**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?!

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**Aims of presentation:**

- Basic concepts in interfacial dynamics.
- Illustrative examples.

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**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

![Diagram showing surface perturbations in foam rheology]

2. Surface stress in the process of foam drainage

![Diagram showing matching bulk and surface flows]

Viscous bulk stress
\[ \tau_V = \mu \frac{dV_z}{dx} \]

Matching bulk and surface flows
\[ V_S = V_Z \ (x = 0) \]
\[ \tau_S = \tau_V \]
B. Interfacial rheology.

1. Phenomenological approach - shear deformation

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)**

\[ \tau = \tau_0 + \eta \dot{\alpha} \]

**Shear thinning (power law)**

\[ \tau = k \dot{\alpha}^n \]
2. Phenomenological approach
- dilatational deformation.

**Surface dilatational elasticity**

\[ \tau_d = E_d \alpha_d \quad \alpha_d = \frac{\delta A}{A_0} \]

For insoluble monolayers:

\[ \Delta \sigma = E_G \alpha_d \Rightarrow E_d = E_G = \frac{d \sigma}{d \ln A} \]

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

**Surface dilatational viscosity**

\[ \tau_d = \eta_d \dot{\alpha}_d \quad \dot{\alpha}_d = \frac{d \alpha_d}{dt} = \frac{d (\ln A)}{dt} \]

**Apparent viscosity**

Characteristic times:
- Experimental time, \( t_{\text{EXP}} \)
- Adsorption time, \( t_{\text{ADS}} \)

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

\[ \approx E_G \left( \frac{t_{\text{ADS}}}{t_{\text{EXP}}} \right) \delta \ln A \approx (E_G t_{\text{ADS}}) \left( \frac{\delta \ln A}{t_{\text{EXP}}} \right) = \mu_{\text{APP}} \dot{\alpha}_d \]

- Similarly for the molecule rearrangement in the monolayer, \( t_R \)
1. Balance of bulk and surface stress

- **Equal velocities**
  \[ V_S = V_B(z = z_S) \]

- **Stress balance**
  \[ \tau_B = \tau_S \]

- **Bulk viscous stress**
  \[ \tau_B = \mu \frac{\partial V_x}{\partial z} \approx \frac{V_0}{h} \]

- **Surface stress**
  \[ \tau_S = -\frac{d\sigma}{dx} + \mu_S \frac{d^2u}{dx^2} \]

2. Surface mass balance for the surfactant

- **Equations for determining**
  \[ \frac{\partial \Gamma}{\partial t} = -D_S \frac{\partial \Gamma}{\partial x} + \frac{\partial (V_S \Gamma)}{\partial x} + J_{\text{BULK}} \]

- **Equations**
  \[ J_{\text{BULK}} = -D_B \left( \frac{\partial C}{\partial z} \right)_{z=z_S} \]

- **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

- **Couette geometry**
- Expanding or oscillating drop

### Dilatational mode

\[
\sigma(t) = (\sigma_{EQ} + \tau_D) = (\sigma_{EQ} + E_d \alpha_d + \eta_d \dot{\alpha}_d)
\]

### Expanding or oscillating drop

\[
P_C = \frac{2\sigma}{R_d}
\]

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

#### Shear

\[
\tau_S = \tau_S(\dot{\alpha}_S)
\]

#### Dilatational

\[
d(\ln A)/dt = \text{const}
\]

For diffusion control, steady-state is difficult to achieve.
2. Stress-relaxation experiments

Maxwell model

\[ \dot{\alpha} = \frac{\dot{\tau}}{E} + \frac{\tau}{\eta} \]

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

\[ t_R = \frac{\eta}{E} \quad E \approx \frac{\Delta \tau}{\Delta \alpha} \]

The relaxation is not exponential for diffusion controlled adsorption

\[ \Delta \sigma(t) \propto \frac{1}{\sqrt{t}} \]

3. Strain-relaxation experiments (creep flow)

Kelvin model

\[ \alpha(t) = \frac{\Delta \tau}{E} \left[1 - \exp\left(-t/t_R\right)\right] \]
4. Oscillatory measurements (shear, dilatation)

**Kelvin model**

\[
\tau = \tau_{EL} + \tau_V = E\alpha + \eta \frac{d\alpha}{dt}
\]

\[
\alpha = A_\alpha \sin(\omega t) \Rightarrow \dot{\alpha} = A_\alpha \omega \cos(\omega t)
\]

\[
\tau = A_\tau \left[ E \sin(\omega t) + \eta \omega \cos(\omega t) \right] = A_\tau \left[ \sin(\omega t + \phi) \right]
\]

\[
\frac{A_\tau}{A_\alpha} = \sqrt{E^2 + (\eta \omega)^2}
\]

**Surface modulus**

\[
\sin \phi = \frac{\eta \omega}{\sqrt{E^2 + (\eta \omega)^2}}
\]

**Example: Diffusion controlled adsorption- dilatation**

(Lucassen, van den Tempel)

**Elasticity**

\[
E(\omega) = E_G \frac{\omega_D + \sqrt{\omega_D^2/2}}{\omega_D + \sqrt{2\omega_D + 1}}
\]

\[
\omega_D = \frac{\omega}{D \left(\frac{dr}{dC}\right)^2}
\]

**Apparent viscosity**

\[
\eta(\omega) = \left(\frac{E_G}{\omega}\right) \left(\frac{\sqrt{\omega_D^2/2}}{\omega_D + \sqrt{2\omega_D + 1}}\right)
\]

**Insoluble monolayers or fast oscillations:**

\(\omega_D \rightarrow \infty \Rightarrow E = E_G; \eta = 0\)

**Slow oscillations:**

\(\omega_D \rightarrow 0 \Rightarrow E(\omega) \approx E_G \omega_D \rightarrow 0; \eta \rightarrow E_G \frac{\sqrt{\omega_D^2/2}}{\omega} \rightarrow \infty; \omega \eta(\omega) \rightarrow 0\)
### Expected rheological response in various systems

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<th>Schematics</th>
<th>Note</th>
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<td>Synthetic polymers</td>
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<td>Globular proteins</td>
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<td>Solid particles</td>
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<td>Plastic, Slow adsorption</td>
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### 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

\[ \gamma_F = \gamma_{\text{APP}} - \frac{V_W}{d} \]

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

Example: Effect of wall-slip on shear stress

Foam stabilised by 3 wt % Betaine, \( \Phi = 90 \% \)
Theoretical approach to describe wall-slip friction

Friction Force Bubble-Wall

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

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

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

\[ \mu \left( \frac{\partial V_x}{\partial z} \right)_{z=b} = -\frac{d\sigma}{dx} + \mu_s \frac{d^2 u}{dx^2} \]

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)

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

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

Tangentially mobile surface (low surface modulus)

\[ \tau_W \propto \left( \frac{\sigma}{R_{32}} \right) Ca^{2/3} \]
Experimental results

Effect of surface mobility on foam-wall friction

Dimensionless shear rate, $Ca$

Dimensionless Stress

$\tau W = kV_0^n$

$n = 1/2$

$n = 2/3$

Soap

Synthetic surfactants

Scaling of the data with solution viscosity

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

$1$ wt % Na Laurate
$2$ wt % K Cocoyleglycinate
$3$ wt % Betaine
$0$ to $60$ % Glycerol
Sheared bulk foam - effect of surface mobility

\[ \tau_F = \tau_0 + k \dot{\gamma}^n \]

\[ Ca_F = \left( \frac{\mu \dot{\gamma} R}{\sigma} \right) \]

**Conclusions**

*Interfacial dynamic properties* play a very important role in foam dynamics (rheology, drainage, foam generation, ...)

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

These phenomenological parameters are governed by the *adsorbed surfactant species* (incl. exchange with the solution)

*Two limiting cases* are often recognized:
- Tangentially immobile (alkylcarboxylates, proteins, synthetic polymers, particles)
- Tangentially mobile (most synthetic surfactants)
SINCERE THANKS

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