

# Back to the basics: Wettability, icing and ice adhesion

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**Abstract:** Icing in the wet growth regime is caused by water drops on a surface, the dynamics of which are determined by external forces, such as gravity and wind drag. However, the drop dynamics also depend on the wetting characteristics of the surface material. The static contact angle determines the area of a drop that is in contact with the solid, and the difference between the advancing contact angle and receding contact angle, i.e., the contact angle hysteresis, determines the critical external force at which the drop begins to slide. Many studies have been made on the contact angles and their relation to runback icing and ice adhesion, but no quantitative theory for the contact angle hysteresis exists. Here, the contact angle hysteresis is explained by a first principles theory, and good quantitative agreement between the theory and experimental data is found. The implications of the theory to icing and ice adhesion are outlined.

**Keywords:** icing, wettability, hydrophobicity, contact angle

## INTRODUCTION

Freezing of runback water is a significant concern during wet growth icing, and also during dry growth icing when thermal ice prevention is applied. Freezing of drops causes aerodynamically dangerous rough ice accretions [1] and initiates icicle growth [2,3]. The dimensions and dynamics of the drops on a solid surface are determined by external forces that include gravity, wind drag and, in the case of rotors and wind turbines, the centrifugal force.

In addition to external forces, the drop dynamics depend on the wetting properties of the surface material, characterized by the solid-liquid contact angles. When a drop slides on a surface, its contact angle at the advancing and receding side of the drop no longer corresponds to the static equilibrium contact angle. The difference between the advancing contact angle and receding contact angle, called the contact angle hysteresis, determines the external force at which the drop begins to slide. These relations are vital in understanding of the icing process, because the rate of freezing of the drops during sliding depends on the liquid-solid contact area and contact time [4-6]. Furthermore, bouncing of impacting drops [7,8] and eventual shedding of the unfrozen water [9,10] are closely related to the receding contact angle.

Many studies have been made in order to estimate the critical external force that causes water to be removed from various surfaces [9,11-17]. In the simplest case, the critical tilt angle of a plane, at which a drop starts to slide, has been studied for different drop sizes and surfaces [14-17]. However, the fundamentals of wetting have not been fully resolved. In fact, the classical theory of wetting does not predict any contact angle hysteresis on a homogenous smooth surface. Experimental studies have been made on the dynamic contact angles and their relation to runback icing [7,10,18,19] and ice adhesion [20-27], but no quantitative theory exists. This has

considerably hampered the selection of optimal surface materials for the applications that include icing due to runback drops.

Wetting of solid surfaces by a liquid is a classical and familiar physics problem [28,29]. When a drop does not spread completely, it forms a specific angle of contact with the solid at the three-phase contact line (Figure 2). This Young's equilibrium angle [30], i.e. the static contact angle  $\theta$  measured on a horizontal surface, is widely used as a measure of the wetting characteristics of surfaces.

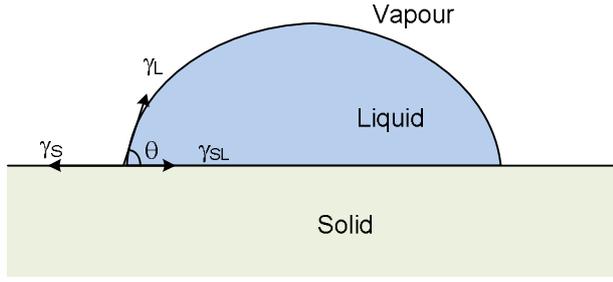


**Figure 1:** Drop of water sliding on an inclined polymer surface.

Under the influence of an external force, a drop becomes asymmetric in shape, and upon a sufficient force being exerted, it begins to slide (Figure 1). At that time, there is a difference between its front (advancing) contact angle  $\theta_a$  and back (receding) contact angle  $\theta_r$ . This is called contact angle hysteresis. Here, the contact angle hysteresis,  $H$ , is specified as  $H = \cos \theta_r - \cos \theta_a$ . Since a liquid does not transfer stress at low flow rates, the external force on the drop manifests itself as the force vector of the magnitude  $H$ . Accordingly,  $H$  determines the external force at which drops are removed from the surface.

Numerous experimental and theoretical studies have been made on the contact angle hysteresis, and were reviewed by De Gennes [28] and more recently by Eral et al. [29]. The origin of contact angle hysteresis has been explained by surface roughness and heterogeneities, surface deformation, liquid adsorption and retention, viscous dissipation, molecular rearrangement upon wetting, and interdiffusion [29]. However, there is no consensus on the origin of the contact hysteresis, and no quantitative theoretical models for it exist.

In the following, the fundamental origin of contact angle hysteresis is revealed and a first-principles physical theory of it is presented. The theory is quantitatively compared with experimental data.



**Figure 2:** Young's equilibrium of surface tensions at a three-phase line of a droplet on a solid surface.

## I. THEORY

The balance of tensions at a contact line was proposed in 1805 by Thomas Young [30]. Formally, this is

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

Here  $\gamma_S$ ,  $\gamma_{SL}$  and  $\gamma_L$  are, respectively, the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions (Figure 2). In this classical construction, the three mechanical surface tensions  $\gamma_S$ ,  $\gamma_{SL}$  and  $\gamma_L$  are at equilibrium in the direction parallel to the solid surface.

Equation (1) has been understood as the mechanical balance of the three surface tensions, but also as a result of minimizing the total free energy. In the latter interpretation  $\gamma_S$ ,  $\gamma_{SL}$  and  $\gamma_L$  in figure 2 represent scalar thermodynamic surface energies  $\Gamma_S$ ,  $\Gamma_{SL}$  and  $\Gamma_L$ , instead of mechanical tension vectors.

While the surface tensions involving a liquid phase can be interpreted either way, the mechanical surface tension of a dry solid,  $\gamma_S$ , is a contentious concept [32-35]. In particular, it is hard to explain how the solid could do work in moving the drop laterally, considering that the net atomic imbalance of forces is perpendicular to the interface. A perpendicular force can do work laterally only when the molecules are free to move, i.e. at an interface that involves a liquid. Thus, we conclude that only the surface energy interpretation of Young's Equation is valid. Then, the tension  $\gamma_S$  is a passive force that can only resist, but not cause, motion of a contact. Using the energy interpretation, Young's equation is written as

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

Taking that  $\gamma_S$  is a passive force, on the left side of Figure 2, there is no force on the solid that could move the contact line to the left. On the other hand, moving the contact line to the right at a constant  $\theta$  would increase the free energy of the system, since  $\Gamma_S > \Gamma_{SL}$ . Hence, the equilibrium contact line of a drop on a solid surface is pinned and an external force is required to make it move in either direction.

The fundamental mechanism that controls  $\theta$  by surface energies is nevertheless valid here. Due to the pinning, the surface chemical potential at the contact line is

$$P = [\Gamma_S - (\Gamma_{SL} + \Gamma_L \cos \theta)] / \rho \quad (3)$$

where  $\rho$  is the surface particle density, can be reduced only by the adjustment of the free coordinate  $\theta$ . At equilibrium,  $P$  equals zero, i.e.,  $\theta$  adopts the value given by Eq. (2).

Equation (2) describes the selection of the contact angle due to minimizing the chemical potential at the contact line that is pinned. However, when the drop is forced to move, a mechanical balance must exist in the direction of the motion. Since an interface involves surface energy, work is spent when new solid-liquid surface is being created. Hence, when the

contact line on the left side of Figure 2 moves to the left, an additional tension,  $\gamma_{SL}$ , arises. The disappearing solid-vapor interface at the advancing contact line does not affect the mechanical balance, as long as  $\gamma_S$  has no such interpretation that it could do mechanical work laterally. The additional tension, initiated by the motion and resisting it, must equal the change in the tension exerted to the contact line via the drop. This change can occur only by adjusting the contact angle. We thus have the mechanical balance at the advancing contact line as

$$\gamma_{SL} = \gamma_L \cos \theta - \gamma_L \cos \theta_a \quad (4)$$

Noting that  $\Gamma_L = \gamma_L$  and  $\Gamma_{SL} = \gamma_{SL}$ , Eq. (4) can be written as

$$\Gamma_{SL} = \Gamma_L \cos \theta - \Gamma_L \cos \theta_a \quad (5)$$

We next consider the receding contact line, i.e. the situation when the left side of the drop in Figure 2 moves to the right. This motion brings in an additional tension,  $\gamma_S$ , owing to the work spent in creating new solid-vapor interface behind the receding contact line. The disappearance of the solid-liquid interface at the receding contact line does not affect this mechanical balance, because the surface tension of the liquid-solid interface is fixed at the value  $\gamma_{SL}$ . We thus obtain the mechanical balance at the receding contact line as

$$\gamma_S = \gamma_L \cos \theta_r - \gamma_L \cos \theta \quad (6)$$

Since  $\gamma_S$  in Eq. (6) represents the tension that arises due to creating new solid-vapor surface, its scalar value equals  $\Gamma_S$  and Eq. (6) can be written as

$$\Gamma_S = \Gamma_L \cos \theta_r - \Gamma_L \cos \theta \quad (7)$$

We next employ Berthelot's rule [36], which provides the solid to liquid surface energy ratio as a function of the equilibrium contact angle as

$$\Gamma_S / \Gamma_L = [(1 + \cos \theta) / 2]^2 \quad (8)$$

Inserting Eq. (8) into Eqs. (5) and (7) gives analytical expressions for the contact angles of a sliding drop as a function of the static contact angle.

For the advancing contact angle we have

$$\cos \theta_a = [-(\cos \theta)^2 + 6 \cos \theta - 1] / 4 \quad (9)$$

The maximum contact angle is  $180^\circ$ , so that  $\cos \theta_a$  has a lower limit at  $-0.464$  ( $\theta = 117.7^\circ$ ), below which  $\cos \theta_a = -1$  and  $H$  is determined by  $\theta_r$  alone.

For the receding contact angle we have

$$\cos \theta_r = [(\cos \theta)^2 + 6 \cos \theta + 1] / 4 \quad (10)$$

The minimum contact angle is  $0^\circ$ , so that  $\cos \theta_r$  has an upper limit at  $\cos \theta = 0.464$  ( $\theta = 62.3^\circ$ ), above which  $\cos \theta_r = 1$  and  $H$  is determined by  $\theta_a$  alone.

## II DISCUSSION

According to the theory above,  $\theta_a$  and  $\theta_r$  and  $H$  depend on  $\theta$  only. The theory thus explains the empirically observed features that the contact angle hysteresis is inherent to all surfaces, and independent of the contact line velocity [37] and the effective vertical force [38].

Quantitative predictions of the theory are in good agreement with the experimental data that are available from experiments

on relatively smooth surfaces [39,40]. This is encouraging considering that the data cover many different liquid-solid combinations, and that the theoretical model here is purely physical, i.e. it includes no experimental ingredients or fitting parameters.

The model presented cannot be directly applied to a rough solid. This is because the contact angles depend on the surface morphology at the contact line in a complicated way, especially when the surface texture is directionally non-isotropic [41-44]. However, the understanding of the process that determines the contact angle hysteresis on a rough surface  $H^R$ , is important when developing superhydrophobic materials by surface modification. To that end, it is noteworthy that, for isotropic surfaces, when applied to the Wenzel state, the theory gives  $H^R = r H$ , where  $r$  is the ratio of the total surface area of the solid to its apparent surface area ( $r > 1$ ). This shows that increasing the roughness increases the contact angle hysteresis in the Wenzel state, i.e. on a hydrophilic material.

In the Cassie state, i.e. on a hydrophobic material, the roughness affects via air entrapment and the fraction  $\Phi_s$  of the apparent interface where a true solid-liquid contact exists. Then, the dynamic balances in Eqs. (5) and (7) become

$$\cos \theta_a = \Phi_s (\cos \theta - \Gamma_{SL}/\Gamma_L) - 2(1 - \Phi_s) \quad (11)$$

$$\cos \theta_r = \Phi_s (\cos \theta + \Gamma_S/\Gamma_L) - (1 - \Phi_s) \quad (12)$$

It follows from Eqs. (10) and (12) that the apparent advancing contact angle  $\theta_a^R$  gets to  $180^\circ$  at all angles  $\theta$  when the surface roughness factor is  $\Phi_s < 0.5$ . Thus, the equation for the contact angle hysteresis  $H^R$  on a reasonably rough hydrophobic and isotropic solid becomes

$$H^R = \Phi_s [(\cos \theta)^2 + 6 \cos \theta + 5] / 4 \quad (13)$$

This shows that under these conditions, making the surface rougher decreases the contact angle hysteresis. This effect is linear with respect to the true solid-liquid contact area, and is in agreement with the recent experiments [45, Figs. 7 and 11]. Equation (13) can also be expressed in terms of the intrinsic contact angle on the rough surface  $\theta^R$  by inserting into it the Cassie relation,  $\cos \theta = (\cos \theta^R + 1 - \Phi_s) / \Phi_s$ . The resulting values of  $H^R$  are in good agreement with the data by Morrow [46, Fig. 11].

Thus, the theory provides new insights into drop dynamics also on a rough surface, and removes many misunderstandings in the literature. A particular implication of the theory is that hydrophobicity should not be defined in a simple way. For example, the critical tilt angle may be smaller in a situation where the static contact angle is higher.

The implications of this theory to the adhesion of ice can be outlined as follows. The thermodynamic work of adhesion  $W_a$  is defined as

$$W_a = \Gamma_S + \Gamma_L - \Gamma_{SL} \quad (14)$$

whereas the contact angle hysteresis from Eqs. (5) and (7) is

$$H = \Gamma_S + \Gamma_{SL} \quad (15)$$

This shows that the relations between the dynamic contact angles and the work of adhesion are not straightforward. However, they are solvable by the theory, since the surface energies, and thus both  $W_a$  and  $H$ , are all functions of  $\theta$ . Furthermore, the theory shows that making a surface superhydrophobic by increasing its roughness may either decrease or increase its adhesion strength, as recently observed [47,48].

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