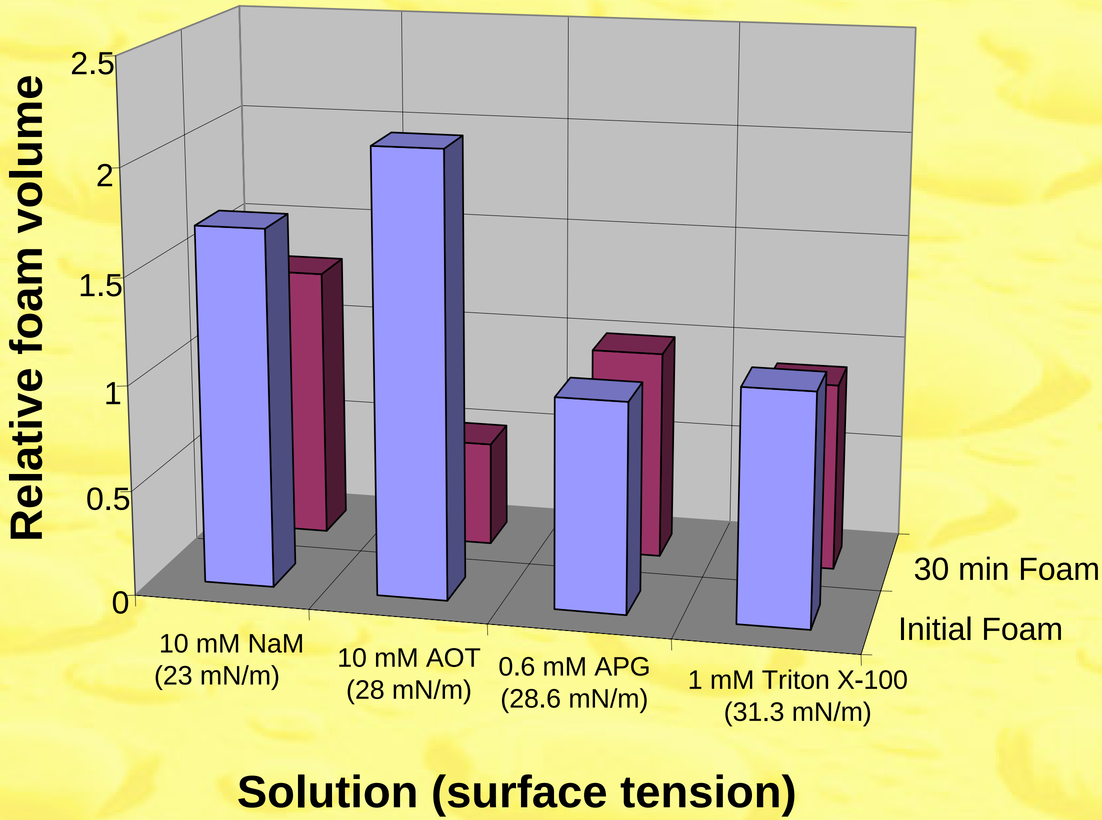
Interfacial Rheology

EDM Expanding Drop Method

ODM Oscillating Drop Method

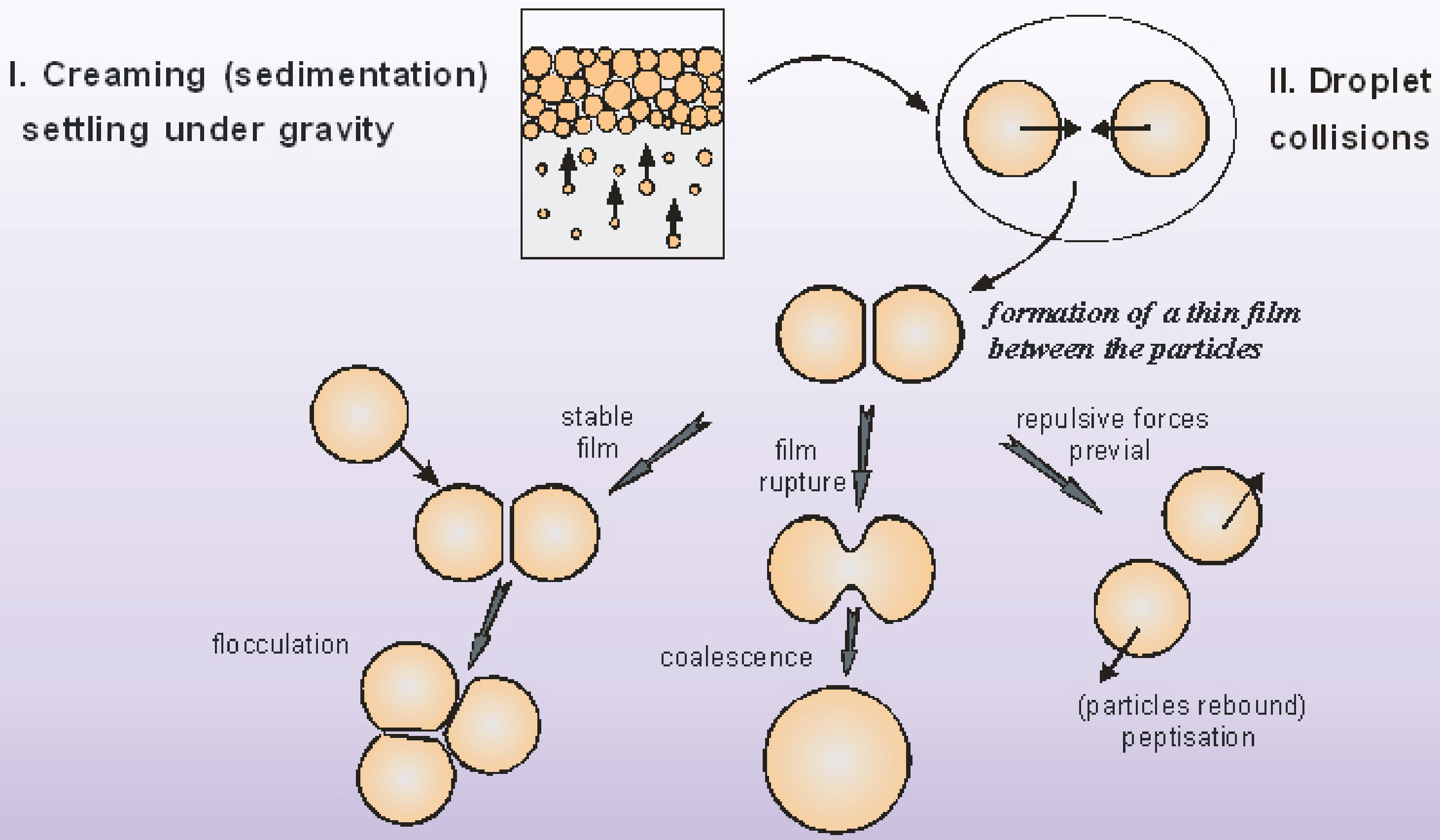
Need to study interfacial rheology – motivation.



The differences in the foam stability arises from the difference stability of the thin liquid films and the different surface rheology!!!

Stability of foams and emulsions

The foams and emulsions are thermodynamically unstable!



Stability of foams and emulsions depend mostly on the stability of the thin liquid films between the bubbles and droplets!

Application

- Foam ability, foam stability
- Stability of emulsions

EDM/ODM Method

Γ = Surface Excess Concentration,
Surface Excess : Measure for concentration increase of surfactants at interface

$$E_G \text{ (Gibbs elasticity)} = \frac{\partial \sigma}{\partial \ln \Gamma}$$

$$\sigma = \sigma(\Gamma, T)$$

Surface elasticity E_A is a measure for dependence of surface tension σ and change of surface area A:

$$E_A \text{ (Surface elasticity)} = \frac{\partial \sigma}{\partial \ln A}$$

Determination of surface tension by pressure measurement

$$P(t) = P_{hydr+} + P_C(t) + P_{visc}(t)$$

$$U(t) = \frac{P(t)}{k_P}$$

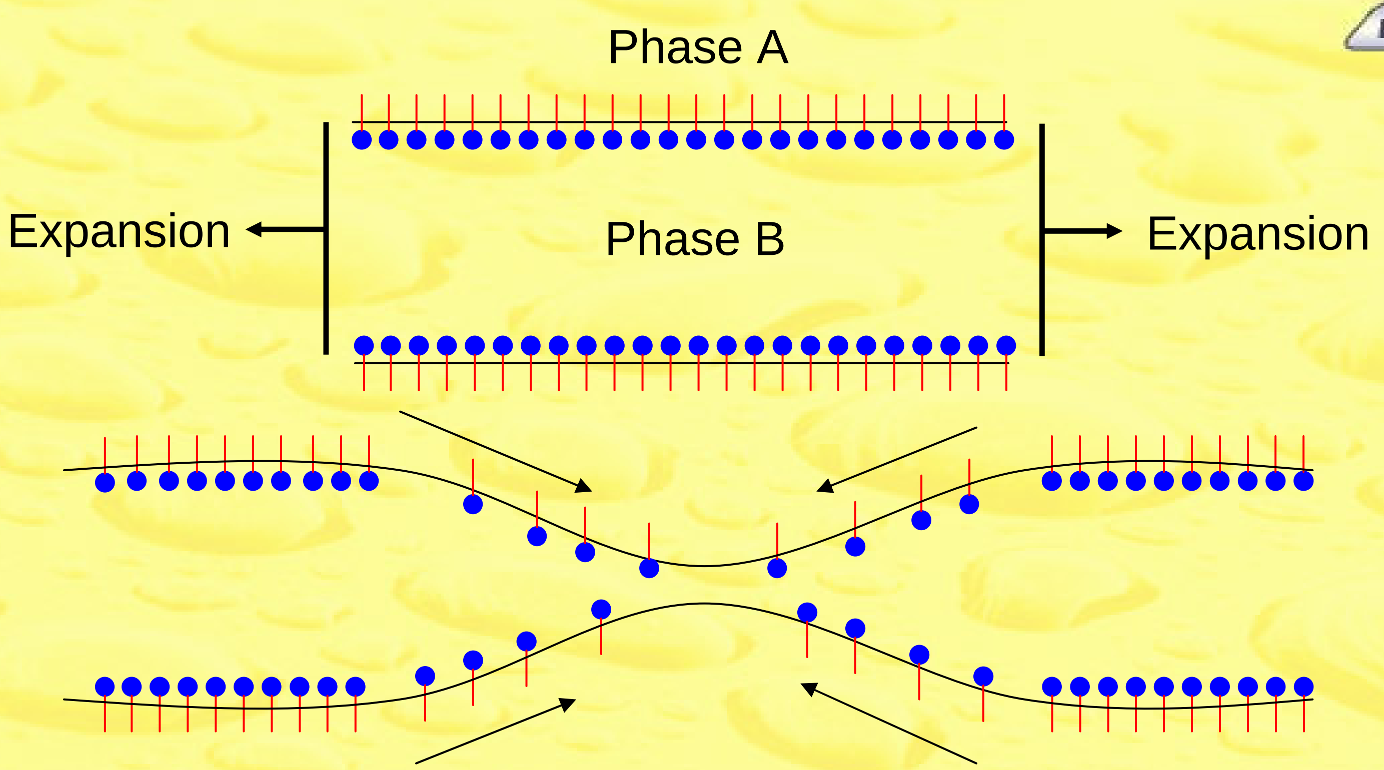
k_P = transducer constant
P_{hydr} = const., hydrostatic pressure
$P_{visc}(t)$ = pressure due to liquid flow in narrow capillary

$$P_C(t) = \frac{2\sigma(t)}{R(t)}$$

Capillary pressure of droplet at capillary tip with surface tension σ and radius R

$$\sigma(t) = R(t)\frac{k_P U(t) - P_{hydr+} - k_{visc} Q(t)}{2}$$

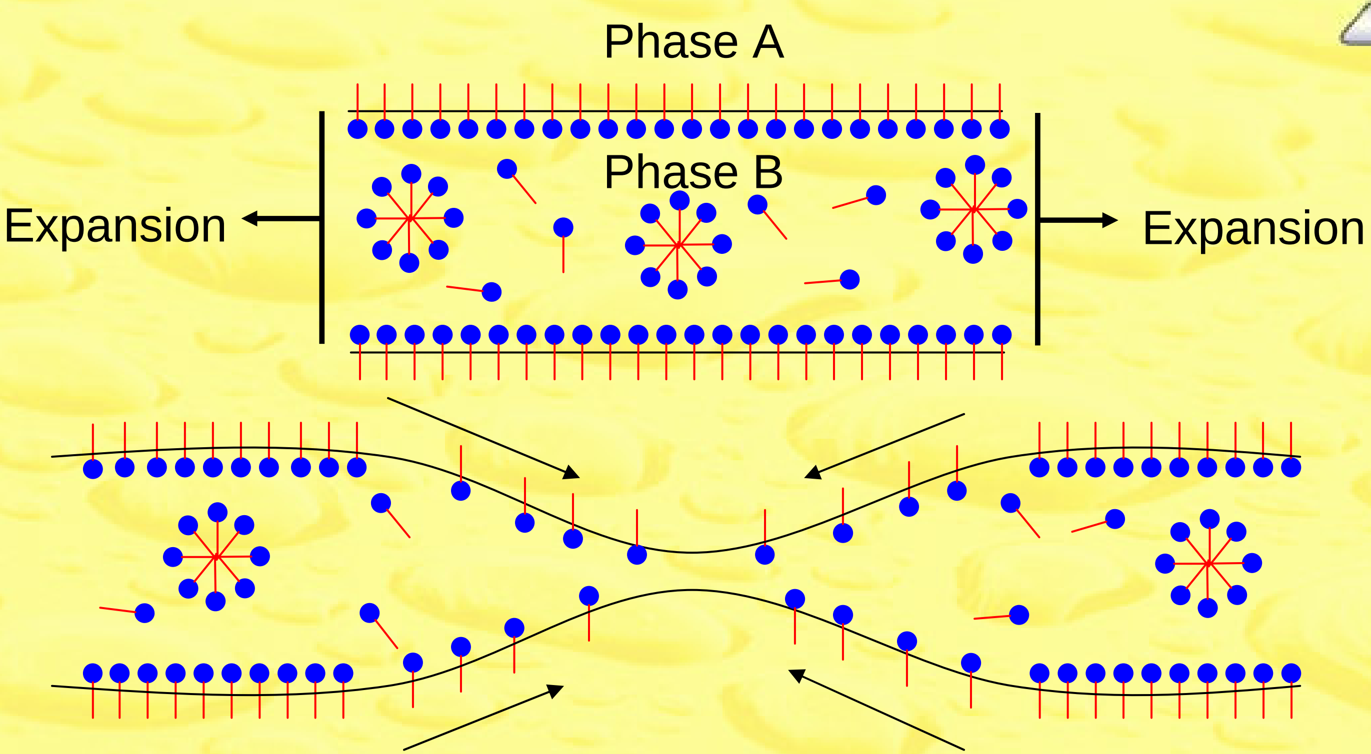
EDM/ODM Method



Insoluble Adsorptions Layer:

$$E_A \text{ (Surface elasticity)} = \frac{\partial\sigma}{\partial \ln A} = \frac{\partial\sigma}{\partial \ln \Gamma} = E_G \text{ (Gibbs elasticity)}$$

EDM/ODM Methode



Soluble Adsorptions Layer :

$E_A \neq E_G$

E_G = Constant for a given system

$E_A = E_A(t)$

EDM/ODM Method

Surface Rheology describes the dependence of surface stress on deformation and rate of deformation:

$$\tau = \tau_{el} + \tau_{vis}$$

τ = Surface stress: Change of surface tension depending on change of surface area

τ_{el} = Elastic component: Depending on surface deformation

τ_{vis} = Viscous component : Depending on rate of deformation

Surface Rheology – Data interpretation

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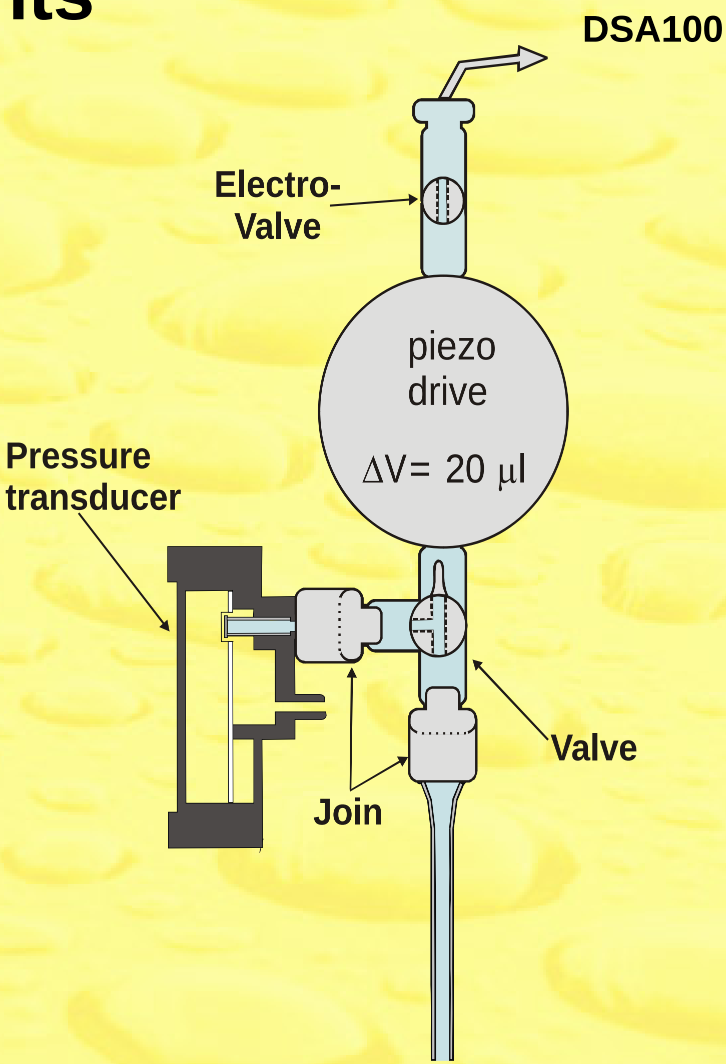
$$\Delta\sigma = \left(\frac{\partial\sigma}{\partial\Gamma}\right)_{eq}\Delta\Gamma + \eta_{dil}\frac{d}{dt}\left(\frac{\Delta\Gamma}{\Gamma_{eq}}\right)$$

η_{dil}= Surface Dilatational Viscosity

Elastic term	Viscous term
↓	↓
Elastic (storage) Module E´	Loss Module E´´

ODM / EDM Module for DSA Krüss instruments



DSA100 with EDM/ODM Module

ODM / EDM Module for Krüss DSA-instruments

Detection of the surface tension in both new methods can be realized by two different detection methods:

– Usual Drop Shape analysis

(–) *nonspherical axisymmetric drop shape – larger volume, more vibrations, data acquisition rate limited by video system speed; not applicable to liquids with similar (same) densities.*

(+) *less sensitive to viscous effects.*

– Direct Capillary Pressure determination

(+) *spherical drops - less volume, less sensitive vibrations, faster acquisition rate; applicable to liquids with same density.*

(–) *more sensitive to viscous effects (can be accounted for)*.

Comparison of Oscillating Drop (ODM) and Expanding Drop (EDM) Methods

EDM on Krüss system:

- Uniform deformation and constant rate of deformation;
- Spherical drop ⇒ pure dilatation ⇒ true dilatational surface viscosity;
- Additional information from the relaxation curve (diffusion time).

  At fast expansion ⇒ Gibbs elasticity is directly obtained.

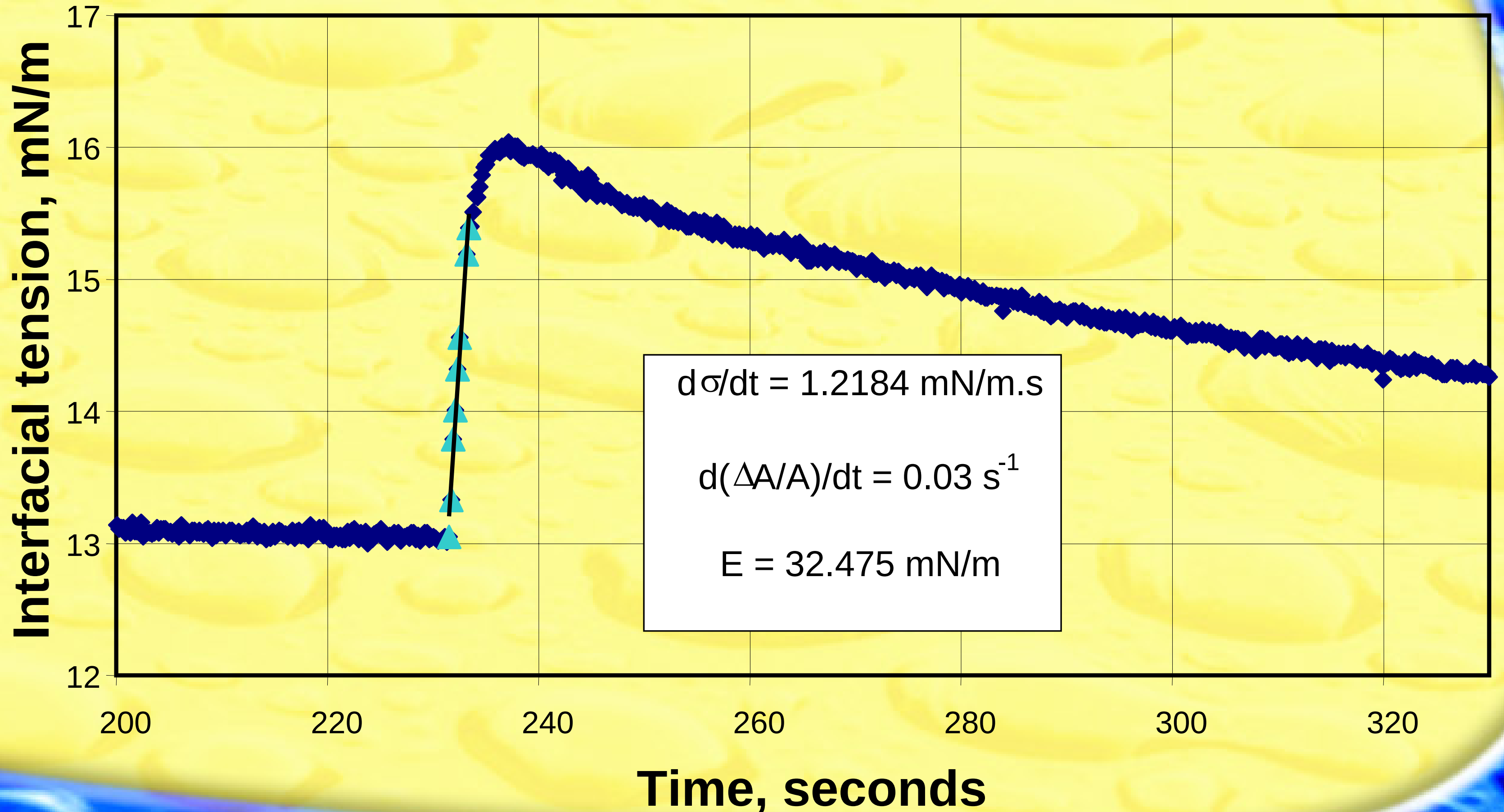
  Applicable for highly viscous fluids like silicone oils, crude oils, etc.; and for liquid/liquid systems with the same density.

ODM on Krüss system:

- Applicable to any linear system ⇒ description by two parameters;
- Fourier Analyses.

Representative data with the new EDM/ODM Module

EDM experiment (Brij 58)



Representative data with the new EDM/ODM Module

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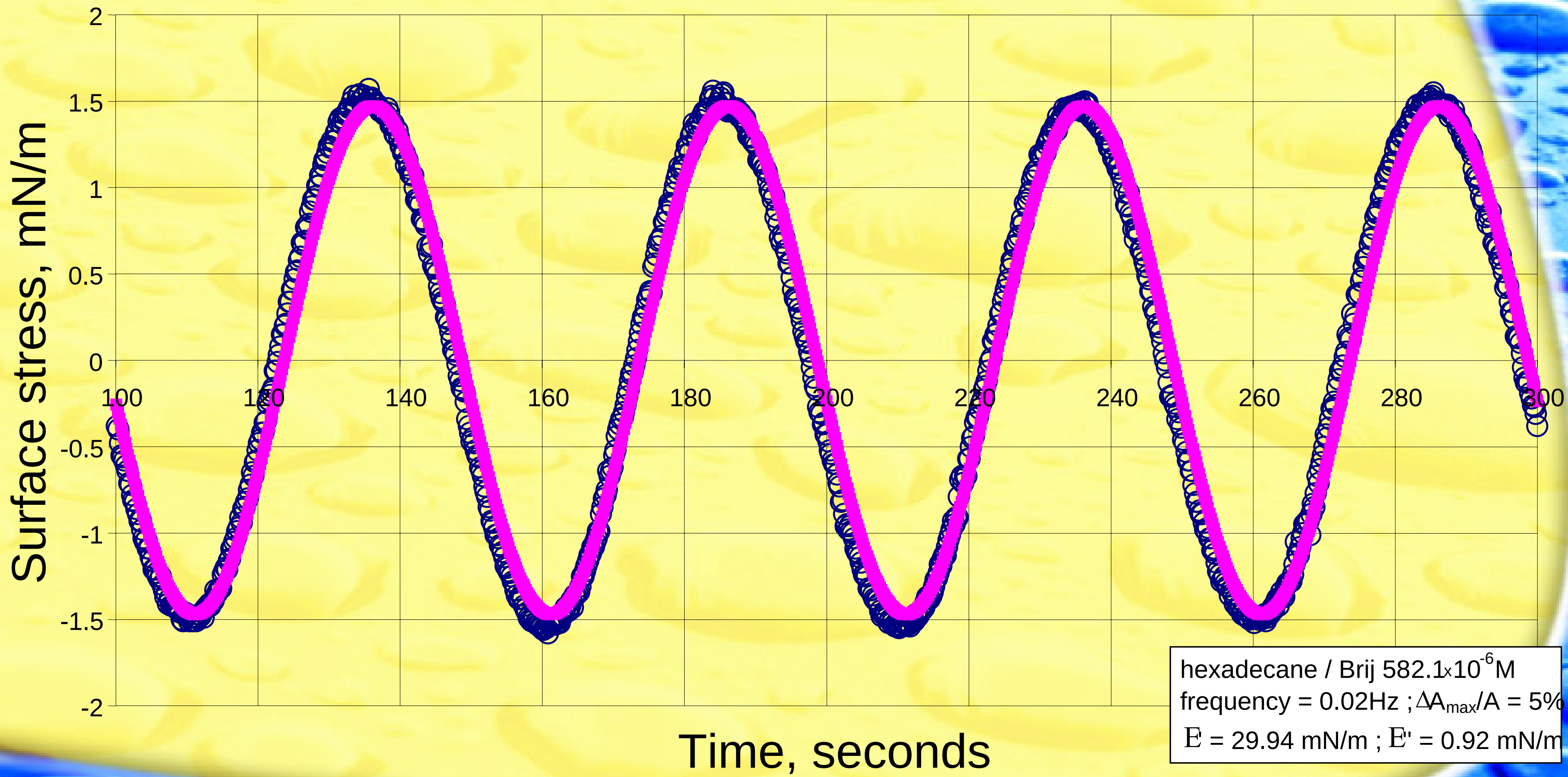
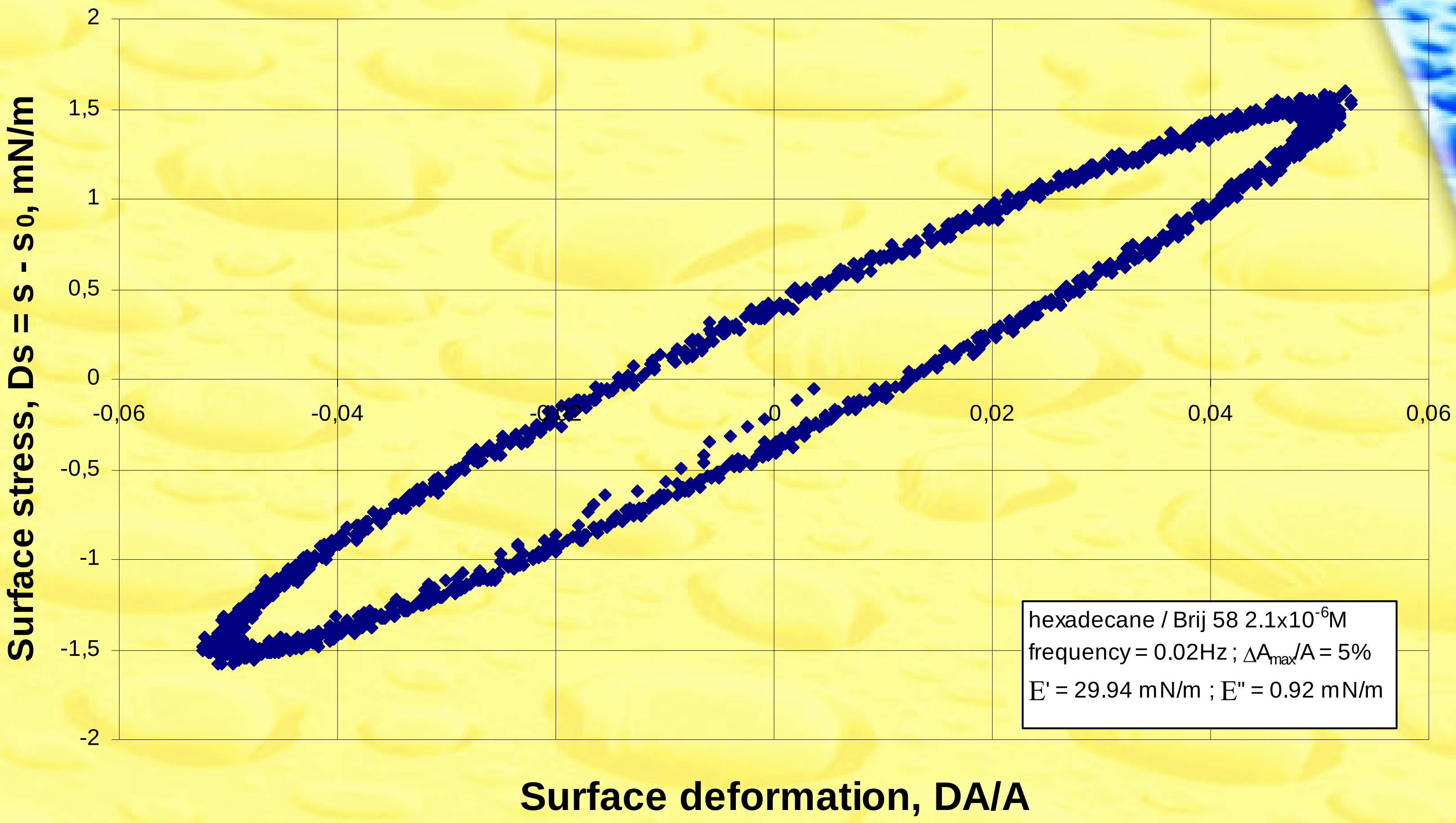
ODM experiment (Brij 58)



Representative data with the new EDM/ODM Module



Adsorption of Brij 58 is slow and the elastic modulus determined in the two type of measurements coincides.

Summary

- Characterization of surfactant dynamics is an important tool for process-near optimization
- The maximum bubble pressure method is a fast and easy to use technique to characterize fast diffusion of surfactants at the liquid / gas interface
- The drop volume technique is a method to characterize diffusions of surfactants at liquid / liquid - interface
- A special capillary tip design increases reproducibility and minimises experimental error