Interfacial Rheology

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

**Motivation – Dispersion Stability**

**Driving force:** $\Delta \Pi$
Dilatation [Expansion/Compression]; Change of $A$

\[ \delta \alpha = u : U_s \]

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

\[ \delta \beta = u : q \]

\[ u = \frac{1}{2} (u : U_s) U_s + \left[ u - \frac{1}{2} (u : U_s) U_s \right] \]

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

\[ \text{Tr} u = u : U_s = u_1 + u_2 \quad \text{isotropic deformation} \]

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?

\[ u - \frac{1}{2} (u : U_s) U_s = \frac{1}{2} (u_1 - u_2) (e_1 e_1 - e_2 e_2) \]

relative shear:

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

\[ U_s = e_1 e_1 + e_2 e_2 ; \quad q = e_1 e_1 - e_2 e_2 \]

\[ u = \frac{1}{2} (\delta \alpha) U_s + \frac{1}{2} (\delta \beta) q \]
Surface Deformation – Curvature

\[ b = -\nabla_s n = HU_s + Dq \]

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 \( B = M_1 + M_2, \quad \Theta = M_1 - M_2 \)

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

if \( w_f = 2k_c(H - H_0)^2 + \bar{k}_cK \) (and \( K = c_1c_2 \)),

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}_cD \quad \text{(and \( B_0 = -4k_cH_0 \))} \]

\( k_c \sim 10-20 \ k_B T \)

for lipid bilayers

Fig. 1. Independent modes of surface deformation.
## Dilatational Surface Elasticity – Low MW Surfactants

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

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 \( \Gamma_1 \to \Gamma_\infty \), \( E_G \to \infty \) (not observed – out-of-plane escape)
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, $(\delta A)/A$.


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

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

which gives, upon rearrangement:

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

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

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

where

\[ \zeta = \frac{dc}{\Gamma} \sqrt{\mathcal{D}} \]  
and \( \epsilon_0 = -\frac{d\sigma}{d\ln \Gamma} \).

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

![Fig. 1. Illustrating phase relations between deformation and surface tension variations.](image)
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.

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

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

\[
E^* = E' + iE''; \quad E' = \left|E^*\right| \cos \varphi; \quad E'' = \left|E^*\right| \sin \varphi
\]

$\Delta \sigma_m, \varphi$ = measured quantities
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 \( \tau \).

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

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

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

\[
\tau(t) = E' \sin(\omega t) + E'' \cos(\omega t)
\]
Presence of irreversibly adsorbed molecules (that cannot be exchanged with the bulk phase)
Polymers, proteins, …

- Extended Maxwell model
  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.
Symmetric motion of the barriers

♦ Linear translation with constant speed

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

UNI-AXIAL DEFORMATION – superposition of dilatation and shear.

If shear is not important for a particular system:

\(\gamma\) – the relative area expansion,

\[ d\gamma = \frac{dA}{A}, \quad \gamma = \ln\left(\frac{A}{A_0}\right) = \alpha \]

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

Dynakoll 0.01%, Solvitose 0.1%, barrier speed = 20 mm/min
The negatively charged acids adsorb easily; to them, polymer molecules with cationic groups can attach.

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

**Linear viscoelasticity – Extended Maxwell Model**

In the Langmuir trough:

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

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

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

Abietic acid
Dynakoll VS 50 FS from Akzo Nobel

Levopimaric acid

Cationized starch
~4-4.5% trimethylammonium-groups
Solvitose BPN from AVEBE Germany
Rheological parameters (at $d\gamma/dt = 0.00247$ s$^{-1}$)

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

$$\alpha = \ln\left(\frac{A}{A_0}\right)$$

$$\tau = \Delta \sigma, \text{ dyn/cm}$$

$$\alpha = \ln\left(\frac{A}{A_0}\right) = \gamma$$
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

Figure 3. HFB1 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.)

AFM data showing displacement of B-lactoglobulin protein film (green) from 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 (≠ from phase transition – spots of condensed phase)

Shear elasticity → 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 β-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)
In the case of pure elasticity:

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

(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

\[ \Delta \sigma_1 = (K + \mu) \alpha = \Delta \sigma_\parallel \quad \Delta \sigma_2 = (K - \mu) \alpha = \Delta \sigma_\perp \]  

(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:

\[ K + \mu = \frac{d\sigma_\parallel}{d \ln A} \quad K - \mu = \frac{d\sigma_\perp}{d \ln A} \]  

(3)
Dilatational and shear elasticity of BLG layers: after ageing for hours, or at high concentrations

Anisotropic Stress Method

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 $1\times10^{-4}$ 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% β-lactoglobulin. The barrier rate was set to 0.5 mm/s.
Anisotropic Stress – Visco-Elastic Behavior

\[ \tau_{11,el} = (K + \mu)u_{11,el} \quad \tau_{22,el} = (K - \mu)u_{11,el} \]
\[ \tau_{11,visc} = (\zeta_s + \eta_s)D_{11,visc} \quad \tau_{22,visc} = (\zeta_s - \eta_s)D_{11,visc} \]

In the frames of the Maxwell model:

\[ \tau_{11} = \tau_{11,el} = \tau_{11,visc} \quad \tau_{22} = \tau_{22,el} = \tau_{22,visc} \]
\[ u_{11} = u_{11,el} + u_{11,visc} \quad D_{11} = D_{11,el} + D_{11,visc} \]

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

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

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

\[ \frac{d\alpha}{dt} = \frac{1}{K + \mu} \frac{d\tau_{11}}{dt} + \frac{\tau_{11}}{\zeta_s + \eta_s}; \quad \frac{d\alpha}{dt} = \frac{1}{K - \mu} \frac{d\tau_{22}}{dt} + \frac{\tau_{22}}{\zeta_s - \eta_s} \]
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, \( \tau_{11} = \sigma_{||} - \sigma_{eq} \); \( \tau_{22} = \sigma_{\perp} - \sigma_{eq} \)

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

We observe different types of rheological behavior
Globular protein – the ageing and the concentration are important.

Disordered protein – absence of network.

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

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Type of rheological behavior</th>
<th>Determined parameters (expansion)</th>
</tr>
</thead>
</table>
| 1   | BLG $1\times10^{-4}$ wt% + 0.15 M NaCl Freshly prepared | Dilatational elasticity only  
No shear elasticity  
No viscous dissipation | $K= 53.0$ dyn/cm  
$\mu= 0$ |
| 2   | BLG $1\times10^{-4}$ wt% + 0.15 M NaCl Aged overnight | Dilatational and shear elasticity  
No viscous dissipation | $K= 70.5$ dyn/cm  
$\mu= 7.5$ dyn/cm |
| 3   | $\beta$-casein 0.001 wt% + $1\times10^{-5}$ M Tween 20 | Dilatational viscoelasticity  
Negligible shear elasticity and viscosity | $K= 42.6$ dyn/cm  
$\mu << K$  
$\zeta_s = 127.9$ dyn.s/cm  
$\eta_s << \zeta_s$ |
| 4   | BLG 0.01 wt% + 0.15 M NaCl | Full dilatational and shear visco-elasticity | $K= 83.2$ dyn/cm  
$\mu= 16.2$ dyn/cm  
$\zeta_s = 1654.8$ dyn.s/cm  
$\eta_s = 113.9$ dyn.s/cm |
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).

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

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

**Figure 6.** Dependence of the strain in the layer on the applied stress. \( \Delta \chi_{\text{th}} - \Delta \chi_{\text{exp}} = 0 \) 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); \( T = 22 \, ^{\circ}\text{C} \).

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


Additional References


**Additional References**


Additional References


