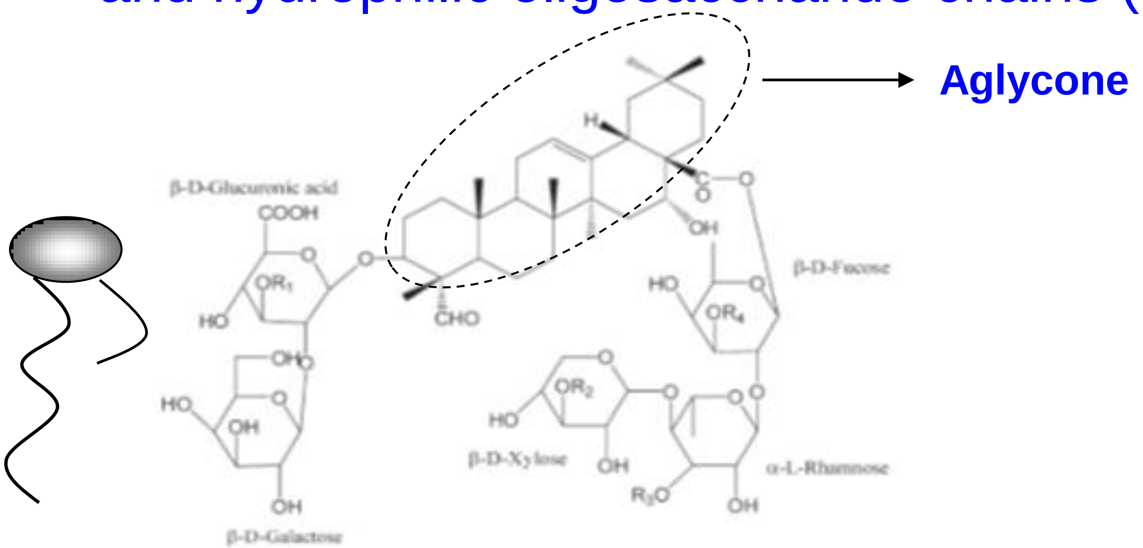
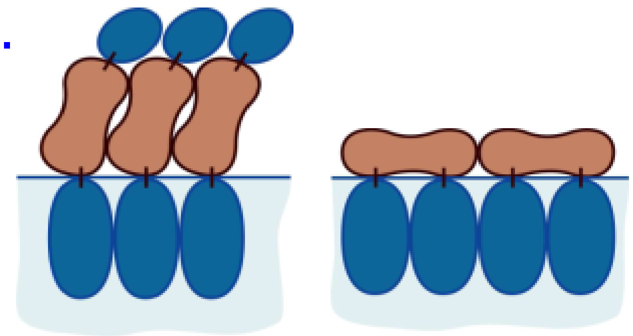
Soft Matter Challenges in Surface Science

Why Saponins !?!

- Natural surfactants found in more than 500 plant species (can reach ≈10-15 % of the dry mass) -> natural /sustainable sourcing feasible
- Molecules consist of hydrophobic part (triterpenoid or steroid aglycone) and hydrophilic oligosaccharide chains (1÷3).





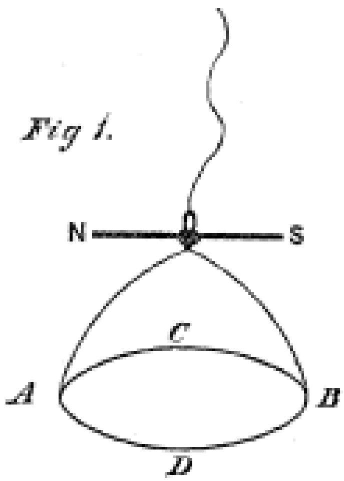
Quillaja Saponin:

- **Triterpenoid aglycone.**
- **2 sugar chains (2÷5 residues).**

- One of oldest detergents (x00 years of usage in America/Asia)
- In1890 saponins were used by Lord Rayleigh “solve” dispute between Maragoni & Plateau on the existence of surface viscosity

IV. "On the Superficial Viscosity of Water." By Lord Rayleigh, Sec. R.S. Received May 15, 1890.

Fig 1.



silk fibre, so that it may turn freely about its centre. To give a definite set, and to facilitate forced displacements, a magnetised sewing needle, NS, is attached with the aid of wax. In order to make an experiment, the ring is adjusted to the surface of water contained in a shallow vessel. When all is at rest, the surface is dusted over with a little fine sulphur,* and the suspended system is suddenly set into rotation by an external magnet. The result is very distinct, and contrasts strongly with that observed by Plateau. Instead of the surface enclosed by the ring being carried round with it in its rotation, not the smallest movement can be perceived, except perhaps in the immediate neighbourhood of the wire itself. It is clear that an ordinary water surface does not appreciably resist shearing.

behaved in much the same manner as the distilled water of the first category. On the other hand, solutions of albumen, and notably of saponine, exercised at their surfaces an altogether abnormal resistance.

Fig 3.

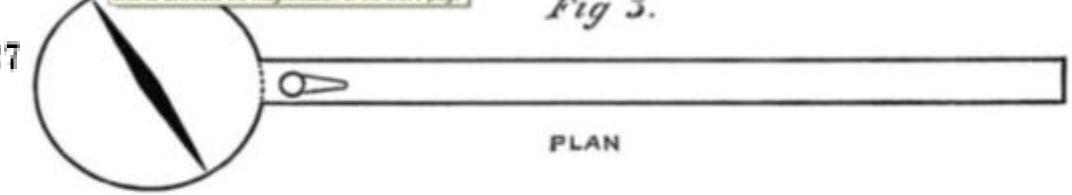
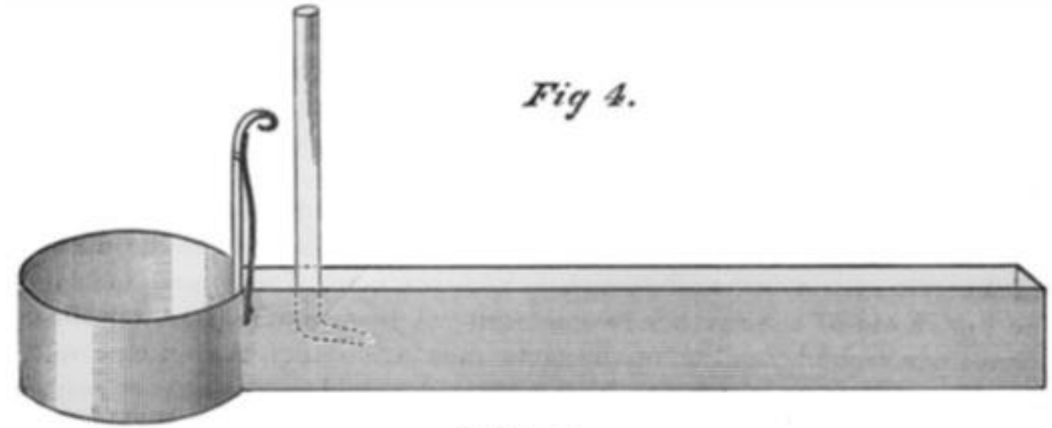
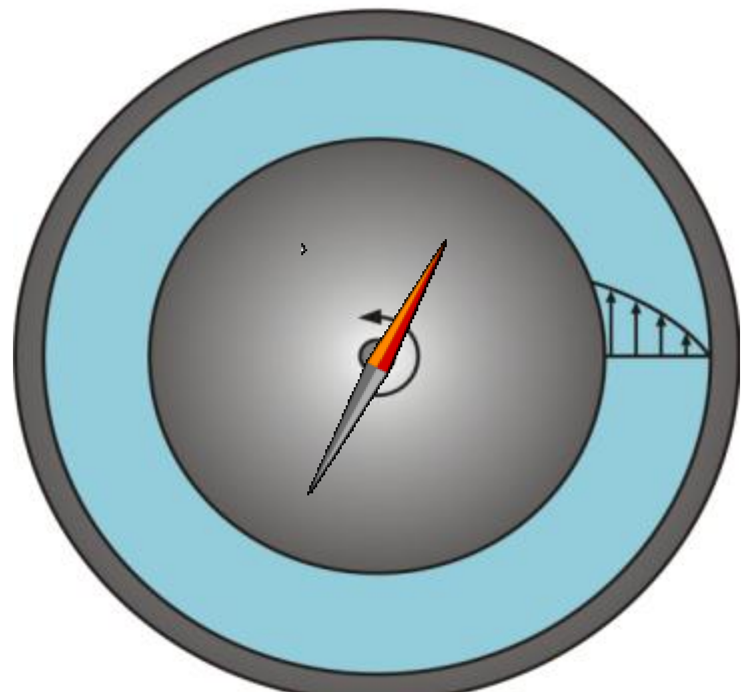
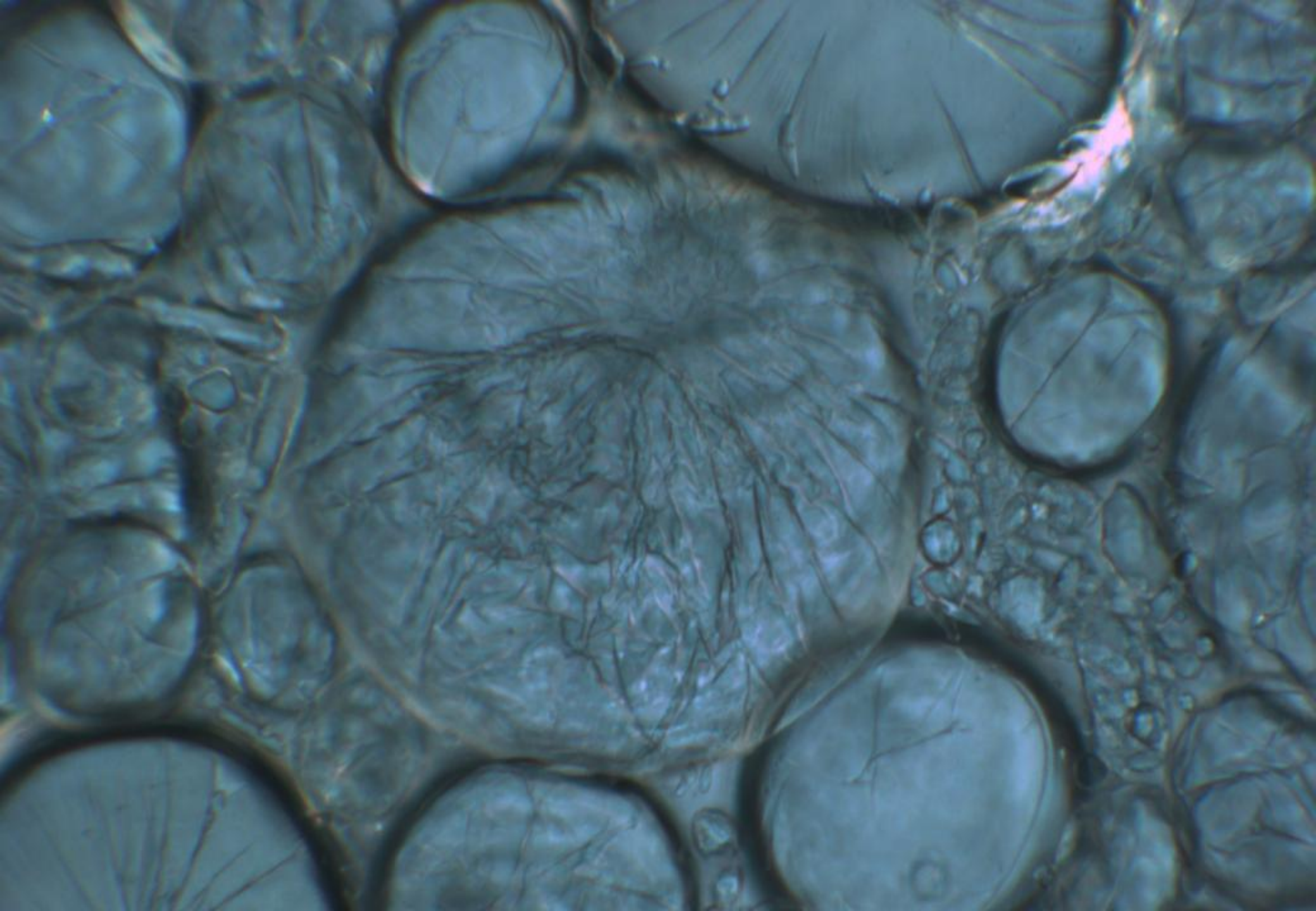


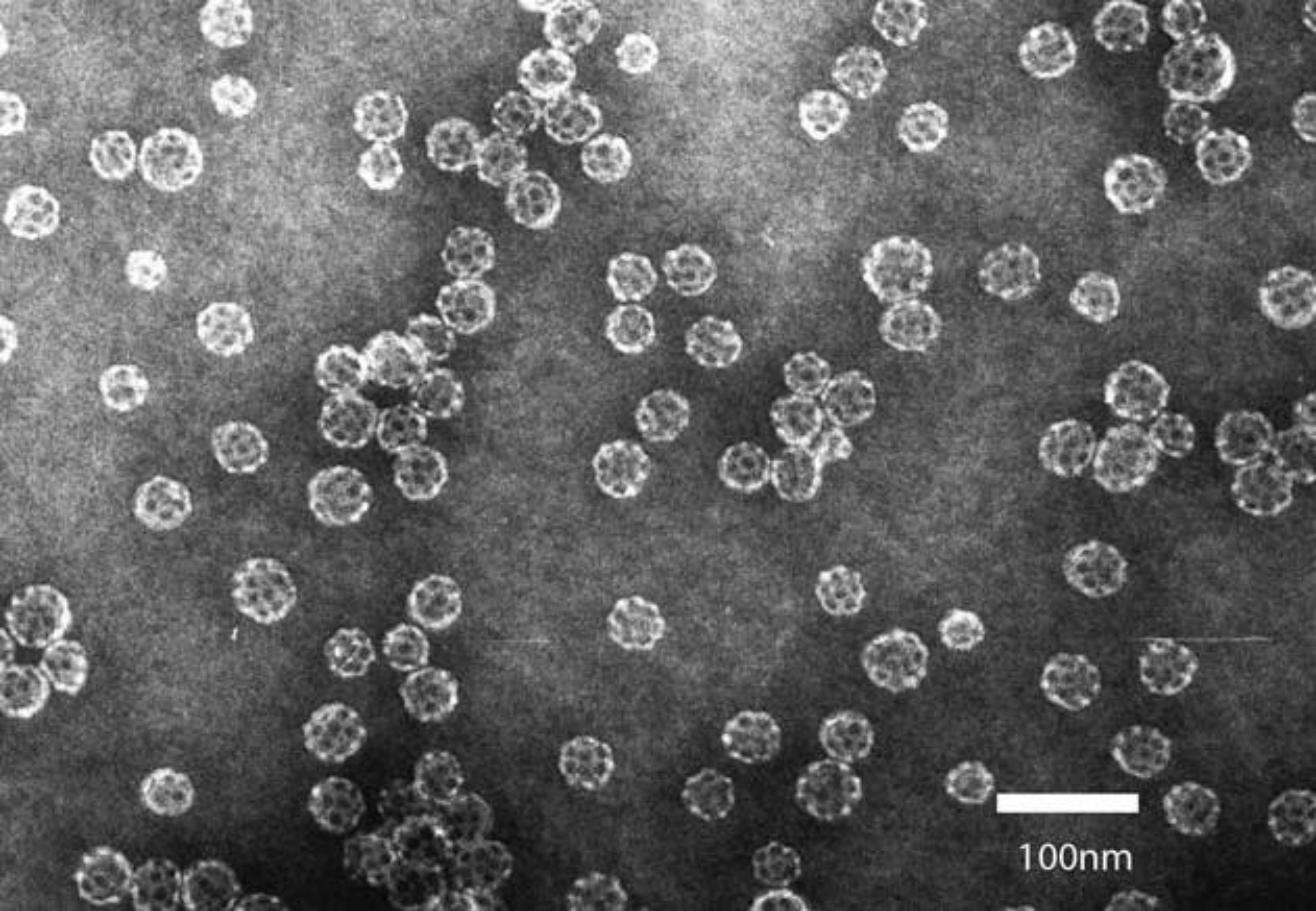
Fig 4.



Scale = ½.






100nm

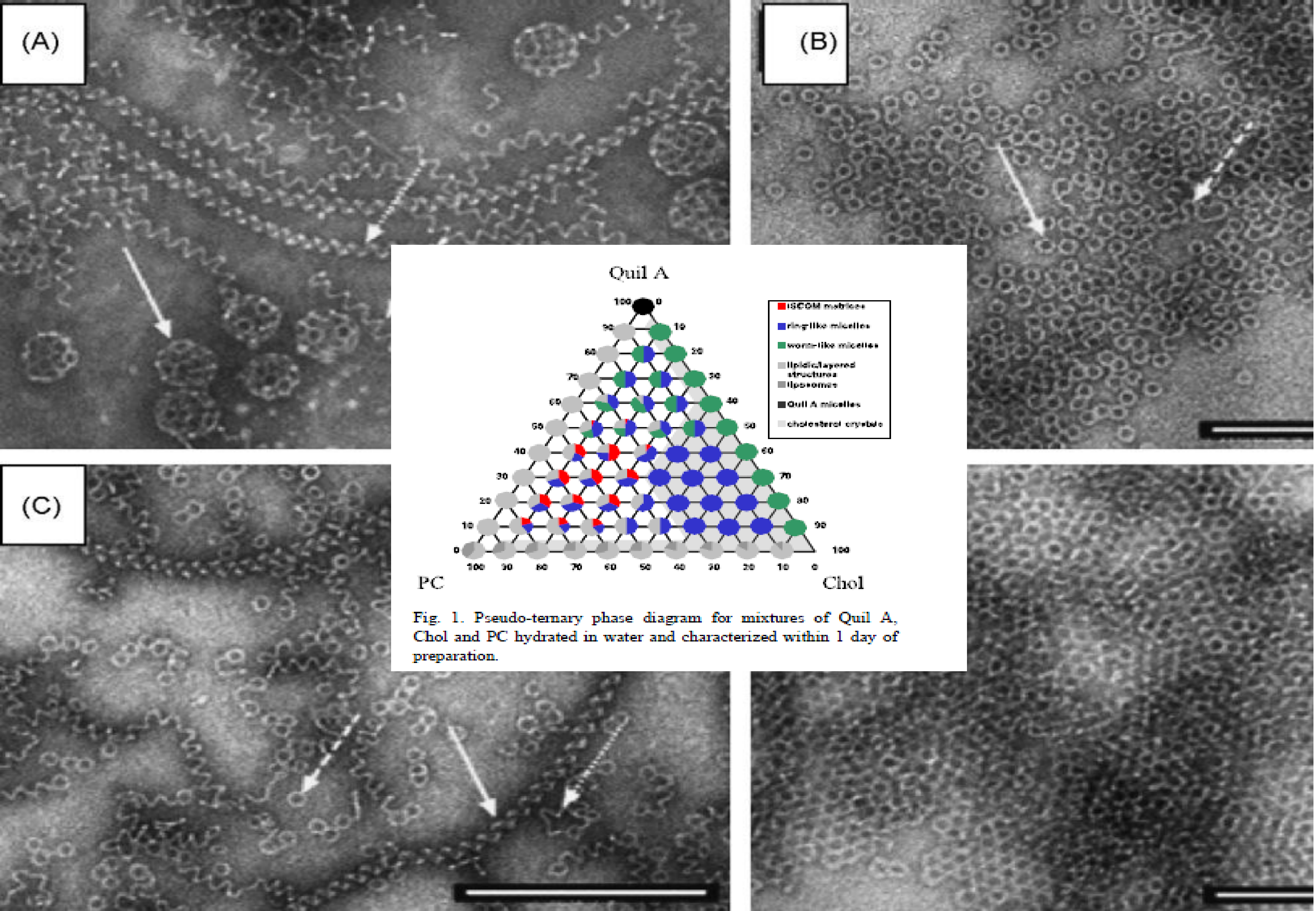


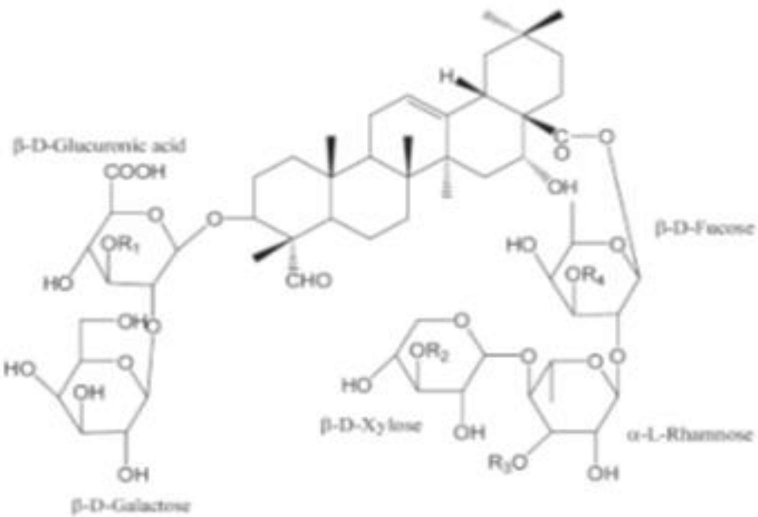
Fig. 1. Pseudo-ternary phase diagram for mixtures of Quil A, Chol and PC hydrated in water and characterized within 1 day of preparation.

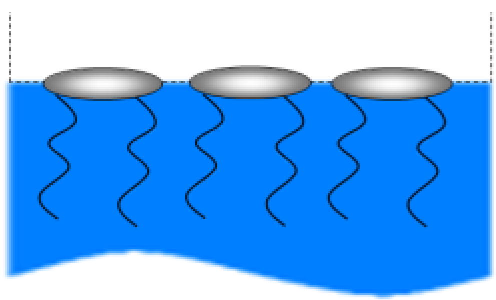
So let use saponins and

1. Characterize the surface shear & dilatational behavior of adsorption layers of saponins from various sources and structures

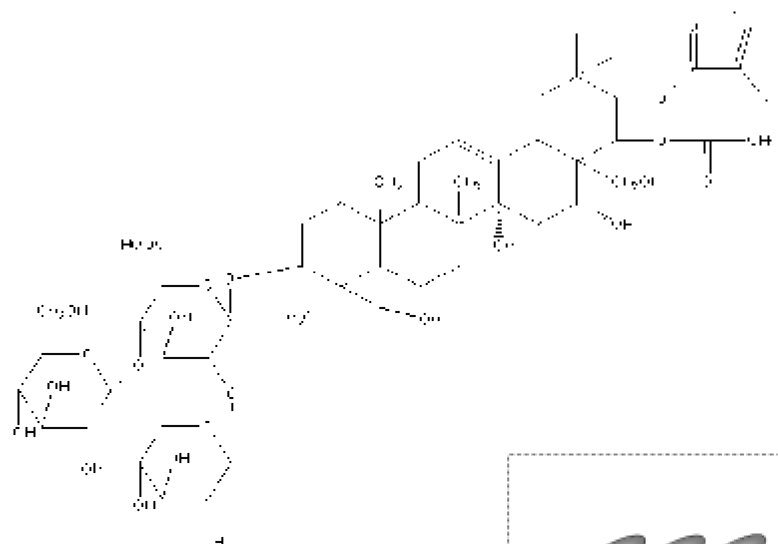
2. Establish structure ↔ functionality relation.

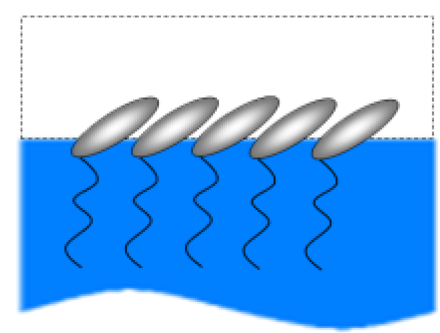
Quillaja (2 sugar chains)





Escin (1 sugar chains)





Studied saponins

Horse Chestnut
(Aesculus hippocastanum)

Sapindus Mukurossi

Camellia Oleifera Abel

Panax Ginseng

Acacia concinna

Sapindus Trifoliatus

Quillaja Saponaria Molina

Tribulus Terrestris

Yucca Schidigera

Trigonella foenum graecum

Licorice

Mono/Bidesmosidics

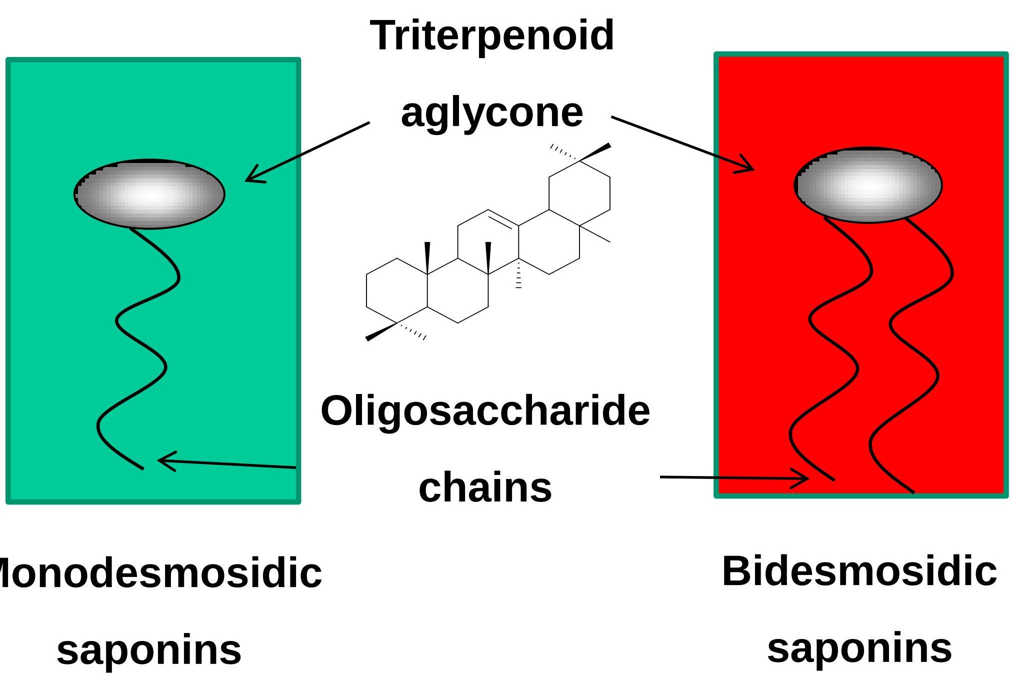
Horse Chestnut (HC/ES)
(Aesculus hippocastanum)

Sapindus Mukurossi (BSC
(Berry Saponin)

Camellia Oleifera Abel (TS)
(Tea seed saponin)

Panax Ginseng
(GS)

Quillaja Saponaria Molina
(QD)



Purity of Studied saponins

How we can make science out of the mess ?

Type of aglycone	Trade Name	Abbreviation	Saponins in extract %
Triterpenoid	Horse chestnut extract	HC	20
	Escin	ES	≥ 95
	Tea Saponin	TS	96.2
	Berry Saponin Concentrate	BSC	53
	Sapindin	SAP	50
	Quillaja Dry 100	QD	26
	Ginsenosides	GS	80
	Ayurvedic Saponin Concentrate	ASC	30
Steroid	Tribulus terrestris extract	TT	45
	Foamation Dry 50	FD	9
	Fenusterols®	FEN	50

Surface Tension vs Bulk Pressure

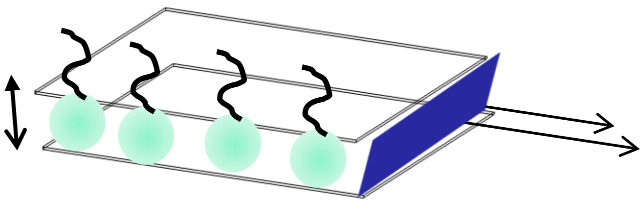
Surface tension – Energy per unit area or Force per unit length

Pressure - Energy per unit volume or Force per unit area

Surface tension vs bulk pressure:

$$P_{eq} = \Delta F / (L\delta) \sim \gamma / \delta$$

$E \sim Es/\delta \sim$ 1 mN/m / 1 nm ~ 10 atm

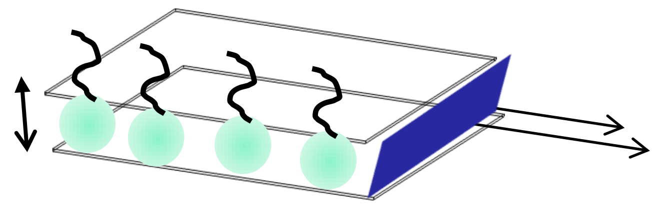


$$\gamma = \Delta F / L$$

Equivalent bulk modulus:

$$E = \Delta F / (L\delta) \sim Es/\delta$$

$E \sim Es/\delta \sim$ 30 mN/m / 1 nm ~ 300 atm

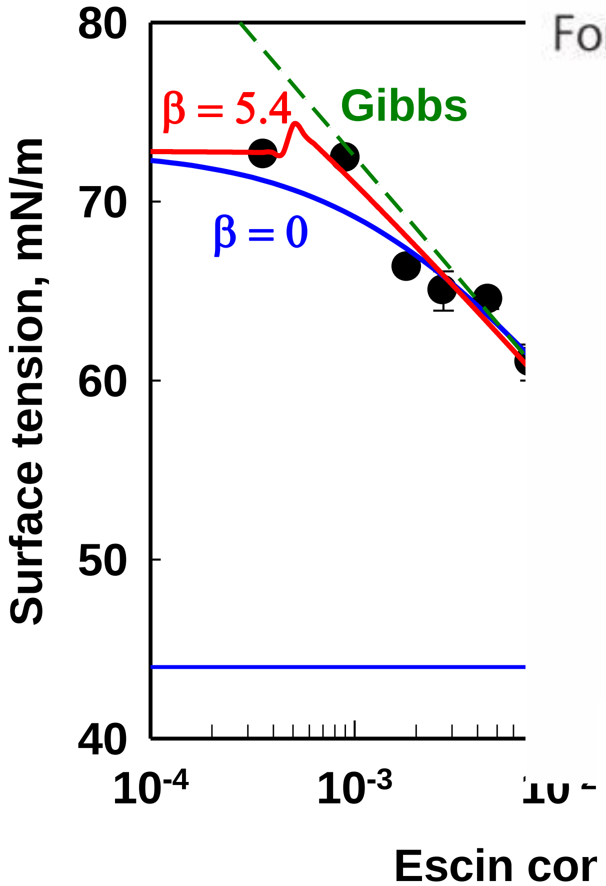


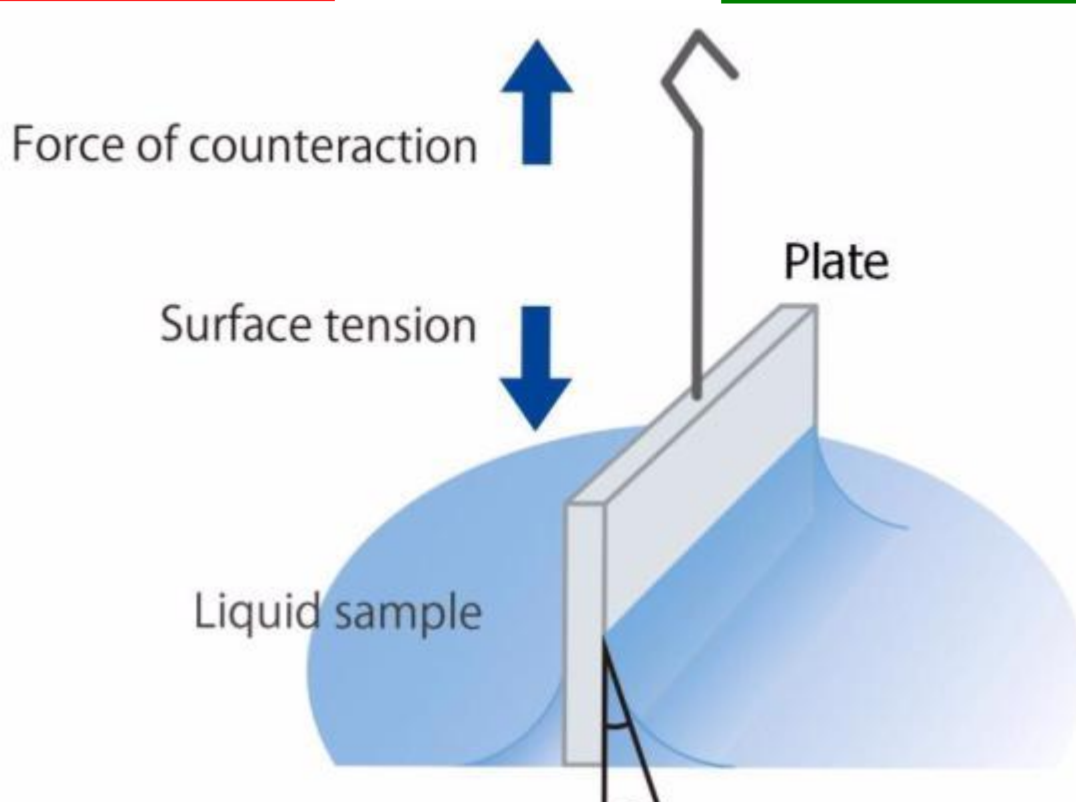
$$Es = \Delta F / L$$

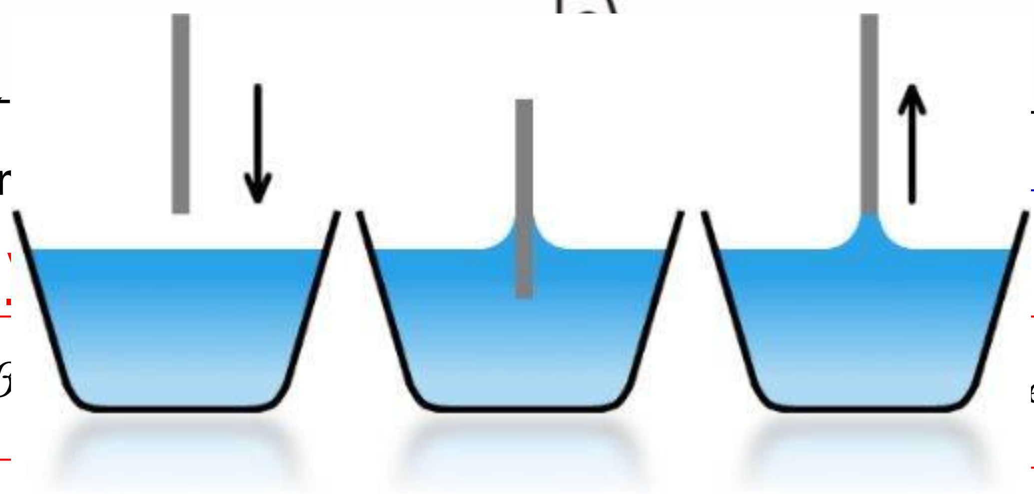
$E \sim Es/\delta \sim$ 1000 mN/m / 1 nm ~ 1 GPa

Surface tension isotherms

Gibbs adsorption isotherm







$-kT\Gamma d\ln(C)$

$kT\Gamma$

$-\frac{kT}{c}\frac{d\Gamma}{dc}$

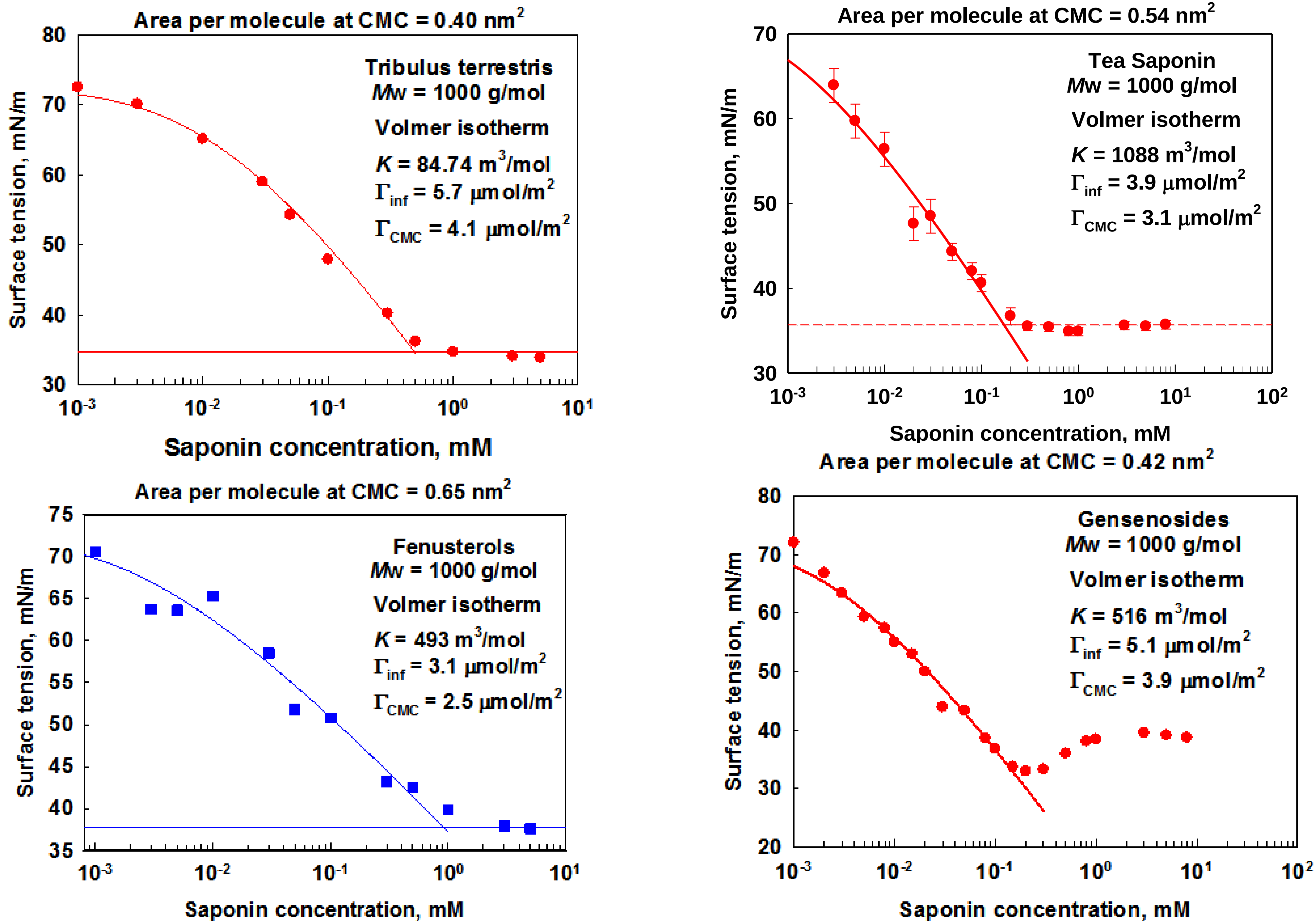
on isotherm

$\Gamma_\infty \frac{\Gamma}{\Gamma_\infty - \Gamma}$

$\overline{\Gamma} \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma}\right)$

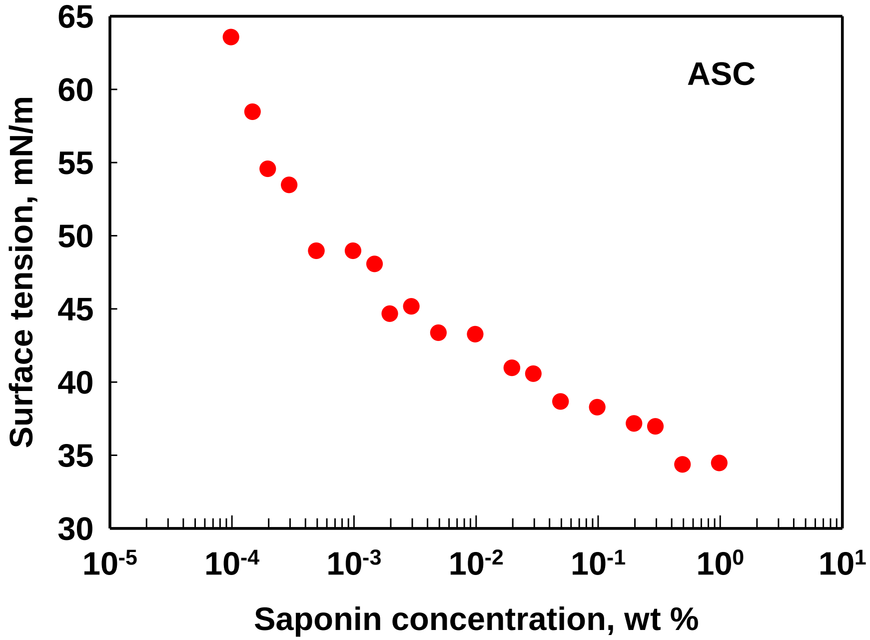
$\sigma = \sigma_0 - k_B T \Gamma_\infty \frac{\Gamma}{\Gamma_\infty - \Gamma} + \beta$

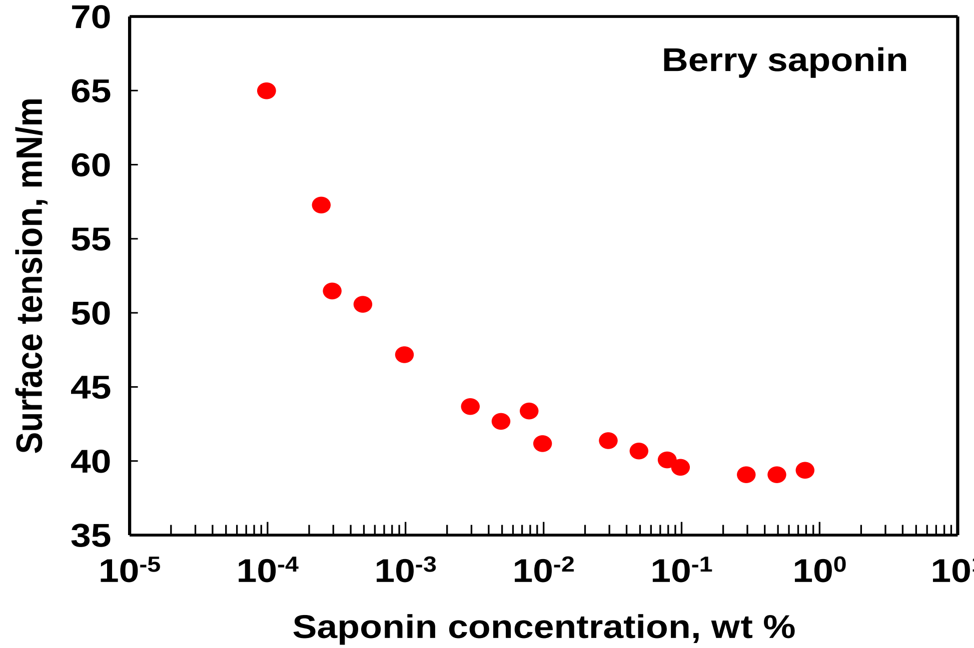
$e^{-\frac{U(r)}{k_B T}}\Big) rdr \approx -\pi \int_{r_0}^{\infty} U(r) rdr$

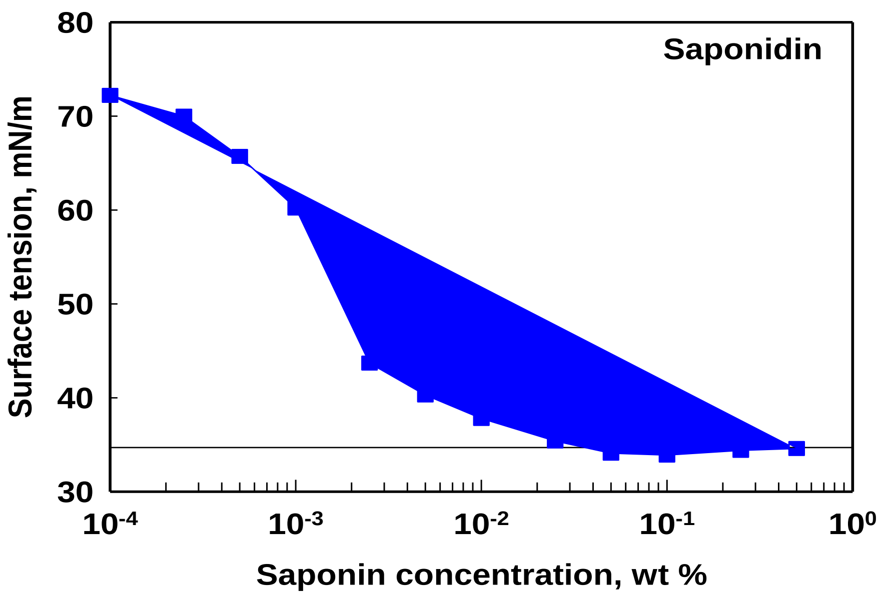


Area per molecule at CMC = 0.40 nm²
Tribulus terrestris
Mw = 1000 g/mol
Volmer isotherm
K = 84.74 m³/mol
Γinf = 5.7 μmol/m²
ΓCMC = 4.1 μmol/m²
Surface tension, mN/m
80
70
60
50
40
30
10-3
10-2
10-1
10⁰
10¹
Saponin concentration, mM
Area per molecule at CMC = 0.54 nm²
Tea Saponin
Mw = 1000 g/mol
Volmer isotherm
K = 1088 m³/mol
Γinf = 3.9 μmol/m²
ΓCMC = 3.1 μmol/m²
Surface tension, mN/m
70
60
50
40
30
10-3
10-2
10-1
10⁰
10¹
10²
Saponin concentration, mM
Area per molecule at CMC = 0.65 nm²
Fenusterols
Mw = 1000 g/mol
Volmer isotherm
K = 493 m³/mol
Γinf = 3.1 μmol/m²
ΓCMC = 2.5 μmol/m²
Surface tension, mN/m
75
70
65
60
55
50
45
40
35
10-3
10-2
10-1
10⁰
10¹
Saponin concentration, mM
Area per molecule at CMC = 0.42 nm²
Gensenosides
Mw = 1000 g/mol
Volmer isotherm
K = 516 m³/mol
Γinf = 5.1 μmol/m²
ΓCMC = 3.9 μmol/m²
Surface tension, mN/m
80
70
60
50
40
30
20
10-3
10-2
10-1
10⁰
10¹
10²
Saponin concentration, mM

Surface tension isotherms for ASC, BSC and Sapindin





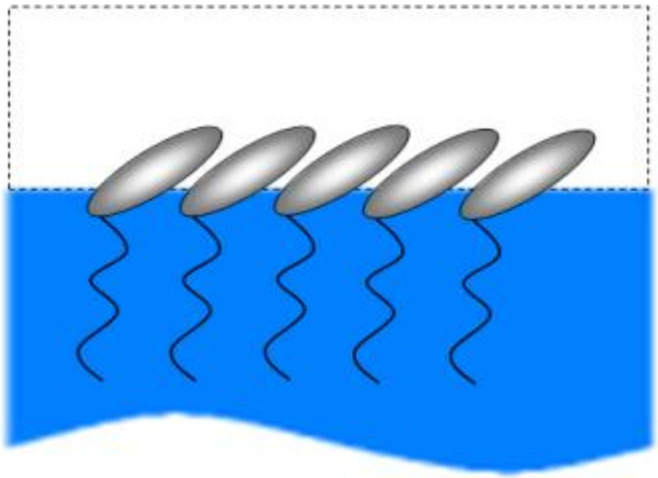


Positive Curvature !!!!

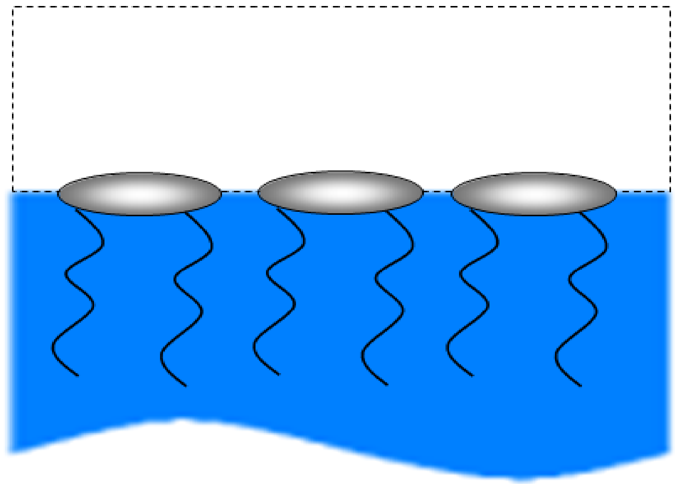
For these saponins we cannot determine the characteristics of adsorption layer (slope of the curves contradicts Gibbs isotherm)

Mixture of components and presence of aggregates?!

Molecular packing mono vs bi desmosides

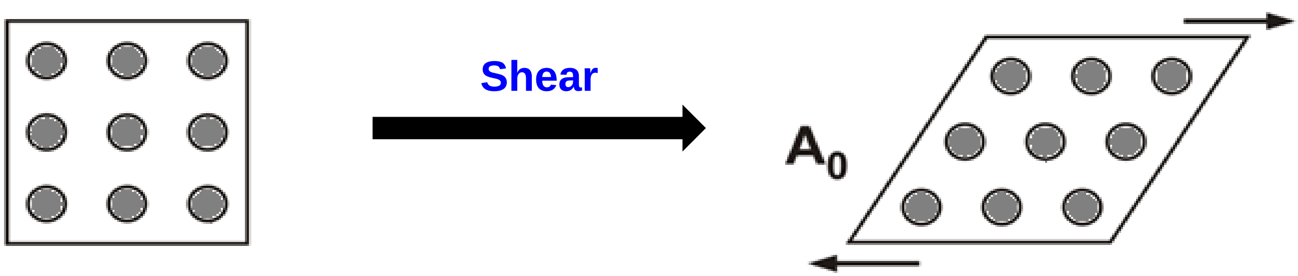


$A \approx 0.4\text{-}0.5\ nm^2$

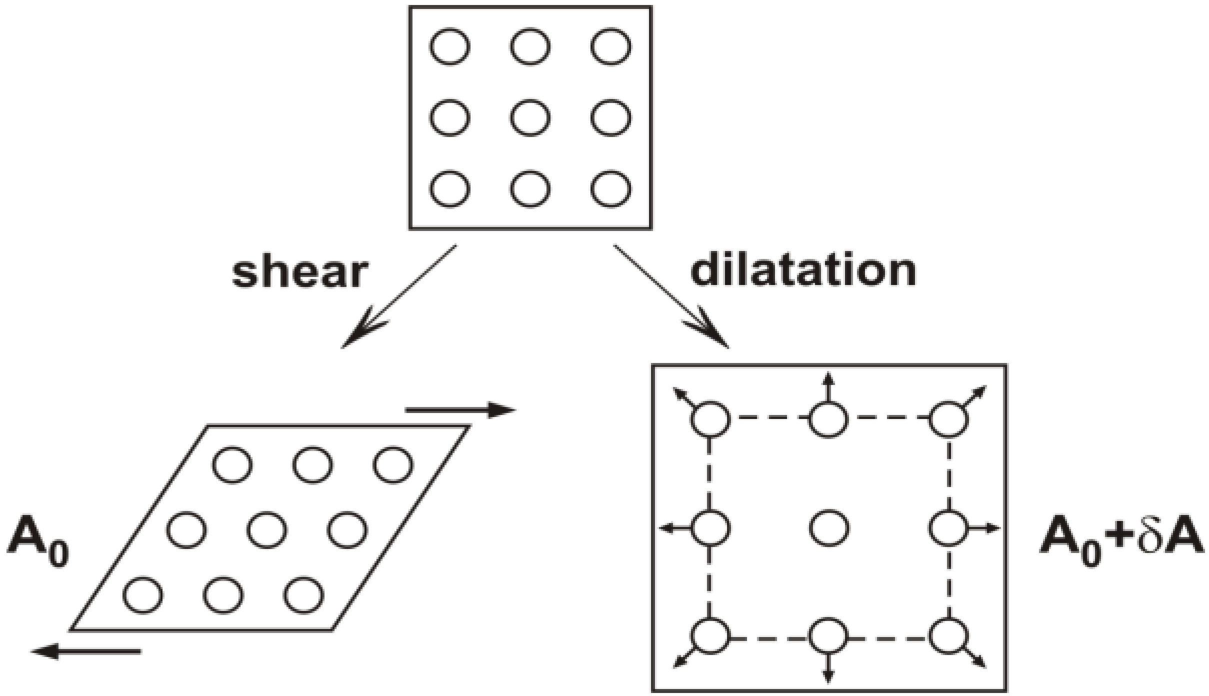


$A \approx 0.8\text{-}1.0\ nm^2$

Is there a link between molecular packing & surface modulus



Surface Rheology

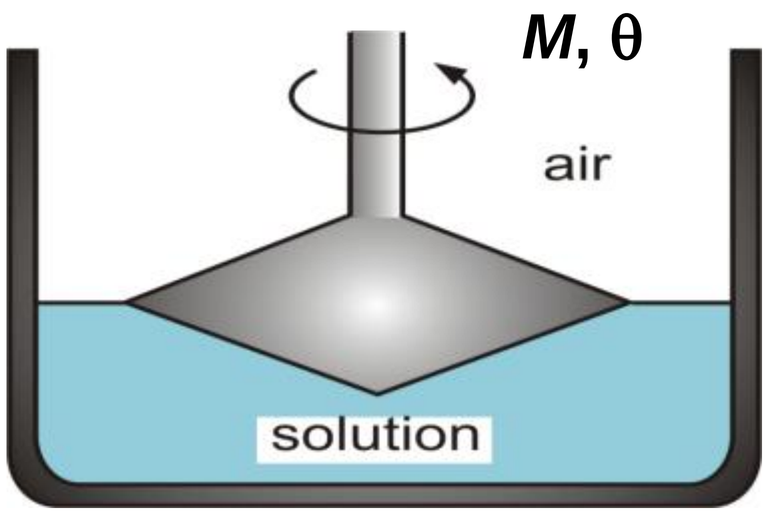


- Interactions between the molecules
- Kinetics of adsorption / desorption

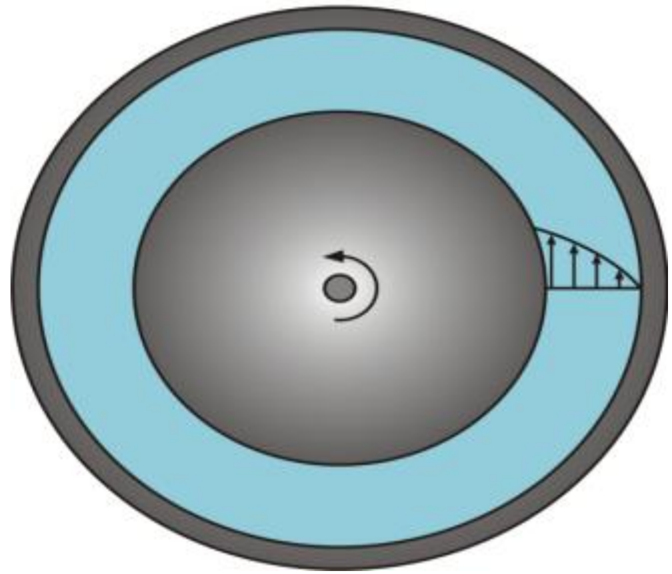
➡ $\tau(\gamma), \tau(\dot{\gamma})$

Surface Shear Rheology: bicone tool

Lateral view



Top view

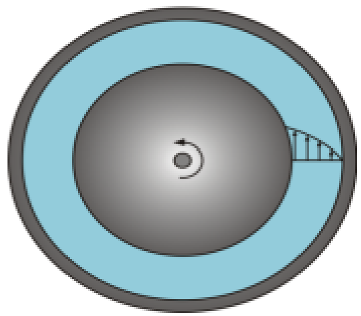


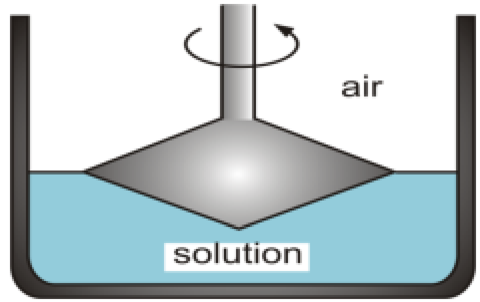
Shear stress: $\tau = M / \left(2\pi R_1^2\right)$

Shear deformation: $\gamma = \theta (R_2 + R_1) / \left[2(R_2 - R_1)\right]$

The Boussinesq number

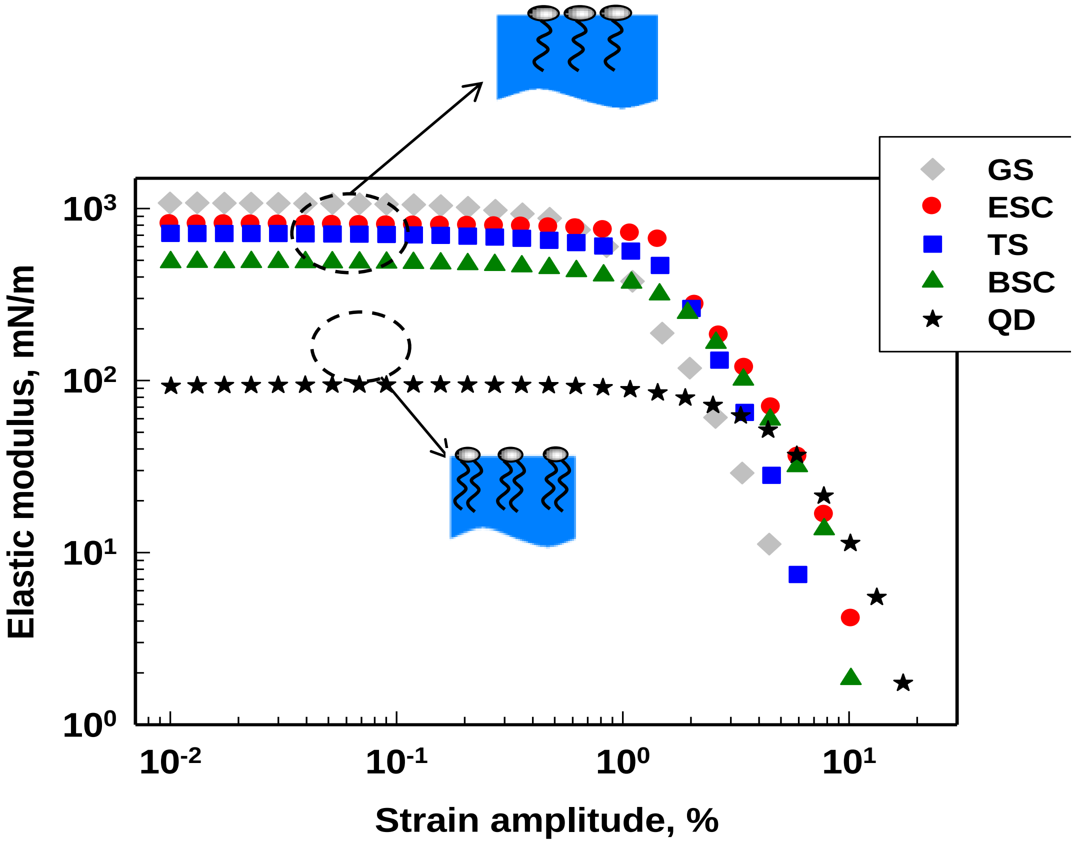
$$Bo = \frac{\text{surface viscous drag}}{\text{bulk viscous drag}} = \frac{\eta_S}{\eta_B . L}$$

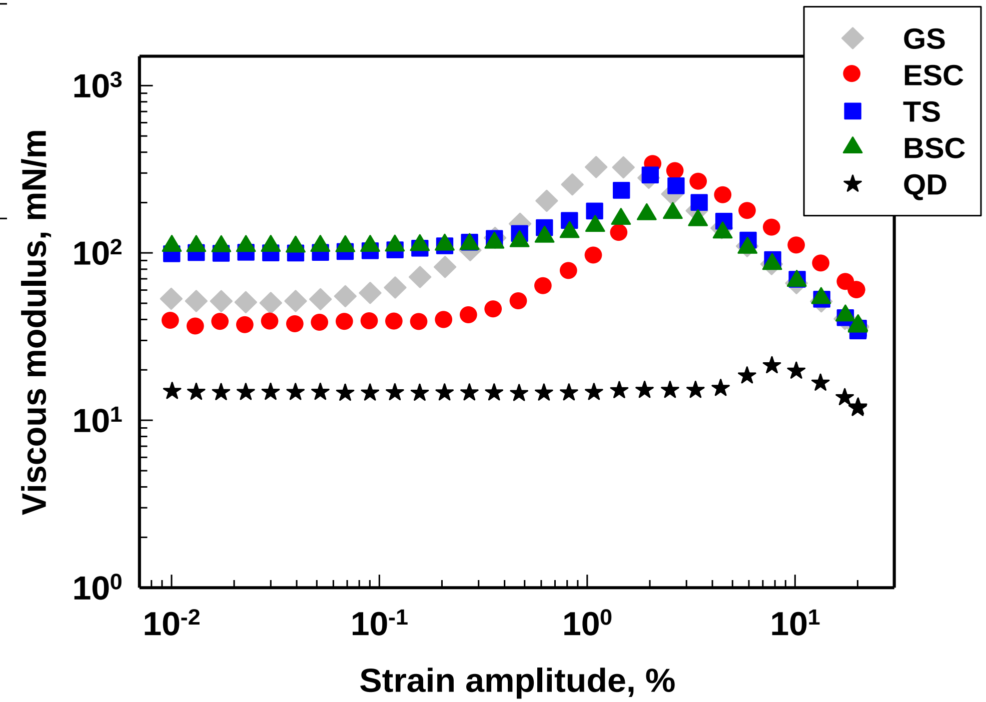




- **At *Bo* < 200:**
  - **Surface and sub-surface flows coupling.**
  - **Numerical procedure needed to calculate the surface viscosity.**
- **Surfactant layer regarded as a 2D body at *Bo* > 200.**

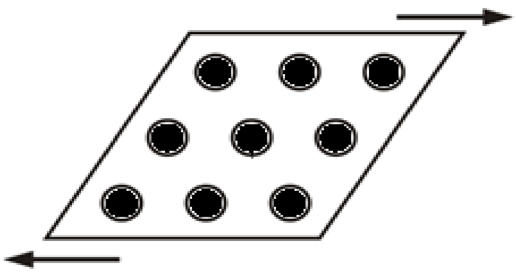
Oscillatory Amplitude sweep (t_A = 30 min)





The bidesmosidic saponins have lower elastic and viscous modulus.

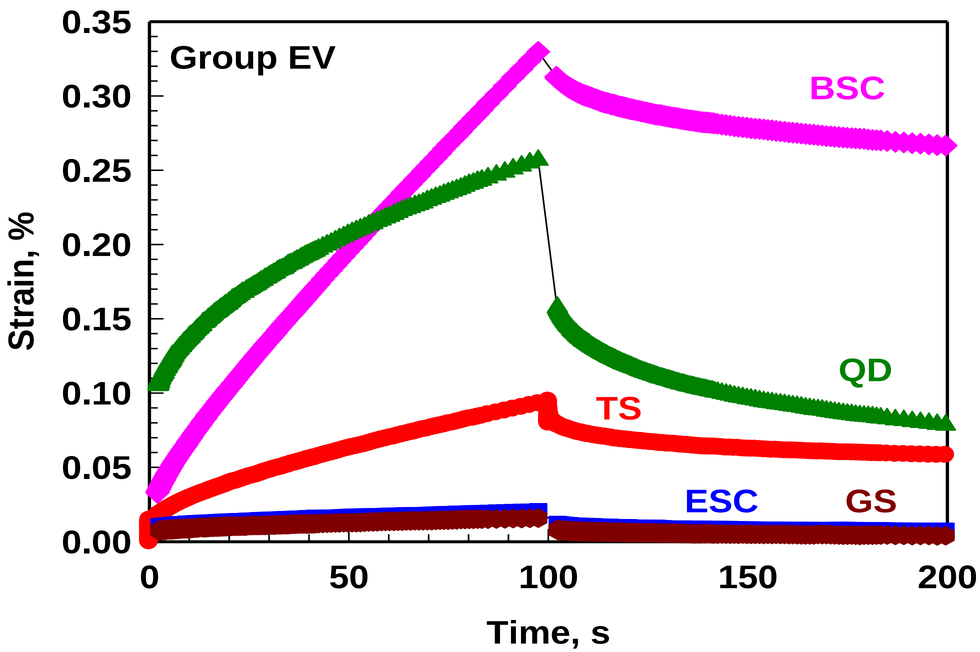
Creep Relaxation Experiments



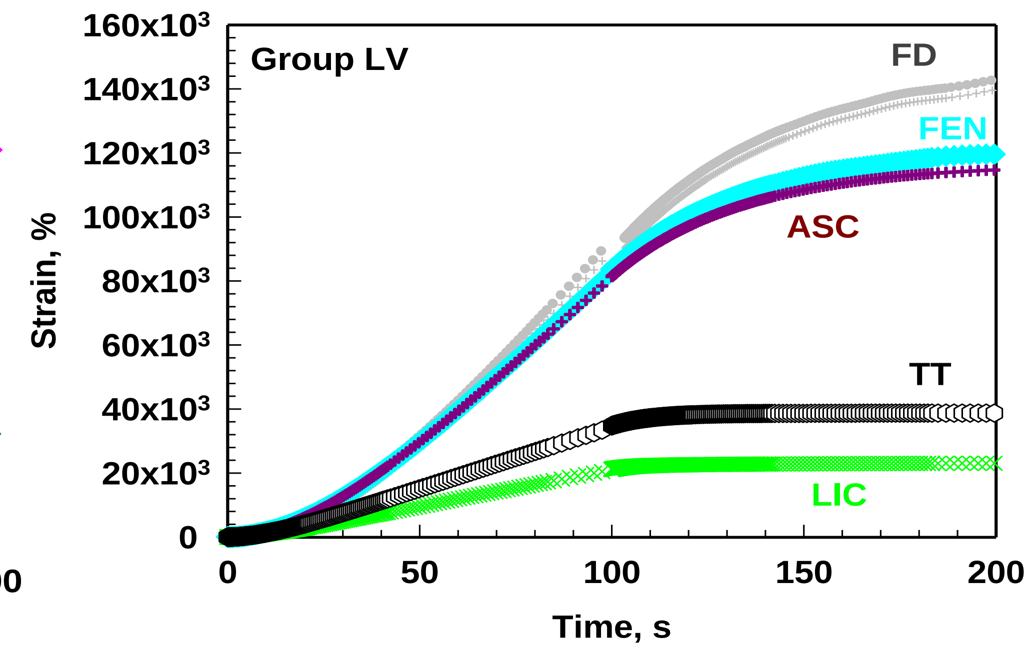
(1) Deformation at constant torque (1 μN.m).

(2) Strain relaxation.

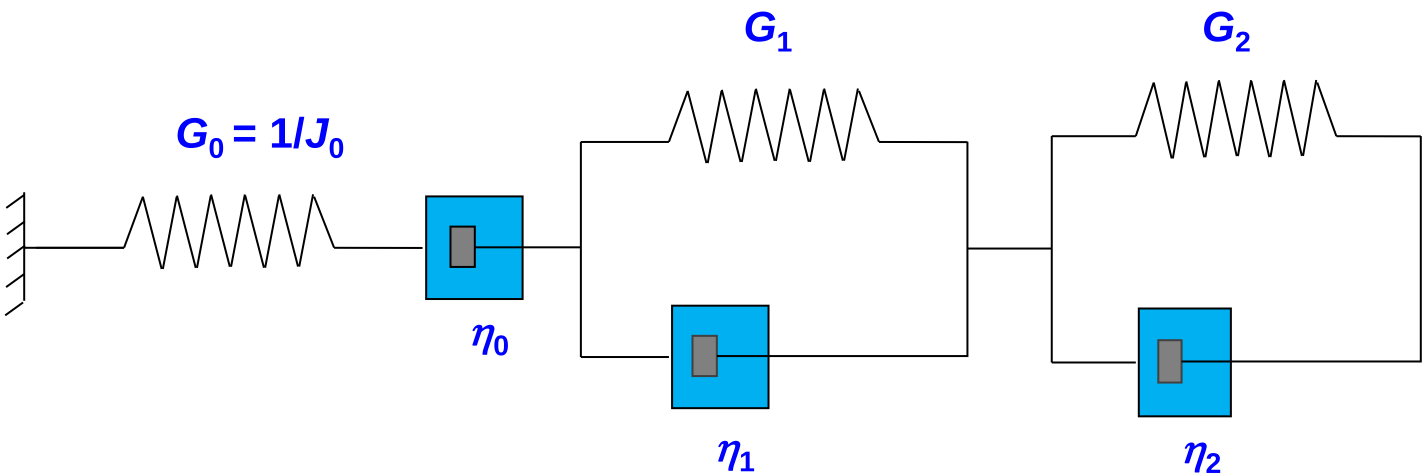
Visco-elastic (some of triterp/mono)



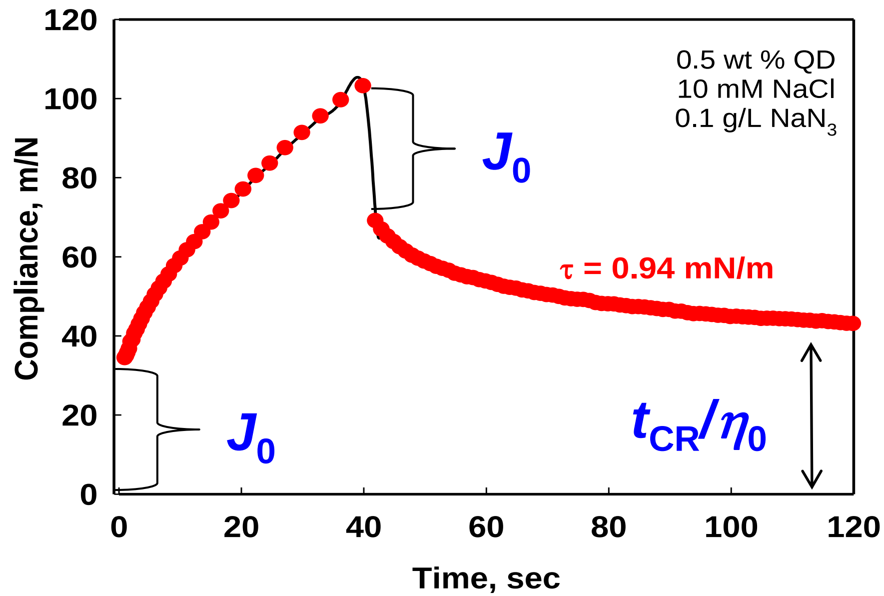
Viscous (main steroidal)



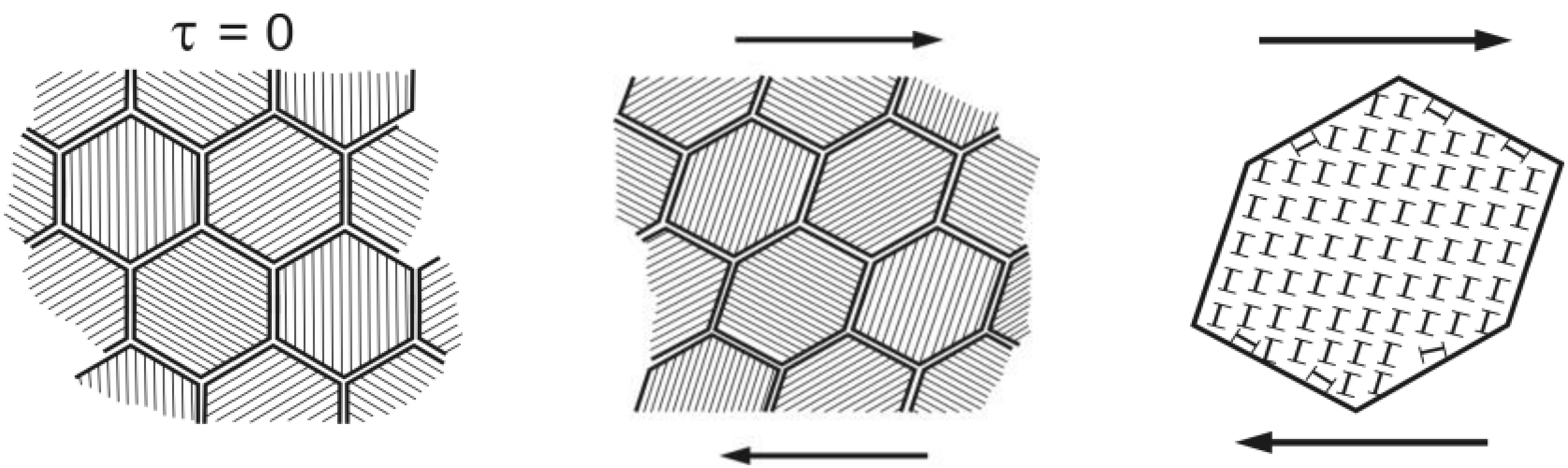
Rheological model (compound Voigt)



- Quillaja saponin.
- Maxwell + Kelvin (1) + Kelvin (2).
- 6 parameters (3 viscous and 3 elastic).
- 2 relaxation times.



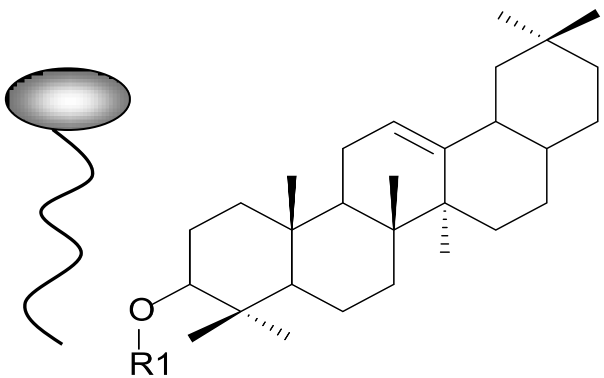
Molecular interpretation

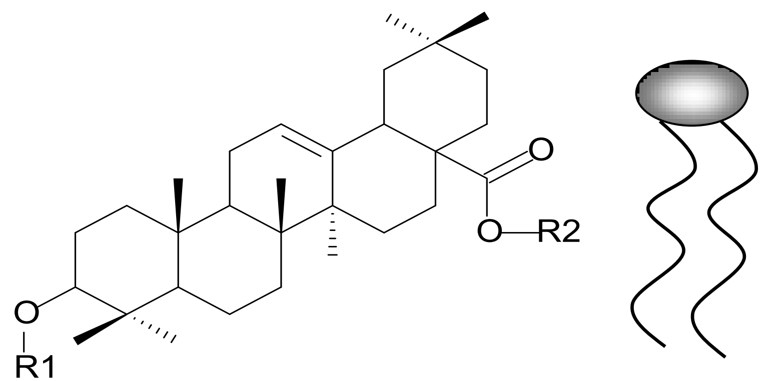


- **Molecules aggregated in domains.**
- **Burger Element: [Maxwell + 1st Kelvin element] – deformation and re-arrangement of domains.**
- **2nd Kelvin Element – re-arrangement of molecules <u>within</u> the domains.**

Viscoelasticity of triterpenoid saponins

- Highly elastic surface layer, *G*`>>*G*``.
- *G*` increases for more than 12 hours of aging of the layer.
- *G*`` decreases or stays constant.
- Saponins with one sugar chain exhibit much higher elasticity.



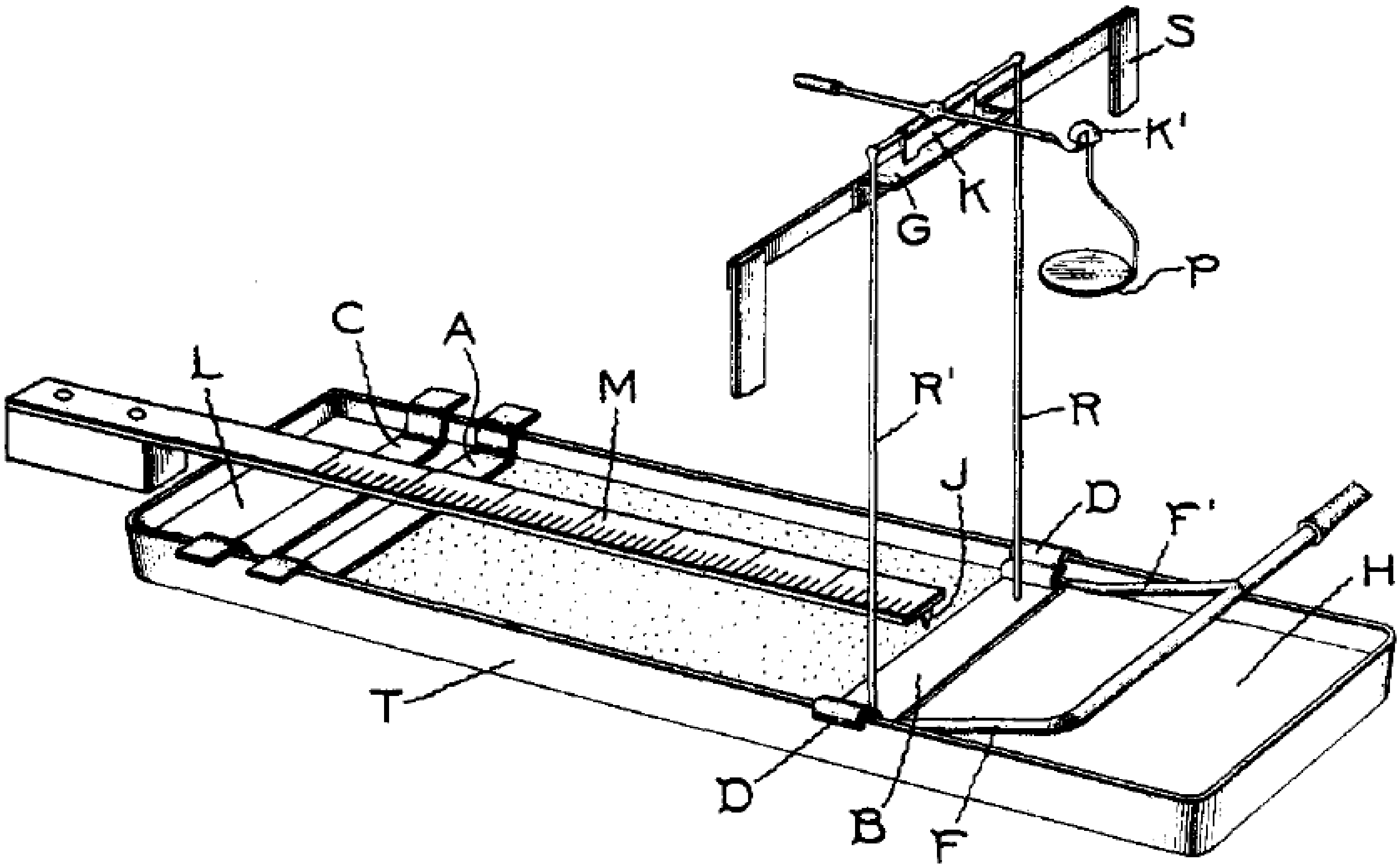


G` ~ 1000 mN/m

G` ~ 100 mN/m

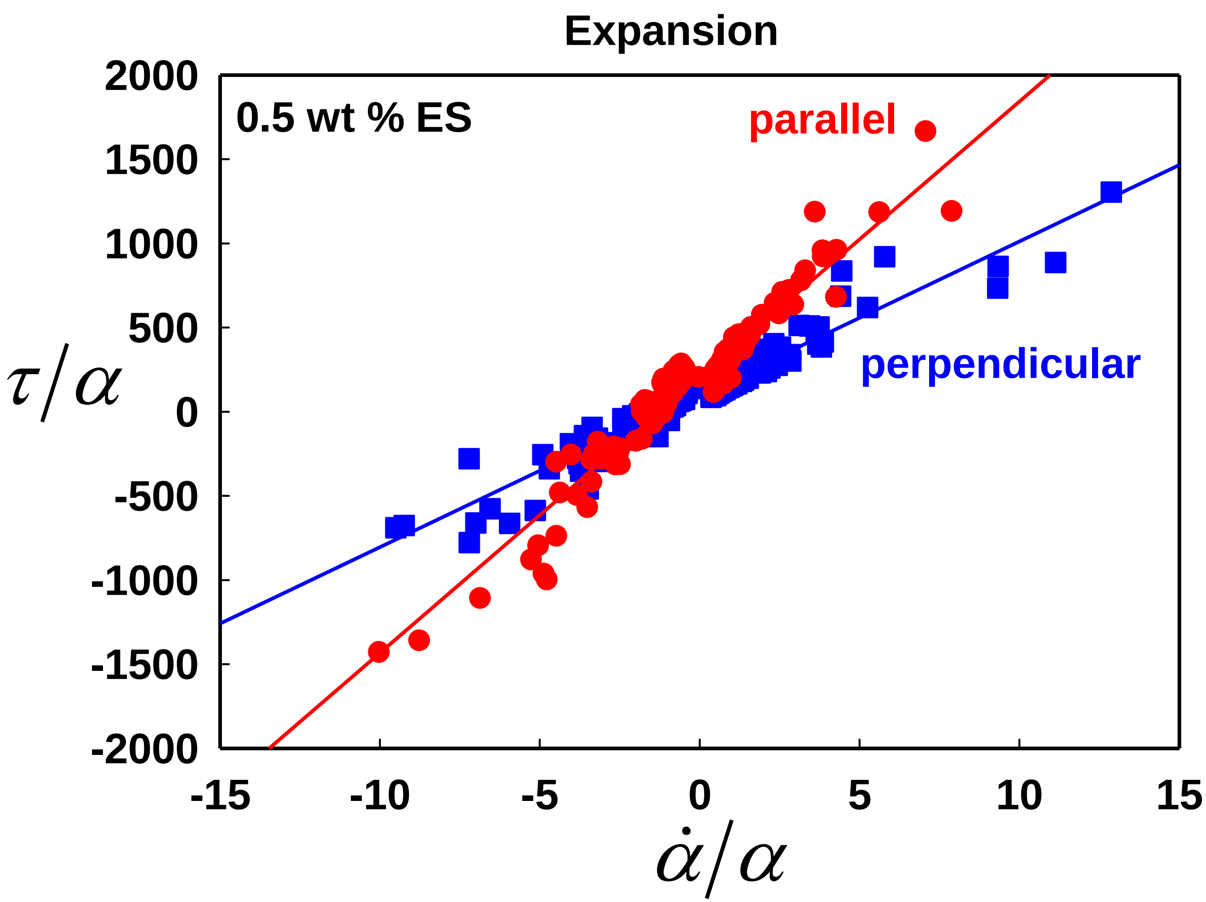
theory of McBain.

Langmuir I.
The constitution and fundamental properties of solids
and liquids. II Liquids.
JACS, **1917,** *39*, 1848-1906



Adsorbing system: 0.5 wt % saponins + 10 mM NaCl

Oscillatory experiments done after equilibration has been reached (>30 min)



Parallel plate

$$\frac{\tau_{\parallel}}{\alpha} = (K+\mu) + (\zeta_s + \eta_s)\frac{\dot{\alpha}}{\alpha}$$

From the best fit

***K*+μ = 204 mN/m**

$\zeta_s + \eta_s$ = 163 mN.s/m

Perpendicular plate

$$\frac{\tau_{\perp}}{\alpha} = (K-\mu) + (\zeta_s - \eta_s)\frac{\dot{\alpha}}{\alpha}$$

From the best fit

***K*-μ = 103 mN/m**

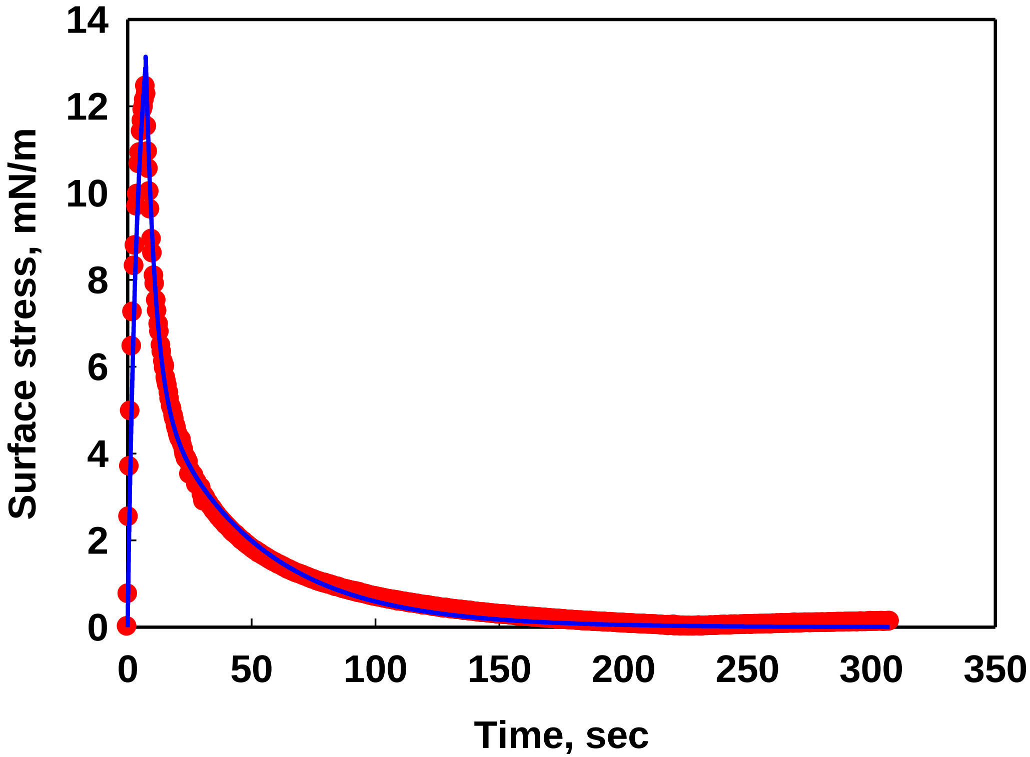
$\zeta_s - \eta_s$ = 91 mN.s/m

For expanding Escin layer

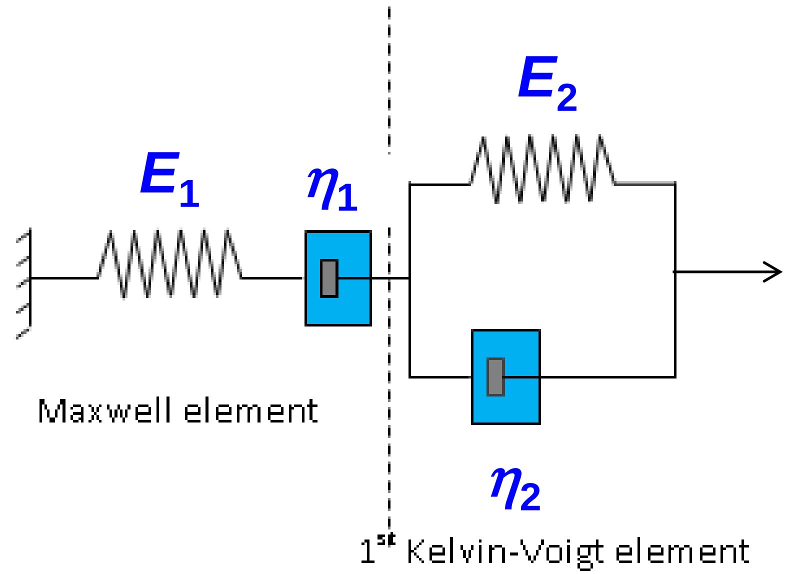
***K* = 154 mN/m; μ = 50 mN/m;**

ζ_s = 127 mN.s/m; η_s = 36 mN.s/m

Analysis of experimental data from dilatation stress-relaxation experiments



Burger model



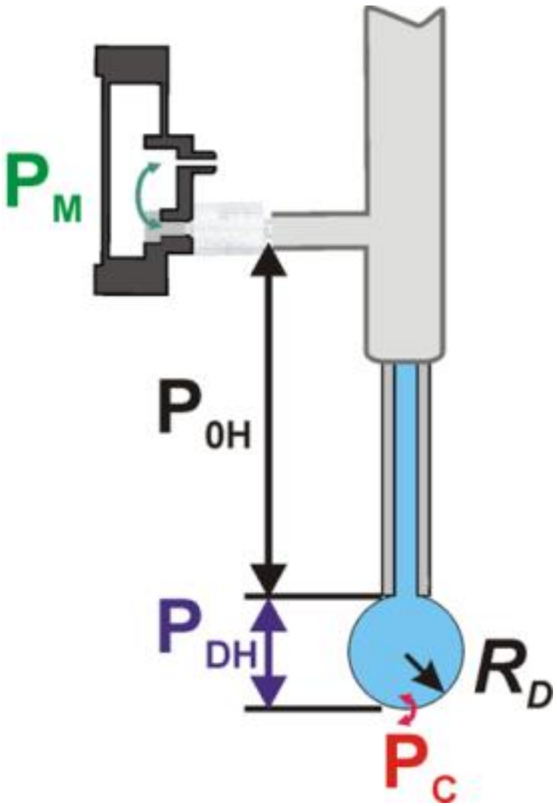
$t_{R1} = \eta_1 / E_1$

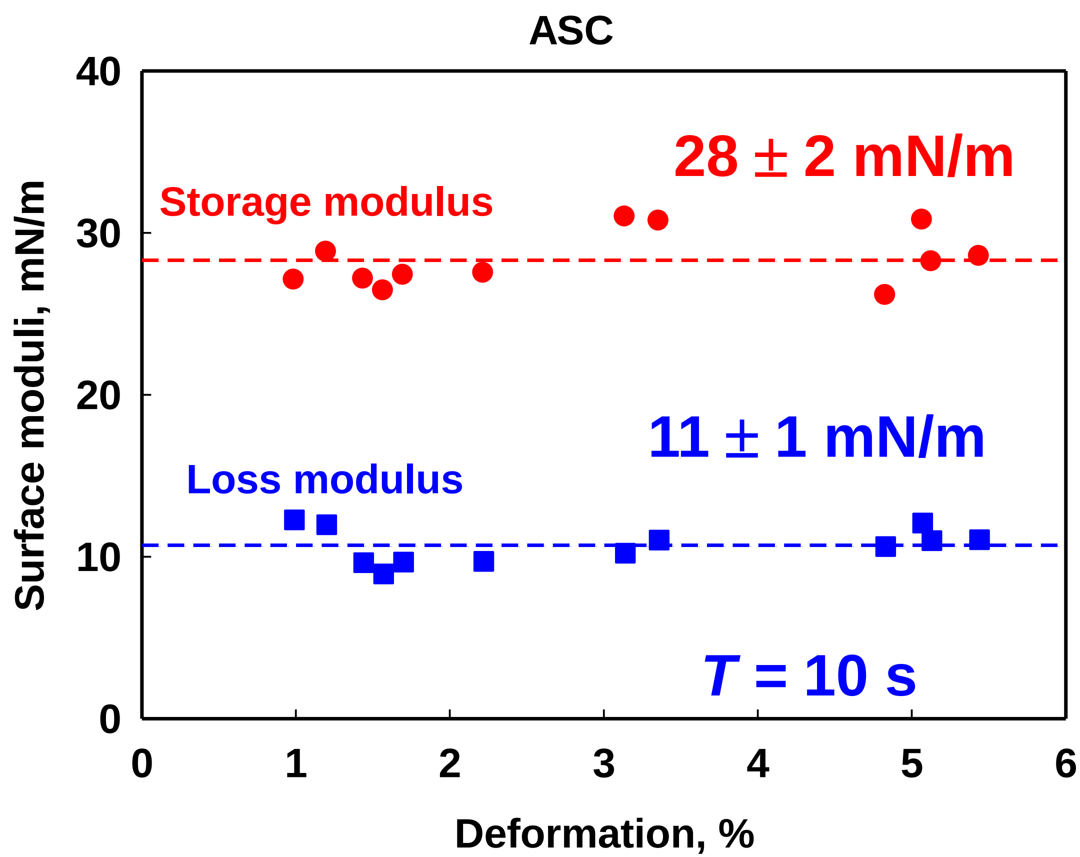
$t_{R2} = \eta_2 / E_2$

$$\ddot{\tau} + \frac{1}{t_{R1}}\left(1 + \frac{E_1}{E_2}\frac{t_{R1}}{t_{R2}} + \frac{t_{R1}}{t_{R2}}\right)\dot{\tau} + \frac{1}{t_{R1}t_{R2}}\tau = E_1\left(\ddot{\gamma} + \frac{\dot{\gamma}}{t_{R2}}\right)$$

From the best fit of deformation and relaxation stages we determine E_1, E_2, t_{R1} and t_{R2}

Surface rheological properties, as determined by oscillating drop method

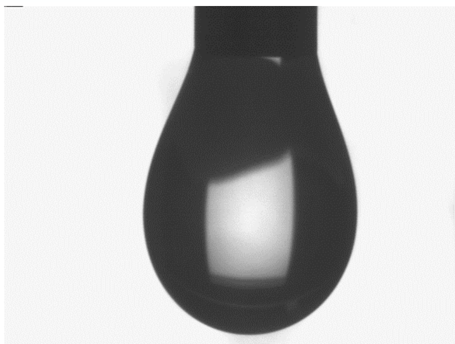




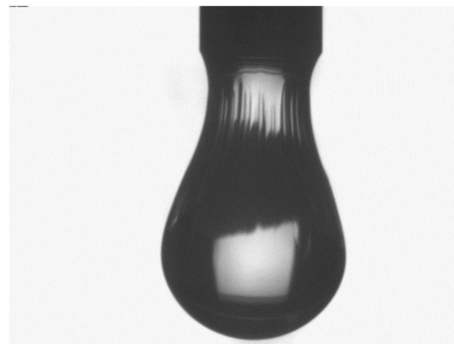
From this experiment we determine the surface dilatational moduli, as functions of surface deformation.

Expansion and contraction of large pendant drop

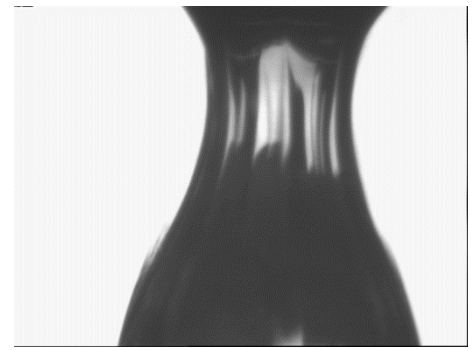
QS



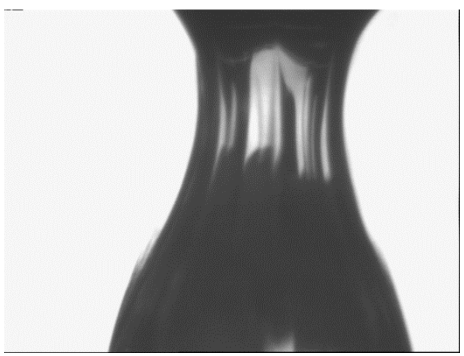
initial state



contraction

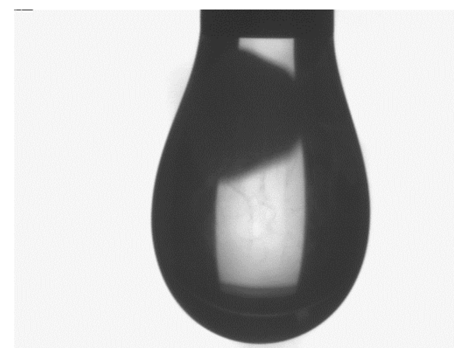


final state



equilibrium contraction state after 100 s

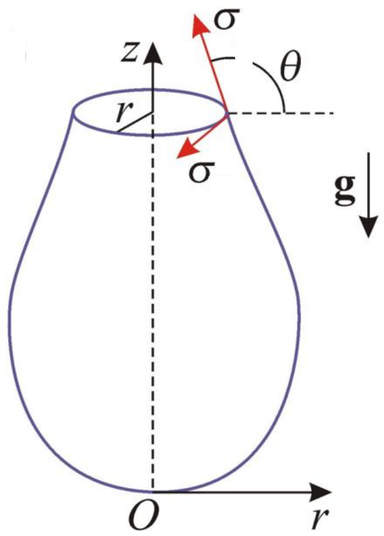
expansion



final state – very close to the initial one

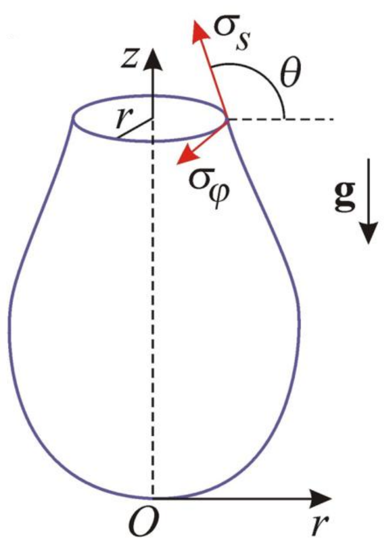
The formation and destruction of elastic membrane is reversible!

Isotropic vs. Anisotropic Interfaces



Fluid Interfaces:

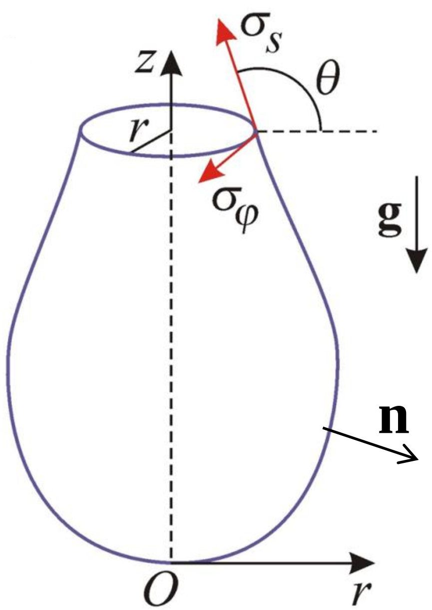
- **Zero surface shear elasticity;**
- **Isotropic: Single surface tension, σ, which is the same along the "meridians" and "parallels";**
- **Uniform: The surface tension σ is the same in all points of the interface;**
- **Method: DSA based on fit of meniscus profile by Laplace equation; σ and p – adjustable parameters.**



Solid Interfaces (Membranes):

- **Nonzero surface shear elasticity;**
- **Anisotropic: Two different surface tensions, σ_s and σ_φ, along the "meridians" and "parallels";**
- **Noniform: The surface tensions σ_s and σ_φ vary from point to point throughout the interface;**
- **Method: CMD (capillary meniscus dynamometry) based on fit of data for meniscus profile and p.**

Force Balances per Unit Area of a Curved Interface



Balance of linear momentum per unit surface area:

$$\nabla_s \cdot \boldsymbol{\sigma} = p_s \mathbf{n}$$

p_s **– pressure difference across the interface;**

$\mathbf{n}$ **– running unit normal to the surface;**

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_s & 0 \\ 0 & \sigma_\varphi \end{pmatrix}$$

Surface stress (tension) tensor (axial symmetry)

$$\sigma_\varphi = \frac{\mathrm{d}}{\mathrm{d}r}(\sigma_s r) \quad \text{(tangential projection)}$$

$$\sigma_s = const. \Rightarrow \sigma_\varphi = \sigma_s = \sigma$$

(uniformity ⇔ isotropy)

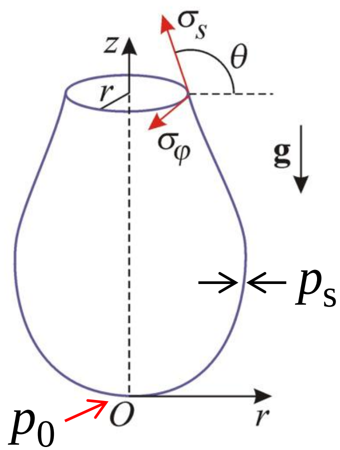
(non-uniformity ⇔ anisotropy)

$$\kappa_s \sigma_s + \kappa_\varphi \sigma_\varphi = p_s \quad \text{(normal projection)}$$

(κ_s , κ_φ – the two principal curvatures)

⟶ For $\sigma_\varphi = \sigma_s = \sigma$ reduces to Laplace equation

Balance of Integral Surface Tension and Pressure Forces



$$\int_0^r \mathrm{d}r$$

$$\frac{\mathrm{d}}{\mathrm{d}r}(\sigma_s r \sin\theta) = p_s r$$

hydrostatic pressure: $p_s \equiv p_{\text{in}} - p_{\text{out}} = p_0 - \varepsilon g z \Delta\rho$

The result of integration can be expressed in the form:

$$2\pi r \sigma_s \sin\theta = F_p$$

$$F_p \equiv \pi r^2 p_0 - \pi\varepsilon g \Delta\rho [r^2 z - \int_0^z r^2(\tilde{z})\,\mathrm{d}\tilde{z}]$$

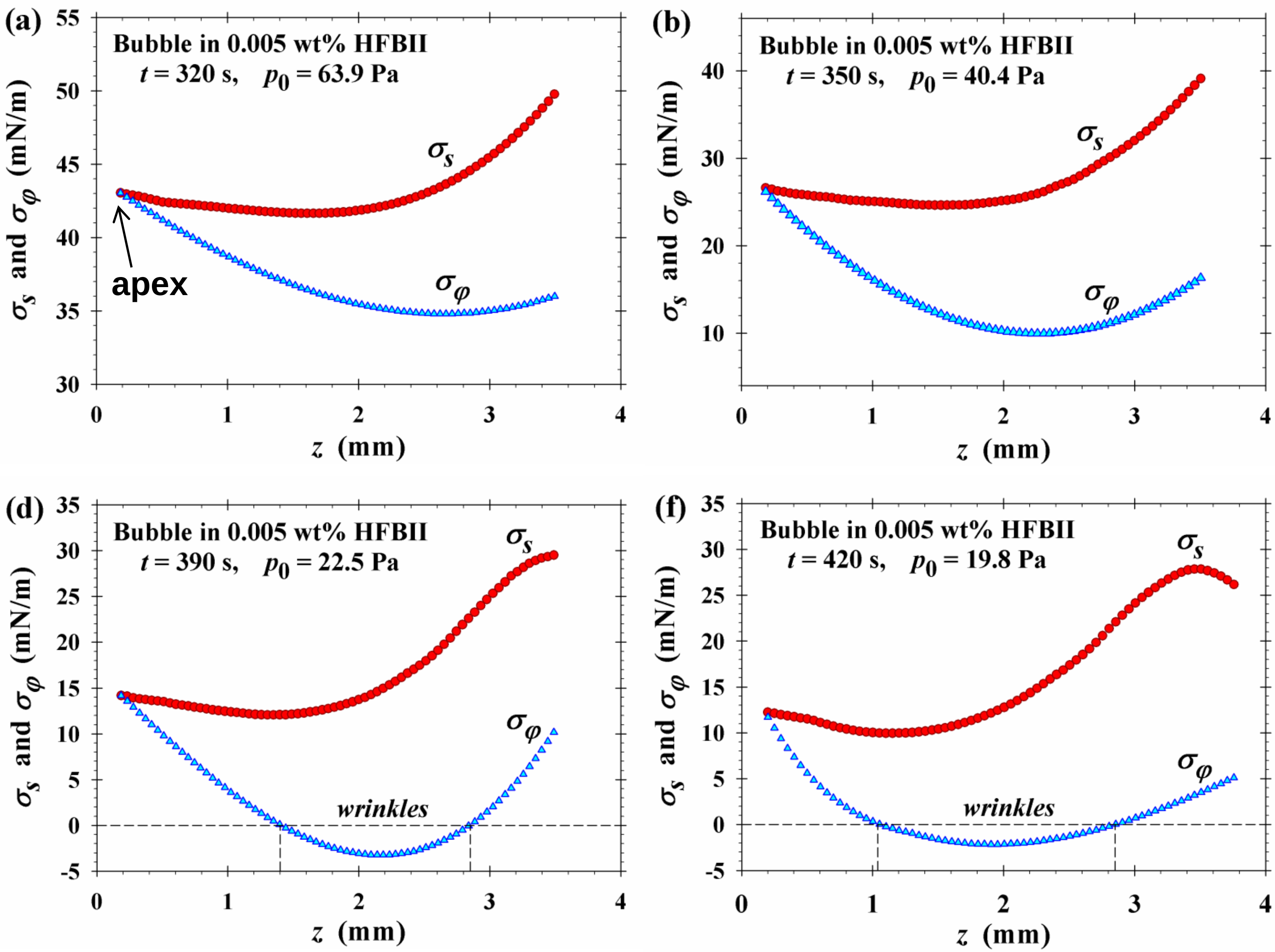
integral surface tension force

integral pressure force

contribution of hydrostatic pressure

Details in: **Danov et al., J. Colloid Interface Sci. 440 (2015) 168.**

Variations of σ_s and σ_φ along the Bubble Profile

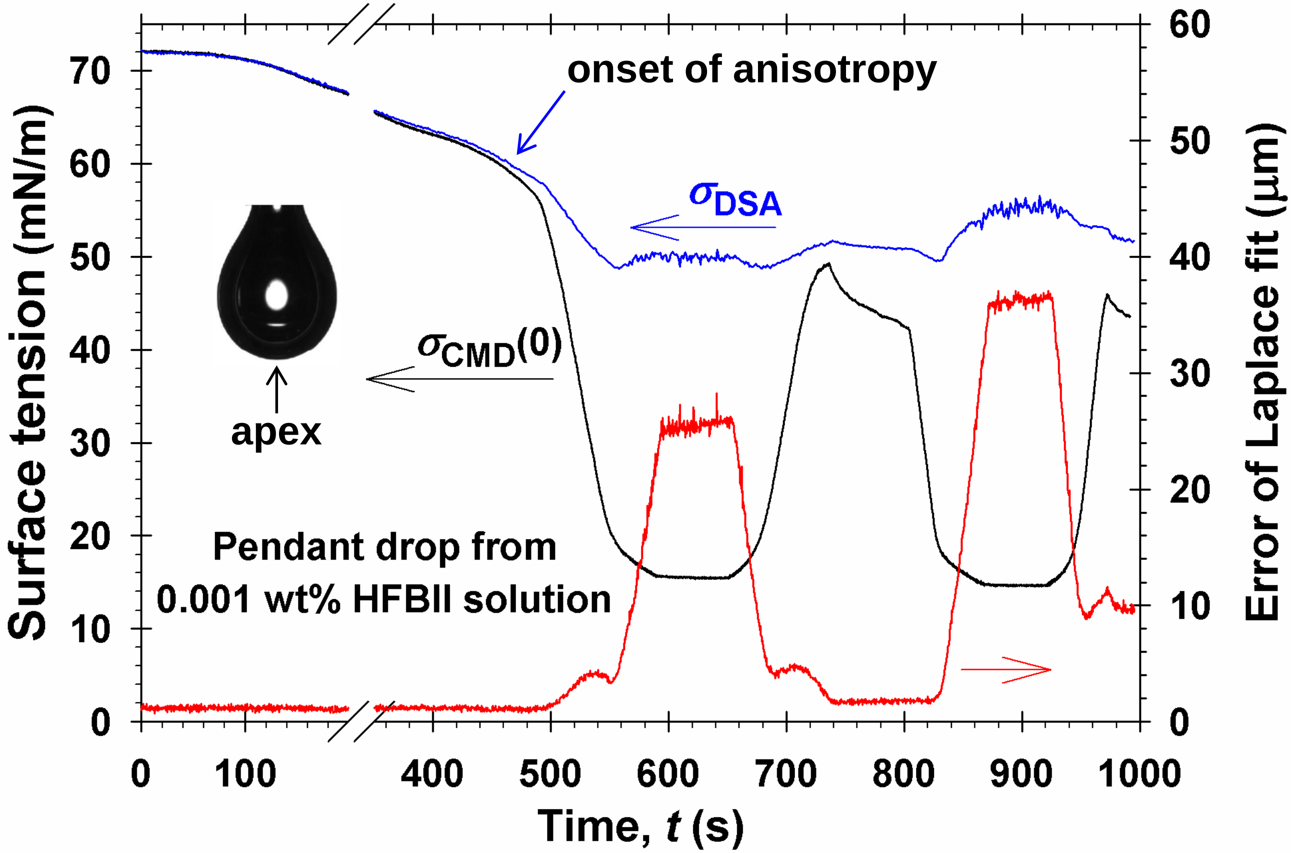


Anisotropic non-uniform surface tension

Wrinkles in the zones with negative σ_φ.

Wrinkles theory: Danov, Kralchevsky, Stoyanov, Langmuir 26 (2010) 143.

DSA vs. CMD



For **anisotropic** surface DSA gives **greater nonphysical values** σ_{DSA}

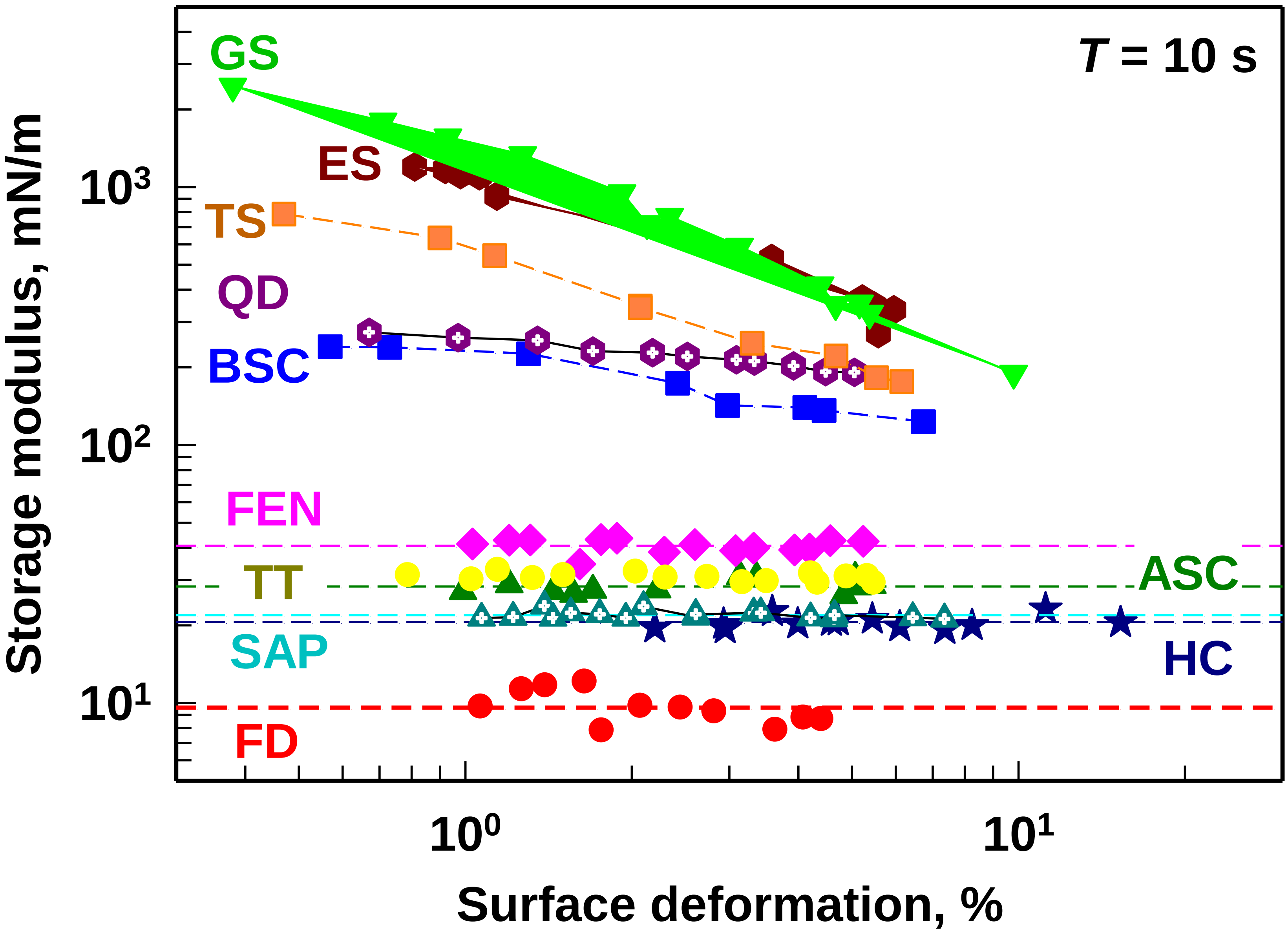
The **error of the DSA fit** is not so sensitive to surface stress **anisotropy**

The **onset of deviation** of **DSA** from **CMD** may serve as **criterion** for surface stress **anisotropy**

Surface tension σ_{DSA} and the error of the Laplace fit given by the DSA apparatus,

vs. surface tension at the drop apex, $\sigma_{CMD}(0)$, measured by CMD.

Surface storage modulus



Take home messages & (Soft Matter) challenges

- The old new challenge -> The origin of interfacial rheology (1890, Rayleigh) is linked with saponins
- There are still unresolved theoretical & experimental issues with respect of surface rheology
  - How we separate/extract/QC naturals ?
  - How/did we measure surface stress [tensor] and strain correctly
    - Can we do in plane measurements / if not how we estimate local/global deformations due to the measurement
  - Did we use the right constitutive and measurement protocols in order to convert surface storage and loss moduli into surface elasticity and viscosity ?
- Saponins are large class of natural surfactants with unique architecture and surface properties, with multiple functionalities, which despite of old history of use and long list of functionalities are yet poorly understood -> and could be used as a proxy for validation of next generation theoretical and experimental soft matter studies
- Some of these natural compounds challenge our standard concepts of surfactants and surface behavior and might be at the limit of what our current methods can measure
- Naturals are hot consumer trend and we need to develop appropriate soft matter tools that allow us to study and conceptualize them -> similar to what we have for synthetic polymers and surfactant systems

Thank You!