ELASTIC LANGMUIR LAYERS AND MEMBRANES SUBJECTED TO UNIDIRECTIONAL COMPRESSION: WRINKLING AND COLLAPSE

Presented by: Peter A. Kralchevsky

Coauthors: Krassimir D. Danov and Simeon D. Stoyanov*

Department of Chemical Engineering, Faculty of Chemistry

Sofia University, 1164 Sofia, Bulgaria

*Unilever Food and Health Research Institute, 3133AT Vlaardingen, The Netherlands

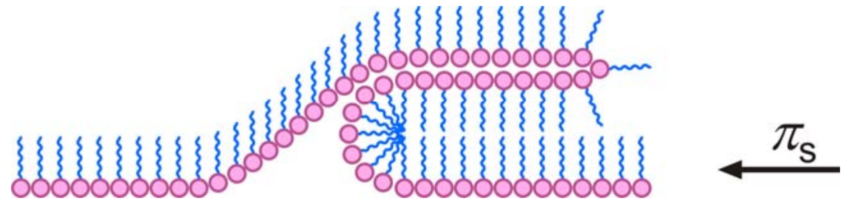
Presentation at the Joint Meeting of Workgroups 3, 4, 5, 6 of COST Action D43 with a Special Session: Nanoparticles & Interfaces for Energetics Technologies

CNR – Consiglio Nazionale delle Ricerche, Genoa, Italy

16–18 March, 2010

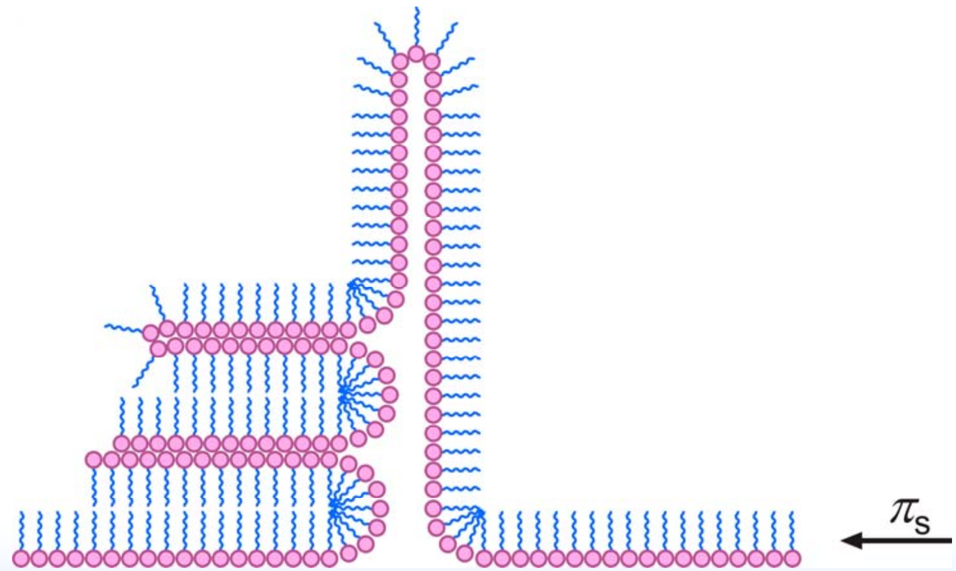
Monolayers of Low Bending Rigidity: Collapse

Langmuir trough

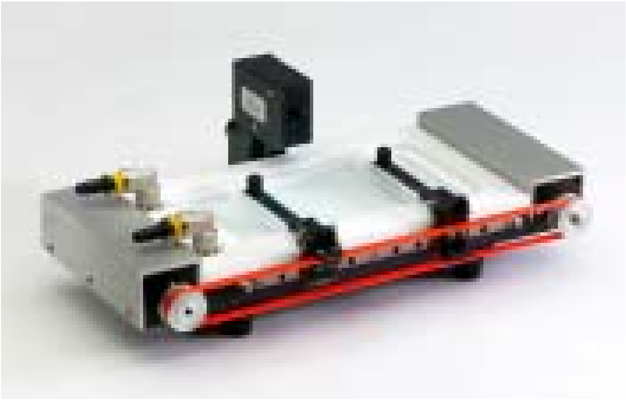


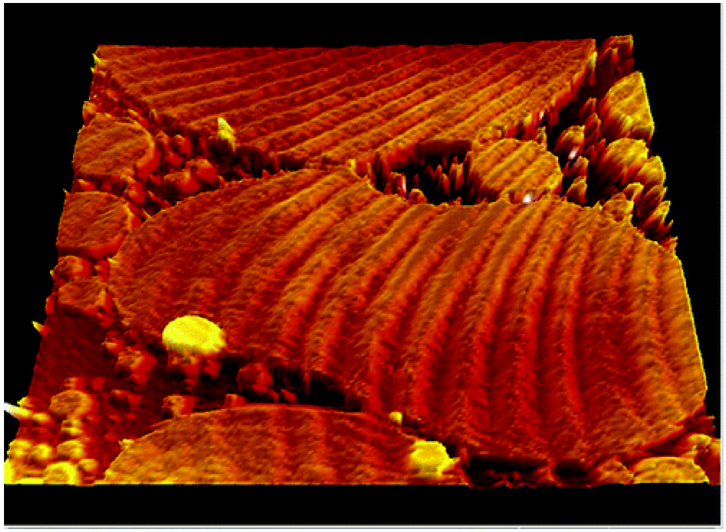
Three-layer structures observed upon a significant compression of an adsorption monolayer, at collapse.

More complex 3D structures at a greater compression →



Monolayers of Higher Bending Rigidity: Wrinkling





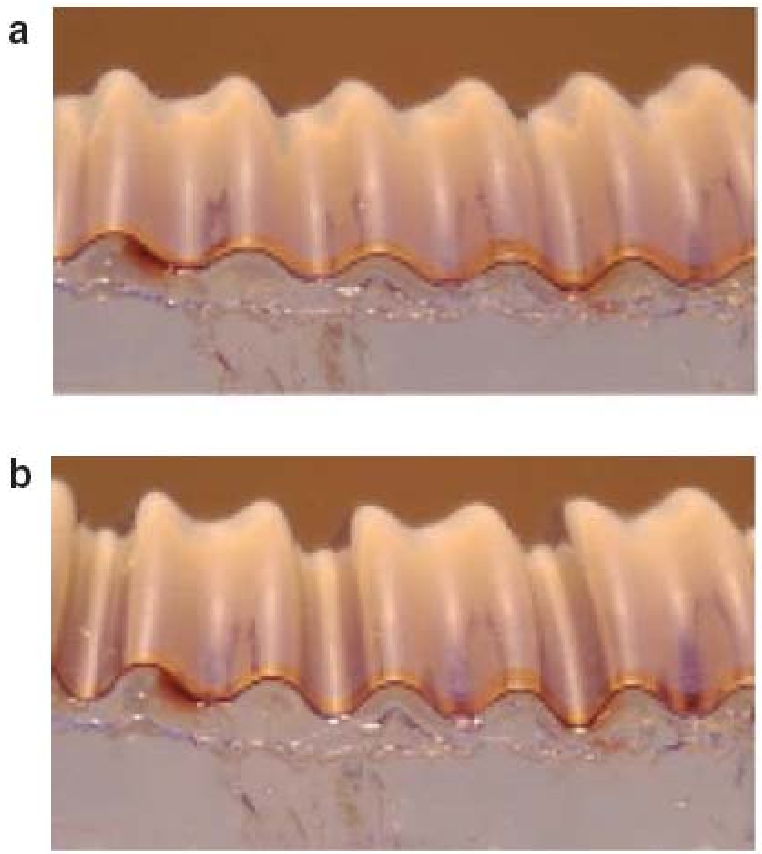
Phospholipid monolayer; J. Saccani et al. *Langmuir* 2004, *20,* 9190–9197.

Surface-active metalorganic complexes, Leontidis et al., *J. Colloid Interface Sci*. 2008, *317*, 544–555. (Brewster angle microscopy)

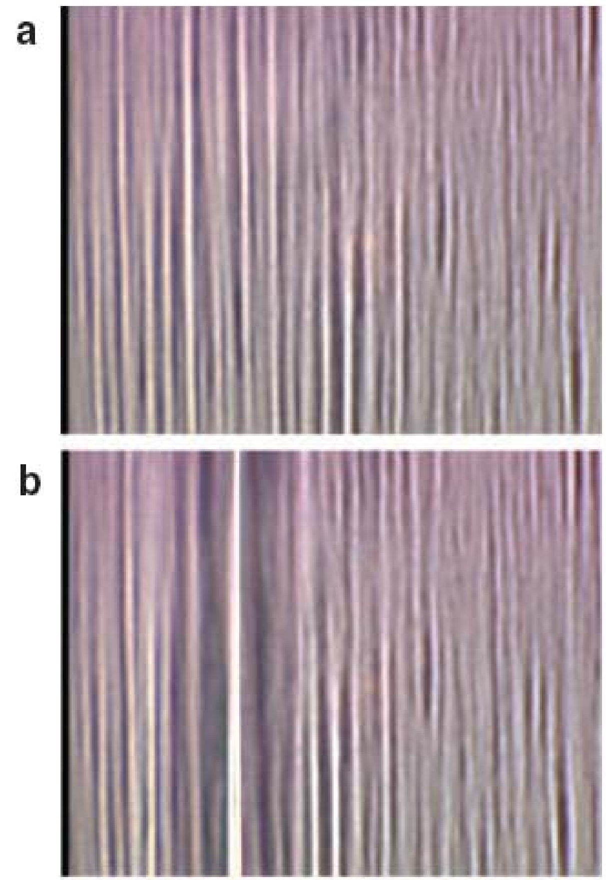
What determines the wavelength and amplitude of wrinkles?

What information can be extracted?

Additional Examples (Pocivavsek, et al. *Science* 2008, *320*, 912–916)

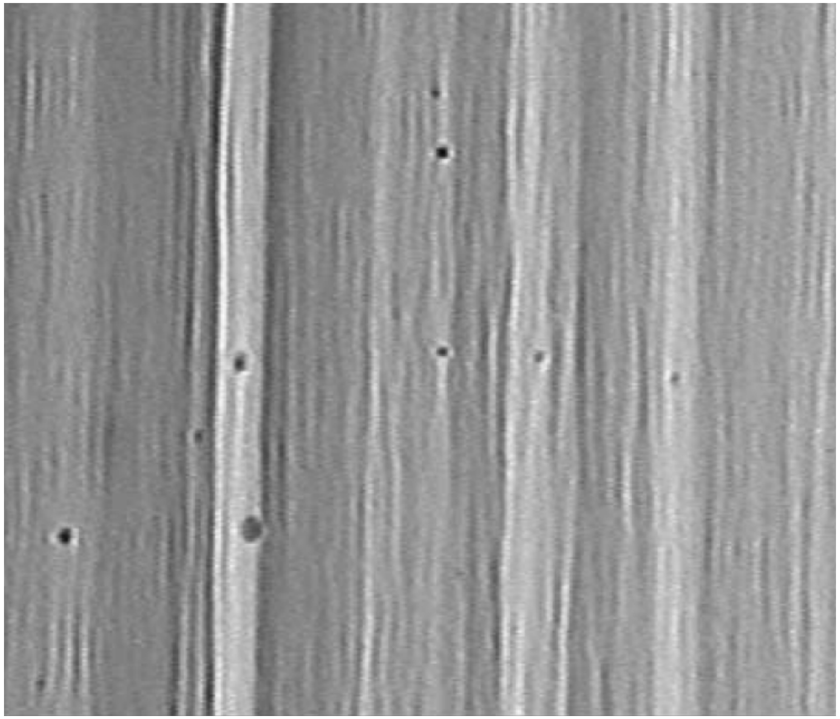


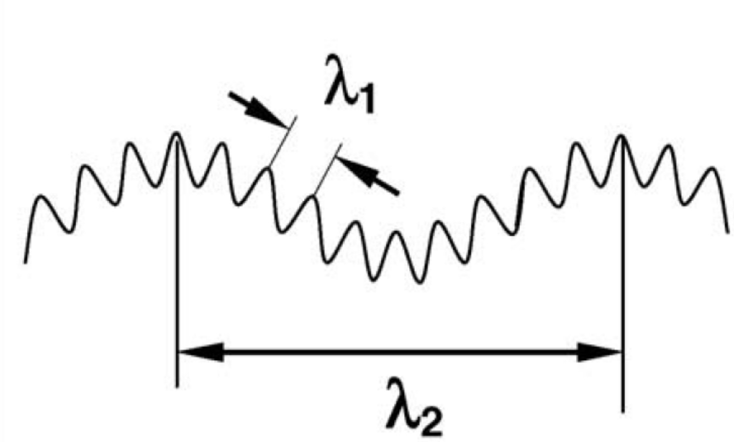
Polyester film (10 μm)
on gel substrate



Trilayer (15 nm) of
colloidal gold
nanoparticles on water

Wrinkling with two wavelengths



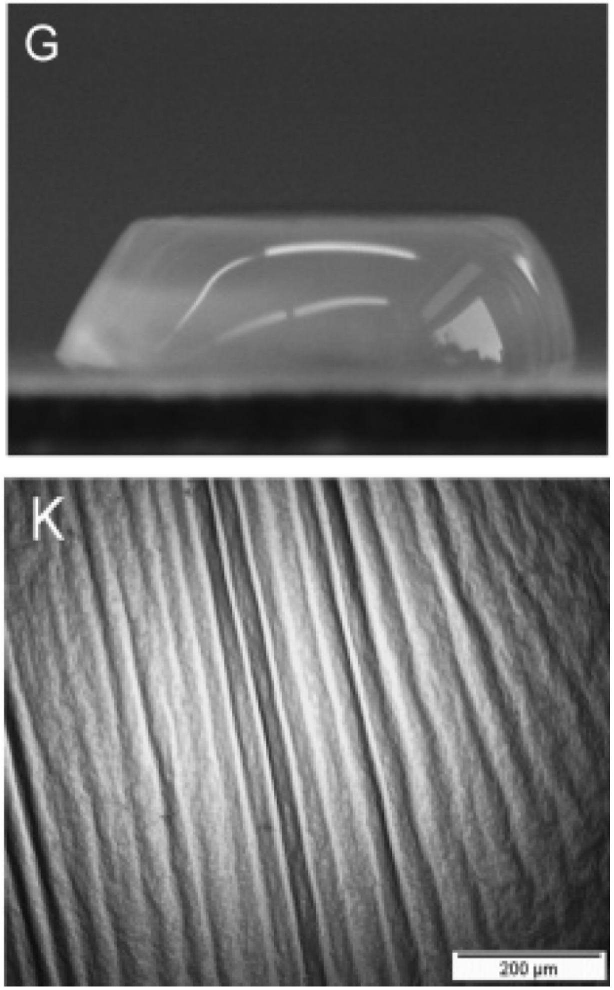


Two characteristic wavelengths: λ_1 = 8 µm and λ_2 = 63 µm

Monolayers from 200 nm hydrophobized silica particles on n-octane/water interface;

Horozov et al. *Colloids Surf. A* 2006, *282*, 377–386.

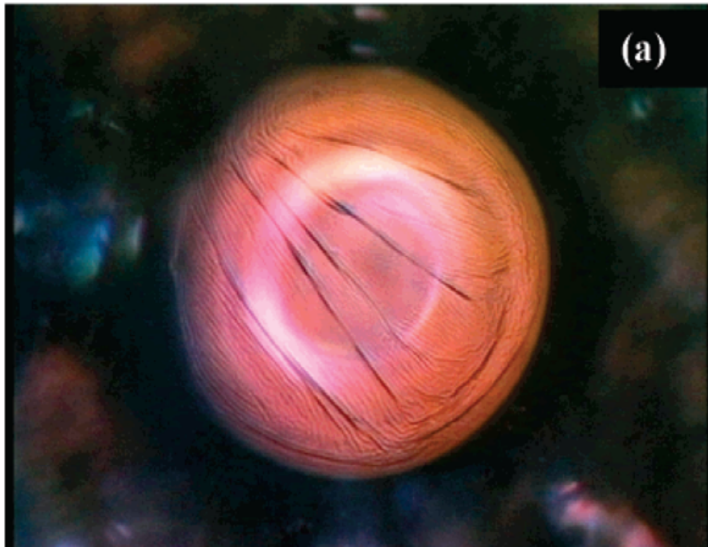
Wrinkling with drops and bubbles covered by proteins

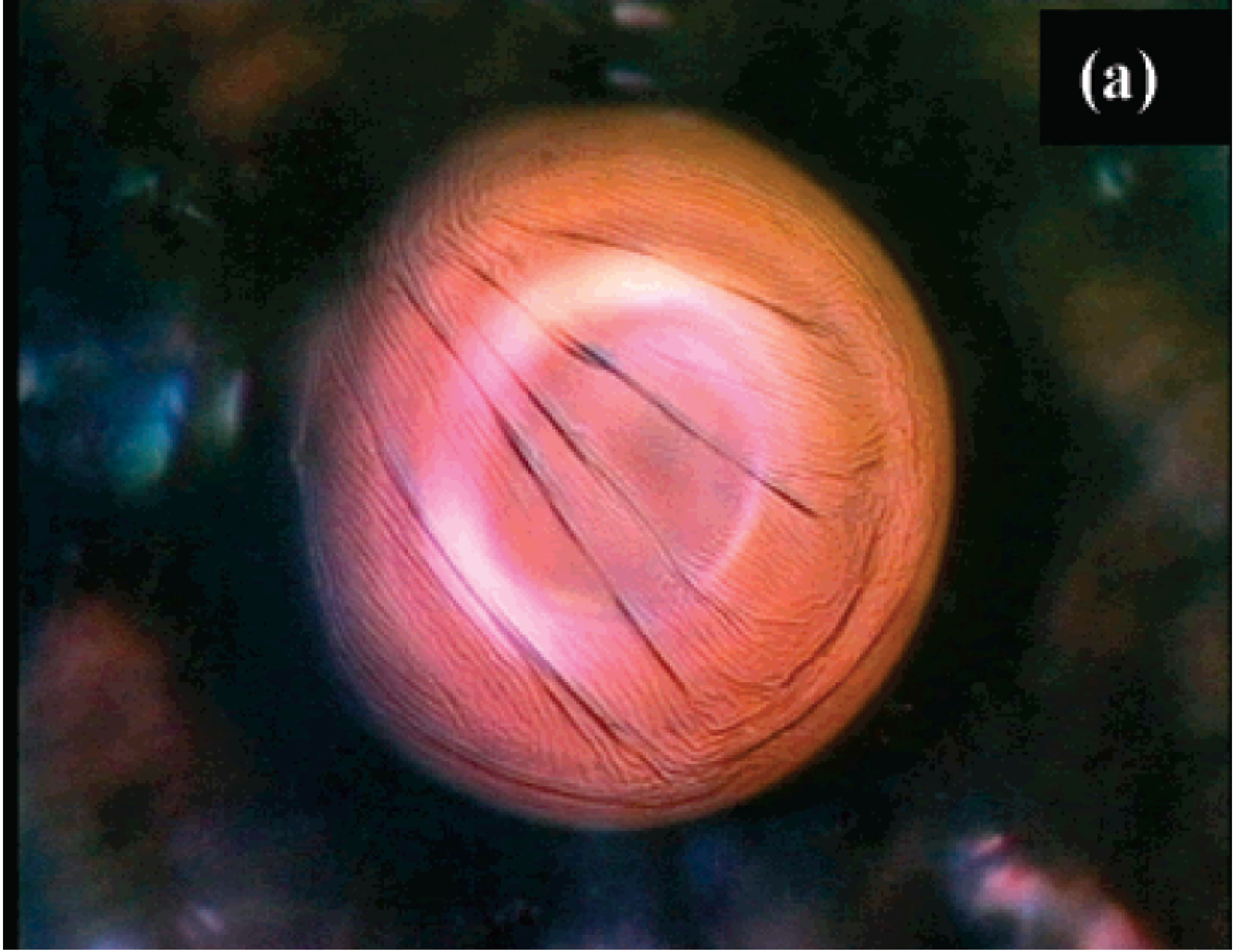


Drop of HFBI solution; wrinkles on its surface.
Szilvay et al., *Biochemistry* 2007, *46,* 2345.

The hydrophobins, HFBI and HFBII, are amphiphilic proteins (~ 3 nm) produced by filamentous fungi.

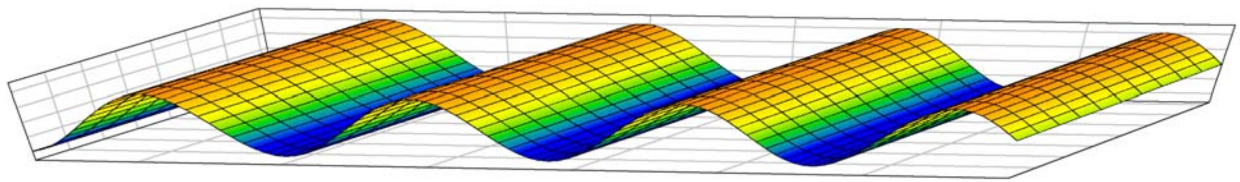
A. Cox et al., *Langmuir* 2007, *23,* 7995–8002:
A bubble in 0.7 mM solution of HFBII:





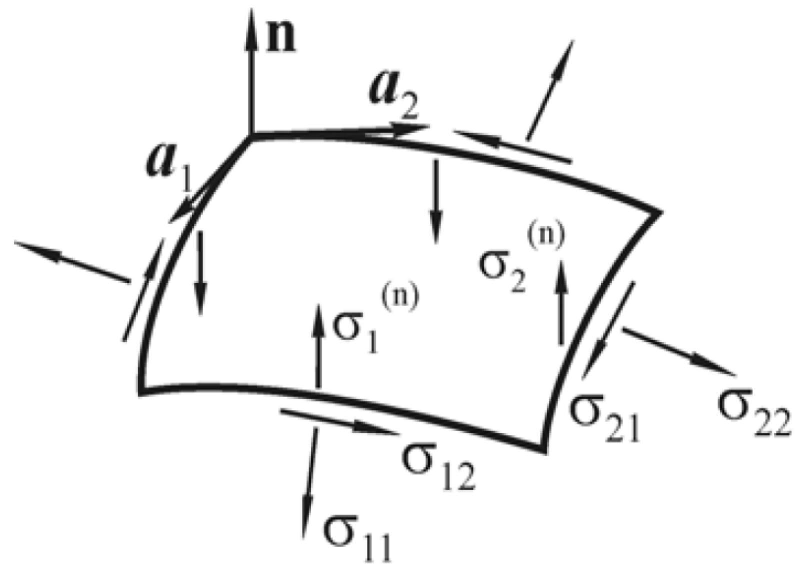
The whole bubble is covered with wrinkles of similar wavelength (A. Cox et al., *Langmuir* 2007, *23,* 7995–8002).

The Two-Dimensional Elastic Continuum Model



The surface stress tensor:

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_1^{(n)} \\ \sigma_{21} & \sigma_{22} & \sigma_2^{(n)} \end{pmatrix}$$



tangential stresses, σ_{11}, σ_{12},… and
transverse stress resultants $\sigma_1^{(n)}$, $\sigma_2^{(n)}$

Rheological constitutive relation:

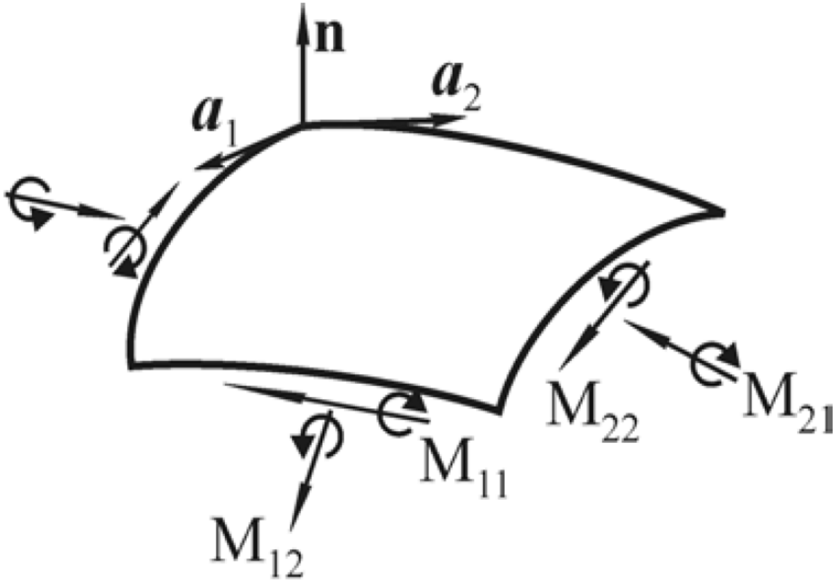
$$\boldsymbol{\sigma}_{\mathrm{s}} \equiv \sigma^{\alpha\beta}\mathbf{a}_\alpha \mathbf{a}_\beta = \sigma_0 \mathbf{I}_{\mathrm{s}} + E_{\mathrm{d}}\,\mathrm{Tr}(\mathbf{d})\,\mathbf{I}_{\mathrm{s}} + 2E_{\mathrm{sh}}[\mathbf{d} - \frac{1}{2}\mathrm{Tr}(\mathbf{d})\,\mathbf{I}_{\mathrm{s}}]$$

E_d and E_{sh} – surface dilatational and shear elasticities; Tr = trace
σ_0 – isotropic tension; I_s – unit tensor; d – surface strain tensor.

The Tensor of Surface Moments (Torques)

Helfrich's rheological constitutive relation:

$$\mathbf{M} = \frac{B_0}{2}\mathbf{I}_s + (k_c + \bar{k}_c)\,\mathrm{Tr}(\mathbf{b})\,\mathbf{I}_s - \bar{k}_c \mathbf{b}$$



k_c – bending elasticity (rigidity);

$\bar{k}_c$ – Gaussian elasticity (rigidity);

$B_0 = -4k_cH_0$ – bending moment of the planar interface;

H_0 – spontaneous curvature; b – curvature tensor.

Interfacial balance of the angular momentum yields a relation between the surface moments and the transverse stress resultants:

$$\sigma^{\alpha(n)} = -2k_c a^{\alpha\mu}\nabla_\mu H$$

The Interfacial Balance of the Linear Momentum

$$\nabla_\mu \sigma^{\mu\alpha} + 2k_c b^{\alpha\mu} \nabla_\mu H = 0$$

(tangential projection)

$$b_{\mu\nu}\sigma^{\nu\mu} - 2k_c a^{\mu\nu}\nabla_\mu \nabla_\nu H = (p_{II} - p_I)_s$$

(normal projection)

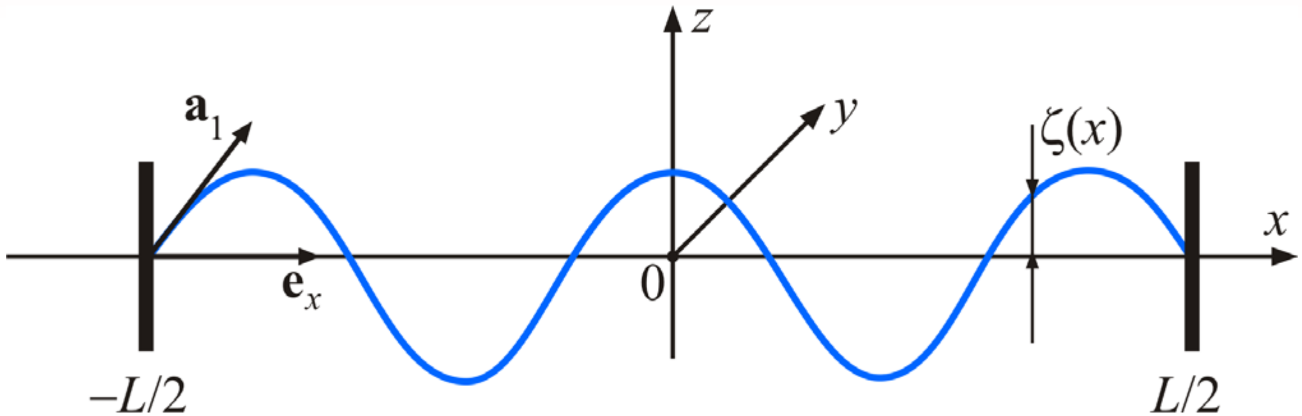
In the projections of the linear-momentum balance, we substitute the rheological constitutive relation for the surface stress tensor, where the surface strain tensor is:

$$d_{\alpha\beta} = \frac{1}{2}(\nabla_\beta u_\alpha + \nabla_\alpha u_\beta) - b_{\alpha\beta} u^{(n)} - \frac{1}{2}\frac{\partial \mathbf{u}}{\partial x^\alpha} \cdot \frac{\partial \mathbf{u}}{\partial x^\beta}$$

(u_1,u_2,u_3) – components of the displacement vector.

All terms in the expression for $d_{\alpha\beta}$ are of the same order of magnitude, and none of them can be neglected!

Unidirectional compression of the surface layer (along the x–axis)



The tangential (first integral) and normal components of the momentum balance are:

$$\frac{\mathrm{d}u_x}{\mathrm{d}x} + \frac{1}{2}\left[\left(\frac{\mathrm{d}\zeta}{\mathrm{d}x}\right)^2 - \left(\frac{\mathrm{d}u_x}{\mathrm{d}x}\right)^2\right] = \left[\sigma_{\mathrm{m}} - \sigma_0 - \frac{k_{\mathrm{c}}}{2}(2H)^2\right]\frac{a}{E_{\mathrm{m}}}$$

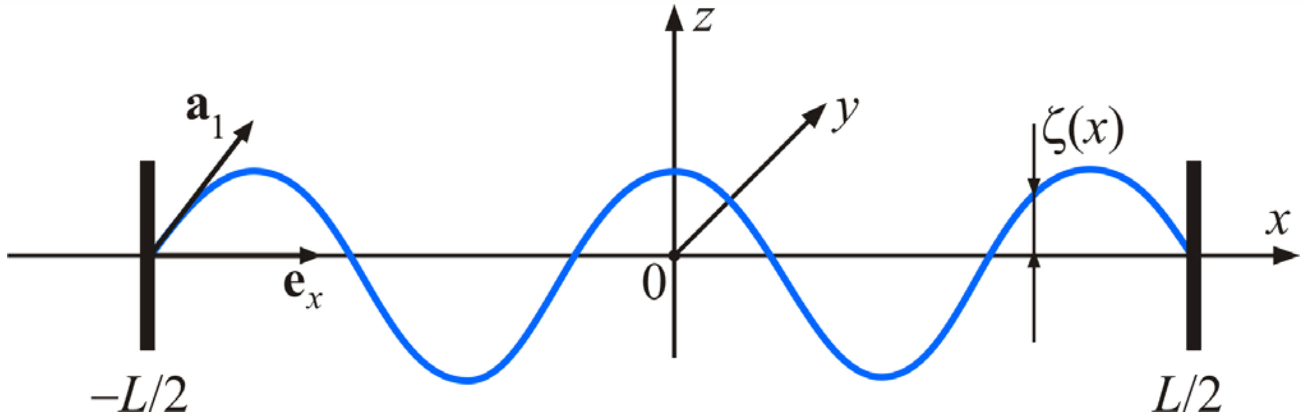
$$(2H)\sigma_{\mathrm{m}} - \frac{k_{\mathrm{c}}}{2}(2H)^3 - \frac{k_{\mathrm{c}}}{a^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{1}{a^{1/2}}\frac{\mathrm{d}(2H)}{\mathrm{d}x}\right] = g\Delta\rho\,\zeta$$

Two <u>nonlinear</u> equations for determining $u_x(x)$ and $\zeta(x)$; σ_{m} – integration constant

$$E_{\mathrm{m}} \equiv E_{\mathrm{d}} + E_{\mathrm{sh}}\,, \qquad 2H = \frac{1}{a^{3/2}}\frac{\mathrm{d}^2\zeta}{\mathrm{d}x^2}\,, \qquad a = 1 + \left(\frac{\mathrm{d}\zeta}{\mathrm{d}x}\right)^2$$

The Full System of Equations

Boundary conditions:



$$\zeta\big|_{L/2} = \zeta\big|_{-L/2} = 0$$

$$u_x\big|_{L/2} = -\Delta L/2, \qquad u_x\big|_{-L/2} = \Delta L/2$$

To obtain an unique solution of the problem, we need one additional equation !

For this goal, we will use the physical requirement that the actual shape of the membrane must correspond to the *minimal energy* of the system.

$$\Delta W \equiv W_\mathrm{m} - W_\mathrm{p} \to \min$$

W_p and W_m – energies of the system in states with planar and deformed membrane.

Calculation of the Energy of Deformation

$$\Delta W = \Delta W_{\mathrm{g}} + \Delta W_{\mathrm{s}}$$

gravitational energy:

$$\Delta W_{\mathrm{g}} = \frac{g\Delta\rho}{2L} S_{\mathrm{p}} \int_{-L/2}^{L/2} \zeta^2 \,\mathrm{d}x$$

S_p – projected area;

surface energy:

$$\Delta W_{\mathrm{s}} = \int_0^{\theta} \delta W_{\mathrm{s}} = \int_0^{\theta} \int_{S_{\mathrm{m}}} \delta w_{\mathrm{s}} \,\mathrm{d}S$$

θ – dimensionless area parameter

Continuum mechanics: The variation of surface energy per unit membrane area is:

$$\delta w_{\mathrm{s}} = \boldsymbol{\sigma}^{\mathrm{T}} : [\nabla_{\mathrm{s}}(\delta \mathbf{u}) + \mathbf{I}_{\mathrm{s}} \times \delta \boldsymbol{\omega}] + \mathbf{N}^{\mathrm{T}} : \nabla_{\mathrm{s}}(\delta \boldsymbol{\omega})$$

δu and $\delta\omega$ denote infinitesimal displacement and rotation.

$$\frac{\Delta W}{S_{\mathrm{p}}} = \frac{g\Delta\rho}{2L} \int_{-L/2}^{L/2} \zeta^2 \,\mathrm{d}x + \frac{2k_{\mathrm{c}}}{L} \int_{-L/2}^{L/2} a^{1/2} H^2 \,\mathrm{d}x + \frac{\Delta L}{L} \int_0^{\theta} \sigma_{\mathrm{m}}(\tilde{\theta}) \,\mathrm{d}\tilde{\theta}$$

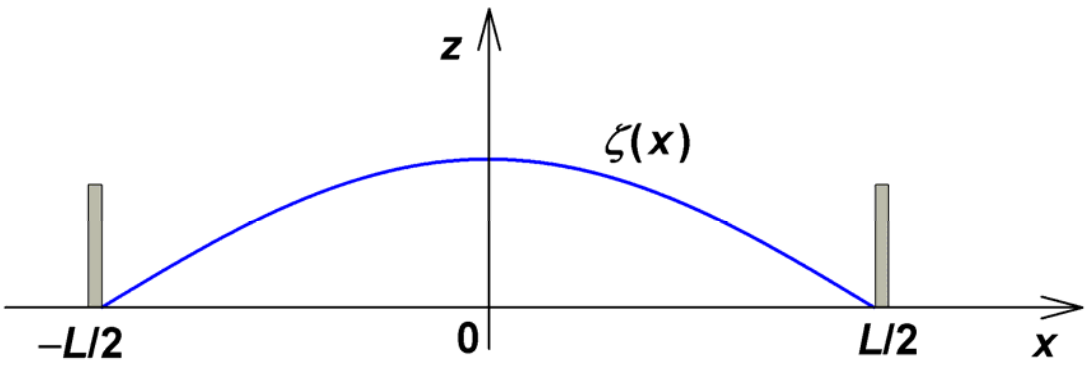
Contributions: gravitational energy, membrane bending and compression;

σ_m – thermodynamic surface tension.

Results for predominant effect of bending elasticity (negligible gravity)

Linearized problem:

The minimum of $\Delta W(\sigma_m)$ corresponds to half-wave shaped membrane:



$$\zeta = 0 \quad \text{for} \quad \frac{\Delta L}{L} < N_c \qquad \text{(flat membrane)}$$

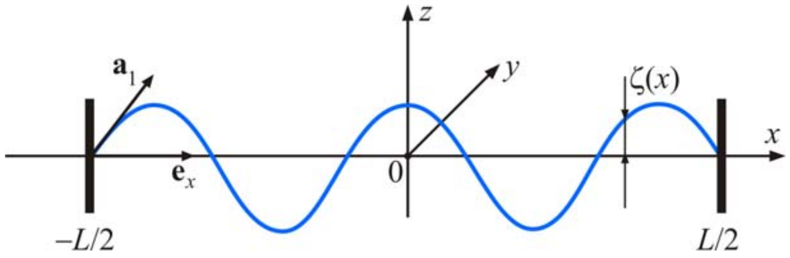
$$\zeta = \pm\frac{2}{\pi}\sqrt{\theta L \Delta L}\cos\left(\pi\frac{x}{L}\right) \quad \text{for} \quad \frac{\Delta L}{L} > N_c \qquad \text{(half wave)}$$

$-L/2 \leq x \leq L/2$ and $\theta = 1 - N_c L/\Delta L$; $N_c = k_c\pi^2/(E_m L^2)$ is a dimensionless number.

The maximum possible wavelength is realized.

The Linearized Problem in the Absence of Bending Elasticity ($k_c = 0$)

Solution: Oscillatory profile



$$\zeta_k = \pm \frac{2}{k\pi}(\theta_k L \Delta L)^{1/2} \cos(\frac{k\pi}{L}x) \quad \text{for } k = 1,3,5,...$$

$$\text{Energy}: \quad \frac{\Delta W_k}{S_p} = -\frac{E_m}{2}(1 - \frac{N_g L}{k^2 \Delta L})^2 (\frac{\Delta L}{L})^2$$

For shorter waves, $k \to \infty$, we have $\Delta W_k \to$ min and $\zeta_k \to 0$ (and $\sigma_m < 0$).

The energetically most advantageous membrane profile is that with infinitesimally small wavelength and amplitude (buckling instability).

The finite size of the molecules and the finite k_c do not allow too short waves.

At finite k_c, the minimum of energy corresponds to a finite wavelength. Find it!

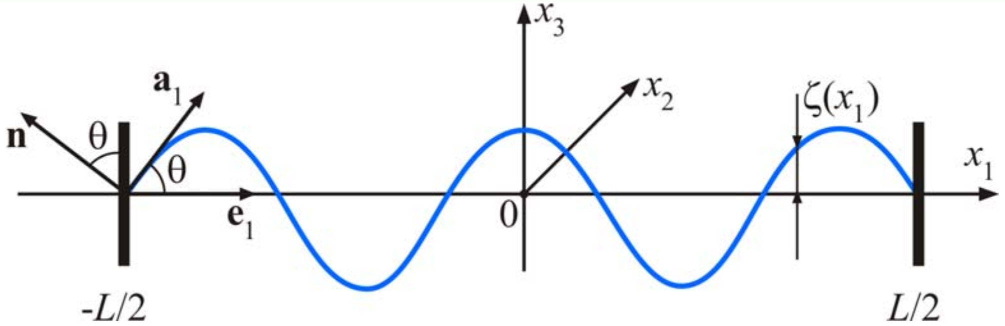
Wrinkling at Small Deformations (Linearized Problem)

$$k_c \frac{d^4\zeta}{dx^4} - \sigma_m \frac{d^2\zeta}{dx^2} + g\Delta\rho\,\zeta = 0$$

$$k_c q^4 + \sigma_m q^2 + g\Delta\rho = 0$$

$$\boxed{\sigma_m = -\left(\frac{g\Delta\rho}{q^2} + k_c q^2\right)}$$

(Milnler, Joanny, Pincus, *EPL* 1989)



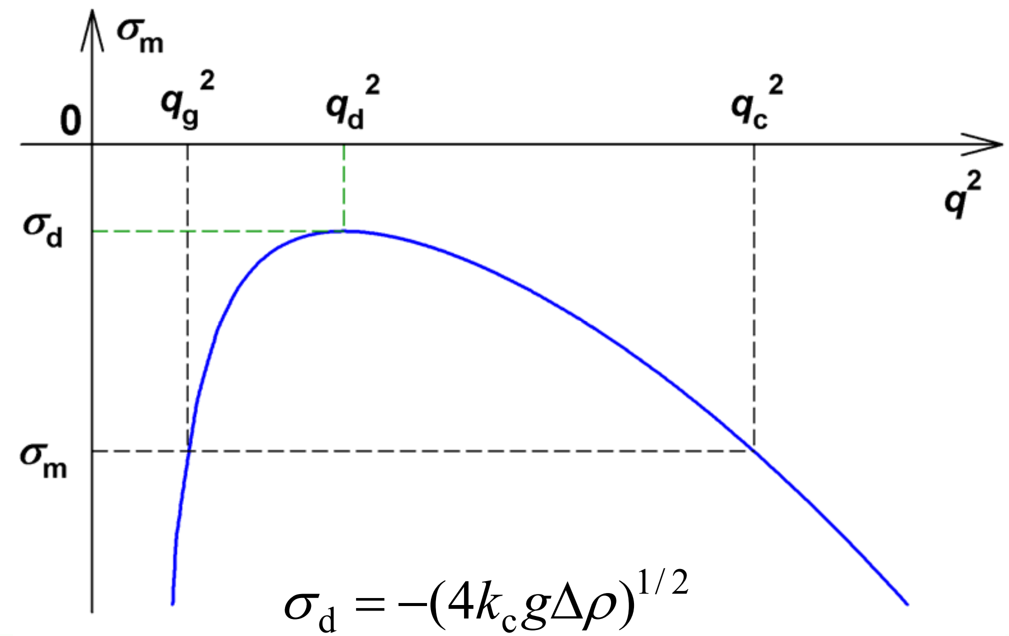
$$\zeta(x) \propto \cos(qx)$$

Minimization of energy:

$$q_d = (g\Delta\rho / k_c)^{1/4} = \frac{2\pi}{\lambda}$$

$$\boxed{k_c = \frac{\Delta\rho\, g \lambda^4}{16\pi^4}}$$

(Danov, Kralchevsky, Stoyanov, *Langmuir* 2010)



Minimum of energy at $[\sigma_m(q_k)]_{max}$, where $q_k = (2k + 1)\pi/L$, $k = 1, 2, 3, \ldots$

Wrinkling of Langmuir layers upon compression

Film from surface-active metalorganic complexes, Leontidis et al., *J. Colloid Interface Sci*. 2008, *317*, 544–555. (Brewster angle microscopy)

Bending elastic constant:

$$k_c = \frac{\Delta\rho g \lambda^4}{16\pi^4}$$

Experimental wavelength:

$$\lambda \approx 15.8\ \mu\text{m}$$

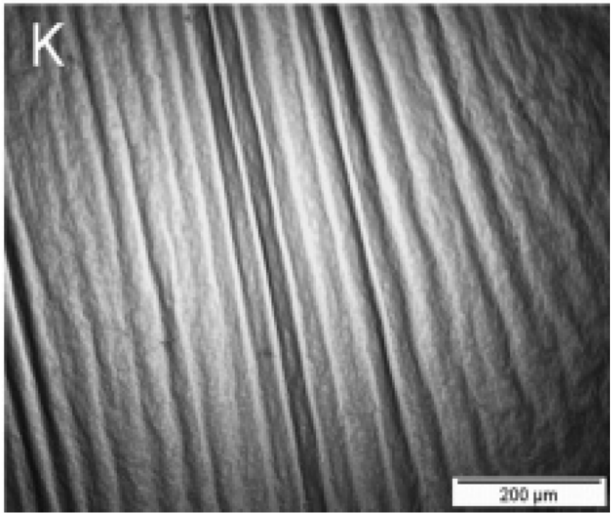
$$\Delta\rho = 1000\ \text{kg/m}^3; \quad g = 9.807\ \text{m/s}$$

$$\Rightarrow \quad k_c = 3.9 \times 10^{-19}\ \text{J}$$

(close to that for bilayer lipid membranes)

Membrane tension: $\sigma_m = -(4 k_c g \Delta\rho)^{1/2} = -1.2 \times 10^{-4}\ \text{mN/m}$

Wrinkling of hydrophobin HFBI layers upon compression



Wrinkles on the surface of a drop of HFBI solution; Szilvay et al., *Biochemistry* 2007, *46,* 2345.

Bending elastic constant:

$$k_c = \frac{\Delta\rho g \lambda^4}{16\pi^4}$$

Experimental wavelength:

$$\lambda \approx 43.2 \ \mu\text{m}$$

$$\Delta\rho = 1000 \ \text{kg/m}^3; \quad g = 9.807 \ \text{m/s}$$

$$\Rightarrow \quad k_c = 2.2 \times 10^{-17} \ \text{J}$$

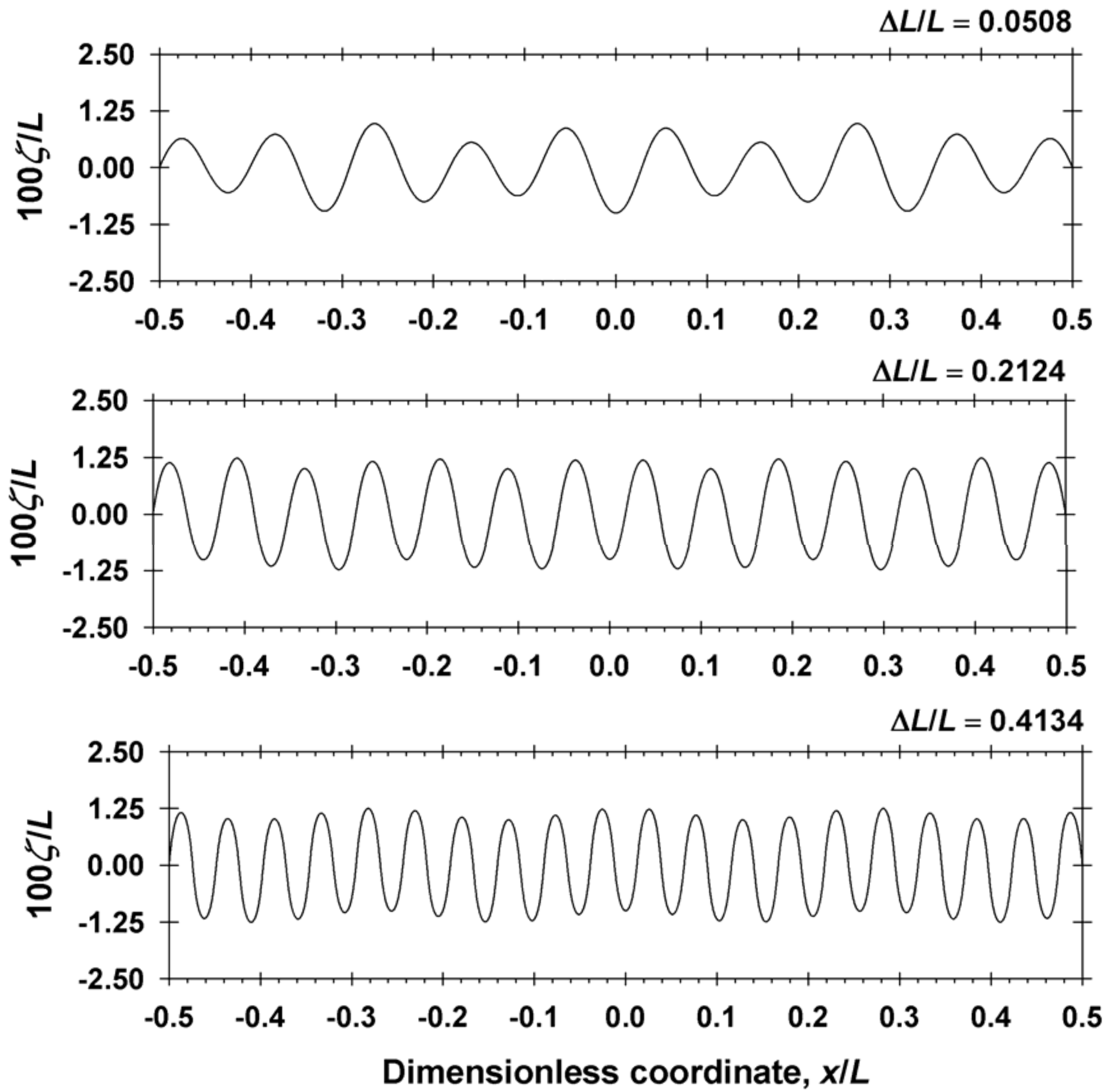
(100 times greater than that for bilayer lipid membranes)

Membrane tension:

$$\sigma_m = -(4k_c g \Delta\rho)^{1/2} = -0.93 \times 10^{-3} \ \text{mN/m}$$

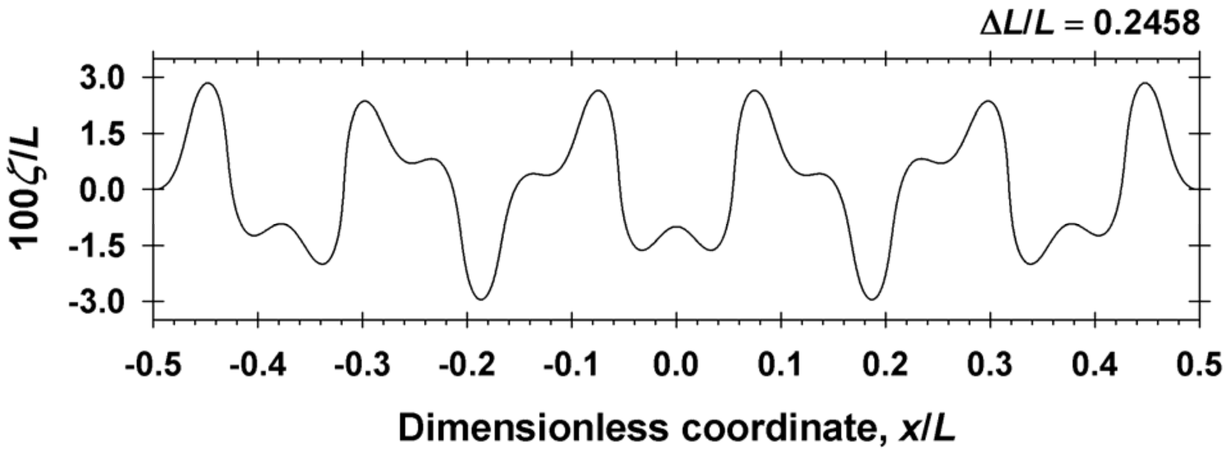
Numerical Solutions of the **Nonlinear Problem** (Larger Deformations)

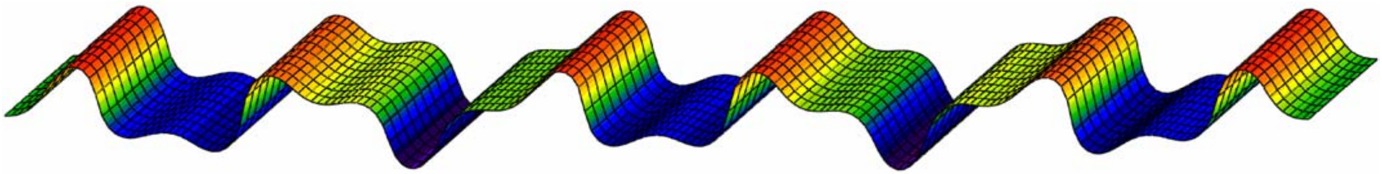
In the non-linear case the undulations are not harmonic (sinusoidal) and their average wavelength depends on L and ΔL. The case of concave profile at $x = 0$:



Numerical Solutions of the Nonlinear Problem (Larger Deformations)

The case of convex profile at x = 0, Toothed profiles:

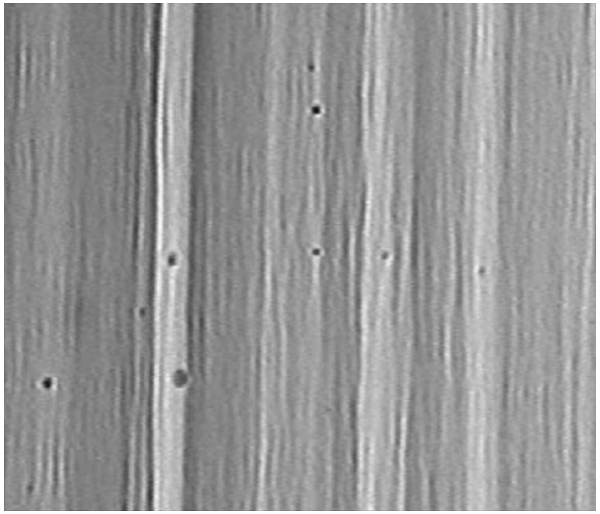


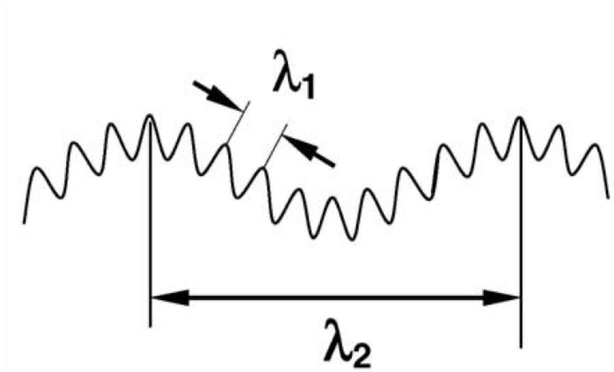


The criterion for minimal energy can be also applied to the nonlinear problem (larger out-of-plane deformations), to find the membrane shape, which is realized under given physical conditions.

However, the application of this criterion is related to heavy computations, which are out of the scope of the present study.

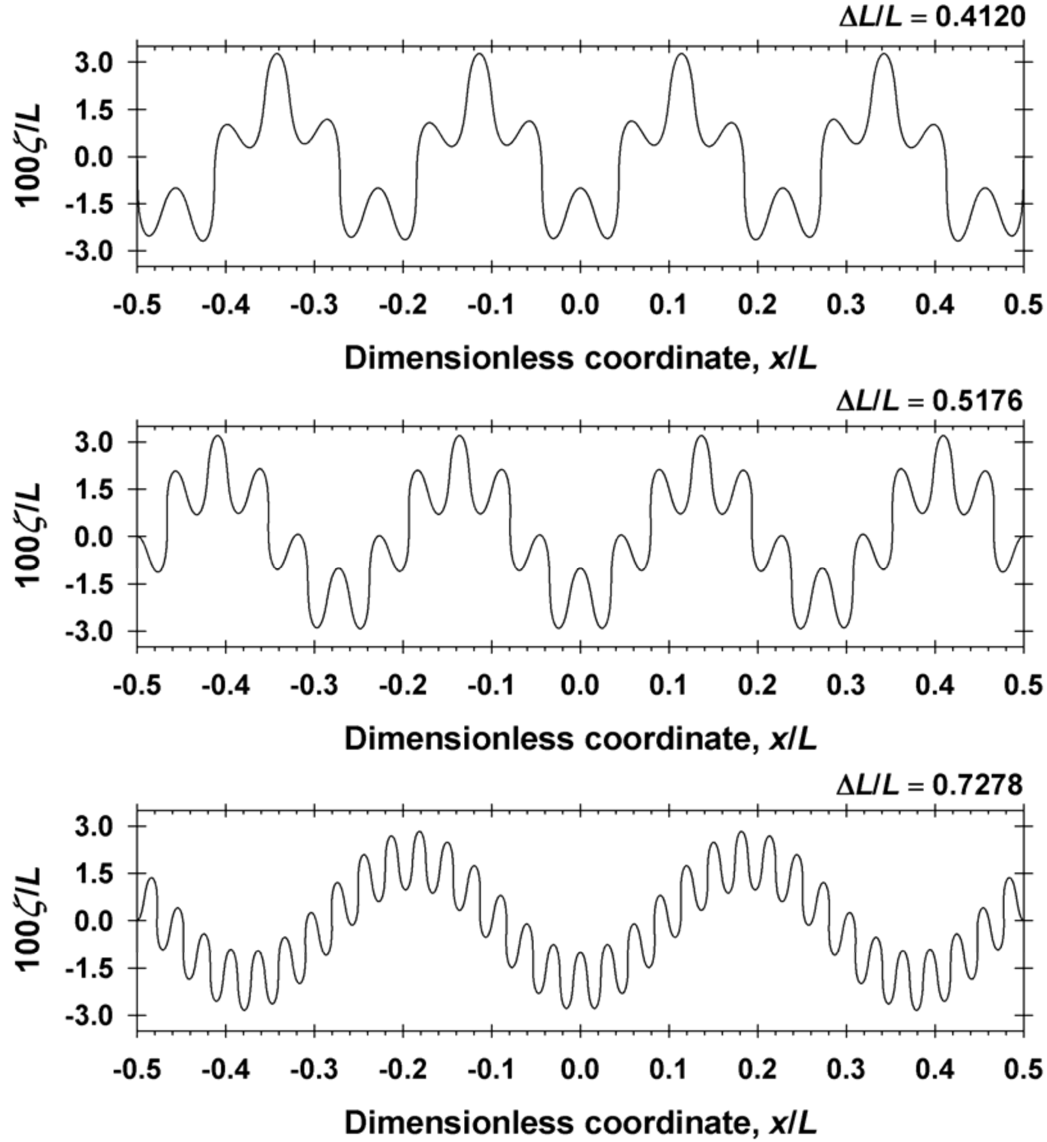
Profiles with **two** characteristic wavelengths





Horozov et al. (2006) obtained wrinkles with two characteristic wavelengths,
λ_1 = 8 μm and λ_2 = 63 μm
for monolayers from 200 nm silica particles

Predictions of the nonlinear theory at larger compressions $\Delta L/L$:



Summary and Conclusions:

(1) The two-dimensional elastic continuum model is used to describe the wrinkling of elastic Langmuir layers (membranes) subjected to unidirectional compression; effects of the dilatational, shear and bending elasticities.

(2) If the gravitational and bending energies are comparable, the membrane shape exhibits multiple periodic wrinkles. An expression is derived for calculating the bending elasticity (rigidity) from the wrinkle wavelength.

(3) This expression, which is independent of L and ΔL, can be used for determining the bending elastic modulus of Langmuir films (membranes): upon compression in linear regime, the amplitude increases at fixed λ.

(4) To determine the membrane shape at larger out-of-plane deformations, we solved numerically the respective nonlinear problem. Depending on the values of the physical parameters, the theory predicts various shapes: non-harmonic oscillations; toothed profiles, and profiles with two characteristic wavelengths.

Published: K.D. Danov, P.A. Kralchevsky, S.D. Stoyanov, *Langmuir* 2010, 26(1), 143–155.