Modeling thin-film free surface flow of nematic liquid crystal (NLC)

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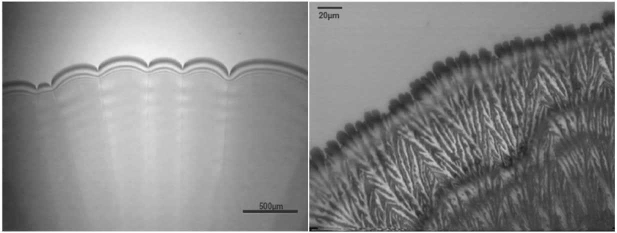
Thin NLC films exhibit intriguing behavior on many scales

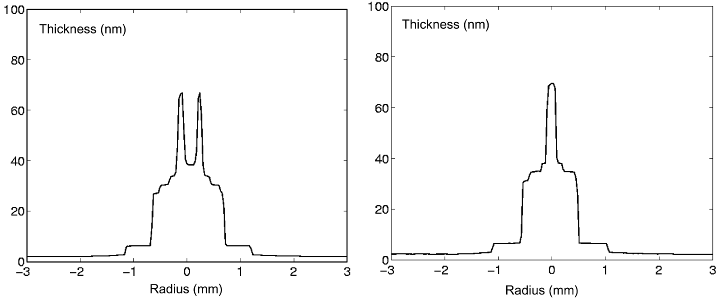
Nematic Liquid Crystal (5CB) drops ($\sim 100\mu$m height) spreading on a silicon substrate



Poulard & Cazabat, Langmuir 2005

Thin NLC films exhibit intriguing behavior on many scales

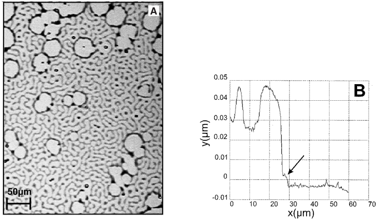
Ellipsometric profiles of very thin nematic droplets on silicon



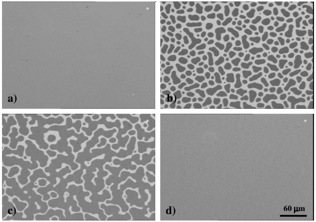
Bénichou *et al.*, Adv. Coll. Int. Sci., 2003

Thin NLC films exhibit intriguing behavior on many scales

"Ultrathin" films ($\sim$ 40nm) of 5AB$_4$ and 5CB dewetting after coating uniformly onto silicon wafers



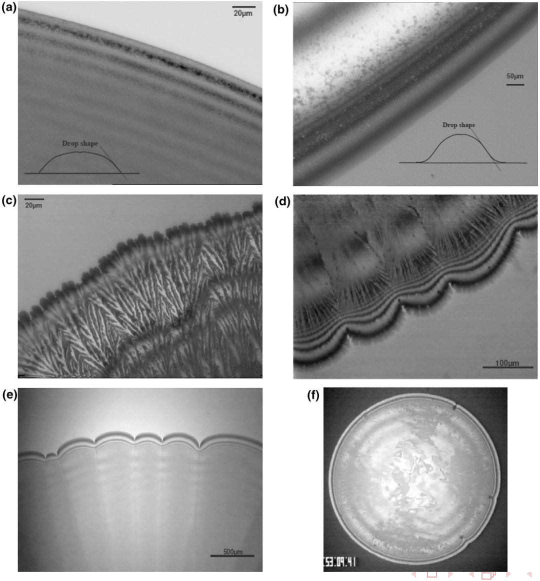
Herminghaus *et al.*, Science 1998



van Effenterre *et al.*, PRL 2001

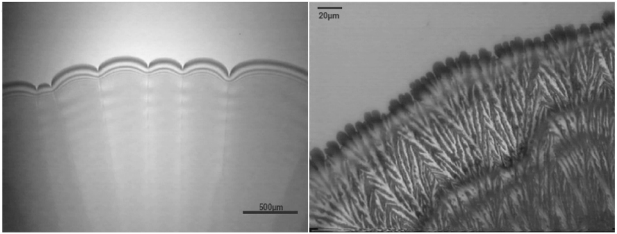
Many external factors influence outcome

6272 *Langmuir, Vol. 21, No. 14, 2005* *Poulard and Cazabat*



This talk:

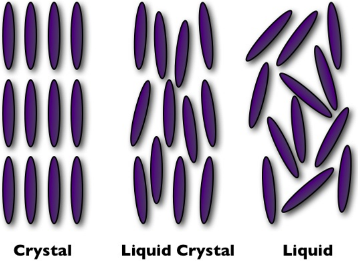
- Spreading nematic films and droplets: Discuss experiments, modeling & simulations, in various "thin film" flow scenarios.
- Systematic asymptotic derivation of simplified models for free surface 3D flow of these complex materials.
- Motivation: Can we predict and explain spontaneous instabilities?



Poulard & Cazabat, Langmuir 2005

Nematic liquid crystals: complex fluids

- Liquid crystals: "orientationally ordered soft matter" – substances with orientational, but not positional, order.



- Nematics typically composed of long, rod-like molecules. Due to electrostatic interactions they like to align with their neighbors – though they flow, they also have elastic character.

Dynamic modeling of nematic liquid crystals (NLCs)

- Use Ericksen-Leslie formulation.
- Rod-like molecules that align locally – modeled by director field $\mathbf{n}(\mathbf{x}, t)$ (unit vector; local average direction of molecules).
- $\mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, $\theta(\mathbf{x}, t)$, $\phi(\mathbf{x}, t)$.
- As for fluids, velocity field $\mathbf{v}(\mathbf{x}, t)$.
- Evolution of $\mathbf{n}$ determined by elastic stresses within NLC, by local flow, and by any external fields.
- Neglect inertia from the outset.
- Surface effects very important – molecules have a preferred orientation at an interface (anchoring) – can be modeled by a surface energy that is minimized at the appropriate director orientation.

Governing equations: Flow (no inertia)

$$-\frac{\partial \pi}{\partial x_i} + G_k \cancel{\frac{\partial n_k}{\partial x_i}} + \frac{\partial \sigma^V_{ij}}{\partial x_j} = 0 \qquad \text{Momentum}$$

$$\nabla \cdot \mathbf{v} = 0 \qquad \text{Incompressibility}$$

where $\pi = p + W + \rho g z$; $G_k = -\gamma_1(\dot{n}_k - \omega_{kj} n_j) - \gamma_2 e_{kj} n_j$,

$$2W = K_s(\nabla \cdot \mathbf{n})^2 + K_t(\mathbf{n} \cdot \nabla \wedge \mathbf{n})^2 + K_b((\mathbf{n} \cdot \nabla)\mathbf{n}) \cdot ((\mathbf{n} \cdot \nabla)\mathbf{n})$$

viscous stress σ^V_{ij} is defined by

$$\sigma^V_{ij} = \alpha_1 n_k n_p e_{kp} n_i n_j + \alpha_2 N_i n_j + \alpha_3 N_j n_i + \alpha_4 e_{ij} + \alpha_5 e_{ik} n_k n_j + \alpha_6 e_{jk} n_k n_i$$

$$N_i = \dot{n}_i - \omega_{ik} n_k, \quad e_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \quad \omega_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i}\right)$$

and α_i and γ_i are viscosities.

Governing equations: Flow (no inertia)

$$-\frac{\partial \pi}{\partial x_i} + \frac{\partial \sigma_{ij}^{V}}{\partial x_j} = 0 \qquad \text{Momentum}$$

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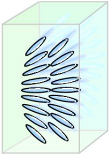
and α_i are viscosities.

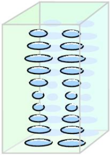
Elastic energy: Splay, twist and bend

$$2W = K_s(\nabla \cdot \mathbf{n})^2 + K_t(\mathbf{n} \cdot \nabla \wedge \mathbf{n})^2 + K_b((\mathbf{n} \cdot \nabla)\mathbf{n}) \cdot ((\mathbf{n} \cdot \nabla)\mathbf{n})$$

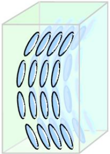
Splay



Twist



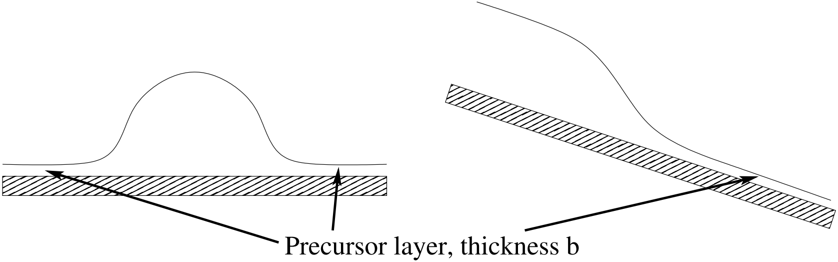
Bend



- Positive definite; minimized globally when distortion-free.
- Simplifies if elastic constants equal: $K_s = K_t = K_b = K$

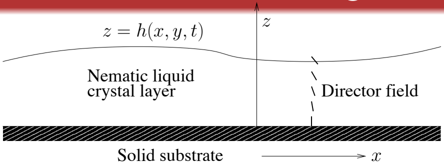
$$2W = K[(\nabla \cdot \mathbf{n})^2 + (\mathbf{n} \cdot \nabla \wedge \mathbf{n})^2 + ((\mathbf{n} \cdot \nabla)\mathbf{n}) \cdot ((\mathbf{n} \cdot \nabla)\mathbf{n})]$$

Physical set-up



We consider a 3D droplet or film, spreading on (and down) a substrate. To avoid issues with the well-known contact line singularity we assume the presence of a very thin precursor layer at the spreading edge.

Horizontal substrate: Thin film scalings



- Thin film (aspect ratio $\delta \ll 1$) so use "lubrication" scalings:

$$(x,y,z) = L(\tilde{x},\tilde{y},\delta\tilde{z}),\ (u,v,w) = U(\tilde{u},\tilde{v},\delta\tilde{w}),\ t = \frac{L}{U}\tilde{t},\ p = \frac{\mu U}{\delta^2 L}\tilde{p}$$

- Viscosity scale here is $\mu = \alpha_4/2$.
- Elastic energy scales as $W = \frac{K}{\delta^2 L^2}\tilde{W}$.
- Provided $\frac{\delta\mu UL}{K} \ll 1$, energy equation decouples, reducing to standard Euler-Lagrange minimization (w.r.t. variations in director angles θ, ϕ) – regime in which fluid flows on a slow timescale and director "instantaneously" adjusts to geometry as drop spreads.

Energy minimization & anchoring

- In thin film regime $(\delta \ll 1,\ \frac{\delta^2 \rho U L}{\mu} \ll 1,\ \frac{\delta \mu U L}{K} \ll 1)$

$$2W = \theta_z^2 + \phi_z^2 \sin^2\theta + O(\delta).$$

- Euler-Lagrange gives bulk equations

$$\theta_{zz} = \frac{\phi_z^2}{2}\sin 2\theta,$$
$$\left(\phi_z \sin^2\theta\right)_z = 0.$$

- On substrate $z = 0$ impose strong planar anchoring $\theta = \pi/2$, $\phi = \phi_0(x, y)$. (Fixed in practice by surface treatment.)
- At free surface $z = h$ impose conical anchoring on ϕ $(\phi_z = 0)$ and weak homeotropic anchoring on θ.

Energy minimization & anchoring: Free surface

- Anchoring energy at free surface independent of azimuthal angle ϕ (conical anchoring):

$$\phi_z = 0 \quad \text{on } z = h \quad \Rightarrow \quad \phi \equiv \phi_0(x, y).$$

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- θ then linear in z: $\theta = a(x, y, t)z + \pi/2$.
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$$ah = -\frac{\pi}{2}$$

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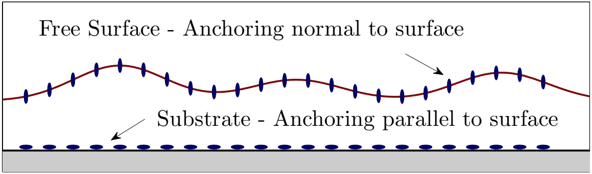
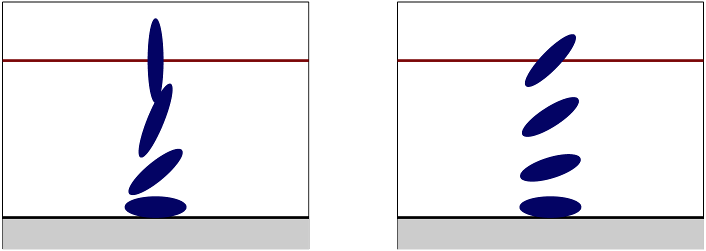
- Director can bend through angle $\pi/2$ for a thick film, but not for very thin films.

$$ah \neq -\frac{\pi}{2}$$

-

Film height & anchoring: schematic





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for some $m(h)$ monotone increasing, $m(\infty) = 1$, and $m(h) \to 0$ as we approach precursor. E.g.

$$m(h) = \frac{(h-b)^2}{\beta^2 + (h-b)^2}$$

- $0 < b \ll 1$ is precursor thickness; $\beta > 0$ is anchoring relaxation length.

Relation to surface energy

More conventional approach is to specify a surface energy $\mathcal{G}$, dependent on the director angle at the free surface $\hat{\theta} = \theta|_{z=h(x,y,t)}$, with minimum at $\hat{\theta} = 0$. A common form is $\mathcal{G}(\hat{\theta}) = \mathcal{A}\sin^2\hat{\theta}$ (Rapini-Papoular).

- Our approach is equivalent: can infer surface energy $\mathcal{G}$ in terms of $m(h)$.
- Can show that the choice

  $$m(h) = \frac{(h-b)^2}{\beta^2 + (h-b)^2}$$

  corresponds to a surface energy $\mathcal{G}(\hat{\theta})$ in good agreement to Rapini-Papoular.
- Easier to work with $m(h)$ though since it gives director angle explicitly in terms of film height: $\theta(h(x,y,t),z)$.

Now deal with momentum equations

- Leading order momentum balance: $\frac{\partial}{\partial x}(p + \tilde{\mathcal{N}} W) \sim \frac{\partial t_{13}}{\partial z}$, $\frac{\partial}{\partial y}(p + \tilde{\mathcal{N}} W) \sim \frac{\partial t_{23}}{\partial z}$, $\frac{\partial p}{\partial z} = -\mathcal{B}$, where $\tilde{\mathcal{N}} = \frac{K}{\mu U L}$, $\mathcal{B} = \frac{\delta^3 \rho g L^2}{\mu U}$, and only the leading-order terms in t_{13}, t_{23} are understood.
- Zero velocity conditions on substrate $z = 0$.
- Impose normal stress balance at free surface.
- Surface energy gradients due to anisotropic contribution (weak anchoring) balance tangential stress.

Derivation of governing equation

Also have kinematic condition which yields flux conservation

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}\left(\int_0^{h(x,y,t)} u\,dz\right) + \frac{\partial}{\partial y}\left(\int_0^{h(x,y,t)} v\,dz\right) = 0$$

Strategy:

- Solve for p (using normal stress b.c.), substitute into x- and y-momentum eqns.
- Solve for u, v as nonlinear functions of director angles $\theta(h,z)$, $\phi_0(x,y)$ using tangential stress b.c.s.
- Substitute in above and simplify to obtain . . .

4th order nonlinear PDE for free surface evolution

$$\frac{\partial h}{\partial t} + \nabla \cdot \left[h^3 \tilde{\nabla} \cdot \left(\mathcal{C} \nabla^2 h - \mathcal{B} h \right) + \mathcal{N} \left(h m m' - m^2 \right) \tilde{\nabla} h \right] = 0$$

with

$$\mathcal{B} = \frac{\delta^3 \rho g L^2}{\mu U,} \quad \mathcal{C} = \frac{\delta^3 \gamma_h}{\mu U}, \quad \mathcal{N} = \frac{\pi^2}{4} \frac{K}{\mu U L}, \quad m(h) = \frac{(h-b)^2}{\beta^2 + (h-b)^2}$$

$$\tilde{\nabla} = \left(\lambda I + \nu \begin{bmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{bmatrix} \right) \cdot \nabla$$

- $\mathcal{C}$, $\mathcal{B}$ are usual inverse capillary and Bond numbers (assigning values fixes length and time scales; $\mathcal{C} = \mathcal{B} = 1$ throughout).
- $\mathcal{N}$ is an inverse Ericksen number, β is dimensionless anchoring relaxation lengthscale; $\lambda > \nu > 0$ (related to viscosities).
- $\tilde{\nabla}$ operator captures effect of substrate anchoring patterns.

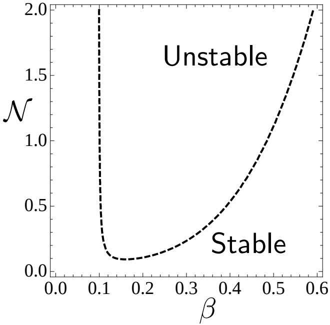
Curiously, weak anchoring needed for instability

$$\frac{\partial h}{\partial t} + \nabla \cdot \left[h^3 \tilde{\nabla} \cdot \left(\mathcal{C} \nabla^2 h - \mathcal{B} h \right) + \mathcal{N} \left(h m m' - m^2 \right) \tilde{\nabla} h \right] = 0$$

$$\mathcal{N} = \frac{\pi^2}{4} \frac{K}{\mu U L}, \qquad m(h) = \frac{(h-b)^2}{\beta^2 + (h-b)^2}$$

- Strong anchoring: $m(h) \equiv 1$, or $\beta \to 0$ in $m(h)$. This leads to a purely diffusive contribution (always stable).
- Analysis complicated in general, but linear stability of flat film $h = h_0$ leads to prediction of unstable regions of parameter space and fastest-growing wavelength.

LSA of flat film $h = h_0 = 0.25$: $\mathcal{C} = \mathcal{B} = 1$, $b = 0.1$



Perturbations $\propto \exp(ikx + \omega t)$ to $h = h_0$ have dispersion relation

$$\omega = -h_0^3[\mathcal{C}k^4 + (\mathcal{B} - \mathcal{N}M(h_0))k^2], \; M(h) = \frac{m(h)}{h^3}(hm'(h) - m(h))$$

hence instability where $M(h_0) > \mathcal{B}/\mathcal{N}$. This analysis provides a good guide for stability of initially-flat 'droplets'.

Unstable 2D droplet: $b = \beta = 0.1, \mathcal{N} = 1$

$h_0 = 0.24$

$h_0 = 0.2$

3D simulations: Simple test case: ϕ constant

To investigate influence of variable substrate anchoring $\phi(x, y)$, compare governing equation for different unidirectional anchoring patterns (with flow only in y-direction).

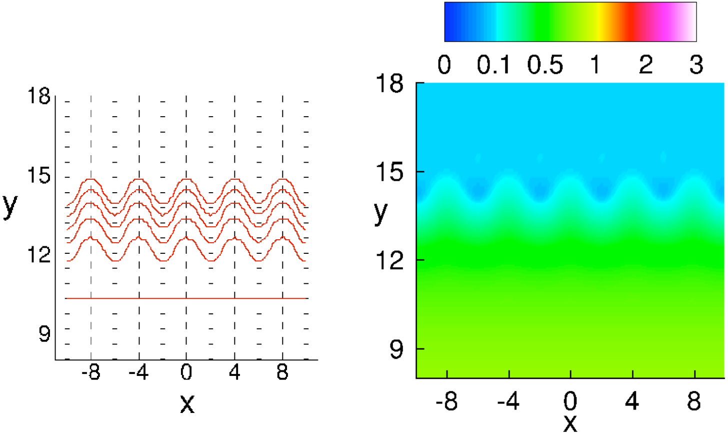
$$\phi \equiv \pi/2: \quad h_t + (\lambda + \nu)\frac{\partial}{\partial y}\left[h^3\left(h_{yyy} - h_y\right) + \mathcal{N}\left(hmm' - m^2\right)h_y\right] = 0$$

$$\phi \equiv 0: \quad h_t + (\lambda - \nu)\frac{\partial}{\partial y}\left[h^3\left(h_{yyy} - h_y\right) + \mathcal{N}\left(hmm' - m^2\right)h_y\right] = 0$$

Difference here appears only in the timescale – spreading is faster in first case with flow parallel to director orientation.

3D test case: ϕ piecewise constant.

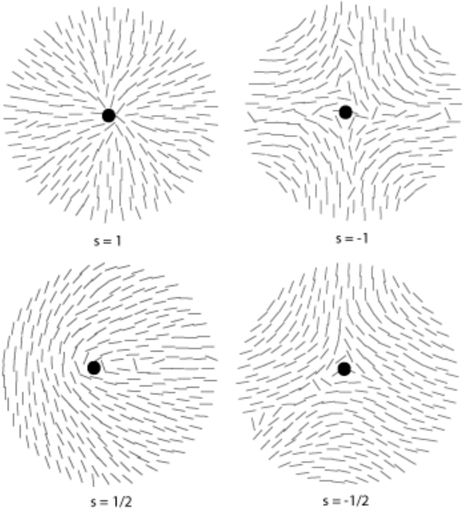
Simple substrate anchoring pattern: Stripes



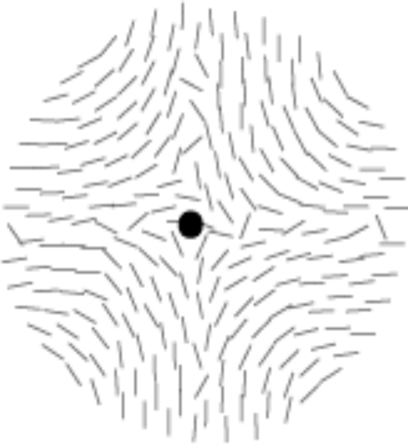
Another possible mechanism for flow patterns to emerge?
Note the absence of any capillary ridge – not unstable.

3D “defect” patterns

Study evolution with various anchoring patterns imposed on the substrate (specify $\phi_0(x, y)$ appropriately)



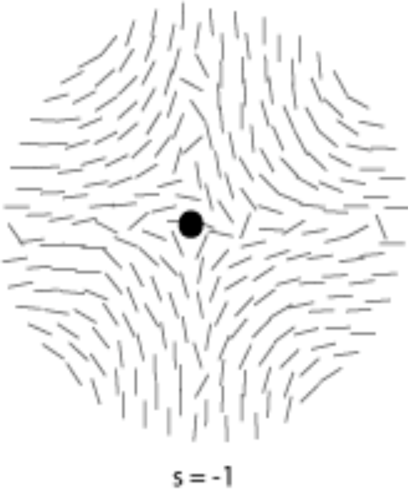
Stable simulation



s = -1

$\mathcal{N} = 1, \beta = 0.1,\ h_0 = 0.24.$

Unstable simulation



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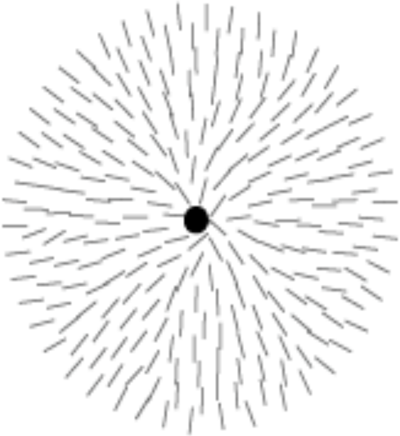
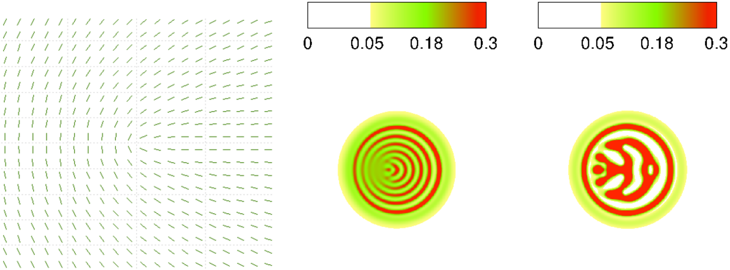


$s = 1$

$\mathcal{N} = 1, \beta = 0.1, \ h_0 = 0.24.$

Unstable simulation



$$\mathcal{N} = 10, \beta = 0.1,\ h_0 = 0.2.$$

Horizontal spreading: key points

- Sufficiently thin spreading films/drops of NLC can be unstable when there is a difference in preferred anchoring angles at surfaces, and anchoring is weak.
  - Predicted wavelength of maximum growth is a few tens of μm for experimentally-appropriate parameters (Poulard & Cazabat) – qualitatively correct.
  - Model suggests that increasing $\mathcal{N} \propto K/\gamma^{3/2}$ makes a drop more unstable – in line with experimental evidence, which suggests that $\mathcal{N}$ increases with humidity.
- What about flow on an incline, where fingering is also anticipated?

Inclined substrate

Governing equation modified for substrate inclined at angle χ:

$$\frac{\partial h}{\partial t} + \nabla \cdot \left[h^3 \tilde{\nabla} \cdot \left(\mathcal{C}\nabla^2 h - \mathcal{B}_c h\right) + \mathcal{N}\left(hmm' - m^2\right)\tilde{\nabla} h\right] + \mathcal{B}_s \mathcal{L}(h^3) = 0$$

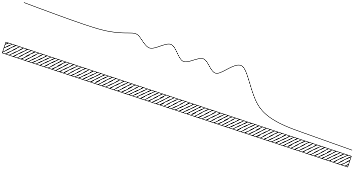
where

$$\mathcal{N} = \frac{\pi^2}{4}\frac{K}{\mu U L}, \; \mathcal{B}_c = \mathcal{B}\cos\chi, \; \mathcal{B}_s = \mathcal{B}\sin\chi, \;\; m(h) = \frac{(h-b)^2}{\beta^2 + (h-b)^2}$$

$$\tilde{\nabla} = \left(\lambda I + \nu \begin{bmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{bmatrix}\right) \cdot \nabla$$

$$\mathcal{L} = [\lambda + \nu\cos 2\phi]\partial_x + \nu \sin 2\phi \partial_y + 2\nu[\phi_y \cos 2\phi - \phi_x \sin 2\phi]$$

2D traveling fronts



- When anchoring $\phi(x, y)$ is parallel to the flow direction ($\phi = 0$) 2D traveling waves exist: $h(x, t) = H(x - Vt)$ with $h \to b$, h_0 as $x \to \pm\infty$; $V = \mathcal{B}_s(h_0^2 + h_0 b + b^2)$.
- By analogy with Newtonian case we expect instability to transverse perturbations.
- But, recalling results for horizontal film, can such traveling waves also be unstable to streamwise perturbations? Yes.

Streamwise stability of traveling fronts

- Can analyze stability of the traveling wave behind the front by linearizing about the simplest traveling wave: the flat film $h = h_0$ in steady shear: unstable whenever

$$\mathcal{N}(h_0 m(h_0) m'(h_0) - m(h_0)^2) > h_0^3 \mathcal{B}_c$$

- But can say more. The linear PDE satisfied by small perturbations may be transformed to the linearized symmetric Kuramoto-Sivashinsky equation, about which much is known.
- In particular, the fate of an initially-localized wave packet or disturbance on the traveling film is known: in terms of our problem parameters the boundaries $x_\pm$ of such a wave packet move in time t according to [Chang et al., PRL 1995]

$$\left(\frac{x}{t}\right)_\pm = 3\mathcal{B}_s h^2 \pm 1.622\sqrt{\frac{\mathcal{N}(hmm' - m^2) - \mathcal{B}_c h^3}{\mathcal{C}h^3}}$$

Streamwise stability of traveling fronts

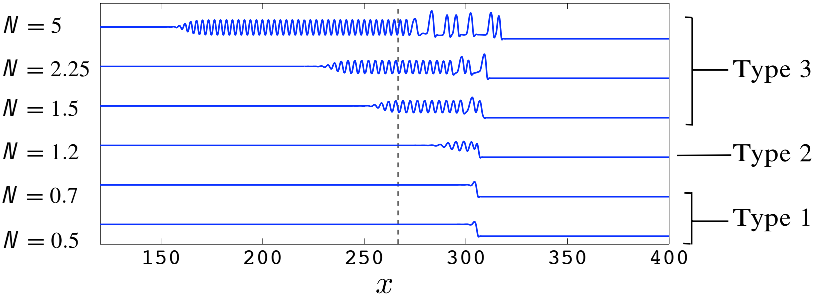
The right hand boundary of the wave-packet always moves faster than the traveling wave $V = \mathcal{B}_s(h_0^2 + h_0 b + b^2)$, but depending on parameter values, three cases may be identified for the left hand boundary:

$$\left(\frac{x}{t}\right)_- \in \begin{cases} (V,\infty) & \text{(1) Stable} \\ (0,V) & \text{(2) Convectively Unstable} \\ (-\infty,0) & \text{(3) Absolutely Unstable} \end{cases}$$

1. The entire wave packet travels faster than the front and disappears into the (stable) precursor.
2. The left-hand boundary of the packet propagates forwards, but more slowly than the wavefront, so that perturbations are always confined to the right of initial position.
3. The left-hand boundary of the packet propagates backwards, so that the entire wave is ultimately destabilized.

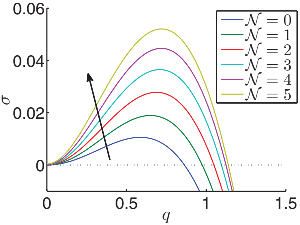
Simulations of streamwise instabilities

With other parameters fixed, as $\mathcal{N}$ increases we move from a stable 2D traveling front, to one that is convectively unstable, and finally absolutely unstable. The values of $\mathcal{N}$ at which the transitions between these instabilities occur are well-predicted by the linear analysis of the flat translating film.



3D traveling fronts: transverse instability

- As with Newtonian fluids, in a real 3D situation a traveling front is unstable to transverse perturbations of sufficiently long wavelength.
- Dependence on model parameters is complicated (linear stability requires evaluation of integrals involving the 2D traveling-wave "base state", known only numerically).



- Can predict accurately coexistence of streamwise and transverse instabilities.

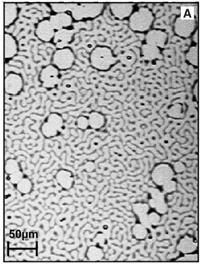
Transverse and streamwise instabilities can coexist

Conclusions & Future work

- Downslope flow of thin NLC films could exhibit interesting instability combinations (experiments?) if elasticity sufficiently strong.
- Increasing $\mathcal{N}$ amplifies the transverse instability.
- Substrate anchoring patterns in the downslope problem?
- Incorporating van der Waals' disjoining forces.

Van der Waals interactions: ongoing study

Herminghaus et al., Science, 1998
Emergence of different lengthscales in dewetting patterns.



3D dewetting simulations

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