Young’s equation revisited

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Abstract
Young’s construction for a contact angle at a three-phase intersection forms the basis of all fields of science that involve wetting and capillary action. We find compelling evidence from recent experimental results on the deformation of a soft solid at the contact line, and displacement of an elastic wire immersed in a liquid, that Young’s equation can only be interpreted by surface energies, and not as a balance of surface tensions. It follows that the a priori variable in finding equilibrium is not the position of the contact line, but the contact angle. This finding provides the explanation for the pinning of a contact line.

Keywords: surface tension, surface energy, Young’s equation, pinning, wetting

(Some figures may appear in colour only in the online journal)

1. Introduction
In 1805, Young [1] proposed that the contact angle at a three-phase contact line is determined by a balance of surface tensions. Formally, this idea results in the equation

\[
\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta. \tag{1}
\]

Here \(\gamma_{SV}\), \(\gamma_{SL}\) and \(\gamma_{LV}\) are, respectively, the solid–vapor, solid–liquid and liquid–vapor interfacial force per unit length of the contact line, i.e. surface tension, and \(\theta\) is the contact angle, see figure 1.

Equation (1) can be understood as the balance of three surface tensions, as originally described by Young [1], but it has also been derived using the principle of minimizing the total free energy of the system [2–4]. The latter thermodynamic derivation relies on interpreting \(\gamma_{SV}\), \(\gamma_{SL}\) and \(\gamma_{LV}\) as scalar thermodynamic surface energies, \(\Gamma_{SV}\), \(\Gamma_{SL}\) and \(\Gamma_{LV}\), instead of tension vectors.

One reason for adopting the surface energy interpretation is that, while \(\gamma_{SL}\) and \(\gamma_{LV}\) can be interpreted either way, the surface tension on a dry solid, \(\gamma_{SV}\), is a contentious concept [2, 5–9]. Specifically, it has been argued that Young’s equation is not a balance of forces [6, 7]. On the other hand, the surface energy interpretation has led to many misunderstandings of the wetting phenomenon on patterned surfaces [10, 11].

Recent critical issues include the validity of equation (1) at the nanoscale [12–15] and on flexible surfaces [15, 16].

2. Interpretation of Young’s equilibrium
In Young’s construction, it is conventionally assumed that all three interfacial tensions \(\gamma_{SV}\), \(\gamma_{SL}\) and \(\gamma_{LV}\) can do work in moving the contact line along the solid surface. The ability of a surface tension to do work on a system can be explained as follows. Owing to a lack of counterparts on the other side of an interface, particles at the interface are at a higher potential than in the bulk liquid. This causes a force that draws the particles from the interface towards the bulk. Without constraints to mobility, i.e. in a liquid, this will happen, and requires replacement of molecules in the direction parallel to the interface. This mechanism, in a system that involves a liquid, makes it possible to transfer the potential energy difference in the direction perpendicular to the surface into mechanical work done by a component of force acting parallel to the surface.

On a solid surface, however, the situation is fundamentally different. The potential energy difference in the direction perpendicular to the surface exists, but atoms are fixed in the crystal lattice and are unable to move from the surface to the bulk. Consequently, at a solid–gas interface there is no such mechanism as described above by which the potential energy difference in the direction perpendicular to the surface can be transferred to work being done parallel to the surface. This argument means that the interpretation of equation (1) as a balance of surface forces has no physical foundation.
Capillarity on an unstrained solid surface (such as \( \gamma_{SV} \)). In this classical scheme, the three mechanical surface tensions \( \gamma_{SV}, \gamma_{SL}, \) and \( \gamma_{LV} \) are in equilibrium in the direction parallel to the solid surface.

Figure 1. Young’s [1] construction of the force balance at a three-phase contact line between a droplet, its vapour, and a solid surface. In this scheme, the three mechanical surface tensions \( \gamma_{SV}, \gamma_{SL}, \) and \( \gamma_{LV} \) are in equilibrium in the direction parallel to the solid surface.

Figure 2. Tension vectors at the three-phase line. The vectors \( \gamma_{LV} \) and \( \gamma_{SL} \), representing interfaces that involve a liquid, induce a resultant vector that is countered by an elastic tension in the solid material, \( \sigma \). The tangential component of the elastic tension \( \sigma_s \) equals \( \gamma_{SL} + \gamma_{LV} \cos \theta \), and the solid at the contact line deforms (not shown) so that a cusp formed is oriented along \(-\sigma\). The contact angle \( \theta \) is not determined by mechanical tensions, but the interface energies (see text).

In view of the argument that the surface of a dry solid cannot do work on a drop in moving it parallel to the surface, how should equation (1) be interpreted? Since \( \gamma_{SL} \) and \( \gamma_{LV} \) involve a liquid surface, there must be a tension, \( \sigma_s \), on the left-hand side of equation (1) that balances the two tangential capillary tensions \( \gamma_{SL} \) and \( \gamma_{LV} \cos \theta \) on the left-hand side of equation (1). However, \( \sigma_s \) does not arise from capillarity on an unstrained solid surface (such as \( \gamma_{SV} \) in Young’s construction), as discussed above. It is simply the counterforce to the sum of the two capillary tensions of the system that pull the contact line from the liquid side. This is illustrated in figure 2. The contact line is pinned because moving it to the liquid side requires doing external work as a solid surface is then being created, causing an additional opposing tension \( \gamma_{SV} \). On the other hand, moving the contact line towards the solid side is opposed by the tension \( \gamma_{SL} + \gamma_{LV}\cos \theta \).

3. Experimental evidence

Here, we provide evidence for our concept based on the interpretation of experimental data. At the end of the paper, we will return to the question of how the contact angle, \( \theta \), is determined by the three-phase contact, given that it is not provided by a balance of mechanical tensions, but the interface energies (see text).

For equation (1) to be valid in its conventional interpretation, the forces parallel to the interface are in equilibrium. Therefore, in Young’s construction the remaining force vector that is not balanced by the tangential tensions is the vertical component of \( \gamma_{LV} \). Thus, in this scheme the deformation of the solid interface at the contact line must be by symmetric, i.e. oriented directly upwards, irrespective of the contact angle \( \theta \). However, recent experiments [17, 18] show convincingly that this is not true. Instead, the orientation angle of the cusp formed by elastic deformation is asymmetric and follows \( \theta \) systematically. This finding is in clear discrepancy with the Young’s construction, but is readily explained by the concept proposed here. According to figure 2, when no active tension \( \gamma_{SV} \) exists, a cusp formed by elastic deformation is oriented in the direction of the resultant of the capillary force, i.e. \(-\sigma\). This prediction is in quantitative agreement with the measured cusp profiles [18].

Owing to the critical importance of the physics at a three-phase contact line, innovative experiments have recently been carried out to measure the capillary tensions in a system where a thin elastomeric wire is partially submerged in a liquid [19], see figure 3. It was found that above the contact line the wire is homogeneously stretched [19]. This suggests that there must be a force at the three-phase contact line pulling downwards.
This finding contradicts Young’s construction (figure 1), where the capillary tensions at the contact line are in equilibrium. However, using the concept proposed here, the tension that balances the two capillary tensions is an elastic counterforce. Stretching of the wire above the contact line then becomes obvious.

Quantitatively, we find (see figure 3 and caption) that above the liquid surface, \( z > 0 \), the elastic tension \( \sigma_z \) at the contact line results in a displacement \( u_a(z) \) relative to the non-submerged state

\[
u_a(z) = [2\sigma_z/(ER) - \rho gL/E] z.
\]

(2)

Here \( E \) is Young’s modulus for the wire material (35 kPa), \( R \) the radius of the wire (150 \( \mu m \)), \( \rho \) the density of the liquid (803 kg m\(^{-3}\)), \( g \) the acceleration due to gravity (9.81 m s\(^{-2}\)), and \( L \) the immersion depth of the wire (11 mm), and \( z \) the distance from the liquid surface. The values in square brackets are those used in the experiments [19]. The tension on the solid \( \sigma_z \) can be deduced from the displacement field \( u_a(z) \) measured for the wire below the liquid surface, \( z < 0 \), for which (see figure 3 and caption)

\[
u_a(z) = [-3\gamma_{SL}/(ER) - \rho g(L + \gamma z)/E] z.
\]

(3)

Best fit to the data [19] at \( z < 0 \) provides \( \gamma_{SL} = 11.2 \) mN m\(^{-1}\), while \( \gamma_{LV} = 22.8 \) mN m\(^{-1}\) and \( \cos \theta = 0.7 \) were directly measured [19]. Consequently, equation (1) provides \( \sigma_z = 27 \) mN m\(^{-1}\). Inserting this into equation (2) predicts a homogenously stretching of the wire above the liquid surface as \( u_a(z) = 7.9 \times 10^{-3} \) \( z \), in excellent agreement with the best fit to the experimental data \( u_a(z) = 8.1 \times 10^{-3} \) \( z \).

Even more striking than the quantitative agreement shown above are the conclusions that can be drawn qualitatively. Not only is it impossible to explain the stretching of the wire at \( z > 0 \) using Young’s construction, but the observed compression of the wire at \( z < 0 \) shows that surface tension does not initiate contraction of the dry solid. If it did, then the dry wire should be in a compressed state due to solid–vapor surface tension, and would relax when submerged into a liquid. Stretching of the wire should then occur, contrary to what is actually observed.

The experimental data above support the theoretical concept presented here, both qualitatively and quantitatively. This indicates that equation (1) can only be interpreted by surface energies. Consequently, the force balance should be written as

\[
\sigma_z = \gamma_{SL} + \gamma_{LV} \cos \theta.
\]

(4)

The elastic tension vector \( \sigma \) opposes the resultant of vectors \( \gamma_{SL} \) and \( \gamma_{LV} \), and is thus directed into the solid at the angle \( \theta \), as shown in figure 2. This also reveals how the ‘excess’ tension perpendicular to the solid interface \( \gamma_{LV} \sin \theta \) in Young’s construction is balanced.

4. Discussion and the derivation of Young’s equation

The remaining critical issue is: what is the fundamental mechanism that controls the equilibrium contact angle \( \theta \)? In terms of the energy interpretation, this mechanism can be explained as follows. The surface chemical potential across the contact line is

\[
P = [(\Gamma_{SV} - (\Gamma_{SL} + \Gamma_{LV} \cos \theta))/\rho]
\]

(5)

where \( \rho \) is the surface particle density. According to the second law of thermodynamics \( P \) will be minimized given a process that makes this possible. Note that motion of the contact line along the solid interface is not such a process, because \( \Gamma_{SV} \), \( \Gamma_{SL} \) and \( \Gamma_{LV} \) are material parameters and \( P \) does not depend on the position of the contact line on a smooth surface. Thus, the spontaneous adjustment of equation (5) to minimize \( P \) can only occur by the free coordinate \( \theta \). At equilibrium, \( P \) is at minimum and equals zero. Consequently, \( \theta \) adopts the value given by the equation.

\[
\Gamma_{SV} = \Gamma_{SL} + \Gamma_{LV} \cos \theta.
\]

(6)

The insight outlined above provides perspectives for understanding many related processes. For example, capillary-driven self-assembly of flexible structures [20] may be explained by the elastic response at the contact line. Deformation of the solid at the contact line can be explicitly determined, which will allow consideration of its effect on the measured contact angles on flexible surfaces [18]. The concept proposed here is consistent with the thermodynamic explanation of sliding friction [21]. The interpretation of Young’s equation in which the three-phase contact line does not move without applying an external force, also explains the pinning of interfacial nanobubbles, which critically affects their stability [22, 23]. The concept can also be used in modeling the contact angle hysteresis, and this will be done in a future paper.

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