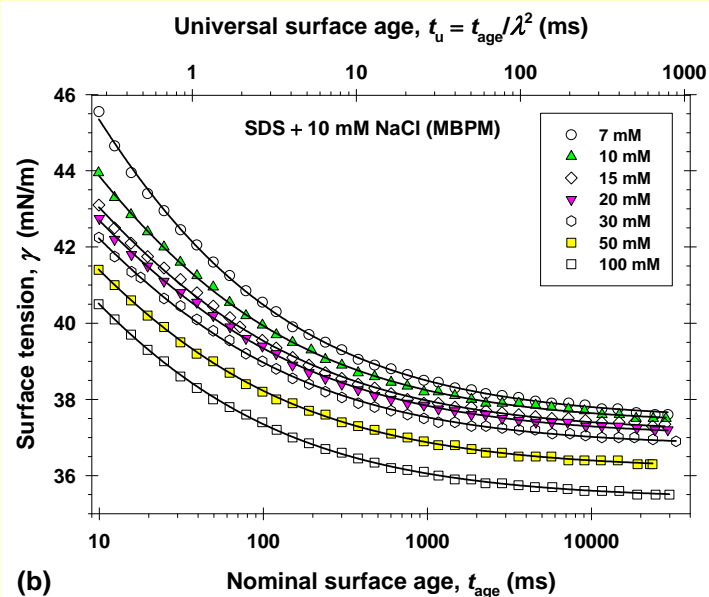


Dynamics of Surfactant Adsorption and Film Stability

Krassimir D. Danov

Department of Chemical Engineering, Faculty of Chemistry
Sofia University, Sofia, Bulgaria

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

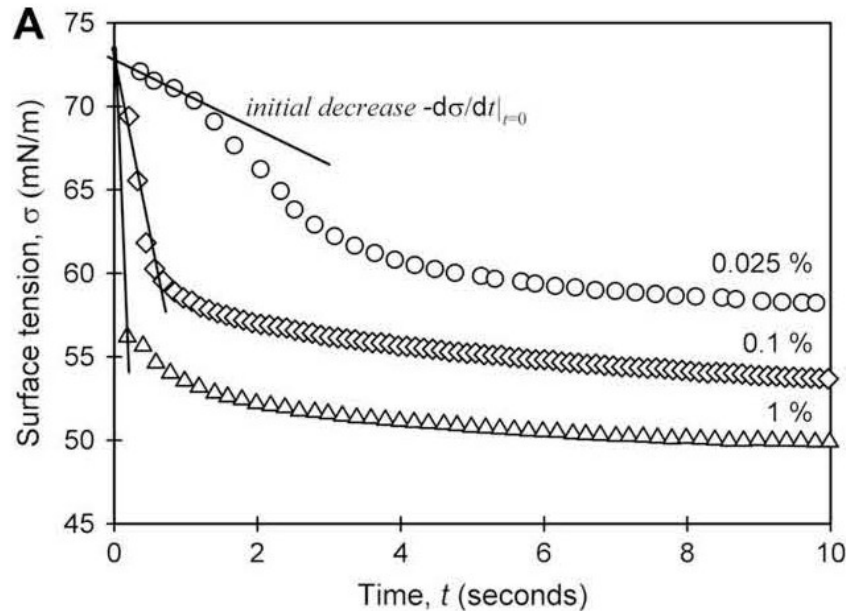


Example:
Dynamic surface
tension measured
by maximum
bubble pressure
method (MBPM)

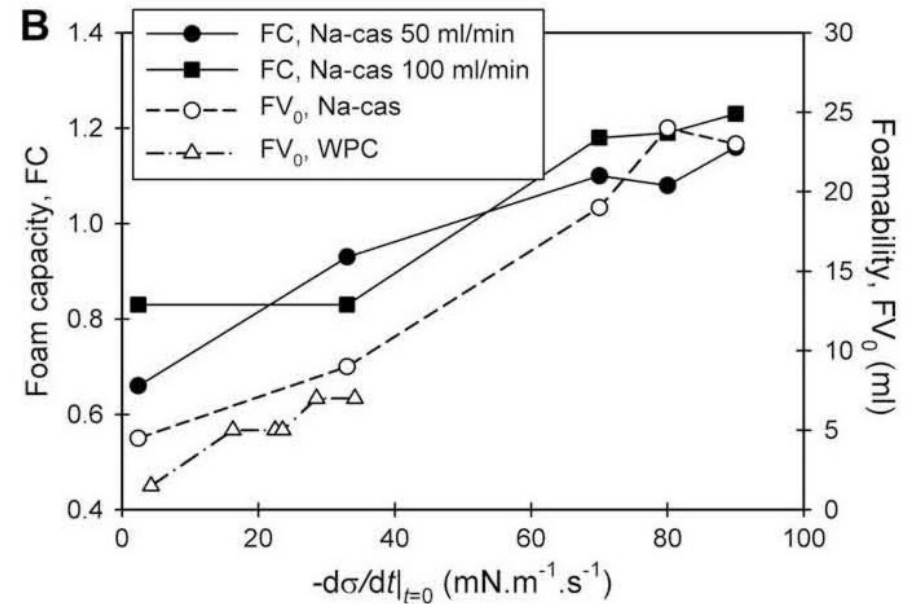


Sofia University

The dynamics of surface tension correlates to the foam capacity and foamability (Examples)

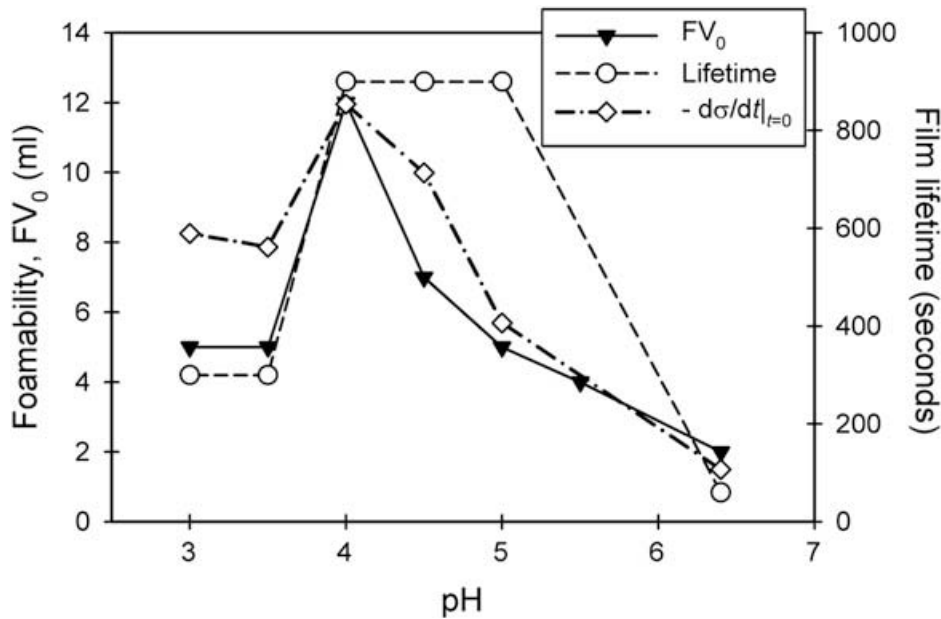


The **initial decrease, $d\sigma/dt$** , of surface tension (Na-cas, natural pH) [5].

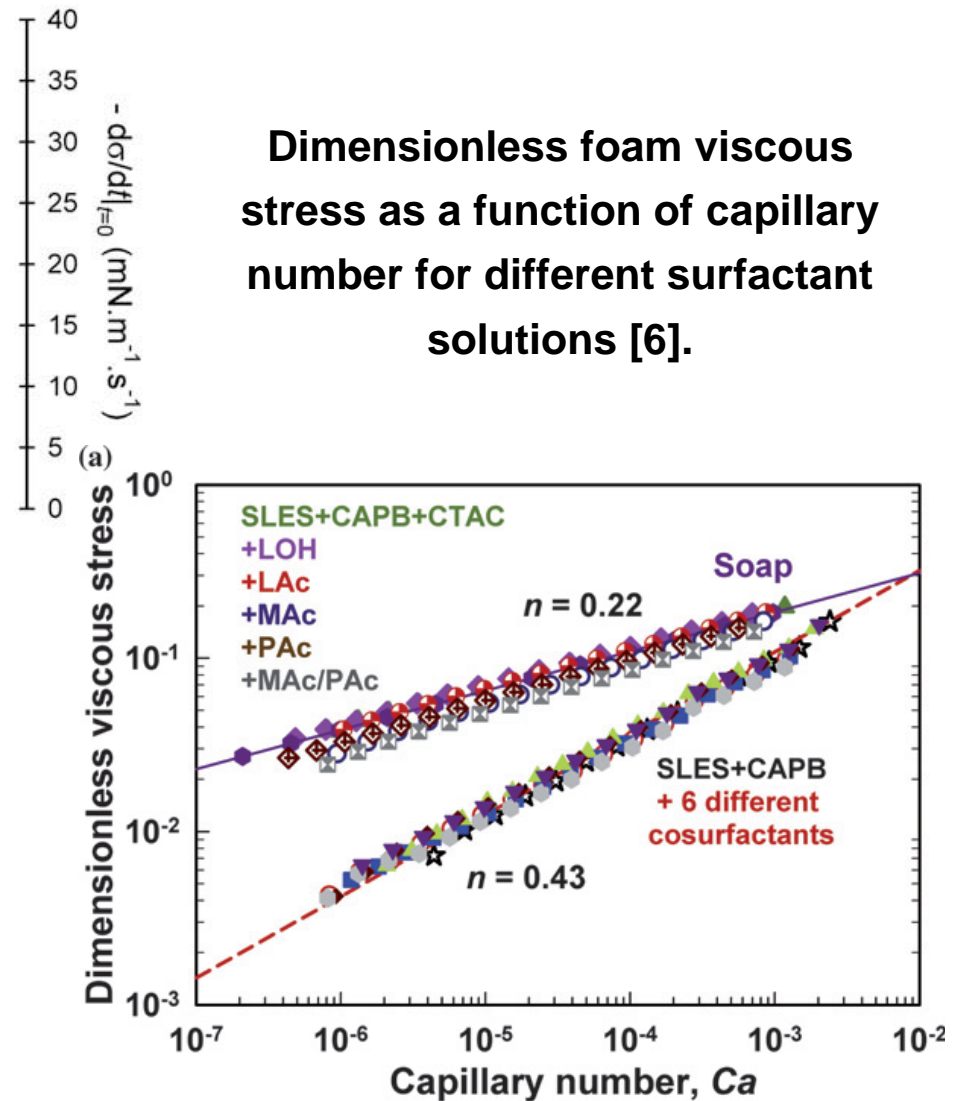


Foam capacity and foamability of Na-cas and WPC solutions vs. $d\sigma/dt$ [5].

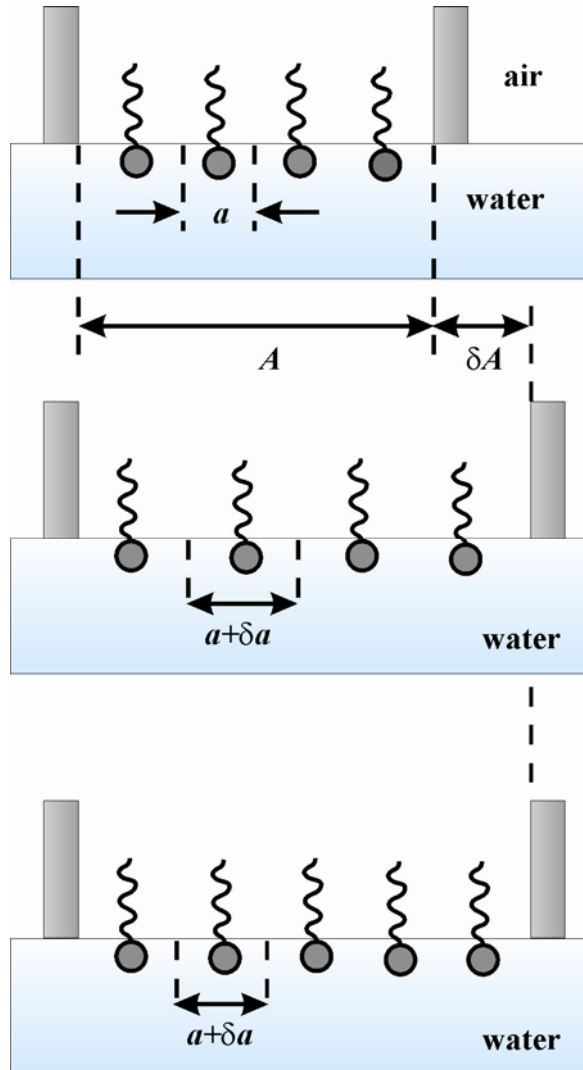
The dynamics of surface tension is related to the film lifetime and foam viscous friction (Examples)



Film lifetime, foamability, and rate of dynamic surface tension decrease for WPC solutions as a function of pH [5].



Surface (total) and adsorption layer (local) deformations



The surface element with an area A is extended to a new area $A + \delta A$ for a time interval from t to $t + \delta t$. The surface dilatation, α , and the rate of surface dilatation are defined as [4]:

$$\dot{\alpha} \equiv \frac{1}{A} \frac{\delta A}{\delta t} \qquad \alpha \equiv \int_0^{\delta t} \dot{\alpha} dt$$

The adsorption changes from Γ to $\Gamma + \delta \Gamma$ and the area per molecule in the adsorption layer – from a to $a + \delta a$. The adsorption layer deformation and its rate [4]:

$$\dot{\varepsilon} \equiv \frac{1}{a} \frac{\delta a}{\delta t} \qquad \varepsilon \equiv \int_0^{\delta t} \dot{\varepsilon} dt$$

For insoluble surfactants the both deformations α and ε are equal.

For soluble surfactants always the adsorption layer deformation is smaller than the surface dilatation, $\alpha > \varepsilon$, because of the bulk diffusion of surfactants.

Surfactant mass balance equations in the bulk phase

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{v}) + \nabla \cdot \mathbf{j} = r$$

convective flux

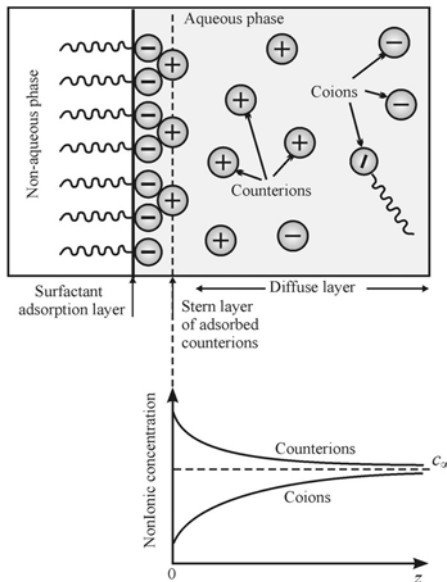
bulk diffusion flux

c – bulk surfactant concentration; \mathbf{v} – fluid velocity; \mathbf{j} – diffusion flux; r – source term accounting for the possible chemical reactions [1,2,4].

The Fick law of diffusion:

$$\mathbf{j} = -D\nabla c$$

where D is the diffusion coefficient (diffusivity).



The diffusion flux is proportional to the gradient of chemical potential. Thus, for ionic surfactants [7]:

$$\mathbf{j}_i = -D_i \left(\nabla c_i + \frac{Z_i e c_i}{kT} \nabla \psi \right)$$

where kT is the thermal energy, Z_i is the valency of the respective ion, ψ is the electric potential.

At equilibrium the diffusion flux is equal to zero and the Boltzmann distribution takes place [7]:

$$c_i = c_{i\infty} \exp\left(-\frac{Z_i e}{kT} \psi\right)$$

Surfactant mass balance equations at surfaces

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{v}_s) + \nabla_s \cdot \mathbf{j}_s = r_s + \langle \mathbf{j} \cdot \mathbf{n} \rangle$$

Γ – adsorption; \mathbf{v}_s – surface velocity; \mathbf{j}_s – surface diffusion flux; r_s – surface source term accounting for the possible chemical reactions [1,2].

↑ **surface convective flux**
 ← **surface diffusion flux**
 ← **surfactants bulk fluxes to the surface**

The Fick law of diffusion: $\mathbf{j}_s = -D_s \nabla \Gamma$ where D_s is the surface diffusion coefficient.

Generally, the surface diffusion flux is proportional to the gradient of the surface chemical potential.

For simplest surface reaction $\Gamma_1 \leftrightarrow \Gamma_2$ one has [8]: $r_1 = -r_2 = -k_+ \Gamma_1 + k_- \Gamma_2$

For surface association reaction $\Gamma_1 + \Gamma_2 \leftrightarrow \Gamma_3$ we have [8]: $r_1 = r_2 = -r_3 = -k_+ \Gamma_1 \Gamma_2 + k_- \Gamma_3$

The rate constant of forward reaction is k_+ and that of the reverse reaction is k_- .

Solution of diffusion equation for simple surfactant

For simple surfactant solution below the CMC when the surface layer is in quasi-equilibrium with the contiguous bulk phase (**diffusion-controlled adsorption processes**):

$$\Gamma(t) = \Gamma(0) + 2c_b \sqrt{\frac{Dt}{\pi}} - \sqrt{\frac{D}{\pi}} \int_0^t \frac{c_s(\tau)}{\sqrt{t-\tau}} d\tau \quad \text{and} \quad \Gamma(t) = \Gamma(c_s) \quad (\text{Ward and Tordai [4,9]})$$

where c_b is the input concentration, c_s is the subsurface concentration, and $\Gamma(c_s)$ is the adsorption isotherm.

General asymptotic expression for the short times reads:

$$\Gamma(t) = \Gamma(0) + 2[c_b - c_s(0)] \sqrt{\frac{Dt}{\pi}}$$

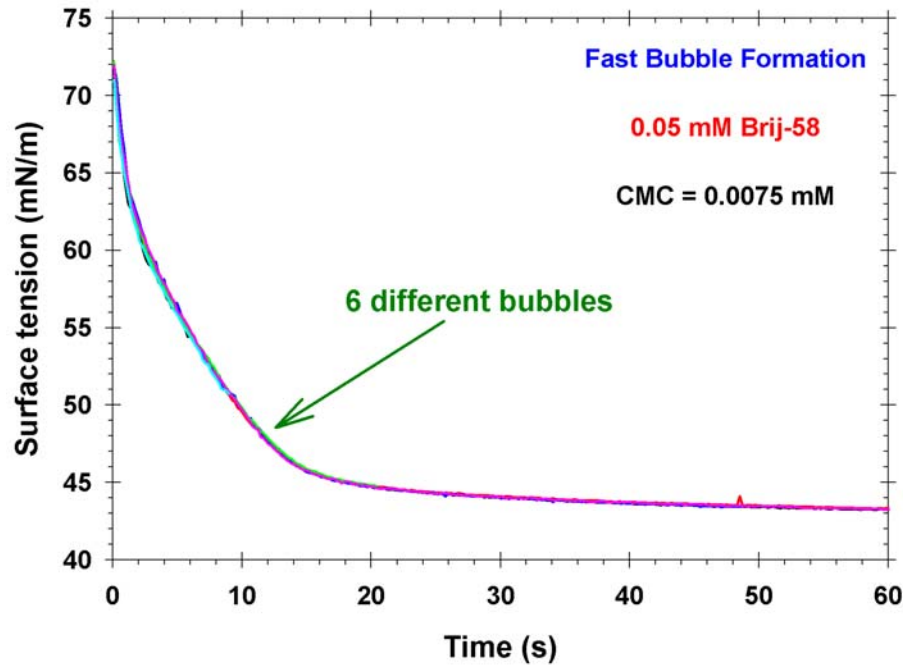
Analogous asymptotic expression for the long times is:

$$c_s(t) = c_b - \frac{\Gamma_e - \Gamma(0)}{\sqrt{\pi Dt}}$$

where Γ_e is the equilibrium value of the surfactant adsorption, that is $\Gamma_e = \Gamma(c_b)$.

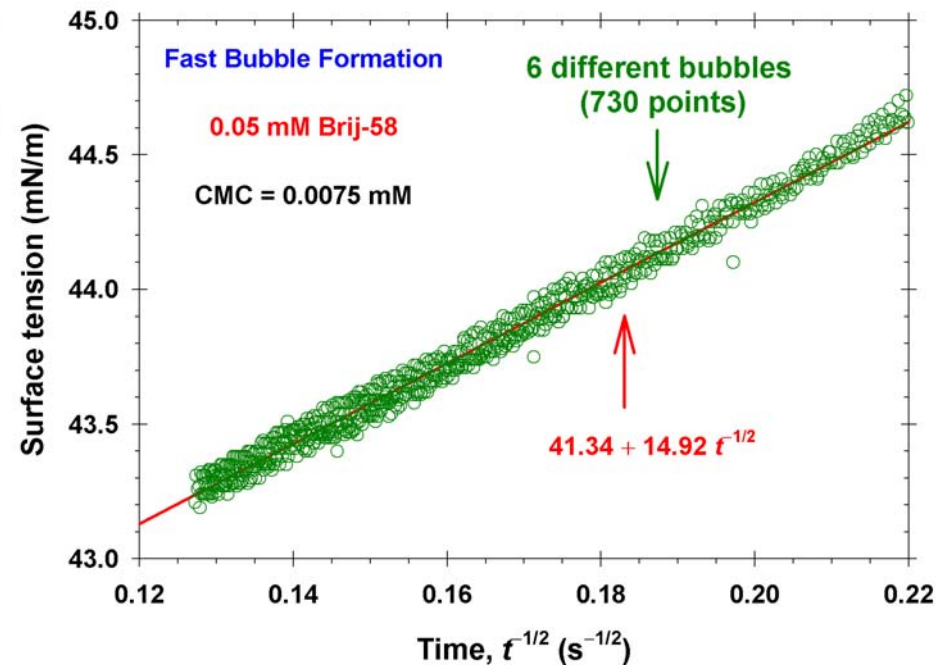
For both asymptotic solutions the two-dimensional equation of state, $\gamma = \chi(\Gamma)$ or $\gamma = \chi(c_s)$, relates the measured surface tension and time.

Diffusion-controlled adsorption (experimental examples)

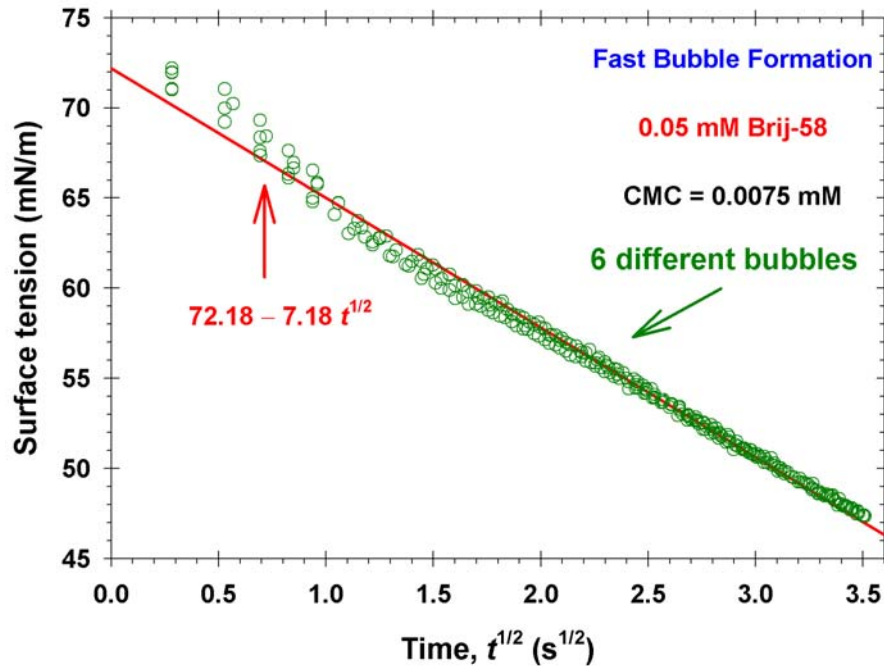


Surface tension vs. time for 6 different bubbles formed in 0.05 mM Brij-58 solution. The bubbles are formed very fast and after their formation the bubble volumes are kept constant.

From the linear plot of the surface tension vs. $t^{1/2}$ we can obtain the equilibrium surface tension (the intercept is 41.34 mN/m) and the slope, which is related to the adsorption at equilibrium.



Diffusion-controlled adsorption (experimental examples)



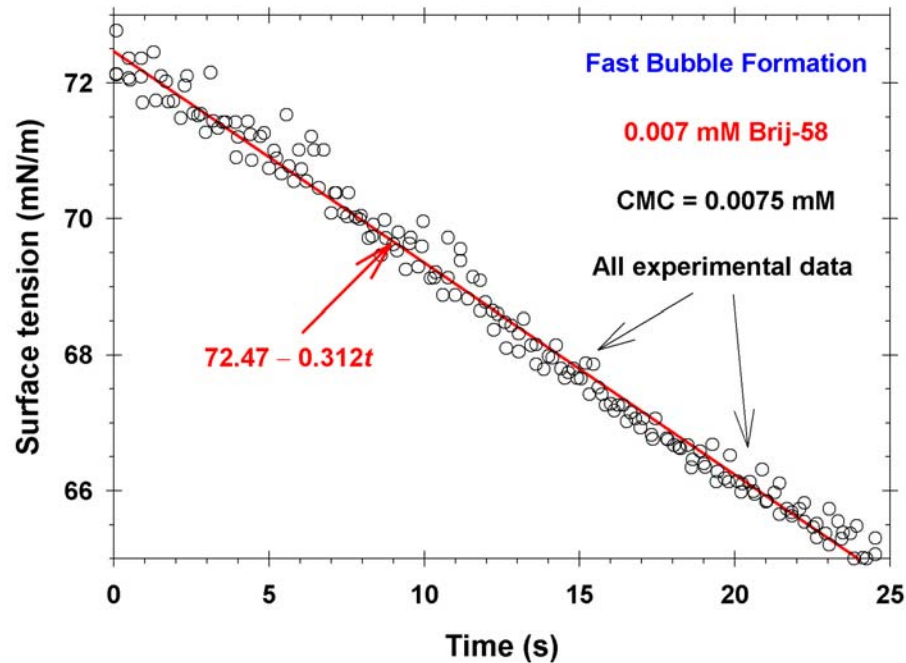
From the linear plot of the surface tension vs. $t^{1/2}$ one checks the mechanism of adsorption processes. The linear plot shows that we start from a clean surface – the intercept is 72.18 mN/m, which corresponds to zero initial adsorption. From the slope one can calculate the value of the diffusion coefficient.

$$\gamma(t) = \gamma(0) - 2kTc_b \sqrt{\frac{Dt}{\pi}}$$

The calculated diffusion coefficient from the slope is 2.6×10^{-9} m²/s, which 6 times greater than the diffusion coefficient of the individual molecule.

Conclusion: For some surfactant systems the mechanism of adsorption above the CMC is diffusion-controlled but with effective diffusion coefficient larger than the diffusion coefficient of the individual molecule (see below).

Barrier-controlled adsorption (experimental examples)



The adsorption is under barrier control when the stage of surfactant transfer from the subsurface to the surface is much slower than the diffusion stage. In this case the change of adsorption is controlled by the rate of adsorption, r_{ads} , and the rate of desorption, r_{des} [1,3]:

$$\frac{d\Gamma}{dt} = r_{\text{ads}}(\Gamma, c_s) - r_{\text{des}}(\Gamma)$$

The solution of the diffusion equation for this regime is:

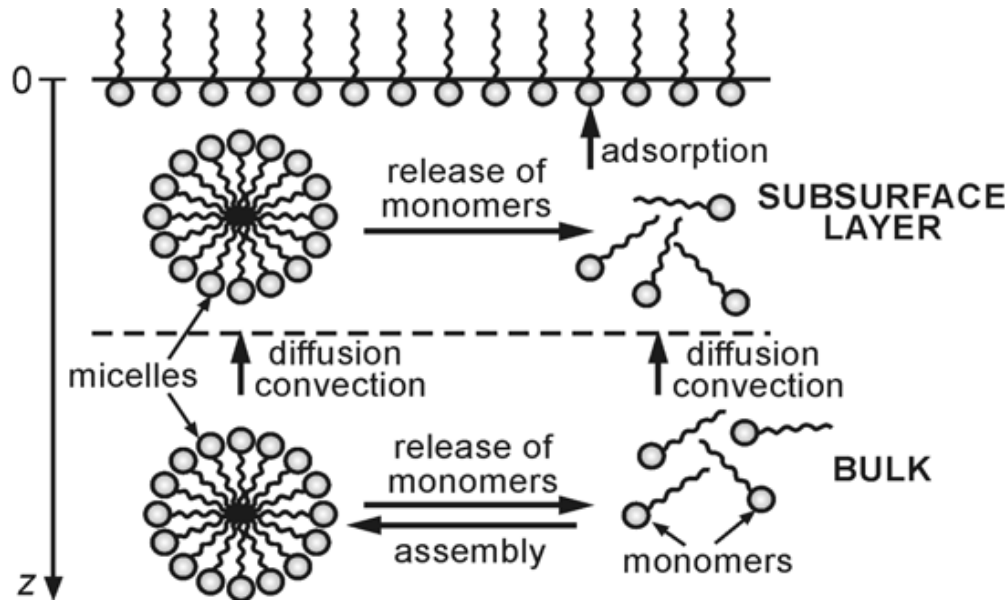
$$\gamma(t) = \gamma_e + [\gamma(0) - \gamma_e] \exp(-t/t_b)$$

The asymptotic expression for the short times is:

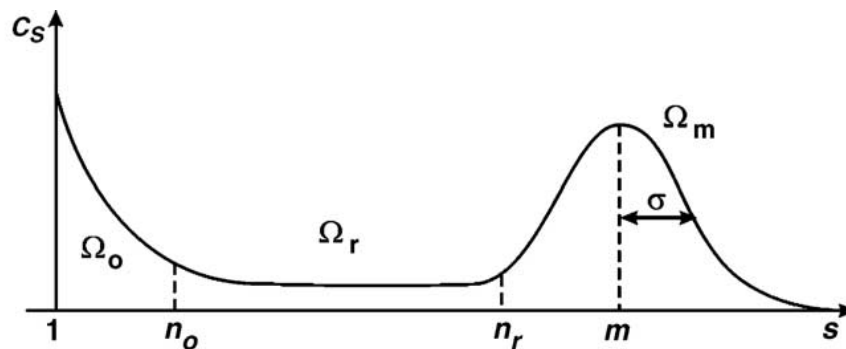
$$\gamma(t) = \gamma(0) - \frac{\gamma(0) - \gamma_e}{t_b} t$$

Conclusion: For barrier-controlled regime of adsorption from the initial slope of the surface tension vs. time one obtains the relaxation time of surfactant, t_b .

Dynamics of adsorption from micellar surfactant solutions



The micelles release monomers to restore the equilibrium concentrations of surfactant monomers at the surface and in the bulk. The concentration gradients give rise to diffusion of both monomers and micelles. The adsorbing component are the surfactant monomers, whereas the micelles do not adsorb.

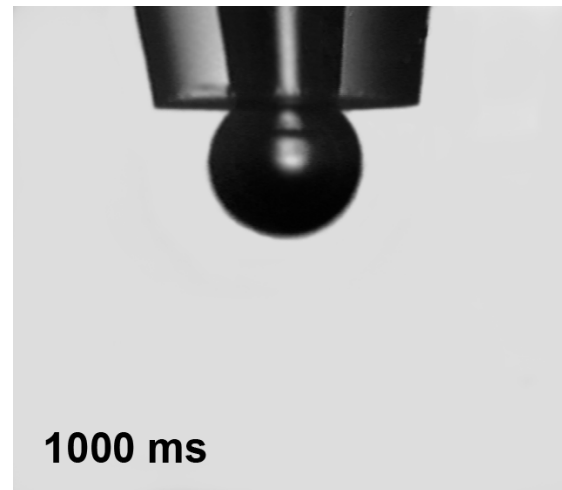
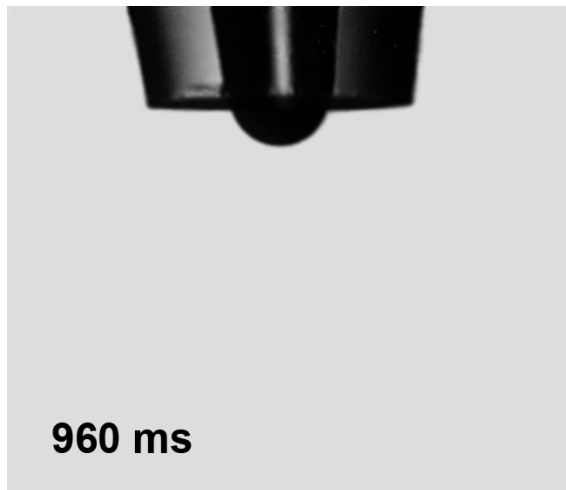
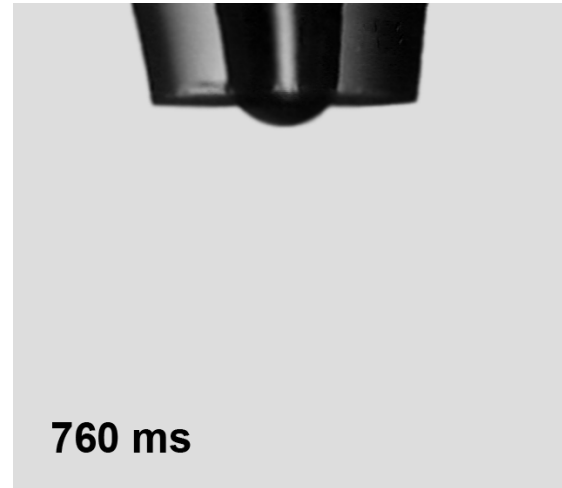
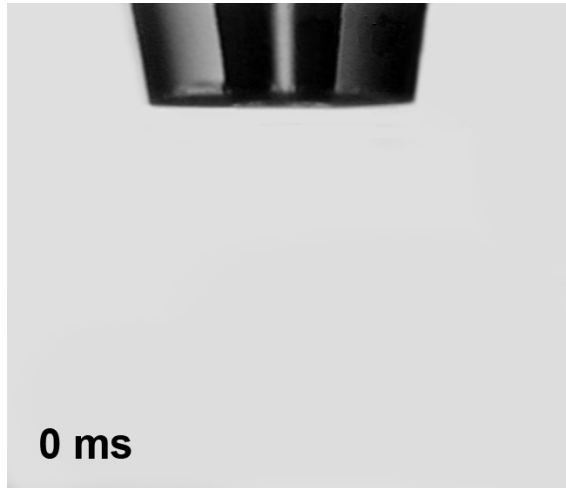


Typical distribution of micellar aggregates: m – the mean aggregation number; σ – the polydispersity of micelles; c_1 – concentration of monomers [11,12] (Aniansson and Wall).

Fast process: exchange monomers between micelles and surrounding solution.

Slow process: decomposition of micelles with critical micellar sizes.

Maximum bubble pressure method



Consecutive photographs of a bubble growing at the tip of a capillary hydrophobized by treatment with silicon oil.

One measures the maximum of pressure difference inside the bubble, which is directly related to the dynamic surface tension through the Laplace equation.

The experimental curve, $A(t)$, is known [3,13].

Maximum bubble pressure method (universal time age)

Bulk diffusion of simple surfactant

$$\frac{\partial c}{\partial t} - \dot{\alpha} z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2} + \dots$$

Mass balance at the interface

$$\frac{d\Gamma}{dt} + \dot{\alpha} \Gamma = D \frac{\partial c}{\partial z} + \dots$$

c – bulk concentration; Γ – adsorption; t – time; z – space coordinate; $d\alpha/dt$ – rate of surface dilatation; $A(t)$ – area of the surface

Time and space transformation [3,13,14]

$$y \equiv \frac{A(t)}{A(0)} z \quad \tau \equiv \int_0^t \frac{A^2(\tilde{t})}{A^2(0)} d\tilde{t}$$

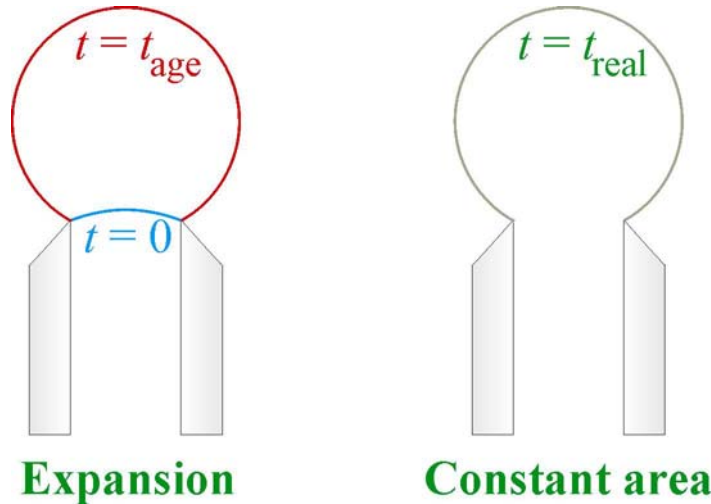
Bulk diffusion (classical problem)

$$\frac{\partial c}{\partial \tau} = D \frac{\partial^2 c}{\partial y^2} + \dots$$

Mass balance (classical problem)

$$\frac{d}{d\tau} \left[\frac{A(\tau)}{A(0)} \Gamma \right] = D \frac{\partial c}{\partial y} + \dots$$

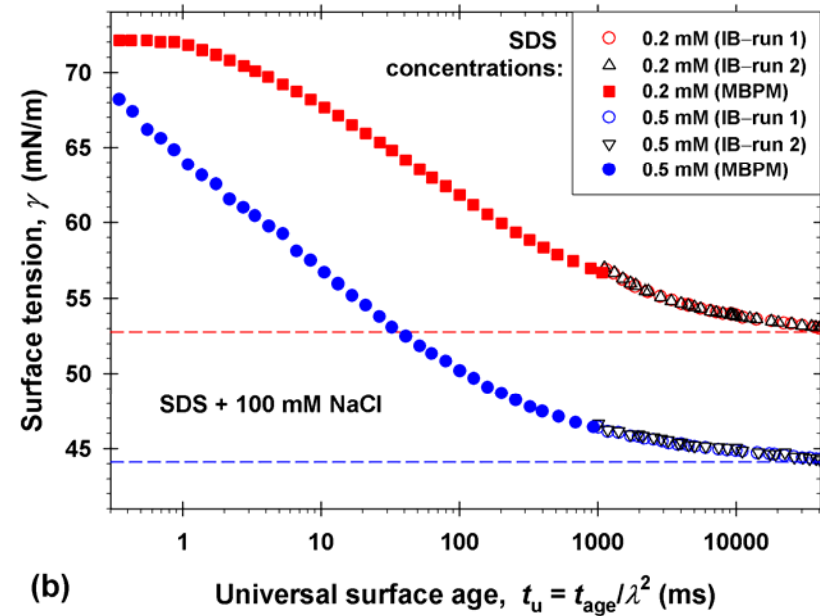
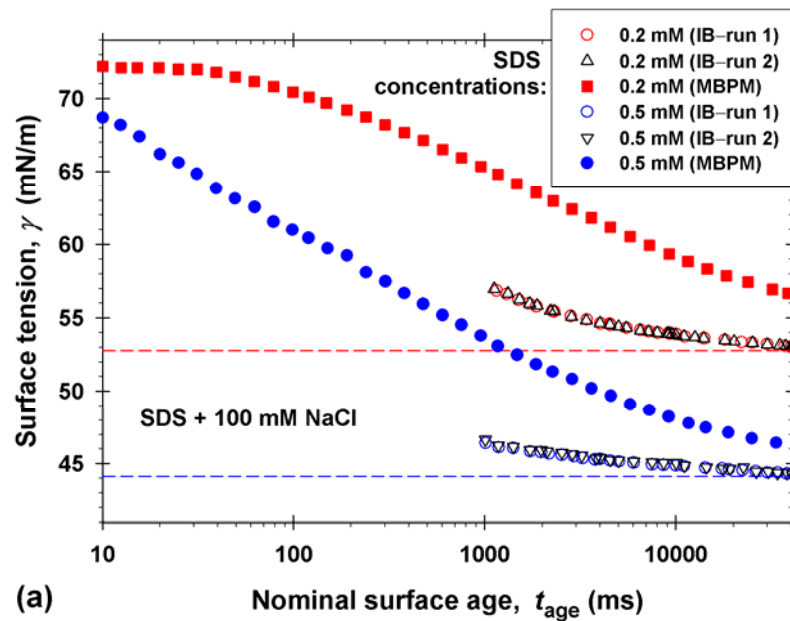
Maximum bubble pressure method (universal time age)



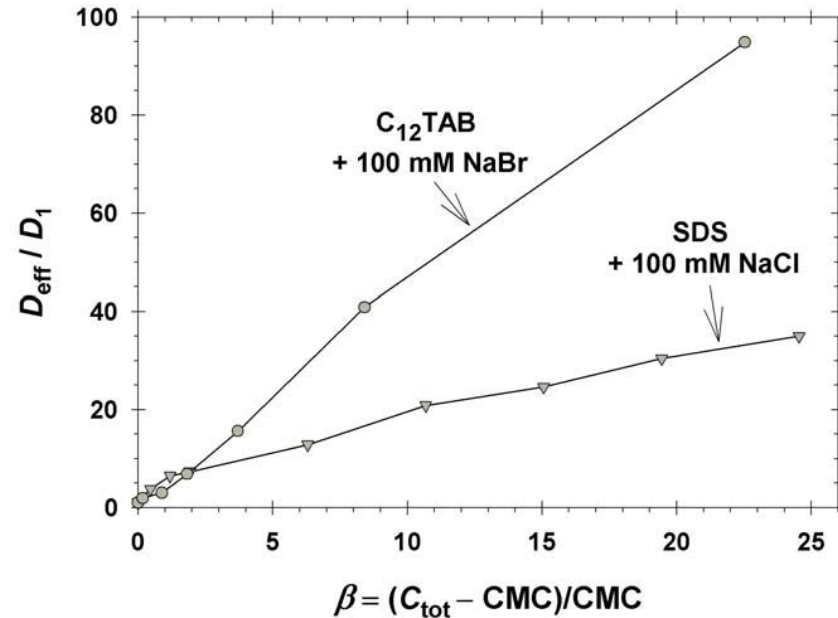
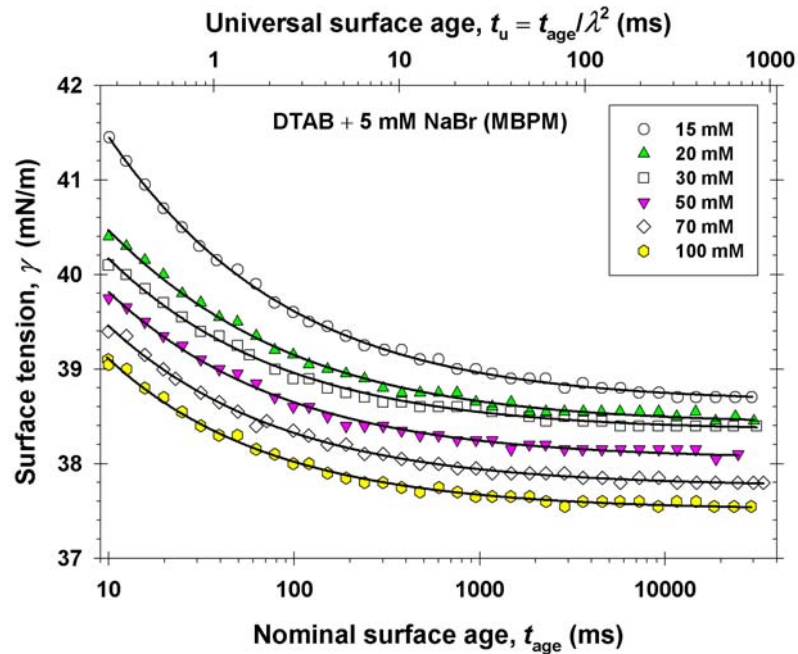
Apparent surface age: t_{age}

Real (universal) surface age $t_{\text{real}} < t_{\text{age}}$ [13]:

$$t_{\text{real}} \equiv t_{\text{age}} / \int_0^1 \frac{A^2(\xi)}{A^2(0)} d\xi$$



Maximum bubble pressure method (universal time age)



Experimental curves are processed with equation [1,13]:

$$\gamma = \gamma_{eq} + \frac{s_\gamma}{a + (t_{age})^{1/2}}$$

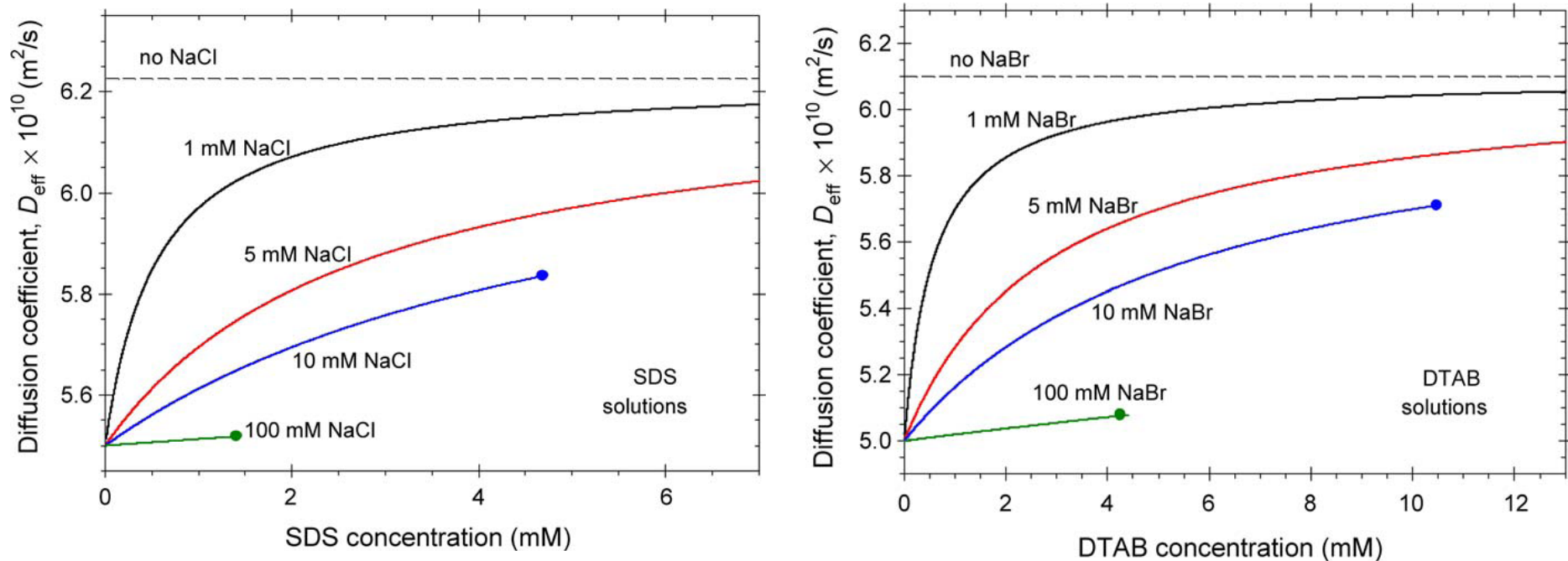
From s_γ we calculate the value of the effective diffusion coefficient.

For slow diffusion process in micellar solutions [10,11]:

$$\frac{D_{eff}}{D} = \left(1 + \beta \frac{\sigma^2}{m}\right) \left(1 + \beta \frac{\sigma^2}{m} \frac{D_m}{D}\right)$$

where D_m is the diffusion coefficient of micelles.

Effective diffusion coefficient of ionic surfactants

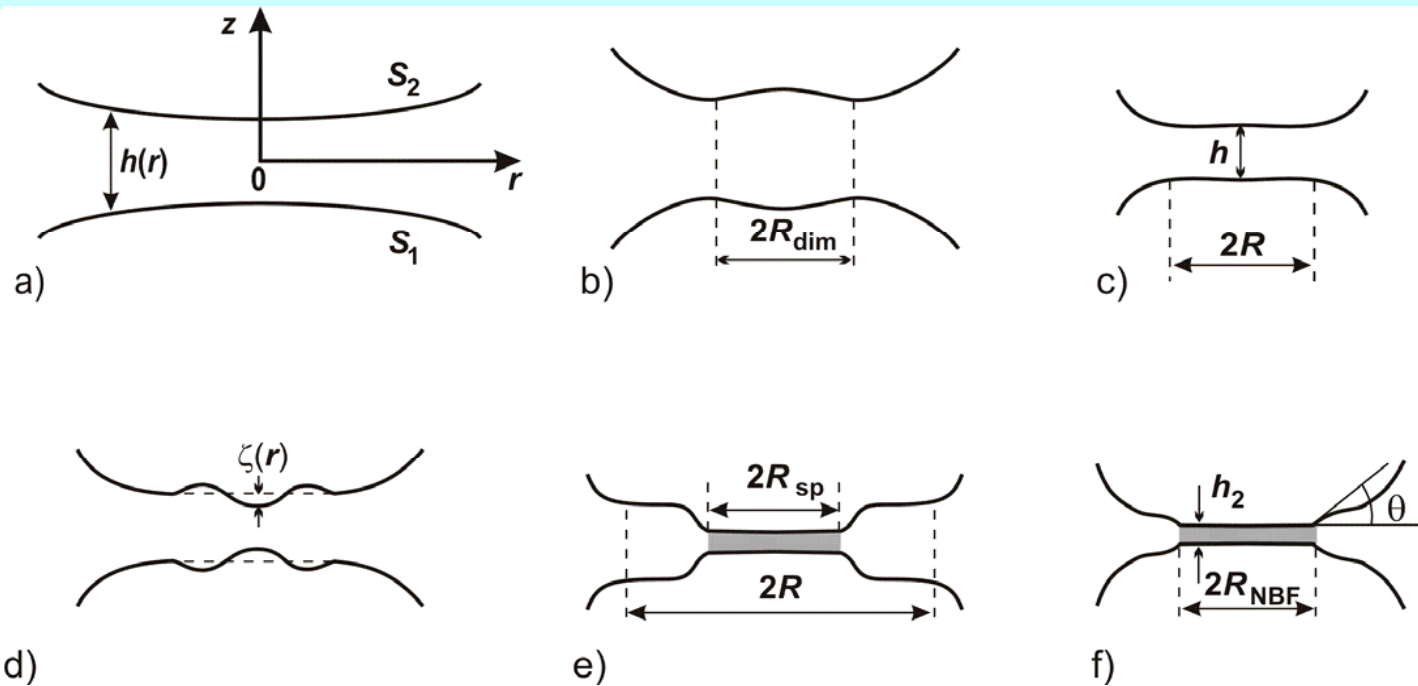


In the case of ionic surfactants the dynamics of surface tension obeys the same rules as for nonionic surfactants but with an effective diffusion coefficients, D_{eff} [15]:

$$D_{\text{eff}} = D_{\text{eff}}(D_1, D_2, D_3, \text{ concentrations})$$

where D_1 is the diffusion coefficient of surface active ion, D_2 of counterions, and D_3 of coions.

Typical consecutive stages of evolution of thin liquid films [4,16]



a) mutual approach of slightly deformed surfaces

b) the curvature at the film center inverts its sign and a "dimple" arises

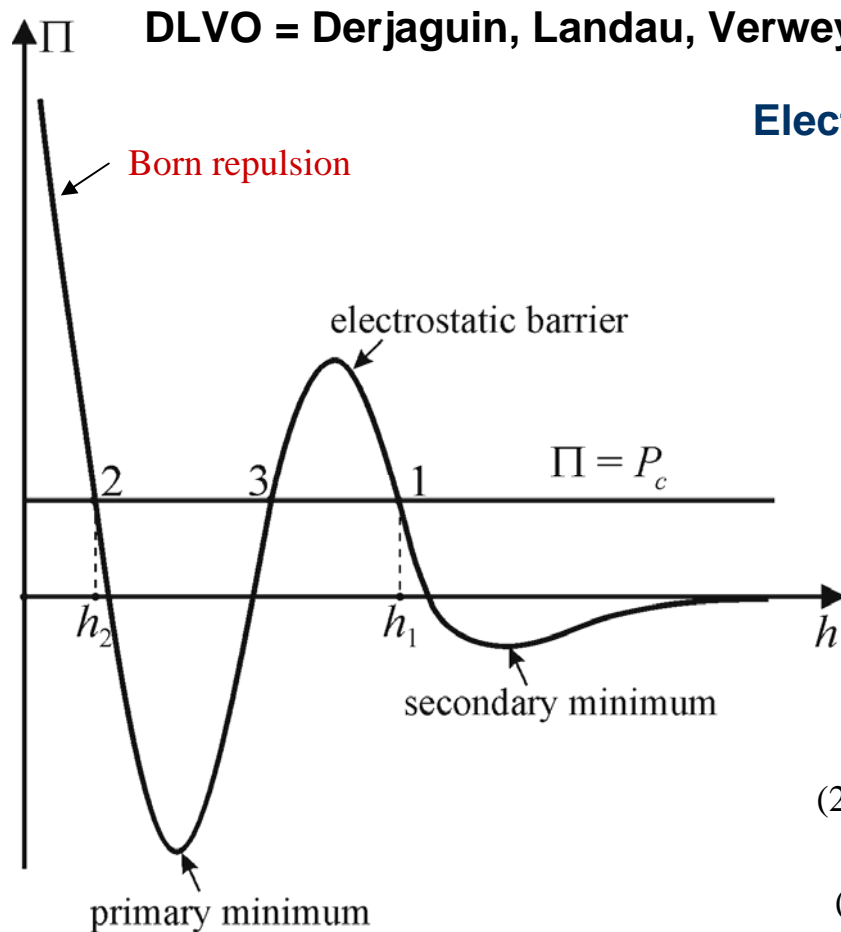
c) the dimple disappears and an almost plane-parallel film forms

d) due to thermal fluctuations or other disturbances the film either ruptures or transforms into a thinner Newton black film

e) Newton black film expands

f) the final equilibrium state of the Newton black film is reached

DLVO Theory: Equilibrium states of free liquid films



Electrostatic component of disjoining pressure [1]:

$$\Pi_{el}(h) = B \exp(-\kappa h) \quad (\text{repulsion})$$

Van der Waals component [1]:

$$\Pi_{vw}(h) = -\frac{A_H}{6\pi h^3} \quad (\text{attraction})$$

h – film thickness; A_H – Hamaker constant;

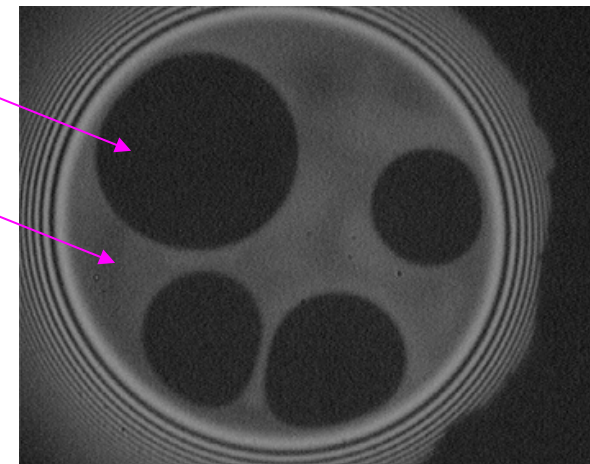
κ – Debye screening parameter

$$\frac{\partial \Pi}{\partial h} > 0 \quad \text{– unstable equilibrium state}$$

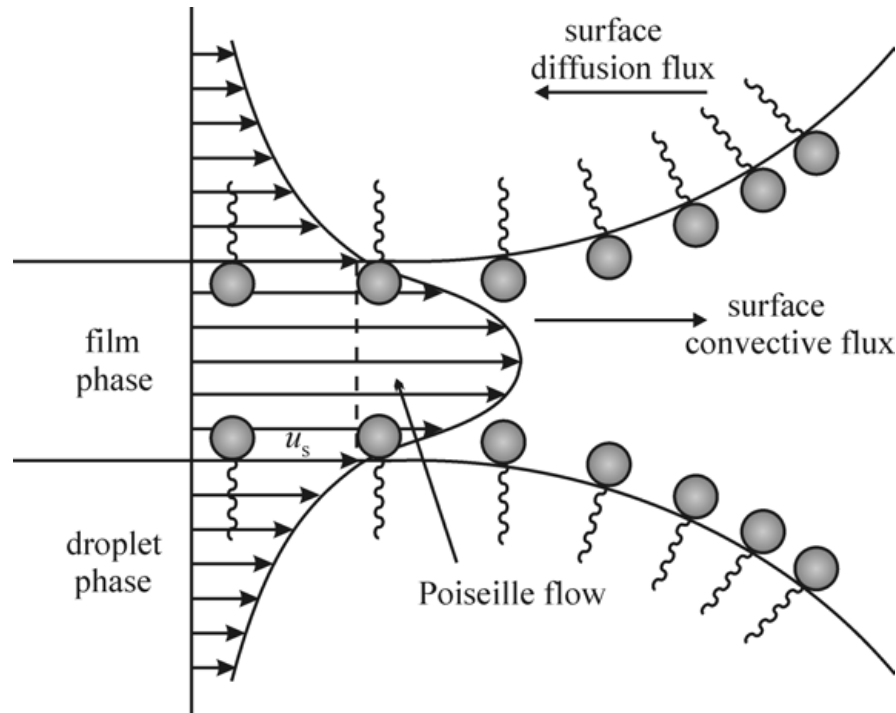
$$\frac{\partial \Pi}{\partial h} < 0 \quad \text{– stable equilibrium state}$$

(2) Secondary film

(1) Primary film



Role of surfactants on the surface mobility [1,2,16,17]



Fluid motion in the film and droplet phases.

The flow in the film phase is superposition of the Poiseuille flow and a flow of constant surface velocity u_s .

Due to the nonuniform interfacial surfactant distribution surface diffusion and convective fluxes appear.

The bulk viscous stresses are balanced with the surface stresses.

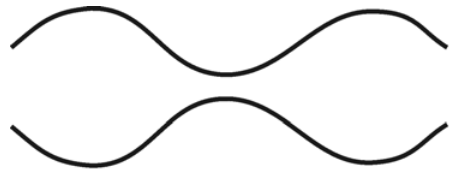
The gradient of surface tension (Marangoni effect) and the surface viscosity (Boussinesq-Scriven effect) suppress the interfacial mobility. Both effects characterize the interfacial rheology! (Interfacial rheology measurements)

The bulk and surface diffusion suppress the gradient of surface tension and increase the mobility of interfaces! (Dynamics surface tension measurements)

The mobility of film surfaces is important for a film (foam) drainage and foam rheology!

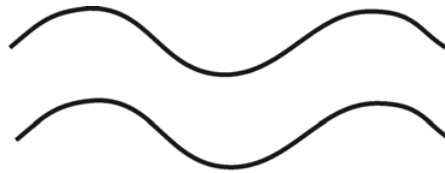
As a rule the film stability is controlled by the disjoining pressure (small effect of the surface mobility is measured)!

Stability film thickness (example for foam films – surface fluctuations)



(a)

Symmetric (squeezing) modes



(b)

Anti-symmetric (bending) modes

The film thickness, h , is presented as a superposition of equilibrium thickness, h_e , and fluctuations, h_f :

$$h = h_e + h_f \quad \text{and} \quad h_f \propto \exp(\omega t) J_0\left(k \frac{r}{R}\right)$$

k is the dimensionless Fourier-Bessel wave number. For **positive** (**negative**) ω the disturbances will **grow** (**decay**).

From mass and momentum balance equations one derives the dispersion relationship [2]:

$$\Omega^2 = \frac{\gamma h_e^3}{48\eta DR^2} \left[\frac{2R^2}{\gamma} \frac{\partial \Pi}{\partial h} - k^2 \right] (1 + F_s) \quad \text{and} \quad \Omega^2 = \frac{\omega h_e^2}{4D} \quad \text{for squeezing modes}$$

F_s – mobility function; D, D_s – bulk and surface diffusivity; η, η_s – bulk and surface viscosity; h_s, E_G – adsorption thickness and Gibbs elasticity; R – film radius:

$$d_s = \frac{12\eta D}{h_e E_G}, \quad B_s = \Omega^2 + \frac{h_e}{2h_s} \Omega \tanh \Omega + \frac{D_s k^2 h_e^2}{4DR^2}, \quad F_s = d_s B_s \left(1 + \frac{\eta_s}{3\eta h_e}\right)^{-1}$$

The stability film thickness, h_{st} , is defined as a thickness at which $\omega = 0$:

$$\frac{\partial \Pi}{\partial h} = \frac{\gamma k^2}{2R^2}$$

Stability film thickness (example for foam films – surface fluctuations)

$$\Omega^2 = \frac{\gamma h_e^3}{48\eta DR^2} \left[\frac{2R^2}{\gamma} \frac{\partial \Pi}{\partial h} - k^2 \right] (1 + F_s)$$

General conclusions:

$$\frac{\partial \Pi}{\partial h} < 0$$

stable fluctuations. The surfactants influence the decrement of surface waves!

$$\frac{\partial \Pi}{\partial h} > 0$$

Two possible cases: a) unbounded films; b) bounded films.

Unbounded films

$$\frac{\partial \Pi}{\partial h} < \frac{\gamma k^2}{2R^2}$$

stable fluctuations

the stability depends on the wave number:

$$\frac{\partial \Pi}{\partial h} < \frac{\gamma k^2}{2R^2}$$

unstable fluctuations

Stability limit of bounded films:

$$\frac{2R^2}{\gamma} \frac{\partial \Pi}{\partial h} = j_1^2 \approx 5.783$$

where j_1 is the first root of the Bessel function, J_0 .

For example:

$$\Pi = \Pi_{vw} = -\frac{A_H}{6\pi h^3} \quad \text{and} \quad \frac{\partial \Pi}{\partial h} = \frac{A_H}{2\pi h^4}$$

$$h_{st} = \left(\frac{A_H R^2}{\pi j_1^2 \gamma} \right)^{1/4} \approx 0.4844 \left(\frac{A_H R^2}{\gamma} \right)^{1/4}$$

Stability, transitional and critical film thicknesses [2,18]

$$\Omega^2 = \frac{\gamma h_e^3}{48\eta DR^2} \left[\frac{2R^2}{\gamma} \frac{\partial \Pi}{\partial h} - k^2 \right] (1 + F_s)$$

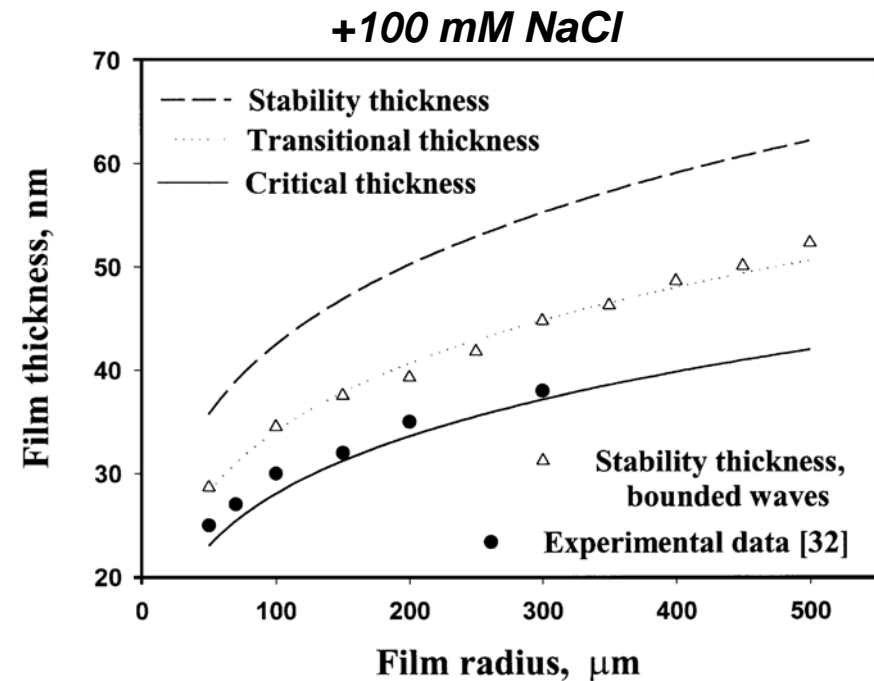
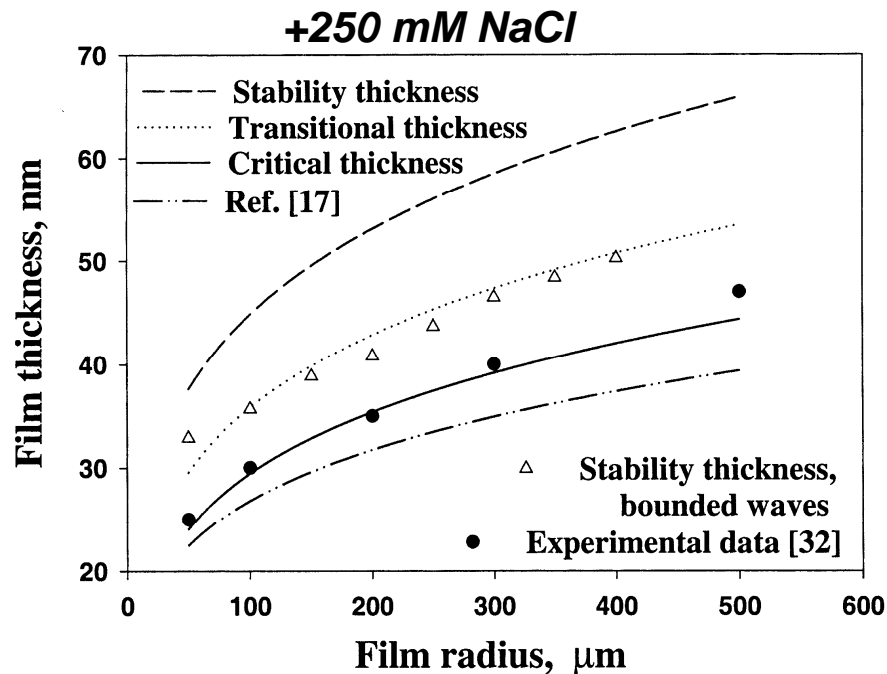
Stability thickness – the first unstable mode appears.

Generally, with the decrease of the film thickness, $d\Pi/dh$ increases and the region of unstable modes becomes wider.

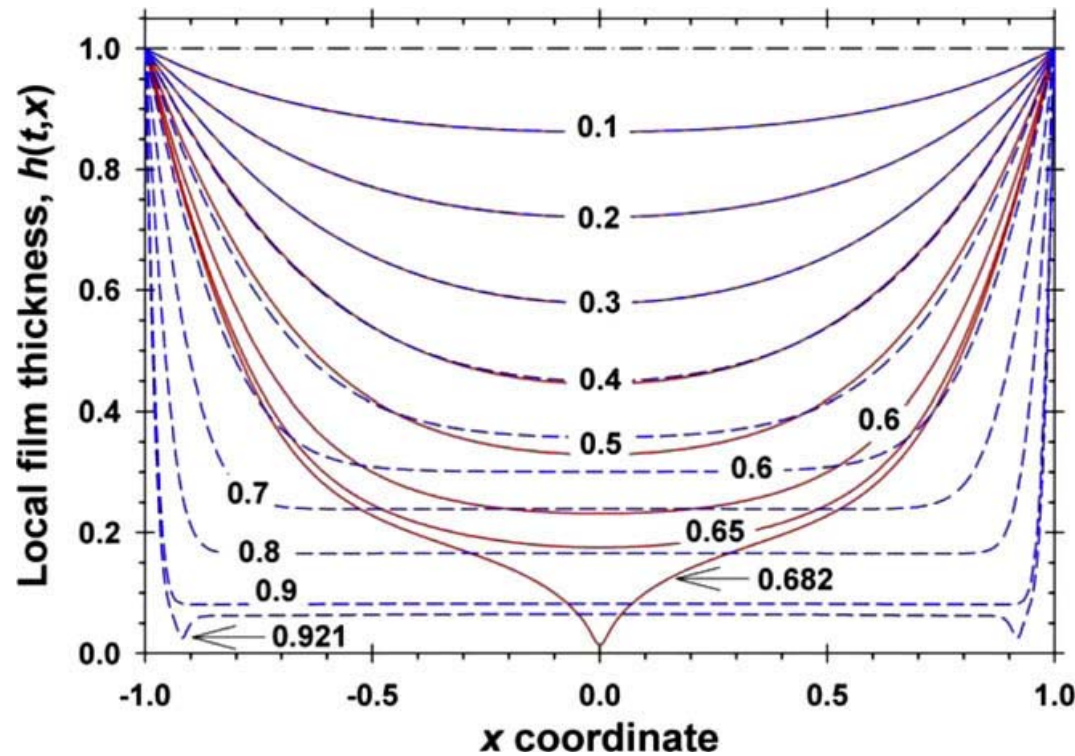
Finally, the film breaks at a given critical film thickness, h_{cr} , with the most dangerous wave number, k_{cr} .

The film thickness at which the most dangerous mode appears, $\Omega(k_{cr}) = 0$, is called transitional film thickness, h_{tr} .

Critical thickness of foam films stabilized with 0.4 mM SDS in the presence of NaCl.



Other possibilities for bubble (drop) coalescence (numerical results)



Red curves: In the presence of VdW component. The film ruptures in its central zone – pimple instability.

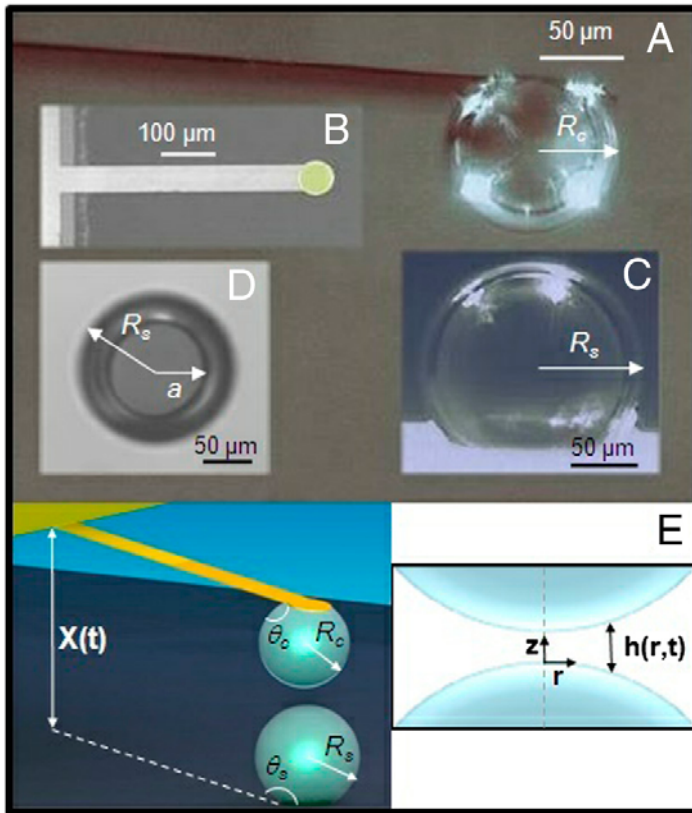
Blue curves: In the presence of VdW and electrostatic components. The film ruptures at its periphery – rim instability.

Evolution of film profile in the presence of different components of disjoining pressure [19].

Example: For raising bubble under the action of buoyancy force, the thickness at which the pimple appears, h_p , is calculated from [2,20]:

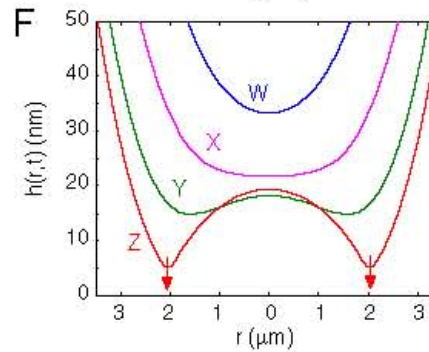
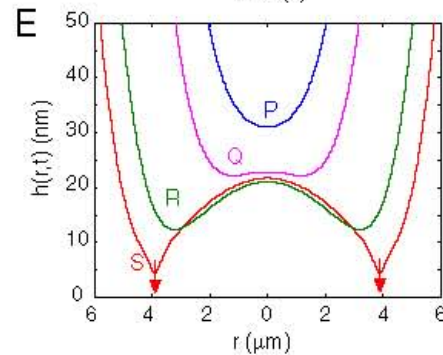
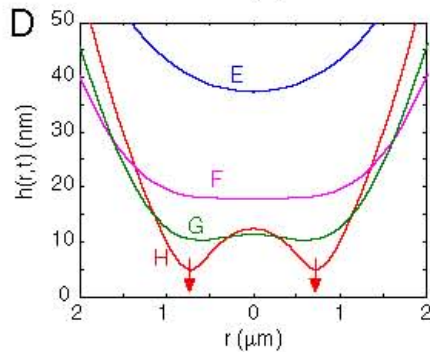
$$h_p = \left(\frac{A_H R}{12 F_b} \right)^{1/2} \quad \text{where} \quad F_b = \frac{4}{3} \pi R^3 g \Delta \rho$$

Bubbles in the AFM [21]



Microscopy photographs of bubbles in the AFM with schematics of the two interacting bubbles and the water film between them:

(A) Side view of the bubble anchored on the tip of the cantilever. (B) Plan view of the custom-made cantilever with the hydrophobized circular anchor. (C) Side perspective of the bubble on the substrate. (D) Bottom view of the bubble showing the dark circular contact zone of radius, a (in focus) on the substrate and the bubble of radius, R_s . (E) Schematic of the bubble geometry.



Evolution of film profiles and rim rupture effect.

Waves at a single interface [2,22]

Capillary waves:

$$\rho\omega^2 = \gamma k^3 + \rho g k \quad \text{for non-damped waves}$$

$$\rho\omega^2 = 2i\eta k^2 \omega + \gamma k^3 + \rho g k \quad \text{for damped waves}$$

Non-damped waves at the surface between two liquids:

$$(\rho_A + \rho_B)\omega^2 = \gamma k^3 - (\rho_A - \rho_B)gk$$

Pure longitudinal waves (longitudinal wave techniques):

$$i\eta(k^2 + n^2)\omega = nk^2(E_* - i\omega\eta_s)$$

Dispersion relationship for simple surfactant solution:

$$\begin{aligned} &(-i\rho\omega^2 - 2\eta k^2 \omega + i\gamma k^3 + i\rho g k)[i\eta(n^2 + k^2)\omega - nk^2(E_* - i\omega\eta_s)] \\ &+ (2i\omega\eta k n + \gamma k^3 + \rho g k)[2\eta k^2 \omega + ik^3(E_* - i\omega\eta_s)] = 0 \end{aligned}$$

k is the wave number; ω is the frequency; η_s is the sum of dilatational and shear surface viscosity; g is the gravity acceleration; ρ is the bulk density; n is the vertical complex wave number and E_* is the complex surface elasticity.

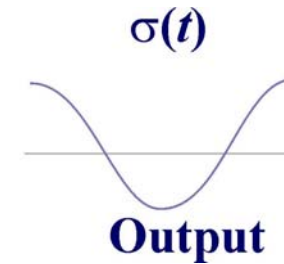
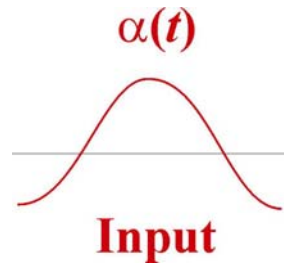
$$n^2 = k^2 - i\omega\rho/\eta, \quad E_* = E_G \frac{1 + \sqrt{q} - i\sqrt{q}}{1 + 2\sqrt{q} + 2q}, \quad q = \frac{D}{2\omega h_s} \quad (\text{Lucassen and van den Tempel [23,24]})$$

Systems with linear and nonlinear response (interfacial rheology experiments – interface with adsorbed surfactants)

Input signal

$$\alpha(t) = \alpha_0 \sin(\omega t)$$

(surface dilatation)



**Output signal
(interfacial tension)**

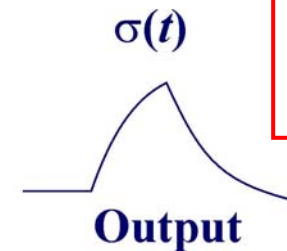
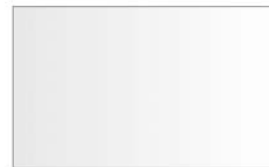
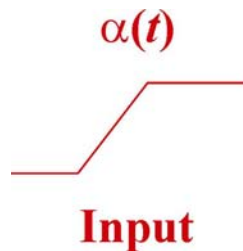
$$\gamma(t) - \gamma_e = E_r(\omega)\alpha_0 \sin(\omega t) + E_i(\omega)\alpha_0 \cos(\omega t)$$

For linear systems: $E_r(\omega)$ – elastic module and $E_i(\omega)$ – loss module and for non-linear systems: $E_r(\omega, \alpha_0)$ and $E_i(\omega, \alpha_0)$!

**Linear system
(arbitrary input)**

**Input signal
(surface dilatation)**

$$\alpha(t) = \int_0^{\infty} \alpha_0(\omega) \sin(\omega t) d\omega$$



**Output signal
(interfacial tension)**

$$\gamma(t) - \gamma_e = \int_0^{\infty} G_r(\omega) \sin(\omega t) d\omega + \int_0^{\infty} G_i(\omega) \cos(\omega t) d\omega$$

Complex elasticity

$$E_* = E_r + iE_i$$

For linear systems: $E_r(\omega) = G_r(\omega)/\alpha_0(\omega)$ and $E_i(\omega) = G_i(\omega)/\alpha_0(\omega)$

Basic References

1. P.A. Kralchevsky, K.D. Danov, N.D. Denkov. Chemical physics of colloid systems and Interfaces, Chapter 7 in *Handbook of Surface and Colloid Chemistry*", (Third Edition; K. S. Birdi, Ed.). CRC Press, Boca Raton, 2008; pp. 197-377.
2. K.D. Danov, P.A. Kralchevsky, I.B. Ivanov, Equilibrium and dynamics of surfactant adsorption monolayers and thin liquid films, in: G. Broze (Ed.), *Handbook of Detergents. Part. A: Properties*, Marcel Dekker, 1999, pp. 303–418.
3. S.S. Dukhin, G. Kretzschmar, R. Miller, *Dynamics of adsorption at liquid interfaces. Theory, experiment, application*, Elsevier, Amsterdam, 1995.
4. K.D. Danov, Effect of surfactants on drop stability and thin film drainage, in: V. Starov, I.B. Ivanov (Eds.), *Fluid Mechanics of Surfactant and Polymer Solutions*, Springer, New York, 2004, pp. 1–38.

Additional References

5. K.G. Marinova, E.S. Basheva, B. Nenova, M. Temelska, A. Y. Mirarefi, B. Campbell, I.B. Ivanov, Physico-chemical factors controlling the foamability and foam stability of milk proteins: Sodium caseinate and whey protein concentrates, *Food Hydrocolloids* 23 (2009) 1864.
6. N.D. Denkov, S. Tcholakova, K. Golemanov, K.P. Ananthpadmanabhan, A. Lips, The role of surfactant type and bubble surface mobility in foam rheology, *Soft Matter* 5 (2009) 3389.
7. W.B. Russel, D.A. Saville, W.R. Schowalter, *Colloidal Dispersions*, Cambridge Univ. Press, Cambridge, 1989.
8. I.B. Ivanov, K.D. Danov, K.P. Ananthapadmanabhan, A. Lips, Interfacial rheology of adsorbed layers with surface reaction: on the origin of the dilatational surface viscosity, *Adv. Colloid Interface Sci.* 114–115 (2005) 61–92.
9. A.F.H. Ward, L. Tordai, *J. Chem. Phys.* 14 (1946) 453.
10. K.D. Danov, D.S. Valkovska, P.A. Kralchevsky, Adsorption relaxation for nonionic surfactants under mixed barrier–diffusion and micellization–diffusion control, *J. Colloid Interface Sci.* 251 (2002) 18–25.

11. K.D. Danov, P.A. Kralchevsky, N.D. Denkov, K.P. Ananthapadmanabhan, A. Lips, Mass transport in micellar surfactant solutions. 1. Relaxation of micelle concentration, aggregation number and polydispersity, *Adv. Colloid Interface Sci.* 119 (2006) 1–16.
12. A.E.G. Aniansson, S.N. Wall, *J. Phys. Chem.* 78 (1974) 1024.
13. N.C. Christov, K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Maximum bubble pressure method: universal surface age and transport mechanism in surfactant solutions, *Langmuir* 22 (2006) 7528–7542.
14. P. Joos, *Dynamic Surface Phenomena*, VSP BV, AH Zeist, The Netherlands, 1999.
15. K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Influence of electrolytes on the dynamic surface tension of ionic surfactant solutions: expanding and immobile interfaces, *J. Colloid Interface Sci.* 303 (2006) 56–68.
16. *Thin Liquid Films* (I.B. Ivanov, Ed.) Marcel Dekker, 1988.
17. I.B. Ivanov, *Pure Appl. Chem.* 52 (1980) 1241.
18. D.S. Valkovska, K.D. Danov, I.B. Ivanov, Stability of draining plane–parallel films containing surfactants, *Adv. Colloid Interface Sci.* 96 (2002) 101–129.
19. S.S. Tabakova, K.D. Danov, Effect of disjoining pressure on the drainage and relaxation dynamics of liquid films, *J. Colloid Interface Sci.* 336 (2009) 273–284.

- 20. D.S. Valkovska, K.D. Danov, I.B. Ivanov, Surfactants role on the deformation of colliding small bubbles, Colloids Surfaces A 156 (1999) 547–566.**
- 21. I.U. Vakarelski, R. Manica, X. Tang, S.Y. O’Shea, G.W. Stevens, F. Grieser, R.R. Dagastine, D.Y.C. Chan, Dynamic interactions between microbubbles in water, 107 (2010) 11177.**
- 22. M.G. Hedge, J.C. Slattery, J. Colloid Interface Sci., 35 (1971) 593.**
- 23. J. Lucassen, M. van den Tempel, Chem. Eng. Sci. 27 (1972) 1283.**
- 23. J. Lucassen, M. van den Tempel, J. Colloid Interface Sci. 41 (1972) 491.**