

Supplemental Information

Detaching droplets in immiscible fluids from a solid substrate with electrowetting

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1. Variation of contact angle (θ) according to applied voltage (V) for electrowetted droplets submerged in oil media with viscosities of 0.65 cSt and 5 cSt, and the relationship between $\cos\theta - \cos\theta_o$ and V^2

The contact angle variations of a droplet in oil with different viscosities were measured with varying DC voltages. The results are compared with the values predicted by the Young–Lippmann equation: $\cos\theta = \cos\theta_o + \varepsilon_d \varepsilon_o V^2 / 2\gamma d$ [Fig. S1]. In this equation, θ_o , ε_d , ε_o , V , d , and γ represent the Young's angle, dielectric constant of the insulator, vacuum dielectric permittivity, applied voltage, thickness of the insulator, and surface tension, respectively. The contact angle acquires a saturated value at voltages higher than 110 V regardless of oil viscosity. Except in the case of contact-angle saturation, the interfacial tension between a droplet and ambient oil with different viscosities can be extracted from the slope ($\varepsilon_d \varepsilon_o / 2\gamma d$) in Fig. S1(b), if the capacitance $C = \varepsilon \varepsilon_o / d$ (per unit area) is determined in advance.

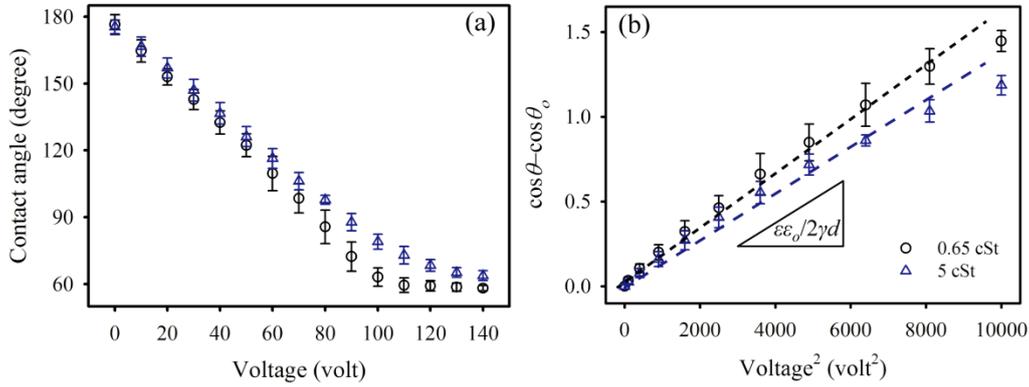


Fig. S1 (a) Variation of contact angle (θ) according to applied voltage (V) for electrowetted droplets submerged in oil with different viscosities. (b) The relationship between $\cos\theta - \cos\theta_0$ and V^2 . Here, θ_0 denotes the Young's angle. Symbols and dashed lines represent the experimentally obtained contact angles and Young-Lippmann equation, respectively. The interfacial tensions between the water droplet and the ambient oil with different viscosities can be extracted from the slope of the relationship curve.

2. Effect of applied voltage on the contact-line speed of retracting droplets

The contact-line speeds of the retracting droplets at different electrowetting (EW) numbers η are extracted from the slope of Fig. 1(c) in the main text. Here, EW η is expressed as $\varepsilon_d \varepsilon_o V^2 / 2d\gamma$, where ε_d is the dielectric constant of insulator, ε_o the vacuum dielectric permittivity, V the applied voltage, d the thickness of insulator.

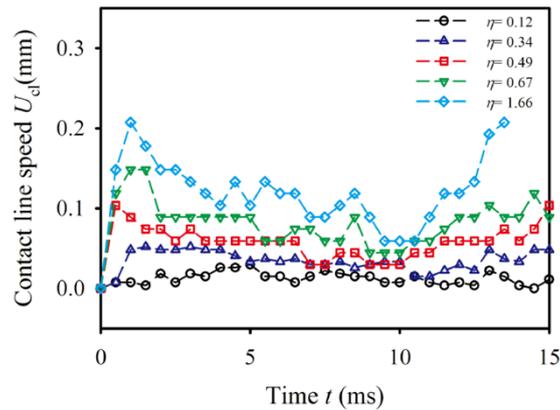


Fig. S2 Temporal variations of contact-line speed (U_c) of retracting droplets at different EW numbers η .

3. Effects of applied voltage on the time elapsed to reach the maximum height of jumping droplets

The time elapsed to reach the maximum height is proportional to the 0.6th power of η : It is approximately linearly proportional to the applied voltage.

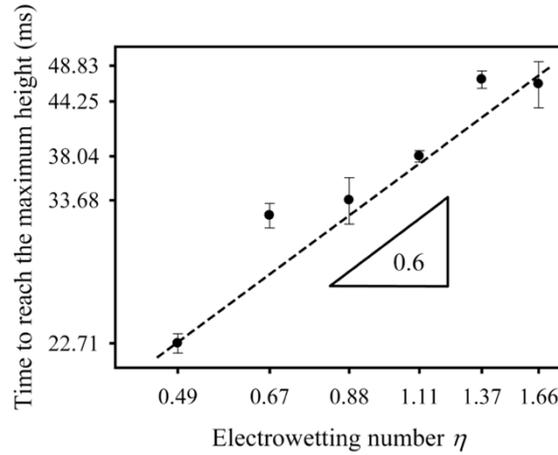


Fig. S3 Power-law dependence of the time elapsed to reach the maximum height of jumping 5 μ L droplets in silicone oil with a viscosity of 0.65 cSt on the EW number η (log-log scale). The error bar denotes the standard deviation. The triangular inset shows that the time elapsed to reach the maximum height is proportional to the 0.6th power of the EW number η (regression $R^2=0.934$).

4. Derivation of the relaxation time from energy balance

The total energy (E_k) of a sessile droplet includes surface energy, potential energy, and pressure energy associated with Laplace pressure, which is given by Eqn (S1).^{s1} In Eqn (S1), the surface energy is expressed as the sum of the areas (S_{ik}) of the interfaces between three phases, the solid substrate, liquid droplet (i.e., water) and ambient fluid (i.e., oil), weighted by the respective interfacial energies (γ_i). Here, subscript $i=$ '1', '2', and '3' represent the 'water/oil', 'water/solid', and 'oil/solid' interfaces, respectively. Therefore, the total energy is expressed by

$$E_k = \gamma_1 S_{1k} + \gamma_2 S_{2k} + \gamma_3 S_{3k} + \rho \Omega g h_k - p_{Lk} \Omega, \quad (S1)$$

where, ρ and Ω denote the density and volume of the droplet, h the center of droplet mass, and p_L the Laplace pressure. The subscript $k=$ 'a' and 'b' represent the 'initial state' (before the application of electrical voltage) and the 'equilibrium state' (after the application of

electrical voltage), as shown Figs. S1(a) and (b), respectively.

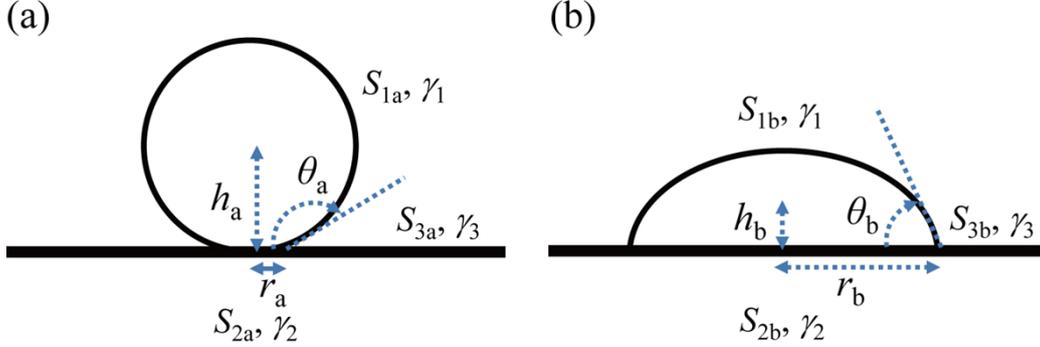


Fig. S4 Cross section of a sessile droplet at the initial (a) and equilibrium (b) states. Here, θ_k and r_k denote the contact angle and the base radius at each state, respectively. The other symbols are defined within the text.

The difference between potential energies at the initial and equilibrium states is assumed to be negligible, due to slight change in h . By using the Young-Dupré equation $\gamma_1 \cos \theta_a = \gamma_3 - \gamma_2$, the difference of total energy ($\Delta E = E_b - E_a$) between the initial and equilibrium states is given by

$$\Delta E = \gamma_1(S_{b1} - S_{a1}) + (\gamma_2 - \gamma_3)\Delta S - \Delta p_{kl}\Omega = \gamma_1(S_{b1} - S_{a1} - \Delta S \cos \theta_a) - \Delta p_{kl}\Omega, \quad (S2)$$

$$\Delta S \equiv S_{b2} - S_{a2} = -(S_{b3} - S_{a3}).$$

Substitution of $S_{k1} = 2\pi r_k^2 / (1 + \cos \theta_k)$, $\Delta S = \pi(r_b^2 - r_a^2)$, and $\Delta p_{kl} = 2\gamma(\sin \theta_b / r_b - \sin \theta_a / r_a)$ into Eqn (S2) leads to the following relation of ΔE as a function of r_k and θ_k .

$$\Delta E = \pi\gamma_1 \left[2 \left(\frac{r_b^2}{1 + \cos \theta_b} - \frac{r_a^2}{1 + \cos \theta_a} \right) - (r_b^2 - r_a^2) \cos \theta_a - 2 \left(\frac{\sin \theta_b}{r_b} - \frac{\sin \theta_a}{r_a} \right) \frac{\Omega}{\pi} \right], \quad (S3)$$

$$\Omega = \frac{\pi r_a^3 (2 - 3 \cos \theta_a + \cos \theta_a^3)}{3 \sin \theta_a^3} = \frac{\pi r_b^3 (2 - 3 \cos \theta_b + \cos \theta_b^3)}{3 \sin \theta_b^3}.$$

When θ_a is given, θ_b can be obtained from the Lippmann-Young equation of $\cos \theta_b = \cos \theta_a + \eta$. Consequently, ΔE can be estimated from Eqn (S3), when θ_a , Ω , and η are given. Our experimental conditions are as follows: $\theta_a = 170^\circ$, $\Omega = 5 \mu\text{L}$, $\gamma_1 = 0.020 \text{ N/m}$, $\varepsilon_d = 3.1$, $\varepsilon_o = 8.854 \times 10^{-12} \text{ F/m}$, $d = 5 \mu\text{m}$, and $V = 0-110 \text{ V}$.

When a droplet is stretched by EW, the stored energy of the electrowetted droplet

(i.e., the difference in total energy ΔE) is expected to be equal to the electrical energy ($E_{el} = \gamma_1 S_{b2} \eta$)^{S1} imparted by the applied voltage, assuming that the dissipation energy caused by viscous drag and the contact-line friction are negligible. By calculating the difference of total energy (ΔE) in Eqn (S3) divided by interfacial tension (γ_1) and contact area (S_{b2}), $\Delta E / (\gamma_1 S_{b2})$ is found to be linearly proportional to η [Fig. S5].

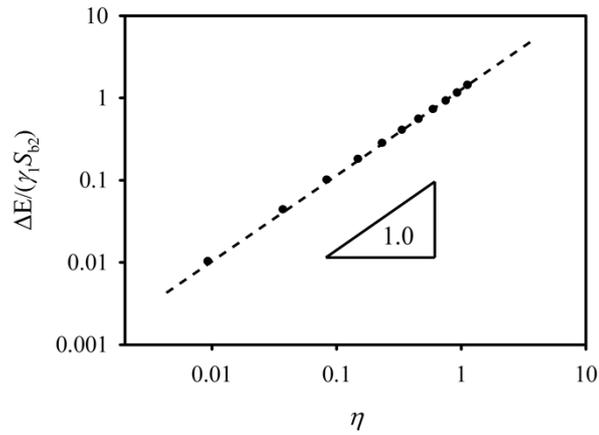


Fig. S5 Power-law relationship between the difference of total energy (ΔE) divided by the interfacial tension (γ_1) and contact area (S_{b2}) and the EW number η (log-log scale). The triangular inset shows that $\Delta E / (\gamma_1 S_{b2})$ is linearly proportional to η (regression $R^2 = 0.999$).

When a droplet retracts after the applied voltage is turned off, the stored energy (ΔE) is converted into kinetic energy $E_{kinetic} = \rho \Omega U^2 / 2$, where U is the velocity of the retracting droplet. Because ΔE is equal to E_{el} , the following relationship can be obtained: $\gamma_1 S_{b2} \eta = \rho \Omega U^2 / 2$. Subsequently, when S_{b2} , Ω , U are scaled as R^2 , R^3 , and R/τ , respectively, the relaxation time, as a characteristic time scale, can be derived as follow: $\tau \sim (\rho R^3 / \eta \gamma_1)^{0.5}$. Here, R denotes the characteristic length, which is set to R is the radius of a spherical droplet in the present study.

Reference

S1. F. Mugele and J.-C. Baret, *J. Phys.: Condens. Matter*, 2005, **17**, R705–R774.

5. Effect of droplet volume on the contact time of retracting droplets

The contact time is approximately proportional to 0.5th power of the droplet volume.

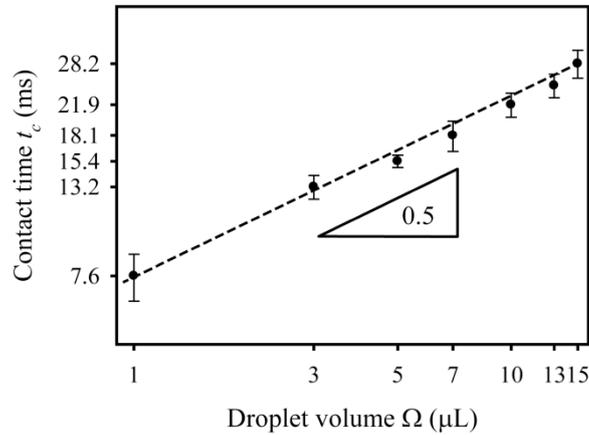


Fig. S6 Power-law dependence of the contact time of retracting droplets in ambient oil with a viscosity of 0.65 cSt on the droplet volume (log-log scale). The error bar denotes the standard deviation. The triangular inset shows that the contact time is proportional to the 0.5th power of the droplet volume (regression $R^2=0.993$).

6. Temporal evolution of base radius of spreading 5 μL drops submerged in oil with viscosity of 5 cSt at different η

The spreading behaviors of 5 μL drops submerged in oil with a viscosity of 5 cSt were observed at $\eta = 0.19$ – 2.69 . The pulse width (T_p) of a square pulse is determined by measuring the spreading time (T_s), defined as the time elapsed to reach the peak of a spreading droplet under DC EW actuation. In this study, T_p is set to 17 ms, regardless of applied voltage.

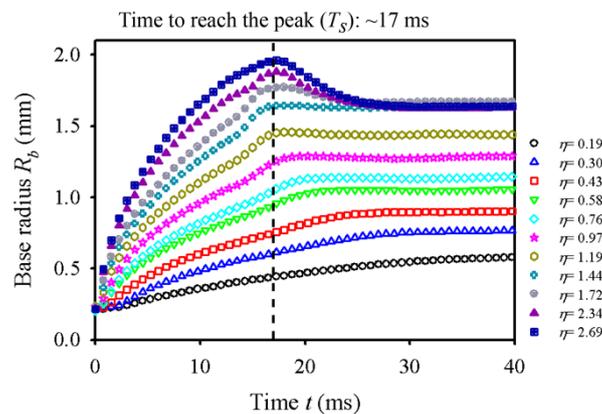


Fig. S7 Temporal variations of base radius (colored symbol) of spreading 5 μL drops

submerged in oil with a viscosity of 5 cSt at different η . The vertical dashed line corresponds to the time elapsed to reach the peak of a spreading droplet (T_s) under DC EW actuation, which the pulse width is set to 17 ms, regardless of η .

7. Comparison of temporal variations of base radii of retracting droplets driven by EW with DC and square pulse signals

Temporal variations of the base radii of retracting droplets by EWs with DC and square pulse signals are shown in Fig. S8. The base radius of an electrowetted droplet with a square pulse voltage of $\eta=0.43$ is larger than that with a DC voltage of $\eta=2.43$. Thus, the former case has a larger surface energy than the latter. On the other hand, the base radius of an electrowetted droplet by applying a square pulse voltage of $\eta=0.19$ is comparable with that by applying a DC voltage of $\eta=0.76$. Even though the two droplets have nearly same amount of surface energy, one droplet can be detached from the solid surface, but the other cannot be detached. These results may be determined whether or not a droplet has the kinetic energy before a droplet starts to retract. For a DC voltage of $\eta=0.76$, an electrowetted droplet rests gently on the solid surface, before it starts to retract (i.e. after the applied voltage is turned off). Thus, the droplet velocity seems to be zero. Accordingly, the surface energy is only converted to kinetic energy during droplet retracting. However, for a square voltage of $\eta=0.19$, the droplet starts to retract as soon as it reaches to the maximum electrowetted radius. Thus, the droplet velocity is not zero. Consequently, the sum of the surface energy and kinetic energy is converted into kinetic energy used for droplet detachment during droplet retracting.

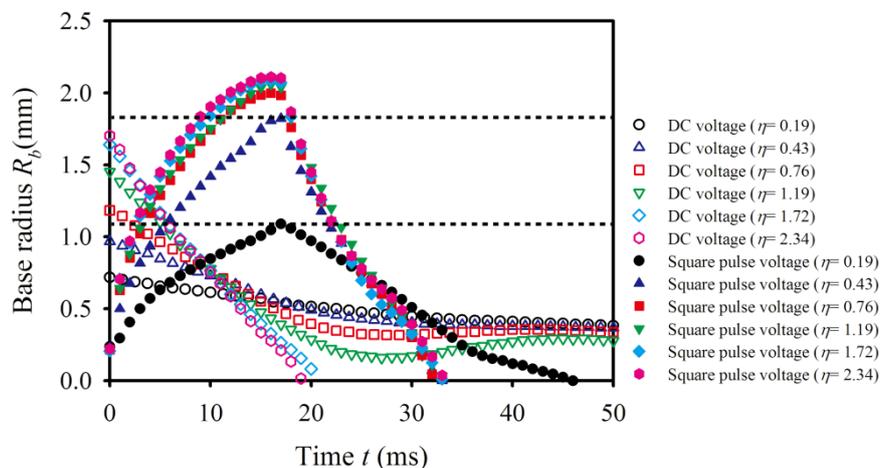


Fig. S8 Comparison of temporal variations of base radii of electrowetted 5 μL droplets

submerged in oil with a viscosity of 0.65 cSt driven by applying DC and square pulse signals.

8. Development of a three-dimensional digital microfluidics (3D-DMF) platform in oil by using patterned electrodes

The experimental apparatus is mainly composed of two parallel plates attached with the same patterned electrode array, as shown in Fig. 6(a). The patterned electrode array was fabricated as follow. A glass wafer (Pyrex® 7740, Corning) is coated with 20 nm thick layer of chromium as an adhesion layer and a 200 ± 10 nm thick layer of gold as an electrode by electron beam deposition. A photoresist (AZ 5214, AZ Electronic Materials) is patterned on the gold layer by photolithography. The gold and chromium layers are patterned by the use of wet etching in sequence. After removing the remained photoresist, an insulating layer of parylene-C is deposited in 5 ± 0.5 μm thickness by vapor deposition using a parylene coating system. The patterned electrode is 2×5 electrode array and the gap between two adjacent electrodes is 20 μm in width and the dimension of one digitized patterned electrode was 1.5 mm \times 1.5 mm. To make the surface hydrophobic, Teflon AF1600® (DuPont) is spin-coated on the top of the insulation layer in 100 nm thickness. The bottom electrode plate is combined with an acrylic cell (length of 3 cm, width of 2.5 cm, and height of 3 cm). The cell is filled with silicone oil (Shin-Etsu Silicone Korea Co., Ltd.), which has a kinematic viscosity of 0.65 cSt. Two droplets with the same volume of 3 μL are dispensed with a micropipette onto the bottom electrode plate. A droplet contains phosphate-buffered saline solution (Gibco) with 20 mM Na_2CO_3 (Sigma-Aldrich), which has a pH value of 8.6. The other droplet contains 0.2 mM phenol red (Sigma-Aldrich), which has a pH value of 5.3. The former and latter droplets exhibit colorless and yellow color, respectively. The interfacial tensions between silicone oil and the two liquids with different pH values are measured as about 0.025 N/m by using a public-domain image-processing program (ImageJ, NIH). DC and AC electrical signals, produced by a function generator (33220A, Agilent) and then amplified (PZD700, Trek), are applied. The signals are transmitted to the electrodes through photo-coupled relays (AQW214, Panasonic) controlled by a digital I/O board (Mega 2560, Arduino) along with a programmed LabVIEW® code. The dynamic behaviors of the electrowetted droplets are consecutively recorded by using a digital camera (Canon EOS 500D).