Surface shear rheology of hydrophobin adsorption layers: laws of viscoelastic behaviour with applications to foam stability

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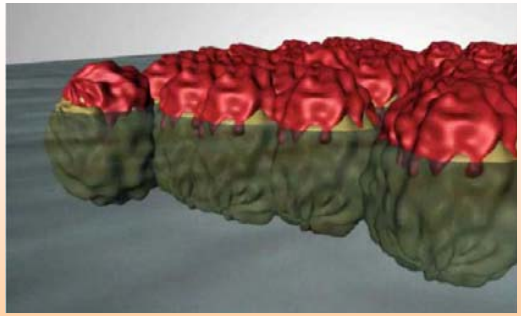
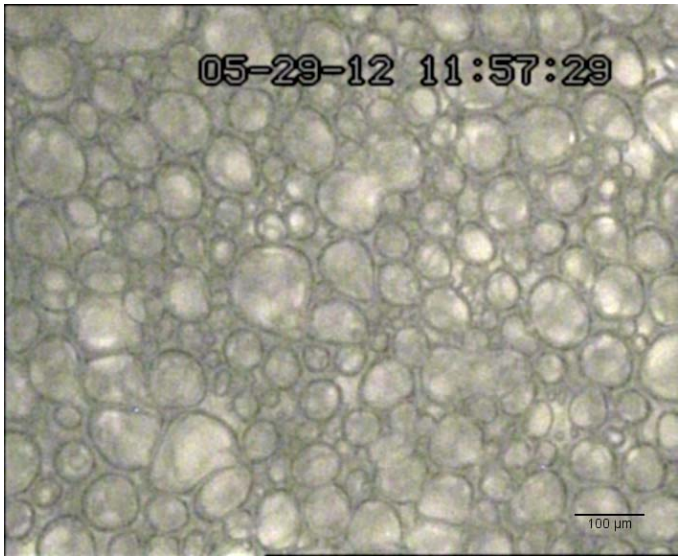
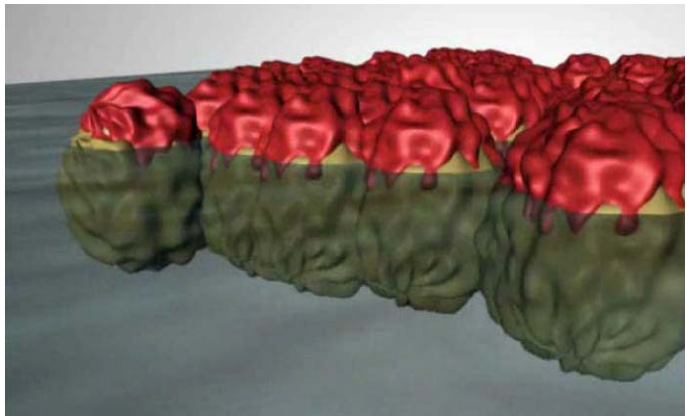


Strategy to Foam Stabilization by Viscoelastic Layers





$$-\frac{dV}{dt} \approx k_g \frac{A}{p_a} \frac{2\sigma}{R}$$

V **– bubble volume decreasing because of Ostwald ripening.**

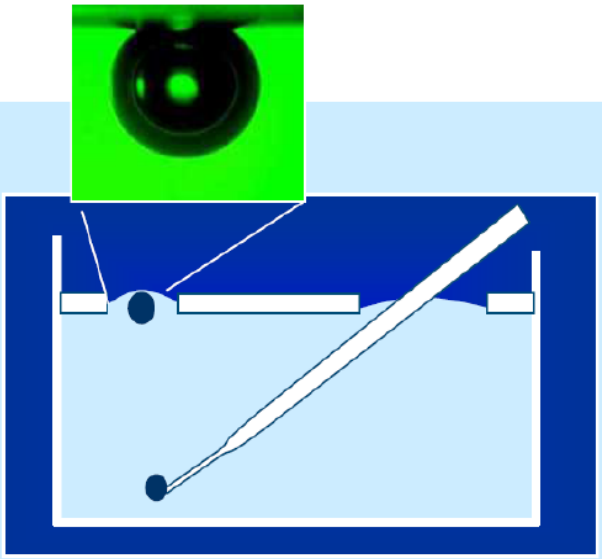
The elasticity of solidified protein adsorption layers can prevent the ripening in two ways:

(1) Decrease of the surface tension *σ*
– close to tension-free state;

(2) Decrease of the permeability k_g of the foam films to gas due to the solid structure.

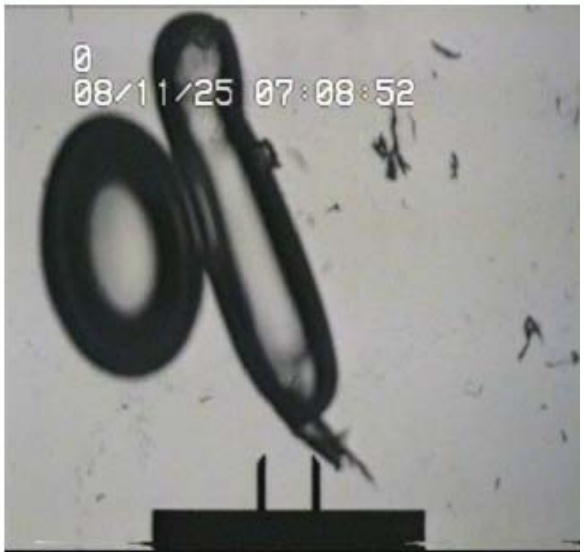
Fast solidifying adsorption layers are formed from the protein Hydrophobin HFBII isolated from filamentous fungi (e.g. button mushroom).

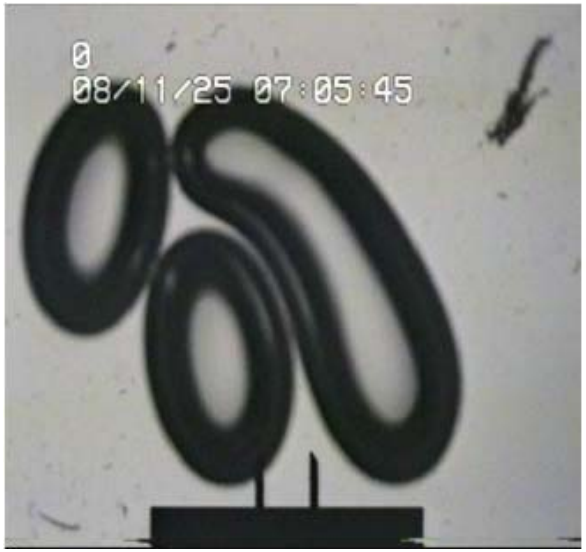
Bubbles of irregular shape – surfaces solidified by HFBII

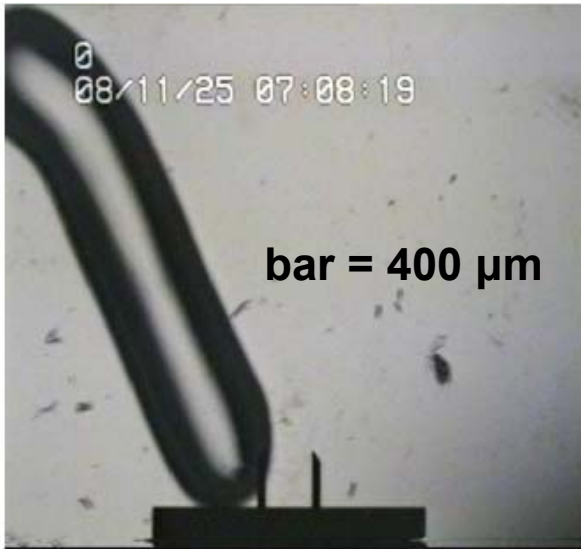


The bubbles released in HFBII solutions acquire peculiar non-spherical shapes;

The adsorption layers of HFBII solidify like shells, which preserve the instantaneous bubble shape. Enhanced surface rheology!



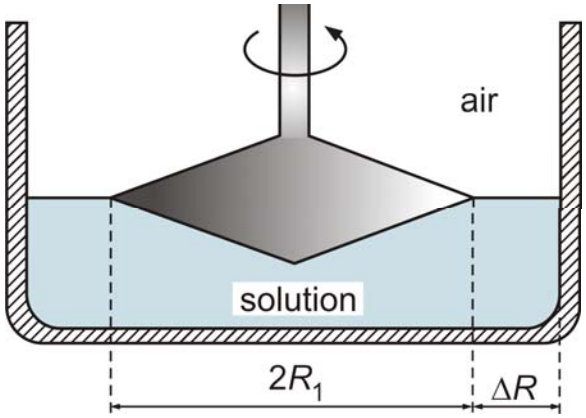


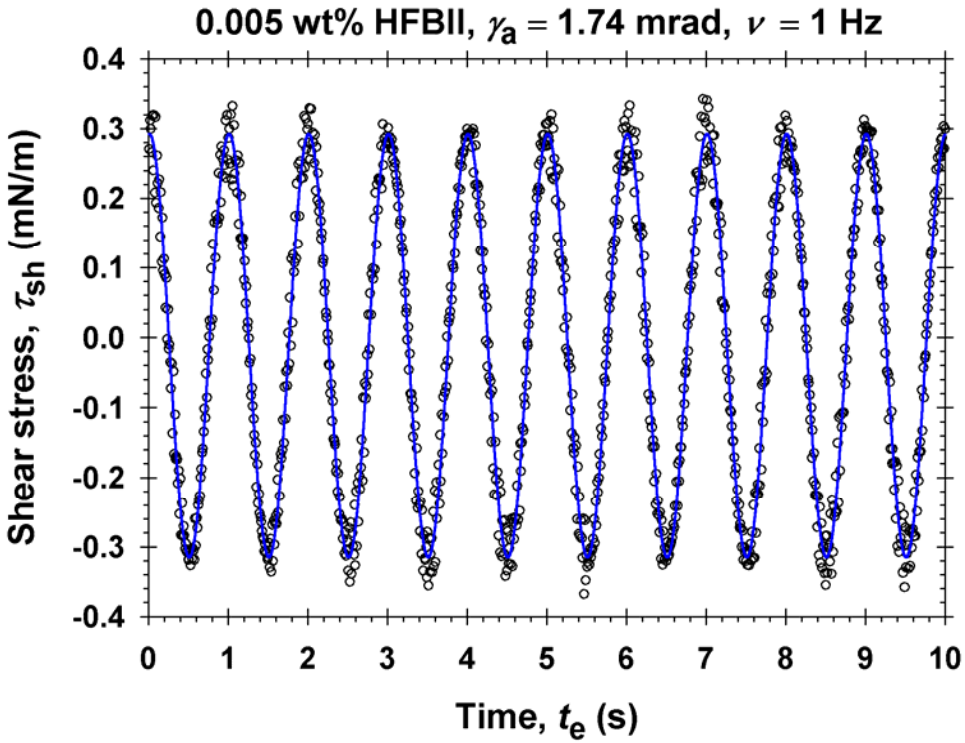


3 nm thick HFBII layer vs. 3 mm large bubble

[E.S. Basheva, P.A. Kralchevsky, N.C. Christov, et al., *Langmuir* 27 (2011) 2382.]

Viscoelastic Properties of Protein Layers – Oscillatory Mode





Shear rheometer; **slow rotation** ⇒ **rheological response only from the film (negligible effect of the subphase).**

Sinusoidal strain: $\gamma(t) = \gamma_a \sin(\omega t)$

⇒ **Sinusoidal stress with phase shift:**

$$\frac{\tau_{sh}}{\gamma_a} = G' \sin(\omega t) + G'' \cos(\omega t)$$

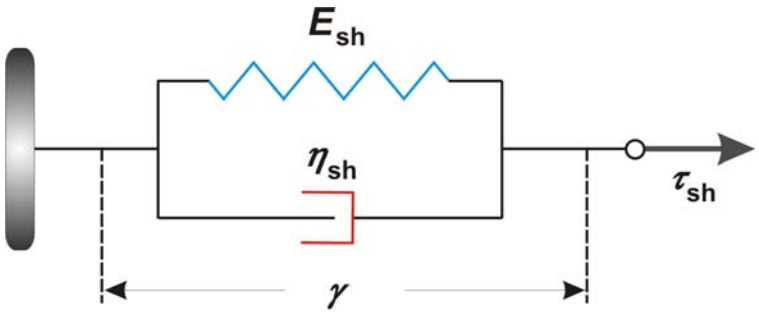
G′ **– storage modulus;** ***G″*** **– loss modulus**

(small amplitude – quasi-linear regime)

The surface shear elasticity, E_{sh}, and viscosity, η_{sh}, can be determined from the experimental *G′* and *G″* only in the framework of an adequate model.

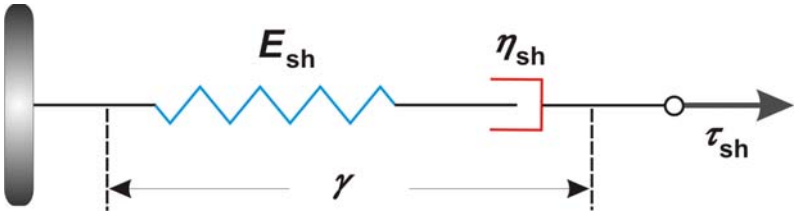
Kelvin Model vs. Maxwell Model of Viscoelastic Bodies

Kelvin model:



Parallel connection of elastic and viscous elements

Maxwell model:



Sequential connection of elastic and viscous elements

The two models lead to different relations (E_{sh} and η_{sh}) $\Leftrightarrow$ (G' and G'')
In the case of constant elasticity and viscosity these are:

Kelvin model:

$$E_{\mathrm{sh}} = G'$$

$$\eta_{\mathrm{sh}} = G''/\omega$$

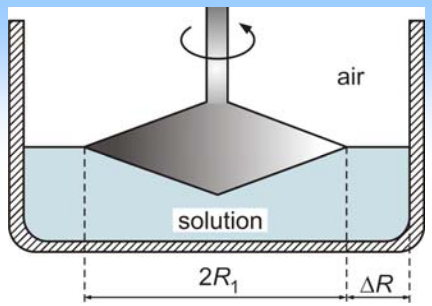
Maxwell model:

$$E_{\mathrm{sh}} = \frac{G'^2 + G''^2}{G'},$$

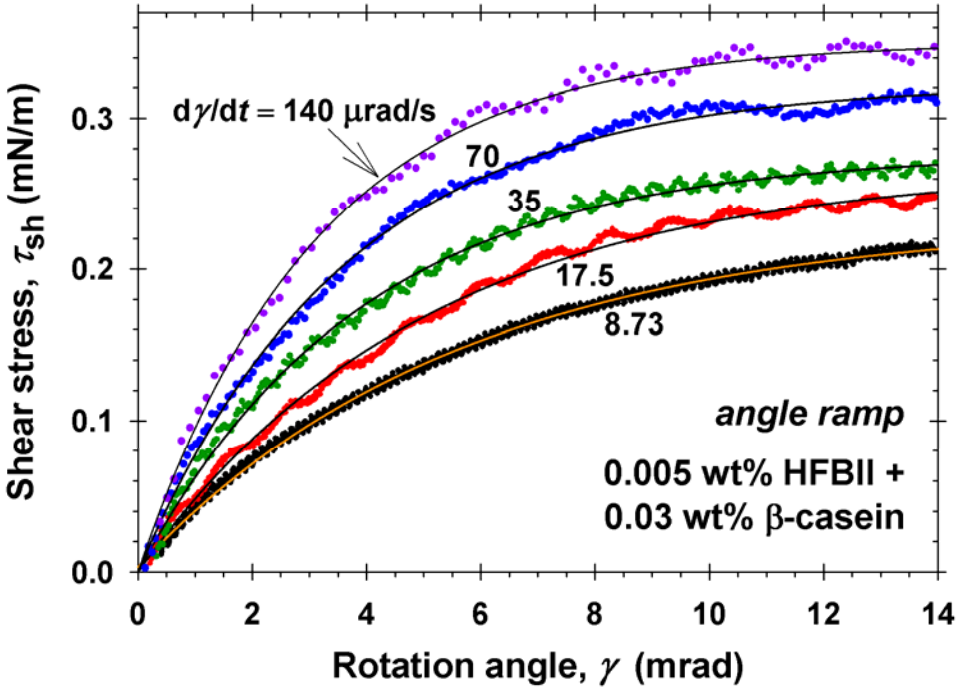
$$\eta_{\mathrm{sh}} = \frac{G'^2 + G''^2}{G''\omega}$$

How to determine the adequate model?

Experiments in Angle-Ramp Regime



Angle ramp = Rotation with constant angular velocity



The experiment gives τ_{sh} vs. γ as an exponential rise to constant.

This behavior complies with the Maxwell model:

$$\tau_{sh} = \eta_{sh}\dot{\gamma}[1-\exp(-\frac{E_{sh}}{\eta_{sh}}\frac{\gamma}{\dot{\gamma}})]$$

From the fit of each curve $\dot{\gamma} = \text{const.}$ **we determine:**

$$E_{sh} = E_{sh}(|\dot{\gamma}|)$$

and

$$\eta_{sh} = \eta_{sh}(|\dot{\gamma}|)$$

For each curve E_{sh} and η_{sh} are constant, but their values are different for the different curves.

Combined Maxwell-Herschel-Bulkley Model

Maxwell model:

Characteristic frequency:

$$\nu_{ch} \equiv \frac{G''}{G'}\omega = \frac{E_{sh}}{\eta_{sh}}$$

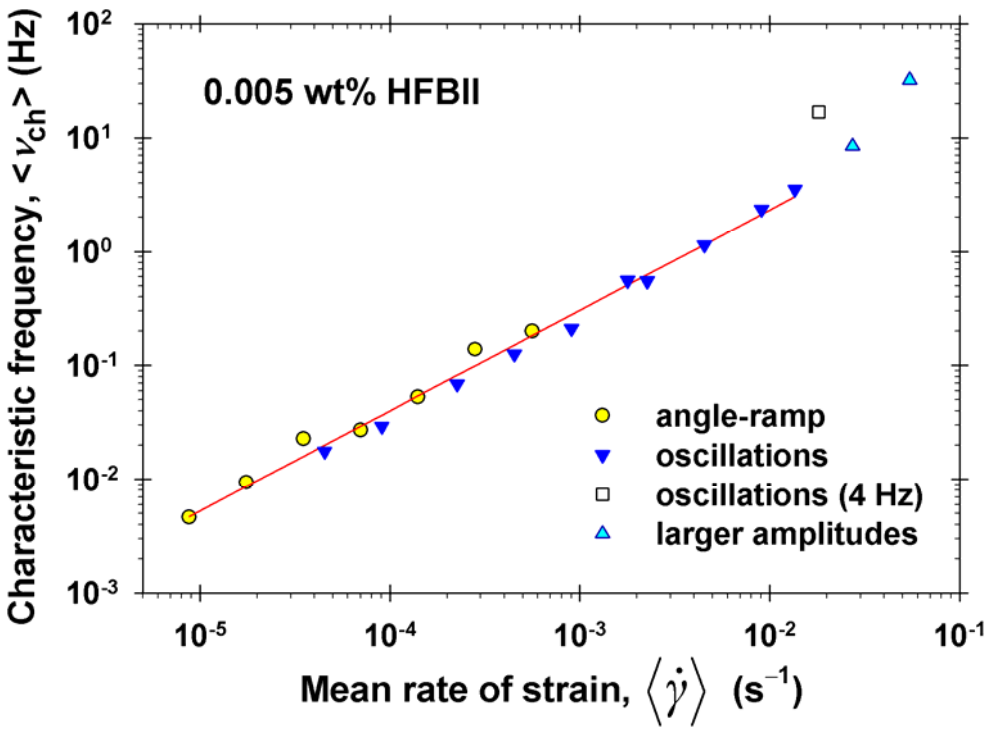
Herschel-Bulkley approach:

Seek ν_{ch} as a power function:

$$\nu_{ch} = Q\,|\dot{\gamma}|^{m}$$

$$E_{sh} = E_{sh}(|\dot{\gamma}|) \qquad \eta_{sh} = \eta_{sh}(|\dot{\gamma}|)$$

Results:



(1) Data from both angle-ramp and oscillatory experiments comply with the same line.

(2) For oscillatory regime, the mean shear rate is plotted:

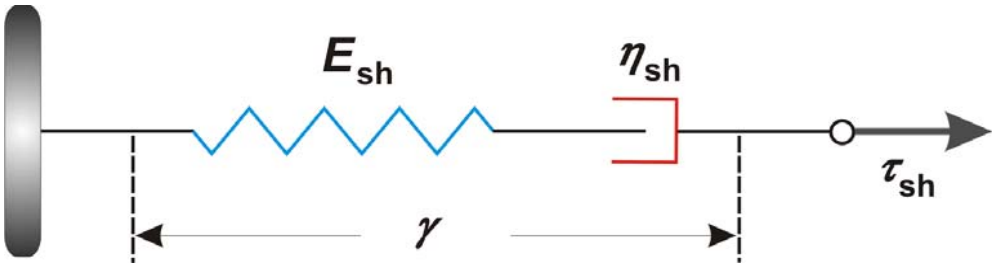
$$\langle\dot{\gamma}\rangle \equiv \mu\,\gamma_a\,\omega$$

***μ*(*m*) is a known parameter**

(3) E_{sh}, η_{sh} and ν_{ch} depend on the product $\gamma_a\omega$, rather than on the amplitude γ_a and frequency ω separately!

Characteristic frequency of the layer's rheological response

$$\nu_{ch} \equiv \frac{E_{sh}}{\eta_{sh}}$$



For a purely elastic layer

$$\eta_{sh} \to \infty, \quad E_{sh} = \text{const.}$$

$$\Rightarrow \nu_{ch} = \frac{E_{sh}}{\eta_{sh}} \to 0$$

For a purely viscous layer

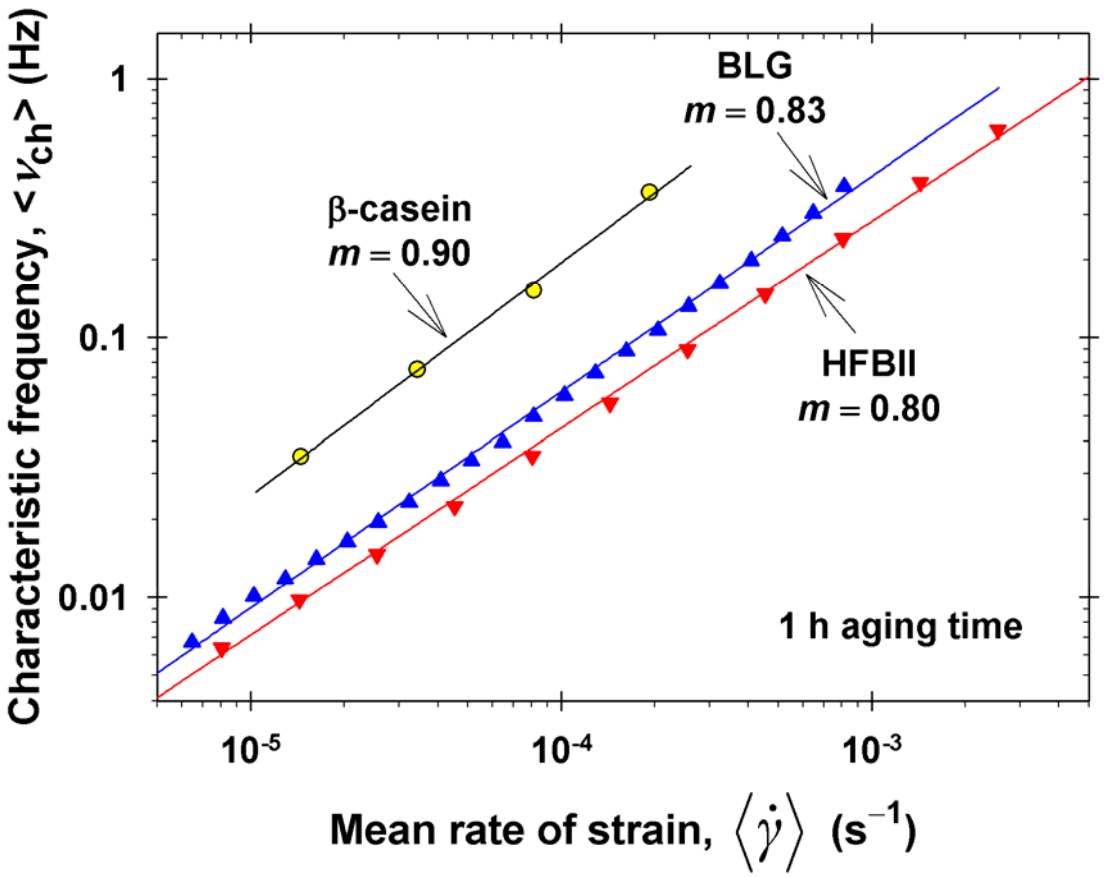
$$E_{sh} \to \infty, \quad \eta_{sh} = \text{const.}$$

$$\Rightarrow \nu_{ch} = \frac{E_{sh}}{\eta_{sh}} \to \infty$$

$$0 < \nu_{ch} < \infty$$

ν_{ch} **characterizes the degree of softness (fluidization) of the adsorption layer**

Comparison of Different Protein Adsorption Layers



Larger $\nu_{ch} \Rightarrow$ more fluid (softer) layer.

The increase of ν_{ch} with the rate-of-strain indicates fluidization upon shearing.

Among the investigated proteins, the layers from HFBII are the most elastic, whereas those from β-casein – the most fluid.

The rheological behavior of the layers from all investigated proteins complies with the combined Maxwell-Herschel-Bulkley model:

$$\nu_{ch} = Q\,|\dot{\gamma}|^{m}$$

Elasticity and Viscosity

Combined Maxwell-Herschel-Bulkley model:

$$\langle E_{sh} \rangle = \frac{G'^2 + (m+1)G''^2}{G'}$$

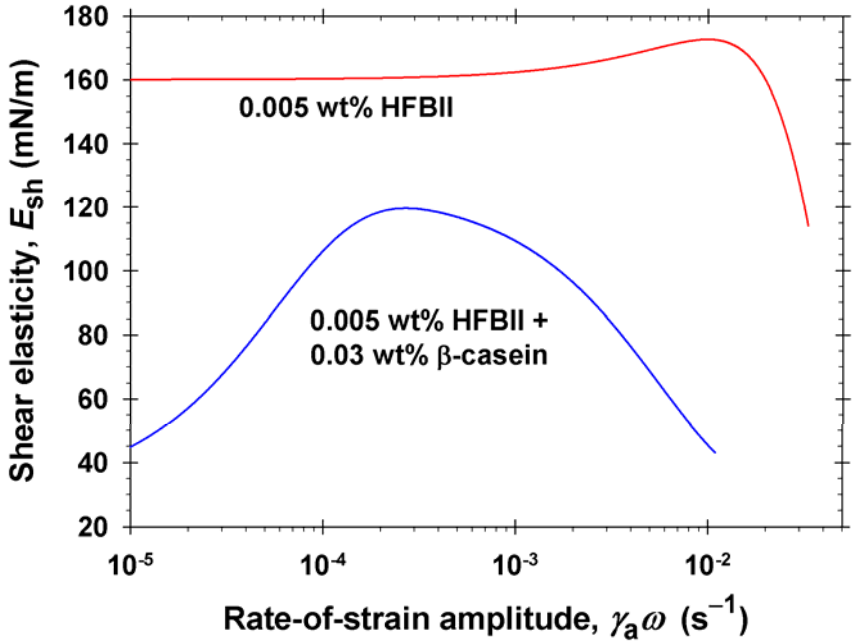
$$\langle \eta_{sh} \rangle = \frac{G'^2 + (m+1)G''^2}{G''\omega}$$

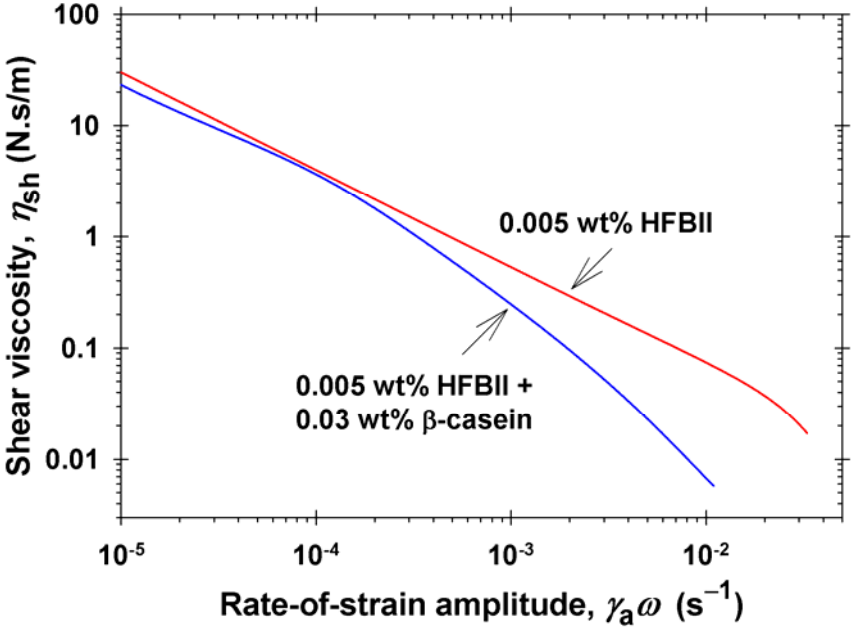
(for $m = 0$, the Maxwell-model expressions)

Unlike ν_{ch} (linear dependence), E_{sh} and η_{sh} exhibit a more complex dependence on the shear rate $\gamma_a\omega$.

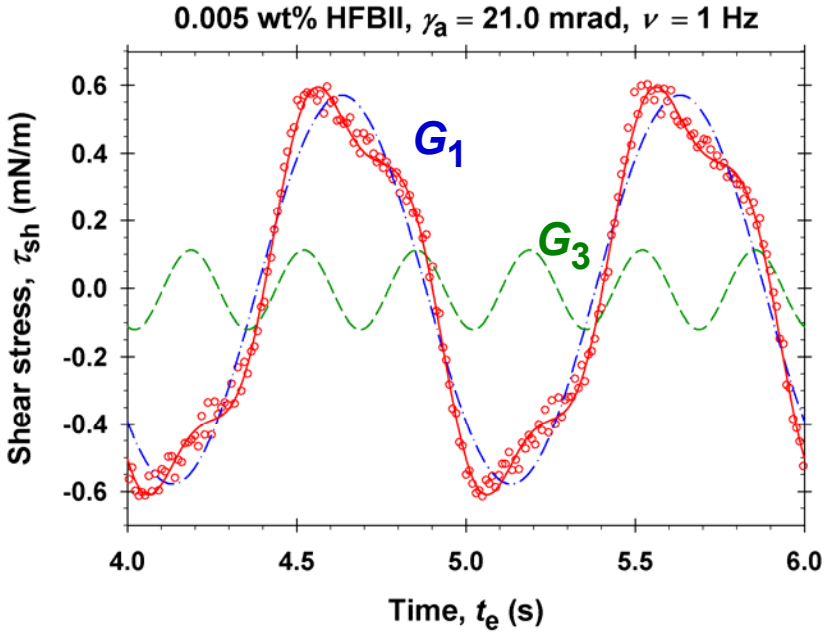
Increasing E_{sh} ⇒ predominant restoration of bonds;

Decreasing E_{sh} ⇒ predominant breakage of bonds.

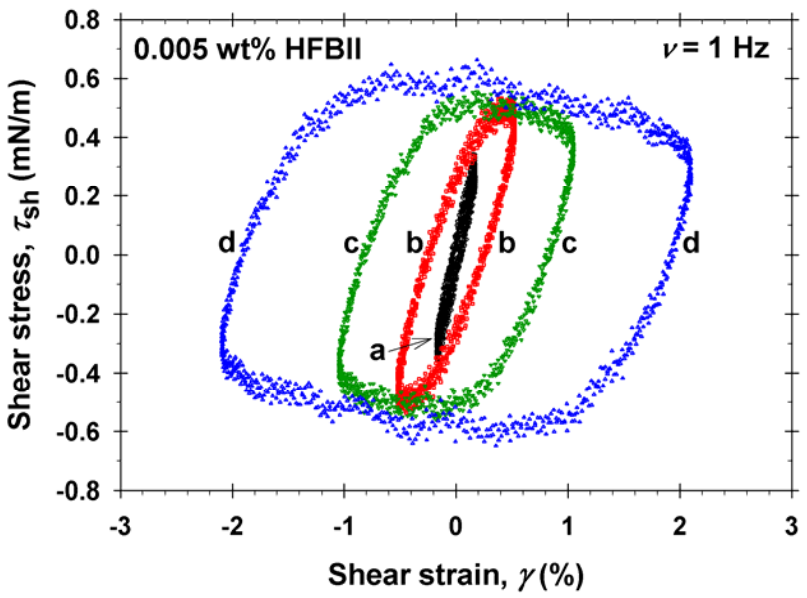




Nonlinear Regime at Higher Amplitudes and Frequencies

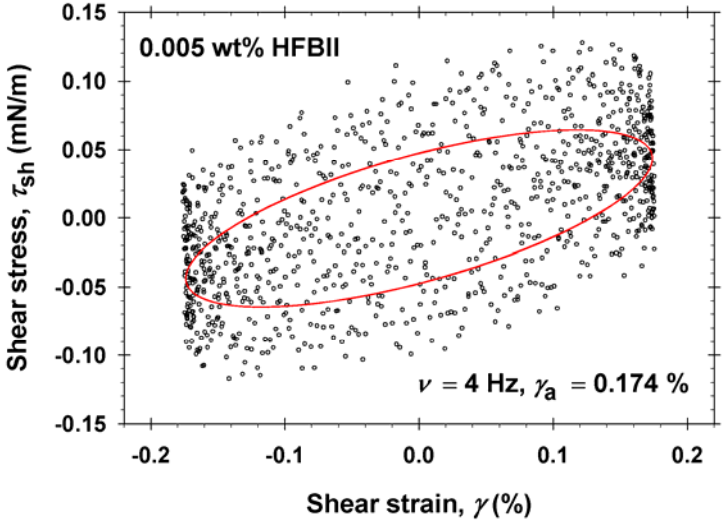


Higher Fourier modes appear

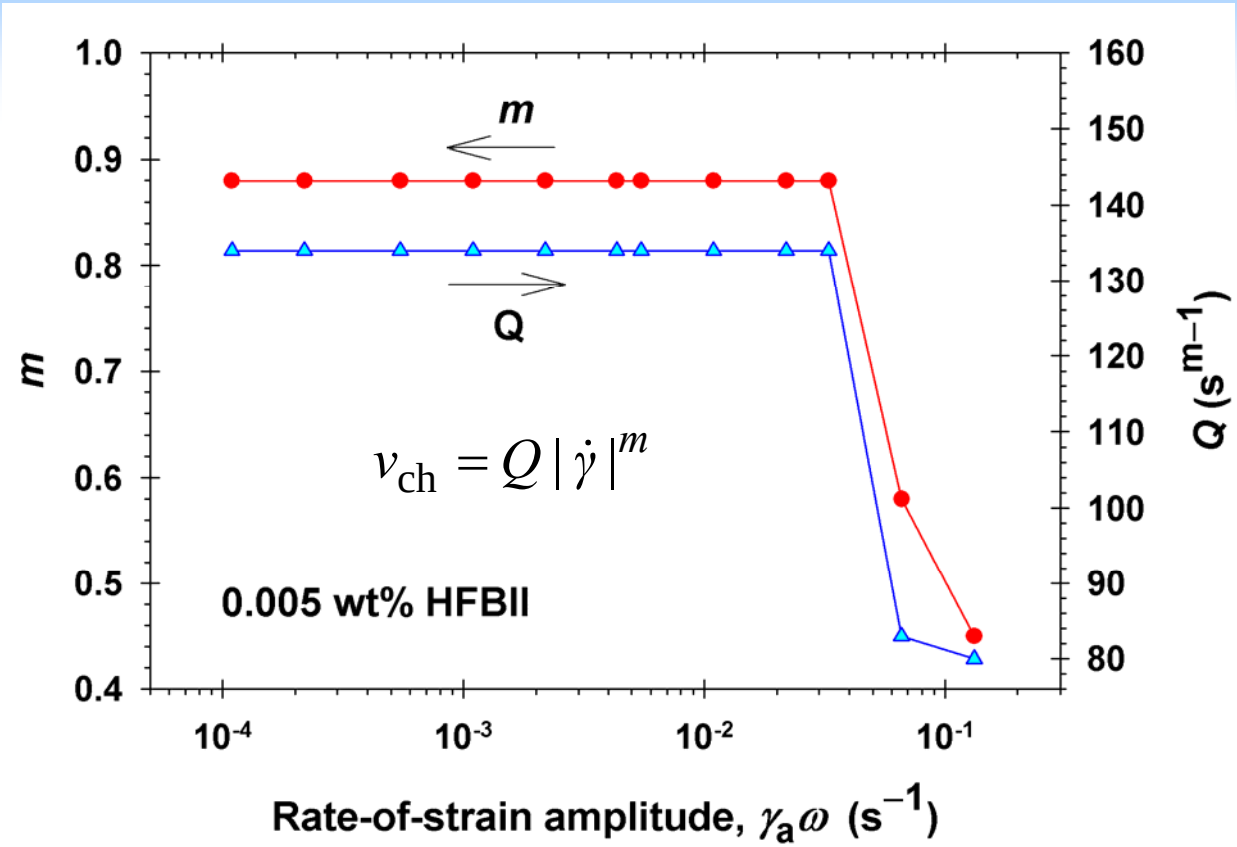


Non-elliptic Lissajous plots

Breakage of the protein elastic network →



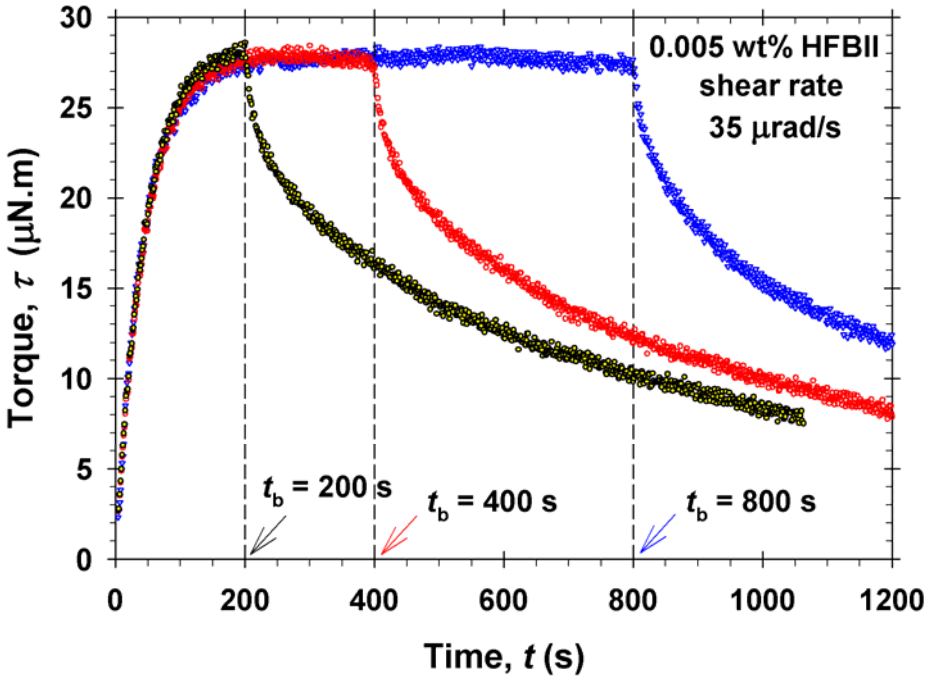
At higher amplitudes and frequencies the elastic protein membrane is destroyed!

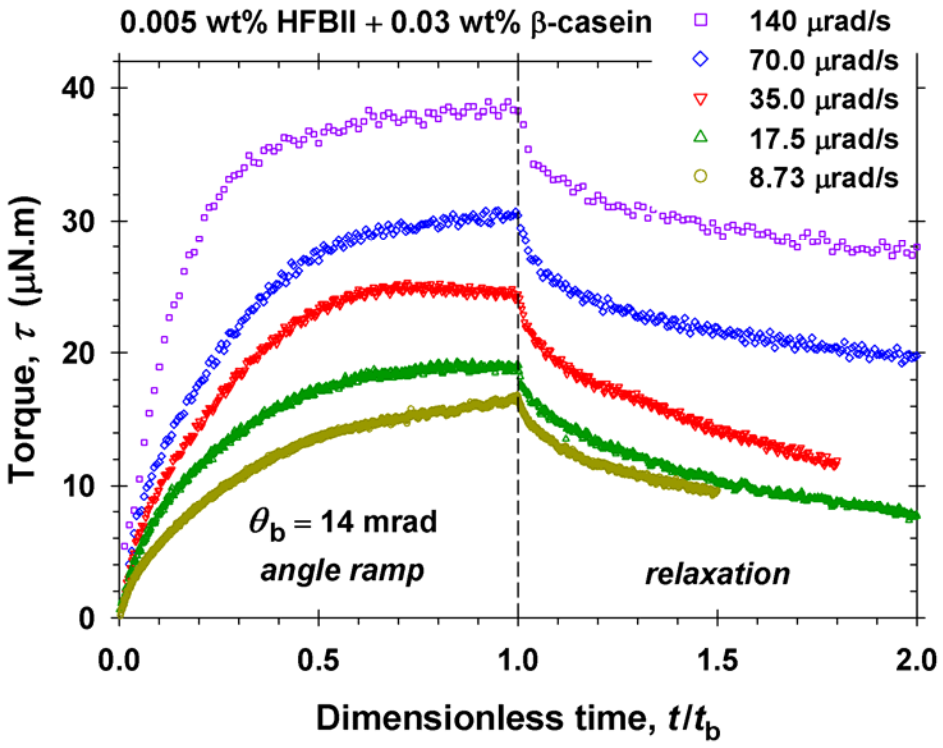


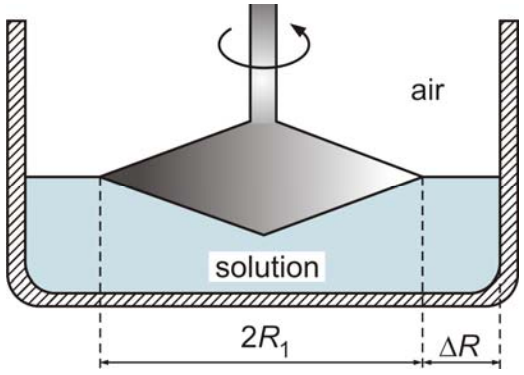
In the case of nonlinear response, both *m* and *Q* sharply decrease, which indicates the occurrence of structural changes in the layer.

<u>Recommendation</u>: Work with not-too-large amplitudes in quasi-linear regime to be dealing with the same viscoelastic body characterized by constant *m* and *Q*.

Stress relaxation at fixed angle after angle-ramp



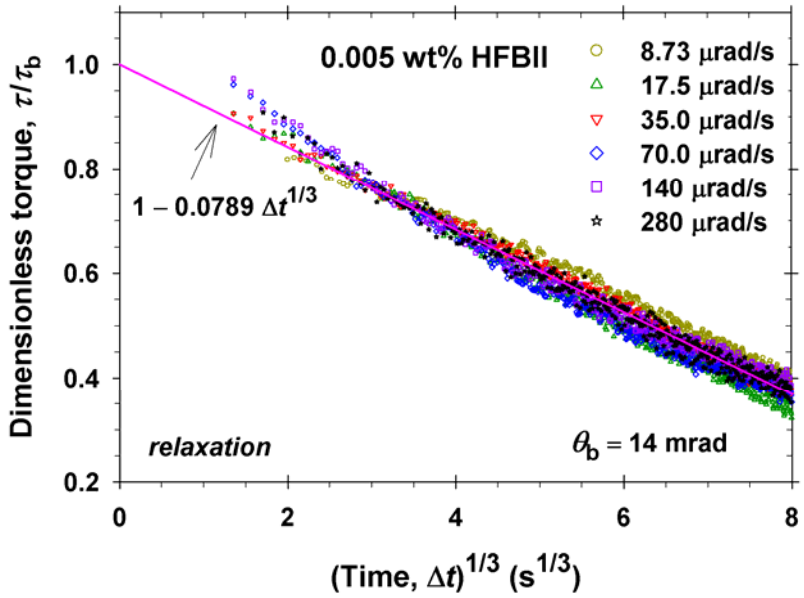




In angle-ramp regime, the rheological response of the system complies with the Maxwell-Hershel-Bulkley law.
(Forced breakage & restoration of molecular bonds)

In relaxation regime, the rheological response of the system complies with the Andrade cubic-root law.
(Spontaneous stress relaxation and solidification)

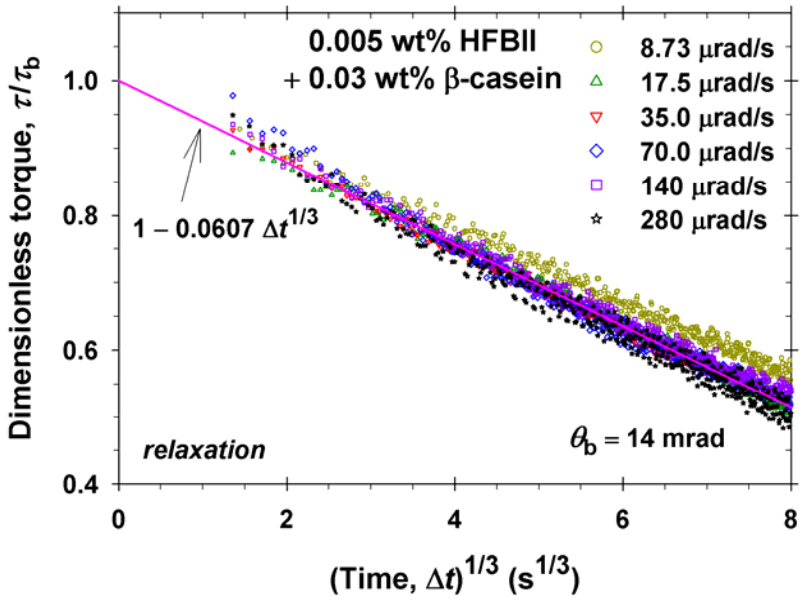
Relaxation Regime: Law and Characteristic Time

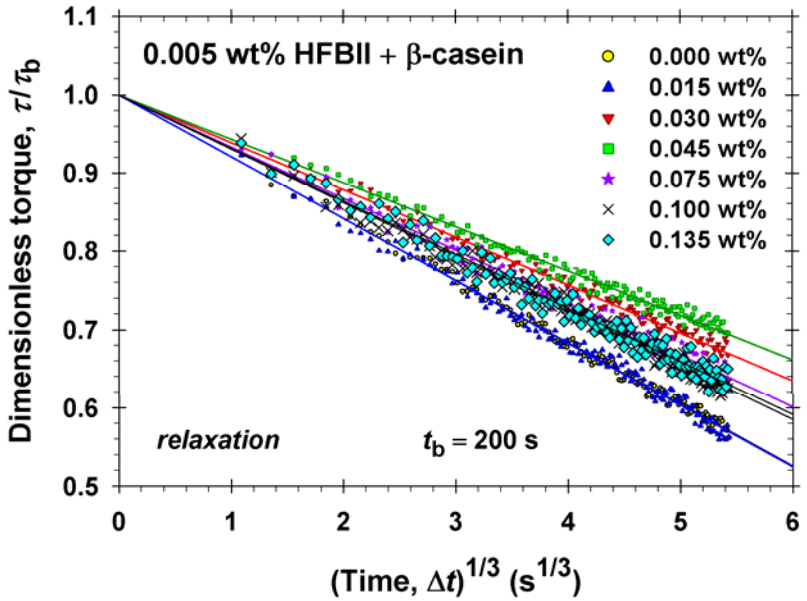


The relaxation of stresses during the solidification of an immobile HFBII adsorption layer follows an Andrade cubic-root law.

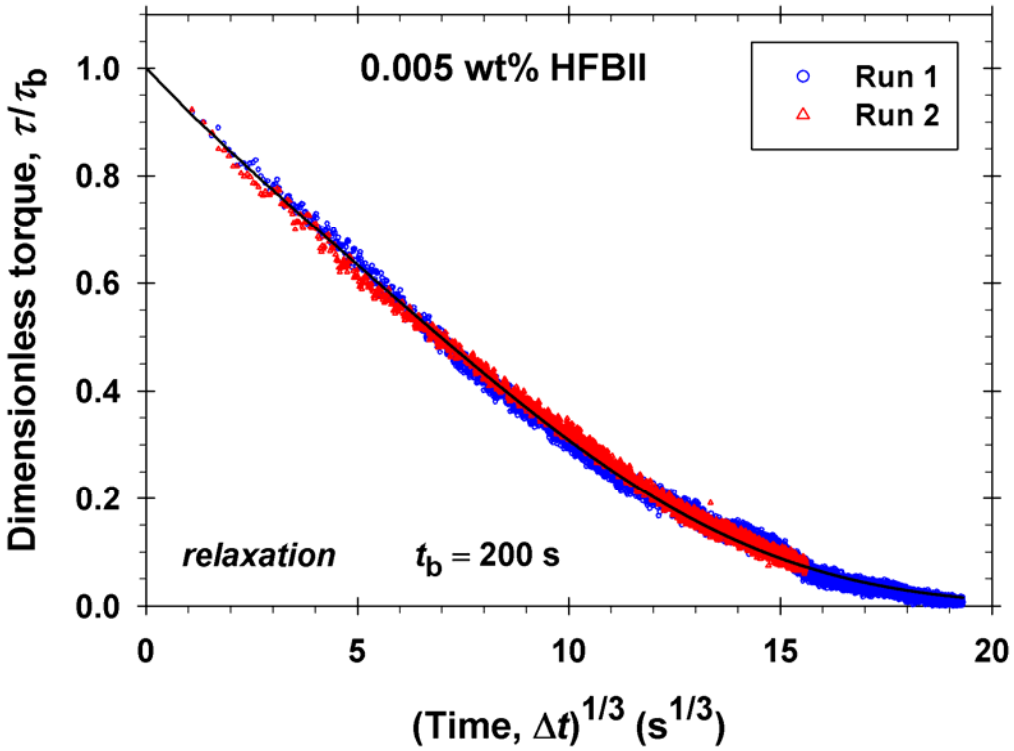
$$\tau \approx \tau_b[1-(\frac{\Delta t}{t_{r1}})^{1/3}], \quad \Delta t \equiv t - t_b$$

$$t_{r1} \approx 30 \text{ min}$$





Long-Time Relaxation and Second Characteristic Time



Modified Andrade's law:

$$\tau = \tau_b \exp[-(\frac{\Delta t}{t_{r1}})^{1/3} - \frac{\Delta t}{t_{r2}}]$$

For $\Delta t \to 0$

$$\tau \to \tau_b[1-(\frac{\Delta t}{t_{r1}})^{1/3}]$$

Two characteristic relaxation times: t_{r1} = 30 min and t_{r2} = 48 min

HFBII layers solidify much faster than those of globular proteins (BLG, BSA, OVA), which solidify for 10-24 hours.

Conclusions

(1) The rheological behavior of viscoelastic protein adsorption layers complies with a combined Maxwell-Herschel-Bulkley model.

(2) Only $\langle \nu_{ch} \rangle$ obeys a simple law of Herschel-Bulkley type, $\langle \nu_{ch} \rangle = Q \left\langle \dot{\gamma} \right\rangle^{m}$, in a wide range – more than three orders of magnitude .

(3) The rise of $\langle \nu_{ch} \rangle$ indicates an increasing fluidization (softening) of the layers with the rise of the shear rate, for both HFBII and HFBII + β-casein.

(4) Expressions for calculating E_{sh}, η_{sh} and ν_{ch} from the experimental G' and G'' are derived.

(5) It is recommended to work in the quasi-linear regime, in which the layer is characterized by constant m and Q. At higher frequencies and amplitudes, structural changes occur, and the layer is eventually broken.

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