



Historical perspective

## Formation, characterization and stability of oil nanodroplets on immersed substrates

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## ABSTRACT

Nanoscale oil droplets locating at solid–liquid interfaces significantly impact the interfacial properties, which are concerned in both industry applications and fundamental studies. This review article presents an overview of the current progress in nanodroplet research. We will start from the characterization of interfacial nanodroplets and the formation of interfacial nanodroplets by direct adsorption from emulsions and by the solvent exchange protocol. Then we will review the experimental and theoretical studies on the evolution of oil nanodroplets including spreading, dissolution, and detachment. We will also cover the emerging applications of the interfacial nanodroplets in the fields of surface functionalization and nanostructure engineering, and particularly, highlight the potential application as capping agents to obtain architectures on microparticle surface. Finally we propose the challenges and the opportunities in this area. In our opinion, the nanodroplets have not only of high relevance to practical applications, but also serve as a model system for understanding many interfacial phenomena, such as phase separation and wetting on a microscopic scale.

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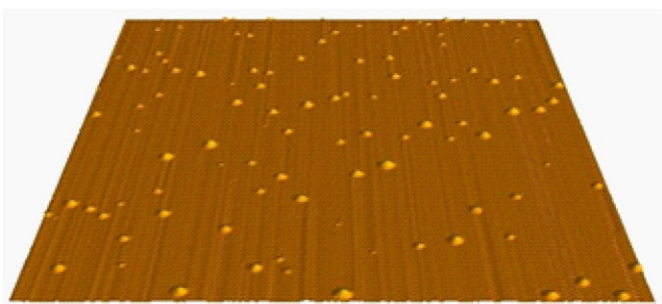
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## 1. Introduction

Small droplets on a solid surface in contact with an immiscible liquid phase are of high relevance to some fundamental interfacial properties, such as spreading and wetting of liquid, surface interactions, surface reactivity, capillary penetration in porous materials, as well as to industrial applications in oil recovery, flotation, microfluidics, printing and others [1–7]. In particular, the adsorption, spreading and detachment of oil droplets are common processes in food, cosmetics, detergent, lubricants, fertilizers, surface protection, pesticides and pharmaceuticals [8–13]. The nanodroplet (ND) is also of interest in respect to nucleation, stability and dynamics of nanoscale fluids confined at the interfaces [14–19]. A large body of literature has investigated the NDs and microdroplets (MDs) on a solid surface in gas phase (vapour or air) [20–38]. Recently the production, characterization and applications of ultrasmall liquid droplets have been reviewed by Méndez-Vilas and co-workers [2]. NDs and MDs at solid–air interfaces have become model systems for wetting studies at microscopic and submicroscopic levels [29–34], and the droplet morphology becomes a mean to characterize the wettability of materials and complicated surfaces [35–38].

Compared to droplets at a solid–gas interface, studies on droplets at a solid–liquid interface are relatively limited. This may be related to the experimental difficulty in the reproducible formation and reliable characterization of such small droplets in a liquid environment. In this perspective article, we focus on the review of recent experimental studies of NDs at solid–liquid interfaces, including formation, characterization, evolution, potential applications, challenges and opportunities in this field. Here interfacial droplets refer to liquid droplets situated on a solid surface immersed in a liquid phase. The dimension of the interfacial droplet determines the prefix of nano- or micro-. The droplet height is usually less than 500 nm, and the volume is 0.1–10 femtolitre, as shown in a representative image in Fig. 1. This article is an extension of the latest review on surface nanobubbles and NDs by Lohse and Zhang where the authors have provided a fresh and comprehensive overview of the current understanding of surface nanobubbles and NDs for the broad audience across multidiscipline of chemistry, physics, nanomaterials and technology [39]. In the present article, we extend several aspects of this topic to meet more specific interest from the community of colloid and interface sciences. As the field is developing very rapidly, we also cover several latest contributions to the field.



**Fig. 1.** An image of oil NDs on a hydrophobized Si substrate. The image was taken by tapping mode atomic force microscopy in water. The image size: 20  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ . The height of the NDs is 5–20 nm.

## 2. Characterization of interfacial NDs

The early detection of NDs was achieved on the substrate in contact with an emulsion system, which was due to the adsorption of the emulsion droplets. The adsorbed NDs were extensively investigated by ellipsometry [8,9], and quartz crystal microbalance [40]. Those measurements were sensitive to the materials at interfaces, although no detailed morphological characteristics could be provided. Recently, atomic force microscope (AFM) [15,16,18,41] and optical microscopy equipped with fluid cell [17,19,42] were applied to in-situ image the interfacial NDs, and study their dynamic evolution.

### 2.1. Analysis of surface physical properties

In 1995, Malmsten and Wårnheim et al. first applied ellipsometric methodology to detect the interfacial oil films [9]. Hydrophilic and methylated hydrophobic silica substrates and phospholipid stabilized oil-in-water emulsions were used as a model system. The change of amplitude ratio ( $\Psi$ ) and the phase difference ( $\Delta$ ) reflected the adsorption of emulsion droplets onto silica surfaces. It was found that emulsion droplets could adsorb on both hydrophilic and hydrophobic silica surfaces. The thickness of the interfacial oil films was measured to be about 100 nm at hydrophilic silica surface and around 35 nm at hydrophobic silica surfaces. The difference in the thickness of adsorbed oil films was attributed to the different contact angle of the adsorbed oil droplets at hydrophilic and hydrophobic silica surfaces.

In 1999 Blomberg and Wårnheim applied an interferometric surface force apparatus (SFA) to investigate the interactions between two solid surfaces immersed in emulsion solution [43]. A repulsive force was detected when the distance of the two surfaces was below 200 nm. The repulsive force increased strongly with decreasing space. The range of the repulsive force was consistent with the thickness of interfacial oil film measured via ellipsometry, suggesting the presence of interfacial oil droplets at solid–liquid interfaces.

Later, quartz crystal microbalance dissipation (QCM-D<sup>TM</sup>) technique was applied to follow adsorption/desorption of emulsions on the gold surfaces [40]. QCM allows the simultaneous measurements of changes in resonance frequency  $f$ , and energy dissipation  $D$ , which were correlated to the adsorption and desorption of emulsion droplets. Based on QCM results, they proposed multistep process in the ND formation from emulsion adsorption, spreading and desorption. It proved a rapid initial adsorption of emulsion droplets, manifesting by an immediate and significant lowering of the resonance frequency and an increase in dissipation factor (Fig. 2). After the initial rapid emulsion adsorption, a relative slow spreading and partial desorption of the interfacial oil droplets took place, which caused the increase in resonance frequency and a decrease in dissipation. Interestingly, an exchange of emulsions with identical composition increased the adsorption of emulsion droplets and slowed the following spreading of interfacial oil droplets as illustrated by the variation of  $f$  and  $D$  within the time of 15–55 min (Fig. 2). It was assumed that the flow of the solution provided the necessary kinetic energy to the emulsion droplets to overcome the energy barrier for further adsorption, thus increasing the adsorption. The slowed spreading was caused by the increased packing density of the interfacial oil droplets that led to the difficulty in spreading process. Repeated exchanges of the emulsion solution led similar results. However, the spreading process became slower for each successive exchange of solution (Fig. 2). Finally, flushing the measuring chamber with pure

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