Physiochemical hydrodynamics of the phase-segregation in an evaporating binary microdroplet
(Supplementary Materials)

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VECTOR VALIDATION OF μPIV MEASUREMENT

In Fig. 1, we show the signal-to-noise ratios (SNR) with the corresponding interrogation window sizes for the two μPIV measurements by using fluorescent particles and dyes, respectively. Fig. 1(a) displays a typical colormap of SNR for the μPIV by using 520 nm diameter fluorescent particle tracers in the binary droplet. The interrogation window size is 16 $\times$ 16 pixels. Fig. 1(b) shows a typical colormap of SNR for the μPIV by using the separated Dextran as the "tracers". The interrogation window size is 32 $\times$ 32 pixels.

Vector validation of the μPIV in our work is based on signal-to-noise ratio and deviation from the median of the neighbouring vectors [1]. Particularly, the threshold of SNR for a valid vector is chosen to be 1.2 in our analysis. Non-valid vectors are less than 9% and 14% in these two cases, and are interpolated from the neighbouring vectors.

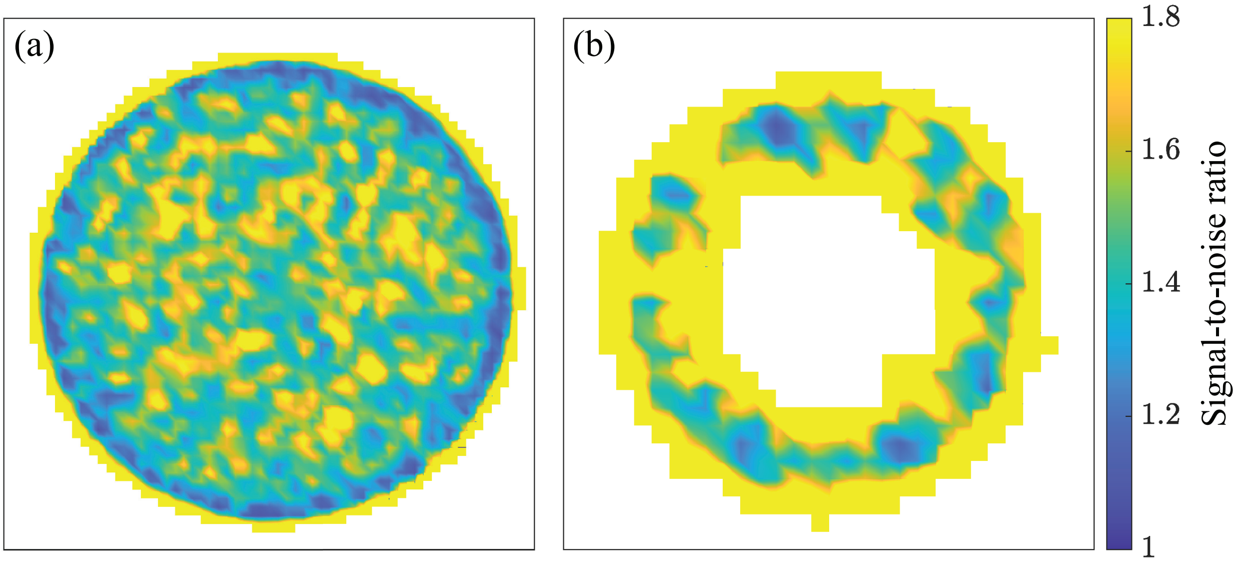

FIG. 1: Signal-to-noise ratio of μPIV by using fluorescent particles (a) and dyes (b).

FLOW STRUCTURE WITHIN SEGREGATIVE PATTERNS

To describe the segregation-induced flow structure within the arch-shaped patterns, a two-dimensional (2D) hydrodynamic model is proposed. As shown in Fig. 2, the expansion of the segregative phase originates from the contact line region, where the segregation emerges due to the evaporation of water. To obtain a theoretical description of the flow structure, we simplify the system by a few assumptions: (i) By neglecting the curvature at the contact line, the region of interest, i.e. every individual segregative pattern, is simplified as a half circular domain. (ii) For the small timescale in which the patterns remain considerably the same shape, the mass conservation holds in the half circular domain which is pushed towards the interior of the droplet by the growing segregation at the contact line regime with the velocity U_E^{sp}. (iii) The coalescence between neighbouring patterns is not considered in the current model. (iv) The flow is two-dimensional due to the flatness of the droplet ($h/R \ll 1$). In a 2D planar geometry, the flow is governed by the incompressible Stokes equation, which reads as the biharmonic equation in polar coordinates (r_{sp}, θ_{sp}),

$$\nabla^4 \psi(r_{sp}, \theta_{sp}) = 0, \tag{1}$$

where $\psi(r_{sp}, \theta_{sp})$ is the stream function. A general solution to the equation is in the form of a Fourier series in θ_{sp}, which is so-called Michell solution [2].

To obtain the exact solution, we take the half-circular domain as the frame of reference and apply the boundary conditions [3], i.e. (i) the periodicity of the stream function and velocity field $\psi(r_{sp}, \theta_{sp}) = \psi(r_{sp}, 2\pi + \theta_{sp}), u_{r,\theta}^{sp}(r_{sp}, \theta_{sp}) = u_{r,\theta}^{sp}(r_{sp}, 2\pi + \theta_{sp})$; (ii) no velocity divergence at $r_{sp} = 0$, $\nabla\psi(0, \theta_{sp}) = 0$; (iii) mass conservation within the domain $\nabla^2\psi = 0$; (iv) the kinematic boundary condition along the contact line $u_r^{sp}(R_{sp}, \theta_{sp}) = 0$; and (v) symmetric azimuthal velocity due to geometry $u_\theta^{sp}(r_{sp}, \theta_{sp}) = -u_\theta^{sp}(r_{sp}, -\theta_{sp})$, $u_r^{sp}(r_{sp}, \theta_{sp}) = u_r^{sp}(r_{sp}, -\theta_{sp})$. As a result, the stream function and velocity vectors are, respectively,

$$\psi(r_{sp}, \theta_{sp}) = \sum_{n=1}^{\infty} B_n r_{sp}^n (r_{sp}^2 - R_{sp}^2) \sin(n\theta_{sp}) \tag{2}$$

$$u_r^{sp}(r_{sp}, \theta_{sp}) = \sum_{n=1}^{\infty} n r_{sp}^{n-1} B_n (r_{sp}^2 - R_{sp}^2) \cos(n\theta_{sp}) \tag{3}$$

$$u_\theta^{sp}(r_{sp}, \theta_{sp}) = -\sum_{n=1}^{\infty} B_n r_{sp}^{n-1} ((n+2) r_{sp}^2 - n R_{sp}^2) \sin(n\theta_{sp}) \tag{4}$$

To determine the prefactor B_n, the kinematic boundary conditions $u_\theta^{sp}(R_{sp}, \theta_{sp})$ at $r_{sp} = R_{sp}$ are still required. As shown in Fig. 2, by taking half of the circular domain as the frame of reference, the flow structure in the growing pattern resembles the flow within a two-dimensional circular cylinder passing a uniform flow. In the current case, the free stream velocity U^{sp} is the summation of the velocity of the convection flow U_{ma}^{sp} induced by the Marangoni effect on the surface and the moving velocity of the domain U^{sp}_E due to the expansion of the pattern, i.e. $U^{sp} = U^{sp}_{ma} + U^{sp}_E$. The outward flow velocity $U^{sp}_{ma} \sim (h_0\Delta\gamma)/(\mu R) \approx 20$ μm/s, and $U^{sp}_E \approx 50$ μm/s, which is estimated from the experimental observations. The flow velocity $u^{sp}_\theta(R_{sp}, \theta_{sp})$ along a circular cylinder in the polar coordinates is given by

$$u^{sp}_\theta(R_{sp}, \theta_{sp}) = -u\text{sin}\theta_{sp} + v\text{cos}\theta_{sp} = U^{sp}[\text{sin}\theta_{sp} - \text{cos}(2\theta_{sp})\text{sin}\theta_{sp} + \text{sin}(2\theta_{sp})\text{cos}\theta_{sp}] = 2U^{sp}\text{sin}\theta_{sp}. \tag{5}$$

By substituting Eq. (5) to Eq. (4), we obtain

$$\sum_{n=1}^{\infty} B_n R^n_{sp}\text{sin}n\theta_{sp} = -\frac{U^{sp}}{R_{sp}}\text{sin}\theta_{sp}, \tag{6}$$

with

$$B_1 = -\frac{U^{sp}}{R^2_{sp}}, B_n = 0 \text{ for } n \neq 1. \tag{7}$$

The expression of the stream function and the velocity in the polar coordinates, reads

$$\psi(r_{sp}, \theta_{sp}) = -\frac{U^{sp}}{R^2_{sp}} r_{sp}(r^2_{sp} - R^2_{sp})\text{sin}\theta_{sp} \tag{8}$$

$$u^{sp}_\theta(r_{sp}, \theta_{sp}) = -\frac{U^{sp}}{R^2_{sp}}(3r^2_{sp} - R^2_{sp})\text{sin}\theta_{sp} \tag{9}$$

$$u^{sp}_r(r_{sp}, \theta_{sp}) = \frac{U^{sp}}{R^2_{sp}}(r^2_{sp} - R^2_{sp})\text{cos}\theta_{sp} \tag{10}$$

Finally we obtain the velocity vectors by transferring the polar coordinates (r, θ_{sp}) to the Cartesian coordinates (x, y) in the laboratory frame of reference,

$$u^{sp}_x = -u^{sp}_r\text{cos}\theta_{sp} + u^{sp}_\theta\text{sin}\theta_{sp} + U^{sp}_E = (1 - \frac{x^2 + 3y^2}{R^2_{sp}})U^{sp} + U^{sp}_E, \tag{11}$$

$$u^{sp}_y = -u^{sp}_r\text{sin}\theta_{sp} - u^{sp}_\theta\text{cos}\theta_{sp} = \frac{2xy}{R^2_{sp}}U^{sp}. \tag{12}$$

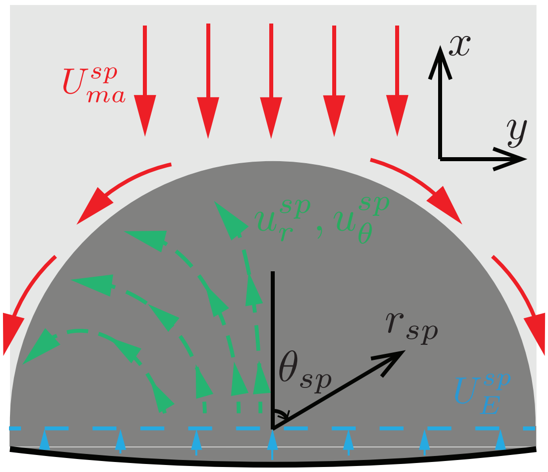

FIG. 2: Schematics of the flow structure within a segregative pattern, described in a polar coordinate system (R_{sp}, θ_{sp}).

SUPPLEMENTARY MOVIES

Movie S1 Confocal microscopic imaging for a 1,2-hexanediol-water droplet evaporating on a glass slide.

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