2

Capillarity and Gravity

Liquids display rather peculiar properties. They have the ability to defeat gravity and create capillary bridges (see Figure 2.1), move up inclined planes, or rise in very small capillary tubes.[1] Moreover, drops may lose their spherical shape under the influence of gravity.

2.1 The Capillary Length κ^{-1}

There exists a particular length, denoted κ^{-1}, beyond which gravity becomes important. It is referred to as the *capillary length.* It can be estimated by comparing the Laplace pressure γ/κ^{-1} to the hydrostatic pressure $\rho g \kappa^{-1}$ at a depth κ^{-1} in a liquid of density ρ submitted to earth's gravity $g = 9.8$ m/s^2. Equating these two pressures defines the capillary length:

$$\boxed{\kappa^{-1} = \sqrt{\gamma/\rho g}} \tag{2.1}$$

The distance κ^{-1} is generally of the order of few mm (even for mercury, for which both γ and ρ are large). If one wants to increase κ^{-1} in a liquid by a factor 10 to 1,000, it is necessary to work in a microgravity environment or, more simply, to replace air by a non-miscible liquid whose density is similar to that of the original liquid.

Gravity is negligible for sizes $r < \kappa^{-1}$. When this condition is met, it is as though the liquid is in a zero-gravity environment and capillary effects

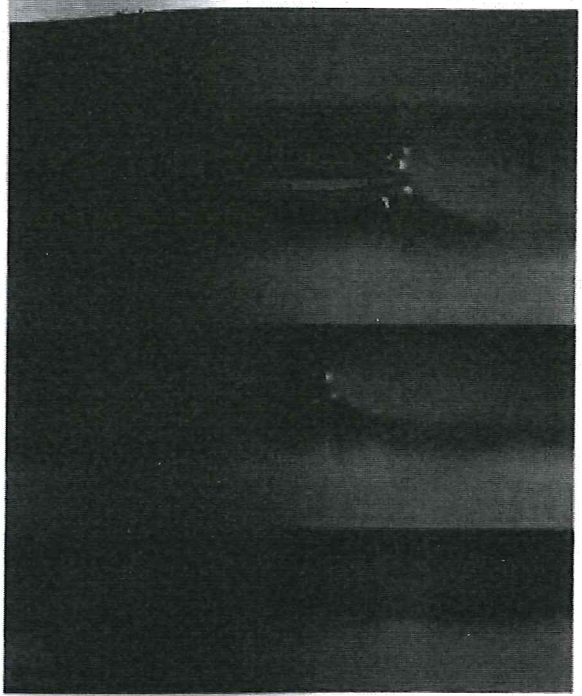

FIGURE 2.1. Liquid bath rising to form a capillary bridge (From "Nucleation Radius and Growth of a Liquid Meniscus," by G. Debregeas and F. Brochard-Wyart. In *Journal of Colloid and Interface Science, 190*, p. 134 (1997), © 2001 by Academic Press. Reproduced by permission.)

dominate. The opposite case, when $r > \kappa^{-1}$, is referred to as the "gravity" regime.

The distance κ^{-1} can also be thought of as a *screening length.* If one perturbs an initially horizontal liquid surface by placing on it a small floating object (Figure 2.2a), the perturbation induced on the surface dies out in a distance κ^{-1}.

It is convenient to consider the one-dimensional situation illustrated in Figure 2.2b. Here, the perturbing object is a solid vertical wall located at $x = 0$. In the vicinity of the wall, the surface of a liquid is no longer flat but, instead, rises to a height $z(x)$. Assume that the height z remains small (which is always true far enough from the wall, when $\kappa x > 1$). The local

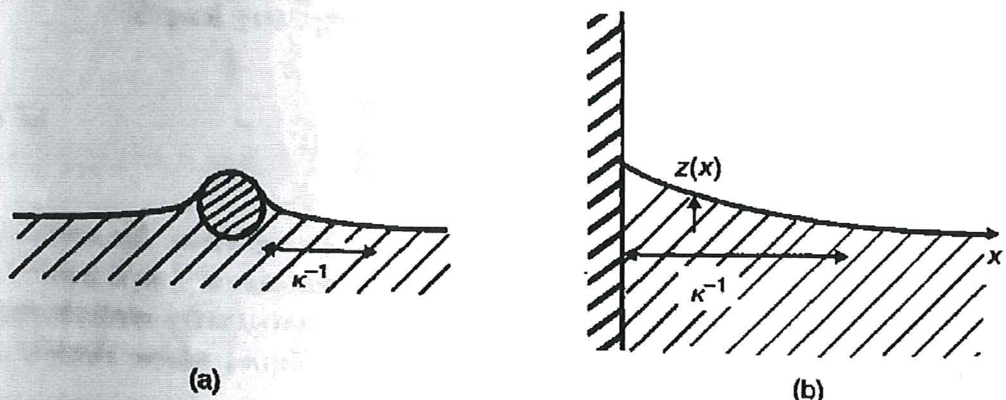

FIGURE 2.2. A small floating object (a) or a wall (b) perturbs the surface of the liquid over a distance κ^{-1} called the "capillary length."

curvature is then simply $-\frac{\partial^2 z}{\partial x^2}$, and Laplace's equation dictates that the pressure immediately under the surface be

$$p_A = p_{atm} - \gamma \frac{\partial^2 z}{\partial x^2} \tag{2.2}$$

where p_{atm} is the atmospheric pressure. At the same time, the pressure must also conform to the laws of hydrostatics, that is to say,

$$p_A = p_{atm} - \rho g z. \tag{2.3}$$

Equating these last two equations yields

$$\gamma \frac{\partial^2 z}{\partial x^2} = \rho g z \tag{2.4}$$

or, equivalently,

$$\frac{\partial^2 z}{\partial x^2} = \kappa^2 z. \tag{2.5}$$

The solutions to this last equation are of the form $z = z_0 \exp(\pm \kappa x)$. In the problem at hand, we are restricted to $z \to 0$ when $x \to \infty$. Therefore, we retain only the exponentially decaying solution:

$$z = z_0 \cdot \exp(-\kappa x) \tag{2.6}$$

Conclusion. Surface perturbations decay *exponentially* with distance with a characteristic length κ^{-1}, which is the capillary length. In the immediate vicinity of the wall, the exact solution is more complicated because the height z is no longer necessarily small. This case will be discussed shortly (section 2.3).

2.2 Drops and Puddles in the Partial Wetting Regime

2.2.1 *The Shape of Drops*

Imagine that we place drops of increasing sizes on a piece of silanized glass or on a horizontal sheet of plastic. The largest drops tend to flatten under the influence of gravity (Figure 2.3).

We have seen in the previous chapter that, when the spreading parameter S is negative (partial wetting regime), a drop of liquid deposited on a horizontal substrate exhibits a contact angle θ_E determined by Young's law. The shape of the drop will therefore change from perfectly spherical to almost completely flat depending on whether its radius R is small or large compared to the capillary length κ^{-1}.[2]

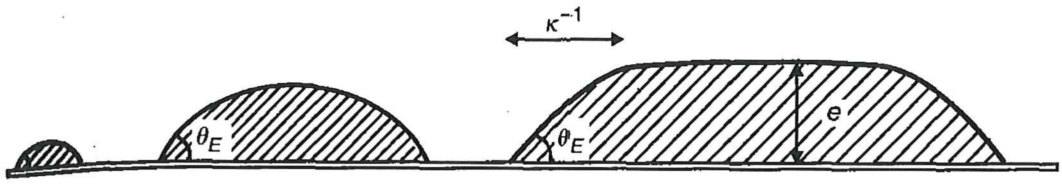

FIGURE 2.3. Water drops of increasing size on a sheet of plastic. Gravity causes the largest drops to flatten.

2.2.2 Droplets ($R \ll \kappa^{-1}$)

For small drops of radius less than κ^{-1}, the capillary forces are the only ones to come into play. In accordance with Laplace's equation, their curvature must be constant. Therefore, a drop deposited on a horizontal surface takes on the shape of a spherical cap whose edges intersect the substrate at angle θ_E. Measuring that angle enables us to determine the spreading parameter (negative in the present case) through the expression $S = \gamma \cdot (\cos\theta_E - 1)$.

Drops Deposited on Dirty Surfaces. We have implicitly assumed an ideal surface. On a real surface, the contact angle of a drop is often slightly dependent on the preparation conditions. Its value lies between two limits θ_A (larger) and θ_R (smaller). The *hysteresis* of the contact angle, determined via the force $\delta = \gamma \cdot (\cos\theta_R - \cos\theta_A)$, will be discussed in chapter 3. The difference $\theta_A - \theta_R$ is a measure of the state of cleanliness and roughness of a surface. It is used as a test in the automobile industry to ensure that surfaces are perfectly clean before applying paint. $\theta_A - \theta_R$ must be sufficiently small for good adhesion.

2.2.3 Heavy Drops ($R \gg \kappa^{-1}$)

For large drops whose radius exceeds κ^{-1}, gravitational effects dominate. A drop is flattened by gravity. At equilibrium, it takes on the shape of a liquid pancake of thickness e. The value of e can be calculated by expressing the equilibrium of the horizontal forces acting on a portion of the liquid.

The forces involved are shown in Figure 2.4. They are of two types:

1. Surface forces, which add up to $\gamma_{SO} - (\gamma + \gamma_{SL})$,
2. Hydrostatic pressure $\tilde{P}$, integrated over the entire thickness of the liquid, which amounts to $\tilde{P} = \int_0^e \rho g(e - \tilde{z})\, d\tilde{z} = \frac{1}{2}\rho g e^2$.

The equilibrium of forces per unit length can be expressed by the equation

$$\frac{1}{2}\rho g e^2 + \gamma_{SO} - (\gamma + \gamma_{SL}) = 0 \tag{2.7}$$

which leads to:

$$S = -\frac{1}{2}\rho g e^2. \tag{2.8}$$

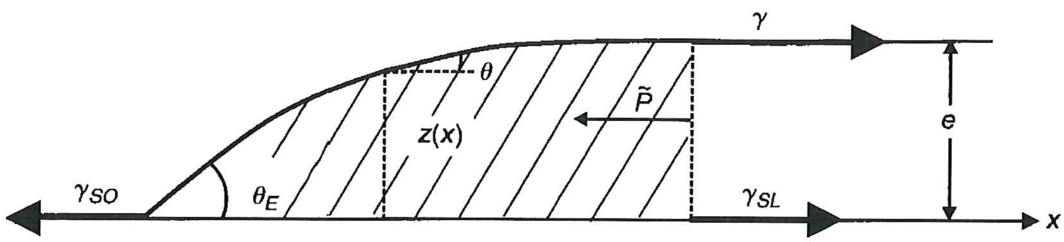

FIGURE 2.4. Equilibrium of the forces (per unit length of the line of contact) acting on the edge of a puddle. $\tilde{P} = \rho g e^2/2$ is the hydrostatic pressure.

Young's law, which describes the equilibrium of forces acting on the line of contact, implies that $\gamma_{SO} - (\gamma \cos\theta_E + \gamma_{SL}) = 0$. Therefore,

$$\gamma \cdot (1 - \cos\theta_E) = \frac{1}{2}\rho g e^2. \tag{2.9}$$

From the preceding equation, the thickness e of a puddle can be recast in terms of the capillary length:

$$e = 2\kappa^{-1} \sin\left(\frac{\theta_E}{2}\right). \tag{2.10}$$

When $\theta_E \ll 1$, the thickness simplifies to $e = \kappa^{-1}\theta_E$.

Alternatively, the thickness e can be calculated by minimizing the energy F_g of the puddle. If the surface area A of the drop is very large ($\sqrt{A} \gg \kappa^{-1}$), it is legitimate to neglect the energy associated with the edges. The energy of the drop can then be written as

$$F_g = -SA + \frac{1}{2}\rho g e^2 A. \tag{2.11}$$

The procedure consists in minimizing the energy F_g while keeping the volume $\Omega = Ae$ constant, which leads straight back to equation (2.8).

The Housewife Problem: A bucket containing 6 liters of water is emptied onto the ground. Calculate the wet surface area A for $\theta_E = 180°$ and for $\theta_E = 1°$. (Answers: 1 m^2; 120 m^2.)

Detailed Profile

To calculate the profile of a drop near its edge, one can still express the equilibrium of the horizontal forces acting on a portion of the drop near the boundary (Figure 2.4):

$$\gamma_{SO} + \tilde{P} = \gamma \cos\theta + \gamma_{SL} \tag{2.12}$$

where $\tilde{P} = \int_0^z \rho g(e - \tilde{z})\, d\tilde{z} = \rho g(ez - \frac{z^2}{2})$ is the hydrostatic contribution exerted on a slice of liquid at height z. One can write $\cos\theta$ in terms of $\dot{z} = \tan\theta$. The relevant expression is $\cos\theta = 1/\sqrt{1+\dot{z}^2}$. This approach produces a differential equation that, after integration, yields the profile $z(x)$. With the help of this detailed profile, one can calculate the border energy per unit length, called the *line tension* $\Im$, which has been neglected in equation (2.11).

2.2.4 *Experimental Techniques for Characterizing Drops*

The goal is to measure all the relevant parameters that characterize the process of spreading, that is to say, the time evolution of a drop and its final steady state. The techniques used generally involve an optical setup and a camera to record the process continuously in real time. We will now review several basic methods used to determine specific parameters, such as the contact angle, the thickness of a liquid film, and the radius of a drop.

Measuring the Contact Angle of a Liquid on a Solid

Drop Acting as a "Mirror" ($1° < \theta < 45°$). This measurement is based on optical reflectometry.[3] The drop (with a typical diameter d of 5 mm) is used as a convex mirror whose edges contact the horizontal support with an angle θ to be determined. When illuminated by a collimated laser beam (diameter of the order of 5 mm) normally incident on the substrate, the drop reflects a cone of light whose total angular divergence is 4θ (Figure 2.5a). A simple method is to place a horizontal screen (translucent glass or wax paper) at a height h above the substrate and to measure the diameter D

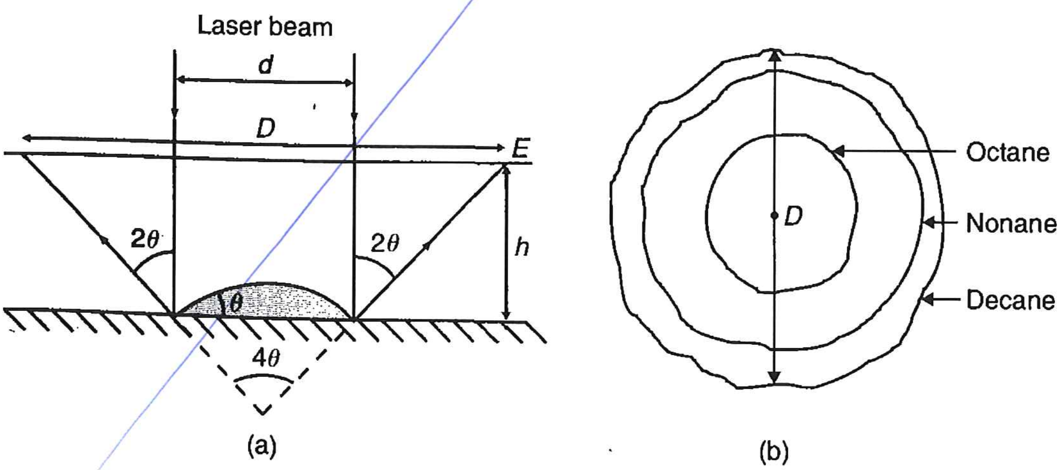

FIGURE 2.5. (a) Drop illuminated by a collimated light beam. The drop reflects a cone of light that can be observed on a translucent screen E placed at a height h above the substrate. (b) Record of the diameter of a laser beam reflected by a drop of alkane deposited on silanized glass.

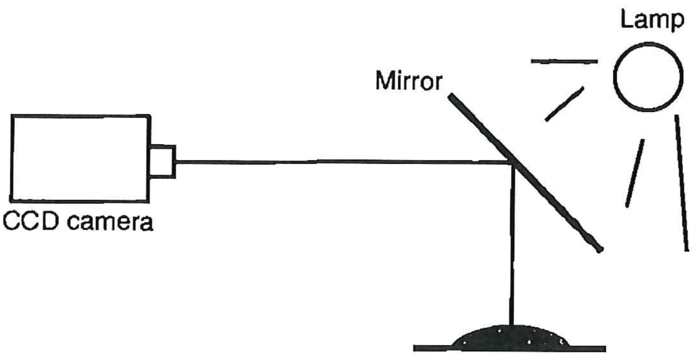

FIGURE 2.11. Apparatus for measuring the radius of a drop as a function of time.

the reaction at the upper contact even provides an excellent measurement accuracy, which is limited only by the resolution of the micrometer, or about 10 µm. Contact with the solid surface is signaled by the bending of the needle as its tip touches the solid. This bending is detected through the sudden and drastic change in the diffraction pattern of a collimated laser beam skimming over the straight needle.[6] Accuracy is again 10 µm.

This technique is able to determine liquid film thicknesses over a wide range (preferably more than 100 µm). It works equally well for opaque and transparent liquids. In the case of fluids (viscosity η of the order of one mPa-s), the relaxation time following contact is quite short and measurements can be repeated in rapid succession, making it possible to follow the dynamical evolution of a drop in the process of spreading.

Measuring the Radius of a Drop

A simple technique for measuring the radius of a drop is to image it on a screen with a video camera equipped with a zoom lens (using a magnification of typically 20×) (Figure 2.11). Lengths can be measured with an accuracy of about 100 µm.

For surfaces exhibiting wetting hysteresis, the advancing angle θ_A and the receding angle θ_R, to be studied in chapter 3, are measured using the optical techniques just described. The liquid is deposited on a surface placed within an enclosed sample chamber (to curb evaporation) by means of a syringe. The angle θ_A is measured as the liquid is inserted; the angle θ_R is measured as the liquid is withdrawn.

2.3 Menisci

2.3.1 Characteristic Size

A liquid is normally contained in a solid vessel with vertical walls. The surface of the liquid is horizontal because of gravity, except near the walls where Young's relation [equation (1.23)] induces a distortion. When the liquid is of the mostly wetting type (characterized by $\theta_E < 90°$), it rises slightly near the walls, whereas when it is non-wetting ($\theta_E > 90°$), it drops. The meniscus (from the Greek *mêniskos*, meaning "crescent") is the region where the liquid surface is curved.

The shape of the meniscus is determined by the equilibrium between the capillary forces (responsible for the curvature) and gravity forces (which oppose it). One can invoke the following pressure argument: Immediately underneath the surface, Laplace's pressure [equation (1.6)] is equal to the hydrostatic pressure. This can be written as

$$P_0 + \frac{\gamma}{R(z)} = P_0 - \rho g z \tag{2.14}$$

where z is the height of the surface above the level of the bath, P_0 is the outer pressure, and $R^{-1}(z)$ is the curvature at a particular point. This expression shows that for $z > 0$ (ascending meniscus), the curvature is negative, which does indeed correspond to a liquid under suction. Since the height z varies from point to point along the interface from 0 (the altitude of the bath proper) to h at the wall, so does the radius of curvature of the interface. As a result, the meniscus is not shaped like a circle. Equation (2.14) simplifies to

$$-Rz = \kappa^{-2} \tag{2.15}$$

where, again, we run into the capillary length $\kappa^{-1} = \sqrt{\gamma/\rho g}$. Ordinary experience indicates that the typical dimension of the meniscus is of the order of a millimeter. Note, however, that as told before the capillary length can be much larger if the densities of the liquid and the fluid above it are comparable. In this case, the density ρ of the liquid, which enters the expression of the capillary length, should be replaced by the difference $\Delta\rho$ between the densities of the two fluids. Likewise, in a reduced gravity environment ($g \to 0$), the capillary length diverges, in which case the meniscus extends over the entire surface of the bath, as illustrated in Figure 2.12. Some people believe that without gravity a wetting liquid would simply float out of a glass; in actuality, it experiences an underpressure because of surface tension and has no reason whatsoever to escape.

As a general rule, the characteristic size of a meniscus is either the capillary length κ^{-1} or the size l of the vessel itself, whichever is smaller.

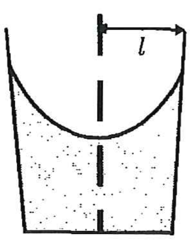

FIGURE 2.12. Meniscus in a glass of water in reduced gravity.

2.3.2 Shape of a Meniscus Facing a Vertical Plate

We study here the meniscus of a liquid facing a vertical plate, shown in Figure 2.13. We now return to the general equation (2.15). Here one of the curvature radius is infinite. The curvature $C = 1/R$ can be expressed as

$$\frac{1}{R} = -\frac{d\theta}{ds} \tag{2.16}$$

where θ is the angle between the tangent to the curve at a particular point and the vertical direction, and s is the curvilinear coordinate.

Switching to a Cartesian coordinate system in the (x, y) plane (Figure 2.13), equation (2.16) translates to

$$\frac{1}{R} = -\frac{\dfrac{d^2 z}{dx^2}}{\left[1 + \left(\dfrac{dz}{dx}\right)^2\right]^{3/2}}. \tag{2.17}$$

Equation (2.17) is a second-order differential equation for the profile $z(x)$ of the meniscus, subject to the appropriate boundary conditions. A first

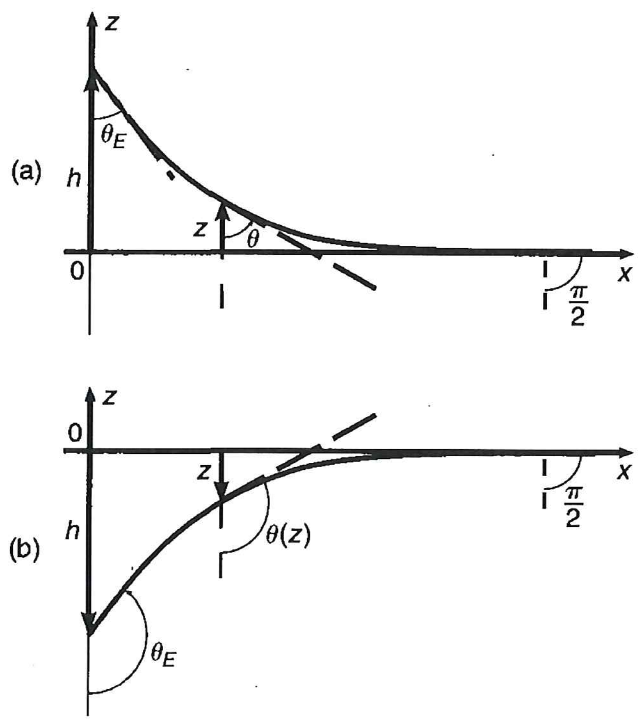

FIGURE 2.13. Menisci for a liquid that is (a) attracted to or (b) repelled by a vertical wall. Case (a) corresponds to $\theta_E < \pi/2$ and case (b) to non-wetting ($\theta_E > \pi/2$). The profile $z(x)$ goes exponentially to zero when $\kappa x > 1$ [equation (2.6)].

integration, together with the boundary condition $\frac{dz}{dx} = z = 0$ when $x \to \infty$ (where the profile merges with the horizontal surface of the bath), yields

$$\frac{1}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}} = 1 - \frac{z^2}{2\kappa^{-2}}. \tag{2.18}$$

The same result can be derived independently without any calculus by expressing the equilibrium of the forces acting a portion of the meniscus extending between x and infinity. The pertinent contributions are the capillary forces and the forces associated with the hydrostatic pressure P_0 outside the liquid and $P_z = P_0 - \rho g \tilde{z}$ inside the liquid. The resultant pressure force $\tilde{P} = \int_0^z \rho g \tilde{z}\, d\tilde{z} = \frac{1}{2}\rho g z^2$ exerts itself in the direction $x < 0$. The argument is similar to the one used in connection with Figure 2.3, even though the substrate is now vertical. In *horizontal* projection, the equilibrium can be written as

$$\gamma \sin\theta + \frac{1}{2}\rho g z^2 = \gamma \tag{2.19}$$

which is but a slightly disguised version of Equation (2.18).

Equation (2.19) allows us to calculate the height h to which the meniscus rises. At $z = h$, Young's condition gives $\theta = \theta_E$, which leads to

$$h = \sqrt{2} \cdot \kappa^{-1} \cdot (1 - \sin\theta_E)^{1/2}. \tag{2.20}$$

The maximum height is reached when $\theta = 0$, at which point $h = \sqrt{2}\kappa^{-1}$. When observing water on clean glass, the height of the meniscus turns out to be 4 mm, which gives direct information on the value of the capillary length.

Remark. Equation 2.20 can be derived more directly from equations (2.14) and (2.16) leading to $\gamma\, d\theta/ds = \rho g z$. With $ds = -dz/\cos\theta$, we get $\rho g z\, dz = -\gamma \cos\theta\, d\theta$. By interpretation, with the boundary condition $\theta = \frac{\pi}{2}$ for $z = 0$, we get $\frac{1}{2}\rho g z^2 = \gamma(1 - \sin\theta)$. The height h of the meniscus is the value of z for $\theta = \theta_E$.

To obtain an explicit relation for the profile $z(x)$, one must integrate equation (2.18) once more. The result is rather cumbersome and uninspiring:

$$x - x_0 = \kappa^{-1} \cosh^{-1}\left(\frac{2\kappa^{-1}}{z}\right) - 2\kappa^{-1}\left(1 - \frac{z^2}{4\kappa^{-2}}\right)^{1/2} \tag{2.21}$$

where x_0 is the distance such that (2.21) gives $z = h$ at $x = 0$ (i.e., at the wall).

Finally, the equilibrium of forces over the entire meniscus in *vertical* projection is

$$\gamma \cos\theta_E = \int \rho g z(x)\, dx. \tag{2.22}$$

In the partial wetting regime, $\gamma \cos\theta_E = \gamma_{SO} - \gamma_{SL}$. This shows that $\gamma_{SO} - \gamma_{SL}$ is the force per unit length that supports the weight of the meniscus $W_{meniscus}$ (also expressed per unit length). In the total wetting regime, the meniscus connects smoothly with the wall with an angle $\theta_E = 0$. The weight of the meniscus is therefore $W_{meniscus} = \gamma < \gamma_{SO} - \gamma_{SL}$. The total force $\gamma_{SO} - \gamma_{SL}$ offsets not only the weight of the meniscus (γ), but also that of the wetting film rising high above the liquid bath (the existence of this film will be discussed in more detail later). In summary,

In total wetting regime:	*In partial wetting regime:*
$\left.\begin{array}{l}\gamma = W_{meniscus}\\ S = W_{film}\end{array}\right\}$ (2.23)	$\left.\begin{array}{l}\gamma_{SO} - \gamma_{SL} = W_{meniscus}\\ \text{No Film}\end{array}\right\}$ (2.24)

2.3.3 *Meniscus on a Vertical Fiber*

We have already touched on this case in chapter 1 [section (1.6)] as an example of a surface with zero curvature. We can carry the analysis further by including the range of the perturbation created on the liquid surface far from the fiber, where gravity is no longer negligible. If the solid is a capillary rod of radius b less than the capillary length κ^{-1}, experiments show that the height of the meniscus is clearly smaller than that predicted by equation (2.20), because it must join with the surface of the fiber, which has a high curvature.

As in the case of a planar wall, the profile of the interface can be calculated by equating the Laplace and hydrostatic pressures. However, because of the additional curvature of the fiber, equation (2.14) must be modified to

$$P_0 + \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = P_0 - \rho g z \tag{2.25}$$

where R_1 and R_2 are the two principal radii of curvature at any point on the interface. We could, of course, integrate equation (2.25) numerically. Instead, we will try to give a more physical picture of what goes on. Near the line of contact, curvatures are of the order of b^{-1}. In other words, they are much more dominant here than in the planar case, when they were of the order of κ. Each curvature term here far exceeds the hydrostatic term in equation (2.25), to the point that gravity can be neglected altogether. This approximation is valid in the vicinity of the fiber only, at distances $r < \kappa^{-1}$. This constitutes an a posteriori justification of the argument used in section 1.1.6. The equation of the meniscus is then that of a surface with zero curvature

$$\frac{1}{R_1} + \frac{1}{R_2} = 0. \tag{2.26}$$

consistent with what anyone can observe when turning a water faucet on. The water emerges as a laminar flow from the faucet but gets completely fragmented by the time it splashes against the sink (the best way to verify this fact is to place your hand in the lower part of the stream and clearly feel individual drops striking your skin). There also exists a viscous version of the calculation applicable to the case of highly viscous fluids (or fluids surrounded by another, highly viscous, fluid).[2,13] This can be used to advantage for measuring the surface tension of molten polymers, which can be deduced from the dynamical properties of the instability.

5.3 Forced Wetting

When trying to coat a solid with a liquid, a time-honored practice is to help the process along with some kind of movement. We all know that a paintbrush wiped against a wall or a piece of paper leaves a trace of liquid in its wake. Likewise, most industrial processes intended to deposit a fluid layer rely on a relative motion between solid and fluid. As an example, to apply a photographic emulsion on a suitable supporting medium, the standard method is to immerse a plastic strip in an emulsion bath and take it out gently so that the liquid "sticks" to the plastic. In any event, it is important to know the parameters that determine the thickness of the coating, which must be controlled precisely in many cases. This section is devoted to this particular problem. We shall confine our attention here to wetting liquids (the case of partial wetting will be discussed in chapter 6).

5.3.1 The Landau-Levich-Derjaguin Model (and Variant Thereof)

Consider first a solid plate partially immersed in a liquid, as we are about to pull it out. If the liquid is wetting ($S > 0$), the surface of the bath connects with the solid with a zero angle, which creates a meniscus in the vicinity of the line of contact. We have already discussed in chapter 2 some of the characteristics of this meniscus, including its height, which is of the order of the capillary length κ^{-1} [equation (2.20)].

Figure 5.10 depicts what happens when the plate is being slowly drawn out of the bath. The upper part of the meniscus (shown as a dotted line) finds itself perturbed by the liquid film dragged along by the plate. The junction between the static meniscus and the film being dragged along is referred to as the *dynamical meniscus*, and its length—unknown as of yet—is denoted l.

If the film is being pulled slowly enough, the film it drags along is thin since it would not exist at all absent the drag effect (ignoring the possible

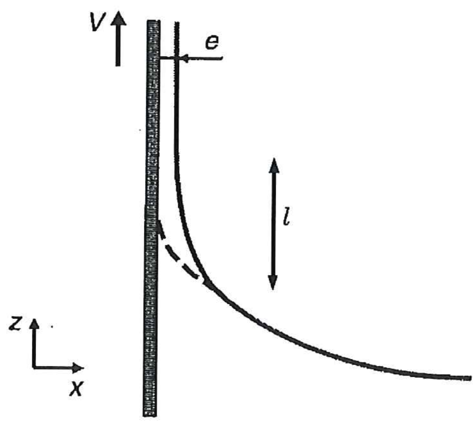

FIGURE 5.10. Plate being pulled out of a pool of wetting liquid. The plate drags a liquid film along with it.

existence of a microscopic wetting film). Therefore, the key role is played by the interfaces:

1. The solid/liquid interface, because the associated boundary condition is actually responsible for the liquid coating. By virtue of its viscosity, the liquid in the vicinity of the solid moves at the same velocity as the solid and is being dragged by it,
2. The liquid/vapor interface, which is being distorted by the film despite the opposing action of the surface tension of the liquid. Of course, gravity causes the film to flow downwards as well and is therefore also opposed to its movement, although we will see that, when the so-called capillary number is small, the contribution of this force is negligible when compared to that of the surface tension.

In short, viscosity and capillarity play opposing roles. The number that compares these two forces (written per unit length) is called the *capillary number*, denoted Ca:

$$\boxed{Ca = \frac{\eta V}{\gamma}} \tag{5.26}$$

This number is dimensionless, unlike the thickness itself. Therefore, there must be a normalizing length that is naturally associated with the meniscus from which the film originates. It happens to be the capillary length. Accordingly, the thickness is expected to be of the form $e = \kappa^{-1} f(Ca)$.

What follows is the argument originally proposed by Landau, Levich, and Derjaguin (LLD for short) in 1942–1943 to evaluate the thickness of the coating and to specify the functional form of $f(Ca)$. We present the LLD calculation in a simplified form. Here again the interested reader is encouraged to read the original papers, which qualify as veritable jewels in the field of interfacial hydrodynamics.[14, 15]

In steady state and for low Reynolds numbers (when viscosity dominates over inertia), we can legitimately work in the lubrication approximation.

Within the dynamical meniscus, the velocity of the liquid and its thickness are of orders magnitude V and e, respectively. The viscous force can therefore be written dimensionally as $\eta V/e^2$. The capillary force, on the other hand, is related to the gradient of the curvature of the dynamical meniscus [the curvature of the film makes a transition from that of the static meniscus to the curvature (equal to zero) of the film being dragged along]. Since the static meniscus is hardly perturbed at all by the flow (LLD hypothesis), the curvature at the point where the static meniscus matches the dynamical one is essentially that which exists at the top of the static meniscus. In other words, it is of the order of κ, the inverse of the capillary length [equation (2.15)]. The gradient of the Laplace pressure associated with this curvature gradient is then equal to $\gamma\kappa/l$.

Equilibrium between these two forces is written dimensionally as

$$\frac{\eta V}{e^2} \approx \frac{\gamma\kappa}{l}. \tag{5.27}$$

This equation has two unknowns (e and l), and finding the solution requires an additional equation. The second equation derived by LLD expresses the matching between the static and the dynamical meniscus. We have already pointed out that the order of magnitude of the curvature is κ. The dynamical meniscus is nearly flat since it merges with a planar film. Therefore, its curvature can be taken to be equal to the second derivative of the profile $e(z)$, which is dimensionally given by e/l^2. These two curvatures have the same sign (both regions are in an underpressure condition with respect to the atmosphere). Setting them equal leads to

$$\frac{e}{l^2} \approx \kappa. \tag{5.28}$$

The extent of the dynamical meniscus therefore turns out to be the geometric mean of the other two relevant lengths in the problem, namely, the thickness e and the capillary length κ^{-1}:

$$l \propto \sqrt{e\kappa^{-1}} \tag{5.29}$$

which "happily" reduces to zero when the thickness e vanishes, in other words, when one stops pulling the plate. Equation (5.29) enables us to eliminate l in equation (5.27), which yields the law describing the thickness of the coating (known as the *LLD law*):

$$\boxed{e \propto \kappa^{-1} Ca^{2/3}} \tag{5.30}$$

With the help of equations (5.29) and (5.30), one can also derive the length of the dynamical meniscus:

$$l \propto \kappa^{-1} Ca^{1/3}. \tag{5.31}$$

In their rigorous calculations, LLD were able to evaluate the numerical coefficient in equation (5.30). Its turns out to be equal to 0.94. The calculation is done by writing the matching condition between the two menisci based on the mathematical expression for the profile of the free interface. At any rate, the underlying principle remains the same as before in the sense that the curvatures of both menisci are evaluated asymptotically. The curvature of the static meniscus is calculated at its summit (even though the actual matching may occur slightly above), while that of the dynamical meniscus is calculated in the limit when its thickness is large in comparison with e (it can be shown by numerical calculation that the matching takes place over a thickness of the order of $10e$). A prerequisite for the previous argument to be valid is that the static and dynamical menisci differ only by a slight perturbation, which can be written in terms of their respective lengths $l \ll \kappa^{-1}$. Based on equation (5.31), we conclude that the LLD result holds as long as

$$Ca \ll 1 \tag{5.32}$$

which amounts to restricting the velocity to low values (more rigorously, the requirement is $Ca^{1/3} \ll 1$, which is more restrictive). In practice, the LLD law will be valid for capillary numbers less than 10^{-3}. Another requirement is that the flow be nearly parallel to the plate, so that the velocity vector can be taken equal to it scalar component in the direction of the plate. This imposes $e \ll l$. In light of equations (5.29) and (5.30), this condition is completely equivalent to the one spelled out previously.

It becomes clear that the LLD model adequately describes situations in which the capillary number is low. When we drink a glass of water, for instance, the velocity at which the glass is emptied is of the order of one cm/s, and the capillary number is 10^{-4}. The LLD model is then suitable for evaluating the thickness of the residual film. The result is about 6 μm. When you scramble out of your bath, perhaps to answer an untimely phone call, V is of the order of 1 m/s (the validity of the LLD model is then borderline), in which case you are covered by a thickness of about 150 μm of water. On an average adult human body (about 1.7 m^2), this corresponds to a weight of about 250 g.

When the capillary number approaches 1, both the thickness and the extent of the dynamical meniscus tend toward the capillary length. Derjaguin has shown that gravity then becomes the dominant force, and limits the thickness of the film. Up to this point, we have neglected the effect of gravity in comparison to that of surface of tension. The condition for this approximation to hold is $\rho g \ll \gamma\kappa/l$ (gravity negligible when compared to the gradient of the Laplace pressure). Again, this leads to the condition $l \ll \kappa^{-1}$, which is equivalent to the criterion (5.32). When Ca exceeds unity, the LLD visco-capillary regime is replaced by a visco-gravitational one. In this case, viscous and gravitational forces balance each other out, and equation (5.27) must be rewritten as

$$\frac{\eta V}{e^2} \approx \rho g. \tag{5.33}$$

From this we easily derive *Derjaguin's law:*[16]

$$\boxed{e \approx \kappa^{-1} Ca^{1/2}} \tag{5.34}$$

which does indeed merge seamlessly with the LLD law [equation (5.30)] when $Ca = 1$, in which case the thickness of the deposited liquid layer is equal to the capillary length. Equation (5.34) can be derived from an even more direct argument. Since a gravity regime takes the place of a capillary regime, Derjaguin looked for a law of the form $\kappa^{-1}Ca^n$, where the exponent n must be such as to make the latter expression independent of γ.[16] This happens only when $n = 1/2$.

5.3.2 Soapy Liquids

We have assumed up to now that the liquid being dragged is *pure.* That is rarely the case in real life. In most practical situations, the liquids one deals with are dispersed mixtures (suspensions or emulsions) containing surfactants (a detailed discussion of surfactants is deferred until chapter 8). Even in the supposedly "simple" case of soap water, the problem proves far more difficult than in the case of pure water. We will see later on that the main effect of a surfactant is to lower the surface tension of water (typically by a factor of 2). This has repercussions on the capillary length as well as on the capillary number, both of which intervene in the LLD law. But the primary difficulty has to do with the fact that when a solid is being pulled out of a liquid, the surface gets diluted, which creates a concentration gradient of surfactant at the surface, and thus a gradient of surface tension. The physical consequence is a certain "stiffening" of the free surface, which causes it to behave somewhat like a solid. The surface can become the seat of a viscous stress, which can be balanced by the gradient in surface tension.

When a plate is pulled out of soap water, it is as though two interfaces (as opposed to just one as in the case of pure water) drag the liquid along with them, which results in a film about twice as thick as it otherwise would be.[17] The precise value of the extra thickness is difficult to calculate. It has to depend on the surfactant concentration since the behavior of a pure liquid must be recovered at very low concentrations. Nevertheless, it is useful to hold on to the qualitative notion of a soapy interface endowed with *drawing power*, that is to say, with the ability to drag a liquid along with it, very much as a solid would. As it turns out, there is in this respect a