Foam films:
Properties and Stability

A. Chemistry of foam stabilizers.

B. Foam films – basic properties and methods for investigation.

C. Antifoams.

A. Chemistry of foam stabilizers

Aim of presentation

Relation between surfactant chemical structure and mode of foam stabilization

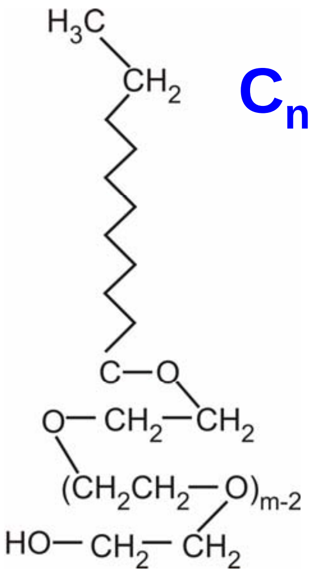
CONTENTS

1. Nonionic, ionic, and amphoteric surfactants.
2. Polymeric surfactants.
3. Particles as foam stabilizers.

Low-molecular mass surfactants

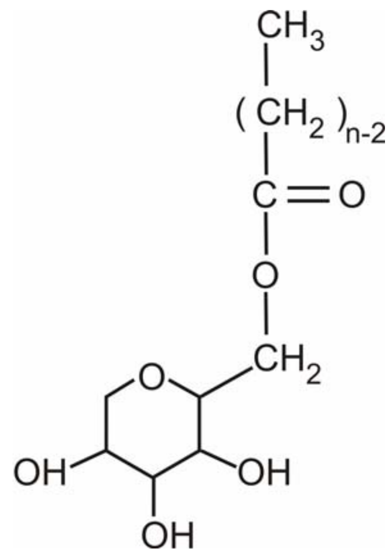
1. Nonionic surfactants

Alkylpolyoxyethylenes

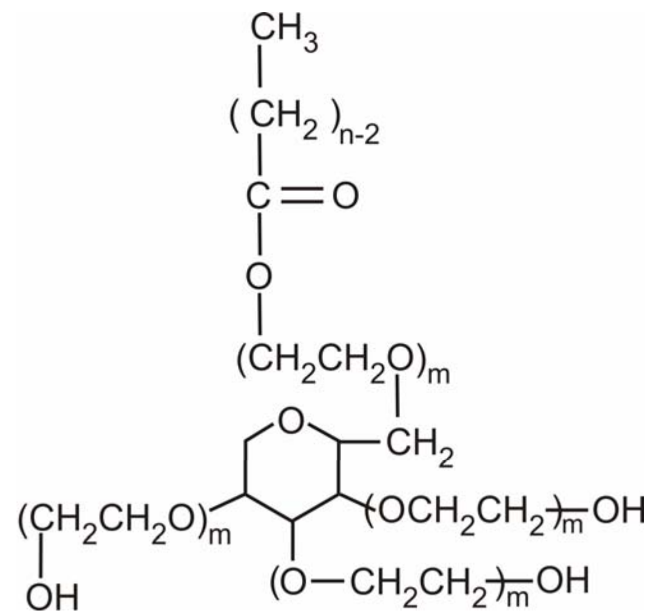


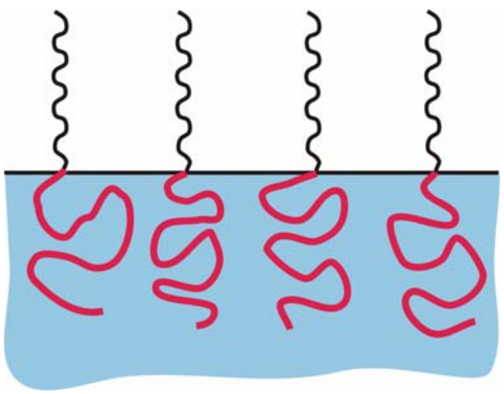
C_nEO_m

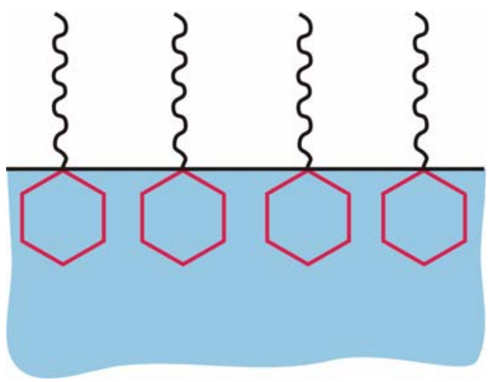
Spans

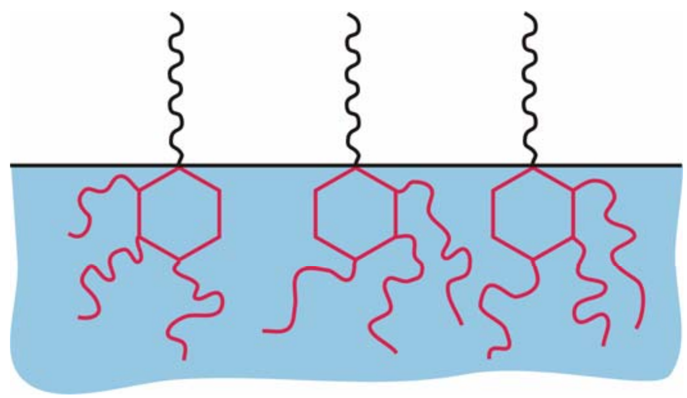


Tweens



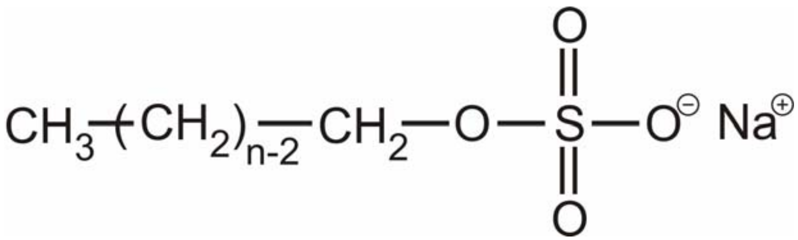


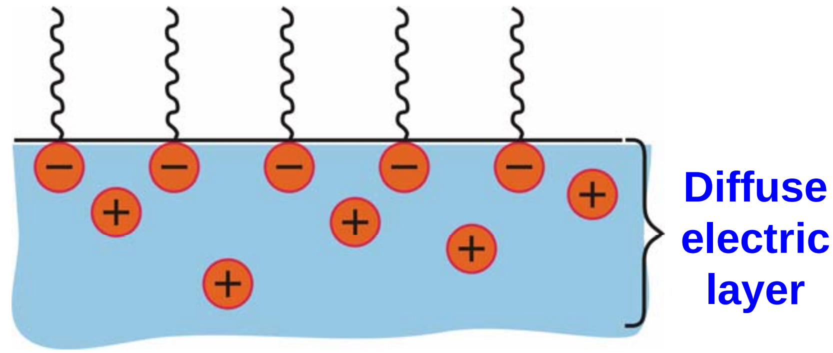




2. Ionic surfactants

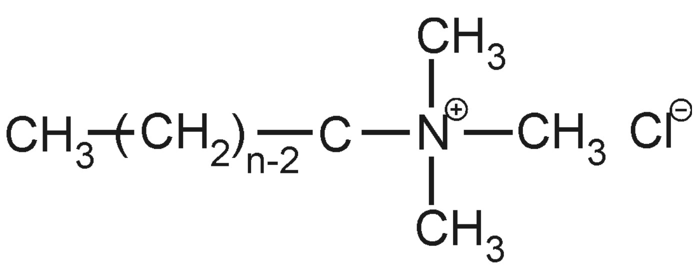
(a) Anionic

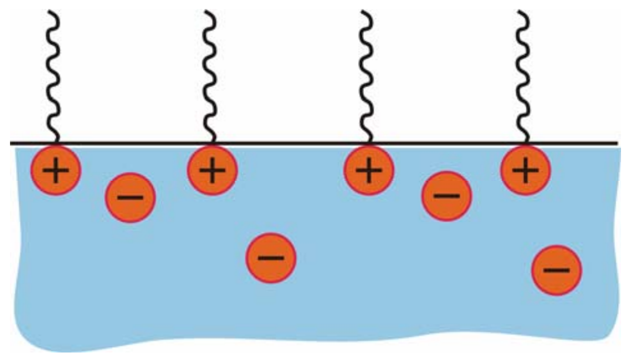




***n*=12 ⇒ sodium dodecyl sulfate, SDS**

(b) Cationic

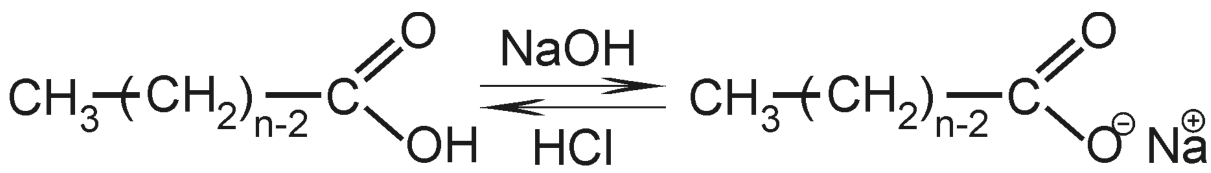


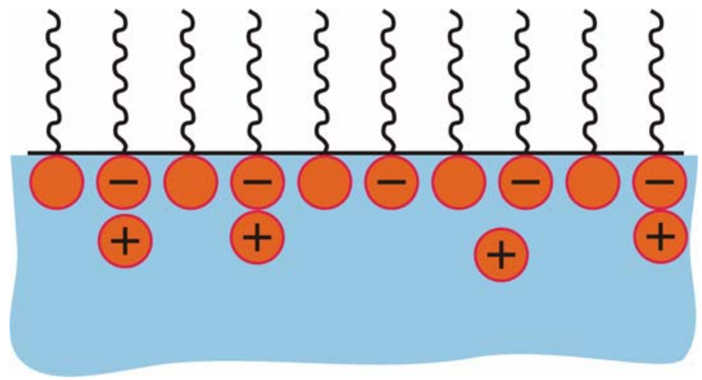


***n*=12 ⇒ dodecyl trimethyl ammonium chloride, DTAC**

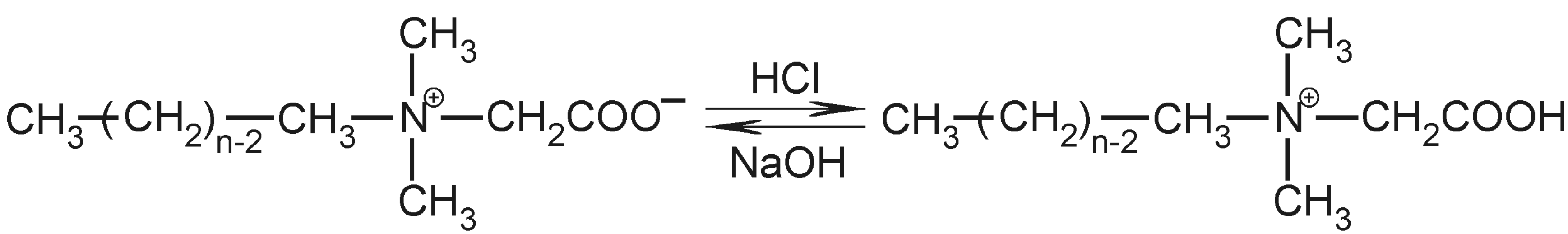
3. Amphoteric surfactants

(a) Natural soaps (alkylcarboxylates), Lipids





(b) Betaines



Comparison of the low-molecular mass surfactants

Sensitivity*	Nonionic	Ionic	Amphoteric
Electrolytes	NO	YES	Depends on pH
Temperature	YES	NO	NO
pH	NO	NO	YES

*Adsorption, surface tension, CMC, micelle size and shape, foaminess and foam stability

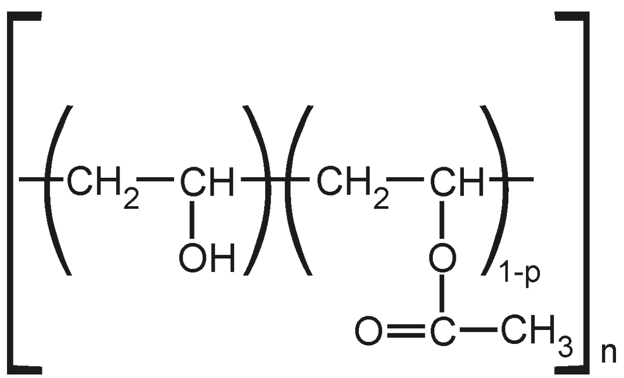
Surfactant mixtures are usually used in applications (main surfactant + cosurfactants)

Polymeric surfactants

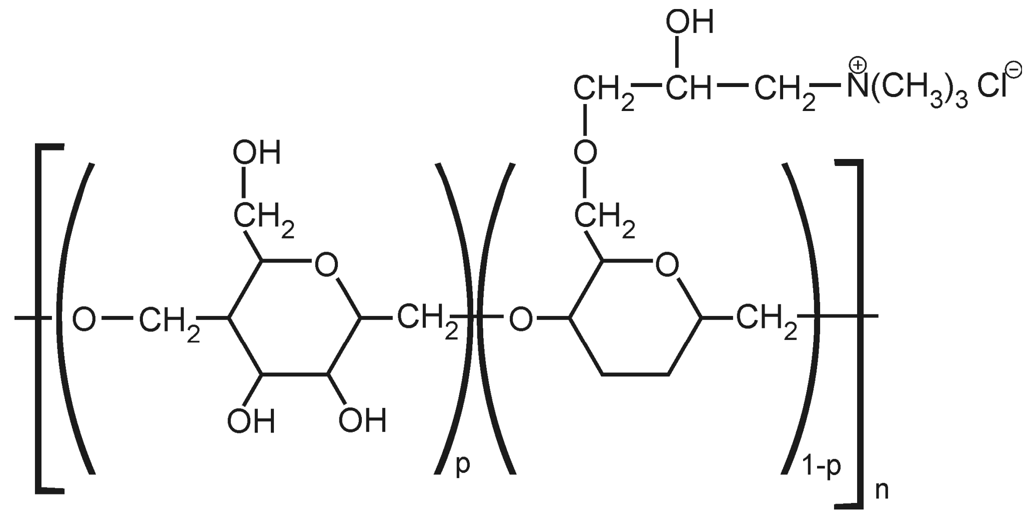
1. Synthetic polymers

(a) Homopolymers

Polyvinyl alcohol, PVA



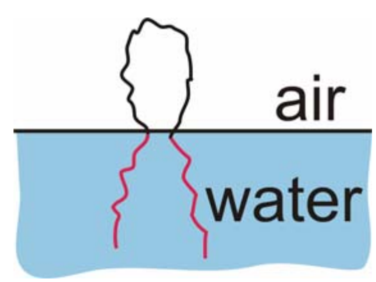
Modified polysacharides

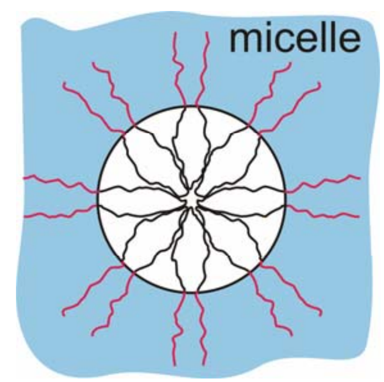


(b) Block-copolymers

$$HO-(CH_2CH_2O)_n-(CH_2CH_2CH_2O)_m-(CH_2CH_2O)_n-H$$

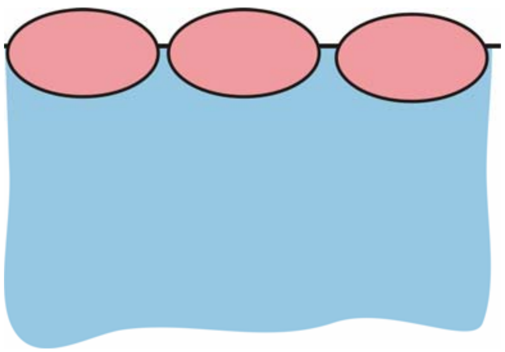
Synperonics, $EO_nPO_mEO_n$





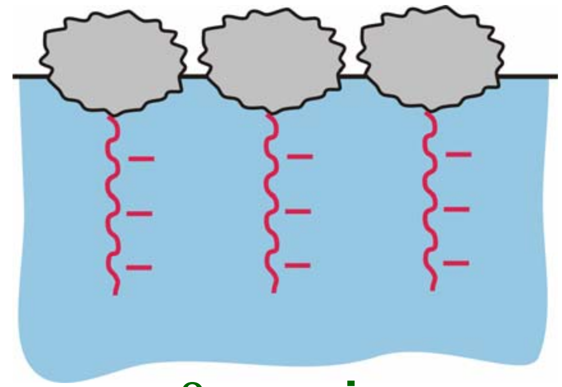
2. Natural polymers (proteins)

(a) Globular



Bovine serum albumin, BSA
β-lactoglobulin, BLG

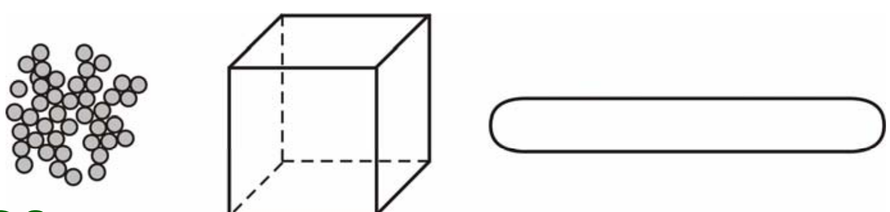
(b) Fibrilar



β-casein
κ-casein

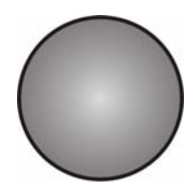
3. Solid particles

(a) Mineral



SiO_2
Ore particles

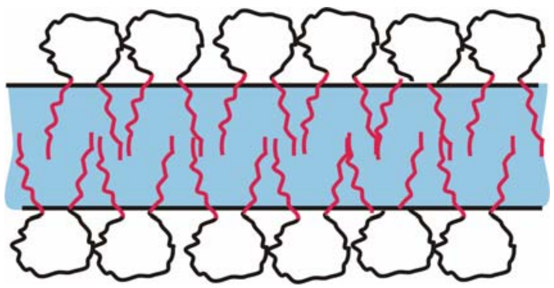
(b) Polymeric



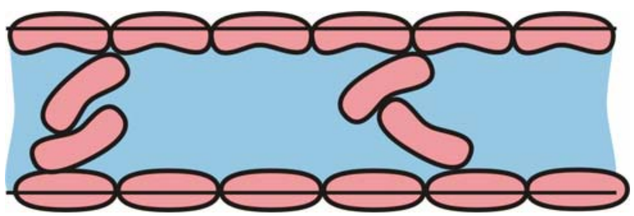
Latex particles

Modes of foam stabilization by polymeric surfactants

Synthetic polymers



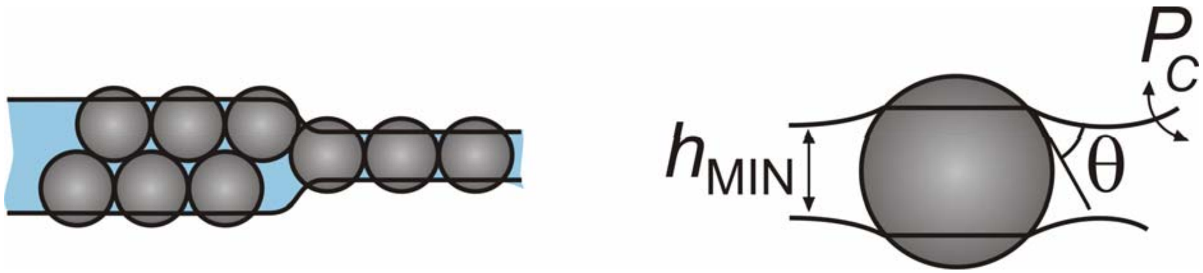
Natural polymers



Usually: combination of steric + electrostatic stabilization

Polymer-surfactant mixtures are often used!

Foam film stabilization by solid particles



Relatively thick foam films.
The foams could be very stable against coarsening!

Difficult to produce:
Slow adsorption ($D = kT/6\pi\eta R$)
No Marangoni effect ($E_G = -(d\sigma/d\ln\Gamma) \approx \Gamma kT = kT/A_0$)
Strong capillary attraction between particles
$\Rightarrow$ **Creation of "weak" spots (free of particles) in the films!**

Mixture of particles + surfactants
(ice-cream, whipped cream, chocolate mousse, …)

B. Foam films

Aims of presentation:

Information gained by studying foam films.

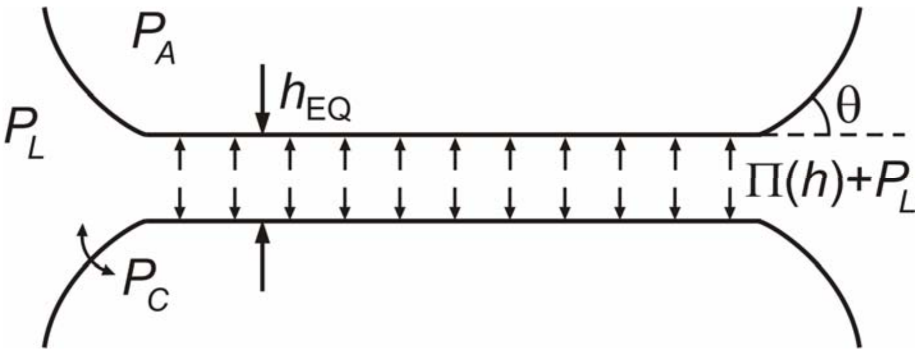
Illustration of differences between surfactants.

CONTENTS

1. Properties of equilibrium foam films.
2. Rate of thinning of foam films.
3. Methods for studying foam films.
4. Illustrative examples

1. Basic properties of equilibrium foam films.

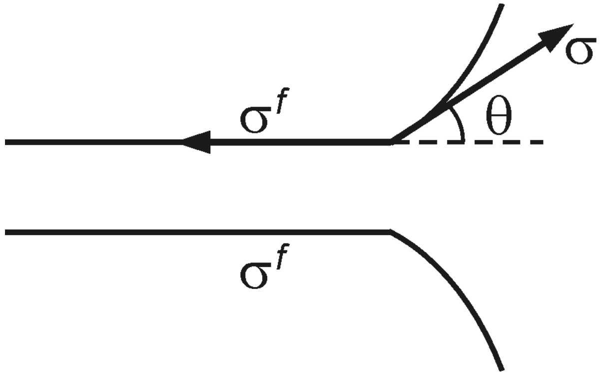
1. Equilibrium film thickness



Pressure balance

$$\Pi\left(h_{EQ}\right)=P_A-P_L=P_C$$

2. Contact angle film-meniscus



Film tension

$$\sigma^f=\sigma\cos\theta;\quad \sigma^f\left(h\right)=\sigma+f\left(h\right)/2$$

Interaction energy

$$f\left(h\right)=\int_h^\infty \Pi\left(h\right)dh$$

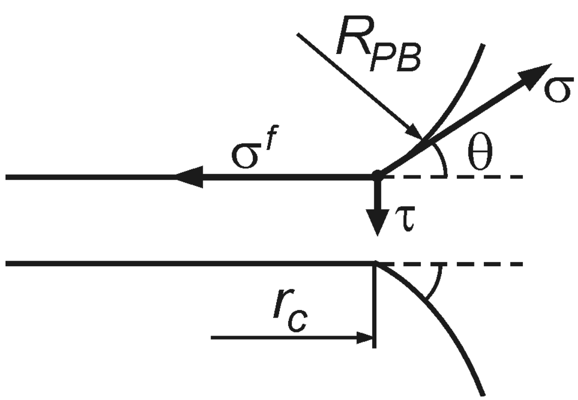
$$f\left(h\right)=2\sigma\left(\cos\theta-1\right)$$

Transition zone film-meniscus

Open questions from the thermodynamic approach:

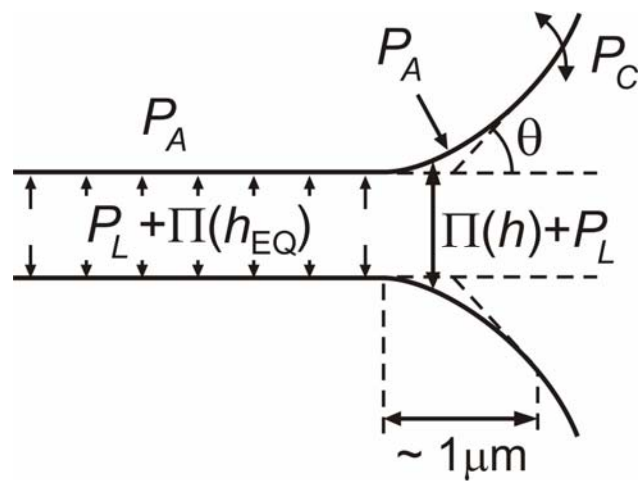
- **Do we have a sharp kink in the shape?**
- **What does compensate the vertical projection of σ?**

Idealized profile



$$\tau = \sigma \sin\theta$$

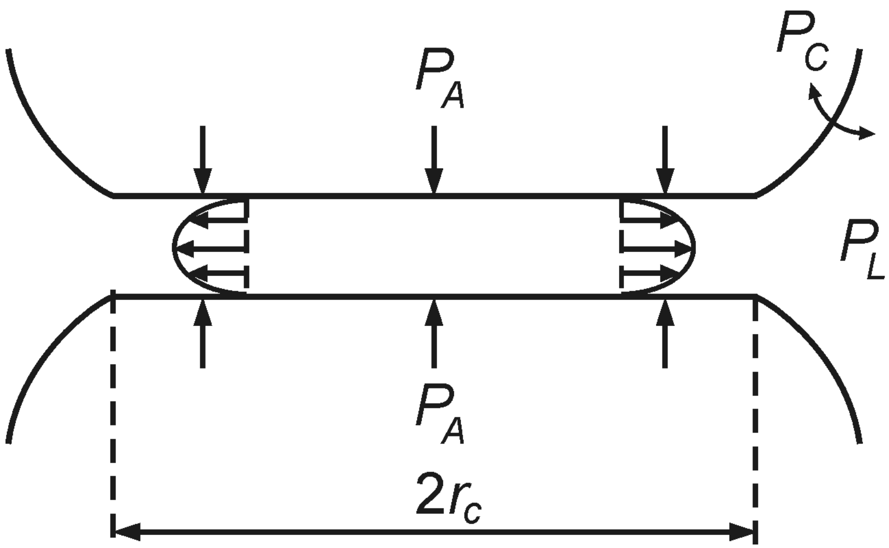
Real profile



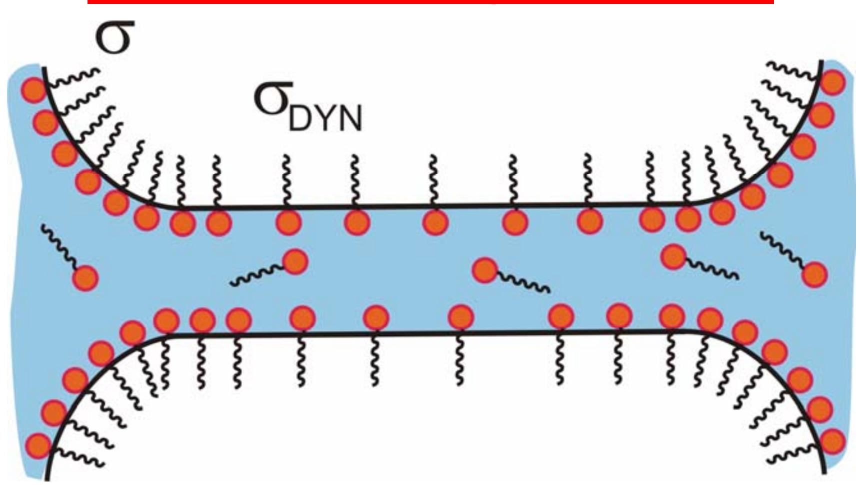
Local stress balance

$$\Pi(h) + \underbrace{(P_L - P_A)}_{-P_C} = -\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Rate of thinning of foam films



Role of Marangoni effect



Driving force

$$P_C = P_A - P_L > 0$$

Reynolds equation for film thinning

$$V_{Re} = -\frac{dh}{dt} = \frac{2\left(P_C - \Pi\right)h^3}{3\eta R^2}$$

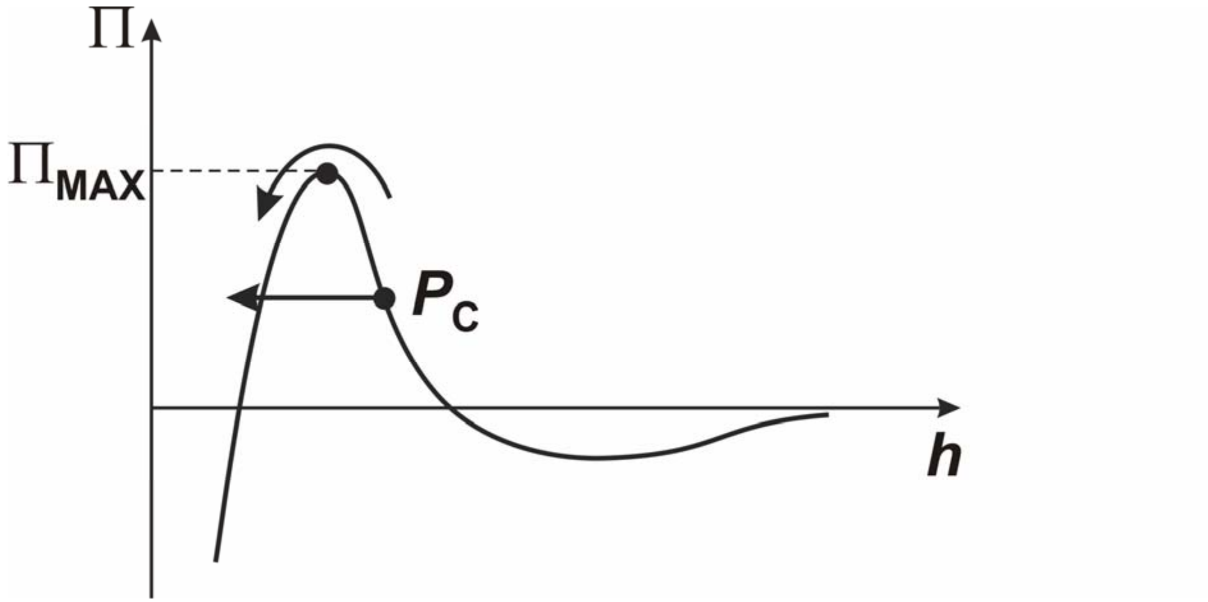
Limitations of Reynolds equation:

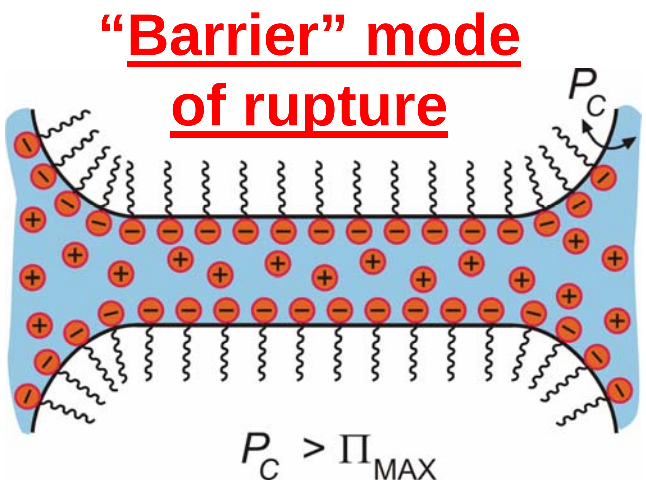
Tangentially immobile surfaces

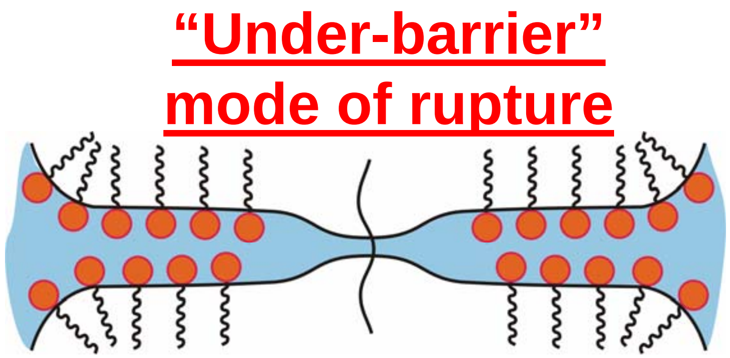
Plane-parallel films

The real films thin faster!

Rupture of foam films

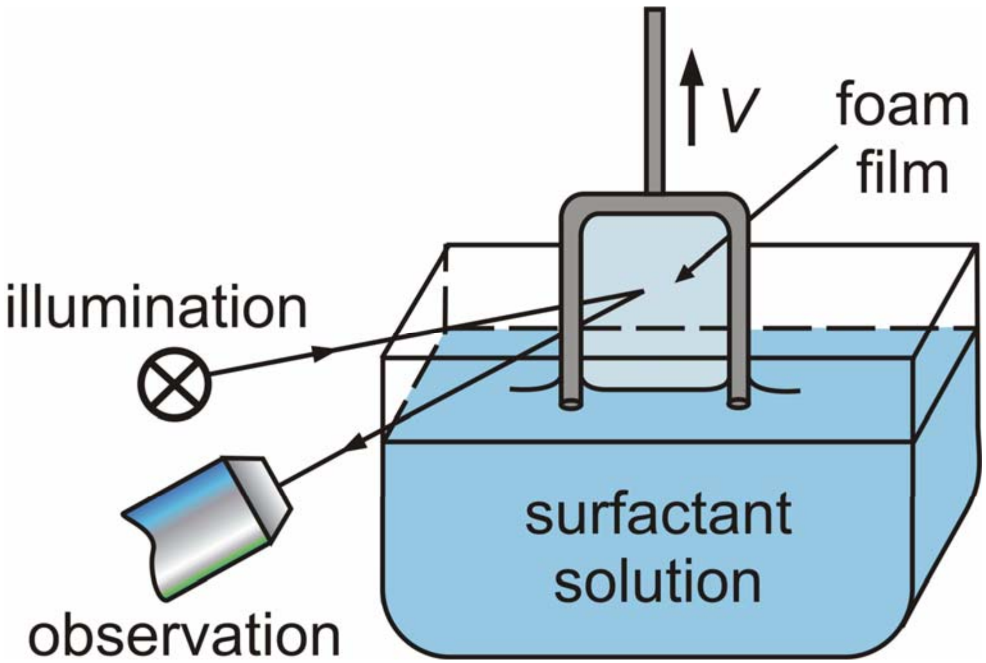






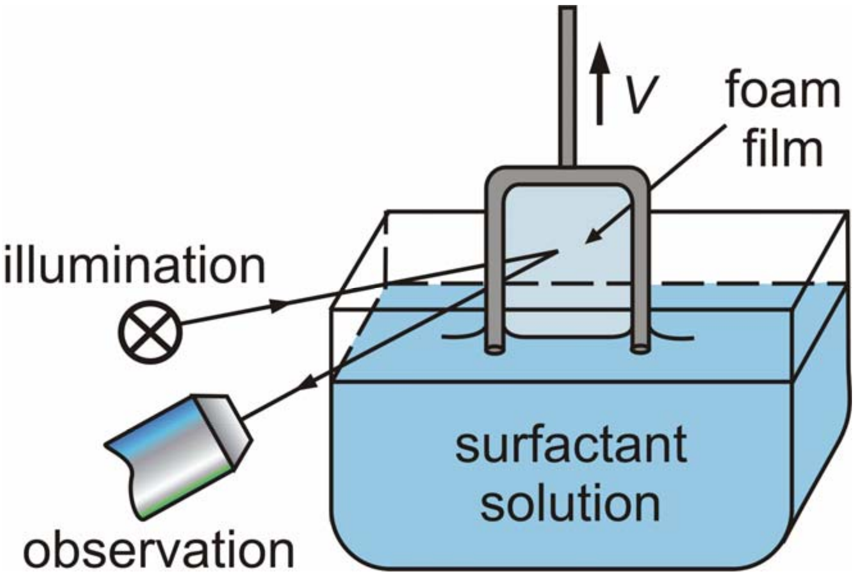
Methods for studying foam films

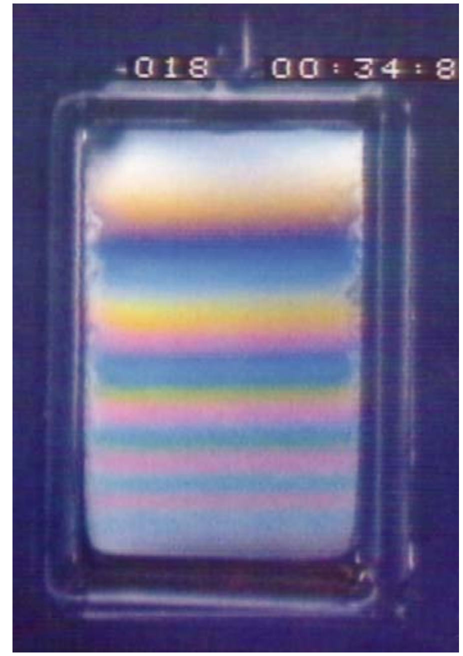
1. Large foam films suspended on a glass frame



White light – beautiful colors (light interference)

Monochromatic light – dark and bright stripes (film thickness)





Film thickness

$$h = \frac{\lambda}{2\pi n}\left(k\pi + \arcsin\sqrt{\frac{I - I_{MIN}}{I_{MAX} - I_{MIN}}}\right)$$

λ - light wavelength
n **- refractive index of solution**
k **- order of interference**

Measured

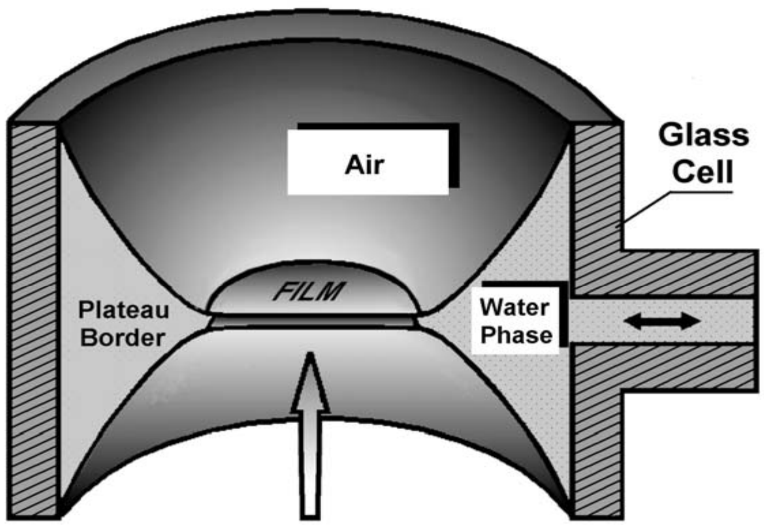
h **(time),** ***h*** **(position)**

Example

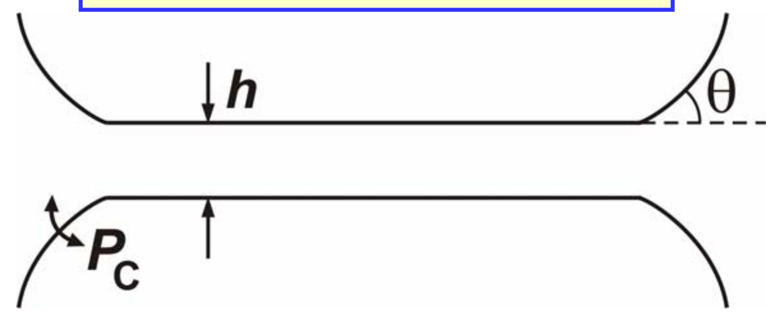
$h_D = k\ Ca^{2/3}$

$Ca = (\mu V/\sigma)$

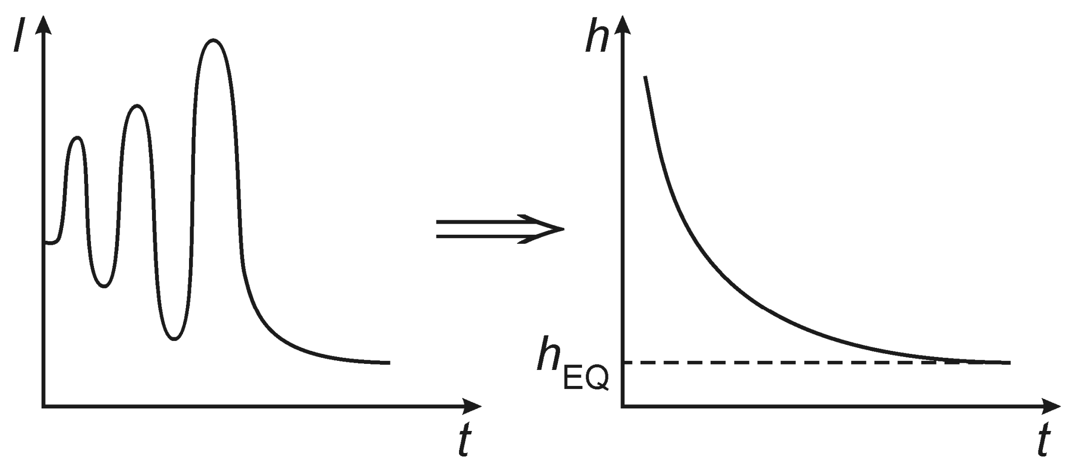
2. Microscopic foam films in a capillary cell



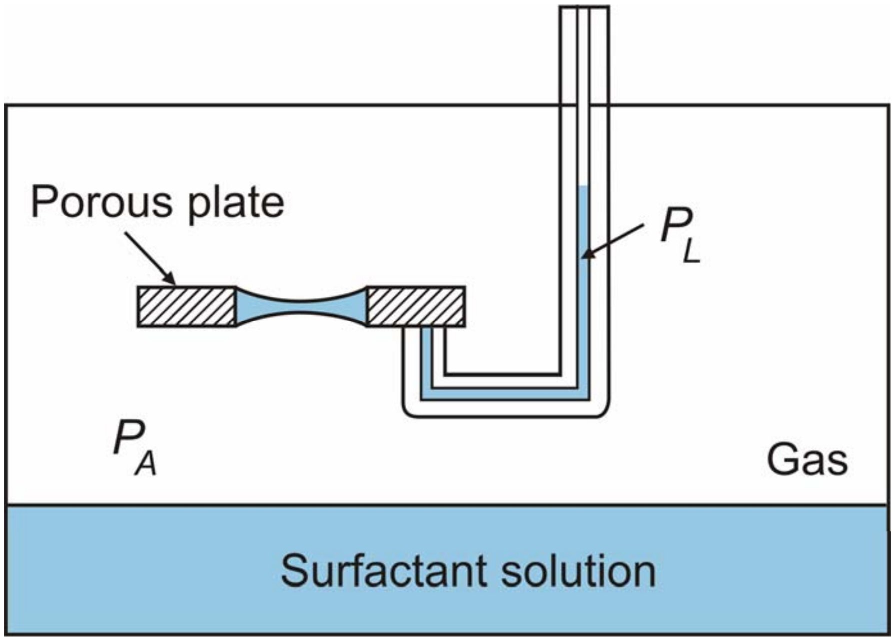
Measured
***h*(t), h_{EQ}**
Contact angle, θ



Film thickness vs time

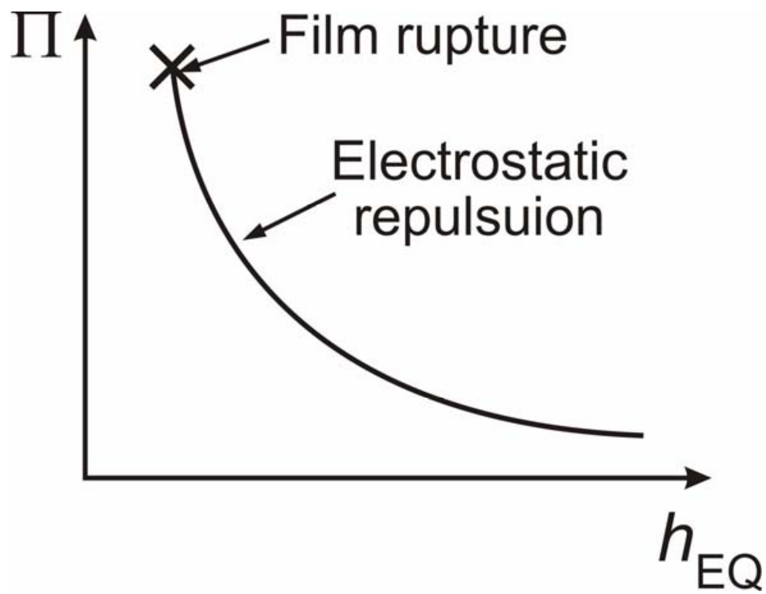


3. Porous plate method



$$P_C = (P_A - P_L) = \Pi(h_{EQ})$$

Disjoining pressure isotherm



Measured:

- **Equilibrium thickness, $h_{EQ}(P_C)$**
- **Disjoining pressure, $\Pi(h)$**
- **Critical pressure for film rupture, Π_{CR}**

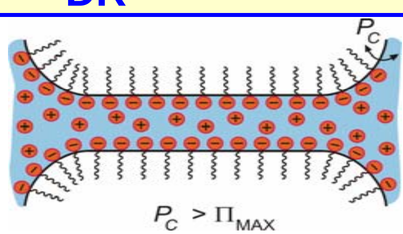
Illustrative examples

Anionic surfactant, SDS

Speed: ×1

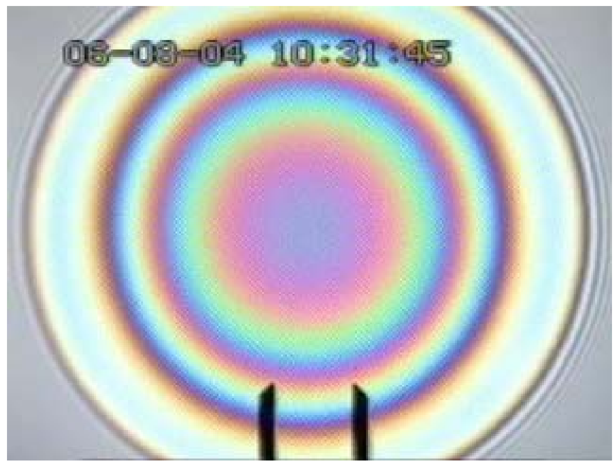
$h_{EQ} \approx$ **10 nm**

$\tau_{DR} \approx$ **60 sec**



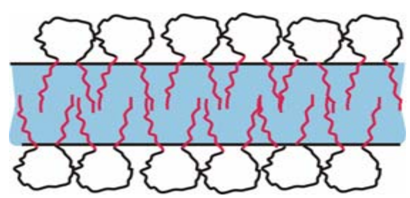
Polymeric surfactant, PVA

Speed: ×4



$h_{EQ} \approx$ **120 nm**

$\tau_{DR} \approx$ **300 sec**

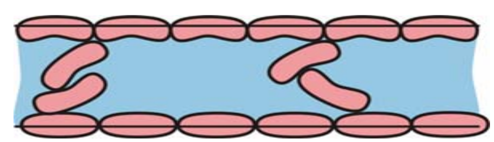


Protein, Na caseinate

Speed: ×8

$h_{EQ} \approx$ **30 nm**

$\tau_{DR} \approx$ **600 sec**



No surfactant

Speed: 1/4

Very rapid film thinning

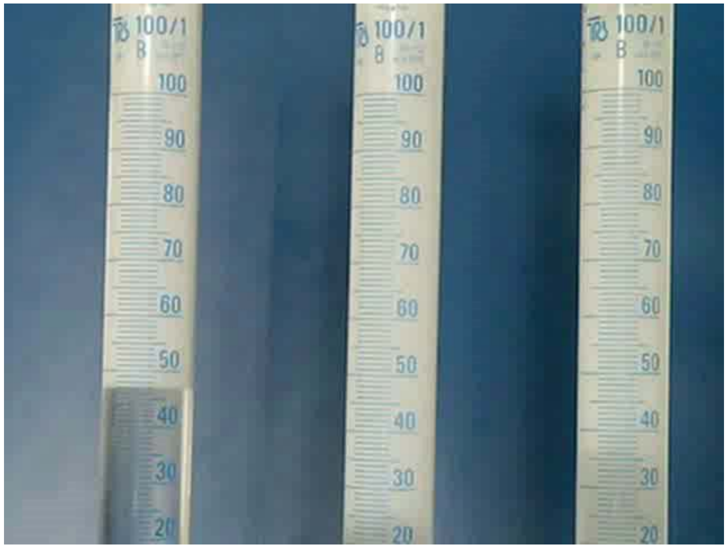
Film rupture at large thickness

(no Marangoni effect)

C. Antifoams

antifoam effect of hydrophobic particles and oils

What is "antifoam effect"?



TECHNOLOGY

- Pulp and paper production
- Oil industry (non-aqueous foams)
- Fermentation
- Textile dying

CONSUMER PRODUCTS

- Powders for washing machines
- Paints
- Drugs

Aims of presentation:

Mechanisms of foam destruction by antifoams.

Illustrative examples.

CONTENTS

1. **Composition of typical antifoams.**
2. **Mechanisms of foam destruction.**
3. **Examples of antifoam actions.**

Composition of Typical Antifoams

1. Hydrophobic solid particles

- Silica (SiO_2)
- Polymeric particles

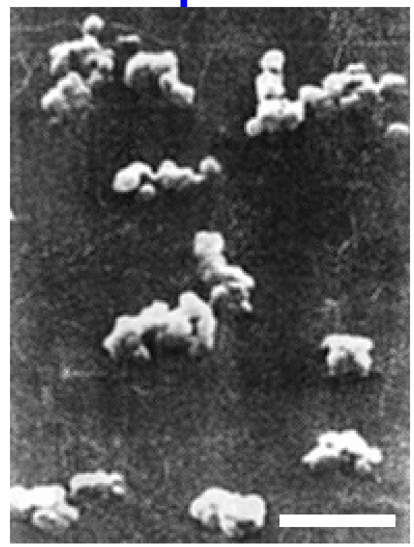
2. Oil

- Silicone oils (PDMS)
- Hydrocarbons (mineral oil, aliphatic oils)

3. Compound

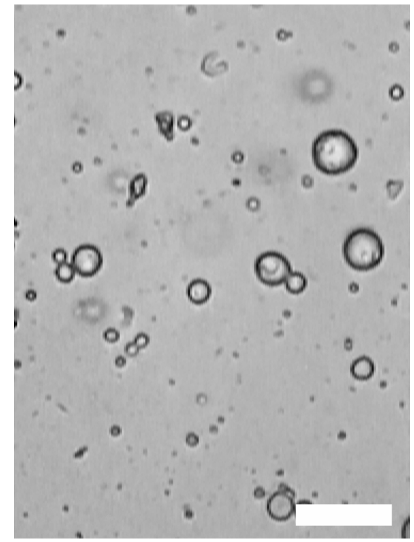
- Oil + particles

Silica particles

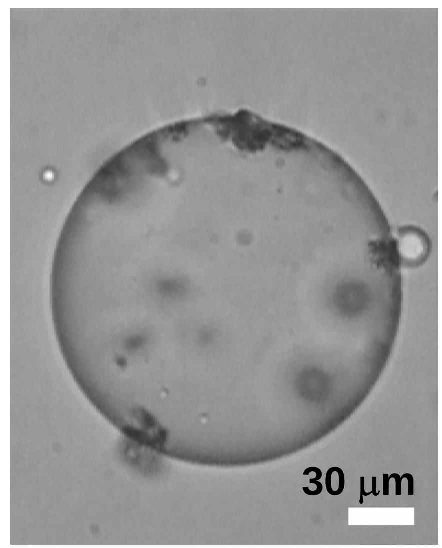


100 nm

Emulsified oil

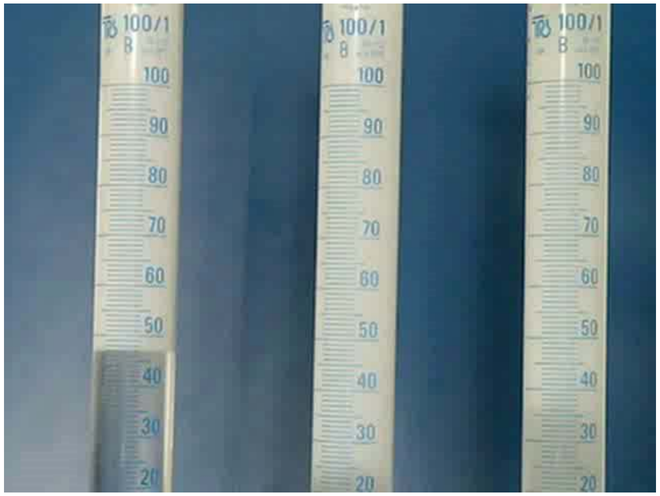


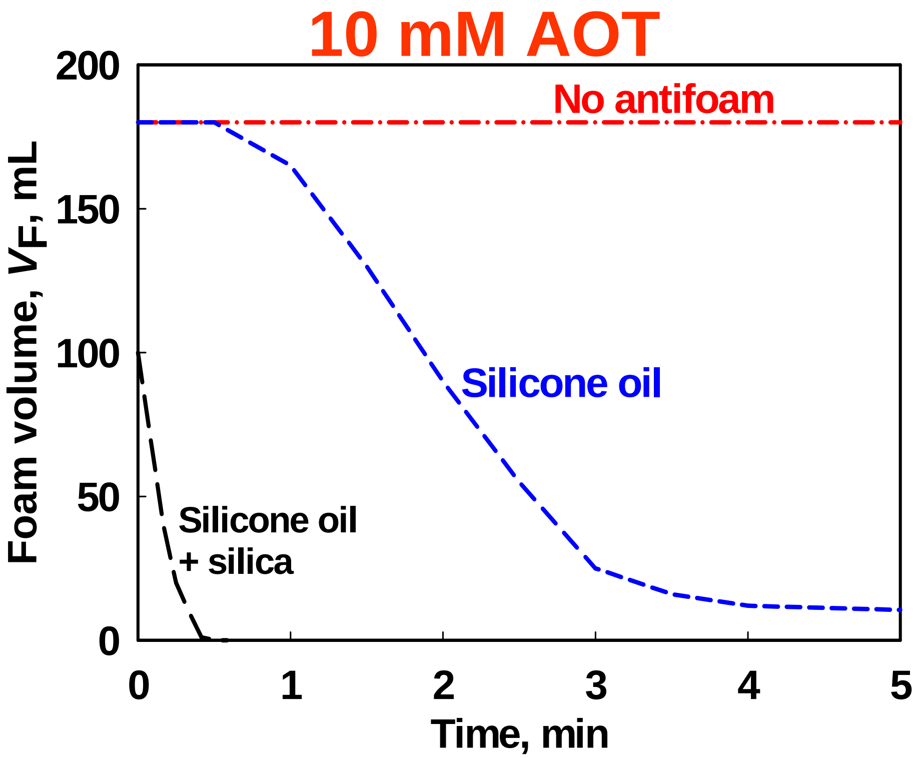
30 μm



Compound globule

Mechanisms of antifoam action: Fast and Slow antifoams

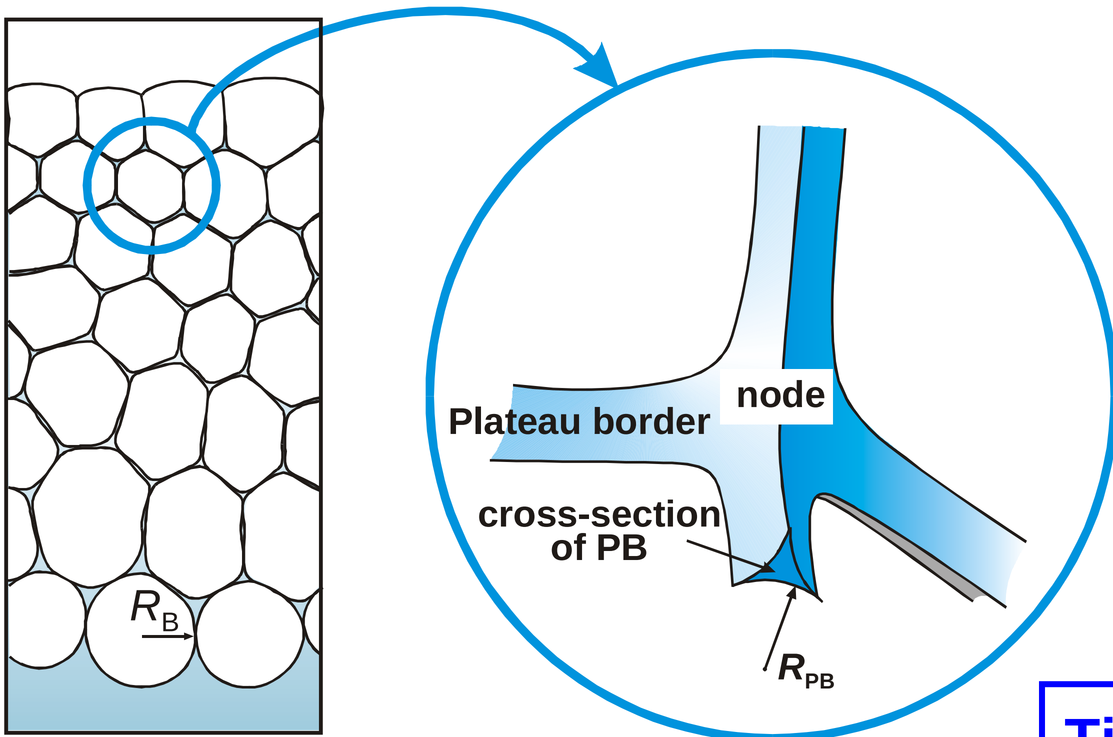


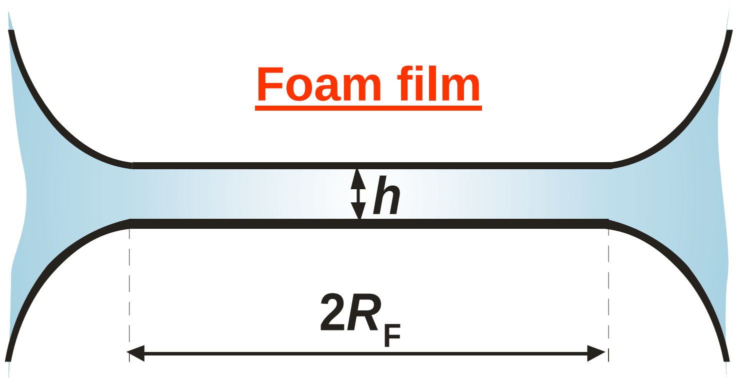


Fast Antifoams
- Foam lifetime ~ seconds
- Foam completely destroyed

Slow Antifoams
- Foam halftime ~ minutes
- Residual foam

Characteristic size- and time-scales in foam





Size scales:

- **Foam films**

  eq. thickness ~ 15 nm

- **Plateau borders (PB)**

  section ~ 100 to 1 μm

- **Nodes**

  section ~ 100 to 1 μm

Time scales:

Foam films

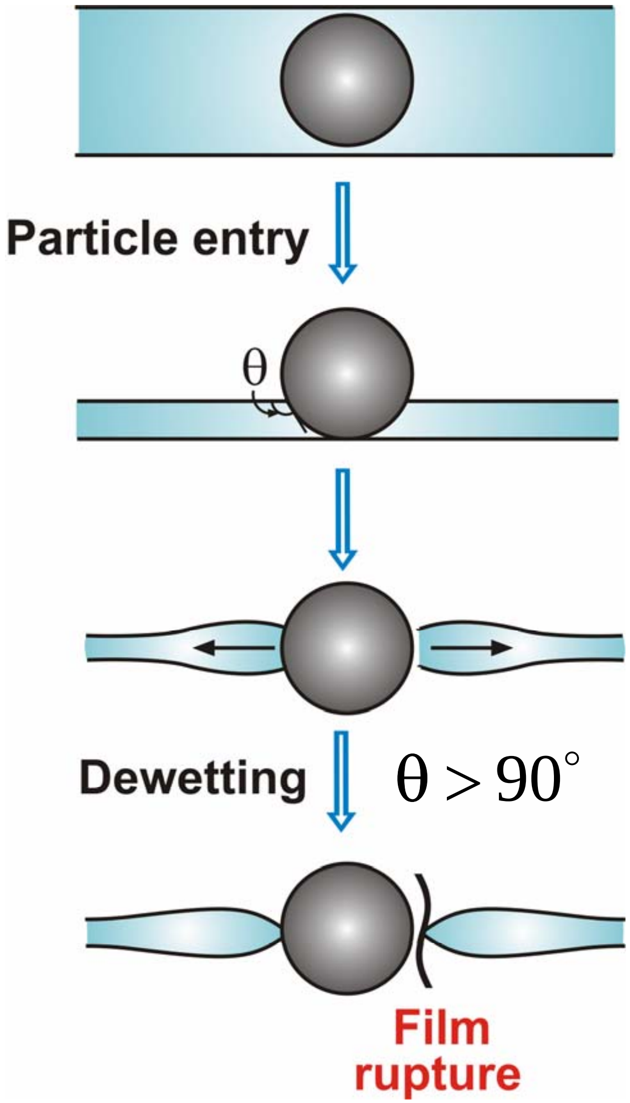
to 1 μm for several seconds

Plateau Borders

at R_B = 1 mm ➔ $\tau_{DR} \approx$ 80 s

at R_B = 300 μm ➔ $\tau_{DR} \approx$ 800 s

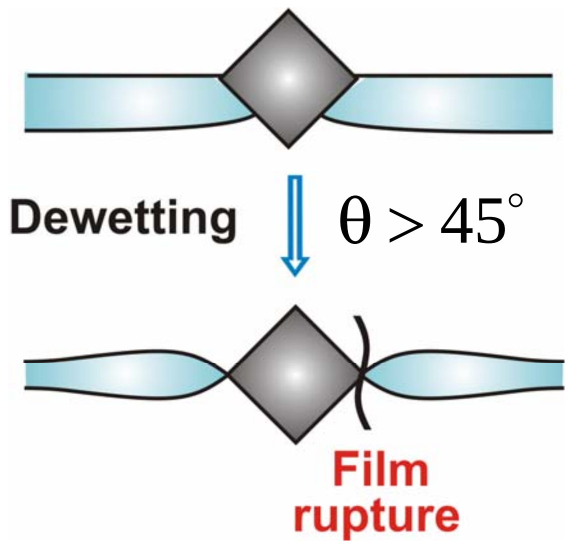
Film rupture by solid particles: <u>bridging-dewetting mechanism</u>



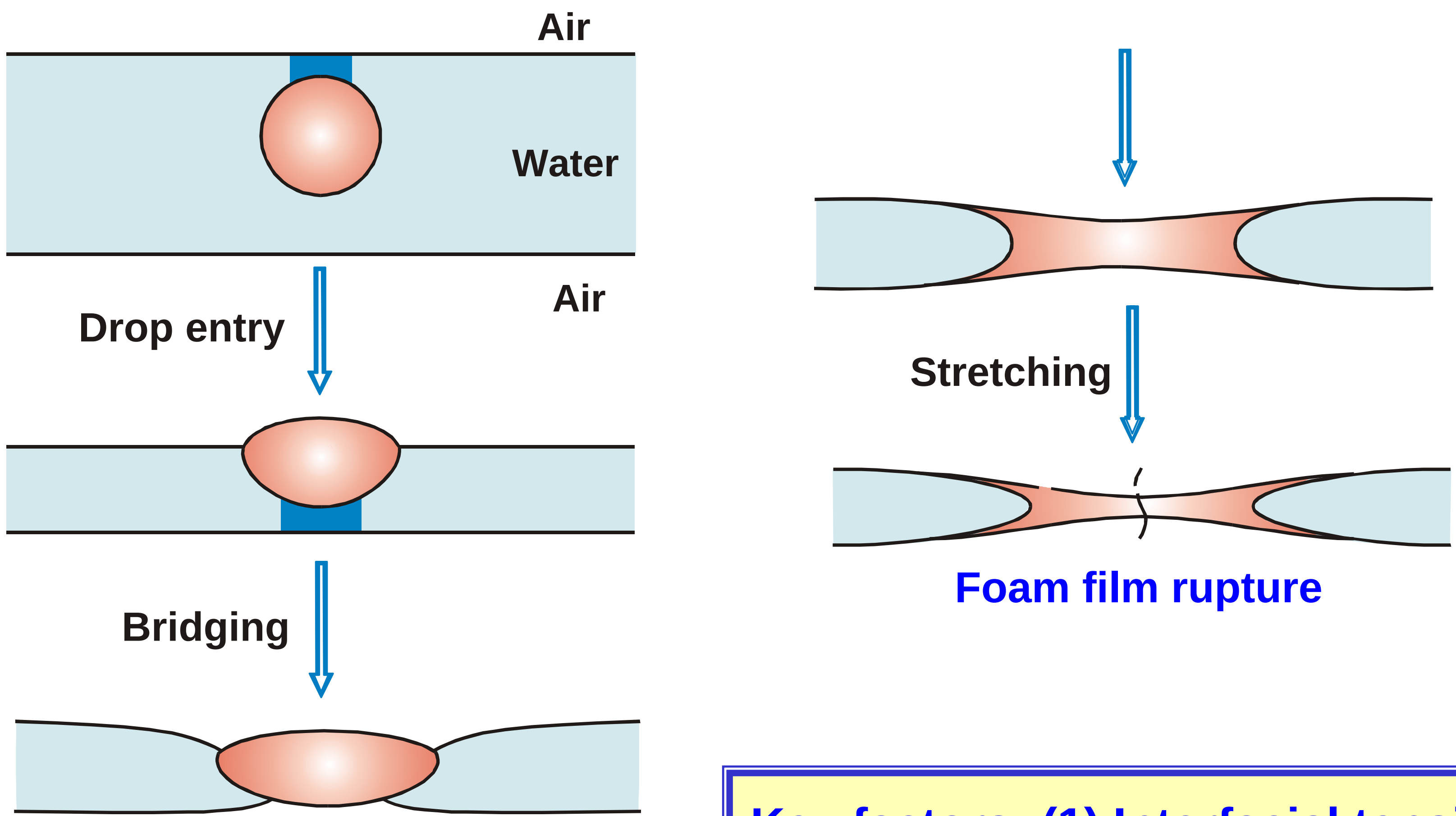
<u>Key factors</u>:

(1) Contact angle

(2) Particle size and shape

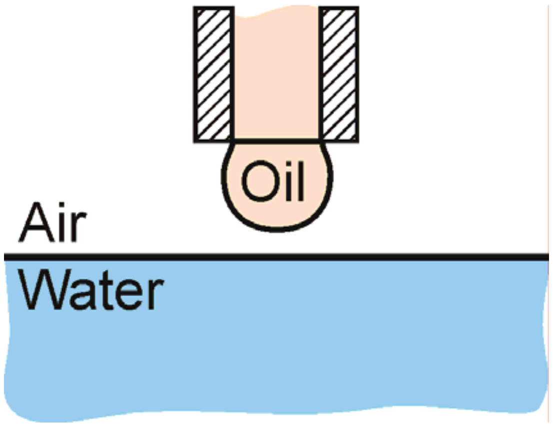


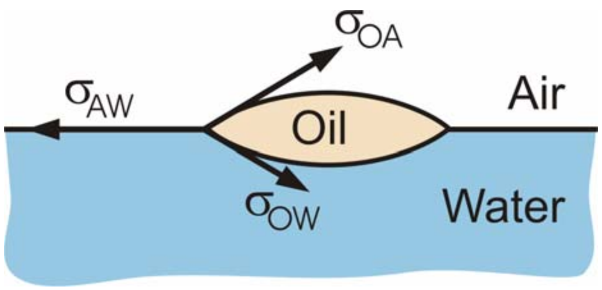
Film rupture by oil-solid compounds: <u>bridging-stretching mechanism</u>



<u>Key factors</u>: (1) Interfacial tensions
(2) Oil rheology

Film rupture after oil spreading



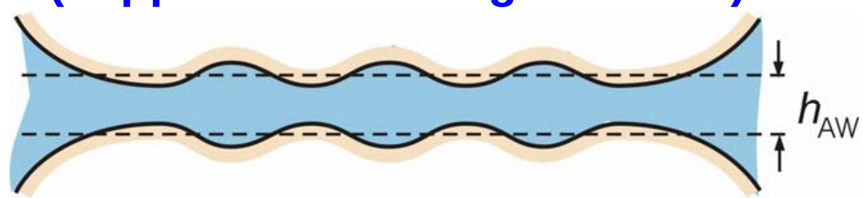


Spreading coefficient

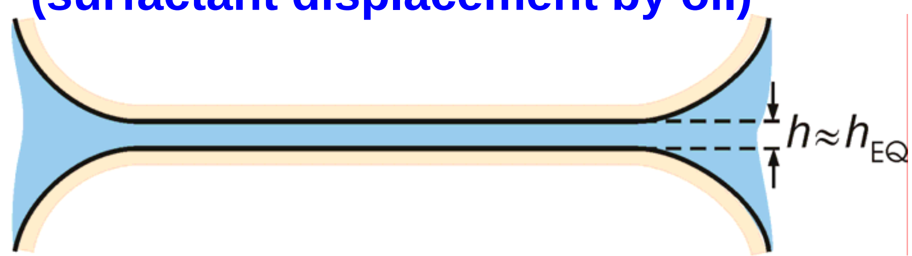
$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA}$$

Modes of film rupture by spread oil

(a) Rupture of thick foam films (suppressed Marangoni effect)



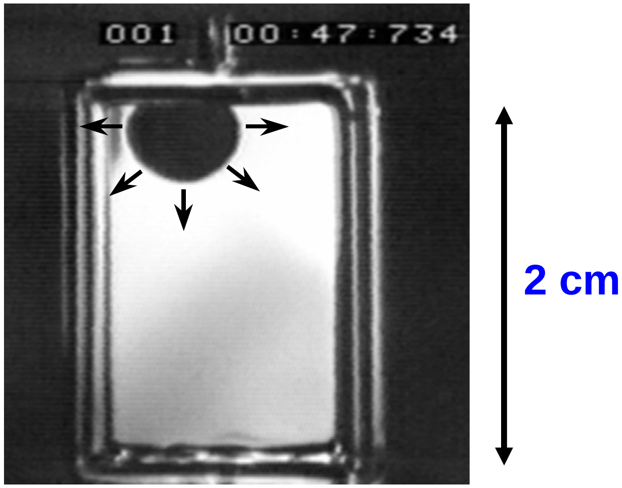
(b) Rupture of thin foam films (surfactant displacement by oil)



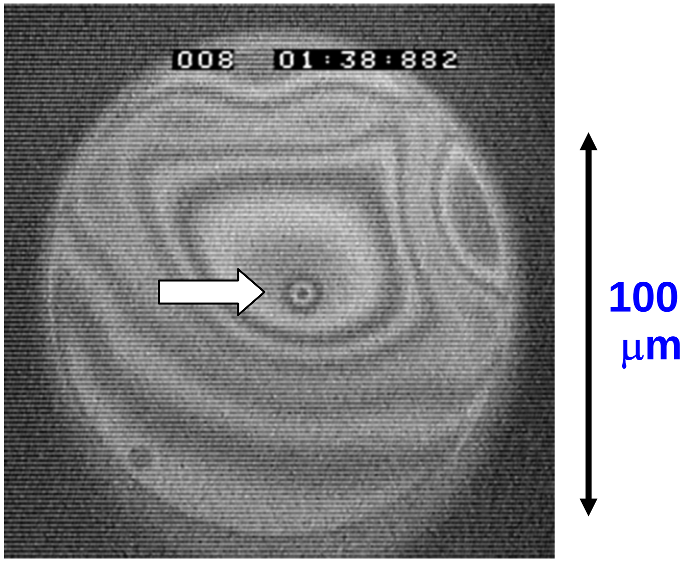
Key factors: (1) Rate of oil spreading
(2) Thickness and structure of spread layer

Optical observation of film rupture (fast antifoams)

Large foam film suspended on glass frame - expanding hole
(high speed camera, 500 fps)



Microscopic film - initial stage of film rupture

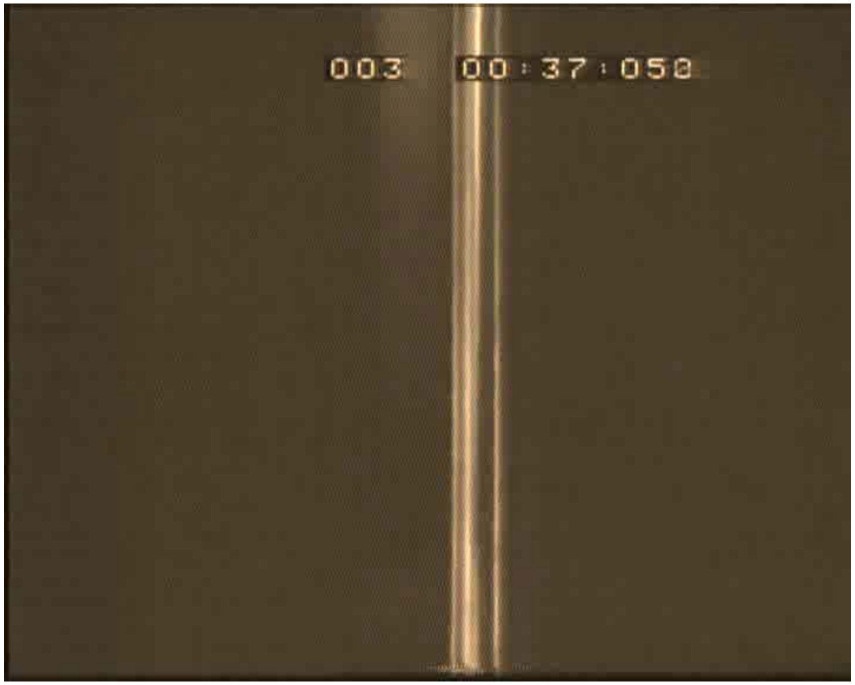


The fast antifoams rupture the films almost immediately after film formation at thickness ~ 1 μm

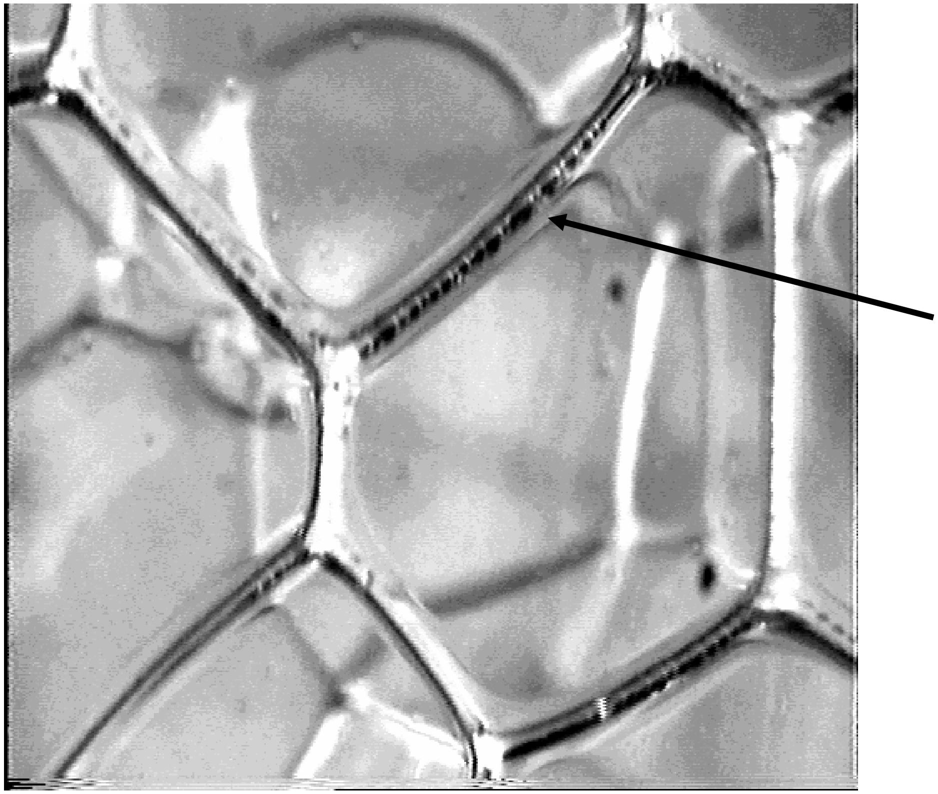
Optical observation of film rupture (fast antifoams)

Large foam film suspended on glass frame

(high speed camera, 500 fps)



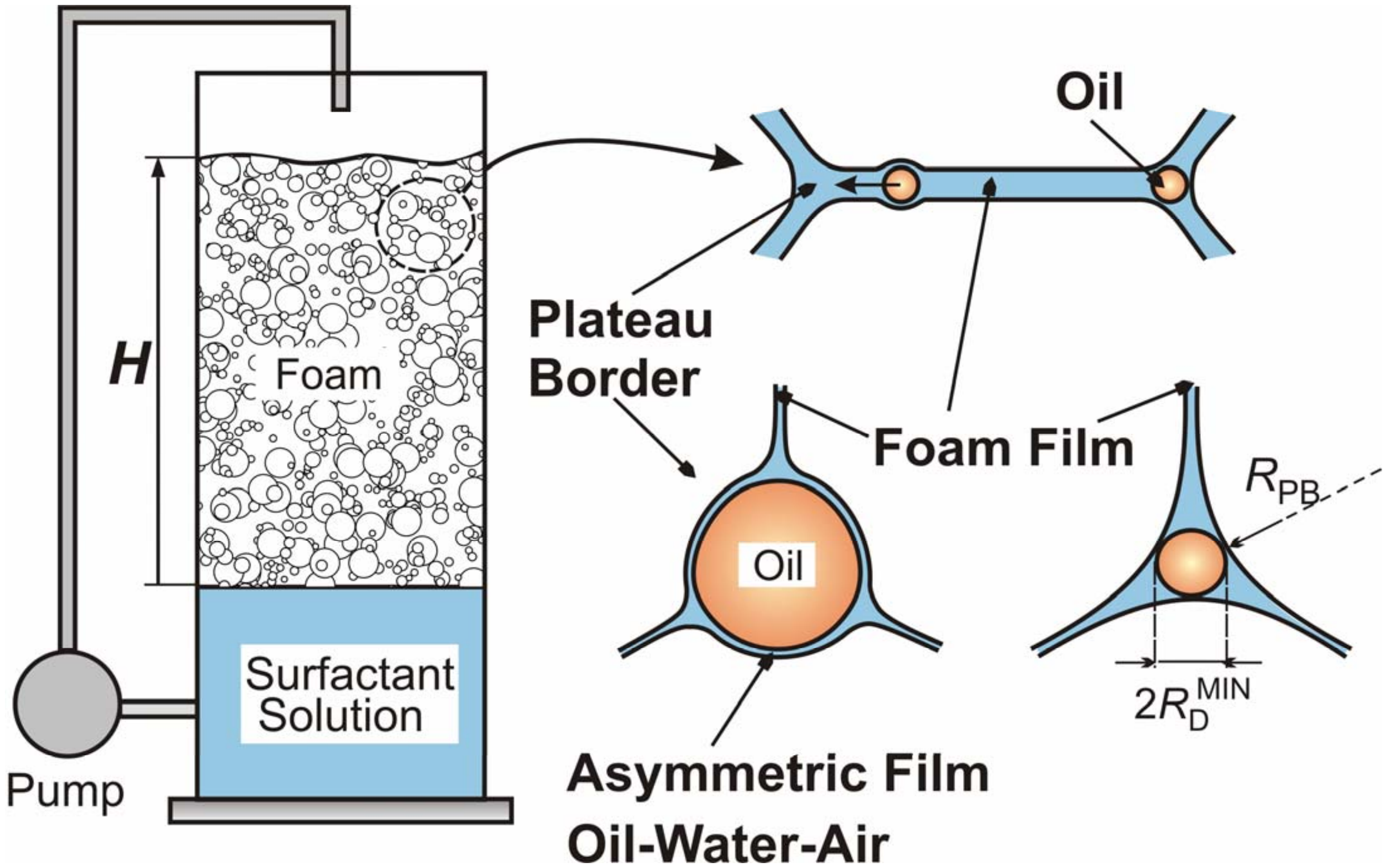
Slow antifoams: Oils drops trapped in Plateau channels



Slow Antifoams – the oil drops:

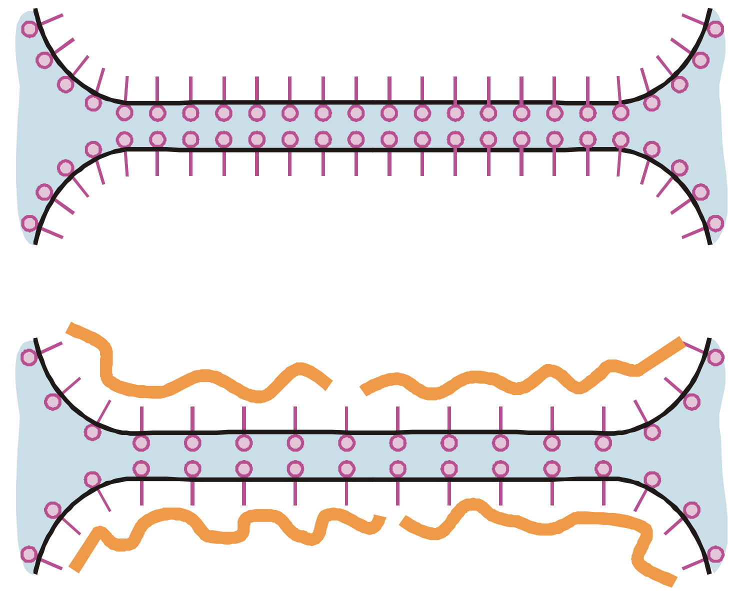
- Escape from the foam films without rupturing them
- Accumulate in the Plateau channels of the foam
- Break the foam films after entry in the Plateau channel

Slow antifoams -
Entry in the Plateau borders



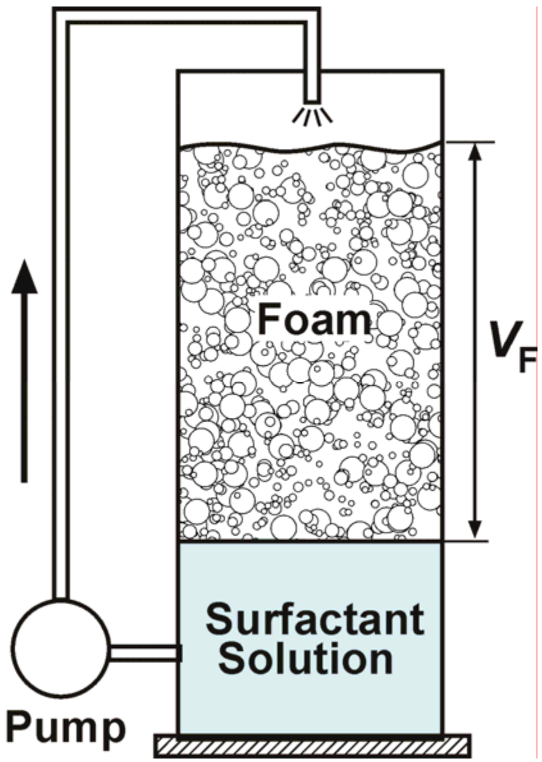
Key factors: (1) Critical pressure for drop entry (entry barrier)
(2) Drop size

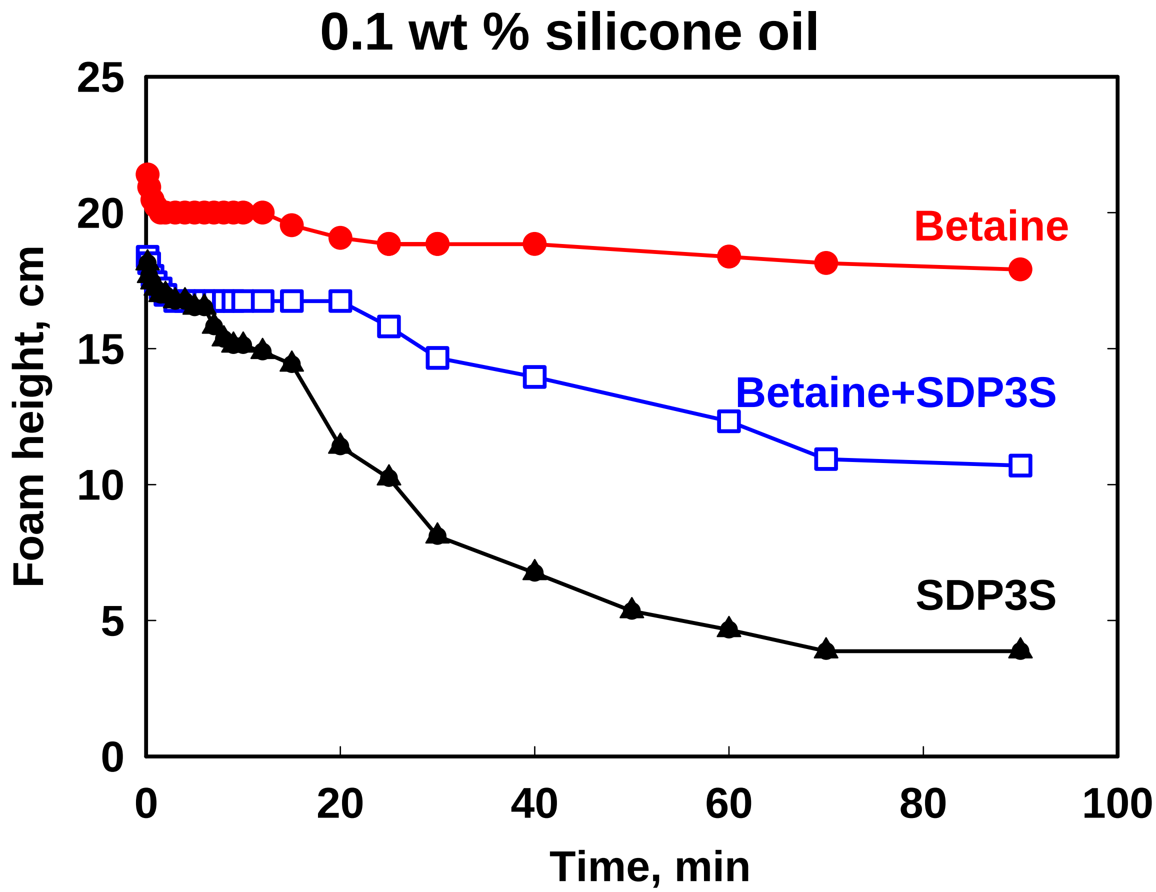
Foam film rupture by slow antifoam (silicone oil)



The spread oil ruptures the thin foam films probably by surfactant displacement

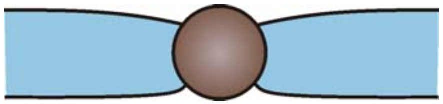
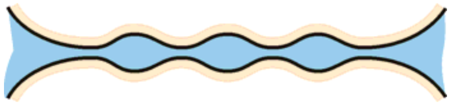
Enhanced foam stability by using Cosurfactants





Classification:

Types of antifoam and mechanisms of antifoam action

Antifoam composition	Type of action	Mode of foam destruction	Schematic presentation
Solid particles	Slow (fast)	Bridging-dewetting	
Oils	Slow	Spreading	
Oil-solid	Fast	Bridging-stretching Bridging-dewetting	

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