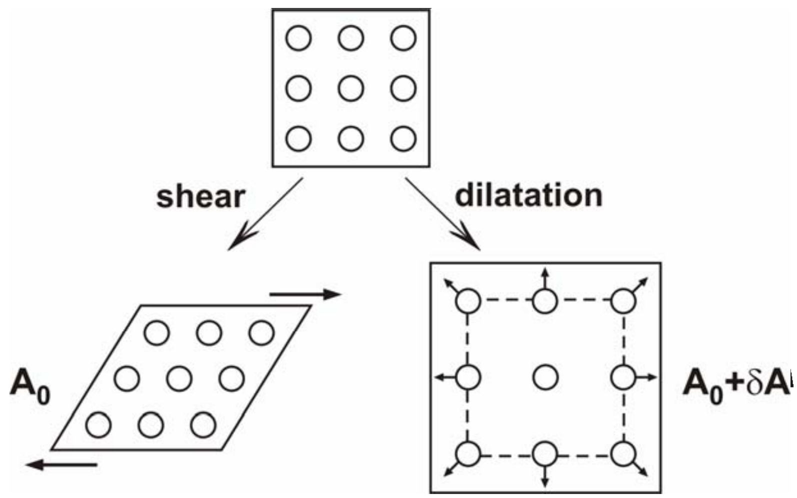
# Interfacial dynamics

**Interfacial dynamics = dynamic processes at fluid interfaces upon their deformation**




**Interfacial rheological properties: elasticity, viscosity, yield stress, …**

**Relation between macroscopic and molecular levels of description?!**

## Aims of presentation:

- **Basic concepts in interfacial dynamics.**
- **Illustrative examples.**

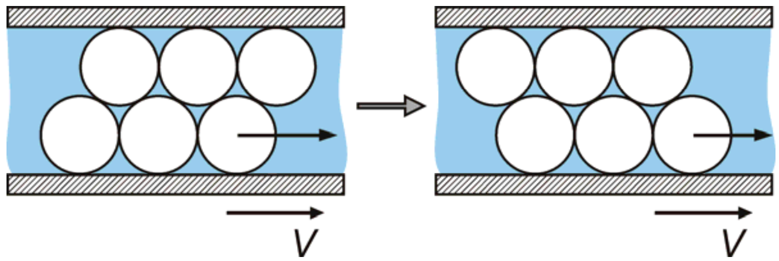
## A. Role of interfacial dynamics.

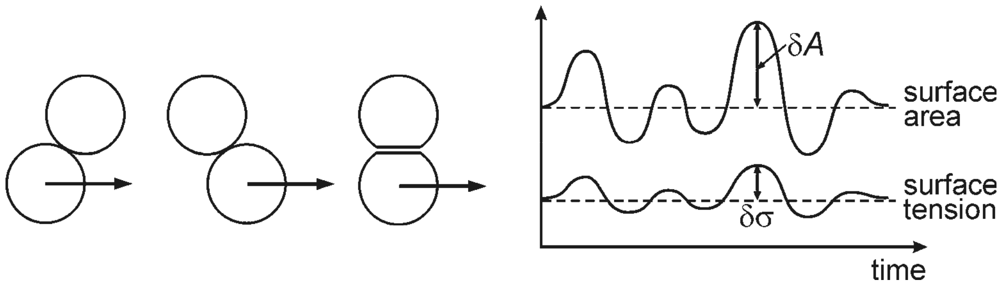
## B. Interfacial rheology.

## C. Foam-wall viscous friction.

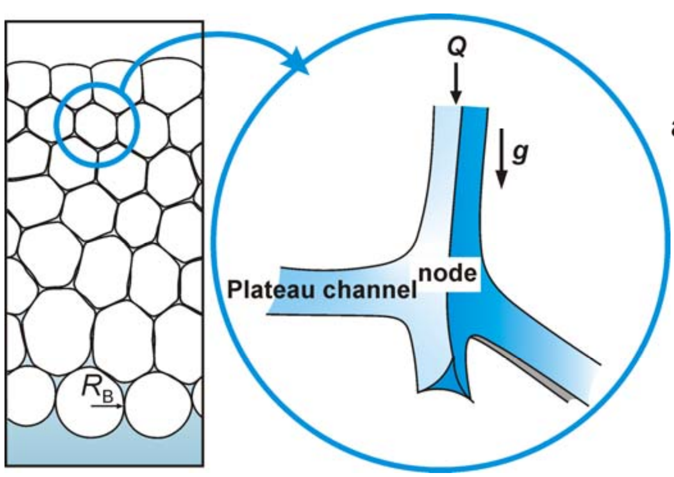
# A. Role of interfacial dynamics in foams - two selected examples

## 1. Surface perturbations in foam rheology

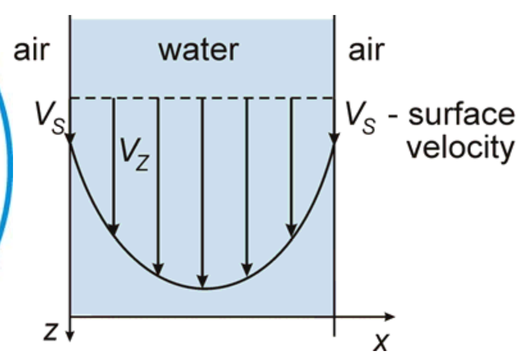



## 2. Surface stress in the process of foam drainage




**Longitudinal section of the Plateau channel**




**Viscous bulk stress**

$$\boxed{\tau_V = \mu \frac{dV_z}{dx}}$$

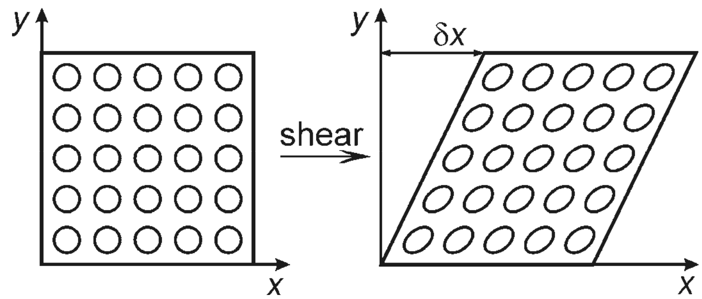
**Matching bulk and surface flows**

$$V_S = V_Z\left(x = 0\right)$$

$$\tau_S = \tau_V \qquad \boxed{\tau_S = ?}$$

# B. Interfacial rheology.

## 1. Phenomenological approach - shear deformation




$$\alpha_S = \frac{\delta x}{y}$$

**Surface shear elasticity**

$$\tau_S = E_S \alpha_S$$

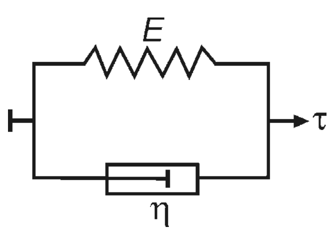
**Surface shear viscosity**

$$\tau_S = \eta_S \frac{d\alpha_S}{dt} = \eta_S \dot{\alpha}_S$$

**The shear rheological properties are sensitive to the molecular interactions in the adsorption layer.**

## More complex models (constitutive equations)

### Visco-elastic (Kelvin)

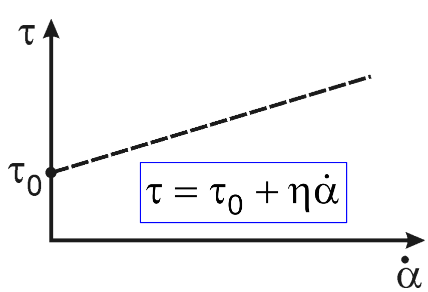



$$\tau = E\alpha + \eta\dot{\alpha}$$

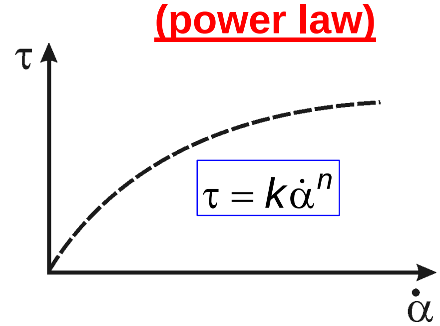
### Visco-elastic (Maxwell)


$$\dot{\alpha} = \frac{\dot{\tau}}{E} + \frac{\tau}{\eta}$$

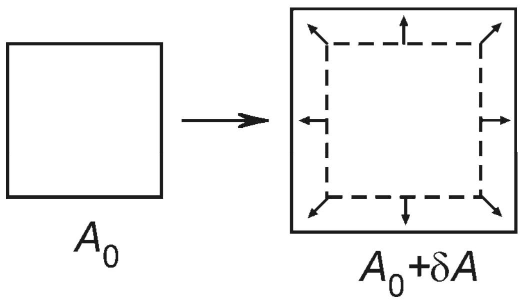
### Visco-plastic (Bingham)




### Shear thinning (power law)



# 2. Phenomenological approach - dilatational deformation.

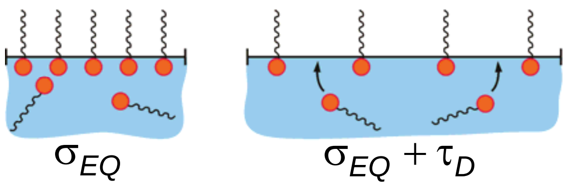



**Surface dilatational elasticity**

$$\tau_d = E_d \alpha_d \qquad \alpha_d = \frac{\delta A}{A_0}$$

**For insoluble monolayers:**

$$\Delta\sigma = E_G \alpha_d \ \Rightarrow \ \boxed{E_d = E_G} = \frac{d\sigma}{d\ln A}$$

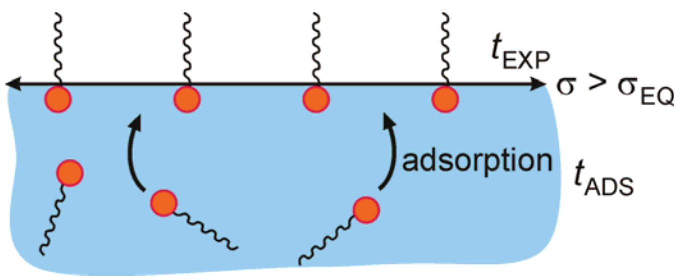



**Surface dilatational viscosity**

$$\tau_d = \eta_d \dot{\alpha}_d \qquad \dot{\alpha}_d = \frac{d\alpha_d}{dt} = \frac{d(\ln A)}{dt}$$

**The dilatational rheological properties are sensitive to both, molecular interactions and adsorption kinetics**

# Apparent viscosity



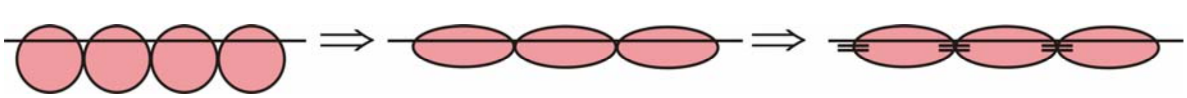

**Characteristic times:**

- **Experimental time, $t_{\mathrm{EXP}}$**
- **Adsorption time, $t_{\mathrm{ADS}}$**

$$\tau_d \equiv \delta\sigma = \left(\frac{d\sigma}{d\Gamma}\right)\delta\Gamma = -\left(\frac{d\sigma}{d\Gamma}\right)\frac{\delta A_M}{A_M^2} = -\left(\frac{d\sigma}{d\ln\Gamma}\right)\delta\ln A_M$$

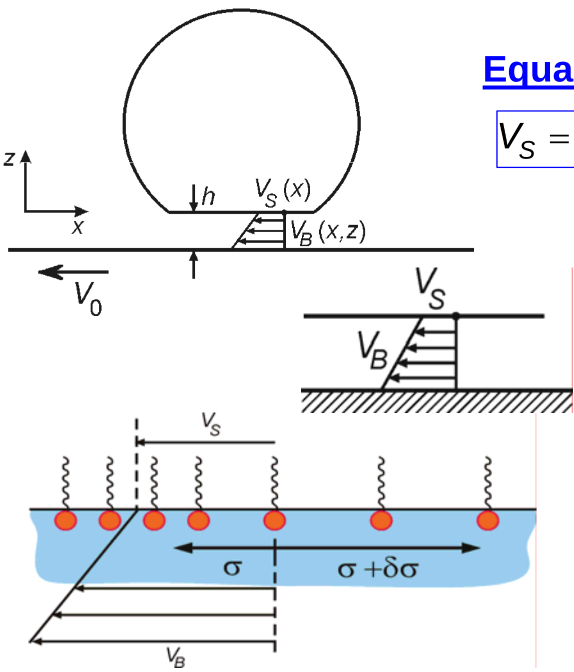
$$\approx E_G\left(\frac{t_{\mathrm{ADS}}}{t_{\mathrm{EXP}}}\right)\delta\ln A \approx \left(E_G\, t_{\mathrm{ADS}}\right)\left(\frac{\delta\ln A}{t_{\mathrm{EXP}}}\right) = \mu_{APP}\,\dot{\alpha}_d$$

- **Similarly for the molecule rearrangement in the monolayer, $t_{\mathrm{R}}$**



# Coupling between bulk and surface flows

## 1. Balance of bulk and surface stress




**Equal velocities**

$$\boxed{V_S = V_B\left(z = z_S\right)}$$

**Stress balance**

$$\boxed{\tau_B = \tau_S}$$

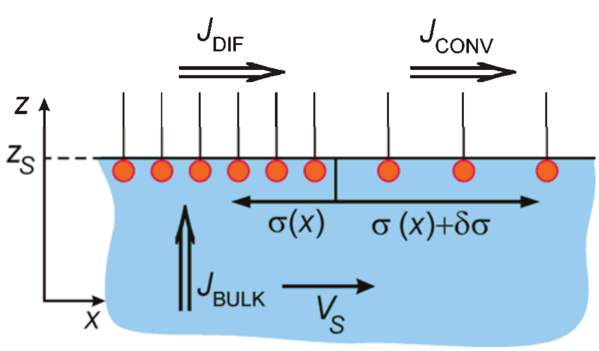
**Bulk viscous stress**

$$\boxed{\tau_B = \mu \frac{\partial V_x}{\partial z} \approx \mu \frac{V_0}{h}}$$

**Surface stress**

$$\boxed{\tau_S = \underbrace{-\frac{d\sigma}{dx}}_{\text{surface elasticity}} + \underbrace{\mu_S \frac{d^2u}{dx^2}}_{\text{surface viscosity}}}$$

## 2. Surface mass balance for the surfactant




$$\frac{\partial \Gamma}{\partial t} = -D_S \frac{\partial \Gamma}{\partial x} + \frac{\partial \left(V_S \Gamma\right)}{\partial x} + J_{BULK}$$

$$J_{BULK} = -D_B \left(\frac{\partial C}{\partial z}\right)_{z=z_S}$$

**Equations for determining**

**$\Gamma(x,t)$ and $\sigma(x,t)$**

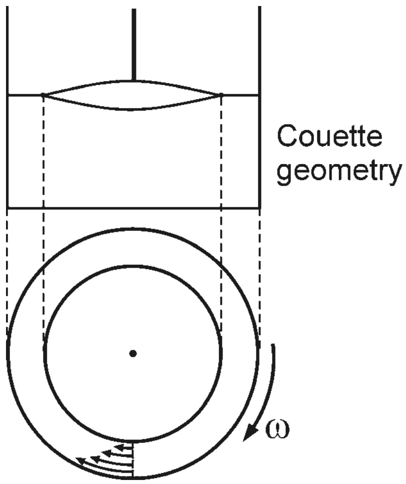
$$\sigma = \sigma\left(\Gamma\right)$$

**Coupled set of equations for $C(x,z)$, $V_x(x,z)$, $\Gamma(x)$, $V_S$**

**Very complex hydrodynamic problem!**

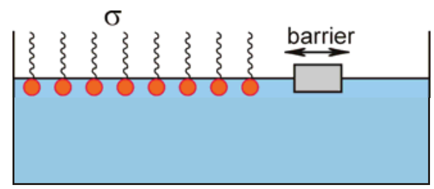
# Experimental methods for studying the interfacial rheological properties

## Shear mode



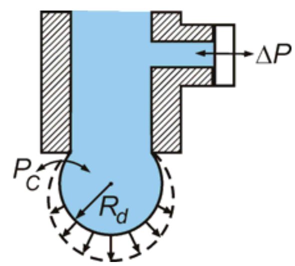

**Continuous shear or oscillations**

## Dilatational mode




$$\sigma(t) = \left(\sigma_{EQ} + \tau_D\right) = \left(\sigma_{EQ} + E_d\alpha_d + \eta_d\dot{\alpha}_d\right)$$

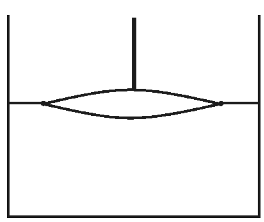
**Expanding or oscillating drop**



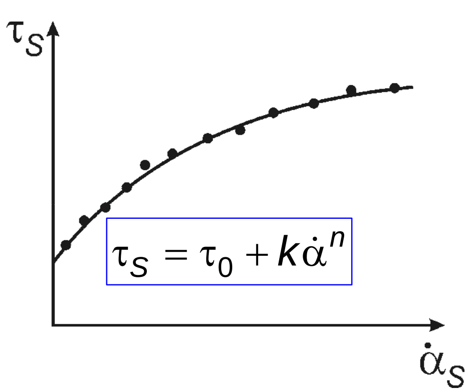

$$P_C = \frac{2\sigma}{R_d}$$

# 1. Continuous type of measurement (steady-state flow)

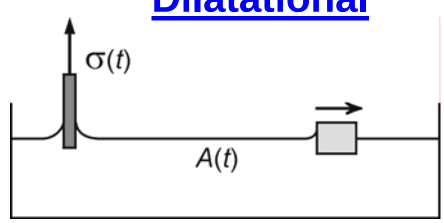
## Shear



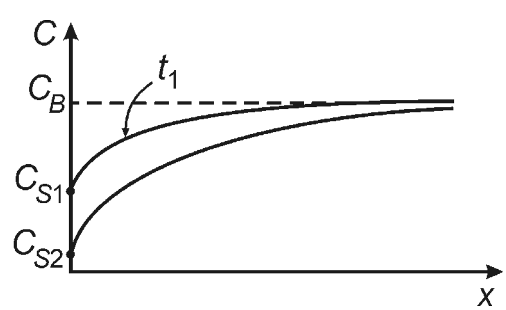
$$\tau_S = \tau_S\left(\dot{\alpha}_S\right)$$




## Dilatational



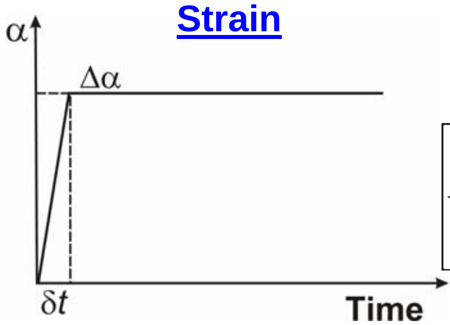

$$d\left(\ln A\right)/dt = \text{const}$$

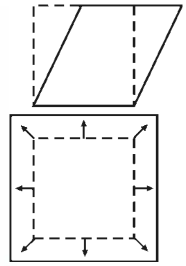



**For diffusion control, steady-state is difficult to achieve**

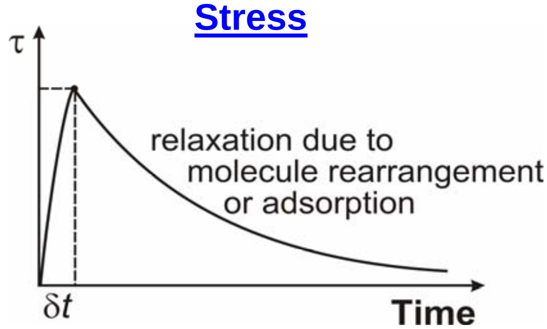
## 2. Stress-relaxation experiments

**Strain**



**Stress**




**Maxwell model**

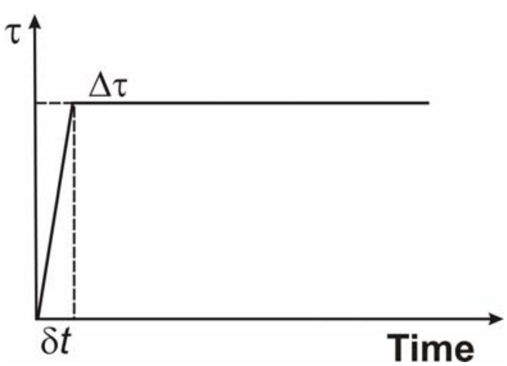

$$\boxed{\dot{\alpha} = \frac{\dot{\tau}}{E} + \frac{\tau}{\eta}}$$

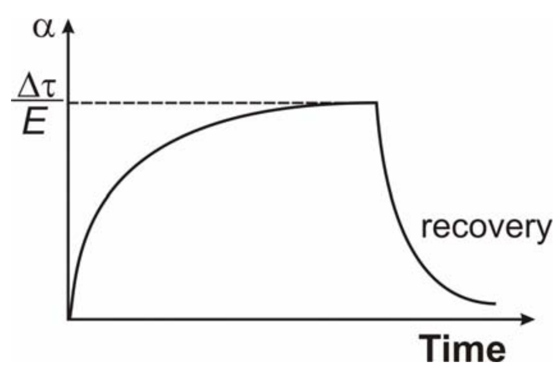
$$\boxed{\tau(t) = \Delta\alpha\, E \exp\left(-\frac{t}{t_R}\right)}$$

$$t_R = \eta / E \qquad E \approx \Delta\tau / \Delta\alpha$$

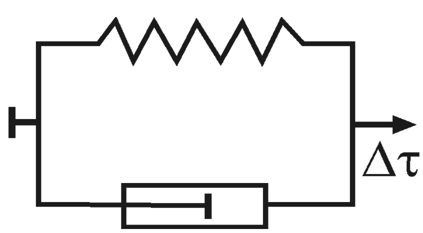
**The relaxation is not exponential for diffusion controlled adsorption**
**$\Delta\sigma(t) \propto 1/\sqrt{t}$**

## 3. Strain-relaxation experiments (creep flow)



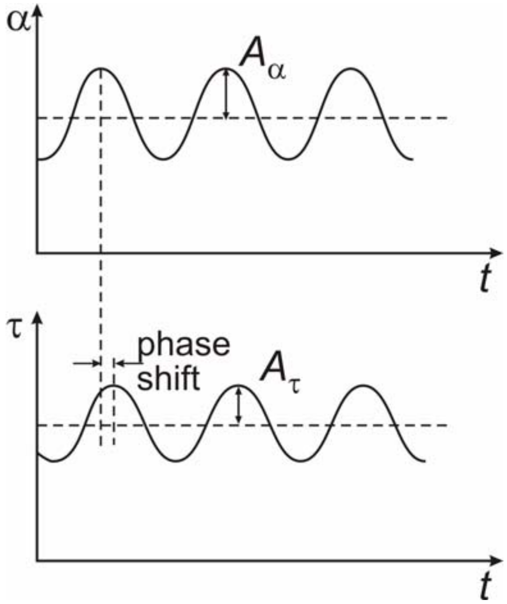




**Kelvin model**




$$\boxed{\alpha(t) = \frac{\Delta\tau}{E}\left[1 - \exp\left(-t / t_R\right)\right]}$$

# 4. Oscillatory measurements (shear, dilatation)




$$\boxed{A_\tau, \varphi \Rightarrow E(\omega), \eta(\omega)}$$

**Kelvin model**

$$\boxed{\tau = \tau_{EL} + \tau_V = E\alpha + \eta \frac{d\alpha}{dt}}$$

$$\boxed{\alpha = A_\alpha \sin(\omega t) \Rightarrow \dot{\alpha} = A_\alpha \omega \cos(\omega t)}$$

$$\boxed{\begin{aligned} \tau &= A_\alpha \left[E \sin(\omega t) + \eta\omega \cos(\omega t)\right] = \\ &= A_\tau \left[\sin(\omega t + \varphi)\right] \end{aligned}}$$

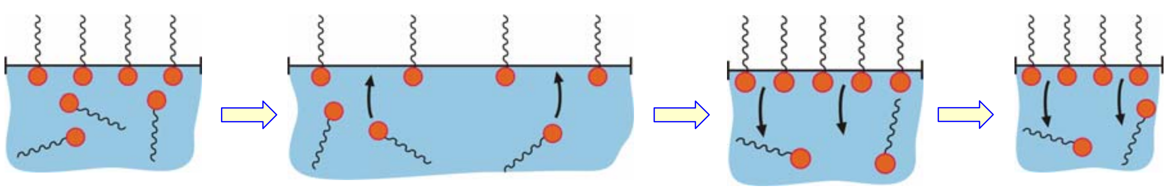
$$(A_\tau / A_\alpha) = \sqrt{E^2 + (\eta\omega)^2}$$

**surface modulus**

$$\sin\varphi = \frac{\eta\omega}{\sqrt{E^2 + (\eta\omega)^2}}$$

# Example: Diffusion controlled adsorption- dilatation

## (Lucassen, van den Tempel)

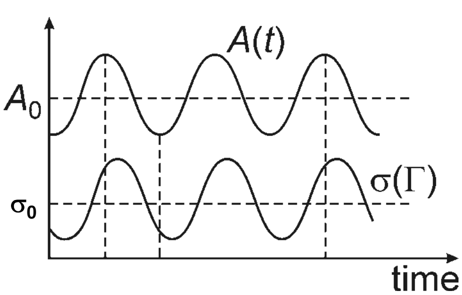


$A_0, \Gamma_0, \sigma_0$

$A_0 + \delta A_0$; $\Gamma < \Gamma_0$; $\sigma > \sigma_0$

$A_0$; $\Gamma > \Gamma_0$; $\sigma < \sigma_0$

$A_0 - \delta A_0$; $\Gamma > \Gamma_0$; $\sigma < \sigma_0$




**Elasticity**

$$\boxed{E(\omega) = E_G \frac{\omega_D + \sqrt{\omega_D/2}}{\omega_D + \sqrt{2\omega_D} + 1}} \qquad \omega_D = \frac{\omega}{D}\left(\frac{dr}{dC}\right)^2$$

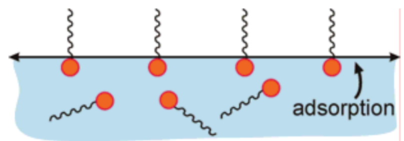
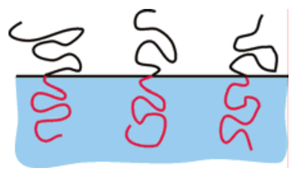
**Apparent viscosity**

$$\boxed{\eta(\omega) = \left(\frac{E_G}{\omega}\right)\left(\frac{\sqrt{\omega_D/2}}{\omega_D + \sqrt{2\omega_D} + 1}\right)}$$

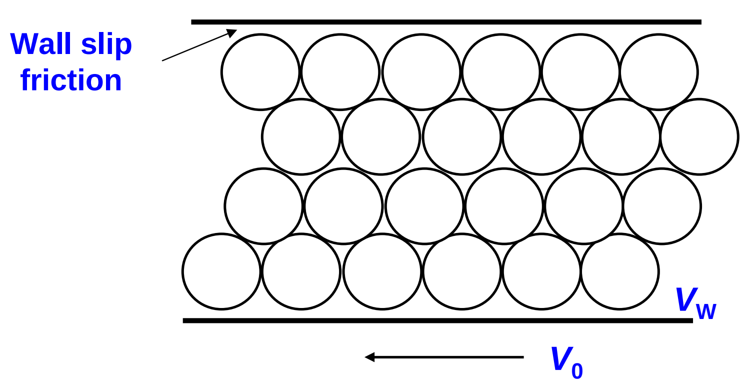
**Insoluble monolayers or fast oscillations:** $\omega_D \to \infty \Rightarrow E = E_G;\ \eta = 0$

**Slow oscillations**: $\omega_D \to 0 \Rightarrow E(\omega) \approx E_G\omega_D \to 0;\ \eta \to E_G \frac{\sqrt{\omega_D/2}}{\omega} \to \infty;\ \omega\eta(\omega) \to 0$

## Expected rheological response in various systems

| System | Schematics | Note |
|---|---|---|
| Low molecular mass surfactants |  | Adsorption |
| Synthetic polymers |  | Visco-elastic<br>Shear thinning |
| Globular proteins |  | + Yield stress<br>Time dependence |
| Solid particles |  | Plastic<br>Slow adsorption |

## C. Friction between foam and solid wall




- **Wall slip is usually significant (incl. rheo-experiments)**
- **Role of surface mobility of the bubbles.**

## Aims of the presentation:

- **Approaches for studying foam-wall friction.**
- **Illustration of role of interfacial properties.**

## CONTENTS

1. **Role of wall-slip in foam rheology.**
2. **Theoretical approach for description.**
3. **Illustrative experimental results.**

## Foam rheological properties

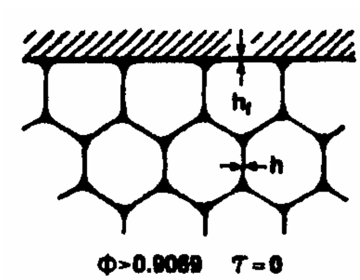
**Constitutive rheological relation**

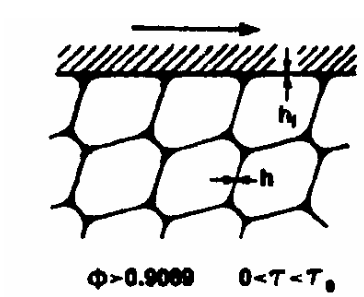
$$\tau = \tau_0 + k\dot{\gamma}_F^n$$

$\tau_0$ - yield stress (elastic origin)

$\dot{\gamma}_F$ - shear rate [1/s]

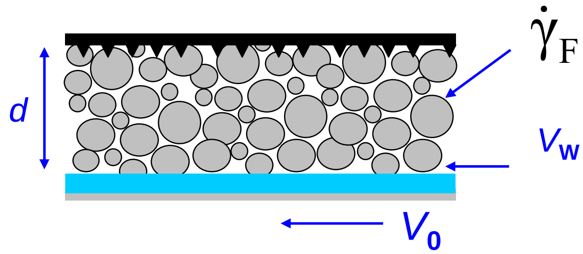
Herschel-Bulkley fluid (HB fluid)




Princen, 1985

# Role of wall-slip in foam rheology



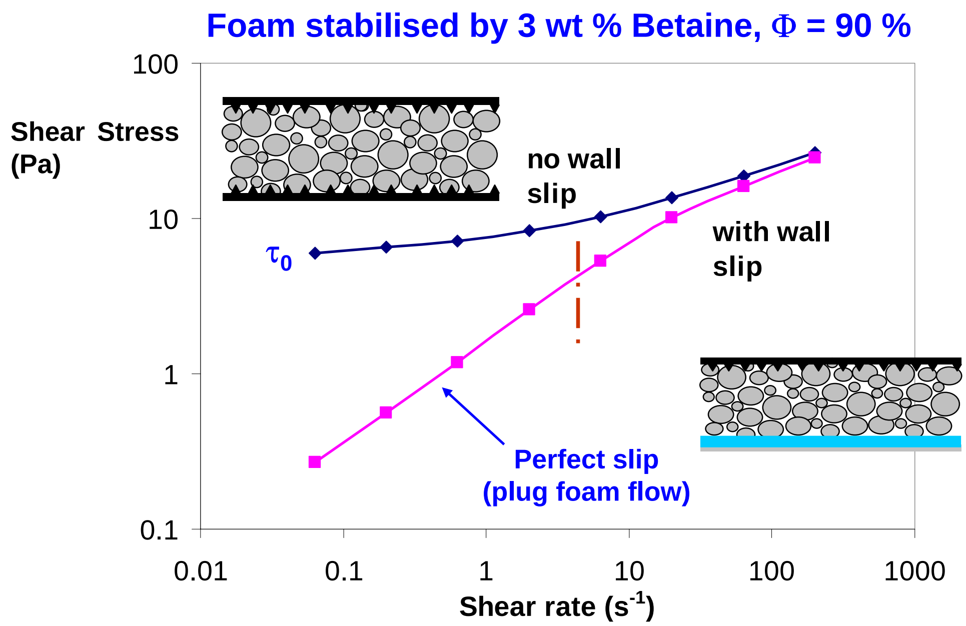

$$\dot{\gamma}_{APP} = \frac{V_0}{d}$$

$$\tau = \tau_0 + k\dot{\gamma}_F^n$$

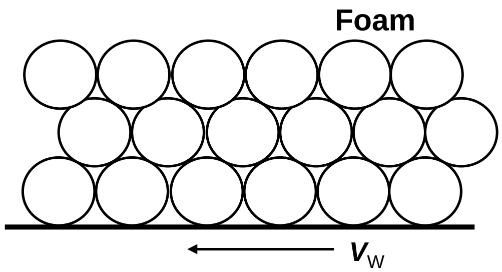
$$\dot{\gamma}_F = \left(\dot{\gamma}_{APP} - \frac{V_W}{d}\right)$$

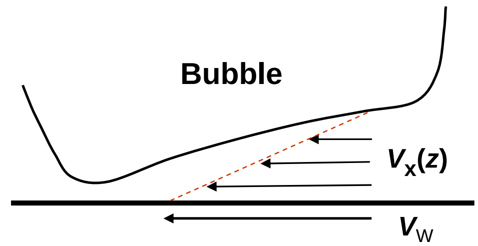
**The true shear rate in the foam, $\gamma_F$, is lower in presence of wall-slip**

# Example: Effect of wall-slip on shear stress



# Theoretical approach to describe wall-slip friction

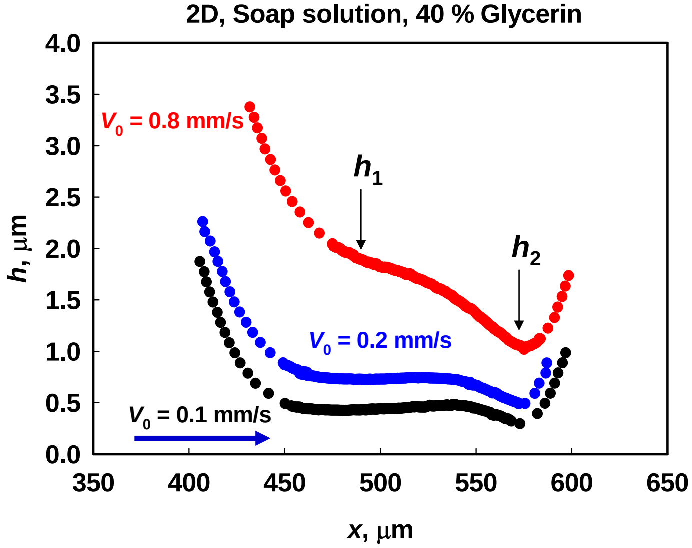


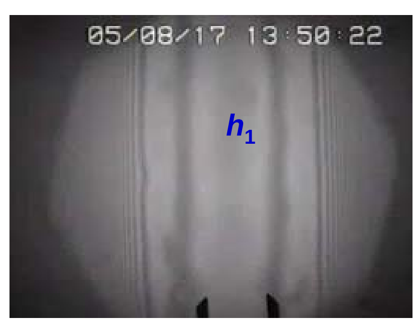




## Friction Force Bubble-Wall

$$F_{FR} = \int_{\text{Contact zone}} \mu \left(\frac{\partial V_x}{\partial z}\right)_{z=0} dA$$

# Shape of the dynamic wetting film formed between bubble and solid wall



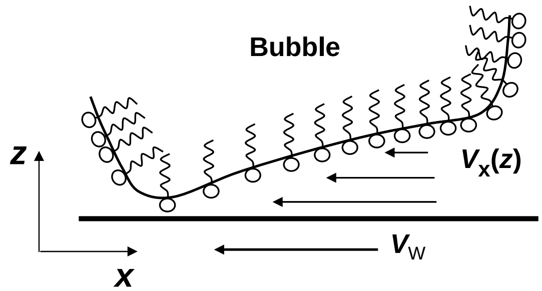




$V_0$ = 0.2 mm/s

**The film thickness increases with the increase of $V_0$**

## Lubrication equation for bubble-wall friction

$$\frac{dP}{dx} = \mu \frac{\partial^2 V_x}{\partial z^2}$$




### Surface stress balance

$$\mu \left( \frac{\partial V_x}{\partial z} \right)_{z=h} = -\frac{d\sigma}{dx} + \mu_S \frac{d^2 u}{dx^2}$$

Surface elasticity

Surface viscosity

**Important factors:**

- **Relative velocity, $V_W$**
- **Bubble size, $R_B$, and volume fraction, $\Phi$**
- **Liquid viscosity, $\mu$**
- **Surface mobility (surface elasticity and viscosity)**

## Two limiting cases are theoretically predicted

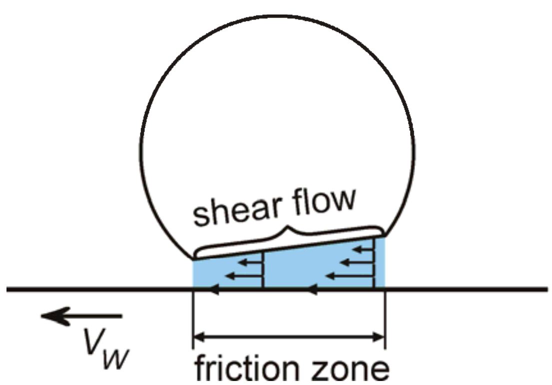
Tangentially immobile surface
(high surface modulus)

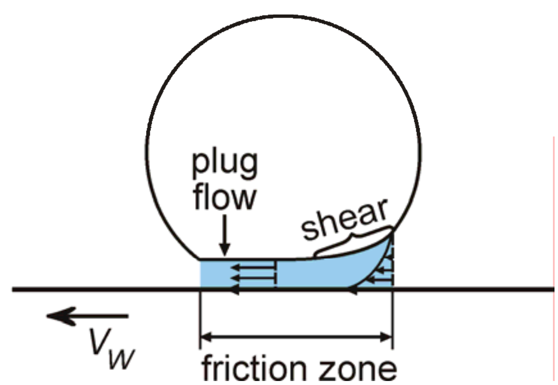
$$\boxed{\tau_W \propto \left( \frac{\sigma}{R_{32}} \right) Ca^{1/2}}$$

$$Ca = \left( \frac{\mu V_W}{\sigma} \right)$$

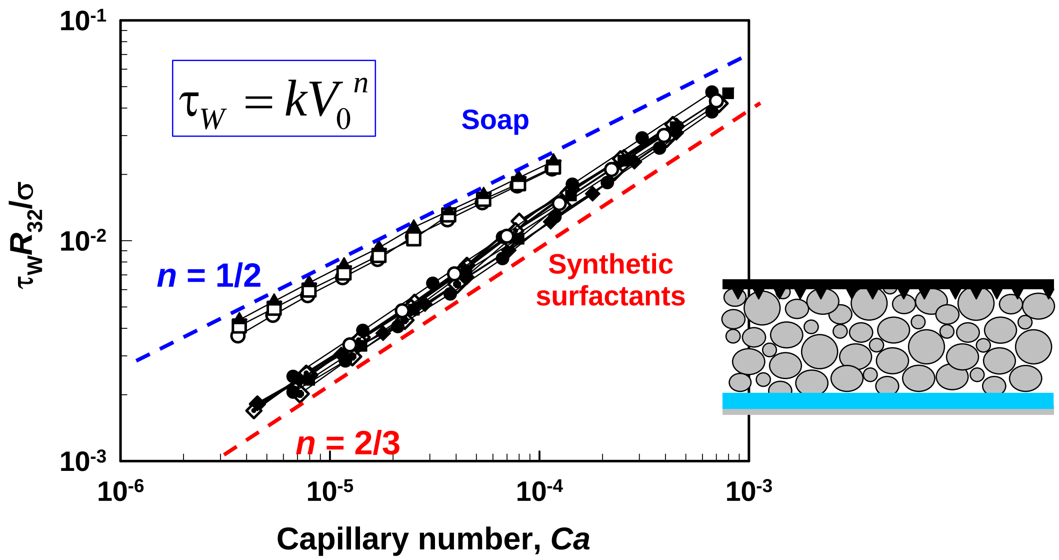
Tangentially mobile surface
(low surface modulus)

$$\boxed{\tau_W \propto \left( \frac{\sigma}{R_{32}} \right) Ca^{2/3}}$$



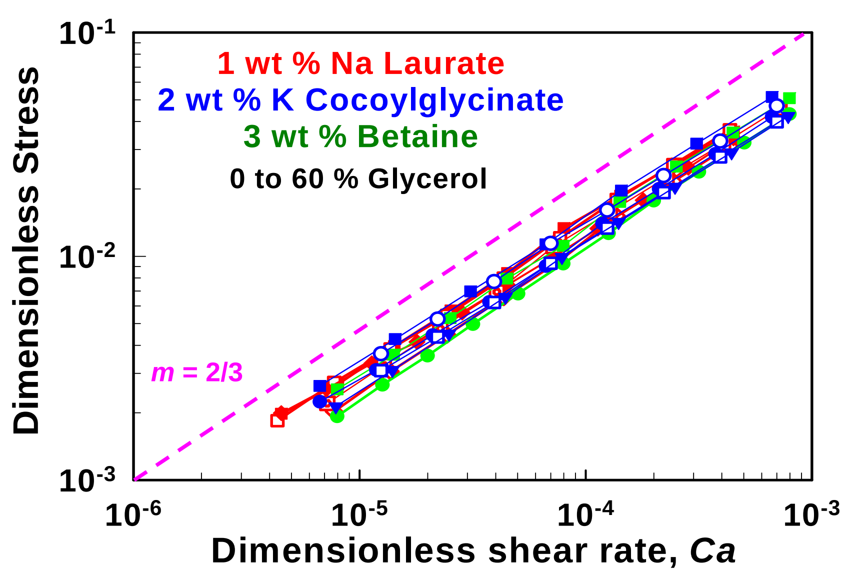



## Experimental results
## effect of surface mobility on foam-wall friction

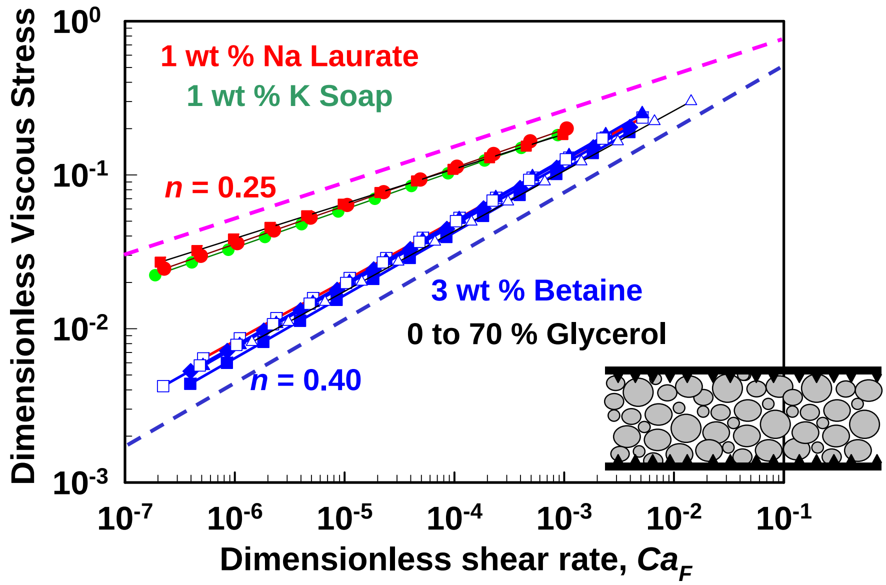



## Scaling of the data with solution viscosity

$$\left(\frac{R_{32}}{\sigma}\tau_W\right) \propto Ca^{2/3} \qquad Ca = \left(\frac{\mu V_W}{\sigma}\right)$$



## Sheared bulk foam - effect of surface mobility




$$\boxed{\tau_F = \tau_0 + k\dot{\gamma}_F^n} \qquad Ca_F = \left(\frac{\mu\dot{\gamma}R}{\sigma}\right)$$

## Conclusions

<u>Interfacial dynamic properties</u> play a very important role in foam dynamics (rheology, drainage, foam generation, …)

Interfacial properties can be characterized by <u>phenomenological parameters</u> (e.g., surface viscosity, elasticity, and yield stress)

These phenomenological parameters are governed by the <u>adsorbed surfactant species</u> (incl. exchange with the solution)

<u>Two limiting cases</u> are often recognized:

- Tangentially immobile (alkylcarboxylates, proteins, synthetic polymers, particles)
- Tangentially mobile (most synthetic surfactants)

## SINCERE THANKS

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