Oscillatory coalescence of droplets in an alternating electric field

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Partial coalescence of microdroplets is of interest for a number of microfluidic applications where a controlled fluid transfer from one droplet to another is required for mixing, dispensing, and metering of chemical and biological fluids. We report a phenomenon of oscillatory coalescence of water droplets situated in an alternating electric field. The oscillatory coalescence exists in a range of electric capillary numbers and fluid conductivities and proceeds through a finite number of cycles. Each cycle includes attractive and repulsion stages and results in a partial fluid transfer through a liquid bridge formed between droplets during the repulsion stage. We propose an energy model to describe the phenomenon and define its limit of existence.

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I. INTRODUCTION

The excess energy of a fluid surface defines shape of individual droplets and free jets. A role of the surface energy increases with a transition to micro- and nanoscale where electric fields have been successfully applied to balance surface effects in DC and AC electrosprays [1–4], electrospinning [5], droplet manipulation, breakup [6,7], emulsification [8,9], and electrically enhanced coalescence [10]. A conducting droplet freely suspended in an insulating fluid accepts spherical shape in the absence of an electric field. Upon application of a field, the droplet becomes elongated along the direction of the field and bursts at high electric fields. The droplet deformation and break up is controlled by a balance of the surface tension and electric forces typically expressed in the form of the electric capillary number $\mathrm{Ca}_E = \varepsilon\varepsilon_o E^2 R/\gamma$, where ε_o is the permittivity of free space, ε is the relative permittivity of the liquid, E is the magnitude of the electric field, R is the radius of the drop, and γ is the surface tension. A conducting droplet in a dielectric fluid breaks up when the electric capillary number reaches a well-defined critical value of $\mathrm{Ca}_E^* = 0.21$ [6]. The effects of droplet and media conductivity, viscosity, and dielectric permittivity on shape and stability of the droplet have been extensively studied [11].

The reverse process, coalescence of a droplet pair, is rich in physical effects and is the subject of continuous research efforts. The electric capillary number for a pair can be defined using the radius of the single spherical droplet with the equivalent total volume. At low capillary numbers the droplet attraction leads to complete coalescence [10]. At an intermediate range of capillary numbers a noncoalescence [12,13] or a partial coalescence [14,15] of oppositely charged droplets is observed, when the droplets repel and bounce back from each other after contact and partial fluid and electric charge transfer. Theoretically, the complete coalescence of a pair is possible at $\mathrm{Ca}_E < \mathrm{Ca}_E^*$; however, the droplets in the pair often emit electrified jets and disintegrate well below Ca_E^* [14]. In this work, we report a phenomenon of oscillatory coalescence of water droplets. Two droplets situated in an alternating electric field coalesce through multiple repetitive stages of attraction, liquid bridge formation, fluid transfer, and repulsion. The goal of this study is to characterize this phenomenon, define its region of existence, and uncover the underlying physical mechanisms.

II. EXPERIMENTAL

In our experiments, a pair of water droplets with the same conductivity is dispensed by a micropipette in the middle of the oil-filled cell. The cell is filled with silicone oil with the conductivity

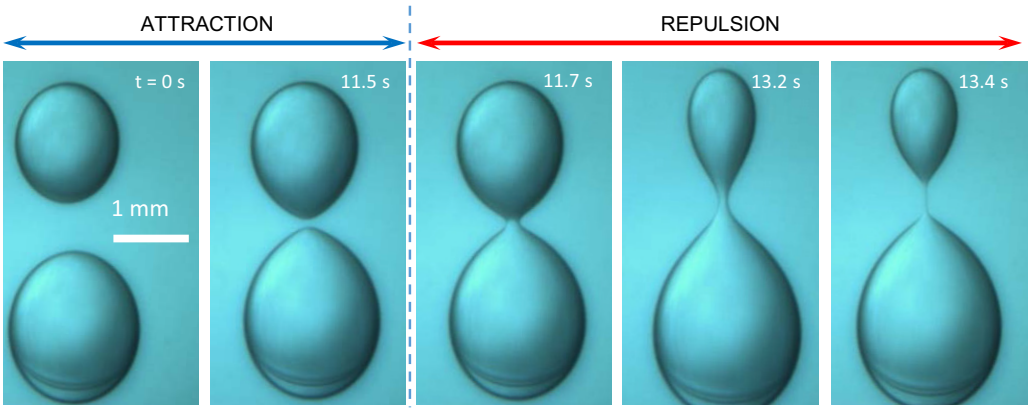

FIG. 1. Attraction and repulsion stages of the first oscillatory coalescence cycle for a pair of water droplets suspended in silicone oil ($E = 0.38\,\mathrm{kV/mm}$, $\sigma_w = 1.1\,\mu\mathrm{S/cm}$, $\alpha = 0.5$). The liquid bridge formed at the repulsion stage alters the droplet dynamics by allowing charge and fluid transfer between droplets (see Movie 1 [16]).

$\sigma_{so} = 10^{-11}\,\mu\mathrm{S/cm}$, kinematic viscosity $\nu_{so} = 10\,000\,\mathrm{cSt}$, and relative permittivity $\varepsilon_{so} = 2.7$. A droplet pair is characterized by radii of the top and bottom droplets r_1 and r_2, the droplet size ratio $\beta = r_1/r_2$, and the droplet volume ratio $\alpha = V_1/V_2$. The total volume of the droplet pair is fixed at $7.5\,\mu\mathrm{L}$. The initial volume ratio is set in an interval from 0.5 to 1.5. The conductivity of water σ_w is adjusted in the range from 0.5 to $235\,\mu\mathrm{S/cm}$ by salt addition. The alternating electric field E with the RMS value from 0.3 to 0.6 kV/mm is applied parallel to the line of centers of the droplets. The following applied frequencies f_{AC} are used: 60 Hz, 10.3 kHz, 16.8 kHz, and 41.7 kHz. In all studied cases the charge relaxation frequencies of water $f_w = \sigma_w/\varepsilon_w\varepsilon_o$ and silicone oil $f_{so} = \sigma_{so}/\varepsilon_{so}\varepsilon_o$ satisfy the following relationship $f_w > f_{AC} \gg f_{so}$, representing a classic case of a leaky dielectric droplet pair suspended in a pure dielectric fluid. A CCD camera equipped with a scientific grade zoom lens is used to capture droplet dynamics at a rate of 10 frames per second. Captured images are analyzed with custom MATLAB code to infer positions, shapes, and volumes of the droplets.

III. RESULTS AND DISCUSSION

Figure 1 shows a representative dynamics of a droplet pair. Initially freely suspended droplets polarize in the applied electric field, slightly elongate, and start to migrate towards one another. Polarization charges induced in the droplets affect the field uniformity enhancing electric fields at top and bottom surfaces of the droplets and especially in the region between the droplets. The droplets assume characteristic egglike shape. At 11.7 s, the local electric field between droplets reaches a critical value and the liquid bridge forms between droplets. The bridge formation allows charge and fluid transfer between the droplets. The droplets assume the same potential. Positive and negative charges are shifted to the opposite ends of the continuous fluid structure. These charges alternate with the applied frequency using the conducting bridge. The Maxwell stresses act on the opposite ends of the interconnected pair and the droplets start to move away from each other (13.2 s). Concurrently, the difference of the droplet diameters creates a pressure difference that drives the fluid flow through the bridge. A visual increase of one droplet and a decrease of another is observed between 11.7 and 13.4 s. The bridge stretches and reduces in diameter but remains stable until $\sim$13.4 s. The bridge breaks up thereafter, and two partially coalesced droplets become electrically isolated forming two attracting dipoles. The attraction-repulsion sequence repeats itself with the oscillatory coalescence frequency f_c until the complete coalescence of the droplets.

At some experimental conditions, more than a few hundred cycles are required to achieve complete coalescence. In Fig. 2(a), the droplet contact repeats about two hundred times and the volume of the

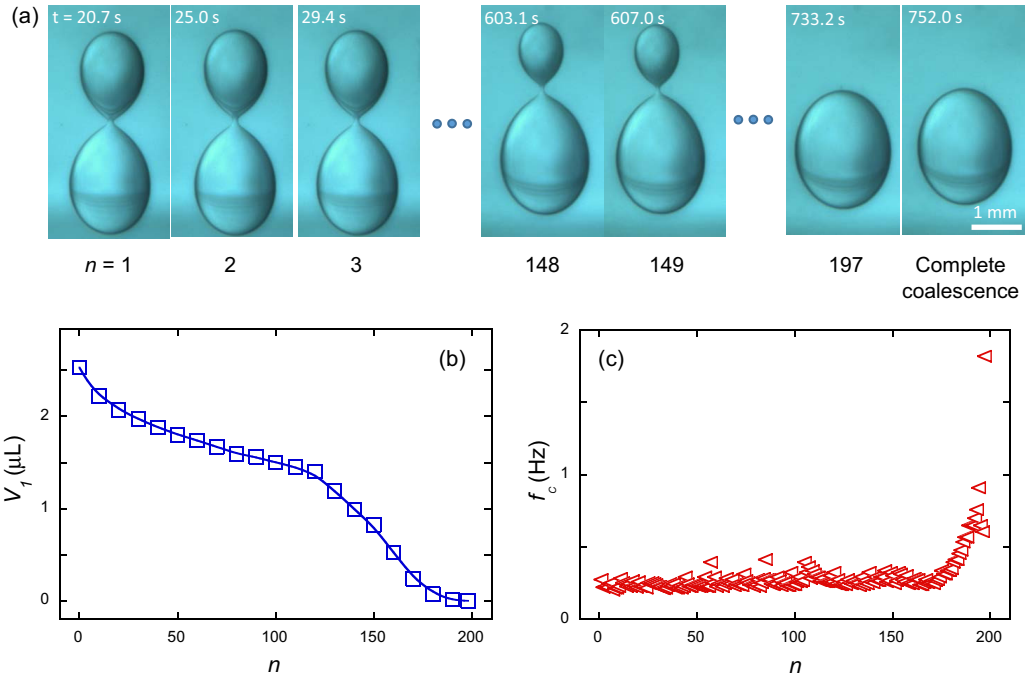

FIG. 2. (a) The oscillatory coalescence between a pair of droplets proceeds through 197 cycles ($E = 0.42\,\mathrm{kV/mm}$, $\sigma_w = 1.1\,\mu\mathrm{S/cm}$, $f_{\mathrm{AC}} = 10.3\,\mathrm{kHz}$). The liquid transfer reduces the droplet volume ratio from $\alpha = 0.5$ to $\alpha \approx 10^{-5}$. The small satellite droplet completely coalesces during the last cycle. (b) The volume of the top droplet monotonically decreases with each cycle. (c) The oscillatory coalescence frequency remains practically constant for nearly 170 cycles.

top droplet decreases with each cycle n as the fluid is transferred from the top to the bottom droplet (see Movie 2 in Ref. [16]). The volume ratio of the droplets consequently decreases from $\alpha = 0.5$ to $\alpha \approx 10^{-5}$. The amount of fluid transfer per cycle ($\sim$12.5 nl/cycle on the average) demonstrates a complex behavior: it first decreases (cycles from 0 to 120), then increases and peaks at $n \approx 150$, and finally exponentially decreases until the final cycle of the oscillatory coalescence [Fig. 2(b)]. The droplet oscillation frequency f_c remains practically constant ($\sim$0.26 Hz) for nearly 170 cycles ($0.06 < \alpha < 0.5$) and steeply increases during the final cycles of the process [Fig. 2(c)].

The fluid transfer is controlled by the pressure difference across the bridge and its geometry. The effect of gravity is negligible in comparison to the surface tension: the characteristic Bond number of the system $\mathrm{Bo} = \Delta\rho g R^2/\gamma$, evaluated using the density difference of the two fluids $\Delta\rho$ and the gravitational acceleration g, is less than 10^{-2}. The excess pressure in the droplets is created by the surface tension and the Maxwell stresses. For an isolated droplet, the Laplace pressure is inversely proportional to the droplet diameter and the Maxwell stresses are size independent. In a pair of unequal droplets, the smaller droplet has higher internal pressure. This forces the fluid transfer through the liquid bridge in the direction from the small to the large droplet. The Laplace pressure difference increases with the number of cycles. It is also expected that field nonuniformity and Maxwell stresses affect the fluid transfer in extremely unequal pairs ($\alpha \ll 1$ and $\alpha \gg 1$). The experiments with droplet pairs at $\alpha = 0.5$ and 1.5 show the fluid transfer from smaller to larger drops (see Movie 3 in Ref. [16]). Oscillatory coalescence of the pair at $\alpha = 0.5$ proceeds through decrease of the top droplet in each consecutive cycle. Conversely, the coalescence of the pair at $\alpha = 1.5$ shows monotonic increase of the top droplet. The system is metastable at the symmetry point ($\alpha = 1$). Two equal droplets in a uniform electric field have the same internal pressure and perform oscillatory motion without noticeable fluid transfer until small initial difference in droplet

size, field nonuniformity, or other body forces shift the system from the metastable point. This noncoalescence phenomena is observed at $\alpha = 1$.

The bridge geometry in a single cycle is changing from a short and wide neck just after the contact to a long thin thread interconnecting the droplets at the late repulsion stage (Fig. 1). This affects the fluid transfer rate. Fluid velocities in the bridge can be evaluated by measuring volumes of the droplets and bridge cross sectional areas. The fluid velocity at the moment of bridge formation reaches ~0.17 m/s ($t = 11.7$ s, Fig. 1). This agrees well with the velocity evaluation based on the Bernoulli equation $v \sim \sqrt{2\Delta P/\rho_w}$, where ΔP is the difference of Laplace's pressures in the droplets, and ρ_w is the water density. This also matches the characteristic velocities of the fluid reported for partial coalescence of droplets in DC field [15]. The fluid velocity drops as the bridge thins out and elongates. For long thin bridges, the characteristic velocity values of ~1 mm/s ($t = 13.4$ s, Fig. 1) are in a good agreement with the estimates based on Poiseuille flow.

The oscillating coalescence has a limit of existence in terms of the electric field strength. The effect of the electric field on the droplet coalescence frequency is shown in Fig. 3(a). The oscillation frequency remains practically constant ~0.2 Hz for electric field strengths from 0.38 to 0.47 kV/mm. The complete coalescence of the droplets after the first contact is observed at the electric fields lower than 0.38 kV/mm ($Ca_E < 0.09$). The bridge thins out and becomes unstable at electric fields greater than 0.47 kV/mm. The droplet oscillation and periodic formation of the thin bridge is observed at $Ca_E = 0.156$ (see Movie 4 in Ref. [16]). However, the bridge is unstable and frequently breaks up generating a fine water-in-oil emulsion in the area between two droplets [8]. The fluid transfer rate drops by two orders of magnitude with the electric field increase from 0.38 to 0.47 kV/mm [Fig. 3(b)]. Only 24 cycles are required for complete coalescence at 0.40 kV/mm, 200 cycles are needed at 0.42 kV/mm, and less than 10% of the fluid is transferred at 0.47 kV/mm after 150 cycles. In contrast, more than 50% of the fluid is transferred during the first cycle at $E = 0.38$ kV/mm, where the two droplets almost completely coalesce, but, then, break up again and continue to oscillate for another 14 cycles reaching $\beta \approx 40$ before the last cycle. The average flowrate is ~2 nl/cycle at $E = 0.47$ kV/mm compared with ~100 nl/cycle at $E = 0.38$ kV/mm. The higher is the electric field strength, the less volume is transferred per cycle. Thinner and longer bridges formed at high electric fields generate significant flow resistance.

The region of existence of the oscillatory oalescence is shown in Fig. 4 in terms of the electric capillary number and the nondimensional frequency f_{AC}/f_w defined as a ratio of the applied frequency to the charge relaxation frequency of water. As expected, the complete coalescence on the first contact is observed at low electric fields ($Ca_E < 0.09$) where the surface tension is dominant. The complete coalescence is also observed at $f_{AC}/f_w > 0.1$. The region of $f_{AC} \approx f_w$ corresponds to the transition from leaky dielectric to pure dielectric behavior of water. A transfer of free charges responsible for the repulsion forces in a coalescing pair is negligible in a pure dielectric fluid. As a result, only attractive forces exist between the droplets in this region and complete coalescence occurs on the first contact. Oscillatory coalescence is observed in the range of capillary numbers $0.09 < Ca_E < 0.15$ and nondimensional frequencies $3 \times 10^{-3} < f_{AC}/f_w < 10^{-1}$. A mode of droplet interaction is changing from oscillatory coalescence to noncoalescence when f_{AC}/f_w drops below 3×10^{-3}. In this mode the droplets first attract towards one another, deform, and develop electrified menisci on the adjacent surfaces. The electrically induced emission of mass starts at a certain distance and results in a partial charge transfer between the droplets. The droplets stabilize without contacting each other interacting via electrified jets. At $f_{AC}/f_w < 3 \times 10^{-3}$, a droplet pair is effectively emulsified into a cloud of fine microdroplets (see Movie 5 in Ref. [16]). A noncoalescence pattern observed at $Ca_E > 0.15$ involves droplets oscillation and periodic formation of unstable thin bridges (see Movie 4 in Ref. [16]). A fine water-in-oil emulsion is created in the region between two droplets by frequent capillary breakups of unstable bridges.

It is interesting to consider oscillatory coalescence of two equal droplets using an energy-based model. The kinetic energy of the droplets is negligible in the highly viscous oil and only surface and electric energies can be considered in the quasistatic approximation. Let the radii of the identical droplets be r and the center-to-center spacing be h. To avoid computational complexity the droplets

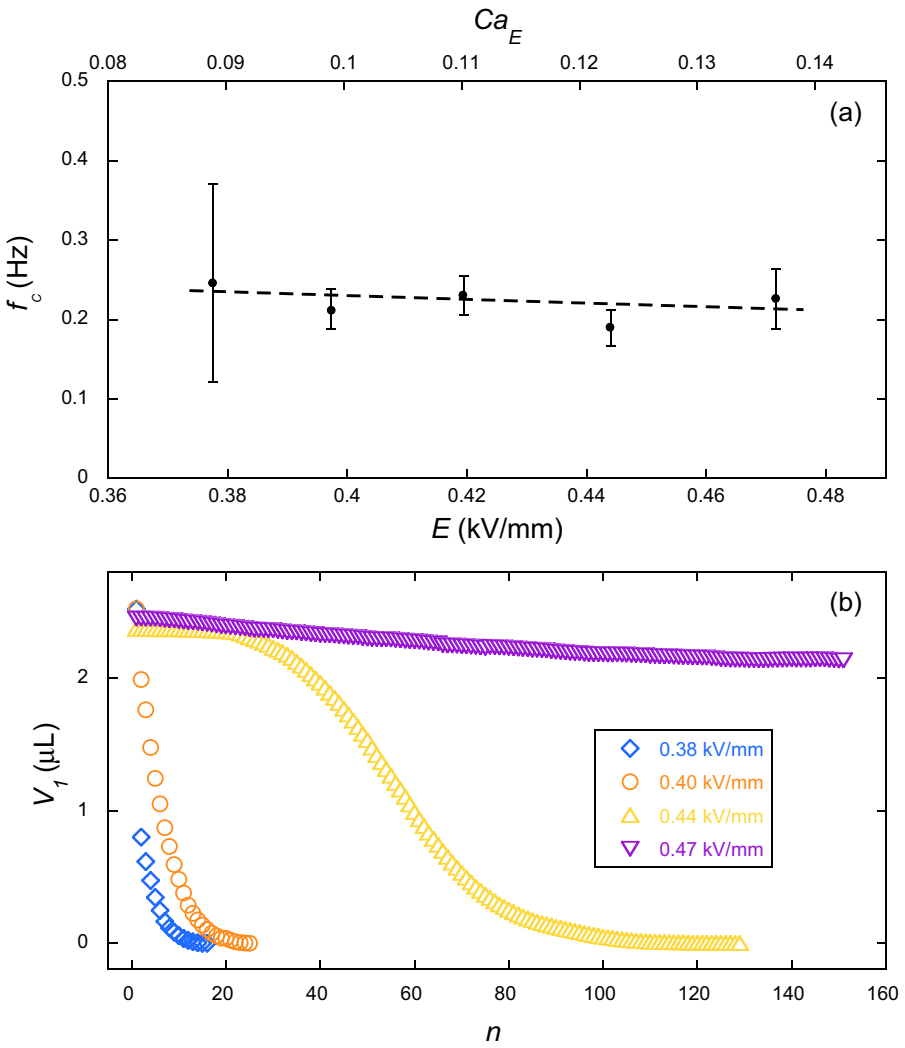

FIG. 3. Effect of the electric field strength on the oscillatory coalescence frequency (a) and fluid transfer (b) for $\sigma_w = 1.1\,\mu$S/cm, $f_{\rm AC} = 10.3$ kHz, and initial $\alpha = 0.5$. The oscillation frequency is averaged over the first 10 cycles. Electric capillary numbers Ca_E are provided for reference.

are considered spherical for $h \geqslant 2r$, and the intersecting spheres model with total volume constraint is employed at $0 \leqslant h < 2r$ [17]. We have further normalized the surface energy of the system by the surface energy of two isolated droplets $8\pi\gamma r^2$ [Fig. 5(a)]. For noncontacting droplets the normalized surface energy u_s is equal to 1; it reduces during the coalescence dropping to $u_s = 1/\sqrt[3]{2}$ for the fully coalesced droplets. The electrical energy of the system U_e is evaluated as $-pE$, where p is the dipole moment of the droplet pair. The dipole moments for isolated, equipotential, and intersecting droplet pairs are calculated numerically using the method of images [17–19]. The magnitudes and locations of the first 100 image charges are considered. The dipole moments available as functions of spacing allow evaluation of the electrical energy of the system. The normalized electrical energy is defined as $u_e = U_e/8\pi\varepsilon\varepsilon_o r^3 E^2$, where $8\pi\varepsilon\varepsilon_o r^3 E^2$ is the electrical energy of two isolated droplets of radius r placed at the electric field E. The normalized energy is equal to -1 for two isolated ($h \to \infty$) and for two fully coalesced ($h = 0$) droplets [Fig. 5(a)]. Electrically isolated droplets attract each other

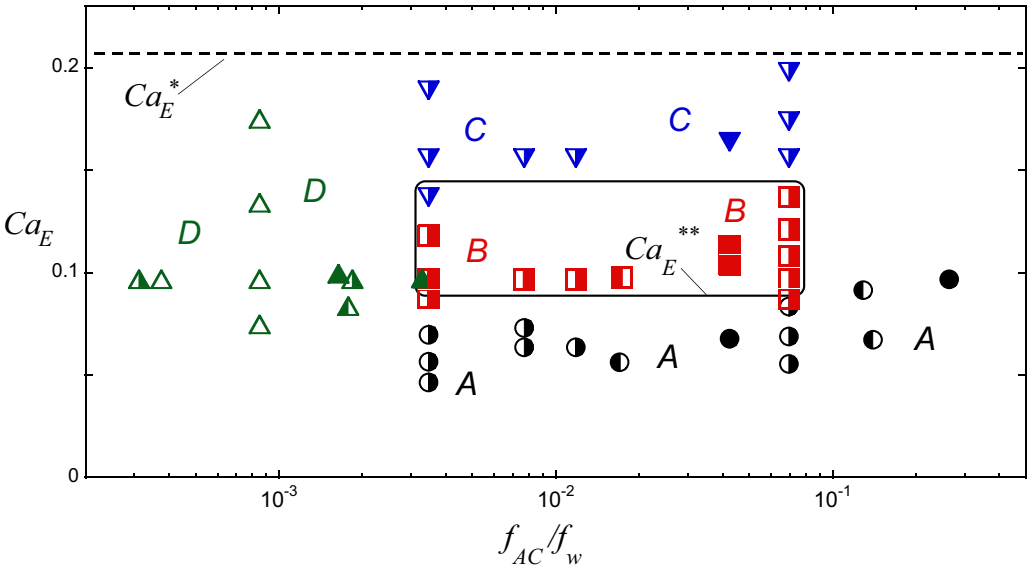

FIG. 4. Diagram illustrating the various coalescence regimes: (*A*) complete coalescence on the first contact, (*B*) oscillatory coalescence, (*C*) noncoalescence with the oscillatory motion of the droplet pair, unstable bridge formation and emulsification, and (*D*) noncoalescence with droplets attraction, deformation and stabilization at a certain distance with electrified jet emissions. The results are obtained with the water conductivities in the range from 0.5 to 235 μS/cm and four applied frequencies: 60 Hz (hollow symbols), 10.3 kHz (symbols solid on the right), 16.8 kHz (symbols solid on the left), 41.7 kHz (solid symbols).

and minimize the electrical energy up to the point of contact $h = 2r$ [Fig. 5(a)]. After contact, the droplets are considered equipotential if $h < 2r$ or if $h > 2r$ and the liquid bridge connection exists. The electric energy of equipotential droplets monotonically decreases with an increase in the droplet spacing [Fig. 5(a)].

We have further normalized the total energy of the system by the surface energy of two isolated droplets $8\pi\gamma r^2$ obtaining the total energy of the droplet pair as

$$u = (U_s + U_e)/8\pi\gamma r^2 = u_s + u_e(8\pi\varepsilon\varepsilon_o r^3 E^2/8\pi\gamma r^2) = u_s + u_e \mathrm{Ca}_E/\sqrt[3]{2}. \tag{1}$$

Using Eq. (1) the total energy of the system can be evaluated for various electric capillary numbers using normalized surface and electrical energies shown in Fig. 5(a).

Two sets of curves for $\mathrm{Ca}_E = 0.06$ and 0.15 show characteristic droplet evolution in the energy space [Fig. 5(b)]. At $\mathrm{Ca}_E = 0.15$, two isolated droplets first minimize the total energy by moving towards each other and making a contact at $h = 2r$. The droplet potentials equalize after the fluid contact. Two scenarios are possible at this point: coalescence or recoil. The outcome is defined by a balance of the attraction and repulsion forces at the point of contact. The magnitudes of the attraction and repulsion forces can be evaluated from the absolute values of the left and right derivatives of du/dh at $h = 2r$ taken along the equipotential curve. At $\mathrm{Ca}_E = 0.15$, the repulsion force proportional to the slope on the right side of the contact point is stronger than the attraction force (the slope on the left side of the contact point). The droplets start to move apart, the liquid bridge forms, elongates and finally breaks up at a certain droplet spacing. The droplets become electrically isolated, transfer to the attraction curve, and the cycle repeats. In contrast, at $\mathrm{Ca}_E = 0.06$, two initially isolated droplets are attracted and fully coalesce after the first contact according to the energy diagram. The model predicts the existence of the critical Ca_E^{**} number that separates regions of complete and oscillatory coalescence. Comparing the absolute values of the left and right derivatives at $h = 2r$ it is possible to evaluate Ca_E^{**} numerically as $\sim$0.1. This value is in a good agreement with our experimental results

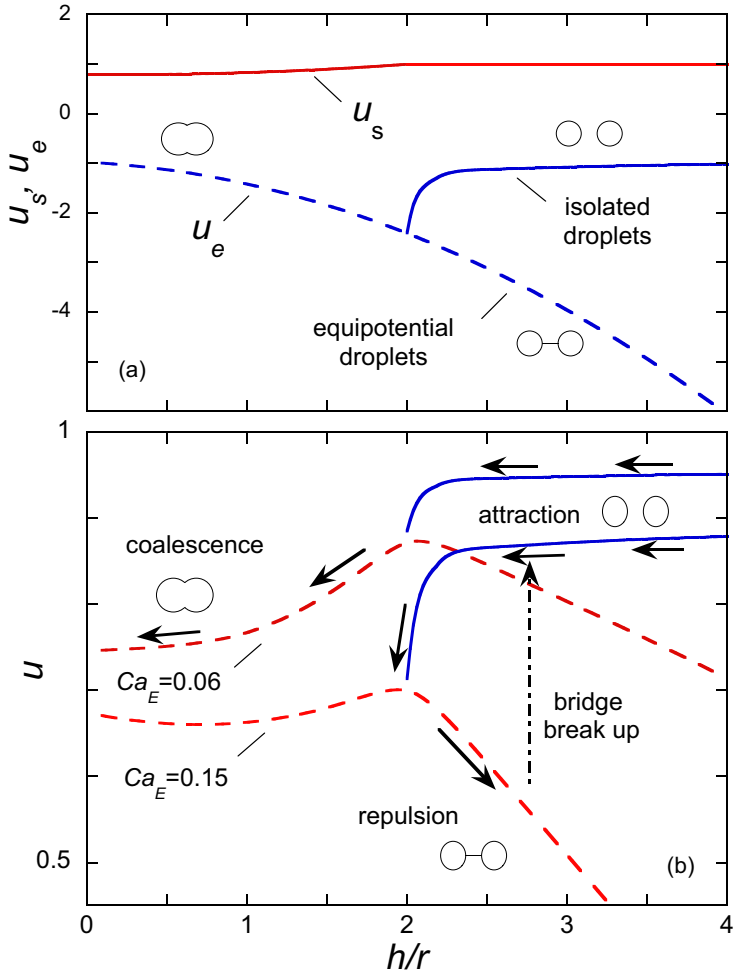

FIG. 5. (a) Normalized surface and electric energies of two equal droplets as functions of relative distance between droplets. (b) Total energy of the pair for electrically isolated droplets (solid line) and for equipotential droplets (dashed line) is obtained by combination of normalized surface and electrical energies using Eq. (1). The droplet coalescence path is defined by the electric capillary number. At $\mathrm{Ca}_E = 0.06$ the droplets coalesce after the first contact. At $\mathrm{Ca}_E = 0.15$ the droplets coalesce through oscillatory motion. The arrows specify direction of the droplet motion. The dashed vertical arrow qualitatively indicates the bridge breakup and corresponding transfer from the equipotential to the isolated energy line.

(Fig. 4) and also with the results on partial droplet coalescence in DC electric fields [13,14]. The region of existence for oscillatory coalescence can be defined as $\mathrm{Ca}_E^{**} < \mathrm{Ca}_E < \mathrm{Ca}_E^{*}$. The electric capillary number in this range is necessary but not sufficient condition of the oscillatory coalescence. Other important conditions involve bridge stability in terms of electric field and charge relaxation frequency.

The high viscosity of the continuous phase is also critically important. The kinetic energy of the droplets in low viscosity fluids could lead to the complete coalescence of the droplet pair on the first contact. The energy model assumes that the kinetic energy of the droplets at the point of contact is negligible in comparison with the electrical energy of the droplets. This assumption can

be expressed using the following inequality:

$$8\pi r^3 \rho v^2/6 \ll 8\pi \varepsilon \varepsilon_o r^3 E^2, \tag{2}$$

where ρ is the droplet density, and v is the droplet velocity at the point of contact. Comparing the Stokes drag force $6\pi\mu r v$ in the continuous phase with the viscosity μ and dielectrophoretic attraction force $\sim 4\pi\varepsilon\varepsilon_o r^2 E^2$ yields

$$v \approx \varepsilon \varepsilon_o r E^2/\mu. \tag{3}$$

The substitution of the characteristic velocity value in Eq. (2) gives

$$\rho r^2 \varepsilon \varepsilon_o E^2/6\mu^2 \ll 1. \tag{4}$$

Using the electric capillary number and the Ohnesorge number defined as $Oh = \mu/\sqrt{\rho\gamma r}$ then yields

$$\mathrm{Ca}_E \ll \mathrm{Oh}^2. \tag{5}$$

For characteristic value of $\mathrm{Ca}_E = 0.09$ the model assumption is valid for $\mathrm{Oh} \gg 0.3$. This scale analysis agrees well with the experimental range of the Ohnesorge numbers reported for the partial coalescence of droplets in DC fields [15]. The characteristic Ohnesorge number for the 10 000 cSt silicone oil used in our experiments is ~50. This suggests that a reduction in the viscosity of the continuous phase by ~50 times could be possible for oscillatory/partial coalescence in AC electric fields. However, in our experiments, droplet pairs coalesce on the first contact in the silicone oil with the kinematic viscosity of 1000 cSt ($\mathrm{Oh} \approx 5$). We partially attribute this inconsistency to the experimental difficulties associated with the initial stabilization of the droplet pairs settling in the gravity field and plan to use alternative experimental arrangements to investigate low viscosity phases.

The viscosity of the continuous phase also affects the dynamics of droplets and liquid bridge thinning. The characteristic viscocapillary frequency $f_\mu = \gamma/\mu r$ that describes the thinning of a viscously dominated thread with radius r is ~5 Hz for the 10 000 cSt silicone oil and $r = 1$ mm. This is an order of magnitude higher than the observed oscillatory coalescence frequency. The latter is defined by the droplet attraction, the longest stage in the oscillatory coalescence cycle. The evaluation of f_c using the characteristic velocity at the point of contact Eq. (3) yields $f_c = v/r = f_\mu \mathrm{Ca}_E/\sqrt[3]{2}$. For $\mathrm{Ca}_E = 0.1$, the characteristic value of $f_c \sim 0.4$ Hz agrees in the order of magnitude with the experimentally recorded values.

The critical electric capillary number obtained from the simplified energy model agrees well with the results obtained for the partial droplet coalescence in DC fields [13,14]. The model of coalescence of two droplets based on the critical angle of two contacting liquid cones suggested the existence of the critical capillary number $\mathrm{Ca}_E^{**} \approx 0.1$. The droplets in DC field fully coalesced below this critical number and recoiled above it. Previously, Brazier-Smith *et al.* [14], numerically predicted a partial fluid transfer and complex coalescence behavior of an electrified droplet pair at $\mathrm{Ca}_E > 0.1$. A contact between droplets in DC electric field leads to one-time transfer of charges across the point of contact. If the electric field is sufficiently strong, the attraction is changed to the repulsion and droplets start to travel in the opposite directions. As a result, the oscillatory coalescence is not observed in DC electric fields. It should be noted, that a direct comparison and extrapolation of our results to DC case is inappropriate as another characteristic interval of the applied frequencies $f_w \gg f_{\mathrm{so}} > f_{\mathrm{AC}}$ exists between the region of frequencies studied in this work and DC.

According to the experimental results, once initiated at the droplet size ratio $\beta \approx 1$ the oscillatory coalescence enhances the droplet disparity to extreme size and volume ratios. The complete coalescence is the final step of the sequence at β of ~20 to 50. At this point one of the droplets is a very small satellite droplet oscillating near the surface of the large droplet. The final coalescence is expected as this point: the surface energy of the satellite droplet is reduced $\sim r^2$ and the electrical energy is reduced $\sim r^3$. The surface energy dominates during the final oscillation steps resulting in

the complete coalescence. The above energy model qualitatively predicts this behavior, however, it fails to predict extreme volume and size ratios observed in the experiments.

The existence and stability of the liquid bridge between the droplets is crucial for oscillatory coalescence. High aspect ratio bridges in pure dielectric fluids are stabilized by polarization charges and resulting tangential stresses on the surface of the bridge [20]. In contrast, the classical leaky dielectric model applied to the bridge results in zero electric field inside the fluid and predicts the bridge instability at high aspect ratios [21]. In AC electric field, the leaky dielectric model is applicable at $f_{\mathrm{AC}} < f_w$. However, this criterion is only valid for the bulk fluid. The specific geometry of the bridge limits the charge transfer in the system. Essentially, the liquid bridge can be considered as a conductor with the resistance R_e that interconnects two oppositely charged droplets with the capacitance C. The response of the system to a change of the electric field will have the characteristic frequency of $f_{RC} \approx 1/R_eC$, which is lower that the bulk charge relaxation frequency f_w. As a result, the electric field in the bridge remains finite at $f_{\mathrm{AC}} < f_w$ generating longitudinal stresses and stabilizing the bridge. Finally, at $f_{\mathrm{AC}} \ll f_w$, the electric field in the bridge relaxes to near zero and the bridge becomes unsustainable. This agrees well with the experimental observations on the transition from the oscillatory coalescence to the noncoalescence at $f_{\mathrm{AC}} \ll f_w$ (Fig. 4). Additional complexity comes from a variable self-organized geometry of the bridge. For a given conductivity, the bridge thins out and becomes unstable at high electric fields (see Movie 4 in Ref. [16]). A fine emulsion cloud is formed as a result of the bridge instability.

IV. CONCLUSIONS

In summary, we have found that in a certain range of electric capillary numbers and fluid conductivities, a pair of droplets in an alternating electric field coalesces through oscillatory sequence that includes the following stages: dipole-dipole attraction, formation of liquid bridge, repulsion of equipotential droplets, bridge elongation and breakup. The liquid bridge formed between droplets is stabilized by the charge transfer in an alternating electric field. Concurrently, the pressure difference between the droplets generates fluid flow through the bridge. Once initiated, the oscillatory coalescence proceeds until complete coalescence in a finite number of steps. The region of the existence of the phenomenon is bounded by the complete coalescence on the first contact at $\mathrm{Ca}_E < 0.09$ and $f_{\mathrm{AC}}/f_w > 10^{-1}$ and noncoalescence with the bridge instabilities and electrified jet emissions at $\mathrm{Ca}_E > 0.15$ and $f_{\mathrm{AC}}/f_w < 3 \times 10^{-3}$. The proposed model describing oscillatory motion of the droplets in energy space shows a good agreement with the experiments. The findings are useful for understanding electrically enhanced coalescence of water-in-oil emulsions, electrified droplet dynamics, and development of droplet manipulation methods. The main potential application of the phenomenon is the electrically controllable droplet-to-droplet fluid transfer and precise dispensing of bio and chemical reagents from freely suspended droplets in microfluidic devices based on the lab-on-a-chip and lab-in-a-droplet platforms. At the same time the high viscosity of the continuum medium limits direct applications of the phenomena in microfluidic flow devices because of the high viscous losses.

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