Supplementary Information for

Explosive electrostatic instability of ferroelectric liquid droplets on ferroelectric solid surfaces

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**Supporting Information Text**

**RM734 droplets preparation**

RM734 droplets were obtained following two steps. First of all a small amount of RM734 powder is deposited at room temperature on a clean glass slide and heated to 150°C to have a melt. To create the initial droplets, a cold stainless needle is dipped into the melt and retracted, so that the droplet on its tip solidifies at contact with the surrounding air. To increase the size of the RM734 “pearl”, rapid (to avoid re-melting) successive dipping are performed. Then, the pearl is remolten into a droplet on the glass substrate. The glass slide is then cooled down to room temperature so that solidified droplets can be peeled off and reused on the proper substrate. The sizes of the droplets are controllable (size before peeling vs size of the remolten droplet) and are measured by means of a calibration slide. The average diameter ranges from 1.25 mm down to 250µm.

**Contact angle**

Measurements of the contact angle as a function of temperature were performed with the set-up shown in Fig. S1, made of a collimated light source, an imaging system, and a hot stage. A white LED, an iris and a collimating lens are used to produce the collimated light source, while the imaging system is made of a collecting and an imaging lens with their focal back-to-back, an iris and a CMOS camera. Such a configuration provides the needed tele-centricity and a constant magnification ratio. To control the LC temperature, we use a slotted aluminium plate able to host resistive cartridges powered by a programmable power supply. The temperature of the hot stage is sampled with a thermocouple connected to a DAQ. The desired set point and the measured temperature are sent to a Labview PID controller that drives the programmable power supply.

![Fig. S1. Set up for measuring the contact angle of RM734 droplets on LN substrates. L1 collimating lens. L2 and L3 imaging and collecting lens. The first iris is used to reduce the width of the LED, the second is as an aperture stop (A.S.). The CMOS sensor is placed in the focal plane of L3. The temperature of the LN substrate is controlled by a heating stage made of a slotted aluminum plate fitted with resistive heater cartridges powered by a programmable power supply unit (PSU). The setting point is precisely controlled (within 1.5°C) by feeding the measured temperature with a thermocouple (T.C.) and DAQ to a PID controller that drives the PSU.](image)

**Homeotropic alignment of RM374 in the nematic phase on lithium niobate substrates**

A thin cell was built using two diffused-doped LN substrates and 6µm mylar spacers. The cell was filled by capillarity with RM734 in the I phase and then cooled down to 175°C, which correspond to the LC N phase. As shown in Fig. S2, the LC alignment in this phase is homeotropic.

**Conventional Rayleigh Instability**

The qualitative numerical evaluations proposed in the main text differ from the threshold of the classic Rayleigh instability of charged spherical droplets expressed through the so-called fissility parameter \( X \). In that case, the increase of surface requires a break of spherical symmetry that does not apply to the sessile droplets, free to expand their interface with LN to compensate for the Coulombic pressure as in fact they do at the N-N\(_F\) transition. Indeed, the threshold condition typically marking Rayleigh instability of a charged droplet of radius \( a \) and surface tension \( \gamma \) is achieved when its total charge \( Q \) is such that the ratio \( Q^2/64\pi^2\varepsilon_0\gamma a^3 \), defining the so-called “fissility parameter” \( X \), is equal to 1. When expressed in terms of charge density at the droplet surface, \( X \) takes the form:

\[
X = \sigma^2 a/64\pi^2\varepsilon_0\gamma
\]
The condition $X = 1$ enables, via Eq. 1, quantitative estimates of $\sigma_{RI}$, the values of $\sigma$ necessary to yield the Rayleigh instability, as a function of the droplet size. We find that in the explored range, $\sigma_{RI} \approx 0.1 \mu\text{C/cm}^2$. This quantity should be responsible for the total screening of the fringing field $E_f$ generated by the LN substrate, which, being $E_f \approx 10^3$ times the internal field, should develop a surface charge density of the order of $10^3 \sigma_{RI} \approx 100 \mu\text{C/cm}^2$, which is definitely too high to be pyroelectrically generated. On the other hand, the fissility parameter has been defined for a charged conductive spherical droplet, Rayleigh instability being in this case a discontinuous phenomenon where the loss of sphericity leads to an even less stable state and thus to a runaway effect by which initial lumps develop into fluid jets. Those described here are instead sessile droplets in contact with a solid substrate, they are not conductive but ferroelectric, thus they do not possess free charges but only polarization charges. The observed shape instability and jet ejection can be better understood as due to a local buildup of polarization charges, in turn due to the growth of the spontaneous polarization $P$ around topological defects and constraints from the droplet boundaries, as discussed in the main text. When the electrostatic repulsion from the rest of the droplet due to this charge accumulation compensate the surface tension, a jet is started and the instability develops as described in the manuscript.

**Droplets images**

![Fig. S2. 6µm thick cell filled with RM734 observed between crossed polarizers in two different orientations: a) cell edges parallel to the axis of the two polarisers and b) cell rotated by an angle about 45 degrees. No birefringence variation can be detected, which indicates homeotropic alignment of the LC in the N phase. T = 180°C. The reddish appearance is due to the Iron dopant.](image)

![Fig. S3. RM734 droplet on a doped LN substrate. Two of the ejected jets are retracted from the droplet and carry back liquid crystalline material, as it is well visible in the blow up. Average droplet diameter: 450µm. White bar = 500µm. Extracted from Video S3.](image)
Fig. S4. RM734 droplet on a diffused doped LN substrate in a temporary quiescent state after jets ejection. Several secondary smaller droplets generated by the ejected jets are visible in the neighbourhood. Line defects in the mother droplet texture can also be observed. Average droplet diameter 400 µm. White bar = 500 µm.

Fig. S5. RM734 droplets of similar size (average diameter = 1.2 × 10^3 µm) on an undoped LN substrate right in the centre (a) and close to the edges (b), at three different moments during cooling from T = 125°C. A comparison between the two figures shows that droplets instabilities develop with different strength, being more violent in case b) where the fringing field is larger. White bar = 500 µm.
Fig. S6. Frames extracted by a video showing a rare event of 3D jet ejection (see main text). Three vertical jets are marked with letters. The vertical ejection occurs at 80 °C, after several conventional 2D instability events. A sketch of the side view is also reported. Undoped LN substrate. White bar = 500 µm.
Movie S1. 300µm RM734 droplet on a diffused doped LN substrate. In the first part of the video the substrate temperature ranges between 134 and 130°C and the transition from N to N_{F} is observed at T = 133°C. The corresponding texture variation is clearly visible. In the second part, T goes from 125°C to 100°C and shape instability occurs at T = 109°C. Droplet shrinkage after explosion is also visible. In order to visualize the director rearrangement induced by the phase transition, the cooling rate was kept slow (0.01°C/s) in the first part and then faster (0.2°C/s) in the second part.

Movie S2. 320µm RM734 droplet on an undoped LN substrate observed under a polarised optical microscope. The substrate temperature ranges between 165 to 125°C. It is possible to observe the N/N_{F} transition at T = 137°C resulting in a change of the LC texture with the appearance of defect lines that move as the temperature decreases. Droplet explosive instability starts at T = 128°C. Cooling rate: 0.3°C/s.

Movie S3. 450µm RM734 on a diffused doped LN substrate. Substrate temperature ranges between 125 and 60°C with a cooling rate of 0.1°C/s. Up to seven instability events are observed, the first occurring at T = 104°C. Jets retraction is well visible. By the end of the video it is possible to observe the beginning of RM734 crystallization.

Movie S4. 500µm RM734 droplet on a diffused doped LN substrate. Temperature ranges between 165 and 125°C with a cooling rate 0.2°C/s.

Movie S5. 250µm RM734 droplet on a diffused doped LN substrate. Temperature ranges between 125 to 65°C with a cooling rate of 0.07°C/s. Several instability events are observable after the first at T = 124°C. Interestingly, the droplet tends to regain a dome shape after each instability. By the end of the video it is possible to observe the beginning of crystallization.

Movie S6. 1.1 × 10^{3}µm RM734 droplet on an undoped LN substrate. Temperature range: 133 – 123°C. Cooling rate 0.3°C/s. Several instabilities with fast jets ejection rapidly forming satellite small droplets are observable, the first one occurring at T = 131°C. The last shape instability is instead characterized by a violent ejection of fluid material, resulting in a kind of droplet destruction.