

# Soft Matter

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Comment on Sorenson *et al.*, ‘Discovery of a tetracontinuous, aqueous lyotropic network phase with 3D hexagonal Symmetry’

## The tricontinuous 3etc(193) phase with 3 identical network domains: a nearly stable morphology even in diblock copolymers

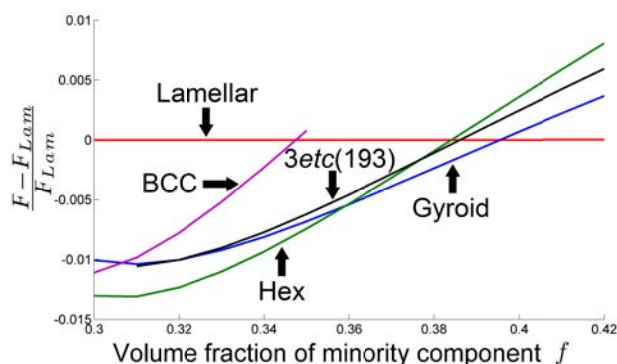
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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

The article by Sorenson *et al.* (Softmatter **10**, 8229, 2014) reports a novel phase formed by gemini surfactants in water, of symmetry  $P6_3/mcm$  and based on a triple intergrowth 3etc(193) of three identical degree-three networks. This phase is the first lyotropic liquid crystalline phase based on the intergrowth of a triplet of network- or labyrinth-like hydrophobic domains. We provide here results from self-consistent field theory that demonstrate that the same morphology is almost stable in standard AB diblock copolymer melts; at the phase transition between the double Gyroid phase and the hexagonal columnar phase, the 3etc(193) morphology only incurs a marginal free energy penalty compared to the equilibrium phases. Interestingly, the ratio of lattice parameters  $c/a = 0.954$  of the diblock phase is very close to that of the gemini surfactant phase and of the related IBN-9 mesoporous silicate phase (Han *et al.*, Nat. Chem. **1**, 123, 2009). Based on the combination of these results, we hypothesise that the 3etc(193) morphology will become a generic phase in various soft materials, rather than an oddity.

Figure 1 presents spectral SCFT calculations<sup>1</sup> for diblock copolymer melts. The data compare free energies for experimentally well-known mesophases, namely the classical lamellar, hexagonal cylindrical and body-centred cubic spherical phases, with that of a novel tricontinuous morphology, composed of three interwoven and identical hexagonal labyrinths whose skeleta are degree-three networks. Since bicontinuous mesophases have two interwoven and equivalent network-like labyrinths, patterns composed of three intergrown network-like labyrinths are referred to as ‘tricontinuous’, see Fig. 2. The hexagonal tricontinuous structure analysed here, first postulated as a candidate morphology for lyotropic phases in ref.<sup>2</sup>, is threaded by a triplet of interwoven nets, each corresponding to Wells (8,3)-c net<sup>3</sup>, now called ‘etc’<sup>4</sup>. According to a naming schema published earlier<sup>5</sup>, this pattern is called 3etc(193).

We hypothesise that the free energy penalty of the 3etc(193) morphology compared to the equilibrium morphologies is so small that small changes to the molecular architecture or composition may suffice to make the 3etc(193) a thermodynamically stable phase. While SCFT free energies for polymeric melts do not afford rigorous estimates of relative stabilities for generic amphiphile-water mixtures subject to hydrogen-bonding<sup>6,7</sup>, we interpret the small free energy penalty of the 3etc(193) phase in diblock copolymers as an indication of its



**Fig. 1** Free energies of a monodisperse AB diblock copolymer melt with  $\chi N = 16$ , relative to the lamellar phase, as function of the volume fraction  $f$  of the minority component.

likely formation in a range of soft materials.

This hypothesis is supported by the observation of a common value for the lattice parameter ratio  $c/a$ . The equilibrium ratio of lattice parameters of the 3etc(193) phase of  $c/a = 0.954$  in our SCFT calculations of the diblock melt is close to the values of  $c/a = 0.95$  observed in the solid IBAN-9 mesoporous silicate phase<sup>8</sup> and  $c/a = 0.91$  in the recently reported 3etc(193) phase in aliphatic gemini surfactants<sup>9</sup>, and commensurate with the geometric frustration analysis in<sup>10</sup>.

In combination, these results demonstrate that the 3etc(193) morphology is likely to be found more generically in soft materials, between the bicontinuous and the hexagonal columnar phases.

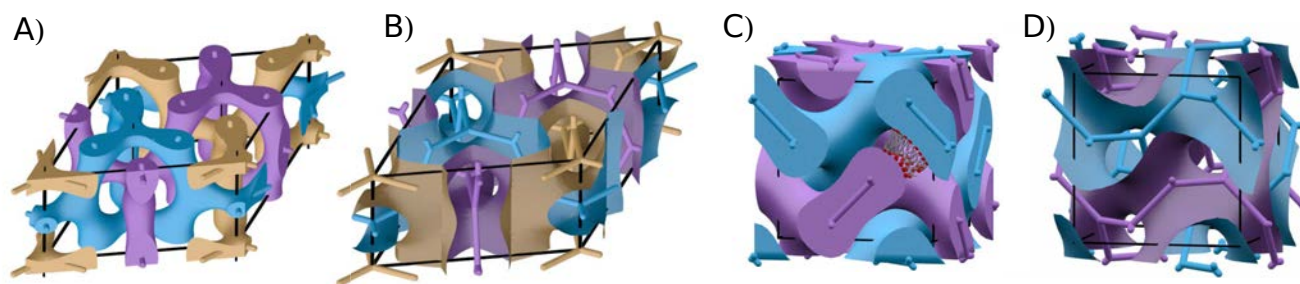
In contrast to the nomenclature used by Sorenson *et al.*<sup>9</sup>,

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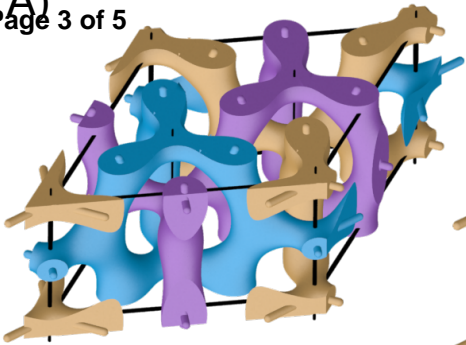


**Fig. 2** The  $P6_3/mcm$  phase in gemini surfactants, based on the tricontinuous  $3etc(193)$  geometry, consists of three identical network-like hydrophobic domains (A, yellow, purple & blue) separated by the hydrophilic matrix which is a single connected branched sheet-like domain (B). The bicontinuous cubic phases, for example the inverse  $Ia\bar{3}d$  Gyroid mesophase illustrated here, consist of two identical network-like domains (C, blue & purple) separated the matrix domain (for type II phases, the lipid bilayer) which is a single connected sheet-like component draped onto a triply-periodic minimal surface (D).

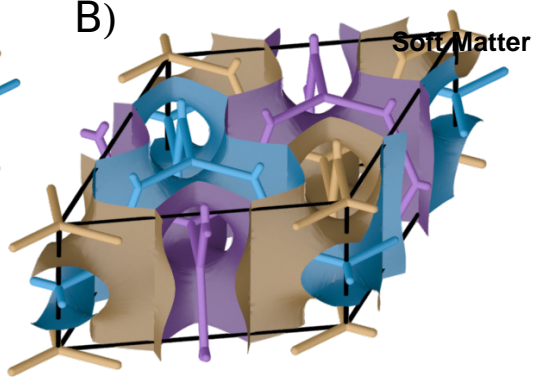
who denote this phase as 'tetracontinuous', the descriptor 'tri-continuous' is closer to the conventional nomenclature of lyotropic phases and consistent with previous definitions and usage<sup>2,5,8,10</sup>. Although the nomenclature by Sorenson *et al.* is motivated by the fact that the aqueous matrix separating the three hydrophobic labyrinths is in itself a single continuous connected component and a related nomenclature is sometimes used in the copolymeric literature<sup>11</sup>, it is inconsistent with previous usage in lyotropic systems. Clearly, the conventional inverse bicontinuous cubic phases are labelled 'bicontinuous' with reference to the two continuous aqueous network domains, even though the bilayer itself can be regarded as a third continuous component.

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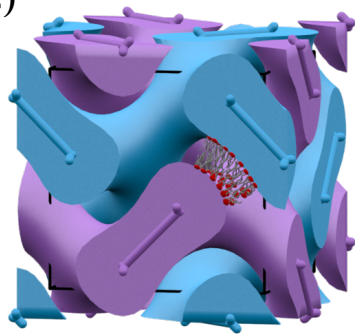
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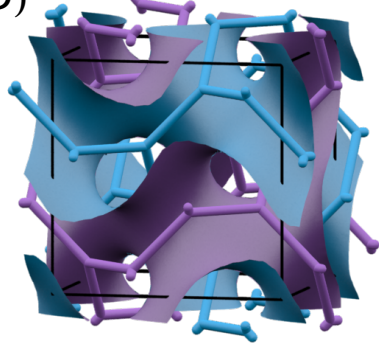
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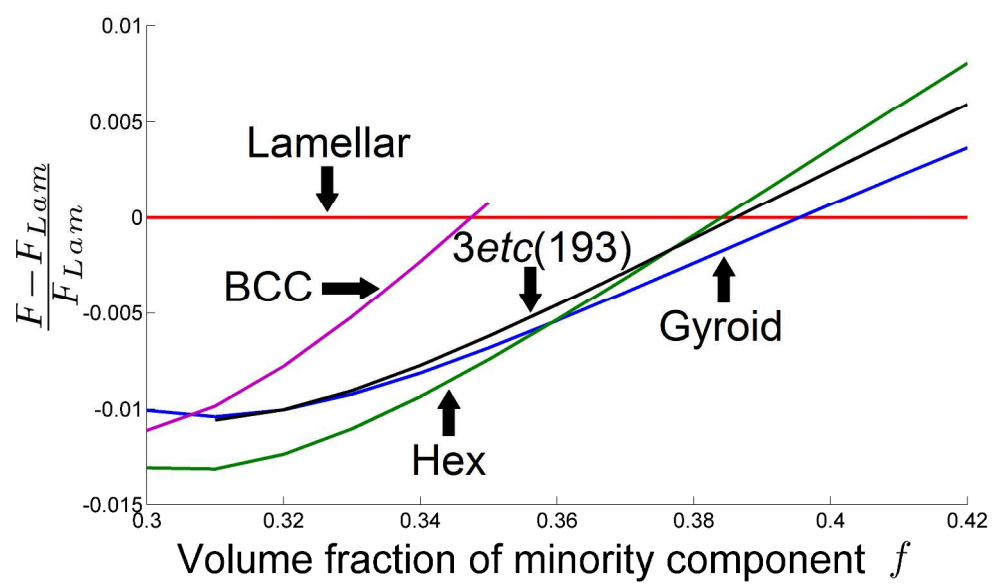


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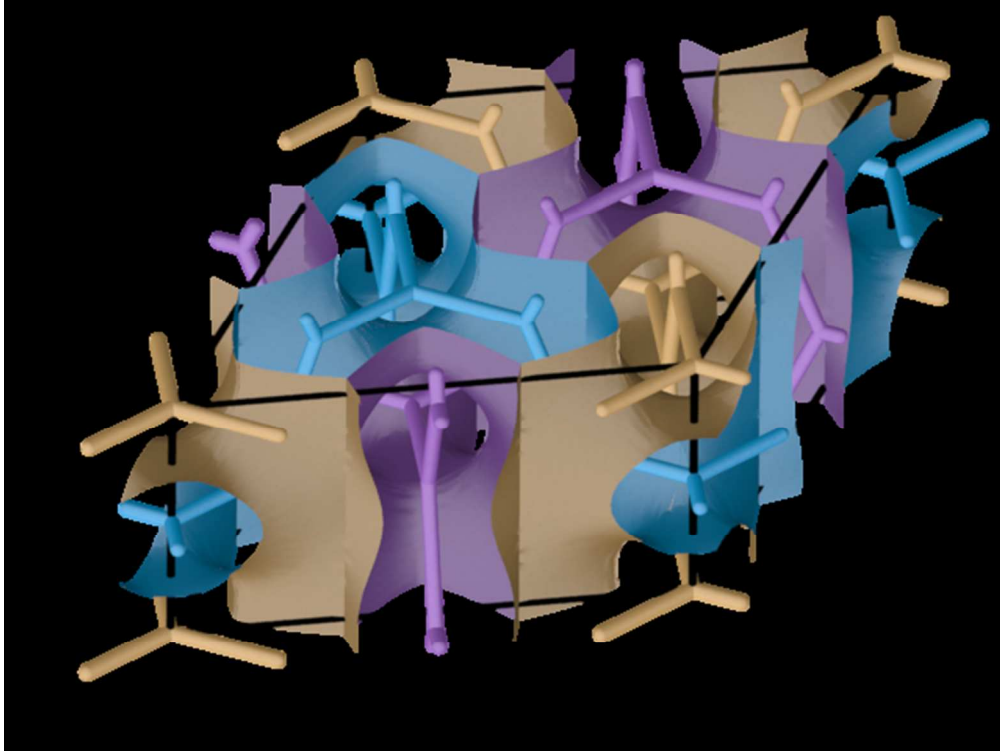


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