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### Historical perspective Chronicles of foam films

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#### ARTICLE INFO

#### ABSTRACT

Available online xxxx Keywords: Foam films Soap films Film thickness Film stability Black foam films Stratified foam films The history of the scientific research on foam films, traditionally known as *soap films*, dates back to as early as the late 17th century when Boyle and Hooke paid special attention to the colours of *soap bubbles*. Their inspiration was transferred to Newton, who began systematic study of the science of foam films. Over the next centuries, a number of scientists dealt with the open questions of the drainage, stability and thickness of foam films. The significant contributions of Plateau and Gibbs in the middle/late 19th century are particularly recognized. After the "colours" method of Newton, Reinold and Rücker as well as Johhonnot developed optical methods for measuring the thickness of the thinner "non-colour" films (first order black) that are still in use today. At the beginning of the 20th century, various aspects of the foam film science were elucidated by the works of Dewar and Perrin and later by Mysels. Undoubtedly, the introduction of the disjoining pressure by Derjaguin and the manifestation of the DLVO theory in describing the film stability are considered as milestones in the theoretical development of foam films. The study of foam films gained momentum with the introduction of the microscopic foam film methodology by Scheludko and Exerowa, which is widely used today. This historical perspective serves as a guide through the chronological development of knowledge on foam films achieved over several centuries.

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#### 1. Introduction

Soap bubbles<sup>\*</sup> have been an attractive object of art since ancient times  $[1]^{\dagger}$ . One can find *soap bubbles* in classic paintings from artists such as Rembrandt, Hanneman and Chardin. Meanwhile, in the second

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\* For the sake of curiosity we afford ourselves to use original terms, phrases and longer pieces of text taken from the cited documents, these we have written in italic.

half of the 17th century, Robert Boyle and Robert Hooke were the first to study foam films, traditionally known as *soap films*. Foam films are the subject of many studies in colloid and interface science. Pioneers like Boyle, Hooke [2], Newton [3], Plateau [1] and Gibbs [4,5] discovered the fundamentals of our present knowledge in this field. With their curiosity and scientific approach, they observed many basic phenomena and gave the first scientific explanations of objects and phenomena that were aspects of daily life. Later, many scientists were dealing with this topic opened new horizons in the physics of surfaces. Charles Vernon Boys was possibly the one who made the most effective publicity for *soap films* and *soap bubbles*. He gave many lecture-demonstrations with live experiments to people of different ages and backgrounds. His lectures were quite popular, so many people knew of him before Boys

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<sup>&</sup>lt;sup>†</sup> In § 315 in Ref.[1]: "...the museum of the Louvre has an Etruscan vessel of highest antiquity, coming from the Campana collection, and on the sides of which are represented children who are blowing on pipes and having fun making soap bubbles."

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published his book entitled "Soap bubbles and the forces which mould them" in 1890 [6]. The most intensive work on fundamental properties of foam films was performed in the 20th century. This historical perspective paper, however, is focused mainly on the early findings in this field and comprises the history of *soap films* from the pioneering observations of the above mentioned scientists until the 1960s.



1) Rembrandt Harmenszoon van Rijn: Cupid with the Soap Bubble, 1634, Liechtenstein Museum, Vienna



2) Adriaen Hanneman3) Jean-Baptiste-Siméon Chardin(1603/04-1671):(1699-1779): The Soap BubbleTwo boys blowingPainting. National Gallery of Art,

Washington

Gallery paintings<sup>‡</sup>

#### 2. From the roots in the 17th to 19th century

In his seminal book "Statique experimentale et theoryque des liquides soumis aux seules forces moleculaires" (Experimental and Theoretical Statics of Liquids Subject to Only Molecular Forces), subsequently referred to as "Statique", published in 1873 [1], Plateau – the blind Belgian scientist – critically comments on the findings of scientists who had preceded him. Below we discuss the early knowledge of foam films mainly on the basis of this source [1].

bubbles. West Palm Beach, Norton Museum

of Art

According to § 317 in *"Statique"*, Boyle and Hooke were the first who paid attention to the phenomenon of foam films in the second half of the 17th century [1,2,7]. Boyle is well known for his achievements in chemistry and physics and is considered one of the founders of modern chemistry. In 1663 he published a work entitled *"Experiments and observations upon colours"* and below we present part of the original text [1]:

"To show the chemists that one can make appear or disappear colours where there is neither increase nor change of the sulphurous, saline or mercurial principles of the bodies, I did not resort to the iris produced by the glass prism, nor to the colours which one sees, on a serene morning, in those dewdrops which reflect or refract suitably towards the eye the rays of the light; but I will point out to them what they can observe in their laboratories: because if a chemical essential oil or concentrated spirit of wine is shaken until bubbles develop at its surface, those offer brilliant and varied colours which disappear all at the moment when the liquid which constitutes the films falls down in the remainder of oil or spirit of wine; one can thus make it so that a colourless liquid shows various colours and loses them in one moment, without increase nor reduction in any of its hypostatic principles. And, to say in passing, it is worthy of remark that certain bodies, either colourless, or coloured, being brought to a great thinness, acquire colours which they did not have before; indeed, besides the variety of colours that water made, viscous by soap acquires when it is inflated in spherical bubbles, terpentine, when air in a certain manner is insufflated there, provides bubbles variously coloured, and, although these colours disappear as soon as the bubbles burst, those would probably continue to express varied nuances on their surface, if their texture were sufficiently durable."

Hooke had rather broad scientific interests and activities, such as physics and architecture. His interest in the colouring of foam bubbles was most probably related to the fact that he was an assistant to Boyle for several years. In 1672, Hooke communicated to the Royal Society a work entitled "*On holes (Black Film) in Soap bubbles*" [2,8]. This text seems to be the first documented observation of the phenomenon of black spots in foam films. His astonishment about the experiments with foam bubbles is evidenced by his own words. We have underlined some of them in the facsimile of the original publication shown in Fig. 1. One can see that Hooke writes about "*holes*" in the film wondering "*what kind of invisible body it is...or what kind of magnetism it is...*" (see Fig. 1). Later, Newton explained this phenomenon by the existence of a very thin "*black*" film which reflects only a very small portion of light (for detailed definitions and classification of foam films see Section 4)







Robert Boyle (25 JanuaryRobert Hooke (28 July 1635-1627-31 December 1691)3 March 1703) OxfordLondonUniversity

Sir Isaac Newton (25 December 1642– 20 March 1727) University of Cambridge

Gallery portraits<sup>§</sup>

Isaac Newton put forth the basics of the foam film studies. These basics were later developed further by many scientists who contributed to different aspects of the science of soap films. Newton investigated mostly film caps resting on a soap solution. He explained the colours appearing on the films with analogies to his earlier observations of the colours of air wedge between two glass plates (the Newton rings) [3]. In obs. 17 and 18 in "The Second Book of Optics" [3], Newton observed the appearance of colours in a very regular order as concentric rings encompassing the bubble apex. The colour successions formed bands of several orders (see Table 1, also in [9]). Subsequently, the colour rings started dilating, flowing down and spreading over the whole bubble area and becoming more distinguishable. Newton related this phenomenon to film thinning due to drainage caused by gravity. He wondered why there was no reflection from the small circular black spot emerging at the cap apex. After a more detailed inspection of the black portion of the film, he noticed several smaller round spots that appeared even "blacker". The faint images of the sun or of a candle reflected by these black areas made him realize that there is some reflection from all parts of the film of different "blackness". Newton was the first who attempted to estimate the thickness of the film for a given colour. He found experimentally that the thicknesses of different media interposed, at which a given tint is seen, are in inverse ratio to their refractive indices. The thickness of the white of the first order produced in vacuum or air was found to be 1/178,000 in. [3, Book II, obs. 6] which is about 143 nm. Therefore, the white produced by a water slab should be 1/1.33 part of that thickness, e.g. a foam aqueous film appearing white (1st order) has a thickness of about 107 nm.

After Newton, a number of scientists performed numerous and curious experiments with *soap bubbles and films* and developed step-bystep the knowledge on this matter. In chapter VIII § 317–356, Plateau gives a comprehensive overview of the literature up to the time *"Statique"* was published. However, we will not repeat this information, only mention some interesting facts. In 1773, Wilke [10, *"Statique"* §

<sup>§</sup> Photos and text in *Gallery portraits* taken from www.wikipedia.org.

<sup>&</sup>lt;sup>‡</sup> 1) http://www.liechtensteincollections.at.

<sup>2)</sup> http://www.codart.nl.

<sup>3)</sup> http://www.metmuseum.org.

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