Electrostatic cloaking of surface structure for dynamic wetting

Satoshi Nita, Minh Do-Quang, Jiayu Wang, Yu-Chung Chen, Yuji Suzuki, Gustav Amberg, Junichiro Shiomı

Dynamic wetting problems are fundamental to understanding the interaction between liquids and solids. Even in a superficially simple experimental situation, such as a droplet spreading over a dry surface, the result may depend not only on the liquid properties but also strongly on the substrate-surface properties; even for macroscopically smooth surfaces, the microscopic geometrical roughness can be important. In addition, because surfaces may often be naturally charged or electric fields are used to manipulate fluids, electric effects are crucial components that influence wetting phenomena. We investigate the interplay between electric forces and surface structures in dynamic wetting. Although surface microstructures can significantly hinder spreading, we find that electrostatics can “cloak” the microstructures, that is, deactivate the hindering. We identify the physics in terms of reduction in contact-line friction, which makes the dynamic wetting inertial force dominant and insensitive to the substrate properties.

INTRODUCTION

From splashing around solid objects in water to the way plants and insects imbibe water and moisture, surface tension and wetting of solid surfaces are key phenomena (1–3). A water surface is itself a habitat for many species that use capillarity and wetting to maintain themselves there (4), and there are classical examples of self-cleaning water-repellent surfaces in nature (1). In technology, the ongoing miniaturization of assays in chemistry and biotechnology (5) has generated strong interest in wetting phenomena as a means to control and manipulate small samples and droplets (6), often realized by using electrostatics (7). Inspired by these technological innovations, droplets colliding with or moving over dry surfaces have recently received considerable attention (8–12).

In many situations, it has been experimentally (13–16) that the fast early spreading is insensitive to the substrate properties and is governed by an inertial time scale (13, 14) for low-viscosity liquids. Recent experiments (17) have shown that the early spreading may have an initial viscous regime even for not very viscous liquids. This regime is replaced by an inertial development once the length scale of the flow near the contact line has increased above a threshold value. For more viscous fluids, this threshold value is never exceeded, and the entire spreading is viscous.

Another line of research discusses dynamic evolution in terms of a nonhydrodynamic energy dissipation at the contact line (18–23), which can be quantified in terms of a contact-line friction parameter μf (in Pa-s) (19)

$$w = \mu_f U^2$$

Here, U is the contact-line speed, and w is the energy dissipation rate at the contact line per unit length. Note that the parameter μf has been discussed for many years and is at the center of molecular kinetic theory (MKT) (18–23). As should be expected, the molecular origin of contact-line friction is complex, in view of the many different ways in which different surfaces, liquids, and liquid interfaces may interact.

However, irrespective of its molecular origin, the parameter μf can be thought of as a material parameter, much as viscosity or a surface tension, which parameterizes the nanoscopic interactions. Values of μf have not been tabulated to any great extent and are not generally available in the literature for practical systems, but they can be determined experimentally from straightforward spreading experiments (23, 24) on flat smooth surfaces.

Because most real surfaces are, to some extent, rough, it is intriguing to know how the properties of mesoscopic roughness will influence the dynamics of spreading. In the study of Wang et al. (24), a series of spreading experiments was carried out on well-controlled microstructured surfaces. Liquids were partially wetting, but such that the spreading was always in the Wenzel state, with liquid filling the pattern as the contact line advances. Under these circumstances, it was found that the nanoscopic interactions quantified in terms of the line friction for a geometrically flat surface (μ(flatt)) could be decoupled from the geometrical properties of the structure and be described as an effective line friction parameter (μf)

$$\mu_f = \mu_{flatt} S$$

where S measures the roughness as the ratio of the total wet surface area to the projected footprint area, and μflatt is the line friction obtained on a (smooth) flat surface of the same material.

Another physics parameter that can influence μf is surface electrostatic effects. With decreasing length scale, electric effects could be of importance also in the absence of external electric effects. On rough surfaces, electric fields may be locally modified by roughness geometry and may either help or hinder the spreading. By applying electric fields (that is, dynamic electrowetting), the sensitivity to these issues can be tested.

Electrowetting on dielectric (EWOD) experiments on a flat surface have shown that application of voltage can speed up spreading (25, 26). Decamps and De Coninck (27) developed a model for this experiment by including the electric contribution to surface energy in their MKT model for spreading. They assumed the contact-line friction to be independent of voltage; thus, the increase in spreading speed in their model is due to the decrease in static contact angle. This model has been successfully compared to experiments in several studies (28–30). These experiments...
were made with water-glycerol mixtures on smooth substrates covered with hydrophobic coatings of polyethylene terephthalate (PET), Teflon, or the like. They are also generally made for voltages below saturation voltage, where the Young-Lippmann equation for the static contact angle holds. Thus, for those systems, and at limited voltages, the assumption that a line friction is independent of voltage is correct.

Here, we investigate how the interplay between surface microstructure and electrostatics determines $\mu_f$ and the spreading speed. We use silicon oxide–covered surfaces that have a different surface chemistry than Teflon or PET and a lower saturation voltage than in the experiments (25, 29–31). This not only provides us with insights into the key physics of dynamic wetting on solid surfaces, which are naturally rough and charged, but also grants us the means to actively control the speed of dynamic wetting.

RESULTS AND DISCUSSION
Dynamic EWOD experiments of 1-mm-diameter droplets were performed on flat substrates and on microstructured surfaces with periodic arrays of pillars with square cross sections with side length $a$ and spacing $b$ (Fig. 1, A to C, and figs. S1 and S2). The pillar height ($h$) is kept constant at 1.3 µm, while $a$ and $b$ vary between 0.3 and 5.3 µm to scan over a range of roughness parameters, $S = 1 + 4ha/(a + b)^2$. We have chosen water as a partially wetting liquid to realize Wenzel wetting throughout the study. The apparent static contact angle on a flat substrate is 45° at 0 V and 34° at 200 V (fig. S4). The variation due to the surface structure is smaller unless the structure wicks the water at the late stage of wetting, where static contact angle is no longer a proper measure of the driving force (see the Supplementary Materials for effects of wicking and hysteresis).

---

Fig. 1. Dynamic electrowetting experiments on microstructured surfaces. (A) Schematic of the dynamic EWOD experiment with microstructured surface. (B and C) Scanning electron microscopy (SEM) images of microstructures with (B) $(a,b) = (1.7,0.3)$ and (C) $(a,b) = (1.1,0.9)$. (D) Droplet shapes during spreading on the flat (first row) and (1.7,0.3) structured surfaces (second row) without electric field and on the flat (third row) and (1.7, 0.3) structured surfaces (fourth row) with an applied voltage of 200 V. The structural indices $(a,b)$ are written in micrometers.
In Fig. 1D, the top two rows show spreading of pure water without the electric field on a flat and on a structured surface. The spreading is significantly slower on the structured surface (second row), and the dynamic contact angle is further away from the equilibrium value, showing that the structure considerably hinders spreading. However, this effect greatly changes when a voltage of 200 V is applied, as shown in the bottom two rows. The most striking observation here is that the structure considerably hinders spreading. However, this effect greatly changes when a voltage of 200 V is applied, as shown in the bottom two rows. The most striking observation here is that the evolution is very similar on the flat (third row) and on the structured (fourth row) surfaces; with the voltage applied, the geometric features of the substrate surface are “cloaked.”

In Fig. 2A, spreading radii \( r \) are shown as functions of time for 0 and 200 V, on all substrates, for pure water. For 0 V, the spreading speed varies significantly with the microstructure, but when 200 V is applied, all the spreading histories coincide. This again demonstrates that the influence of the surface microstructure disappears when the voltage is applied. Figure 2B shows spreading of water with NaCl on the same substrates. The time histories are qualitatively similar to those in Fig. 2A, indicating that cloaking occurs in a similar way with the presence of the electrolyte. However, by further quantifying the average spreading speed (Fig. 2, C and D), at intermediate voltages, the pure water shows a much more gradual increase in spreading speed with voltage, whereas for the electrolyte, the hindrance to spreading from the microstructures is essentially removed already at 50 V.

Figure 3A shows comparisons between the spreading experiments and the Cahn-Hilliard/Navier-Stokes (CHNS) simulations of a flat surface for different values of \( \mu_F \). By choosing an appropriate value of \( \mu_F \), the simulation can reproduce the spreading radius and the droplet shapes (as shown in Fig. 3B) for the time instant when the wetting radius is 0.25 mm. When voltage is applied, the droplet adjacent to the substrate forms a conical tip that touches the substrate at a finite angle (see section S5.3). In the simulations, the initial droplet shape was taken from the experiments, but otherwise, the electric forces are not included. Thus, the good agreement between the simulated and experimental droplet shapes suggests that the effect of the electric field is primarily to alter
the initial shape and to change the process very close to the contact line, that is, the line friction (and the equilibrium contact angle).

Therefore, the value of $\mu_f$ can be thought of as the measure of contact-line friction modified by the electric field. As shown in Fig. 4A, for the pure water case, $\mu_f$ decreases as the voltage increases for all the substrates. The decrease is gradual up to 150 V but essentially levels off at 200 V. With electrolyte (Fig. 4B), the effects of the electric field appear at lower voltages, with most of the decrease in $\mu_f$ taking place between 0 and 50 V. Our finding contrasts with those of previous works (27, 28), which state that values of $\mu_f$ on flat surfaces are insensitive to the

---

**Fig. 3. Evaluation of contact-line friction.** (A) Time histories of spreading radius of a pure water droplet on microstructures with $a = 2.2 \mu m$ and $b = 1.8 \mu m$ compared with those of CHNS simulations, indicating the values of $\mu_f$ to be 0.20, 0.08, and 0.05 Pa·s for voltages of 0, 100, and 200 V, respectively. (B) Snapshots of a pure water droplet spreading on different microstructured surfaces at the spreading radii of 0.25 mm in experiments (left half) and simulations with optimized $\mu_f$ (right half). See section S6 for the comparison at various times.
voltage. We speculate that this may be because the voltages here are high enough to cause static contact angle saturation (fig. S5), which in turn should affect the value of $m_f$. In the study of Decamps and De Coninck (27) with water-glycerol mixtures on Teflon, where the static angle saturation voltage is 1000 V, it is shown that the contact-line friction $m_f$ does significantly decrease with the voltage when it exceeds 700 V. In our experiments, the static angle saturation voltage is about 100 V, which is in the middle of the voltage range that we have explored. Note that we have confirmed that extraction of $\mu_f$ from dynamic contact angles through MKT results in a similar voltage dependence (fig. S20), with a significant decrease at high voltages.

Another observation is that the value of $\mu_f$ satisfies Eq. (2). In Fig. 4 (C and D), we show the ratio $\mu_f/S$ as a function of voltage. For both the pure water and the electrolyte, the curves collapse around the values for the flat substrate, indicating that Eq. (2) is valid even with the presence of electric fields. This suggests that the effect of the electric field on contact-line friction can be considered as local and uniform, and spatial variation induced by the surface structure mainly comes in as a geometrical factor that can be incorporated by scaling with the roughness parameter $S$. To illustrate the validity of the scaling from a microscopic viewpoint, we showed in Fig. 5 the result of a full numerical simulation for a droplet spreading over a two-dimensional (2D) ridged surface, with rectangular ridges of width $a = 2 \mu m$, height $h = 1 \mu m$, and spacing $b = 2 \mu m$. Figure 5A shows the horizontal spreading on the substrate as a function of time. The blue stepwise curve is the actual horizontal position of the contact line, showing how it moves in bursts as it passes over the ridges and troughs. The black smooth curve shows the evolution of the contact line over a flat surface, where the line friction has been increased by a factor of $S = 1 + 2h(a+b) = 1.5$, the ratio of the wet to the projected area for the ridged structure. The perfect coincidence of the two curves again shows that the effect of the surface structure can be parameterized according to Eq. (2).

The mechanism by which structure slows down the spreading can be elucidated by referring to Fig. 5B. This shows the absolute speed $ds/dt$ of the contact line as a function of time. Note that this also shows

---

**Fig. 4. Dependence of contact-line friction on applied voltage.** (A and B) Dependence of the extracted values of $\mu_f$ on applied dc voltage for (A) pure water and (B) water with NaCl. (C and D) Effective line friction $\mu_f$ divided by the geometric factor $S$ according to Eq. (2) for (C) pure water and (D) water with NaCl. The structural indices $(a,b)$ are written in micrometers.
the vertical speed when the contact line is moving up or down along the sides of the ridges. The spreading speed is highly fluctuating, with slow advancement down the forward-facing side of the ridge and fast advancement over the bottom and the rearward face of the next ridge. However, it should be noted that the velocity here is never zero, and the reason it is slow on the forward-facing “adverse” side of the ridge is that the local dynamic contact angle there is not very far from the equilibrium one. On other parts of the structure, it differs substantially from the equilibrium angle, and the driving force for moving the contact line is strong. Because the limiting factor for advancement is then the slowest part of the substrate, it is the presence and relative size of these adverse faces that determine the reduction of contact-line speed. The ratio of the wet to the projected area then naturally appears as a measure of how much microscopic adverse vertical face there is on a projected area of the substrate.

It is worth discussing the current effect in terms of the power-law dependence of the spreading time histories, a phenomenon that has been widely discussed in the literature (14, 32). As shown in Fig. 6A, the time histories of spreading radius can be fitted well by the power-law dependence $Ct^a$, where $t$ is the time. It can be seen that, without the voltage applied (0 V), the structure inhibits wetting, but the exponent $a$ remains the same. When voltage is applied (200 V), the profiles with
and without the structures collapse on top of each other, as discussed earlier (cloaking). At the same time, $\alpha$ significantly increases because of the transition from the spherical to conical tip shape of the droplet, whose $\alpha$ in the complete wetting scenario has been derived in analogy to coalescence as $\sqrt[2]{/3}$ and $\sqrt[3]{/2}$ respectively. As observed in the study of Bird et al. (14), in the case of partial wetting, $\alpha$ becomes smaller than the complete wetting values and approaches them as the contact angle decreases. The values of $\alpha$ are mapped in Fig. 6B. Without the voltage applied, $\alpha$ and its dependence on the contact angle are in line with previous researches of the partial wetting on flat (14) and structured (24) surfaces. From these results, we see that, for cases both with and without electric field, the presence of surface structure does not give rise to abrupt transition in the overall spreading characteristics, which is consistent with the above discussion related to Eq. (2).

We next investigated the mechanism of cloaking. Given the values of $\mu_s$, the consequences of line friction for macroscopic phenomena can be studied. Previous work (24, 33), has shown that in many practical cases, the line friction is actually the factor that limits dynamic spreading speed. The seeming contradiction between experiments that report insensitivity to the substrate properties, and those that claim them to be determining, was resolved when the relative importance of inertia, line friction, and viscous stress was estimated in the flow. This yields a set of parameter regimes and criteria for identifying the factor that limits spreading (24, 33) in terms of the liquid and surface Ohnesorge numbers $Oh = \mu/\sqrt{\rho R T}$ and $Oh_l = \mu_l/\sqrt{\rho R T}$ (where $\mu$ is the liquid viscosity, $\rho$ is the density, $T$ is the surface tension, and $R$ is the initial droplet radius). Note that, in a recent experiment (17), the very viscous liquid spreading results seem to fit nicely in the parameter range of “viscous coalescence analogy” identified by Do-Quang et al. (33), as it is valid for $Oh > 1$ and $Oh_l > Oh$.

In Fig. 7, the parameter map of dominant physics for droplet spreading is constructed in terms of Oh and Ohf. With this, the question of whether the surface properties (particularly, the surface roughness) will be important for spreading can be answered by using the effective line friction according to Eq. (2) in the definition of $Oh_l$. For low-viscosity liquids, such as a millimeter-size droplet of water, Oh is typically $10^{-2}$ or less. Because the line friction $\mu_s$ is often more than 100 times larger than the liquid viscosity (33), the surface Ohnesorge number Ohf can be both greater or smaller than 1. For $Oh_f < 1$, the spreading is inertial and independent of the substrate. In reference to the short initial viscous phase of the spreading described by Mitra et al. (17), we note that, as expressed in terms of our notation, this viscous phase would hold until the ratio of the spreading radius and the initial radius becomes equal to Oh. For a millimeter-size water droplet, this would be quite small and hardly distinguishable in an experiment.

For cases where $Oh_f > 1$, contact-line friction dominates and determines the spreading speed. Among the open marks corresponding to the present experiments, the cases with a voltage of 0 V have Ohf values of $\sim 1$, with the largest Ohf value being 1.95 for the $(a,b) = (1.7,0.3)$ substrate. The higher voltages all have lower values of Ohf with the smallest being 0.053 for 150 V on the flat surface. As the voltage increases, the value of Ohf decreases below 1 because $\mu_{s,flat}$ in Eq. (2) decreases with increasing voltage. We conclude that the spreading becomes insensitive to the substrate because the intrinsic line friction $\mu_{s,flat}$ decreases in the presence of the electric field, in such a way as to reduce the value of Ohf below 1.

In summary, we have shown that the effect of surface structure to hinder dynamic wetting can be deactivated by applying the voltage. Surface structures are cloaked because the line friction of the material itself is reduced with increasing voltage, and this makes the inertial force dominant and the spreading insensitive to the surface structures. Another notable observation is that the influence of the surface structure on line friction can be described through the roughness parameter $S$ even with applied electric field and that the influence of roughness on dynamic electrowetting is precisely the same as for wetting at 0 V. From a practical viewpoint, this allows us to predict the contact-line friction on a structured surface based on the knowledge of the contact-line friction on a flat surface, which can be determined from straightforward spreading experiments. Because the resulting surface Ohnesorge number identifies the importance of the surface structure, this predictability can be useful in designing reproducible and reversible EWOD systems. The findings presented here provide new insights into how dynamic wetting can be sensitive or insensitive to the surface structures and electrostatics that are omnipresent and how surface structures and electrostatics can actively slow down and speed up dynamic wetting in various engineering setups.

**MATERIALS AND METHODS**

**Fabrication of microstructured surfaces**

Pillars with square cross sections were fabricated on the surface of a silicon wafer by using electron beam lithography and non–Bosch etching (34). Figure S1 shows the flow of fabrication. By thermally oxidizing the surface of the samples, uniform insulation layers with a thickness of $286 \pm 2$ nm were formed. We prepared five structures with different pillar side length $a$ and interpillar spacing $b$: $(a,b) = (5.3,4.7), (1.1,2.9), (2.2,1.8), (1.1,0.9)$, and $(1.7,0.3)$ (in micrometers). The pillar height $h$ was fixed at 1.3 μm. The flat surface was also processed in the same way to ensure the same surface chemistry. The surfaces were designed to span a range of surface roughness parameters, $S = 1 + 4ha/(a + b)^3$ (values are listed in Fig. 2, C and D). SEM images of all the fabricated microstructures are
shown in fig. S2. More details on the fabrication processes can be found in section S1.

Selection of the working liquids
We chose ultrapure water and water with NaCl (0.1 mol kg\(^{-1}\)) as working liquids, which have different electric properties and thus result in different Debye lengths of about 100 and 1 nm, respectively (table S2).

Static contact angle measurements
The equilibrium contact angles were measured by fitting a circle to the steady droplet shape. Hysteresis (advancing and receding contact angles) was also measured (see section S3).

Dynamic spreading experiment
Dynamic electrowetting experiments were carried out on the two types of liquid and on the six different surface structures (including the flat surface). For each trial, the desired substrate was placed under a thin needle (33-gauge, 90°) with an outer diameter of 0.21 mm. For electrowetting, the prescribed voltage (0, 50, 100, 150, or 200 V) was applied between the needle and the substrate by a dc power supply. The distance between the needle tip and the substrate was accurately fixed at 1.0 mm, and the droplet was then gradually enlarged by feeding liquid with a syringe pump at 0.04 ml/hour. When the droplet touched the surface, the spreading process was captured and recorded by a Photron FASTCAM SA2 camera at 54,000 frames/s under a sufficiently intensive light. After the experiments, the histories of spreading radius were extracted through image processing (see sections S4.1 and S4.2).

Measurement of average spreading speed
The average spreading speeds were calculated on the basis of the observed time histories of the spreading radii. The average was obtained from the history of spreading from 0.1 to 0.4 mm in radius. As shown in Fig. 2A, the spreading radius is not linear with time, and thus, the values here are no more than the effective ones. However, the dependence on the structures and trends of saturations was confirmed to be insensitive to the choice of the averaging window. Details of the averaging method are summarized in section S4.3.

CHNS simulations
The numerical simulations were carried out by finite element simulations of the coupled CHNS equations in axisymmetry, using adaptively refined and derefined meshes to ensure mesh resolution along the interface and the surface [with the toolbox femLego (35)]. The effect of microstructures was incorporated through the contact-line friction factor \(\mu_c\). The voltage-dependent equilibrium contact in the simulation was set to the value obtained from the experiment for flat substrate at the corresponding voltage. The inputs to the simulation are the liquid equilibrium contact angle and \(\mu_c\) as the boundary conditions. When simulating the spreading with an applied electric field, the initial droplet shape was taken from the experiment, just before the spreading started. More details can be found in section S5. The CHNS simulation was also performed for a droplet spreading over a 2D ridged surface by solving the ridges to confirm the validity of Eq. (2) even with a fluctuation of spreading speed induced by the surface structures. More details can be found in section S8.

REFERENCES AND NOTES

Acknowledgments
Funding: This work was financially supported, in part, by the JSPS (to S.N., J.W., and J.S.), the Swedish Agency for Innovation Systems (to M.D.-Q. and G.A.), and the JST through CREST (to S.N., J.W., and J.S.). Author contributions: J.S. directed and designed the project. S.N., J.W., and J.S. carried out the experiments with support from Y.-C.C. and S.N., G.A., and J.S. contributed to the discussions and wrote the paper. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 11 September 2016
Accepted 27 January 2017
Published 24 February 2017
10.1126/sciadv.1602202

Electrostatic cloaking of surface structure for dynamic wetting
Satoshi Nita, Minh Do-Quang, Jiayu Wang, Yu-Chung Chen, Yuji Suzuki, Gustav Amberg and Junichiro Shiomi

Sci Adv 3 (2), e1602202.
DOI: 10.1126/sciadv.1602202