Supplementary Information for

Electrochemical characterization of individual oil micro-droplets by high-frequency nanocapacitor array imaging

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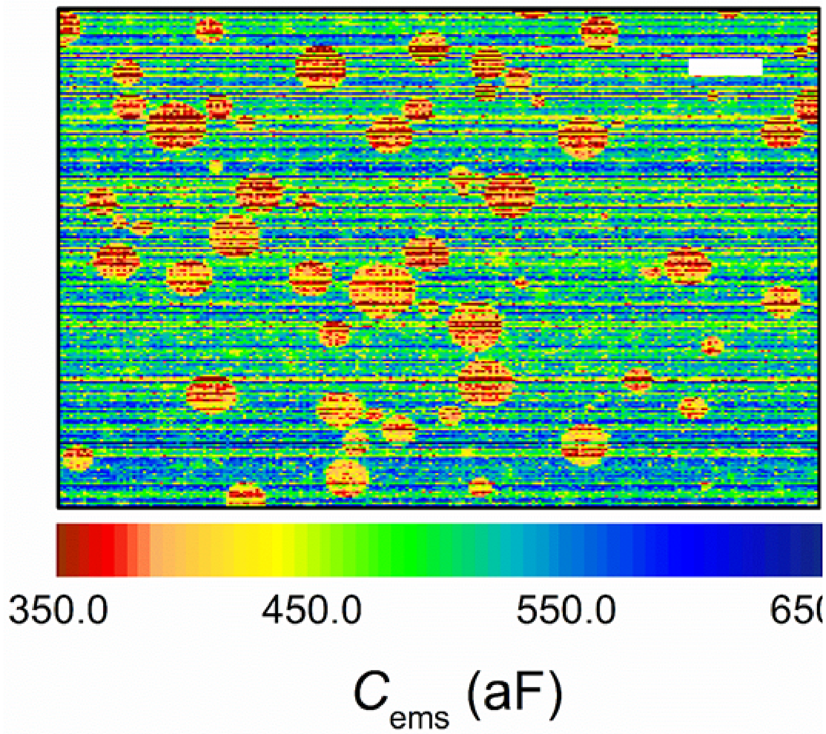

Figure S1. Raw single-frame capacitance image measured with a chip incubated 1 min in an oDCB in water emulsion. The scale bar represents 20 µm.

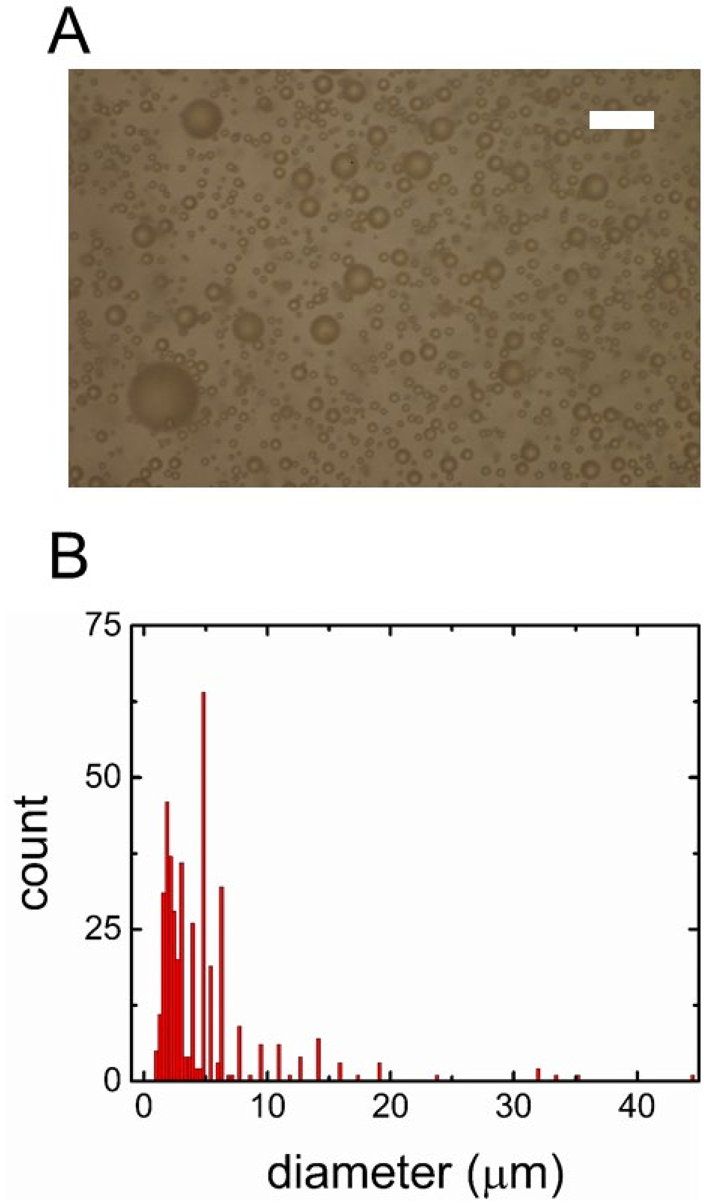

Figure S2 (A) Optical micrograph of an *o*DCB droplets sedimented on a glass slide. The micrograph was taken 1 min after preparation of the emulsion. The scale bar represents 10 μm. (B) Size distribution of the droplets measure from the analysis of optical micrographs as shown in (A).

Numerical simulations of oDCB droplets and calibration curves for size estimation. We rely on ENBIOS simulations to estimate the size of measured oil droplets. We run ENBIOS simulations of spheres of different sizes with a permittivity of ε_r = 9.9 (i.e., the permittivity of oDCB) immersed in milliQ water, thereby obtaining effective capacitance (C_{eff}) maps for each considered droplet. We then apply two different algorithms (described below) to estimate the size of the sphere based on the capacitance response at the nanoelectrodes. Consequently, we obtain an estimated size (r_{app}) vs real size (r_{p}) curve, which can be used to extract the true size of a droplet based on its measured capacitance profile in real experiments. To this end, we consider the following approaches: an approach based on the second-momentum of the electrodes' capacitance response, and an approach based on estimating the sphere's projected area on the array plane upon binarizing the capacitance response.

Second momentum approach. This approach estimates the radius of the sphere r_{app} based on the following equation:

$$-r_{app}^2 = \frac{\sum_i \sum_j \left[(j\,p_x - d_x)^2 + \left(i\,p_y - d_y\right)^2\right] \Delta C_{\mathrm{eff}}(i,j)}{\sum_i \sum_j \Delta C_{\mathrm{eff}}(i,j)}$$

where $\Delta C_{\mathrm{eff}} = C_{\mathrm{eff}}$ *(w/ analyte)* – C_{eff} *(w/o analyte)* is the capacitance variation between a measurement with the droplet and a measurement without the droplet, p_x and p_y represent the intra-electrode pitch along the x- and y-directions, and (d_x, d_y) is the projected center of mass of the analyte, which is known a-priori in simulations and can be extracted from experiments as

$$\left(d_x, d_y\right) = \frac{\sum_i \sum_j \left[(j\,p_x\hat{x}) + \left(i\,p_y\hat{y}\right)\right] \Delta C_{\mathrm{eff}}(i,j)}{\sum_i \sum_j \Delta C_{\mathrm{eff}}(i,j)}$$

where here $\Delta C_{\mathrm{eff}}(i,j)$ is the measured (experimental) capacitance variation at electrode (i,j). To identify which electrodes have to be considered for the calculation, we first apply a threshold: all electrodes whose response ΔC_{eff} is lower than the threshold are not used in the equation. Figure S3 shows the estimation curves (estimated size as a function of real size) for different choices of the threshold. Clearly, higher thresholds entail a smaller number of electrodes considered, and consequently smaller r_{app} values. For the analysis a threshold of 5 aF was selected.

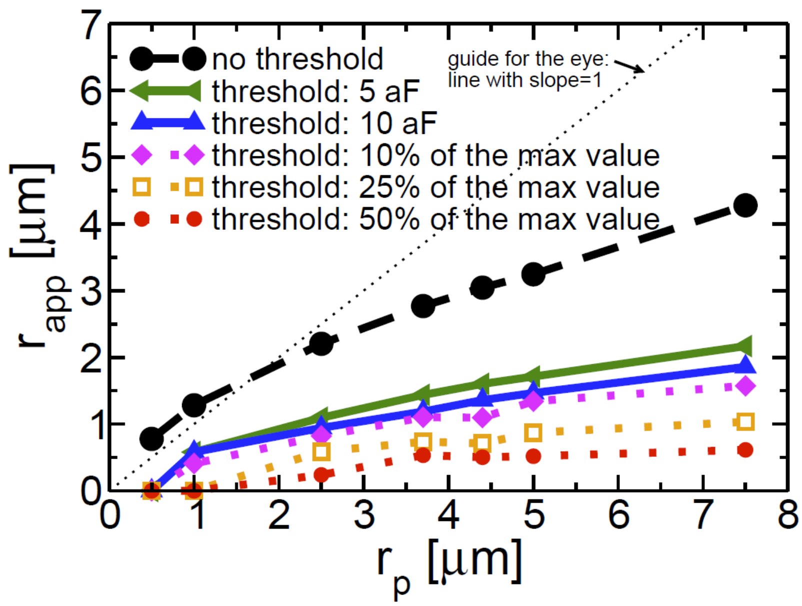

Figure S3. Apparent radius as a function of the real radius of *o*DCB droplets, as calculated with the second-momentum equation. Different curves correspond to different choices for the threshold (i.e., neglecting the electrodes whose response is lower than the threshold). If the threshold excludes all electrodes but the central one, the apparent size drops to zero.

Binarized projected area approach. We consider also this alternative approach, since it proved to perform better than the second-momentum equation for small droplets in noisy environments (results not shown). The first step consists of binarizing the capacitance response of the array: electrodes whose response exceeds a threshold are assigned a value of '1', all others '0'. The apparent radius is then estimated following the approach used in the *bwarea* MATLAB function:

1) the area of a pixel is calculated as $A_{pixel} = p_x \cdot p_y$, where p_x and p_y are the intra-electrodes pitch along the x- and y- directions
2) A weight w_i is assigned to each pixel
3) using the weights and the area of each pixel, we calculate an *effective* pixel area: $A_{pixel,i}^{eff} = w_i A_{pixel}$
4) the projected area of the object is calculated as the sum of the effective areas of its pixels:

$$A_{object} = \sum_{i=1}^{N_{pixels}} A_{pixel,i}^{eff}$$

5) the apparent radius is calculated as: $r_{app} = \sqrt{A_{object}/\pi}$

For each pixel, the calculation of the weight is based on inspecting the value ('1' or '0') of all its neighbor pixels. Each pixel can be seen as the central pixel of a 3x3 pixel matrix, and within such 3x3 pixel matrix, we can identify four 2x2 pixel subsets (top-left, top-right, bottom-left, bottom-right). For each 2-by-2 subset, we first calculate a partial weight. Then, the total weight w_i of the pixel is the summation of the partial weights of the 2-by-2 subsets.

For a given 2-by-2 subset of pixels, there are six possible scenarios of pixel configuration:
- All the four pixels are off: in this case the 2-by-2 subset is assigned a partial weight of 0
- Only one pixel is ‘1’: the assigned partial weight is 1/4
- Two adjacent pixels are ‘1’: the assigned partial weight is 1/2
- Two diagonal pixels are ‘1’: the assigned partial weight is 3/4
- Three pixels are ‘1’: the assigned partial weight is 7/8
- All four pixels are ‘1’: the assigned partial weight is 1

Consequently, pixels surrounded by all ‘1’-pixels get a higher weight, pixels surrounded by ‘0’-pixels get a smaller weight. Figure S4 shows the calculated estimation curves, again for different choices of the threshold. These curves are also much closer to the ideal line ($r_{app}=r_p$) than for the second momentum approach.

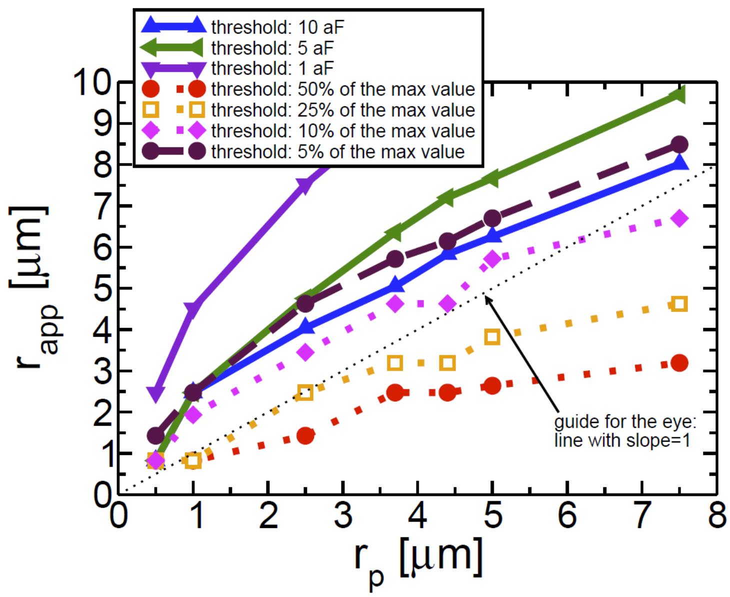

Figure S4. Apparent radius as a function of the real radius of *o*DCB droplets, as calculated with the binary projected-area approach. Different curves correspond to different choices for the threshold (i.e., neglecting the electrodes whose response is lower than the threshold).

Determination of the droplet height.

A spherical droplet with radius r_0 has a volume:

$$V = \frac{4\pi}{3} {r_0}^3 \tag{S1}$$

Assuming that the droplet has a constant volume and wets the surface of the chip forming a spherical dome (Figure S5) of radius r_1 and height h_1 we obtain the following relation:

$$V = \int_{r_1-h_1}^{r_1} \pi x^2 dy = \int_{r_1-h_1}^{r_1} \pi({r_1}^2 - y^2)dy = \pi\left(r_1 - \frac{1}{3}h_1\right){h_1}^2 \tag{S2}$$

From the relation

$$ {r_{wet}}^2 + (r_1 - h_1)^2 = {r_1}^2$$

where r_{wet} is the measured footprint radius of the sedimented drop on the chip, it follows that:

$$r_1 = \frac{{r_{wet}}^2 + {h_1}^2}{2h_1} \tag{S3}$$

Substitution into eq (S2) we obtain:

$$V = \frac{\pi}{6}\left(3{r_{wet}}^2 h_1 + {h_1}^3\right) \tag{S4}$$

Substituting V from eq (S1) and solving for h_1 gives:

$$h_1 = \left(\sqrt{{r_{wet}}^6 + 16\,{r_0}^6} + 4{r_0}^3\right)^{1/3} - \left(\sqrt{{r_{wet}}^6 + 16\,{r_0}^6} - 4\,{r_0}^3\right)^{1/3} \tag{S5}$$

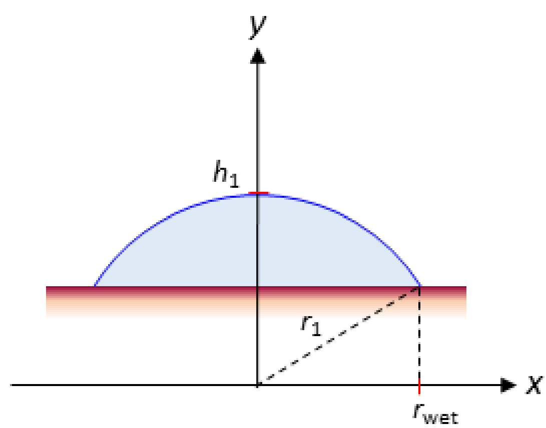

Figure S5. Droplet's geometry at the surface of the chip.

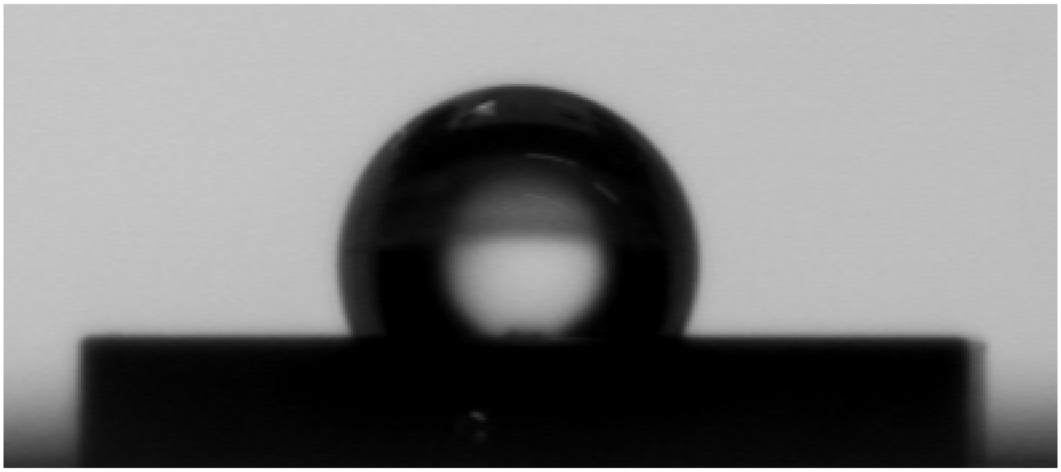

Figure S6. Typical optical micrograph of a 1 µL *o*DCB droplet at the surface of a chip. The measurement is made in DI-water at room temperature.

Movie S1. Real-time capacitance imaging of an oDCB in DI-water emulsion. At the beginning of the movie the array is in contact with pure DI-water and the emulsion is added at c.a. 4 s (real time, frame 20 in the movie). The movie was generated with an in-house program coded in Matlab. The axes are plotted in pixel length. The pitch of the array defines the distance between pixel's centers; the pitch is 0.6 um and 0.89 um in the X and Y directions, respectively. The movie is played at 3.25 times the real speed. The color map describes the capacitance variation (in aF) between the average of the first five frames of the movie (recorded in DI-water) and the following frames.

Movie S2. Real-time tracking and trajectory analysis of *o*DCB droplets. Panel (A) shows the row images analyzed by the particle tracking code. The code (run on Matlab 2012) is freely provided by Daniel Blair and Eric Dufresne at the following address: http://site.physics.georgetown.edu/matlab/. A median filter was added to the code to remove the small droplets (< 5 μm diameter). Panel (B) shows the filtered image. The axes are in pixels. The centroid of the peaks found on the filtered image are plotted in panel (C). Note that despite using a code designed for locating the peaks with sub-micron resolution, the number of pixel per peak (typically 10) is not enough to reliably locate the centroid of the peak with a sub-micron resolution and thus we round the position to the micron digit. All the centroids in each frame are analyzed to reconstruct the trajectory of each droplet as shown in panel (D).