; Gorevski, N.; Kotsmar, Cs.; Leser, M. E.; Miller, R. *Colloids Surf., A* 2008, 319, 13.

## Coaxial double capillary

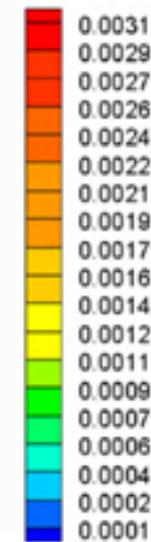
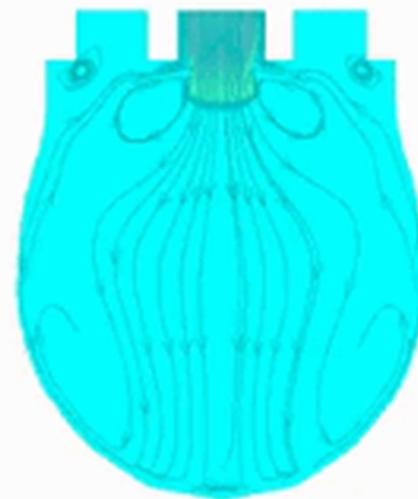
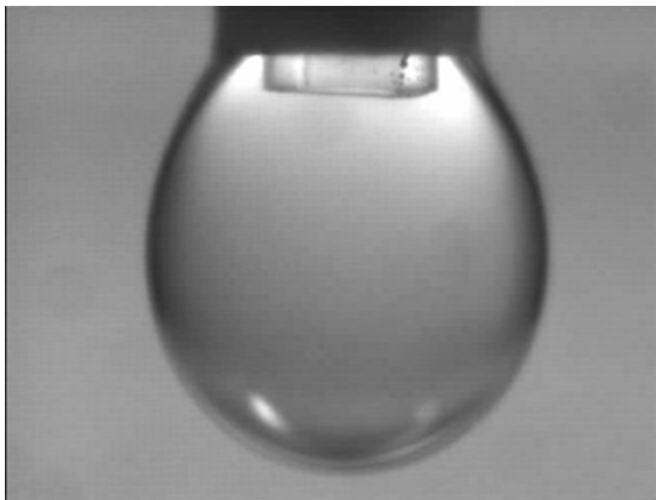


## Drop profile Analysis Tensiometry PAT-1 with coaxial capillary and double dosing system



A. Javadi, J.K. Ferri, T.D. Karapantsios and R. Miller, Interface and bulk exchange:  
Single drop experiments and CFD simulations, *Colloids Surfaces A*, 365 (2010) 145

## Drop profile analysis tensiometry with drop bulk exchange

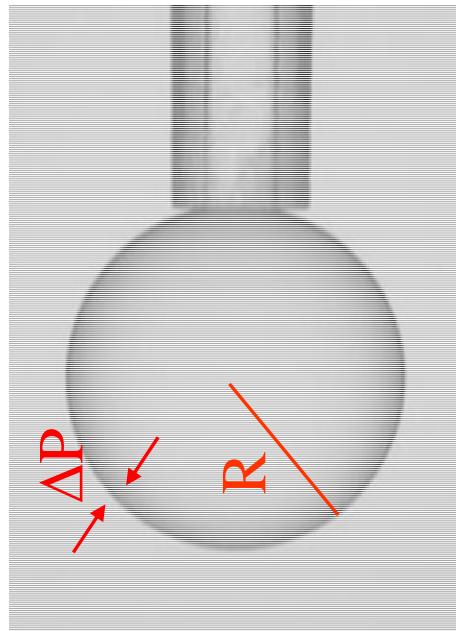


Drop exchange rate  $dt = 0.1$ ,  $dv = 0.1$ ,  $V = 30\text{mm}^3$ ,  $t = 65\text{ s}$

A. Javadi, J.K. Ferri, T.D. Karapantsios and R. Miller, Interface and bulk exchange:  
Single drop experiments and CFD simulations, *Colloids Surfaces A*, 365 (2010) 145

## Capillary pressure technique for fast dynamic Interfacial tension measurements

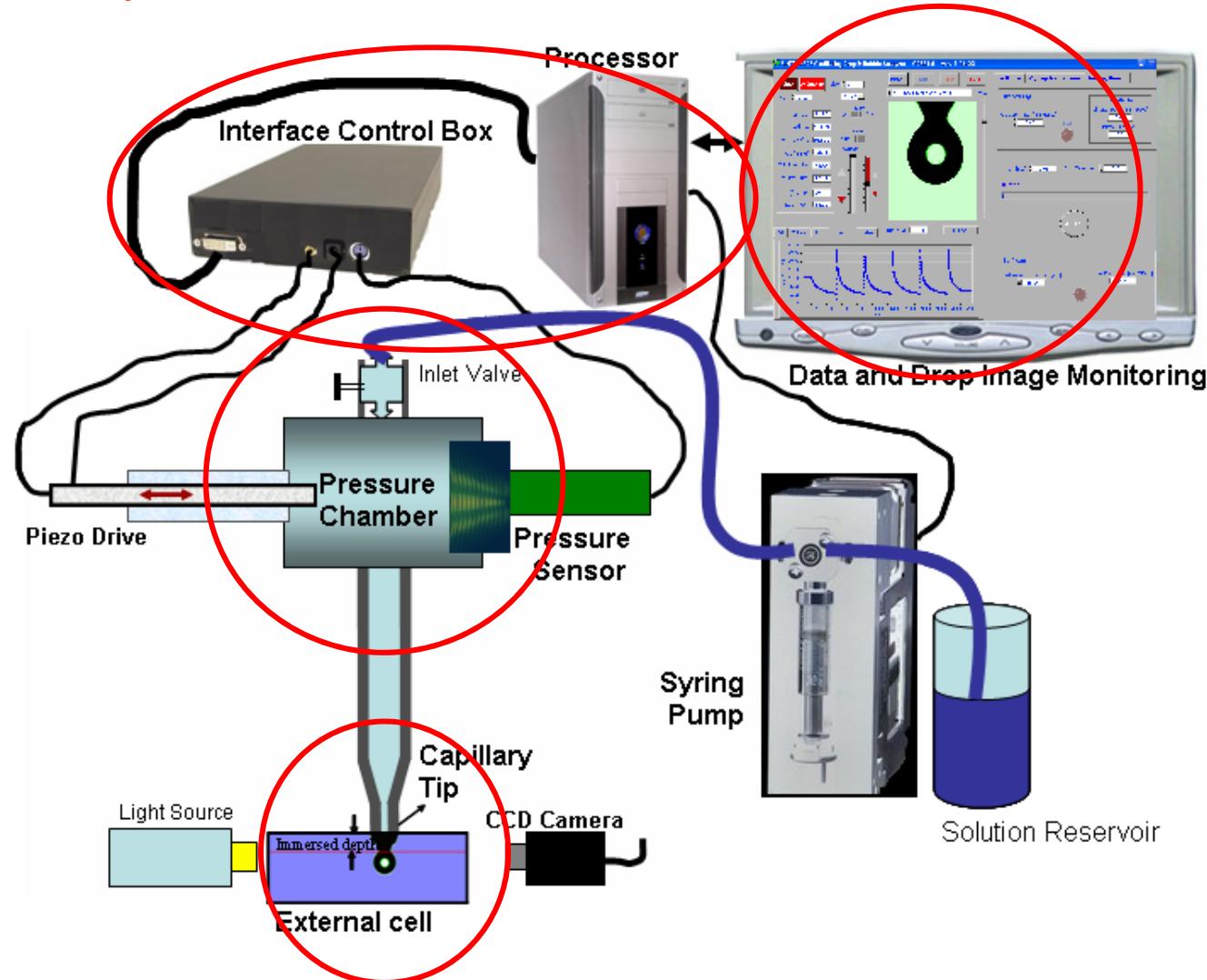
Fast dynamics (<0.01 s)  
Low density differences  
Microgravity conditions



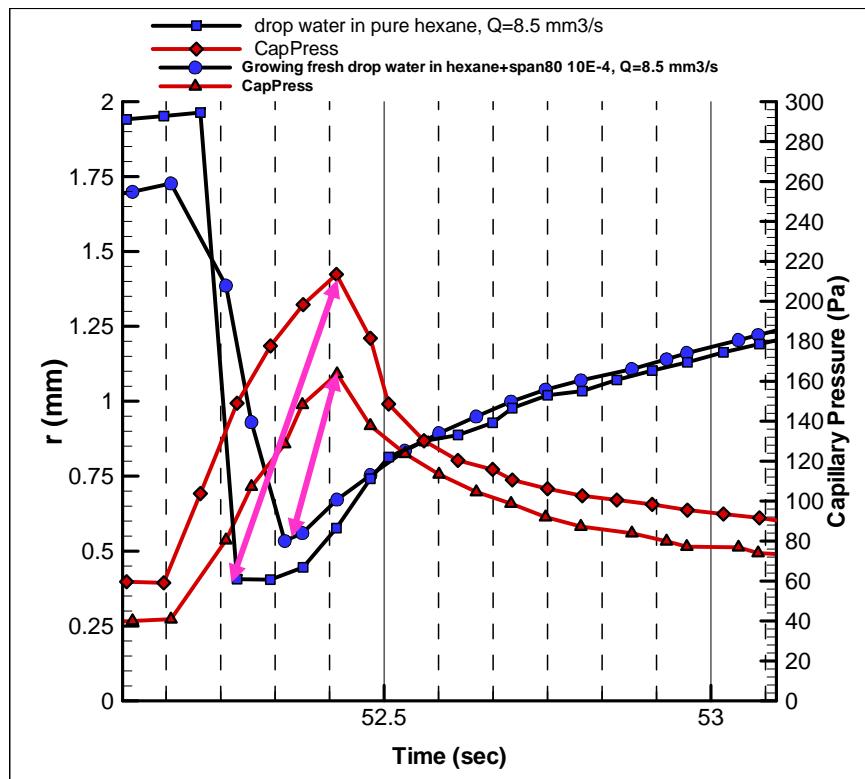
$$\Delta P(t) = 2 \frac{\gamma(t)}{R(t)}$$

- A. Passerone, L. Liggieri, N. Rando, F. Ravera, E. Ricci, J. Colloid Interface Sci., 146 (1991) 152.  
R. Nagarajan, D.T. Wasan, J. Colloid Interface Sci., 159 (1993) 164.  
C. A. Macleod, C. J. Radke, J. Colloid Interface Sci., 166 (1994) 73.  
X. Zhang, M.T. Harris, O.A. Basaran, J. Colloid Interface Sci., 168 (1994) 47.  
L. Liggieri, F. Ravera, A. Passerone, J. Colloid Interface Science, 169 (1995) 226.

## Capillary pressure technique for fast dynamic Interfacial tension measurements

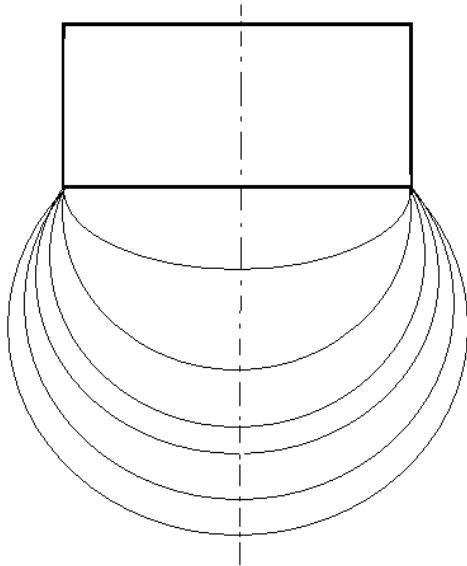


## Continuously Growing Drop (CGD)



There can be various reasons for the time shift between maximum capillary pressure and minimum drop radius at high liquid flow rates

## Adsorption on Growing Drop Surfaces



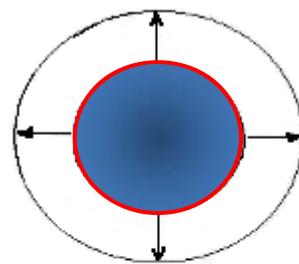
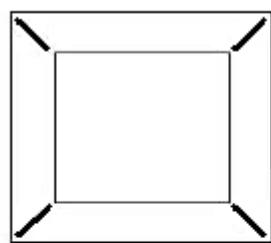
$$\Gamma(t) = \Gamma(0) + \frac{1}{R^2(t)} \sqrt{\frac{D}{\pi}} \int_0^t \frac{R^4(\tau)(c_0 - c(\tau))}{\left[ \int_{\tau}^t R^4(\xi) d\xi \right]^{1/2}} d\tau$$

$\Gamma(t)$  - time dependence of adsorption  
 $c$  - surfactant bulk concentration  
 $\Gamma(0)$  - initial load of the drop surface  
 $R(t)$  - change of drop radius with time

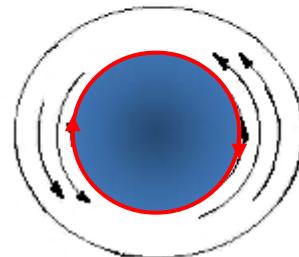
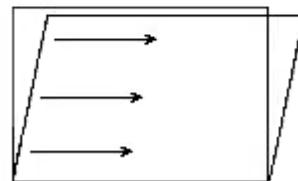
**18 years old but yet the best that we have to describe the adsorption at a growing drop.**

C.A. MacLeod and C.J. Radke, J. Colloid Interface Sci., vol. 166, pp. 73-78 (1994)

## Interfacial Rheology



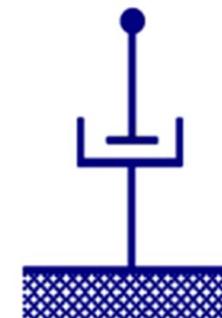
Expansion /  
Compression



Shear



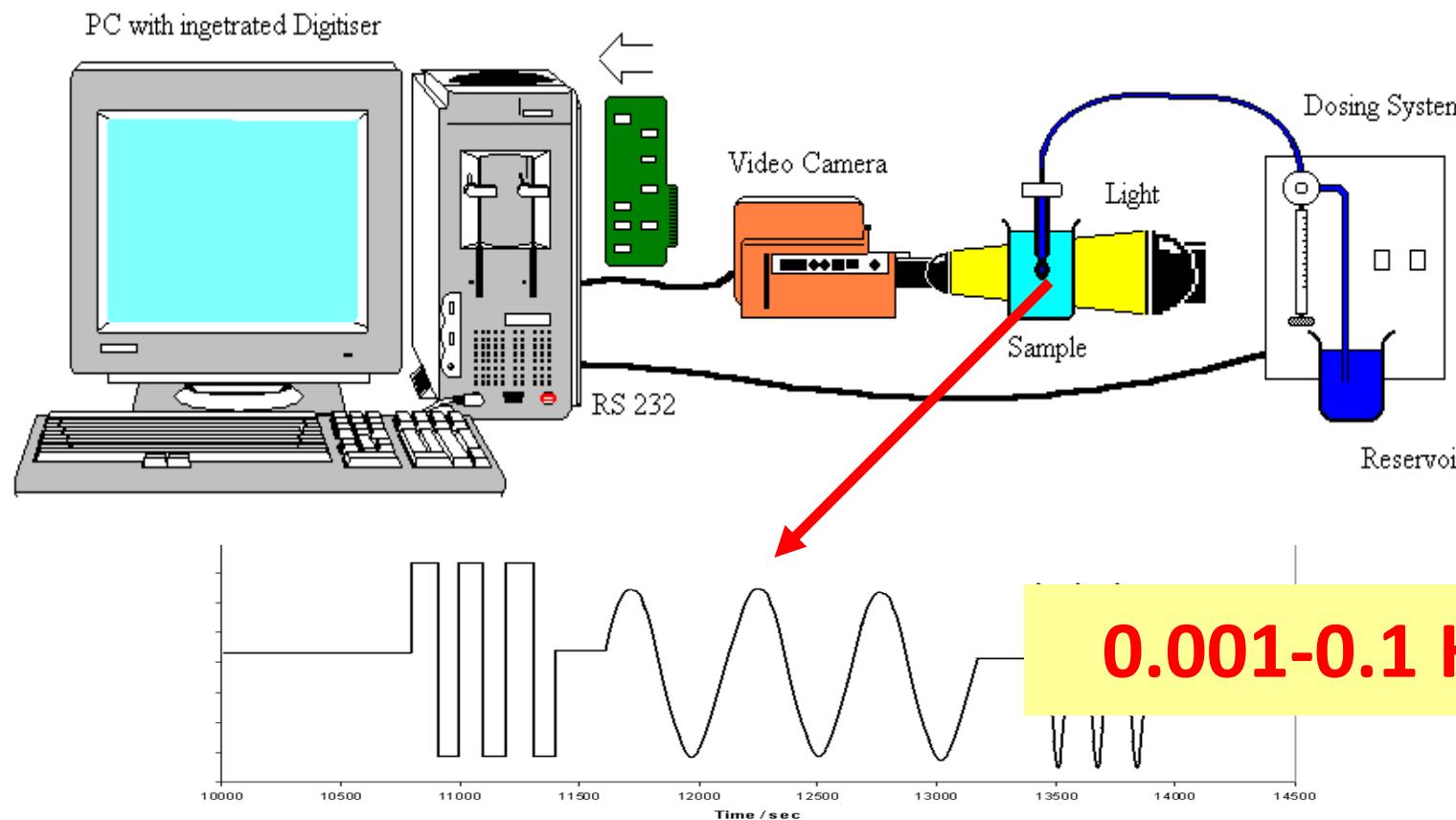
Elasticity

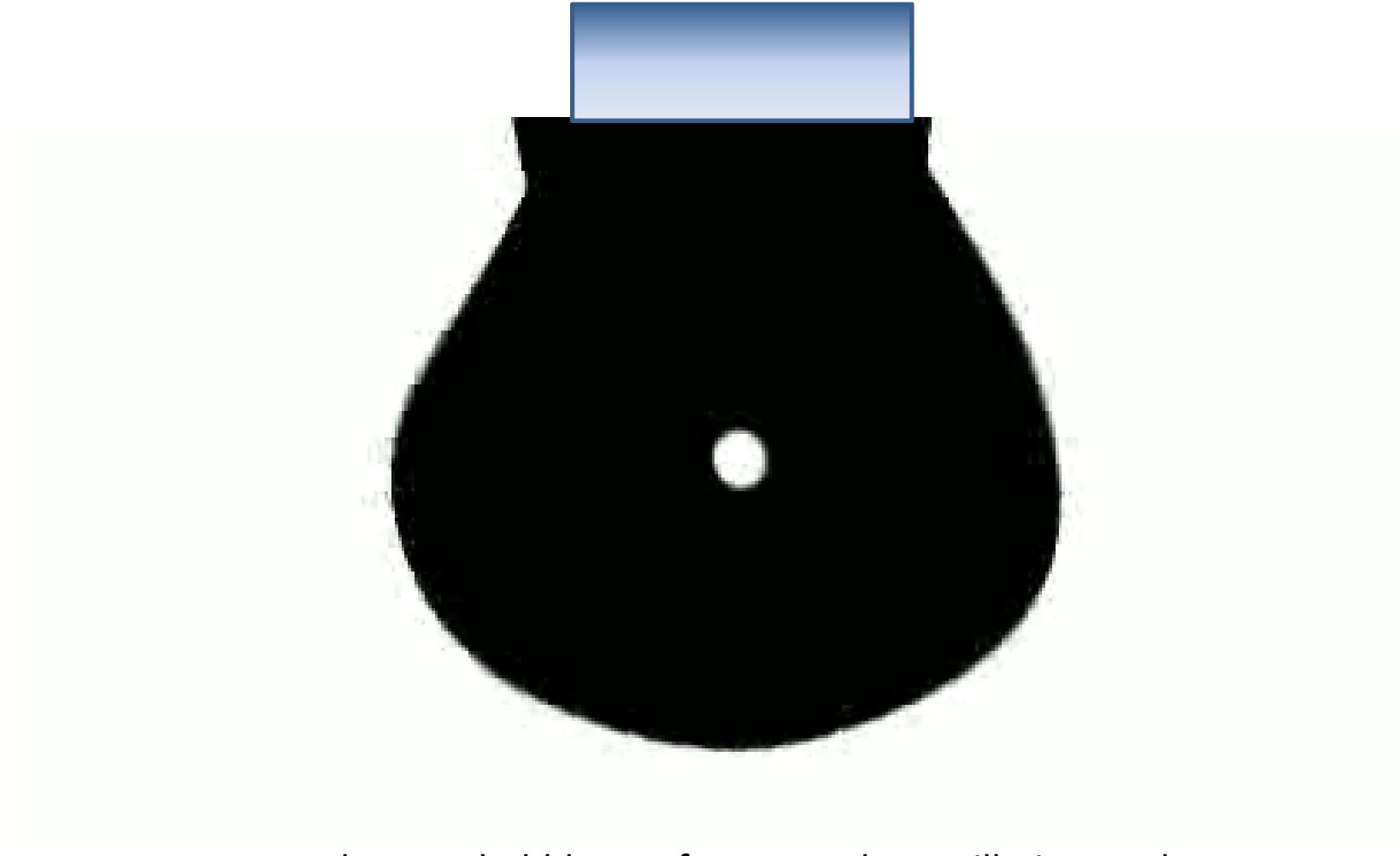


Viscosity

# Drop Profile Analysis Tensiometer PAT-1

Drop/ Bubble Oscillations generated via the Dosing System



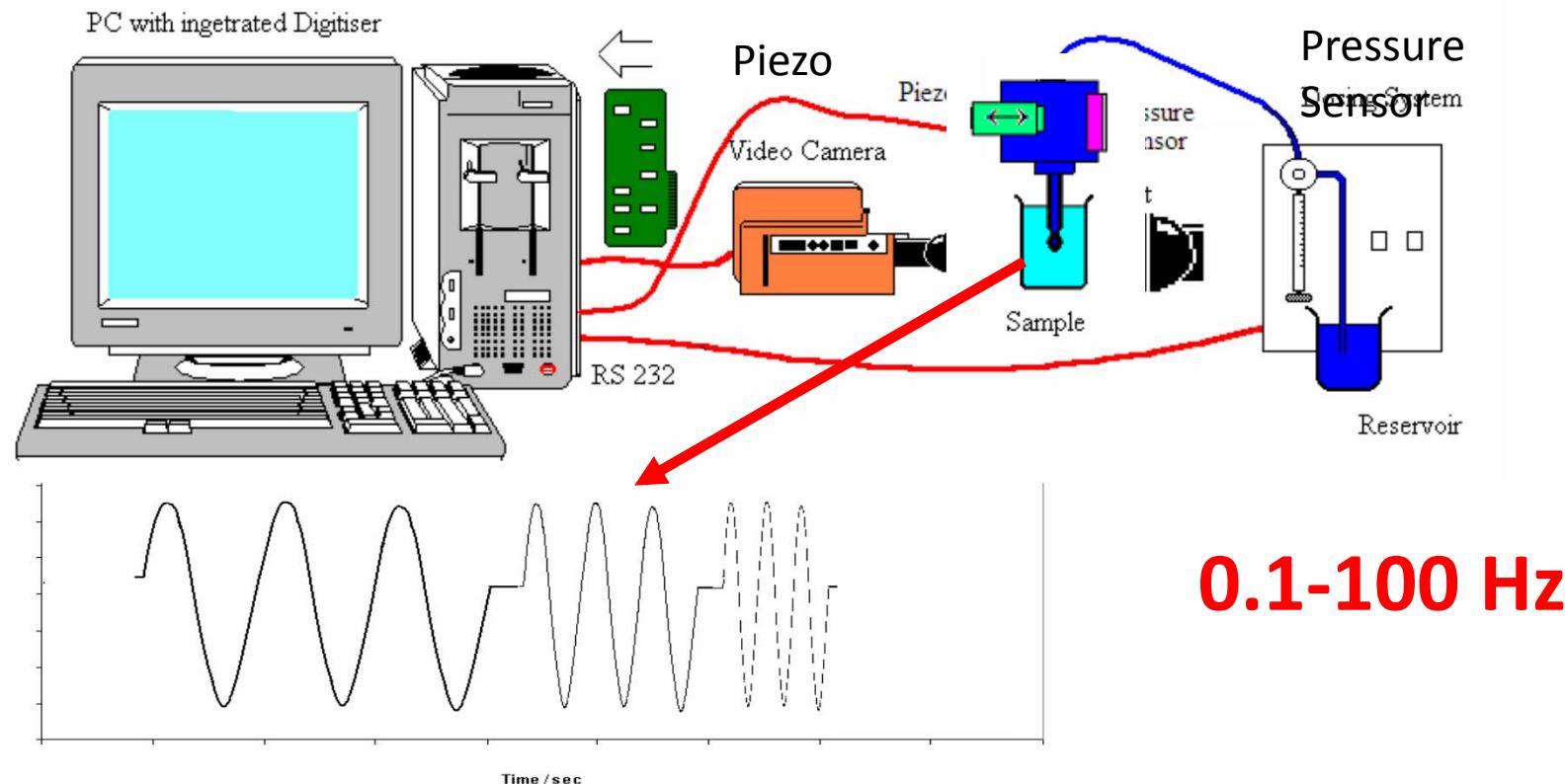


Large drops or bubbles perform complex oscillating modes.

**Looks nice but is useless from a scientific point of view.**

# Extra Equipment for PAT-1

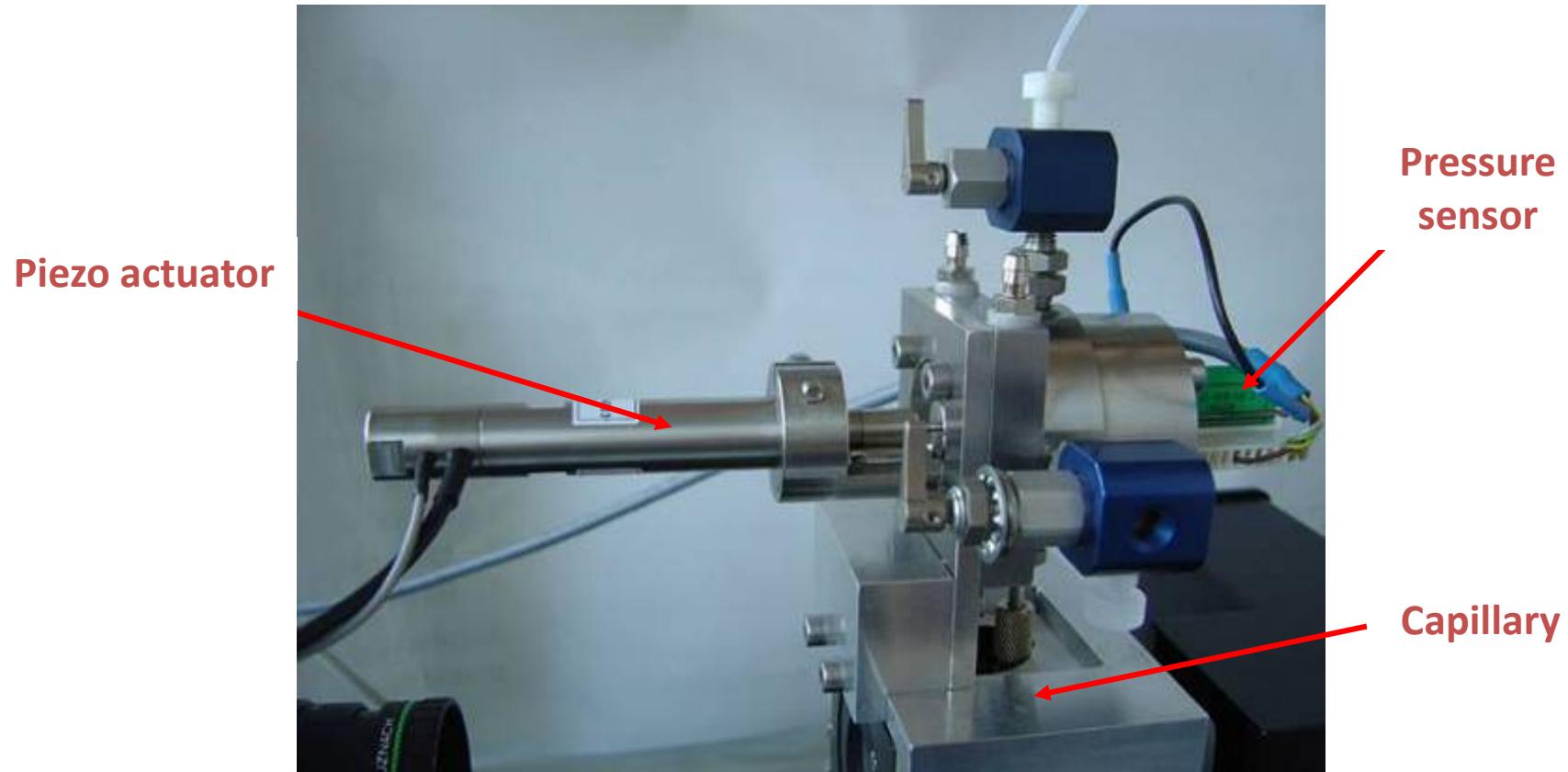
## Fast Drop/ Bubble Oscillations with ODBA-1



*A piezo system allows fast drop oscillations up to 100 Hz and more.  
The change in surface tension is monitored by capillary pressure measurements*

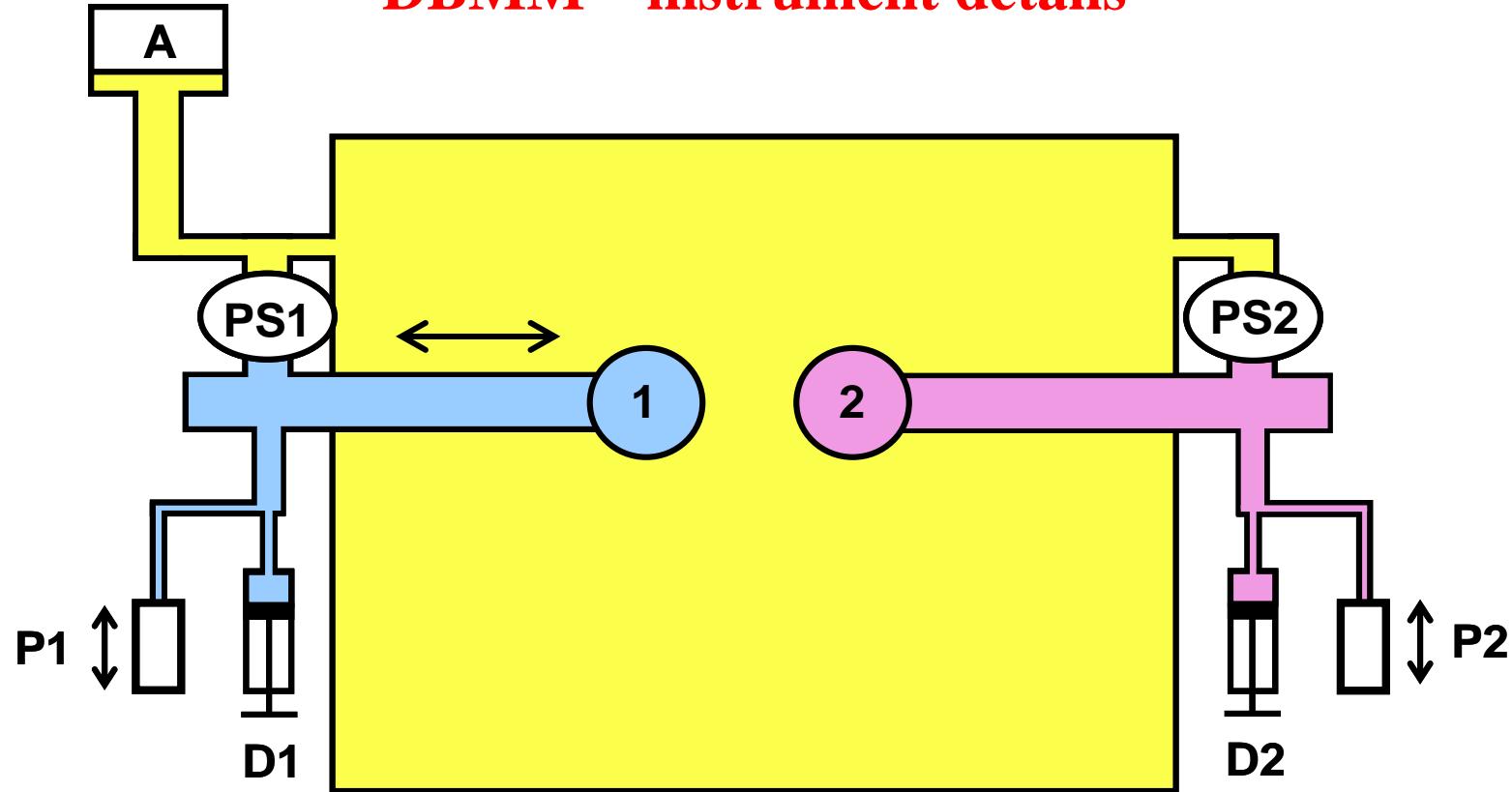
## Extra Equipment for PAT-1

### Fast Drop/ Bubble Oscillations with ODBA-1



*Oscillating Drop and Bubble Analyser as extra module for PAT1 from SINTERFACE Technologies Berlin*

## DBMM – instrument details



*Schematic of the Drop Bubble Micro Manipulator DBMM with its main elements*



10e<sup>-4</sup> CTAB in water drops in air  
real time - 0.003s  
Running time : 30s



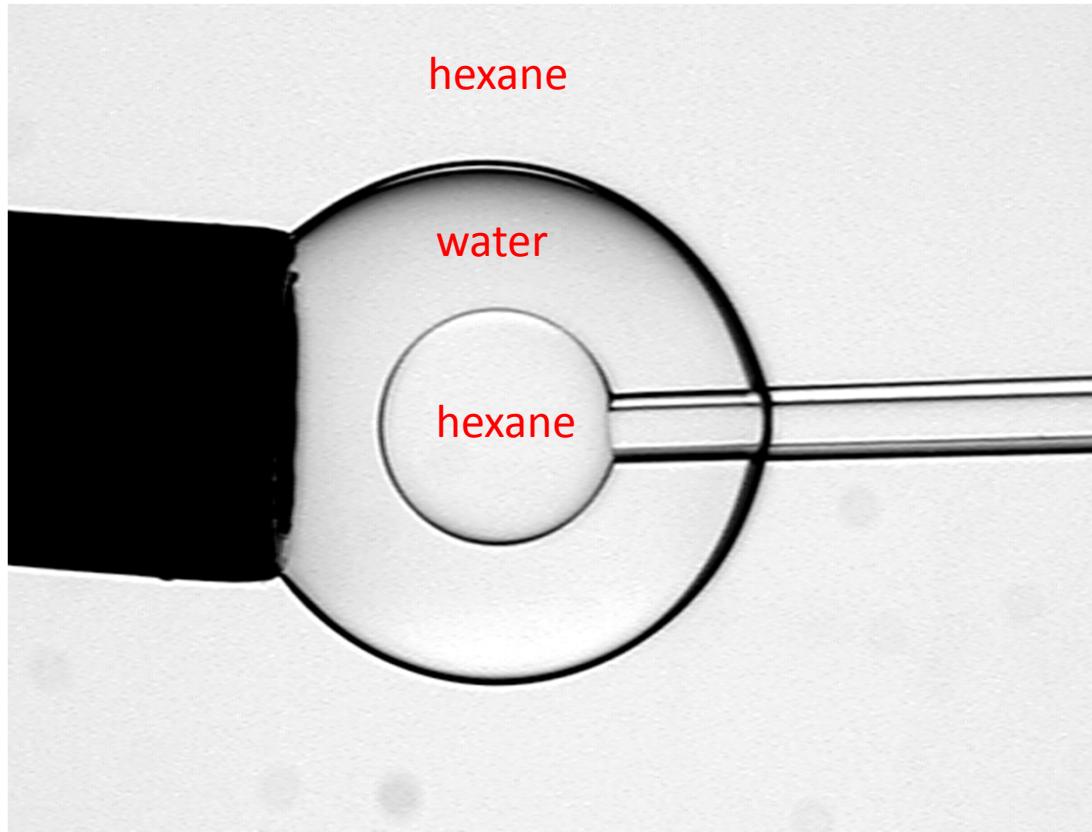
10e<sup>-4</sup> CTAB in water drops in hexane  
real time - 0.002s  
Running time : 20s



Pure water drops in hexane  
real time - 0.002s  
Running time : 20s

## Coalescence of droplets in air or hexane

## Extended to Droplet/Bubble inside of droplet/bubble – Water droplet in hexane droplet in water



Suitable tool for *investigations with two drops (or bubbles)*  
*for a quantitative analysis of the role of emulsifiers in “multiple emulsions”*

## Drops under dynamic conditions – high liquid inflow

150mm<sup>3</sup>/s flowing water in air through a 0.45mm cylindrical capillary



On ground

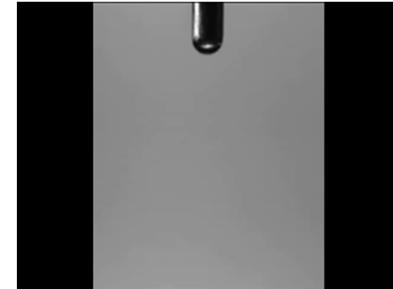


Under microgravity Conditions

83mm<sup>3</sup>/s flowing water in air through a 0.45mm cylindrical capillary



On ground

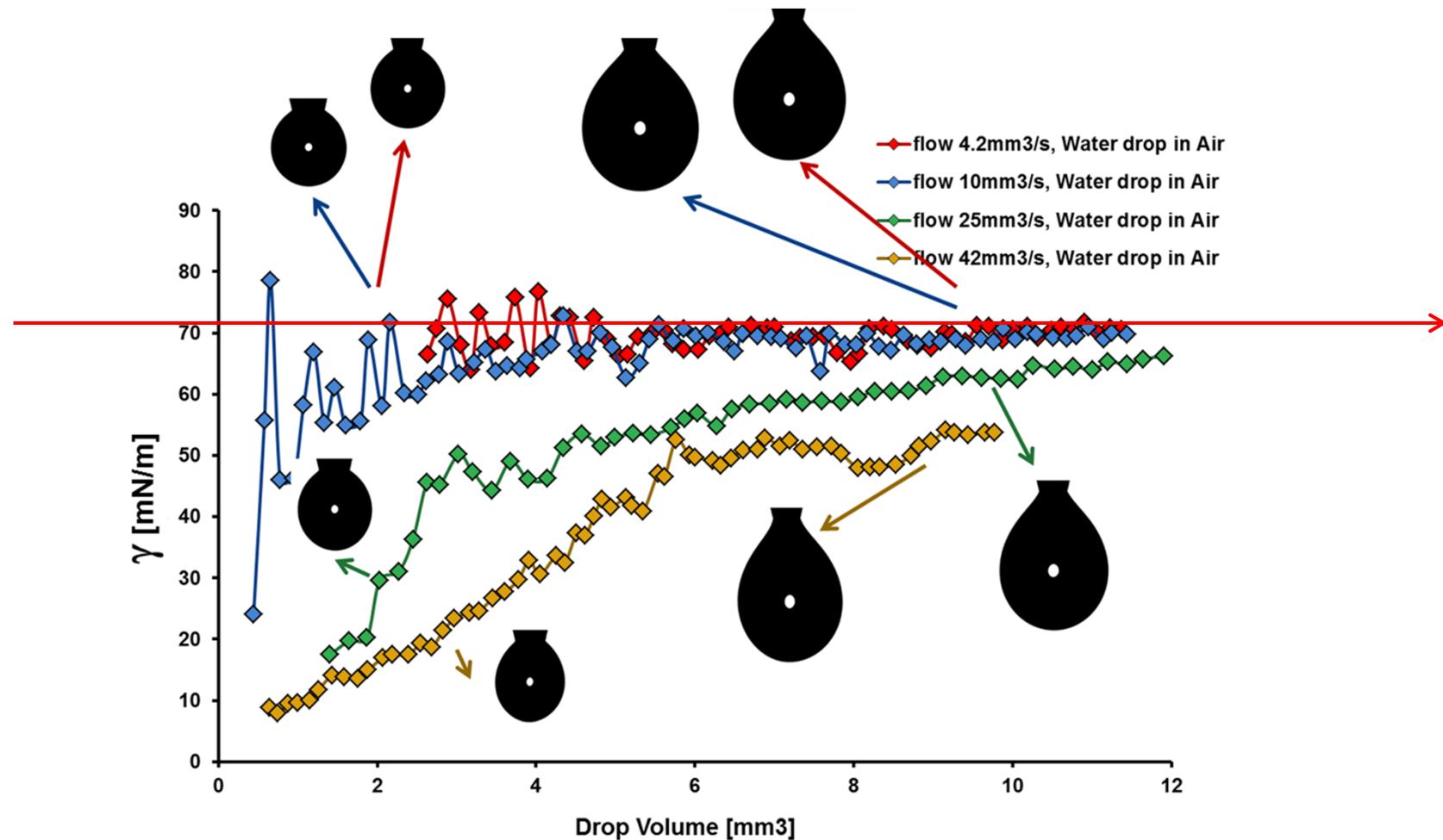


Under microgravity Conditions



Drop Tower Bremen

## Profile Analysis Tensiometry applied under dynamic conditions

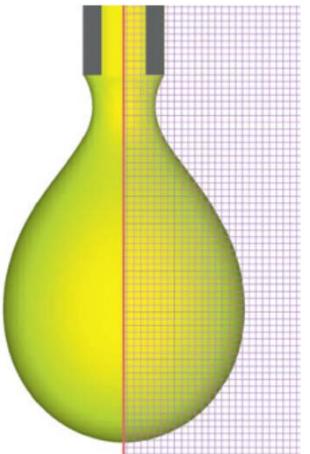


The obtained surface tension values extracted from dynamic drop profiles depend on the flow rate.

## Computational Fluid Dynamics simulations (VOF)

The complete Navier-Stokes equations should be solved in conjunction with relevant equations regarding multiphase systems and surface forces

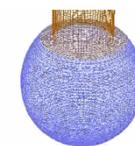
$$\frac{D\rho}{Dt} + \rho \vec{\nabla} \cdot \vec{u} = 0 \quad \rho \frac{D\vec{u}}{Dt} = -\vec{\nabla}P + \mu \vec{\nabla}^2 \vec{u} + \rho \vec{g} \quad \frac{DC_i}{Dt} = D_i \vec{\nabla}^2 C_i$$



Volume of Fluid technique applied to describe multiphase systems

$$\varphi = \frac{V_{Fluid,II}}{V_{Fluid,II} + V_{Fluid,I}} \quad \frac{\partial \varphi}{\partial t} + \frac{\partial}{\partial x_i} (u_i \varphi) = 0$$

$$\rho = \rho_{Fluid,II}\varphi + \rho_{Fluid,I}(1-\varphi) \quad \frac{1}{\mu} = \frac{\varphi}{\mu_{Fluid,II}} + \frac{1-\varphi}{\mu_{Fluid,I}}$$

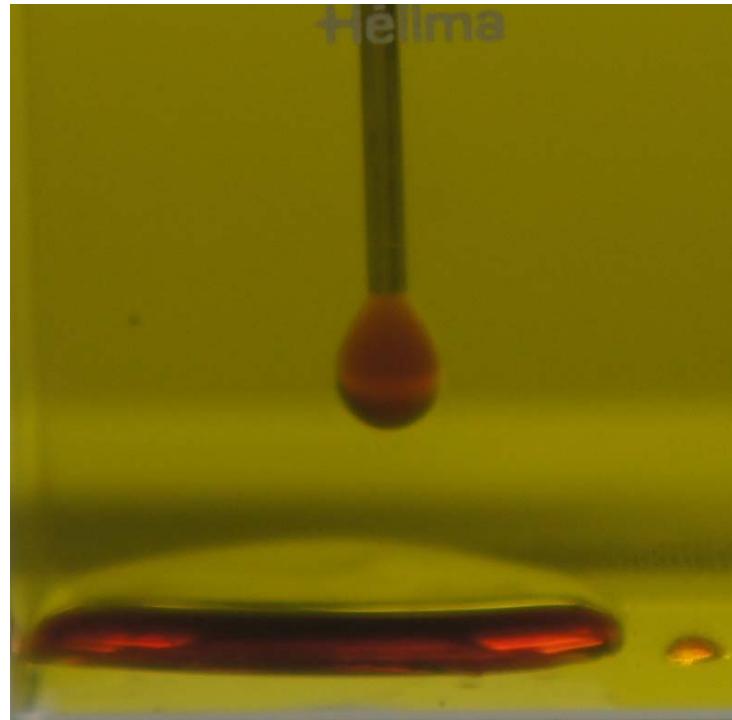


Continuum Surface Force Model for surface tension effects

$$F_{sv}(x) = -\gamma \kappa \underline{n} \delta(\varphi) \quad \kappa = -\vec{\nabla} \cdot \underline{n} \quad \underline{n} = \vec{\nabla} \varphi / |\vec{\nabla} \varphi|$$

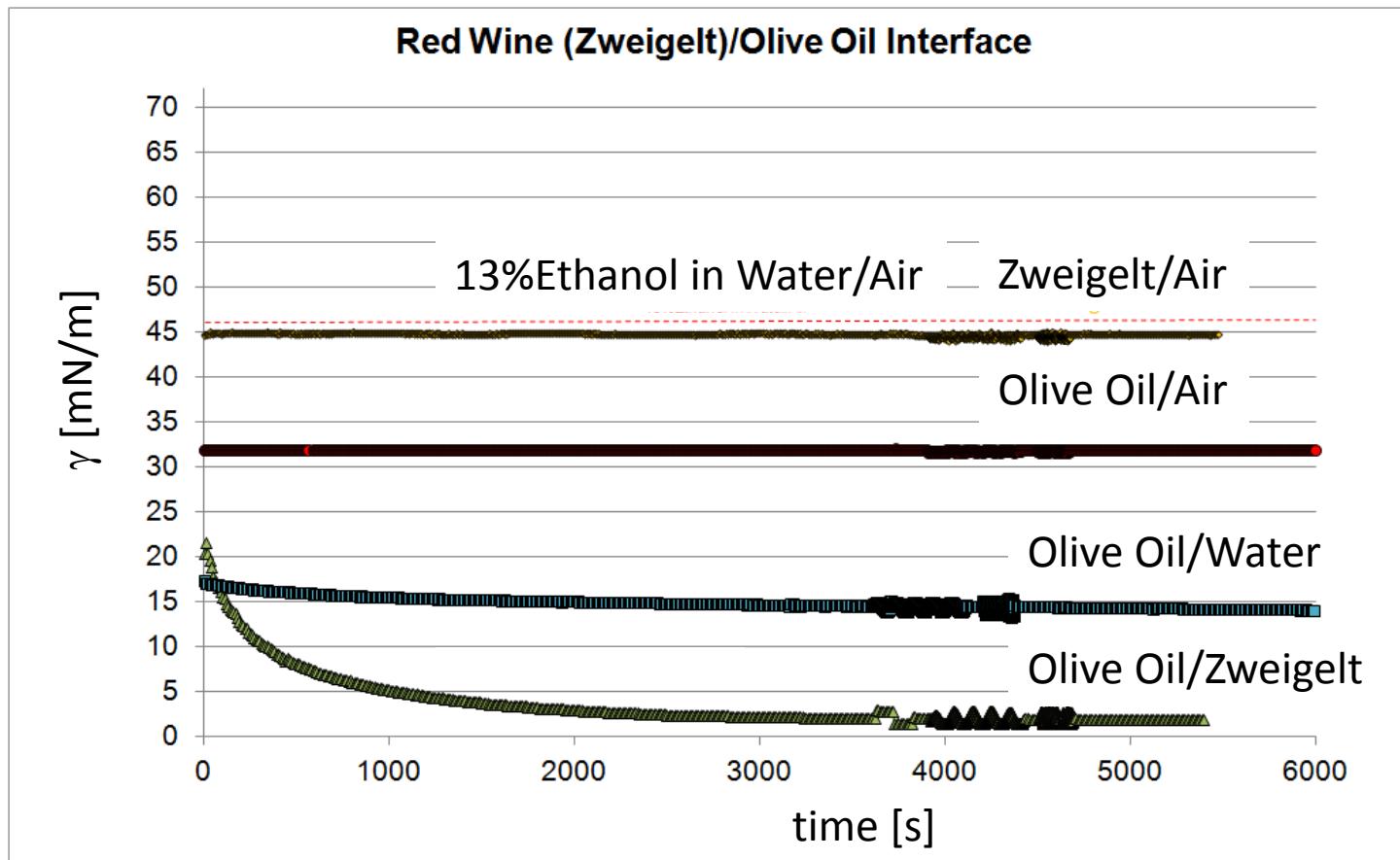
# A real example in daily life

## Interfacial studies of an aqueous solution in oil



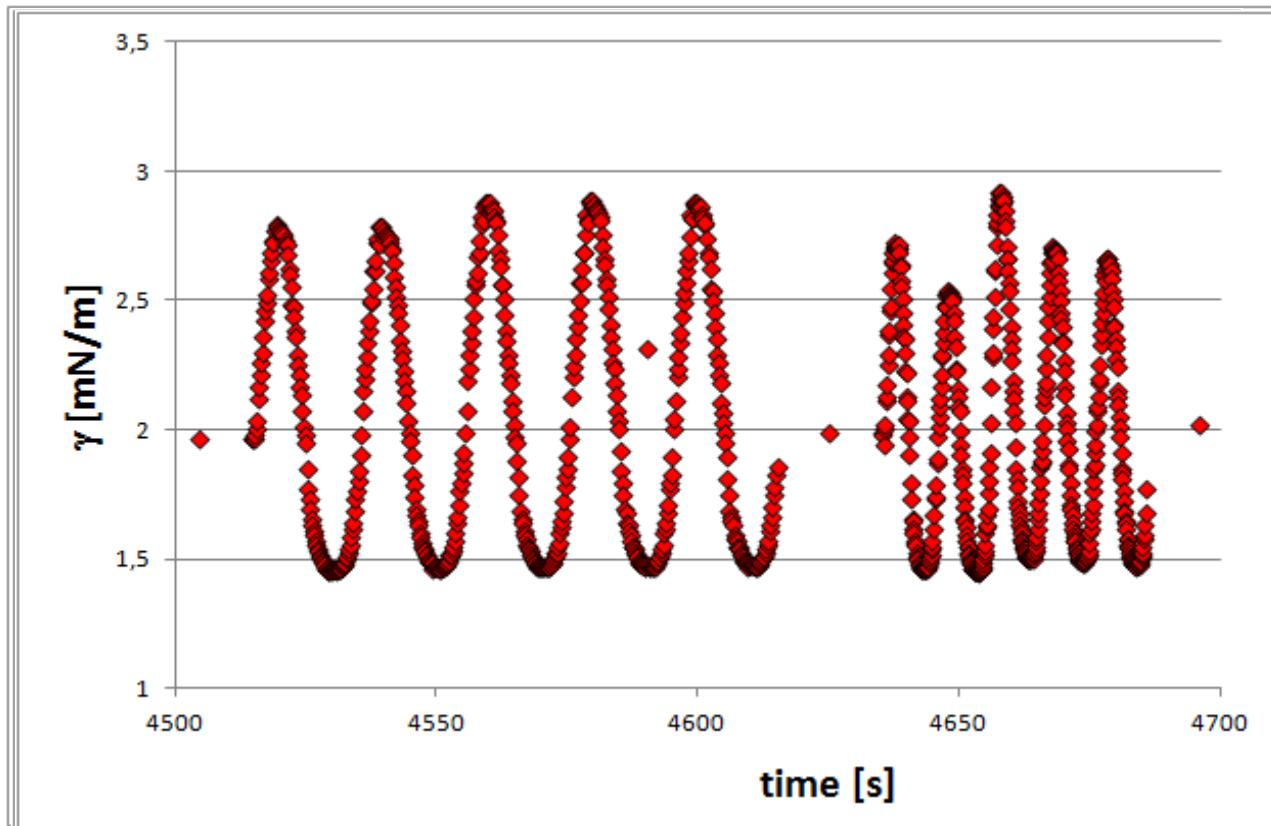
Red wine ( Zweigelt, Austria) in olive oil (extra virgin, Spain)

# A real example in daily life



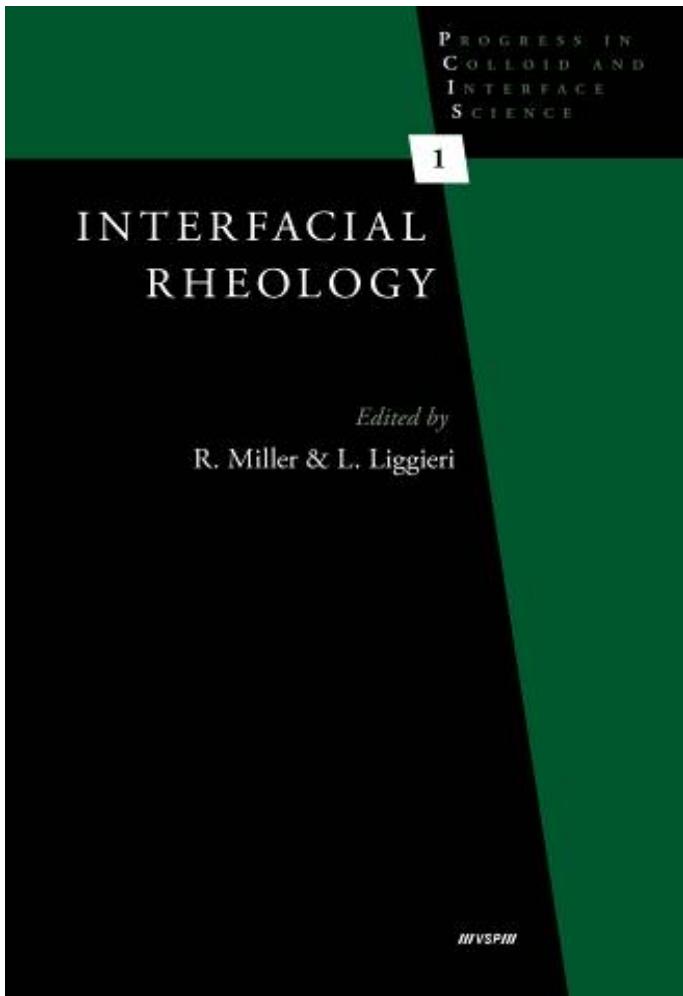
Aqueous solution in oil: red wine (Zweigelt, Austria) in olive oil (extra virgin, Spain)

## A real example in daily life



Aqueous solution in oil: red wine (Zweigelt, Austria) in olive oil (extra virgin, Spain)

## Recently published books on the topic



### Interfacial Rheology

R. Miller and L. Liggieri (eds.)

Progress in Colloid and Interface Science

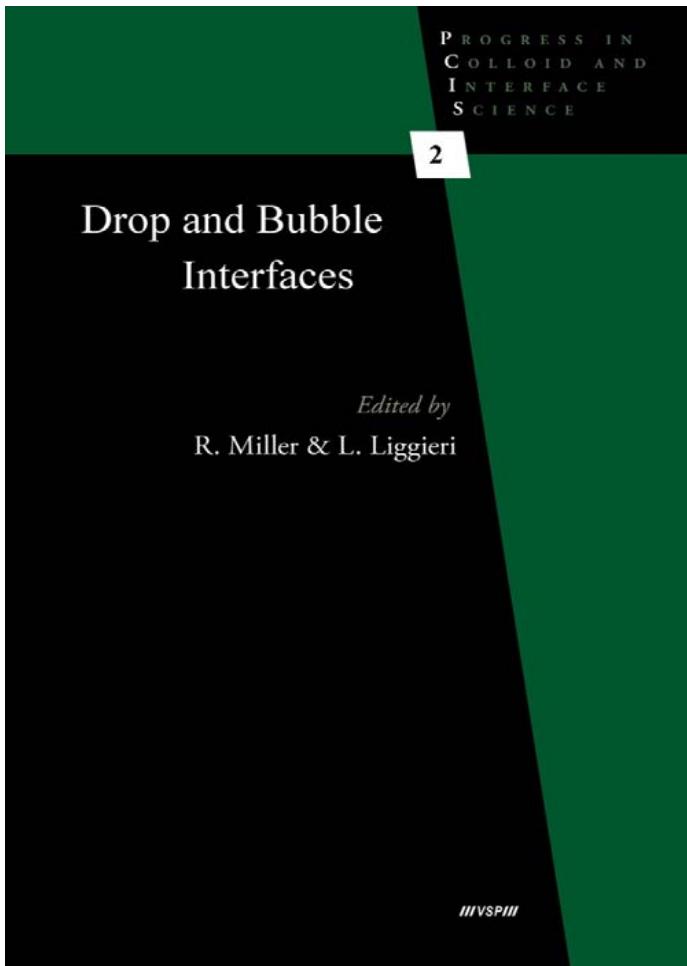
Volume 1

VSP, Brill Publ.

ISBN 978 90 04 17586 0

Leiden 2009

## Recently published books on the topic



### Drop and Bubble Interfaces

R. Miller and L. Liggieri (Eds.)

Progress in Colloid and Interface Science

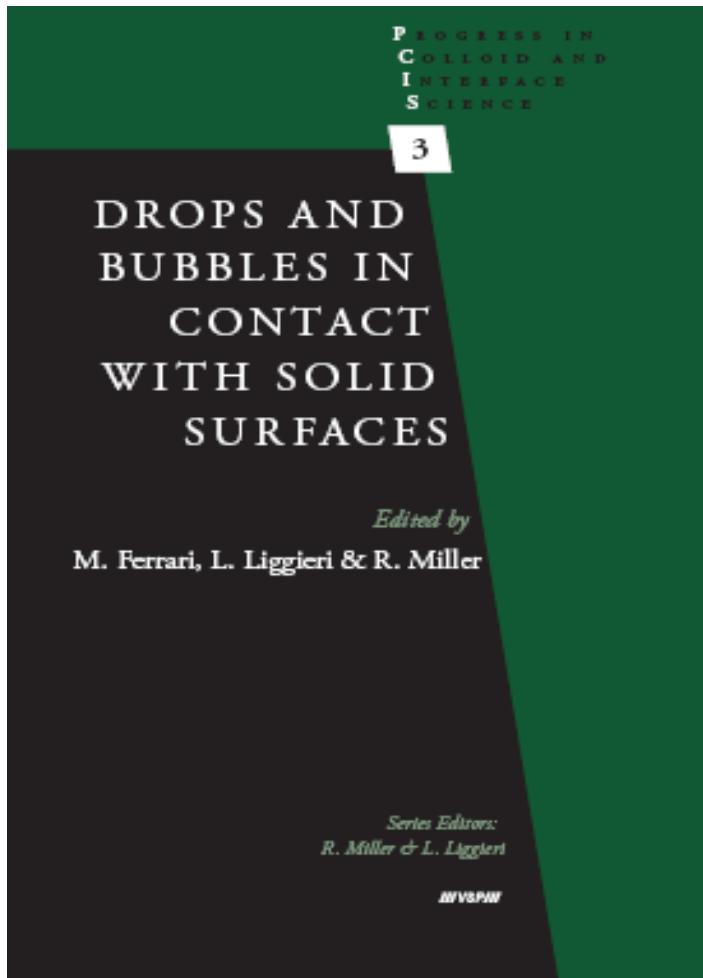
Volume 2

VSP, Brill Publ.

ISBN 978 90 04 17495 5

Leiden 2011

## Recently published books on the topic



### Drops and Bubbles in Contact with Solid Surfaces

M. Ferrari, L. Liggieri and R. Miller (eds.)

Progress in Colloid and Interface Science

Volume 3,  
VSP, Brill Publ.  
ISBN 9789004203198  
Leiden 2012

**The work was financially supported by  
the DFG (SPP 1506), the DLR (50WM1129),  
and COST MP1106.**

Many thanks to the team at the MPI in Potsdam.



**Thank you for your attention!**