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Response to Fischer *et al.* "The Tricontinuous 3etc(193) Phase with 3 Identical Network Domains: A Nearly Stable Morphology Even in Diblock Copolymers"

Structure versus Function in Polycontinuous Network Phases: What's in a name?

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A new calculation by Fischer *et al*. suggests that the 3**etc** network phase with 3D-hexagonal symmetry (space group #193: $P6_3/mcm$) may be a generic phase adopted by self-assembling soft materials, thereby broadening the context for our recent report of its spontaneous formation in lyotropic liquid crystals. The experimental observation of the 3**etc** phase further validates early theoretical models used to predict its stability, provocatively suggesting that other polycontinuous network phases predicted by these models may be discovered in the future. While these network phase morphologies are often mathematically described in terms of their underlying triply periodic minimal surfaces (TPMS), the numerous potential applications of these functional nanostructured soft materials require the development of a concise, consistent, and unambiguous nomenclature for their complete description. In this comment, we propose adoption of a nomenclature that describes each mesophase more generally in terms of the total number of non-intersecting domains into which three-dimensional space is partitioned.

Lyotropic liquid crystals (LLCs) are nanostructured functional soft materials, with wide ranging potential applications to areas of societal significance, including solar fuels generation and utilization,[1] drug delivery,[2, 3] and transmembrane protein crystallization and structure determination.[4, 5] Of these LLC materials, lyotropic network phases are valued in many applications as a natural consequence of their three-dimensional labyrinths of percolating, chemically functional nanopores arising from the water concentration-dependent self-assembly of small molecule surfactants. Three common network phase morphologies that arise from small molecule amphiphile self-assembly in water are the double gyroid (G), double diamond (D), and primitive (P) networks, which are based on interpenetrating nets of 3-, 4-, or 6-fold connectors.[6] Over the last 15 years, theoretical calculations by Hyde, Schröder-Turk and co-workers have suggested the stability of a plethora of other polycontinuous network phase LLCs with both cubic and non-cubic symmetries comprising three or more interpenetrating networks of multivalent connectors.[7-9]

The nomenclature associated with network phase LLCs stems from their mathematical derivation from triply periodic minimal surfaces (TPMS), which partition space into two or more non-intersecting subvolumes.[6, 10] Type II (water-poor or "inverse") G_{II}, D_{II}, or P_{II} LLC morphologies, in which the hydrophobic/hydrophilic domain interfaces curve toward the aqueous domains, may be conceptually described by situating the midplane of a lipid bilayer on either a G, D, or P cubic minimal surface, respectively. In these lyotropic phases, the lipid bilayer partitions space into two interwoven and non-intersecting aqueous subdomains. Hence, these phases are typically referred to as "bicontinuous cubic" morphologies, wherein the finite size of the lipid bilayer is not taken into account in the partitioning of space. The TPMS description of a Type I (water-rich or "normal") G_I phase, in which the domain interfaces curve toward the hydrophobic tails of the amphiphile, is less intuitive. These experimentally observed Type I phases[11] comprise two interpenetrating lipid networks in a matrix of water, wherein the TPMS is at the midplane of the aqueous domains. Application of this TPMS-derived nomenclature to the recently reported Type I H_I^{193} or 3**etc**(193) network phase in aliphatic gemini surfactant LLCs[12] would catalog this morphology as "tricontinuous," based on its derivation from a tricontinuous TPMS with 3D-hexagonal symmetry.

However, the mathematical TPMS classification scheme for LLC, block copolymer, and other supramolecular network phases is generally limited in its ability to unambiguously describe these useful soft materials. Figure 1 depicts four different triply periodic network morphologies formed by LLCs and block copolymers that derive from the gyroid TPMS, which would necessarily be categorized as bicontinuous phases. Except for the anticipated single gyroid phase, all of these morphologies have been experimentally observed in either

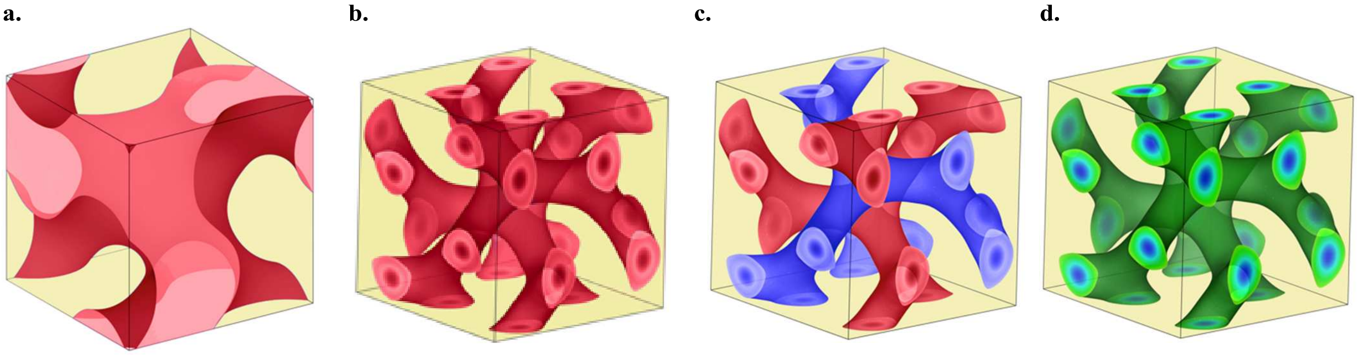

Figure 1. The (a) single gyroid (SG; space group 214: $I4_132$ symmetry), (b) double gyroid (G; space group 230: $Ia\overline{3}d$ symmetry), (c) alternating gyroid (AG; space group 214: $I4_132$ symmetry), and (d) core-shell gyroid (CSG; space group 230: $Ia\overline{3}d$ symmetry) mathematically derive from the G minimal surface and are thus classified as bicontinuous phases. However, this classification fails to capture the number of distinct, non-intersecting, and potentially chemically different domains present in each structure. We instead suggest that the SG phase is bicontinuous, DG and AG are tricontinuous, and the CSG phase is pentacontinuous to reflect the potentially different chemical transport properties of each different domain in these four different morphologies.

LLCs or microphase separated block copolymers.[6, 13-15] Careful inspection of these morphologies reveals that the single gyroid (SG) consists of two distinct and non-intersecting domains, whereas the double gyroid (G) and alternating gyroid (AG) phases comprise three non-intersecting domains. (The three-domain nature of the structurally related Type II double diamond (D_{II}) LLC mesophase is highlighted by recent work from Zabara *et al.*,[16] in which pH-responsive membrane proteins are embedded in the lipid bilayer to create channels that connect the two distinct water channels.) Following this line of reasoning, the core-shell gyroid (CSG) morphology comprises five distinct domains. Thus, the TPMS categorization of these phases fails to capture the obvious structural differences between these four morphologies, since it does not enumerate the distinct and non-intersecting domains present in each structure.

Thus, we suggest adoption of a functional nomenclature for these polycontinuous morphologies, wherein each structure is classified in terms of the total number of distinct and non-intersecting volumes into which space is partitioned. Under this convention, the SG phase is bicontinuous, the G and AG phases are tricontinuous, and the CSG is pentacontinuous. Practically, let us consider a hypothetical lithium-ion battery with an AG morphology (Fig. 1C), in which the blue domain is an anode, the red domain is a cathode, and the yellow domain is a lithium-transporting electrolyte. By virtue of the chemically distinct nature of each of the components, this morphology is functionally tricontinuous. One could alternatively imagine a Li-ion battery in a CSG morphology (Fig. 1d), in which the yellow matrix is the cathode, the green sheath of the cables is the Li-conductive electrolyte, and the blue core of the cables is the anode. Analogous arguments related to the mathematically "tricontinuous" 3**etc**(193) network phase imply that this morphology is functionally tetracontinuous (Fig. 2), as described in our recent experimental report.[12]

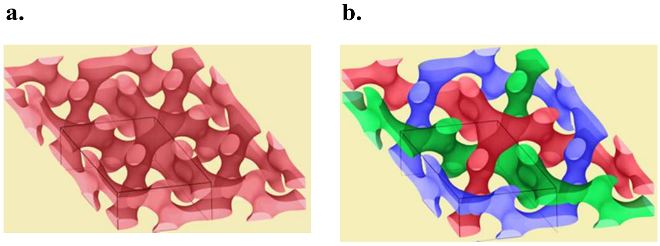

Figure 2. (a) The normal **3etc**(93) (space group 193: $P6_3/mcm$ symmetry) LLC morphology is mathematically tricontinuous, whereas (b) it is functionally a tetracontinuous network phase comprising three non-intersecting lipidic networks embedded within a chemically distinct matrix.

The need for a consistent and unambiguous nomenclature for describing the structure and functionality of soft matter network phases will only grow, with the advent of new phases with unusual symmetries and connectivities that beget new applications. Given the natural evolution from structure to functionality in soft materials science, the nomenclature associated with these intricate network phase materials should evolve to reflect their potential applications.

Notes and references

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Recent discoveries of new soft matter network phases with complex structures and potentially useful functionalities suggest a revision of the nomenclature used for their unambiguous description.