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ТЕМПЕРАТУРНО-ИНДУЦИРАНО ОБРАЗУВАНЕ НА БИКОНТИНУАЛНА ФАЗА: CRYO-TEM ВИЗУАЛИЗАЦИЯ И КАН–ХИЛИАРД ИНТЕРПРЕТАЦИЯ

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TEMPERATURE-INDUCED FORMATION OF A BICONTINUOUS PHASE: CRYO-TEM VISUALIZATION AND CAHN–HILLIARD INTERPRETATION

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Abstract
Cryogenic transmission electron microscopy (Cryo-TEM) provides direct visualization of bicontinuous sponge (L_3) phases, where a surfactant bilayer meanders through space, dividing solvent into two continuous domains. Temperature increase destabilizes lamellar order by lowering the bending rigidity and driving the Gaussian modulus toward values that favor handle formation. We captured this transition as the loss of layered registry and the emergence of a labyrinthine bilayer network rich in saddle regions. A Cahn-Hilliard-type phase-field model reproduces these features: small shifts in the free-energy landscape and interfacial penalty are sufficient to convert stripe-like lamellae into bicontinuous structures. This synergy between imaging and modeling highlights how thermal fluctuations push membranes into topologies inaccessible at lower temperatures, offering a predictive framework for designing temperature-responsive surfactant systems.

Keywords: Cryo-TEM; Sponge phase; Cahn–Hilliard phase-field; Bicontinuous phase.

1. INTRODUCTION

Bicontinuous sponge (L_3) phases occupy a distinctive place in soft matter science. They are formed when a surfactant bilayer folds into a highly connected labyrinth, partitioning solvent into two interpenetrating but disconnected domains. Unlike lamellar phases, which preserve

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long-range positional order, sponge phases are globally isotropic yet microscopically structured. Their unusual topology underlies applications ranging from drug solubilization to templating of nanostructured materials [1,2].

The stability of such bicontinuous phases reflects a balance between curvature elasticity and thermal fluctuations. In the Helfrich framework, the areal free energy of a bilayer is expressed as:

$$f = \frac{k_c}{2}(2H - C_0)^2 + \bar{k}K \qquad (1)$$

where k_c is the bending rigidity, C_0 the spontaneous curvature, and $\bar{k}$ the Gaussian modulus [3]. Lamellar stacks are favored when k_c is large and $\bar{k}$ negative, penalizing topology changes. By contrast, sponge phases emerge when heating reduces k_c and drives $\bar{k}$ toward zero or positive values, lowering the barrier to pore formation and bilayer connectivity [4,5].

While reciprocal-space techniques such as small-angle scattering provide statistical signatures of this transition, they cannot directly capture the real-space connectivity. Cryogenic transmission electron microscopy (Cryo-TEM) has recently enabled direct visualization of sponge bilayers as saddle-rich, multiply connected networks, making it possible to distinguish genuine L_3 morphology from perforated lamellae or multilamellar vesicles [6,7].

Alongside experimental advances, phase-field modeling offers a complementary conceptual framework. The Cahn–Hilliard equation, originally introduced to describe spinodal decomposition [8], can be extended with bilayer-specific free-energy terms to generate diffuse interfaces that reproduce lamellar and bicontinuous morphologies [9,10]. This formalism naturally accommodates topological transitions, such as handle formation, that are difficult to treat in sharp-interface models.

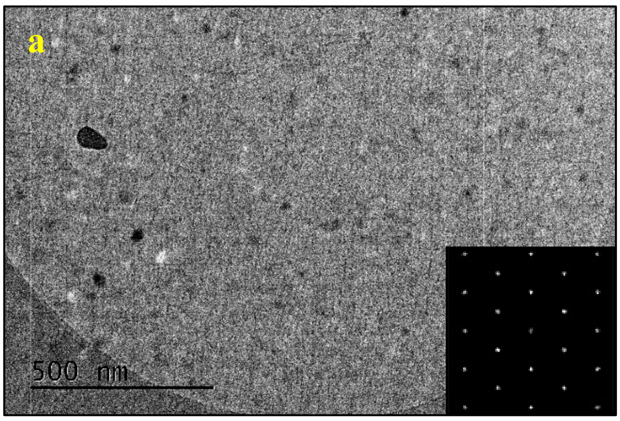
The present study combines Cryo-TEM imaging with a Cahn–Hilliard interpretation of temperature-induced phase transitions in surfactant bilayers. We focus on the lamellar-to-sponge transformation, demonstrating how direct visualization and diffuse-interface modeling converge to explain the role of thermal softening in generating bicontinuous connectivity.

2. RESULTS AND DISCUSSION

Samples were prepared following the standard protocol described by Georgiev et al. [11].

2.1 Temperature-driven morphological changes observed by Cryo-TEM

At lower temperatures the surfactant bilayers arrange in lamellar stacks, clearly visible in Cryo-TEM micrographs as parallel density bands with long-range registry. Upon heating, this order is lost: the images reveal a bicontinuous labyrinth where bilayers curve through space and form saddle-shaped passages. The disappearance of parallel alignment and the emergence of multiply connected motifs mark the transformation into a sponge (L_3) morphology. Fast Fourier transforms (FFTs) of the images support this distinction, with sharp lamellar reflections at low temperature giving way to a diffuse ring at higher temperature, corresponding to a characteristic mesh size in the tens of nanometers.



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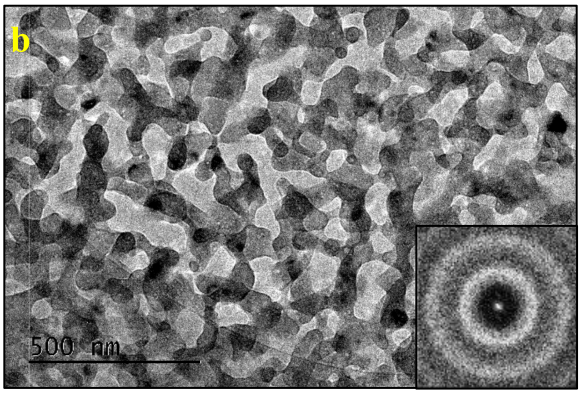

Fig. 1. *Cryo-TEM images of surfactant bilayers at two temperatures. (a) Lamellar morphology with parallel registry (T = 15 °C). (b) Sponge morphology with bicontinuous connectivity (T = 25 °C). Insets: FFTs showing the disappearance of lamellar reflections and the appearance of a diffuse ring (illustrative)[12]. Scale bars: 500 nm.*

2.2 Cahn–Hilliard phase-field interpretation

The lamellar–sponge transition can be reproduced within a diffuse-interface framework. In the Cahn–Hilliard formulation, an order parameter $\phi(\boldsymbol{r}, t)$ distinguishes solvent domains, while the free energy includes both bulk and gradient terms:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (M \nabla \mu)$$
$$\mu = \frac{\delta F}{\delta \phi} \qquad (2)$$
$$F[\phi] = \int \left[f(\phi) + \frac{\kappa}{2} |\nabla \phi|^2 + \lambda (\nabla^2 \phi)^2 \right] dV$$

Here, κ penalizes interfaces, while λ selects bilayer-type structures. Reducing κ mimics the effect of heating, which lowers the bilayer bending modulus and softens interfaces. Simulations show that under these conditions, stripe-like lamellae destabilize and reorganize into bicontinuous labyrinths. The transition occurs through handle formation, a process naturally allowed in the phase-field framework but difficult in sharp-interface models.

The order parameter $\phi(\boldsymbol{r})$ reveals how gradual softening of the system destabilizes lamellae and enables bicontinuous connectivity, mirroring the morphological transition observed in experiments.

2.3 Mechanistic picture

At lower temperature, the Cryo-TEM images (Fig. 1a) show parallel, registry-preserving fringes characteristic of lamellae. This morphology reflects a regime with high k_c and negative $\bar{k}$: the membrane pays a large energy to bend or nucleate passages, so it minimizes curvature by stacking into nearly flat layers (small $|H|$ and $K \approx 0$ almost everywhere). Upon heating, lamellar registry is lost and the micrographs display a labyrinth of saddle regions (Fig. 1b). These saddles are the real-space fingerprint of negative Gaussian curvature ($K < 0$), i.e., handles and necks that thread the bilayer into a bicontinuous network (L_3). Mechanically, this is exactly the scenario where k_c has decreased and $\bar{k}$ has shifted toward values that no longer penalize connectivity. The FFT insets reinforce the picture: sharp lamellar reflections at low T give way to a diffuse ring at higher T, consistent with the emergence of a characteristic mesh size ξ in the bicontinuous state. In practice, ξ is set by a competition between bending costs (via k_c) and an effective interfacial penalty; larger thermal softening tends to increase ξ (coarser networks), whereas residual constraints (e.g., hydration, additives) can pin ξ at smaller values.

The phase-field simulations (Fig. 2) reproduce these morphological regimes by tuning a single control parameter $\boldsymbol{r}$ that plays the role of an effective temperature/softening knob. More negative $\boldsymbol{r}$ yields stripe/lamellar patterns, numerical analogs of Fig. 1a, because the model’s gradient and higher-order penalties suppress handle formation. As $\boldsymbol{r}$ is increased, stripes destabilize via handle nucleation and coalescence into a bicontinuous labyrinth (Fig. 2b), mirroring the sponge morphology in Fig. 1b. Near $\boldsymbol{r} \to \boldsymbol{0}$ the amplitude weakens (Fig. 2c), consistent with a softened interface where long-range

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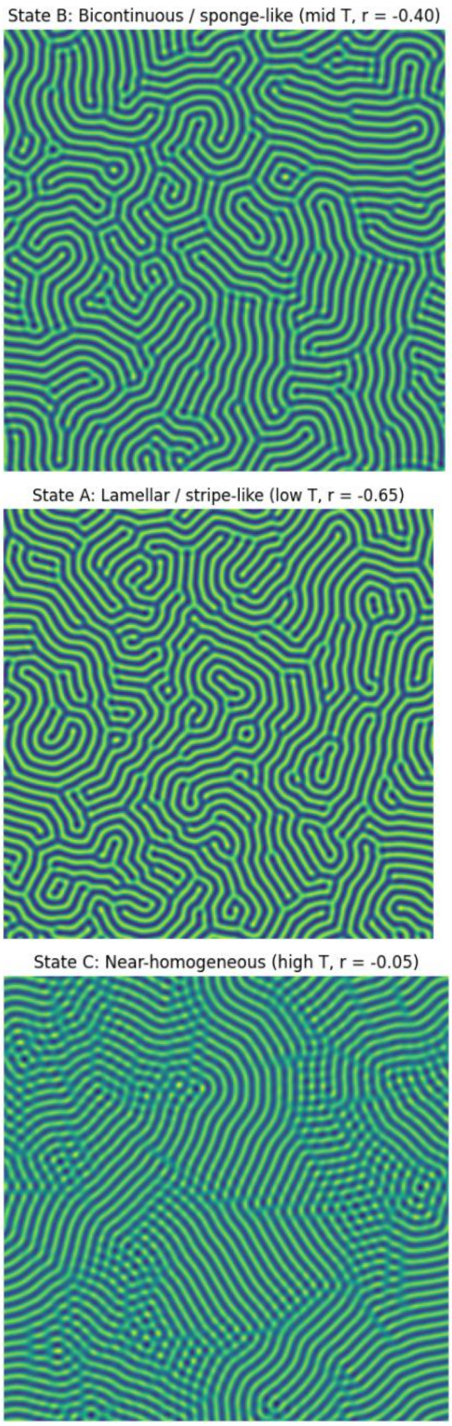

Fig.2. Two-dimensional phase-field simulations of the conserved Swift–Hohenberg equation illustrate temperature-induced transitions in surfactant bilayer morphology. (a) Stripe-like (lamellar) state at low effective temperature ($\boldsymbol{r} = -0.65$), (b) Bicontinuous "sponge"-like state at intermediate temperature ($\boldsymbol{r} = -0.40$), (c) Weakly modulated, near-homogeneous state at high temperature ($\boldsymbol{r} = -0.05$).

order is absent and connectivity is easily reconfigured. Topologically, this progression corresponds to an increase in genus (number of handles) and a more negative Euler characteristic, the same topological signature implied by the saddle richness in the Cryo-TEM. Thus, the agreement is not merely visual: the simulations encode the same mechanical trade-offs as the membrane (bending vs. interface vs. topology) and the transition pathway (stripe breakup → neck formation → networking) is the algorithmic counterpart of what the microscope reveals.

3. CONCLUSIONS

Temperature acts as a clean control parameter for topology in surfactant bilayers. Cryo-TEM directly reveals a lamellar-to-sponge transformation as heating disrupts layer registry and generates a saddle-rich, bicontinuous network. A minimal phase-field (Cahn–Hilliard with higher-order interfacial penalty) reproduces this pathway: modest shifts in the control parameter destabilize stripe-like lamellae and yield labyrinthine connectivity via handle formation.

Taken together, the real-space imaging and the diffuse-interface model provide a compact, predictive framework in which thermal softening—interpretable as reductions in effective bending rigidity and a shift of the Gaussian modulus—lowers the barrier to topological change. This framework explains why small thermal nudges produce large morphological consequences and offers practical levers for design: tune temperature to set connectivity and mesh size, and use phase-field simulations to pre-screen parameter space before formulation. Future work should quantify the temperature-dependence of the effective elastic moduli, extend to 3D reconstructions (e.g., cryo-electron tomography), and couple the model to transport/rheology to link morphology with function.

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Continuation. As a next step, we will extend the structural readout to the liquid–air interface using imaging ellipsometry (IMME) to extract independent parameters, effective optical thickness, refractive-index contrast (Δn), surface coverage, and lateral domain statistics, thereby cross-validating and tightening the Cryo-TEM/phase-field picture [13].

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