Electronic Supplementary Material (ESI) for Soft Matter.

Patterned Surface Anchoring of Nematic Droplets at Miscible Liquid—Liquid Interfaces

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Electronic Supplementary Information (ESI)

Calculation of temporal evolution of aqueous—glycerol interfaces.

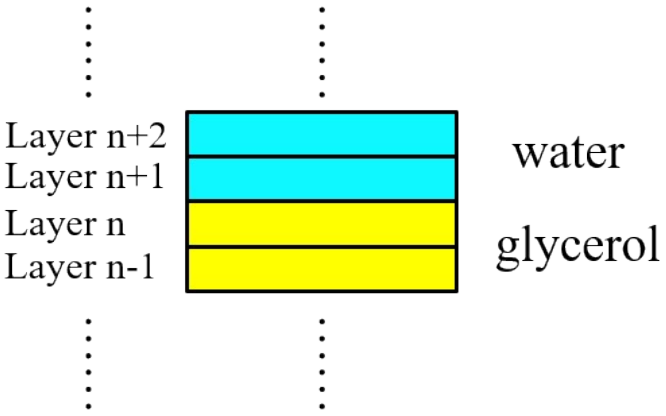

Fig. S1 Schematic illustration of an aqueous—glycerol interface. Blue and yellow color represent water and glycerol, respectively.

In the calculation, we divide the aqueous—glycerol system into multilayers with thickness Δz = 100 nm, as shown in Fig. S1. We assume that there is no concentration gradient in each layer. At t = 0, the aqueous—glycerol interface locates at z = 0 (x_{glycerol} = 0 for z > 0, and x_{glycerol} = 1 for z < 0). As time increases, both water and glycerol will diffuse from layers of high concentration to those of low concentration. At time t, the flux of glycerol from Layer z - Δz to Layer z can be written as:

$$J_{z-\Delta z \to z}^{t} = -D\left(x_{g,z}^{t}\right)\frac{x_{g,z-\Delta z}^{t} - x_{g,z}^{t}}{\Delta z} \quad \text{(S1)}$$

where $D\left(x_{g,z}^{\ t}\right)$ is the mutual diffusion coefficient, which depends on local volume fraction of glycerol. D'Errico et al. measured $D\left(x_{g,z}^{\ t}\right)$ for glycerol—water mixtures by using Gouy interferometry, and correlated the data as:[1]

$$D\left(x_{g,z}^{\ t}\right) = \frac{1.024 - 0.91x_{g,z}^{\ t}}{1 + 7.5x_{g,z}^{\ t}} \times 10^{-9}\ m^2 s^{-1} \quad \text{(S2)}$$

Similarly, the flux of glycerol from Layer z to Layer $z + \Delta z$ can be written as:

$$J_{z \to z+\Delta z}^{\ t} = -\ D\left(x_{g,z+\Delta z}^{\ t}\right)\frac{x_{g,z}^{\ t} - x_{g,z+\Delta z}^{\ t}}{\Delta z} \quad \text{(S3)}$$

The net change in the amount of glycerol in Layer z within time interval Δt can be written as:

$$N_z^t = -J_{z-\Delta z \to z}^{\ t} V_{layer}\Delta t + J_{z \to z+\Delta z}^{\ t} V_{layer}\Delta t \quad \text{(S4)}$$

in which V_{layer} is the volume of the layer. Substitution of Eqn (S1) and (S3) into (S4) leads to:

$$N_z^t = -\ D\left(x_{g,z+\Delta z}^{\ t}\right)\frac{x_{g,z}^{\ t} - x_{g,z+\Delta z}^{\ t}}{\Delta z}V_{layer}\Delta t + D\left(c_{g,z}^{\ t}\right)\frac{x_{g,z-\Delta z}^{\ t} - x_{g,z}^{\ t}}{\Delta z}V_{layer}\Delta t \quad \text{(S5)}$$

The change in the volume fraction of glycerol in Layer z after Δt can be written as:

$$x_{g,z}^{\ t+\Delta t}V_{layer} - x_{g,z}^{\ t}V_{layer} = N_z^t \quad \text{(S6)}$$

Substitution of Eqn (S5) into (S6) leads to:

$$x_{g,z}^{\ t+\Delta t}V_{layer} - x_{g,z}^{\ t}V_{layer} = -\ D\left(x_{g,z+\Delta z}^{\ t}\right)\frac{x_{g,z}^{\ t} - x_{g,z+\Delta z}^{\ t}}{\Delta z}V_{layer}\Delta t + D\left(x_{g,z}^{\ t}\right)\frac{x_{g,z-\Delta z}^{\ t} - x_{g,z}^{\ t}}{\Delta z}V_{layer}\Delta t \quad \text{(S7)}$$

By dividing both sides of Eqn (S7) by V_{layer} and rearrangement, we obtain:

$$x_{g,z}^{\ t+\Delta t} = x_{g,z}^{\ t} - D\left(x_{g,z+\Delta z}^{\ t}\right)\frac{x_{g,z}^{\ t} - x_{g,z+\Delta z}^{\ t}}{\Delta z}\Delta t + D\left(x_{g,z}^{\ t}\right)\frac{x_{g,z-\Delta z}^{\ t} - x_{g,z}^{\ t}}{\Delta z}\Delta t \quad \text{(S8)}$$

Eqn (S8) is Eqn (2) in the main text."

Observation of temporal evolution of aqueous—glycerol interfaces.

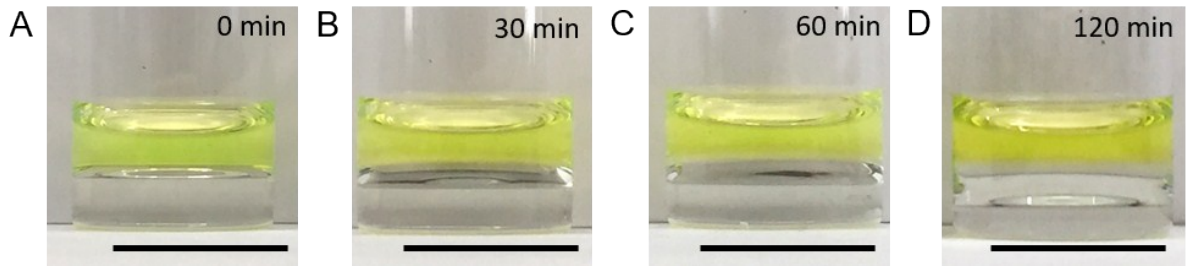

Fig. S2 Images of temporal evolution of an aqueous—glycerol interface. Fluorescein isothiocyanate-dextran (average molecular weight is 70,000 g/mol) was added to the aqueous phase for better imaging of aqueous—glycerol interfaces. Scale bars: 1 cm.

To support our calculation above, we observe the temporal evolution of aqueous—glycerol interfaces. We first added 0.5 mL of pure glycerol to the bottom of a glass vial, and subsequently added another 0.5 mL of Fluorescein dye in water on the top of the glycerol. As shown in Fig. S2, a sharp aqueous—glycerol interface was still observed even after 2 hours, which is consistent with our calculation result.

Topology conservation law of LC droplets.

In this section, we sought to analyze the configuration of LC droplets with patterned surface anchoring by using Poincaré and Gauss theorem.[2-6] Poincaré theorem indicates that the total charges m of surface defects must be equal to Euler characteristic number E ($\sum m = 2$ for a sphere (3D) and $\sum m = 1$ for a disk (2D)). The theorem is valid only when the projection of director on the nematic boundary exists (not valid for a homeotropic anchoring). In most cases, solving Poincaré theorem in 3D geometries is not trivial (*e.g.*, Figs. 4-6 of the main text). For convenience, therefore, one can solve the theorem by simplifying the 3D geometry to 2D (*e.g.*, a sphere to a disk). Gauss theorem describes that the summation of charges of bulk defects (hedgehogs) must be equal to $E/2$: $\sum N = 1$ for a sphere. Contrary to Poincaré theorem, Gauss theorem is independent on a surface anchoring and only valid for 3D geometry.

First, we analyze the simplest cases, bipolar and radial LC droplets in which directors are aligned tangentially and perpendicularly to the droplet surface (in 3D aspect), respectively; in 2D aspect (disk), directors are aligned tangentially with respect to a disk for both radial and bipolar structures. As shown in Fig. S3A, in bipolar LC droplets, each boojum at the poles possesses m_1(3D) = m_2(3D) = +1 in 3D aspect (a sphere, $E = 2$) and m_1(2D) = m_2(2D) = +1/2 in 2D aspect (a disk, $E = 1$), both of which satisfy Poincaré theorem ($\sum m = 2$ for a sphere (3D) and $\sum m = 1$ for a disk (2D)). Although there is no bulk defect in a bipolar droplet, it still satisfy the Gauss theorem ($\sum N = 1$) because boojums also possess the 'bulk characteristics' A. We note here that $\hat{n}$ is treated as a vector in the calculation of bulk characteristics A. By using Eqn (3) in the main text, $A = +1/2$ for the boojum at the north pole of the bipolar droplet whereas $A = -1/2$ for the boojum at the south pole. From these values of A, we can get $N = 1$ for the boojum at the north pole whereas $N = 0$ for the boojum at the south pole, as shown in Fig. S3A. These results satisfy Gauss theorem ($\sum N = 1$). For radial LC droplets (Fig. S3B), since the surface anchoring of LCs is perpendicular, only Gauss theorem is applicable. The hedgehog point defect possesses bulk topological charge $N = 1$, which satisfies the Gauss law.

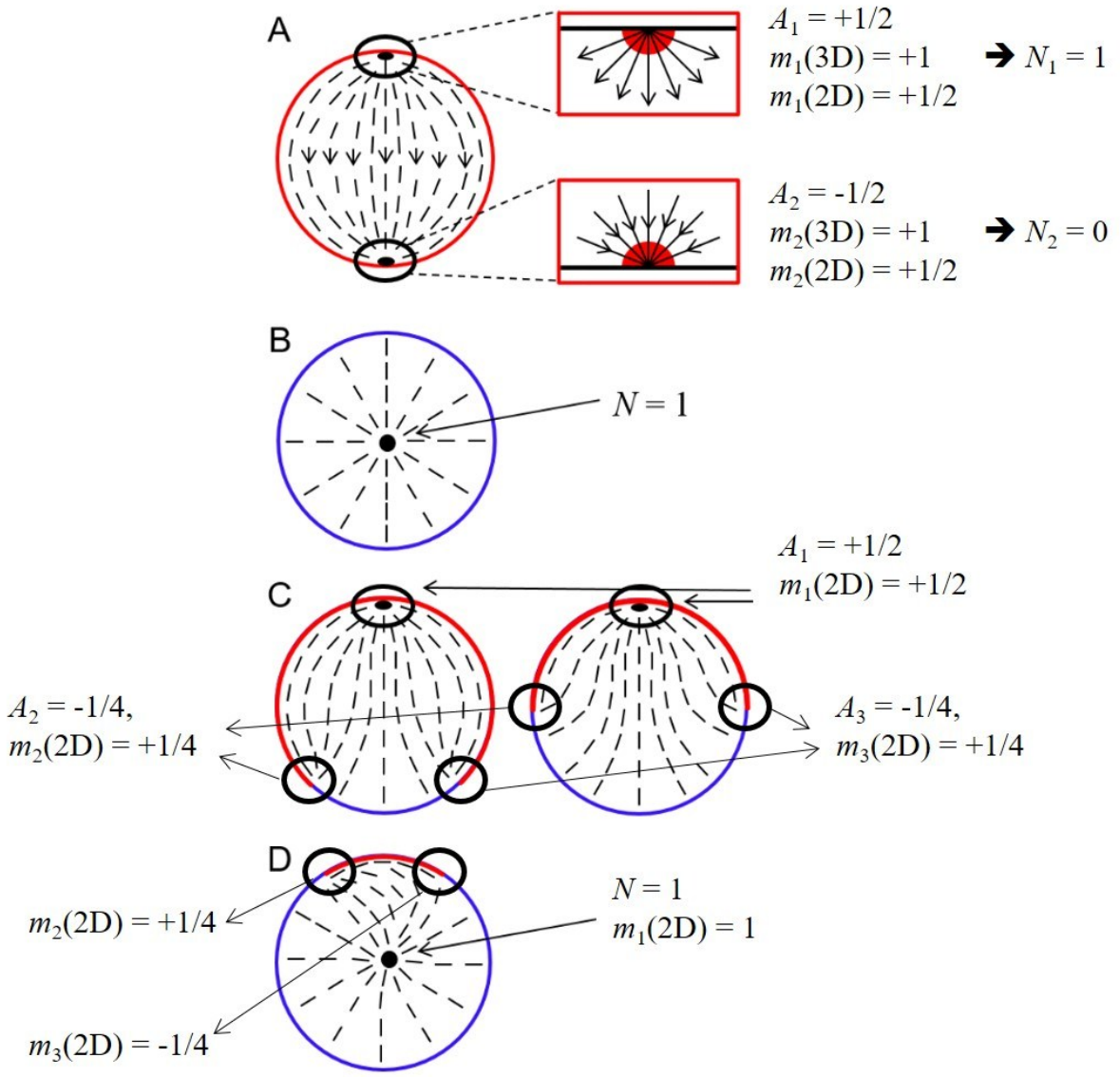

Fig. S3 Analysis of topological charge in LC droplets with different surface boundary conditions (red: tangential; blue: perpendicular).

Next we analyze the LC droplets with patterned surface anchoring. For simplification, we solved the Poincaré theorem for this complex system in 2D aspect.

1) Droplets possessing a surface boojum defect and a disclination loop

Initially, the droplets had the radial configuration, as shown in Fig. S3B. As an anchoring transition (from homeotropic to tangential) occurred, a boojum appeared at a north pole and was merged with a hedgehog after the transition was completed.[3] At an equilibrium state, the droplet possesses a boojum at a north pole and a disclination loop at the boundary between homeotropic and tangential anchoring. The boojum at a north pole has $A_1 = +1/2$, $m_1(2D) =$

+1/2 and each boojum at the boundary of different surface anchoring has $A_1 = A_2 = -1/4$, $m_2(2D) = m_2(2D) = +1/4$. Therefore, it satisfies both Poincaré ($\sum m(2D) = m_1(2D) + m_2(2D) = 1$, E=1 for a disk) and Gauss theorem ($|A_1| + |A_2| + |A_3| = E/2 = 1$; $E = 2$ for a sphere) even in the absence of bulk defects.

2) Droplets possessing a disclination and a hedgehog

In 2D aspect, a point defect at the center of a disk has $m_1(2D) = +1$ and two boojums at the boundary between different anchoring have $m_2(2D) = +1/4$ and $m_3(2D) = -1/4$, which is in agreement with Poincaré theorem ($\sum m(2D) = m_1(2D) + m_2(2D) + m_3(2D) = 1$, E=1 for a disk). In 3D aspect, the droplet satisfies the Gauss theorem because it possesses the hedgehog of N =1.

ESI Video S1: Ordering transition of a 4 μm-in-diameter LC droplet.
ESI Video S2: Ordering transition of a 3 μm-in-diameter LC droplet.

Reference:

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