New insights into the capillary retention force and the work of adhesion

Rafael de la Madrid,* Huy Luong,† Jacob Zumwalt
Department of Physics, Lamar University, Beaumont, TX 77710

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Abstract

We calculate the normal capillary retention force that anchors a drop to a solid surface in the direction perpendicular to the surface, and study the relationship between such force and the Young-Dupré work of adhesion. We also calculate the work necessary to create or destroy a patch of solid-liquid interface by moving the triple line on a solid substrate. We argue that when the capillary number is small and a drop is sliding on a surface at constant speed, the lateral retention force is the major source of energy dissipation, whereas viscous dissipation plays a minor role.

Keywords: Wetting, dewetting, adhesion, work of adhesion, lateral retention force, normal retention force.

1 Introduction

The adhesion of droplets to solid surfaces has been studied extensively due to its intrinsic scientific interest and its wide range of important applications, such as self-cleaning, microfluidics, ink-jet printing, mist eliminators, and carbon dioxide capture, to name just a few. Three very important quantities that characterize the adhesion properties of a solid-liquid pair are the lateral retention force $\vec{f}_\parallel$ (which quantifies the opposition to lateral motion of a drop moving on a solid substrate), the normal force of adhesion $\vec{f}_\perp$ (which quantifies the resistance of a drop to be detached from a surface), and the Young-Dupré work of adhesion $w_{\text{adhesion}}$ (which quantifies the energy per unit area necessary to detach a drop from a surface without changing the shape of the drop).

*E-mail: rafael.delamadrid@lamar.edu
†Current address: Sage Automation, Beaumont, TX 77705
Although the lateral retention force has been studied extensively (see Refs. [1–14] and references therein), its normal counterpart $\vec{f}_\perp$ has not received nearly as much attention [14–31], in spite of the fact that it plays an essential role in many situations. A familiar situation is a pendant drop, which must be anchored to the surface by a force that is normal to the surface. In this paper, our first objective is to derive an expression for $\vec{f}_\perp$ using the same kind of arguments used to derive the expression for $\vec{f}_\parallel$. The resulting expression for $\vec{f}_\perp$ turns out to be essentially the same as that of Refs. [14, 28].

The expression for the Young-Dupré work of adhesion has been known for over 150 years [32], and it is part of the standard theory of wetting [33–36]. However, its precise measurement has proved to be elusive. In a recent experiment [26], Tadmor et al. presented a new way to measure $w_{\text{adhesion}}$. That experiment was re-analyzed by Extrand [27]. Our second objective is to use the expression for $\vec{f}_\perp$ to provide a new theoretical description of that experiment. We will show that the normal retention force per unit of triple line is different from the Young-Dupré work of adhesion, and we will compare the (apparent) contact angles predicted by $\vec{f}_\perp$ with those of Refs. [26, 27].

The work of adhesion quantifies the energy needed to detach a drop from a surface when the drop is in thermodynamic equilibrium. However, the energy needed to move the triple line along the surface in dynamical situations where the drop may not be in thermodynamic equilibrium has been rarely discussed [1]. Our third objective is to calculate the work done (i.e., energy dissipated) by the lateral retention force when the triple line is moving on a surface. We will introduce two new quantities, the advancing ($w_a$) and the receding ($w_r$) works of adhesion, which arise from the energy dissipated by $\vec{f}_\parallel$ as the triple line moves on a surface. The parameter $w_a$ ($w_r$) will quantify the work needed to create (destroy) a unit of solid-liquid contact area by expanding (contracting) the triple line. The expressions for $w_a$ and $w_r$ will be derived using purely mechanical arguments (work done by the lateral retention force) and can be applied to dynamical situations where the drop may not be in thermodynamic equilibrium. We will see that, even though $w_a$ and $w_r$ are not thermodynamic equilibrium quantities, their expressions resemble that of $w_{\text{adhesion}}$.

Our fourth objective is to use the expressions for $w_a$ and $w_r$ to re-derive Furmidge’s expression [1] for the sliding work of adhesion, $w_{\text{sliding}}$, and to argue that, when a drop is moving at constant speed and the capillary number is small, viscous dissipation can be neglected and $\vec{f}_\parallel$ is the main source of energy dissipation.

Our overall objective is that the results of this paper contribute to a complete description of the adhesion properties of droplets in terms of forces and energy, in both the parallel and the normal directions to the surface.

The structure of the paper is as follows. In Sec. 2.1 we recall the main arguments used to derive the expression for the lateral retention force. We also recall the expressions for the works of adhesion (Young-Dupré) and cohesion. In Sec. 2.2 we calculate $\vec{f}_\perp$. In Sec. 2.3 we introduce $w_a$ and $w_r$. In Sec. 2.4 we re-derive the expression for
In Sec. 3 we discuss the details of a simple experiment that will be used to test the expressions for $w_a$, $w_r$ and $w_{sliding}$. In Sec. 4.1 we analyze the relationship between $f_{\perp}$ and the Young-Dupré work of adhesion, and provide a new theoretical description of the experiment of Ref. [26]. In Sec. 4.2 we obtain the experimental values of $w_a$, $w_r$, $w_{sliding}$ and $w_{adhesion}$, and we infer from such values that viscous dissipation can be neglected in our solid-liquid system. Finally, Sec. 5 contains our conclusions.

2 Theoretical section

2.1 The lateral retention force, and the Young-Dupré work of adhesion

To better understand how the expressions for $f_{\perp}$, $w_a$ and $w_r$ arise, it is useful to first recall a derivation [2, 13] of the lateral retention force $f_{\parallel}$.

Let us consider a drop on top of a flat surface. Let us denote the liquid-vapor, solid-vapor and solid-liquid surface tensions by $\gamma = \gamma_{lv}$, $\gamma_{sv}$ and $\gamma_{sl}$, respectively. Such surface tensions act on a given infinitesimal section $dl$ of the triple line at point P as shown in Fig. 1.

![Figure 1: Surface tensions and contact angle $\theta$ at a generic point P of the triple line. The infinitesimal section $dl$ (not shown in the figure) is perpendicular to the page at point P.](image)

When the contact angle $\theta$ is the Young, equilibrium angle $\theta_Y$, the net force on the element $dl$ is zero. This balance of forces leads to the Young equation,

$$\gamma \cos \theta_Y + \gamma_{sl} - \gamma_{sv} = 0.$$  \hspace{1cm} (2.1)

When the contact angle $\theta$ at $dl$ is not $\theta_Y$, the forces due to the surface tensions do not cancel each other [15],

$$\gamma \cos \theta + \gamma_{sl} - \gamma_{sv} \neq 0,$$  \hspace{1cm} (2.2)
and therefore there is a non-zero capillary force per unit of length acting at point P in the direction parallel to the surface. If we denote by $\hat{n}_\parallel$ the unit vector that is parallel to the surface, perpendicular to the triple line and pointing outwardly, then such capillary force per unit of length is given by

$$(-\gamma \cos \theta - \gamma_{sl} + \gamma_{sv}) \hat{n}_\parallel.$$  \hspace{1cm} (2.3)

However, if the infinitesimal element $dl$ at point P does not move, there must be a force that cancels that in Eq. (2.3), and therefore has the same magnitude but opposite direction. The force that cancels that in Eq. (2.3) is the lateral retention force per unit of length,

$$\text{retention force per unit of length} = (\gamma \cos \theta + \gamma_{sl} - \gamma_{sv}) \hat{n}_\parallel.$$  \hspace{1cm} (2.4)

where in the last step we have used the Young equation. Hence, the (infinitesimal) lateral retention force on an (infinitesimal) segment $dl$ of triple line is

$$\gamma (\cos \theta - \cos \theta_Y) dl \hat{n}_\parallel.$$  \hspace{1cm} (2.5)

The total retention force on a drop can be calculated by integrating Eq. (2.5) along the triple line. When the triple line has a quasi-rectangular shape, and when the advancing (receding) contact angle is constant along the advancing (receding) edge of the drop, integration of Eq. (2.4) along the triple line yields [2] exactly Furmidge’s expression [1],

$$f_\parallel = \gamma w (\cos \theta_r - \cos \theta_a),$$  \hspace{1cm} (2.6)

where $w$ is the width of the drop, and $\theta_a (\theta_r)$ is the angle that the liquid-air interface makes with the solid at the advancing (receding) edge of the drop.

In principle, the derivation of Eq. (2.5) applies when the drop is not moving. When the drop is moving, an additional source of opposition to lateral motion arises from viscous dissipation [15]. However, even though the drop is moving, there is still an imbalance of forces [15], and we expect Eq. (2.5) to hold, although now $\theta$ is a dynamical contact angle [15]. In fact, if the capillary force of Eq. (2.5) suddenly disappeared when the drop starts to move, right after the onset of the motion, when the speed is very low, the viscous force would be very small, and the drop would first accelerate dramatically and later slow down when viscous dissipation sets in. However, it is well known that when a drop starts to move due to a slowly increasing lateral force, the drop speeds up slowly, and therefore there must be a retention force at low speeds that is not due to viscous dissipation. Hence, when the drop is in motion, we will assume that Eq. (2.5) accounts for the capillary contribution to the lateral retention force. In addition, in situations where the capillary number is low, we expect that viscous dissipation can be neglected and that the (capillary) retention force of Eq. (2.5) provides the main opposition to the motion of the drop.
The work per unit area necessary to detach a drop from a solid substrate without changing the shape of the drop is given by \[33\] \[36\]

\[ w_{\text{adhesion}} = \frac{W_{\text{adhesion}}}{A} = \gamma + \gamma_{sv} - \gamma_{sl}, \] (2.7)

where \(W_{\text{adhesion}}\) is the total work of adhesion, \(A\) is the area of the solid-liquid interface, and \(w_{\text{adhesion}}\) is the work of adhesion per unit area \[37\]. Thanks to the Young equation, Eq. (2.7) can be written as the Young-Duprè equation,

\[ w_{\text{adhesion}} = \frac{W_{\text{adhesion}}}{A} = \gamma (1 + \cos \theta_Y). \] (2.8)

When we separate a liquid from itself, Eq. (2.7) must be replaced by the work of cohesion \[33\],

\[ w_{\text{cohesion}} = \frac{W_{\text{cohesion}}}{A} = 2\gamma, \] (2.9)

where \(A\) is the area of the newly created liquid-vapor interface.

### 2.2 The normal retention force

In the previous section, we used classic arguments \[2\] \[15\] to derive the well-known expression of the lateral retention force. We are now going to use the same arguments \[15\] to calculate the normal retention force.

Let us assume that there is an external force in the vertical direction pulling the drop away from the surface. Even if there was no gravity, the drop would not be detached from the surface unless the pulling force is strong enough, because there is a normal force of adhesion that pins the drop to the surface. From Fig. 1, we can see that \(\gamma \sin \theta\) is the only component of surface tension acting in the normal direction. Because the infinitesimal element \(dl\) does not move in the normal direction, there must be a force pointing in the opposite direction and pinning the triple line to the surface \[15\]. Hence, the normal force of capillary adhesion per unit length should be

\[ \frac{d\vec{f}_\perp}{dl} = \gamma \sin \theta \hat{n}_\perp, \] (2.10)

where \(\hat{n}_\perp\) is a unit vector perpendicular to the surface and pointing away from the drop. To obtain the total retention force that pins the drop in the normal direction, we just need to integrate Eq. (2.10) along the triple line,

\[ \vec{f}_\perp = \oint \gamma \sin \theta \, dl \, \hat{n}_\perp. \] (2.11)

For the particular case that the contact angle remains constant along the triple line and that the triple line is a circumference of radius \(r\), Eq. (2.11) yields

\[ \vec{f}_\perp = 2\pi r \gamma \sin \theta \hat{n}_\perp. \] (2.12)
Not surprisingly, Eq. (2.12) has a resemblance with Tate’s law [34].

It is important to realize that the magnitude of the actual external force $f_d$ necessary to detach a drop from a surface is in general different from $f_\perp$. For example, the force necessary to detach a sessile drop is different than for a pendant drop, because weight opposes (helps) the detachment of a sessile (pendant) drop. In addition, even in the absence of gravity, the Laplace pressure [14,28,31] produces a force in the normal direction that needs to be taken into account. However, even though $f_\perp$ is different from $f_d$, in this paper we will refer to $f_\perp$ as the normal force of adhesion for two reasons. First, $f_\perp$ is the only force that is exerted by the solid on the triple line and that tries to anchor the drop on the solid in the normal direction. The force produced by the pressure at the solid-liquid contact area points away from the surface [14,28], and therefore it seems natural to take $f_\perp$ to be the force that truly anchors a drop to a solid surface in the direction perpendicular to the surface. Second, the conceptual comparison of Eqs. (2.11) and (2.12) with the approaches of Refs. [26,27] and with the Young-Dupré work of adhesion must be done using $f_\perp$, because in Refs. [26,27] the force produced by pressure was not taken into account.

To the best of our knowledge, Eq. (2.11) has been studied (with a different notation and for different situations) only in Refs. [14,28,31]. Our approach is essentially the same as that of Refs. [14,28,31], the only real difference being that for us the normal force of adhesion does not take the (Laplace) pressure into account, whereas in Refs. [28,31] the normal force of adhesion is implicitly taken to be the same as the detachment force, which does include the contribution of the force produced by pressure.

Historically, the role played by the normal component of surface tension, $\gamma \sin \theta$, has been either neglected or just briefly mentioned [15]. Some authors [16] have even dismissed it. For soft materials, however, it has been realized [17–25] that $\gamma \sin \theta$ deforms the solid and produces a “wetting ridge” whose height is of the order of $\gamma / G$, where $G$ is the shear modulus of the solid. Based on the work of Shanahan and co-workers [18–25], Tadmor [7] proposed a new formula for the lateral retention force $f_\parallel$. The main difference between our approach and that of Tadmor is that for us the normal component of $\gamma$, $\gamma \sin \theta$, affects the normal retention force, whereas for Tadmor it affects the lateral retention force. The point of view of the present paper is the same as that of Ref. [15]: The normal component of surface tension is balanced out by a reaction force exerted by the solid at the triple line. If the solid is hard, there is no significant wetting ridge. When it is soft (e.g., rubber or a coat of paint), $\gamma \sin \theta$ distorts the solid at the triple line and the results of Refs. [17–25] need to be used.

## 2.3 The lateral advancing and receding works of adhesion

Let us assume for simplicity that the only external force acting on the drop of Fig. 1 is a force normal to the surface that is pulling the drop away from the surface. As the drop is deformed, the contact angle changes from its initial equilibrium angle. When
the contact angle becomes the receding angle $\theta_r$, the triple line starts receding. Since $f_\parallel$ is the force that needs to be overcome to move the triple line, the work necessary to move a segment of triple line $dl$ a distance $dr$ (see Fig. 2) is given by [38]

$$dW_r = f_\parallel dr = \gamma (\cos \theta_r - \cos \theta_Y) dl dr.$$ \hspace{1cm} (2.13)

Figure 2: Contraction of the triple line by an amount $dr$. The shape of the triple line is arbitrary.

Hence, the work per unit area necessary to destroy an amount of contact area $dA = dr dl$ is

$$w_r = \frac{dW_r}{dA} = \gamma (\cos \theta_r - \cos \theta_Y).$$ \hspace{1cm} (2.14)

To calculate the total work necessary to destroy an area $A$ as the triple line recedes, we need to integrate Eq. (2.14) over the whole triple line,

$$W_r = \gamma \int_A (\cos \theta_r - \cos \theta_Y) dA.$$ \hspace{1cm} (2.15)

If the external force acting on the drop pushes the drop towards the surface and the triple line expands, analogous equations hold by replacing the receding angle with the advancing one,

$$w_a = \frac{dW_a}{dA} = \gamma (\cos \theta_Y - \cos \theta_a),$$ \hspace{1cm} (2.16)

$$W_a = \gamma \int_A (\cos \theta_Y - \cos \theta_a) dA.$$ \hspace{1cm} (2.17)

Several comments are in order. First, similar to the Young-Dupré work of adhesion, Eqs. (2.14) and (2.16) show that the energy per unit area needed to create or destroy a patch of solid-liquid interface is a constant that depends only on surface tension.
and contact angles. Second, the work $w_a$ needed to create a solid-liquid patch by expanding the triple line is the same as the work $w_r$ needed to destroy the same patch by contracting the triple line only when the following relationship holds:
\[
\cos \theta_Y = \frac{\cos \theta_a + \cos \theta_r}{2}.
\] (2.18)

Third, similar to the Young-Duprée work of adhesion [36], the advancing and receding works of adhesion do not take into account the energy needed to change the shape of the drop. Only the energy needed to create or destroy an area of solid-liquid interface is taken into account. Fourth, conceptually, the main difference between the work of adhesion and the lateral works of adhesion is that $w_{\text{adhesion}}$ is a thermodynamic quantity that measures the energy needed to detach a drop from a surface, whereas $w_a$ and $w_r$ quantify the energy dissipated by $f_\parallel$ as the triple line moves on a surface. Fifth, in principle, we can use Eqs. (2.15) and (2.17) to calculate the total lateral work of adhesion needed to create or destroy a solid-liquid contact area $A$. In practice, however, we need to know how the contact angle changes along the triple line as the contact area expands or contracts. For some special cases, we can calculate such total lateral work exactly. For example, when the contact angle $\theta_r$ ($\theta_a$) remains constant as the solid-liquid contact area contracts (expands), the total work to destroy (create) an area $A$ is
\[
W_r = \gamma(\cos \theta_r - \cos \theta_Y)A,
\] (2.19)
\[
W_a = \gamma(\cos \theta_Y - \cos \theta_a)A.
\] (2.20)

It may be surprising that Eqs. (2.19) and (2.20) mix up thermodynamic, equilibrium quantities (such as $\theta_Y$) with metastable, non-equilibrium ones (such as $\theta_a$ and $\theta_r$). The apparent inconsistency is resolved by realizing that the way we calculated $W_a$ and $W_r$ uses a purely mechanical approach (work done by the lateral retention force), without invoking equilibrium thermodynamics. In addition, one can always use the Young equation to express $\cos \theta_Y$ in terms of surface tensions and therefore make $W_a$ and $W_r$ depend explicitly on non-equilibrium quantities.

### 2.4 The lateral work of sliding

When a drop slides on a surface at a low, constant velocity, the solid-liquid contact area has a quasi-rectangular shape [12], and as an amount of solid-liquid contact area is destroyed, the same amount is created. Hence, the work per unit area necessary to slide the drop is
\[
W_{\text{sliding}} = W_r + w_a = \gamma(\cos \theta_r - \cos \theta_a).
\] (2.21)

Equation (2.21) was first introduced by Furmidge [13]. However, Furmidge assumed an expression for the advancing and receding works of adhesion based on the Young-Dupré work of adhesion,
\[
w_a = -\gamma(1 + \cos \theta_a), \quad [\text{Ref. 1}],
\] (2.22)
\[
w_r = \gamma(1 + \cos \theta_r), \quad [\text{Ref. 1}].
\] (2.23)
Although the sum of Eqs. (2.22) and (2.23) does yield the same result as Eq. (2.21), it is problematic to assume that the Young-Dupré equation can be applied freely to non-equilibrium situations.

The quantities $w_a$, $w_r$ and $w_{sliding}$ do not take into account the energy lost due to viscous dissipation. However, in situations where the capillary number is low, it would not be surprising that viscous dissipation plays a minor role compared to the energy dissipated by the lateral retention force.

### 3 Experimental section

Our experimental apparatus consists of a metallic box [13] that sits on top of a platform, see Fig. 3.

![Experimental apparatus](image)

Figure 3: Experimental apparatus: 1-platform; 2-screw; 3-inclinometer; 4-top camera; 5-side camera; 6-PMMA sheet with drop; 7-remote-controlled LED light. Inside the box (not shown in the picture) there is an LED panel that provides the necessary illumination for the top camera.

Using a screw, the box can be inclined at any desired angle. Each turn of the screw changes the inclination of the box by around 0.6°. An inclinometer is attached to the box to measure the tilt angle $\alpha$. The box has two cameras placed on top and on the side, which provide top and side views of the drops. On the door of the metallic box, a poly methyl methacrylate (PMMA) sheet (Optix, by Plaskolite) can be mounted such that, when a (distilled) water drop is placed on the sheet and the door is closed, the cameras have side and top views of the drop. Illumination for the side camera is provided by a remote-controlled LED. Lighting for the top camera is provided by an LED panel and an optical gradient [40]. The remote-controlled LED is used to set a common starting time in the videos of the cameras. To remove any remnants
of their protective films, the PMMA sheets were initially washed with hot water and soap. Afterward, before each run, the PMMA sheets were cleaned with 70% isopropyl alcohol and paper tissue, and dried with lamplight \cite{13,41}. To place the (distilled) water droplets on the PMMA sheet, we used a syringe from Hamilton. The volume of the water drops was 60 \(\mu\)L.

For each run, we placed a drop on the PMMA sheet, closed the door, and used the screw to tilt the box. After the drop started to slide down the surface, the inclination was slightly lowered to make the drops move with a slow, constant velocity. When this was achieved, the contact area of the drop had a quasi-rectangular shape, see Fig. 4.

![Figure 4: Top (a) and side (b) views of a drop moving with nearly constant velocity.](image)

We used the videos of the side camera and custom-made software to determine the position and speed of the receding edge of the drop. When the speed was about constant and the contact area was quasi-rectangular, we used ImageJ \cite{42} to obtain the contact angles \(\theta_a\) and \(\theta_r\) from the videos of the side-view camera, and the width and the contact area from the videos of the top-view camera. Before the box was tilted, we measured the equilibrium angle \(\theta_Y\). In both theory and experiment, the angles are the apparent, macroscopic angles.

Our experimental apparatus is not able to detach drops, and therefore we cannot directly measure \(\vec{f}_\perp\). However, using the so-called Centrifugal Adhesion Balance (CAB), Tadmor et al. \cite{26} were able to detach drops from surfaces. The CAB has a centrifugal arm that rotates in a horizontal plane. At one end of the arm, there is a chamber where a solid substrate can be placed. This chamber can rotate around an axis that is orthogonal to the centrifugal rotation. As the centrifugal rotation proceeded and the centrifugal force increased, the chamber was tilted in such a way that the external lateral force acting on the drop was always zero, whereas the external normal force increased. Thus, essentially, the CAB provided an external force that was ever increasing and normal to the surface. When the normal force was strong enough, the drop was detached from the surface, and the work of adhesion was calculated. We will analyze the experiment of Ref. \cite{26} in the light of Eq. (2.12).
4 Results and discussion

4.1 The normal retention force

In Ref. [26], the value of \( f_{\perp} \) was used to obtain the Young-Dupré work of adhesion as the ratio of the pulling force to the length of the (circumferential) triple line,

\[
\frac{f_{\perp}}{2\pi r} = w_{\text{adhesion}} = \gamma (1 + \cos \theta_Y), \quad \text{[Ref. 26].} \tag{4.24}
\]

In Ref. [27], a different approach to the problem leads to a different expression for the work of adhesion,

\[
\frac{f_{\perp}}{2\pi r} = w_{\theta} = \pm \gamma \cos \theta_c, \quad \text{[Ref. 27],} \tag{4.25}
\]

where \( \theta_c \) is the critical angle at which the drop is detached from the surface, and where the + (−) sign corresponds to the case \( \theta_c < 90^\circ \) (\( \theta_c > 90^\circ \)). By contrast, when we apply Eq. (2.12) to the same situation, and assuming that we neglect the force due to pressure, we obtain

\[
\frac{f_{\perp}}{2\pi r} = \gamma \sin \theta_c, \quad \text{[this work].} \tag{4.26}
\]

Clearly, Eq. (4.24), (4.25) and (4.26) assign different values and meanings to one and the same quantity, \( f_{\perp}/2\pi r \).

The experiment of Ref. [26] measured the values of the detachment force \( f_d \) and radius \( r \) of water drops on three different surfaces (hydrophobic silicon, microporous PTFE, and hydrophilic glass). The values were compiled by Extrand in Ref. [27], and are listed in Table 1 [43]. Using the experimental value of \( f_d/2\pi r \), and assuming that the pressure force can be neglected (i.e., assuming that \( f_d = f_{\perp} \)), we can use Eqs. (4.24), (4.25) and (4.26) to obtain the corresponding contact angles, see Table 1.

In Table 1 we also list the measured, apparent, macroscopic contact angles \( \theta_{\text{measured}} \).

| Solid surface         | \( \frac{f_{\perp}}{2\pi r} \) (mJ/m²) | \( \theta_Y^{(o)} \) | \( \theta_c^{(o)} \) | \( \theta_{\text{measured}}^{(o)} \) |
|-----------------------|----------------------------------------|-----------------------|-----------------------|-------------------------------------|
| Hydrophobic silicon   | 50                                     | 107                   | 46                    | 44                                  | 81                                  |
| Microporous PTFE      | 26                                     | 130                   | 111                   | 159                                 | 123 *                               |
| Hydrophilic glass     | 72                                     | 90                    | 0                     | N/A                                 | 20                                  |

* This value is a rough estimate based on Fig. 9 of Ref. [26].

For hydrophobic silicon, our critical contact angle \( (44^\circ) \) is very close to that of Extrand \( (46^\circ) \). The value of \( \theta_Y \) that comes out of Eq. (4.24) is, however, much larger...
(107°). All of those angles are far from the apparent, measured angle (81°). For mPTFE, all the contact angles are again far from the (rough estimate of the) apparent contact angle, and ours is the farthest of all. The most dramatic differences occur for hydrophilic glass. When a drop of water was detached from a glass surface, a nanometric layer of water was left behind, and Tadmor et al. concluded that they were “in practice separating water from water” [26]. As is well known [33], when a liquid is separated from itself, the relevant work is the work of cohesion, which according to Eq. (2.9) is \( w_{\text{cohesion}} = 2\gamma \). However, the experimental value of Ref. [26] is 71.3 mJ/m\(^2\) \( \approx \gamma \). To match this value of \( w_{\text{adhesion}} \), a Young contact angle of 90° is needed, which seems too high for water on glass [27], even when the increase of the contact angles due to the large value of the effective acceleration of gravity is taken into account. Extrand’s approach, Eq. (4.25), yields a critical angle of 0°. Our approach uses the work of cohesion, and therefore does not yield any contact angle.

It is clear from Table 1 that the predictions of all three approaches do not match the apparent, measured angles. Tadmor et al. [26] have argued that the mismatch occurs because the true nanoscopic Young contact angle is different from the macroscopic, apparent contact angle. In our approach, however, it is possible to account for the apparent measured angles by including the effect of the force due to pressure. As mentioned in Sec. 2.2, Eq. (4.26) does not include the effect of the normal reaction force \( f_p \) on the liquid-solid contact area that is due to the pressure of the drop. In general, calculating the force due to pressure is difficult, because it involves the Laplace pressure. However, for drops that are detached without a neck formation (like mPTFE), Farhan and Tafreshi [28] were able to estimate the pressure force to be \( f_p = \gamma \pi r \), where \( r \) is the radius of the (circular) contact area. Because the pressure force points away from the surface, it combines with the detachment force \( f_d \) to produce the normal force of adhesion, \( f_\perp = f_d + f_p \). Hence,

\[
\gamma \sin \theta_c = \frac{f_\perp}{2\pi r} = \frac{f_d}{2\pi r} + \frac{\gamma}{2},
\]

which yields [28] a value of \( \theta_c = 121° \), very close to the apparent contact angle (123°) of Table 1. If we took the effect of \( f_p \) into account, for mPTFE Tadmor’s approach would yield a Young angle of 98°, and Extrand’s approach would yield a contact angle of 149°.

As can be seen in the movie of the Supporting Information of Ref. [26], the rotation of the CAB produces wild vibrations on the drops. Hence, the values of the contact angles and the detachment force are subject to a systematic error, and the comparison of the contact angles of Table 1 cannot lead to firm conclusions as to which approach best describes the detachment of a drop. Without systematic-proof data, it is more useful to compare the conceptual foundations of the three approaches.

Conceptually, the main differences between Tadmor’s approach and ours are the following: First, in Tadmor’s approach, thermodynamic equilibrium quantities such as \( w_{\text{adhesion}} \) and \( \theta_Y \) are measured in a seemingly non-equilibrium situation, whereas we use
a completely mechanical approach without any recourse to equilibrium thermodynamics. Second, the data of Ref. [26] has a dependence on the receding, critical angle \( \theta_c \), and therefore needs to be described by a formula that involves such angle instead of \( \theta_Y \). Third, when water is separated from water, we use the work of cohesion rather than the Young-Dupré work of adhesion. Fourth, Eq. (4.24) is obtained by a loose analogy with Tate’s law, whereas we have provided a thorough derivation of Eq. (4.26).

Conceptually, the main differences between Extrand’s approach and ours are the following: First, Extrand assumes that \( f_{\perp} \) is equal to a force \( f_s \) that is parallel to the surface and that is given in terms of the component of surface tension that is parallel to the surface, whereas in our approach \( f_{\perp} \) is obtained in terms of the component of surface tension that is perpendicular to the surface. Second, as long as we assume that the contact angle \( \theta_c \) remains constant along the circumferential triple line (as Extrand seems to assume), the force \( f_s \) parallel to the surface that would arise from integrating Eq. (2.5) along the triple line would be zero, whereas Extrand estimated that \( f_{\perp} = f_s = 2\pi r \gamma \cos \theta_c \).

Conceptually, our approach is very much the same as that of Farhan and Tafreshi [28], the main difference being simply a matter of definition: For us the normal retention force is not the same as the actual detachment force, our normal retention force is the sum of the detachment force and the force due to pressure.

Because the experimental values of Table 1 suffer from a known systematic (vibration), the only way to elucidate the proper way to describe the normal retention force is by performing new experiments that avoid the vibrations of the CAB. Such experiments can be easily performed using the same technique of Refs. [12,28–30], but substituting the fibrous surface by a flat solid surface. A ferrofluid droplet can be detached from a flat surface, and all the relevant experimental quantities can be easily measured.

4.2 The advancing and receding works of adhesion

Table 2 lists our experimental data for drops sliding down a PMMA surface.

| Angles     | Speed | Area   | Width |
|------------|-------|--------|-------|
| \( \alpha \) \( ^{(o)} \) | \( \theta_s \) \( ^{(o)} \) | \( \theta_r \) \( ^{(o)} \) | \( \theta_Y \) \( ^{(o)} \) | \( v \) (mm/s) | \( A \) (mm\(^2\)) | \( w \) (mm) |
| 24.1 ± 0.2 | 72.8 ± 0.5 | 39.4 ± 0.4 | 60.7 ± 0.4 | 0.79 ± 0.07 | 54.8 ± 0.2 | 7.1 ± 0.2 |

The Young, equilibrium angle was measured when the PMMA surface was placed horizontally, whereas the rest of the quantities were measured when the surface was
tilted at an angle $\alpha$ and the drop was moving at a nearly constant speed with a quasi-
rectangular triple line. In our experiments, we used 21 different PMMA sheets, and
did 3 runs with each sheet, for a total of 63 runs.

By plugging the data of Table 2 into Eqs. (2.8), (2.14), (2.16) and (2.21), we obtain
the results of Table 3.

Table 3: Experimental results.

| Works of adhesion (mJ/m$^2$) | $w_a$  | $w_r$  | $w_{\text{sliding}}$ | $w_{\text{adhesion}}$ |
|-------------------------------|--------|--------|-----------------------|-----------------------|
|                               | 13.9 ± 0.7 | 20.4 ± 0.5 | 34.3 ± 0.9 | 107.2 ± 0.4 |

We can draw several conclusions from the results of Table 3. First, the work of sliding
is somewhat larger than the advancing and receding works of adhesion. Second, the
Young-Dupré work of adhesion is significantly larger than any of the lateral works
of adhesion. Third, the result that $w_a < w_{\text{sliding}} < w_{\text{adhesion}}$ is consistent with the
experimental fact that the force necessary to spread a drop on a surface is smaller than
the force necessary to slide the drop on the surface, which in turn is much smaller than
the force needed to detach the drop from the surface [9][11][26]. Fourth, the advancing
and receding works of adhesion are different. Although it is possible that $w_a$ and $w_r$
are truly different, it is also possible that their actual values are the same. The reason
is the following: It is believed that the apparent, equilibrium angles of sessile drops
often lie in between the true Young contact angle and the advancing contact angle, due
to the way the drop is deposited on the surface. Because overestimating $\theta_Y$ leads to
overestimating $w_r$ and underestimating $w_a$, the difference between $w_a$ and $w_r$ may be
simply due to not having measured the true Young contact angle. If $w_a$ and $w_r$ were
actually equal, Eq. (2.18) would provide the true Young equilibrium angle. For our
system, the Young angle predicted by Eq. (2.18) is 57.7°, which is smaller than, but
very close to, the apparent Young angle we measured (60.7°). Hence, although it is
a speculative proposal, it may well be that the true Young contact angle is given by
Eq. (2.18), and that $w_a = w_r$.

The capillary number, defined as $Ca = \frac{\eta v}{\gamma}$, where $\eta$ is the viscosity of the liquid and
$v$ its speed, measures the importance of viscous forces relative to capillary forces. In
our experiment, $Ca \sim 10^{-5}$, which suggests that in our experiment the dissipation by
the lateral retention force (quantified by the sliding work of adhesion) dominates over
viscous dissipation.

To calculate how much gravitational potential energy is dissipated by $f_{\parallel}$, we are
going to compare the gravitational potential energy of the drop with the energy dissipated by $f_{\parallel}$, or, equivalently, we are going to compare the work per unit area done by the weight with the sliding work of adhesion. To calculate the work done by the weight, let us consider a drop of quasi-rectangular contact area $A$, length $L$, and width $w$ that
is sliding down the incline with constant velocity. When the drop travels a distance $L$, its center of mass drops a height $h = L \sin(\alpha)$, and therefore the work done by the weight is

$$W_g = mgh = mgL \sin(\alpha). \quad (4.28)$$

Since $A = Lw$, the work per unit area done by the weight is

$$\frac{W_g}{A} = \frac{mgL \sin(\alpha)}{A} = \frac{mg \sin(\alpha)}{w}. \quad (4.29)$$

By plugging the values of Table 2 into Eq. (4.29), we obtain the following experimental value:

$$\frac{W_g}{A} = (34 \pm 1) \text{ mJ/m}^2, \quad (4.30)$$

which agrees within 1% with the value of $w_{\text{sliding}}$ in Table 3. Hence, viscous dissipation can be neglected in our experiment, since all the gravitational potential energy is dissipated by the lateral retention force.

Theoretically, the condition that $\frac{W_g}{A}$ equals $w_{\text{adhesion}}$ is equivalent to the condition that the lateral retention force equals the component of the weight parallel to the surface,

$$f_\parallel = mg \sin(\alpha). \quad (4.31)$$

Hence, Eq. (4.31) is another way to check that viscous dissipation can be neglected. By plugging the values of Table 2 into Eqs. (4.31) and (2.6), we obtain the following experimental agreement:

$$f_\parallel = \gamma w (\cos \theta_r - \cos \theta_a) = (244 \pm 8) \mu \text{N}, \quad (4.32)$$

$$mg \sin(\alpha) = (240 \pm 2) \mu \text{N}. \quad (4.33)$$

Hence, both energy- and force-wise, viscous dissipation plays no significant role in our water-PMMA system.

Since the gravitational potential energy is dissipated by the lateral retention force, viscoelastic dissipation [17–25] can also be neglected in our system. This is not surprising, since the height of the “wetting ridge” of the water-PMMA system is of the order of $\gamma/G \sim 42 \text{ pm}$, certainly negligible on a macroscopic scale.

Although we have only studied water droplets sliding on a PMMA surface, we would like to note that Furmidge’s experimental values [1] are consistent with Eq. (4.31), and therefore viscous dissipation can also be neglected for the solid-liquid pairs considered by Furmidge [1].

From the discussion above, it should be clear that our claim that the gravitational potential energy is dissipated (mostly) by the lateral retention force rests on the assumption that Eq. (2.6) provides the exact lateral retention force. Such assumption holds only when the advancing (receding) contact angle is constant along the advancing (receding) edge of the drop. However, in Ref. [6] it has been shown that neglecting the variation of the contact angle along the triple line may lead to an erroneous value of
the lateral retention force. Hence, to check that Eq. (2.6) provides a very good approximation of the actual lateral retention force, one needs a measurement of the variation of the contact angle along the triple line. Although our experimental apparatus is not able to measure such variation, the so-called IBAFA methodology of Ref. [6] could measure it, thereby characterizing how accurately Eq. (2.6) describes $f_\parallel$ and how much gravitational potential energy is dissipated by $f_\parallel$.

We would like to note that the typical size of a 60 $\mu$L drop (around 7 mm) is larger than the capillary length of water (around 2.7 mm), and therefore in our experiment gravity dominates over surface tension. This makes 60 $\mu$L water drops sliding on an incline have a quasi-rectangular shape, a situation where we expect Furmidge’s expression for the lateral retention force to be accurate. However, small drops whose characteristic length is less than the capillary length will have a more circular-like triple line, Furmidge’s expression may not be so accurate, and viscous dissipation may be more important for them than for larger drops.

5 Conclusions

We have calculated the normal capillary retention force $\vec{f}_\perp$ on a drop that is in contact with a solid surface. We have seen that, essentially, $\vec{f}_\perp$ is determined by the component of surface tension that is perpendicular to the solid substrate. We have used the expression for $\vec{f}_\perp$ to provide a new theoretical description of a recent experiment on the work of adhesion [26,27], and concluded that the normal retention force per unit length of triple line is different from the Young-Dupré work of adhesion. We have also compared the conceptual foundations of $\vec{f}_\perp$ with the approaches of Refs. [26,27]. However, because of the wild vibrations of the CAB [26], further experimental work is needed to elucidate which approach is more appropriate to describe the detachment of a drop from a surface. We have proposed that separating ferrofluid droplets from a flat surface using the experimental apparatus of Refs. [12,28–30] can provide the necessary data to elucidate the proper way to describe the normal force of adhesion.

By calculating the work done by the lateral retention force, we have obtained the energy needed to contract (expand) the triple line on a surface, and have identified the resulting energy with the advancing (receding) work of adhesion $w_a$ ($w_r$). We have used the expressions for $w_a$ and $w_r$ to re-derive [1] the expression for the sliding work of adhesion, $w_{\text{sliding}}$.

We have seen that the main similarity between the Young-Dupré and the lateral works of adhesion is that all of them represent work per unit area that is equal to a constant that depends only on surface tension and contact angles. Another similarity is that those works do not quantify any change in the shape of the drop that may occur, or the energy needed to create or destroy the concomitant liquid-vapor contact area. The main difference between them is that whereas the Young-Dupré work of adhesion quantifies the energy needed to create/destroy the solid-liquid contact area
by attaching/detaching a drop to/from a surface, the lateral works of adhesion quantify the energy necessary to create/destroy the solid-liquid contact area by moving the triple line along the surface. Conceptually, the main difference is that the Young-Dupré work of adhesion is a thermodynamic equilibrium quantity, whereas the lateral works of adhesion are based on apparent angles and describe dynamical, non-equilibrium situations in which the triple line is moving on the surface.

We have argued that when the capillary number is low and the drop is moving at constant speed, viscous dissipation can be neglected compared to the energy dissipated by the lateral retention force. Because neglecting viscous dissipation in our system is equivalent to assuming that Furmidge’s expression for the lateral retention force is exactly true, to know how much gravitational potential energy is truly dissipated by $f_{\parallel}$, we need to know how truly Furmidge’s expression describes $f_{\parallel}$. We have proposed that an experiment similar to that of Ref. [6] should be able to determine how much gravitational potential energy is truly dissipated by the lateral retention force.

Our results are valid for flat surfaces. When the surface is not flat, or if we considered a fiber [12][28–30], the general principles are the same, although the integrations needed to calculate the forces are more complicated [12, 28–30].

Finally, we would like to stress that both $f_{\parallel}$ and $f_{\perp}$ have a capillary (surface tension) origin. Hence, when other non-capillary forces (e.g., viscous and viscoelastic forces) cannot be neglected, our results would need to be modified.

CRediT authorship contribution statement

Rafael de la Madrid: Conceptualization, data acquisition, writing-review & editing.
Huy Luong: Design and construction of experimental apparatus.
Jacob Zumwalt: Data analysis.

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Throughout the paper, we will use upper case $W$ to denote total work, and lower case $w$ to denote work per unit of area.

To simplify the derivation, we are going to assume that the contact angles are smaller than 90°. When some of (or all) the contact angles are greater than 90°, we need to change the signs in the final formulas appropriately to make the works of adhesion positive, because it takes energy to move the triple line.

It should be noted that Furmidge \cite{Furmidge1995} did not explicitly use the nomenclature of advancing, receding and sliding works of adhesion.

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The values listed by Extrand \cite{Extrand2000} are slightly different from the experimental values listed in Ref. \cite{Wenzel1928}. However, to keep the discussion simple, we will ignore such difference because it does not affect our conclusions.

Semih Gulec, private discussions.