Dynamic contact angle model for resolving low-viscosity droplet oscillations during spreading over a surface with varying wettability

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(Received 4 December 2021; accepted 2 March 2022; published 15 March 2022)

Droplet oscillations of low-viscosity liquids spreading over textured surfaces arise from pinning of the three-phase contact line that is, in turn, related to hysteresis in the wetting behavior of real surfaces. A dynamic contact angle model proposed in the present work improves the existing models by including the pinning of contact line motion. Experiments are conducted on four substrates of distinct hydrophobicity. The initial Weber number of the drop is deliberately kept small (<0.34) so that surface characteristics dominantly influence spreading. Specifically, a superhydrophobic surface with small hysteresis is shown to display small oscillations, while a hydrophobic surface with large hysteresis has large persistent oscillations. Numerical simulations are subsequently performed with the proposed dynamic contact angle model and compared with experiments. The model is also validated against experiments reported in the literature at a higher Weber number of 31.67. The model successfully predicts the contact angle evolution on the chosen surfaces, including oscillations. Specific experimental trends such as spreading, retraction, pinning of the contact line and underdamped oscillations of the drop height emerge as part of the numerical solution. With the proposed contact angle model, propagation of surface waves at the gas-liquid interface from and toward the apex is revealed as a factor responsible for the observed behavior of drop spreading.

DOI: 10.1103/PhysRevFluids.7.034002

I. INTRODUCTION

Droplet spreading is of immense interest in applications [1–6], but its modeling is limited by the complex nature of the motion of the three-phase contact line (TPL) [7,8]. The singularity of contact line motion was first described by Huh and Scriven [9], who showed that the no-slip condition of the liquid-solid interface does not carry over to the liquid-solid-gas boundary. Resolving the singularity has been a numerical challenge, and recent literature on the subject has addressed the treatment of the TPL boundary condition [9–13]. Cox [12] used matched asymptotic analysis to blend the outer macroscopic region, the inner microscopic region close to TPL, and an intermediate region between the two limits. A slip model was used in the microscopic region while the outer region was dominated by viscous dissipation. The intermediate or mesoscopic region was defined by a balance of viscous forces and surface tension. Up to zeroth order expansion in capillary number, the macroscopic contact angle was derived as [12]

\[
g(\theta_d, \mu_r) = g(\theta_m, \mu_r) + Ca \ln(\epsilon^{-1}),
\]

(1)
where

\[ g(\theta, \mu_r) = \int_0^\theta \frac{d\tilde{\theta}}{f(\theta, \mu_r)}. \quad (2) \]

Here, \( \theta_d \) and \( \theta_m \) are the macroscopic dynamic contact angle and microscopic contact angle, respectively. In hydrodynamic theory, the dynamic contact angle is estimated by extrapolating the static-like shape of the liquid-gas interface away from the contact line and outside the region of viscous bending. Further, \( \mu_r \) is the ratio of dynamic viscosity of the continuous phase to the dynamic viscosity of the dispersed phase in a two-phase system. The small parameter is defined in terms of \( \epsilon^{-1} \), the ratio of the macroscopic length scale such as the drop radius \( (R) \) and the slip length \[14\] \( (\epsilon^{-1} = R/b, \text{with } b \text{ the slip length}) \). The integrand appearing in Eq. (2) is defined as \[12\]

\[ f(\tilde{\theta}, \mu_r) = \frac{2 \sin \tilde{\theta} (\mu_r^2 (\tilde{\theta}^2 - \sin^2 \tilde{\theta}) + 2 \mu_r [\tilde{\theta} (\pi - \tilde{\theta}) + \sin^2 \tilde{\theta}] + [(\pi - \tilde{\theta})^2 - \sin^2 \tilde{\theta}])]}{\mu_r (\tilde{\theta}^2 - \sin^2 \tilde{\theta})(\pi - \tilde{\theta} + \sin \tilde{\theta} \cos \tilde{\theta}) + [(\pi - \tilde{\theta})^2 - \sin^2 \tilde{\theta}] (\tilde{\theta} - \sin \tilde{\theta} \cos \tilde{\theta})}. \quad (3) \]

In Eq. (1), \( \text{Ca} \) is the capillary number defined as \( \mu u_{cl} / \gamma \). Here, \( u_{cl} \) is the three-phase contact line velocity, \( \mu \) is the dynamic viscosity of the liquid, and \( \gamma \) is the coefficient of surface tension at the gas-liquid interface. Equation (1) is applicable to advancing and receding contact lines in the sense that the capillary number can be positive or negative. For small values of \( \mu_r \) and \( \theta_d \leq 3\pi / 4 \), Eq. (1) with the help of Eqs. (2) and (3) can be simplified as

\[ \theta_d^3 = \theta_m^3 + 9 \text{Ca} \ln(\epsilon^{-1}). \quad (4) \]

A contact angle equation of this form is referred to as the Cox-Voinov law \[7,15,16\]. The microscopic contact angle \( (\theta_m) \), measured at a distance of the order of slip length from the contact line, could be constant, as suggested by Cox \[12\] for some surfaces, though, in general, it is a function of the contact line velocity \[17\]. For the low capillary number regime, Eq. (4) was shown to model experimental data even for \( \theta_d > 3\pi / 4 \) \[18,19\]. Later, Cox and Pearson \[20\] addressed the issue of inertia in the dynamic contact angle model. The authors extended the previous work of Cox \[12\] and presented the model for a range of Reynolds numbers. Here, the intermediate region was subdivided into the viscous, transition, and inviscid subregions. In the transition subregion, inertia and viscous effects are of similar order. In the present context, the inertia effect on the dynamic contact angle is not substantial, and is discussed further in Sec. III B.

The hydrodynamic description leading to Eq. (4) fails to capture the detailed flow structure close to the contact line. Contrary to continuum modeling, atomistic interaction of the surface with the liquid in the presence of surrounding gas has emerged as a new modeling technique and is referred to as the molecular-kinetic theory (MKT) \[15,21,22\]. Instead of viscous dissipation in the inner and intermediate regions, it treats contact line friction as the primary energy dissipation mechanism. The local adsorption and desorption of liquid molecules at the solid surface near the contact line changes the regional surface tension, resulting in force imbalance, causing the three-phase boundary to move with a velocity \( u_{cl} \). Nonhydrodynamic dissipation occurring at the molecular level could be seen to affect the macroscopic dynamic contact angle. Thus two regions are necessary to explain the MKT model. In MKT, the dynamic contact angle related to the capillary number has the following form \[23\]:

\[ \theta_d = \text{acos} \left[ \cos \theta_e - \frac{2k_B T}{\gamma \lambda^2} \text{asinh} \left( \frac{\gamma \text{Ca}}{2 \mu K_0 \lambda} \right) \right]. \quad (5) \]

Here, \( K_0 \) and \( \lambda \) are molecular parameters representing the equilibrium frequency of displacement of any random molecule primarily located at the three-phase zone and an average length of the displacement, respectively; in addition, \( k_B \) is Boltzmann constant and \( T \) is the absolute temperature. Parameters \( K_0 \) and \( \lambda \) are often calculated by curve fitting the experimental data and fall in the range.
of MHz and nm [23], respectively. The contact angle $\theta_e$ is velocity independent, symbolizing an equilibrium value. For small argument inside the inverse sine hyperbolic function, the full MKT model, Eq. (5) can be simplified as [24]

$$\theta_d = \cos\left(\theta_e - \frac{\xi \text{Ca}}{\mu}\right),$$

(6)

where $\xi = k_B T / K_o \lambda^3$ is interpreted as the contact line friction coefficient in units of dynamic viscosity though it is usually greater than the dynamic viscosity of the liquid [25,26]. Equations (4) and (6) can be interpreted as the hydrodynamic and molecular approaches to contact angle modeling. These are not independent since adjustable parameters in one model can be derived using the other as a limiting condition. Further, Rothstein [23] and Petrov and Petrov [27] compared the combined model of MKT, Eq. (5), and the hydrodynamic, Eq. (4), with experiments using the glycerine-water solution and showed a favorable match. Recently, Fernández-Toledano et al. [28] highlighted the importance of the combined model by comparison against large-scale MD simulation.

The theoretical background and the analytical formulation of the dynamic contact angle rarely include substrate heterogeneity. Inhomogeneous surfaces arise from both physical texturing as well as chemical coatings. Here, the scale of inhomogeneity is taken to be smaller than the capillary length scale that makes the Bond number unity. For the present study, the Bond number is defined as [19]

$$\text{Bo} = \frac{\Delta \rho g R_0^2}{\gamma}.$$  

(7)

Further, in drop spreading applications, $\text{Bo} < 1$, making surface tension a dominant influence. In Eq. (7), $\Delta \rho$ is the density difference of the liquid droplet and the gas phase, $g$ is gravitational acceleration, and $R_0$ is the initial radius of the impacting droplet. The minimum and maximum contact angles at the onset of droplet motion are the receding and advancing angles, respectively, while the difference between them is the static contact angle hysteresis (CAH) [29–32]. Dynamic hysteresis angles are needed in applications such as digital microfluidic devices with electric droplet actuation and microchannel bioreactors and can be similarly defined [31,33]. Surface details are particularly important in modeling the spreading of low-viscosity droplets at a low Weber number ($\text{We} = \rho u_0^2 D_0 / \gamma$ where $u_0$ is the impact velocity and $D_0$ is the initial diameter of the droplet undergoing the impact process).

Finite hysteresis is desirable in several applications, such as adhering pesticides onto leaves and efficient coating and printing processes [31]. In other applications, contact angle hysteresis should be small. An example is dropwise condensation, where low CAH allows early slide-off of liquid droplets leading to fresh nucleation and thus accelerating the vapor condensation rate [34].

Droplet spreading of a low-viscosity liquid such as water on a textured surface is known to be accompanied by oscillations [35–38] [Fig. 1(a)]. The oscillations are clearly visible at a low Weber number of impact [35]. Previous models [37,39] have captured these oscillations in analogy to a spring-mass-dashpot system. However, numerical simulation of multiphase flow as a boundary-value problem has not been fully attempted. The specification of the contact angle at the three-phase contact line is one source of difficulty. An incorrect specification leads to inappropriate oscillations of drop shapes and a substantial mismatch with experiments, particularly at low Weber numbers and highly hysteretic surfaces. In a VOF simulation with a constant contact angle [40], capillary wave formation was unrepresented and oscillations were seen to continue till damped by viscous dissipation in bulk. Arkhipov [41] reported oscillatory behavior of the dynamic contact angle for a water droplet making contact with a substrate whose equilibrium contact angle was 76° for an impact velocity as low as 0.02 m/s. Liu et al. [42] reported damped oscillations in maximum height during the impact of a water droplet at low Weber numbers ($\text{We} < 0.5$). Yokoi et al. [43] carried out a CLSVOF simulation of droplet impact and spreading where the contact angle model was
FIG. 1. (a) Spreading and postpinning events of the water droplet. (b) Definitions of the equilibrium contact angle $\theta_e$, advancing contact angle $\theta_a$, and receding contact angle $\theta_r$. During spreading, an advancing droplet attains a contact angle of $\theta_a$ while a receding drop attains a contact angle of $\theta_r$. The difference between the two angles is hysteresis and is a characteristic feature of the surface. In a simulation, these conditions are related to the sign of the contact line velocity. The thick black line shows the treatment of hysteresis adopted in the present work wherein contact angle discontinuity is represented as a continuous function of the contact line velocity. (c) Schematic showing advancing and the receding contact angle of an oscillatory drop. (d) Demonstration of droplet oscillations for the pinned contact line. Following the advancing phase, the contact line is pinned while the contact angle oscillates between $\theta_a$ and $\theta_r$. After prolonged oscillations, the droplet attains the equilibrium shape with viscosity having damped fluid motion. Inset shows the initial shape of the spreading droplet with a scale bar of 1 mm.

Based on experimental observations. With a correct contact angle variation specified, the simulation predictions were shown to match experiments.

The present study seeks to improve the contact line model so that drop oscillations and their damping jointly with the pinning of the contact line are correctly realized in both early- and late-spreading simulations of a low-viscosity liquid drop over a variety of surfaces. A dynamic contact angle model that has built-in hysteresis at zero capillary number is first proposed. Second, the model includes contact line friction derived under pinning conditions. The model is an extension of the one based on molecular kinetic and hydrodynamic theories. To highlight surface characteristics such as hysteresis, simulations and experiments have been carried out at a low Weber number, $\text{We} < 0.34$. In addition, the liquid viscosity is low, viscous dissipation in the bulk is small, and energy losses arising from surface-droplet adhesion play a significant role in spreading. In this respect, pinning and friction introduced in the contact angle model are validated against experiments. In the second part of the study, the model is tested against higher Weber number experiments as well ($\text{We} = 31.67$), where viscous dissipation in the bulk is equally significant. Specifically, the dynamic contact angle model is used as a contact line boundary condition within COMSOL®, a commercial fluid flow solver. High-speed imaging experiments of the present study have been carried out.
over four surfaces with distinct wettability characteristics: Glaco, FluoroPel, polydimethylsiloxane (PDMS), and glass. The instantaneous drop shapes and other geometric parameters are measured and compared against the numerical data.

II. INCLUSION OF HYSTERESIS IN THE DYNAMIC CONTACT ANGLE MODEL

The droplet gently placed on the substrate can have many quasi-stable positions and contact angles. All possible equilibrium contact angles lie between the static advancing \( \theta_a \) and the static receding contact angle \( \theta_r \), while contact angle hysteresis \( H \) is defined as

\[
H = \theta_a - \theta_r. \tag{8}
\]

Apart from roughness and chemical inhomogeneity, hysteresis may be displayed by a smooth homogeneous surface as well [44]. As a result, the contact line is pinned while the contact angle changes to a point from where fluid motion is reinitiated. Figure 1(b) schematically shows the jump in contact angle due to hysteresis; the advancing \( \theta_a \) and receding \( \theta_r \) contact angles are the maximum and the minimum contact angles when the contact line velocity is practically zero. The thick black line in Fig. 1(b) shows a smoothed distribution of contact angle including hysteresis with a unique equilibrium contact angle \( \theta_e \) at zero capillary number. This distribution, localized at zero capillary number, is restricted by the static advancing and the static receding contact angles on each side. The pinning coefficient associated with hysteresis is defined as [25,26]

\[
C_{pin} = \begin{cases} 
\gamma (\cos \theta_e - \cos \theta_d) & u_{cl} > 0, \\
\gamma (\cos \theta_r - \cos \theta_e) & u_{cl} < 0.
\end{cases} \tag{9}
\]

Owing to pinning, the contact line itself has only a small velocity though the fluid medium inside the droplet is in motion. The physical nature of fluid motion accompanied by the movement of the interface is shown in Figs. 1(c) and 1(d); here, the contact line is pinned while the droplet motion is oscillatory. As a result, contact angle oscillations are observed until damped by fluid viscosity. It should be expected that oscillations in contact angle will be underdamped to an extent determined by the surface texture.

In the past literature [45–47], the advancing and receding contact angles were directly used in place of the equilibrium contact angle, depending on the sign of the contact line velocity. The equilibrium contact angle is assigned as a wetting condition when the dynamic contact angle falls within the range of the hysteresis [48,49]. This methodology does not provide for the dynamic contact angle distribution for a pinned contact line for small but nonzero capillary numbers.

The initial form of the dynamic contact angle model is derived from a force balance at the contact line under pinning conditions. The horizontal component of the capillary force is balanced by friction and pinning forces leading to the expression

\[
\gamma (\cos \theta_d - \cos \theta_e) = F_{friction} + F_{pinning}. \tag{10}
\]

The friction force is modeled here as a linear dashpot

\[
F_{friction} = -\xi u_{cl}. \tag{11}
\]

The pinning force is selected in such a way that it smoothens the representation of the hysteretic jump in contact angle. Specifically, a smoothing parameter \( C \) multiplying capillary number \( (Ca) \) as the argument of a hyperbolic tangent function is selected, along with the pinning coefficient as a multiplier in dimensional form; hence

\[
F_{pinning} = C_{pin} \tanh (C \times Ca). \tag{12}
\]

On including these expressions in Eq. (10), the dynamic contact angle model is obtained as

\[
\theta_d = \cos^{-1} \left[ \cos \theta_e - \frac{\xi Ca}{\mu} - C_{pin} \frac{\tanh(C \times Ca)}{\gamma} \right]. \tag{13}
\]
FIG. 2. Illustration of the effect of model parameters. (a) Variation of the dynamic contact angle (DCA) with the capillary number (Ca) from Eq. (13) for $\theta_e = 76^\circ$, $\mu = 10^{-3}\text{Pa s}$, $\gamma = 0.072\text{N/m}$ and $C_{pin} = 0.009\text{N/m}$ with advancing and receding motions shown; smoothing parameter $C = 2.0 \times 10^4$; (b) a similar plot for $\xi = 0.1\text{Pa s}$. A higher value of parameter $C$ in (b) satisfactorily models hysteresis as a jump.

The smoothing parameter ($C$) has a value of the order of $10^4$. Thus, $\tanh(C \times \text{Ca})$ approaches the limits of $+1$ or $-1$ when the droplet is about to advance ($u_{cl} \to 0^+$) or recede ($u_{cl} \to 0^-$) around the region of hysteresis. Under these circumstances, Eq. (13) approaches the static advancing (for $\text{Ca} \to 0^+$) or the static receding angle (for $\text{Ca} \to 0^-$).

The third term in Eq. (13) is a smoothly distributed form of hysteresis with the following properties:

1. The jump caused by hysteresis is re-formulated as a continuous line [black line in Fig. 1(b)] having a single equilibrium contact angle.
2. The hyperbolic tangent function has values lying between $+1$ and $-1$.
3. The argument of the hyperbolic tangent function changes sign depending on that of the capillary number.
4. When the drop is trapped in the hysteresis region, it is practically stationary though $|\text{Ca}| \sim O(10^{-4})$. Hence, a smoothing parameter $C \sim 10^4$ is used as a premultiplier for the capillary number. Thus, the following limiting conditions are realized: $\theta_d \to \theta_a$ for $u_{cl} \to 0^+$, $\theta_d \to \theta_r$ for $u_{cl} \to 0^-$ and $\theta_d = \theta_e$ for $u_{cl} = 0$.

Such a treatment of hysteresis has not been reported earlier. The advantages of this approach are as follows. It smoothes the contact angle jump at hysteresis and prevents convergence difficulties in a numerical simulation during the advancing-receding transition. This difficulty is particularly severe when the contact line velocity is obtained as the time derivative of the spreading radius ($u_{cl} = dr/dt$) [50,51]. Second, it allows for the resolution of real droplet oscillations that are common in low Weber number spreading applications.

The consequence of the selection of the smoothing parameter ($C$) in Eq. (13) is discussed here. Figure 2 is a plot of the dynamic contact angle as a function of the capillary number for various choices of the smoothing parameter. Curves in the figure are drawn for a CAH of 14.81°. In Fig. 2(a), $C = 2.0 \times 10^4$ reproduces the jump clearly over a range of values of the friction coefficient; advancing ($\text{Ca} > 0$) and receding ($\text{Ca} < 0$) trends are distinctly reproduced. The importance of the smoothing parameter is brought out in Fig. 2(b) where the choice substantially affects the advancing and receding angle distributions.

In Eq. (13), the physical origin of the parameters related to friction and local pinning is connected to surface morphology and its interaction with the droplet near the three-phase zone. These are estimated from drop-scale imaging experiments over surfaces with a uniform distribution of microstructures on the nanoscale (see the SEM images, Fig. S1, of four surfaces in the Supplemental Material [52]). In high-viscosity liquids and also at higher Weber numbers, the liquid-vapor interface will bend, leading to additional dissipation. In this context, the dynamic contact angle model, Eq. (13), is further extended using the Cox-Voinov model, Eq. (4) leading to the macroscopic contact
angle with the following form:

$$\theta^3_d = \left\{ \cos \theta_e - \frac{\xi \text{Ca}}{\mu} - \frac{C_{\text{pin}} \tan h(C \times \text{Ca})}{\gamma} \right\}^3 + 9\text{Ca} \ln(\epsilon^{-1}).$$

Equation (13) can be viewed as contributing to the microscopic interactions in the Cox-Voinov model. Equation (14) is a composite dynamic contact angle model where hysteresis, as well as wall friction, depend upon the physico-chemical nature of the substrate relative to the droplet. The slip length parameter $\epsilon^{-1}$ has to be chosen carefully in order to avoid the slip length to fall below the subatomic scale [23, 53]. Parameter C determines the sharpness of the hysteresis jump. It has been estimated in the present work to be $\sim 10^4$. Equations (13) and (14) may be referred to as the two- and three-region approaches to contact line modeling. They, however, do not resolve the local distortions in the droplet-vapor interface in the immediate vicinity of the contact line where mesoscale physical laws prevail. The mesoscale model coupled with the continuum scale Navier-Stokes equations, including surface tension and body forces, will provide the details of the near-field as well as the far field of the spreading drop. In contrast, the approach adopted here is a detailed near-field model that resolves instantaneous macroscopic features, including drop shape, its height, and footprint radius.

The present study expresses the contact angle model [Eq. (14)] as a time-independent relationship, where, for unsteady droplet spreading, capillary number is interpreted as an instantaneous value. Time does not appear as an independent variable in it. This approach, common in studies that derive equations of state, is justified because the model parameters are obtained by curve fitting the expression against time-dependent experimental data. The applicability of the proposed dynamic contact angle in steady drop motion on an inclined surface is discussed in the Supplemental Material [52] (Fig. S2) where experimental data are adopted from [53]. Overall, it is confirmed that the present formulation can be used for steady as well as unsteady contact line motion.

The above formulation of the contact angle model is expected to be widely applicable for various surfaces and cover a wide range of spreading regimes. The generality of this approach is demonstrated in the following sections against published experiments as well as those of the present study.

### III. DESCRIPTION OF EXPERIMENTS

#### A. Materials, surface preparation, and surface characterization

Apart from experimental data from the literature, additional experiments on droplet spreading have been carried out in the present work. In these experiments, a deionized water droplet of volume $11.26 \pm 0.6 \mu l$ with a Bond number of $0.26 \pm 0.008$ is used. Spreading experiments have been carried out at room temperature of $20 \pm 0.4 ^\circ C$. The physical properties of the water [41] are density, $998 \, \text{kg/m}^3$; viscosity, $0.001 \, \text{Pa s}$; and water-air surface tension, $0.072\,\text{N/m}$. The four substrates studied are prepared using glass slides, while three of them are coated with Glaco spray, FluoroPel liquid, and PDMS. The fourth surface is the bare glass slide itself. These surfaces are superhydrophobic (low hysteresis), hydrophobic (moderate hysteresis), hydrophobic (large hysteresis), and hydrophilic (moderate hysteresis), respectively, and represent a wide range of possibilities to test the proposed contact angle model.

Glaco Mirror Coat Zero spray (Soft 99 Ltd, Japan) and FluoroPel 1601V (Cytonix, USA) are used as superhydrophobic and hydrophobic coatings, respectively over a glass surface. The superhydrophobic nature of Glaco™ arises from nanoparticles (average size $\sim 30 \, \text{nm}$) suspended in alcohol. It is uniformly sprayed over the glass slide and cured at $100 \, ^\circ C$ for 5 min using a hot air gun. The hydrophobic coating of FluoroPel over the glass slide uses a spin coater at $180 \, ^\circ C$ for 30 s. It is subsequently cured at $180 \, ^\circ C$ for 30 min using a hot plate. PDMS is prepared by mixing the monomer (liquid PDMS) and curing agent in a 10:1 ratio. Bubbles formed during mixing are removed in the desiccator. The sample is poured over a glass slide and spin-coated at $3000 \, \text{RPM}$
FIG. 3. (a) Schematic of the experimental setup and recording arrangement developed to study drop spreading over surfaces varying from superhydrophobic to hydrophilic. (b) Static shapes of the water droplet recorded on the four substrates studied, from left to right: Glaco, FluoroPel, PDMS, and bare glass. The volume of the droplet dispensed is $11.26 \pm 0.6 \mu l$. The bar within the image represents a scale of 1 mm. The respective equilibrium contact angles on the four surfaces are $160.2 \pm 2^\circ$, $116 \pm 2^\circ$, $106 \pm 2^\circ$, and $57 \pm 2^\circ$.

for 30 s. The resulting PDMS coating is then cured on a hot plate at 100 °C for 60 min. The fourth surface, the glass slide, is washed in acetone and dried but is otherwise untreated.

Figure 3(a) shows the schematic of the experimental apparatus used for droplet spreading experiments. Before conducting experiments, the bench is made horizontal using a spirit level. The substrate is kept close to the needle of the syringe. The dispensing mechanism of the syringe pump is a part of a goniometer that is software-controlled while volume flow rate and total liquid volume are fixed ahead of the experiment. The droplet is first generated at the tip of a 0.517 mm outer diameter needle. The distance between the needle and the substrate is prefinalized so that the droplet makes gradual contact with it. The maximum impact velocity [41] has been found to be $\sim 0.093 m/s$. Gentle deposition of the droplet over the substrate makes the initial Weber number quite small ($<0.34$), as required in the present study.

The wetting characteristics of the four chosen surfaces are shown in Fig. 3(b) in the form of equilibrium shapes of the droplet. These are representative images that were found to be practically identical at several locations over a substrate size of $25 \times 25$ mm. In addition, FESEM images (Fig. S1 [52]) were recorded at three locations for each sample with identical magnification. Surface uniformity was observed at these locations, leading to repeatability in the drop spreading characteristics.

B. High-speed imaging and analysis

Droplet spreading sequence has been imaged using a high-speed camera (Photron-FASTCAM SA-3) at 7500 fps mounted with a 200 mm Nikon zoom lens for close-up work. However, the three-phase contact line is not fully resolved, being limited by the imaging extent of the high-speed camera. Image acquisition continued for a time period of $\sim 3$ s. The recorded images were processed using MATLAB®. The Canny edge detection algorithm was applied to derive pixel-level information at the droplet interface leading to quantities such as the footprint and its height at various instants of time. During image analysis, the left and right contact angles of the droplets were obtained using Image J software on a resolution of a pixel, namely, $17.83 \mu m \times 17.83 \mu m$. 
The near-wall interface slope sequence is extrapolated to the wall and is recorded as the applicable contact angle (Fig. S3 [52]). This process, however, does not yield the macroscopic contact angle during drop spreading since there is no closed form of an outer solution that can be extrapolated to the wall.

The molecular-level surface inhomogeneity, adherence of suspended microparticles to the substrate, and other reasons may cause slight differences between the left and right contact angles. Hence, the measured dynamic contact angle, resolved on a scale of 18–200 μm near the wall, was calculated as the average of the left and right contact angles. In experiments, surface nonuniformity was found to have only a small influence on droplet spreading, and the difference between the instantaneous left and right contact angles was uniformly within ±1°.

Further, based on the maximum contact line velocity, we examine We and Re (ρuclmaxlc/μ) at the length scale of pixels where contact angle measurement is carried out. In images, for the near-wall length scale (lc = 17.83 μm), Re = 7.68, We = 0.046, and Ohnesorge number (Oh = μ/√ρlcγ) = 0.0279. In experiments discussed in the present work, the range of capillary numbers is small (<0.006). For these nondimensional numbers, surface tension is dominant at the length scale of the dynamic contact angle measurement, and viscous bending is expected to be low. Additionally, with the droplet approaching the pinning stage, the contact line velocity, and hence the Reynolds number, diminish substantially, in effect reducing the role of inertia. Hence, additional interface bending at the mesoscopic length scale and the inertia effect on the contact angle measurement are expected to be small [53]. As a result, the uncertainty in the dynamic contact angle measurement by near-wall imaging at the pixel scale could be estimated to be ±2.5° for the superhydrophobic substrate and within ±2° for other substrates.

IV. NUMERICAL SIMULATION AND VALIDATION

Droplet spreading simulation in axisymmetric coordinates has been performed in COMSOL® Multiphysics finite element software, in which fluid flow is represented by the Navier-Stokes equations. For an incompressible fluid, mass balance and momentum equations can be written in a coordinate-free form as

\[ \nabla \cdot \mathbf{u} = 0, \]  
\[ \rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -p \mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \right] + \mathbf{F}_{st}. \]  

Equations (15) and (16) are solved for velocity and pressure in the air-water domain. In Eq. (16), \( \mathbf{F}_{st} \) is surface tension at the air-water interface, shown here as a body force term. The interface between the two fluids (air and water) is tracked by the phase-field method [54,55], where the minimization of mixing energy density over the interface thickness determines the position of the interface. The resulting Cahn-Hilliard equation is of the advection-diffusion form and advances the air-water interface in time. Here, the diffusion term is simplified as the gradient of a chemical potential leading to the equation for the phase-field parameter:

\[ \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \gamma_1 \lambda_1 \nabla^2 \left[ -\nabla^2 \phi + \frac{\phi (\phi^2 - 1)}{\alpha^2} \right]. \]  

The phase-field parameter (\( \phi \)) has values of +1 and −1 for the two pure fluids and varies smoothly over the interface. Further, capillary width \( \alpha \) scales with interface thickness and \( \lambda_1 \) denotes the mixing energy density; in addition, \( \gamma_1 \) represents mobility that is kept constant during the formulation of Eq. (17). In the COMSOL framework, Eq. (17), a fourth-order partial differential equation is decomposed into two second-order PDEs as follows:

\[ \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \nabla \cdot \left[ \frac{\gamma_1 \lambda_1}{\alpha^2} \nabla \psi \right], \]  
\[ \psi = -\nabla \cdot \alpha^2 \nabla \phi + (\phi^2 - 1)\phi. \]
Parameters $\lambda_1$ and $\alpha$ are related to the interfacial tension coefficient as

$$\gamma = \frac{2\sqrt{2}}{3} \frac{\lambda_1}{\alpha}.$$

The mobility parameter is associated with capillary width as $\gamma_1 = \chi \alpha^2$ where $\chi$ is the mobility tuning parameter. Mass loss of the liquid phase during the simulation as well as the convergence of the nonlinearity iterations are strongly controlled by the tuning parameter when sharp interfaces are encountered. Values of $\chi$ adopted in the present work are discussed later in the present section. The volume fraction of each phase, air and water, is defined as

$$V_f = \min\left(\max\left(\left(\frac{1 + \phi}{2}\right), 0\right), 1\right).$$

Here, $V_f = 0.5$ denotes the interface. Properties such as density $\rho$ and dynamic viscosity $\mu$ are calculated as a weighted average:

$$\rho = \rho_1 + (\rho_2 - \rho_1)V_f, \quad \mu = \mu_1 + (\mu_2 - \mu_1)V_f.$$  \hspace{1cm} (20)

The contribution of surface tension in Eq. (16) is computed as

$$F_{st} = G \nabla \phi,$$  \hspace{1cm} (21)

where $G$ is the chemical potential defined as

$$G = \lambda_1 \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\alpha^2} \right].$$

From Eq. (21), it is clear that surface tension is nonzero only within the thickness of the interface. The Navier-Stokes equations and the Cahn-Hilliard equation are coupled. Thus, pressure, velocity field, and droplet shape evolution are jointly extracted from a coupled system of differential equations.

### A. Initial and boundary conditions

The initial droplet shape is a circle; in an axisymmetric coordinate system, it is a half-circle placed just above the substrate [Fig. 4(a)]. The droplet may also be assigned an initial velocity to represent nonzero Weber numbers of impact. The reference pressure $p = 0$ is enforced in the air domain by introducing a pressure point constraint node. Initial velocities within the air domain are set to zero. In contrast, the initial pressure distribution within the droplet is derived from the Young-Laplace equation by reference to the droplet shape prescribed. The side and top boundaries define the far field whose dimensions are chosen in such a way that the drop shape evolution is unaffected. Open boundary conditions are enforced on these boundaries. The wetted wall condition is assigned on the lower substrate, while the no-slip condition is enforced at the solid-liquid interface within the three-phase contact line. The axis $r = 0$ is a line of symmetry where normal velocities and shear stresses are zero.

### B. Dynamic contact angle (DCA)

On the wetted wall, the dynamic contact angle is prescribed as a function of the capillary number over the three-phase contact line. In the present discussion, Eq. (14) is the dynamic contact angle model of choice. Capillary number, specifically, the contact line velocity is determined at the point where the volume fraction is 0.5. The line integral of volume fraction on the wetted wall up to this point with respect to the wall coordinate is also the instantaneous footprint radius. In the present study, the location of the contact point at the wall is tracked in time, and the time derivative of this data set provides the contact line velocity. With this velocity, Eq. (14) is enforced as a wetted wall condition by the solver within an iterative framework.
FIG. 4. (a) Schematic of the computational domain. (b) Variation of footprint radius of the spreading water droplet with time for equilibrium contact angles of 0°, 65°, and 115°. The solid line is from simulation using Eq. (14) as the dynamic contact angle model, while symbols denote experimental data adapted from Winkels et al. [59]. Parameters in the contact angle model are summarized in Table I. (c) Validation of contact angle variation with time for a water droplet spreading over a substrate with an initial impacting speed of 0.02 m/s. Open circles are experimental data from Arkhipov et al. [41]. The black line represents the numerical simulation of the present study conducted with the dynamic contact angle model given by \( \theta_d \): Eq. (14). Model parameters used are \( \theta_e = 76°, C_{pin} = 0.018 \text{ N/m for } u_{i,t} > 0, \xi = 0.03 \text{ Pa s, } \ln(\epsilon^{-1}) = 10, \text{ and } C = 2.5 \times 10^4 \). Further, \( \theta_{d,k} \): Eq. (24) refers to simulation data obtained by using the dynamic contact angle model of Kistler [62].

C. Mass loss, convergence, and validation

The finite thickness of the gas-liquid interface as well as large interface deformation results in a cumulative mass loss of the liquid drop during time advancement [56,57]. A mass loss of less than 0.6% over the entire duration of the simulation is taken as appropriate for resolving the details of interface deformation. In this respect, the mobility tuning parameter and grid refinement can be judiciously selected to minimize mass loss. Specifically, the element size at the gas-liquid interface should be small enough for a physically meaningful simulation. The mobility tuning parameter can be estimated as

\[
\chi = \frac{2}{3\sqrt{2}} \times \frac{u_{\text{max}}}{\gamma(h_{\text{max}}/\alpha)}.
\]  

(22)

Here, \( h_{\text{max}} \) is the maximum element size and \( u_{\text{max}} \) is the expected magnitude of the maximum velocity in the interfacial region. Often \( h_{\text{max}}/\alpha = 0.5 \), and we get the simplified expression

\[
\chi = \frac{4u_{\text{max}}}{3\sqrt{2}\gamma}.
\]

(23)
Large values of the parameter result in a diffuse interface [58], while small values result in highly localized surface tension, leading to a delay in the convergence of the numerical computation. Optimum values are to be selected jointly with the grid.

Validation of simulation is discussed here against experiments reported in the literature [Figs. 4(b) and 4(c)]. The spreading validation in Fig. 4(b) employs mobility tuning parameters of \( \chi = 57.62 \text{ m/s/kg}, \ 34 \text{ m/s/kg}, \ \text{and} \ 7.85 \text{ m/s/kg} \) for equilibrium contact angles of 0°, 65°, and 115°, respectively. Simulation in Fig. 4(c) has been performed for \( \chi = 2.62 \text{ m/s/kg} \) and 875154 cells distributed over a domain of size 9.1 mm \times 9.1 \text{ mm}. The highest mass loss seen over a time frame of 250 ms was less than 0.6%. A discussion on the effect of the mobility tuning parameter on mass loss and the numerical solution is presented in Figs. S4 and S5 [52]. For droplet spreading simulations carried out to validate the experiments conducted by the authors, the mobility tuning parameters were selected from mass balance and grid independence studies as 6.54 \text{ m/s/kg}, 2.62 \text{ m/s/kg}, 2.62 \text{ m/s/kg}, and 39.28 \text{ m/s/kg} \) for the substrates of Glaco, FluoroPel, PDMS, and plain glass, respectively. These values depend on \( \mu_{\text{max}} \) and, in turn, the parameters appearing in the dynamic contact angle model. Hence, the tuning parameter is finalized after performing trial simulations with a given initial condition and contact angle parameters.

The match between experiment and simulation is seen to be quite good in Figs. 4(b) and 4(c), thus validating the extended model proposed here. Application of Eq. (14) requires the specification of several parameters that are dependent on the experimental details. In Fig. 4(b), the pinning coefficient is extracted from the static advancing and receding contact angles available in the work of Winkels et al. [59]. In Fig. 4(c), it is obtained by assessing the dynamic contact angle behavior. As shown in Fig. 4(c), the droplet undergoes oscillations with the minimum and maximum contact angles during oscillations being \( 62.44° \) and \( 91.6° \), respectively. These values may be taken as the static receding and advancing contact angles while the equilibrium contact angle is 76°. For water \( \gamma = 0.072 \text{ N/m}; \) from Eq. (9), the pinning coefficient corresponding to these data is 0.018N/m and 0.017N/m for \( u_{\text{cl}} > 0 \) and \( u_{\text{cl}} < 0 \), respectively. The contact line friction coefficient and the slip length are not prescribed in the work of Winkels [59] and Arkhipov [41]. These parameters are to be obtained by curve fitting the experimental dynamic contact angle data with respect to capillary number by using the dynamic contact angle model [Eq. (14)]. Owing to unavailability of experimental data, the friction parameter \( \xi \) in the contact line model is iteratively determined and summarized in Table I for Winkels et al. [59], and \( \ln(e^{-1}) \) has been taken \( \sim 10 \) consistent with the literature [14,60,61]. Consequently, for droplet radii of 0.5 mm and 1.5 mm, slip lengths of 22.3 nm, and 68 nm were obtained for the data of Winkels [59] and Arkhipov [41], respectively. However, low Weber number spreading is quite insensitive to the choice of slip length.

Along with the proposed dynamic contact angle model, Eq. (14), Fig. 4(c) also shows results obtained for the dynamic contact angle model of Kistler [62] against the experimental results of Arkhipov et al. [41]. Here, the Kistler model is given as

\[
\theta_{d,k} = \cos^{-1}\left(1 - 2 \tanh\left\{5.16 \left[\frac{\text{Ca} + fHI}{1 + 1.31(\text{Ca} + fHI)^{0.99}}\right]^{0.706}\right\}\right),
\]

\[
fHI^{0.706} = \frac{1}{5.16} \left(1 + 1.31 fHI^{0.99}\right)^{0.706} \tanh^{-1}\left(\frac{1 - \cos\theta_e}{2}\right).
\] (24)

Figure 4(c) shows that Eq. (24) can neither capture the experimental trends during the initial time steps nor the oscillatory nature beyond \( t = 12 \text{ ms} \). These details are well realized with the present approach. Further, the present simulations capture the experimental contact angle variation in time but with a slight time delay during the oscillatory phase of 15 ms to 44 ms. This difference may be related to small differences in the initial drop shape between experiments and simulation.
Table I. Surface characteristics in experiments and parameters used in the proposed dynamic contact angle model.

<table>
<thead>
<tr>
<th></th>
<th>Glaco</th>
<th>FluoroPel</th>
<th>PDMS</th>
<th>Glass</th>
<th>Winkels et al. [59]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_e$</td>
<td>160.2±2°</td>
<td>116 ±2°</td>
<td>106±2°</td>
<td>57 ±2°</td>
<td>0</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>-</td>
<td>123.3±2°</td>
<td>123.5±2°</td>
<td>82 ±2°</td>
<td>-</td>
</tr>
<tr>
<td>$\theta_r$</td>
<td>-</td>
<td>110 ±2°</td>
<td>84.5±2°</td>
<td>48.5±2°</td>
<td>-</td>
</tr>
<tr>
<td>Contact angle hysteresis (H)</td>
<td>~0°</td>
<td>13.3°</td>
<td>39°</td>
<td>33.5°</td>
<td>-20°</td>
</tr>
<tr>
<td>$C_{\text{pin}}$ (N/m) (for $u_{ij} &gt; 0$)</td>
<td>-</td>
<td>0.00791</td>
<td>0.0205</td>
<td>0.0292</td>
<td>-</td>
</tr>
<tr>
<td>$C_{\text{pin}}$ (N/m) (for $u_{ij} &lt; 0$)</td>
<td>-</td>
<td>0.00693</td>
<td>0.0267</td>
<td>0.0085</td>
<td>-</td>
</tr>
<tr>
<td>$\xi$ (Pa s) (advancing)</td>
<td>0.012</td>
<td>0.04</td>
<td>0.06</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>$\xi$ (Pa s) (receding)</td>
<td>0.012</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>$C(\times10^3)$</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>$\ln(\epsilon^{-1})$</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Mobility tuning parameter (MTP)</td>
<td>6.54</td>
<td>2.62</td>
<td>2.62</td>
<td>39.28</td>
<td>57.6</td>
</tr>
<tr>
<td>Maximum mass loss (%)</td>
<td>0.634</td>
<td>0.589</td>
<td>0.473</td>
<td>0.346</td>
<td>0.4</td>
</tr>
</tbody>
</table>

V. RESULTS AND DISCUSSION

The physical problem of a liquid drop spreading over a solid surface is initiated at a molecular level by surface chemistry and progresses over to the continuum, creating a hierarchy of length and time scales. On the continuum scale, the droplet immediately creates a small but finite patch over the substrate before the onset of the spreading phase. As discussed in the literature [8], the unbalanced contact line force is proportional to the contact perimeter. Simultaneously, the initial contact angle differs significantly from the equilibrium value. The combined effect of an expanding perimeter and departure of the contact angle from the equilibrium value causes a force imbalance at the three-phase contact line. The contact line velocity impacts the drop shape via the dynamic contact angle model, alters pressure distribution within the liquid phase, and generates bulk motion inside the droplet. Relative magnitudes of these changes depend on surface hydrophobicity along with thermophysical and interfacial properties of the droplet. For a low-viscosity liquid such as water spreading on a partially wetted substrate, the deformation originating from the contact line tends to propagate towards the top of the droplet. The change in curvature of the droplet close to the contact line establishes a curvature gradient along with the water-air interface. The droplet curvature is related to the droplet pressure through the Young-Laplace equation in a hydrostatic setting and is modified by the Navier-Stokes equations when the fluids are in motion. Curvature gradient, specifically the pressure gradient at the gas-liquid interface, causes fluid motion from the apex of the droplet towards its contact line. The curvature near the apex is convex, while a highly wetting surface makes the contact line curvature closer to concave [8,63]. The two curvatures are equalized by the flow set up within the drop from the apex region of high pressure to a contact line region of low pressure. The propagation of interface deformation has the appearance of a wave and has been referred to as a capillary wave [8,60]. The characteristics of the capillary wave depend on the departure from the equilibrium contact angle, initial Weber number, Bond number, Reynolds number, and surface hysteresis.

Results are presented here in three sections. In the first, simulation based on the proposed dynamic contact angle, Eq. (14), is compared against imaging experiments of water droplet spreading over four distinct surfaces (Table I). In this part of the study, the maximum Weber number based on the initial droplet velocity is ~0.34. The second section discusses the influence of the injection needle on droplet spreading experiments in terms of the numerically determined velocity distribution inside the droplet. In the last section, the application of the proposed dynamic contact...
FIG. 5. (a) and (b) illustrate the dynamic contact angle variation with the capillary number. Symbols denote experimental data, and the solid line represents the contact angle model, $\theta_d$: Eq. (14). The contact line friction coefficient ($\xi$), parameter $\epsilon^{-1}$, and the smoothing parameter ($C$) are obtained from the experimental data fitted with Eq. (14). The contact angle data derived from experiments have an uncertainty of $\pm 2.5^\circ$ in Glaco and $\pm 2^\circ$ for other substrates. The uncertainty arises from the difficulty in edge detection and identification of the contact point in the instantaneous image.

angle model is discussed for experiments reported in the literature at a higher Weber number, We = 31.67.

A. Spreading at a low Weber number

A comparison of the proposed model [Eq. (14)] against the experiments of the present study for four distinct surfaces is discussed in the present section. Figure 5(a) shows this comparison for the Glaco and FluoroPel-coated surfaces in terms of the dynamic contact angle variation as a function of the capillary number, and Fig. 5(b) shows the plot for PDMS and glass. A coating of Glaco leads to a superhydrophobic substrate with small hysteresis, and the dependence of contact angle on capillary number is relatively weak. A hysteretic jump at zero capillary number is seen for the other three surfaces. For the four surfaces, the contact angle increases with the capillary number during the advancing phase. However, an observable receding phase is seen only for Glaco and FluoroPel [Fig. 5(a)] when the droplet retracts with contact angle reduction in the negative capillary number regime. For PDMS and glass, the degree of hysteresis is higher, and the jump is abrupt. Specifically, for PDMS, the jump is sharper than glass, as seen in the inset of Fig. 5(b) for $Ca < 1 \times 10^{-4}$. Hence, the water droplet continues to spread with a low contact line velocity over the glass. On the other hand, PDMS being sticky hinders contact line motion, generating large changes in contact angle for near-zero contact line velocity. In Glaco, hysteresis is practically absent, and the contact angle changes continuously with the capillary number. The contact angle model, Eq. (14), reproduces these trends, and the match between experiments and the model equation is quite close (Fig. 5).

In addition to a good match with Eq. (14), experimental data were found to be in good match with Eq. (13) as well. Hence, referring to Sec. II, it is concluded that the inner scale model based on friction and pinning are primary to spreading and losses arising from viscous bending are secondary. Against this perspective, observations from Fig. 5 are summarized as follows. Low Weber number spreading over glass is well modeled by both Eqs. (13) and (14), indicating that viscous bending is of secondary importance. For PDMS, a slight difference (1.184° at $\sim Ca = 0.00452$) is seen when the capillary number exceeds 0.003. For FluoroPel, differences (1.02° at $\sim Ca = 0.0032$) become visible for $Ca > 0.002$ while for Glaco, differences remain small. At a higher Weber number (We $\sim 31.67$), the generalized model given by Eq. (14) shows a better match with experiments as discussed later in Sec. VC.
FIG. 6. Dynamic contact angle variation with time for a water droplet spreading on various surfaces. Symbols represent data from the experiments of the present study, while continuous solid lines represent simulation using the dynamic contact angle model, Eq. (14). Surfaces studied are (a) Glaco (green), (b) FluoroPel (blue), (c) PDMS (black), and (d) glass (red). The equilibrium contact angle ($\theta_e$), static advancing ($\theta_a$), and the static receding ($\theta_r$) angles are also shown for each substrate. Uncertainty in the measured contact angle is estimated to be $\pm2.5^\circ$ in Glaco, and $\pm2^\circ$ for other surfaces.

The parameters appearing in the proposed model are listed in Table I for the four substrates. The static advancing and receding contact angles are the global maximum and minimum values of the dynamic contact angle around the pinning phase. These are also recognizable in the time domain plots of the contact angle and spreading ratio shown in Figs. 6 and 7. The contact line over a FluoroPel surface is pinned for $t \geq 27$ ms (Fig. 7); correspondingly, from Fig. 6(b), $\theta_a = 123.25^\circ$ and $\theta_r = 110^\circ$. The pinning phases for PDMS and glass can be similarly identified for $t \geq 12.6$ and 12 ms, respectively. The time-dependent behavior of the spreading drop on the four surfaces is further discussed below.

Simulations using the proposed dynamic contact angle model are shown using solid lines in Figs. 6 and 7. Experimental data are superimposed on these plots using appropriate symbols. The match is seen once again to be quite good. The spreading data can be divided on the time axis into two parts: ahead of oscillations and post the onset of oscillations. These two regions are also visible on the capillary number axis in Fig. 5, close to $Ca \sim 0$ and away from it. The FluoroPel-coated surface has a hysteresis of 13.3$^\circ$ when compared to 39$^\circ$ for PDMS and 33.5$^\circ$ for glass. Thus, the FluoroPel-coated surface shows low-amplitude oscillations [Fig. 6(b)] compared to PDMS [Fig. 6(c)]. In contrast, the droplet shows persistent finite-amplitude oscillations over PDMS, while for the glass substrate, oscillations decay gradually with time. The simulation data reproduced these experimental trends, confirming that the proposed extended dynamic contact angle model can be effectively used for drop spreading simulations over various surfaces with distinct wettability characteristics.
FIG. 7. Instantaneous distribution of spreading ratio and height factor with time: experimental data are represented by symbols while the solid line represents simulation using the dynamic contact angle model, Eq. (14). The experimentally determined spreading distance from image processing using pixel counts is estimated to have an uncertainty of $\pm 0.01$ mm, whereas the height calculations from image data have an uncertainty of $\pm 0.08$ mm.

The spreading behavior of a droplet over a chosen surface impacts its height variation in time along with the contact angle. During the pinning phase, spreading is arrested, and the changes in height correlate with the contact angle; see Fig. 1(d). Two relevant dimensionless parameters are the footprint spreading ratio $\beta = D/D_0$ and the height factor $\delta = H/D_0$; the latter is defined as the ratio of the instantaneous height at the axis and the initial diameter of the droplet. The variation of the spreading ratio and height with time are shown in Fig. 7. Numerical and experimental data are once again seen to be quite close. Height and spreading ratio (Fig. 7) vary jointly in time for a superhydrophobic surface with negligible hysteresis as for Glaco. The two quantities become decoupled for a surface with large hysteresis such as PDMS as well as the hydrophilic surface with high hysteresis, such as glass, where spreading is accompanied by the pinning of the contact line. An intermediate result is seen for a hydrophobic surface such as FluoroPel that has a measurable hysteresis. FluoroPel and PDMS surfaces are hydrophobic, having an equilibrium contact angle of 116º and 106º, respectively, while the hysteresis exhibited by the latter is high. Thus, arising entirely from differences in hysteresis, their dynamic characteristics show differences in height factor and spreading ratio, especially before the start of the pinning phase. After achieving a peak in spreading, the water droplet on a FluoroPel-coated surface shows retraction of the contact line and subsequently shows smaller growth rates (Fig. 7).

Glass and PDMS are further compared here with reference to Fig. 7. For the glass surface, the drop spreads rapidly (up to $\sim 12.4$ ms) and later, the footprint radius becomes practically constant. The resulting oscillations in height are damped in the long run owing to the hydrophilicity of the
surface that results in a large surface area. This observation has also been reported by Liu et al. [42] during water droplet spreading on the nano-SiO$_2$-coated aluminum substrate with a 10º equilibrium contact angle. With decaying oscillations in height, the spreading ratio of the drop placed on glass increases slowly in time (Fig. 7), keeping the volume constant. Since the Weber number is low, only a small amount of kinetic energy is initially available for droplet spreading. The release of surface energy due to reduction in average curvature balances an increase in kinetic energy of the liquid mass along with viscous dissipation in the bulk and contact line dissipation. For PDMS, hysteresis is considerable; hence, an initially stationary droplet has insufficient energy to overcome the surface energy barrier. As a result, PDMS shows large-amplitude DCA oscillations, a practically fixed contact line, and oscillations in the droplet height. For glass, the surface is hydrophilic, hysteresis is moderate, retraction is absent, and the spreading continues slowly over a longer time period.

The time $t_s$ required to reach maximum spreading is compared for the four substrates against the inertia-capillary time scale [64] defined as $t_i = \sqrt{\rho R_0^3/\gamma}$. For Glaco $t_s \simeq 10$ ms, for FluoroPel, it is 11.46 ms, and for PDMS-coated substrates and glass $t_s$ is $\sim 12.4$ ms. In comparison, $t_i = 6.086$ ms; thus $t_s/t_i = 1.64$ for Glaco, 1.88 for FluoroPel, and 2.037 for PDMS and glass, and the ratios of the time scales are numerically comparable. For low Weber number, We $< 0.5$, Liu et al. [42] found that the ratio of $t_s$ and $t_i$ is only weakly dependent on the substrate wettability. Bird [65] reported

FIG. 8. Experiment (black shade) and numerical simulation (grey) of the droplet shape evolution on (a) Glaco, (b) FluoroPel, (c) PDMS, and (d) glass. In the numerical simulation, the dynamic contact angle model (14) is used as a wetted wall condition. The simulation parameters are listed in Table I. The bars shown in the first image represent a length of 1 mm.

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FIG. 9. Understanding the role of the needle in droplet spreading via simulation; absolute velocity distribution inside the water droplet spreading on (a) Glaco substrate and (b) glass substrate. For the superhydrophobic Glaco substrate, surface waves generated at the droplet apex cause the droplet to spread. For the glass substrate, surface waves are damped and overtaken by the capillary wave originating from the contact line.

that $t_s/t_i$ decreases with an increase in surface hydrophobicity, thus confirming the trends discussed here.

The simulated shapes of the droplet are compared with experiments and are shown in Fig. 8. The multimedia views of the experimental drop shapes on the four substrates are included in the supplementary material [52] (videos S1–S4). A comparison of drop shapes at identical time instants requires a careful specification of the initial condition in numerical simulation, particularly at low Weber numbers. To facilitate the comparison of experiments and simulation, the needle continued to be in touch with the drop while the rest of it formed a sphere over the substrate. With this alignment in initial conditions, the drop shape evolution in experiments and simulation matched quite well (Fig. 8) on the short as well as the long-time scales. A correct initial condition is also important for resolving waves generated at the apex of the droplet, as in the Glaco-coated surface [Fig. 8(a)].

B. Appearance of surface waves

The superhydrophobic substrate created by Glaco spray shows a distinct droplet spreading pattern [Figs. 7 and 8(a)] that is visible in simulations as well as experiments. Owing to small adhesion to the surface, the droplet tends to recoil even if the initial Weber number is zero. The first peak in footprint radius is attained at $\sim 10$ ms, but for other substrates, this time instant delayed to the range of 12–13 ms (Fig. 7). The dynamic contact angle variation with time for the Glaco
surface is nonoscillatory (Fig. 6(a)), while the spreading ratio and height factor (Fig. 7) show clear oscillations. Experiments reveal that waves are generated at the apex due to drop detachment from the needle, as discussed below.

Figure 9 provides numerically determined velocity distribution inside the droplet for spreading over Glaco-coated and glass substrate. The contact line dissimilarity for the superhydrophobic Glaco surface, namely the difference between the equilibrium and the instantaneous contact angles, is small, and a weak capillary wave is formed at the contact line. For the glass substrate, contact line dissimilarity is significantly larger and drives stronger capillary waves. During detachment of the droplet from the needle, a concave curvature is momentarily formed, pressures are low, and relatively large velocities are generated near the apex; see the time instant of 0.5 ms for Glaco and 1.67 ms over the glass, Fig. 9. The localized high-velocity zone drives shape deformation, which propagates towards the contact line. Jointly, a capillary wave related to contact angle mismatch propagates from the contact line to the apex. The two opposing waves create a region of low velocity at the middle of the bulge. See time instant of 2.17 ms for glass [Fig. 9(b)] followed by time instants of 3.17 ms to 6.17 ms when the capillary waves overtake surface waves and surface deformation proceeds toward the apex. The trend is reversed for the Glaco substrate since a stronger surface wave drives fluid flow toward the contact line; see Fig. 9(a) for time instants of 0.5 ms to 6 ms. During this time period, the spreading rate is low. Later (6–9 ms), excess energy released due to the motion of the contact line increases the spreading rate. Without any observable deformation of the contact line, the droplet spreads and retracts due to the shape deformation initiated by the surface waves. For other surfaces, the detachment of the droplet from the needle does not affect spreading. Here, ahead of the wave reaching the contact line from the apex, it is damped and overtaken by the capillary waves. Unlike other substrates, the superposition of these waves is relevant and observable for the Glaco substrate in the early time height and footprint oscillations (Fig. 7).

During spreading and retraction phases over the Glaco-coated surface, the droplet shows small rebounds at multiple time instants [Fig. 8(a) at ~25 ms; also see the multimedia view of the experimental results on Glaco substrate (video S1 [52])] for other rebounds. The present study,
along with the proposed contact angle model, reveals rebounds, oscillations, and superposition of interface waves on surfaces of varying wettability at a low Weber number.

C. Spreading at a high Weber number

A comparison of simulation with the proposed contact angle against experiments at $We = 31.67$ is discussed in the present section. The droplet deformation increases with an increase in impact velocity. Along with surface-droplet adhesion, viscous losses in the bulk of the droplet significantly increase. Energy dissipation additionally takes place when the drop is pinned over the surface leading to interface oscillations. The experiment data of water droplet spreading on hydrophobic silane surface have been adapted from the work of Yokoi et al. [43]. The simulation parameters are obtained by fitting the experimental data of contact angle as a function of the capillary number to Eq. (14). The pinning coefficients for advancing and the receding menisci are 0.024 N/m and 0.0225 N/m, respectively. The contact line friction factor is $0.2 \times 10^{-2}$ Pa s, and the smoothing parameter $C = 0.9 \times 10^4$. The parameter $\epsilon^{-1} = 8.88 \times 10^6$, thus the slip length of $\sim 0.128$ mm was obtained for the droplet radius of 1.14 mm, which is physically intuitive and in accordance with a previous study [53]. The dynamic contact angle variation in Fig. 10(a) shows a good match with experiments. The simulation outcome of the spreading ratio is shown in Fig. 10(b); again a good match with experiments is obtained. The corresponding drop shapes derived from the simulation are shown in Fig. 10(c) at selected time instants. Large deformation as appropriate for a higher Weber number is clearly to be seen. The applicability of Eq. (14) in this context is further confirmed.

VI. CONCLUSIONS

A dynamic contact angle model is proposed to describe contact line spreading, retraction, and pinning of a water droplet approaching surfaces of varying textures at low and intermediate Weber numbers. The model parametrically accounts for hysteresis in contact line motion as well as wall friction and is in a form that can be readily included in numerical simulation platforms. The choice of a low Weber number makes droplet adhesion with the surface a determining feature of spreading and is a good test of the model developed. Specifically, a correct dynamic contact angle model can account for droplet shapes and height oscillations during late spreading over surfaces with large hysteresis. The model proposed is shown to resolve these details correctly in relation to imaging experiments. Simulation and experiments have been carried out in the present study for $We < 0.34$ on four substrates: Glaco-coated (superhydrophobic with low hysteresis), FluoroPel (hydrophobic with moderate hysteresis), PDMS (hydrophobic with large hysteresis), and glass (hydrophilic with moderate hysteresis). For a Glaco-coated substrate, low hysteresis damps the contact angle oscillations and the timescale of maximum spreading is relatively short. At the other extreme, large hysteresis leads to pinning of the contact line on PDMS, leading to long-time oscillations in the dynamic contact angle and height. For a glass substrate, the combination of hydrophilic texture and hysteresis leads to damped oscillations as the contact line itself moves slowly over the surface. On FluoroPel, the contact line initially retracts and is later pinned into a practically immobile state, causing height and contact angle oscillations. While Kistler’s [62] contact angle model fails to reproduce oscillations of a pinned drop, the predictions of the proposed model are quite close to experiments in terms of the dynamic contact angle and drop shapes over the range of parameters considered.

The underlying mechanism that reveals control of spreading by surface texture is shown to be related to capillary waves that propagate over the gas-liquid interface. These are visible in experimental data and can also be analyzed via velocity fields derived from simulation. Two contrasting waves are generated when a drop touches a surface at a low Weber number: one, at the contact line (capillary wave), and the other, at the droplet apex (surface wave). The capillary wave moves from the contact line to the droplet apex, while the surface wave moves from the apex to the contact line. The capillary wave is quite weak for a superhydrophobic surface, and the surface
wave causes the droplet to spread and recoil. The surface wave effect is negligible for other surfaces because the nature of spreading is overtaken by the capillary wave.

The proposed dynamic contact angle model has been further utilized to explain other experimental data reported in the literature. The application of interest relates to the impact of a droplet at a higher Weber number of \( \text{We} = 31.67 \). The spreading ratio and droplet shapes are well simulated in comparison to experiments.

The predictions of the simplified model, Eq. (13), match the generalized model, Eq. (14), as well as experiments at low Weber numbers, indicating that spreading is dominated by friction and pinning. At a higher Weber number, Eq. (14) provides a better match with experiments, showing additionally the importance of viscous bending.


See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevFluids.7.034002 for the applicability of the dynamic contact angle model during steady motion of the contact line. It also includes the surface morphology of the four substrates, multimedia views of the experimental drop shapes on these substrates, a discussion on the dynamic contact angle measurement, mobility tuning parameter and its effect on the mass loss, and the final numerical solutions.


