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

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Monolayers of Low Bending Rigidity: Collapse

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

Langmuir trough

More complex 3D structures at a greater compression →
Monolayers of Higher Bending Rigidity: Wrinkling


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?

Polyester film (10 μm) on gel substrate

Trilayer (15 nm) of colloidal gold nanoparticles on water
Wrinkling with two wavelengths

Two characteristic wavelengths: $\lambda_1 = 8 \, \mu\text{m}$ and $\lambda_2 = 63 \, \mu\text{m}$

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

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:

Drop of HFBI solution; wrinkles on its surface.

Szilvay et al., *Biochemistry* 2007, 46, 2345.
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:

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

tangential stresses, \( \sigma_{11}, \sigma_{12}, \ldots \) and transverse stress resultants \( \sigma_1^{(n)}, \sigma_2^{(n)} \)

Rheological constitutive relation:

\[
\sigma_s \equiv \sigma^{\alpha\beta} a_\alpha a_\beta = \sigma_0 I_s + E_d \text{Tr}(d) I_s + 2E_{sh} [d - \frac{1}{2} \text{Tr}(d) I_s]
\]

\( E_d \) and \( E_{sh} \) – surface dilatational and shear elasticities; \( \text{Tr} = \) trace
\( \sigma_0 \) – isotropic tension; \( I_s \) – unit tensor; \( d \) – surface strain tensor.
The Tensor of Surface Moments (Torques)

Helfrich’s rheological constitutive relation:

\[ M = \frac{B_0}{2} I_s + (k_c + \bar{k}_c) \text{Tr}(b) I_s - \bar{k}_c b \]

- \( k_c \) – bending elasticity (rigidity);
- \( \bar{k}_c \) – Gaussian elasticity (rigidity);
- \( B_0 = -4k_c H_0 \) – 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)

\[ b_{\mu\nu} \sigma^{\nu\mu} - 2k_c a^{\mu\nu} \nabla_\mu \nabla_\nu H = (p_\Pi - p_I)_s \]  
(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:

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

\((u_1, u_2, u_3)\) – 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:

$$\frac{d u_x}{d x} + \frac{1}{2} \left[ \left( \frac{d \zeta}{d x} \right)^2 - \left( \frac{d u_x}{d x} \right)^2 \right] = \left[ \sigma_m - \sigma_0 - \frac{k_c}{2} (2H)^2 \right] \frac{a}{E_m}$$

$$(2H)\sigma_m - \frac{k_c}{2} (2H)^3 - \frac{k_c}{a^{1/2}} \frac{d}{d x} \left[ \frac{1}{a^{1/2}} \frac{d(2H)}{d x} \right] = g \Delta \rho \zeta$$

Two **nonlinear** equations for determining $u_x(x)$ and $\zeta(x)$; $\sigma_m$ – integration constant

$$E_m \equiv E_d + E_{sh} , \quad 2H = \frac{1}{a^{3/2}} \frac{d^2 \zeta}{d x^2} , \quad a = 1 + \left( \frac{d \zeta}{d x} \right)^2$$
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.

\[ \Delta W \equiv W_m - W_p \rightarrow \min \]

\( W_p \) and \( W_m \) – energies of the system in states with planar and deformed membrane.
Calculation of the Energy of Deformation

\[ \Delta W = \Delta W_g + \Delta W_s \]

**Gravitational energy:**

\[ \Delta W_g = \frac{g\Delta \rho}{2L} S_p \int_{-L/2}^{L/2} \zeta^2 \, dx \]

\( S_p \) – projected area;

**Surface energy:**

\[ \Delta W_s = \int_0^{\theta} \delta W_s = \int_0^{\theta} \int_{S_m} \delta w_s \, dS \]

\( \theta \) – dimensionless area parameter

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

\[ \delta w_s = \sigma^T : \left[ \nabla_s (\delta \mathbf{u}) + \mathbf{I}_s \times \delta \mathbf{\omega} \right] + \mathbf{N}^T : \nabla_s (\delta \mathbf{\omega}) \]

\( \delta \mathbf{u} \) and \( \delta \mathbf{\omega} \) denote infinitesimal displacement and rotation.

\[ \frac{\Delta W}{S_p} = \frac{g\Delta \rho}{2L} \int_{-L/2}^{L/2} \zeta^2 \, dx + \frac{2k_c}{L} \int_{-L/2}^{L/2} a^{1/2} H^2 \, dx + \frac{\Delta L}{L} \int_0^{\theta} \sigma_m(\tilde{\theta}) \, d\tilde{\theta} \]

**Contributions:** gravitational energy, membrane bending and compression;

\( \sigma_m \) – 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:

$$-L/2 \leq x \leq L/2$$

$$\zeta = 0 \quad \text{for} \quad \frac{\Delta L}{L} < N_c$$

(flatten membrane)

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

(half wave)

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

The maximum possible wavelength is realized.
The Linearized Problem in the **Absence of Bending Elasticity** \((k_c = 0)\)

**Solution:** Oscillatory profile

\[
\zeta_k = \pm \frac{2}{k\pi} \left( \theta_k L \Delta L \right)^{1/2} \cos\left( \frac{k\pi}{L} x \right) \text{ for } k = 1, 3, 5, \ldots
\]

Energy:

\[
\frac{\Delta W_k}{S_p} = - \frac{E_m}{2} \left( 1 - \frac{N_g L}{k^2 \Delta L} \right)^2 \left( \frac{\Delta L}{L} \right)^2
\]

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)

\[ k_c \frac{d^4 \zeta}{d x^4} - \sigma_m \frac{d^2 \zeta}{d x^2} + g\Delta\rho \zeta = 0 \]

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

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

(Milnler, Joanny, Pincus, EPL 1989)

Minimization of energy:

\[ q_d = \left( \frac{g\Delta\rho}{k_c} \right)^{1/4} = \frac{2\pi}{\lambda} \]

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

(Danov, Kralchevsky, Stoyanov, Langmuir 2010)

Minimum of energy at \([\sigma_m(q_k)]_{\text{max}}\), where \(q_k = (2k + 1)\pi/L\), \(k = 1, 2, 3, \ldots\)
Wrinkling of Langmuir layers upon compression

Bending elastic constant:

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

Experimental wavelength:

\[ \lambda \approx 15.8 \, \mu m \]

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

\[ \Rightarrow k_c = 3.9 \times 10^{-19} \, \text{J} \]

(close to that for bilayer lipid membranes)

Membrane tension:

\[ \sigma_m = -(4k_c g \Delta \rho)^{1/2} = -1.2 \times 10^{-4} \, \text{mN/m} \]

Film from surface-active metalorganic complexes, Leontidis et al., J. Colloid Interface Sci. 2008, 317, 544–555. (Brewster angle microscopy)
Wrinkling of hydrophobin HFBI layers upon compression

Bending elastic constant:

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

Experimental wavelength:

\[ \lambda \approx 43.2 \ \mu m \]

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

\[ \Rightarrow k_c = 2.2 \times 10^{-17} \ \text{J} \]

(100 times greater than that for bilayer lipid membranes)

Membrane tension:

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

Wrinkles on the surface of a drop of HFBI solution; Szilvay et al., Biochemistry 2007, 46, 2345.
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 $\Delta L$. 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.
Horozov et al. (2006) obtained wrinkles with two characteristic wavelengths, \( \lambda_1 = 8 \mu m \) and \( \lambda_2 = 63 \mu m \) for monolayers from 200 nm silica particles.
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 $\Delta L$, can be used for determining the bending elastic modulus of Langmuir films (membranes): upon compression in linear regime, the amplitude increases at fixed $\lambda$.

(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.