2. Definition and Scaling of Surface Tension

These lecture notes have been drawn from many sources, including textbooks, journal articles, and lecture notes from courses taken by the author as a student. These notes are not intended as a complete discussion of the subject, or as a scholarly work in which all relevant references are cited. Rather, they are intended as an introduction that will hopefully motivate the interested student to learn more about the subject. Topics have been chosen according to their perceived value in developing the physical insight of the students.

2.1 History: Surface tension in antiquity

Hero of Alexandria (10 AD - 70 AD) Greek mathematician and engineer, *"the greatest experimentalist of antiquity"*. Exploited capillarity in a number of inventions described in his book *Pneumatics*, including the water clock.

Pliny the Elder (23 AD - 79 AD) Author, natural philosopher, army and naval commander of the early Roman Empire. Described the glassy wakes of ships. *"True glory comes in doing what deserves to be written; in writing what deserves to be read; and in so living as to make the world happier."* *"Truth comes out in wine"*.

Leonardo da Vinci (1452-1519) Reported capillary rise in his notebooks, hypothesized that mountain streams are fed by capillary networks.

Francis Hauksbee (1666-1713) Conducted systematic investigation of capillary rise, his work was described in Newton's Opticks, but no mention was made of him.

Benjamin Franklin (1706-1790) Polymath: scientist, inventor, politician; examined the ability of oil to suppress waves.

Pierre-Simon Laplace (1749-1827) French mathematician and astronomer, elucidated the concept and theoretical description of the meniscus, hence the term Laplace pressure.

Thomas Young (1773-1829) Polymath, solid mechanician, scientist, linguist. Demonstrated the wave nature of light with ripple tank experiments, described wetting of a solid by a fluid.

Joseph Plateau (1801-1883) Belgian physicist, continued his experiments after losing his sight. Extensive study of capillary phenomena, soap films, minimal surfaces, drops and bubbles.

2.2   Motivation: Who cares about surface tension?

As we shall soon see, surface tension dominates gravity on a scale less than the capillary length (roughly 2mm). It thus plays a critical role in a variety of small-scale processes arising in biology, environmental science and technology.

Biology

- all small creatures live in a world dominated by surface tension

- surface tension important for insects for many basic functions

- weight support and propulsion at the water surface

- adhesion and deadhesion via surface tension

- the pistol shrimp: hunting with bubbles

- underwater breathing and diving via surface tension

- natural strategies for water-repellency in plants and animals

- the dynamics of lungs and the role of surfactants and impurities

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Please see the image on page http://news.sciencemag.org/sciencenow/2011/06/spiders.html#panel-2.

Figure 2.1: The diving bell spider

Geophysics and environmental science

- the dynamics of raindrops and their role in the biosphere

- most biomaterial is surface active, sticks to the surface of drops / bubbles

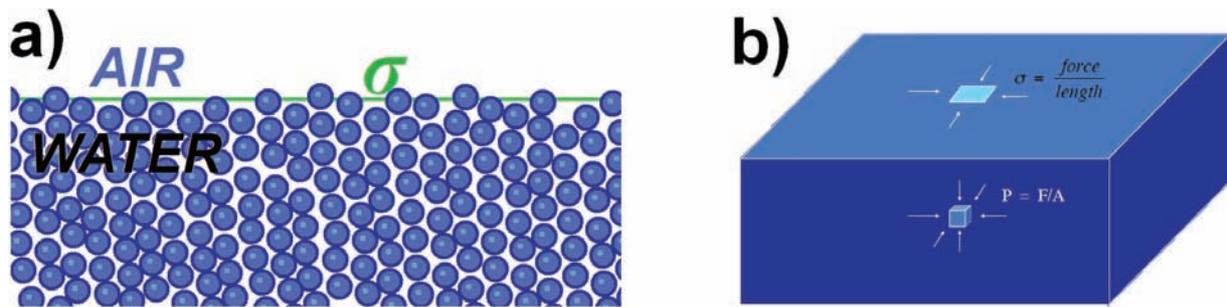- chemical, thermal and biological transport in the surf zone

- early life: early vessicle formation, confinement to an interface

- oil recovery, carbon sequestration, groundwater flows

- design of insecticides intended to coat insects, leave plant unharmed

- chemical leaching and the water-repellency of soils

- oil spill dynamics and mitigation

- disease transmission via droplet exhalation

- dynamics of magma chambers and volcanoes

- the exploding lakes of Cameroon

Technology

- capillary effects dominant in microgravity settings: NASA

- cavitation-induced damage on propellers and submarines

- cavitation in medicine: used to damage kidney stones, tumours ...

- design of superhydrophobic surfaces e.g. self-cleaning windows, drag-reducing or erosion-resistant surfaces

- lab-on-a-chip technology: medical diagnostics, drug delivery

- microfluidics: continuous and discrete fluid transport and mixing

- tracking submarines with their surface signature

- inkjet printing

- the bubble computer

Figure 2.2: **a)** The free surface between air and water at a molecular scale. **b)** Surface tension is analogous to a negative surface pressure.

2.3 Surface tension: a working definition

Discussions of the molecular origins of surface or interfacial tension may be found elsewhere (e.g. *Israelachvili 1995, Rowlinson & Widom 1982*). Our discussion follows that of *de Gennes, Brochard-Wyart & Quéré 2003.*

Molecules in a fluid feel a mutual attraction. When this attractive force is overcome by thermal agitation, the molecules pass into a gaseous phase. Let us first consider a free surface, for example that between air and water (Fig. 2.2a). A water molecule in the fluid bulk is surrounded by attractive neighbours, while a molecule at the surface has a reduced number of such neighbours and so in an energetically unfavourable state. The creation of new surface is thus energetically costly, and a fluid system will act to minimize surface areas. It is thus that small fluid bodies tend to evolve into spheres; for example, a thin fluid jet emerging from your kitchen sink will generally pinch off into spherical drops in order to minimize the total surface area (see Lecture 5).

If U is the total cohesive energy per molecule, then a molecule at a free surface will lose $U/2$ relative to molecules in the bulk. Surface tension is a direct measure of this energy loss per unit area of surface. If the characteristic molecular dimension is R and its area thus R^2, then the surface tension is $\sigma \sim U/(2R)^2$. Note that surface tension increases as the intermolecular attraction increases and the molecular size decreases. For most oils, $\sigma \sim 20$ dynes/cm, while for water, $\sigma \sim 70$ dynes/cm. The highest surface tensions are for liquid metals; for example, liquid mercury has $\sigma \sim 500$ dynes/cm. The origins of interfacial tension are analogous. Interfacial tension is a material property of a fluid-fluid interface whose origins lie in the different energy per area that acts to resist the creation of new interface. Fluids between which no interfacial tension arises are said to be miscible. For example, salt molecules will diffuse freely across a boundary between fresh and salt water; consequently, these fluids are miscible, and there is no interfacial tension between them. Our discussion will be confined to immiscible fluid-fluid interfaces (or fluid-gas surfaces), at which an effective interfacial (or surface) tension acts.

Surface tension σ has the units of force/length or equivalently energy/area, and so may be thought of as a negative surface pressure, or, equivalently, as a line tension acting in all directions parallel to the surface. Pressure is generally an isotropic force per area that acts throughout the bulk of a fluid: small surface element $\mathrm{d}S$ will feel a total force $p(\mathbf{x})\mathrm{d}S$ owing to the local pressure field $p(\mathbf{x})$. If the surface S is closed, and the pressure uniform, the net pressure force acting on S is zero and the fluid remains static. Pressure gradients correspond to body forces (with units of force per unit volume) within a fluid, and so appear explicitly in the Navier-Stokes equations. Surface tension has the units of force per length, and its action is confined to the free surface. Consider for the sake of simplicity a perfectly flat interface. A surface line element $\mathrm{d}\ell$ will feel a total force $\sigma\mathrm{d}\ell$ owing to the local surface tension $\sigma(\mathbf{x})$. If the surface line element is a closed loop C, and the surface tension uniform, the net surface tension force acting on C is zero, and the fluid remains static. If surface tension gradients arise, there may be a net force on the surface element that acts to distort it through driving flow.

2.4 Governing Equations

The motion of a fluid of uniform density ρ and dynamic viscosity μ is governed by the Navier-Stokes equations, which represent a continuum statement of Newton's laws.

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u} \right) = -\nabla p + \mathbf{F} + \mu \nabla^2 \mathbf{u} \tag{2.1}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0 \tag{2.2}$$

This represents a system of 4 equations in 4 unknowns (the fluid pressure p and the three components of the velocity field $\mathbf{u}$). Here $\mathbf{F}$ represents any body force acting on a fluid; for example, in the presence of a gravitational field, $\mathbf{F} = \rho \mathbf{g}$ where $\mathbf{g}$ is the acceleration due to gravity.

Surface tension acts only at the free surface; consequently, it does not appear in the Navier-Stokes equations, but rather enters through the boundary conditions. The boundary conditions appropriate at a fluid-fluid interface are formally developed in Lecture 3. We here simply state them for the simple case of a free surface (such as air-water, in which one of the fluids is not dynamically significant) in order to get a feeling for the scaling of surface tension. The normal stress balance at a free surface must be balanced by the curvature pressure associated with the surface tension:

$$\boldsymbol{n} \cdot \boldsymbol{T} \cdot \boldsymbol{n} = \sigma (\boldsymbol{\nabla} \cdot \boldsymbol{n}) \tag{2.3}$$

where $\mathbf{T} = -p\mathbf{I} + \mu \left[\boldsymbol{\nabla} \boldsymbol{u} + (\boldsymbol{\nabla} \boldsymbol{u})^T \right] = -p\mathbf{I} + 2\mu \mathbf{E}$ is the stress tensor, $\mathbf{E} = \frac{1}{2} \left[\boldsymbol{\nabla} \boldsymbol{u} + (\boldsymbol{\nabla} \boldsymbol{u})^T \right]$ is the deviatoric stress tensor, and $\mathbf{n}$ is the unit normal to the surface. The tangential stress at a free surface must balance the local surface tension gradient:

$$\boldsymbol{n} \cdot \boldsymbol{T} \cdot \boldsymbol{t} = \boldsymbol{\nabla} \sigma \cdot \mathbf{t} \tag{2.4}$$

where $\mathbf{t}$ is the unit tangent to the interface.

2.5 The scaling of surface tension

Fundamental Concept   The laws of Nature cannot depend on arbitrarily chosen system of units. Any physical system is most succinctly described in terms of dimensionless variables.

Buckingham's Theorem   For a system with M physical variables (e.g. density, speed, length, viscosity) describable in terms of N fundamental units (e.g. mass, length, time, temperature), there are $M - N$ dimensionless groups that govern the system.

`E.g.  Translation of a rigid sphere through a viscous fluid:`
Physical variables: sphere speed U and radius a, fluid viscosity ν and density ρ and sphere drag D; $M = 5$.
Fundamental units: mass M, length L and time T; $N = 3$.
Buckingham's Theorem: there are $M - N = 2$ dimensionless groups: $C_d = D/\rho U^2$ and $\mathcal{R}e = Ua/\nu$.
System is uniquely determined by a single relation between the two: $C_d = F(\mathcal{R}e)$.
We consider a fluid of density ρ and viscosity $\mu = \rho \nu$ with a free surface characterized by a surface tension σ. The flow is marked by characteristic length- and velocity- scales of, respectively, a and U, and evolves in the presence of a gravitational field $\mathbf{g} = -g\hat{\mathbf{z}}$. We thus have a physical system defined in terms of six physical variables $(\rho, \nu, \sigma, a, U, g)$ that may be expressed in terms of three fundamental units: mass, length and time. Buckingham's Theorem thus indicates that the system may be uniquely described in terms of three dimensionless groups. We choose

$$\mathcal{R}e = \frac{Ua}{\nu} = \frac{\text{Inertia}}{\text{Viscosity}} = \text{Reynolds number} \tag{2.5}$$

$$\mathcal{F}r = \frac{U^2}{ga} = \frac{\text{Inertia}}{\text{Gravity}} = \text{Froude number} \tag{2.6}$$

$$\mathcal{B}o = \frac{\rho g a^2}{\sigma} = \frac{\text{Gravity}}{\text{Curvature}} = \text{Bond number} \tag{2.7}$$

The Reynolds number prescribes the relative magnitudes of inertial and viscous forces in the system, while the Froude number those of inertial and gravity forces. The Bond number indicates the relative importance of forces induced by gravity and surface tension. Note that these two forces are comparable when $\mathcal{B}o = 1$, which arises at a lengthscale corresponding to the capillary length: $\ell_c = (\sigma/(\rho g))^{1/2}$. For an air-water surface, for example, $\sigma \approx 70$ dynes/cm, $\rho = 1\text{g/cm}^3$ and $g = 980$ cm/s^2, so that $\ell_c \approx 2$mm. Bodies of water in air are dominated by the influence of surface tension provided they are smaller than the capillary length. Roughly speaking, the capillary length prescribes the maximum size of pendant drops that may hang inverted from a ceiling, water-walking insects, and raindrops. Note that as a fluid system becomes progressively smaller, the relative importance of surface tension over gravity increases; it is thus that surface tension effects are critical in many in microscale engineering processes and in the lives of bugs.

Finally, we note that other frequently arising dimensionless groups may be formed from the products of $\mathcal{B}o$, $\mathcal{R}e$ and $\mathcal{F}r$:

$$\mathcal{W}e = \frac{\rho U^2 a}{\sigma} = \frac{\text{Inertia}}{\text{Curvature}} = \text{Weber number} \tag{2.8}$$

$$\mathcal{C}a = \frac{\rho \nu U}{\sigma} = \frac{\text{Viscous}}{\text{Curvature}} = \text{Capillary number} \tag{2.9}$$

The Weber number indicates the relative magnitudes of inertial and curvature forces within a fluid, and the capillary number those of viscous and curvature forces. Finally, we note that if the flow is marked by a Marangoni stress of characteristic magnitude $\Delta\sigma/L$, then an additional dimensionless group arises that characterizes the relative magnitude of Marangoni and curvature stresses:

$$\mathcal{M}a = \frac{a\Delta\sigma}{L\sigma} = \frac{\text{Marangoni}}{\text{Curvature}} = \text{Marangoni number} \tag{2.10}$$

We now demonstrate how these dimensionless groups arise naturally from the nondimensionalization of Navier-Stokes equations and the surface boundary conditions. We first introduce a dynamic pressure: $p_d = p - \rho \boldsymbol{g} \cdot \boldsymbol{x}$, so that gravity appears only in the boundary conditions. We consider the special case of high Reynolds number flow, for which the characteristic dynamic pressure is ρU^2. We define dimensionless primed variables according to:

$$\mathbf{u} = U\mathbf{u}' , \qquad p_d = \rho U^2 p_d' , \qquad \mathbf{x} = a\mathbf{x}' , \qquad t = \frac{a}{U}t' \qquad , \tag{2.11}$$

where a and U are characteristic lenfth and velocity scales. Nondimensionalizing the Navier-Stokes equations and appropriate boundary conditions yields the following system:

$$\left(\frac{\partial \mathbf{u}'}{\partial t'} + \boldsymbol{u}' \cdot \boldsymbol{\nabla}' \boldsymbol{u}'\right) = -\boldsymbol{\nabla} p_d' + \frac{1}{\mathcal{R}e}\nabla'^2 \mathbf{u}' , \ \ \boldsymbol{\nabla}' \cdot \boldsymbol{u}' = 0 \tag{2.12}$$

The normal stress condition assumes the dimensionless form:

$$-p_d' + \frac{1}{\mathcal{F}r}z' + \frac{2}{\mathcal{R}e}\boldsymbol{n} \cdot \boldsymbol{E}' \cdot \boldsymbol{n} = \frac{1}{\mathcal{W}e}\boldsymbol{\nabla}' \cdot \boldsymbol{n} \tag{2.13}$$

The relative importance of surface tension to gravity is prescribed by the Bond number $\mathcal{B}o$, while that of surface tension to viscous stresses by the capillary number $\mathcal{C}a$. In the high $\mathcal{R}e$ limit of interest, the normal force balance requires that the dynamic pressure be balanced by either gravitational or curvature stresses, the relative magnitudes of which are prescribed by the Bond number.

The nondimensionalization scheme will depend on the physical system of interest. Our purpose here was simply to illustrate the manner in which the dimensionless groups arise in the theoretical formulation of the problem. Moreover, we see that those involving surface tension enter exclusively through the boundary conditions.
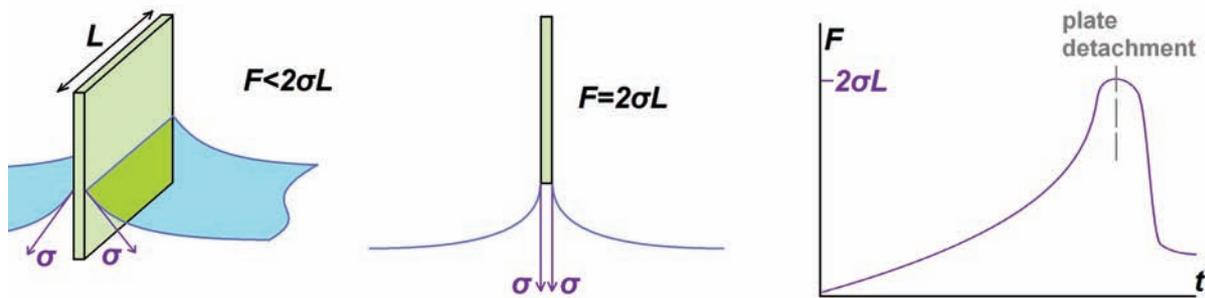
Figure 2.3: Surface tension may be measured by drawing a thin plate from a liquid bath.

2.6 A few simple examples

Measuring surface tension. Since σ is a tensile force per unit length, it is possible to infer its value by slowly drawing a thin plate out of a liquid bath and measure the resistive force (Fig. 2.3). The maximum measured force yields the surface tension σ.

Curvature/ Laplace pressure: consider an oil drop in water (Fig. 2.4a). Work is required to increase the radius from R to $R + dR$:

$$dW = \underbrace{-p_o \mathrm{d}V_o - p_w \mathrm{d}V_w}_{mech.\ E} + \underbrace{\gamma_{ow} dA}_{surface\ E} \qquad (2.14)$$

where $\mathrm{d}V_o = 4\pi R^2 dR = -\mathrm{d}V_w$ and $dA = 8\pi R dR$.
For mechanical equilibrium, we require
$dW = -(p_0 - p_w)4\pi R^2 dR + \gamma_{ow} 8\pi R dR = 0 \Rightarrow$
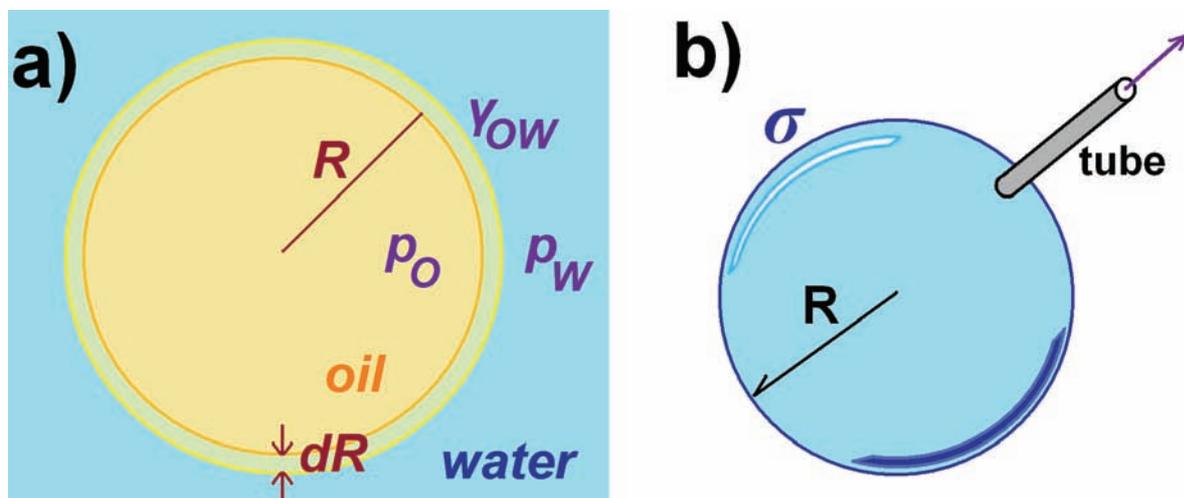$\Delta P = (p_o - p_w) = 2\gamma_{ow}/R$.

Figure 2.4: **a)** An oil drop in water **b)** When a soap bubble is penetrated by a cylindrical tube, air is expelled from the bubble by the Laplace pressure.

`Note:`

1. Pressure inside a drop / bubble is higher than that outside $\Delta P \sim 2\gamma/R \Rightarrow$ smaller bubbles have higher Laplace pressure $\Rightarrow$ champagne is louder than beer.
   Champagne bubbles $R \sim 0.1mm$, $\sigma \sim 50\ dynes/cm$, $\Delta P \sim 10^{-2}\ atm$.

2. For a soap bubble (2 interfaces) $\Delta P = \frac{4\sigma}{R}$, so for $R \sim 5\ cm$, $\sigma \sim 35$dynes/cm have $\Delta P \sim 3\times 10^{-5}$atm.

More generally, we shall see that there is a pressure jump across any curved interface:

Laplace pressure $\Delta p = \sigma \boldsymbol{\nabla} \cdot \boldsymbol{n}$.
`Examples:`

1. **Soap bubble jet - Exit speed** (Fig. 2.4b)
   Force balance: $\Delta p = 4\sigma/R \sim \rho_{air} U^2 \Rightarrow U \sim \left(\frac{4\sigma}{\rho_{air}R}\right)^{1/2} \sim \left(\frac{4\times 70 dynes/cm}{0.001g/cm^3 \cdot 3cm}\right) \sim 300 cm/s$

2. **Ostwald Ripening**: The coarsening of foams (or emulsions) owing to diffusion of gas across interfaces, which is necessarily from small to large bubbles, from high to low Laplace pressure.

3. **Falling drops**: Force balance $Mg \sim \rho_{air} U^2 a^2$ gives
   fall speed $U \sim \sqrt{\rho g a / \rho_{air}}$.
   drop integrity requires $\rho_{air} U^2 \sim \rho g a < \sigma/a$
   raindrop size $a < \ell_c = \sqrt{\sigma/\rho g} \approx 2$mm.
   If a drop is small relative to the capillary length, σ maintains it against the destabilizing influence of aerodynamic stresses.

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