

Solid-Liquid Work of Adhesion

S. Gulec^{*,1}, R. Tadmor^{*,#}, R. Das^{*}, J. Liu^{*}, H. N'guessan^{*}, M. Shah^{*}, P. Wasnik^{*}, S. B. Yadav^{*}

^{*}Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont TX 77710
¹sgulec@lamar.edu

[#]Department of Mechanical Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel,
 tadmorr@bgu.ac.il

ABSTRACT

We establish a tool for direct measurements of the work needed to separate a liquid from a solid. This method mimics a drop that is subjected to a gravitational force that is slowly increasing until the solid–liquid contact area starts to shrink spontaneously. The work of separation is then calculated in analogy to Tate’s law. The values obtained for the work of separation are independent of drop size and are in agreement with Dupré’s theory, showing that they are equal to the work of adhesion.

Keywords: wetting, adhesion, work of adhesion, CAB

1 INTRODUCTION

Surface tension was established as a measurable property in the nineteenth century. In 1863 Wilhelmy introduced measurement of surface tension via Wilhelmy plate method [1]; in 1864, Tate [2] laid the foundation for measuring surface tension from a falling drop weight; and in 1869, Dupré constituted solid–liquid work of adhesion via contact angle measurements. These three methods are still extensively used, with the work of adhesion being restricted to an estimation via the Young–Dupré equation [3–6]. The contact angle values needed in the Young–Dupré equation are obscured by contact angle hysteresis, and by an unknown difference between macroscopic and nanoscopic contact angle values. Thus, many papers use it qualitatively [7–10].

In our study, we allow a controlled gradual increase of a force pulling the drop, and then calculate the work of separation in analogy to Tate’s law [2].

Tate’s law for the drop weight method [5] determines the surface tension, γ , and considers the entire weight of the liquid under the tube. Similarly, we will also consider the entire weight of the drop under the surface.

Here we consider a system of a drop on a flat surface for which the detachment starts from the solid–liquid interface. We increase the weight by increasing the force field and look for a critical depinning beyond which, no pinning can stop the reduction in drop width.

To increase the drop’s weight we use modified Centrifugal Adhesion Balance (CAB) [11,12].

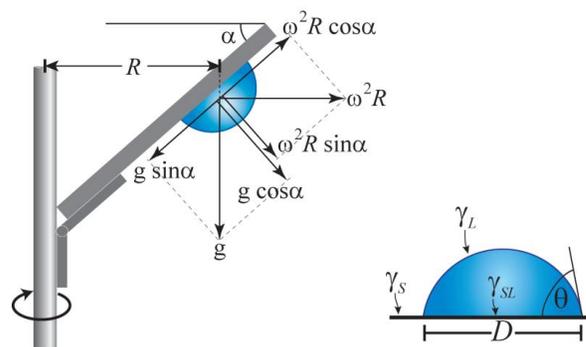


Figure 1: Left: Schematics of CAB alignment for total zero lateral force ($\omega^2 R \cos \alpha = g \sin \alpha$). At this alignment the drop can only move (fly) normal to the surface. Right: Some drop parameters used in this study.

2 THEORY

The CAB, shown schematically in figure 1, combines gravitational and centrifugal forces to manipulate normal and lateral forces according to eq 1 and eq 2 [12]:

$$f_{\parallel} = m(\omega^2 R \cos \alpha - g \sin \alpha) \quad (1)$$

$$f_{\perp} = m(\omega^2 R \sin \alpha + g \cos \alpha) \quad (2)$$

where f_{\perp} and f_{\parallel} are the normal and lateral force acting on the drop, ω is the CAB angular velocity, R is the drop’s distance from the CAB’s center of rotation, α is the tilt angle with respect to the horizon, and m is the drop’s mass.

For our purpose, it is required to change the normal force when the centrifugal and gravitational components cancel each other in the lateral direction but add up in the normal direction. Such an alignment, seen in figure 1, shows that $f_{\parallel} = 0$ when

$$\tan \alpha = \frac{\omega^2 R}{g} \quad (3)$$

This setup follows the Dupré gedanken experiment [4] according to which, the solid-liquid work of adhesion, W_{SL} , is given by:

$$W_{SL} = \gamma_s + \gamma_L - \gamma_{SL} \quad (4)$$

where γ_s , γ_L and γ_{SL} are the solid-liquid, liquid-vapor, and solid-vapor interfacial energies respectively.

The Dupré equation (Eq. 4) combined with the Young-Laplace equation (Eq. 5),

$$\cos\theta = \frac{\gamma_s - \gamma_{SL}}{\gamma_L} \quad (5)$$

results in eq. (6), where θ is the contact angle that the liquid makes with the surface:

$$W_{SL} = \gamma_L(1 + \cos\theta) \quad (6)$$

Eq. (6), which was derived by Dupré [3], is often called the Young-Dupré equation. It relates the work of adhesion to the equilibrium contact angle.

In accordance with the falling drop weight technique, the work of separation per area equals the pull off (separation) force per triple line circumference. In analogy to Tate law for measuring surface tension, the work of separation per area equals the pull off (adhesion) force per triple line circumference [5], i.e.,

$$W_{SL} = \frac{F_D}{\pi D_P} \quad (7)$$

where F_D is the pull-off force, or the Dupré force and D_P is the pull off diameter of the triple line: D represents the drop's diameter (see fig. 1(B)), and the index P stands for pull off.

Equation 4 shows that the work of adhesion per unit area can also be described as force per unit length (similar to describing surface energy per area as force per length) and equation 5 shows this as well.

Since W_{SL} is an intensive property, it does not depend on the length, i.e.:

$$\left. \frac{\partial(F_D/(\pi D))}{\partial(\pi D)} \right|_{D=D_P} = 0 \quad (8)$$

Graphically, this is presented schematically in figure 2A.

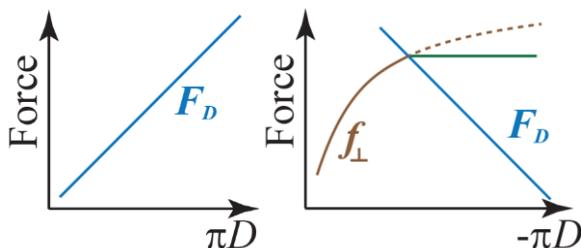


Figure 2. Schematics plotting the Dupré force variation with (A) the drop's pull off circumference. (B) The drop's circumference as a negative abscissa (i.e. negative x axis), superimposed on the drop retention force, f_{\perp} . Following f_{\perp} intersection with F_D (the negative abscissa represents a

positive time axis), the circumference will need to continue decreasing spontaneously without further force investment, as represented by the horizontal green line.

3 EXPERIMENTAL

3.1 Centrifugal Adhesion Balance (CAB)

The Centrifugal Adhesion Balance (CAB) [11,12] used was a Wet Scientific model CAB15G14. CAB pictures are shown in fig. 3.

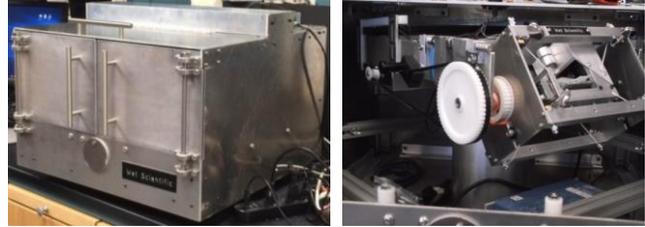


Figure 3. Pictures of CAB model CAB15G14. Left: closed CAB; Right: the CAB interior.

3.2 Experimental Procedure

The experiments were conducted when the lab environment was at 23 ± 1 °C and 96% relative humidity inside the CAB chamber. OTS coated silica was placed in the CAB sample holder and near saturation conditions [13–15] were maintained.

4 RESULTS AND DISCUSSION

In our experiment, the pull off force is one datum in a growing force curve, f_{\perp} . We note that D decreases as f_{\perp} values increase. Thus, if we superimpose the trend shown in figure 2A on the curve of f_{\perp} versus D , we get qualitatively what is shown in figure 2B. Once the functions cross, $f_{\perp} = F_D$ and $D = D_P$, the drop diameter, D , will decrease spontaneously, while the applied force-ramp will not have the time to increase significantly. This is marked as green line in figure 2B. To identify this value experimentally, we need to look for the first moment in the experimental plots in which

$$\left. \frac{\partial f_{\perp}}{\partial(\pi D)} \right| = 0 \quad (9)$$

At that point, the force corresponds to the work of adhesion, and reaches the value of eq 7, i.e.,

$$f_{\perp} = F_D = \pi D_P W_{SL} \quad (10)$$

following which the triple line circumference will decrease at no additional force, as implied from eq 8. Further circumference reduction will be spontaneous.

Figure 4 shows selected pictures from an experimental run.

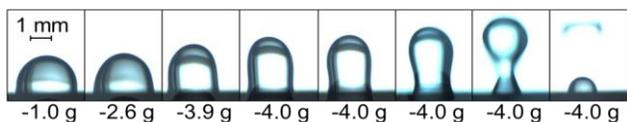


Figure 4. Pictures of water drops during a CAB run of an increasing effective gravity field which pulls on the drop from the silanized (C18) silicon surface from which it is suspended.

There are two processes that occur in tandem: *first*, reduction in the solid–liquid interfacial area and *second*, drop elongation, namely, increase in liquid–air interfacial area. At some point the force pulling on the drop above the neck will equal the neck capillary pulling force, and a liquid–liquid snap will occur. This happens long after the time at which a spontaneous reduction in the solid–liquid interfacial area is initiated (several frames). Therefore, the point considered for the pull off is when the solid–liquid area starts to reduce spontaneously and not when the liquid–liquid separation occurs a few frames later.

As the effective gravity pulling on the drop reaches -4.0 g (for this particular drop), the drop’s diameter starts decreasing spontaneously. This is the point that needs to be considered for the work of adhesion.

Force and the circumference are plotted in figure 5: panels A and C show the overall trend, while panels B and D magnify the final stages. The first point in the experimental plot that obeys eq 9 is marked with blue arrows in figure 5B,D.

Taking the values to which the blue arrows point in the plots and substituting in eq 7, we get from figure 5B

$$W_{SL} = \frac{f_{\perp}}{\pi D_p} = \frac{487 \mu\text{N}}{9.58 \text{ mm}} = 50.8 \frac{\text{mJ}}{\text{m}^2} \quad (11)$$

and from figure 5(D):

$$W_{SL} = \frac{f_{\perp}}{\pi D_p} = \frac{361 \mu\text{N}}{7.19 \text{ mm}} = 50.2 \frac{\text{mJ}}{\text{m}^2} \quad (12)$$

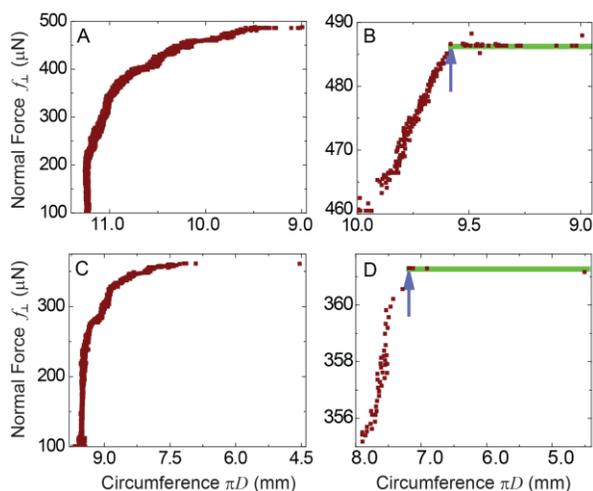


Figure 5. Water drop triple line circumference on OTS coated silica versus the effective gravitational force pulling on the drops. The blue arrows show the values taken for the pull off force and the pull off diameter in equations 11 and 12. The green line corresponds to the green line in figure 2. Drop sizes are $10.5 \mu\text{L}$ (A and B); $9.2 \mu\text{L}$ (C and D).

The linear trend of figure 6 for different experimental runs, similar to figure 2A, supports the Dupré theory, and provides a unique W_{SL} value (which for our particular system is 51.9 mJ/m^2). This shows that the work of separation is an intensive property and therefore equals the work of adhesion.

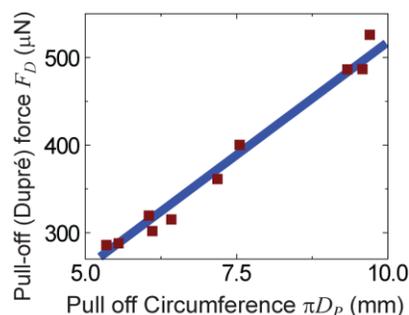


Figure 6. A set of points for which different experimental runs like those shown in figure 5 obey eq 9 for the first time, together with a fit based on eq 7 using $W_{SL} = 51.9 \text{ mJ/m}^2$.

From eq 6, the contact angle that corresponds to the work of separation above is 106° . This value is close to the apparent measured advancing angle (107°), suggesting that the nanoscopic value of the contact angle may be higher than the macroscopic (observed) one. This is in line with refs [8], [9], and [16].

To test this, we consider a solid–liquid interface of known work of adhesion: glass is known to form a nanometric water layer on its surface [17]. Therefore, for a glass–water system, we are in practice separating water from water and expect to have the water surface tension as the work of adhesion.

An example of such an experiment is shown in figure 7, and the average value obtained for that system is $71.3 \pm 2.4 \text{ mJ/m}^2$.

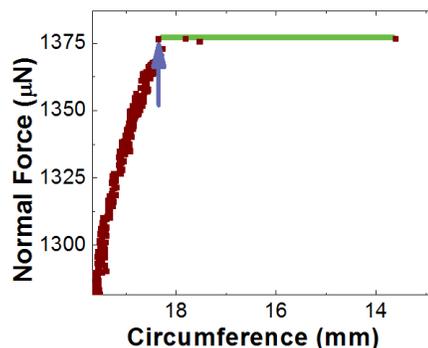


Figure 7. Water drop triple line circumference on a glass surface versus the normal (effective gravitational) force pulling on the drops (zoomed in on the end of the run). The blue arrow shows the values taken for the pull off force and the pull off diameter in equation 7. The green line corresponds to the green line in figure 2.

The macroscopic (observed) contact angle value of this system is roughly 20° , which is in agreement with measurements of Pashley et al. [17] and lower than the back calculated contact angle based on the work of separation experiments (but again corresponds well with references [8], [9], and [16]). Therefore, we conclude that our work of separation measurements correlate well with the thermodynamic work of adhesion.

We also made some measurements with rough systems. Surface roughness plays a significant role in wetting phenomena. Similar to the way it influences spontaneous spreading [18,19], it should also influence spontaneous triple line retraction, namely work of adhesion measurements.

In the experiments shown below, a smaller droplet is left on the solid surface behind the flying drop, but sometimes the departing drop leaves a clean surface behind.

The existence, or lack, of a remainder drop, as explained above, is related to a later stage after the spontaneous solid-liquid area reduction already commenced and the work of separation already determined. In the few systems that we considered so far, we found for water drops that adhere to solids with work of separation that is lower than 30 mJ/m^2 there is no drop left behind, and when it is higher than 30 mJ/m^2 , there is a drop left behind.

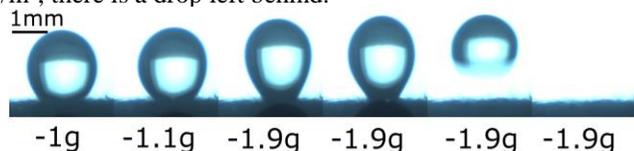


Figure 8. Pictures of water drops on a microporous layers polytetrafluoroethylene surface during a CAB run of an increasing effective gravity field. No droplet is left after the detachment.

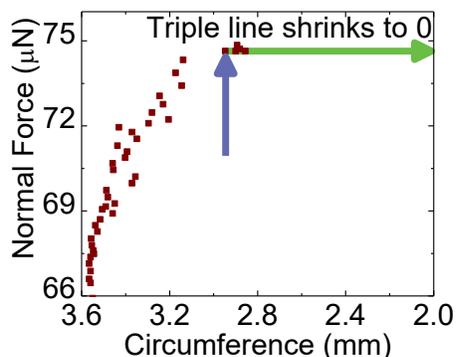


Figure 9. The force pulling a $4 \mu\text{L}$ water drop from MPL-PTFE surface versus drop's circumference at CAB run. (only the end of the run is shown).

For example, we show in figure 8, frames from a CAB experiment with water drops on a microporous layers (MPL) of polytetrafluoroethylene (PTFE), and in figure 9 we show that, for this experiment, $\text{WSL} < 30 \text{ mJ/m}^2$.

The work of adhesion that corresponds to this series of images is 25 mJ/m^2 .

5 CONCLUSION

We apply an ever increasing effective gravity using CAB, thereby forcing a drop to detach from a solid surface in the normal direction. From this we demonstrate how to directly obtain the work of separation. The values of work of separation correlate well with the expected work of adhesion and are irrespective of drop size or initial conditions in agreement with the Dupré equation.

6 ACKNOWLEDGEMENTS

This study was supported by NSF grants CMMI-1405109 and CBET-1428398 and CBET-0960229 and supported in part at the Technion by a fellowship from the Lady Davis Foundation.

7 REFERENCES

- [1] L. Wilhelmy, *Ann. Phys.* **195**, 177 (1863).
- [2] T. Tate, *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **27**, 176 (1864).
- [3] M. A. Dupré, *Ann. Chim. Phys.* **4**, 194 (1867).
- [4] J. N. Israelachvili, *Intermolecular and Surface Forces: Second Edition* (1991).
- [5] a W. Adamson and a P. Gast, *Physical Chemistry of Surfaces Sixth Edition* (1997).
- [6] P.-G. de Gennes, F. Brochard-Wyart, and D. Quéré, *Capillarity and Wetting Phenomena* (2004).
- [7] M. Staykova, M. Arroyo, M. Rahimi, and H. A. Stone, *Phys. Rev. Lett.* **110**, (2013).
- [8] J. J. Kuna, K. Voitchovsky, C. Singh, H. Jiang, S. Mwenifumbo, P. K. Ghorai, M. M. Stevens, S. C. Glotzer, and F. Stellacci, *Nat. Mater.* **8**, 837 (2009).
- [9] K. Voitchovsky, J. J. Kuna, S. A. Contera, E. Tosatti, and F. Stellacci, *Nat. Nanotechnol.* **5**, 401 (2010).
- [10] L. Heepe, A. E. Kovalev, A. E. Filippov, and S. N. Gorb, *Phys. Rev. Lett.* **111**, (2013).
- [11] H. E. N'guessan, A. Leh, P. Cox, P. Bahadur, R. Tadmor, P. Patra, R. Vajtai, P. M. Ajayan, and P. Wasnik, *Nat. Commun.* **3**, 1242 (2012).
- [12] R. Tadmor, P. Bahadur, A. Leh, H. E. N'Guessan, R. Jaini, and L. Dang, *Phys. Rev. Lett.* **103**, 1 (2009).
- [13] P. S. Wasnik, H. E. N'guessan, and R. Tadmor, *J. Colloid Interface Sci.* **455**, 212 (2015).
- [14] W. Xu, R. Leeladhar, Y. T. Kang, and C. H. Choi, *Langmuir* **29**, 6032 (2013).
- [15] N. Belman, K. Jin, Y. Golan, J. N. Israelachvili, and N. S. Pesika, *Langmuir* **28**, 14609 (2012).
- [16] A. P. Defante, T. N. Burai, M. L. Becker, and A. Dhinojwala, *Langmuir* **31**, 2398 (2015).
- [17] R. M. Pashley and J. A. Kitchener, *J. Colloid Interface Sci.* **71**, 491 (1979).
- [18] E. Chen, Q. Yuan, X. Huang, and Y.-P. Zhao, *J. Adhes. Sci. Technol.* **4243**, 1 (2016).
- [19] Q. Yuan, X. Huang, and Y. P. Zhao, *Phys. Fluids* **26**, 1 (2014).