

## Supplemental Information: Spreading of volatile droplets in a humidity-controlled environment

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### Close-up of ethanol droplet contact line spreading on an acrylic surface

A confocal microscope with a spatial resolution of  $2.5 \mu\text{m}/\text{pixel}$  was employed to meticulously examine the motion of the droplet's contact line. An observable precursor film forms at the periphery of the droplet when deposited on a sapphire surface, as detailed in the main text. However, this precursor film is less prominent on the acrylic substrate (see Fig. S1). We instead observe small fluid masses dispersed alongside the contact line, rather than a continuous precursor film. We speculate that as the droplet spreads, water accumulates due to the hygroscopic nature of ethanol, leading to its expulsion from the contact line. This phenomenon can be recognized in Fig. S1 as darker regions adjacent to the contact line. These islands become more pronounced at higher relative humidity levels (Fig. S1(b)).

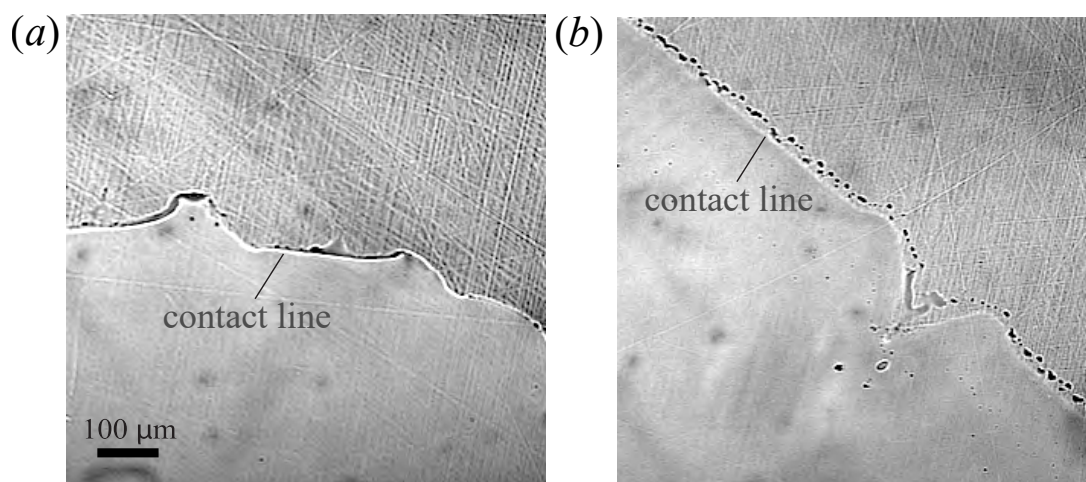


Fig. S1. Confocal microscopy images illustrating the contact lines of spreading droplets on an acrylic substrate ( $T_s = 25^\circ\text{C}$ ) at (a)  $\text{RH} = 10\%$  and (b)  $\text{RH} = 60\%$ . The accumulation of the water phase around the contact line is visibly pushed out from the droplet, represented as dark regions.

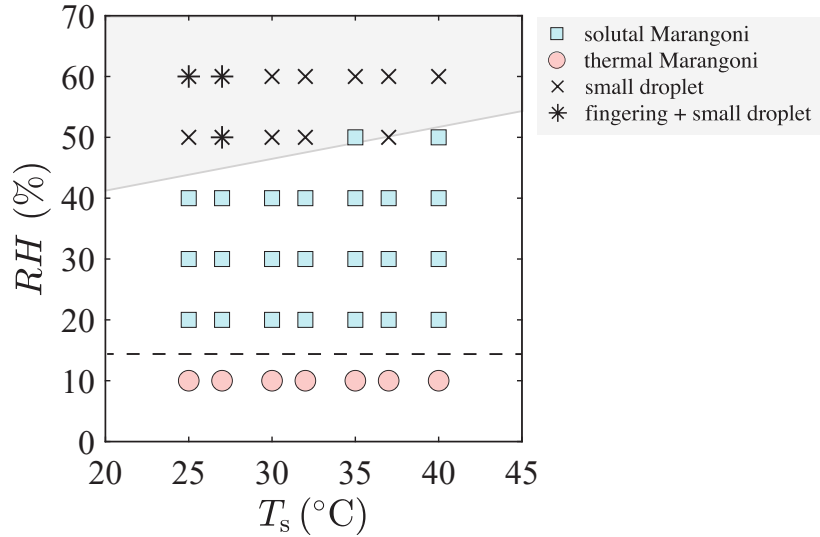


Fig. S2. Regime maps in a space spanned by the surface temperature  $T_s$  across the relative humidity RH for acrylic surface. Different symbol shapes represent various spreading behaviours of evaporating ethanol droplets.

#### Phase diagram for spreading behaviours of ethanol droplets on an acrylic surface

Figure S2 depicts the different dynamics of droplet spreading depending on  $T_s$  and RH. In the main text, it is noted that thermal Marangoni appears for droplets on the sapphire surface at relatively high  $T_s$  and low RH. In contrast, for droplets on the acrylic surface (Fig. S2), spreading motion is enhanced above  $\text{RH} = 20\%$  across all  $T_s$  ranges but is less prone to fingering compared to the sapphire surface under the same conditions. Instead, breakup into smaller droplets occurs more frequently. The prolonged spreading duration on the acrylic surface allows ample time for water vapour absorption by the droplet. We attribute the breakup into small droplets to Rayleigh-Plateau instability [1, 2]. However, it's important to note that fingering on a macroscopic scale doesn't always manifest, despite leaving behind numerous tiny droplets at the end of evaporation.

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- [1] A. P. Mouat, C. E. Wood, J. E. Pye, and J. C. Burton, *Tuning contact line dynamics and deposition patterns in volatile liquid mixtures*, *Physical Review Letters* **124**, 064502 (2020).  
 [2] J. Shi, L. Yang, and C. D. Bain, *Wetting and Drying of Aqueous Droplets Containing Nonionic Surfactants* *Chemical Communications*, *Langmuir* **37**, 4091 (2021).