

# Interfacial Rheology

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Lecture at COST P21 Student Training School  
*Physics of droplets: Basic and Advanced Topics*  
12 – 13 July, 2010, Borovets, Bulgaria

## Contents:

- ▶ Description of surface deformation (strain)
- ▶ Types of surface rheological behavior (elastic, viscous, plastic; combinations thereof)
- ▶ Examples of measurements, methods



**Sofia University**

# Motivation – Dispersion Stability

Role of the interfacial rheology:

❖ **At short times**

-Slows down the drainage of films

-Damps fluctuations

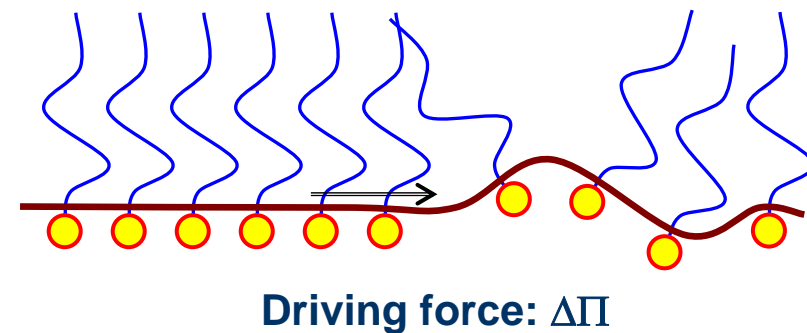
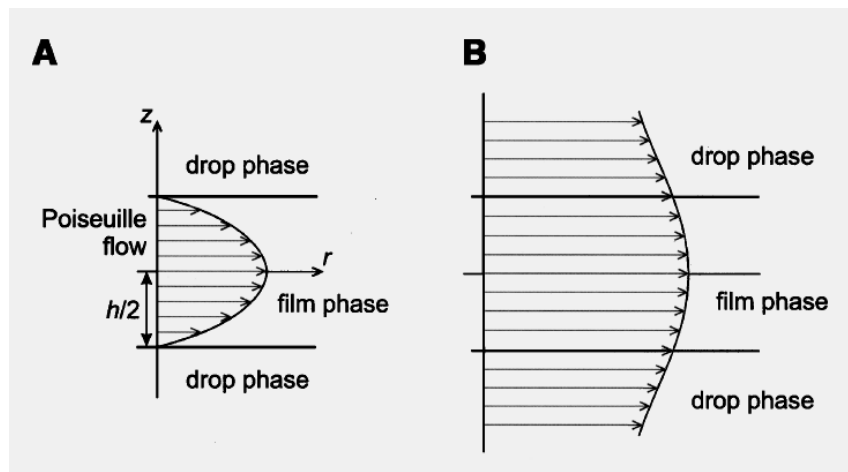
of area expansion/compression, by opposing stresses

of adsorption layer density,  $\delta\Gamma$ , by the Marangoni effect (motion toward lower surface pressure)

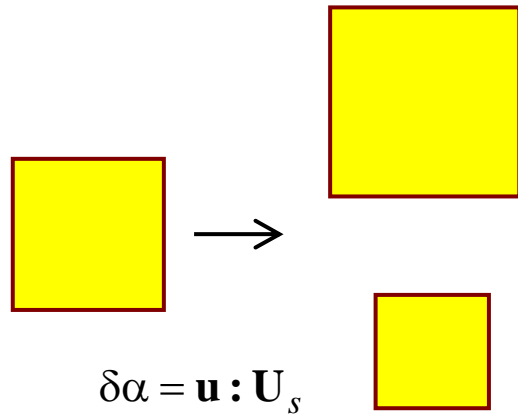
of film thickness

❖ **At long times**

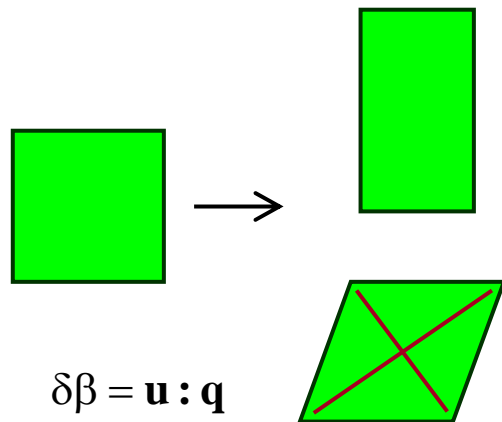
-Plastic behavior of surfaces – fracture of fragile layers and exposure of bare fluid interface



# Surface Deformations



**Dilatation [Expansion/Compression];  
Change of  $A$**



**Shear ( $A = \text{const.}$ )**

$$\mathbf{u} = \frac{1}{2}(\mathbf{u} : \mathbf{U}_s)\mathbf{U}_s + \left[ \mathbf{u} - \frac{1}{2}(\mathbf{u} : \mathbf{U}_s)\mathbf{U}_s \right]$$

$$\text{Tr} \left[ \mathbf{u} - \frac{1}{2}(\mathbf{u} : \mathbf{U}_s)\mathbf{U}_s \right] = 0 \quad \text{deviatoric part}$$

$$\text{Tr} \mathbf{u} = \mathbf{u} : \mathbf{U}_s = u_1 + u_2 \quad \text{isotropic deformation}$$

**relative extensions:**

$$u_1 = \frac{\delta L_1}{L_1} = \delta \ln L_1; \quad u_2 = \frac{\delta L_2}{L_2} = \delta \ln L_2$$

**relative dilatation:**

$$u_1 + u_2 = \delta \ln(L_1 L_2) = \frac{\delta A}{A} = \delta \ln A = \delta\alpha$$

**how to describe shear deformation?**

$$\mathbf{u} - \frac{1}{2}(\mathbf{u} : \mathbf{U}_s)\mathbf{U}_s = \frac{1}{2}(u_1 - u_2)(\mathbf{e}_1\mathbf{e}_1 - \mathbf{e}_2\mathbf{e}_2)$$

**relative shear:**

$$u_1 - u_2 = \delta \ln(L_1 / L_2) = \frac{\delta(L_1 / L_2)}{L_1 / L_2} = \delta\beta$$

$$\mathbf{U}_s = \mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2; \quad \mathbf{q} = \mathbf{e}_1\mathbf{e}_1 - \mathbf{e}_2\mathbf{e}_2$$

$$\mathbf{u} = \frac{1}{2}(\delta\alpha)\mathbf{U}_s + \frac{1}{2}(\delta\beta)\mathbf{q}$$

# Surface Deformation – Curvature

$$\mathbf{b} = -\nabla_s \mathbf{n} = HU_s + D\mathbf{q}$$

In the basis of principal curvatures:

$$H = \frac{1}{2}(c_1 + c_2), \quad D = \frac{1}{2}(c_1 - c_2)$$

$$\delta w_s = \gamma \delta \alpha + \xi \delta \beta + B \delta H + \Theta \delta D$$

where  $B = M_1 + M_2$ ,  $\Theta = M_1 - M_2$

The behavior of  $B(H)$ ,  $\Theta(D)$  is usually elastic:

if  $w_f = 2k_c(H - H_0)^2 + \bar{k}_c K$  (and  $K = c_1 c_2$ ),

then  $B = \left( \frac{\partial w_f}{\partial H} \right)_D = B_0 + 2(2k_c + \bar{k}_c)H$

$\Theta = \left( \frac{\partial w_f}{\partial D} \right)_H = -2\bar{k}_c D$  (and  $B_0 = -4k_c H_0$ )

$k_c \sim 10\text{-}20 k_B T$   
for lipid bilayers

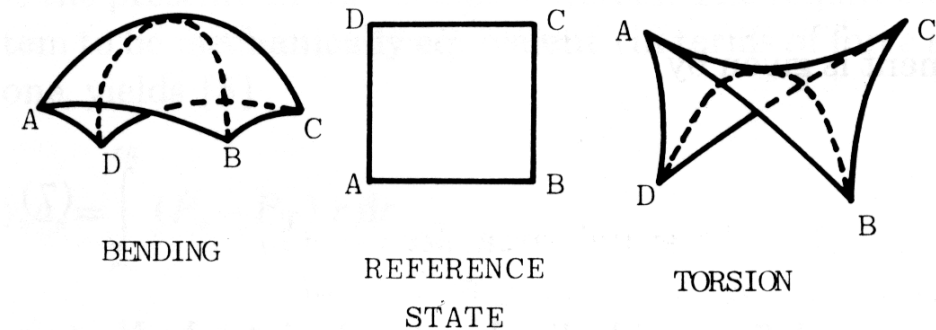
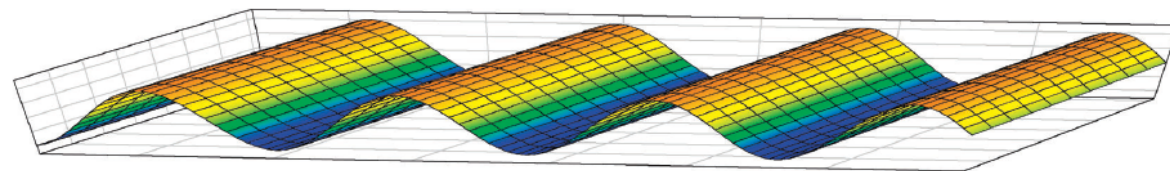
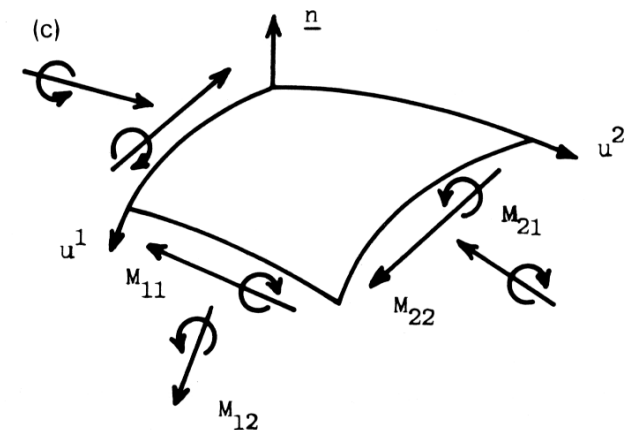


Fig. 1. Independent modes of surface deformation.



## Dilatational Surface Elasticity – Low MW Surfactants

Type of surface tension isotherm	Surface tension isotherm $\sigma = \sigma_0 - kTJ$	Gibbs elasticity, $E_G$
Henry	$J = \Gamma_1$	$E_G = kT\Gamma_1$
Freundlich	$J = \frac{\Gamma_1}{m}$	$E_G = kT\frac{\Gamma_1}{m}$
Langmuir	$J = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right)$	$E_G = kT\Gamma_1 \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1}$
Volmer	$J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1}$	$E_G = kT\Gamma_1 \frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2}$
Frumkin	$J = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) - \frac{\beta\Gamma_1^2}{kT}$	$E_G = kT\Gamma_1 \left( \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT} \right)$
van der Waals	$J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{\beta\Gamma_1^2}{kT}$	$E_G = kT\Gamma_1 \left[ \frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2} - \frac{2\beta\Gamma_1}{kT} \right]$

**In presence of surfactant,**  
 $\sigma = \sigma(\Gamma)$

**Elasticity:**

$$E = \frac{d\sigma}{d \ln A}$$

**Gibbs elasticity:**

$$E_G = -\frac{d\sigma}{d \ln \Gamma}, \quad \Gamma = \frac{N}{A}$$

$E = E_G$  **only when  $N = \text{const.}$**

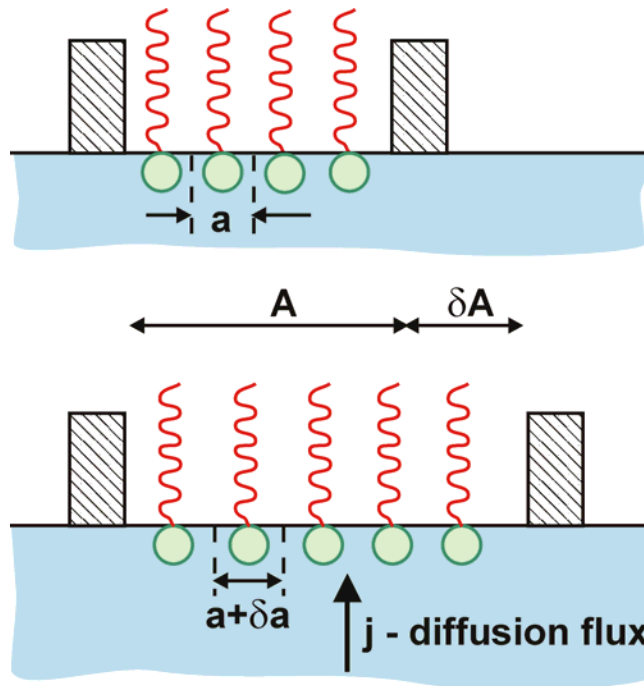
**(insoluble surfactant, or absence of exchange with bulk)**

**In general,**

$$E = \left( \frac{d\sigma}{d \ln \Gamma} \right) \left( \frac{d \ln \Gamma}{d \ln A} \right)$$

**Interesting feature: At  $\Gamma_1 \rightarrow \Gamma_\infty$ ,  $E_G \rightarrow \infty$  (not observed – out-of-plane escape)**

# Diffusional Exchange Model



a) Initial state

b) Expanded state

$$\frac{\delta A}{A} > \frac{\delta a}{a}$$

With soluble surfactants, when the interface is expanded, the diffusion flux,  $j$ , brings new molecules to the interface. For this reason, the relative increase of the area per one adsorbed molecule,  $(\delta a)/a$ , is always smaller than the relative increase of the total area,  $(\delta A)/A$ .

Lucassen & van den Tempel, *Chem. Eng. Sci.*, 27 (1972) 1283.

Sinusoidal oscillations of a barrier in the plane of the interface – compression/expansion

$$\xi = \xi_B \frac{L-x}{L} e^{i\omega t}.$$

For small deformations  $\varepsilon = \left( \frac{d\sigma}{d \ln \Gamma} \right)_{eq} \frac{d \ln \Gamma}{d \ln A}$

# Diffusional Exchange Model

$$\frac{1}{A} \frac{d(\Gamma A)}{dt} + \mathcal{D} \left( \frac{\partial c}{\partial y} \right)_{y=0} = 0 \quad (11)$$

which gives, upon rearrangement:

$$\frac{d \ln \Gamma}{d \ln A} = - \left\{ 1 + \mathcal{D} \frac{dc}{d\Gamma} \left( \frac{\partial c / \partial y}{\partial c / \partial t} \right)_{y=0} \right\}^{-1} \quad (12)$$

Combination of Eqs. (8)–(10) and (12) finally gives for  $\epsilon$ :

$$\epsilon = \epsilon_0 \frac{1 + \zeta + i\zeta}{1 + 2\zeta + 2\zeta^2} \quad (13)$$

where

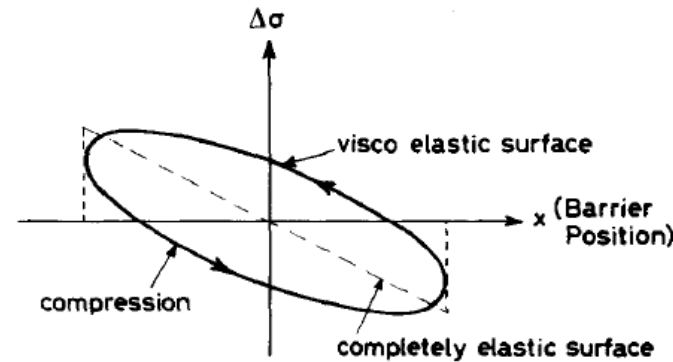
$$\zeta \equiv \frac{dc}{d\Gamma} \sqrt{\frac{\mathcal{D}}{2\omega}} \quad \text{and} \quad \epsilon_0 \equiv - \frac{d\sigma}{d \ln \Gamma}.$$

The dimensionless parameter  $\zeta$  is determined by the ratio of the time scales of the experiment and of the diffusion process. Its magnitude depends mainly on the slope of the equilibrium-adsorption isotherm of the surface-active solute. This slope is usually large at low concentrations

## Visco-elastic behavior

- ❖ The elasticity and viscosity depend on frequency,  $\omega$
- ❖ "Apparent" viscosity, due to the mass exchange

(a)



(b)

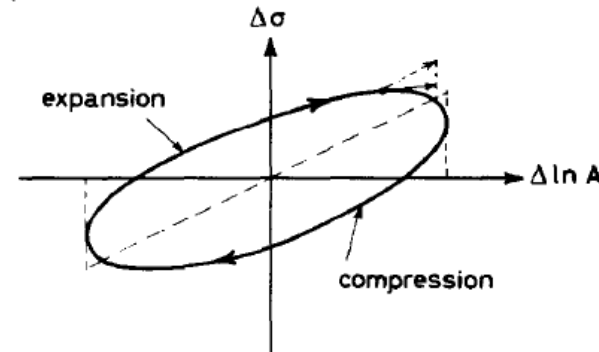
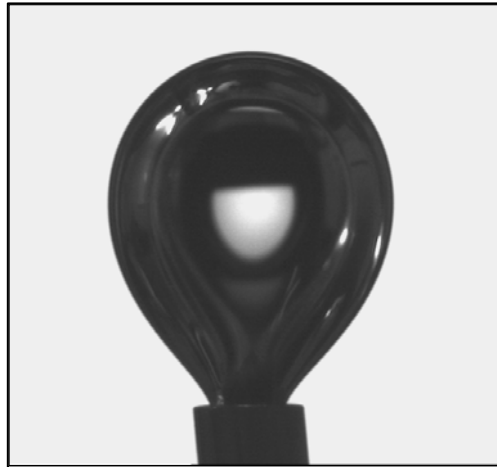


Fig. 1. Illustrating phase relations between deformation and surface tension variations.

$$\zeta = \sqrt{\frac{1}{\omega \tau_D}}$$

$$\tau_D = \frac{2}{D} \left( \frac{\partial \Gamma}{\partial c} \right)_{eq}^2$$

# Harmonic Oscillations



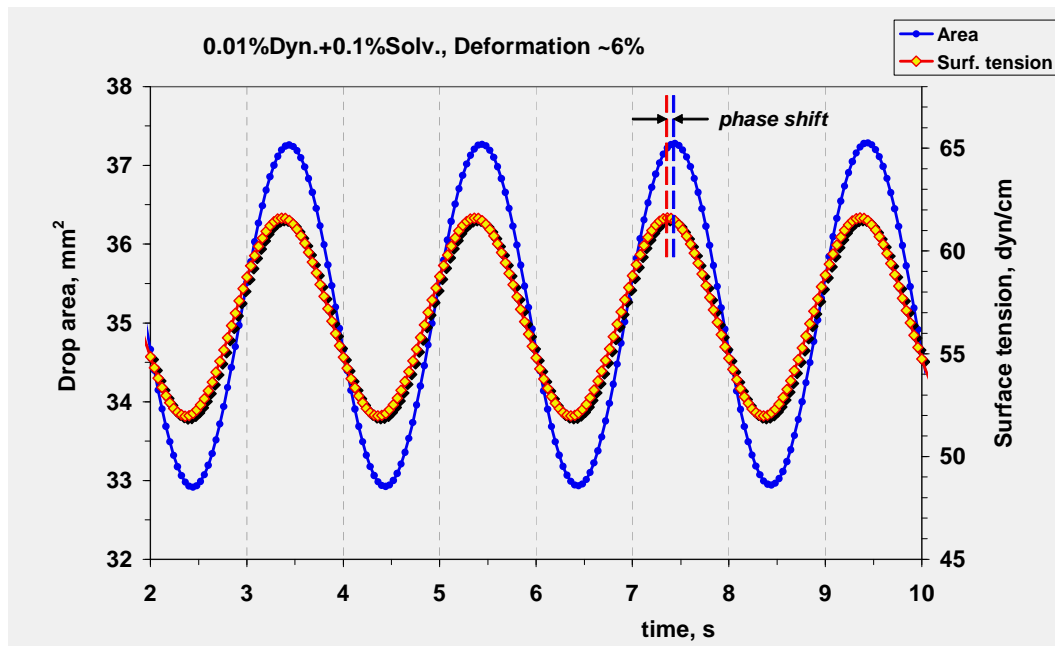
Oscillating deformable drop

$$\Delta\sigma_m e^{i(\omega t + \varphi)} = \tau = E^* \gamma = E^* \frac{\Delta A_m}{A_0} e^{i\omega t}$$

$$|E^*| = \sqrt{E'^2 + E''^2} = \frac{\Delta\sigma_m}{\Delta A_m / A_0} = \text{ratio of amplitudes}$$

$$E^* = E' + iE''; \quad E' = |E^*| \cos \varphi; \quad E'' = |E^*| \sin \varphi$$

$\Delta\sigma_m, \varphi =$  measured quantities



From the experimentally measured amplitude ratio and the phase shift, one determines  $E', E''$ .

Interpretation of the storage modulus,  $E'$ , and the loss modulus,  $E''$ , can only be made in terms of rheological models.

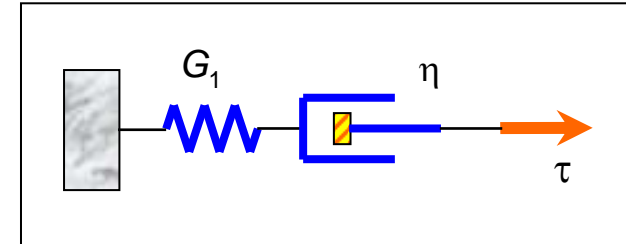


# Linear Visco – Elasticity (Maxwell)

Maxwell model [summation of strains]

Constitutive relation:

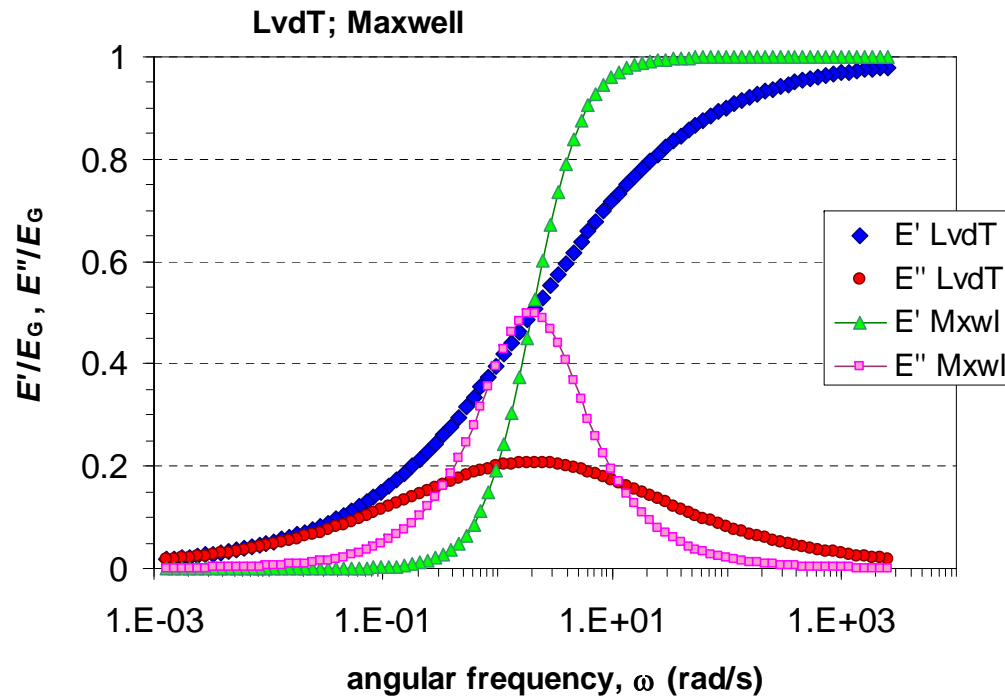
$$\frac{d\gamma}{dt} = \frac{1}{G_1} \frac{d\tau}{dt} + \frac{1}{\eta} \tau$$



Oscillatory  $\gamma(t)$  is substituted; the equation is solved for  $\tau$ .

$$E' = G_1 \frac{(\omega t_r)^2}{1 + (\omega t_r)^2}$$

$$E'' = G_1 \frac{\omega t_r}{1 + (\omega t_r)^2} \quad t_r \equiv \frac{\eta}{G_1}$$



At high frequencies, the behavior becomes fully elastic, with  $E' = G_1$ . Besides,  $G_1 = E_G$ .

If  $\gamma(t) = \sin(\omega t)$ , then

$$\tau(t) = E' \sin(\omega t) + E'' \cos(\omega t)$$

## A More Complex Linear Visco-Elastic Model

Presence of **irreversibly adsorbed molecules** (that cannot be exchanged with the bulk phase)

Polymers, proteins, ...

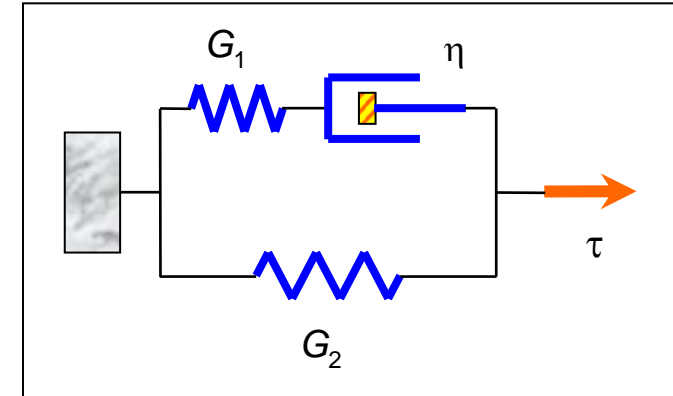
❖ **Extended Maxwell model**

Freer et al. (+Radke), *Langmuir*, 20 (2004) 10159

Saulnier et al. (+Panayotov), *Langmuir*, 17 (2001) 8104

Constitutive equation:

$$\left(1 + \frac{G_2}{G_1}\right) \frac{d\gamma}{dt} + \frac{G_2}{\eta} \gamma = \frac{1}{G_1} \frac{d\tau}{dt} + \frac{1}{\eta} \tau$$



### Very fast deformation:

▶ **Elastic behavior**, with elasticity =  $G_1 + G_2$

The viscosity is **“apparent”**: related to the **exchange** of molecules with the bulk.

At fast deformation, this cannot happen.

Slow exchange  $\Leftrightarrow$  **LARGE** viscosity;  $t_r = \eta / G_1$  is long

### Very slow deformation:

▶ The elasticity =  $G_2$  ; it is due only to the **irreversibly adsorbed molecules**.

Full relaxation of the mass exchange ( $G_1$  is inactive);  $\Gamma$  of the exchangeable molecules has equilibrium value.

# Langmuir Trough Method

Symmetric motion of the barriers

◆ Linear translation with constant speed

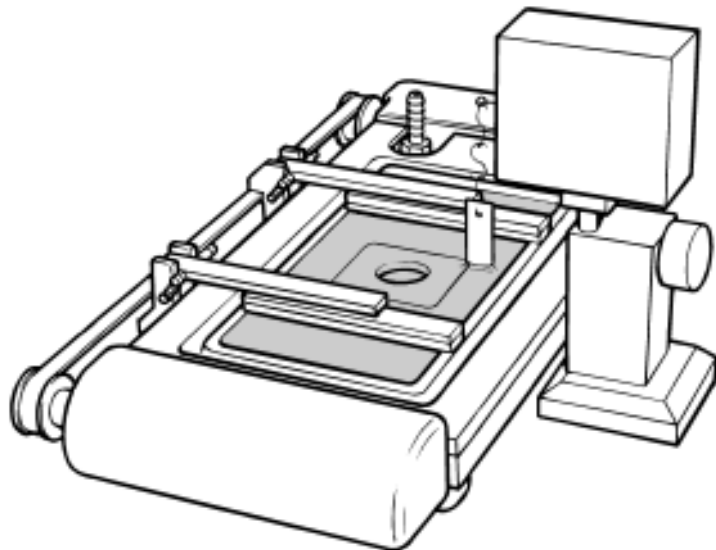
The deformation rate is relatively small (to avoid ripples);  $d\gamma/dt < 0.01 \text{ s}^{-1}$ .

UNI-AXIAL DEFORMATION – **superposition of dilatation and shear.**

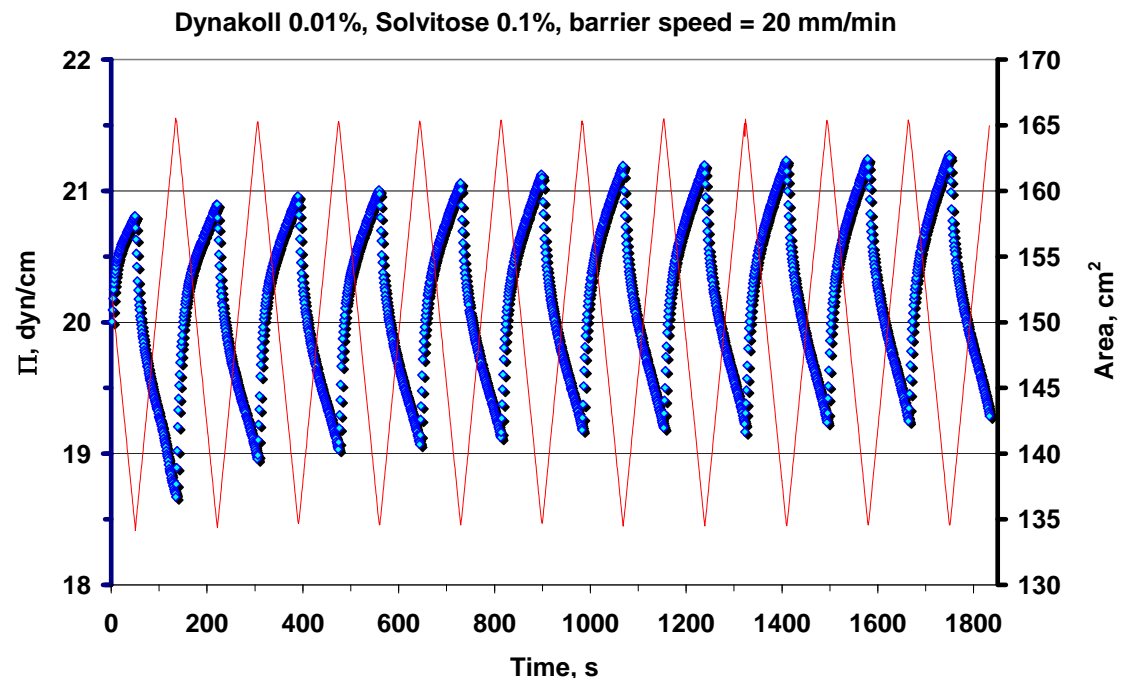
If shear is not important for a particular system:

$\gamma$  – the relative area expansion,

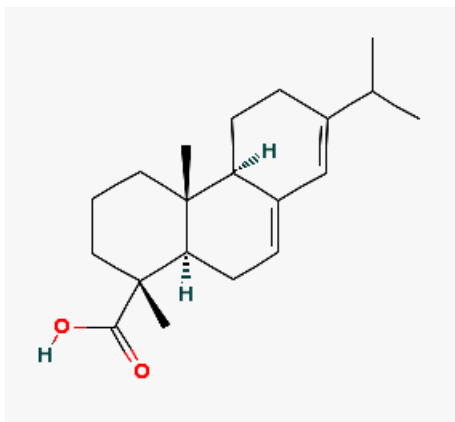
$$d\gamma = dA/A, \quad \gamma = \ln(A/A_0) \equiv \alpha$$



The surface pressure is measured with Wilhelmy plate (made of chromatographic paper)

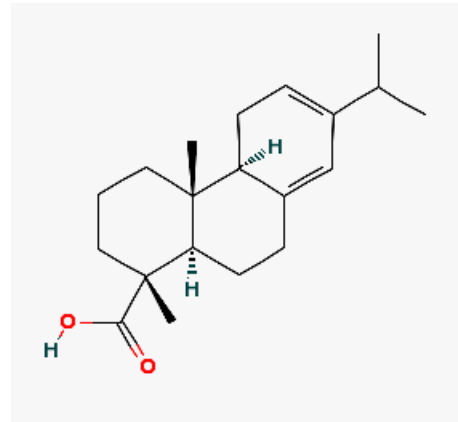


## Linear viscoelasticity – Extended Maxwell Model



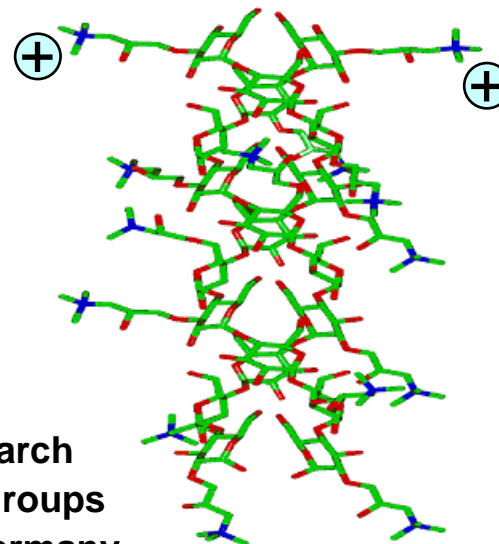
Abietic acid

Dynakoll VS 50 FS from Akzo Nobel



Levopimaric acid

~4-4.5% trimethylammonium-groups  
Solvitose BPN from AVEBE Germany



Cationized starch

The negatively charged acids adsorb easily; to them, polymer molecules with cationic groups can attach

In the Langmuir trough:

For small deformations,  $d\gamma / dt \approx \text{constant}$ . Hence,  
for the particular rheological model:

$$\tau = \eta \frac{d\gamma}{dt} \left\{ 1 - \exp \left[ - \frac{G_1}{\eta(d\gamma / dt)} \gamma \right] \right\} + G_2 \gamma$$

We use the model  
with two elasticities  
and one (apparent)  
viscosity

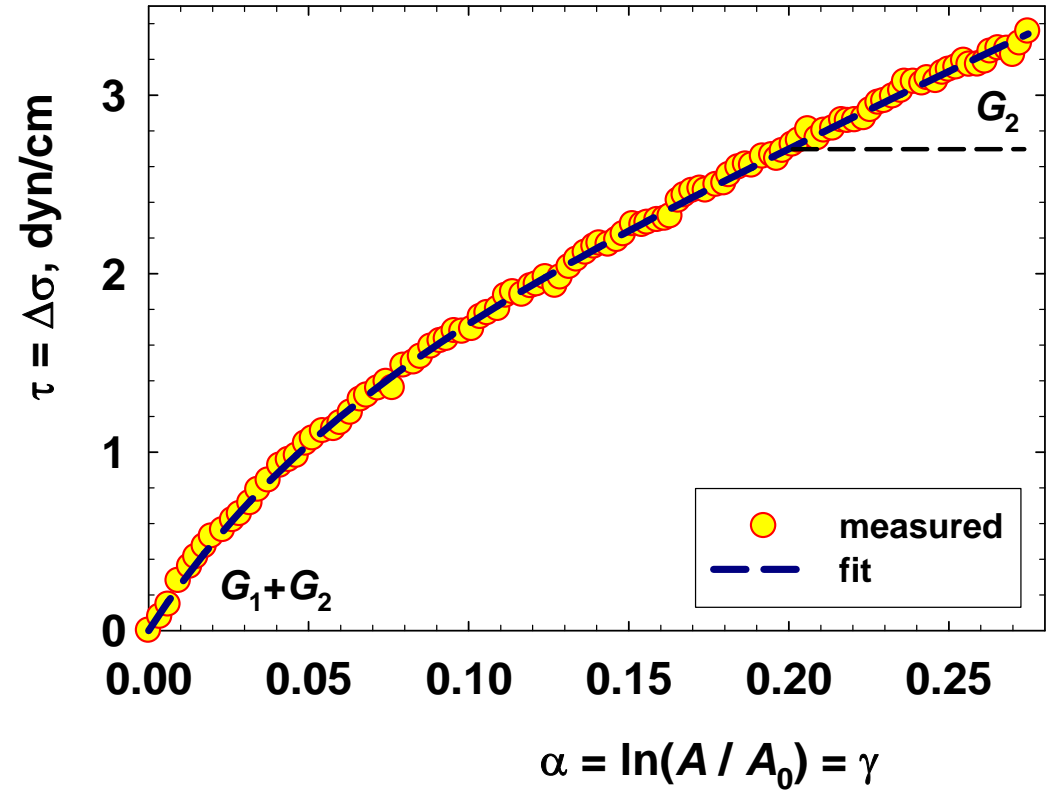
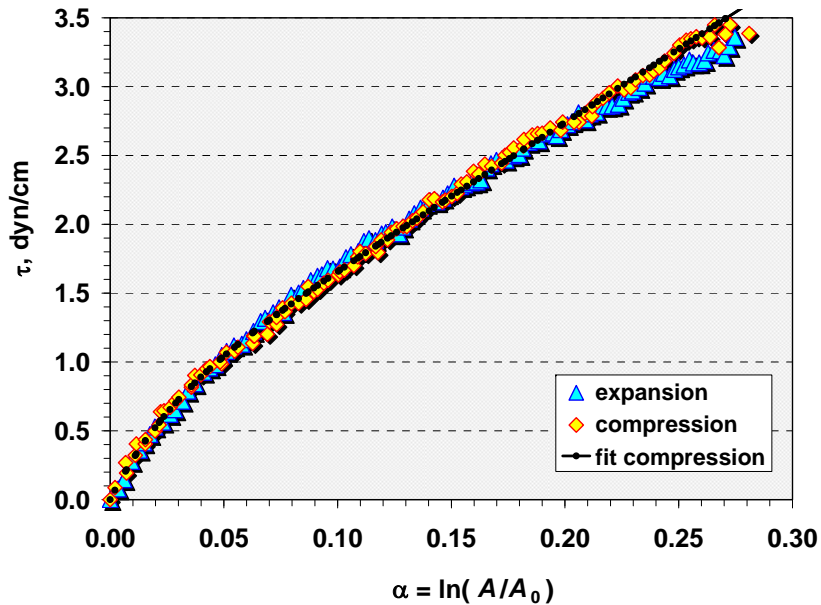
The experimental dependence  $\tau(\gamma)$  is fitted;  
 $G_1$ ,  $G_2$  and  $\eta$  are determined.

Rheological parameters (at  $d\gamma/dt = 0.00247 \text{ s}^{-1}$ )

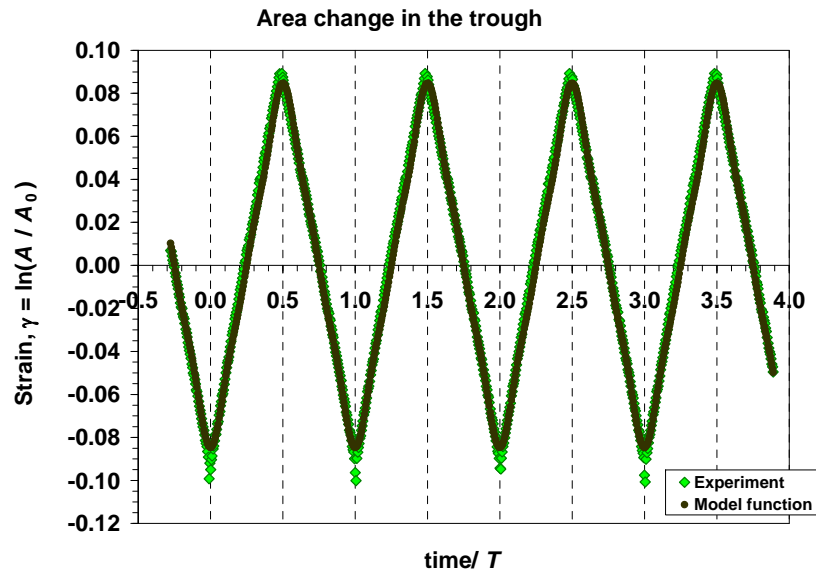
System	$\sigma$ , dyn/cm	$G_1+G_2$ , dyn/cm	$G_1$ , dyn/cm	$G_2$ , dyn/cm	$\eta$ , dyn.s/cm
1. Dyn. 0.01%, Solv. 0.1%, 40°C (expansion)	51.1	27.37	19.02	8.35	427.8
1a. Dyn. 0.01%, Solv. 0.1%, 40°C (compression)	50.9	32.88	22.20	10.68	244.3

**Data from  
Langmuir trough**

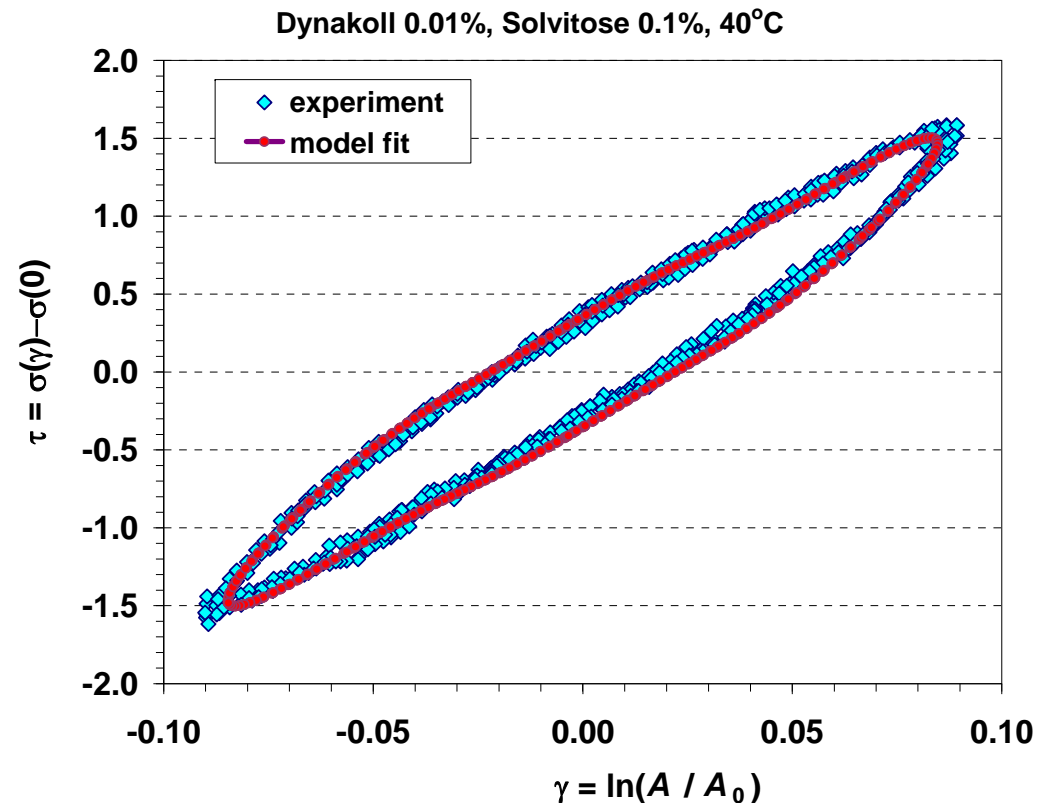
$d\gamma/dt = 0.00247 \text{ s}^{-1}$



# Oscillatory Stress



Alternative way to analyse data:  
The oscillatory strain  $\gamma(t)$  is inserted into the constitutive equation, and the solution for  $\tau(t)$  is found in the form of Fourier series.



$$\sigma(\gamma=0) = 23.4 \text{ dyn/cm}$$

$$G_1 = 12.8 \text{ dyn/cm}$$

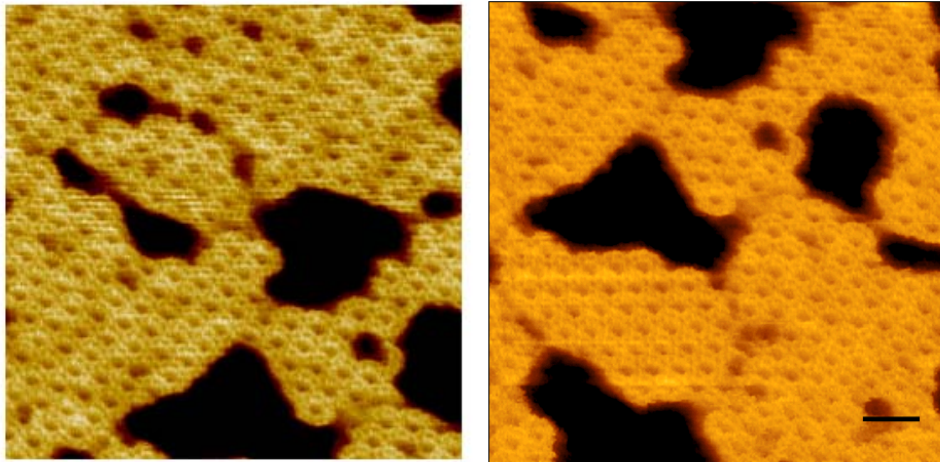
$$G_2 = 13.6 \text{ dyn/cm}$$

$$\eta = 206.4 \text{ dyn.s/cm}$$

It is impossible to fit the results with only one  $G$  and  $\eta$ .

# Shear Elasticity – Entangled Gel-Like Layers

Hydrophobins

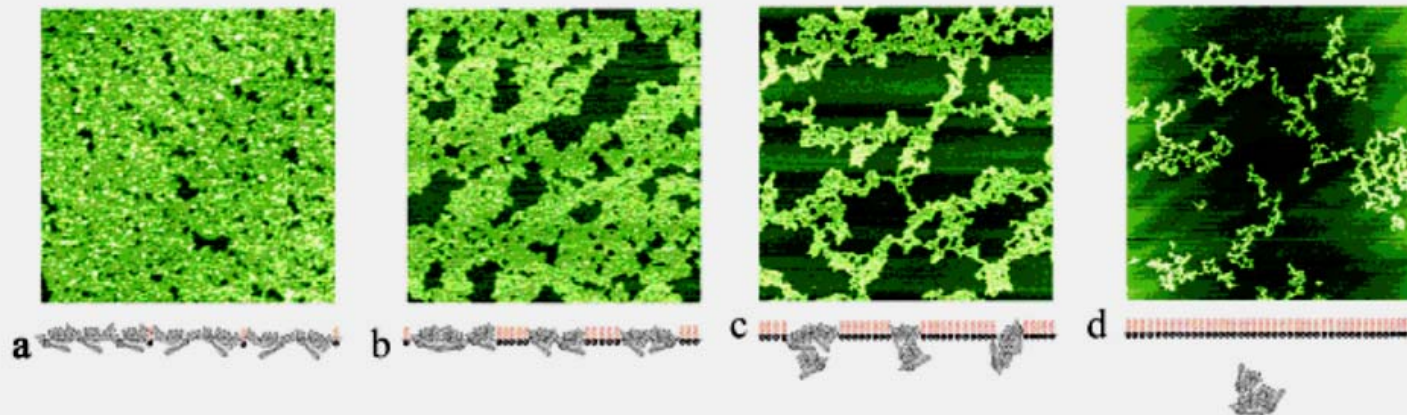
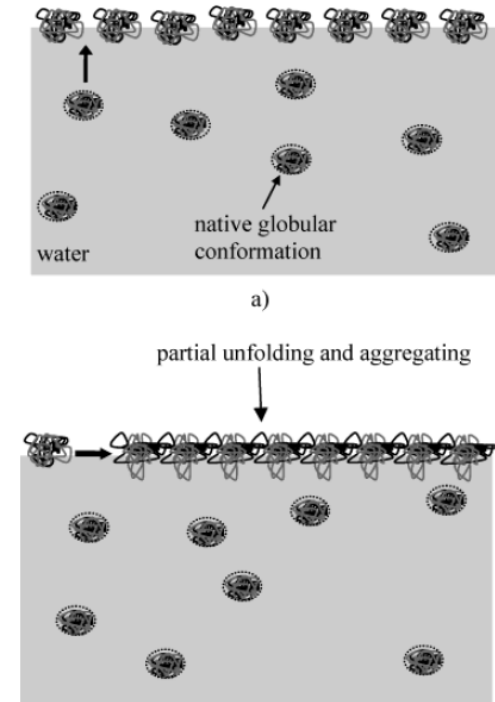


picture size – 100 nm

Paananen et al, Biochemistry 2003

Figure 5. HFBI self-assembles at the air-water interface into a hexagonally ordered monolayer. Imaged with tapping mode AFM in air, image size is 100 nm x 100 nm. (Image courtesy of Arja Paananen.)

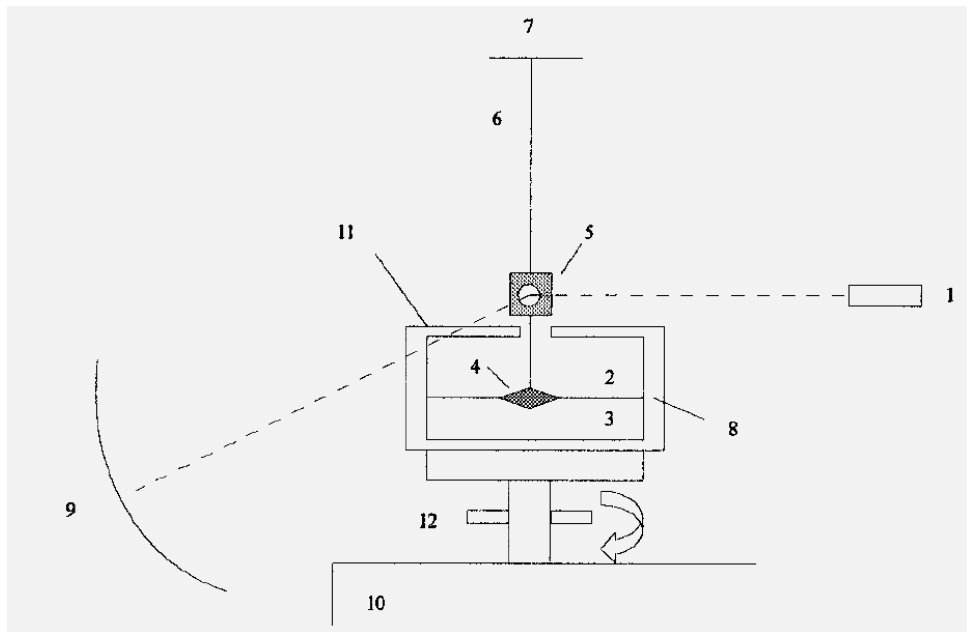
Proteins,  
Polymers,  
...



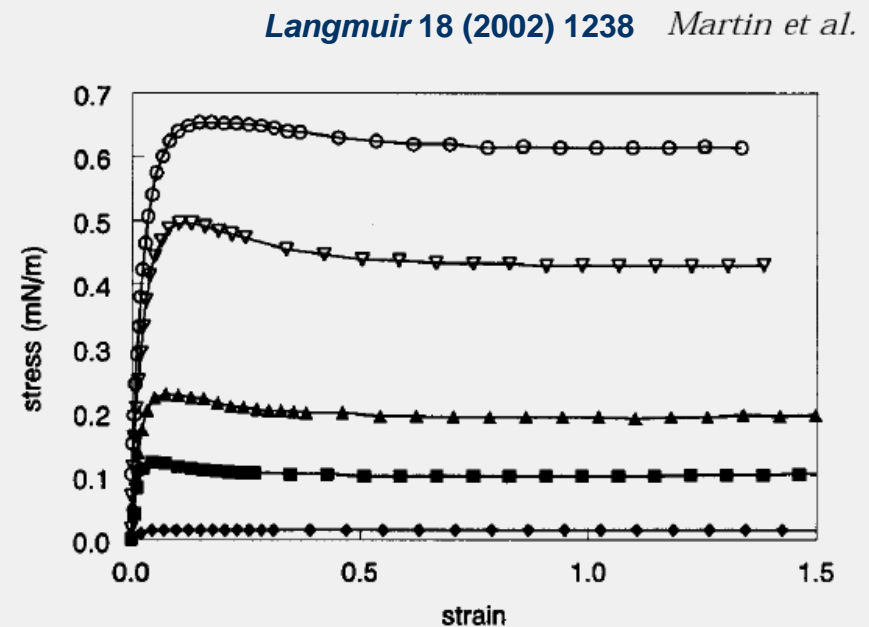
AFM data showing displacement of a B-lactoglobulin protein film (green) from an air-water interface by progressive addition of surfactant Tween 20 (black). Image sizes (a) 1.0 x 1.0 μm, (b) 1.6 x 1.6 μm, (c) 3.2 x 3.2 μm and (d) 10.0 x 10.0 μm. A schematic model of the displacement is illustrated below the images.

# Rheological Behavior under Shear

- ❖ Specific conformation on the interface – irreversible adsorption
  - ❖ Aggregation – 2D network ( $\neq$  from phase transition – spots of condensed phase)
- Shear elasticity  $\rightarrow$  solid-like behavior



**Figure 1.** The setup of the surface shear rheometer: 1, light source; 2, air; 3, protein solution; 4, biconical disk; 5, mirror; 6, torsion wire; 7, support for wire; 8, thermostated water in water jacket; 9, circular scale; 10, vibration-free bench; 11, Perspex lid; 12, coq for attachment to motor.

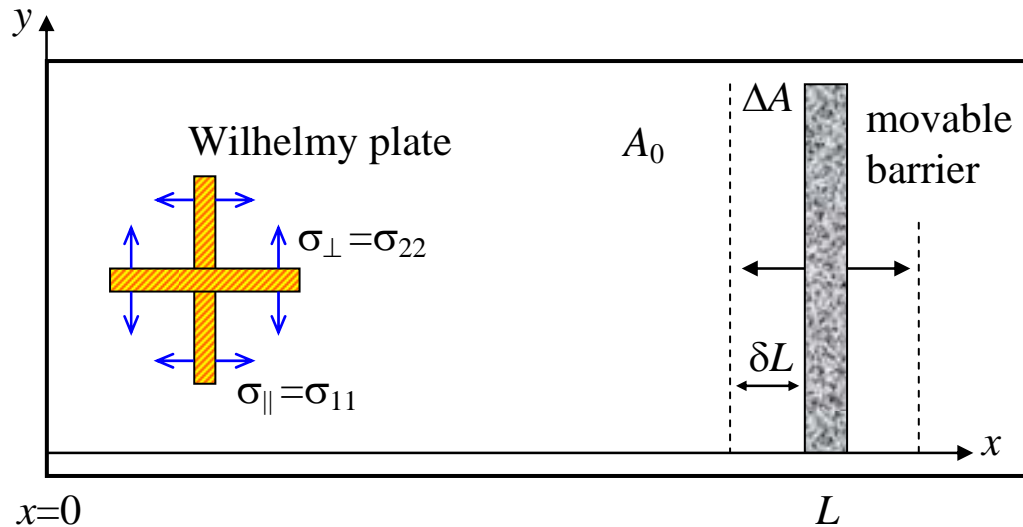


**Figure 4.** Stress–strain curve for  $\beta$ -lactoglobulin (0.1 g/L, pH 6.7, 30 mM) at different aging times of the protein film: (◆)  $t = 0$  h 53 min; (■)  $t = 2$  h 30 min; (▲)  $t = 3$  h 53 min; (▽)  $t = 5$  h 53 min; (○)  $t = 7$  h 07 min.

## Plastic behavior (Bingham)



# Anisotropic Stress Method



The deformation is anisotropic  
 $\Rightarrow$  for solid-like layers, the measured  $\sigma$  will depend on the orientation of the Wilhelmy plate.

Langmuir trough:  
 Uniaxial deformation =  
 = Superposition of dilatation and shear

In the case of **pure elasticity**:

$$\Delta\sigma_j = K(u_1 + u_2) + 2\mu\left[u_j - \frac{1}{2}(u_1 + u_2)\right] \quad j=1,2 \quad (1)$$

$u_1$  refers to the direction perpendicular to the barriers, while  $u_2$  is in parallel direction. For uni-axial deformation,  $u_1 = \ln(A/A_0)$ ,  $u_2 = 0$ . With  $\alpha \equiv \ln(A/A_0)$ , Eq. (1) becomes

$$\Delta\sigma_1 = (K + \mu)\alpha = \Delta\sigma_{\parallel} \quad ; \quad \Delta\sigma_2 = (K - \mu)\alpha = \Delta\sigma_{\perp} \quad (2)$$

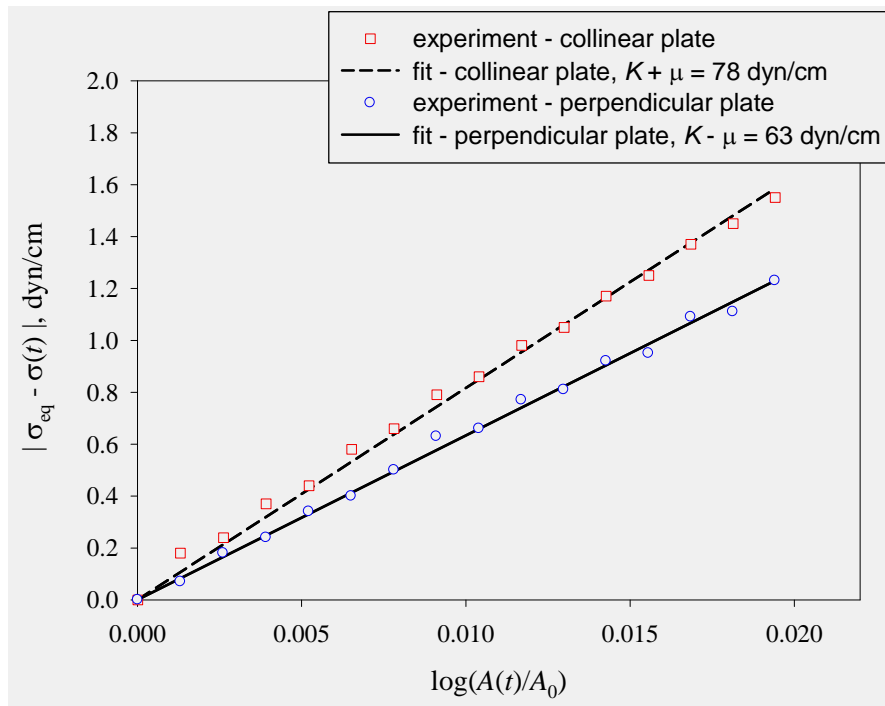
$\Delta\sigma_1$ , acting perpendicularly to the barriers, is measured when the Wilhelmy plate is oriented in parallel with the barriers, hence the notation  $\Delta\sigma_{\parallel}$  (similar reasoning holds for  $\Delta\sigma_{\perp}$ ). Dilatation ( $K$ ) and shear ( $\mu$ ) elasticity moduli:

$$K + \mu = \frac{d\sigma_{\parallel}}{d \ln A} \quad ; \quad K - \mu = \frac{d\sigma_{\perp}}{d \ln A} \quad (3)$$

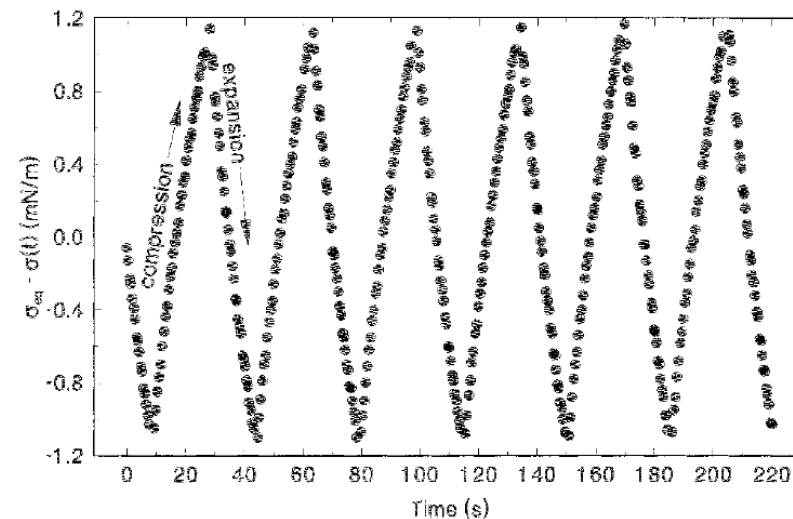
# Anisotropic Stress Method

## Dilatational and shear elasticity of BLG layers: after ageing for hours, or at high concentrations

*Petkov et al.*



**Figure 2.** Elastic stress response of the surface, as a function of the relative area deformation during expansion for two different orientations of the Wilhelmy plate: collinear (squares), and perpendicular (circles). The system contains  $1 \times 10^{-4}$  wt% BLG and 0.15 M NaCl (at the "natural" pH, 6.2). **The interface was aged overnight.**



**Figure 4.** A typical reading of the sensor for the surface tension measurement, as a result of periodic compression/expansion of the layer. The system contains 0.1 wt %  $\beta$ -lactoglobulin. The barrier rate was set to 0.5 mm/s.

# Anisotropic Stress – Visco-Elastic Behavior

$$\tau_{11,el} = (K + \mu)u_{11,el}$$

$$\tau_{22,el} = (K - \mu)u_{11,el}$$

$$\tau_{11,visc} = (\zeta_s + \eta_s)D_{11,visc}$$

$$\tau_{22,visc} = (\zeta_s - \eta_s)D_{11,visc}$$

In the frames of the Maxwell model:

$$\tau_{11} = \tau_{11,el} = \tau_{11,visc}$$

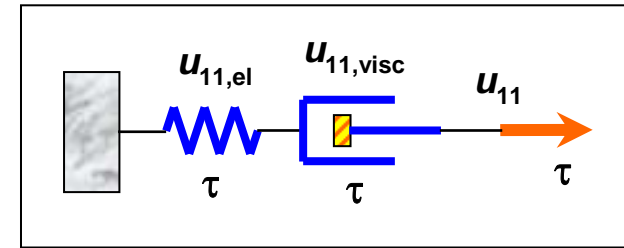
$$\tau_{22} = \tau_{22,el} = \tau_{22,visc}$$

$$u_{11} = u_{11,el} + u_{11,visc}$$

$$D_{11} = D_{11,el} + D_{11,visc}$$

where  $\frac{d}{dt}u_{11,el} = D_{11,el}$  ;  $\frac{d}{dt}u_{11,visc} = D_{11,visc}$  is the rate of strain.

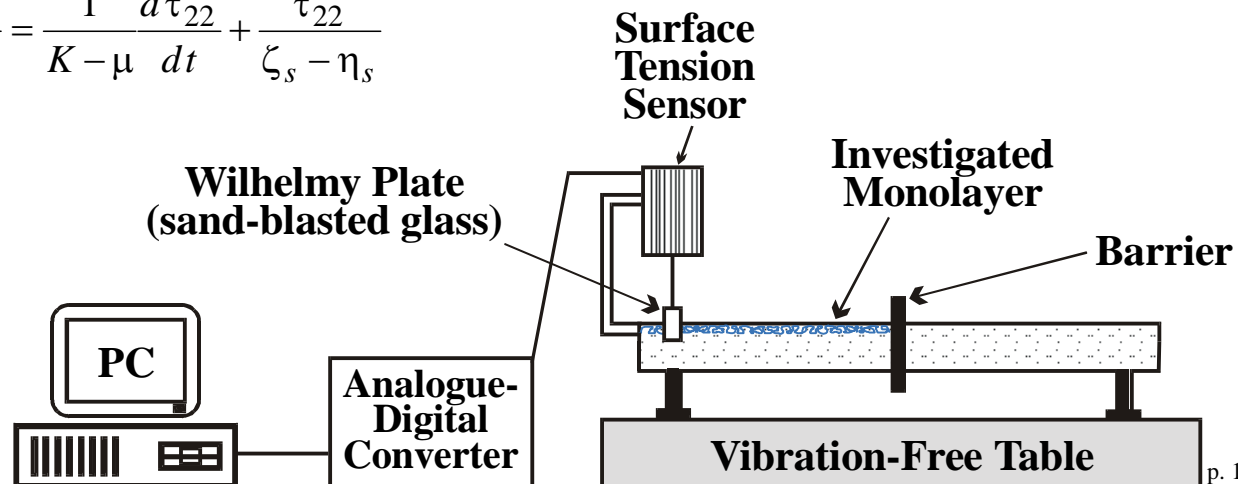
$$u_{22} = 0$$



The displacement is a linear function of the  $x$ -coordinate, and  $u_{11}, D_{11}$  do not depend on  $x$ . In such a case the rate of total deformation is

$$D_{11} = \frac{d\alpha}{dt}, \text{ where } \alpha = u_{11} = \ln \frac{A}{A_0}.$$

$$\frac{d\alpha}{dt} = \frac{1}{K + \mu} \frac{d\tau_{11}}{dt} + \frac{\tau_{11}}{\zeta_s + \eta_s}; \quad \frac{d\alpha}{dt} = \frac{1}{K - \mu} \frac{d\tau_{22}}{dt} + \frac{\tau_{22}}{\zeta_s - \eta_s}$$



## Anisotropic Stress – Visco-Elastic Behavior

In the Langmuir trough, we carry out deformation with constant rate (fixed  $d\alpha/dt$ ). Then,

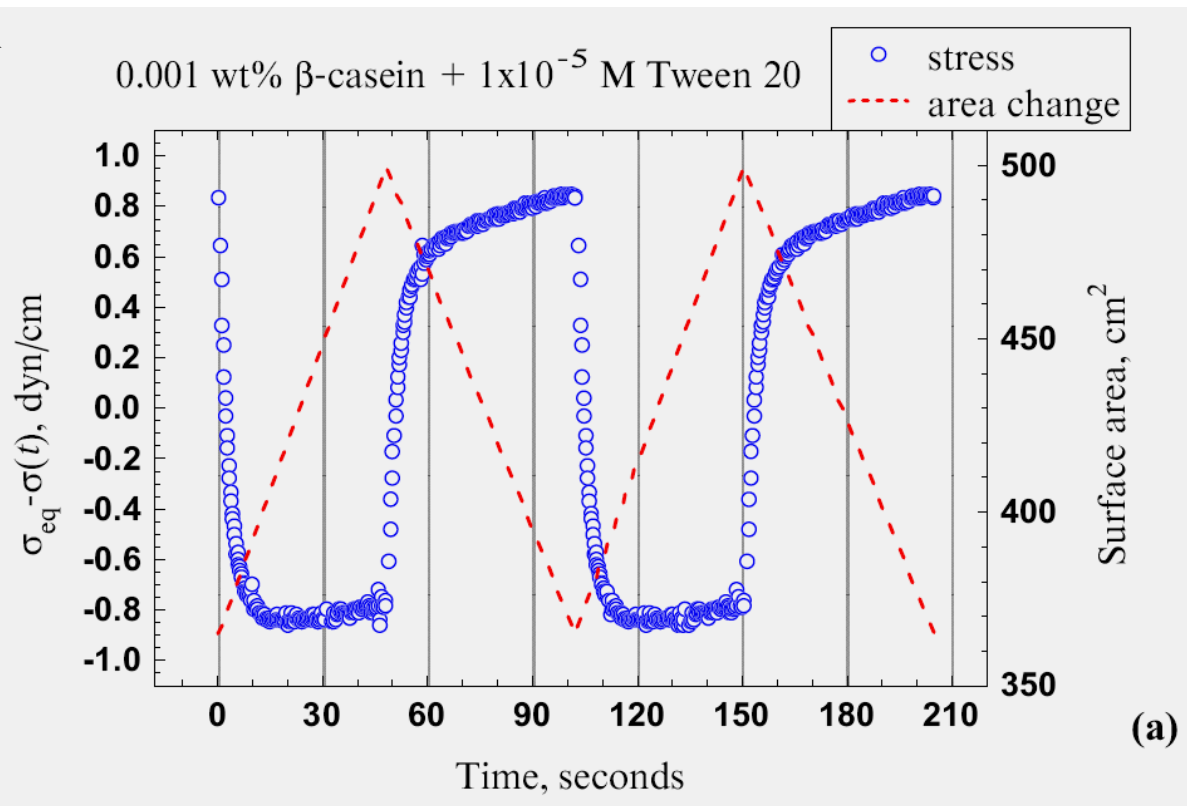
$$\tau_{11}(t) = \left[ \tau_{11}(0) - \frac{d\alpha}{dt}(\zeta_s + \eta_s) \right] \exp\left( -\frac{K + \mu}{\zeta_s + \eta_s} t \right) + \frac{d\alpha}{dt}(\zeta_s + \eta_s)$$

$$\tau_{22}(t) = \left[ \tau_{22}(0) - \frac{d\alpha}{dt}(\zeta_s - \eta_s) \right] \exp\left( -\frac{K - \mu}{\zeta_s - \eta_s} t \right) + \frac{d\alpha}{dt}(\zeta_s - \eta_s)$$

besides,  $\tau_{11} = \sigma_{\parallel} - \sigma_{eq}$  ;  $\tau_{22} = \sigma_{\perp} - \sigma_{eq}$

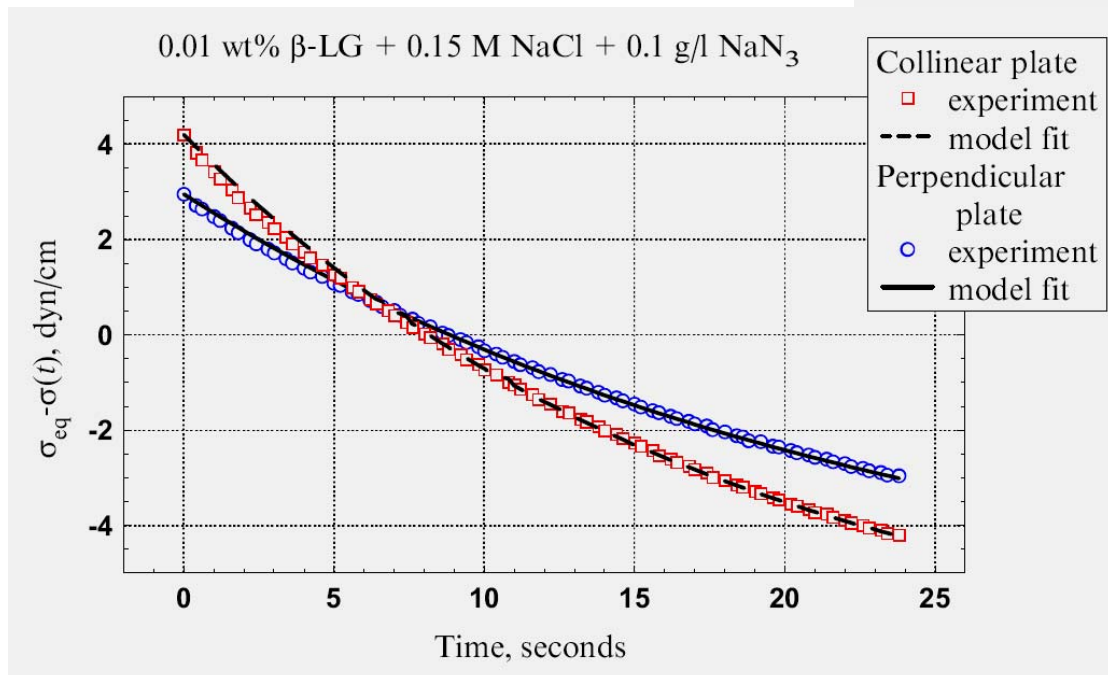
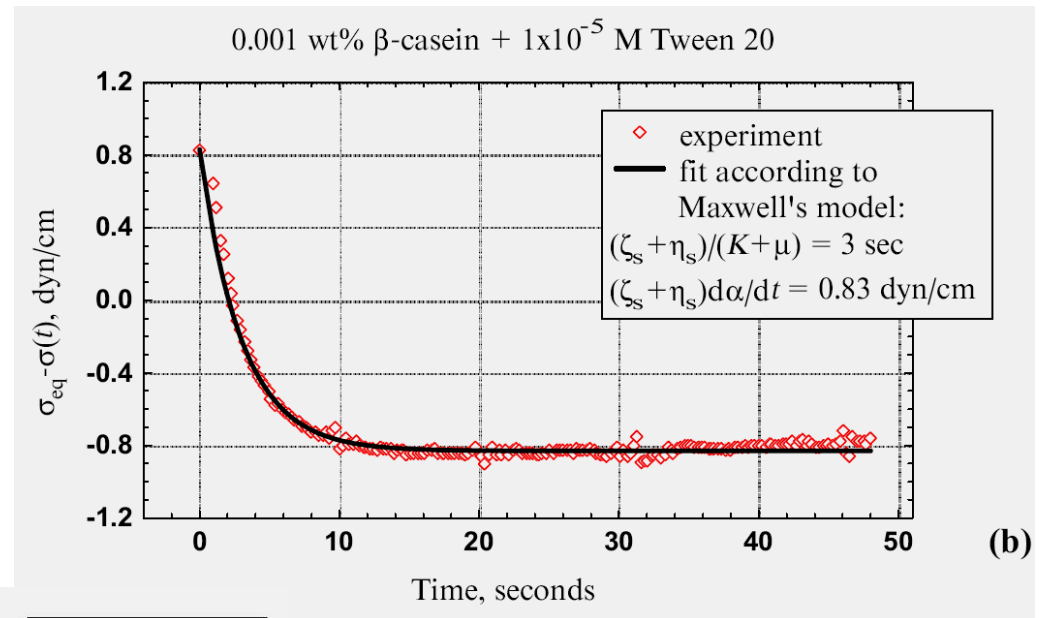
The functions  $\tau_{11}(t)$ ,  $\tau_{22}(t)$  are fitted with the model expressions.

- If the shear parameters are negligible, then  $\tau_{11} = \tau_{22}$ .
- The viscous dissipation leads to curvature of the plot.
- Difference between compression and expansion.



# Anisotropic Stress – Visco-Elastic Behavior

Data fit  $\Rightarrow$   
 Values of the material parameters  
 $K, \mu, \zeta_s, \eta_s$   
 (see the Table below).



We observe different types of rheological behavior

# Surface Rheological Behavior of Proteins

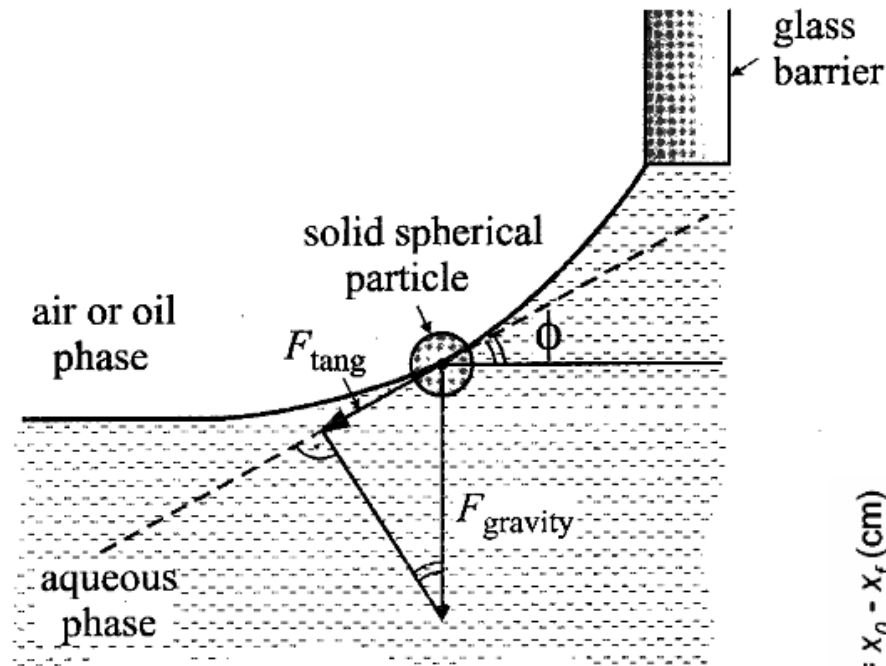
**TABLE 1.** Summary of results for the studied systems

No.	System	Type of rheological behavior	Determined parameters (expansion)
1	BLG $1 \times 10^{-4}$ wt% + 0.15 M NaCl Freshly prepared	<b>Dilatational elasticity only</b> No shear elasticity No viscous dissipation	$K = 53.0$ dyn/cm $\mu = 0$
2	BLG $1 \times 10^{-4}$ wt% + 0.15 M NaCl Aged overnight	<b>Dilatational and shear elasticity</b> No viscous dissipation	$K = 70.5$ dyn/cm $\mu = 7.5$ dyn/cm
3	$\beta$ -casein 0.001 wt% + $1 \times 10^{-5}$ M Tween 20	<b>Dilatational viscoelasticity</b> Negligible shear elasticity and viscosity	$K = 42.6$ dyn/cm $\mu \ll K$ $\zeta_s = 127.9$ dyn.s/cm $\eta_s \ll \zeta_s$
4	BLG 0.01 wt% + 0.15 M NaCl	<b>Full dilatational and shear visco-elasticity</b>	$K = 83.2$ dyn/cm $\mu = 16.2$ dyn/cm $\zeta_s = 1654.8$ dyn.s/cm $\eta_s = 113.9$ dyn.s/cm

**Globular protein – the ageing and the concentration are important.**

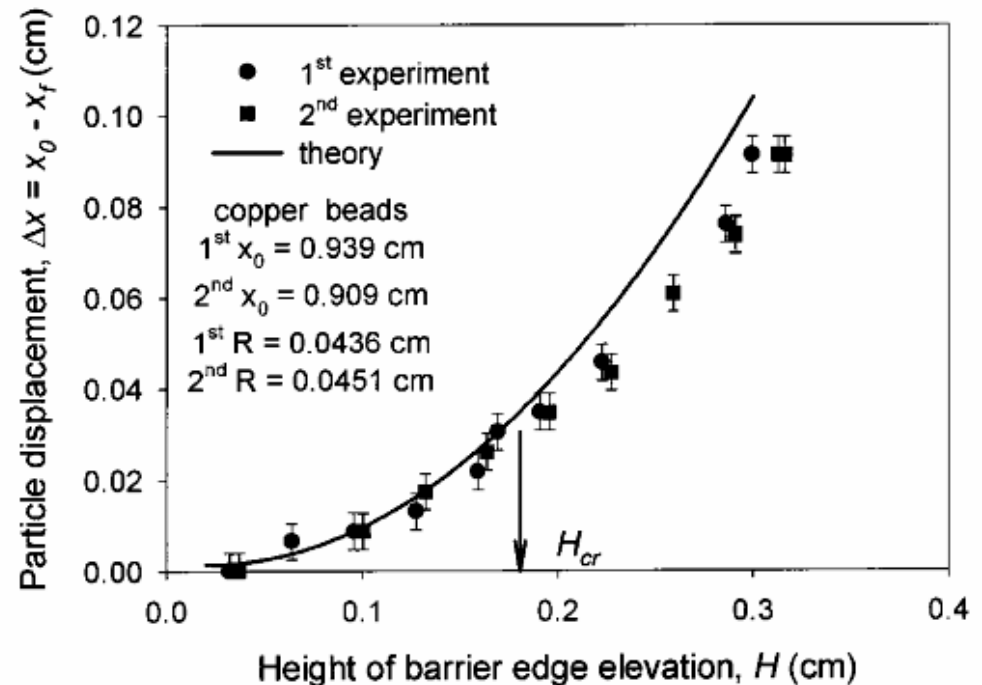
**Disordered protein – absence of network.**

# Method for Measuring the Surface Yield Stress

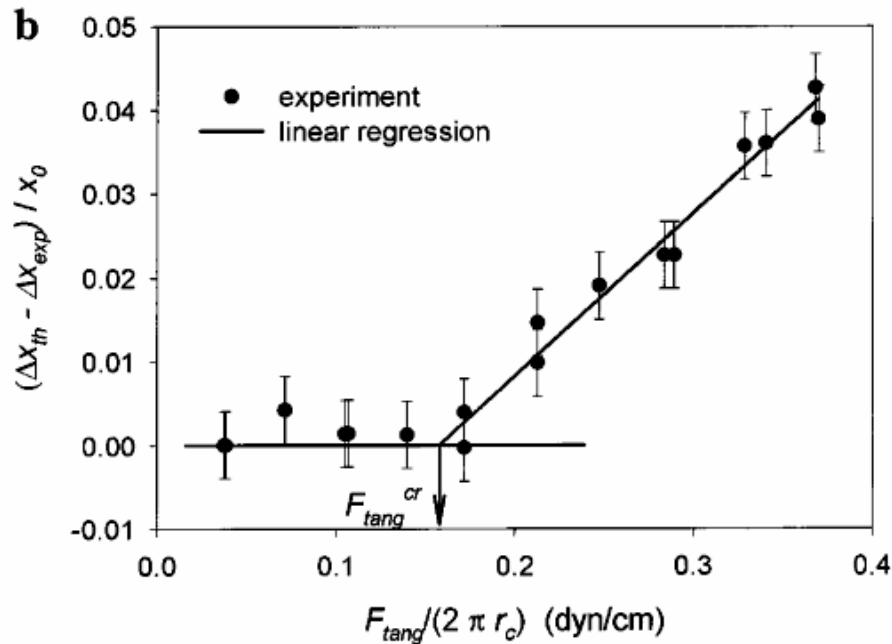


The barrier rises and the tangential force on the particle increases gradually, until the layer breaks. **The method is suitable for small stresses (starting from Zero).**

The layer breakdown is detected when the position of the particle starts to deviate from the predicted position according to the Laplace equation of capillarity (the curve).

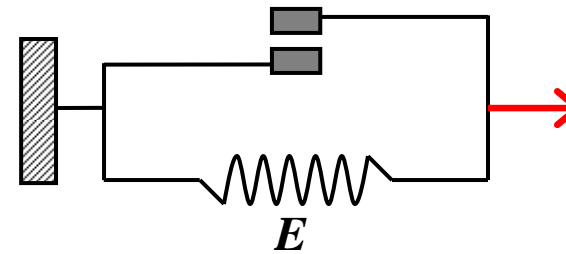


# Yield Stress of Entangled Protein Layers



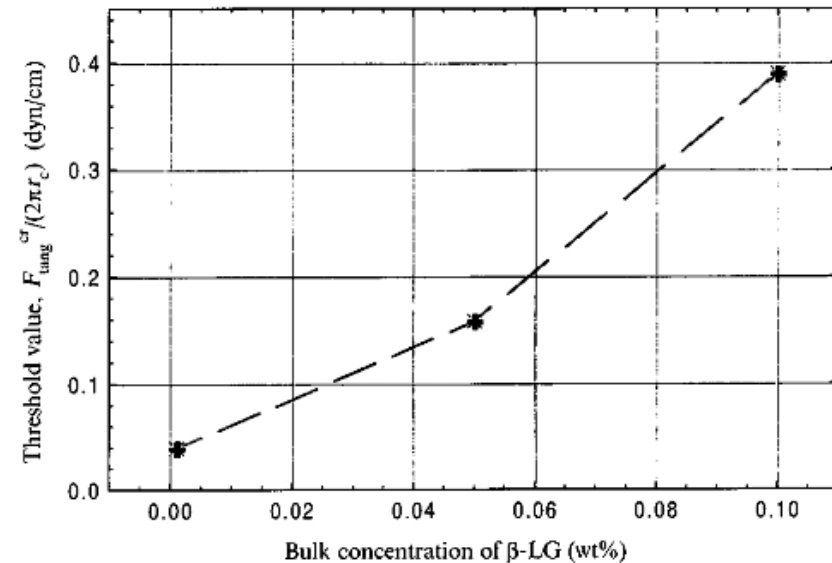
**Figure 6.** Dependence of the strain in the layer on the applied stress.  $\Delta x_{th} - \Delta x_{exp} = 0$  means that the particle follows exactly the displacement of the surface material points (and thus just serves as a marker). The system contains: (a) 0.001 wt %  $\beta$ -LG; (b) 0.05 wt %  $\beta$ -LG; (c) 0.1 wt %  $\beta$ -LG. No electrolyte was added; the pH was natural (6.2);  $T = 22^\circ\text{C}$ .

**With increasing protein concentration, the layer gains more strength (against disruption)**



**After the plastic element is activated, the behavior is elastic.**

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**Figure 7.** Concentration dependence of the yield threshold stress in adsorbed protein layers.



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