# Dynamics of complex fluid-fluid interfaces


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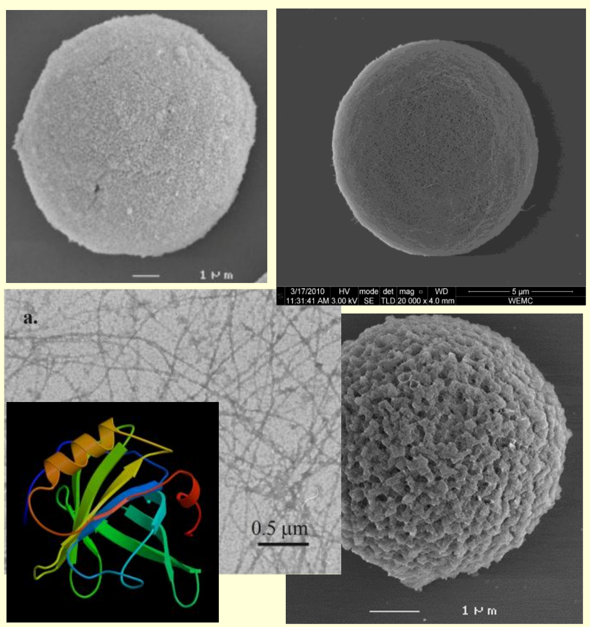


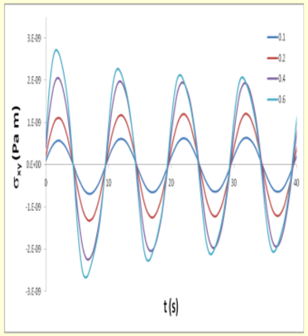


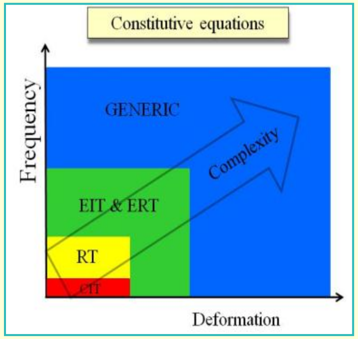


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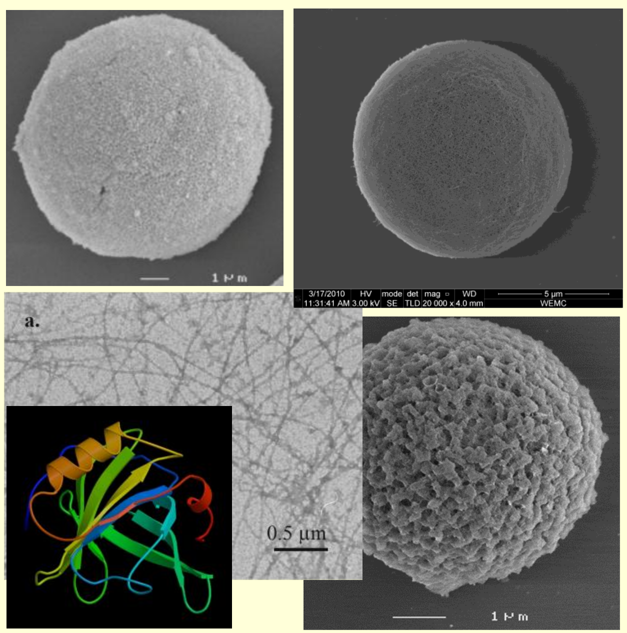
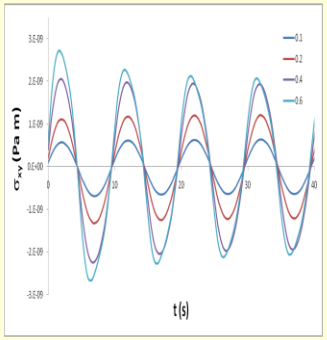
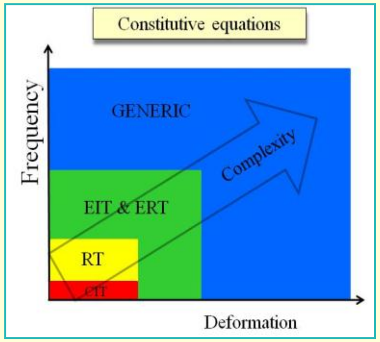


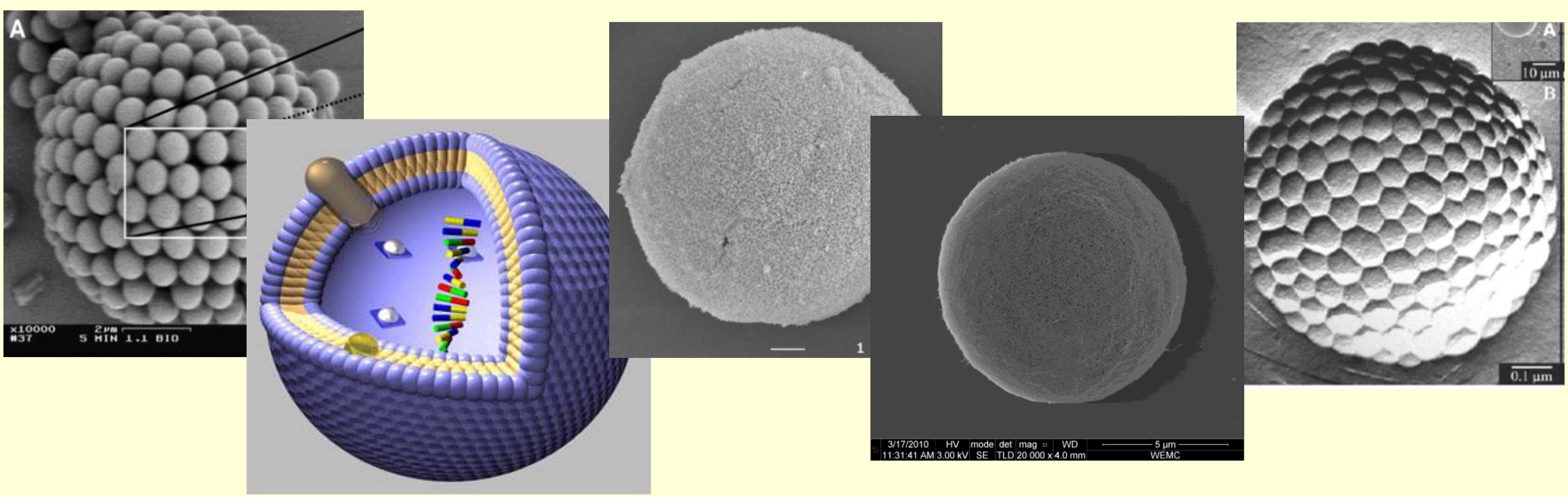
# Aim:

- Investigate effect of surface rheology on macroscopic behavior and stability of emulsions, foam, encapsulation systems
- Link nonlinear surface rheology to deformation induced changes in surface microstructure

- block oligomers
- colloidal particles
- rod-like particles
- proteins
- complexes
- (mixtures of ) lipids

→

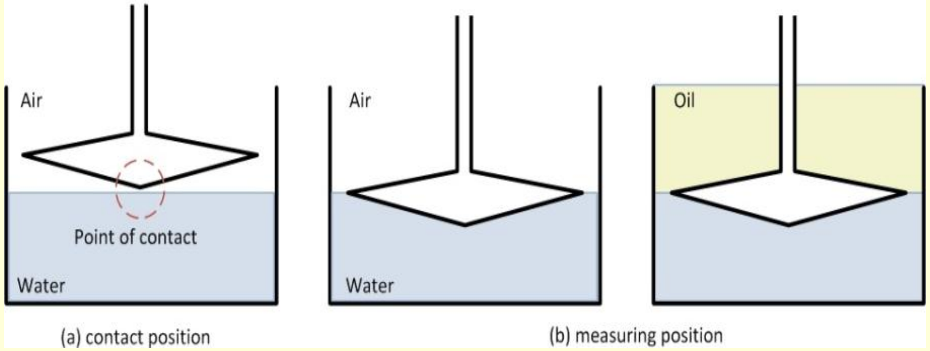
Interfacial structure:
- 2D suspensions
- 2D glasses
- 2D gels
- 2D (liquid) crystalline phases
- 2D nano-composites

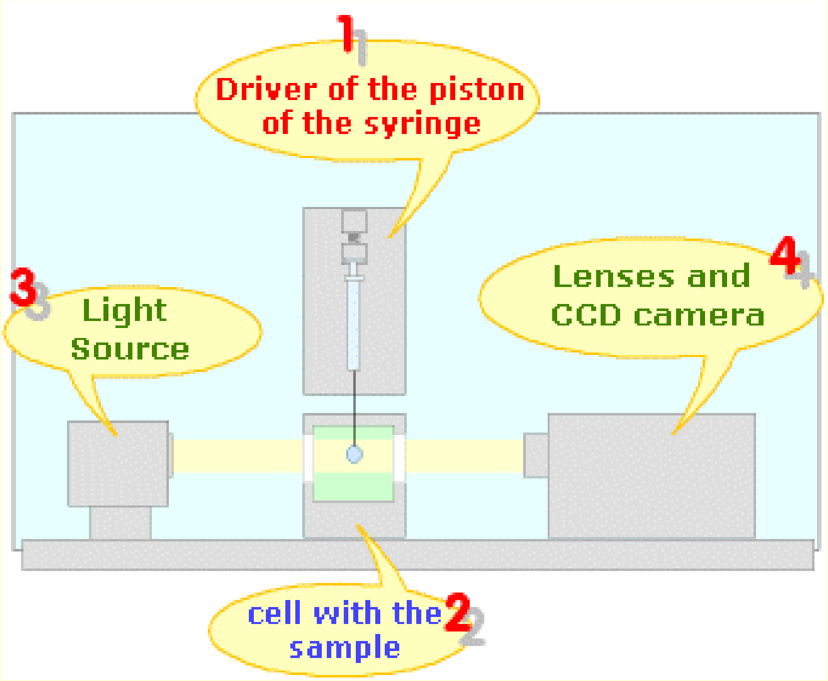


# Determination of surface rheological properties of complex interfaces

Stress controlled rheometer
with biconical disk geometry

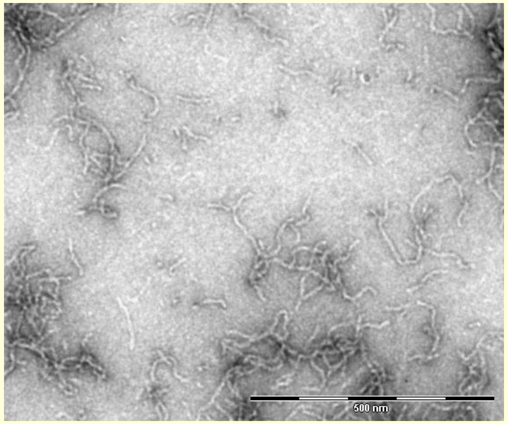
Automated drop tensiometer

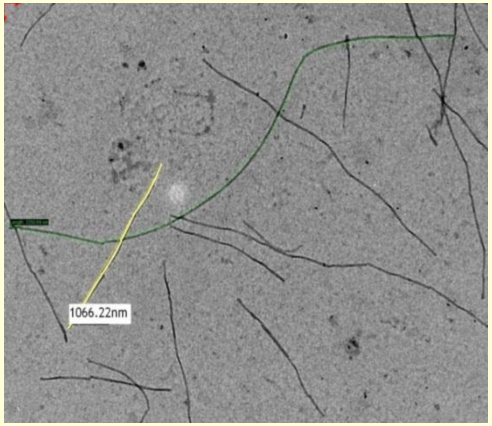


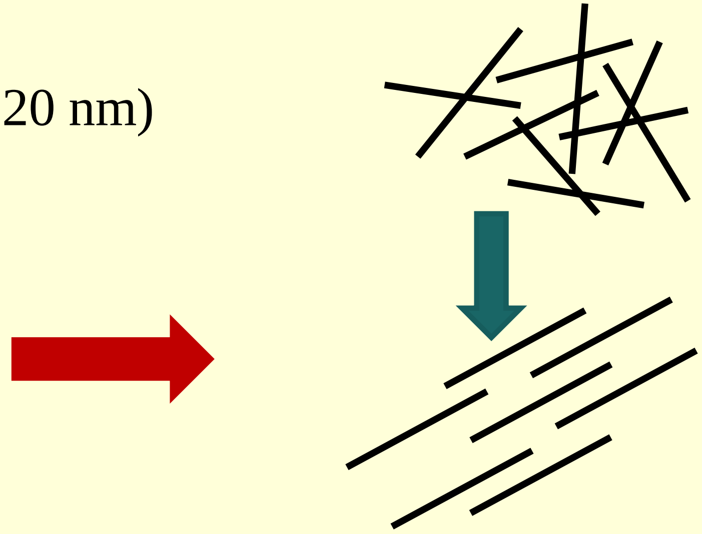



## Typical structures we are investigating:

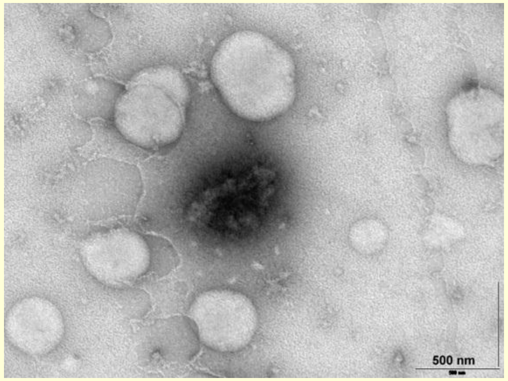
Protein fibrils ($L_c$ = 200 – 2000 nm, D = 5 – 20 nm)

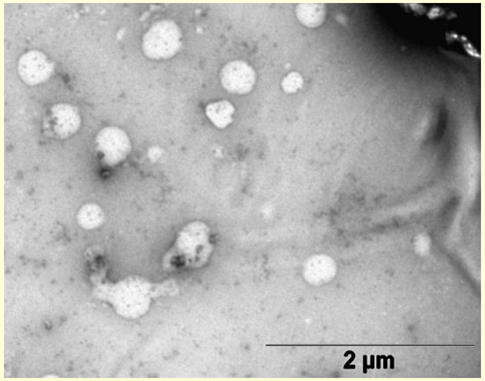


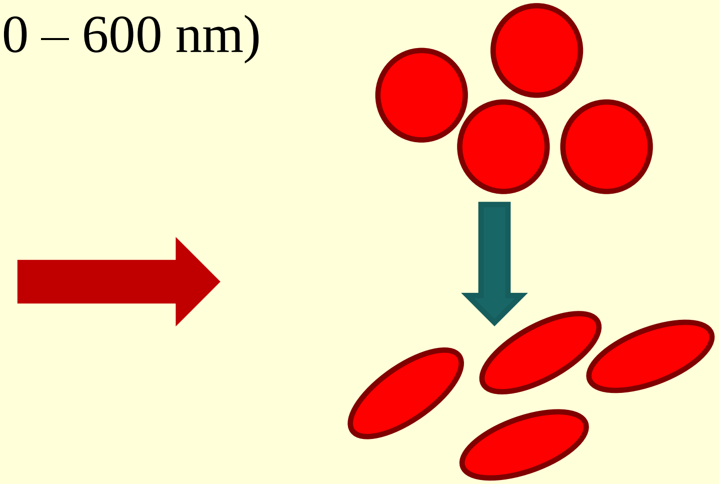



Protein – polysaccharide complexes (D = 200 – 600 nm)



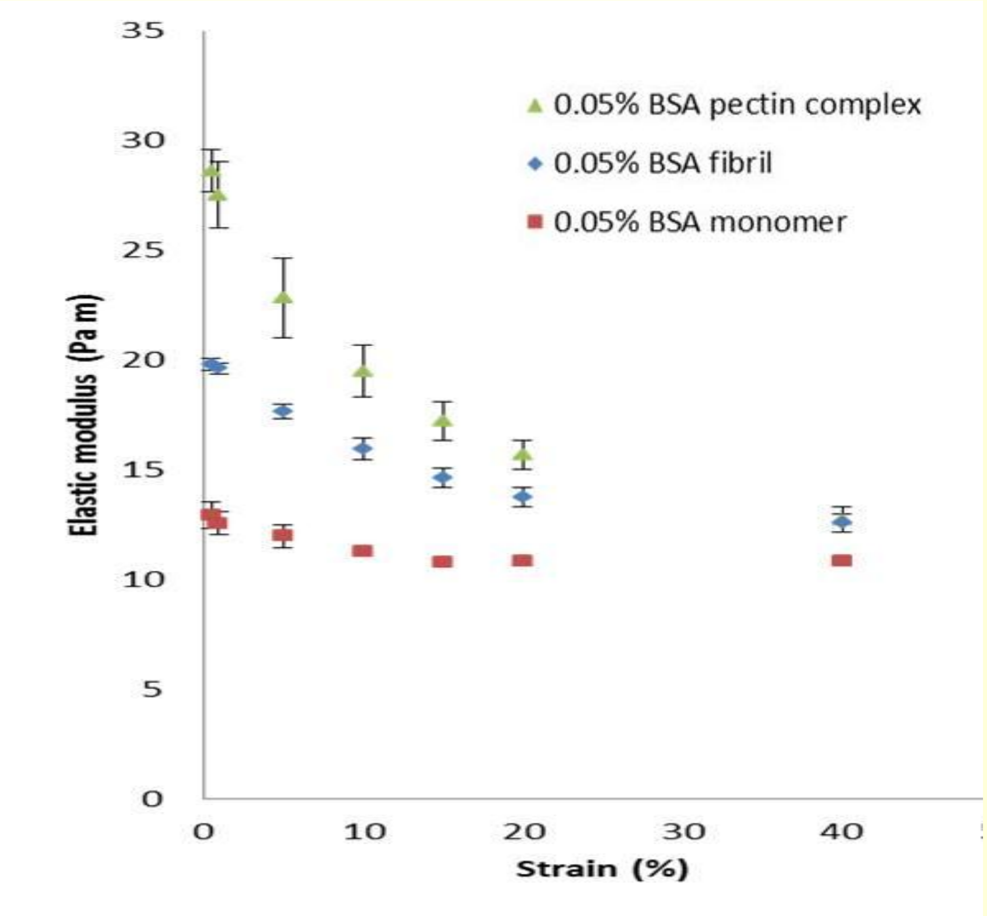



Focus of this presentation: anisotropic structures and effect of flow on their orientation

## Surface dilatational modulus for single layers

- MCT/W interface
- Frequency strain sweep: 0.01 Hz
- Strain of frequency sweep : 5%




Nonlinear behavior even at lowest strains that can be applied (~0.02)

Most dilatational studies do not even apply strain sweeps

No useful constitutive equations for nonlinear surface stresses

L.M.C. Sagis, *Rev. Mod. Phys.* **83**, 1367 (2011)

Excellent opportunity for NET to fill this "knowledge gap"

# Modeling surface rheology with Nonequilibrium Thermodynamics (NET)

## Properties constitutive models for in-plane surface fluxes should have:

- Link surface stress to the microstructure of the interface
- Give structure evolution as a function of applied deformation
- Incorporate a coupling with the bulk phase
- Be valid far beyond equilibrium

L.M.C. Sagis, *Rev. Mod. Phys.* **83**, 1367 (2011)

## What is “far beyond equilibrium” for surface rheology of complex interfaces:

- Fluid-fluid interfaces with complex microstructure show changes in that structure at very low strains
- First nonlinear contributions to surface stress: $10^{-5} \leq \gamma \leq 10^{-3}$
- Significant deviations from linear behaviour: $\gamma > 0.1$
- Most industrial applications: $\gamma >> 1$
- CIT models typically start to fail at: $10^{-3} \leq \gamma \leq 10^{-2}$

# GENERIC for multiphase systems with complex interfaces:

$$\frac{dA}{dt} = \{A, E\} + \{A, B\}^{\text{mint}} + [A, S]$$

Reversible dynamics for bulk phase and interface variables

Ensures structural compatibility of GENERIC in presence of moving interfaces

Dissipative processes bulk phase and interface

E = total energy of the system

S = total entropy of the system

$$A = \int_R a \, dV + \int_S a^s \, dA$$

H.C. Öttinger, D. Bedeaux and D.C. Venerus, *Phys. Rev. E.*, 80, 021606 (2009)
L.M.C. Sagis, *Advances in Colloid & Interface Science* **153**, 58 (2010)
L.M.C. Sagis, *Rev. Mod. Phys.* **83**, 1367 (2011)

## GENERIC for multiphase systems with complex interfaces:

$$\{A,E\} = \frac{\partial A}{\partial x} \cdot L \cdot \frac{\partial E}{\partial x}$$

$$L = -L^T$$

Poisson matrix

$$[A,S] = \frac{\partial A}{\partial x} \cdot M \cdot \frac{\partial S}{\partial x}$$

$$M = M^T$$

Independent system variables:

$$\mathbf{x}^T = \left(\rho, \mathbf{m}, \bar{U}, \rho_{(1)}, \ldots, \rho_{(N-1)}, \bar{\Gamma}, \bar{\mathbf{C}}\right)$$

$$\mathbf{x}^{sT} = \left(\rho^s, \mathbf{m}^s, \bar{U}^s, \rho^s_{(1)}, \ldots, \rho^s_{(N-1)}, \bar{\Gamma}^s, \bar{\mathbf{C}}^s\right)$$

Structural variables

# GENERIC for structured interfaces

Surface extra stress tensor:

$$\boldsymbol{\sigma}^s_{tot} = \boldsymbol{\sigma}^s + 2\bar{\mathbf{C}}^s \cdot \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s} + \mathbf{G}^s \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s}$$

Configurational Helmholtz free energy

$$\mathbf{G}^s = G^s_1 \bar{\mathbf{C}}^s + G^s_2 \mathbf{P} + G^s_3 \left(\bar{\mathbf{C}}^s\right)^{-1}$$

Coupling of $\Gamma$ with velocity gradient

Upper convected surface derivative

$$\frac{d_s \bar{\mathbf{C}}^s}{\partial t} - \bar{\mathbf{C}}^s \cdot \left[(\nabla_s \mathbf{v}^s)^T \cdot \mathbf{P}\right] - \left[\mathbf{P} \cdot (\nabla_s \mathbf{v}^s)\right] \cdot \bar{\mathbf{C}}^s$$
$$+ \mathbf{R}^s_2 : \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s}\right) - \nabla_s \cdot \left[\mathbf{D}^s_C \odot^3 \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s}\right)\right]$$
$$+ \left[\!\left[ \bar{\mathbf{C}} \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi} - \left[\mathbf{D}_C \odot^3 \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\mathbf{C}}}\right)\right] \cdot \boldsymbol{\xi} \right]\!\right] = 0$$

Diffusion term

Relaxation term

Coupling with the bulk phase

# GENERIC for structured interfaces

We can create a wide range of models by specifying:

$$\overline{F}_c^{\,s}, \mathbf{G}, R_1^s, \mathbf{R}_2^s, \mathbf{D}_\Gamma^s, \mathbf{D}_C^s$$

Admissible models:

$$[S, S] \geq 0 \quad \Rightarrow \quad R_1^s \geq 0$$

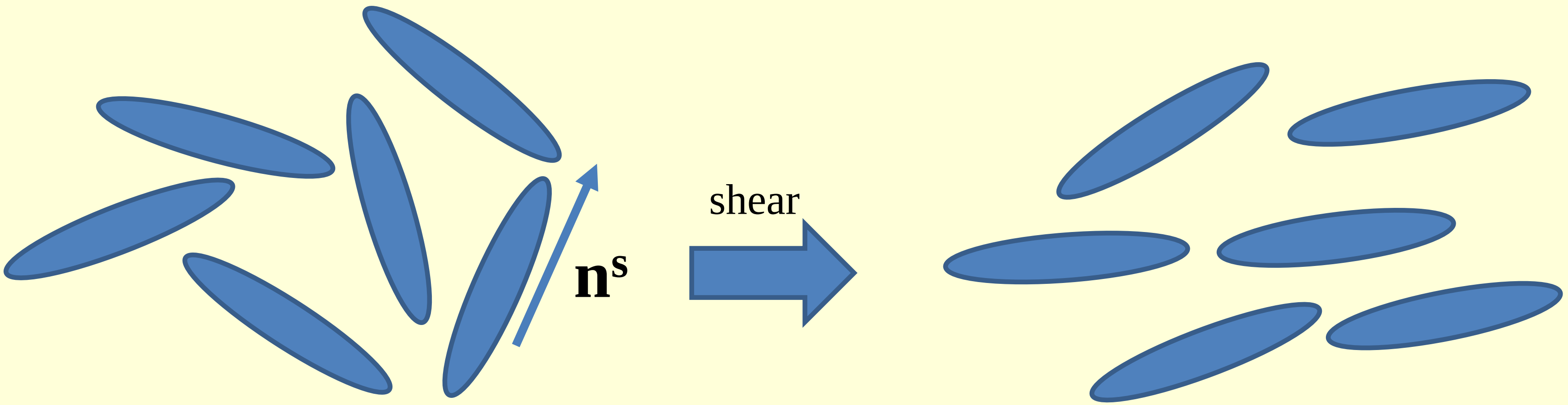
$$\left.\begin{array}{l} \mathbf{R}_2^s \geq \mathbf{0} \\ \mathbf{D}_\Gamma^s \geq \mathbf{0} \\ \mathbf{D}_C^s \geq \mathbf{0} \end{array}\right\}$$

Symmetric positive semi-definite tensors

# Example:

Interface stabilized by a mixture of rod-like particles and low molecular weight surfactant (dilute 2D particle dispersion)

Structural parameter: particle orientation tensor $\mathrm{C}^s = 2 < \mathrm{n}^s \mathrm{n}^s >$




Assumptions: No inhomogeneity caused by the flow, and no exchange with the bulk phases

$\bar{\Gamma}^s = \rho_P{}^s =$ a constant (= $\rho^s \omega_P{}^s$ with $\omega_P{}^s$=0.01)

## Orientation of rod-like particles as a function of shear rate:

Expression for the surface structural Helmholtz free energy (per unit area):

$$F_c^s = -\frac{k_B T^s \rho^s \omega_P^s}{m}\left(-\ln \omega_P^s + \tfrac{1}{2}\left[\mathrm{tr}\left(\mathbf{P} - \mathbf{C}^s\right) + \ln \det \mathbf{C}^s\right]\right)$$

Expression for the surface relaxation tensor:

$$\mathbf{R}_2^s = \frac{m}{k_B \rho^s \omega_P^s}\frac{1}{\tau}\left(a_{\alpha\mu} C^s_{\beta\nu} + a_{\alpha\nu} C^s_{\beta\mu} + \beta\left[C^s_{\alpha\mu} C^s_{\beta\nu} + C^s_{\alpha\nu} C^s_{\beta\mu}\right]\right)\mathbf{a}^\alpha \mathbf{a}^\beta \mathbf{a}^\mu \mathbf{a}^\nu$$

Balance equations for the surface structural tensor:

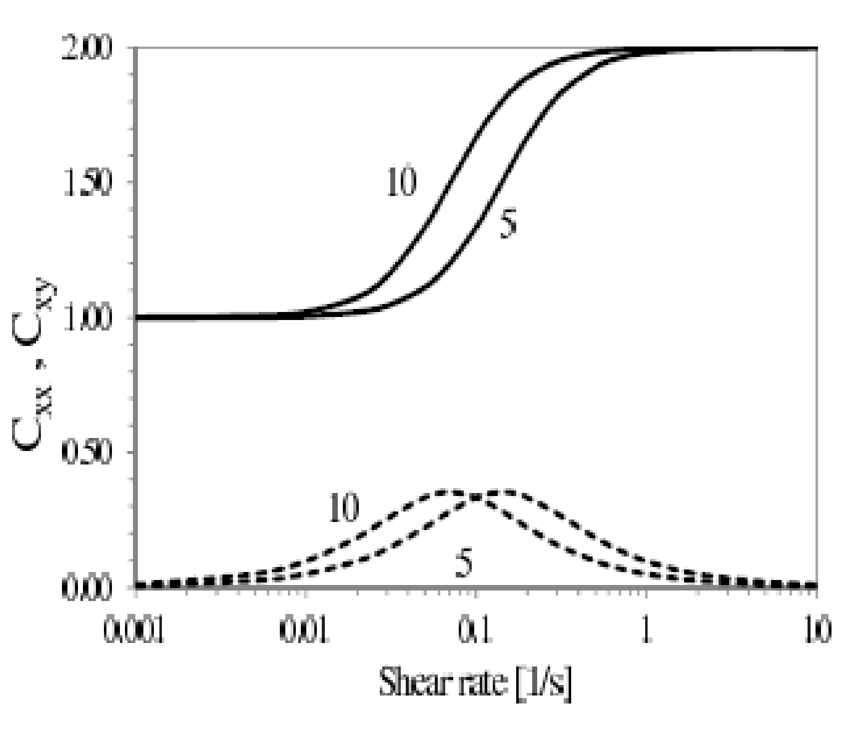
$$\frac{\partial C^s_{xx}}{\partial t} = 2\dot{\gamma} C^s_{xy} - \frac{1}{\tau}\left([1-\beta]C^s_{xx} - 1 + \beta\left[(C^s_{xx})^2 + (C^s_{xy})^2\right]\right)$$

$$\frac{\partial C^s_{xy}}{\partial t} = \dot{\gamma}\left(2 - C^s_{xx}\right) - \frac{1}{\tau}[1+\beta] C^s_{xy}$$

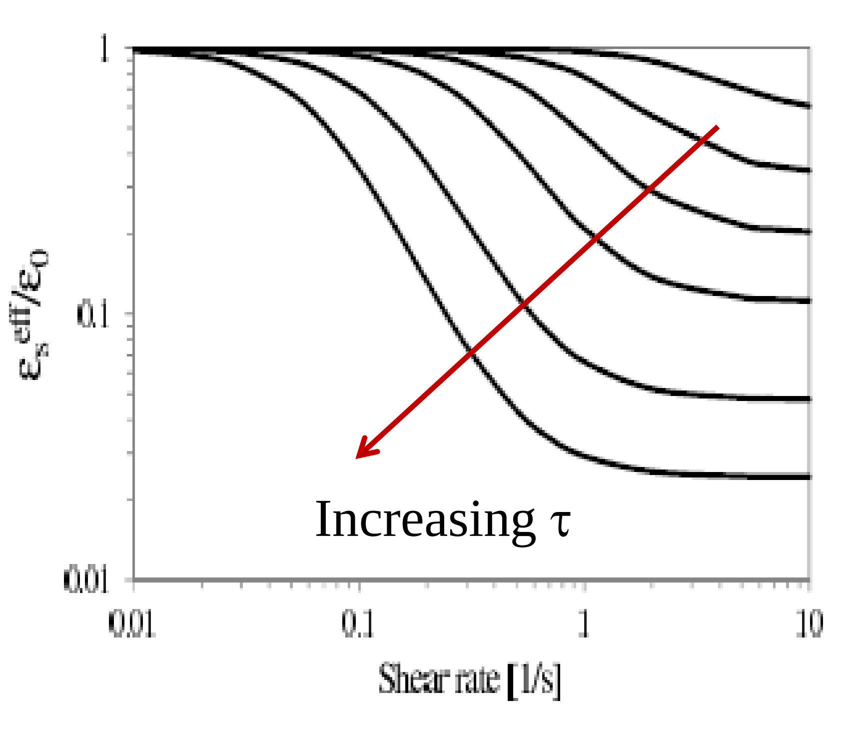
Initial condition: $\mathbf{C}^s(0)=\mathbf{P}$

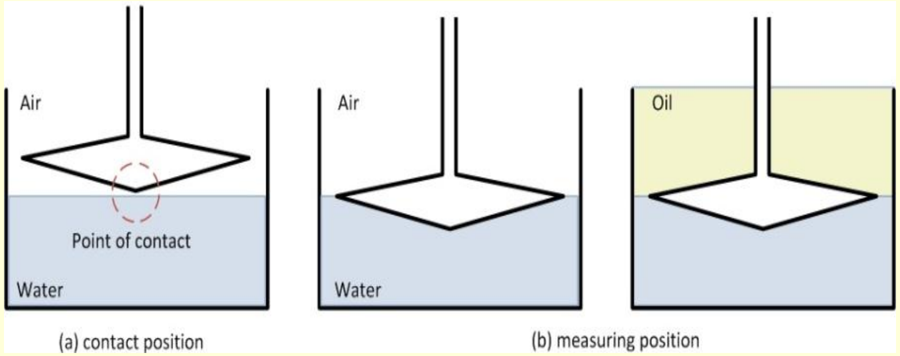
# Flat interface with anisotropic particles in a constant in-plane shear field

Steady state values orientation tensor (β=0)




Effective surface shear viscosity



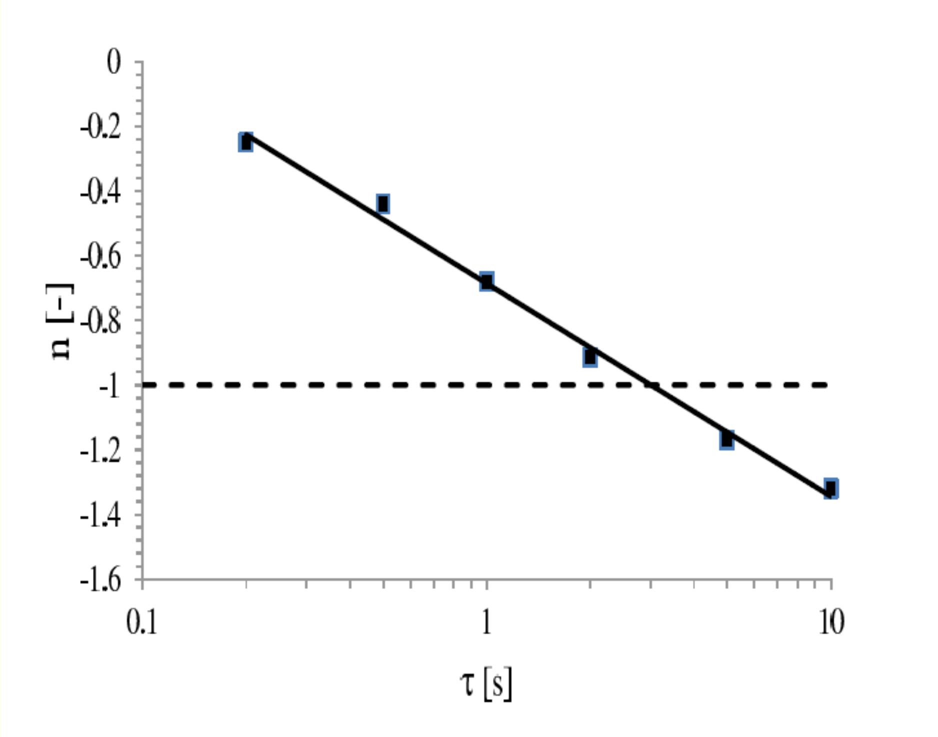




Orientation –> surface shear thinning

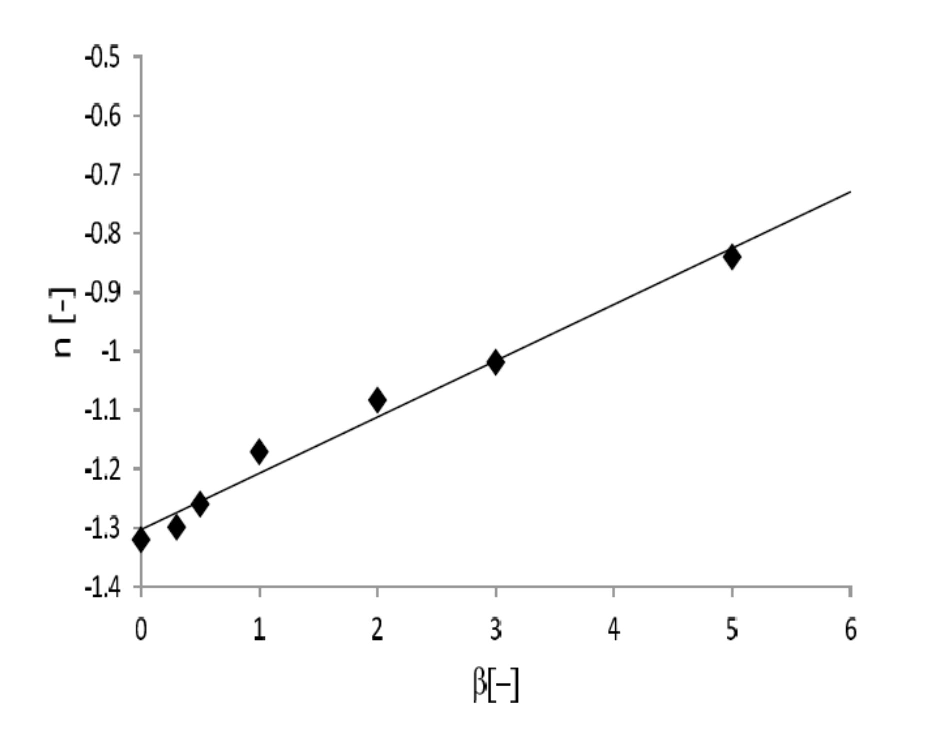
# Flat interface with anisotropic particles in a constant in-plane shear field

$$\varepsilon_s^{\mathrm{eff}} / \varepsilon_0 \sim \dot{\gamma}^n$$

Exponent *n* as a function of τ for β=0

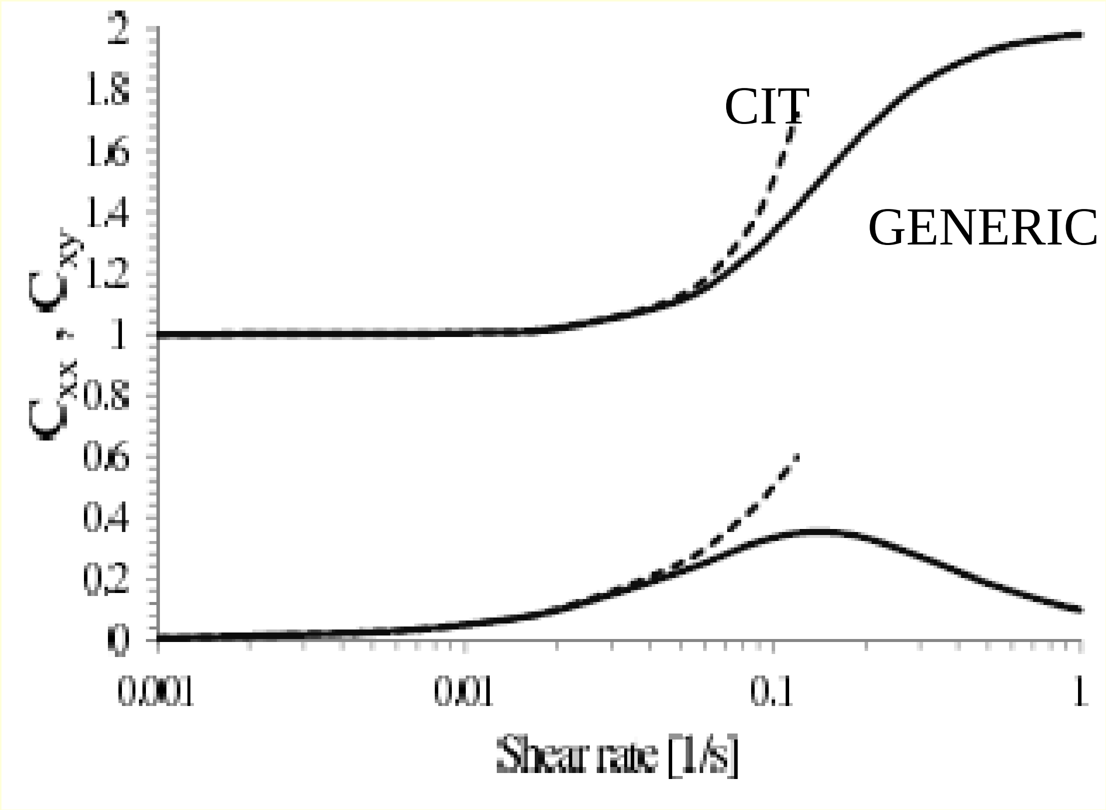



Exponent *n* as a function of β for τ=10



# Flat interface with anisotropic particles in a constant in-plane shear field

Comparison with a CIT model (8 parameters)*:




$\tau = 5$ s ; $\beta = 0$

* L.M.C. Sagis, *Soft Matter* **17**, 7727 (2011) .

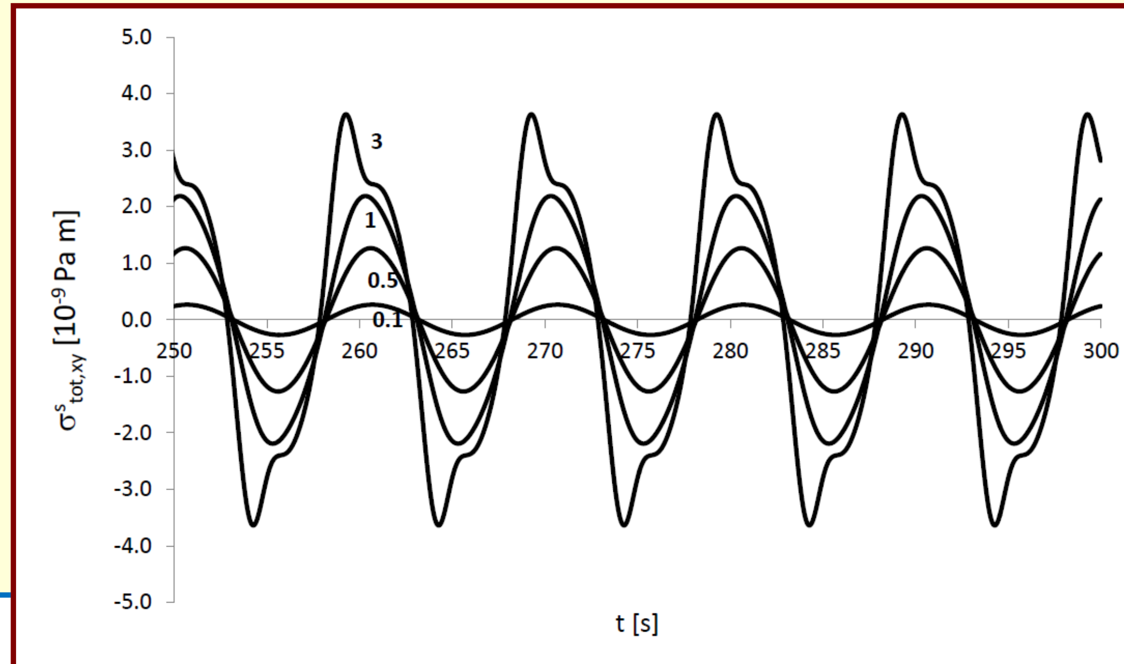
# Flat interface with anisotropic particles in oscillatory in-plane shear field

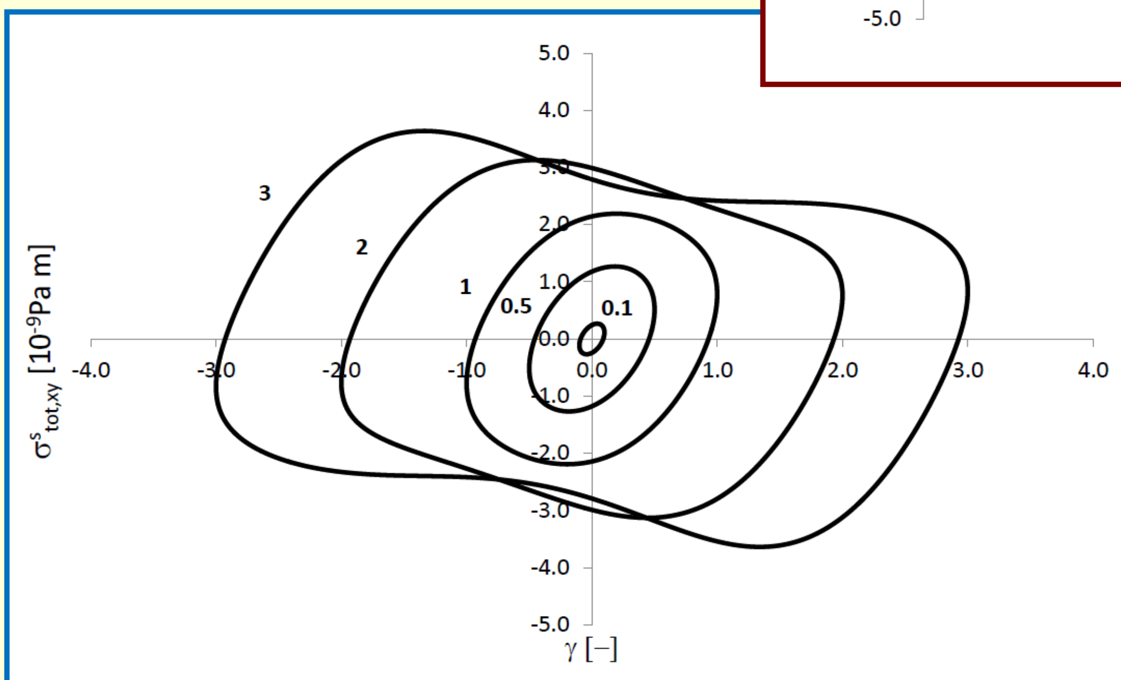
$\gamma_{xy}(t) = \gamma_0 \sin(2\pi\omega t)$

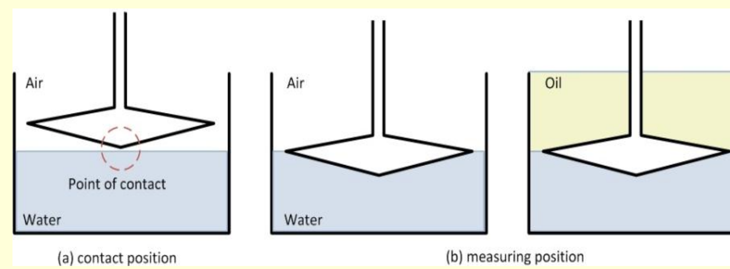
$\omega$=0.1 Hz

$\tau$= 1.0 s

$\beta$=0



# Flat interface with anisotropic particles in oscillatory in-plane shear field

$\gamma_{xy}(t) = \gamma_0 \sin(2\pi\omega t)$

$\omega$=0.1 Hz

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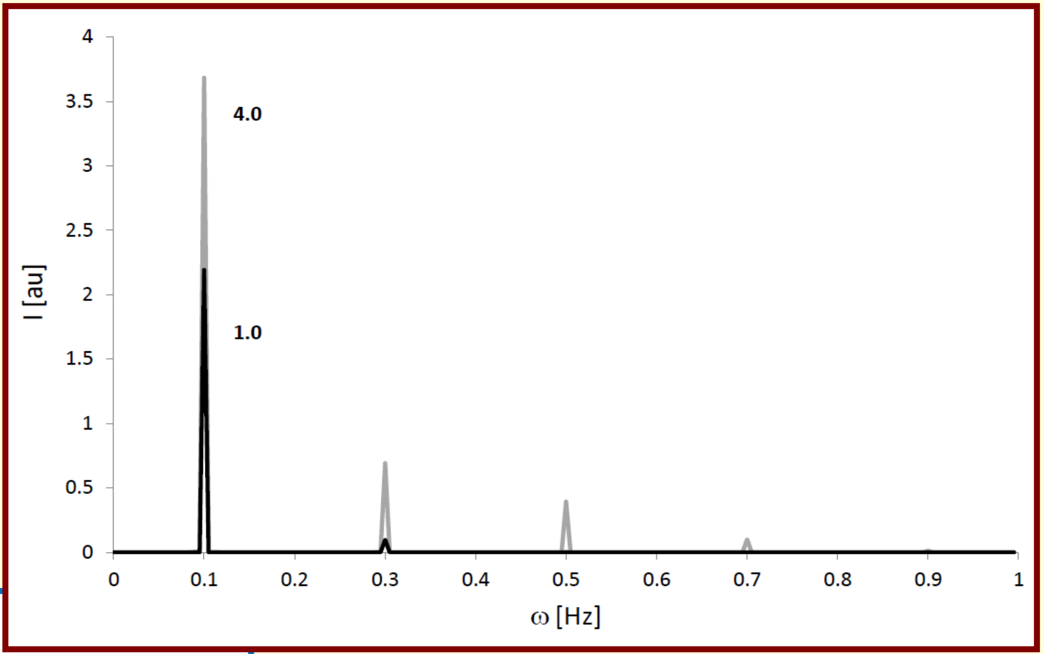
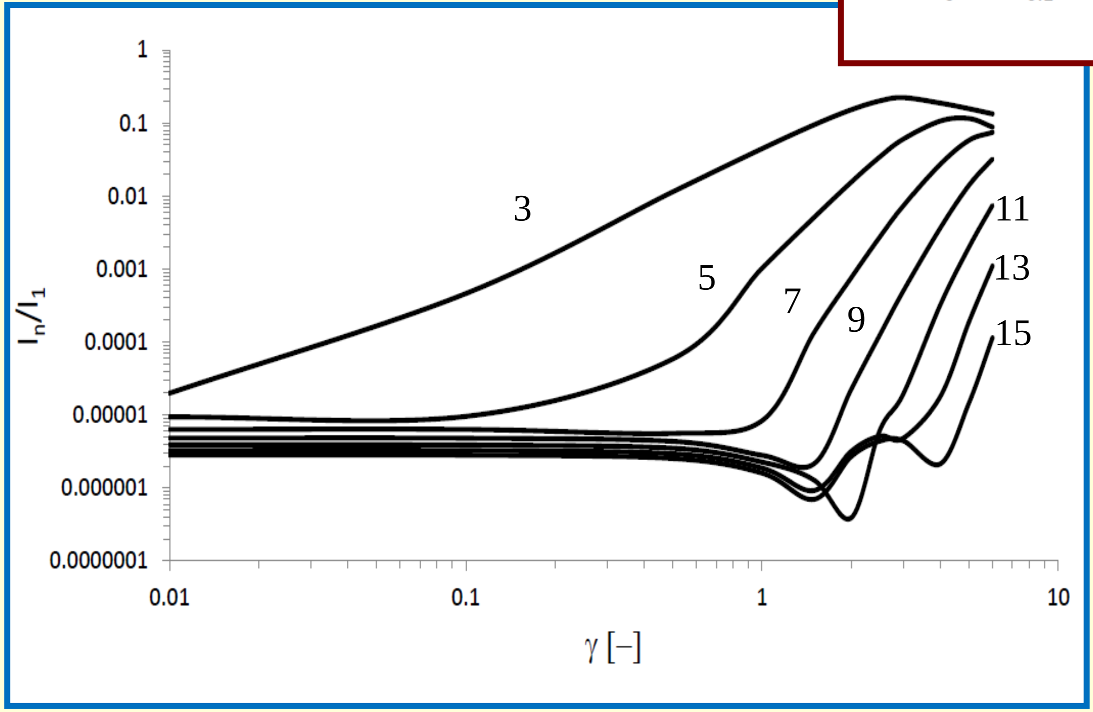
$\beta$=0

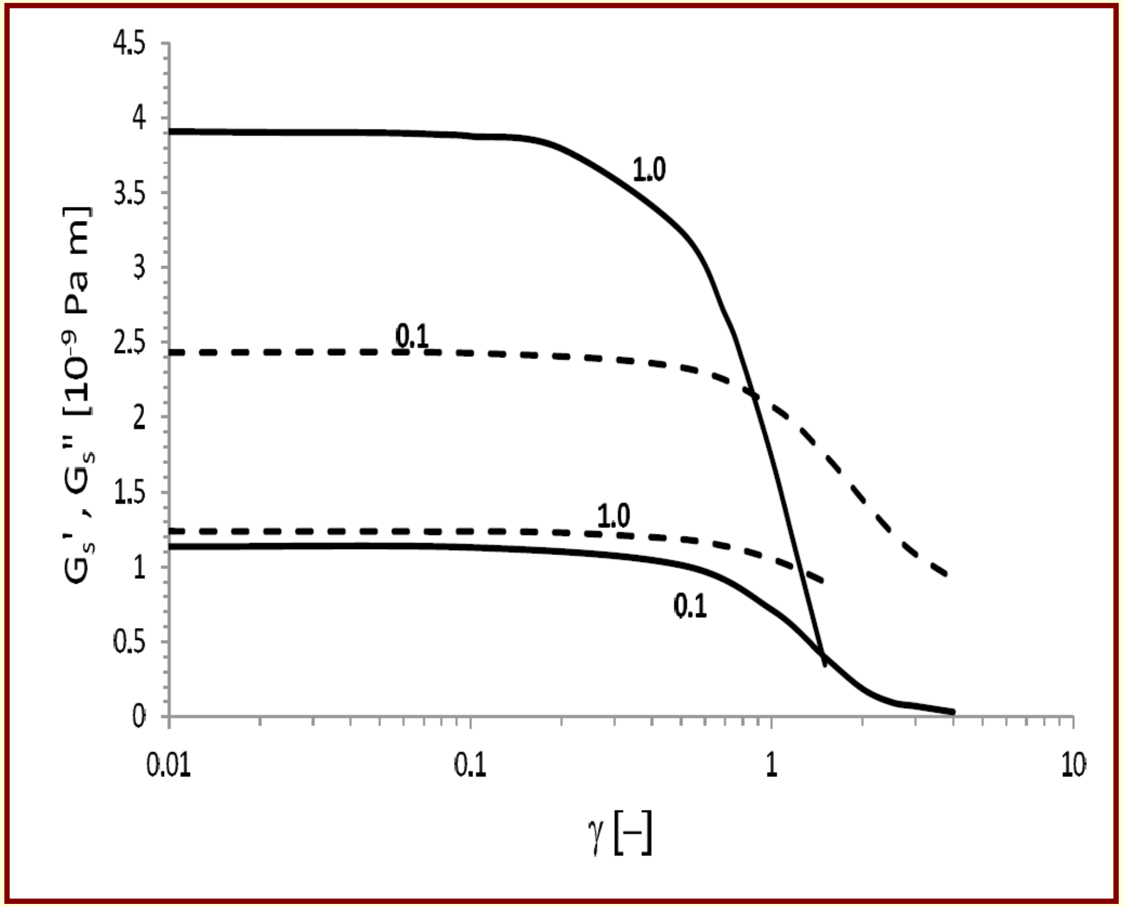



- First nonlinear contributions already at $\gamma < 0.01$
- Highly nonlinear at $\gamma > 1$

# Flat interface with anisotropic particles in oscillatory in-plane shear field

Surface storage modulus, $G_s$' (——) and loss modulus, $G_s$" (- - - - )

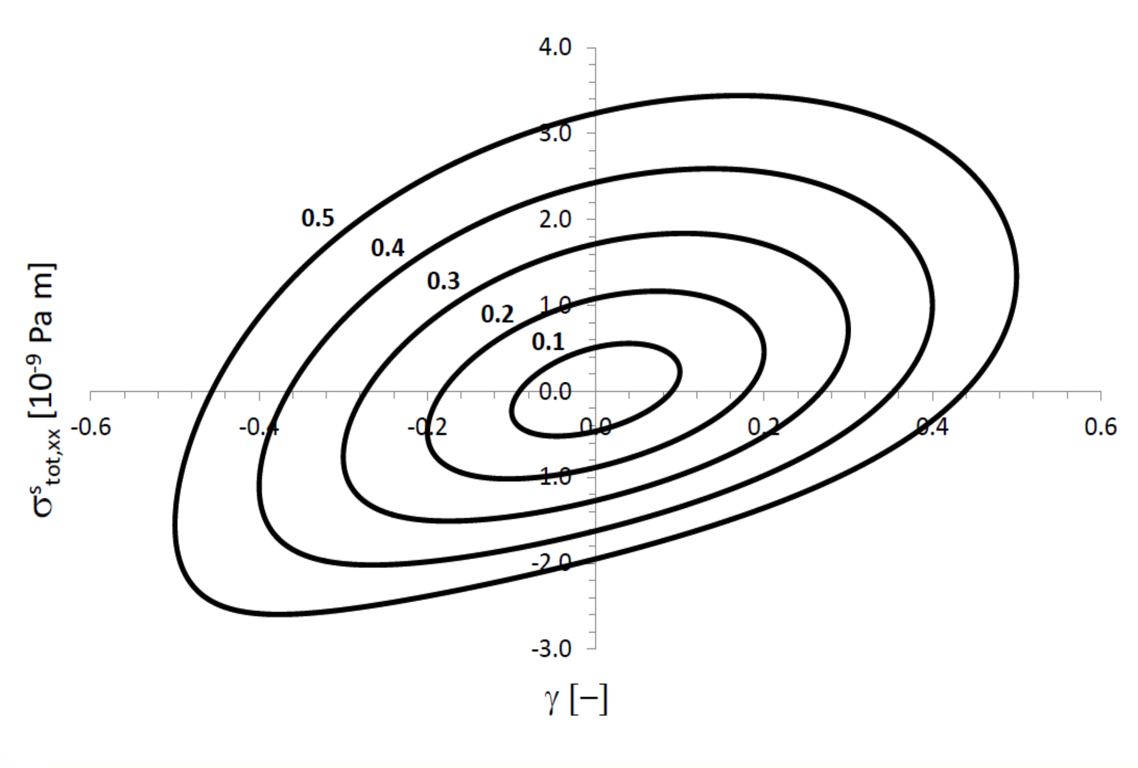


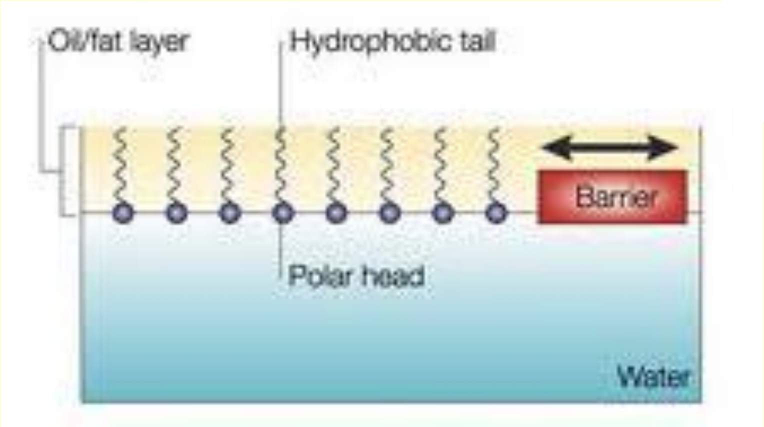

Two values of ωτ:

- 1.0: soft gel-like behaviour
- 0.1: viscoelastic liquid

# Flat interface with anisotropic particles in oscillatory dilatation (Langmuir trough)

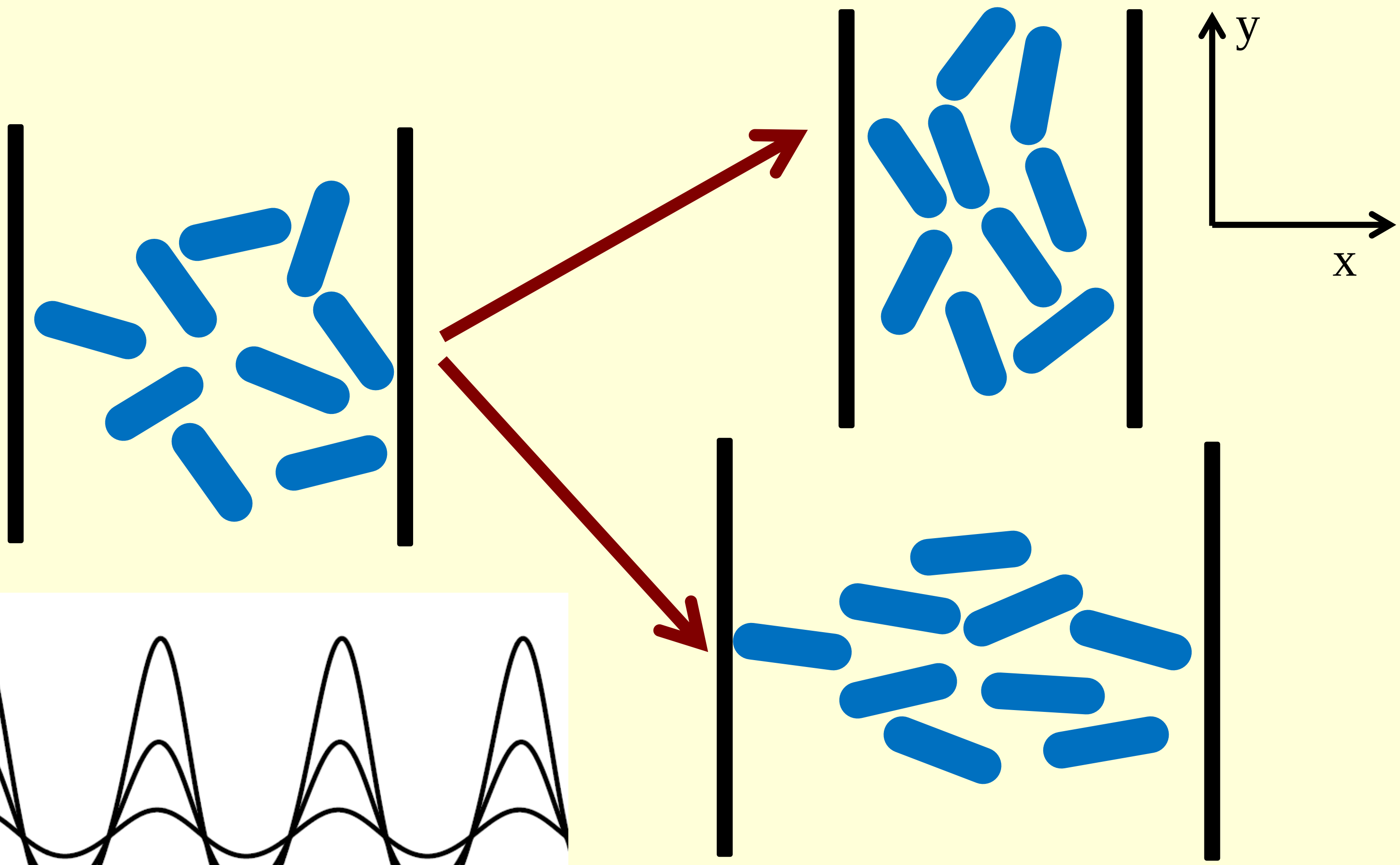
$\gamma_{xx}(t) = \gamma_0 \sin(2\pi\omega t)$,  $\omega$=0.1 Hz, $\tau$= 1.0 s

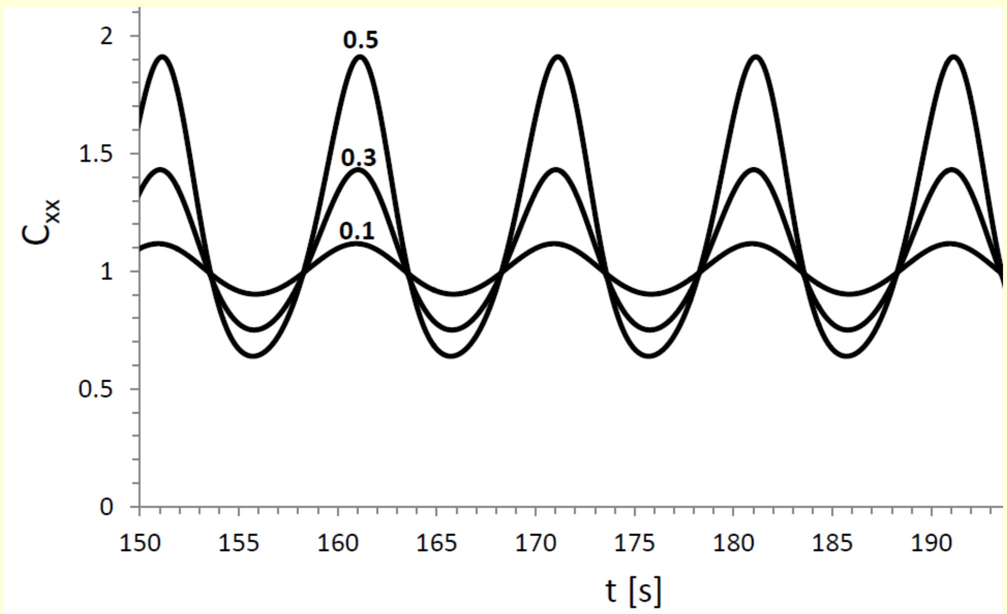



Strictly speaking this experiment determines the surface Young modulus

# Flat interface with anisotropic particles in oscillatory dilatation (Langmuir trough)




Asymmetry in response results from different orientation in compression / extension parts of the cycle

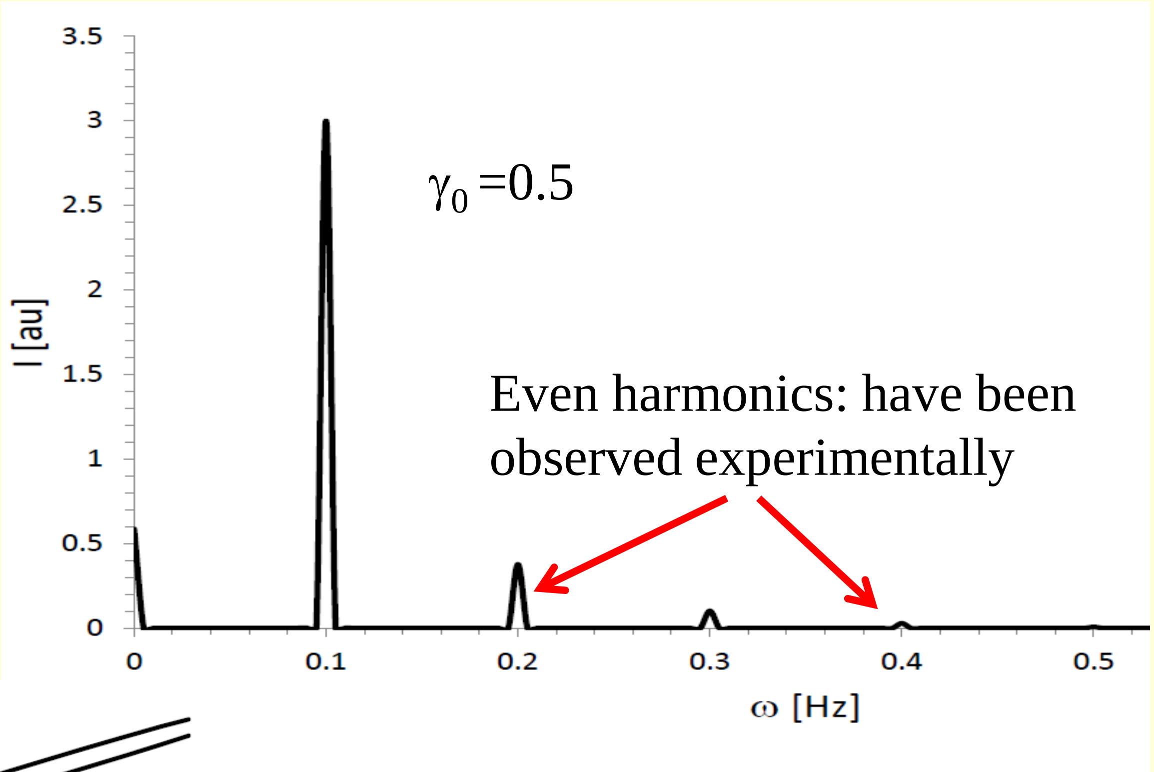
# Flat interface with anisotropic particles in oscillatory dilatation (Langmuir trough)

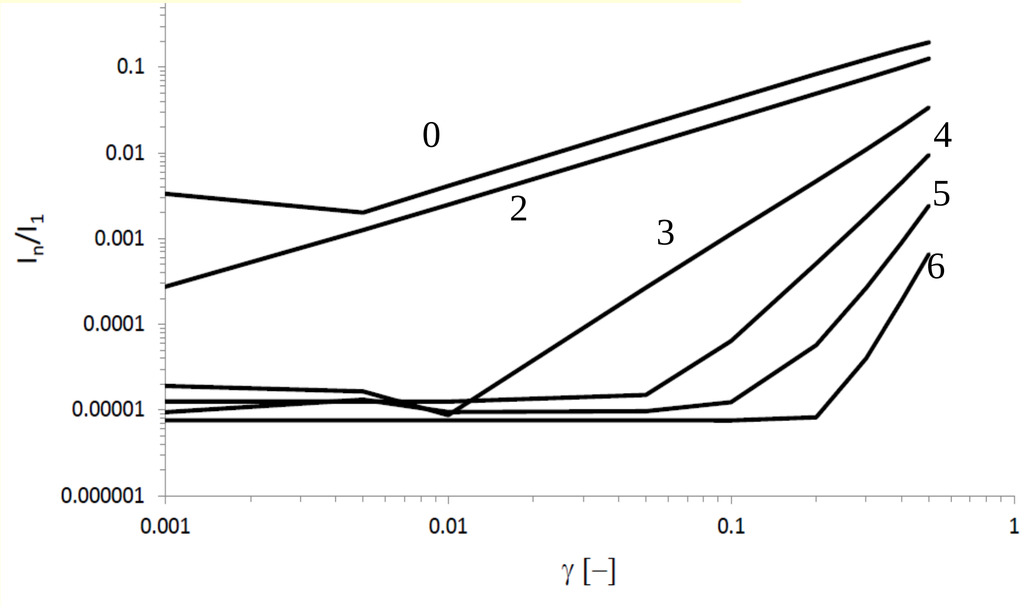
$\gamma_{xx}(t) = \gamma_0 \sin(2\pi\omega t)$

$\omega$=0.1 Hz

$\tau$= 1.0 s

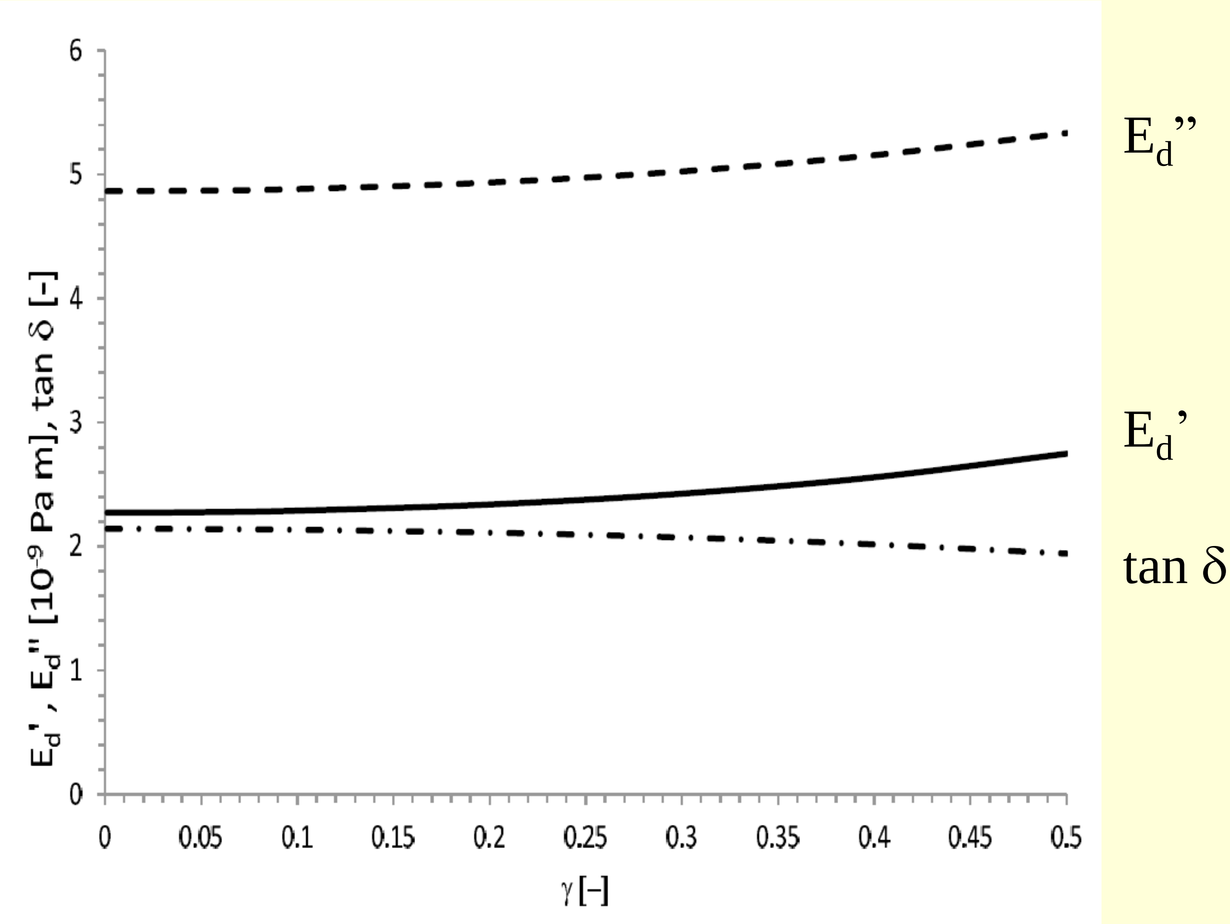
$\beta$=0




- First nonlinear contributions already at $\gamma < 0.001$
- Highly nonlinear at $\gamma > 0.1$

# Flat interface with anisotropic particles in oscillatory dilatation (Langmuir trough)




- Calculated from the intensity of the first harmonic (as in real experiment)
- In spite of the high nonlinearity of the response, modulus plot shows only mild strain hardening.

## Conclusions:

1. GENERIC appears to be a powerful tool to model the nonlinear surface rheological response of complex interfaces.
2. True value of the framework still has to be established by comparison with experimental data

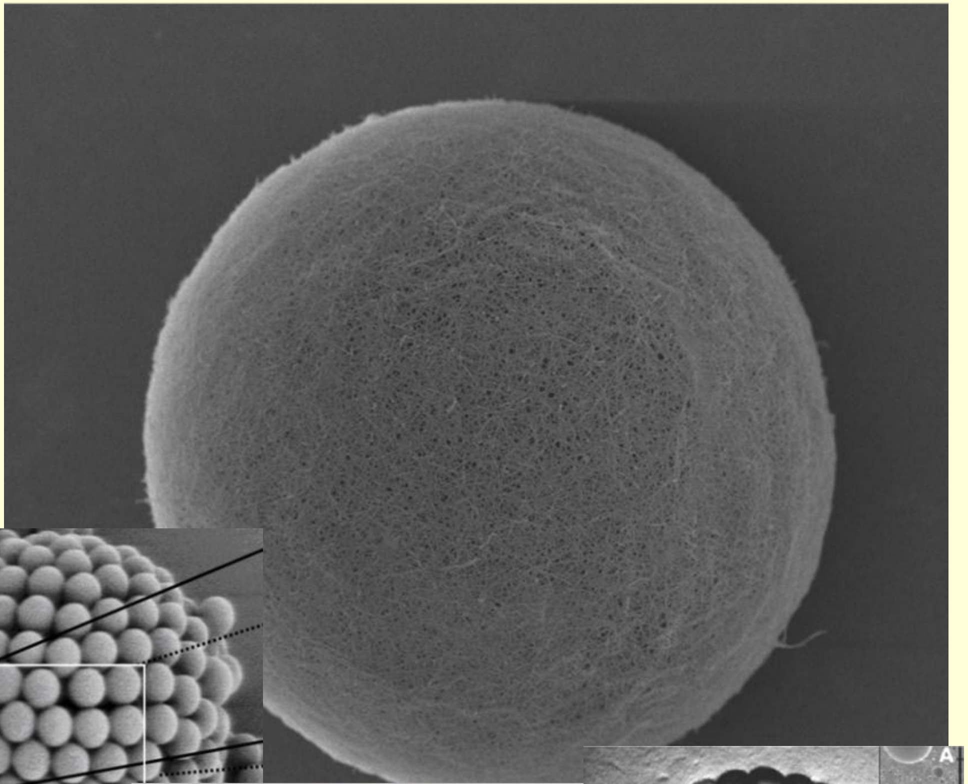
## Future work:

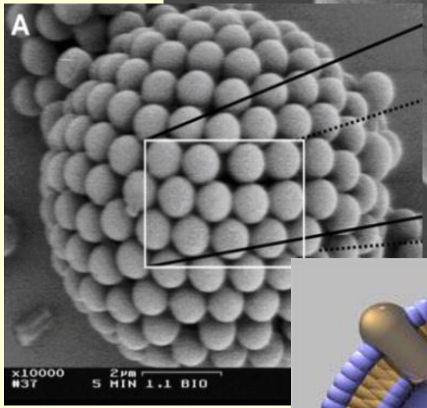
- Comparison with data for surface shear experiments + optical techniques
- Extension to more complex systems

# Perspectives:

Ultimate goal:

understanding the complex dynamic behaviour of biomaterial microcapsules, liposomes, cells, ultrasound microbubbles, ......






NET can play a major role in this field by providing accurate descriptions for the coupled transfer of mass, heat, and momentum, on both microscopic and macroscopic length scales.