



## Wetting–dewetting films: The role of structural forces



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### ABSTRACT

The liquid wetting and dewetting of solids are ubiquitous phenomena that occur in everyday life. Understanding the nature of these phenomena is beneficial for research and technological applications. However, despite their importance, the phenomena are still not well understood because of the nature of the substrate's surface energy non-ideality and dynamics. This paper illustrates the mechanisms and applications of liquid wetting and dewetting on hydrophilic and hydrophobic substrates. We discuss the classical understanding and application of wetting and film stability criteria based on the Frumkin–Derjaguin disjoining pressure model. The roles of the film critical thickness and capillary pressure on the film instability based on the disjoining pressure isotherm are elucidated, as are the criteria for stable and unstable wet films. We consider the film area in the model for the film stability and the applicable experiments. This paper also addresses the two classic film instability mechanisms for suspended liquid films based on the conditions of the free energy criteria originally proposed by de Vries (nucleation hole formation) and Vrij–Scheludko (capillary waves vs. van der Waals forces) that were later adapted to explain dewetting. We include a discussion of the mechanisms of nanofilm wetting and dewetting on a solid substrate based on nanoparticles' tendency to form a 2D layer and 2D inlayer in the film under the wetting film's surface confinement. We also present our view on the future of wetting–dewetting modeling and its applications in developing emerging technologies. We believe the review and analysis presented here will benefit the current and future understanding of the wetting–dewetting phenomena, as well as aid in the development of novel products and technologies.

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### Contents

1. Introduction . . . . .	207
2. Fundamentals: wetting, spreading, and dewetting on solids. . . . .	209
3. Film stability mechanisms . . . . .	210
3.1. Suspended films . . . . .	210
3.2. Liquid films wetting–dewetting solids: the confinement effect . . . . .	213
3.3. Aqueous film wetting–dewetting solids and the role of hydration forces. . . . .	216
3.4. Nanofluid film wetting–dewetting solids and the role of structural forces . . . . .	216
4. Experimental studies of liquid films wetting–dewetting solids: the roles of the capillary pressure and film area . . . . .	218
5. Outlook for the future. . . . .	219
References . . . . .	220

### 1. Introduction

We would like to dedicate this work to Professor M. Velarde; one of his great accomplishments was to make science accessible to everyone. He made seminal and long lasting contributions to fluid physics: wetting and spreading dynamics, hydrodynamic instability, and nonlinear

wave dynamics. He devoted his life to building bridges using science during the difficult period that was the Cold War. He not only succeeded in helping others, but also managed to present the best of the scientific accomplishments in colloid science and hydrodynamics from Eastern Europe to Western European and US scientific societies.

Wetting and dewetting are fundamental phenomena and are involved in many key technological processes: micro- and nano-fabrication by spinodal dewetting, hydrophobic (tailored) surfaces, wetting on gradient surfaces, nano-lithography, induced wetting by capillary or

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electro-capillarity, solid lubrication, chemical or light induced wetting, painting, nano- and macro-particle-coated liquid surfaces, Saramago [1] printing, surface polishing on a nano-level, flotation, gas/oil recovery, and surface self-cleansing. It is actually difficult to find a technological area where the role of surface forces governing wetting–dewetting cannot take place. Here, we briefly review the history of wetting–dewetting research findings, note some of the recent achievements concerning wetting–dewetting on a substrate, and finally present some challenges facing researchers.

Despite the technological importance of the wetting–dewetting phenomena, what governs film stability and its dependence on film size is still not well understood. The film stability–instability (rupture) is the subject of thermal–mechanical and capillary surface waves caused by spatial variations of the surface tension due to the temperature or surfactant concentration. In order to optimize wetting–dewetting, researchers have focused on understanding the processes at the sub-micron, nano-, and molecular levels.

When a bubble or droplet in a liquid approach a substrate (e.g., an ideal solid: rigid, insoluble, smooth, and having a homogenous energy), the capillary force, hydrostatic force, and adhesion force balance that govern the bubble/droplet tend to allow the spreading or wetting on the solid substrate. The classical understanding of wetting is based on a mechanistic approach for a macroscopic reversible three-phase contact angle: the liquid spreads over an ideal solid until it reaches its equilibrium macroscopic contact angle ( $\theta_{eq}$ ), as defined by Young's horizontal force balance equation (1805):

$$\cos \theta_{eq} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}. \quad (1)$$

There are four parameters: the contact angle ( $\theta_{eq}$ ), the interfacial tension of the solid/vapor ( $\gamma_{sv}$ ), the interfacial tension of the solid/liquid ( $\gamma_{sl}$ ), and the surface tension of the liquid/vapor ( $\gamma_{lv}$ ). Only two of the four parameters can be measured experimentally: the surface tension of the liquid/vapor and the contact angle when the tension of the solid/vapor and liquid/vapor are unknown. Only the difference ( $\gamma_{sv} - \gamma_{sl}$ ) can be calculated if Young's contact angle and the surface tension are known. Young's contact angle requires an understanding of the method used to determine the value and the knowledge to correctly interpret the contact angle's value. The fundamental understanding of the three-phase contact angle is associated with a consideration of the structure, texture, and energy of the solid substrate and surface forces operating at the three-phase contact region where the three phases merge. The methods used to provide information about the contact angle are optical and based on three principles. The first is the sessile droplet's side-view goniometry, which is commonly used in industrial purposes for substrate surface characterization and is limited to contact angles larger than  $10^\circ$ . The second is the drop/bubble shape analysis based on the Laplace equation, which is a more reliable approach than that of the side-view. Finally, there are the reflected light interference methods – common and differential – which are used in conjunction with the Laplace equation and the disjoining pressure isotherm (these are the most reliable methods). All of these methods are accurate for smaller contact angles or small film thicknesses. The light reflected inference methods are limited to a meniscus thickness of 100 nm, which is above where the surface forces operate. At distances less than 100 nm, the use of the SFA (surface force apparatus) to measure contact angles is also limited because of the forced interference of the cantilever with the substrate. In summary, Young's three-phase contact angle measured by the goniometry view method on non-ideal substrates is not necessarily a thermodynamic one and the correct interpretation is not a simple task—it requires considerable skill and knowledge to interpret.

Often, the surfaces of substrates are not ideal; the three-phase contact angle is irreversible and is commonly characterized as advancing and receding. Two distinct models regarding the role of the substrate

surface roughness and inhomogeneous energy on the contact angle were proposed by Wenzel [2] and Cassie and Baxter [3]. Their models are commonly used to explain the role of the substrate surface non-ideality on the contact angle and the wetting dynamics are explained by Melanie et al. [4]. When dealing with the actual non-ideal substrate, the substrate surface roughness and inhomogeneous surface energy play crucial roles on wetting, film stability, and dewetting. The photos presented in Fig. 1 depict how nature creates artistic aqueous droplet patterns on the hydrophobic surface of a leaf and a spider web.

Men learned from nature how to create artistic wetting patterns (Fig. 2).

Scientists created tailored surfaces of nano-scaled energy patterns or by surface engraving to create super-hydrophobic surfaces, micro-fluidic devices, and labs on chips. Manipulating a solid substrate to have repeating hydrophobic and hydrophilic regions is an important subject with a long history: Blodgett [5] and Blodgett and Langmuir [6] proposed a method to build up successive molecular layers on flat solid surfaces and manipulate their wettability. Later, their approach became a tool to develop patterned surfaces (Krupenkin et al. [7]).

Another intriguing observation of a liquid suspension wetting solids is when the three-phase contact line is “pinned” (e.g., a non-ideal substrate) and used to create 2D nano- or micro-structured materials. The phenomenon is known as “coffee stains” (Deegan et al. [8], Hu and Larson et al. [9], Nikolov and Wasan [10], Truskett and Stebe [11], Askounis et al. [12], and Yunker et al. [13]). This occurs when an aqueous drop of a colloidal fluid or nanofluid is deposited on a smooth, clean partially-hydrophilic substrate (e.g., glass). At the beginning, the drop partially spreads over the substrate and a wedge film is formed at the advancing three-phase contact line region. Over time, the liquid evaporates and the drop volume diminishes. It was observed that, as the liquid evaporates, the three-phase contact line remains “pinned” for a time; the three-phase contact angle decreases continuously (e.g., from  $25^\circ$  to  $10^\circ$ ) and then the particles begin to move from the central part of the droplet to the three-phase contact region, where they tend to self-assemble into a 2D hexagonal formation (Fig. 3).

The value of the wetting angle governs the direction of the particle flow. For a colloidal aqueous suspension at a small contact angle (e.g.,  $10^\circ$ ), the convection flow is toward the meniscus region. At a large wetting angle, the convection flow is toward the central part of the drop (Hu and Larson [9]). The convection flow governs the particle flow direction. However, what is less understood is the reason particles self-assemble into regular 2D hexagonal patterns. It was proposed that capillary forces drive particles to self-assemble by Denkov et al. [14] and Kralchevsky et al. [15]. Nikolov and Wasan [10] established that what drives particles to self-assemble in “coffee stains” at the wedge region is a stagnation flow rather than capillary forces.

Truskett and Stebe [11] and Nikolov and Wasan [10] studied the influence of surfactants on particle deposition patterns and the creation of the outward flow to the three-phase contact line, the formation of periodic hexagonal Marangoni–Bernard cells, and also observed the formation of circular mounds of particles. Particle structural transitions at the contact line, the disorder–order following the stick–slip motion of the three-phase contact line, was reported by Askounis et al. [16] and Orejon et al. [17], and the order-to-disorder transitions in ring-shaped colloidal stains were reported by Nikolov and Wasan [10] and Marin et al. [18]. The coffee ring effect caused by ellipsoidal particles carried to the three-phase contact line at the air–water interface by capillary interactions was studied by Yunker et al. [13]. The authors reported using ellipsoidal particles floating at the air–aqueous interface to supersede the coffee ring effect. It is not unusual for scientists to have different perceptions of phenomena, but over time, the correct view prevails.

Our goal is to primarily provide a fundamental understanding of the wetting, film stability, and dewetting phenomena as well as the role of the structural forces and film area. Because of the wetting complexity of non-ideal substrates, they will not be considered here for their

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