Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Colloid and Interface Science 272 (2004) 420–429
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

# Local thermodynamic derivation of Young's equation

P. Roura and Joaquim Fort *

GRMT, Departament de Física, Universitat de Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain

Received 24 June 2003; accepted 13 January 2004

**Abstract**

A derivation of Young's equation based on the energy balance near the contact line is presented. Our proposal is rigorous and avoids the errors identified in the usual local derivation. It is valid under very general conditions (for any geometry, in a gravitational field and for compressive fluids). Deviations of the contact angle from Young's equation are discussed in several cases: surfaces of high curvature and line tension. Finally, the relationship between surface tensions and surface energies comes as an additional, natural result. Our derivation also provides a new physical insight into the equilibrium of forces acting near the contact line. Its local character makes the recourse to integral analysis unnecessary, which results in a great simplification when compared to other general treatments.

*Keywords:* Surface tension; Young's equation; Contact angle

## 1. Introduction

As early as 1805, Thomas Young [1] stated that when a liquid makes contact with a solid surface it will approach the contact line following a dihedral angle, $\theta$, that depends on the solid and liquid surfaces according to his famous equation

$$\sigma_{\mathrm{LV}} \cos\theta = \sigma_{\mathrm{SV}} - \sigma_{\mathrm{SL}}, \tag{1}$$

where $\sigma_{ij}$ are called the "surface tensions" of the interfaces. He argued that Eq. (1) reveals an equilibrium of "three forces acting on the angular particles (of the liquid), one in the direction of the surface of the fluid only ($\sigma_{\mathrm{LV}}$), the second in that of the common surface of the solid and fluid ($\sigma_{\mathrm{SL}}$), and the third in that of the exposed surface of the solid ($\sigma_{\mathrm{SV}}$)." In 1830, Gauss introduced the concept of surface energy and applied it to the phenomenon of capillarity [2]. However, it was several decades later (around 1880), when Gibbs [3] developed the thermodynamics of solid–liquid–vapor systems very elegantly and, thus, founded the study of phenomena related to surface tension on more solid ground. In particular, he showed that surface tensions result from the excess free energy that can be assigned to the atoms at the surfaces when compared to the bulk. From this point of view, the shape of liquid surfaces is governed by the condition of minimum energy and, consequently, Young's equation could be derived from this condition. In fact, this nonlocal approach has been applied to special, elementary cases (such as drops in contact with solid surfaces in the absence of gravity and thin capillaries [4] or the meniscus formed on a vertical solid wall [5]) where the total energy can be calculated analytically. In more general cases, where analytical solutions do not exist (e.g., drops under gravity [6] or menisci inside thick capillaries [7]), variational methods are used or, alternatively, the energy is calculated numerically [6,8]. The conclusion is always the same: minimization of the total energy in any particular case leads to Young's equation. In contrast with these particular situations, the analysis by Gibbs is valid for any geometry and includes gravity explicitly. In fact, the scope of Gibbs' work goes far beyond the problem of the contact angle and, for this reason, makes use of a formalism that results cumbersome when one is interested in this particular subject. This is perhaps the reason that, aside from Johnson's paper (see below), we have not found Gibbs' derivation reproduced nor adapted by any later author [9]. Instead, a local analysis is usually followed.

Let us briefly review the existing local derivation. From the geometrical point of view, Young's equation is a boundary condition on the liquid–vapor surface. Consequently, it

---

* Corresponding author.
*E-mail address:* joaquim.fort@udg.es (J. Fort).

0021-9797/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2004.01.028

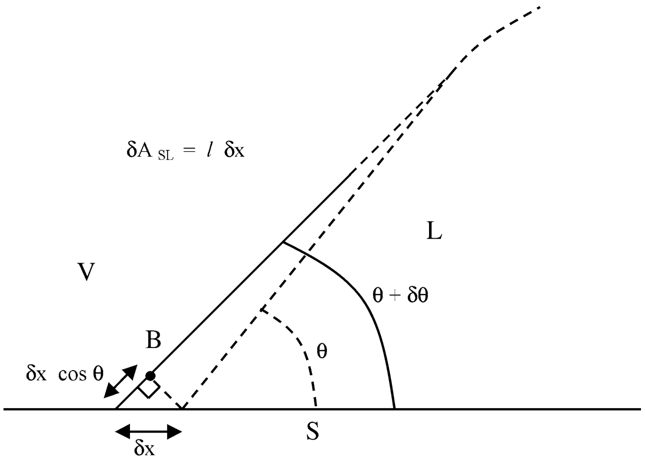


Fig. 1. When the liquid advances, the area of the LV surface will increase by a value proportional to $\cos\theta$, provided that the new surface meets the initial one asymptotically. This geometrical construction is the basis of the most popular "derivation" of Young's equation.

should be possible to derive it by quantifying the energy near the contact line. The arguments of this local approach can be easily understood with the help of the geometrical construction detailed in Fig. 1. Let $\theta$ correspond to equilibrium; therefore, the energy will not change up to first order after a slight increase, $\delta\theta$, of the contact angle. According to the geometrical construction of Fig. 1, it is argued that this perturbation induces a variation of the liquid–vapor surface area, $\delta A_{\mathrm{LV}}$, which is proportional to the liquid–solid $\delta A_{\mathrm{SL}}$ through

$$\delta A_{\mathrm{LV}} = \delta A_{\mathrm{SL}} \cos\theta. \tag{2}$$

This relationship allows the calculation of the energy increments related to surfaces:

$$\begin{aligned}\delta U_\sigma &= \sigma_{\mathrm{LV}}\delta A_{\mathrm{LV}} + (\sigma_{\mathrm{SL}} - \sigma_{\mathrm{SV}})\delta A_{\mathrm{SL}} \\ &= \left[\sigma_{\mathrm{LV}}\cos\theta + (\sigma_{\mathrm{SL}} - \sigma_{\mathrm{SV}})\right]\delta A_{\mathrm{SL}}.\end{aligned} \tag{3}$$

In the absence of other contributions to the energy variations (e.g., gravity), the equilibrium condition $\delta U = 0$ implies Young's equation (1). Despite the easy criticism that can be addressed to this derivation (see Section 2), it has survived as the most popular general proof of Young's equation. For instance, we find it in the textbook of physics by Poynting and Thomson [10] and in the treatise of surface chemistry by Adamson [11]; Sommerfield [12] used it in the case of a meniscus; etc. [13–16].

The correctness of this local derivation has been the subject of great debate, which from time to time has led several authors to doubt the validity of Young's equation itself. A good example of the confusion created around this subject is the discussions held during a conference devoted to surface activity in 1957, where it was argued that Young's equation fails under gravity [17]. In order to test this hypothesis, several papers followed this conference which gave rigorous and valuable derivations [5,6] that apply, in fact, to particular geometries under gravity. Perhaps the most celebrated contribution was that by Johnson [18] which was considered at that time as correct [19,20] or even "definitive" in the review of the subject by Zisman [21]. However, Johnson followed the steps already outlined by Gibbs' almost one century before and should therefore be considered an attempt to simplify Gibbs' derivation [22]. This aim was not fulfilled, it seems, because Johnson's approach has not been reproduced by any later author.

Despite its inherent problems (see Section 2), the geometrical construction of Fig. 1 still survives [13,16] and continues raising doubts about the validity of Young's equation. Several examples can illustrate these doubts. The recent development of extensive numerical calculations has made it possible to test Young's equation from first principles. Initial attempts that treated each of the phases in contact as a continuum gave negative results [23,24]. The interesting aspect of this failure is that these authors did not conclude that their method had some problems, but that Young's equation was erroneous [25]. Once again, one sees that although anyone working in the field of surface phenomena will often deal with contact angles, the equation governing their value at equilibrium is usually under suspicion. Which would otherwise be the reason for doing measurements of contact angles during free fall [26] or for computing the energy of a drop under gravity [8]? At present there is a paper [27] where more elaborate simulations confirm Young's equation on a microscopic basis [28]. Finally, we should point out that direct experimental verifications of Young's equation are very scarce [29,30] because, in most cases, it is impossible to measure $\sigma_{\mathrm{SL}}$ and the determination of $\sigma_{\mathrm{SV}}$ is usually problematic.

The main purpose of this paper is to present an original and general derivation of Young's equation, founded on thermodynamic grounds. The analysis is local, in the sense that the energy balance is applied to a small volume near the contact line (local analysis). Despite that any displacement of the contact line will produce energy changes in the rest of the system (nonlocal perturbation), our method allows us to write down a rigorous local balance equation. In fact, to our knowledge it constitutes the single rigorous local derivation of Young's equation (1). It is valid within a number of general, clearly stated hypotheses. In particular, it is shown that Young's equation is obeyed under gravity and for all geometries.

## 2. Criticism of the existing local derivation

From the historical review in our Introduction, it follows that the only general derivation of Young's equation based on a local analysis of the contact line is that illustrated by the geometrical construction of Fig. 1, and reproduced in Section 1. In this section we will give some arguments (based on the energy balance of particular cases) that invalidate this local derivation.

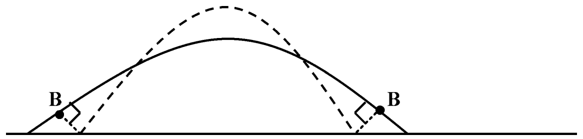


Fig. 2. Changes in the shape of a drop when the wetted surface area increases.

### 2.1. Local status of the geometrical construction

The validity of the construction in Fig. 1 would be general (for any geometry without gravity) provided that its presumed local character were really local. That would be so, if the energy variations near the contact line could be used to compute the energy variation of the whole system. In the absence of gravity, only the surface energy varies. Consequently, the local derivation assumes that the variations of the whole surface areas are equal to the local variations $\delta A_{\mathrm{LV}}$ and $\delta A_{\mathrm{SV}}$ shown in Fig. 1. In other words, beyond point B in Fig. 1 the LV surface area should not change up to first order in $\delta x$. This point could be ensured if, as sketched in Fig. 1, far enough from the contact line, the LV surfaces remained unchanged [32]. However, this asymptotic behavior is not true in general. In the particular case of a drop (Fig. 2), volume conservation obviously implies that the whole LV interface is modified. We conclude that the local geometrical construction of Fig. 1 cannot be considered as a correct way for computing the variations of the whole surface energies and, therefore, it cannot be the basis of a rigorous derivation of Young's equation.

It is worth noting that, without gravity, minimization of the total energy is equivalent to $\delta U_\sigma = 0$ and, therefore, the validity of Young's equation ensures that the variations of the whole surface areas always follow Eq. (2). Thus, we arrive at the striking conclusion that, in the absence of gravity, from Young's equation (1) (by introducing it into Eq. (3)) one can derive Eq. (2) but the reverse is not true, because there is no a priori proof of Eq. (2).

### 2.2. Drop under gravity

Let us show that the problems with the geometrical construction leading to Eq. (2) become still more apparent when analyzing the case of a drop under gravity. We will explicitly show that, in this particular case, Eq. (2) is no longer valid even when considering the whole surface (because the area beyond point B in Fig. 2 has now varied). This can be proved very easily, as follows. In equilibrium, a small displacement will not increase the total energy. That is,

$$\delta U = \delta U_g + \delta U_\sigma = 0, \tag{4}$$

where $\delta U_g$ and $\delta U_\sigma$ correspond to the increments of gravitational and surface energies, respectively. From Eq. (4) one can write:

$$\delta U_\sigma \equiv (\sigma_{\mathrm{SL}} - \sigma_{\mathrm{SV}})\delta A_{\mathrm{SL}} + \sigma_{\mathrm{LV}}\delta A_{\mathrm{LV}} = -\delta U_g. \tag{5}$$

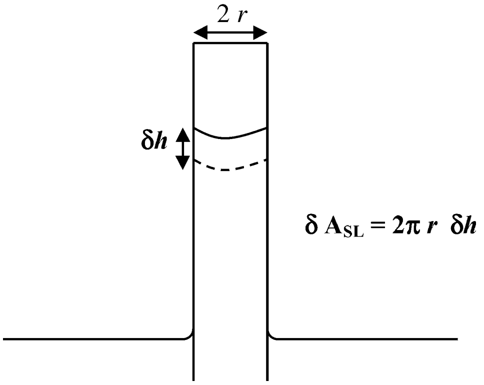


Fig. 3. An increment of the height, $h$, of the column of liquid inside a thin capillary increases the $A_{\mathrm{SL}}$ area but leaves the $A_{\mathrm{LV}}$ surface area unchanged.

An elementary geometrical inspection of Fig. 2 leads to

$$-\delta U_g = \alpha \frac{1}{2} \rho g \delta A_{\mathrm{SL}} H^2,$$

where $\rho$ and $g$ are the liquid density and the acceleration of gravity, respectively, $H$ is the drop height, and $\alpha$ is a numerical factor near unity. Therefore, $U_g$ is not minimal but varies in first order of $\delta A_{\mathrm{SL}}$ and cannot be neglected in Eq. (4). Now, introduction of Eq. (2) and that for $-\delta U_g$ above into Eq. (5) would lead to the conclusion that Young's equation is not valid. However, precisely because Young's equation is valid in general [3] and in this particular case [6,8], it follows from our argument that Eq. (2) is false under gravity. This makes it absolutely clear that the usual, widely quoted local proof of Young's equation (Section 1) is not valid in general.

In general terms, we can then state that $\delta U_g$ and $\delta U_\sigma$ are coupled. Obviously, also this fact makes the geometrical construction of Fig. 1 of questionable applicability. This aspect will become clearer below. We can say, in passing, that simultaneous consideration of Eqs. (2) and (5) as valid led Pethica and Pethica [17] and others [32] to conclude that the contact angle progressively deviates from the value given by Young's equation when drops become large. This suggestion was later ruled out, both from numerical calculations based on precise drop shapes [8] and experimentally [33].

### 2.3. The geometrical construction under gravity

Although we think that the arguments given above should leave few doubts about the inapplicability of the geometrical construction of Fig. 1, we will now give an additional example showing that under gravity this construction does not relate correctly the $\delta A$ increments (i.e., Eq. (2) is not valid) and, consequently, $\delta U_g$ and $\delta U_\sigma$ are necessarily coupled.

Consider the case of a thin capillary (Fig. 3). A small increment (in fact a reduction) of the contact angle will increase the height of the water column by $\delta h$. The corresponding variation in $A_{\mathrm{SL}}$ will not be accompanied by any variation of $A_{\mathrm{LV}}$ (in contrast to Eq. (2)). If $h$ is just the equilibrium value, then the corresponding increment of the solid surface energy, namely $(\sigma_{SL} - \sigma_{SV})\delta A_{LV}$, will be exactly balanced by the gravitational energy decrease. Clearly, in Fig. 3 $\delta A_{LV} = 0$ and $\delta A_{SL} \neq 0$, and thus Eq. (2) breaks down for sure.

Before leaving this section, we must say that the arguments that follow the geometrical construction in Fig. 1 are not a simplified version of any rigorous analysis of the local energy balance. This analysis does not exist and, consequently, this local "derivation" is not founded on solid ground.

## 3. Local thermodynamic derivation

### 3.1. The derivation

In the former sections, we have shown that the existing local, general derivation of Young's equation is erroneous. This is why an alternative derivation, valid for all geometries and under gravity, is proposed below. Consider the following conditions:

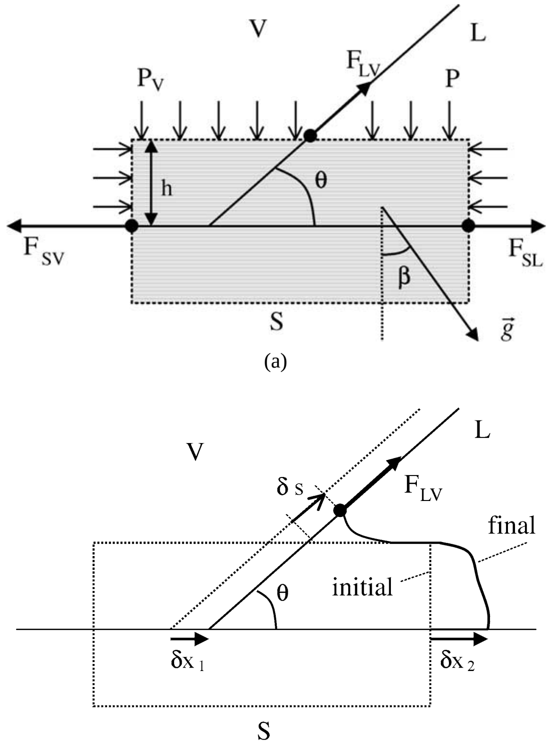
1a. Every phase is homogeneous and continuous up to the corresponding interface.
1b. Every interface is geometrically defined by a surface (i.e., a region of zero thickness).
1c. The free energy per unit volume of any region is independent of its proximity to the interfaces.
2. The LV, SL, and SV interfaces have a free energy per unit area equal to $\sigma_{LV}$, $\sigma_{SV}$, and $\sigma_{SL}$ [34], respectively, and their dependence on surface curvature is negligible.
3. The energy of the contact line is negligible.
4. The variations of free energy related to the vapor phase are negligible.

It will be shown below that, under these conditions, a displacement of the contact line is reversible when Young's equation holds,

$$\sigma_{LV}\cos\theta = \sigma_{SV} - \sigma_{SL},$$

where $\theta$ is the contact angle measured at a distance asymptotically close to the contact line (under the conditions above).

The derivation will rely on the energy balance of a small volume around a short portion of the contact line (Fig. 4a). Its length $l$ in the direction orthogonal to the paper will be short, up to the point that it can be considered as a straight line, but much longer than the thickness of the element of fluid, $h$. This is possible irrespective of the curvature of the contact line, provided that conditions 1 are fulfilled. The volume element considered is extended along the solid surface beyond the contact line in both directions and into the solid (Fig. 4a) in order to be sure about which are the external forces that will contribute to the work done on it during a reversible displacement.



(b)

Fig. 4. (a) Definition of the volume element (dashed) used for the energy balance when the contact line recedes. All of the external forces contributing to the work done on the volume element are shown. $g$ is the acceleration of gravity. (b) Deformation of the liquid part of the volume element during a reversible displacement of the contact line ($\delta s \ll h$).

First of all, let us identify the forces acting on the boundaries of the volume element (Fig. 4a). The surrounding liquid and vapor will act through the hydrostatic pressure exerted at the boundary surfaces. Viscous forces are absent in whatever process as long as it is reversible. In addition, it can be proved (see Appendix A) that, under very general assumptions, any force acting at the upper edge of the LV surface limiting the liquid element, $F_{LV}$, will be tangential to the surface. Although we all know that $F_{LV}$ will be proportional to $\sigma_{LV}$, we do not need a priori such information. This relationship will come out in a natural way as an additional result of our derivation. A similar argument can be applied to the possible forces $F_{SV}$ and $F_{SL}$ (see Fig. 4a). Finally, any forces arising from the boundaries located in the solid are not relevant, because at these regions the boundary does not move.

When the contact line recedes, the liquid fraction of the volume element will be deformed on the side of the LV interface (Fig. 4b). One may think that the usual nonslip boundary condition of hydrodynamics forbids any displacement of the fluid element at the LS interface. However, this is not always the case. Microscopic analyses [35] have shown that, for nonwetting solid–liquid systems, large slippage of the liquid boundary layer is possible. Consequently, in general, we must allow a certain degree of movement on the side of the liquid opposite to the LV surface (Fig. 4b).

After the displacement of the contact line, the internal energy of the volume element, $U$, will change and, according to the first law of thermodynamics, this variation can be computed from the heat exchanged, $\delta Q$, and the work done by the forces acting on the boundaries, $\delta W$:

$$\delta U = \delta W - \delta Q \neq 0.$$

If this process is reversible and at constant temperature, the former equation can be written as

$$\delta G = \delta W + P\delta V + V\delta P, \tag{6}$$

where $\delta U$ has been written in terms of the Gibbs free energy, $G$ (see Appendix B) [36].

Due to the fact that the solid portion of the volume element remains unchanged (its boundaries do not move) and that, for the sake of simplicity, variations of energy are neglected in the vapor phase (condition 4), the thermodynamic functions and variables of Eq. (6) correspond to the liquid phase and the interfaces located inside the volume element. First of all, we will calculate the changes in free energy,

$$\delta G = \delta G_L + \delta G_\sigma + \delta G_g, \tag{7}$$

where the subindexes $L$, $\sigma$, and $g$ refer to the liquid "intrinsic" free energy (see Appendix B), the interface, and the gravitational free energies, respectively,

$$\delta G_L = V\delta P, \tag{8a}$$

$$\delta G_\sigma = l\sigma_{\mathrm{LV}}\delta s + l(\sigma_{\mathrm{SV}} - \sigma_{\mathrm{SL}})\delta x_1 + l\delta x_2\sigma_{\mathrm{SL}}(L), \tag{8b}$$

$$\delta G_g \simeq \frac{1}{2}\rho g h^2 l(\delta x_1 - \delta x_2)\cos\beta, \tag{8c}$$

where $\rho$ is the liquid density and, except $\sigma_{\mathrm{SL}}(L)$, all of the other parameters have been defined previously or are defined in Fig. 4. The meaning of $\sigma_{\mathrm{SL}}(L)$ will be clarified in Section 4 (there, it will be shown that it is not exactly the same as the SL surface energy, $\sigma_{\mathrm{SL}}$, and this is why we use a different notation; in fact, $\sigma_{\mathrm{SL}}(L)$ is the fraction of $\sigma_{\mathrm{SL}}$ that can be assigned to the liquid).

Now we shall calculate the work done by the external forces acting on the boundaries,

$$\delta W = \delta W_\sigma + \delta W_P, \tag{9}$$

where $\delta W_\sigma$ and $\delta W_P$ are the work done by the surface forces and by the pressure, respectively. The work done by $F_{\mathrm{LV}}$ can be evaluated through its components parallel and normal to the solid surface:

$$\delta W_x = (F_{\mathrm{LV}}\cos\theta)(\delta x_1 + \delta s\cos\theta),$$
$$\delta W_y = (F_{\mathrm{LV}}\sin\theta)(\delta s\sin\theta).$$

Therefore

$$\delta W_{\mathrm{LV}} = \delta W_x + \delta W_y = F_{\mathrm{LV}}\delta s + F_{\mathrm{LV}}\delta x_1\cos\theta. \tag{10}$$

The work done by $F_{\mathrm{SL}}$ is simply

$$\delta W_{\mathrm{SL}} = F_{\mathrm{SL}}\delta x_2. \tag{11}$$

The work done by the pressure is (see Appendix C)

$$\delta W_P = -P\delta V + hl(P_V - P)\delta x_1, \tag{12}$$

where $P_V$ and $P$ are the pressures in the vapor and liquid phases, respectively. In Eqs. (8c) and (12) the terms proportional to $h$ and $h^2$ can be neglected because, by virtue of conditions 1, the value of $h$ can be arbitrarily small. Consequently, in the limit where $h$ tends to zero, substitution of Eqs. (8), (10), (11), and (12) into (6) leads to a simplified equation of energy balance:

$$\delta G_\sigma = \delta W_\sigma. \tag{13}$$

In the way leading from Eq. (6) to this simplified version, we have seen that both gravity and pressure have a negligible contribution to the energy balance of the volume element in the limit where its boundary at the LV surface tends to the contact line. This fact does not constitute any kind of limitation on the validity of our derivation but simply shows, in a rather easy way, that Young's equation is still valid under gravity. Of course, if the volume element had a finite height, $h$, then our analysis would say that the angle $\theta$ measured at height $h$ would deviate from Young's equation because of gravity and pressure contributions. This is equivalent to saying that, in general and according to Laplace's law, the LV surfaces are curved and that this fact is explained by our Eqs. (9) and (12).

Finally, because in general the displacements $\delta x_1$, $\delta x_2$, and $\delta s$ are not related, the condition of a reversible process (Eq. (13)) splits into three new equations:

$$F_{\mathrm{LV}}\delta s = \sigma_{\mathrm{LV}} l\delta s,$$
$$F_{\mathrm{SL}}\delta x_2 = \sigma_{\mathrm{SL}}(L) l\delta x_2,$$
$$F_{\mathrm{LV}}\cos\theta\delta x_1 = (\sigma_{\mathrm{SV}} - \sigma_{\mathrm{SL}}) l\delta x_1. \tag{14}$$

The first and second ones identify the forces as arising from the surface energies (the exact meaning of $\sigma_{\mathrm{SL}}(L)$ will be clarified in Section 4), whereas a combination of the first and the third equations delivers Young's equation (1). This completes our derivation of Young's equation.

### 3.2. *Relaxation of the general conditions*

The derivation above has been done by assuming that the general conditions 1–4 are fulfilled. Now, we will relax some of these conditions in order to clarify whether they are necessary or not for the validity of Young's equation.

Due to the very low densities of the vapor phase, its contribution to the free energy is negligible, indeed (condition 4). If the vapor phase were substituted by a second liquid phase, its free energy would have to be taken into account. Its volume element would be deformed, similarly to the first liquid, with the constraint that at the L–L interface both deformations should be the same. In the energy balance equation, additional terms corresponding to this new phase will appear, but without any effect on the Young equation. Let us stress, in passing, that the contribution of the solid bulk

Fig. 5. Near the contact line, the LV surface deviates from the angle given by Young's equation ($\theta$) due to the finite range of the atomic interactions.

phase to the energy balance is exactly zero because during the reversible displacement it remains unchanged (Fig. 4b).

The atomic structure of matter raises the question about the localization of surface energy. The energy of molecules will depart from its value in bulk wherever their distance to anyone of the interfaces is similar to, or less than, the range of intermolecular interactions, $\Delta$. Therefore, surface energies are localized, in fact, not on a surface but in a volume of small but nonvanishing thickness (relaxation of conditions 1). Our derivation is still valid in this case, provided that the volume element is thick enough (thermodynamic limit, $h \gg \Delta$ in Fig. 4a) (see, for instance, De Gennes [13], who adapts the geometrical construction of Fig. 1 to this situation). At shorter distances from the contact line (microscopic limit), the liquid surface will change its slope and the angle can depart considerably from the value given by Young's equation (Fig. 5) (see the experimental measurements shown in Fig. 3 of Ref. [37]).

Similarly to the atoms near the surface, those near the contact line will have a different energy from that in the bulk. This is the origin of what is usually called the contact line tension, $\tau$. Its contribution to the energy balance leading to the contact angle value has been treated by Boruvka and Neumann [38], who generalized Gibbs' thermodynamical analysis of the whole solid–liquid–vapor system. The contribution of $\tau$ adds an extra term to the Young's equation, which now becomes

$$\sigma_{\mathrm{LV}} \cos\theta = (\sigma_{\mathrm{SV}} - \sigma_{\mathrm{SL}}) - \frac{\tau \cos\alpha}{R}, \tag{15}$$

where $R$ is the curvature radius of the contact line, and the angle between the plane containing the contact line and the plane tangent to the surface of the solid ($\alpha = 0$ for a flat solid surface). It can be shown that our local approach can be extended without any difficulty to take into account this effect of $\tau$ (relaxation of condition 3).

Before passing to the next point, we want to discuss the localization of the contact line energy. Although it is strictly defined as the excess free energy of the atoms at the contact line, the finite range of molecular interactions discussed above implies that the region affected will be localized within a radius of the order of $\Delta$ around the contact line. The excess free energy in this region has thus the same origin as the surface energy. Consequently, the deviation of $\theta$ from the value given by Young's equation when one approaches the contact line (microscopic limit) can be used to evaluate $\tau$. This has been done recently [37], and the value obtained in this way agrees with Eq. (15). Finally, the common origin of $\sigma_{ij}$ and $\tau$ (namely, interatomic interactions) has led, recently, to the surprising result that, in general, the line tension depends on the contact angle [39], i.e., $\tau(\theta)$. This dependence is presumably more relevant than the dependence of the surface tension on curvature. Consequently, before the curvature of the interfaces would have an effect on the values of $\sigma_{ij}$ (relaxation of condition 2), Young's equation should be substituted by its generalized form, Eq. (15). Although the dependence of the excess free energy on surface curvature has been included in the general derivation by Boruvka and Neumann [38], in our opinion their generalization of Young's equation is only formal. In the limit of highly curved surfaces, we think that the Gibbsian concept of "curvature" [38] is not adequate to describe the complexity of the new situation.

In summary, most of the conditions listed above are not necessary for our derivation of Young's equation, and the contribution of the contact line energy (condition 3) can be taken into account, giving rise to the generalized Eq. (15). Our derivation is, therefore, valid under very general conditions (with gravity, for all geometries and for compressible fluids) provided that interfaces are not curved "in excess." However, this does not constitute any limitation of our derivation because, in this situation, Young's equation fails.

## 4. Young's equation as equilibrium of forces

Despite the immense progress achieved in the understanding of surface phenomena since the original formulation by Young of his equation, its elementary interpretation as equilibrium of forces survives (Fig. 6a) [40]. If one assumes that the LV, SL, and SV interfaces are in a state of biaxial tension, then mechanical equilibrium requires that

$$\gamma_{\mathrm{LV}} \cos\theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}, \tag{16}$$

where $\gamma_{ij}$ are surface tensions (forces per unit length), whereas the symbols $\sigma_{ij}$ (used in Sections 1–3) denote Gibbs free energies per unit area. Although experiments and theory state that $\gamma_{\mathrm{LV}} = \sigma_{\mathrm{LV}}$ (e.g., from our Eqs. (14)), the same correspondence cannot be established for the solid surface tensions, because it is difficult to understand how an nondeformable solid surface can exert a force on the contact line. In fact, Eq. (16) reduces to Young's equation if

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \sigma_{\mathrm{SV}} - \sigma_{\mathrm{SL}},$$

that is, if the solid surface tensions differ from surface energies by a constant amount, $\sigma_{S_0}$:

$$\begin{aligned} \gamma_{\mathrm{SL}} &= \sigma_{\mathrm{SL}} - \sigma_{S_0}, \\ \gamma_{\mathrm{SV}} &= \sigma_{\mathrm{SV}} - \sigma_{S_0}. \end{aligned} \tag{17}$$

Gibbs was aware of this, and proposed that surface tensions and surface energies were related through Eq. (17), where $\sigma_{S_0}$ would be the solid surface energy on vacuum [41]. However, this reformulation of Young's equation cannot be deduced from Gibbs' derivation because, in his energy balance of the whole system, forces do not appear explicitly.

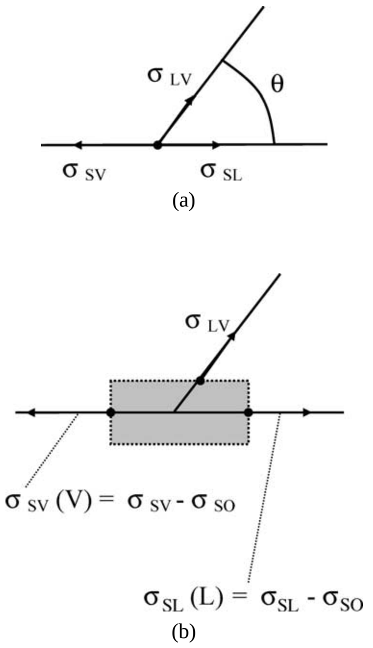


Fig. 6. (a) The classic interpretation of Young's equation as an equilibrium of forces. All surfaces are thought to be under biaxial tension. (b) The forces that actually act near the contact line differ from the surface energies on the solid–fluid surfaces. $\sigma_{S_0}$ is the surface energy of the solid in vacuum. In contrast with the LV surface, the surface of the fluids in contact with the solid can be under tension or compression.

In contrast, in our local analysis forces do appear and their relationship with surface energies is deduced, as follows. From Eqs. (14) we can write

$$\gamma_{\mathrm{LV}}\left(\equiv\frac{F_{\mathrm{LV}}}{l}\right)=\sigma_{\mathrm{LV}},$$
$$\gamma_{\mathrm{SL}}\left(\equiv\frac{F_{\mathrm{SL}}}{l}\right)=\sigma_{\mathrm{SL}}(L), \tag{18}$$

and, for completeness,

$$\gamma_{\mathrm{SV}}\left(\equiv\frac{F_{\mathrm{SV}}}{l}\right)=\sigma_{\mathrm{SV}}(V).$$

The meaning of $\sigma_{\mathrm{SL}}(L)$ and $\sigma_{\mathrm{SV}}(V)$ can be discussed now, once conditions 1 have been relaxed. In view of Fig. 4b, the displacement $\delta x_2$ increases the SL surface of the volume element on the side of the liquid, only. So, $\sigma_{\mathrm{SL}}(L)$ (which multiplies $\delta x_2$ in Eq. (8b)) represents the contribution of the atoms of the liquid to the SL surface energy. Combination of Eqs. (17) and (18) states that $\sigma_{S_0}$ is simply the contribution of the atoms of the solid to $\sigma_{\mathrm{SL}}$ and $\sigma_{\mathrm{SV}}$. Now, Young's equation will be consistent with the equilibrium of forces only if $\sigma_{S_0}$ is independent of which fluid is in contact with the solid surface. If the "fluid" is vacuum, then $\sigma_{\mathrm{SV}}(V)$ will be zero because no free energy can be assigned to vacuum and, consequently, $\sigma_{S_0}$ will coincide with $\sigma_{\mathrm{SV}}$ in this particular case. In this way we arrive to the same conclusion as Gibbs, namely that $\sigma_{S_0}$ is the surface energy of the solid in vacuum.

Beyond its consequences for the understanding of Young's equation, this result gives valuable information about the microscopic structure of the solid–fluid interfaces. The contributions of the atoms on the side of the solid to $\sigma_{\mathrm{SL}}$ and $\sigma_{\mathrm{LV}}$ are independent of the fluid. This means that the free energy of the solid does not change when it comes into contact with a fluid. In the particular case of immiscibility, this means that the microscopic structure of the solid near the surface (the position, and the interactions of its atoms) is not affected at all by the presence of the fluid. This general conclusion could probably be useful for microscopic analyses of the solid–fluid interactions.

Previous authors usually decompose the value of $\sigma_{\mathrm{SL}}$ into three terms [41,42], as follows

$$\begin{aligned}\sigma_{\mathrm{SL}}&=\sigma_{S_0}+\sigma_{L_0}+\Delta\sigma_{\mathrm{SL}}\\&=\left(\sigma_{S_0}+\frac{\Delta\sigma_{\mathrm{SL}}}{2}\right)+\left(\sigma_{L_0}+\frac{\Delta\sigma_{\mathrm{SL}}}{2}\right),\end{aligned} \tag{19}$$

where $\Delta\sigma_{\mathrm{SL}}$ accounts for the interaction between the atoms of the L and S phases, respectively. In principle, the energy of interaction belongs to both phases and cannot be distributed among them. However, from the very beginning of this kind of analyses [41] it is considered that $\Delta\sigma_{\mathrm{SL}}$ is equally shared by the L and S phases, as implicitly indicated by the right-hand side of Eq. (19). But this assignation is quite arbitrary and enters in contradiction with our own conclusion (namely, if $\sigma_{\mathrm{SL}}(L)=\sigma_{\mathrm{SL}}-\sigma_{S_0}$, then $\sigma_{\mathrm{SL}}(L)=\sigma_{L_0}+\Delta\sigma_{\mathrm{SL}}$).

To conclude this section we can say that Young's equation cannot be interpreted as the equilibrium of forces of Fig. 6a. The forces that actually act on the volume element containing the contact line are detailed in Fig. 6b. $\sigma_{\mathrm{SL}}(L)$ and $\sigma_{\mathrm{SV}}(V)$ are the surface tensions of the fluid surfaces in contact with the solid. So, the force exerted from the SV side of the contact line is due to the interactions with the molecules of the gas phase adsorbed onto the solid surface, the contribution of the molecules of the solid phase being zero. In contrast with $\sigma_{\mathrm{SL}}$, depending on the value of $\sigma_{S_0}$, the liquid surfaces in contact with the solid can be in a state of biaxial tension or compression. Additionally, Fig. 6b is more exact because the mechanical equilibrium of the three surface tensions is only meaningful on a finite volume element around the contact line (and not on the contact line itself, because at the microscopic limit Young's equation is no longer valid).

The conclusions of this section follow from the assumption that slippage of the liquid over the solid surface is possible (at least at the microscopic level) [33]. If not, probably the distribution of the interaction energy among phases, or the decomposition of surface mechanical tensions in contributions of liquid and solid surfaces, would be nonsense. Anyway, the validity of our derivation of Young's equation does not depend on this assumption.

## 5. Comparison with Gibbs' derivation

As it was already noted in the Introduction, Gibbs' treatment of the equilibrium conditions for a solid–fluid system relies on the general condition that the total energy must be a minimum (global derivation). Although this is conceptually clear, important difficulties arise when this condition must be applied to an arbitrary geometry. The surface and volume energies cannot be calculated analytically but, instead, they appear as surface and volume integrals where the integration range is not specified. In this case, the only option is to follow a variational method and impose that $\delta U = 0$ (at constant entropy and temperature) for any departure from the equilibrium geometry. By doing so, the variation in the shape of the surfaces results in a term that accounts for the displacement of the contact lines. Since the geometry is arbitrary, the integrand of this term must be identically zero and Young's equation results. Following Gibbs, a local condition at the contact line is obtained from the global condition $\delta U = 0$.

In our local derivation, we analyze the effect of a displacement of the contact line on a volume element near the contact line. Of course, now the energy of this volume element will be, in general, modified according to Eq. (6) (and, thus, in contrast with the geometrical analysis of Fig. 1). However, if the displacement is reversible, then $\delta U = 0$ for the whole system. This means simply that the work done by the forces acting on the boundary of the volume element is just the same and opposite in sign than the one done by the volume element on the rest of the system (the same can be stated for the heat exchanged). In general, gravitational as well as surface energy changes will occur in the rest of the system, whereas only surface energies are relevant for the volume element under analysis. So, our approach avoids any explicit calculation of the energy terms that are impossible to calculate beyond the volume element boundaries in a general configuration where the geometry is not defined. In other words, the contact line displacement will have for sure an effect on, say, the gravitational and strain energies of the whole system (Section 2); however, we are not worried about it because this effect is negligible as compared to that of the surface energies when the volume element near the contact line is analyzed.

Apart from the simplicity inherent in avoiding recourse to integral calculus, in our method, the displacements of the boundaries have an extra benefit. The energy balance equation (6) contains both thermodynamic functions ($G$ or $U$) and mechanical terms (the forces that do work). So, in fact, our derivation mixes thermodynamics and mechanics, which results in an explicit relationship between surface energies and surface tensions (Eq. (18)). We think that, up to now, this relationship had not been previously derived by any rigorous method.

## Appendix A. Surface forces are tangential

Consider a thin element of liquid, whose free surface extends from point $A$ to $B$ and is orthogonal to the plane of the figure (Fig. 7). Let $\vec{F}_A$ be the force exerted by the surface of the liquid located at the right side of point $A$. We want to prove that the component orthogonal to the surface, $F_{A\perp}$, will necessarily be zero.

Our element of liquid will exert a force $\vec{F}'_B$ on the rest of the liquid located on its left side and this force will be similar to $\vec{F}_A$. In fact, by virtue of continuity, if the distance $d_{AB}$ between points $A$ and $B$ is short enough, $\vec{F}'_B$ will tend to $\vec{F}_A$ and, consequently, the reaction of the liquid on the left side, $\vec{F}_B$ $(= -\vec{F}'_B)$ will tend to $-\vec{F}_A$. Let us now calculate the torque of all external forces with respect to the midpoint $O$. For a thin element of liquid its weight can be neglected and, if $d_{AB}$ is short enough, pressure can be considered uniform. Their contribution, and that of the tangential components of the forces, will be of second or higher order in $d_{AB}$. So, up to first order, the net torque will depend only on the perpendicular components of the surface forces:

$$M_O = F_{A\perp}\frac{d_{AB}}{2} + |F_{B\perp}|\frac{d_{AB}}{2} = (2F_{A\perp})\frac{d_{AB}}{2}. \tag{A.1}$$

From Eq. (A.1), we are led to the conclusion that mechanical equilibrium ($M_O = 0$) requires that the normal component of the force acting on the surface be zero.

## Appendix B. Thermodynamical relationships

For a reversible process, the first law of thermodynamics accounts for the variation of the internal energy, $\delta U$, in terms of the work done on the system, $\delta W$, and the variation of entropy,

$$\delta U = \delta W + T\delta S. \tag{B.1}$$

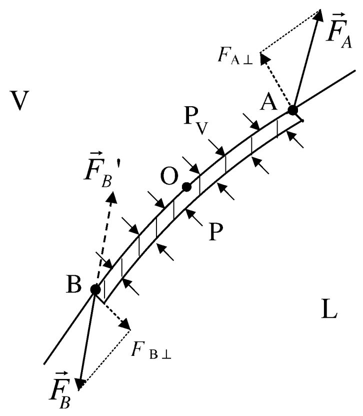


Fig. 7. Analysis of the mechanical equilibrium of a thin volume element (dashed) containing the LV surface between points $A$ and $B$. The net torque will be zero only if the normal components of surface forces, $F_{B\perp}$ and $F_{A\perp}$, vanish.

For our purposes, it is more convenient to express $U$ as a function of the Gibbs free energy,

$$G \equiv U + PV - TS. \tag{B.2}$$

Substitution of Eq. (B.2) into Eq. (B.1) leads to

$$\delta G = \delta W + P\delta V + V\delta P - S\delta T, \tag{B.3}$$

which, for a process at constant temperature, reduces to

$$\delta G = \delta W + P\delta V + V\delta P. \tag{B.4}$$

If this equation is applied to a bulk phase, the work $\delta W$ is just $-P\delta V$ and, therefore,

$$\delta G = V\delta P, \tag{B.5}$$

which is called the intrinsic free energy.

## Appendix C. Work done by pressure

The work done by pressure on our element of volume can be decomposed into two contributions,

$$\delta W_P = \delta W_V + \delta W_L, \tag{C.1}$$

where $V$ and $L$ refer to the surrounding vapor and liquid, respectively. The work done by the vapor phase, $\delta W_V$, can be computed in the limit where the displacement of the contact line is very small ($\delta s \ll h$ in Fig. 4b). This leads to

$$\begin{aligned} \delta W_P &= P_V lh\delta x_1 + \delta W_L \\ &= (P_V - P)lh\delta x_1 + Plh\delta x_1 + \delta W_L. \end{aligned} \tag{C.2}$$

The last two terms can be easily interpreted with the help of Fig. 8. They correspond to the work done by the liquid surrounding the bulk portion of our volume element. Consequently, whatever the deformation of the volume element, we know that their addition will be equal to $-P\delta V$, and we arrive to the desired result:

$$\delta W_P = (P_V - P)lh\delta x_1 - P\delta V. \tag{C.3}$$

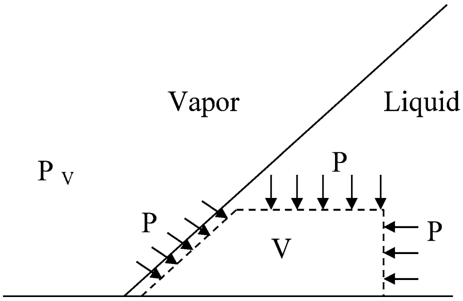


Fig. 8. The pressure acting on any boundary surface of the bulk portion of the liquid element near the contact line is the pressure in the liquid, $P$.

## References

[1] T. Young, Philos. Trans. R. Soc. 95 (1805) 65.
[2] K.F. Gauss, Comment. Soc. Regiae. Scient. Gottingensis Rec. 7 (1830), reprinted in Werke, vol. 5, Gottingen, 1876, p. 29 (in Latin).
[3] J.W. Gibbs, The Collected Works of J. Willard Gibbs, vol. I, Thermodynamics, Yale Univ. Press, New Haven, 1928, pp. 314–331.
[4] J. Pellicer, J.A. Manzanares, S. Mafe, Am. J. Phys. 63 (1995) 542.
[5] J.E. McNutt, G.M. Andes, J. Chem. Phys. 30 (1959) 1300.
[6] E.M. Blokhuis, Y. Shilkrot, B. Widom, Mol. Phys. 86 (1995) 891.
[7] R.E. Collins, C.E. Cooke Jr., Trans. Faraday Soc. 55 (1959) 1602.
[8] H. Fuji, H. Nakae, Philos. Mag. A 72 (1995) 1505.
[9] At this point it should be emphasized that a much more recent nonlocal derivation due to Boruvka et al. [35] (see also the main text) generalizes Gibb's results to include additional energy terms.
[10] J.H. Poynting, J.J. Thomson, A Textbook of Physics. Properties of Matter, eighth ed., Griffin, London, 1902, pp. 139–140.
[11] A.W. Adamson, Physical Chemistry of Surfaces, sixth ed., Wiley, 1997, p. 353.
[12] A. Sommerfield, Mechanics of Deformable Bodies, in: Lectures on Theoretical Physics, vol. 2, Academic Press, New York, 1964, p. 127.
[13] De Gennes, Rev. Mod. Phys. 57 (1985) 827.
[14] C.G. Sumner, in: Symposium on Detergency, Chemical Pub. Co., New York, 1937, pp. 15–17.
[15] R. Shuttleforth, G.L.J. Bailey, Dis. Faraday Soc. 3 (1948) 16.
[16] J. Bico, C. Marzolin, D. Quéré, Europhys. Lett. 47 (1999) 220.
[17] B.A. Pethica, T.J. Pethica, in: Second International Congress on Surface Activity, vol. III, Electrical Phenomena, Solid–Liquid Interface, Butterworth, London, 1957, pp. 131–135.
[18] R.E. Johnson Jr., J. Phys. Chem. 63 (1959) 1655.
[19] A.S. Michaelis, S.W. Dean, J. Phys. Chem. 66 (1962) 1790.
[20] A.W. Adamson, I. Ling, Adv. Chem. Ser. 43 (1964) 57–73.
[21] W.A. Zisman, Adv. Chem. Ser. 43 (1964) 1–51.
[22] This point of view is also shared by W.A. Zisman: see his comments at the end of the paper in Ref. [15].
[23] G.J. Jameson, M.C.G. del Cerro, J. Chem. Soc. Faraday Trans. I 72 (1976) 883.
[24] C.A. Miller, E. Ruckenstein, J. Colloid Interface Sci. 48 (1974) 368.
[25] In addition, it is significant that these authors do not try to invalidate Gibbs' derivation.
[26] S. Shimizu, T. Kusunase, H. Kimura, M. Ooyama, M. Imura, S. Ishikura, K. Sahira, H. Kitamura, H. Shiraishi, Y. Nakada, M. Wada, M. Suzuki, T. Narite, NASDA-JSUP 1 (1991) 49.
[27] M.J.P. Nijmeijer, C. Bruin, A.F. Bakker, J.M.J. van Leeuwen, Phys. Rev. A 42 (1990) 6052.
[28] A microscopic derivation based on statistical mechanics does exist: J. De Coninck, et al., Phys. Rev. E 65 (2002) 036139. Of course, any microscopic approach relies on several particular assumptions, e.g., concerning the molecular interactions. Thus, any microscopic approach necessarily has a lesser degree of generality compared to a thermodynamical derivation.
[29] J.N. Israelachvili, Adv. Colloid Interface Sci. 16 (1982) 31.
[30] A. Michaels, S.W. Dean, J. Phys. Chem. 66 (1962) 1790.
[31] Although implicitly, this assumption is also made in Ref. [11].
[32] T. Wada, T. Fukumoto, J. Jpn. Inst. Welding 37 (1968) 845.
[33] W.J. Herzberg, J.E. Marian, J. Colloid Interface Sci. 33 (1970) 161.
[34] R.C. Tolman, J. Chem. Phys. 16 (1948) 758, several equivalent definitions of $\sigma_{ij}$ are presented.
[35] J.L. Barrat, L. Bocquet, Phys. Rev. Lett. 82 (1999) 4671.
[36] Although in our derivation the energy balance is written in terms of the Gibbs free energy, the results are *exactly* the same if the Hemoltz free energy is used instead. It should be remarked here that the process is not carried out at constant pressure nor at constant volume (both $\delta V$ and $\delta P$ are, in general, different from zero in Eq. (6)).
[37] T. Pompe, S. Herminghaus, Phys. Rev. Lett. 85 (2000) 1930.
[38] L. Boruvka, A.W. Neumann, J. Chem. Phys. 66 (1977) 5464.

[39] A. Marmur, B. Krasovitski, Langmuir 18 (2002) 8919.
[40] L.D. Landau, E.M. Lifshitz, Statistical Physics, Part 1, Pergamon, Oxford, 1980, p. 532.
[41] F.M. Fowkes, J. Phys. Chem. 67 (1963) 2538.
[42] D.K. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13 (1969) 1741.