18. Spreading

`Recall`: gravity currents, the spreading of heavy fluid under the influence of gravity.
further reading: **John E. Simpson - Gravity Currents: In the Environment and the Laboratory**.

Stage I: $\mathcal{R}e \gg 1$
Flow forced by gravity, and resisted by fluid inertia:

$\frac{\Delta \rho g h}{R} \sim \rho \frac{U^2}{R} \Rightarrow U \sim \sqrt{g'h}$ where $g' = \frac{\Delta \rho}{\rho} g$.

Figure 18.1: Spreading of a fluid volume under the influence of gravity.

Continuity: $V = \pi R^2(t) h(t) = const. \Rightarrow h(t) \sim \frac{V}{R^2(t)}$
$\Rightarrow U \equiv \frac{dR}{dt} \sim \sqrt{g'V} \frac{1}{R} \Rightarrow R dR \sim \sqrt{g'V} dt \Rightarrow R(t) \sim (g'V)^{1/4} t^{1/2}$

> `Note`: $U \sim \sqrt{g'h}$ decreases until $\mathcal{R}e = \frac{UR}{\nu} \leq 1$.

Stage II: $\mathcal{R}e \ll 1$
Flow forced by gravity, resisted by viscosity: $\frac{\partial p}{\partial r} = \nu \frac{\partial^2 u}{\partial z^2} \Rightarrow \frac{\Delta \rho g h}{R} \sim \nu \frac{U}{h^2}$
now substitute for $h(t) = V/R^2(t)$ to obtain:

$$U = \frac{dR}{dt} \sim \frac{R}{t} \sim \frac{\rho g' V^3}{\nu R^7} \qquad \Rightarrow \qquad R \sim \left(\frac{\rho g' V^3}{\nu} \right)^{1/8} t^{1/8} \tag{18.1}$$
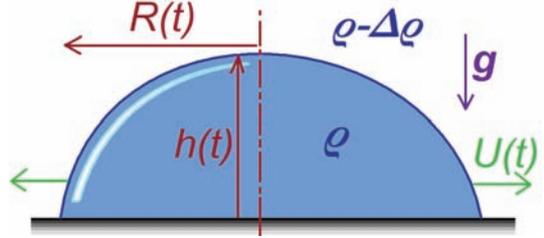
18.1 Spreading of small drops on solids

For a drop of undeformed radius R placed on a solid substrate, spreading will in general be driven by both gravity and curvature pressure.
Gravity: $\nabla p_g \sim \frac{\rho g h}{R}$, Curvature: $\nabla p_c \sim \frac{\gamma h}{R^3}$.
Continuity $V = \pi R^2(t) h(t) =$ const.
Which dominates? $\frac{\Delta p_g}{\Delta p_c} \sim \frac{\rho g R^2}{\gamma} =$ Bond number. $\mathcal{B}o = \frac{\rho g V}{\gamma h} \sim \frac{1}{h} \Rightarrow$ gravity becomes progressively more important as the drop spreads !?
`Recall`:

- drop behaviour depends on $S = \gamma_{SV} - \gamma_{SL} - \gamma$.

- When $S < 0$: Partial wetting. Spreading arises until a puddle forms.

- When $S > 0$: Complete wetting. Here, one expects spreading forced by the unbalanced tension at the contact line.

$$\underbrace{\frac{\mu U}{h}}_{viscous\ stress} \cdot \underbrace{\pi R^2}_{drop\ area} \sim \underbrace{S}_{contact\ line\ force} \cdot \underbrace{2\pi R}_{perimeter} \tag{18.2}$$

Thus, we expect $R \frac{dR}{dt} \sim \frac{S}{\mu} h \sim \frac{S}{\mu} \frac{U}{R^2} \Rightarrow R^3 \frac{dR}{dt} \sim \frac{SU}{\mu}$

$$\Rightarrow \qquad R \sim \left(\frac{SU}{\mu} \right)^{1/4} t^{1/4} \tag{18.3}$$

But this is not observed; instead, one sees $R \sim t^{1/10}$. **Why?**

Hardy (1919) observed a precursor film, the evidence of which was the disturbance of dust ahead of the drop. This precursor film is otherwise invisible, with thickness $e \sim 20\text{Å}$
Its origins lie in the force imbalance at the contact line ($S > 0$) and its stability results from interactions between the fluid and solid (e.g. Van der Waals)

Physical picture

Force at Apparent Contact Line: $F = \gamma + \gamma_{SL} - \gamma\cos\theta_d - \gamma_{SL} = \gamma(1 - \cos\theta_d) \approx \gamma\frac{\theta_d^2}{2}$ for small θ_d.

Note: $F \ll S$. Now recall from last class: $FU = \frac{3\mu\ell_D}{\theta_d}U^2$.

Letting $F \to \frac{\gamma\theta_d^2}{2}$, we find $U = \frac{dR}{dt} = \frac{\theta_d}{3\ell_D\mu}F = \frac{U^*}{6\ell_D}\theta_d^3$, where $U^* = \frac{\gamma}{\mu}$. Since the drop is small, it is a section of a sphere, so that

$$U = \frac{\pi}{4}R^3\theta_d \qquad (18.4)$$

Hence $\frac{3}{R}\frac{dR}{dt} = -\frac{1}{\theta_d}\frac{d\theta_d}{dt}$. Substituting in $\frac{dR}{dt}$ from above, we find: $\frac{1}{\theta_d}\frac{d\theta_d}{dt} = \frac{-U^*}{R}\theta_d^3$.

Now substitute $R = L\theta_d^{-1/3} \approx (U/\theta_d)^{1/3}$ and $L \equiv U^{1/3} \Rightarrow \frac{d\theta_d}{dt} = -\frac{U^*}{L}\theta_d^{13/3} \Rightarrow$

$$\theta_d = \left(\frac{L}{U^*t}\right)^{3/10} \qquad (Tanner's\ Law) \qquad (18.5)$$

so using (18.4) yields $R \sim L\left(\frac{U^*t}{L}\right)^{1/10}$, which is consistent with observation.
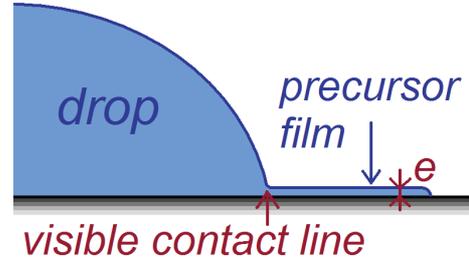

Figure 18.2: The precursor film of a spreading drop.

18.2 Immiscible Drops at an Interface *Pujado & Scriven 1972*

Gravitationally unstable configurations can arise ($\rho_a < \rho_b < \rho_c$ or $\rho_c < \rho_a < \rho_b$).

- weight of drops supported by interfacial tensions.

- if drop size $R < l_{bc} \sim \sqrt{\frac{\gamma_{bc}}{(\rho_b - \rho_c)g}}$, it can be suspended by the interface.

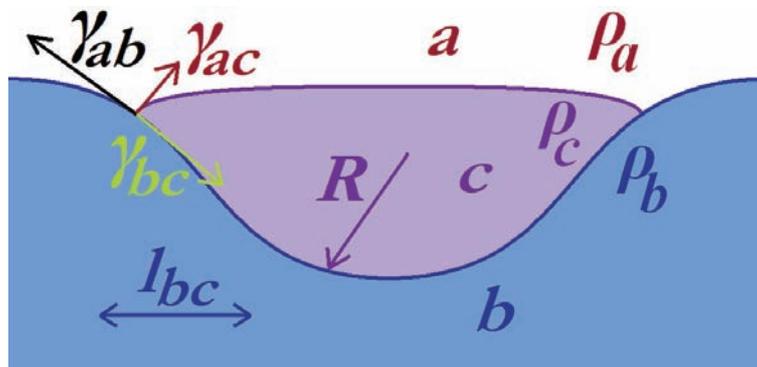Sessile Lens, $\rho_a < \rho_c < \rho_b$: stable for drops of any size, e.g. oil on water.

Figure 18.3: An immiscible liquid drop floats on a liquid bath.

18.3 Oil Spill

3 Distinct phases:

Phase I Inertia vs. Gravity: $U \sim \sqrt{g'h(t)} \Rightarrow R(t) \sim (g'U_0)^{1/4} t^{1/2}$

Phase II Viscosity vs. Gravity : as previously, $R \sim \left(\frac{\rho g' V_0^3}{\nu}\right)^{1/8} t^{1/8}$

Phase III Line tension vs. Viscosity: For $S < 0$, an equilibrium configuration arises $\Rightarrow$ drop takes the form of a sessile lens. For $S > 0$ the oil will completely cover the water, spreading to a layer of molecular thickness.

Phase IIIa Viscous resistance from dissipation within oil. As previously:
$\frac{\mu U}{h}\pi R^2 \sim 2\pi R S \Rightarrow R \sim \left(\frac{SU}{\mu}\right)^{1/4} t^{1/4}$

Phase IIIb Spreading driven by S, resisted by viscous dissipation in the underlying fluid.
Blasius boundary layer grows on base of spreading current like $\delta \sim \sqrt{\nu t}$.
$\mu \frac{U}{\delta}\pi R^2 \sim S \cdot 2\pi R$ where $\delta \sim \sqrt{\nu t} \Rightarrow R\frac{dR}{dt} \sim \frac{S}{\mu}\sqrt{\nu} t^{1/2} \Rightarrow R \sim \left(\frac{S}{\mu}\right)^{1/2} \nu^{1/4} t^{3/4}$.

18.4 Oil on water: A brief review

When an oil drop is emplaced on the water surface, its behaviour will depend on the spreading coefficient

$$S \equiv \sigma_{aw} - \sigma_{oa} - \sigma_{ow} \tag{18.6}$$

For $S > 0$, the droplet will completely wet the underlying liquid, and so spread to a layer of molecular thickness.
References: *Franklin (1760); Fay (1963); DePietro & Cox (1980); Foda & Cox (1980); Joanny (1987); Brochard-Wyart et al. (1996); Fraaije & Cazabat (1989).*

For $S < 0$, an equilibrium configuration arises: the drop assumes the form of a sessile lens.
The statics of the sessile lens have been considered by *Langmuir (1933)* and *Pujado & Scriven (1972)*.
their dynamics has been treated by *Wilson & Williams (1997)* and *Miksis & Vanden-Broeck (2001)*.
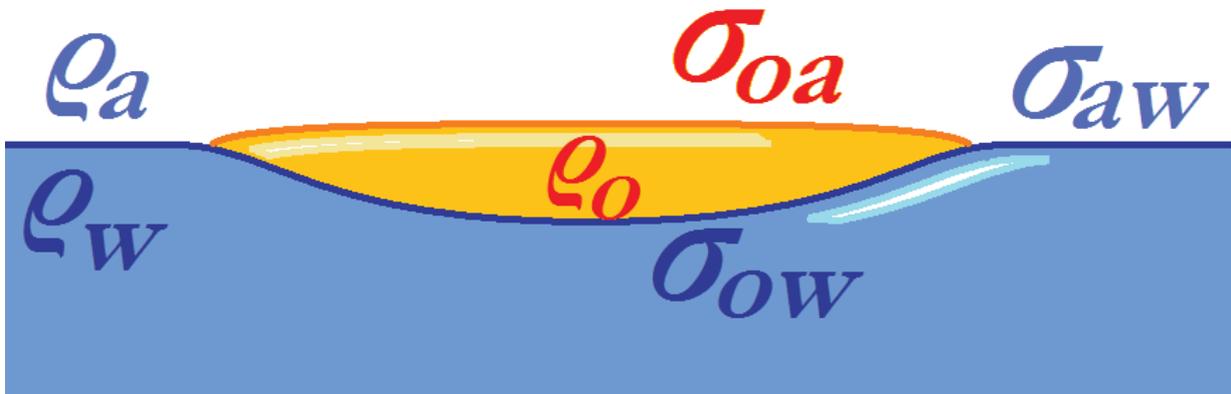

Figure 18.4: An oil drop spreading on the water surface.

18.5 The Beating Heart *Stocker & Bush (JFM 2007)*

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When a drop of mineral oil containing a small quantity of non-ionic, water-insoluble surfactant (Tergitol)

Figure 18.5: An oil drop oscillates on the water surface. Note the ring of impurities that marks the edge of the internal circulation.

is so emplaced, a sessile lens with $S < 0$ is formed. However, **no equilibrium shape emerges**; the lens is characterized by periodic fluctuations in radius, and so resembles a beating heart.

The phenomenon was first reported by *Buetschli (1894)*, a professor of Zoology at the University of Heidelberg, in his treatise *Investigations on Protoplasm*. It was subsequently described qualitatively by *Sebba (1979, 1981)*.

Motivation: *"The ultimate goal of physiologists is to be able to explain living behaviour in terms of physicochemical forces. Thus, any expansion of our knowledge of such forces, based on inanimate systems, should be examined to see whether this might not offer insight into biological behaviour"*. Sebba (1979).

Many biological systems exhibit periodic behaviour; e.g. oscillations of cells of nerves and muscle tissue, oscillations in mitochondria, and biological clocks. Conversion of chemical into mechanical energy is one of the main processes in biological movements; e.g. chloroplast movements and muscle contraction.

Observations:

- lens behaviour is independent of water depth, strongly dependent on surfactant concentration Γ

- for $\Gamma = 0$ no beating - stable sessile lens

- for moderate Γ steady beating observed

- for high Γ drop edges become unstable to fingers

- for highest Γ, lens explodes into a series of smaller beating lenses.

- beating marked by slow expansion, rapid retraction

- odour of Tergitol always accompanies beating

- placing lid on the chamber suppresses the oscillations $\Rightarrow$ evaporation is a critical ingredient.

Physical picture

`Stage I`: Slow expansion of drop.
Adsorption of surfactant onto oil-water interface $\Rightarrow \sigma_{ow}$ decreases. Evaporation of surfactant from air-water surface $\Rightarrow \sigma_{aw}$ increases.

`Stage II`: Rapid retraction.
Flushing of surfactant onto air-water interface $\Rightarrow \sigma_{aw}$ decreases and σ_{ow} increases. BUT WHY?

Internal circulation: confined to the outer extremities of the lens, absent in the flat central region. Marangoni flow associated with gradient in Γ - indicates Γ is lowest at the drop edge.   Consistent with radial gradient in adsorption flux along surface. Reflects geometric constraint - less surfactant available to corners than bulk.

Such **Marangoni shear layers** are unstable to longitudinal rolls or *transverse waves* (as in the wine glass).
The flushing events are associated with breaking Marangoni waves (*Frenkel & Halpern 2005*).

Figure 18.6: Internal circulation of the "beating heart".

Another surfactant-induced auto-oscillation: `The Spitting Drop` *(Fernandez & Homsy 2004)*

- chemical reaction produces surfactant at drop surface

- following release of first drop, periodic spitting

- rationalized in terms of *tip-streaming* (Taylor 1934), which arises only in the presence of surfactant (de Bruijn 1993) for $\mu/\mu_d \approx 10^4$ and $\mathcal{Ca} = \mu G/\sigma > 0.4$

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