Direct observation of stick-slip movements of water nanodroplets induced by an electron beam

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Dynamics of the first few nanometers of water at the interface are encountered in a wide range of physical, chemical, and biological phenomena. A simple but critical question is whether interfacial forces at these nanoscale dimensions affect an externally induced movement of a water droplet on a surface. At the bulk-scale water droplets spread on a hydrophilic surface and slip on a nonwetting, hydrophobic surface. Here we report the experimental description of the electron beam-induced dynamics of nanoscale water droplets by direct imaging the translocation of 10- to 80-nm-diameter water nanodroplets by transmission electron microscopy. These nanodroplets move on a hydrophilic surface not by a smooth flow but by a series of stick-slip steps. We observe that each step is preceded by a unique characteristic deformation of the nanodroplet into a toroidal shape induced by the electron beam. We propose that this beam-induced change in shape increases the surface free energy of the nanodroplet that drives its transition from stick to slip state.

Results and Discussions

Hydrodynamic slip of water that results in the movement of water over the surfaces generally occurs on hydrophobic surfaces (16, 17). However, it may be possible that a hydrophilic surface with dense favorable absorption sites for water molecules can promote water slip at nanoscale as water molecules easily migrate across the closely spaced atomic absorption sites (15). The atomic spacing in hydrophilic amorphous silicon nitride (Si3N4) is suitably dense, 1.73 Å between Si and N atoms (22), making flat Si3N4 membrane a great candidate for observing the movement of interfacial water. Here, we report the dynamic TEM imaging of structural changes in 10- to 80-nm-diameter droplets of water induced by an electron beam that directly lead to deformation and translocation of these nanodroplets on flat Si3N4 membranes. Thus in our study, electron beam directly deforms and forces the movement of nanodroplets, which differs from general discussion of interfacial water flow focused on substrate-water interaction.

Water movement at the interface plays a crucial role in the function of biological membranes (1), fluid of liquids through pores (2, 3) and over surfaces (4), hydration of biomolecules (5–7), and chemical reactions in aqueous solutions (8). Although much is known about the movement of bulk water, most of what is known about interfacial water results from modeling and computational simulations (9, 10). Nanometer-diameter water droplets, because of their high surface-to-volume ratio and small number of molecules, present an ideal system for theoretical explorations of interfacial water dynamics induced by external forces. Such studies describe how external driving forces imposed by thermal (11), chemical (12), and topographic gradients (13) can lead to motion of nanometer-diameter droplets, and local fluctuations may result in the breakup of liquid nanojets (14). These theories imply that perturbations, either from external physical forces or chemical nonuniformities are coupled to dynamics of a nanodroplet through changes in shape and thus causing translocation of nanoscale droplets. Interestingly, very recent simulations also predict that nanometer-diameter water droplets will slip on hydrophilic surfaces (15) similar to those on hydrophobic surfaces (16, 17). However, studying the structural dynamics of nanodroplets is experimentally challenging because one needs to be able to externally induce the movement and be able to image the subsequent dynamic process of nanoscale droplets. Although atomic force microscopy probes have measured the interfacial forces between liquids (18) and scanning transmission electron microscopy (TEM) has imaged small numbers of static water molecules confined in carbon nanotubes (19), these approaches fail to directly relate structure and dynamics of nanoscopic liquids. The ability to externally induce the movement and directly study the motion of model nanodroplets in contact with substrate interface may provide an insight to dynamic properties of interfacial water by experimentally complementing theoretical simulations. Such studies will be critical in the design of materials tailored to the adhesion and flow of liquids at the interface (20, 21).


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charged suggests the dewetting of the window membrane is not caused by modification of the window surface.

When irradiated by the same 120-kV electron beam of the TEM, a nanodroplet moves in discrete steps on the hydrophilic surface and not by a continuous flow (Fig. 1B). We visualized the internal dynamics of the water inside a nanodroplet by mapping the relative water mass from the electron absorbance (Fig. 1C). Within a stationary nanodroplet, the liquid mass exhibits small fluctuations under a uniform electron beam during which the water redistributes to the droplet rim (see Movie S2) and assumes a torus-like structure with nonuniform thickness (Fig. 1C and D). The droplet advances at the steepest side of the torus when a thin lamella extends from the rim as schematically illustrated in Fig. 1D and E. The mass of water then shifts into this protrusion, causing the torus shape to flatten and the rear of the nanodroplet to recede. The angles at which both the advancing (θ_{adv}) and receding (θ_{rec}) contact lines slip are set by molecular interactions at the liquid–solid interface, surface roughness, and chemical heterogeneities (26, 27). This type of motion is characteristic of a stick-slip mechanism (28, 29) in which the nanodroplet slips when the redistribution of water overcomes interfacial forces between the nanodroplet and the substrate.

The stick-slip motion is clearly seen when the dynamics of a 50-nm nanodroplet are plotted and quantified (Fig. 2A and B) through six stick-slip cycles. Each step is characterized by a burst of movement (20–80 nm/s peak velocity) that coincides with a transient increase in area (Fig. 2C). These bursts are separated by a pause which reduces the average speed to approximately 10 nm/s (189 nm total travel distance in 19.2 s). The change in interface area during slipping is limited by the initial size of the nanodroplet.

To investigate the relationship between dynamics and nanodroplet size, we compared two nanodroplets with diameters of approximately 30 nm (droplet 1) and 60 nm (droplet 2) under identical electron beam conditions as shown in Fig. 3A (see Movies S3 and S4). During a 20-s period, the 30-nm droplet traveled 276 nm while the 60-nm droplet traveled 353 nm (see SI Text, Figs. S4 and S5). Similarly, very small nanodroplets (less than 20 nm) often tend to get pinned on the surface and do not move (see Movie S5). A histogram of the nanodroplet size at different average speeds obtained with the electron flux in the range of 60–80 e/Å²s (Fig. 3B) shows that larger diameter nanodroplets are on average faster than the smaller nanodroplets and that very small nanodroplets are essentially immobile. A distribution of average stick times, a time interval between two consecutive slipping attempts, indicates that these stick times are independent of nanodroplet size (Fig. 3C and D). It has also been shown that the velocity of macroscopic droplet increases with droplet size when driving force is introduced by either physically (30) or chemically (31, 32) induced surface energy gradient (33, 34). However, contrary to smooth flow observed in macroscopic droplets driven by surface energy gradient, the induced movement of nanodroplets happens in discrete slip steps only when deformation causes sufficient change in surface free energy.

Generally, the step size (lamella extension from the rim of the droplet) will depend on the balance between surface and adhesion energies of the droplet interfaces. To estimate the slip step size, we consider a simplified hemispherical droplet sitting on a solid surface that undergoes a shape deformation induced by electron beam, with surface area of πR² at the solid–liquid interface and 2πR² at the liquid–air interface. The surface free energy of such droplet is G(R) = 2γR² + πR²(γ_{LS} – γ_{SG}), where γ = 72 mJ/m², γ_{LS}, and γ_{SG} are surface energy density at liquid–gas, liquid–solid, and solid–gas interfaces, respectively (35). The small steps of ΔR can result from a deformation-induced increase in the surface energy, ΔG = G(R + ΔR) – G(R) ≈ (dG/dR)_{R=0}ΔR + 1/2(d²G/dR²)_{R=0}ΔR² = π(γ_{LS} – γ_{SG})ΔR², where (dG/dR)_{R=0} = 0, as the droplet deforms because the surface energy of the unperturbed droplet is at a minimum (36). Therefore, such a change in surface energy can lead to a step of

$$\Delta R = \sqrt{\frac{\varepsilon}{\pi \gamma (2 - \cos \theta_c)}}$$

where ΔG = ε is the energy barrier that needs to be overcome for a nanodroplet to slip by ΔR. This barrier energy for a nanodroplet with 2R = 50 nm is an adhesion energy at the interface between the water and the surface. Using macroscopic equili-
brium contact angle measurement of $\theta_c = 16^\circ$, where contact angle can be expressed as $\cos \theta_c = (\gamma_{SG} - \gamma_{LS})/\gamma$: $\epsilon = \pi R^2 \gamma(1 + \cos \theta_c)$, we obtain a step size of $\Delta R \approx 34$ nm, similar to our experimental observations (Fig. 1B).

The nanodroplet deformation and the subsequent translocation are observed above a threshold electron flux. The relation between average speeds of nanodroplets and electron flux of imaging beam is plotted in Fig. 4A. The influence of a power delivered by electron flux on average speed of nanodroplets can be qualitatively described by the Kramer’s type transition-state relation (37). The nanodroplet moving with velocity $v$ experiences an interfacial drag force at the droplet–substrate interface that is proportional to the velocity of the nanodroplet: $F_d \sim v$. The driving power for such a nanodroplet can be estimated to be $P = F_d \cdot v \sim v^2$. Because the driving power, $P$, must be linearly proportional to the electron flux, $\Phi$, we have phenomenological description of velocity as

$$v = \frac{v_0 \sqrt{\Phi}}{1 + e^{-\alpha(\Phi - \Phi_0)}} \quad [2]$$

where $v_0$ is a velocity factor, $\Phi_0$ is the threshold flux for droplet to move, $\Phi$ is the irradiating electron beam flux, and $\alpha$ is the transfer coefficient. The average translocation speeds for nanodroplets are plotted in Fig. 4A, qualitatively capturing the relation between the average velocity and the electron flux. The fit of Eq. 2 to speed data reveals that the threshold flux (Fig. 4A) required to overcome the nanodroplet’s adhesion to substrate are $37 \pm 5$, $32 \pm 2$, and $31 \pm 1$ e/($A^2 \cdot s$) for droplets 20–40, 40–60, and 60–80 nm diameter, respectively. The corresponding slip step (lamella extension) sizes for moving nanodroplets are bigger for larger nanodroplets and appear to be independent of electron flux as predicted by Eq. 1 (Fig. 4B). It is unlikely that the slight temperature change in droplet and the substrate may induce the substantial redistribution of water in a nanodroplet because temperature increase in a nanodroplet in reference to substrate is calculated to be uniform and insignificant (SI Text, Figs. S6–S8).

However, the formation of toroidal nanodroplets under electron flux raises interesting issues about the possible role of electrostatic forces on water redistribution. One possible mechanism is that charging of a nanodroplet when high-energy electrons ionize a small fraction of water molecules and repulsive forces inside the nanodroplet may lead to formation of the toroidal structure (see SI Text). The exact nature of the mechanism that drives the motion of the nanodroplets remains an open question, and future theoretical explorations may elucidate the mechanism.

Fig. 3. Size effects on a nanodroplet translocation. (A) TEM micrograph of 30 nm (droplet 1) and 60 nm (droplet 2) along with their corresponding paths during 20 s (see Movies S3 and S4). (B) Distribution of droplet diameters for droplets moving with an average speed of less than 3 nm/s (stuck), 3–10 nm/s (slow), and 10–20 nm/s (fast) when exposed to an electron flux of 60–80 e/($A^2 \cdot s$). (C) Distribution of droplet stick times for droplets moving at 3–10 nm/s (slow), and 10–20 nm/s (fast) when exposed to an electron flux of 60–80 e/($A^2 \cdot s$). Solid lines represent average value of stick time (horizontal lines) and diameter (vertical lines).

Fig. 4. Nanodroplet movement as a function of the electron flux. (A) Average speed as a function of electron flux for droplets that are greater than 20 nm in diameter. (B) Step size of moving nanodroplet where the shaded regions represents the step size range set by Eq. 1 for nanodroplets with the diameter of 20–40 nm (green), 40–60 nm (blue), and 60–80 nm (red).
On a final note, there is an ongoing debate about the role of deformation in nanoscale friction (38, 39). For example, atomically thin sheets susceptible to out-of-plane deformation are observed to exhibit stick-slip movement due to enlarged contact area and therefore increased static friction between the sliding surfaces as a result of deformation (39). It is therefore very interesting to note that in the case of electron beam-induced movement of liquid nanodroplets, the deformation at liquid–air interface that does not result in increase of interfacial contact area promotes slipping and not sticking. Our real-time imaging of the electron beam-induced movements of water nanodroplets associated with the intradroplet redistribution of water mass differs from other examples of movements where the driving force is induced by introducing physical or chemical gradients on a substrate. However, our study reveals that a sufficient deformation area promotes slipping and not sticking. Our real-time imaging of the electron beam-induced deformation and subsequent motion of the water droplets may bear important consequences for movement of other deformable nanoscale objects residing on adherent surfaces. The direct observations of beam-induced movement of nanodroplets presented may serve as a platform for future studies of liquid dynamics at the nanoscale, which has not yet been accessible and is a highly debated topic among many disciplines. Of liquid nanodroplets, the deformation at liquid–air interface promotes slipping and not sticking. Our real-time imaging of the electron beam-induced deformation and subsequent motion of the water droplets may bear important consequences for movement of other deformable nanoscale objects residing on adherent surfaces. The direct observations of beam-induced movement of nanodroplets presented may serve as a platform for future studies of liquid dynamics at the nanoscale, which has not yet been accessible and is a highly debated topic among many disciplines. By studying the dynamics of water at these scales, it is possible to understand the energy dissipation and conversion at liquid–solid interfaces. Dynamics properties of water and other liquids at the nanoscale have potential applications in the future design of flexible liquid nanodevices and will aid in designing new lubrication techniques for nanoelectromechanical systems.

**Materials and Methods**

**TEM Liquid Cell.** A low-stress silicon nitride (Si₃N₄) film with a thickness of approximately 20 nm was deposited by low-pressure chemical vapor deposition on both sides of 300-μm-thick, 4-in silicon (Si) wafers (Ultrasil). The fabrication details of liquid cells were described previously (25). Prior to the experiment, chips were cleaned with hydrochloric acid [with 10% (vol/vol)] to remove any metal residues. Next, the Si₃N₄ membrane surface was rinsed with acetone, isopropanol alcohol, and water followed by plasma cleaning (P = 3.3 W) for 45 s. Finally, the two pieces (bottom and top) were aligned by their windows and bonded together at 125 °C in a vacuum for 2 h to form a single liquid chamber (see SI Text). The liquid cell was filled with spectroscopic grade water (320072-2L, Sigma), and both reservoirs were sealed with a copper gasket and placed in specimen holder of an FEI T12 TEM. The images were acquired at the rate of 10 and 20 frames per second with a GATAN Orion SC200 camera. Electron flux was measured post specimen and represents transmitted electrons.

**Image Processing.** We applied the segmentation algorithm in Definiens Developer-XD to find the boundaries of the droplet area, centroid position of the droplet area, border length, and mean intensity. If the change in the centroid positions of the droplet area between two consecutive frames were within a range of a few pixels (less than 10 pixels), then it was considered to be the same object. The droplet boundaries were defined in three consecutive steps. First, images were smoothed using a median filter with a 3 × 3 or 5 × 5 matrix size. Next, a rolling disk algorithm was used to reduce the intensity gradient over the whole image plane to efficiently implement an autothreshold algorithm. Finally, upon identifying the probable droplets in the image, a pixel-based shrink and grow algorithm of both probable droplets and background was used to identify the actual droplet with its original shape (see Movie S2).

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Supporting Information

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SI Text

Transmission Electron Microscopy (TEM) Liquid Cell. We characterized the topography and the surface potential of freestanding Si$_3$N$_4$ membrane window prior and postglow discharge using commercial atomic force microscope (X-120; Park Systems) to match the surface properties of our conditions. The cleaning and glow discharge was similar to those of actual membranes used for study as described above. The topography in Fig. S1B and C shows that plasma treatment does not affect surface topography of Si$_3$N$_4$ membrane and the rms roughness for untreated and glow discharging surface of freestanding Si$_3$N$_4$ membrane is about 0.5 nm. Scanning kelvin probe microscopy revealed that the surface potential of freestanding Si$_3$N$_4$ membrane postglow discharge is uniform and about 300 mV.

**Droplet Formation.** Water loaded into liquid cell is sandwiched between the two Si$_3$N$_4$ membranes. Exposing this water layer to intense electron flux (greater than 100 electron/(Å$^2$·s)) causes water to rapidly retract from the beam, leaving a thin water film (approximately 5–20 nm) behind. Recent macroscopic observations show that a small volume of water can be pushed by an electron field leaving water film behind (1), and we suspect that similar phenomenon is occurring here when water is exposed to an electron beam. The thin layer of water in our liquid cell then slowly recedes under intense electron flux as captured by series of micrographs, shown in Fig. S2. The receding water film leaves nanometer size droplets on the surface of the membrane window.

**Change in the Surface Potential of the Si$_3$N$_4$ Membrane Window Due to the 120-keV Electron Beam.** We measured the change in the surface potential of Si$_3$N$_4$ membrane prior and postelectron beam irradiation under the similar conditions used in our experiments (approximately 60 e/Å$^2$·s for approximately 4 min). Several measurements were performed within 1–2 h of irradiation. These measurements clearly indicate that the membrane potential is slightly offset (approximately 130 mV) (Fig. S3) when irradiated by electron beam. However, we do not attribute the liquid movement during dewetting to this surface modification because water starts flowing back within a few minutes and wetting the film once the beam intensity is reduced or turned off while the surface clearly remains charged, as shown in Movie S1. Therefore, we think it is the interaction between electron beam and the liquid film (possibly the voltage gradient at the edges of the film and not just a uniform offset of the membrane potential) that causes dewetting of Si$_3$N$_4$ membrane window.

**Thickness Estimates.** We can roughly estimate the thickness of the nanodroplet using the relative intensity of the transmitted electrons (electron count) through the droplet ($N_{\text{drop}}$) and through the droplet free area of the image ($N_1$) using

$$\frac{N_{\text{drop}}}{N_1} \approx \exp(-l_{\text{drop}}/l_{\text{water}}),$$

where $l_{\text{drop}}$ is the thickness of the nanodroplet and $l_{\text{water}}$ is the mean free path for electron passing through water. The thickness is then

$$l_{\text{drop}} \approx l_{\text{water}} \ln \left( \frac{N_1}{N_{\text{drop}}} \right).$$


The images in Fig. S4 illustrate the thickness estimates of a stationary droplet and as droplet readiness to take a step. The higher contrast relative to the substrate represents the thicker liquids. It is unlikely that the change in image contrast within the droplet as it prepares to step is from nanobubbles, because liquid droplet of almost the same volume has been recovered in the following process. In addition, no other configurations have been observed, although the nucleation of a bubble within the center of the droplet is not energetically more favorable compared to the edges or off centers.

**Comparison Between 30- and 60-nm Droplets.** See Fig. S5.

**On the Heating of the Nanodroplet Due to the Electron Beam. Droplet temperature.** We would like to consider the possible effect of electron beam-induced heating of water nanodroplets because they may have an effect on dynamics of water. The energy is delivered to droplet in the form of the electron energy loss as electrons undergo inelastic scattering in water. The electron energy loss can be estimated using Bethe function (2):

$$\frac{dE}{dx} = \frac{2\pi e^4 N_4 Z \rho}{AE} \ln \left( \frac{AE}{T} \right).$$

where $E$ is the incident electron energy, $x$ is distance traveled through the medium, $J$ is estimated ionization energy, $Z$ is atomic number of the material, $e$ is electron charge, $N_4$ is Avogadro’s number, $\rho$ is density of the material, $A$ is atomic mass of the material, and the relativistic factor constant at 120 keV is $\alpha = 1.16$. Using Eq. S1, electron energy loss of 120 keV electrons transmitting through water and Si$_3$N$_4$ is calculated to be $dE/dx = 0.21$ eV/nm and $dE/dx = 0.2$ eV/nm, respectively.

Next, we assume that all the electron energy loss transfers into heat and that the heat dissipation is only possible via two-dimensional thermal conduction through the thin Si$_3$N$_4$ membrane (3). Then, the temperature increase of the thin membrane can be calculated using a two-dimensional heat conduction equation and ignoring the heat loss through other mechanisms. At steady state, the two-dimensional heat conduction equation in cylindrical coordinates can be expressed as

$$\kappa_{\text{memb}} \left( \frac{d^2 T}{dr^2} + \frac{1}{r} \frac{dT}{dr} \right) = J.$$  

where $\kappa_{\text{memb}}$ is thermal conductivity of Si$_3$N$_4$ membrane, $T$ is temperature, $r$ is the distance to the center of heat source, and $J$ is the heat density flux. Heat flows from the electron beam irradiated area of radius $R_b$ to the heat sink at the edge of membrane window (Si frame of the chip at $r = R_w \approx 10$ μm–window radius) where we assume the heat sink temperature to be at ambient temperature, $T = T_0$. Outside the irradiated area ($R_b \leq r \leq R_w$) there is no net heat flux ($J = 0$) and the boundary conditions are $T(R_b) = T_0$ and $dT(R_w)/dr = Q/(2\pi R_w \kappa_{\text{memb}})$, where $Q$ is the net heat power input and $t$ is the membrane thickness. The solution to Eq. S2 results in the temperature expression

$$T = T_0 + \frac{Q}{2\pi \kappa_{\text{memb}}} \ln(R_w/r).$$  

At the boundary between the irradiated and nonirradiated area ($r = R_b$) we get

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However, within the irradiated area \((r \leq R_b)\), the heat flux density is \(J = Q/(\pi R_b^2 \kappa_{\text{memb}}) = n(dE/dx)\), where \(n\) is the electron flux (i.e., number of electrons arriving per unit area per unit time) and \(\kappa_{\text{memb}}\) is the membrane thickness. In this case, the solution to Eq. S2 yields the temperature at the illuminated area to be

\[
T = T_0 + \frac{Q}{2\pi \kappa_{\text{memb}}} \ln(R_w/R_b).
\] [S4]

Now let us consider the droplet residing on a surface of Si₃N₄ membrane and assume that it is in the center of the irradiated area (Fig. S6) at \((r = 0)\) where the membrane temperature is

\[
T_{\text{memb}} = T_0 + \frac{Q}{2\pi \kappa_{\text{memb}}} \ln(R_w/R_b) + \frac{R_b^2}{4\kappa_{\text{memb}}} J_{\text{memb}}.
\] [S5]

Next, we consider the droplet residing on top of this Si₃N₄ membrane (where \(R_{\text{drop}} \ll R_b\)). As illustrated in Fig. S6, we make an assumption that heat flows through a thin contact interface layer of thickness \(l_0\) as drop temperature reaches \(T_{\text{drop}}\), due to heat power input, \(Q\), from electron beam. Then, the one-dimensional heat transfer equation is given by

\[
-k_{\text{drop}} \frac{d^2 T}{dz^2} = 0
\] [S7]

with the simple solution

\[
T_{\text{drop}} = \frac{Q}{k_{\text{drop}} A} z + T_{\text{memb}},
\] [S8]

where, if we assume that droplet transfers heat across the contact (with height of \(l_{\text{drop}}\), and area of \(\pi R_{\text{drop}}^2\)) to a membrane, and that total power delivered to droplet is \(Q \approx J_{\text{memb}} \pi R_{\text{drop}}^2 l_{\text{drop}} t\), we arrive at final expression that defines the temperature in terms of membrane, droplet properties, and beam conditions. The final expression for drop temperature is then

\[
T_{\text{drop}} = T_0 + \frac{J_{\text{memb}} R_b^2}{2\pi \kappa_{\text{memb}}} \ln(R_w/R_b) + \frac{J_{\text{memb}} R_b^2}{4\kappa_{\text{memb}}} + \frac{J_{\text{drop}} l_{\text{drop}}}{k_{\text{drop}}}.
\] [S9]

Fig. S7 plots the temperature change of the nanodroplet with respect to the ambient temperature \((\Delta T = T_{\text{drop}} - T_0)\) as a function of electron beam flux for our experimental conditions \([T_0 = 293 \, \text{K}, \ R_w \approx 10 \, \text{μm}, \ R_b \approx 5 \, \text{μm}, \ k_{\text{memb}} \approx 4.9 \, \text{W/}(\text{m·K}), \text{ref. 4, } k_{\text{water}} \approx 0.6 \, \text{W/}(\text{m·K}), \ R_{\text{drop}} \approx 25 \, \text{nm, } l_{\text{droplet}} \approx 10 \, \text{nm, } l_0 \approx 0.37 \, \text{nm}].\) Therefore, TEM imaging doesn’t result in substantial heating of the nanodroplets.

**Convective flow of water.** Based on our temperature estimates at the length scales of our nanodroplets, we will not have convective movement of water because the Rayleigh number defined as (5)

\[
Ra = \frac{\alpha g \Delta T L^3}{\nu \mu} \approx 2 \times 10^{-17}
\] [S10]

is extremely small and we rule out the possibility of convection redistribution of water \((Ra > 10^3 \text{ needed for convective flow to occur})\). Here, \(\alpha = 2 \times 10^{-5} \, \text{K}^{-1}\) is the thermal expansion coefficient of water, \(g = 9.8 \, \text{m/} \text{s}^2\) is the gravitational acceleration, \(\Delta T = 0.1 \, \text{K}\) is the possible temperature difference across the drop, \(L = 50 \, \text{nm}\) is the droplet length scale, \(\nu = 1.4 \times 10^{-7} \, \text{m}^2/\text{s}\) is the thermal diffusivity of water, and \(\mu = 9 \times 10^{-4} \, \text{Pa·s}\) is the water viscosity.

**Temperature gradient.** The temperature gradient is reported to induce the movement of the droplet (6). If we assume typical imaging conditions \(n = 100 \, \text{e}/(\sqrt{\text{A}}^2 \text{·s})\) and that we are imaging at most halfway between the center of the beam and its edge \((0 < r < R_b/2)\) of Eq. S5, we find the temperature radiant of a substrate with the nanodroplet

\[
\frac{dT}{dr} = -\frac{J_{\text{memb}} r}{2\pi \kappa_{\text{memb}}} < 1.6 \times 10^{-5} \, \text{K/\text{nm}}.
\] [S11]

In order for a temperature gradient to induce a droplet movement, the contact angle hysteresis for a droplet movement on that surface, \(\Delta \theta = \theta_{\text{adv}} - \theta_{\text{rec}}\), should satisfy the following condition (6):

\[
\Delta \theta < R_{\text{drop}} \theta_{\mu} \frac{1}{\tau} \frac{dT}{dr}.
\] [S12]

From a quick estimate for water \((\text{surface tension, } \gamma = 72 \, \text{mN/m}; \text{surface tension gradient}, \, d\gamma/dT \approx 0.2 \, \text{mN/(m·K)}; \text{droplet radius, } R_{\text{drop}} = 25 \, \text{nm; critical angle, } \theta_c = 0.3 \, \text{rad})\) we find that contact angle hysteresis is \(\Delta \theta < 3.4 \times 10^{-6} \, \text{rad} \approx 2 \times 10^{-4}\). This condition is practically impossible to satisfy even in recently fabricated ultralow contact angle hysteresis surfaces \((\Delta \theta > 1^\circ)\) (7, 8). Therefore, we safely rule out the possibility of temperature gradient induced movement of nanodroplets.

Nonuniform electron beam profile may potentially be a source for temperature gradient, but our beam is considerably uniform (Fig. S8).

**Possible Role of Electron Beam-Induced Radiation Pressure on Droplet Deformation.** To consider the effect of the radiation pressure exerted by electron beam on a specimen that is being image due to electron scattering, we need to consider only the fraction of the electrons that are scattered, which is given by

\[
\frac{N_{\text{scat}}}{N_{\text{tot}}} = 1 - \exp(-t/\lambda),
\] [S13]

where \(N_{\text{scat}}\) is the number of scattered electrons. \(N_{\text{tot}}\) is total number of electrons impacting the sample, \(t\) is specimen thickness, and \(\lambda\) is mean free path of the 120-keV energy electron in water.

The momentum change, \(\Delta p\), of each scattered electron during the time interval, \(\Delta t\), when an electron interacts with the sample is \(\Delta p = p(1 - \cos \theta) = (2m_e E)^{1/2}(1 - \cos \theta)\), where we have neglected relativistic effects for simplicity. This momentum change exerts a force and therefore a pressure on a sample area of \(A\):

\[
P = \frac{F}{A} = \frac{N_{\text{scat}} \Delta p}{A \Delta t} = \frac{N_{\text{scat}} \sqrt{2m_e E (1 - \cos \theta)}}{A \Delta t} = \frac{N_{\text{tot}} \lambda}{A \Delta t} (1 - \exp(-t/\lambda)) \sqrt{2m_e E (1 - \cos \theta)},
\] [S14]

where \(\theta\) is the scattering angle (usually a few degrees), \(m_e = 9.1 \times 10^{-31} \, \text{kg}\) is the mass of the electron, and \(E = 120 \, \text{keV}\) is the energy of the electron. If we assume that electrons undergo complete backward scattering (\(\theta = 180^\circ\)) which yields the maximum possible pressure, we calculate a pressure of 0.31 Pa, which is negligible compared to Laplace pressure inside the nanodroplet:

\[
P = \frac{\gamma}{R} = 2.9 \, \text{MPa}.
\]
Here we used known values of $\gamma = 0.072$ N/m, $m_e = 9.1 \times 10^{-31}$ kg, $E = 120$ keV, $(N_{\text{ex}}) = 100$ electrons/(A$^2$·s) – typical experimental values, $t = 20$ nm, $\lambda = 232$ nm (9), $R = 25$ nm. Therefore, we conclude that it is unlikely that radiation pressure will induce any noticeable deformation of the nanodroplet.

Possible Role of Electrostatic Forces in Deformation of the Nanodroplet. Electrostatic effects may also deform the nanodroplets. We can model the nanodroplet of radius $R$ to be a spherical capacitor with the capacitance of $C = 4\pi\varepsilon_0 R$ that charges up with charge $q$ when exposed to energetic electron beam as a result of ionization ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m). The energy stored in this nanodroplet capacitor is then $E = q^2/2C$. In order for the electrostatic energy to induce a deformation, it should be comparable to the surface energy of the nanodroplet, $E = \gamma A = 4\pi\varepsilon_0 R^2$, where $A = \pi R^2$ is the surface area of the sphere. Setting electrostatic energy equal to the surface energy of the nanodroplet ($R = 25$ nm), we obtain total charge necessary to induce the deformation of

$$q = 4\pi(2\varepsilon_0\gamma R^3)^{1/2} = 350e.$$ 

Nanodroplet with a radius of 25 nm contains about $2.2 \times 10^7$ water molecules. Such ionization of a very small fraction of water molecules ($350/2.2 \times 10^7 = 0.0016\%$) can lead to internal electrostatic repulsive force that results in toroidal shape as water is pushed toward the rims of the nanodroplet, leading to an increase in contact angle until the advancing contact angle is reached. As the droplet steps forward it may lose some outward charge diffusion (to membrane and air interface) and because of the enlarged total area, which will reduce the overall charge of the droplet as it comes to rest and this cycle repeats, forcing the nanodroplet to undergo stick-slip movement.


Fig. S1. The liquid cell. (A) Si$_3$N$_4$ membrane windows both on top and bottom frame are aligned and attached together with indium spacer providing a gap for liquid to be loaded from two large openings at the top of the chip. Once liquid is loaded, the chip is sealed by a copper gasket that prevents the liquid from being exposed to vacuum of TEM. Surface topography of Si$_3$N$_4$ membrane window (B) before and (C) after glow discharge.

Fig. S2. Water nanodroplet formation. TEM micrograph showing the droplet formation as thin water film recedes when exposed to an electron beam with flux of $>120$ e/(A$^2$·s).
Fig. S3. Influence of electron beam on the surface potential of the membrane obtained by scanning kelvin probe microscopy. (A) Prior to an electron beam exposure. (B) After the exposure to an electron beam (approximately $60 \text{ e/Å}^2\text{s}$ for duration of approximately 4 min; measured approximately 60 min after electron beam exposure). (C) Histogram of voltage distribution of Si$_3$N$_4$ before (blue) and after (red) the electron beam exposure obtained from 512 x 512 pixel scanning kelvin probe micrographs.

Fig. S4. Estimating the rough thickness of a nanodroplet. (A) Thickness of a stationary 30-nm water droplet. (B) Thickness as 30-nm droplet prepares to step by forming a torus structure. (C) Thickness of a stationary 60-nm water droplet. (D) Thickness as 60-nm droplet prepares to step by forming a torus.
Fig. S5. Nanodroplet parameters. (A) Droplet 1 and droplet 2. (B) Coordinates x-y of two droplets. (C) Instantaneous velocities of the droplet 1 (blue) and droplet 2 (green). (D) Area of the droplet 1 (blue) and droplet 2 (green).

Fig. S6. Schematic of droplet under e-beam. Electron beam (yellow region) interacts both with the substrate and freestanding Si$_3$N$_4$ membrane. Absorbed energy from droplet dissipates into the membrane, while the energy input into membrane dissipates to thick Si frame of the chip, which is in direct contact with the specimen holder.

Fig. S7. Estimated temperature dependence on electron dose. (A) Temperature difference between the membrane and the ambient environment due to the electron beam. (B) The difference between the nanodroplet and the membrane temperature in the presence of the 120 keV electron beam.
Fig. S8. Typical beam profile used during imaging of droplet movement recorded by camera appears to be considerably flat (within 5% of incident beam intensity).

Movie S1. Movie of water film flowing back and rewetting the membrane surface after beam was turned off for a few minutes.

Movie S2. Movie of a approximately 50-nm nanodroplet (red outline) executing stick-slip movement on a flat $\text{Si}_3\text{N}_4$ film imaged with electron flux of $52 \text{ e}/(\text{Å}^2\cdot\text{s})$.

Movie S2 (MOV)
Movie S3.  Movie of an approximately 30-nm nanodroplet executing stick-slip movement on a flat Si$_3$N$_4$ film imaged with electron flux of 95 e/Å$^2$·s.

Movie S3 (MOV)

Movie S4.  Movie of an approximately 60-nm nanodroplet executing stick-slip movement on a flat Si$_3$N$_4$ film imaged with electron flux of 95 e/Å$^2$·s.

Movie S4 (AVI)

Movie S5.  Movie of an approximately 15-nm nanodroplet executing attempting stick-slip movement on a flat Si$_3$N$_4$ film imaged with electron flux of 95 e/Å$^2$·s. However, the droplet remains pinned to the surface and immobile.

Movie S5 (MOV)