Theory of pattern formation in Langmuir-Blodgett transfer systems

Thomas Wulf

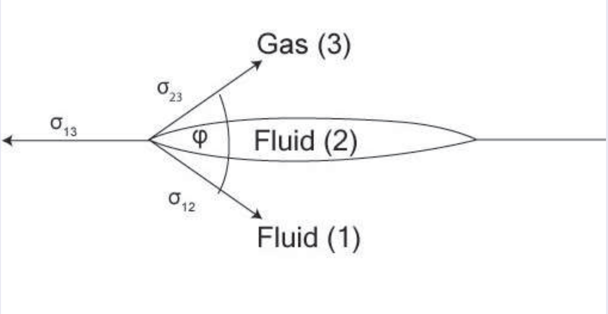
26.08.2007

Inhalt

Quote by Benjamin Franklin (1774)

...I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface...the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square,which spread amazingly and extended itself gradually until it reached the leeside.

Spreading of a drop



Equilibrium

$$\cos\varphi = \frac{\sigma_{12}^2 - (\sigma_{13}^2 + \sigma_{23}^2)}{2\sigma_{13}\sigma_{23}}$$

For $|\sigma_{12}| > |\sigma_{13}| + |\sigma_{23}|$ spreading of the drop to a monolayer arises.

Langmuir-Blodgett-Films

- built up from monolayer, which are spread at air-water interface
- mostly amphiphilic substances (which consist of a hydrophilic headgroup and hydrophobic hydrocarbon chains) are used to be spread

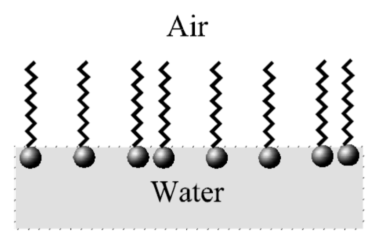


Figure: Schematic illustration of a spread monolayer

- to superimpose the organic molecules on the water interface, often water insoluble surfactants are needed (e.g. DPPC in chloroform)

Experiment

Experimental setup

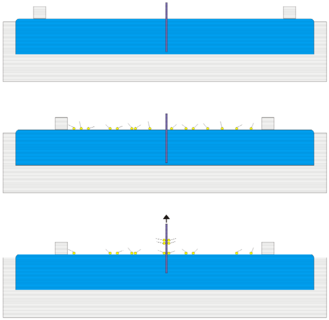


Figure: Experimental setup [1]

- barriers are used to maintain the lateral pressure and to adjust different phases of the monolayer
- deposition of monolayer on solid substrate by dipping the substrate up

Experiment

Experimental setup

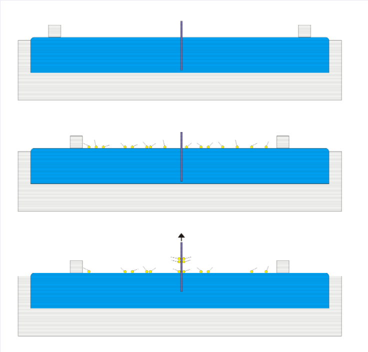
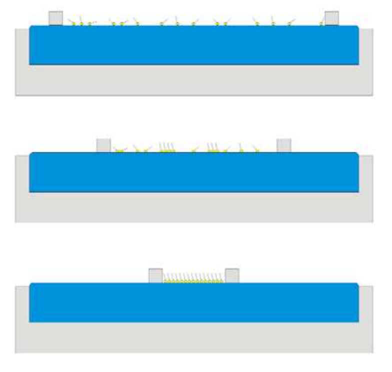
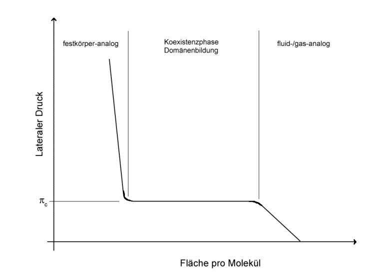


Figure: Experimental setup [1]

- barriers are used to maintain the lateral pressure and to adjust different phases of the monolayer
- deposition of monolayer on solid substrate by dipping the substrate up

Phases according to lateral pressure





One could assume the monolayer to be deposed homogenously on the substrate but under circumstances (e.g. decomposition is carried out in liquid-expanded phase regime) stripe pattern can be observed.

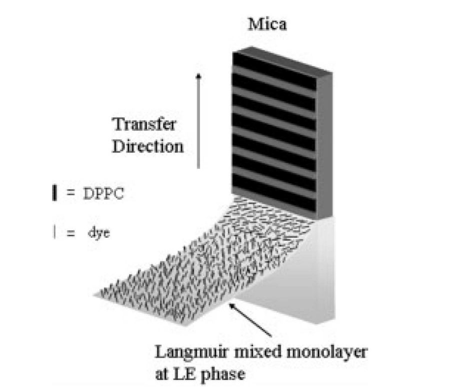


Figure: Stripe pattern [2]

Thin liquid films

Navier-Stokes equation

$$\varrho(\partial_t \vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla p + \vec{F}$$

- $\vec{F}$ is conservative force ($\vec{F} = -\nabla\phi$)
- fluid assumed to be incompressible ($\nabla\vec{v} = 0$)
- $\vec{v} = (u, w) = (v_x, v_z)$

with generalized pressure $P = p + \phi$:

$$\varrho(\partial_t \vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla P$$

Thin liquid films

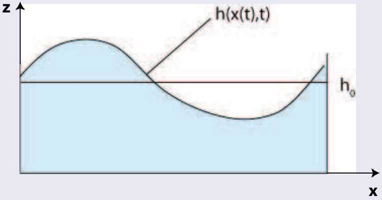
Navier-Stokes equation

$$\varrho(\partial_t \vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla p + \vec{F}$$

- $\vec{F}$ is conservative force ($\vec{F} = -\nabla\phi$)
- fluid assumed to be incompressible ($\nabla\vec{v} = 0$)
- $\vec{v} = (u, w) = (v_x, v_z)$

with generalized pressure $P = p + \phi$:

$$\varrho(\partial_t \vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla P$$



$$\frac{d}{dt}h(x(t),t) \stackrel{!}{=} v_z|_h$$
$$\Leftrightarrow \partial_t h = v_z|_h - v_x|_h \partial_x h$$

Integrating the continuity equation with respect to z and using boundary condition $v_z(z=0)=0$ leads to:

$$\partial_t h = -\partial_x \int_0^{h(x,t)} v_x dz$$

Lubrication approximation

Consider cases where the length-scales (λ) of the emerging patterns are large compared to the film mean thickness (h_0). After

- introducing a small parameter $\varepsilon = h_0/\lambda$ and
- scaling

one obtains:

$$x = \frac{\varepsilon}{h_0}\tilde{x} \qquad z = h_0\tilde{z} \qquad t = \tau\tilde{t}$$
$$U_0 = \frac{\lambda}{\tau} \qquad u = \frac{\lambda}{\tau}\tilde{v_x} \qquad w = \frac{\lambda}{\tau}\varepsilon\tilde{v_z} \qquad P = \frac{\mu}{\varepsilon^2\tau}\tilde{P}$$

Dropping the "$\sim$" yields:

$$\begin{aligned} \varepsilon Re(\partial_t u + u\partial_x u + w\partial_z u) &= -\partial_x P + \varepsilon^2\partial_x^2 u + \partial_z^2 u \\ \varepsilon^3 Re(\partial_t w + u\partial_x w + w\partial_z w) &= -\partial_z P + \varepsilon^2(\varepsilon^2\partial_x^2 w + \partial_z^2 w) \end{aligned}$$

Dropping the "$\sim$" yields:

$$\begin{aligned} \varepsilon Re(\partial_t u + u\partial_x u + w\partial_z u) &= -\partial_x P + \varepsilon^2 \partial_x^2 u + \partial_z^2 u \\ \varepsilon^3 Re(\partial_t w + u\partial_x w + w\partial_z w) &= -\partial_z P + \varepsilon^2(\varepsilon^2 \partial_x^2 w + \partial_z^2 w) \end{aligned}$$

$\lim\limits_{\varepsilon \to 0}$:

$$\begin{aligned} \partial_z^2 u &= -\partial_x P \\ 0 &= \partial_z P \end{aligned}$$

$\Rightarrow P$ independent of z

$$\Rightarrow u(x,z) = f(x)z + \frac{1}{2}(\partial_x P(x))z^2$$

- Estimation of $f(x)$ by boundary conditions (e.g. $\mu \partial_z u|_h = \partial_x \gamma$)

$$
\begin{aligned}
v_x(x,z) = u(x,z) &= f(x)z + \frac{1}{2}(\partial_x P(x))z^2 \\
\partial_t h &= -\partial_x \int_0^{h(x,t)} v_x dz \\
\Rightarrow \partial_t h &= -\partial_x \int_0^{h(x,t)} (f(x)z + \frac{1}{2}(\partial_x P(x))z^2)dz
\end{aligned}
$$

Evolution equation for thin liquid films:

$$
\partial_t h = -\partial_x(\frac{1}{2}f(x)h^2 + \frac{1}{6}h^3\partial_x(P(x))
$$

Surface tension

Surface tension

- $\sigma = \frac{\Delta W}{\Delta A}$
- at the interface of a fluid the difference between the stresses is balanced by surface tension

  $$(\underline{\underline{T}}^{fl} - \underline{\underline{T}}^{a})\vec{n} = [\sigma \frac{h''(x,t)}{(1+(h'(x,t))^2)^{3/2}}]\vec{n} = \sigma\kappa\vec{n}$$

  with: $\underline{\underline{T}}^{fl}_{ij} = -P^{fl}\delta_{ij} + \varrho\mu[\frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j}]$
- $\kappa = \frac{h''(x,t)}{(1+(h'(x,t))^2)^{3/2}}$ is the local curvature
- neglecting stress due to viscous forces:

  $-P^{fl} + P^{a} = \sigma\kappa$

Surface tension

free energy

$$F(h(x)) = \sigma \int dA - p \int dV + g \int z dV$$

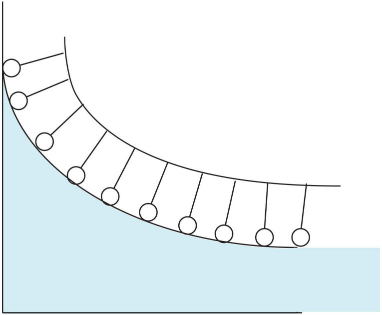
$$F(h(x)) = \sigma \int \sqrt{1 + h'(x)^2} dx - p \int dx \int_0^h dz + g \int dx \int_0^h z dz$$

Variation of functional $F(h(x)) = \int f(x, h(x), h'(x)) dx$ (see analytical mechanics)

$$\delta F = \int dx \left(-\sigma \frac{h''(x)}{(1 + h'(x))^{3/2}} - P + gh\right) \delta h \overset{!}{=} 0$$

Additional surface tension

Motivation:



- Similarity to deflection of a thin beam (see membrane-physics)

Free energy

$$F(h(x)) = \sigma_I \int dA + \sigma_{II} \int \kappa^2 dA - p \int dV + g \int z dV$$

Variation of $F(h(x))$ leads to:

$$\delta F = \int dx \delta h[-\sigma_I \frac{h''(x)}{(1+h'(x))^{3/2}} - P + gh + \underbrace{\sigma_{II} \frac{d}{dx}(2\frac{h'''(x)}{(1+h'(x)^2)^{5/2}} - 5\frac{h'(x)h''(x)^2}{(1+h'(x)^2)^{7/2}})}_{\text{additional pressure}}] \stackrel{!}{=} 0$$

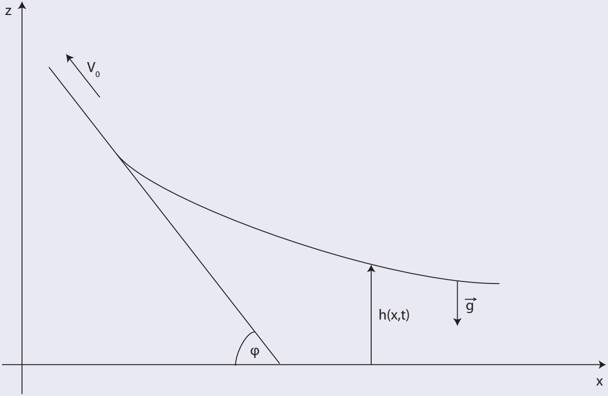


Figure: Initial situation

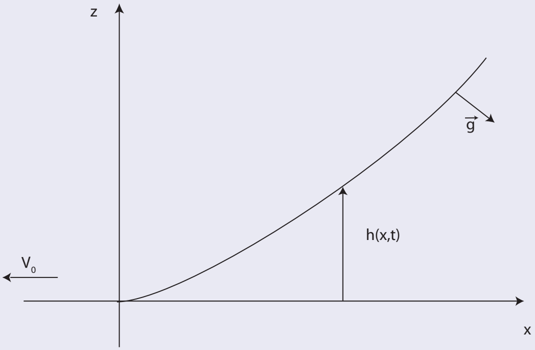
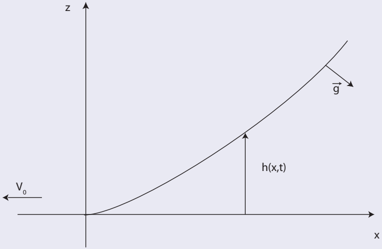


Figure: Coordinate system rotated clockwise by φ



$$\varrho(\partial_t\vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla p + \vec{F}$$
$$\vec{F} = -\nabla\phi, \quad \phi = -\varrho g \sin\varphi x + \varrho g \cos\varphi z$$
$$\vec{v} = (u, w) = (v_x, v_z)$$

- Fluid is assumed to be incompressible: $\Rightarrow \partial_x u + \partial_z w = 0$

$$\varrho(\partial_t \vec{v} + (\vec{v}\nabla)\vec{v}) - \mu\Delta\vec{v} = -\nabla P$$

Boundary conditions

$$z = 0, \quad u = -v_0, \quad w = 0$$

$$z = h, \quad \frac{dh(x,t)}{dt} = u|_{z=h}\partial_x h + \partial_t h \stackrel{!}{=} w$$

$$\underline{\underline{T}}\vec{n} = \kappa\sigma_I\vec{n} + \sigma_{II}\frac{d}{dx}\left(2\frac{h'''}{(1+h'^2)^{5/2}} - 5\frac{h'h''^2}{(1+h'^2)^{7/2}}\right)\vec{n} + \frac{\partial\sigma_I}{\partial s}\vec{t} + a\frac{\partial\sigma_{II}}{\partial s}\vec{t} + \vec{f}$$

$\vec{f} = \pi\vec{n} + \tau\vec{t}$: prescribed force at the interface

κ: local curvature

$\underline{\underline{T}}$: tension tensor of the fluid

- Navier-Stokes equation and boundary conditions are scaled and lubrication approximation is performed (analogous to thin liquid films).

Scaled equations in lubrication approximation

$$\begin{aligned} \partial_z^2 U &= -\partial_x P \\ 0 &= \partial_z P \\ \partial_t H &= -\partial_x \left(\int^H U dz \right) \end{aligned}$$

Boundary conditions provide an expression for P and $\partial_z U$, thus the evolution equation can be obtained.

Evolution equation

Rescaled evolution equation

$$\mu\partial_t h = -\partial_x\Big[-\frac{1}{3}h^3\partial_x\{-\pi - \sigma_I\partial_x^2 h - 2\sigma_{II}\partial_x^4 h + \phi|_{z=h}\} + \frac{1}{2}(\partial_x\{\sigma_I + a\sigma_{II}\} + \tau)h^2 - \mu v_0 h\Big]$$

Consider equations of type: $h_t + F(h) = 0$, with $F(h) = \nabla f(h)$ (conservative form).
Time discretization by backward Euler method:

$$h^{n+1} - h^n = -\Delta t \cdot F(h^{n+1}), \qquad h^n = h(n\Delta t)$$

Introducing $\delta = h^{n+1} - h^n$ yields:

$$\Rightarrow \delta = -\Delta t \cdot F(\delta + h^n)$$

Linearizing the right-hand side:

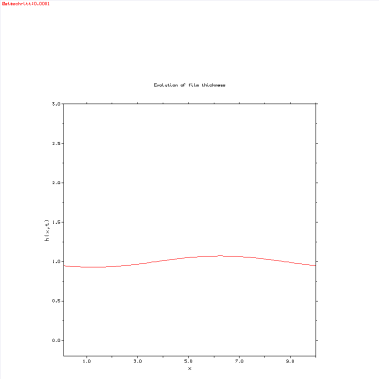
$$\Rightarrow \delta = -\Delta t \cdot (F(h^n) + F_h(h^n)\delta + O(\delta^2))$$

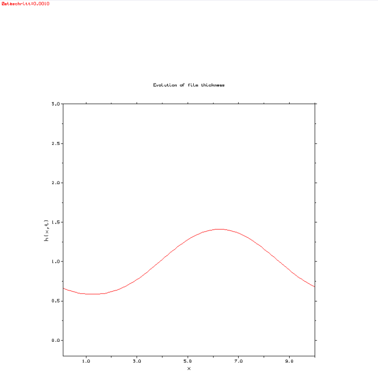
$$\delta + \Delta t \cdot F_h(h^n)\delta = -\Delta t \cdot F(h^n)$$

$\Rightarrow \delta \Rightarrow h^{n+1} = h^n + \delta$

$$\partial_t h = \partial_x[(-B_0 h^3 + \frac{BMh^2}{2(1+Bh)^2})\partial_x h] + \partial_x[h^3 \partial_x^3 h]$$

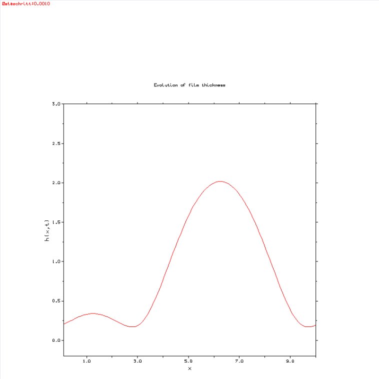
$L = 10, \quad B_0 = 0.1, \quad B = 0.1, \quad M = 25.0, \quad \Delta t = 0.001$

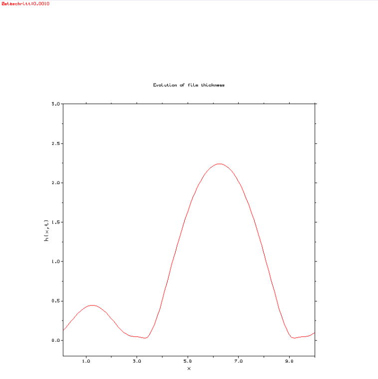




$$\partial_t h = \partial_x[(-B_0 h^3 + \frac{BMh^2}{2(1+Bh)^2})\partial_x h] + \partial_x[h^3 \partial_x^3 h]$$

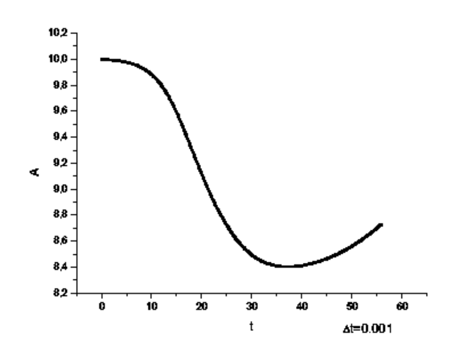
$$L = 10, \quad B_0 = 0.1, \quad B = 0.1, \quad M = 25.0, \quad \Delta t = 0.001$$





$$\partial_t h = \partial_x[(-B_0 h^3 + \frac{BMh^2}{2(1+Bh)^2})\partial_x h] + \partial_x[h^3 \partial_x^3 h]$$

$L = 10, \quad B_0 = 0.1, \quad B = 0.1, \quad M = 25.0, \quad \Delta t = 0.001$



References

Xiaodong Chen, Michael Hirtz, Harald Fuchs and Lifeng Chi,
Self-Organized Patterning: Regular and spatially tunable luminescent stripes over large areas

Michael Hirtz, *Selbstorganisierte Musterbildung von DPPC auf Plasma- und RCA-behandeltem Silizium*