LETTERS

Non-coalescence of oppositely charged drops

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Electric fields induce motion in many fluid systems, including polymer melts[1], surfactant micelles[2] and colloidal suspensions[3]. Likewise, electric fields can be used to move liquid drops[4]. Electrically induced droplet motion manifests itself in processes as diverse as storm cloud formation[5], commercial ink-jet printing[6], petroleum and vegetable oil dehydration[7], electrospray ionization for use in mass spectrometry[8], electrowetting[9] and lab-on-a-chip manipulations[10]. An important issue in practical applications is the tendency for adjacent drops to coalesce, and oppositely charged drops have long been assumed to experience an attractive force that favours their coalescence[11–13]. Here we report the existence of a critical field strength above which oppositely charged drops do not coalesce. We observe that appropriately positioned and oppositely charged drops migrate towards one another in an applied electric field; but whereas the drops coalesce as expected at low field strengths, they are repelled from one another after contact at higher field strengths. Qualitatively, the drops appear to 'bounce' off one another. We directly image the transient formation of a meniscus bridge between the bouncing drops, and propose that this temporary bridge is unstable with respect to capillary pressure when it forms in an electric field exceeding a critical strength. The observation of oppositely charged drops bouncing rather than coalescing in strong electric fields should affect our understanding of any process involving charged liquid drops, including de-emulsification, electrospray ionization and atmospheric conduction.

The non-coalescence behaviour is readily demonstrated experimentally (Fig. 1, left), using a container with the bottom half filled with water and the top half with an immiscible and poorly conducting oil. Metal wires are inserted into each liquid (at top and bottom) to serve as electrodes. A high-voltage power supply provides a potential difference of the order of 1 kV over approximately 1 cm. Although the applied potential is large, the total current density is low because of the insulating oil. After application of the field, a water drop is pipetted manually into the oil near the top electrode. Dielectrophoretic forces[14] cause the drop to move towards and contact the top electrode, thereby providing the drop a net charge. The drop then moves down towards the oppositely charged oil/water meniscus. Drop motion is recorded with high-speed video.

The behaviour of a 2-μl water drop (0.2 mM KCl) in silicone oil is captured in the series of images shown in Fig. 1, right. For low field strengths (Fig. 1, top), the drop slowly approaches the oil/water meniscus and coalesces immediately on contact (Supplementary Movie 1). This behaviour is consistent with prior work on electro-coalescence[13,15], where it was found that application of a field simply increases the rate of coalescence; this increase was attributed to charge polarization induced by the applied field. For our experimental configuration shown in Fig. 1, the bottom edge of the small droplet becomes positively charged, whereas the oil/water meniscus beneath it becomes negatively charged. The opposite charges attract, forcing the drop into contact and hastening the overall rate of coalescence.
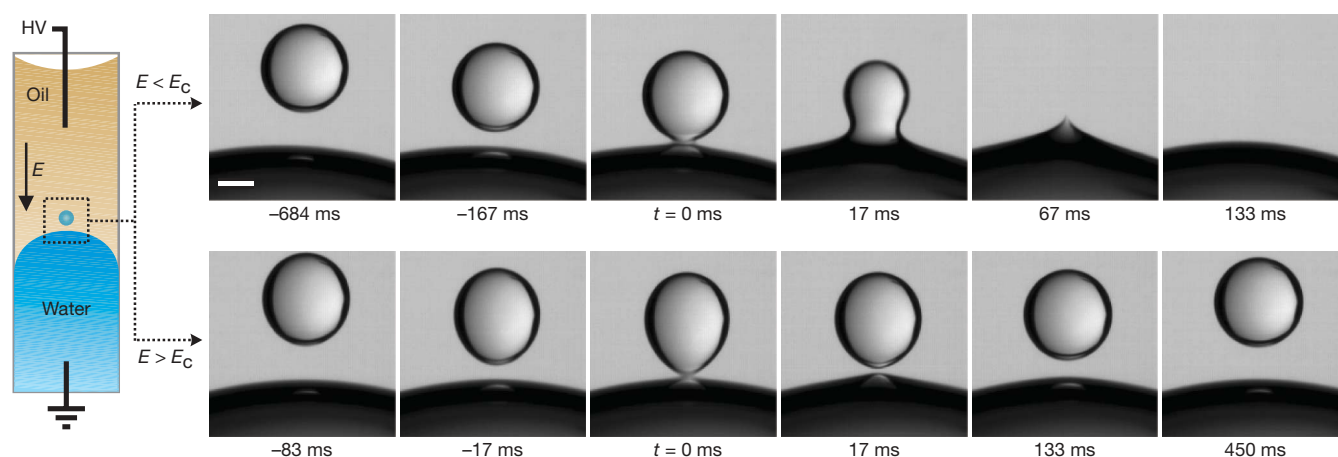

Figure 1 | Electrically driven bouncing of water in oil. Left, diagram of the experimental apparatus ('water' indicates 0.2 M KCl). A high-voltage (HV) power supply provides the electric field. Right, droplet coalescence (top) and bouncing (bottom); time (*t* in ms) is relative to the video frame labelled *t* = 0. Top, *E* = 160 V mm⁻¹, d.c. The drop slowly approached the oil/water interface, and then coalesced on contact. Bottom, *E* = 300 V mm⁻¹, d.c. The drop quickly approached the oil/water meniscus, briefly made apparent contact, then moved away in the opposite direction. Scale bar, 0.5 mm. Oil is 1,000 centistokes (1,000 cSt) polydimethylsiloxane.

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Above a critical field strength E_c, however, drops fail to coalesce (Fig. 1, bottom). Before contact, the leading edge of the drop noticeably elongates. This elongation results from the electrical stress acting on the charged liquid/liquid interface; the resulting conical shape is often referred to as a Taylor cone[16,17]. In this configuration, the cone is positively charged and therefore attracted towards the negatively polarized oil/water meniscus. After apparent contact with the meniscus, however, the cone recoils and the drop reverses direction, moving upwards against gravity (Supplementary Movie 2). After bouncing, the drop typically moves back to the top electrode. On contact with the metal, the drop again reverses direction and migrates back to the oil/water meniscus, whereupon it bounces again, repeating the cycle. In this fashion, individual drops are observed to bounce back and forth indefinitely (Supplementary Movie 3). We emphasize that the applied potential difference remains constant throughout the experiment, and that coalescence does not occur until the applied field is sufficiently reduced. Although water drops are known to bounce off metallic electrodes[18,19,20], to our knowledge the only previous observation of bouncing off a water/oil meniscus was by Allan and Mason[21], who reported that water drops in silicone oil 'repelled' one another after the drops moved within a critical separation distance. They speculated that an electrical discharge had occurred, but did not otherwise explain the bouncing behaviour.

Why do the droplets bounce? The familiar bouncing of a ball occurs because of a combination of inertia and elasticity, but scaling arguments based on the observed droplet velocities indicate that here inertia does not have a dominant role (Supplementary Information). Instead, the bouncing demonstrated in Fig. 1 appears to be driven entirely by charge transfer dynamics. Recalling that the applied field remains constant, the only way for the drop to travel upwards against gravity is if the electrostatic force is oriented in that direction. The reversal of direction following each bounce indicates that the net charge in the drop switches sign, which means charge must be transmitted during the bounce. A striking consequence of this charge transfer is demonstrated in Fig. 2, in which multiple water drops were inserted into the oil phase. The drops rapidly arranged into a chain extending from the oil/water meniscus, whereupon individual droplets within the chain oscillated back and forth between their neighbours in a coordinated fashion. The leading edges of neighbouring drops extended towards each other in a 'double-cone' geometry, briefly made contact, then recoiled. The bouncing events propagated up and down the chain, suggesting that charge is conducted through the chain in this manner (Supplementary Movie 4). The behaviour qualitatively resembles the motion in 'Newton's cradle' (a series of vertically aligned pendula, set into motion by contact with one another), except here linear momentum is apparently conveyed via charge transfer and is not necessarily conserved. For example, drops were frequently observed with a larger absolute velocity after contact, yielding an apparent coefficient of restitution larger than unity. Because the motion is electrically driven, the increased velocity indicates that an increased net charge was acquired during the bounce.

As the charge consists of dissociated ionic species (for example, K^+ and Cl^-) in the water phase, the ions must transfer from one drop to another during each bounce. There are several possible mechanisms for charge transfer, including conduction through the oil, dielectric breakdown or electrospray[8] of smaller drops, but our direct high-speed observations show that, at least in silicone oil, a short-lived aqueous bridge forms between the drops. By zooming-in on a bounce (with a ×10 microscope objective) and capturing images at 25,000 frames s^{-1}, an image of such a bridge was captured (Fig. 3a, Supplementary Movie 5). The bridge was short lived—the frames immediately before and after show a gap of oil between the drops, indicating that the bridge existed for less than 80 μs. Charge transfer presumably occurs by ionic conduction through the water phase during the short lifespan of the bridge.

A temporary meniscus bridge is thus the conduit of charge between bouncing drops, but it is not obvious why it pinches off. Coalescence would reduce the system's energy by minimizing the total surface area and corresponding surface energy. The usual explanations for drop stability invoke prevention of direct contact by the presence of surfactants, polymers or colloids at the oil/water interface[22,23], but these do not apply because the drops clearly make physical contact (as shown in Fig. 3a).

To explore possible driving forces for pinch-off, we systematically measured the critical field strength E_c above which bouncing occurs. The threshold field strength depended sensitively on the magnitude of charge on the droplet, Q, which itself depends on the details of charge transfer between the droplet and the previous interface it contacted (for example, the metal electrode). We determined Q using Stokes' drag for a sphere and the measured drop velocity (Supplementary Information). By taking into account both Q and E, we found that the threshold between bouncing and coalescence for water in silicone oil is well defined in terms of a critical electric force $F_E^{crit} = QE_c$, the magnitude of which depends on the dissolved salt concentration. Whenever drop charge and applied field are such that $QE_c > F_E^{crit}$, the drops invariably bounced (the upper region of Fig. 3c).

The data in Fig. 3c rule out thermal Marangoni flows or Maxwell stresses as the driving force for pinch off (see Supplementary Information for details), and suggest instead that capillary forces render the meniscus bridge intrinsically unstable above a critical cone angle. The experimental observations show that drops assume a 'double-cone' geometry in the vicinity of the meniscus bridge (Fig. 3b). The Young–Laplace equation approximates the capillary pressure inside the bridge as
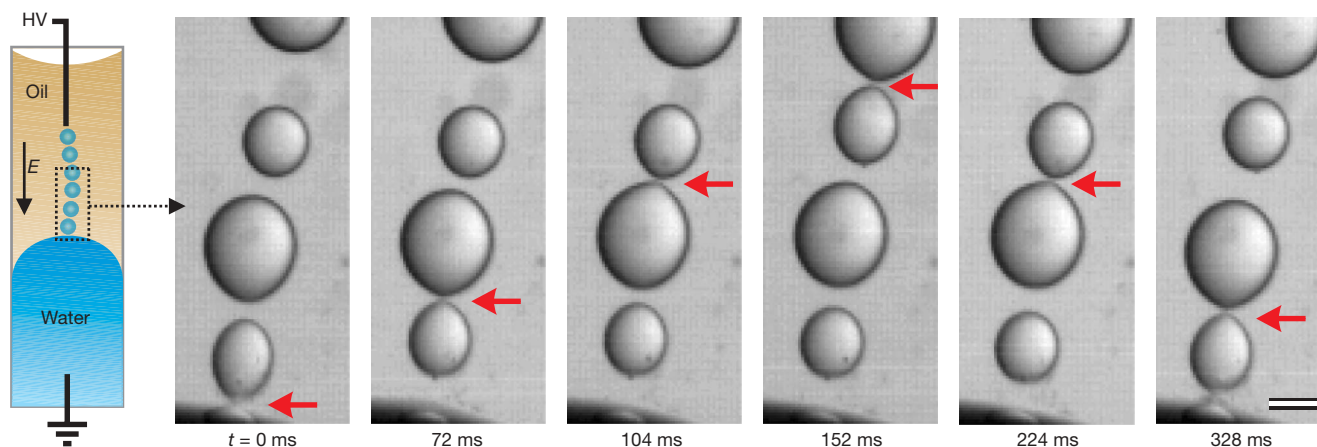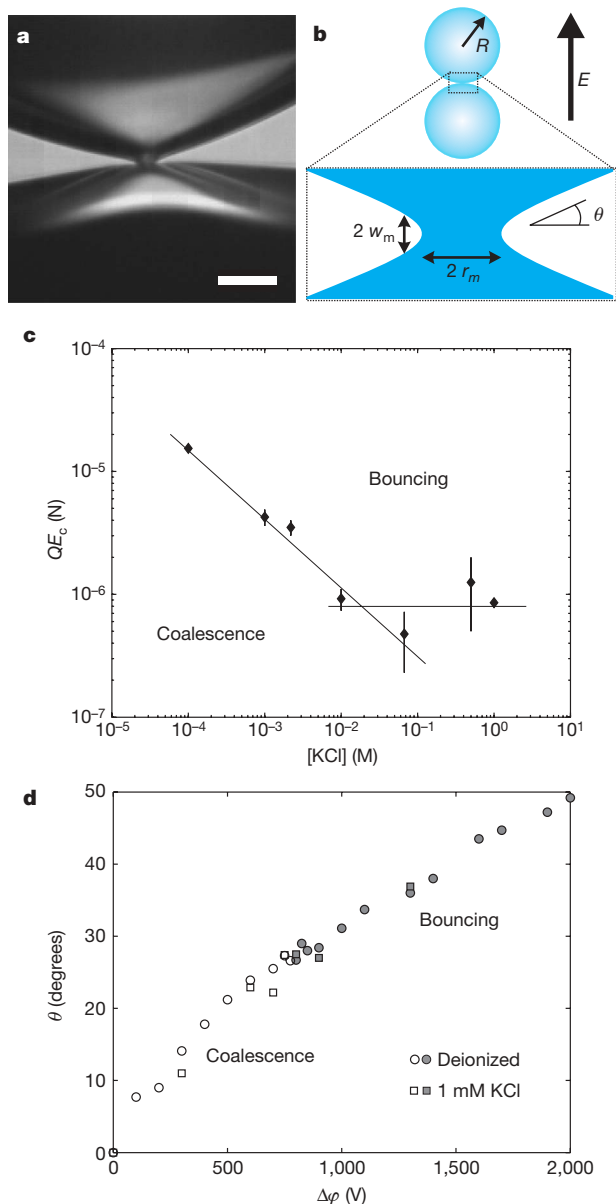

Figure 2 | Bouncing within a chain of water droplets in oil. Left, diagram of the apparatus, showing area magnified at right ('oil' and 'water' as Fig. 1). Right, bouncing of droplets. Arrows indicate the location of charge exchange during each bounce. $E = 300\ V\ mm^{-1}$, d.c. Scale bar, 0.5 mm.

difference between the bulk of the drop and the meniscus bridge is $\Delta p \equiv p_{drop} - p_{bridge} = \frac{2\gamma}{R} - \frac{\gamma}{r_m}(1 - \cot\theta)$. The meniscus bridge is small, so the inequality $r_m \ll R$ holds and to good approximation the pressure difference is:

$$\Delta p \approx \frac{\gamma}{r_m}(\cot\theta - 1) \qquad (2)$$

The sign of the pressure difference and corresponding flow direction thus depend only on θ. For sufficiently steep cones ($\theta > 45°$), the pressure is higher in the meniscus bridge (that is, $\Delta p < 0$), so fluid moves from the meniscus back into the drop, driving pinch-off. The cone angle between approaching drops increases with field strength, as evidenced by the observations here and in previous numerical studies[24,25] (which did not consider the behaviour after contact). Likewise, drops with larger net charge form cones more readily when a field is applied[16], which is consistent with the observed dependence of

Figure 3 | Meniscus bridge, critical field strength and critical cone angle.
a, High-magnification, high speed image of the temporary meniscus bridge between two bouncing water drops (1 M KCl) in silicone oil (1,000 cSt). Dark regions are water, the brighter areas within the water are reflections. $E = 200\,\text{V mm}^{-1}$; scale bar, 0.1 mm. **b**, Definition sketch of the meniscus bridge. **c**, The critical electric force as a function of salt concentration for 2-μl water droplets in 1,000 cSt silicone oil. Lines are to guide the eye. Error bars indicate the range of observed transitions between bouncing and coalescence. **d**, The cone angle at the time of contact between water drops in air as a function of applied potential ($\Delta\varphi$). Open symbols denote coalescence; filled symbols denote bouncing. Circles, deionized water (4 μS cm^{-1}); squares, 1 mM KCl (163 μS cm^{-1}).

$$p_{bridge} = p_0 + \gamma\left(\frac{1}{r_m} - \frac{1}{w_m}\right) \qquad (1)$$

where p_0 is the ambient pressure, γ is the oil/water interfacial tension, and the two curvatures are defined by the radius and width of the meniscus bridge, r_m and w_m, respectively (Fig. 3b). This approximate expression neglects dynamic effects, but helps estimate the flow direction in the meniscus bridge. For the double-cone angle θ formed by the intersection of two Taylor cones, the meniscus width scales as $w_m \approx r_m \tan\theta$, and since the capillary pressure in the bulk of the drops (each assumed to have radius R) is $p_{drop} = p_0 + 2\gamma/R$, the pressure
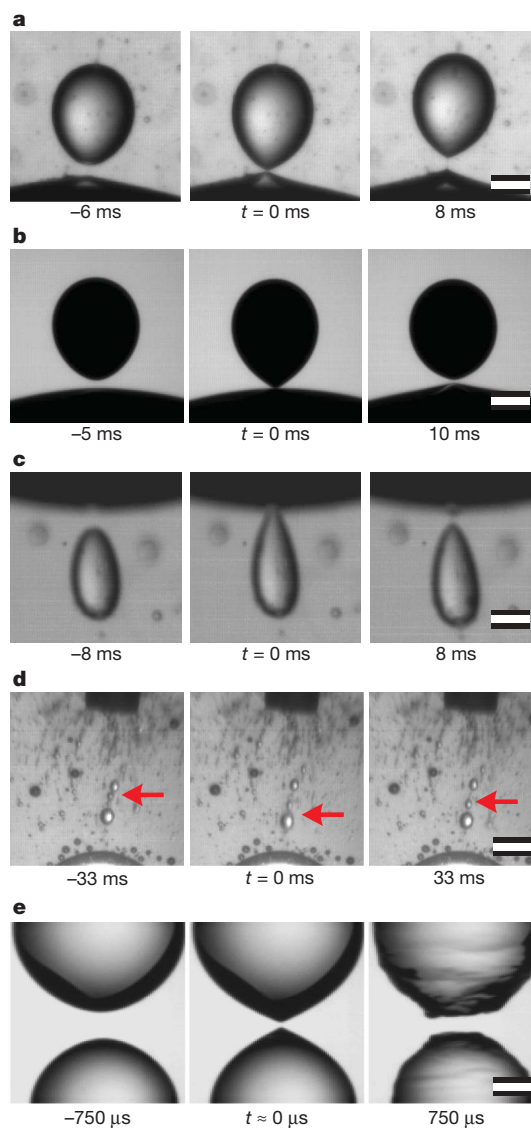

Figure 4 | Non-coalescence behaviour in different liquid systems.
a, Vinegar (5% acetic acid) in olive oil. $E = 600\,\text{V mm}^{-1}$. **b**, Deionized water with polystyrene particles (0.82-μm diameter, 2.2%) in 1,000 cSt silicone oil. $E = 300\,\text{V mm}^{-1}$. **c**, Ethanol (95%, at top in dark regions) in mineral oil. $E = 400\,\text{V mm}^{-1}$. **d**, Multiple droplets of 1 M KCl in light Louisiana Gulf sweet crude oil. $E = 300\,\text{V mm}^{-1}$. Dark rectangle near top is the electrode; curved dark region near bottom is the water/oil meniscus. **e**, Deionized water drops in air. $E = 500\,\text{V mm}^{-1}$. The drops are attached directly to electrified nozzles. Scale bars: **a**–**d**, 0.5 mm; **e**, 0.3 mm.

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the bouncing threshold on the drop charge for a given applied field strength.

The preceding model says nothing about the conductivity of the droplet, whereas Fig. 3c shows that it can have an important role, especially for lower salt concentrations. We therefore measured the cone angle at the time of contact between two water droplets in air as a function of the applied potential (Fig. 3d). To isolate the cone dynamics from the drop motion, the water drops were attached directly to electrified nozzles and slowly brought together; this procedure also ensured that the cones contacted at a known location, simplifying the high-speed photography (67,000 frames s^{-1}). Two significant results were obtained. First, the drops invariably coalesced for $\theta \lesssim 30°$, but recoiled for larger angles. Second, the critical angle was the same for drops with no added salt (deionized water) and for drops with 1 mM KCl, concentrations that correspond to the regime of high sensitivity to salt concentration shown in Fig. 3c. The data indicate that conductivity plays a significant part in determining how large an electric force must be applied to a moving charged drop to achieve a certain cone angle; but whether coalescence occurs or not depends only on the cone angle following contact.

Inspection of Fig. 3d suggests that the critical cone angle is closer to 30° than 45°, and a more detailed analysis of the nonlinear free-boundary problem for the capillary pressure (J.C.B., W.D.R., A.B. and H.A.S., manuscript in review) predicts in fact a critical cone angle of approximately 31°. But the key point here is that above a critical field strength pinch-off is inherently favoured, with other material parameters having only an indirect role in governing the coalescence behaviour. Specifically, interfacial tension, conductivity and electric field define the cone angle before contact; but after contact, only the geometry of the meniscus bridge matters. A significant implication of this model is that non-coalescence will occur for any liquid/liquid or gas/liquid system, provided that the electric field induces a sufficiently steep meniscus bridge. Indeed, our experiments show that the bouncing behaviour is quite general, occurring in a variety of systems including olive oil, crude oil and air (Fig. 4). That non-coalescence occurs in such diverse systems is consistent with the independence of this phenomenon on system material properties as predicted by the capillary pinch-off model.

The universal nature of the non-coalescence behaviour can explain observations in very different fields. For example, a study[26] of atmospheric charge conduction reported that the coalescence efficiency of oppositely charged water drops in air plateaus above a critical charge density. A similar plateau has been observed in the context of oil dehydration [27,28], while experiments[29] on drop pairs in microfluidic devices revealed that adjacent water drops repelled one another above a frequency-dependent critical field strength. Although the applied waveform differed in these studies, the stresses giving rise to Taylor cones (and hence the double-cone geometry) scale as the square of the applied field[17]. Electric fields that are steady, oscillatory or pulsed will thus all fail to induce coalescence above some critical field strength. Reviewing de-emulsification experiments using pulsed fields[30], Eow et al. noted[7] that "…chains of water droplets are usually created during periods of high voltage, followed by rapid coalescence during periods of reduced or no voltage". The capillary pinch-off mechanism presented here helps to explain the above observations.

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