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Impingement dynamics of water drops onto four graphite morphologies: From triple line recoil to pinning

Paola G. Pittoni [a], Heng-Kwong Tsao [b], Yi-Lin Hung [a], Jen-Wei Huang [a], Shi-Yow Lin [a,*]

[a] *Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Rd., Sec. 4, Taipei 106, Taiwan*
[b] *Department of Chemical and Materials Engineering, National Central University, Chung-Li 320, Taiwan*

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A B S T R A C T

Droplet impingement experiments at low Weber number ($W_e = 7.61$) were conducted by digitizing silhouettes of impacting water drops onto four graphite surfaces with different hydrophobicities. The relaxation of the wetting diameter, the droplet height and the dynamic contact angle were determined for characterizing the peculiar impact and spreading dynamics for the unalike surfaces, typified by four distinctive topographies carefully analyzed by scanning electron microscopy. After the initial inertially dominated phase, during which the drops spreading onto all substrates showed a similar behavior, the expected recoil phase was not observed for droplets impacting onto graphite surfaces characterized by 90° and 120° advancing contact angles. A few milliseconds after the impact, the drops exhibited a pinned configuration due to the peculiar morphology of these graphite substrates: randomly distributed cavities on a generally smooth surface, in fact, stopped the movement of the triple line. This behavior, however, was not detected for water droplets impinging onto graphite surfaces characterized by 160° advancing contact angles, which instead presented the usual retraction phase. Finally, the graphite surface characterized by 140° advancing contact angles showed a mixed behavior due to a transition of the drop configuration from Cassie-Baxter to Wenzel state.

1. Introduction

Due to its extensive industrial applications, such as ink-jet printing, pesticide spraying, metal forming, spray coating, and various additional chemical-related industrial processes, the droplet impact phenomenon has attracted researchers' interest since the 19th century and has been the subject of investigation of numerous experimental studies, mostly summarized in Rein's and Yarin's extensive reviews [1,2]. Theoretical and computational simulation models, based on fluid dynamics and surface physics, have been also reported [3–11].

Impingement of liquid droplets onto dry surface substrates is a complex process that encompasses fluid dynamics, physics, and interfacial chemistry. Sundry parameters, such as drop size, impact velocity, liquid viscosity, surface tension, addiction of surfactants, and substrate morphology have been found intensely influencing the droplet impacting and spreading processes [3,4,6,9–23]. Additional studies scrutinizing distinctive environmental impinging conditions, such as the presence of magnetic or electric fields, have also been reported [24,25].

After detaching from the tip of the needle, the droplet follows a free falling body dynamics. Immediately after impact, a thin film forms at the solid surface and the liquid expands horizontally [5]; this is generally termed as the spreading phase [1,2]. Subsequently, the liquid may form a donut-like shape, which is due to the accumulation of mass at the edge of the droplet [7]. The spreading phase ends as the drop achieves its maximum spreading diameter [6,26]. Generally, a droplet retraction or recoil starts right after this phase [1,2]. However, the presence or the extent of this retraction phase and the subsequent three phases contact line movement depend on the initial impact velocity [27–29] and specific characteristics of the substrate morphology, as intensively analyzed in the present work. These spreading and recoil processes may also repeat and, for a droplet that has gained adequate energy before the impact, splash or rebound phenomena may occur [10].

In recent years, the study of the dynamics of the triple line during evaporation, forced dewetting or forced wetting, also has been delved into by numerous works [30–44]. Considering these dynamic processes as a sequence of quasi-steady states, the well-known Young's equation predicts that the contact angle should remain unchanged during the movement of the three phases contact line, while the droplet wetting diameter decreases (or increases) with time. This "ideal" behavior has actually been observed in dynamic processes involving several systems, such as a series of n-alkanes on poly(ethene-alt-N-(4-(perfluoroheptylcarbonyl)aminobutyl)maleimide) films [34], pure ethanol on PTFE [35], or water on Cytop and PTFE [36]. However, it has also been observed that, for plenty of distinct systems, the triple line

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* Corresponding author. Fax: +886 2 2737 6644.
E-mail address: sylin@mail.ntust.edu.tw (S.-Y. Lin).

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movement shows instead a pinned behavior: the wetting diameter remains constant while the droplet mass loss (of gain) is accommodated by a decreasing (or increasing) contact angle [37–43]. This pinned phase may be followed by a depinning, after which the three phases contact line moves as described by the "ideal" behavior [36,38–41,43] or, alternatively, the drop may remain pinned until the end of the measurements [42,43]. Finally, numerous studies have reported an intermediate behavior, termed "stick–slip", in which the drop alternates short pinned phases with abrupt sliding phases [32,34–36,43,44].

Peculiar interface morphologies, mechanic or chemical characteristics of the substrate, and wetting–dewetting methods have been indicated as the main factors influencing these aforementioned different three phases contact line movement behaviors [30–44]. Particularly, the "ideal" behavior has been related to extreme non-wetting conditions of superhydrophobic surfaces due to highly rough substrate topographies. In these conformations, the liquid drop sits on top of the substrate roughness with air remaining trapped in the ditches and troughs under the droplet (Cassie-Baxter state), allowing a continuous triple line movement. On the contrary, the pinned phase dynamics have been mathematically modeled and seen as caused by the presence of random surface defects in, generally, smooth surfaces [37]. Ridges, cavities, grooves or other energetic barriers due to specific chemical or molecular characteristics of the substrates, stop the movement of the triple line and the drop remains "anchored" on singles defects. The balance between two opposite forces determines the observed dynamic behaviors of the three phases contact line: the force due to the single defect, which pins the triple line; and the elastic restoring force, which tends to bring the line to the undisturbed original position. Up to a definite concentration of random defects, the pinning phase is more and more promoted. However, when the number of defects is sufficiently high, their collective effect along the triple line favorites the depinning of the drop.

All the above mentioned works [30–44] have analyzed accurately the three phases contact line movement behaviors during rather slow dynamic processes (mostly for evaporating systems) and have all been conducted at large time scales. Therefore the purpose of this study was determining if such "ideal", pinned or "stick–slip" triple line movements could be observed during drops impacting and spreading onto solid surfaces, taking, instead, millisecond time scales and highly dynamic processes into consideration. Moreover, although in recent years sundry works [1–29] have been conducted for investigating drop impacts on substrates typified by unalike topographies, to the best of our knowledge no mention to observed pinning behaviors for drops impacting on a generally smooth surface with randomly distributed cavities or defects has been reported.

To fully investigate the dynamics of the three phases contact line and the potential influence of surface morphology during the spreading and the retraction phases, we examined, thus, impacting and spreading behaviors of water drops impinging at low Weber number on four distinct graphite surfaces characterized by different surface morphologies. The impact dynamics were measured in terms of the variation of the contact angle, the wetting diameter, the drop height and shape.

2. Experimental

2.1. Apparatus

A similar apparatus of the droplet impingement imaging system detailed in Wang et al. [22] was used to do the following: create silhouettes and top-view images of impacting and spreading drops; take video-images of the silhouettes; and digitize the images. The apparatus consisted of a halogen light source, a plano-convex lens system for generating a collimated beam, an objective lens, and a solid-state camera, as schematized in Fig. 1. The video image system digitized the pictures into 128 lines × 128 pixels (for CCD_1, PhotonFocus DS1-1024-CL-10) and 400 lines × 400 pixels (for CCD_2, Optronis CR3000X2) each of which was assigned a grey level value with an eight-bit resolution. The rate of image acquisition was 6770 images per second.

An edge detection routine was devised in the following way. The change in the grey level ranged from the black inside (0 level) to the bright outside (255 level) in a few pixels. The change was not a step increase from 0 to 255 but instead was continuous. The variation was symmetric at around 127.5, and therefore, the edge was defined at the position with 127.5 grey level.

Therefore, the drop edge was obtained by first interpolating a straight line between the two points that bound the grey level 127.5. The edge was defined as the x or y position that, for the interpolated line, corresponded to an intensity of 127.5. The uncertainty for the edge location in this work was around 0.2 pixels. The image forming system was calibrated by digitizing a stainless-steel ball with a known diameter of 2.498 ± 0.002 mm. The coordinates of the digitized sphere were processed to calibrate the average length between pixels along a row and along a column. The calibration procedure yielded values of 55.3 μm/pixel horizontally and 55.1 μm/pixel vertically for the side-view camera.

2.2. Materials

The water used was purified by a Millipore water purification system with a specific conductance of 0.056 μS/cm. Four distinctive graphite substrates were prepared following the methods illustrated by Hong et al. [45]. These peculiar graphite surface morphologies were characterized by different advancing water contact angles (θ_a): 90°, 120°, 140°, and 160°. In the present work, these surfaces were termed as "graphite-90°", "graphite-120°", "graphite-140°" and "graphite-160°", respectively. The advancing contact angles measurements were obtained at room temperature by using a sessile drop tensiometer [46] and a scanning electron microscope (SEM) analysis was conducted for characterizing their unlike topographies (Fig. 2).

The advancing contact angle was obtained from the location of the air/solid interface and a theoretical drop profile curve generated from the video-recorded silhouettes of the sessile drop and a best-fitting algorithm based on the Laplace equation, as fully described in Lin et al. [46]. This technique is capable of giving advancing contact angles measurements of ±0.2° precision.

The graphite sheets were purchased from NTC (IGS-743, 99.7%) and, after a rinse in acetone, the advancing water contact angles measured about 120°. The SEM analysis showed a generally mid-rough surface featured by the presence of irregular hollows (Fig. 2c and d). After the sheet was ground by a 4000-grit sandpa-

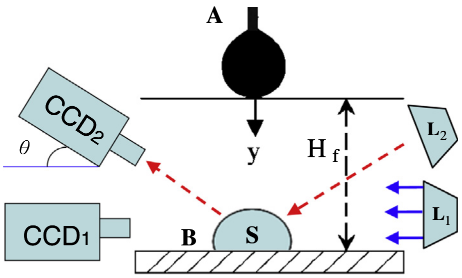

Fig. 1. Experimental design for studying the impingement behavior of a free falling droplet. A: needle; B: solid substrate; CCD: high-speed video camera; H_f: height of the droplet before falling; L: parallel light surface.