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Review

Droplet spreading on liquid–fluid interface

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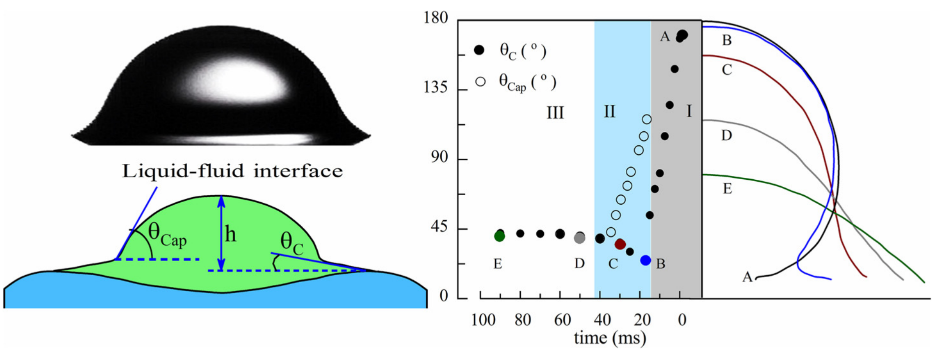
GRAPHICAL ABSTRACT



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ABSTRACT

We studied the early time dynamics of viscous drop spreading on a liquid–fluid interface. Unlike spreading on solid substrate, a drop deforms at the base as it spreads on a liquid–fluid interface. Hence the dynamics are seen to deviate from the classical power law of spreading. Experimental observations allowed us to establish a simple empirical expression to predict the temporal growth of the contact radius. Further, inertial oscillations were observed for spreading of less viscous liquid drop that can be described by the inertial capillary model.

1. Introduction

The dynamics of droplet spreading on solid substrates is a classical moving boundary problem in fluid mechanics that has long been studied for complete and partial wetting scenario [1–7]. The interfacial and viscous forces determine the spreading rate of small viscous drops and this temporal evolution often follows the well known Tanner's law [3,8,9]. For lower contact angle cases, the spreading of the bulk drop is indeed preceded by the progression of a pre-cursor that justifies the universality of the Tanner's law [10–12]. However, a wide range of variation in the exponents for this law can be attributed to the liquid and solid properties [13–17] and wetting scenario such as partial wetting [18] and electro-wetting [19].

Recently, the early time dynamics of drop spreading has attracted researchers from varied fields. Eddi et al. [20] observed that initial stage of spreading is independent of the contact line dissipation and wettability. Importantly, very different dynamic law has been observed in the first steps of spreading before attaining the Tanner's law behavior [18,21,20]. The dissimilarity has been further manifested in the study of Carlson et al. [22] where the initial stage of viscous drop spreading is seen to follow a square root growth with dependency on the liquid viscosity.

It is needless to mention that characteristics of the interface, on which the droplet spreads, play a vital role in governing the dynamics.

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For perfectly rigid and flat substrates, forces normal to the three phase contact line (TPCL) can be neglected. In such case, balancing the competing forces acting along the TPCL results in the classical Young's equation [1]. However, in situations where the rigidity of the solid substrate is not significantly larger, the normal force component can deform the solid–liquid interface [23–25]. Therefore, in the case of liquid–fluid interface, the drop attains a lense form. Equilibrium configuration of this lense can be identified with Neumann's triangles [26,13] and this transformation from Young's to Neumann's condition has been studied in detail by numerous authors [27,28].

Though the spreading dynamics of small drops on solid substrates has been very well documented, surprisingly a limited attention is given on the dynamics of drop spreading on a completely deformable interface, *i.e.*, liquid–fluid interface. The physical understanding of such a phenomenon is important in numerous applications, including but not limited to, drug and food encapsulation and targeted delivery [29–31], oil recovery processes, surface water proofing and bio-locomotion [32–34]. A few studies have investigated the spreading on liquid–fluid interface mainly focused on the equilibrium configuration [35,36]. The attainment of this equilibrium is fundamentally as rich as drop spreading on a solid or soft substrate and it is worthwhile to study this dynamics. However, how a drop spreads on such a stretchable interface and how the spreading dynamics differ from its solid counterpart remain unanswered till date. More importantly, the role of drop viscosity in dictating the early spreading of a drop on a flexible liquid–air interface has been ignored in the literature. This present study addresses these situations and concentrates on the early time dynamics.

2. Materials and methods

A silicon oil droplet of 1.5 ± 0.1 μL was carefully generated inside a water bath in a cuvette and brought in the vicinity of liquid–fluid (water–air) interface. This inverted gravity arrangement facilitate the recording of drop spreading on liquid–fluid interface in desired liquid medium. The oil drop detached at the interface due to the appropriate interfacial tension and attempts to attain equilibrium configuration through a transient spreading process. This phenomenon was recorded at high frames per second that allowed us to observe any event occurring within one-fourth of a millisecond. Four different grades of Silicon oil (Paragon Scientific Ltd. and Cargille Laboratories) were used to observe the effect of drop liquid viscosity on spreading. Properties of the considered liquids are reported in Table 1. De-ionized water was used as the liquid medium in a controlled environment with its free surface as the water–air interface. It is to be noted that the magnitudes of interfacial tensions between the water and respective oils are presented in Table 1. The interfacial tensions were measured by Wilhelmy plate technique with a force tensiometer (K100, KRÜSS GmbH). Please refer to Ref. [37] for further experimental details. Each experimental case was repeated for at least thrice and corresponding deviation in the data is reported in appropriate sections. A special attention is required to study the role of fluid flow motion inside the surrounding fluid or to identify the different spreading behaviors dominant by inertial, viscous or combined effects. In this study, the surrounding liquid volume (~70 mL) is much larger than the drop volume, additionally, the size of liquid–fluid interface is also much larger (5 cm × 5 cm) than the drop size. The large volume of the water dissipates the perturbation easily and by the time counteraction from bulk water affects the drop, the drop attains the equilibrium, hence, we can safely assume that the inertial or viscous effects from the water bulk can be ignored. The viscosity ratio between water and drop is the criteria that is varied in this analysis which is in the order of 10–1000. To avoid any dependency on the liquid–fluid interface, only one liquid as the surrounding liquid, i.e., water, was selected. One can carefully study the importance of medium by alternative combinations where the order of viscosity ratio is 1–0.1 or even less. The unavailability of liquids of viscosity lower than D10 (viscosity ratio 10), with appropriate interfacial and physical properties, restricted further analysis but the detailed investigation with multiple combinations is warranted.

Table 1
Properties of droplet liquids.

Drop liquid	Viscosity (mPa s)	Interfacial tension (mN/m)	Density (g/cm^3)
D10	10.32	40.6	0.846
S60	100.6	40.4	0.857
Laser liquid	197	24.2	1.064
D1000	990	40.6	0.870

3. Results and discussions

Spreading starts immediately as the drop detaches from the needle at the interface. Within a few milliseconds contact angle reaches its abyss and a precursor footing becomes visible. Unlike spreading on a rigid substrate, in case of spreading on a liquid fluid interface, the vertical interfacial force component at the three phase contact line assists the deformation of the underlying interface. At the same time, drop spreads along the horizontal direction. The competition between the horizontal and vertical force components results in the appearance of two angles, θ_c and θ_{cap} (please refer to Supplementary Video S1 for detailed elaboration). These two angles as well as the drop height are schematically shown in Fig. 1(a). We will first discuss the spreading of viscous drops in Section 3.1 and then extend our discussion on the observations of inertial oscillation for a drop of lower viscosity in Section 3.2 of this article.

3.1. Viscous drop spreading

Fig. 1(b) shows snap shots of Regime (I) – initial spreading with no visible precursor, Regime (II) – appearance of precursor as well as cap angle and, Regime (III) – merging of the two angles into one that approaches equilibrium. In this representation, a silicon (S60) drop spreading on water–air interface is shown. These three distinct regimes can be identified in Fig. 1(c) where the temporal variation of the two angles is plotted for the same combination of drop-interface in Panel – L, whereas the corresponding drop profiles are presented in Panel – R. Initially (in Regime I), the interface behaves as if it repels the drop – similar to the observations in numerous study for drop spreading on solid substrate [38] and a near 180° contact angle can be observed as seen at point A. Respective drop profile is (labeled as A in panel R) also depicts this scenario. The evolution of drop shape can be witnessed from drop profiles A–E. In Regime I, the contact angle rapidly decreases and at the end a large cap angle appears (B) in the beginning of Regime II. The cap angle θ_{cap} (shown by empty symbols in panel L) decreases fast while the contact angle θ_c (shown by the filled symbols) starts to increase slightly. At the end of the Regime II, these two angles approach each other (at C) and in Regime III (at D), they converge into a single contact angle. Eventually the balance between the components of interfacial tensions results in lens formation with an equilibrium contact angle (at E). We find similar behavior for other liquids considered in this study and Fig. 1(d) shows the spreading of laser liquid drop on water–air interface. The quantified analysis of contact angles as well as the drop shapes for varied combinations of drop viscosity is studied in detail to identify the spreading behavior as depicted in Fig. 2.

Fig. 2(a)–(c) show the temporal variations in the quantified drop shape properties, *i.e.*, contact angle, θ_c, drop base radius r (non-dimensionalized by equilibrium radius, R_e) and drop height h (non-dimensionalized by initial drop diameter, $h_o = 2R_o$) for all the four different grades of Silicon oil. It is evident that increase in viscosity prolongs the spreading time. Also the spreading rate is much higher at early stage which slows down as spreading continues and approaches equilibrium. We observe an interesting oscillatory behavior in the