

# Faulty Intuitions of Wetting

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Theories of wetting have a long history and they are intensively used in interpreting experimental data. Nevertheless, many basic aspects, such as the pinning of a contact line and contact angle hysteresis, are still poorly understood. The development of a rigorous consensus theory has suffered from concepts that are based on faulty intuitions. These include the force interpretation of Young's equation, the use of the principle of minimizing the global free energy, and the concepts of the work of adhesion and the mechanical surface tension on a solid. In this paper, the appropriate treatment of the basic ingredients of surface thermodynamics is discussed and the route towards the physically justified theoretical approach on wetting is outlined.

*Keywords: Wetting, hydrophobicity, contact angle, contact angle hysteresis, surface energy, surface tension, surface thermodynamics*

## 1 INTRODUCTION

Theories of contact angles and wettability have been developed for over two centuries and the literature on them includes a huge number of publications. Nevertheless, many basic phenomena, such as the pinning of a contact line and contact angle hysteresis are so poorly understood that even their origin is controversial [1, 2]. The development in the field has been hampered by many widely-used concepts that are based on intuitions and dubious assumptions.

The coherent state-of-the art can be demonstrated by reviewing the derivations of Young's equation, which is the main paradigm of the science of wet-

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ting. Over a period of more than a hundred years, dozens of attempts to prove Young's equation have been published. Yet, as will be outlined below, none of them is valid. The problems in these "rigorous" derivations include dubious assumptions of mechanical surface tension on a solid, misuse of the Second Law of Thermodynamics and an inappropriate assumption of the reversibility of contact line displacement.

Since already the most fundamental foundation of the wetting theory, Young's equation, is under vigorous controversy in the literature, it is no wonder that more complex issues, such as the contact angle hysteresis, are far from settled. Worse still, there are scientists who believe that they do have a solution, even if that solution does not convince others, who may believe that they have a solution of their own. Such a separation of wetting science into schools makes presentation and publication of novel ideas difficult for everyone.

In this paper, the problems encountered with the basic ingredients of the theory of wetting are analysed, and an attempt to direct future research on the right track is made. The discussion is structured in sections, each of which deals with a specific wide-spread faulty intuition which has hampered the development of a sound physical theory. In each section, suggestions on how to deal with the prevailing misconceptions are made, and the appropriate theoretical framework for future work is outlined.

## 2 FAULTY INTUITION: SOLID SURFACE CAN DO LATERAL WORK

Prior to Gibb's development of surface thermodynamics [3], no concept of surface energy existed. Thus, Young's idea of an "appropriate angle of contact" [4] could only be interpreted as an equilibrium of forces at the contact line, see Figure 1.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta. \quad (1)$$

Here  $\gamma_S$ ,  $\gamma_{SL}$  and  $\gamma_L$  are, respectively, the solid-vapor, solid-liquid and liquid-vapor interfacial forces per unit length of the contact line, i.e., surface tensions, and  $\theta$  is the equilibrium contact angle, see Figure 1. In the discussions that follow we refer to the tensions in Figure 1 as "forces".

It has sometimes been argued that Young's equation does not represent a balance of forces [5, 6]. However, the exactly opposite view [7] has dominated the literature and was summarized by Gao and McCarthy [8] in their extensive review by stating that dealing with Young's equation in terms of surface energies is "a confusing substitution", and that "This equation is not derived or proven, nor does it need to be; it is the simple balance of forces in a plane operating on a line".

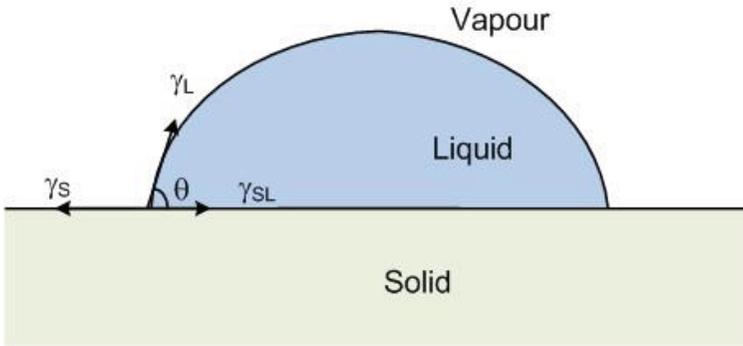


FIGURE 1

Classical construction of the force balance at a three-phase contact line between a drop, its vapour, and a solid surface. In this scheme, the components of three applied mechanical surface tensions  $\gamma_L$ ,  $\gamma_S$  and  $\gamma_{SL}$  and are at equilibrium in the direction parallel to the solid surface, and this equilibrium determines the equilibrium contact angle  $\theta$ .

Clarity to this issue can only be found by proper understanding of the nature of the forces in question. Consider two men pulling a rope in opposite directions and not moving. Then, there are applied forces that are in equilibrium. Either of the men can make the system move when he applies a higher action force than required at the equilibrium. This is analogous with the conventional understanding of Young's force equilibrium. Consider now a man pulling a rope that is fixed to a box on a floor, and that the box does not yet move. In this situation, there is also equilibrium of forces, but the equilibrium is between the applied force and a friction force. As long as the box does not move, these two force vectors point to the opposite directions and are of the same magnitude. Obviously, the man can make the box move by applying a sufficiently strong force, but the reverse is not true, i.e. a box cannot make the man move. Hence, the nature of a friction force is different from that of an applied force. Specifically,

- An applied force is an active force that can do work.
- A friction force is a passive force that cannot do work.
- Prior to motion, the friction force equals the applied force and it thus controlled by it.
- When motion starts, both forces are at their maximum, usually called the static friction force.

The appropriate question now is: What is the nature of forces  $\gamma_S$ ,  $\gamma_L$  and  $\gamma_{LV}$  in the classical construction in Figure 1?

The ability of a surface tensional force to do work on a system can be explained as follows. Owing to the lack of counterparts on the other side of an interface, particles at the interface are at a higher potential than in the bulk. This causes a net perpendicular force that, given that there are no constraints

to mobility, draws particles from the interface towards the bulk. When the particles leave the interface, replacement of them is required in the direction parallel to the interface. This mechanism, possible in a system that involves a liquid, transfers the potential energy difference that exists in perpendicular to the surface, into mechanical work spent in parallel to the surface. Hence, the interfaces that involve a liquid can do lateral work, and  $\gamma_L$  and  $\gamma_{SL}$  are thus active applied forces.

On a solid, however, the situation is fundamentally different [3, 9-11]. In a solid, atoms are fixed in the crystal lattice and are unable to move from the surface to the bulk. Thus, there is no driver for the replacement of surface molecules laterally. Consequently, on a solid-gas interface, there is no such mechanism, as described above for a liquid, by which the perpendicular potential energy difference can be transferred to work spent in parallel to a surface. Note that basic mechanics tell us that a force will do work only if it has a component in the direction that the object moves. This means that the perpendicular net force due to the imbalance across the solid interface cannot possibly do work on the system in Figure 1. Therefore,  $\gamma_S$  is a friction force.

Yet another way to consider the nature of lateral interfacial forces is that when a liquid surface does work, the energy for that is taken from spontaneously reducing the surface area of the liquid. A solid does not reduce its surface area spontaneously and, therefore, a solid surface cannot do work laterally. Because  $\gamma_S$  is a force that cannot do work on a system, we use a different symbol,  $\sigma_S$ , for it in the discussion that follows.

That  $\sigma_S$  is a friction force has two consequences of paramount importance. Firstly, Young's equilibrium cannot be derived by the concept of forces, because one of the three operating forces,  $\sigma_S$ , is merely a consequence of the two applied forces  $\gamma_L \cos\theta$  and  $\gamma_{SL}$ . In a static situation, the friction force equals the applied force in magnitude, and this is the reason why Equation (1) trivially holds.

Since  $\gamma_L$  and  $\gamma_{SL}$  are material constants,  $\sigma_S$  is, in fact, determined by  $\theta$  alone, i.e.  $\sigma_S = \sigma_S(\theta)$ . In other words, the lateral forces operating at the contact line do not determine the equilibrium contact angle, but the contact angle determines the counter force  $\sigma_S$ . In the framework of the elasticity theory,  $\sigma$  can be interpreted as the elastic reaction force that is caused by the solid material being stretched by the action forces. Indeed, by analyzing data on elastic deformations of a soft material [12-13] it can be shown also experimentally that  $\sigma_S$  is a reaction force [14]. The situation at a contact line, interpreted in terms of  $\sigma_S$ , is shown in Figure 2.

Secondly, a static situation in Figure 2, where two applied forces pull on one side of the contact line without an applied force pulling on the other side, means that the contact line is pinned by the frictional force against receding. In other words, the contact line is fixed so that it will not move in spite of the forces applied on the liquid side. Thus, a range of contact angles is possible in the static situation. In the analogy of men pulling a box by a rope, this is a

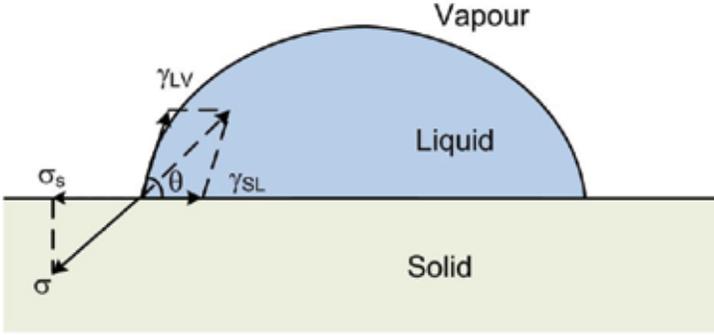


FIGURE 2

Forces at the three-phase contact line. The resultant of the applied force vectors,  $\gamma_L$  and  $\gamma_{SL}$  is countered by the force,  $\sigma$ . The tangential component of  $\sigma$  is the friction force  $\sigma_s$  that equals  $\gamma_{SL} + \gamma_L \cos\theta$ . Adopted from [14].

situation where the force applied by the men is insufficient to cause motion. Only with a sufficiently high force, the box starts to move. At that point, the total applied force equals the maximum frictional force, which is determined by friction at the bottom of the box. This is an important analogy with the contact angle hysteresis, and will be further elaborated in Section 5.

Obviously, a contact line is pinned against advancing motion too, because on the solid side, there is no applied force that could do work and move the contact line, whereas there are two applied forces that pull the contact line towards the liquid side (see Figure 2).

Returning now to Young's equation, the conclusion from what is above is that attempts towards proving Equation (1) by the classical force interpretation are invalid. This is simply because the lateral surface tensional forces do not determine the equilibrium contact angle. The proof must, therefore be sought from the surface energy interpretation of Young's equation. Indeed, numerous attempts have been made to that end, as will be discussed in the following section.

### 3 FAULTY INTUITION: LOCAL EQUILIBRIUM IS SET BY GLOBAL EQUILIBRIUM

Young's equation in terms of scalar specific surface energies  $\Gamma_S$ ,  $\Gamma_{SL}$  and  $\Gamma_L$

$$\Gamma_S = \Gamma_{SL} + \Gamma_L \cos \theta, \quad (2)$$

was derived by Gibbs [3] using the idea that the total free energy of the system is minimized at a certain contact angle. Numerous derivations for different system geometries, including a drop on a surface, have subsequently been proposed [15-19].

This idea of analysing the global thermodynamic equilibrium is based on the Second Law of Thermodynamics which states that all spontaneous processes tend to shift towards the system's minimum total free energy. There are two problems with this approach when applied to wetting. Firstly, the systems considered in wetting include the surface of the dry solid. Such a surface does not deform spontaneously. Secondly, the spontaneity of a process only determines whether or not a process can occur, and does not indicate whether or not the process will occur. In other words, spontaneity is a necessary, but not sufficient, condition for a process to occur. Spontaneity of a large system to find its total free energy minimum requires that the system includes no sub-systems that are not spontaneous. In other words, a global system finds its state of minimum energy only when there are no local constraints for that to happen.

Considering a drop on a solid, it has been shown that, if the global system is at its minimum state in terms of the interfacial energy, then Equation (2) results. However, it was pointed out above that the surface energy of dry solid, which is included in the analysis of the global system, is not a component of the system's free energy, and that the contact line is pinned. Pinning of a contact line is also a well-known empirical fact. Hence, there are local constraints at the contact line that prevent a drop from finding its state of minimum total free energy spontaneously. Thus, strictly speaking, none of the derivations that are based on the principle of minimizing the free energy of the global system provide a valid proof of Young's equation.

Moreover, these derivations are for specific global geometries, and it seems odd that Young's equation would need to be proven for each geometry separately. As advocated in the review by Gao and McCarthy [8], Schwartz [20] argued that physically, the forces at the contact line "operate in each phase within a few molecular diameters of the other two phases. Neither the state nor the geometry of the phase interfaces in the regions remote from the line boundary has any direct effect on the contact angle." This point is crucially important in the derivation of Young's equation, and consideration of the local thermodynamic equilibrium at the contact line is clearly the only rigorous option. This will be discussed in the following section.

#### **4 FAULTY INTUITION: CONTACT LINE DISPLACEMENT IS REVERSIBLE**

Being at least partly aware of the problems discussed in Section 3, many derivations of Young's equation have been presented based on local thermodynamics at the contact line [21-25]. These derivations are based on virtual displacement of the contact line position. As acknowledged in many of these papers, a definite requirement for such an approach to be valid is that the

displacement of the contact line is reversible. The wide-spread intuition that this is indeed the case naturally follows from the classical construction in Figure 1, which suggests no constraints on the motion of a contact line. However, applying such an intuition in the derivation is circular deduction: Young’s equation is proved by employing a critical assumption that follows from the same equation.

Worse still, the intuition of a reversible displacement of a contact line is false. This can be concluded already from the fact, discussed in Section 3, that a contact line is pinned. Because of the pinning, external work is required to make a contact line move. This means that contact line motion is a dissipative process. To outline this crucial aspect more specifically, we emphasize the most basic definition of the Gibbsian surface thermodynamics:

Work must be spent when creating new surface.

This work defines the thermodynamic surface energy  $\Gamma$  ( $\text{Jm}^{-2}$ ). Obviously, when a three-phase contact line recedes along the solid surface, new solid surface is formed behind it. Correspondingly, when a contact line advances, new solid-liquid surface is formed behind it. Noting the above cited argument [20] on the spatial range of atomic forces, these processes are strictly local. Surface creation at the contact lines in the case of a sliding drop is schematically illustrated in Figure 3.

Since work is spent in creating surface, a frictional force  $F$  against which the work is done, must exist at a sliding contact line. This is analogous with the thermodynamic origin of sliding friction of solids [26]. Consider a liquid body of width  $w$  moving in complete contact by an increment  $dx$ , so that an area  $dA$  is formed. Then, work  $dE$  is spent in creating new surface. From the definition of force, we find that the scalar value of the resisting force, when creating new surface in the  $x$ -direction, is  $F = dE/dx = \Gamma dA/dx = \Gamma w$ . It follows that the frictional tension that resists the motion is  $F/w = \Gamma$ .

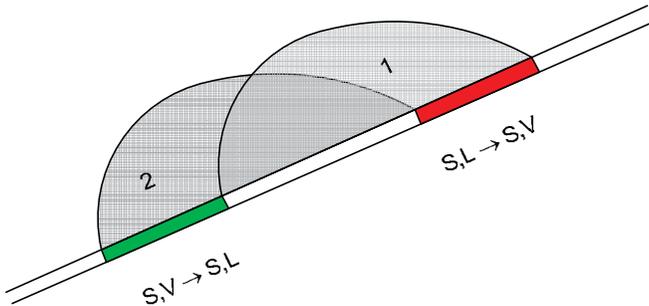


FIGURE 3  
 Displacement of a sliding drop. Solid-vapor interface (S,V) disappears and solid-liquid interface (S,L) is created at the advancing contact line. Correspondingly, solid-liquid interface disappears and solid-vapor surface is created at the receding contact line.

In other words, the magnitude of the frictional force  $F$  is such that the related tension equals the thermodynamic surface energy  $\Gamma$  of the interface being created. Note again, that the frictional force  $F$  cannot do work on the system, but the system, when forced to move, must do work against  $F$ . Since the nature of the contact of a liquid on a smooth solid does not change upon initiating motion, the dynamic friction force equals the maximum static friction force. Note that  $F$  is independent of the velocity of the contact line motion.

Intuitively, one could argue that when creating new interface behind a moving contact line, the surface energy of the disappearing surface on the other side of the contact line is available as free energy. In that case,  $F$  would be related to the difference of the solid and solid-liquid surface energies, and one could apply the concept of work of adhesion in analyzing the motion of a contact line [25, 27, 28]. However, surface energy is a thermodynamic concept, and in the thermodynamic theory [3], surface energy is not a property associated to a volume, but a property of a discrete interface. Therefore, the surface energy of the surface that arrives the contact line is not stored anywhere and, thus, cannot be transferred to the other side of the contact line. Consequently, upon moving a three-phase contact line, the surface energy of the disappearing surface must dissipate into thermal energy. This is analogous to frictional heating [26].

The inevitable conclusion from what is above is that the concepts of surface free energy and reversible work of adhesion are inapplicable in the context of wetting, because contact line motion is a dissipative process. It follows that all local derivations of Young's equation based on a reversible displacement of the contact line are dubious. This, together with the conclusions made in the previous sections regarding derivations by the force interpretation and by the global free energy balance, leaves us with a striking observation: Young's equation is the foundation of the science of wettability, and yet, there is no valid proof of it. A relief to this situation will be provided in the following section.

## **5 FAULTY INTUITION: DERIVATION OF YOUNG'S EQUATION IS COMPLEX**

From the discussions in the previous sections three crucial aspects of Young's equation become clear. Firstly, considering Young's equation as representing a balance of lateral forces is problematic and prone to misconceptions about the nature of the related phenomena. Secondly, Young's equation describes a small scale local equilibrium based on surface energies, and thirdly, Young's equation cannot be appropriately derived based on displacement of a contact line, because a contact line is pinned and its displacement is irreversible.

Hence, even the methods utilizing rather complicated calculus [7,19, 29] do not provide an appropriate derivation of Young's equation. This would seem to indicate that the problem is mathematically very complex, or that a comprehensive proof does not exist. Fortunately, this is not the case.

Due to the pinning of a contact line, the adjustment of a system to the final equilibrium at the contact line does not happen spontaneously by lateral motion. On the other hand, all parameters in Equation (1), except the contact angle, are material constants. Hence, the system at the contact line can find its local equilibrium only by the adjustment of the contact angle  $\Theta$ . In mechanical analogy, the change in  $\Theta$  towards the equilibrium angle  $\theta$  is driven by generalized force along generalized coordinate  $\Theta$ .

Of course, the adjustment of  $\Theta$  has been considered in the previous derivations, but it has been inappropriately combined with a displacement of the contact line. This has been justified e.g. by retaining a constant drop volume. Such an argument is poor, not only because the contact line is pinned, but also because the equilibrium is strictly local and, thus, unaffected by events far from the contact line. It is another matter that external forces may shift the contact angle away from its Young's equilibrium value, as will be discussed in Section 6.

We are now in the position to derive Young's equation appropriately [14]. Along the solid surface with a particle surface density  $\rho_S$ , the sum of the surface chemical potentials

$$\Sigma\mu_S = [\Gamma_S - (\Gamma_{SL} + \Gamma_L \cos \Theta)] / \rho_S, \quad (3)$$

can be minimized only by a change in the contact angle  $\Theta$ . The minimum, at which  $\Theta = \theta$ , is at  $\Sigma\mu_S = 0$ . In its simplicity, this gives Young's equation, Equation (2).

## 6 FAULTY INTUITION: CONTACT ANGLE HYSTERESIS IS ABSENT ON AN IDEAL SURFACE

Gray [27] proposed that the contact angle hysteresis is always caused by surface heterogeneities. This idea, promoted by Joanny and De Gennes [30], found its way to text books, e.g. [31], and is widely adopted today. In other words, it is presumed that the contact angle hysteresis does not exist on an ideally smooth and homogenous surface. This intuition has initiated many extraordinary explanations of the origin of contact angle hysteresis, such as liquid adsorption and retention, line tension, viscous dissipation, molecular rearrangement upon wetting, inter-diffusion, and shape of the disjoining isotherms (dozens of references, for review, see [2]). However, as discussed above, and by Bomarshenko [32], the irreversibility of contact line motion

and the pinning of a contact line reveal that the idea of surface heterogeneity as the fundamental origin of the contact angle hysteresis is faulty.

It was shown in Section 3 that, due to the laws of surface thermodynamics, moving a three-phase contact line along a solid surface requires an external force. Consequently, upon applying an external force, the contact angle will change until the net applied force exceeds the maximum friction force, i.e. the force that arises from creating new interface. Then, the system will move, and keeping the external force constant, this happens at a constant speed and with a constant dynamic contact angle. This is the fundamental mechanism of the contact angle hysteresis.

It is noteworthy that, although Equation (1) cannot be derived by forces, it represents a necessary mechanical equilibrium of tensions in parallel to the solid surface when  $\gamma_S$  is appropriately interpreted as  $\sigma_S$ , i.e., a friction force. Obviously, a mechanical equilibrium at the contact line must exist also when it moves. The interpretation of frictional force that affects the dynamic contact angles has been made before [33-37], but without understanding its true origins, this has remained a qualitative argument.

We will now point the way to quantify the friction force and the contact angle hysteresis. Consider a system where an external force, e.g. gravity, affects a drop on a solid and alters the contact angle, i.e. changes the term  $\Gamma_L \cos\Theta$  in the force balance at the contact line [38]. When the magnitude of the external force is such that it changes the contact angle from its static equilibrium angle to the limiting angle at which motion begins, then the magnitude of the lateral external force equals the frictional force  $F$ .

Based on the analysis in Section 4, we know the scalar magnitude of  $F$ . It equals the surface energy  $\Gamma$  of the interface that is being created at the contact line. Therefore, when the contact line advances, the decrease in  $\Gamma_L \cos\Theta$  from the static equilibrium state is compensated by  $\Gamma_{SL}$ , i.e.

$$\Gamma_{SL} = \Gamma_L (\cos \theta - \cos \theta_a), \quad (4)$$

where  $\theta_a$  is the advancing contact angle.

Similarly, when the contact line recedes, the increase in  $\Gamma_L \cos\Theta$  from the static equilibrium angle is compensated by  $\Gamma_S$ , i.e.

$$\Gamma_S = \Gamma_L (\cos \theta_r - \cos \theta), \quad (5)$$

where  $\theta_r$  is the receding contact angle.

As discussed in many textbooks, the geometric mean combining rule of intermolecular forces provides Berthelot's rule in the form

$$\Gamma_S / \Gamma_L = [(1 + \cos \theta) / 2]^2. \quad (6)$$

Combining Equations (2), (4) and (6), the advancing contact angle  $\theta_a$  is obtained from

$$\cos \theta_a = [-(\cos \theta)^2 + 6 \cos \theta - 1] / 4, \tag{7}$$

(when  $\theta > 117.7^\circ$ , then  $\theta_a = 180^\circ$ ), and the receding contact angle  $\theta_r$  from

$$\cos \theta_r = [(\cos \theta)^2 + 6 \cos \theta + 1] / 4, \tag{8}$$

(when  $\theta < 62.3^\circ$ , then  $\theta_r = 0^\circ$ ).

Hence, the physical theory [39] outlined above not only explains the origin of contact angle hysteresis, but also provides quantitative estimates for the dynamic contact angles as the function of the static Young’s equilibrium contact angle. These predictions are shown in Figure 4. Figure 4 also includes the available experimental data on these relationships on “smooth” surfaces.

Comparing the theory and experiments in Figure 4 shows good quantitative agreement for  $\theta_a$  in the whole range of angles. The agreement is also

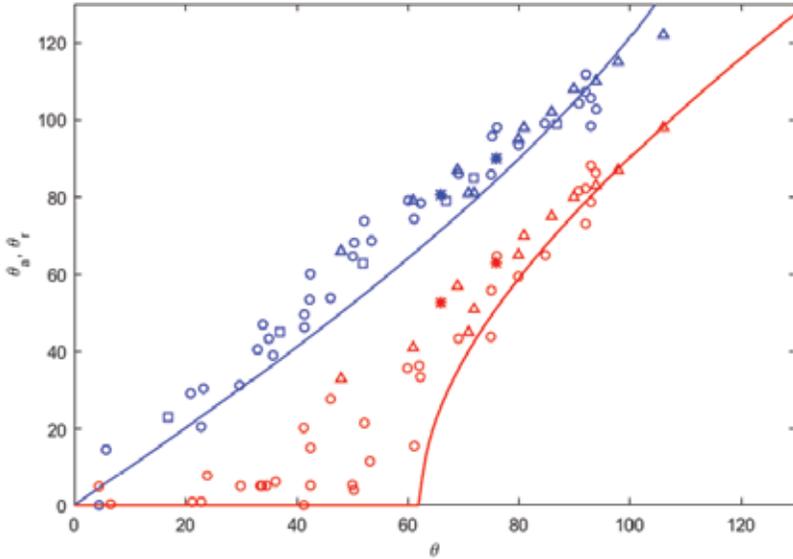


FIGURE 4 Advancing ( $\theta_a$ , blue) and receding ( $\theta_r$ , red) contact angles as a function of Young’s contact angle on a smooth surface,  $\theta$ . The lines show the prediction of the theory. The circles are experimental data for water on plasma polymer surface coatings [36], triangles for different water-ethanol mixtures on a  $\text{Si}_3\text{N}_4$  surface [40], squares for water on untreated and treated PET and PHMS surfaces [41] and stars for water on PMMA and PC surfaces [42].

good for  $\theta_r$  at high angles. The large scatter in  $\theta_r$  at low angles is due to sorption of the liquid onto the solid during a receding angle experiment as shown by Lam et al. [43]. As to the advancing contact angle  $\theta_a$ , the agreement in Figure 4 is a strikingly good considering the experimental uncertainties and that the surfaces in the experiments may not have been ideally smooth. When using the Wilhelmy plate method repeatedly on a slightly rough surface,  $\theta_a$  is larger for the first immersion and remains at a smaller constant value thereafter [44]. The circles in Figure 4 represent the first immersion [36], and this may explain the small systematic difference with the theoretical curve.

For polar materials, Berthelot's rule requires an interaction correction factor due to the non-dispersive interactions across interfaces [45]. That there is, nevertheless, a good agreement in Figure 4 between the predicted and measured  $\theta_a$  without employing such a correction suggests that the advancing contact angle is quite insensitive to variations in the interaction correction factor [29].

These results, together with the fundamental issues discussed in the previous section, point out that the fundamental origin of the contact angle hysteresis has escaped from earlier researchers. This is not to say that other mechanisms, particularly liquid adsorption, would not affect the dynamic contact angles [43, 46], but Figure 4 shows that they, particularly  $\theta_a$ , can be predicted theoretically well without considering any other mechanisms than surface creation. It is noteworthy that experimentally, the contact line hysteresis is observed on all surfaces, even the smoothest and hardest surfaces that can be manufactured [47, 48]. This is hard to explain by the conventional theory.

Roughness of the surface is, of course, an important factor in the contact angle hysteresis, as it makes the contact at the solid-liquid interface incomplete in the Cassie-Baxter state and thus modifies the geometry of the contact line. The theory discussed here can be readily expanded to include textured surfaces. This will provide the necessary basic understanding for developing e.g. super-hydrophobic surfaces.

## **7 FAULTY INTUITION: ADVANCING CONTACT ANGLE PROVIDES ESTIMATES OF SURFACE ENERGIES BY YOUNG'S EQUATION**

The surface energies of solids and of the solid-liquid interfaces are commonly determined by making contact angle measurements. The practical procedure, i.e., Zisman's method [49], involves a series of liquids by which the critical surface energy is extrapolated. As discussed in the previous sections, Young's equation and Berthelot's rule are valid for the static equilibrium contact angle.

Yet, for the last sixty years, measurements of the surface energy of solids have been based on the advancing contact angle. The argument behind this

procedure has been that “the advancing contact angle is thermodynamically significant and can be used in Young’s equation” [50]. This is vague intuition, since the thermodynamic significance of  $\theta_a$  is not the same as its equality with  $\theta$ . The use of  $\theta_a$  has also been defended by arguing that the static and advancing contact angles should be the same on an ideal surface [51]. This belief was shown to be fundamentally false in Section 6 above. A better argument is that Young’s equilibrium angle is difficult to obtain due to the contact line pinning, and that for practical reasons  $\theta_a$  must, therefore, be used [32]. In any case, the wide-spread use of the advancing contact angle in determining surface energy of solids is curious, as it is clear from the discussion in Section 6 that  $\theta_a$  and  $\theta$  are consequences of different equilibria.

To obtain a consistent solid surface tension by using different liquids, empirical corrections to Berthelot’s rule have been devised. The most popular of them is the so-called Equation of State [52]

$$\Gamma_S / \Gamma_L = [(1 + \cos \theta_a) / 2]^2 / e^{2\beta(\Gamma_L - \Gamma_S)^2}, \quad (9)$$

where  $\beta$  is an empirical constant based on a fit to experiments with various solid-liquid combinations. Equation (6) is derived for the static contact angle, and the theory on the dynamic contact angles discussed above agrees well with data when applying Equation (6) as such (Figure 4). One then wonders if the empirical correction in Equation (9) is necessary only because a wrong contact angle is used.

To investigate this, we utilize the data by Kwok and Neumann [52], who presented their experimental results on the surface tension of a solid  $\Gamma_S$  as a function of the advancing contact angle  $\theta_a$  measured when using different liquids. We wish to find out how consistently  $\Gamma_S$  is obtained by varying the liquid, when the calculation is based on

- Berthelot’s rule using  $\theta_a$
- Equation of State using  $\theta_a$
- Berthelot’s rule using  $\theta$  derived by the theory from  $\theta_a$

As for the latter method, it follows from Equations (2), (6) and (7) that the surface energy of the solid can be calculated based on the advancing contact angle as

$$\Gamma_S / \Gamma_L = [2 - (2 - \cos \theta_a)^{1/2}]^2, \quad (10)$$

Equation (10) is used to obtain the theoretical result in Table 1, where the comparison of the consistency of the three calculation methods is shown.

Table 1 shows that, when varying the liquid, the analytical theory provides equally consistent values of the solid surface tension as the empiri-

TABLE 1

Surface energy  $\Gamma_S$  of FC722-coated mica surface calculated based on the advancing contact angle  $\theta_a$  of various liquids from Berthelot's rule, Equation of State, and the analytical theory. Partly adopted from [52].

Liquid	$\Gamma_L$ (mJ m <sup>-2</sup> )	$\theta_a$ (°)	$\Gamma_S$ (mJ m <sup>-2</sup> )		
			Berthelot's Rule by $\theta_a$	Equation of State Equation (9)	Equation (10)
Decane	23.88	67.36	11.5	11.9	12.7
1-Pentanol	26.01	72.95	10.9	11.5	12.5
trans-Decalin	27.19	73.38	11.2	11.9	13.0
Hexadecane	27.62	75.94	10.7	11.4	12.6
1-Decanol	28.99	78.84	10.3	11.2	12.5
cis-Decalin	32.32	79.56	11.3	12.4	13.7
Ethyl cinnamate	37.17	86.54	10.5	12.2	13.7
Dibenzylamine	40.80	90.70	10.0	12.2	13.8
Dimethyl sulfoxide	42.68	90.95	10.3	12.9	14.3
1-Bromonaphthalene	44.31	93.81	9.7	12.4	14.0
Diethylene glycol	44.68	94.22	9.6	12.4	14.0
Ethylene glycol	47.55	97.87	8.9	12.1	13.8
Diiodomethane	49.98	101.18	8.1	11.7	13.5
2,2'-Thiodiethanol	56.26	104.56	7.9	12.7	14.0
Formamide	59.08	108.49	6.9	12.0	13.5
Glycerol	65.02	111.73	6.5	12.8	13.8
Water	72.70	118.69	4.9	12.2	13.1

cal Equation of State. The absolute values are quite similar as well. The relative standard deviation of the values of  $\Gamma_S$  in Table 1 is 4.0% for the Equation of State and 4.4% for the theory. This shows that the need to correct Berthelot's rule by empirical equations such as Equation (9) arises from inappropriately using the advancing contact angle instead of the static contact angle.

We further demonstrate this aspect by considering the scaled surface energy of a solid,  $\Gamma_S/\Gamma_L$ , as obtained by the Equation of State, for three hypothetical values of the liquid surface energy, 30, 50, and 70 mJ/m<sup>2</sup> [52]. In Figure 5, these data are compared with the purely theoretical result, showing that the theory provides essentially the same result as the empirical fitting method. These results indicate that the analytical theory allows determining the surface energy of a solid quite accurately based on a measurement with a single liquid. This opens the door for simplifying the experimental procedure considerably.

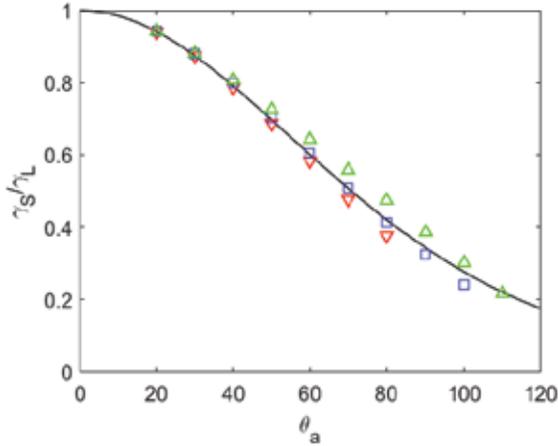


FIGURE 5

Surface energy of the solid scaled by that of the liquid,  $\Gamma_s/\Gamma_L$ , as a function of the advancing contact angle  $\theta_a$ . The curve is the prediction of the theory, Equation (10), and the data [52] are obtained by the empirical Equation of State for three hypothetical values of  $\Gamma_L$ ,  $30 \text{ mJm}^{-2}$  (dots),  $50 \text{ mJm}^{-2}$  (squares) and  $70 \text{ mJm}^{-2}$  (triangles).

## 8 CONCLUSIONS

The analysis of the problems of the prevailing wetting theory and how to solve them makes us to draw the following conclusions. These conclusions should direct future work.

- On a solid, there is no independent applied force that balances the capillary forces on the liquid side of the contact line. The force on a solid is a friction force which balances the applied capillary forces at the prevailing contact angle.
- Most of the faulty intuitions of wetting originate from the inappropriate classical interpretation of Young's equation that three active applied forces are effective at the contact line. Should this be true, even the slightest external force would make the contact line move on an ideal surface. This has led to the wrong belief that the contact line motion is reversible and that the origin of contact angle hysteresis must be found by assuming surface heterogeneities.
- Derivation of Young's equation cannot be appropriately done by the principle of minimizing the global free energy of a system or by variational calculus based on a reversible displacement of the contact line.
- In the local system at the contact line, the equilibrium contact angle is the free generalized coordinate, and adjusts to the minimum of chemical potential a priori. This directly results in Young's equation.
- Motion of a contact line is an irreversible and dissipative process. This explains the origin of the contact angle hysteresis.

- Contact angle hysteresis is a fundamental phenomenon that occurs already on an ideally smooth and homogenous surface.
- The limits of overcoming the pinning, and the dynamic contact angles, can be quantified and modelled theoretically. This theory of contact angle hysteresis can be extended to textured surfaces.
- The new theory can be used to determine the surface energy of solids more easily. Empirical equations, such as the Equation of State, are unnecessary, when the static equilibrium contact angle is used. The static equilibrium contact angle can be derived from the theory based on the measured advancing contact angle.

## 9 ACKNOWLEDGEMENTS

I wish to thank K. Kolari, M. Tikanmäki and K. Kanervo for fruitful discussions. This work was supported by the Academy of Finland, grant 297278.

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