Wetting and spreading: sharp interface models

Selected topics in between a mini-course and a workshop

Lorenzo Giacomelli
University of Rome “La Sapienza"

Foreword

These slides cover four over five lectures given in Trieste in May 07 during the informal school and workshop on wetting and friction — in fact they don't cover the "blackboard part", marked with [• • •] . The audience included physicists, engineers and mathematicians (including Sissa and Ictp Ph.D. students), more or less equally distributed.
The main goal of the lectures was to try conveying a few ideas and structures. For this reason, these slides are not to be taken as reviews. In particular, the referencing is not accurate – I apologize for that. Anyone wishing to have a reasonable picture of the literature on some particular topic, especially analytical ones, is warmly invited to contact me.

Master references (MR)

- P.G. de Gennes – Wetting: statics and dynamics – Rev. Mod. Phys. 57 (85)
- A.Oron, S.H. Davis, S.G. Bankoff – Long-scale evolution of thin liquid films – ib. 69 (97)
- P.G. de Gennes, F. Brochard-Wyart, D. Quéré – Capillarity and wetting phenomena – Springer (03)
- D. Bonn, J. Eggers, J. Meunier, E. Rolley – Wetting and spreading – preprint

Plan

I Basics

- Laplace and Young laws
- lubrication approximation
- the no-slip paradox and the ways out

II Rough surfaces

- Wenzel and Cassie-Baxter models
- A systematic study of minimizers
- metastability and contact angle hysteresis

III Dynamics of wetting

- macroscopic contact angle in a capillary flow
- droplet spreading: Tanner's law
  - slippage, long-range forces

IV Partial wetting and dewetting

- models of partial wetting
- dewetting: rupture, droplet and coarsening

V Eventually a few PDEs !

What I will not mention

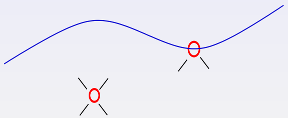
- gravity !, inertia! (MR)
- surface tension gradient (thermal gradient, surfactant) creates drag forces (“Marangoni effect") (MR, Bertozzi, Shearer, Münch, Bowen, ...)
- reactive wetting (MR)
- ...
- Three-dimensional phenomena (MR)
  - flow past a defect
  - fingering
  - ...

I. Basics

- Laplace and Young laws
- lubrication approximation
- the no-slip paradox and the ways out

The name of the game: Surface tension

- Molecular origin: liquid molecules are happier when surrounded by other liquid molecules



- Macroscopic definition: the work required to increase surface area of *dA* is proportional to the number of molecules brought to the surface, i.e. to *dA*:

$$\delta W = \gamma \, dA$$

$$\boxed{\gamma = \text{energy required to create one unit of surface area}}$$

Surface tension as a force

Γ curve on the surface
$\mathbf{t}$ tangent unit vector to Γ
$\mathbf{n}$ normal unit vector to the surface

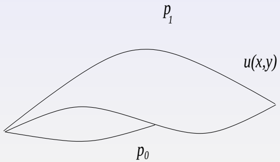
$$\gamma(\mathbf{t} \times \mathbf{n}) = \textit{force per unit length pulling the curve}$$

A Gerris Remigis (1 cm) supported by the capillary forces generated by its distorting the free surface. (John Bush)

Laplace law

- Represent the surface separating to immiscible liquids in equilibrium by a graph $u(x, y)$

[• • •]

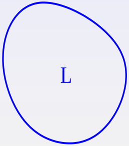


- Jump in hydrostatic pressure = $2\gamma H$:

$$\boxed{p_1 - p_0 = \gamma \operatorname{div}\left(\frac{\nabla u}{\sqrt{1+|\nabla u|^2}}\right) = 2\,\gamma\,H}$$

where H is the mean curvature of the surface, i.e. half the sum of the principal curvatures

It follows from the previous computation that, in equilibrium, L is a stationary point of



$$U = \gamma|\partial L| - p|L|$$

If we fix the mass $|L|$, then

> L is a stationary point of $E = \gamma|\partial L|$ with $|L| = \mathit{constant}$
>
> In fact it is a minimizer: L is a circle in $\mathbb{R}^2$ and a sphere in $\mathbb{R}^3$ (if ∂L is not self-intersecting, else counter-example by Wente 85)

Laplace law

In other words:

- At equilibrium, the interface between two liquids satisfies

$$H = \frac{1}{2\gamma}\Delta p = constant$$

- Volume constraint determines the radius:

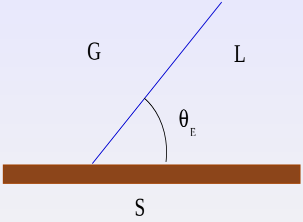
smaller drops have larger pressure inside

- “Ostwald ripening”: due to thermodynamic instability, smaller drops vanish in favor of larger ones.

Young's law

- γ_{SG}, γ_{SL} and $\gamma =: \gamma_{LG}$ defined with each pair of phases in equilibrium
- zoom into triple junction
- interface is straight

[• • •]

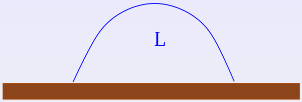


$$\boxed{\cos\theta_E = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma}} \quad \dots$$

... if possible: else $\theta_E = 0$ (=complete wetting) or $\theta_E = \pi$ (complete drying)

$$\boxed{S = \gamma_{SG} - \gamma_{SL} - \gamma \text{ = spreading coefficient}}$$

$S \geq 0$ implies complete wetting



- Neglect gravity

$$\begin{cases} \textit{minimize } E(L) = \gamma|\partial_G L| + (\gamma_{SL} - \gamma_{SG})|\partial_S L| \\ \textit{among all } L \textit{ such that } |L| = \textit{volume} \end{cases}$$

Rewrite E:

$$\begin{aligned} E(L) &= \gamma\left(|\partial_G L| - \cos\theta_E |\partial_S L|\right) \qquad (\textit{enlights } \theta_E) \\ E(L) &= \gamma\left(|\partial_G L| - |\partial_S L|\right) - S|\partial_S L| \quad (\textit{enlights } S) \end{aligned}$$

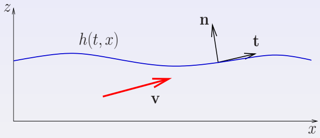
Corrections to Young's law

- θ_M= contact angle (macroscopic, i.e. measured by optical setups)
- $\theta_M \neq \theta_E$ – it can be varied by microscopically texturing the substrate (lecture II)
  - roughness
  - chemical heterogeneity
- For similar reasons, in a dynamical situation θ_M displays hysteresis effects (lecture II)
- Even on an ideal substrate, in a dynamical situation $\theta_M \neq \theta_E$ (lecture III)
  - microscopic phenomena near a moving contact line

Lubrication approximation: the systematic approach

Simplest setting:

- no external or molecular forces
- incompressible Newtonian liquid



- Navier-Stokes equations in the bulk
- at the (unknown) free interface: kinematic condition, zero shear, dynamic Laplace law

$$(T \cdot \mathbf{n}) \cdot \mathbf{n} = -p_G + \gamma H$$

- at the L/S interface: kinematic condition, no-slip (temporarily)

Lubrication approximation: the systematic approach

Separation of lengthscales X, Z, T

$$V = \frac{X}{T} \quad \textit{average horizontal velocity}$$

Three dimensionless constants:

$$\begin{aligned}
\varepsilon &= \frac{Z}{X} = \frac{\textit{vertical lengthscale}}{\textit{horizontal lengthscale}} \\
Re &= \frac{\rho V Z}{\eta} = \frac{\textit{inertial forces}}{\textit{viscous forces}} \\
Ca &= \frac{V\eta}{\gamma} = \frac{\textit{viscous forces}}{\textit{capillary forces}}
\end{aligned}$$

Lubrication approximation: the systematic approach

- At leading order in $\varepsilon \ll 1$, assuming $Re = O(1)$ and $\varepsilon^3 Ca = O(1)$,
- or in two steps: first $Re \ll 1$ (neglect inertia), then $\varepsilon \ll 1$ (separate lengthscales)

$$\boxed{3\,\eta\,h_t + \gamma\,(h^3 h_{xxx})_x = 0}$$

Lubrication approximation revisited

Sloppy derivation (see Appendix for details on the systematic one) enlighting the main features

Think of a periodic (in x) “thick" film (i.e. $E(L) = \gamma|\partial_G L|$)

- $Z \ll X$: at leading order, surface energy and rate of dissipation of kinetic energy via viscous friction read as

$$
\begin{aligned}
E(h) &= \gamma \int \left(\sqrt{1+h_x^2} - 1 \right) dx \sim \frac{\gamma}{2} \int h_x^2 \\
D &= \frac{\eta}{2} \int \int_0^h |\nabla v + (\nabla v)^T|^2 \sim \eta \int \int_0^h |u_z|^2
\end{aligned}
$$

- Energy balance: $\boxed{\partial_t E = -D}$

Lubrication approximation revisited

- Describe the film in terms of its height h and its average horizontal velocity V:

$$h_t + (hV)_x = 0, \quad V = \frac{1}{h}\int u \, dz$$

- u is a slowly modulated Poiseuille velocity profile determined by h and V:

$$\left\{ \begin{array}{l} u_{zz} = constant \\ u(z=0) = 0 \\ u_z(z=h) = 0 \end{array} \right\} \Rightarrow u = -\frac{3V}{2}\left(\left(\frac{z}{h}\right)^2 - 2\frac{z}{h}\right)$$

- Then

$$D = \eta \int \int_0^h |u_z|^2 = \int \frac{3V^2}{h}$$

Lubrication approximation revisited

- Recall: $h_t + (hV)_x = 0$
- Compute $\partial_t E$:

$$\begin{aligned} \partial_t E &= \frac{\gamma}{2}\partial_t \int h_x^2 = \gamma \int h_x h_{xt} \\ &= -\gamma \int h_{xx}\ h_t = \gamma \int h_{xx}(h\ V)_x = -\gamma \int h\ V\ h_{xxx} \end{aligned}$$

$$\boxed{\partial_t E = -D} = -\eta \int \frac{V^2}{h} \quad \text{``}\Rightarrow\text{''} \quad \boxed{3\eta V = \gamma h^2 h_{xxx}}$$

$$\boxed{3\ \eta\ h_t + \gamma\ (h^3 h_{xxx})_x = 0}$$

From liquid films to drops

- In order to extend the previous theory to the case of drops, we first need to encode

$$E(L) = \gamma\left(|\partial_G L| - |\partial_S L|\right) - S|\partial_S L|$$

- In lubrication approximation

$$E(h) \quad \sim \quad \frac{\gamma}{2}\int h_x^2\,dx - S|supp\,h|$$

- In principle, all equilibrium properties (such as γ_{SL}) should be related to molecular interaction potentials (e.g. Lennard-Jones) and should be continuous:

$$E(h) = \frac{\gamma}{2}\int h_x^2 + U(h)$$

where $U(\infty) = -S$ and $U(0) = 0$. U accounts for long-range forces (a few details in lecture III)

From liquid films to drops

Redo the previous formal argument $\boxed{\text{EX}}$ with E replaced by

$$E(h) = \frac{\gamma}{2} \int h_x^2 + U(h)$$

$$\boxed{3\, \eta\, h_t + \gamma(h^3(h_{xx} - U'(h))_x)_x = 0}$$

Same structure:

$$h_t + (hV)_x = 0, \quad V = h^2(h_x x - U'(h))_x$$

$$\partial_t E = -D := -\eta \int \frac{V^2}{h}$$

Down to $h = 0$: the no-slip paradox

- Obstruction to push lubrication approximation down to $h = 0$:
- "...not even Herackles could sink a solid" (Huh-Scriven 71, Dussan-Davis 74)
- That is, an infinite rate of energy dissipation is needed for the contact line to move – very transparent in lubrication approximation:

$$D = \int \frac{V^2}{h} = +\infty \quad \forall h'(0) \in [0, +\infty)$$

Open problem

Prove that weak solutions to the thin-film equation with no-slip don't move.

Relieving the paradox

... but liquids do spread !

- (Navier) slip condition (Greenspan, Hocking, ...)
- long-range forces and the precursor film (MR)
- diffuse interface models (Qian's lectures)
- non-Newtonian rheology (Davis, Schwartz, ...)
- black boxes (Barenblatt-Beretta-Bertsch)

- All of them introduce (at least) a microscopic lengthscale

Navier slip condition

- Navier slip condition in lubrication approximation:

$$u = b\, u_z \quad at \quad z = 0$$

- Going through the previous computations $\boxed{\text{EX}}$

$$3\eta\, h_t + \gamma\, ((h^3 + bh^2)(h_{xx} - U'(h))_x)_x = 0$$

- Energy balance:

$$\partial_t E = -\int \frac{V^2}{h + b}$$

- Traveling waves exist for any value of the “microscopic" (“mathematical") contact angle $\theta_m := h_x|_{h=0}$:

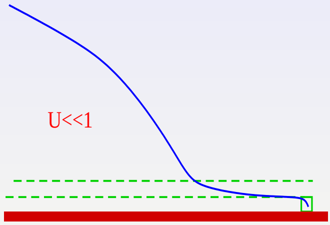
$$\begin{aligned} \theta_m = 0 \quad &\Rightarrow \quad \textit{advancing} \\ \theta_m > 0 \quad &\Rightarrow \quad \textit{both advancing and receding} \end{aligned}$$

Slip conditions

- More general forms:
  - $u = b^{3-n} h^{n-2} u_z$
  - Generalized Navier (Qian)
- Motivations:
  - Mechanical: homogeneization of surface roughness (Hocking, Jäger-Mikelic, Schweizer)
    (but roughness yields hysteresis, too...)
  - Some systems (polymer melts) display strong slippage (yielding a macroscopic protruding foot near the contact line) (MR)
  - Molecular dynamic simulations (Qian's lectures)

Precursor film

Separation of lengthscales:



We shall see in lecture III that this leads to a relatively flat precursor film, ahead of the macroscopic contact line, over which the film can spread

Experimentally observed (Hardy 19)

Power-law fluids

- Speculative: further investigations (Oldroyd) might be interesting for polymeric liquids
- Simplest constitutive equation with non-constant viscosity (Bird et al):

$$T_0 := T + pI \;=\; \eta\left(|\nabla v + (\nabla v)^T|\right)\,\left(\nabla v + (\nabla v)^T\right)$$

- $|T_0|$ increases with $|\nabla v + (\nabla v)^T|$ (i.e. $s\eta(s)\uparrow$):

$$\nabla v + (\nabla v)^T \;=\; \frac{1}{\eta(|T_0|)}\,T_0, \quad \eta(s) = \frac{s}{\overline{\eta}^{-1}(s)}, \quad \overline{\eta}(s) \;=\; s\,\eta(s)$$

Power-law fluids

- Simplest model-case: Ellis law

$$\eta_0 \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) = \left(1 + (\varepsilon |T_0|)^{p-2} \right) T_0, \quad p > 2$$

ε = threshold magnitude of T_0 such that viscosity is decreased by a factor 1/2

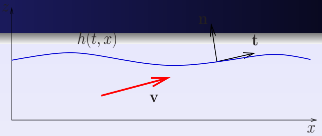
- In lubrication approximation

$$3\eta_0 h_t + \gamma (h^3 (1 + |\varepsilon h h_{xxx}|^{p-2}) h_{xxx})_x = 0$$

- Advancing t.w. ($\theta_m = 0$), advancing and receding t.w. ($\theta_m > 0$)

Appendix I

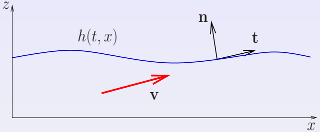
Systematic derivation of the thin-film equation



Simplest setting:

- no external forces
- incompressible Newtonian liquid
- no-slip condition

two space dimensions

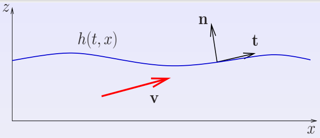


In the bulk:

- mass balance: $\operatorname{div} \mathbf{v} = 0$
- force balance: $\rho(\mathbf{v}_t + (\mathbf{v} \cdot \nabla)\mathbf{v}) = \operatorname{div} T$
- Newtonian liquid: $T = -pI + \eta(\nabla\mathbf{v} + (\nabla\mathbf{v})^T)$

$$\begin{cases} \operatorname{div} \mathbf{v} = 0 \\ \rho(\mathbf{v}_t + (\mathbf{v} \cdot \nabla)\mathbf{v}) = -\nabla p + \eta\Delta\mathbf{v} \end{cases}$$

Navier-Stokes – the L/V interface



L/G interface:

- kinematic condition:

$$h_t + \mathbf{v} \cdot \nabla(h - z) = 0$$

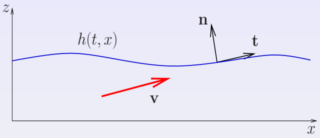
- continuity of shear stress (no shear stress in gas):

$$(T \cdot \mathbf{n}) \cdot \mathbf{t} = 0$$

- dynamic Laplace law:

$$(T \cdot \mathbf{n}) \cdot \mathbf{t} = -p_G + \gamma H$$

Navier-Stokes – the L/S interface



L/S interface:

- kinematic condition:

$$\mathbf{v} \cdot \mathbf{e}_3 = 0$$

- for the time being, no-slip condition:

$$\mathbf{v} \cdot \mathbf{e}_1 = 0$$

Lubrication approximation – Separation of lengthscales

Separation of lengthscales X, Z, T

$$V = \frac{X}{T} \quad \textit{average horizontal velocity}$$

Three dimensionless constants:

$$\begin{aligned}
\varepsilon &= \frac{Z}{X} = \frac{\textit{vertical lengthscale}}{\textit{horizontal lengthscale}} \\
Re &= \frac{\rho V Z}{\eta} = \frac{\textit{inertial forces}}{\textit{viscous forces}} \\
Ca &= \frac{V\eta}{\gamma} = \frac{\textit{viscous forces}}{\textit{capillary forces}}
\end{aligned}$$

Bulk:

$$\begin{aligned} \varepsilon\ Re\ D_t\hat{u} &= -\hat{p}_x + \varepsilon^2\hat{u}_{xx} + \hat{u}_{zz} \\ \varepsilon^3\ Re\ D_t\hat{v} &= -\hat{p}_z + \varepsilon^4\hat{v}_{xx} + \varepsilon^2\hat{v}_{zz} \\ u_x + v_z &= 0 \end{aligned}$$

- pressure normalized to retain $\hat{p}_x$ as driving force
- $Re = O(1)$
- $\varepsilon \ll 1$

$$\begin{aligned} \hat{p}_x &= \hat{u}_{zz} \\ \hat{p}_z &= 0 \\ u_x + v_y &= 0 \end{aligned}$$

Lubrication approximation – Rescaling

L/G interface:

$$\begin{aligned} \hat{h}_t + \hat{u}\hat{h}_x - v &= 0 \\ \hat{u}_z &= O(\varepsilon^2) \\ -\hat{p} + O(\varepsilon^2) &= \frac{\varepsilon^3}{Ca}\hat{h}_{xx} \qquad \left(H = \frac{\hat{h}_{xx}}{(1+\varepsilon^2\hat{h}_x^2)^{3/2}} \right) \end{aligned}$$

- Small capillary number: $\varepsilon^{-3}\, Ca = O(1)$
- Scheme may be simplified by splitting the limits:
  - first $Re \ll 1$ (evolution is slow)
  - $\varepsilon \ll 1$ (separation of lengthscales)

Lubrication approximation – Rescaled

Back to dimensional variables:

$$\textit{Bulk} \quad \begin{cases} p_x = \eta u_{zz} \\ p_z = 0 \\ u_x + v_z = 0 \end{cases}$$

$$L/G \quad \begin{cases} h_t + u h_x - v = 0 \\ u_z = 0 \\ -p = \gamma h_{xx} \end{cases}$$

$$L/S \quad u = v = 0$$

Lubrication approximation – Outcome

Solve the prevuous system $\boxed{\text{EX}}$:

$$3\eta h_t + \gamma(h^3 h_{xxx})_x = 0$$

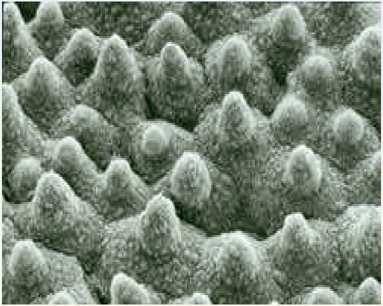
II. Rough surfaces

- Wenzel and Cassie-Baxter models
- A systematic study of minimizers
- metastability and contact angle hysteresis

Soon after the lectures, I became aware of recent, related works by L.A. Caffarelli and A. Mellet which are not mentioned hereafter

Contact angle on rough surfaces

Rough surfaces magnify the wetting properties of a system, making hydrophilic (hydrofobic) substrates even more so:



A lotus leaf: two-scale texturing

Contact angle on a rough surface

A water drop on a lotus leaf

Wenzel's model

- $R = roughness = \dfrac{real\ surface\ area}{apparent\ surface\ area} \geq 1$

[• • •]

- $$\boxed{\cos\theta_M = R\ \cos\theta_E}$$

- Captures the enhancement of wetting properties:

$$\theta_M < \theta_E \quad \text{if} \quad \theta_E < \frac{\pi}{2}$$
$$\theta_M > \theta_E \quad \text{if} \quad \theta_E > \frac{\pi}{2}$$

- ... but yields complete wetting (drying) at finite roughness

Cassie-Baxter model

- solid surface made of two species:

$$\phi_1 = \frac{\textit{surface area of 1}}{\textit{total surface area}}, \quad \phi_2 = 1 - \phi_1$$

[• • •]

$$\boxed{\cos\theta_M = \phi_1 \cos\theta_{E1} + (1 - \phi_1) \cos\theta_{E2}}$$

- In Wenzel's model, liquid fills asperities; assume instead that vapour does:

$$\boxed{\cos\theta_M = 1 - \phi_S(1 - \cos\theta_E), \quad \phi_S = \textit{fraction of solid}}$$

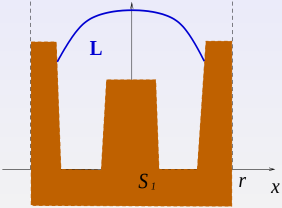
- Complete wetting (drying) reached only ideally ($\phi_S = 0$)

A systematic study of minimizers (Alberti-DeSimone)

- S_1 symmetric
- $S_\varepsilon = \{\varepsilon x : \; x \in S_1\}$
- normalized energy ($\gamma = 1$)

$$E = |\partial_V L| - \cos\theta_E \, |\partial_S L|$$

- hydrophobic case



Theorem

$$E_\varepsilon \xrightarrow{\Gamma} E_M(L) := |\partial_V L| - \cos\theta_M |\partial_S L|,$$

$$-\cos\theta_M := \inf_L \frac{1}{2r} E(L; (-r, r) \times [0, \infty)), \quad L \text{ symmetric}$$

Systematic study of minimizers – consequences

- recall: hydrophobic case

$$-\cos\theta_M := \inf_L \frac{1}{2r} E(L; (-r,r)\times[0,\infty))$$

- Roughness magnifies hydrophobicity:

$$\boxed{\cos\theta_M \le \cos\theta_E}$$

$$\begin{aligned} E(L) &= |\partial_V L| + |\cos\theta_E|\,|\partial_S L| \\ &\ge |\cos\theta_E|(|\partial_V L| + |\partial_S L|) \\ &\ge |\cos\theta_E| \quad \forall\ L \end{aligned}$$

Systematic study of minimizers – consequences

- recall: hydrophobic case

$$-\cos\theta_M := \inf_L \frac{1}{2r} E(L; (-r,r)\times[0,\infty))$$

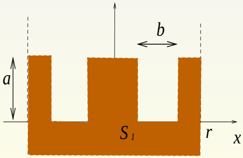
- Wenzel's is an upper bound:

$$\boxed{|\cos\theta_M| \le \frac{\partial S_1}{2r}|\cos\theta|}$$

(fill with liquid)

  - Achieved if

$$\frac{a}{b} \le \frac{1-|\cos\theta|}{2\cos\theta}$$



Systematic study of minimizers – consequences

- recall: hydrophobic case,

$$-\cos\theta_M := \inf_L \frac{1}{2r} E(L; (-r,r)\times[0,\infty))$$

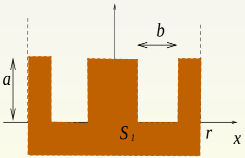
- Cassie-Baxters is an upper bound:

$$\boxed{|\cos\theta_M| \le 1 - \phi_S(|\cos\theta_E| - 1)}, \qquad \phi_S = |\partial S_1 \cap \{z = a\}|$$

(fill asperities with vapour)

  - Achieved if

$$\frac{a}{b} \ge \frac{1 - |\cos\theta|}{2\cos\theta}$$



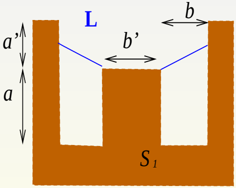
Systematic study of minimizers – consequences

- recall: hydrophobic case,

$$-\cos\theta_M := \inf_L \frac{1}{2r} E(L; (-r,r)\times[0,\infty))$$

Both not achieved if

$$\frac{a'}{b'} \le \frac{1-|\cos\theta|}{2\cos\theta} \le \frac{a}{b}$$



A systematic study of minimizers – discussion

Two experimental evidences not captured:

- a hydrophilic surface turned into a hydrophobic one
- asymmetry between hydrophobic and hydrophilic landscapes
    - metastability, hysteresis

Contact-angle hysteresis

- First exp. by Johnson-Dettre 64 (water on wax)
- moderate *R*: hysteresis increases
- large *R*: hysteresis drops, the receding contact angle increases

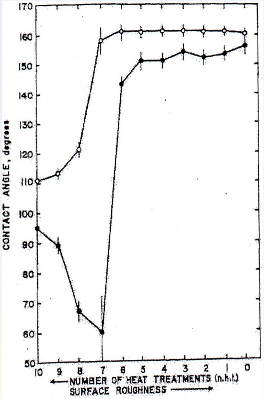


Figure 1. Water contact angles on TFE-methanol telomer wax surface as a function of roughness

○ Advancing angle
● Receding angle

Contact-angle hysteresis

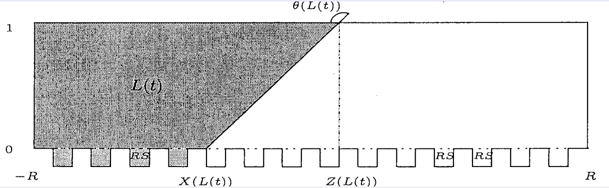
Model by DeSimone-Grunewald-Otto

- “critical loading" before system unlocks
- rate-independent model (loading at double rate yields the same response at twice the speed)

critical load: the system unlocks whenever

$$\left.\begin{array}{l} \textit{energy reduced} \\ \textit{by moving} \end{array}\right\} > \left\{\begin{array}{l} \textit{energy dissipated} \\ \textit{through the motion} \end{array}\right.$$

Contact-angle hysteresis – setting



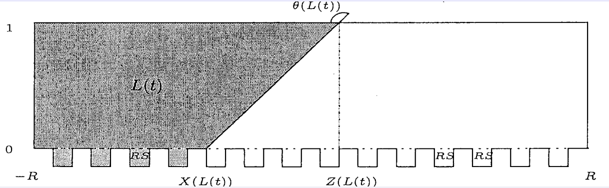
- normalized surface energy: $E(L) = |\partial_V L| - \ cos\theta_E|\partial_S L|$
- Dissipation = change in wetted solid area

  (i.e. neglect viscous dissipation, straight LV-interface)

$$diss(L,[t_0,t_1]) := \lambda \int_{-R}^{R}\int_{t_0}^{t_1}\left|\frac{d}{dt}|\partial_S L(t)|\right|$$

$\lambda > 0$ phenomenological – 0-scaling in t (rate-indep.)

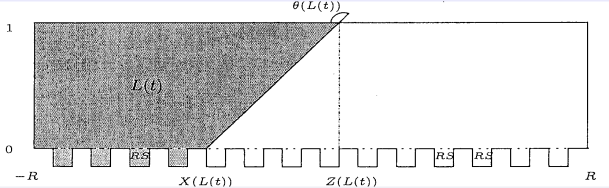
Contact-angle hysteresis – setting



- recall: $$diss(L,[t_0,t_1]) := \lambda \int_{-R}^{R}\int_{t_0}^{t_1}\left|\frac{d}{dt}|\partial_S L(t)|\right|$$
- distance between two configuration = minimal dissipation to join them:

$$\begin{aligned} dist(L_0,L_1) \quad &:= \quad inf\,\{diss(L,[0,1]);\ L(0)=L_0,\ L(1)=L_1\} \\ &\qquad \text{(monotone, rate-independent)} \\ &= \quad \lambda\int_{-R}^{R}\big||\partial_S L_1| - |\partial_S L_0|\big| \end{aligned}$$

Contact-angle hysteresis – notion of stability



- Recall: $E(L) = |\partial_V L| - \cos\theta_E |\partial_S L|$

$$dist(L_0, L) = \lambda \int_{-R}^{R} ||\partial_S L| - |\partial_S L_0||$$

- A drop L_0 is stable if

$$\begin{cases} E(L_0) - E(L) \leq dist(L_0, L) \\ among\ all\ L: \ Z(L_0) = Z(L) \end{cases}$$

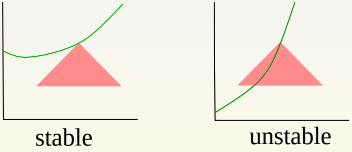
Contact-angle hysteresis – notion of stability

A drop L_0 is stable

$$\iff \begin{cases} E(L_0) - E(L) \leq dist(L_0, L) \\ among\ all\ L:\ Z(L_0) = Z(L) \end{cases}$$

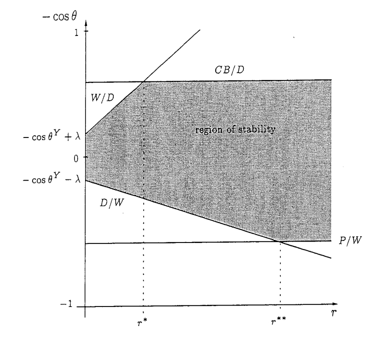
Rewrite:

$$E(L) \geq E(L_0) - dist(L_0, L)$$



Stability – Wenzel drop on a dry substrate

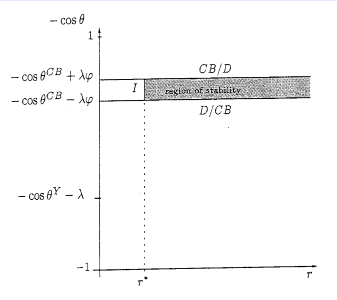
- Wenzel drop (fills pores)
- dry substrate (no L in pores)
- $\theta_E = \theta^Y > \frac{\pi}{2}$
- W/D: advance filling pores
- CB/D: advance keeping pores empty
- D/W: recede and dewet pores
- P/W: recede leaving puddles



$$\boxed{2\lambda = \text{hysteresis on a smooth substrate}}$$

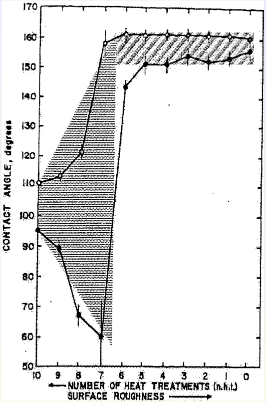
Stability – Cassie-Baxter drop on a dry substrate

- Cassie-Baxter drop (empty pores)
- dry substrate (no L in pores)
- $\theta_E > \frac{\pi}{2}$, $\varphi = \phi_S$
- CB/D: advance keeping pores empty
- D/CB: recede and dewet pores
- I: fill pores underneath



Discussion

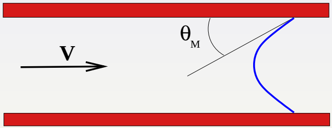
- metastability of CB-drops
- no decrease from CB to W if $-\cos\theta_E - \lambda > 0$
- tail indep. of the sign of $\cos\theta_E$ (again metastability)



III. Dynamics of wetting

Ideal surface: smooth, homogeneous (no hysteresis)

$$\boxed{\theta_M > \theta_E}$$



Dynamics of spreading – capillary tube

First experiments by Hoffmann 75 (MR)

Complete wetting, $Ca = \frac{V\eta}{\gamma}$

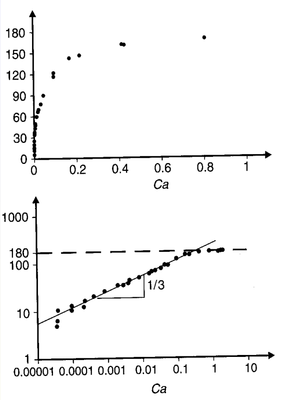
Data suggest $\boxed{\theta_M \approx V^{1/3}}$

Macroscopic force balance, $S \leq 0$:

[• • •]

$$\boxed{V \sim \frac{\gamma}{\eta}\theta_M(\theta_M^2 - \theta_E^2)\frac{1}{\log\left(\frac{R}{\ell}\right)}}$$

$\theta_M, \theta_E \ll 1$, R macroscopic lengthscale, ℓ microscopic cut-off



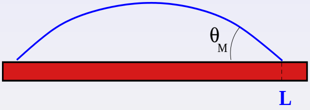
Capillary tube – discussion

- The purely macroscopic argument fails if $S > 0$:
- it would yield a dependence of θ_M on S which is (almost?) not seen in reality, in the sense that different positive S yield (almost?) the same relation between V and θ_M.
- ... we'll see where S is hidden.

Droplet spreading – complete wetting

Simplest unforced scenario:

- Droplet spreading over a smooth homogeneous substrate
- $S \geq 0$ ($\theta_E = 0$)

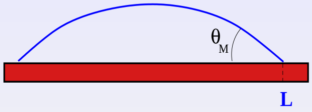


first experiments by Tanner 79:

"Tanner's law" $\boxed{\theta_M \sim t^{-3/10}}$

Droplet spreading – complete wetting

Our framework:



- two-dimensional geometry
- ideal substrate
- $S \geq 0$
- lubrication approximation ($\theta_M \ll 1$)

Our goals:

- discuss the notion of R and ℓ depending on the model
- get a scaling law for θ_M
- get an estimate for the deviation of L from the microscopic contact line (i.e. of the precursor or the foot)
- where's S ?

Two scenarios

We'll look at two scenarios in order to separate the different issues:

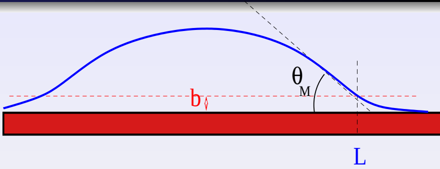
- $S = 0$, Navier slip: this will lead to an understanding of the first three issues;
- $S > 0$, long-range forces: this will also cover the fourth

Droplet spreading – Navier slip, $S = 0$

(elaboration from Cox, Hocking, de Gennes, Bertsch-DalPasso-Davis-G, G-Otto)

$$h_t + ((h^3 + bh^2)h_{xxx})_x = 0$$

$$E = \frac{1}{2}\int h_x^2, \quad \int h = \frac{4}{3}$$



- most of the mass in $(-L, L)$
- macroscopic profile in equilibrium given mass and L

$$h \sim \frac{1}{L}\left(1 - \left(\frac{x}{L}\right)^2\right)_+, \quad \theta_M \sim \frac{1}{L^2}$$

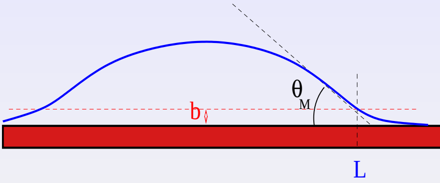
- most of the energy contained in $(-L, L)$

$$E \sim \frac{1}{L^3}, \quad \overset{\circ}{E} \sim -\frac{\overset{\circ}{L}}{L^4}$$

- simplest compatible velocity profile: $\qquad V \sim \frac{x}{L}\overset{\circ}{L}$

Energy balance ($\mathring{E} = -D$)
[• • •] yields

$$\boxed{\mathring{L} \sim \frac{\theta_M^3}{\log\left(\frac{1}{bL}\right)}}$$



and integrating [• • •] we recover Tanner's law:

$$\theta_M \sim \left(\frac{t}{\log\left(\frac{1}{b^7 t}\right)}\right)^{-2/7} \quad \text{if} \quad L_0^7 \log\left(\frac{1}{bL_0}\right) \ll t \ll b^{-7}$$

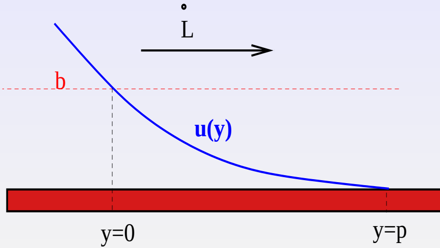
Theorem (G.-Otto 02)

These asymptotic hold true with L_0 replaced by the microscopic initial support

Droplet spreading – Navier slip $S = 0$

Rough estimate for the width of the foot

$$h_t + ((h^3 + bh^2)h_{xxx})_x = 0$$



- For $x > L$, h has a traveling wave profile u with speed $\overset{\circ}{L}$
- linearize around $u = b$ (better ones produce no change):

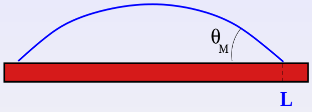
$$\begin{cases} b^2 u''' = \overset{\circ}{L} \\ u(0) = b, \ u'(0) = -1/L^2 \\ u(p) = u'(p) = 0 \end{cases} \Rightarrow \boxed{p \sim bL^2 \sim b/\theta_M}$$

Open problem

Prove the estimate for p

Droplet spreading – complete wetting

Recall our setting:



- two-dimensional geometry
- ideal substrate
- $S \geq 0$
- lubrication approximation ($\theta_M \ll 1$)

Recall our goals:

- discuss the notion of R and ℓ depending on the model
- get a scaling law for θ_M
- get an estimate for the deviation of L from the microscopic contact line (i.e. of the precursor or the foot)
- where's S ?

Digression: a few details on effective interface potentials

To understand where S is, we preliminarily need a few details on the structure of the effective interface potential U we introduced in lecture I.

Disjoining pressure

- In principle, all equilibrium properties (such as γ_{SL}) should be related to molecular interaction potentials (e.g. Lennard-Jones).
- Take a liquid pellicule of thickness e: one should have

$$\frac{\textit{energy}}{\textit{surface area}} \to \begin{cases} \gamma_{SL} + \gamma & e \uparrow +\infty \\ \gamma_{SG} & e \downarrow 0 \end{cases}$$

- Therefore, define an effective interface potential $P(e)$ such that

$$\frac{\textit{energy}}{\textit{surface area}} = \gamma_{SL} + \gamma + P(e), \quad P(e) \to \begin{cases} 0 & e \uparrow +\infty \\ S & e \downarrow 0 \end{cases}$$

- Disjoining pressure: $\quad \Pi(e) = -P'(e)$

Long-range forces

- Consider only the energy of attraction between two molecules:
$$V \sim -\frac{1}{dist^6}$$
- Integrate over volume (Israelachvili 92):
$$P(e) \sim \frac{A}{e^2} \quad e >> a$$
$a =$ molecular lengthscale, $A =$ Hamaker constant
- sign of A: positive if $S > 0$ (water on bare glass), negative if $A < 0$ (water on plastic)
- This represents the large-e tail of P – for small e, $P(e)$ reconnects to S.

The “pancake" thickness

- Equilibrium of a uniform film of finite width and height e_* (a “pancake") with the dry solid yields [• • •]

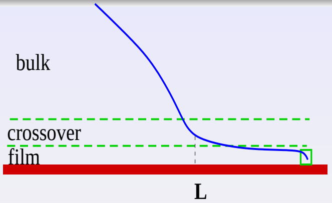
$$e_* \sim (A/S)^{1/2}$$

The larger S, the thinner the pancake (spreading is enhanced)

Droplet spreading – long-range forces, $S \geq 0$
(Hervet-deGennes '84)

$$E = \frac{1}{2}\int h_x^2 + U(h)$$

BULK



- energy is oblivious to variations of the macroscopic support ($|U'| \ll 1$):
$$\overset{\circ}{E} \sim \frac{d}{dt}\int h_x^2$$
- follow the previous approach:

$$D \sim \int_0^{L-\ell} \frac{V^2}{h} \quad \Rightarrow \quad L^6 \log\left(\frac{L}{\ell}\right) \overset{\circ}{L} \sim 1$$

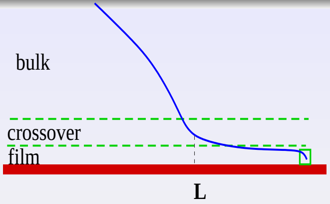
$\ell =$ microscopic horizontal lengthscale to be determined

Droplet spreading – long-range forces, $S > 0$

(Hervet-deGennes '84)

$$E = \frac{1}{2}\int h_x^2 + U(h)$$

$\boxed{\text{CROSSOVER}}$



- h has a traveling wave profile determined by $\overset{\circ}{L}$ and A:

$$\begin{cases} \overset{\circ}{L} = h^2(h'' + \frac{A}{h^3})' \\ h''(-\infty) = 0, \; h(+\infty) = 0 \end{cases}$$

  (the solution exists)

- Non-dimensionalize to infer scaling:

$$x = X\hat{x} = \frac{A^{1/2}}{(\overset{\circ}{L})^{2/3}}\hat{x}, \quad h = H\hat{h} = \frac{A^{1/2}}{(\overset{\circ}{L})^{1/3}}\hat{h}$$

Droplet spreading – long-range forces, $S \geq 0$
(Hervet-deGennes '84)

- Recall:

$$\begin{cases} \mathring{L} = h^2(h'' + \frac{A}{h^3})' \\ h''(-\infty) = 0, \ h(+\infty) = 0 \end{cases}$$

$$x = X\hat{x} = \frac{A^{1/2}}{(\mathring{L})^{2/3}}\hat{x}, \quad h = H\hat{h} = \frac{A^{1/2}}{(\mathring{L})^{1/3}}\hat{h}$$

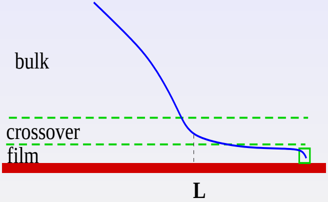
- hence, in particular,

$$\theta_M^3 \sim \left(\frac{H}{X}\right)^3 = \mathring{L}, \quad \ell \sim X = \frac{A^{1/2}}{\theta_M^2} \sim A^{1/2}L^4$$

Droplet spreading – long-range forces, $S > 0$ (Hervet-deGennes '84)

$$E = \frac{1}{2} \int h_x^2 + U(h)$$

FILM



- S determines the length p of the precursor film:

  Cut-off the crossover solution at the pancake thickness $e_* = (A/S)^{1/2}$:

$$p \sim \frac{(AS)^{1/2}}{\mathring{L}}$$

Droplet spreading – complete wetting

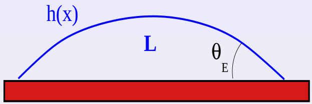
- Universality of Tanner's law, up to log corrections which depend on the model
- Most of the dissipation mechanism occurs in the transition region and in the film
- In the long-range model, we neglected dissipation *at* the microscopic contact line

Open problem

Prove Tanner law and log corrections for the long-range, $S \geq 0$ model.
Challenge: need for a self-consistent model from the bulk down to the microscopic contact line (diffuse interface ? Qian)

IV. Partial wetting and dewetting

Surface energy in partial wetting – lubrication approximation



$$E(L) = \gamma|\partial_G L| + (\gamma_{SL} - \gamma_{SG})|\partial_S L|$$

$$\frac{1}{\gamma}E(L) = |\partial_G L| - \cos\theta_E|\partial_S L|, \qquad \gamma\cos\theta_E = \gamma_{SG} - \gamma_{SL}$$

$$= |\partial_G L| - |\partial_S L| + (1 - \cos\theta_E)|\partial_S L|$$

- ∂D is the graph of h, $\dfrac{\textit{vertical lengthscale}}{\textit{horizontal lengthscale}} \ll 1$

$$E = \frac{\gamma}{2}\left(\int h_x^2\,dx + \theta_E^2|supp\ h|\right)$$

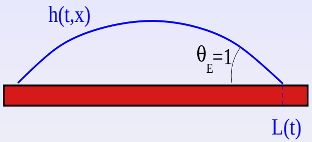
The contact angle as a Neumann condition – the static case

$$\begin{cases} \textit{minimize} \quad E = \frac{\gamma}{2}\left(\int h_x^2\, dx + \theta_E^2 |\textit{supp}\ h|\right) \\ \textit{among all } h \geq 0 \textit{ with } \int h\, dx = M \end{cases}$$

$\Rightarrow$ *h is (up to translations) the parabola with* $|h_x|_{h=0}| = \theta_E$

- mass-preserving variations in the bulk $\Rightarrow$ $h_{xx} = -C$
- one-parameter family: $h_\lambda = \frac{3M}{4\lambda}\left(1 - \left(\frac{x}{\lambda}\right)^2\right)$
- $\boxed{\text{EX}}$: $\min_\lambda E(h_\lambda)$ attained when $(h_\lambda)_x|_{h=0} = -\theta_E$

Dynamic formulations



ideal surface, $\gamma = 1$, $\theta_E = 1$

$m(h)$ =mobility ($m(h) = h^3 + bh^2$)

$$(P) \begin{cases} h_t + (m(h)h_{xxx})_x = 0 & x \in (-L(t), L(t)) \\ h = 0,\ \mathring{L} = \frac{m(h)}{h} h_{xxx} & x = \pm L(t) \end{cases}$$

No disjoining pressure: expect $\theta_M = \theta_d = 1$

Formal (but subtle) :

$$\boxed{\begin{array}{c} (P) \text{ and } \mathring{E} = -D := -\int m(h)h_{xxx}^2 \\ \Longleftrightarrow \\ (P) \text{ and } |h_x(L)| = 1 \end{array}}$$

Dynamic formulations – slippage

$$(P)\begin{cases} h_t + (hm(h)h_{xxx})_x = 0 & x \in (-L(t), L(t)) \\ h = 0,\ \mathring{L} = \frac{m(h)}{h} h_{xxx},\ |h_x| = 1 & x = \pm L(t) \end{cases}$$

Recovering the gradient-flow structure $\mathring{E} = -D$ requires:

- knowledge on the behavior of h at $x = L$ (i.e. regularity) in the classical formulation (P)
- knowledge of the metric induced by D (non Euclidean) in the corresponding weak formulation

Open problem

Existence for (P)

- $m(h) = h$: solved (Otto)
- $m(h) = h^3 + bh^2$: attacked (Bertsch-G-Karali)
- regularity of 0-c.a. solutions, $m(h) = h$: (G-Knüpfer-Otto)

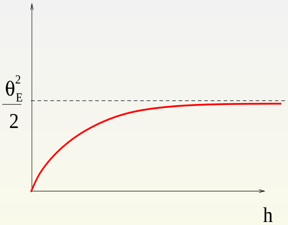
Dynamic formulations – long-range potentials

Relieve the $[E/m^2]$ discontinuity via long-range potentials

$$E = \frac{1}{2}\int \left(h_x^2 + U_0\left(\frac{h}{\varepsilon}\right)\right)$$

$$h_t + \left(m(h) \left(h_{xx} - \frac{1}{\varepsilon} U_0'\left(\frac{h}{\varepsilon}\right)\right)_x \right)_x = 0$$

- long-range forces ($A \sim \varepsilon^2$)
- allow motion via slippage: $m(h) = h^3 + bh^2$



As $\varepsilon \downarrow 0$ one recovers solutions tending to parabolas as $t \uparrow \infty$ (Bertsch-G-Karali) – contact angle ?

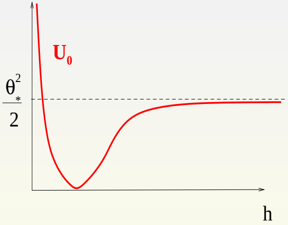
Dynamic formulation – long-short-range potentials

Phenomenological but efficient model

$$E = \frac{1}{2}\int \gamma \left(h_x^2 + U_0\left(\frac{h}{\varepsilon}\right)\right)$$

$$h_t + \left(m(h)\left(h_{xx} - \frac{1}{\varepsilon} U_0'\left(\frac{h}{\varepsilon}\right)\right)_x\right)_x = 0$$

- long range and “short range"
- establishes an ultrathin film of thickness ε (mimicks e_*)
- θ_*=equilibrium c.a. within the model



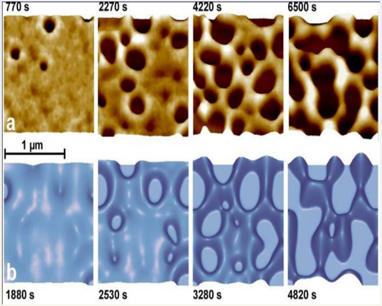
For the analytical state-of-the-art, refs. may be found e.g. in most recent papers by Grün

Dewetting – early stages

- $S > 0 \;\Rightarrow$ dewetting (Reiter 92)
- Perturb a flat film: $h = 1 + \delta e^{ikx+\lambda t}$
- Linearize: $\lambda + k^4 + \frac{1}{\varepsilon^2} \underbrace{U_0''(\frac{1}{\varepsilon})}_{<0} k^2 = 0$
- Only short-long model investigated – three timescales:
  - rupture timescale
  - droplet timescale
  - ... coarsening timescale

Dewetting: experiments and simulations

Thin (4nm) polystyrene film on an oxidized silicon substrate



Three timescales:

- rupture (mismatch)
- droplet (agree)
- coarsening (agree)

Becker-Grün-Seeman-Mantz-Jacobs-Mecke-Blossey

Understanding coarsing timescale

Rescale:

$$h_t + \left(m(h)\left(h_{xx} - U_0'(h)\right)_x\right)_x = 0$$

[• • •]

$$\boxed{\begin{array}{rcl} \textit{drops distance} & \lesssim & t^{2/5} \\ \textit{drops radius} & \lesssim & t^{1/5} \end{array}}$$

Witelski-Glasner (Grün, Bertozzi, ...)

Theorem

Rigorous (averaged) upper bounds for $m(h) = h$
(Otto-Rump-Slepcev)

Open problem

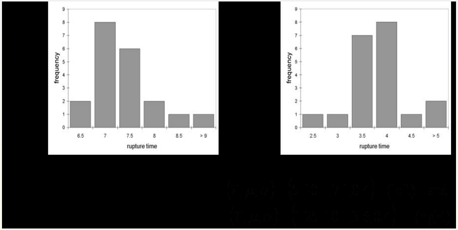
- Identify the rupture and droplet timescales
- qualify dependence on ε
- explore slippage + long-range
- explore $m(h) = h^3$

Corrections to the rupture timescale

- non-Newtonian rheology (unexplored)
- Thermal fluctuations Grün-Mecke-Rauscher

$$h_t + (h^3(h_{xx} - U'(h))_x)_x + (h^{3/2}N(x,t))_x = 0$$

mean$=0$, correlation $= 2\tau\delta(t-t')\delta_\varepsilon(x-x')$



White noise with two different intensities, (deterministic rupture time is around 13)