1. The origins of surface tension

The van der Waals force is an intermolecular force considered to be long-range, in that it acts over distances long relative to the molecular size, typically $10^{-10}$ to $10^{-8}$ m. The Van der Waals potential is given by $\phi = -k/r^6$, where $k$ is some constant. (It is the Van der Waals force that initiates the coalescence of fluid drops when they get sufficiently close to a fluid surface).

a) Show that the Van der Waals potential of a fluid molecule a distance $h$ above the horizontal surface of a fluid with $\rho$ molecules per unit volume is $\phi = -k\rho\pi/6h^3$.

b) Show that the Van der Waals potential per unit area between two planar fluid layers separated by a thin air layer of thickness $d$ is $\phi = -k\pi\rho^2/(12d^2)$, and that the associated attractive force per unit area $F = -A/(6\pi d^3)$, where $A = k\pi^2\rho^2$ is called the Hamaker constant.

c) Show that the total Van der Waals force between a small spherical fluid drop of radius $b$ and a fluid plane separated by a distance $d$ is given by $F = Ab/6d^2$.

d) Consider the Van der Waals potential acting on a fluid molecule inside a spherical drop of radius $b$, a distance $h \ll b$ from its surface. Calculate the potential arising as a result of the interfacial curvature; specifically, deduce the potential difference arising due to the removal of molecules (of density $\rho$) from the tangent plane. Show that this potential is $\phi = \pi\rho/(4bh^2)$ Calculate the resulting force per unit volume. Show that, in equilibrium, this must be balanced by a pressure gradient $dp/dh = A/(2\pi bh^3)$. Noting that this becomes singular at $h = 0$, integrate the pressure gradient from $h$ to the molecular dimension $\epsilon$. Thus show that when $h \gg \epsilon$, the pressure inside the fluid, the Laplace pressure: $P = \sigma/b$, where $\sigma = A/(4\pi\epsilon^2)$ is the surface tension.

2. Drops and bubbles

a) Consider a spherical water drop of radius $a$, density $\rho$, viscosity $\nu$ and surface tension $\sigma$ vibrating in a vacuum. It is perturbed from spherical, and oscillates such that its motion is characterized by a large Reynolds number. What mode of vibration do you expect to be most persistent, and why? Make an estimate for the frequency of this most unstable mode of vibration via scaling arguments. Use the above result to assess the frequency of the most unstable mode of oscillation of a rain drop.

b) Beaming. An optical effect causes incident light to be focused by drops, resulting in a beam of light being emitted by the droplet (T. Timusk, Applied Optics, 48, 1212, 2009). Given the frequency of oscillation of a raindrop along with its fall speed, assess whether or not the two images of rain posted on the class webpage are real or fake. Hazard a guess as to why the streak lengths are different in the two images.

c) A spherical drop of radius $a = 1$ cm is placed on a bath of the same fluid. At time $t = 0$, it merges with the bath. Assume that the drop remains spherical as its contents are evacuated. Estimate the initial exit velocity, and so a characteristic Reynolds number. On the basis of this inference, deduce the dependence of the bubble radius on time, $R(t)$, through consideration of the dominant force balance. When do you expect your solution to break down?

d) Consider now a soap bubble of radius $a = 5$ cm with the same gas inside as out. Estimate its frequency of vibration. Describe what happens when it lands on a planar soap film, merges, then evacuates its contents across the film. How does its radius evolve with time during this evacuation process? How and why are these results similar to or different from those for a droplet?
3. The Euler-Lagrange equations

Since surface energy is proportional to surface area, systems dominated by surface tension will generally tend to minimize their surface area. We here consider a technique that may be applied to find such extremal shapes.

**Calculus of variations:** A functional \( F[y] \) of a function \( y(x) \) defined for \( x_1 < x < x_2 \) is an integral of the form: \( F[y] = \int_{x_1}^{x_2} f(y, y', x) \, dx \), where \( y' = \frac{dy}{dx} \). The value of \( F \) is then minimized (or maximized) by a function \( y(x) \) that satisfies the Euler-Lagrange equation:

\[
\frac{\partial f}{\partial y} - \frac{d}{dx} \left( \frac{\partial f}{\partial y'} \right) = 0.
\]

If \( f \) does not depend explicitly on \( x \), then the Euler-Lagrange equation implies that

\[
\frac{d}{dx} \left[ f - y' \frac{\partial f}{\partial y'} \right] = 0 \iff f - y' \frac{\partial f}{\partial y'} = \text{Const.}
\]

a) Suppose \( y(x) \) describes a curve in the plane between the points \((x_1, y_1)\) and \((x_2, y_2)\). Recall that the length of the curve between \( x_1 \) and \( x_2 \) is given by the formula \( L[y] = \int_{x_1}^{x_2} \sqrt{1 + y'^2} \, dx \). Show that the curve \( y(x) \) of minimal length obeys the equation \( \sqrt{1 + y'^2} = \text{Const} \); thus, deduce that the curve of shortest length between two points in the plane is a straight line.

b) Suppose that two rings, both of unit radius, are dipped in soapy water and then drawn apart a distance \( 2d \), so that the rings lie in parallel planes. Neglecting gravity, the film will form an equilibrium surface of minimal area. The soap film is axisymmetric, and so forms a surface \( r = r(z) \) with surface area \( S = 2\pi \int_{-d}^{d} r \sqrt{1 + r'^2} \, dz \). Use the Euler-Lagrange equations to show that \( r \sqrt{1 + r'^2} = \text{Const} \). Thus, deduce that the shape of the soap film is a catenoid, with \( r(z) = r_0 \cosh z/r_0 \), for some constant \( r_0 \). Under what conditions do you expect the soap film to break (and relax to the form of two circles bounding the rings) on energetic grounds?

Analogous to the method of Lagrange multipliers, the function \( y(x) \) minimizing \( F[y] \), subject to a constraint \( G[y] = G_0 \) where \( G[y] = \int_{x_1}^{x_2} g(y, y', x) \, dx \), is a solution of

\[
\frac{\partial(f + \lambda g)}{\partial y} - \frac{d}{dx} \left( \frac{\partial(f + \lambda g)}{\partial y'} \right) = 0,
\]

the so-called constrained Euler-Lagrange equation. The Lagrange multiplier, \( \lambda \), is selected in order to enforce the constraint.

c) Consider an inextensible string of uniform density \( \rho \) and length \( \ell \) hanging freely under gravity. It is pinned at end points such that its equilibrium shape is \( y = y(x) \), with \( y(-d) = y(d) = 1 \). The potential energy of the string is \( E_p = \rho g \int_{-d}^{d} y \sqrt{1 + y'^2} \, dx \). By imposing the constant-length constraint, use the constrained Euler-Lagrange equation to show that the string’s equilibrium shape is the catenary curve \( y(x) = y_0 + \alpha \cosh x/\alpha \). State the relationship between \( y_0 \) and \( \alpha \).

d) Describe a soap bubble pinned to a circular ring in terms of a surface of revolution \( r = r(z) \) with \( r(-1) = r(1) = 0 \) and a fixed volume \( V = \frac{4}{3} \pi \). Show that the constrained Euler-Lagrange equation implies that

\[
\frac{r}{\sqrt{1 + r'^2}} + \frac{\lambda}{2} r^2 = \text{Const.}
\]

Verify that one possible solution to this constrained minimization problem is a spherical bubble.
4. Chemical propulsion

Gradients in wettability may lead to spatial gradients in surface energy that generate propulsive forces. We consider here a solid substrate with a linear chemical gradient such that the equilibrium contact angle $\theta_e$ increases linearly with distance along the substrate. Neglect the influence of gravity throughout.

a) If a small hemispherical drop is placed on a plane composed of this surface such that its contact line is circular, calculate the resulting force on the drop.

b) Assuming that the resulting motion arises at low Reynolds number (so is resisted primarily by viscous stresses), estimate the rate of dissipation incurred by the drop motion via a scaling argument. Use an energy balance to estimate the speed of propulsion of the droplet.

b) This surface is now rolled up into a small cylindrical tube of radius $R$ such that there is a wettability gradient along its length. If a fluid volume $V \gg 4\pi R^3/3$ is deposited inside the tube, it takes the form of a roughly cylindrical slug of length $L$. What is the resulting driving force on the slug?

c) Assuming that the principal resistance to motion comes from viscous dissipation resulting from the Poiseuille-type flow within the bulk of the slug, calculate its speed via a scaling argument.

5. Geometric propulsion

Gradients in geometry may also lead to spatial gradients in surface energy that generate propulsive forces. Consider a fluid-filled wedge with small opening angle $\alpha$. A bubble of volume $V$ is placed in the wedge, forming a roughly penny-shaped form of radius $R \gg h$ (where $h$ is the local gap width) whose center is a distance $x$ from the corner. The fluid completely wets the solid, so we assume that there is an extremely thin fluid layer separating the bubble from the plate. The curvature at the bubble’s edge is thus prescribed by the local gap width.

a) Calculate the surface energy of the system as a function of $x$. Thereby deduce the force on the bubble. Does the bubble move towards or away from the corner?

b) As the bubble moves, it induces a flow around it. To leading order, provided the bubble is sufficiently far from the corner and $\alpha$ sufficiently small, this may be described as flow around a circular disc in a Hele-Shaw cell (see course notes in 18.355 or 2.25). By calculating the rate of dissipation associated with such a flow, deduce the dependence of bubble speed on distance from the corner.

c) Now orient the wedge vertically, so that its corner is horizontal, and the bubble feels the influence of gravity. Consider gravitational and surface energies in order to deduce the distance from the corner at which the bubble will be in equilibrium.
6. Capillary rise in a corner

a) Consider a bath of oil with density $\rho$, dynamic viscosity $\mu$, and surface tension $\sigma$. The oil wets glass, so that there is an equilibrium contact angle $\theta_e < \pi/2$. Suppose two plates of glass are inserted in the oil so there is a uniform thin gap of thickness $\delta$ between the plates. What shape will the cross-gap meniscus between the oil and air form? What is the Laplace pressure jump across this meniscus in terms of $\delta$ and $\theta_e$?

b) Now suppose that the plates are arranged so as to form a wedge with a small opening angle $\alpha$. Assume that the cross gap thickness remains less than the capillary length of the oil, so that the cross-gap curvature calculated in part (a) is dominant. Show that the equilibrium meniscus takes the form of a hyperbola. In particular, show that the fluid height tends to infinity in the vicinity of the corner.

We proceed by considering the dynamics of capillary rise in the viscous limit, where inertial effects are negligible. Work in a coordinate system in which $x$ points away from the corner, $y$ is in the cross-gap direction and $z$ is vertical. The plate surfaces are thus given by $y = 0$ and $y = \alpha x$. The shape of the meniscus can then be approximated in terms of the curve $z = H(x,t)$. We will consider the dynamics in the region far from the corner, where $x/H \gg 1$.

c) Modeling the region between the two plates as a Hele-Shaw cell with a small, slowly varying thickness, use lubrication theory to find the velocity profile in the wedge in terms of the modified pressure, $P = p + \rho gz$. Specifically, show that the velocity field is prescribed by a Darcy flow of the form: $u = -\frac{1}{2\mu} y(\alpha x - y) \nabla P$.

d) Calculate the flux along the gap $q = \int_0^{\alpha x} u \, dy$, then use the conservation of mass $\nabla \cdot q = 0$ to show that, when $x \gg H$, the pressure $P$ obeys $\frac{\partial P}{\partial z} = 0$. State the appropriate boundary conditions for $P$ at $z = 0$ and $z = H(x,t)$, then solve for $P(x,z)$.

e) Treat the meniscus as a material surface rising at the vertical component of cross-gap averaged velocity, $\bar{u} = q/(\alpha x) = (\bar{u}, 0, \bar{w})$, so that $\frac{\partial H}{\partial t} = \bar{w}$. Thus, show that
$$\frac{\partial H}{\partial t} + \frac{\alpha^2 x^2}{12\mu} \frac{\partial P}{\partial z} = 0 \quad \text{at} \quad z = H(x,t).$$

f) For small times, the effect of gravity is negligible. Calculate the simplified form of $P(x,z)$ in this limit. Use the result of part (e) to show that the height of the meniscus is then given by $H(x,t) = A\sqrt{xt}$. State $A$ explicitly. Compare your result to Washburn’s law for capillary rise in a tube. Estimate the timescale for the meniscus to reach its equilibrium height for $x \gg H$. 