Dynamics of a nanodroplet under a transmission electron microscope

Fong Yew Leong,1, a) Utkur M. Mirsaidov,2,3 Paul Matsudaira,3,4 and L. Mahadevan5

1A*STAR Institute of High Performance Computing, 1 Fusionopolis Way, Connexis, Singapore 138632
2Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551
3Center for BioImaging Sciences, National University of Singapore, Science Drive 4, Singapore 117543
4MechanoBiology Institute, National University of Singapore, 5A Engineering Drive 1, Singapore 117411; Department of Biological Sciences, National University of Singapore, 14 Science Drive 4, Singapore 117543; and Singapore-MIT Alliance for Research and Technology Center, Science Drive 2, Singapore 117543
5School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA and Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

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We investigate the cyclical stick-slip motion of water nanodroplets on a hydrophilic substrate viewed with and stimulated by a transmission electron microscope. Using a continuum long wave theory, we show how the electrostatic stress imposed by non-uniform charge distribution causes a pinned convex drop to deform into a toroidal shape, with the shape characterized by the competition between the electrostatic stress and the surface tension of the drop, as well as the charge density distribution which follows a Poisson equation. A horizontal gradient in the charge density creates a lateral driving force, which when sufficiently large, overcomes the pinning induced by surface heterogeneities in the substrate disjoining pressure, causing the drop to slide on the substrate via a cyclical stick-slip motion. Our model predicts step-like dynamics in drop displacement and surface area jumps, qualitatively consistent with experimental observations. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4862801]

I. INTRODUCTION

Nanodroplets are critically important in a variety of processes, including chemical1 and biological2 processes, as well as technological ink-jet printing.3 Since the size of a nanodroplet is, by definition, smaller than the wavelength of visible light, optical observation is challenging. Consequently, our understanding of such nanodroplets has been mostly limited to computational models, such as molecular dynamics simulations of interfacial water under atomic force microscopy4 and nanodroplets either spreading5 or dewetting6 on substrates. Other approaches include mesoscopic hydrodynamics7,8 as a form of long-wave (or thin film) models,9 and discrete-continuum hybrid methods.10

Despite the prevalence use of electron microscopy in nanotechnology, there are comparatively few reports on experimental observations of nanodroplets. Habenicht et al.11 used a scanning electron microscope to observe 100–250 nm molten gold nanodroplets under intense laser irradiation, while
50–300 nm heat-nucleated nanobubbles have been observed by scanning probe microscope\textsuperscript{12} and more recently, by transmission electron microscope.\textsuperscript{13} Interestingly, the bubble size is seen to exhibit a strong dependence on the magnification of the electron microscope, suggesting that the electron illumination itself affects the nanodroplet shape, even under normal observational electron intensities used in microscopes. Recently, direct observations of water nanodroplets on a hydrophilic silicon nitride substrate under a transmission electron microscope\textsuperscript{14,15} showed that an ultra-thin film of water (\(\sim 5–20\) nm) on the substrate spontaneously dewets into nanodroplets of size 10–80 nm which adopt a toroidal shape and move in a stick-slip fashion. Here, we explain these observations in terms of a minimal theoretical model.

Direct observation of toroidal shaped nanodroplets under a transmission electron microscope\textsuperscript{14} raises questions about the role of the electron beam on the droplet. First, thermal heating of the bulk water sample occurs via inelastic scattering of high speed electrons,\textsuperscript{16} but an estimated increase in temperature of 1 K\textsuperscript{14} is not likely to affect the physical behavior of water droplets in a significant way. Second, surface stress is generated by high-speed electrons propagating through different media: a phenomenon well-known in light optics, where the stress applied by photons is typically referred to as the optical radiation pressure.\textsuperscript{17–20} However, considering experimental electron flux of \(\sim 100 \text{e}/(\text{Å}^2 \text{s})\) and energies of \(\sim 120\) keV, the estimated radiation stress is about 7 orders of magnitude less than the Laplace pressure of the nanodroplet, and is therefore unlikely to lead to significant deformation of the drop (see the Appendix).

Electric charge can also accumulate within a radiated fluid due to direct impact of primary electrons from the incident beam, or secondary electrons scattered on collision with water molecules, or backscattered electrons reflected off the substrate.\textsuperscript{21} In a conducting fluid, the excess charges will be concentrated on its surface, locally increasing the area of the fluid droplet and modifying its contact angle with known applications in electrowetting;\textsuperscript{22} indeed, an estimated total charge of less than 100 elementary charges is sufficient to overcome the surface energy of the droplet.\textsuperscript{14} Since electric charges tend to accumulate in the neighborhood of the contact line, the electrostatic stress distribution on the drop surface is spatially non-uniform, and recent work has shown that the charge can deform drops statically into a concave shape.\textsuperscript{23,24} The similarity in shapes to those seen in the electron beam and our estimates suggests that the droplet behavior observed under an electron beam may also be explained analogously by electrostatic arguments. Electrostatic stress is known to induce instability\textsuperscript{25,26} and patterning\textsuperscript{27} in thin films of dielectric liquids, as well as leaky dielectric\textsuperscript{28} and conducting liquids.\textsuperscript{29}

The dynamic mobility of drops depends strongly on the chemical or topographical nature of substrate. Specifically, a finite driving force is needed to depin the contact line from the heterogeneity, before bulk motion of the drop can be realized\textsuperscript{30,31} The effect of substrate heterogeneity on drop mobility is significant even in cases where the drop size is larger than the heterogeneity length scale.\textsuperscript{32} This is clearly shown by the observed stick-slip motion of macroscopic drops sliding down inclined chemically heterogeneous substrate.\textsuperscript{33} As for smaller sized drops, Moosavi et al.\textsuperscript{34} numerically investigated the motion of nanodrops on a heterogeneous substrate, but due to the large size of the model defect, potential stick slip dynamics was not revealed. This suggests that heterogeneities of lengths closer to the drop size should be considered in order to address the observed stick-slip motion of nanodroplet.\textsuperscript{14}

Here we investigate the dynamic behavior of charged nanodroplets under the electron microscope using a continuum description of drop shape and lateral mobility on a solid substrate. The stress singularity at the contact line can be alleviated using a slip model,\textsuperscript{35–37} where the no-slip condition is relaxed near the moving contact line; or circumvented by having the droplet rest on a precursor film of uniform thickness.\textsuperscript{38,39} Despite their different functional forms, both slip and precursor models exhibit nearly identical behavior under appropriate conditions, and only diverge significantly for cases where multiple droplet equilibria are involved.\textsuperscript{36} While both approaches are practically feasible, we preferred the precursor film approach for its comparative ease of implementation. To explain the observed intermittent stick-slip motion of the drop, we examine the interplay between lateral forcing due to heterogeneous charge distributions and the heterogeneity of the substrate, which could be either chemical\textsuperscript{38} or topographical\textsuperscript{36} in nature.
II. THEORY

We limit ourselves to a consideration of a two-dimensional drop on an inhomogeneous solid substrate subjected to electron irradiation in the vertical direction. Using the long wave approximation to the Stokes equations and neglecting gravity (since the nanometer length scales under consideration are much smaller than the millimetric capillary length), the thickness of the liquid film $h(x, t)$ evolves according to the equations

$$\partial_t h = -\partial_x \left\{ \frac{h^3}{3\mu} \left[ \partial_x \left( \gamma \partial_x h + \Pi(h, x) + \frac{\sigma_s^2}{2\varepsilon_w} \eta^2(h, x) \right) \right] \right\} \quad (1)$$

where $\gamma$ is the water surface tension, $\mu$ is the dynamic viscosity, $\Pi(h, x)$ is the disjoining pressure, and the last term is the electrostatic stress contribution, where $\sigma_s$ is the reference surface charge density at the contact line, $\eta$ is the ratio of local charge density to the reference value $\sigma_s$, and $\varepsilon_w$ is the electric permittivity of water.

The disjoining pressure term is modeled as a sum of short-ranged repulsive and long-ranged attractive force per unit area, given by

$$\Pi(h, x) = \Pi_0 \left[ \xi(x) \left( \frac{h_x}{h} \right)^n - \left( \frac{h_x}{h} \right)^m \right], \quad (2)$$

where $\Pi_0$ and $(n, m)$ are positive exponent pairs chosen to be (4,3) pair based on Oron et al. and Schwartz and Eley. The coefficient $\xi(x)$ is assumed to affect the short range attractive component of the disjoining pressure. The film is stable at $h = h_x$, where $h_x$ is the thickness of the precursor film for $\xi = 1$. We consider $\xi = 1$ as the default value in both Secs. II and III; other values of $\xi(x)$ are explored subsequently in Sec. IV. Sample profiles of normalized disjoining pressure $\Pi/\Pi_0$ as a function of the drop height $h/h_x$ for various values of $\xi$ are shown in Fig. 1(a).

Although the accumulation and distribution of surface electric charges on a droplet due to electron irradiation are not completely understood, we assume that the electrostatic charging time-scale is fast compared to the viscous time-scale, in which case the charge distribution can be considered quasi-steady. The thin disc approximation follows the long-wave theory and produces a charge density which is nearly constant at the center of the drop and grows sharply towards the drop edge, becoming singular at the drop edge, but remains relatively invariant dynamically.

Here, we model the surface charge distribution as the solution to the Poisson equation, for the charge density of a thin parallel plate capacitor with a gap equivalent to the film height, which tends towards the precursor film thickness far from the drop. We write

$$\partial_x [D(h) \partial_x \eta] = -\frac{1}{\xi^2} \left( \frac{h}{h_x} \right), \quad (3)$$

where $\eta$ is the charge density ratio and $\xi$ is a distribution length constant. Since the contact line is not fixed in space, we apply a far-field Dirichlet boundary condition with $\eta(x \gg R) \rightarrow 1$ and a continuous smoothing function in the form of diffusion constant $D(h) = 1 + \exp [5(3 - h/h_x)]$, such that $D \rightarrow 1$ for $h \gg 3h_x$ (drop interior) and $D \rightarrow \infty$ for $h \ll 3h_x$ (precursor film). The latter limit ensures that the drop always has a bounded charge density whose value is close to the far-field value ($\eta \approx 1$), regardless of its shape or area. The selection of the transition height at $3h_x$ is balanced by the need to capture the full extent of the drop size and ensuring numerical stability. Fig. 1(b) shows sample profiles of charge density ratio $\eta$ (continuous lines) plotted incrementally up to $1/\xi^2 \sim 10^{-3}$ (lowest curve) in steps of $10^{-4}$. These curves are based on an idealized drop profile (broken line), with a peak to base height ratio of $h/h_x \sim 10$.

III. DEFORMATION OF A PINNED NON-SPREADING DROP

For the case of a pinned drop, the drop is not free to slide but it can deform under disjoining and electrostatic stresses. First, we investigate the problem of rigid pinning at a defined boundary so that the drop is non-spreading. We solve the full evolution equation (1) numerically for a drop with initial radius $R$ and height $R/2$, resting on a homogeneous precursor film ($\xi = 1$) of thickness $h_x/R \sim 0.05$,
FIG. 1. Sample profiles of (a) normalized disjoining pressure $\Pi/\Pi_0$ against drop height $h/h_s$ for different constant values of $\xi$ ($\xi = 1$ is the default value), and (b) charge density ratio $\eta$ (continuous lines) plotted incrementally from $1/\xi^2 \sim 10^{-3}$ the inverse-square of the characteristic length scale of the charge distribution (lowest curve) in steps of $10^{-4}$ and based on an idealized drop profile (broken line), with a peak to base height ratio of $h/h_s \sim 10$.

but pinned by a boundary condition $h(x = R) = h_s$ until we reach a steady state. All numerical solutions are carried out on a finite element solver COMSOL (v3.5a) and mesh independence is verified in each case to within 5% accuracy for all dependent variables.

Setting the disjoining pressure as $\Pi_0 h_s/\gamma \sim 5$ without electrostatic stress, i.e., $\sigma_s = 0$, we obtain an equilibrium convex drop shape shown as a bold curve in Fig. 2(a). Based on the height distribution obtained, we solve the Poisson equation for the charge density ratio $\eta$ in space, using the boundary value of $\eta(x = R) = 1$. The corresponding solution is plotted as a bold curve in Fig. 2(b) for the charge distribution parameter $h_s^2/\xi^2 \sim 10^{-3}$. We verify that the depression of the charge density ratio $\Delta \eta \equiv 1 - \eta$ scales linearly with the distribution parameter $h_s^2/\xi^2$. Note that a negative density ratio $\eta < 0$ is physically unrealistic and is not considered.

When electrostatic stress is applied non-uniformly ($\sigma_s, \Delta \eta > 0$), the drop deforms until the electrostatic stress is balanced by the capillary stress and a new steady state is reached. Introducing the electrostatic stress parameter $\sigma_s^2 h_s / 2\varepsilon_w\gamma$, the ratio of the reference electrostatic stress and the capillary stress, in Fig. 2(a), we show that an increase in electrostatic stress parameter causes fluid to be displaced from the drop center outwards towards the pinned end, leading to a concave drop shape. Furthermore, due to coupling between charge density ratio and the drop shape, the charge distribution also shifts to a new steady state. As shown in Fig. 2(b), the corresponding changes in

FIG. 2. (a) Steady shapes of a charged drop pinned at $\alpha R = 1$ and (b) steady distribution of the charge density ratio depending on electrostatic parameter $\sigma_s^2 h_s / 2\varepsilon_w\gamma$. Precursor film is spatially homogeneous ($\xi = 1$) with thickness $h_s/R \sim 0.05$ and disjoining pressure $\Pi_0 h_s/\gamma \sim 5$. 
drop height results in a redistribution of charges from the contact line region towards the drop center, reducing the depression in the charge density ratio $\Delta \eta$.

Next we consider the extent of the height depression at the drop center due to electrostatic stress. As before, the drop is pinned by an imposed boundary condition $h(x = R) = h_0$ on a spatially homogeneous substrate ($\xi = 1$). Here, we define the drop depression as $\Delta h = h^c - h_0$, where $h_0$ is the reference center height where the drop radius is characteristically defined by the imposed boundary radius $R$, here taken at the point when the curvature near $x/R = 1$ changes from concave to convex (refer to Fig. 2(a) the curve for $\sigma^2 s h_0 / 2 \varepsilon_w \gamma \sim 0.145$).

Assuming negligible drop spreading, the electrostatic term $\sigma^2 \eta^2 / 2 \varepsilon_w$ is balanced by the capillary term $\gamma \partial_x h$, so that

$$\frac{\Delta h}{h_0} \sim \left( \frac{\sigma^2 \eta}{2 \varepsilon_w \gamma} \right) E(\Delta \eta^2),$$

where $E(\Delta \eta^2)$ is a charge distribution function of the charge density ratio. To avoid confusion, $h_0$ is used as the reference length scale throughout this work.

Fig. 3(a) shows plots of drop depression $\ln (\Delta h / h_0)$ against the electrostatic stress parameter $\ln (\sigma^2 h^c / 2 \varepsilon_w \gamma)$ for selected values of the distribution parameter $h^2 / \xi^2$. The profiles shown are nearly parallel, shifted only by the independent charge distribution function ($\Delta \eta^2$). For large depression, we see that the depression depth scales linearly with electrostatic stress. For smaller depression, the slope of the curves starts to deviate from linearity, as the electrostatic stress acts to spread the fluid laterally against the pinned ends of the drop thus increasing the apparent contact angle (Fig. 2(a)).

Assuming small drop deformations, the difference in charge density ratio scales with the distribution parameter $\Delta \eta \sim h^2 / \xi^2$. Now we expand and factorize $\Delta \eta^2 \equiv \eta^2_0 - \eta^2 = \Delta \eta (2 - \Delta \eta)$, noting its quadratic form, and rearranging the scaling argument as

$$\frac{2 \varepsilon_w \gamma \Delta h}{\sigma^2 h^2} \sim f \left( \frac{h^2}{\xi^2} \right) + g \left[ \left( \frac{h^2}{\xi^2} \right)^2 \right].$$

We plot $2 \varepsilon_w \gamma \Delta h / \sigma^2 h^2$ against $h^2 / \xi^2$ as shown in Fig. 3(b), which collapsed into a fitted curve using values taken from the linear region in Fig. 3(a). Indeed, the plot shows an approximately linear dependence on the distribution parameter at small values and a quadratic dependence at larger values.
IV. DYNAMICS OF DROPS

Next we consider an unpinned drop which is free to spread and translate on a heterogeneous substrate under electrostatic forcing. Substrate heterogeneity is modeled in the form of spatially varying disjoining pressure.36,39 Typical patterns include two dimensional ridges30–32 and random topographical variations.40,41 Here, we consider a substrate heterogeneity whose length scale is less than the size of the drop,32 and introduce a checkerboard pattern in the form of staggered sinusoidal waveforms in orthogonal x-y directions:

$$\xi(x, y) = 1 - \xi_0 \cos \left( \frac{2\pi}{L_p} x \right) \cos \left( \frac{2\pi}{L_p} y \right),$$

where $\xi_0$ is the amplitude of perturbation and $L_p$ is the heterogeneity wavelength. We solve the full evolution equation (1), coupled with Eqs. (2), (3) and (6), with initial conditions corresponding to steady state solutions without electrostatic forcing.

Under conditions of perfect symmetry, the drop flattens under electrostatic forcing and the drop centroid does not change. However, the electric field generated by excess electrons surrounding the charged drop, the substrate interior, and the electron beam is asymmetrical, leading to gradients in electric potential that create a non-uniform charge distribution. The constant gradient in the charge density ratio imposed by modifying the boundary conditions for the Poisson equation is characterized in terms of a dimensionless charge density gradient $\delta, \eta$, that quantifies the difference in charge density ratio due to the modified boundary conditions, per unit distance normalized by the length scale $R$. This leads to a lateral forcing on the drop that can eventually cause it to slip.

Fig. 4(a) shows the time evolution of the normalized displacement of the drop centroid $(x_c - x_c(0))/R$ as a function of the normalized time $\gamma t/\mu R$, based on assumed values of surface heterogeneity $(\xi_0 = 0.20, L_p/R = 1)$ and the electrostatic stress parameter $(\sigma^2 \delta h_x/2\epsilon_r \mu R \sim 6.4, \delta^2 h_x/\xi_0 \sim 10^{-4})$, for four representative cases. For the smallest charge density gradient, the drop spreads from its original area $A(0)$ to a new steady area $A'$, but does not slip. At some critical charge density gradient $(\delta, \eta \sim 8.4 \times 10^{-3})$, the drop first spreads and later slips and retracts into a new stable position without further slipping. With further increase in charge density gradient, the drop undergoes a continual stick-slip like motion with no stable solution for its centroid displacement. If the lateral forcing is much greater than the resistive heterogeneous substrate, the stick-slip effect disappears and the drop slides at a near constant velocity.

Fig. 4(b) shows the corresponding time evolution of the drop area ratio $A'/A(0)$ against normalized time $\gamma t/\mu R$. In each stick-slip episode, we see that the drop area increases rapidly, as it spreads to contact an attractive “hydrophilic” surface, and retracts to its original area. Characteristics of step-like centroid displacement (Fig. 4(a)) and pulse-like area change (Fig. 4(b)) are in good agreement with experimental observations, as shown in Fig. 5. Furthermore, the fractional area change of the drop during stick-slip (5%–10%) closely matches experimental data (see Fig. S5 of Ref. 14), suggesting that the assumed length scale of the substrate heterogeneity $L_p/R = 1$ is reasonable.

The transition from a static drop to one in motion is typically characterized by the $L^2$ norm,39,30,31 defined here as $\| \delta h \| = \sqrt{\int_A (h(x) - h_c)^2 dA/A}$, where $A$ is the total substrate area $(A \gg R^2)$. Fig. 4(c) shows plots of $L^2$ norm for steady solutions (circles) and time-averaged $L^2$ norm for unsteady solutions (triangles) driven by charge gradient $\delta, \eta$. Vertical dashed lines indicate a depinning transition regime, where steady solution is obtained after a single stick-slip event (square data point). The obtained $L^2$ norm profile compares favorably with the bifurcation analyses for 2D (e.g., Figure 19 of Ref. 39) and 3D depinning (e.g., Figure 2 of Ref. 30) from a hydrophilic line defect. Fig. 4(d) shows a plot of the inverse stick-slip period $T^{-1}$ against charge gradient, which follows a square root dependence (see inset). The power law exponent of one-half suggests that the stick-slip dynamics arose from a Saddle Node Infinite PERiod (SNIPER) type of bifurcation, a result consistent with earlier analyses.39,30,31

We point out that the nanodroplet undergoes stick-slip motion in near cyclical periodicity. However, significant variations in direction and distance covered have been observed by jumps. For comparison, we present in Fig. 6 the numerical simulation of a drop with under base
values of surface heterogeneity ($\xi_0 = 0.20, \frac{L_p}{R} = 1$), electrostatic stress profile ($\sigma_s^2 h_\epsilon \gamma \sim 6.4, \frac{h_s^2 h_\epsilon}{\xi^2} \sim 10^{-4}$), and a charge density gradient of $\delta_n \eta \sim 8.5 \times 10^{-3}$. In both experiments (Fig. 5) and our computational study (Fig. 6), the drops adopt a circular shape (top-down view) before elongating in one direction and re-establishing a new position before the cycle repeats. We see that our model is able to qualitatively reproduce key features of both the torus shape transition and the observed stick-slip events, as a result of the competition between the driving electron beam stress and the resistance from surface heterogeneities.

However, our minimal model does not adequately account for some experimental observations. For example, during the extension of the experimental drop at $t = 1.35$ s (Fig. 5), the depression of the drop does not shift towards the new drop center, but instead remains at its initial position and decays until it is no longer visible by $t = 1.5$ s (Fig. 5). This suggests that there is a time lag between drop motion and redistribution of the charge density, and could result from a modification of our electrostatic model to account for the leaky dielectric effect. Additionally, a constricted bridge separates the original and target site as shown at $t = 1.35$ s (Fig. 5), whereas no such necking behavior is found in the numerical solution. A possible explanation is that as pressure builds up within the drop due to electrostatic stress, some fluid is relieved through a random chemical or topographical defect on the substrate. Therefore, the assumed periodicity may not accurately reflect the actual heterogeneities present in the real substrate. Future work should include an accurate model of electron beam stresses on the drop and elucidating the nanoscale heterogeneity patterns on substrate surfaces.
V. DISCUSSION AND CONCLUSIONS

Using a continuum long wave description, we have shown how electrostatic stresses due to non-uniform charge distribution can deform a pinned nanodroplet into a toroidal shape, and further how a gradient in charge distribution can produce stick-slip motion on a heterogeneous substrate. Our model predicts a step-like response in drop displacement and surface area jumps, in qualitative agreement with experimental observations.

A more quantitative analysis is hindered by uncertainties in estimates of physical properties of interfacial fluid compared to bulk fluid, e.g., the apparent surface tension is expected to decrease sharply with the size of a nanodroplet close to the Tolman length, a relationship supposedly valid for a variety of liquids, although this has not been experimentally measured in the nanometer size range. This is also reflected in the related observation that artificially nucleated nanobubbles on a substrate resist dissolution, despite the extremely large Laplace pressures on the nanometer scale.12

FIG. 5. Stick-slip motion of nanodroplet as observed under a transmission electron microscope. Color map represents relative electron absorbance.

FIG. 6. Simulated stick-slip dynamics of a charged drop under a charge density gradient \( \delta \eta_x \sim 8.5 \times 10^{-3} \). Snapshots of drop height (top row) and charge density ratio (bottom row) are obtained at time points \((\gamma t/\mu)^R\): 0, 105, 140, and 245. Contour lines represent surface heterogeneity in the form of sinusoidally varying disjoining pressure \((\xi_0 = 0.20, \eta_0/R = 1)\). The parameters for electrostatic forcing are \(\sigma_s^2 h_s/2\varepsilon w^2 \sim 6.4\) and \(h_s^2/\xi^2 \sim 10^{-4}\).
Since suspended nanobubbles are apparently more prone to collapse,\textsuperscript{13} it is speculated that the interaction forces should be included in this consideration, a view supported by a recent theoretical development that the Tolman size dependence of surface tension is not unique and it depends on disjoining pressures.\textsuperscript{46}

The present model makes idealized assumptions on the topographical and chemical profile of the heterogeneous substrate, which limits its applicability. For instance, in our analysis of static drop shapes, the artificial rigid pinning is only applicable in the limit of strong contact angle hysteresis due to highly localized asperities or chemical defects. Hence, a more realistic model of the drop shape would necessarily account for weaker forms of pinning, as well as the size and spatial distributions of surface heterogeneities. Topographical information of specific substrates could be obtained or supported through the use of experimental techniques such as Atomic Force Microscopy (AFM).

One considers that the disjoining pressure is dependent on the specific nature of the liquid drop, that is, for instance whether it is solution or suspension.\textsuperscript{47} It would also be interesting to see how other specific properties of the liquid, such as magnetic susceptibility,\textsuperscript{48} would affect its interaction, not only with an electron beam, but other forms of electromagnetic radiation. Our present work has implications for the design of nanofluidic devices involving electronic manipulation of nanodroplets on chemically modified substrates.

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**APPENDIX: OPTICAL RADIATION STRESS**

Optical radiation stress, such as one produced by a focused laser beam, has been shown to be capable of deforming a sessile liquid drop into a torus.\textsuperscript{49} For an electron beam impinging on a water nanodrop, the radiation stress has been estimated to be several orders of magnitude lower than that of the Laplace pressure, so it has been ruled out in favor of the electrostatic stress argument. That said, it could also be argued that if the electron beam were to be focused like an optical laser, the radiation stress would be increased significantly, while the electrostatic charge held by the drop may reach saturation.

The stress is a result of a change in momentum experienced by electrons in the electron beam as they pass between different mediums, in the same manner as photons in optical stretchers.\textsuperscript{50} Following the kinetic view, electrons lose energy and momentum as they pass from air to water.\textsuperscript{51} By conservation of momentum, a localized stress is applied on the air-water interface, thus deforming the drop.\textsuperscript{49} Thereafter, penetrating electrons may be back-scattered on collision with either water or substrate molecules.\textsuperscript{52} These electrons gain momentum upon re-entry to air, so a recoil stress is applied on the air-water interface, thus further depressing the drop.

To quantify this, we introduce an additional optical stress term $\phi(x)$ in the governing lubrication approximation equation as

$$\partial_t h = -\partial_x \left\{ \frac{h^3}{3\mu} \left[ \partial_x (\gamma \partial_{xx} h + \Pi(h, x) + \phi(x)) \right] \right\}.$$  \hspace{1cm} (A1)

Assuming small interfacial slopes, we model the net interfacial stress $\phi(x)$ as the sum of impact and recoil optical stresses due to incident and rebounded electrons,

$$\phi(x) = \frac{\phi_0}{\sqrt{1 + (\partial_x h)^2}} \left[ 1 + \eta_r \exp \left( -\frac{1}{2} \left( \frac{x - x_r}{w} \right)^2 \right) \right],$$  \hspace{1cm} (A2)

where $\phi_0$ is the optical stress due to incident electrons, $\eta_r$ is the fraction of rebounded electrons. Since more electrons rebound towards the focal center of the drop, compared to the periphery, the
rebounded beam is modeled as a Gaussian beam, whose center is \( x_c \) and whose width is \( w \). The Gaussian profile is chosen for its simplicity and its potential relevance to focused optical laser beams.

We approximate the focal center of the electron beam stress by the centroid of the moving drop, \( x_c(t) \), defined as

\[
\frac{\int_{A} (h(t) - h_s) x dA}{\int_{A} (h(t) - h_s) dA},
\]

where \( A \) is the total substrate area \( (A \gg R^2) \). To minimize the computational expense of determining the fluid profile over the entire substrate, we seek an approximation to the centroid of the drop itself, and not the entire substrate. Defining the surface of the drop as a region of fluid \( A' \) whose fluid height is above some specified threshold of the precursor film, and assuming that the film is thin, we neglect the dependence of the centroid on drop height and obtain a computationally tractable approximation,

\[
x_c(t) \approx \frac{\int_{A'(t)} x dA'(t)}{\int_{A'(t)} dA'(t)},
\]

where the drop surface area \( A'(t) \in A \) is defined if \( h(t) > 3h_s \).

We solve the full evolution equation (A1) numerically for a hemispherical drop with initial radius \( R \) and height \( R \), resting on a precursor film of thickness \( h_s/R \sim 0.05 \), pinned at \( x = R \) until steady state is reached. Here we introduce the length scale \( h^* \) representing the equilibrium height of a drop with no optical stress imposed. When optical stress \( (\phi > 0) \) is applied, the drop deforms to a new steady state.

Fig. 7(a) shows that the purely incident component of the optical stress tends to compress and flatten the drop evenly into a pancake shape. Fig. 7(b) shows that the rebounded component of the optical stress creates depression near the focal center of the beam, producing a concave drop shape.

Next we consider the extent of depression created by optical stress. For small drop depressions \( (\partial_x h \ll 1) \), the effect of surface gradient is negligible and the rebounded component of the optical stress term \( (\phi_r) \) approximates to

\[
\phi_r(x) \approx \phi_0 \eta_r g(x),
\]

where \( g(x) \equiv \exp \left[ -(x - x_c/w)^2/2 \right] \) is the Gaussian factor. Assuming that the surface heterogeneity is small compared to drop height \( (\xi_0 h_0 \ll h) \), the imposed optical stress \( (\phi_r) \) is balanced solely by...
FIG. 8. Logarithmic plots of normalized drop depression ($\Delta h/h^*$) against optical stress parameter ($\phi_0 h^*/\gamma$) for small values of Gaussian width ($w/R$).

the capillary term ($\gamma \partial_x h$). Approximating the surface curvature as $\partial_x h \sim \Delta h/(h^*)^2$, we obtain the following linear scaling behavior for small depressions:

$$\frac{\Delta h}{h^*} \sim \left( \frac{\phi_0 h^*/\gamma}{G} \right), \quad (A6)$$

where $\Delta h \equiv h - h^*$ is the depression of drop height, $h^*$ is the equilibrium drop height without optical stress, and $G$ is a function of the gaussian width ($w/R$).

For large depression ($\partial_x h \gg 1$), surface gradient is significant and the rebounded optical stress term is better approximated as

$$\phi_r (x) \approx \frac{\phi_0 h^*/\gamma}{\partial_x h} g(x). \quad (A7)$$

Approximating the gradient as $\partial_x h \sim \Delta h/h^*$, the scaling behavior for large depression is

$$\frac{\Delta h}{h^*} \sim \left( \frac{\phi_0 h^*/\gamma}{G} \right)^{1/2}. \quad (A8)$$

We verify the two scaling relations by solving the full evolution equation (A1) for a drop pinned at $x = R$ with the initial drop height $h^* = R$. Fig. 8 shows a plot of drop depression $\ln(\Delta h/h^*)$ against optical stress parameter $\ln(\phi_0 h^*/\gamma)$ for different values of $w/R$. For small drop depressions, we see that the depression scales linearly with optical stress. Conversely, for large depression depths, the exponent changes to $1/2$.

In addition, we observe that the depression depth is dependent on the Gaussian width $w$ at small values of the width, but this dependence diminishes at larger values of the width. Simply taking derivative of the Gaussian factor with respect to the width, we obtain

$$\partial_w g(x) = \left[ (x - x_c)^2/w^3 \right] g(x),$$

indicating that the width dependence of $g(x)$ scales with $w^{-3}$. For large Gaussian widths ($w \gg (x - x_c)$), the width dependence of $g(x)$ becomes comparatively weak ($\partial_w g(x) \to 0$).


