Confining Geometry Drives Dynamics in Lipidic Mesophases

Matteo Rutsch [1], *Sara Catalini* [1,2,3], *Andrea Lapini* [3,4], *Barbara Rossi* [5], *Mariangela Di Donato* [3,6], *Marco Paolantoni* [7], *Yang Yao* [1*]

[1] *Department of Chemistry, University of Basel, Basel, Switzerland*
[2] *Department of Chemistry "Ugo Schiff", University of Florence, Florence, Italy*
[3] *European Laboratory for Non-Linear Spectroscopy, Florence Italy*
[4] *Department of Chemical, Life and Environmental Sustainability Sciences, University of Parma, Parma, Italy*
[5] *Elettra-Sincrotrone Trieste, Trieste, Italy*
[6] *CNR-ICCOM, Florence Italy*
[7] *Department of Chemistry, Biology and Biotechnology, University of Perugia, Perugia, Italy*
[*] *Corresponding author*

matteo@rutsch.ch

In biological and advanced nanomaterial environments, water and other non-aqueous solvents often exist in confined settings, where dynamics are strongly coupled to surrounding interfaces [1]. While the size of confinement plays a major role, the effect of confining geometry on solvent dynamics remains an open question [2,3]. Lipidic mesophases (LMPs) serve as a versatile platform to study soft confinement effects by offering a range of self-assembled phase structures with nanometer-sized solvent-domains [4]. By tuning composition and temperature, LMPs transition from structures with planar interfaces to curved interfaces with interconnected solvent channels, and further to highly curved, isotropic phases, such as the lamellar (L_α), cubic *Ia* 3 *d* , and reverse micellar (L_2) phases, respectively. Combined X-Ray Scattering and Calorimetry reveal that transitions between these phases occur with modest enthalpic input but trigger discontinuous shifts in lipid- and solvent-dynamics, as probed by complementary spectroscopic techniques: In both water- and glycerol-based LMPs, conductivity increases when systems transition into more fluid phases and solvent-connectivity is increased. H-bonding strength increases as interfaces curve towards planar membranes, revealing dynamically different interfacial and core water populations, while lipid tail packing tightens. Together, these findings establish a clear geometric principle: interfacial curvature and solvent connectivity jointly control the packing of lipids, hydrogen-bonding, solvent dynamics, and charge transport in lipidic mesophase, providing a conceptual framework for the rational design of lipid-based systems.

Keywords:
lipidic mesophase, phase structure, dynamics, spectroscopy

References:

[1] H. Zeng, K. Liang, L. Jiang, D. Y. Zhao, B. Kong 2025 Electrochemical Sensing Mechanisms and Interfacial Design Strategies of Mesoporous Nanochannel Membranes in Biosensing Applications *Accounts Chem Res* **58** , 732-745
[2] Yao Y, Catalini S, Kutus B, Hunger J, Foggi P and Mezzenga R 2021 Probing Water State during Lipidic Mesophases Phase Transitions *Angew Chem Int Edit* **60** 25274-80
[3] Yao Y, Catalini S, Foggi P and Mezzenga R 2024 Water-lipid interface in lipidic mesophases with excess water *Faraday Discuss* **249** 469-84
[4] Mezzenga R, Seddon J M, Drummond C J, Boyd B J, Schroder-Turk G E and Sagalowicz L 2019 Nature-Inspired Design and Application of Lipidic Lyotropic Liquid Crystals *Adv Mater* **31** 35