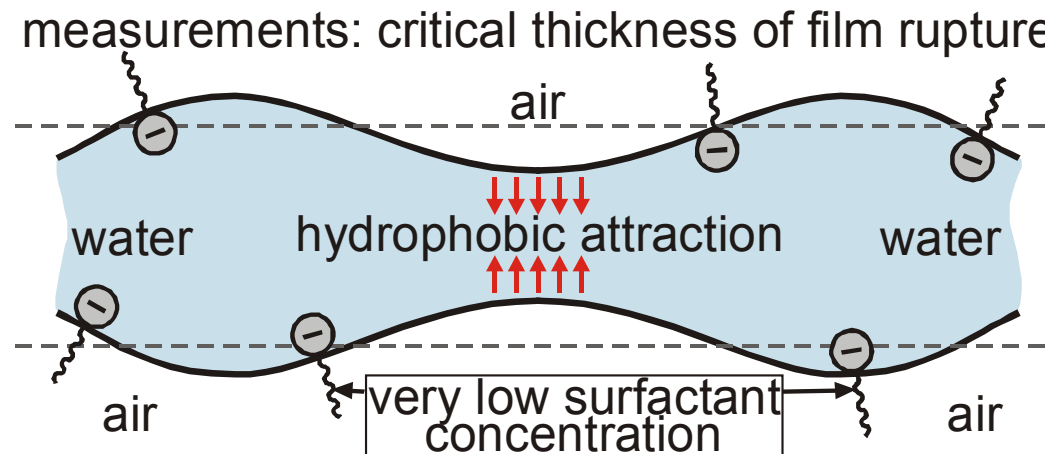


# Critical Thickness of Rupture of Foam Films in Relation to the Acting Surface Forces

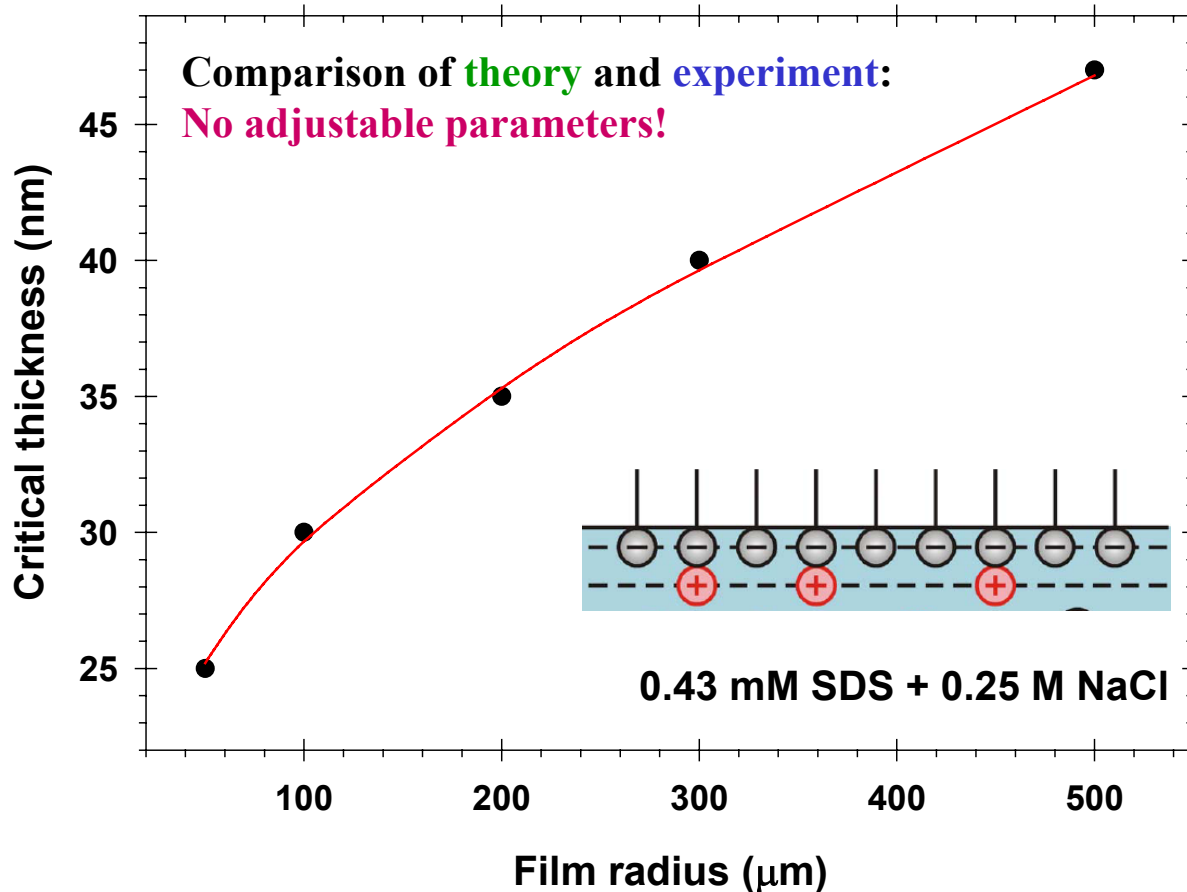
P. Kralchevsky, K. Danov, J. Angarska, B. Dimitrova, K. P. Ananth, Alex Lips

University of Sofia (BG), University of Shumen (BG), Unilever Research (USA)

(Invited Lecture at the Conference “EUFOAM”, Marne la Vallée, France, July 5-8, 2004)

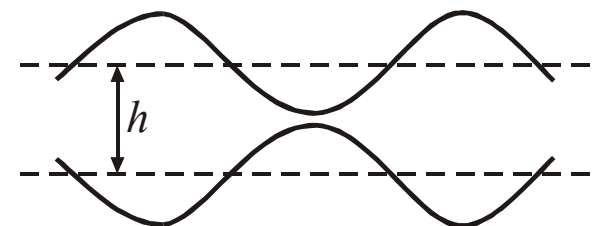


**Basic Idea:** The air is “hydrophobic phase”  $\Rightarrow$  Hydrophobic attraction could be present in foam films  $\Rightarrow$  It would affect the critical thickness of film rupture!



**Foam Films:**  
 Relatively **high SDS concentration**;  
 High **NaCl concentration** – to **suppress the double layer repulsion**;  
**Van der Waals forces** in **retarded regime** taken into account.

**SDS = Sodium Dodecyl Sulfate**



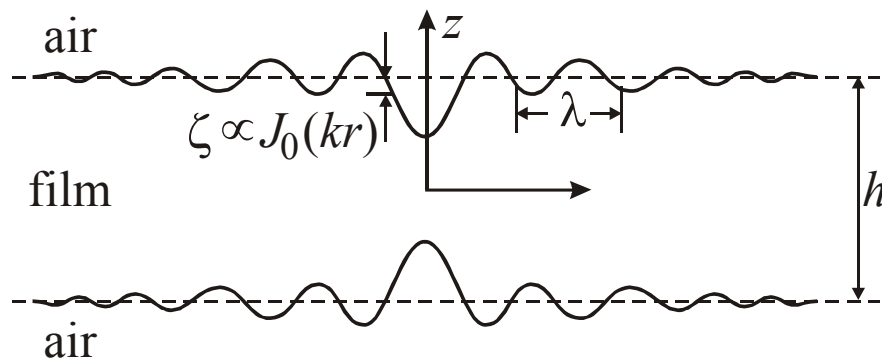
**Experiment:** E. Manev, S. Sazdanova, D.T. Wasan, *J. Colloid Interf. Sci.* 97 (1984) 591.  
**Theory:** D.Valkovska, K. Danov, I. B. Ivanov, *Adv. Colloid Interface Sci.* 96 (2002) 101.

**Theory:** D.Valkovska, K. Danov, I. B. Ivanov, *Adv. Colloid Interface Sci.* 96 (2002) 101:

**Assumptions:**

1. Simultaneous **film drainage** and **growth of interfacial perturbations**;
2. The **critical wave** has amplitude =  $h/2$ ;
3. **Unbounded waves**: Hankel transformation:

$$\zeta(r, t) = \int_0^{\infty} A(k, t) J_0(\xi kr) k dk$$



$$\zeta \propto \exp(\omega t) J_0(kr)$$

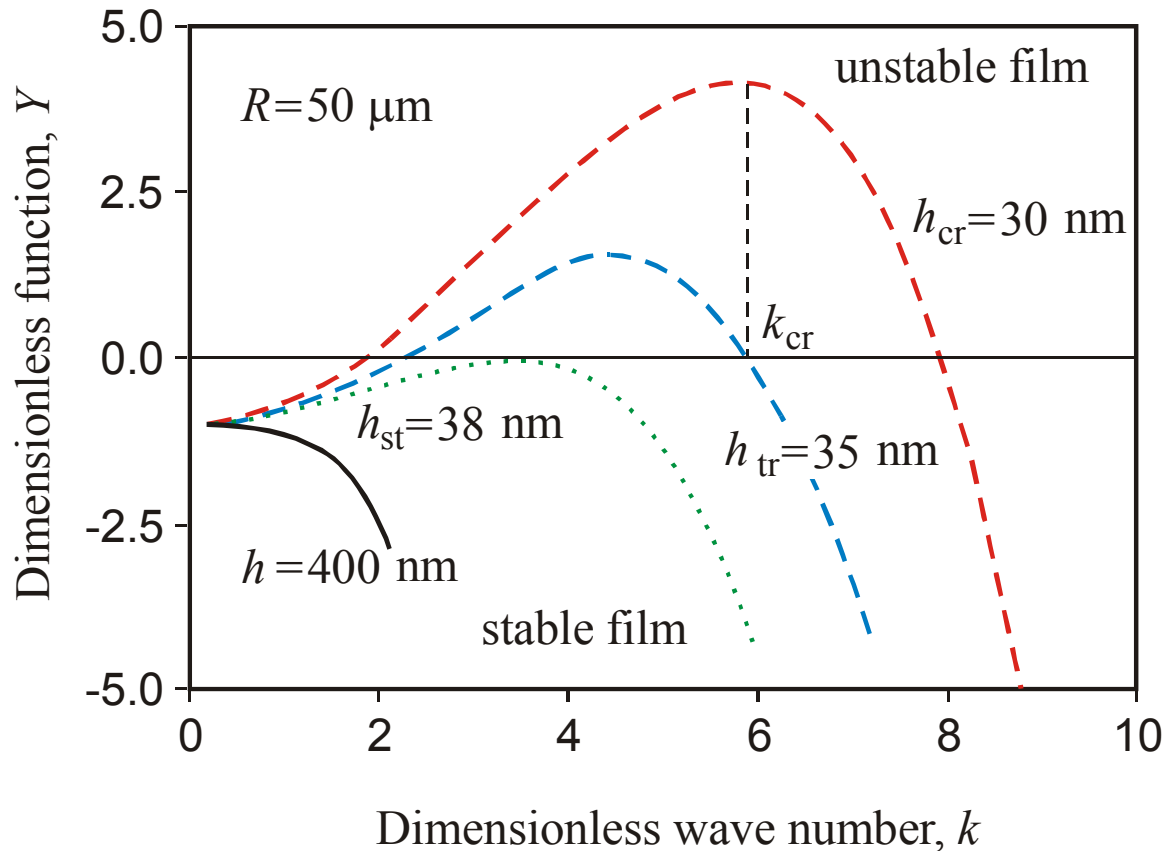
$$\omega = \frac{V}{h} Y(h, k)$$

$\omega < 0 \Rightarrow$  the wave will **decay** (stable film);

$\omega > 0 \Rightarrow$  the wave will **grow** (unstable film);

$\omega = 0 \Rightarrow$  transition from **stability** to **instability**.

**Theory of Critical Thickness: Valkovska, Danov, Ivanov (2002) (continued)**

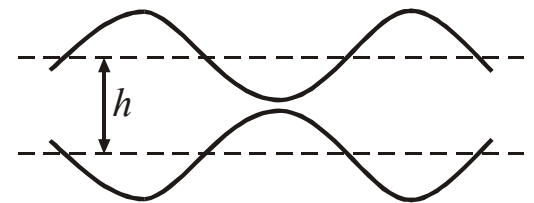


$$\zeta \propto \exp(\omega t) J_0(kr)$$

$$\omega = \frac{V}{h} Y(h, k)$$

$Y > 0 \Rightarrow$  growth

$Y < 0 \Rightarrow$  decay



At  $h = h_{\text{st}}$  – the first unstable wave appears (“**stability**” thickness);

At  $h = h_{\text{cr}}$  – the film breaks (“**critical**” thickness); the respective wave number is  $k_{\text{cr}}$

At  $h = h_{\text{tr}}$  – the “critical wave” becomes unstable (“**transitional**” thickness).

## Critical Thickness, Basic Equations: Valkovska, Danov, Ivanov (2002)

$$\frac{k_{\text{cr}}^2 \sigma}{R^2 h_{\text{cr}}^3} \int_{h_{\text{cr}}}^{h_{\text{tr}}} \frac{h^6}{P_c - \Pi} dh = \int_{h_{\text{cr}}}^{h_{\text{tr}}} \frac{h^3 \Pi'}{P_c - \Pi} dh$$

$$\Pi'(h_{\text{tr}}) = \frac{24h_{\text{cr}}^3}{h_{\text{tr}}^4} [P_c - \Pi(h_{\text{tr}})] + \frac{\sigma h_{\text{tr}}^3 k_{\text{cr}}^2}{2R^2 h_{\text{cr}}^3}$$

$$h_{\text{cr}} = \left( \frac{\sigma h_{\text{tr}}^2}{k_B T} \right)^{1/4} h_{\text{tr}} \exp\left(-\frac{k_{\text{cr}}^2}{32h_{\text{cr}}^3} \int_{h_{\text{cr}}}^{h_{\text{tr}}} \frac{h^3 \Pi'}{P_c - \Pi} dh\right)$$

Three equations for determining  $h_{\text{cr}}$ ,  $k_{\text{cr}}$  and  $h_{\text{tr}}$

Numerical solution:  
Bisection method

Single roots:  
convenient computations

### Input Quantities:

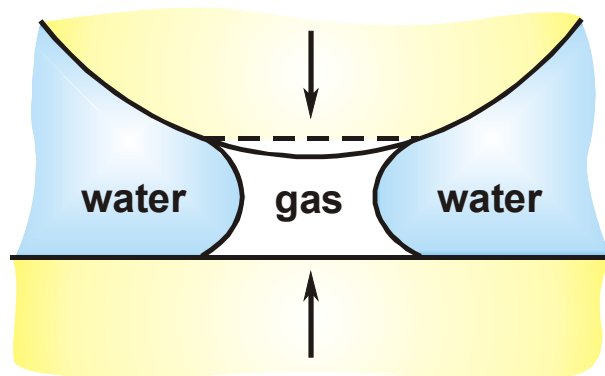
$R$  – Film radius;  $P_c$  – Capillary pressure;  $\sigma$  – Surface tension;  $T$  – temperature

Disjoining pressure:  $\Pi(h) = \Pi_{\text{vw}}(h) + \Pi_{\text{hb}}(h)$  (van der Waals + hydrophobic)

# Physical Origin of the Hydrophobic Surface Force

Two kinds of hydrophobic surface forces:

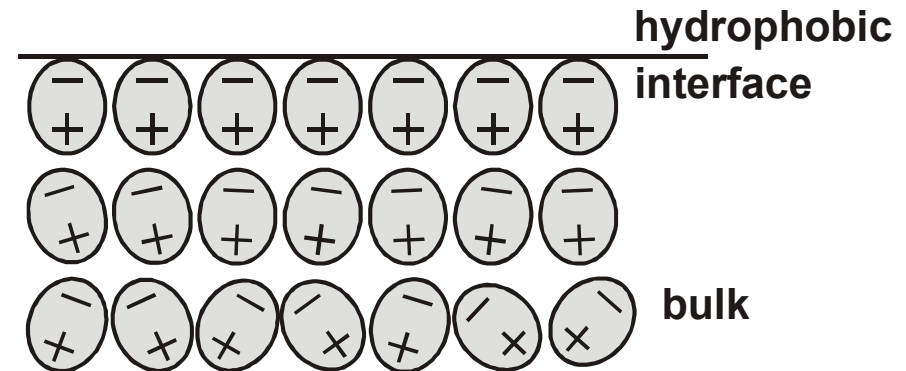
(1) Due to **gaseous capillary bridges** (cavitation) between the hydrophobic surfaces



gas bridge between two hydrophobic surfaces

Yushchenko et al.,  
*J. Colloid Interface Sci.* 96  
(1983) 307

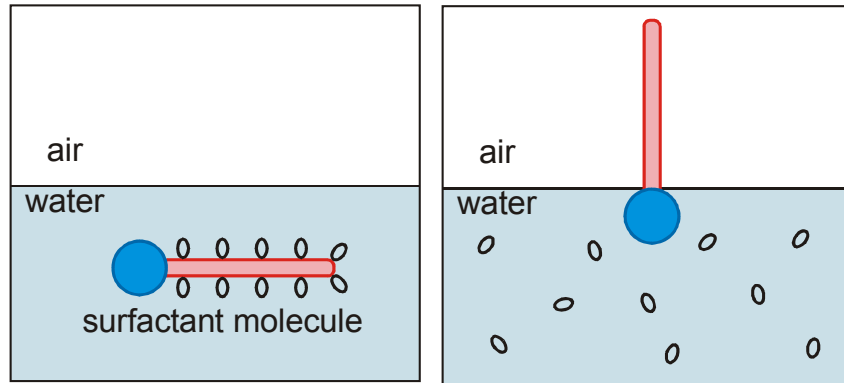
(2) Due to **hydrogen-bond-propagated ordering** of water molecules in the vicinity of hydrophobic surfaces



**Ordered** H<sub>2</sub>O in the **film**,  
**Disordered** H<sub>2</sub>O in the **bulk** ⇒ **Gain of Entropy** !

Eriksson, J. C. et al. *J. Chem. Soc. Faraday Trans. 2* 1989, 85, 163.

## Hydrophobic Surface Force of the Second Kind



**Example:** Structuring of **water** molecules in the vicinity of **paraffin-water** interface, including the **paraffin** tails of **surfactants**:

**Standard free energy** of surfactant adsorption:

$$\Delta G_{\text{ad}}^{\circ} = \Delta H_{\text{ad}}^{\circ} - T\Delta S_{\text{ad}}^{\circ}$$

**Enthalpy:**  $|\Delta H_{\text{ad}}^{\circ}| = 1-7 \text{ kJ/mol}$ ,

**Entropy term:**  $T\Delta S_{\text{ad}}^{\circ} = 23-37 \text{ kJ/mol}$

**Hydrophobic Disjoining Pressure in a water film:**

$$\Pi_{\text{hb}}(h) = -\frac{B}{4\pi\lambda} \frac{1}{\sinh^2(h/2\lambda)}$$

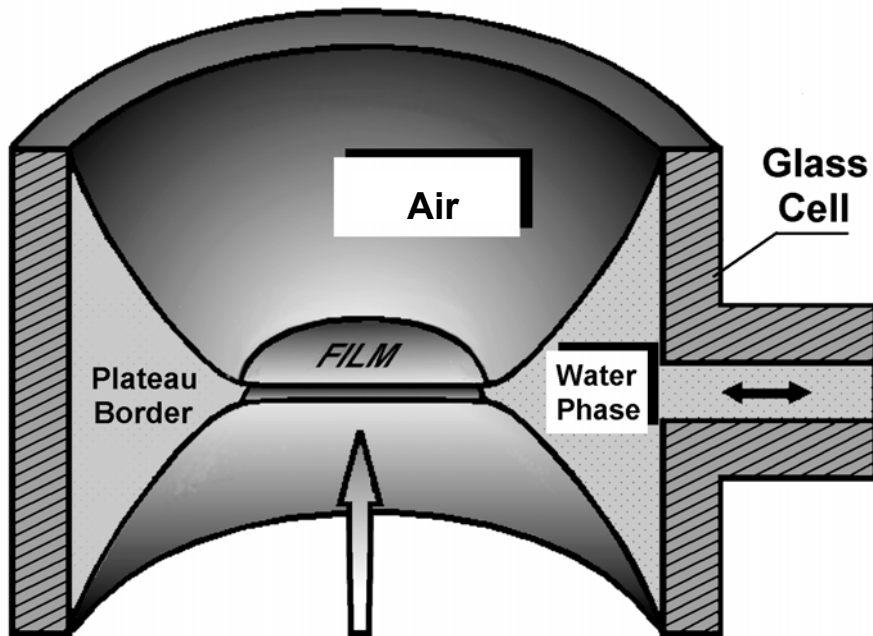
$h$  – film thickness;

$B$  – **strength** of the hydrophobic attraction; depends on the **interfacial hydrophobicity**;

$\lambda$  – **decaylength**; **bulk** property; depends on the **solution** conditions.

Eriksson, J. C. et al. *J. Chem. Soc. Faraday Trans. 2* 1989, 85, 163.

## Experiment with Foam Films

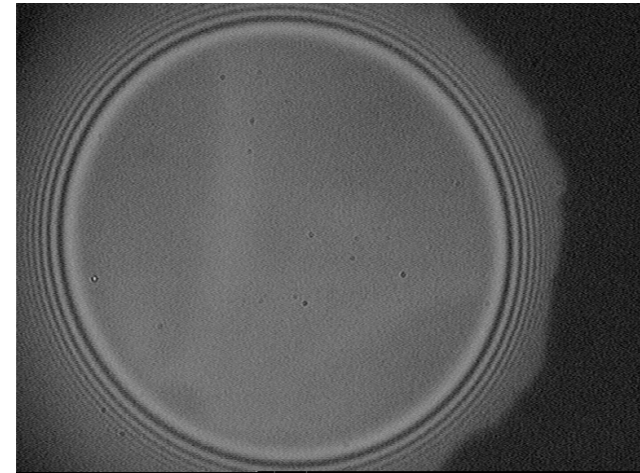


(Experimental cell of Scheludko & Exerowa)

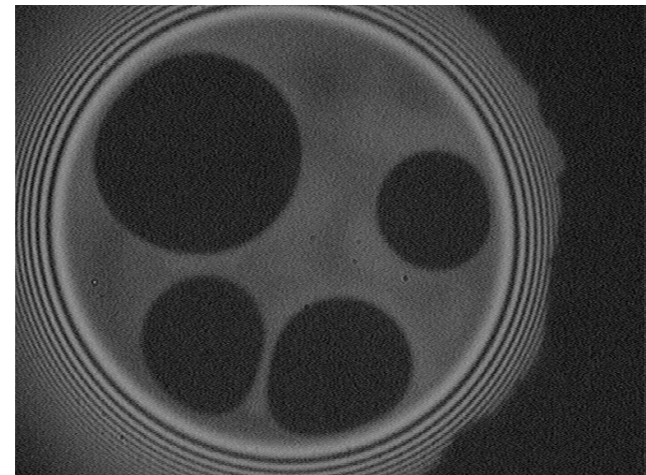
**Film radius  $R = 155 \mu\text{m}$** ; Solutions:  $10 \mu\text{M}$  SDS

**0.3 M NaCl** the film looks dark gray in reflected light just before it ruptures.

**0.1 M NaCl** in primary film, formation of black spots, corresponding to a secondary film, is seen.

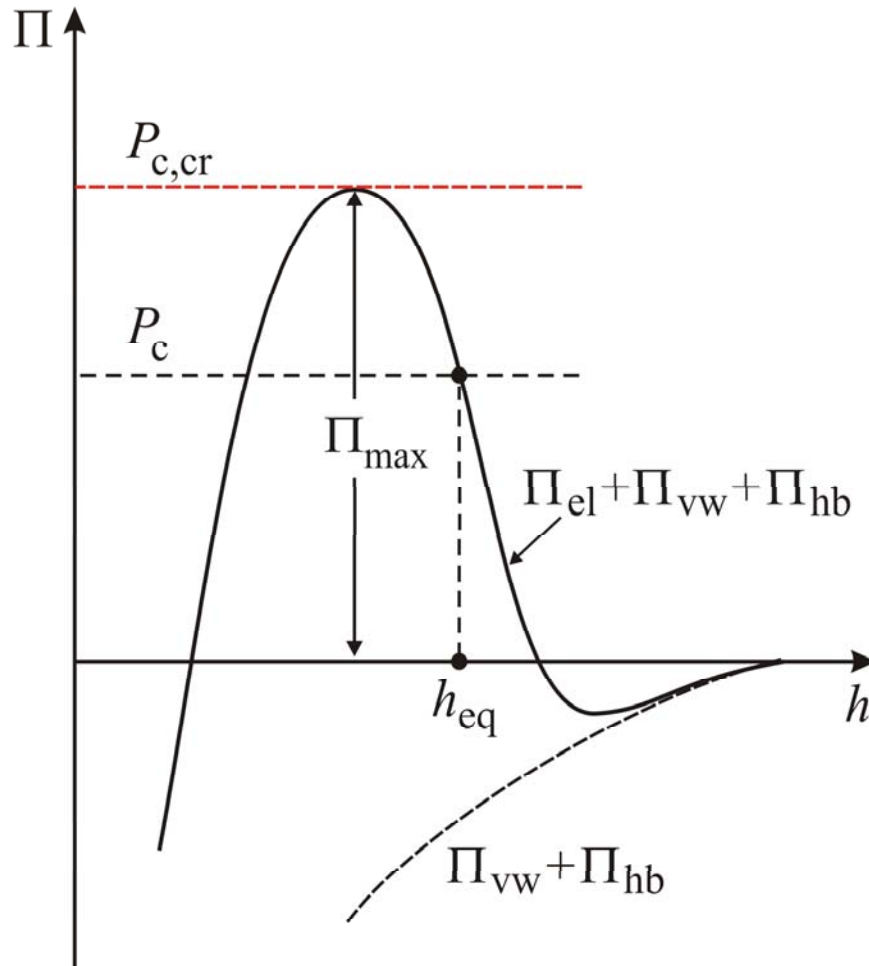


0.3 M NaCl



0.1 M NaCl





At 0.1 M NaCl – indications about existence of primary films and  $\Pi_{el}$  are seen.

At 0.3 M NaCl – the electrostatic effects are suppressed:  
working concentration!

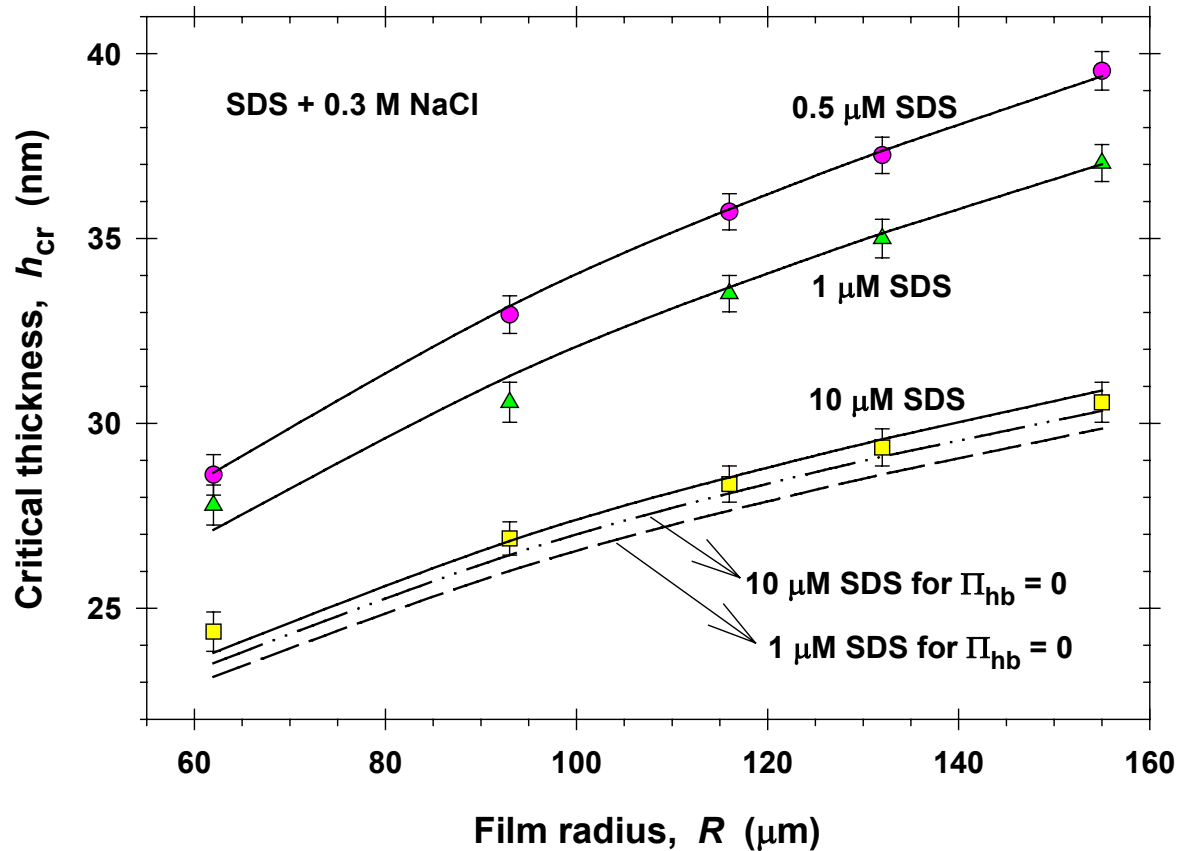
No equilibrium films – only the critical thickness of film rupture is measured.

$\Pi_{vw}$  – only dispersion interaction with account for the electromagnetic retardation effect (Russel et al):

$$\Pi_{vw}(h) = -\frac{A(h)}{6\pi h^3}$$

$$A(h) = \frac{3h_p V_e}{4\pi} \frac{(n_i^2 - n_j^2)^2}{(n_i^2 + n_j^2)^{3/2}} \int_0^\infty \frac{(1 + 2\tilde{h}z) \exp(-2\tilde{h}z)}{(1 + 2z^2)^2} dz$$

# Experimental Results and Theoretical Fits



Disjoining pressure:

$$\Pi(h) = \Pi_{vw}(h) + \Pi_{hb}(h)$$

Eriksson et al.:

$\lambda$  - decay length,  
independent of the  
surface hydrophobicity;

$B$  - characterizes the  
strength of the  
hydrophobic  
interaction, depends on  
surface hydrophobicity.

Eriksson formula:

$$\Pi_{hb}(h) = -\frac{B}{4\pi\lambda} \frac{1}{\sinh^2(h/2\lambda)}$$

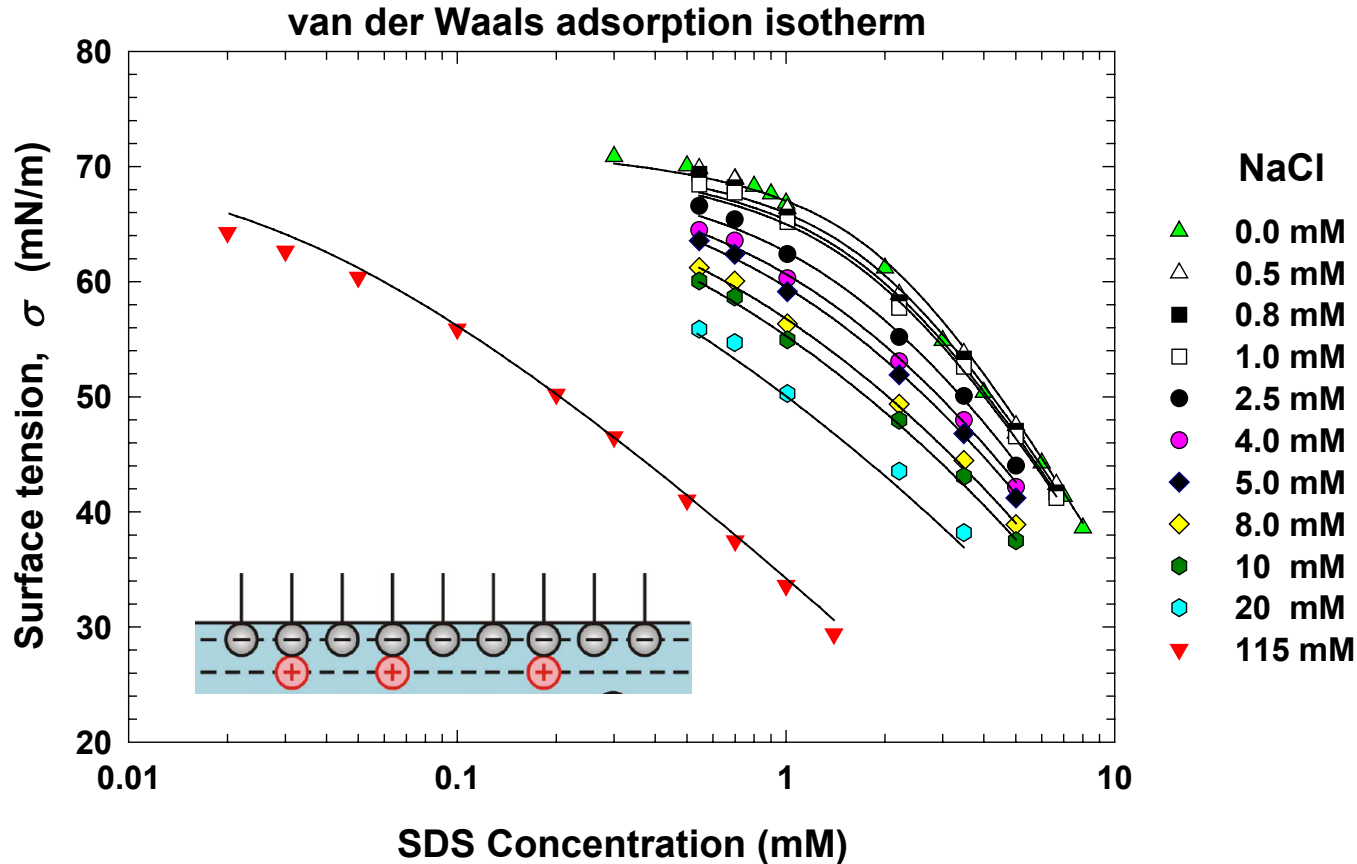
## Parameter Values

System	$\lambda$ (nm)	$B$ (mJ/m <sup>2</sup> )
<b>0.5 <math>\mu</math>M SDS + 0.3 M NaCl</b>	<b>15.85</b>	<b><math>6.56 \times 10^{-4}</math></b>
<b>1.0 <math>\mu</math>M SDS + 0.3 M NaCl</b>	<b>15.85</b>	<b><math>4.71 \times 10^{-4}</math></b>
<b>10 <math>\mu</math>M SDS + 0.3 M NaCl</b>	<b>15.85</b>	<b><math>3.34 \times 10^{-5}</math></b>
<b>DDOA-covered mica*</b>	<b>15.8</b>	<b>0.6</b>
<b>F-surfactant-covered mica*</b>	<b>15.8</b>	<b>0.9</b>

**\*Data by Eriksson et al. DDOA = dimethyl-dioctadecyl-ammonium bromide;  $\lambda$  is constant;  $B$  decreases with the rise of SDS concentration**

**Key:** The adsorption of SDS and Na<sup>+</sup> render the surface hydrophilic.

The adsorptions can be determined from fit of **surface-tension data:**



Data: Tajima et al. (1970-1971)

Parameters of the best fit:

Adsorption energy:

$$E_{\text{SDS}} = 12.5 kT$$

$$E_{\text{Na}} = 1.6 kT$$

Area per SDS molecule:  
**0.30 nm<sup>2</sup>** (cross-section of the SO<sub>4</sub> – group)

The curves for all NaCl concentrations are fitted simultaneously

[Kolev, Danov, Kralchevsky et al., *Langmuir* 18 (2002) 9106–9109]

$C_{\text{SDS}}$ ( $\mu\text{M}$ )	$\Gamma_1/\Gamma_\infty$ (%)	$\Gamma_2/\Gamma_\infty$ (%)	$E_G$ (mN/m)
0.5	4.2 %	1.0 %	0.560
1.0	6.9 %	2.1 %	0.921
10.0	33.2 %	19.4 %	6.15

**Results** from the fit of the SDS surface tension isotherms:

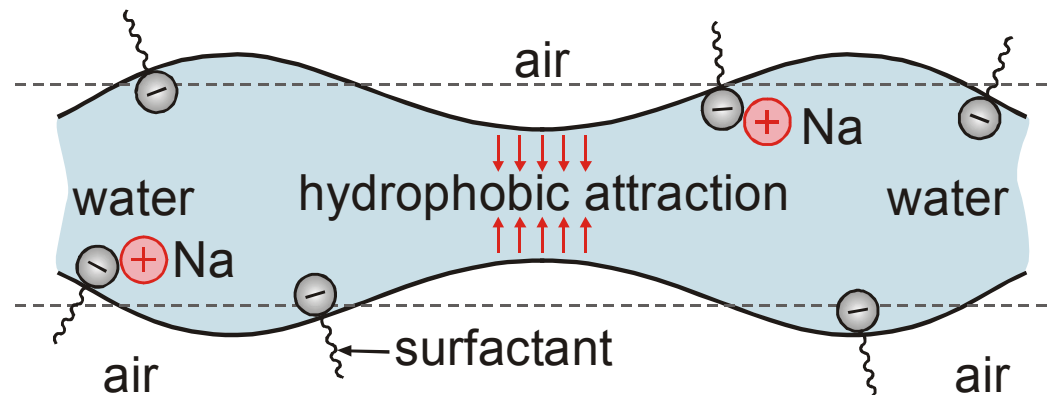
$\Gamma_1$  – surfactant ( $\text{DS}^-$ ) adsorption;

$\Gamma_2$  – counterion ( $\text{Na}^+$ ) adsorption;

$\Gamma_\infty$  – maximal adsorption in a closely-packed surfactant adsorption monolayer;

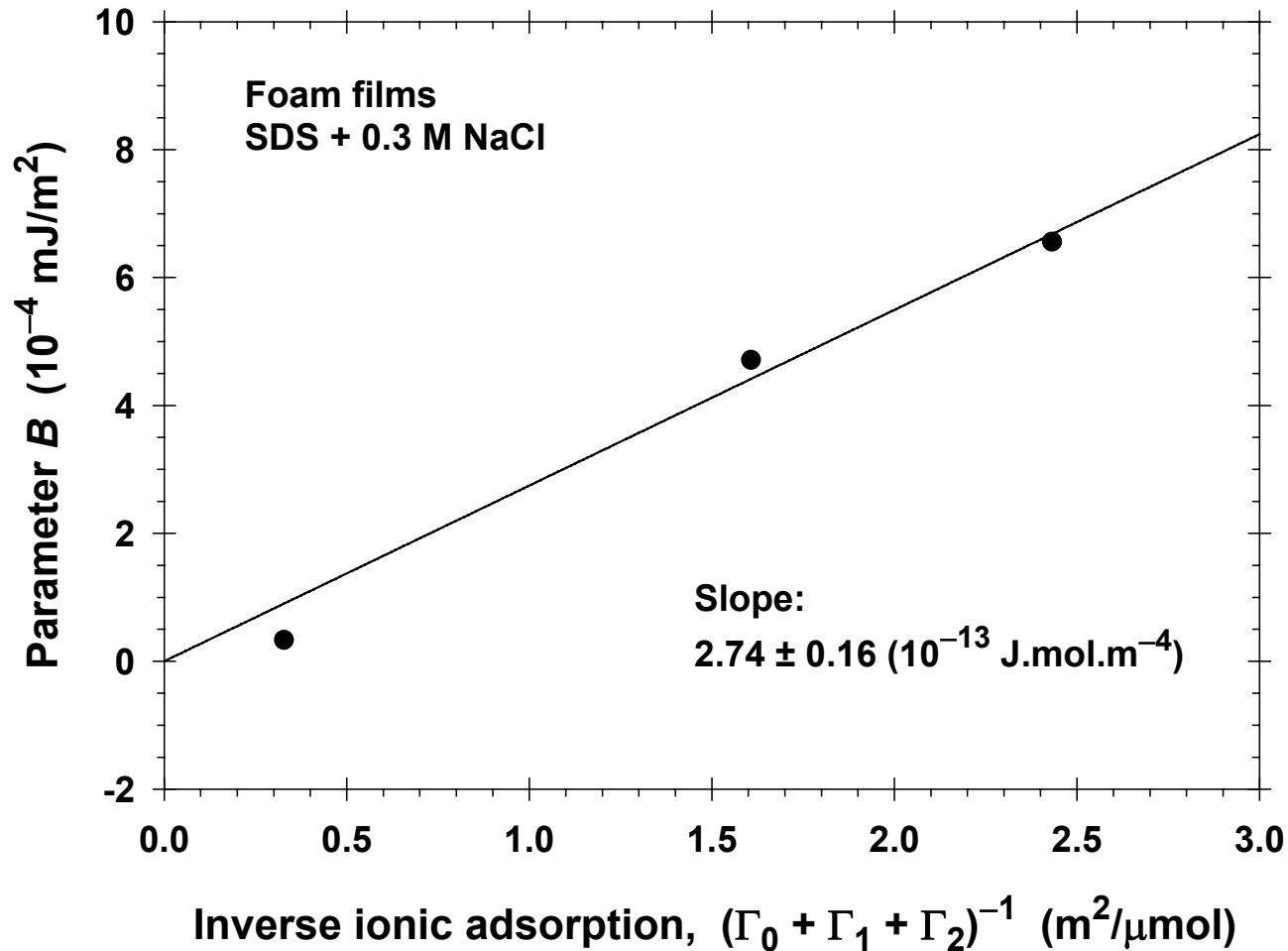
$E_G$  – surface dilatational (Gibbs) elasticity.

(0.3 M NaCl)



Plot of  $B$  vs.  $(\Gamma_0 + \Gamma_1 + \Gamma_2)^{-1}$ ;

$\Gamma_0$ ,  $\Gamma_1$  and  $\Gamma_2$  are the adsorptions of  $\text{OH}^-$ ,  $\text{DS}^-$  and  $\text{Na}^+$  ions  
(the adsorbed ions render the air-water interface hydrophilic)



## Conclusions

1. The **van der Waals attraction**, alone, is **insufficient** to explain the results, especially for the lower SDS concentrations, 0.5 and 1  $\mu\text{M}$ .
2. If the difference is attributed to the **hydrophobic attraction**, then a **very good agreement** between theory and experiment is achieved.
3. From the best fit, we determine **decaylength**  $\lambda \approx 15.8 \text{ nm}$ , which coincides with results by other authors for hydrophobized mica surfaces.
4. The **strength of the hydrophobic interaction**,  $B$ , is found to be inversely proportional to the **surface density of the adsorbed ions**.
5. With the **decrease of SDS adsorption**, greater areas of **bare hydrophobic air-water interface** are uncovered  $\Rightarrow$  **hydrophobic attraction** becomes stronger.

Details can be found in: *Langmuir* 20 (2004) 1799.