Behavior of a Droplet on a Thin Liquid Film

Ellen R. Peterson

Carnegie Mellon University
Department of Mathematical Sciences
Center for Nonlinear Analysis

February 23, 2012

Funded by National Science Foundation

Project Motivation

Goal: Improve treatment for Cystic Fibrosis
- use surfactant to spread medicine over mucus in lungs

Research Group:
CMU Physics: Steve Garoff, Fan Gao

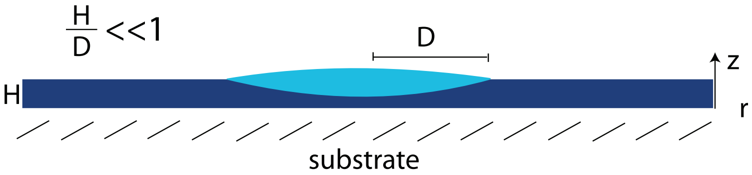
CMU Chemical Engineering:
Todd Przybycien, Robert Tilton, Roomi Kalita, Ramankur Sharma, Amsul Khanal

U. Pitt Medical Center: Tim Corcoran

Questions:

- How does the fluid spread?
- Where is the surfactant?
- How do multiple droplets interact?

Background on Spreading



Drop spreading on a solid substrate:

- Multivalued velocity profile-precursor layer:
  - Dussan, Davis (1974)
  - Bertozzi (1998)
  - Glasner (2003)
- Coarsening of droplets:
  - Otto, Rump, Slepcev (2005)
  - Witelski, Glasner (2003)

Background on Spreading Surfactant

Surfactant spreading on liquid subphase:

- Model: Gaver and Grotberg (1990)

$$h_t + \frac{1}{r}\left(\frac{1}{2}rh^2\sigma(\Gamma)_r\right)_r = \beta\frac{1}{r}\left(\frac{1}{3}rh^3 h_r\right)_r - \kappa\frac{1}{r}\left(\frac{1}{3}rh^3\left(\frac{1}{r}(rh_r)_r\right)_r\right)_r$$

$$\Gamma_t + \frac{1}{r}\left(rh\Gamma\sigma(\Gamma)_r\right)_r = \beta\frac{1}{r}\left(\frac{1}{2}rh^2\Gamma h_r\right)_r - \kappa\frac{1}{r}\left(\frac{1}{2}rh^2\Gamma\left(\frac{1}{r}(rh_r)_r\right)_r\right)_r + \delta\frac{1}{r}\left(r\Gamma_r\right)_r$$

- Asymptotic spreading behavior/similarity solutions: Jensen, Grotberg (1992), Jensen (1994)

$$h_t - \frac{1}{r}\left(\frac{1}{2}rh^2\Gamma_r\right)_r = 0 \qquad \Gamma_t - \frac{1}{r}\left(rh\Gamma\Gamma_r\right)_r = 0$$

  Similarity scaling:

$$h(r,t) = H(\xi), \quad \Gamma(r,t) = \frac{1}{t^{\frac{1}{2}}}G(\xi), \quad \xi = \frac{r}{t^{\frac{1}{4}}}$$

  Similarity solutions:

$$H(\xi) = 2\xi^2, \quad G(\xi) = -\frac{1}{8}\log\xi, \quad \xi = \frac{r}{t^{\frac{1}{4}}}$$

Numerical similarity solutions: ERP, Shearer (2012)

Equations:

$$h_t - \frac{\xi \, \dot r_0(t)}{r_0(t)} h_\xi = \frac{1}{r_0(t)^2} \left(\xi \tfrac{1}{2} h^2 \Gamma_\xi \right)_\xi$$

$$\Gamma_t - \frac{\xi \dot r_0(t)}{r_0(t)} \Gamma_\xi = \frac{1}{r_0(t)^2} \left(\xi h \Gamma \Gamma_\xi \right)_\xi$$

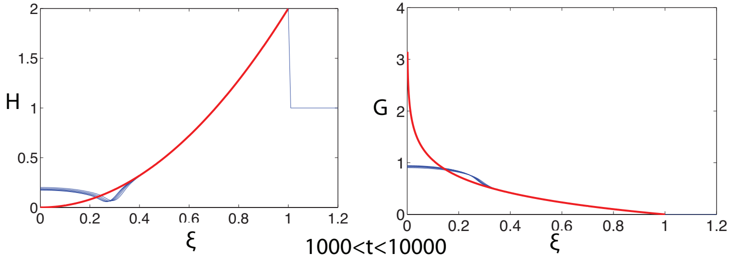
$$\dot r_0 = -\frac{1}{r_0} h(1,t) \Gamma_\xi(1,t)$$

$$\xi = \frac{r}{r_0(t)}$$

Solutions:

$$h(r,t) = H(\xi), \quad \Gamma(r,t) = \frac{1}{t^{\frac{1}{2}}} G(\xi), \quad \xi = \frac{r}{r_0(t)}$$

$$H(\xi) = 2\xi^2, \quad G(\xi) = -\frac{1}{8} \log \xi, \quad \xi = \frac{r}{t^{\frac{1}{4}}}$$

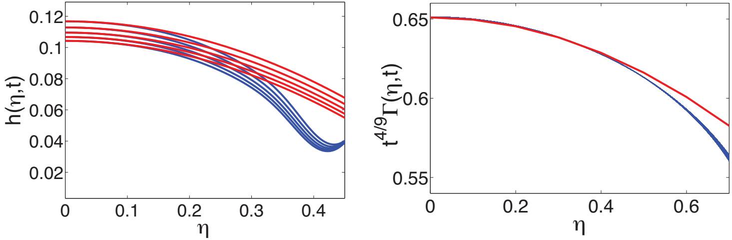


1000<t<10000

Inner Solution: ERP, Shearer (2011)

$$h(r,t) = t^{-\frac{2}{9}}\left(H_0 + \frac{1}{18G_0}\left(\frac{r}{t^{\frac{1}{6}}}\right)^2 + A\left(\frac{r}{t^{\frac{1}{9}}}\right)^2\right) + O(r^4)$$

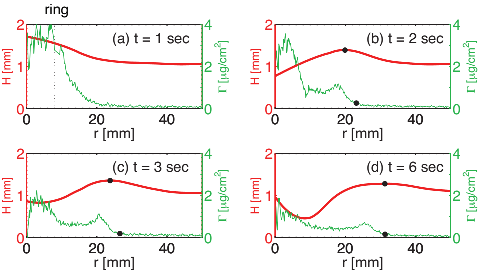
$$\Gamma(r,t) = t^{-\frac{4}{9}}\left(G_0 + \frac{\mu}{H_0}\left(\frac{r}{t^{\frac{1}{6}}}\right)^2\right) + O(r^4)$$



Experimental Goals

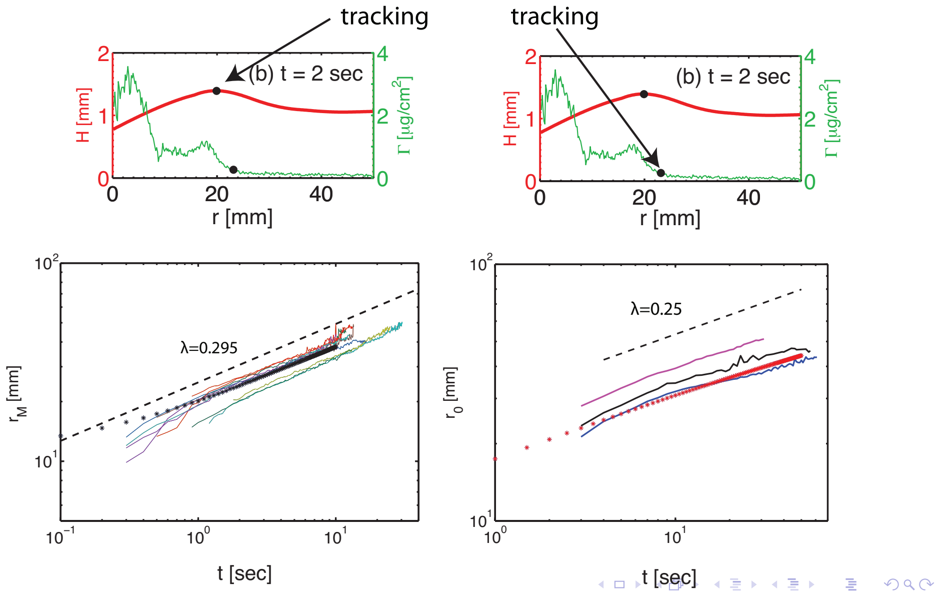
Experimental spreading:
Bull et al (1999), Fallest et al (2010)

- Visualize the height of the film (using laser line)
- Visualize the location of the surfactant (fluorescence)
- Match the experimental data to the PDE model



Karen Daniels's Lab NC State University

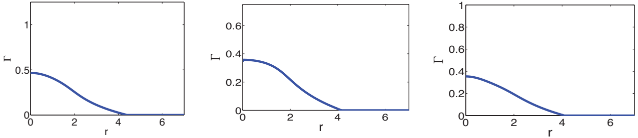
Spreading Behavior



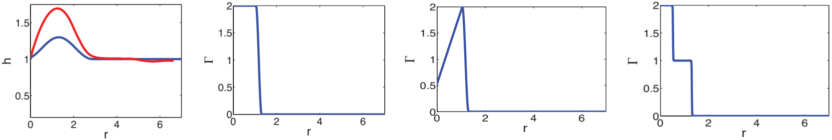
Surfactant Initial Condition

Using time scale $t = t^*$:

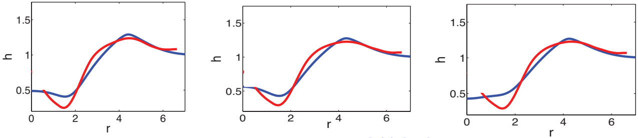
Surfactant at
t=9



Initial Conditions



Height at
t=9

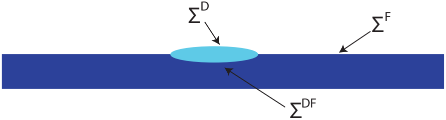


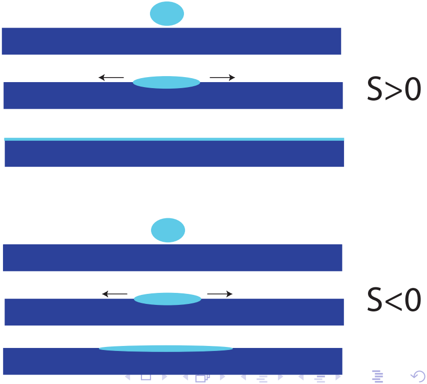
How do we predict the spreading behavior?

Spreading Parameter: (Harkins 1952)

$$S = \Sigma_F - \Sigma_{DF} - \Sigma_D$$

- **Complete spreading** $(S > 0)$
  - Spreading on a Deep Layer:
  Dipietro, Huh, & Cox, 1978; DiPietro & Cox, 1980; Foda & Cox, 1980
  - Spreading Power Law:
  Fraaije & Cazabat, 1989
- **Lens-shape** $(S < 0)$
  - Numerical axisymmetric solution, static lens :
  Pujado & Scriven, 1971

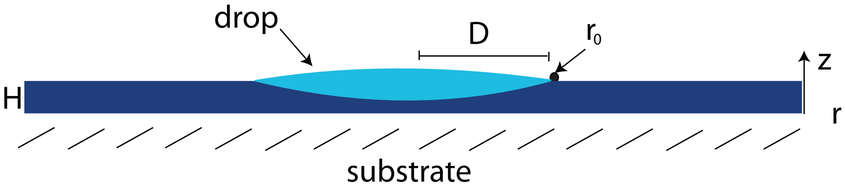




Assumptions

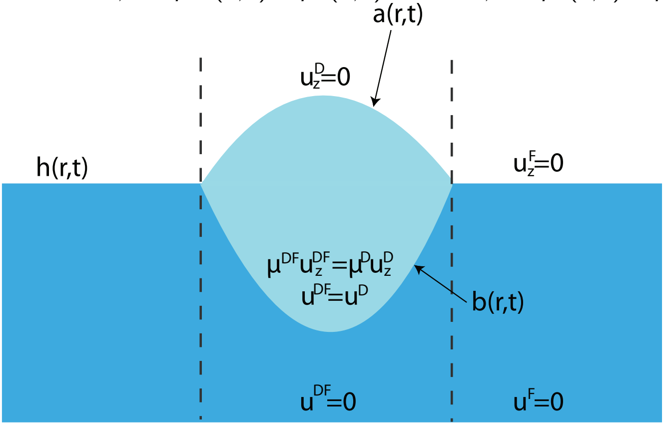
- Newtonian drop on Newtonian fluid
- Fluids immiscible
- Lubrication Approximation $\frac{H}{D} << 1$
- $S < 0$
- axisymmetric spreading

Issue: Contact Line Force Balance



Deriving Droplet Spreading Equations

$$\begin{aligned} p_r^D &= \mu^D u_{zz}^D, \\ p_z^D &= -\rho^D g, \\ p^D(a,t) &= p_{atm} - \Sigma^D a_{rr}, \end{aligned} \qquad \begin{aligned} p_r^{DF} &= \mu^{DF} u_{zz}^{DF}, \\ p_z^{DF} &= -\rho^{DF} g, \\ p^{DF}(b,t) &= p^D(b,t) - \Sigma^{DF} b_{rr}, \end{aligned} \qquad \begin{aligned} p_r^F &= \mu^F u_{zz}^F \\ p_z^F &= -\rho^F g \\ p^F(h,t) &= p_{atm} - \Sigma^F h_{rr} \end{aligned}$$



Droplet Spreading Equations - axisymmetric

$$h_t = \frac{1}{r}\left[r\left(Boh_r - \left(\frac{1}{r}(rh_r)_r\right)_r\right)h^3\right]_r$$

$$b_t = \frac{1}{r}\left[r\left(b^3\left(Bo(1-\beta)b_r - \sigma^{DF}\left(\frac{1}{r}(rb_r)_r\right)_r\right)\right.\right.$$
$$\left.\left. + \left(Bo\beta a_r - \sigma^{D}\left(\frac{1}{r}(ra_r)_r\right)_r\right)\frac{b^2}{2}(3a-b)\right)\right]_r$$

$$a_t = \frac{1}{r}\left\{r\left[\left(Bo(1-\beta)b_r - \sigma^{DF}\left(\frac{1}{r}(rb_r)_r\right)_r\right)\frac{b^2}{2}(3a-b)\right.\right.$$
$$\left.\left. + \left(\frac{1-\lambda}{\lambda}(a-b)^3 + a^3\right)\left(Bo\beta a_r - \sigma^{D}\left(\frac{1}{r}(ra_r)_r\right)_r\right)\right]\right\}_r$$

Bo: Bond number

β: density ratio

λ: viscosity ratio

σ^D: surface tension of drop and air

σ^{DF}: surface tension of drop and fluid

Equilibrium Solutions

$$Boh_r - \left(\frac{1}{r}(rh_r)_r\right)_r = 0$$

$$Bo\beta a_r - \sigma^D\left(\frac{1}{r}(ra_r)_r\right)_r = 0$$

$$Bo(1-\beta)b_r - \sigma^{DF}\left(\frac{1}{r}(rb_r)_r\right)_r = 0.$$

If $\beta \neq 1$ these equations are Bessel equations. We'll assume $\beta < 1$

$$\begin{aligned} h(r) &= C_h + C_{hh} I_0\left(\sqrt{Bo}r\right) + C_{hhh} K_0\left(\sqrt{Bo}r\right) \\ a(r) &= C_a + C_a I_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right) + C_{aaa} K_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right) \\ b(r) &= C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right) + C_{bbb} K_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right) \end{aligned}$$

Related studies: Kriegsmann & Miksis (2003), Pujado & Scriven (1971)

Boundary Conditions

Edge Conditions:

$$a_r(0,t) = 0, \quad b_r(0,t) = 0, \quad h_r(L,t) = 0$$

Continuity of Interface:

$$a(r_0,t) = h(r_0,t), \qquad b(r_0,t) = h(r_0,t)$$

Continuity of Pressure: $\left(p^{DF} = p^F|_{r=r_0}\right)$

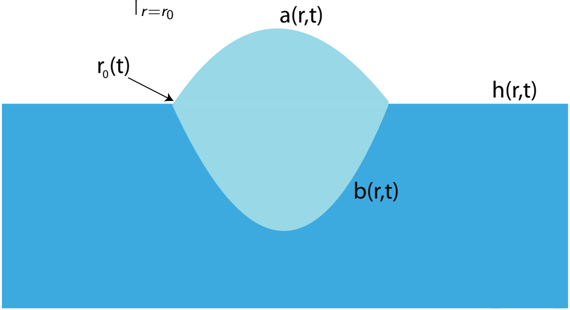
$$\Delta h - \sigma^D \Delta a - \sigma^{DF} \Delta b = 0\Big|_{r=r_0}$$

Height of Film:

$$2\pi \int_0^{r_0} b(r,t) r dr + 2\pi \int_{r_0}^{L} h(r,t) r dr = Mass_F$$

Location of $r_0(t)$:

$$Mass_D = 2\pi \int_0^{r_0} (a(r) - b(r)) r \, dr$$



Boundary Conditions

Balance of Surface Tension Forces:

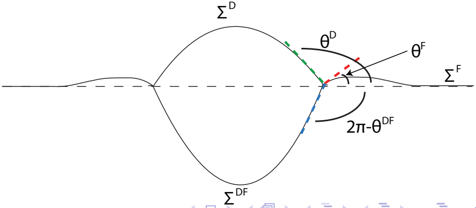
$$\Sigma^F \cos\theta^F + \Sigma^D \cos\theta^D + \Sigma^{DF} \cos\theta^{DF} = 0$$
$$\Sigma^F \sin\theta^F + \Sigma^D \sin\theta^D + \Sigma^{DF} \sin\theta^{DF} = 0$$

Apply approximations:

$$\theta^F \approx \varepsilon h_r, \qquad \theta^D \approx -\varepsilon a_r, \qquad \theta^{DF} \approx -\varepsilon b_r$$

$$\Sigma^F \left(1 + \frac{\varepsilon^2 h_r^2}{2} + \dots\right) - \Sigma^D \left(1 + \frac{\varepsilon^2 a_r^2}{2} + \dots\right) - \Sigma^{DF} \left(1 + \frac{\varepsilon^2 b_r^2}{2} + \dots\right) = 0$$
$$\Sigma^F \left(\varepsilon h_r + \frac{\varepsilon^3 h_r^3}{3} + \dots\right) - \Sigma^D \left(\varepsilon a_r + \frac{\varepsilon^3 a_r^3}{3} + \dots\right) - \Sigma^{DF} \left(\varepsilon b_r + \frac{\varepsilon^3 b_r^3}{3} + \dots\right) = 0$$

$$O(1) : 1 - \sigma^D - \sigma^{DF} = 0$$
$$\implies S \sim O(\varepsilon^2)$$
$$O(\varepsilon) : h_r - \sigma^D a_r - \sigma^{DF} b_r = 0$$
$$O(\varepsilon^2) : h_r^2 - \sigma^D a_r^2 - \sigma^{DF} b_r^2 = -2$$



Applying Boundary Conditions

Apply boundary conditions at edges of domain:

$$a_r(0,t) = 0 \qquad b_r(0,t) = 0 \qquad h_r(L,t) = 0$$

Resulting Equations:

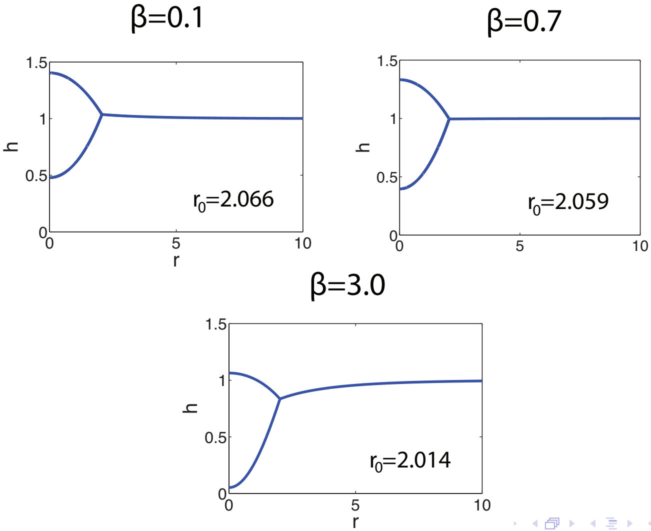
$$\begin{aligned} h(r) &= C_h + C_{hhh} K_0\left(\sqrt{Bo}\, r\right) \\ a(r) &= C_a + C_{aa} I_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}\, r\right) \\ b(r) &= C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}\, r\right) \end{aligned}$$

Find coefficients using remaining boundary conditions and conservation of mass of droplet:

$$V = 2\pi \int_0^{r_0} (a(r) - b(r)) r \, dr$$

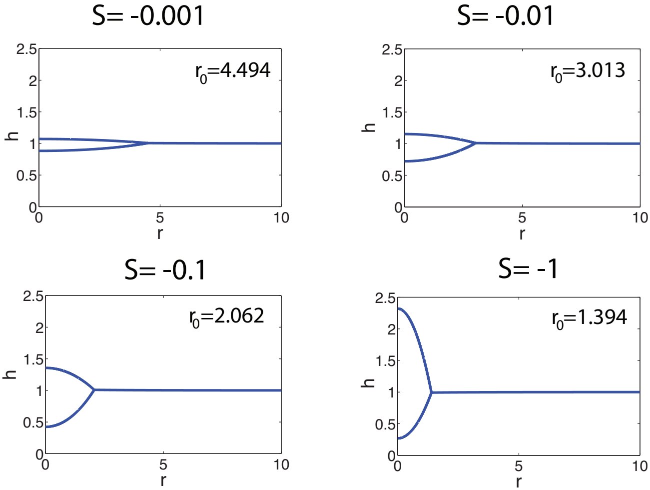
Profiles - fix S, vary β

$Bo = 0.1, \quad \sigma^D = 0.7, \quad S = -0.1$



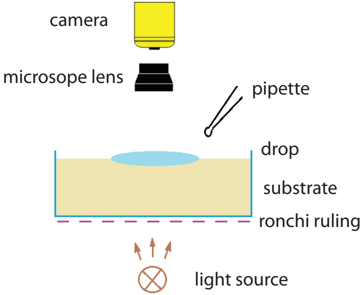
Profiles - fix β, vary S

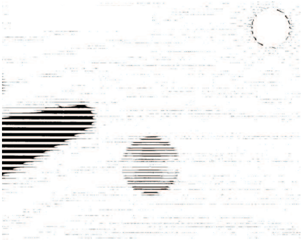
$Bo = 0.1, \quad \sigma^D = 0.7, \quad \beta = 0.5$



Evidence of a Lens - Fan Gao

- Water on Polyacrylimide
- Lens remains for over 10 minutes

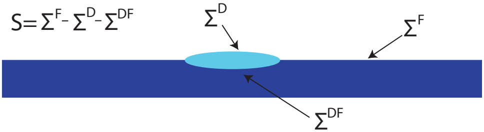




Experimental Systems

Substrate	Drop	S	See Lens??
Glycerol (75%)/water (25%)	Hexadecane	7.53	no
Glycerol(10%)/water (90%)	Hexadecane	−3.71	yes
Glycerol(75%)/water (25%)	Oleic Acid	20.18	yes
Water	Oleic Acid	32.25	yes

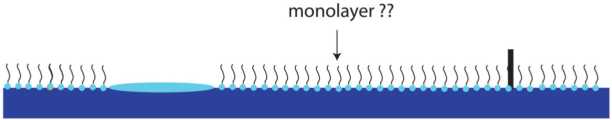
$S = \Sigma^F - \Sigma^D - \Sigma^{DF}$



Interface	Interface Type	Surface Tension (dynes/cm)
Glycerol (75%)/Air	Σ^F	63.63
Glycerol (10%)/Air	Σ^F	71.5
Water/Air	Σ^F	72.75
Hexadecane/Air	Σ^D	26.18
Oleic acid/Air	Σ^D	27.34
Hexadecane/Glycerol (75%)	Σ^{DF}	29.92
Hexadecane/Glycerol (10%)	Σ^{DF}	45.61
Oleic acid/Glycerol (75%)	Σ^{DF}	16.11
Oleic acid/Water	Σ^{DF}	13.16

Autophobing

Is fluid escaping the lens?
Will the lens spread on its own monolayer?



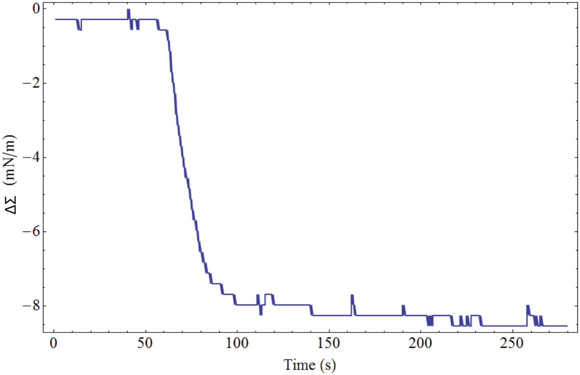
On SOLID surface:

- Langmuir (1917) - first suggested the mechanism of autophobing
- Zisman (1964) - adsorption of solution outside the bulk
- Frank & Garoff (1995) - advancement and retraction of spreading drop

Hexadecane on glycerol (75%)

Σ^F: Glycerol/Air: 63.63 dyne/cm
Σ^D:Hexadecane/Air: 26.18 dyne/cm
Σ^{DF}: Hexadecane/Glycerol: 29.92 dyne/cm

$$S = 7.53 > 0$$

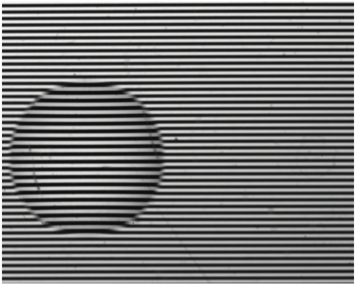


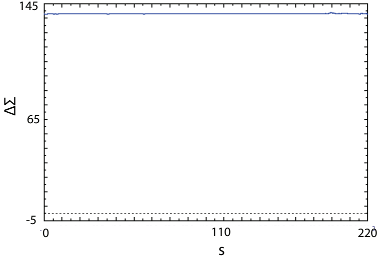
No Lens!!

Hexadecane on glycerol (10%)

Σ^F: Glycerol/Air: 65.76 dyne/cm
Σ^D:Hexadecane/Air: 26.18 dyne/cm
Σ^{DF}: Hexadecane/Glycerol: 43.29 dyne/cm

$$S = -3.71 < 0$$



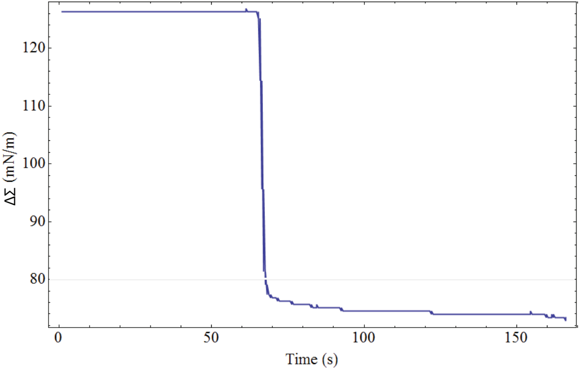


Lens!!

Oleic acid on glycerol (75%)

Σ^F: Glycerol/Air: 63.63 dyne/cm
Σ^D: Oleic acid/Air: 27.34 dyne/cm
Σ^{DF}: Oleic acid/Glycerol: 16.11 dyne/cm

$$S = 20.18 > 0 \quad (1)$$

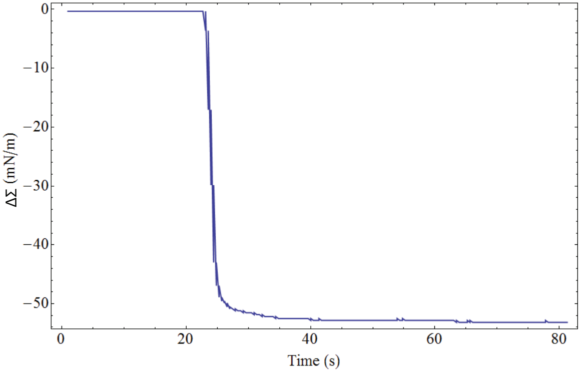


Lens!!

Oleic acid on water

Σ^F: Water/Air: 72.75 dyne/cm
Σ^D: Oleic acid/Air: 27.34 dyne/cm
Σ^{DF}: Oleic acid/Water: 13.16 dyne/cm

$$S = 32.25 > 0 \tag{2}$$



Lens!!

Comparison of spread area

System: Oleic acid spreading on Glycerol (75%)

- Original spreading parameter:

$$S = 63.63 - 27.34 - 16.11 = 20.18$$

- Allow surface tension of substrate (Σ^F) to be altered by escaping monolayer:

$$\begin{aligned} \Sigma^F &= 38.11 \text{ dyne/cm} \\ S &= 38.11 - 27.34 - 16.11 = -5.34 \end{aligned}$$

For the equilibrium solution corresponding to this altered system, find the spread area:

$$2r_0 = 1.91 - 2.22 \text{ mm (Theory)}$$
$$2r_0 \approx 1.6 - 1.72 \text{ mm (Experiment)}$$

Discussion of Thin Film Approximation

Recall the solution form:

$$
\begin{aligned}
h(r) &= C_h + C_{hh} I_0\left(\sqrt{Bo}r\right) + C_{hhh} K_0\left(\sqrt{Bo}r\right)\\
a(r) &= C_a + C_a I_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right) + C_{aaa} K_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right)\\
b(r) &= C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right) + C_{bbb} K_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right)
\end{aligned}
$$

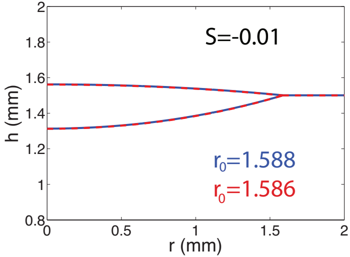
where

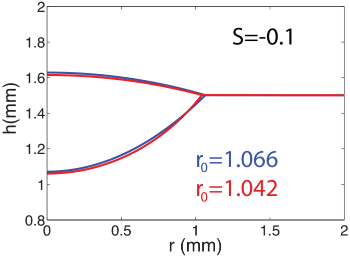
- $Bond = \frac{\rho^F g L^2}{\Sigma^F}$
- $\beta = \frac{\rho^D}{\rho^F}$
- $\sigma^D = \frac{\Sigma^D}{\Sigma^F}$
- $\sigma^{DF} = \frac{\Sigma^{DF}}{\Sigma^F}$

Additional Restriction:

- $S \sim O(\varepsilon^2)$

Varying S comparison

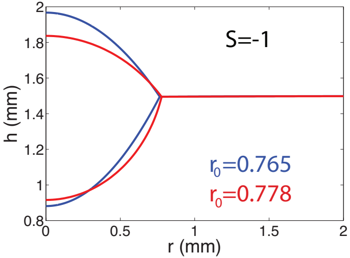




Blue: Thin Film Approximation

Red: Full Curvature,

Pujado & Scriven



What happens if drop touches bottom surface?

Equations:

$$h(r) = C_h + C_{hh} I_0\left(\sqrt{Bo}r\right) + C_{hhh} K_0\left(\sqrt{Bo}r\right)$$

$$a(r) = C_a + C_a I_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right) + C_{aaa} K_0\left(\sqrt{\frac{Bo\beta}{\sigma^D}}r\right)$$

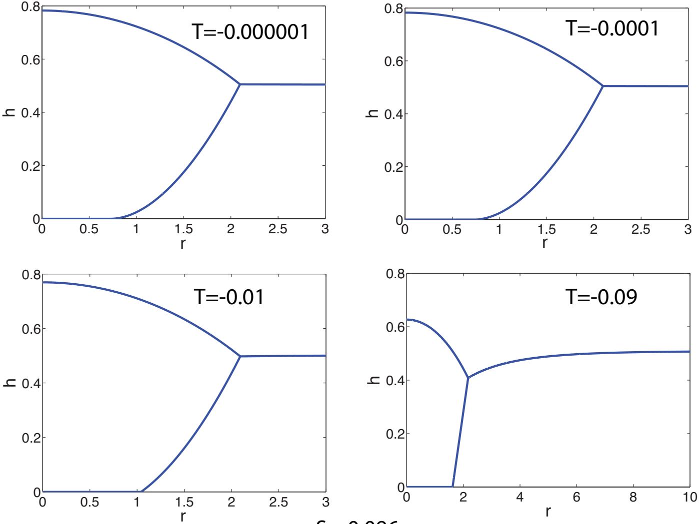
$$b(r) = C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right) + C_{bbb} K_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}r\right)$$

New Force Balance Conditions where drop touches bottom surface ($r = \bar{X}$):

$$C_b + C_{bb} I_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}\bar{X}\right) + C_{bbb} K_0\left(\sqrt{\frac{Bo(1-\beta)}{\sigma^{DF}}}\bar{X}\right) = 0$$

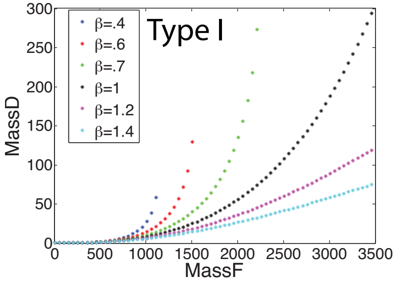
$$b_r(\bar{X}) = \sqrt{\frac{-2T}{\sigma^{DF}}}$$

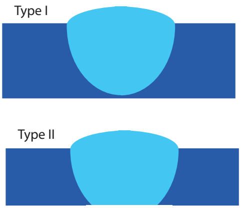
Spreading Coefficients

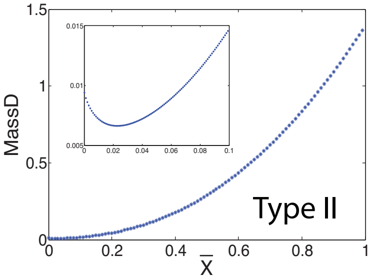


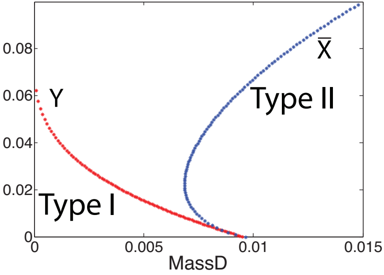
S=-0.096

Mass comparison









Planar Drop

- Only consider $x \geq 0$, solution symmetric

Type I solution:

$$h(x,t) = C_h + C_{hh} e^{-\sqrt{Bond}x}$$

$$a(x,t) = C_a + C_{aa} cosh\left(\sqrt{\frac{\beta Bond}{\sigma^D}}x\right)$$

$$b(x,t) = C_b + C_{bb} cosh\left(\sqrt{\frac{(1-\beta)Bond}{\sigma^{DF}}}x\right)$$

Type II solution:

$$h(x,t) = C_h + C_{hh} e^{-\sqrt{Bond}x}$$

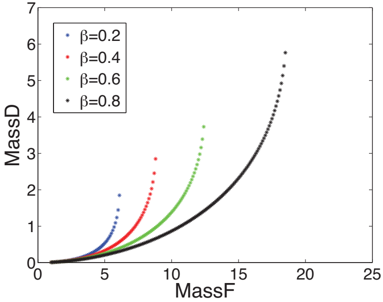
$$a(x,t) = C_a + C_{aa} cosh\left(\sqrt{\frac{\beta Bond}{\sigma^D}}x\right)$$

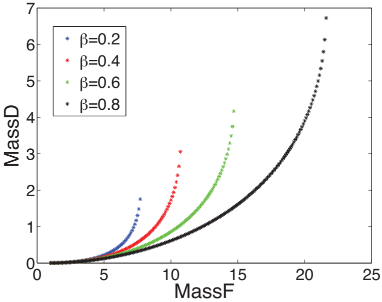
$$b(x,t) = C_b + C_b e^{-\sqrt{\frac{(1-\beta)Bond}{\sigma^{DF}}}x} + C_{bb} e^{\sqrt{\frac{(1-\beta)Bond}{\sigma^{DF}}}x}$$

Mass Comparison

Type I

Type II





Summary

Conclusions:

- Found equilibrium solutions for droplet on thin film
- Explored drop touching bottom surface
- Compared with experiment to confirm mechanism of autophobing

Future (short term) Work:

- Stability analysis of equilibrium solution
- Comparison between thin film approximation and thicker film solution
- Spreading behavior of drop
- Compare experimental shape of the drop with mathematical predictions

Future (long term) Work:

- Non-Newtonian underlying fluid
- Surfactant-laden droplet