Adaptive Two Capacitor Model to Describe Slide Electrification in Moving Water Drops

Pravash Bista∗, Amy Z. Stetten, William S.Y Wong, and Hans-Jürgen Butt
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Stefan A. L. Weber†
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany and
Department of Physics, Johannes Gutenberg University, Staudingerweg 10, 55128 Mainz, Germany
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Slide electrification is a spontaneous charge separation between a surface and a sliding drop. Here, we describe this effect in terms of a voltage generated at the three-phase contact line. This voltage moves charges between capacitors, one formed by the drop and one on the surface. By introducing an adaptation of the voltage upon water contact, we can model drop charge experiments on many surfaces, including more exotic ones with drop-rate dependent charge polarity. Thus, the adaptive two capacitor model enables new insights into the molecular details of the charge separation mechanism.

Introduction.—Spontaneous charge-accumulation of moving drops is commonly observed in sliding (slide electrification) [1–3] , micropipetting [4], aerosolizing [5], bouncing [6–11] or squeezing [12] of drops. It is highly debated whether the source of this charging is electron [3, 12, 13] or ion transfer[14–17]. However, the electric double layer (EDL) is thought to play a key role; some of the charge from EDL is left behind on the surface as the contact line moves. Many studies have highlighted the potential of this charge separation process in energy harvesting [18–28] or sensing [29]. Although this phenomenon has been observed qualitatively for years [30][9], a quantitative understanding of the physical process is required to improve the application.

One simple way to study slide electrification is to measure the charge of a drop sliding down a tilted hydrophobic plate[2, 3, 13, 31]. Using this method, we recently found that the charge accumulated by subsequent drops is drop-number dependent[2]. To describe the data, we assumed that surface charges within the droplet are pinned at the receding contact line. The magnitude of pinning depends on the charge already accumulated by the drop and the pre-existing surface charge, e.g. left behind from previous drops. Important parameters to describe the charge separation include a drop-charge-dependent transfer coefficient, α0, the maximum surface charge density within the sliding drop, σL, and the saturation length, λ, that describes where along the slide path this maximum charge is reached. The dissipation of surface charge in the time between drops is described by the surface discharge time (τ). The resulting model provided a qualitative description of the drop charge dependence on drop number and sliding length. Nevertheless, strong discrepancies between experiment and model and recent observations of surfaces that exhibit drop-rate-dependent polarity flipping motivated the development of a conceptually new approach to describe slide electrification.

In this article, we present a circuit model that is capable of accurately describing the behavior of all experimental data, including polarity flipping and other complex charging behavior. We propose that the three-phase contact line acts as a voltage source influenced by the contact time between surface and drop. Our adaptive two-capacitor model reveals characteristic timescales of this wetting-induced voltage adaptation and enables a deeper, more conceptual understanding of charge separation at moving contact lines.

Experimental.— Charge measurements for multiple drops were performed using a tilted plate setup (Figure 1a). The experiments were done under ambient conditions (Temperature: 21 ± 1°C, Humidity: 30-50%). The charge collected by a neutral drop sliding on a neutral hydrophobic surface (perfluorodecyltrichlorosilane, PFOTS) was measured using a sub femto current amplifier (response time: 0.8 ms, FEMTO DDPCA-300, Berlin, Germany, Figure 1b).

FIG. 1. (a) Illustration of experimental setup, (b) current signal measured as the probe electrode discharges the sliding drop, (c) drop-surface contact time tc at a particular point.

The drop charge vs. drop number measured at a slide length of 2 cm showed a rapid decrease form 1.0 nC to 0.4 nC within the first four drops, followed by a slower decrease over the next 50-75 drops to a value of 0.26 nC (figure 2(a)). We performed the same experiment at different slide lengths and plotted the drop charge values as a function of slide length for the 1st, 5th, 20th and 200th
drops, respectively (Fig. 2(b)), which we call drop charge traces. The first drop accumulated 1.7 nC of charge over a characteristic distance $\lambda = 2.7 \pm 0.2$ cm (SI4). For subsequent drops, the saturation length increased due to the fact that the surface was already partially charged from previous drops, reducing the charge transfer. Additionally, the saturation charge decreased to less than 0.5 nC.

So far, we have only considered surfaces where the drop charge is always positive (pure PFOTS). This is not the case on N-(3-trimethoxysilylpropyl)diethylenetriamine (NTDET) mixed PFOTS surfaces (SI1). Drops sliding on these surfaces at an interval of $\Delta t = 2$ s rapidly decrease in charge from +330 pC, down through 0 pC, eventually saturating at -55 pC for the 200th drop (Fig. 2(c)). This negative drop charge can be explained by amine groups on the NTDET molecules, which protonate upon water contact. Surprisingly, increasing $\Delta t$ to 4 s flips the drop charge back to nearly 0 pC, and to +70 pC for $\Delta t = 16$ s. Returning $\Delta t$ to 2 s at drop number 800 flips the drop charge back to the original negative saturation value of -55 pC. This drop-rate-dependent polarity-switching is impossible to explain within the existing drop charge model.

To explain these experimental observations, we developed a new model for slide electrification based on a circuit diagram, which allows identification of the microscopic physical processes leading to drop charging. The observed dependence of the drop charge polarity on the drop rate for the NTDET:PFOTS surface suggests that some surface relaxation takes place in the time between drops. We therefore introduce the concept of surface adaptation upon drop contact. This adaptive two-capacitor model allows us to identically recreate the original model using conceptually simple, physically measurable observables, and it allows adaptation in various parameters to account for the missing slowly-changing effects with drop number.

The Adaptive Two Capacitor (A2C) Model. — Conceptually, slide electrification can be understood in terms of a voltage, $U_{cl}$, generated by the moving three-phase contact line (circuit diagram in 3(a)). The charges at the solid-liquid interface within the drop partially remain on the surface and the mobile counter charges are pulled by the moving drop. Therefore, the voltage can be understood as the electrostatic work that the moving contact line performs on the charges inside the drop. In our model, we assume that the contact line voltage moves charges between surface and drop. We furthermore assume that the charging is limited by the drop- and surface capacitance, respectively. Experimentally, the contact line voltage manifests as the saturation drop voltage ($U_{cl} = U_D(x = \infty)$) reached by the sliding drop after long distances. It can be measured with a high input impedance oscilloscope and is on the order of 3-7 V for our samples (a simple estimation on the contact line voltage is given in chapter 5.1 in the SI).

At time zero for the first drop, both the drop and the surface are neutral. The charging is then limited by available surface charges under the three-phase contact line, i.e., by the surface capacitance. The maximum charging rate $I_{max}$ occurs just as the drop begins to slide and is coupled to the velocity, $v_D$, and the width, $w$, of the droplet:

$$I_{max} = \frac{dQ_D}{dt} = U_{cl}c_wv_D = \frac{U_{cl}}{R_{int}},$$

(1)

where $Q_D$ is drop charge, and $R_{int} = (c_wv_D)^{-1}$ is the internal resistance of the voltage source. As the drop continues to slide, it accumulates a charge, which generates a drop voltage $U_D = Q_D/C_D$. Thus, still assuming the neutral surface seen by the first drop, we can write:

$$U_{cl} = U_D + R_{int}I = \frac{Q_D}{C_D} + R_{int}\frac{dQ_D}{dt}$$

(2)

$$dQ_D = (U_{cl} - U_D)c_wdx$$

(3)

In the last step, we used the definition for $R_{int}$ and $v_D = dx/dt$. Equation (3) can be rearranged into a familiar form using $\lambda := C_D/c_w$:

$$\frac{dQ_D}{dx} = \frac{Q_D}{\lambda} - c_wU_{cl}w$$

(4)

Solving eq(4) yields the charge as function of sliding distance for the first drop. It saturates exponentially.
FIG. 3. (a) Circuit diagram explaining slide electrification. The moving three-phase-contact line acts as a voltage source with a characteristic voltage, $U_{CL}$, and internal resistance, $R_{int}$, driving charges from the surface to the drop. (b) Graphical representation of surface adaptation and relaxation. Here, $U_w$ and $U_d$ are the maximum and minimum three-phase contact line voltages. $t_w$ and $t_d$ are the characteristic surface adaptation and relaxation time, respectively, $t_c$ is the drop-surface contact time, and $\Delta t$ is drop interval.

with distance, corresponding to the charge on a capacitor saturating with time following a voltage step:

$$Q_D^n(x) = -c_sU_{cl}w\lambda \left[1 - \exp\left(-\frac{x}{\lambda}\right)\right]$$  \hspace{1cm} (5)

So far, we have ignored the effect of the surface charge density ($\sigma(x)$), which also generates a voltage $U_s(x) = \sigma(x)/c_s$. For the first drop on a neutral surface ($\sigma_0 = 0$), $U_s$ is zero. For a series of drops sliding down the surface at constant interval $\Delta t$, we must include the surface charge (for $n$th drop $\sigma^n(x)$) that was left behind by the previous drops:

$$\sigma^n(x) = c_sU^n_s(x) = \sigma^{n-1}(x) \exp(-\Delta t/\tau)$$  \hspace{1cm} (6)

In the time between two drops, $\Delta t$, the surface charge will gradually dissipate, e.g. through non-zero substrate or surface conductivity [32–35] or by neutralization through ionic species in the air [36]. As a first-order approximation, we assume that these processes introduce an effective surface resistance, $dR$ on each surface element $dA$, leading to an exponentially decaying surface charge with characteristic decay time $\tau = dRc_sdA$.

Including $U^n_s(x)$ in equation (2) yields the following differential equations for the $n$th drop:

$$dQ^n = (U_{cl} - U^n_D(x) - U^n_s(x))c_s wd\hspace{1cm}x$$  \hspace{1cm} (7)

$$\Delta \sigma^n(x) = -\frac{dQ}{wdx} = -(U_{cl} - U^n_D(x) - U^n_s(x))c_s$$  \hspace{1cm} (8)

Here, $\Delta \sigma^n(x)$ denotes the change in surface charge caused by the $n$-th drop. We call equations (7) and (8) the two capacitor model for slide electrification.

To explain the slower saturation in the measured drop charge theory, we suggest that one or more of the parameters controlling drop charge are changing with time. The conceptual simplicity of the two capacitor model makes the possible parameters clear: surface capacitance $c_s$, surface discharge time $\tau$, or contact line voltage $U_{cl}$.

A change in surface properties upon contact with a liquid drop is called surface adaptation [37–39]. We therefore call this model the adaptive two capacitor model (A2C model). This adaptation could be occurring in a number of ways. The surface capacitance and contact line voltage might adapt due to slow dielectric relaxation in the substrate, chemical changes or alteration of surface groups under hydration. The surface discharge time might adapt due to a change in surface conductivity. All three of these quantities could adapt with exposure to water or to greater numbers of drops seen by the surface.

The adaptation and relaxation of the surface in terms of a model parameter is graphically illustrated in figure 3(b). Upon drop-surface contact with contact time ($t_c$), $U_{cl}$ will change within a characteristic time $t_w$ from the dry state value $U_d$ towards the equilibrium value in the wet state, $U_w$. When the drop has passed, the surface will relax back to the dry state within a characteristic time $t_d$. The timescales for adaptation and relaxation can be different. We want to emphasize that $t_d$ is fundamentally different from the surface discharge time ($\tau$), which describes the neutralization of the charged surface. In contrast, $t_c$ describes the molecular/physical relaxation of the surface after the drop-surface contact. To calculate the voltage $U^n$ for the $n$-th drop in a succession of drops we can use the following recursive equation:

$$U_n = U_w + (U_d - U_w)e^{(-\Delta t/\tau)} - (U_d - U_{n-1})\exp\left(-\frac{\tau}{t_d}\right).$$  \hspace{1cm} (9)

Using this recursion, we calculate an analytical solution for steady-state drops (i.e. for large drop numbers $n$; complete derivation in the SI):

$$U_{\infty} = U_w + (U_d - U_w)\left[1 - \frac{e^{(-\Delta t/\tau)} - 1}{e^{(-\Delta t/\tau_d)} - 1}\right]$$  \hspace{1cm} (10)

To obtain the saturation parameter values $U_w$ and $U_d$ and the time constants $t_w$ and $t_d$, we can fit this equation to drop voltage at long slide length with varying time between drops ($\Delta t$).

To determine which of the three possible adaptation variables has the largest effect on drop charging, we analyzed the experimental data allowing for A2C model adaptation separately in each variable. We implemented a numerical simulation program based on equations 7 and 8 together with the adaptation equation 9 (see SI, source-code available as supplementary material). Adaptation
FIG. 4. (a) Measured drop charge on PFOTS (dots) and numerical simulation (lines) using the $U_{cl}$ adaptive two capacitor model. Parameters used for the simulation are $\lambda = 2.7$ cm, $U_{dry} = 6.6$ V, $\sigma_0 = -14 \frac{\mu C}{\text{m}^2}$, $C_s = 2.4 \frac{\mu F}{\text{m}^2}$, $\tau = 1.6$ s, $U_w = 1.0$ V, $T_d = 150$ s and $T_w = 0.12$ s. (b) Simulated drop charge traces (lines) of the first, 5th, 20th, and 200th drops plotted with measured drop charge traces (dots). (c) Steady-state three-phase contact line voltage vs. drop interval ($\Delta t$), and the fit with the analytical solution (10) for $U_{cl}$ vs. $\Delta t$.

in the contact line voltage ($U_{cl}$) was able to produce both a slower decrease in drop charge with drop number and a drop-number dependence of the saturation charge at long slide lengths. However, adaptation in surface capacitance and surface discharge time could not account for the two missing behaviors with drop number (SI T).

To get the parameters for the A2C model, we measured the drop charge with increasing time between drops, $\Delta t$, at 15 cm slide length. We converted the drop charge to voltage using a drop capacitance of $C_D \approx 0.3 nF$ [2] (Figure 4(c)). We chose this distance because it is longer than the charge saturation length, $\lambda = 2.7 \pm 0.2$ cm, ensuring that the drops are fully charged and the measured drop voltage corresponds to $U_{cl}$. From the discharge current curves, we estimated the contact time of the drop with the surface to be roughly $t_c \approx 20$ ms (Figure 1(c) and SI). Using this contact time, we fit eq(9) to the saturated drop voltage as a function of $\Delta t$, and obtained the A2C model parameters as follows: $U_d = 6.6 \pm 0.3$ V and $U_w \approx 0.9 \pm 0.2$ V; $t_w = 0.11 \pm 0.01$ s and $t_d = 152 \pm 13$ s. Using these parameters and equation above 9, we calculated $U_{cl}(n)$ and simulated the drop charge versus drop number and slide length.

Figure 4(a) compares the measured (dots) and A2C simulated (lines) drop charge. The simulated data reproduces the slower decay of the drop charge over the first 50 drops and the steady-state value at high drop number for different slide lengths. Moreover, the A2C simulated drop traces for the $1^{st}$, $5^{th}$, $20^{th}$, and $200^{th}$ drops agree with the experimentally observed behavior showing drop-number-dependent saturation charge (Figure 4(b)).

Deviations from the model could be explained by variations in the drop contact time coming from slight changes in drop path or variations in velocity, either caused because the drop not yet reaching terminal velocity, or by electrostatic forces between the drop and surface charges[40]. Furthermore, the observed behavior might be caused by more complex adaptation processes involving several time scales or an additional adaptation in one of the other parameters. Nevertheless, we found a good match between data and the A2C model using contact line voltage adaptation, suggesting that $U_{cl}$ is the most relevant parameter.

The transition into the wet state as obtained from the fitting takes about 100 ms. The relaxation time of an electrostatic double layer is usually much faster than a millisecond. Molecular re-arrangement at the surface, e.g. caused by swelling, is unlikely, because the PFOTS structure is very thin, suggesting faster timescales. One processes that could happen on these timescales would be ion migration in the glass substrate, driven by strong electric fields close to the surface. These timescales give us an indication of which directions would likely yield results in future research.

One particularly exciting new aspect of the A2C model, is that it is able to describe the bipolar charging behavior on mixed surfaces (NTDET:PFOTS) (Fig.2C). This can be achieved by using a dry- and wet-state contact line voltages with opposite polarity. Here we used contact line voltages of $U_d = 2$ V and $U_w = -0.6$ V, respectively, and wetting and drying time constants of $t_w = 0.1 s$ and $t_d = 180 s$, respectively. Using these parameters, we are able to reproduce the polarity flip with increasing the drop interval very precisely (blue line Fig.2(c)). Fully explaining the physical and chemical processes within this experiment is beyond the scope of this paper, however it is likely that the negative drop charge is caused by the change in surface charge of NTDET upon exposure to water.

Summary.-We introduced a slide electrification model that is able to precisely describe experimentally observed drop charges of series of water drops atop hydrophobic surfaces. We propose that the charge separation between capacitors formed by the drop, $C_D$, and surface, $C_s$, is driven by a voltage, $U_{cl}$, generated by the three-phase contact line. The charging of a succession of drops is influenced by residual surface charges that dissipate from the surface on a timescale of $\tau$. To explain gradual changes in the drop charge over the first 10-50 drops, we additionally suggest that $U_{cl}$ changes over time. In particular, we suggest that $U_{cl}$ changes toward $U_w$ within a characteristic time $t_w$ whenever the surface is in con-
tact with water, and relaxes back to $U_d$ within a characteristic time $t_d$ between drops. The inclusion of these dynamic processes allows us to fully model experimental data at multiple drop rates and slide length using a single set of parameters. Further exploration shows that the model even holds for more complicated charge separation scenarios of surfaces with bipolar charging behavior. The adaptation timescales provided through an analysis based on the two capacitor model will open a door to a more detailed investigation of the underlying physico-chemical processes involved. This will ultimately lead to a deeper understanding of the molecular origin and the fundamental limitations of slide electrification.

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*: pravash@mpip-mainz.mpg.de  
†: webers@mpip-mainz.mpg.de

[1] K. Yatsuzuka, Y. Mizuno, and K. Asano, Electrification phenomena of pure water droplets dripping and sliding on a polymer surface, Journal of electrostatics 32, 157 (1994).
[2] A. Z. Stetten, D. S. Golovko, S. A. Weber, and H.-J. Butt, Slide electrification: charging of surfaces by moving water drops, Soft matter 15, 8667 (2019).
[3] S. Lin, L. Xu, A. C. Wang, and Z. L. Wang, Quantifying electron-transfer in liquid-solid contact electrification and the formation of electric double-layer, Nature communications 11, 1 (2020).
[4] D. Choi, H. Lee, I. S. Kang, G. Lim, D. S. Kim, K. H. Kang, et al., Spontaneous electrical charging of droplets by conventional pipetting, Scientific reports 3, 2037 (2013).
[5] P. C. L. Kwok, S. J. Trietsch, M. Kumon, and H.-K. Chan, Electrostatic charge characteristics of jet nebulized aerosols, Journal of aerosol medicine and pulmonary drug delivery 23, 149 (2010).
[6] D. Chate and A. Kamra, Charge separation associated with splashing of water drops on solid surfaces, Atmospheric research 29, 115 (1993).
[7] P. Lenard, Über die electricität der wasserfärre, Ann. Phys 46, 584 (1892).
[8] J. Thomson, Xxxi. on the electricity of drops, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 37, 341 (1894).
[9] Z. Levin and P. V. Hobbs, Splashing of water drops on solid and wetted surfaces: hydrodynamics and charge separation, Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences 269, 555 (1971).
[10] N. Miljkovic, D. J. Preston, R. Enright, and E. N. Wang, Electrostatic charging of jumping droplets, Nature Communications 4, 1 (2013).
[11] D. I. Diaz, D. G. González, P. Bista, S. Weber, H.-J. Butt, A. Z. Stetten, and M. Kappl, Charging of impacting drops onto superhydrophobic surfaces, Soft Matter 6, 3347 (2015).
[22] L. E. Helseth, A water droplet-powered sensor based on charge transfer to a flow-through front surface electrode, Nano Energy 73, 104809 (2020).
[23] Y. Wang, S. Gao, W. Xu, and Z. Wang, Nanogenerators with superwetting surfaces for harvesting water/liquid energy, Advanced Functional Materials 30, 1908252 (2020).
[24] L. Zhao, L. Liu, X. Yang, H. Hong, Q. Yang, J. Wang, and Q. Tang, Cumulative charging behavior of water droplet driven freestanding triboelectric nanogenerators toward hydrodynamic energy harvesting, Journal of Materials Chemistry A 8, 7880 (2020).
[25] W. Xu, H. Zheng, Y. Liu, X. Zhou, C. Zhang, Y. Song, X. Deng, M. Leung, Z. Yang, R. X. Xu, et al., A droplet-based electricity generator with high instantaneous power density, Nature 578, 392 (2020).
[26] N. Miljkovic, D. J. Preston, R. Enright, and E. N. Wang, Jumping-droplet electrostatic energy harvesting, Applied Physics Letters 105, 013111 (2014).
[27] J. Niu, W. Xu, K. Tian, G. He, Z. Huang, and Q. Wang, Triboelectric energy harvesting of the superhydrophobic coating from dropping water, Polymers 12, 1936 (2020).
[28] L. Yang, Y. Wang, Y. Guo, W. Zhang, and Z. Zhao, Robust working mechanism of water droplet-driven triboelectric nanogenerator: Triboelectric output versus dynamic motion of water droplet, Advanced Materials Interfaces 6, 1901547 (2019).
[29] L. Helseth, Interdigitated electrodes based on liquid metal encapsulated in elastomer as capacitive sensors and triboelectric nanogenerators, Nano Energy 50, 266 (2018).
[30] I. Langmuir, Surface electrification due to the recession of aqueous solutions from hydrophobic surfaces, Journal of the American Chemical Society 60, 1190 (1938).
[31] L. E. Helseth, The influence of microscale surface roughness on water-droplet contact electrification, Langmuir 35, 8268 (2019).
[32] C. Moore and B. Vonnegut, Measurements of the electrical conductivities of air over hot water, Journal of Atmospheric Sciences 45, 885 (1988).
[33] V. T. Paiva, L. P. Santos, D. S. da Silva, T. A. Burgo, and F. Galemebeck, Conduction and excess charge in silicate glass/air interfaces, Langmuir 35, 7703 (2019).
[34] A. Soffer and M. Folman, Surface conductivity and conduction mechanisms on adsorption of vapours on silica, Transactions of the Faraday Society 62, 3559 (1966).
[35] R. Umezawa, M. Katsura, and S. Nakashima, Electrical conductivity at surfaces of silica nanoparticles with adsorbed water at various relative humidities, e-Journal of Surface Science and Nanotechnology 16, 376 (2018).
[36] J. North, Cosmos: an illustrated history of astronomy and cosmology (University of Chicago Press, 2008) Chap. 19.
[37] H.-J. Butt, R. Berger, W. Steffen, D. Vollmer, and S. A. L. Weber, Adaptive wetting—adaptation in wetting, Langmuir 34, 11292 (2018).
[38] W. S. Wong, L. Hauer, A. Naga, A. Kaltbeitzel, P. Baumii, R. Berger, M. D, Acunzi, D. Vollmer, and H.-J. Butt, Adaptive wetting of polydimethylsiloxane, Langmuir 36, 7236 (2020).
[39] X. Li, S. Silge, A. Saal, G. Kircher, K. Koynov, R. Berger, and H.-J. Butt, Adaptation of a styrene–acrylic acid copolymer surface to water, Langmuir 37, 1571 (2021).
[40] X. Li, P. Bista, A. Stetten, H. Bonart, M. Schür, S. Hardt, F. Bodziony, H. Marschall, A. Saal, X. Deng, et al., Drop race: How electrostatic forces influence drop motion, https://doi.org/10.21203/rs.3.rs-737950/v1 (2021).
Adaptive Two Capacitor Model to Describe Slide Electrification in Moving Water Drops

Supplemental Information

Pravash Bista\(^1\)*, Amy Z. Stetten\(^1\), William S.Y. Wong\(^1\), Hans-Jürgen Butt\(^1\), and Stefan A.L. Weber\(^1,2\),†

\(^1\) Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
\(^2\) Johannes Gutenberg University, Department of Physics, Staudingerweg 10, 55128 Mainz, Germany

*: pravash@mpip-mainz.mpg.de
†: webers@mpip-mainz.mpg.de

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1 Sample Preparation

To prepare the sample, we used a long glass slide (200 x 20 x 3) mm\(^3\) (window glass, prepared by a glass mechanic at Max-Planck-Institut for Polymer research). We used chemical vapor deposition to coat the glass substrates with perfluorodecyltrichlorosilane (PFOTS) (Sigma-Aldrich Chemie GmbH, Eschenstrasse 5, Germany). Before coating the substrates, they were cleaned with acetone and ethanol and treated in an oxygen plasma cleaner for 10 minutes at 100% power (Diener Electronics Plasma surface: Femto BLS, Ebgausen, Germany), to remove all organic compounds from the surface. After this, we placed the substrates and a 1 mL vial of PFOTS with a magnetic stir bar in a vacuum desiccator. A pump evacuated the desiccator to a pressure of 100 mbar, which vaporized the PFOTS. Then the chamber was left on a stir plate for 30 minutes to complete the silanization process. The motion of the magnetic stir bar provided airflow within the desiccator for more homogeneous deposition. The PFOTS surface has advancing and receding contact angles of (107 ± 2)\(^\circ\) and (89 ± 3)\(^\circ\), respectively.

To synthesize mixed hydrophobic surface (NTDET+PFOTS), PFOTS layer coated substrates were evacuated without any silane for 30 minutes in vacuum before the next step. The secondary layer is synthesized by co-functionalization of N-(3-trimethoxysilylpropyl)diethylenetriamine, NTDET. A fresh desiccator was used to avoid cross-contamination. NTDET was deposited (1 mL) at ca. 11 cm from the center. The pressure was then pumped down to ca. 50 mbar and kept for 6 hours. After functionalization, the glass substrates were kept under 50 mbar for 30 minutes without any silane to vent unreacted silanes. The coated glass substrates were then left to equilibrate with the ambient air environment (T = 20 °C, humidity = 30-70 %) for 5 days (120 h) before testing. The NTDET+PFOTS hydrophobic surface has advancing and receding contact angles of (113 ± 4)\(^\circ\) and (91 ± 4)\(^\circ\), respectively.

2 Experimental

Our experiments is shown in figure 1(A). The experiments were done under ambient conditions (Temperature : 21 ± 1°C, Humidity: 30-50%) where minimal influence of humidity and temperature has...
Figure 1: (A) Illustration of experimental setup, (B) current signal measured as the probe electrode discharges the sliding drop, (C) drop-surface contact time $t_c$, and (D) drop charge estimated by integrating the initial peak of around 2 ms.

been reported [6]. Here, we placed perfluorodecyltrichlorosilane (PFOTS) hydrophobic samples prepared using Chemical vapor deposition method on an inclined grounded plate with a tilt angle of 50°. We neutralized any surface charge using an ionizing air blower (IAB) (Simco-Ion Aerostat PC Ionizing air blower) for 5 minutes (air ion concentration to 300000 ions/cm$^3$, Ionometer, IMS06v3.66687 Wadern, Germany), and waited some minutes until ions in the air dissipated and an equilibrium air ion concentration (200-400 ions/cm$^3$) was reached. Next, a peristaltic pump (Gilson Minipuls 3, Wisconsin, USA) was used to pump deionized water of volume 45 µL (Sartorius Arium Pro VF, 18.2 MΩ resistivity, Germany) into the grounded metallic syringe (diameter 2 mm). We chose a drop interval $\Delta t = 2.1 \pm 0.2$ s between drops for all experiments (unless otherwise noted). The drops fell from the height of (0.5 ± 0.2) cm and slid for (1.0 ± 0.2) cm to a grounding electrode, where they were neutralized to begin the slide electrification experiment. This grounding electrode marked the start point of the slide experiment ($L = 0$). The drop then slid a known distance ($L = 2$ cm) to a probe electrode. A laser trigger system consisting of a 657 nm laser diode (CPS186, Thorlabs, United States) and a laser detector was placed 1cm before the probe electrode and served as a trigger for data acquisition. When the charged droplet touched the probe electrode, a current signal as shown in figure 1B was measured using a sub femto current amplifier (response time: 0.8 ms, FEMTO DDPCA-300, Berlin, Germany). We used a national instrument data acquisition board (NI USB-6366 x-Series) to record the current signal. To calculate
the accumulated drop charge over a chosen slide length, we integrated the initial peak of the measured current signal, which was within the first 2.5 ms of drop probe contact.

3 Numerical Simulation

Both the original slide electrification model proposed in [7] and our newly developed Two Capacitor Model fundamentally consist of a set of coupled differential equations for drop and surface charge. In the case of the original model for sliding drops with time interval $\Delta t$, the drop charge $Q_n$ and surface charge density $\sigma_n$ for the n-th drop are given by

$$dQ_n(x) = w(\sigma^{n-1}(x)exp(-\Delta t/\tau) - \alpha(Q_n(x))\sigma_L)dx$$

$$\sigma_n(x) = \sigma_{n-1}(x)exp(-\Delta t/\tau) - \frac{1}{w} \frac{dQ_n(x)}{dx},$$

where $w$ is the drop width and $\alpha(Q_n(x)) = \alpha_0 - \alpha_1 Q_n(x)$ is the transfer coefficient (dependent on drop charge). The decay rate, $\tau$, takes into account how quickly the surface charge left behind by the drop neutralizes, e.g. via atmospheric ions and cosmic rays [3] or via mobile electrons and ions on the substrate[2, 4, 5, 8]. For the first drop, the surface is neutral, thus $\sigma_0(x) = 0$. Within the new two capacitor model described in the main part of this manuscript, substituting the the contact line voltage with $U_{cl} = -\alpha_0/\alpha_1C_D$, the drop voltage with $U_D^n(x) = Q_D^n/C_D$ and the surface voltage with $U_s^n(x) = \sigma^n(x)/c_s$, we can obtain identical differential equations to equations 1 and 2.

Based on this model, a set of analytical solutions for the first and steady-state drops can be derived[7]. Due to the recursive nature of equations 1 and 2, however, analytical solutions for every drop in a series of drops are difficult to calculate and yield complicated expressions. Furhtermore, experiments with varying drop rate are impossible to simulate this way. Therefore, we wrote a simulation program in Igor Pro (wavemetrics) that solves equations 1 and 2 numerically, generating data sets of drop- and surface charge as a function of distance and drop number. This simulation program can be easily modified to introduce adaptation behavior in a number of variables, which will prove useful in going beyond the limitations of the original slide electrification model. An example of such simulation for PFOTS-NTDET surface (mentioned in the main manuscript) is shown in figure 2. The figure shows the change in drop and surface charge with changing slide length, the time between drop $\Delta t$ and drop number.

Figure 2: (A) Color plot drop charge, (B) color plot surface charge density generated using numerical simulation simulation.
4 Original slide electrification model

4.1 Drop traces measurement and Fit for $\lambda$, $\tau$ calculation, Capacitance measurement, and simulated $U_{cl}$ adaptation.

Figure 3A shows the curve fits on $Q_1$ and $Q_{200}$ to estimate $\lambda$ and $\sigma$, respectively. In Figure 3B, we show surface capacitance measurement where we used a defined voltage impulse (3 V) in a defined area (0.5 cm²). Figure 3C and D, show decrease in decay length and $U_{cl}$ with increasing $\Delta t$, and drop number, respectively.

Figure 3: (A) Simultaneous fit of the drop charge traces. The model parameters obtained are $\lambda = 2.7 \pm 0.2$ cm, $\lambda_{200} = 3.3 \pm 0.2$ cm, $\tau = 1.6 \pm 0.2$s, $\sigma_{Q_1} = 14 \pm 1 \mu C/m^2$, and $\sigma_{Q_{200}} = 3.0 \pm 0.2 \mu C/m^2$. (B) Capacitance per unit area does not change with voltage pulse. (C) Decrease in decay length as a function of the ratio between drop interval time, $\Delta t$, and surface charge decay time, $\tau$. (D) $U_{cl}$ adaptation with a increasing drop number.

Estimation of $\tau$

The gradual charging and discharging of the hydrophobic surface by a succession of drops leads to a slower charging for later drops. After a large number of drops, the charging pattern $Q_D^\infty(x)$ reaches a
steady state which is given by:

\[ Q^\infty_D(x) = -U_{cl} c_s w \lambda \left\{ 1 - \exp \left[ -\frac{x}{\lambda} \left( 1 - \exp \left( -\frac{\Delta t}{\tau} \right) \right) \right] \right\} \]

Comparing this equation for the infinite drop to equation \( Q^1_D(x) = -c_s U_{cl} w \lambda [1 - \exp \left( -\frac{x}{\lambda} \right)] \) for the first drop shows that the charging patterns converge towards a similar exponential shape with an increased decay length for higher drop number \( \lambda_{200} = \lambda/(1 - \exp(-\Delta t/\tau)) \). For shorter drop interval times \( \Delta t \), the saturated decay length \( \lambda_{200} \) becomes longer, whereas it approaches \( \lambda \) for longer \( \Delta t \) times (3(A)). To estimate the surface discharge time \( \tau \), we used the surface charge decay length \( \lambda \) and \( \lambda_{200} \) obtained from the fit (3 C) in the following equation:

\[ \tau = \frac{-\Delta t}{\log (1 - \frac{\lambda_{200}}{\lambda})} \]

4.2 Limitations of the original slide electrification model

We fitted the original slide electrification model to our experimental data to demonstrate its possibilities and limitations. In particular, we obtained the transfer coefficient \( (\alpha_0) \) and the surface charge density within the drop, \( (\sigma_L) \), from fitting the charge saturation length, \( \lambda \), to the drop traces in 4(B). Here, we found that fitting drop traces for different drop numbers yields different fit parameters. Therefore, the expected drop charge vs. drop number dependence expected from fitting the traces of first drops \( (M_1) \) and 200th \( (M_\infty) \) drops show huge deviations from each other and from the experimental data (solid lines in Figure 4(A), SI Figure 3A). For a given set of parameters, the predicted range of charges between the first and the last drop is within the shaded region underneath the model curves in Figure 4(B). This predicted range of drop charges is much smaller than what we observe experimentally, suggesting that some important effects are not captured by the model.
5 Three phase contact line voltage, $U_{Cl}$

5.1 Possible physical origins of $U_{Cl}$

A large part of the voltage difference between the drop and the charged surface behind can be explained by the removal of the dielectric water that surrounds the surface charges within the drop. The Born self-energy of an ion with charge $Q$ and radius $a$ at a solid-water interface is given by [1]

$$\mu = \frac{Q^2}{4\pi(\epsilon_s + \epsilon_{fl})a}.$$ \hspace{1cm} (5)

Here, $\epsilon_s$ and $\epsilon_{fl}$ are the dielectric permittivities of the surface and the fluid, respectively. The voltage of these charges is defined as the energy per charge ($v = \mu/Q$). Thus, the voltage ratio for a surface ion in air compared to a surface ion in water is given by

$$\frac{v_{air}}{v_{fl}} = \frac{\mu_{air}}{\mu_{fl}} \frac{\epsilon_s + \epsilon_{fl}}{\epsilon_s + 1}.$$ \hspace{1cm} (6)

For water ($\epsilon_{water} = 80$) and a glass substrate ($\epsilon_s = 4$), we get a voltage ratio of 17. Even if we assume a relatively high zeta potential on the order of 100 mV, we would get a three phase contact line voltage of 1.7 V, which is much lower than the observed values. Furthermore, the surface will most probably remain partially hydrated after the drop, decreasing the voltage difference. An additional contribution to the drop voltage will be added by the work that the drop does separating the surface and drop charge. The exact value of this voltage will depend on the exact arrangement of the charges at the three-phase-contact line and the mechanism.

5.2 Equation for parameter adaptation

Here we will calculate the expressions for the drop-dependent three phase contact line voltage. As mentioned in the main text and shown in the following chapters of the SI, our results suggest that the adaptation happens in $U_{cl}$, however, the same formalism can be used for other parameters, such as the surface capacitance or the charge decay time. To make the derivation easier to read, we will use the following substitutions:

- $D = U_{dry}$
- $W = U_{wet}$
- $a = -\frac{t_{contact}}{t_{wet}}$
- $b = -\frac{\Delta t}{t_{dry}}$

Upon contact with the first drop, the surface approaches the wet state within the contact time $t_{cont}$, yielding a three phase contact line voltage of $U_1 = W + (D - W) e^a$. In the time between the first and the second drop, the surface will return to the dry state. When the second drop arrives, the surface is in a state $U_2' = U_1 + (D - U_1) e^b$. During contact with the second drop, the voltage again tends towards $U_{wet}$, yielding $U_2 = W + (D - U_2') e^a$. Combining and generalizing these equations, we can get a recursive expression for the drop voltage of the following drop for $n > 1$:

$$U_{n+1} = W + (D - W) e^a - (D - U_n) e^{a+b}.$$ \hspace{1cm} (7)
Using these equations, we can calculate the expressions for the first drops explicitly:

\[ U_1 = W + (D - W)e^a \]
\[ U_2 = W + (D - W)e^a - (D - U_1)e^{a+b} \]
\[ = W + (D - W)[e^a - e^{a+b} + e^{2a+b}] \]
\[ U_3 = W + (D - W)[e^a - e^{a+b} + e^{2a+b} - e^{2a+2b} + e^{3a+2b}] \]
\[ ... \]
\[ U_n = W + (D - W) \left[ 1 + (e^a - 1) \sum_{k=0}^{n-1} e^{k(a+b)} \right] \]

Using the definition of the geometric series we can write:

\[ U_n = W + (D - W) \left[ 1 + \frac{(e^a - 1)e^{n(a+b)} - 1}{e^{a+b} - 1} \right] \] (8)

At large drop numbers \( n \), the exponential term in the numerator will approach zero, yielding

\[ U_\infty = W + (D - W) \left[ 1 - \frac{e^a - 1}{e^{a+b} - 1} \right] \] (9)
6 Drop Charge measurement and numerical simulation of 2019 Stetten et al. data

Figure 5: (A) Drop charge (dots) measured on PFOTS surface and numerical simulation (sold lines) using the $U_{cl}$ adaptive two capacitor model. Parameter used for the simulation are $\lambda \approx 0.014 \text{ m}$, $U_{cl, d} \approx 3.3 \text{ V}$, $\sigma_0 \approx -14 \mu \text{C/m}^2$, $\tau \approx 8\text{s}$, $U_{cl, w} \approx 1.6 \text{ V}$, $t_d \approx 150\text{s}$ and $t_w = 0.3\text{s}$. (B) Simulated drop charge traces of the first, 5th, 2th, and 200th drop plotted on top of the measured drop charge traces.

Here, we tested our new model with the original experiment done by Stetten et. al [7]. We used the initial surface parameters with adaptation for the numerical simulation, which describes the experimental data with a single set of parameters.

7 Surface capacitance $c_s$, and surface discharge time $\tau$ adaptation to describe slide electrification

7.1 Surface capacitance ($c_s$) adaptation

To observe the effect of surface capacitance adaptation in drop charge, we used $c_{s, dry} = \frac{\sigma_0}{U_{cl, dry}} \approx 2.4 \mu \text{F/m}^2$ and the adaptation and relaxation times obtained from the fit in numerical the simulation. We choose the steady-state $c_s \approx 0.7 \mu \text{F/m}^2$ to match the drop charge versus drop number at 2 cm. Although the drop charges at 2 cm slide length match quite well (fig.6 A), the drop charge behaviors at other slide lengths are not described by a $c_s$ adaptation model. This is seen clearly in the drop traces plot (fig.6 B), where the charge of every drop saturates after sliding around 40 cm, which does not match in the experiment.

In addition to simulation, to examine a potential adaptation in surface capacitance, we designed a simple experiment to measure the surface capacitance with increasing contact time with the droplet. In the experiment, we placed a grounded metal electrode of area 0.5 cm$^2$ directly beneath a PFOTS-coated glass substrate (lower plate of the capacitor). On top of the substrate, we placed a drop $V \approx 45\mu\text{L}$ (upper plate of the capacitor). Using a tungsten wire and a function generator (940-WAVESTATION2052, Teledyne LeCroy, 69126 Heidelberg, Germany), we applied a square potential of 3 V to the drop. A current amplifier connected to the bottom electrode measured the capacitive current, from which we calculated the total capacitive charge and the overall capacitance. The experimental geometry corresponds to three capacitors in series: the wire-drop capacitance, the drop-substrate capacitance and the substrate-bottom electrode capacitance. Any changes in any of these capacitances should be visible as change in the overall capacitance. Figure 3 (B) shows the capacitance was stable within 0.3% with the
Figure 6: (A) Measured drop charge (dots) and simulated drop charge dynamic curve with $c_s$ adaptive two capacitor model. Parameters used for the simulation are $\lambda \approx 2.4 \text{ m}$, $\tau \approx 1.5s$, $\sigma_0 \approx -15 \mu \text{C/m}^2$, $c_{s0} \approx 2.2 \mu \text{F/m}^2$, $c_{s200} \approx 0.7 \mu \text{F/m}^2$, $t_d \approx 200s$ and $t_w = 0.1s$. (B) Drop charge traces according to $c_s$ adaptive two capacitor model where every drop charge saturates after a certain slide length and the experimental data of drop charge traces (dots). (C) Measured drop charge (dots) and simulated drop charge dynamic curve with $\tau$ adaptive two capacitor model. Parameter used for the simulation are $\lambda \approx 2.4 \text{ m}$, $\tau_0 \approx 1.6s$, $\sigma_0 \approx -15 \mu \text{C/m}^2$, $\tau_{200} \approx 10s$, $t_d \approx 200s$ and $t_w = 0.1s$. (D) Drop charge traces given by the $\tau$ adaptive two capacitor model which is different than the measured drop charge traces.

increasing number of the voltage pulses over the measurement time of 100 sec. Therefore, we exclude the surface capacitance adaptation case from the model.

### 7.2 Surface charge relaxation time ($\tau$)

To examine whether an adaptation in the surface relaxation time ($\tau$) would explain the slower saturation of the drop charge, we used $\tau_0 \approx 1.6s$ with the adaptation and relaxation times from the fit. We choose the steady-state $\tau \approx 10s$ to match the drop charges at 2 cm. Figure 6 C and 6 D show drop charge vs. drop number curves with their simulations and the drop charge traces with increasing slide length, respectively. Similarly to the adaptive surface capacitance ($c_s$) case, the $\tau$ adaptive two-capacitor model describes the drop charge behavior at 2 cm slide length quite well. But, it does not describe the drop charge behavior at other slide lengths. The steady-state drop charge in drop charge vs. drop number and saturated drop charge in drop charge traces are lower than expected by the model. Therefore, we exclude the $\tau$ adaptive two capacitor model.
References

[1] Jacob N Israelachvili. *Intermolecular and surface forces*. Academic press, 2015.

[2] CB Moore and B Vonnegut. “Measurements of the electrical conductivities of air over hot water”. In: *Journal of Atmospheric Sciences* 45.5 (1988), pp. 885–890.

[3] John North. *Cosmos: an illustrated history of astronomy and cosmology*. University of Chicago Press, 2008. Chap. 19.

[4] Victor TC Paiva et al. “Conduction and excess charge in silicate glass/air interfaces”. In: *Langmuir* 35.24 (2019), pp. 7703–7712.

[5] A Soffer and M Folman. “Surface conductivity and conduction mechanisms on adsorption of vapours on silica”. In: *Transactions of the Faraday Society* 62 (1966), pp. 3559–3569.

[6] Mariana D Sosa et al. “Liquid–polymer triboelectricity: chemical mechanisms in the contact electrification process”. In: *Soft Matter* 16.30 (2020), pp. 7040–7051.

[7] Amy Z Stetten et al. “Slide electrification: charging of surfaces by moving water drops”. In: *Soft matter* 15.43 (2019), pp. 8667–8679.

[8] Ryosuke Umezawa, Makoto Katsura, and Satoru Nakashima. “Electrical conductivity at surfaces of silica nanoparticles with adsorbed water at various relative humidities”. In: *e-Journal of Surface Science and Nanotechnology* 16 (2018), pp. 376–381.