

Mechanics of Interfaces

Lecture notes

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Chapter 1

Introduction to surface tension

The interface between a liquid and its adjoining material (may it be another liquid, a solid, or a gas) is naturally under a mechanical state of tension. It is as if the liquid interface wants to shrink in area, but is held stretched by some forces, just as the rim of a trampoline holds the trampoline sheet in a stretched state (see Figure 1.1 for an illustration). This property of a liquid interface is called *surface tension*.



Figure 1.1: A Waterstrider floating on the surface of water without sinking. The weight of the organism makes depressions in the air-water interface, indicating the tension present on the interface. (source: pxhere.com/en/photo/889347)

Mechanically, the surface tension is represented by an internal force per unit length acting along the interface. By an internal force, we mean a force exerted by one part of the interface on another (see Figure 1.2). It is this internal force that keeps the entire interface in tension.

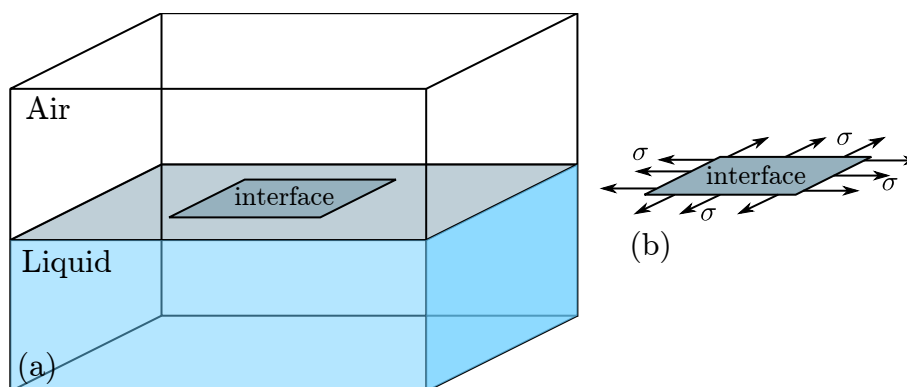


Figure 1.2: Schematic illustrating the concept of surface tension. (a) A container containing a liquid. The panel depicts the liquid-air interface. (b) The interface is under a state of tension depicted schematically by the arrows. The strength of this tension is represented by a force per unit length with magnitude σ .

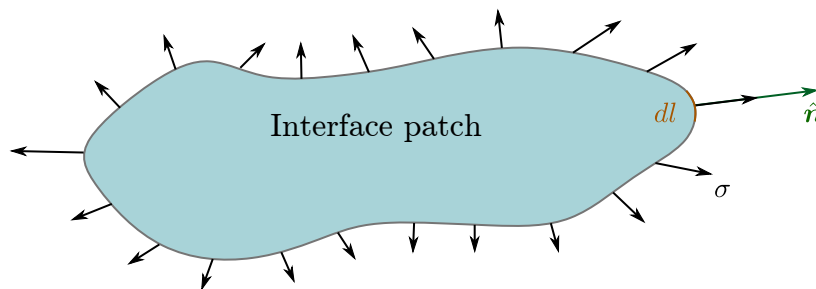


Figure 1.3: Free body diagram depicting the force due to surface tension exerted on a patch of a liquid interface by its neighbouring portion.

Free body diagrams are indispensable tools for analyzing the mechanical consequences of surface tension. For a patch of the interface, whose boundary is given by the curve C , the net force exerted by the neighbouring portion of the interface is given by

$$\mathbf{F} = \int_C \sigma \hat{\mathbf{n}} \, dl, \quad (1.1)$$

where σ is the coefficient of surface tension, $\hat{\mathbf{n}}$ is a unit normal that is tangential to the interface but normal to the curve C , and dl is the arc-length element.

In this chapter, we discuss the molecular origin of surface tension.

1.1 Molecular origin of surface tension

The reason underlying the existence of surface tension on liquid interfaces may be traced back to the reason underlying the existence of the liquid state itself. The chain of reasoning justifying this claim is briefly and informally presented below. For more details, refer to j. Israeliachvili, “Intermolecular and surface forces”, Academic Press, London.

The liquid state exists due to a weak attractive force between the molecules of the liquid. In the absence of such an attractive force, the interaction between the molecules is limited to a short range repulsion, causing collision between the molecules, and leading to a gaseous state. Indeed, an assumption underlying the kinetic theory of gases is that attractive interaction between molecules be negligible (compared to their average kinetic energy). In the absence of such an interaction, the molecules move more or less in a straight line between collisions and this fills the whole volume available to them, which is the defining characteristic of a gas. Violation of this assumption causes a departure from gaseous state and underlies the formation of the liquid state.

A gas condenses when the average kinetic energy of the molecules becomes comparable to the potential energy well formed by a combination of long-range attraction and short-range repulsion between molecules. As the temperature of the gas is reduced, the kinetic energy of the molecules decreases (the kinetic energy is proportional to the temperature according to statistical mechanics). At the melting point, the kinetic energy is comparable to the intermolecular attractive potential energy.

The interaction between molecules may be characterized by an intermolecular potential energy. The depth of the potential well, ϵ , characterizes the scale for the energy needed for molecules to escape from the attractive interaction (see Figure 1.4). This energy is provided to the molecules in the form of random thermal kicks provided by the jiggling of the neighbouring molecules. The magnitude of these kicks is characterized in terms of the average kinetic energy of the molecules, which is given in terms of the absolute temperature as $k_B T$ (k_B being the Boltzmann constant). When $\epsilon \approx k_B T$, molecules start to coagulate because the thermal jiggling is not strong enough to break the attractive bond between the molecules. This is how a gas condenses, typically into a liquid state for small molecules like water.

Thus, an order of magnitude estimate for the interparticle potential well $\epsilon \approx k_B T_m$, where T_m is the boiling temperature. For water, $T_m = 373$ K, which implies $\epsilon \approx k_B T_m = (1.3 \times 10^{-23} \text{ J/K}) (373) \text{ K} \approx 5 \times 10^{-21} \text{ J}$. For liquid Helium, $T_m \approx 4$ K, so $\epsilon \approx 6 \times 10^{-23} \text{ J}$.

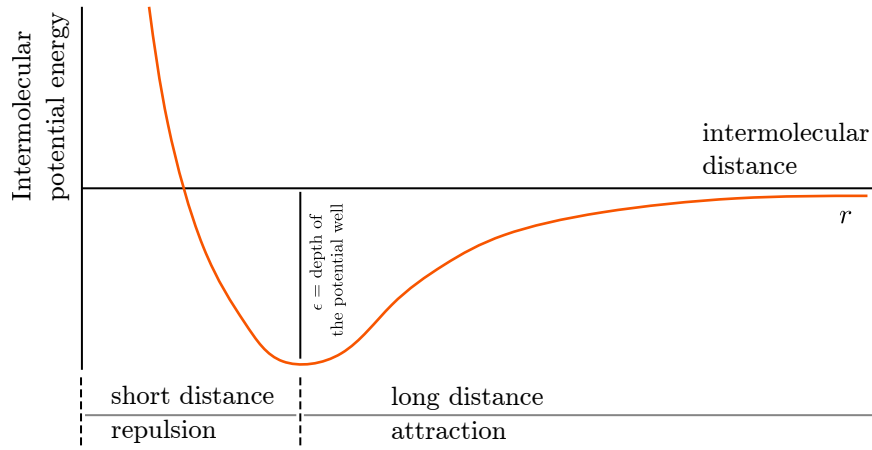


Figure 1.4: A characteristic interaction potential energy between two molecules of a liquid.

Thus, the energy of each molecule is reduced by an amount that scales as $Z\epsilon$, where Z is the average number of neighbours the molecule experiences, approximately 8 (see Figure 1.5). At the interface, the molecules have fewer neighbours, say half that of a molecule in the interior. These molecules have a higher energy due to the reduced number of neighbours. The magnitude of this energy per molecule may be estimated as $Z\epsilon/2$. If a is half the typical intermolecular distance, the excess energy per unit area scales as $Z\epsilon/(2\pi a^2)$. Using $a \approx 1$ nm for small molecules like water, the excess surface energy per unit area is

$$\epsilon_A = \frac{8}{2} \frac{5 \times 10^{-21} \text{ J}}{3.14 \times (10^{-9} \text{ m})^2} \approx 6 \times 10^{-3} \text{ J/m}^2. \quad (1.2)$$

Similarly, for helium

$$\epsilon_A = \frac{8}{2} \frac{6 \times 10^{-23} \text{ J}}{3.14 \times (10^{-9} \text{ m})^2} \approx 7 \times 10^{-5} \text{ J/m}^2. \quad (1.3)$$

This excess energy is closely related to the surface tension.

Excess energy means lower density of molecules at the interface. The molecules at the interface are attracted towards the interior of the liquid. Think of either the unbalanced force or the excess energy for being on the interface. It is energetically not preferable for the molecules to be at the interface. As a result of this attraction, the density of molecules on the interface is less than that in the bulk, as shown schematically in Figure 1.5.

Lower density means larger average distance between molecules on the interface. The average intermolecular distance lies in the range for long-distance attraction. This attraction manifests as a tensile force on the interface, or surface tension. In this manner, an attractive intermolecular force leads both to the existence of the liquid state and the surface tension on the interface.

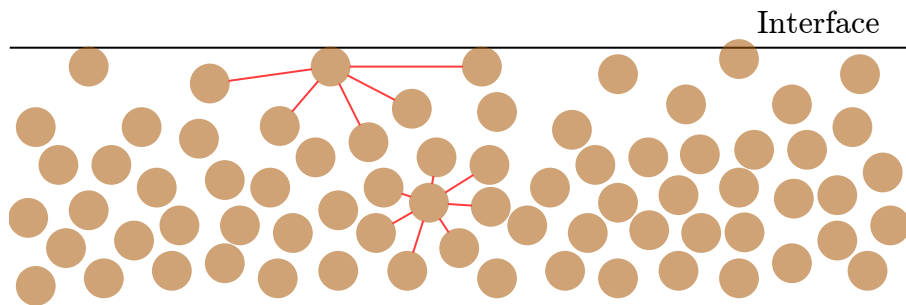


Figure 1.5: Nearest neighbour interaction for liquid molecules in the interior of the liquid phase and for molecules near the interface.

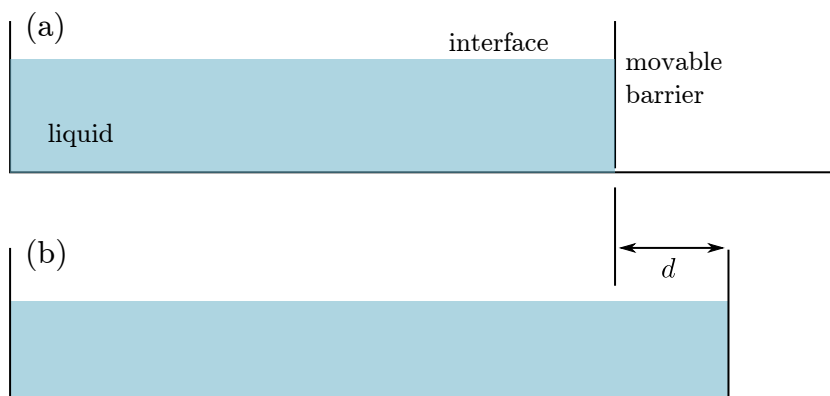


Figure 1.6: Schematic of the thought experiment to illustrate the relation between excess surface energy and surface tension. (a) A column of liquid in a trough with a movable barrier. (b) The barrier moved a distance d to extend the interface.

1.2 Surface energy and surface tension

There is a closer relation between excess surface energy and surface tension. Consider the following thought experiment. A trough with a movable wall is filled with a liquid as shown in Figure 1.6. The trough has width w out of the plane of the paper. The way we defined surface tension, the interface exerts a force σw on the barrier. Imagine a situation with zero gravity.

Now imagine moving the barrier quasi-statically a distance d , as shown in Figure 1.6(b). The area of the interface increases by an amount wd , hence the excess interface energy increases by $\epsilon_A \times wd$. The work done by the force moving the barrier is $(\sigma w) \times d$.

By the law of conservation of energy the work done to move the wall must all appear as an increase in the excess surface energy, because there is no other mechanism for the energy to be stored. As a result

$$\epsilon_A \times wd = (\sigma w) \times d \quad \implies \quad \sigma = \epsilon_A, \quad (1.4)$$

i.e. the excess surface energy is numerically equal to the surface tension.

The dimensions of the two quantities are also identical. The dimensions of ϵ_A are $[E/L^2]$, where $[E]$ is the dimension of energy, while dimensions of σ are $[F/L]$, where $[F]$ is the dimension of force. Because $[E] = [FL]$ (energy is force times displacement), the dimensions of σ and ϵ_A are identical.

We estimated the excess surface energy of water and liquid helium to be $6 \times 10^{-3} \text{ J/m}^2$ and $7 \times 10^{-5} \text{ J/m}^2$, respectively. The corresponding values of surface tension are $70 \times 10^{-3} \text{ N/m}$ and $3 \times 10^{-4} \text{ N/m}$, respectively. The estimates are comparable, especially with very approximate values of parameters.

1.3 Surfactants

Surfactants are chemical compounds, which preferentially adsorb to the liquid interface. For example, consider a common surfactant, sodium dodecyl sulfate (SDS). The molecular structure of this compound consists of a hydrophilic (i.e. water-loving) head and a hydrophobic (i.e. water-hating) tail (see Figure 1.7). When mixed with water, SDS dissolves in it. But the molecules that can adsorb to the interface with their heads immersed in water and tails emerging out of water have a lower energy configuration than that of the molecules in the bulk, where the hydrophobic tails are surrounded by water molecules. Each such molecule adsorbed on the water interface lowers the energy of the interface, and depending on the area density of the adsorbed molecules, reduces the excess energy of the interface per unit area. Since excess energy per unit area is equivalent to surface tension, surfactants when mixed with water reduce the surface tension of water.

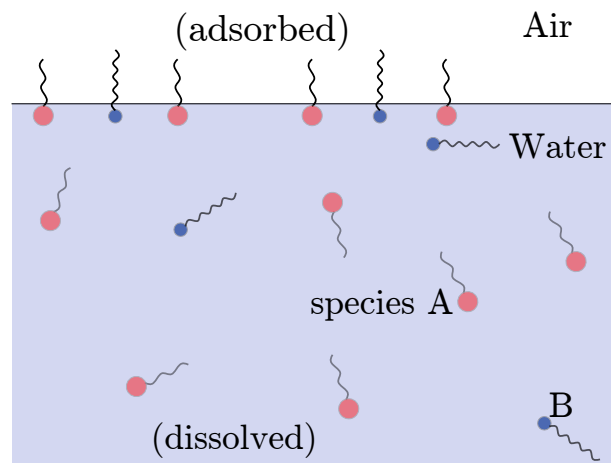


Figure 1.7: Schematic depiction of the action of surfactants showing two chemical species, A and B, in both the dissolved and adsorbed states.

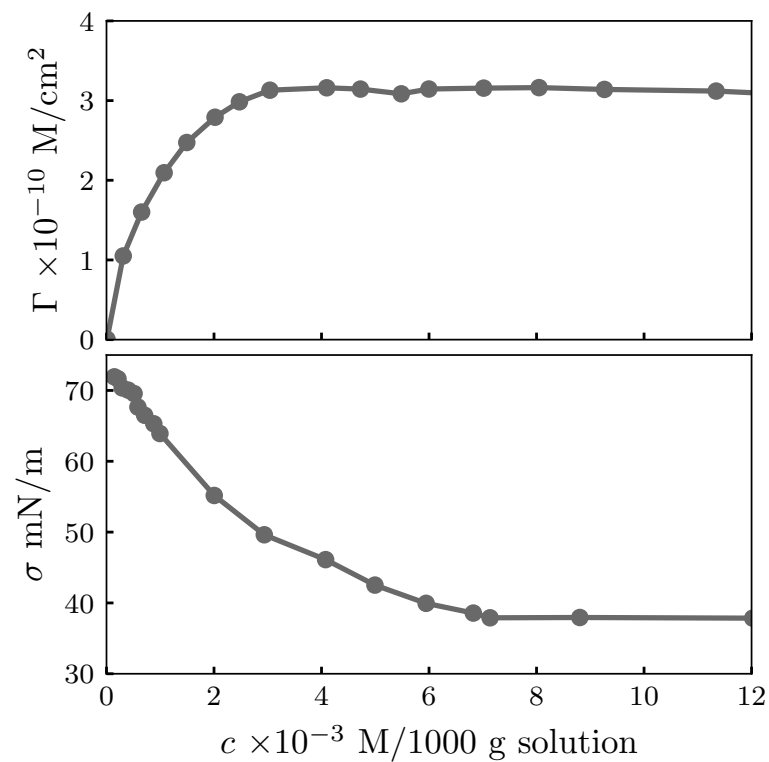


Figure 1.8: Measurements of the equilibrium behaviour of SDS. The adsorbed concentration of SDS (Γ) and the surface tension (σ) for different dissolved concentrations.

1.4 Conclusion

In this chapter, we introduced the concept of excess surface energy and surface tension for liquid interfaces and showed that they are equal. We also described the physical origin of the liquid state and that of surface tension.

Chapter 2

Static equilibrium of liquid interfaces

Surface tension contributes to the balance of forces on the fluid at the interface. We will consider the configuration of the static interfaces on the presence of surface tension.

2.1 Planar liquid interfaces

Consider a patch of planar liquid interface, as shown in Figure 1.3. The patch could enclose the liquid interface itself or some other material, such as a floating body. Let the boundary of the patch be denoted by the closed curve C . According to (1.1), the net force on the patch due to surface tension is

$$\mathbf{F} = \int_C \sigma \hat{\mathbf{n}} \, dl, \quad (2.1)$$

where $\hat{\mathbf{n}}$ is a unit vector normal to C but tangent to the interface and dl is the arc-length element. If the coefficient of surface tension is constant along the curve, then the integral can be demonstrated to vanish as follows:

$$\sigma \int_C \hat{\mathbf{n}} \, dl = -\sigma \mathbf{N} \times \int_C d\mathbf{r} = \sigma \mathbf{N} \times \mathbf{0} = \mathbf{0}, \quad (2.2)$$

where $\mathbf{N}$ is a unit vector normal to the interface (a constant for planar interfaces), and $\mathbf{r}$ is the differential vector arc-length element. The integral of $d\mathbf{r}$ integrates to zero because it is an exact differential and the integral is carried over a closed curve.

Another way to derive this result is to apply the divergence theorem as

$$\mathbf{F} = \int_C \sigma \hat{\mathbf{n}} \, dl = \int_A \nabla \sigma \, dA, \quad (2.3)$$

where A is the area enclosed by the curve C . Here $\nabla \sigma$ vanishes if σ is constant.

Based on this, we conclude that an unbalanced force can exist on a planar interface only if the surface tension is not constant. This unbalanced force is necessarily tangential to the surface. This force may be considered to be composed on an infinite number of infinitesimal contributions $d\mathbf{F}$ arising from small area elements dA making up the interface patch as

$$d\mathbf{F} = \nabla \sigma \, dA. \quad (2.4)$$

Although the force of surface tension is proportional to the length of the curve C , for planar interfaces the unbalanced force on infinitesimal patches is not proportional to the perimeter of the patch but the area of the patch. This is essentially due to the direction along which the force of surface tension applies – always tangent to the interface and normal to the curve being considered. Thus, we have the manifestation of a quantity that behaves like a stress. This quantity, $\nabla \sigma$ is called the *Marangoni stress*, after the Italian physicist Carlo Marangoni (1840-1925). These gradients of surface tension may exist on the interface due to non-uniform distribution of temperatures, solvents or surfactants (such as soap).

Let us now consider the influence of curvature of the interface.

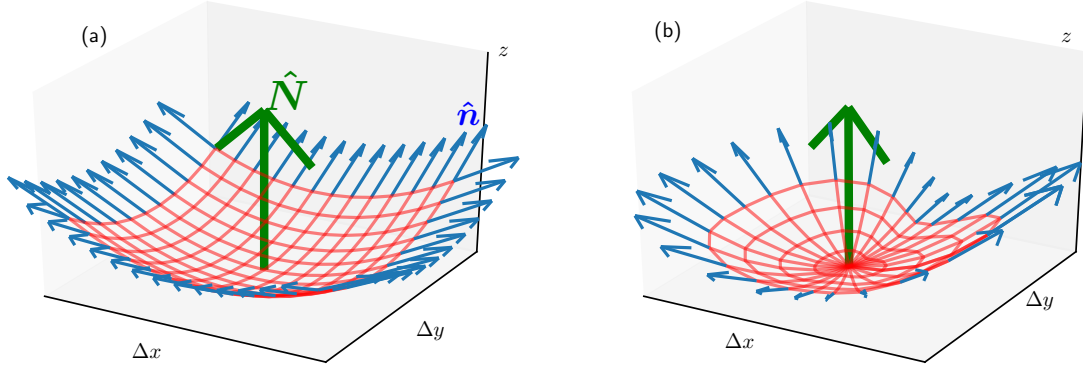


Figure 2.1: Schematic of free body diagram on an infinitesimal element of a curved interface. (a) An approximately rectangular element of the interface aligned with the Cartesian axes. Red mesh indicates the interface patch, blue arrows the force of surface tension, and the green arrow indicates the unit normal to interface $\hat{N}$. (b) An infinitesimal patch of the interface of arbitrary shape.

2.2 Curved liquid interfaces

For a curved interface, the force balance also has a component normal to the interface. This can be readily seen by examining the schematics shown in Figure 2.1, where it can be seen that the component normal to the interface does not cancel out.

2.2.1 Derivation for a rectangular interface patch

To derive the magnitude of this net unbalanced force, let us first consider an infinitesimal patch of the interface, approximately rectangular in shape with sides $\Delta x \times \Delta y$ (see Figure 2.1a). Here we take two orthogonal directions in the tangent plane of the interface to be the x and the y axes of a Cartesian coordinate system, with its origin at the centre of the rectangular patch. The interface normal is then along the z axis. The sum of the forces on the opposite sides, say those aligned along the y direction, can be evaluated as follows. Using the sketch in Figure 2.2, the component of the interfacial force in the direction normal to the interface is

$$\sigma \Delta y \times 2 \sin \theta \approx \sigma \Delta y \times 2\theta \approx \sigma \Delta y \times \kappa_{xx} \Delta x, \quad (2.5)$$

where κ_{xx} is the curvature of the interface patch along the x direction, such that $\theta = \kappa_{xx} \Delta x / 2$. Here, the force along the tangent plane to the interface vanishes. (If surface tension is not constant, then the tangential component evaluates to the Marangoni stress derived in §2.1.) Similarly, the unbalanced force on the sides aligned with the x direction is

$$\sigma \Delta x \times \kappa_{yy} \Delta y, \quad (2.6)$$

where κ_{yy} is the interface curvature along the y direction. The net force may be written as

$$\int_C \sigma \hat{n} \, dl \approx \sigma \Delta x \Delta y \times (\kappa_{xx} + \kappa_{yy}). \quad (2.7)$$

Noting that $\kappa_{xx} + \kappa_{yy}$ is twice the mean curvature κ_{mean} , and in the limit of an infinitesimal patch size, we arrive at

$$\int_C \sigma \hat{n} \, dl \approx \sigma \Delta x \Delta y \times 2\kappa_{\text{mean}} = \sigma \Delta A \times 2\kappa_{\text{mean}}, \quad (2.8)$$

where ΔA is the area of the patch. The result is independent of the choice of x and y axes direction, so long as they are along the tangent plane to the interface, because the mean curvature is an invariant of the interface geometry.

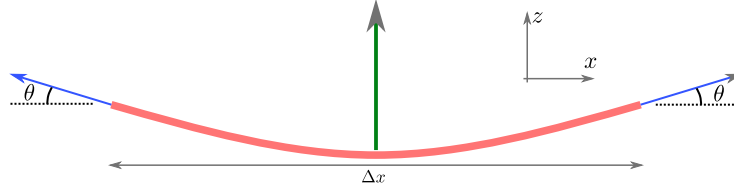


Figure 2.2: Side perspective of a section of the interface in Figure 2.1(a). The side visible is of length Δx . Color code same as Figure 2.1.

2.2.2 General derivation for a curved interface patch

To see that the result is independent of the shape of the patch, and that the Marangoni component of the force is additive, let us consider the net force on an infinitesimal patch of the interface of arbitrary shape, such as shown in Figure 2.1(b). The tangent plane is again used to construct a local Cartesian coordinate system with its origin inside the patch, with the x and y coordinates parameterizing the patch. The curvature at the origin is, say, given by the tensor

$$\boldsymbol{\kappa} = \begin{bmatrix} \kappa_{xx} & \kappa_{xy} \\ \kappa_{xy} & \kappa_{yy} \end{bmatrix}. \quad (2.9)$$

The normal to the interface at any location parameterized by the coordinates (x, y) is given to $O(x, y)$ by

$$\hat{\mathbf{N}} = \hat{\mathbf{z}} + (\kappa_{xx}x + \kappa_{xy}y)\hat{\mathbf{x}} + (\kappa_{xy}x + \kappa_{yy}y)\hat{\mathbf{y}}. \quad (2.10)$$

Noting that $\hat{\mathbf{n}} = \hat{\mathbf{t}} \times \hat{\mathbf{N}}$ and that $\hat{\mathbf{t}} = a\hat{\mathbf{x}} + b\hat{\mathbf{y}} + O(x^2, xy, y^2)$, i.e. it lies in the xy -plane, yields

$$\hat{\mathbf{n}} = \hat{\mathbf{n}}' + \hat{\mathbf{z}} \{ \hat{\mathbf{n}}' \cdot [(\kappa_{xx}x + \kappa_{xy}y)\hat{\mathbf{x}} + (\kappa_{xy}x + \kappa_{yy}y)\hat{\mathbf{y}}] \} + O(x^2, xy, y^2), \quad (2.11)$$

where $\hat{\mathbf{n}}' = \hat{\mathbf{t}} \times \hat{\mathbf{z}} = a\hat{\mathbf{y}} - b\hat{\mathbf{x}}$ is the unit vector in the xy -plane that is perpendicular to $\hat{\mathbf{t}}$. The net force evaluates to

$$\begin{aligned} \int_C \sigma \hat{\mathbf{n}} \, dl &= \int_C \sigma \hat{\mathbf{n}}' \, dl + \hat{\mathbf{z}} \int_C \sigma \hat{\mathbf{n}} \cdot [(\kappa_{xx}x + \kappa_{xy}y)\hat{\mathbf{x}} + (\kappa_{xy}x + \kappa_{yy}y)\hat{\mathbf{y}}] \, dl + O(x^3, x^2y, xy^2, y^3) \\ &= \int_A \boldsymbol{\nabla} \sigma \, dA + \hat{\mathbf{z}} \int_A \sigma \left[\frac{\partial(\kappa_{xx}x + \kappa_{xy}y)}{\partial x} + \frac{\partial(\kappa_{xy}x + \kappa_{yy}y)}{\partial y} \right] dA + O(x^3, x^2y, xy^2, y^3) \\ &= \int_A \boldsymbol{\nabla} \sigma \, dA + \hat{\mathbf{z}} \int_A \sigma (\kappa_{xx} + \kappa_{yy}) dA + O(x^3, x^2y, xy^2, y^3), \end{aligned} \quad (2.12)$$

where the order of the error term arises from the product of $O(x^2, xy, y^2)$ error in the integrand and the $O(x, y)$ extent of the integration domain along the length of the curve. In the limit of an infinitesimal interface patch, the integrals scale as the area of the patch, i.e. $O(x^2, xy, y^2)$, while the error term is one order smaller, and thus vanishes. This leads to

$$\int_C \sigma \hat{\mathbf{n}} \, dl = \underbrace{\int_A \boldsymbol{\nabla} \sigma \, dA}_{\text{Marangoni stress}} + \hat{\mathbf{z}} \underbrace{\int_A \sigma (\kappa_{xx} + \kappa_{yy}) dA}_{\text{Laplace pressure}}. \quad (2.13)$$

As in §2.1, for flat interfaces, (2.13) reduces to the Marangoni stress and for constant σ , it derives its contribution only from Laplace pressure.

2.2.3 Consequences of Laplace pressure – equilibrium shape of a liquid blob

The results so far can be used to determine the shape of a liquid blob in equilibrium. For this determination, we will ignore the influence of gravity. Equilibrium dictates that the surface tension be uniform, i.e. agencies such as temperature and surfactants that cause surface tension to vary are uniform. In the absence of gravity, hydrostatics dictate that the pressure inside p_{in} and outside p_{out} the drop must also be uniform. The force balance on a small patch of the interface then only constitutes the forces of pressure and those acting on the interface as

$$d\mathbf{F} = \int_A (p_{\text{in}} - p_{\text{out}} - 2\sigma\kappa_{\text{mean}}) \, dA = 0. \quad (2.14)$$

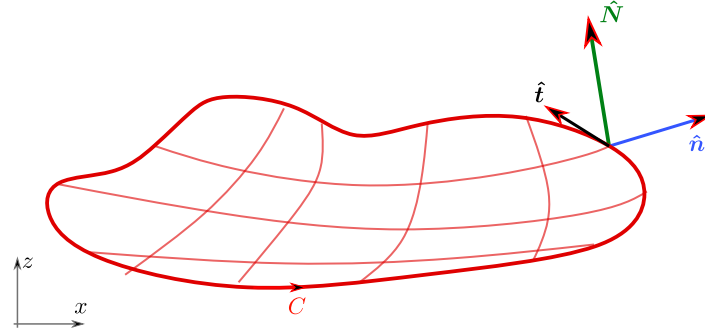


Figure 2.3: Definition of some useful vectors in Figure 2.1(b). Here $\hat{\mathbf{t}}$ is the unit tangent vector to the boundary curve C , $\hat{\mathbf{N}}$ the unit normal to the interface and $\hat{\mathbf{n}}$ the vector normal to $\hat{\mathbf{t}}$ but parallel to the interface.

Consequently,

$$p_{\text{in}} = p_{\text{out}} + 2\sigma\kappa_{\text{mean}}, \quad (2.15)$$

or, in other words, the inside of the blob is pressurized relative to the outside by an amount equal to the Laplace pressure. Since the inside pressure must be uniform, the shape of the blob must be one with constant mean curvature, i.e. a sphere.

Energetic considerations may alternatively be used to arrive at the same conclusion. The thermodynamic energy of the system is derived from the surface energy of the blob. Minimizing this energy is then equivalent to determining the shape the minimizes the surface area, while maintaining a fixed volume equal to the volume of the blob. This shape is a sphere.

Chapter 3

Three-phase contact lines

Now we consider the mechanics at the intersection of the mutual interfaces between three adjoining immiscible phases, the so-called *three-phase contact line*. One of the three phases must be a liquid, so that surface tension between this liquid phase and the other two phases are under tension. There are two cases we consider in this chapter: (i) where the three phases are two immiscible liquids and a third fluid, and (ii) where the three phases are liquid, another fluid and a solid. (Here fluid implies either a liquid or a gas.)

3.1 Liquid-liquid-fluid contact line

At the three-phase contact line between three fluids (naturally, at least two of these must be immiscible liquids), the action of surface tension must form a Neumann triangle. In other words, the sector angles for the three phases (see Figure 3.1a) must adjust themselves in such a way that the force of surface tension from the three interfaces is balanced. Mathematically, projecting the force along and perpendicular to the 1-3 interface, yields

$$\sigma_{13} + \sigma_{12} \cos \theta_1 + \sigma_{23} \cos \theta_3 = 0, \quad (3.1a)$$

$$\sigma_{12} \sin \theta_1 - \sigma_{23} \sin \theta_3 = 0. \quad (3.1b)$$

Either equation (3.1) or the geometric interpretation of the Neumann triangle uniquely determine the angles θ_1 , θ_2 and θ_3 , provided the following inequalities are satisfied:

$$\sigma_{13} \leq \sigma_{12} + \sigma_{23}, \quad (3.2a)$$

$$\sigma_{12} \leq \sigma_{13} + \sigma_{23}, \text{ and} \quad (3.2b)$$

$$\sigma_{23} \leq \sigma_{12} + \sigma_{13}. \quad (3.2c)$$

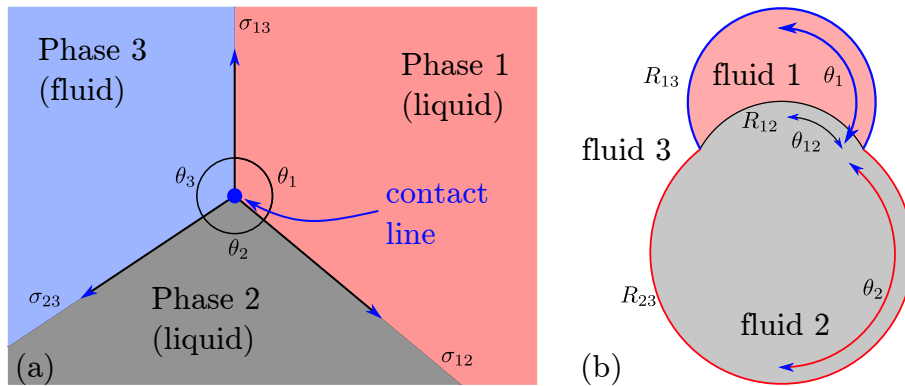


Figure 3.1: Schematic of a three-phase contact line between two liquids and a third fluid. The three phases are labelled 1, 2 and 3, and occupy a sector of angle θ_1 , θ_2 and θ_3 , respectively. The surface tension of the interface between phase i and j is σ_{ij} .

3.1.1 Application: Two drops in contact

The Young-Laplace equation and the Neumann triangle construction is used to determine the geometry of two drops (or bubbles) in contact with each other. The geometry is schematically shown in Figure 3.1(b). The volumes of the two liquid drops (V_1 and V_2) are known, as are the pairwise surface tensions of the interfaces (σ_{12} , σ_{13} , and σ_{23}). Each interface takes the shape of a axisymmetric spherical cap. The unknowns of the geometry are the angles (θ_1 , θ_2 , θ_{12}) and the radii (R_{12} , R_{23} , R_{13}) of the spherical caps, which constitute six unknowns. To determine these six unknowns, we use the following six conditions:

1. The volumes of the two drops depending on the geometry furnish two equations, which are of the form

$$V_1 = V(R_{13}, \theta_1) - V(R_{12}, \theta_{12}), \quad (3.3a)$$

$$V_2 = V(R_{23}, \theta_2) + V(R_{12}, \theta_{12}), \quad (3.3b)$$

where $V(R, \theta) = 2\pi R^3(1 - \cos \theta)/3$ is a function that represents the volume of spherical cap of radius R and angle θ .

2. The pressures difference across the three interfaces is given by Laplace pressure, which furnishes one more equations as follows

$$p_1 - p_3 = \frac{2\sigma_{13}}{R_{13}}, \quad (3.4a)$$

$$p_2 - p_3 = \frac{2\sigma_{23}}{R_{23}}, \quad (3.4b)$$

$$p_2 - p_1 = \frac{2\sigma_{12}}{R_{12}}. \quad (3.4c)$$

Here the pressure differences constitute two additional unknowns, which could be eliminated as

$$\frac{2\sigma_{13}}{R_{13}} + \frac{2\sigma_{12}}{R_{12}} - \frac{2\sigma_{23}}{R_{23}} = 0. \quad (3.5)$$

3. The Neumann triangle condition furnishes two conditions for force balance along two orthogonal directions as

$$\sigma_{13} \cos \theta_1 + \sigma_{23} \cos \theta_2 + \sigma_{12} \cos \theta_{12} = 0, \quad (3.6a)$$

$$\sigma_{13} \sin \theta_1 - \sigma_{23} \sin \theta_2 + \sigma_{12} \sin \theta_{12} = 0. \quad (3.6b)$$

4. Geometric compatibility that radius of the contact line is identical between the three interfaces, which reads

$$R_{13} \sin \theta_1 = R_{12} \sin \theta_{12} = R_{23} \sin \theta_2. \quad (3.7)$$

These appear to be two more equations, but indeed (3.5), (3.6b) and (3.7) are dependent on each other, with only three independent equations. This is a remarkable observation because it implies that the consideration of Laplace pressure jumps (3.5) arises out of a combination of vertical force balance (3.6b) and geometric compatibility (3.7). This dependence can be understood as combination of a local force balance (leading to Laplace pressure jumps) forming the global force balance on the contact line (i.e. Neumann triangle).

These six independent equations in six unknowns can be solved to determine the resultant geometry of the two-drop complex.

3.2 Solid-liquid-fluid contact line

Considerations change when one of the phases is a rigid solid so its interface with the other phases does not deform. A schematic of this situation is shown in Figure 3.2, where without loss of generality, we denote the third fluid to be air. The surface tension on the liquid-air, solid-liquid and solid-air interfaces is denoted σ_{la} , σ_{sl} and σ_{sa} , respectively. Since only the liquid-air interface is deformable in this situation, let us say that it makes an angle θ with the solid surface.

3.2.1 Equilibrium based on energetic considerations

An important variable that determines whether and how the liquid spreads on the solid surface is the differential change in surface excess energy caused by the motion of the interface. If the contact line in Figure 3.2(a) displaces a distance d away from the liquid phase, then this contributes to an additional solid-liquid excess energy of $\sigma_{sl}d$, and a reduction in the solid-air excess energy of $\sigma_{sa}d$. However, such a displacement d would cause the liquid-air interface to expand a distance $d \cos \theta$, costing an additional excess energy of $\sigma_{la}d \cos \theta$. Since thermodynamic systems tend to reduce the excess energy, the decrease in excess energy $(\sigma_{sl} - \sigma_{sa} + \sigma_{la} \cos \theta)d$ can be considered to be a driving force behind the spreading of the liquid. This quantity may be written in terms of the wetting parameter S defined as

$$S = \frac{\sigma_{sa} - \sigma_{sl}}{\sigma_{la}}. \quad (3.8)$$

The decrease in excess energy is $(\cos \theta - S)\sigma_{la}d$.

First, suppose $-1 \leq S \leq 1$. In this case, the contact line has a tendency to advance (i.e. the liquid wets more surface of the solid) if $\cos \theta < S$, and the contact line has the tendency to recede (i.e. the liquid wets less solid surface) if $\cos \theta > S$. Equilibrium corresponds to the case between the two tendencies, i.e. $\cos \theta = S$. The angle that satisfies this condition is called the *equilibrium contact angle*, which we will denote θ_{eq} . Thus,

$$\cos \theta_{eq} = S = \frac{\sigma_{sa} - \sigma_{sl}}{\sigma_{la}}. \quad (3.9)$$

This relation is called the *Young-Dupré* relation.

Now, let us consider the case $S > 1$. (The case $S < -1$ may be treated by exchanging the roles of liquid and air.) The condition $S > 1$ may be interpreted as $\sigma_{sa} > \sigma_{sl} + \sigma_{la}$. If the solid surface is coated by a microscopically thin layer of the liquid, as shown in Figure 3.2(b), the equivalent excess energy of the surface per unit area is $\sigma_{sa,eq} = \sigma_{sl} + \sigma_{la}$. When $S > 1$, this state of the liquid coated solid surface is therefore thermodynamically favourable compared to the pristine solid-air interface. As a consequence, any vapour of the liquid present in the environment spontaneously condenses on the solid surface coating it upto a point where the equivalent excess energy $\sigma_{sl} + \sigma_{la}$ becomes equal to σ_{sa} . In this manner, unless extreme care is exercised to maintain the purity of the interface, surfaces with large values of surface excess energy are spontaneously contaminated by chemical elements present in the environment that reduce the equivalent excess surface energy. Thus, for materials which possess $S > 1$, contaminants spontaneously reduce the excess surface energy to an equivalent value of 1. For this reason, the case $S > 1$ reduces to the situation $S = 1$ (and by argument of exchanging the fluid and the liquid $S < -1$ reduces to $S = -1$).

3.2.2 Equilibrium based on force balance considerations

We now present the same results based on force-balance considerations.

The unbalanced surface tension forces (per unit length perpendicular to the plane of the paper) acting at the contact line is

$$\sigma_{sl} + \sigma_{la} \cos \theta - \sigma_{sa} = (\cos \theta - S)\sigma_{la} = (\cos \theta - \cos \theta_{eq})\sigma_{la}. \quad (3.10)$$

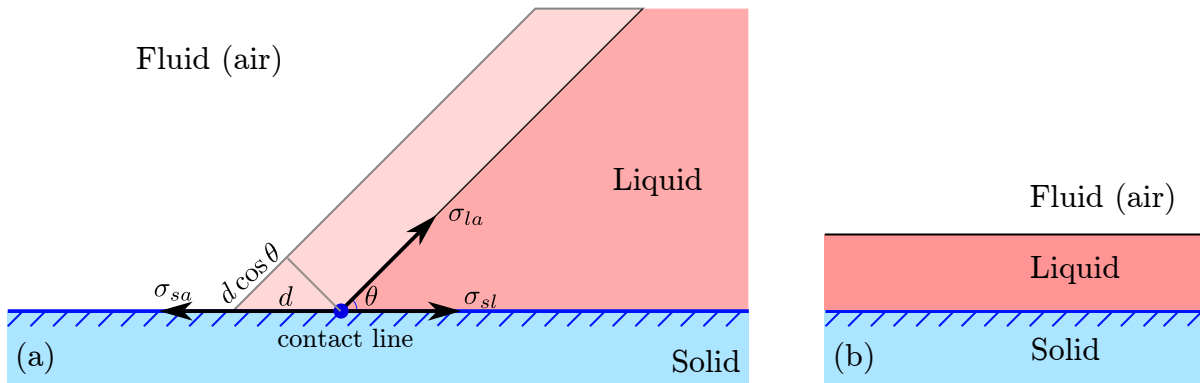


Figure 3.2: Schematics for analysis of the solid-liquid-fluid contact line. (a) Energetics and force balance at a solid-liquid-fluid contact line. (b) A solid surface coated by layer of the liquid.

When $\cos \theta > \cos \theta_{eq}$, i.e. $\theta < \theta_{eq}$, the unbalanced force points into the liquid and the contact line tends to recede and de-wet the solid, whereas when $\cos \theta < \cos \theta_{eq}$, i.e. $\theta > \theta_{eq}$, the unbalanced force points away from the liquid and tends to advance the contact line and the liquid to wet the solid. Equilibrium is attained at $\theta = \theta_{eq}$ when the unbalanced force vanishes.

3.2.3 Contact line motion

Contact lines move in the direction of unbalanced tangential force. The speed with which they move is a topic of current research, but there is no doubt that they move in the direction of unbalanced tangential force, which as argued earlier depends on $(\cos \theta - \cos \theta_{eq})$.

The idealized relations derived in §3.2.2 can only hold for truly flat surfaces. However, real surfaces are rarely flat, which has non-trivial consequences for the motion of the contact line. These consequences are expressed in the literature using terms such as *pinning*, *de-pinning*, *stick-slip motion*, and *contact line hysteresis*. We present a rationalization of these phenomena here.

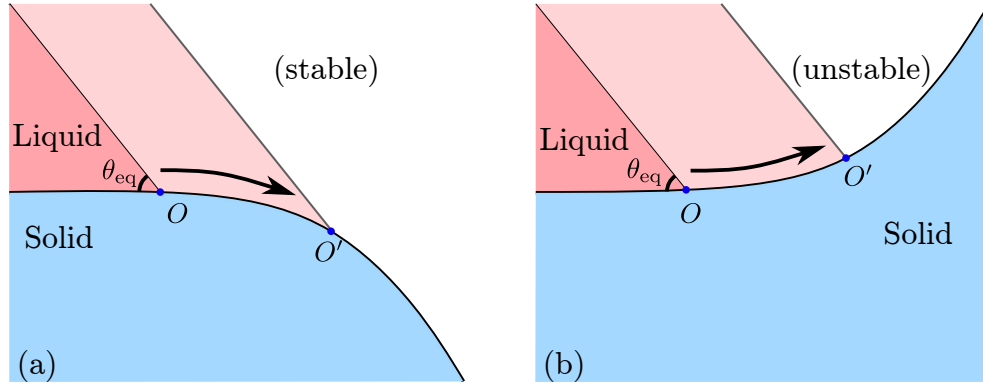


Figure 3.3: Influence of surface curvature on the tendency of a contact line to move. (a) Solid surface with a convex face towards the liquid. Solid black curved arrow denotes imagined displacement of the contact line from O to O' . This displacement reduces the contact angle of the liquid because of the change in orientation of the solid surface and results in a unbalanced force that tends to move the contact line back to O . Therefore, the contact line position in this case is stable. (b) Solid surface with concave face towards the liquid. In this case, the contact angle at the displaced contact line at O' is higher than its original position O , and the resulting imbalance in the surface tension forces tends to move the contact line further away from O . Therefore, the contact line position in this case is unstable and runs away from O .

To understand the basic mechanisms, consider the influence of curvature of a solid surface on the tendency of contact line motion. The two possibilities of convex and concave surfaces is shown schematically in Figure 3.3. In the first case, Figure 3.3(a) shows the contact line on a curved solid surface with the convex face towards the liquid. The liquid initially makes an angle equal to the equilibrium contact angle at the contact line. If we now imagine a small displacement of the contact line as shown in this figure, the contact angle changes in such a way as to push the contact line back to its original location. This contact line configuration is stable. However, if the concave face of the solid is towards the liquid, as shown in Figure 3.3(b), the change in contact angle pushes the contact line further away from its initial location. This contact line configuration is unstable and runs away from its original location.

Next we use the background developed so far to discuss the phenomena emerging from the interaction of contact lines with surfaces that possess microscopic features. To illustrate the simplest such phenomena, consider a axisymmetric drop on a surface with a well-defined concentric geometric asperity, such as the one shown in Figure 3.4. The surface is otherwise smooth and offers a fixed equilibrium contact angle to the liquid in the drop. Consider the asperity to be microscopic, i.e. of a length scale much smaller than the drop radii in question. Depending on the volume of the deposited liquid, the equilibrium shape of the drop is a spherical cap with a contact-line radius R .

Now imagine increasing the volume of the deposited drop on the surface, which advances the contact line. In doing so, the drop volume traverses the path shown in Figure 3.5(a) and the shapes in Figure 3.5(b). For small volumes, the contact line of the deposited drop has a radius smaller than the asperity. As the volume increases and the contact line approaches the asperity, the surface is concave to the liquid and, therefore, unstable. This causes the contact line to slip over a small region, depicted in Figure 3.5(a) from points A to B. On the convex

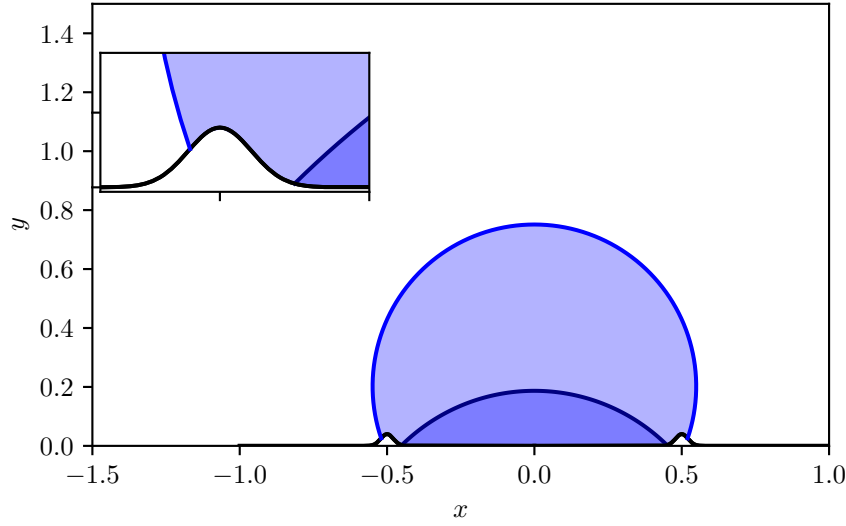


Figure 3.4: Schematic of an axisymmetric drop on an axisymmetric surface. The equilibrium contact angle between the solid and the liquid is 60° . The solid surface has a small axisymmetric bump at a radius of 0.5 from the axis of symmetry. The figure shows the drop shape for two radii of the contact line, one right before the uphill part of the bump and another on its downhill part.

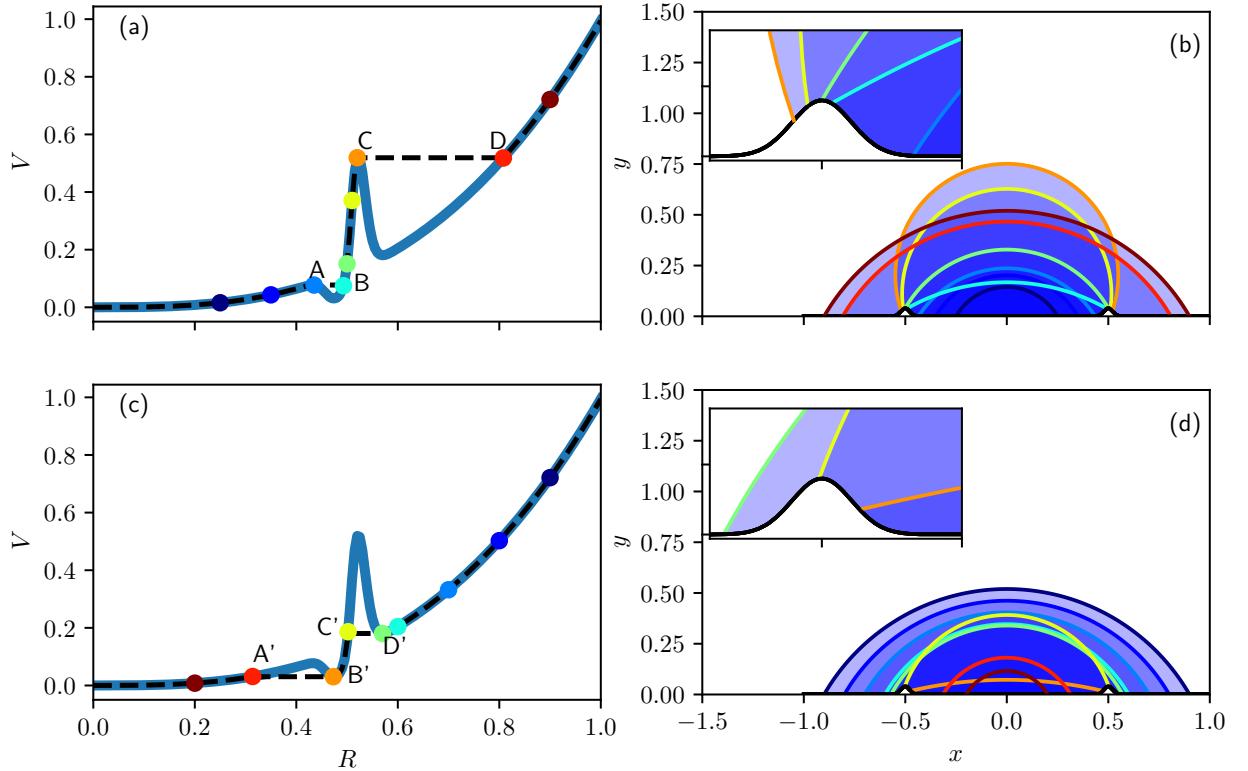


Figure 3.5: Contact line motion, pinning, depinning, stick-slip and hysteresis. (a) Volume of the drop V as a function of the contact line radius R for a drop (blue curve). The dashed curve shows the path taken by a drop of increasing volume. The contact line radius jumps from A to B and then from C to D. Coloured solid circles show specific cases illustrated in panel b. (b) The shape of the drop at the points indicated by solid coloured circles in panel a (corresponding cases coded by identical colour). (c-d) Same as panels a-b but for drops of decreasing volume.

part of the solid surface, the contact line is stable, and offers a range of microscopic orientations to the liquid over the extent of the asperity. This process is depicted in Figure 3.5(a) between points B and C, and the corresponding interface shapes are shown in Figure 3.5(b). As the contact line traverses the asperity, while the microscopic contact angle the liquid surface makes with the local solid surface remains equal to the equilibrium contact angle, the apparent or the “macroscopic” contact angle traverses a range equal to the range of the surface orientation. In this range, the contact line itself moves only by an amount comparable to the asperity scale. For microscopic asperities, the contact line appears to be *pinned* at the asperity, while the angle can take a range of values, say $\theta_{\min} \leq \theta \leq \theta_{\max}$, depending on the precise details of the shape of the asperity. If the volume of the drop exceeds beyond that of point C in Figure 3.5(a), the contact line *depinns* and slips to the position given by D.

Now imagine decreasing the volume below that given by point D, which recedes the contact line. The drop shape then evolves along the geometry described in Figure 3.5(c-d). On the way towards deflating the drop, the path taken by the drop jumps from D' to C' and B' to A', which is distinct from the path taken while inflating. The contact line pins and depins, but between different positions compared to an advancing contact line. The difference in paths taken by an advancing contact line versus a receding contact line is termed as *contact line hysteresis*.

A similar picture is expected at chemical asperities on a flat solid surface. A chemical asperity is a region of the surface where the equilibrium contact angle varies from the rest of the surface. Here we state without proof or demonstration that phenomena similar to pinning, depinning, stick-slip behaviour and contact line hysteresis also exists in the presence of chemical asperities.

The roughness of real surfaces is best characterized as random, composed of a distribution of geometric and chemical asperities on the microscale. Because of the roughness, the contact line pins can pin at any location and only advance if the contact angle exceeds a value θ_{adv} called the advancing contact angle, which is greater than the equilibrium contact angle on a flat surface. Similarly, the contact line recedes when the contact angle decreases below θ_{rec} called the receding contact angle, which is smaller than the equilibrium contact angle.

3.3 Conclusion

In this chapter, we have presented conditions of mechanical equilibrium at the three-phase contact line. The nature of the condition depends on whether all three phases are deformable, or whether one of the three phases is rigid. When one of the phases is rigid, mechanical equilibrium demands the satisfaction of the Young-Dupré relation. However, microscopic geometric and chemical asperities on the rigid surface then lead to phenomena of contact line pinning, depinning, stick-slip and hysteresis. For deformable phases, a Neumann triangle condition on the orientation of the interface applies. In recent years, experiments have confirmed the validity of the Neumann triangle condition for soft solids, such as hydrogels [1].

Another topic we did not discuss in this chapter is that of contact line behaviour on textured surfaces, i.e. surfaces with structured microscopic roughness. Texture systematically changes the energetic considerations of the interface with the solid surface. This leads to the lotus leaf effect, a phenomenon where droplets of water roll off of lotus leaves without wetting the surface. The explanation invokes a state of the interface called the *Cassie-Baxter state*, where the droplet balances gently on the tips of the microstructure without wetting the whole solid surface. However, the effect could be disrupted by transitioning to the so-called *Wenzel state*, where the liquid wets the whole surface. We will be seeing much more research on these topic in the coming years.

This completes the preliminaries necessary to mathematically model physical phenomena with liquid interfaces.

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Chapter 4

Surface tension and gravity

This chapter is dedicated to phenomena where surface tension and gravity govern the dynamics. The balance between these two forces generally leads to a static configuration and the object of interest is the geometric shape of the interface.

4.1 Dimensional analysis

Gravity is characterized by the specific weight of the liquid ρg , where ρ is the liquid density and g is the acceleration due to gravity. The dimensions of specific gravity are F/L^3 , where F denotes the dimensions of force and L those of length. Since the dimensions of surface tension σ are F/L , a balance of surface tension and gravity invariably yields the ratio $(\sigma/\rho g)$, which has the dimensions L^2 . Based on this arises the capillary length defined as $\ell_c = (\sigma/\rho g)^{1/2}$. For a fluid like water, with $\sigma = 72 \times 10^{-3}$ N/m and $\rho g = 9800$ N/m³, the capillary length is $\ell_c = 2.7$ mm.

4.2 Planar capillary meniscus

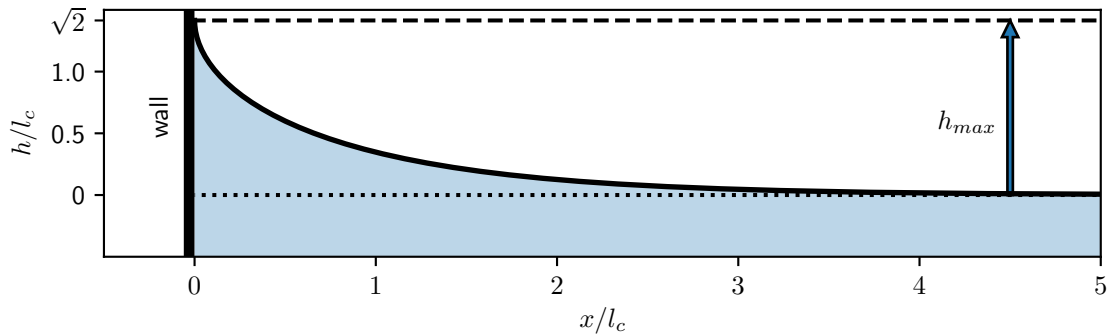


Figure 4.1: Shape of the planar meniscus. Based on the solution shown in ??.