Fitting into and shifting symmetries of block copolymer cubic networks

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Triply-periodic network morphologies constitute "natural forms" of self-assembled soft matter, forming in nearly every class of amphiphilic molecular building blocks, from surfactants and lyotropic liquid crystals to complex shape amphiphiles [1]. By far the most commonly observed network structures are the cubic domain networks: the double-gyroid (DG), double-diamond (DD) and double-primitive (DP). Their global structure reflects a "hybridization" between cylinders and layers, with one domain forming a double network of interconnected tubes (e.g. meeting at 3-, 4-, and 6-valent connections for DG, DD, and DP respectively), interspersed with a slab-like matrix layer, whose undulating shape approximates a triply-periodic minimal surface.

In this talk, I describe recent advances in the ability to connect the thermodynamic principles of self-assembly of block copolymer melts to geometric features of triply-periodic double network morphologies. First, I describe a direct link between the *medial geometry* of double-networks [2], molecular configurations and the selection of the equilibrium DG phase in block copolymer melts, resolving a long-standing puzzle about the strong-segregation phase behavior of networks [3]. This theory shows that among cubic double networks DG is unique in terms of the terminal packing geometry of chains, which is characterized twisted and "corner-free" weblike surfaces threading within tubular domains, accounting for a particularly large chain entropy and a window of thermodynamic stability [4]. Next, I describe efforts to understand the multi-scale morphology of block copolymer double networks distorted from cubic symmetry, motivated by recent in 3D tomographic studies or block copolymer double-networks that show prominent, yet coherent, symmetry-breaking distortions are the rule, rather than the exception [5]. These studies reveal a novel mechanism for non-affine collective rearrangements nodes and struts in acubic networks, which can be largely captured by a geometric principle of length-minimizing "liquid networks" [6]. Last, I describe recent studies of direct and continuous transformations between cubic DD and DG phases (Fig. 1) [7]. While it has long been known that DD phase is not equilibrium in a the phase diagram of linear diblock copolymer melts, we show the surprising result that DD is *not even metastable* and is generically unstable to DG via an non-affine tetragonal distortion pathway.

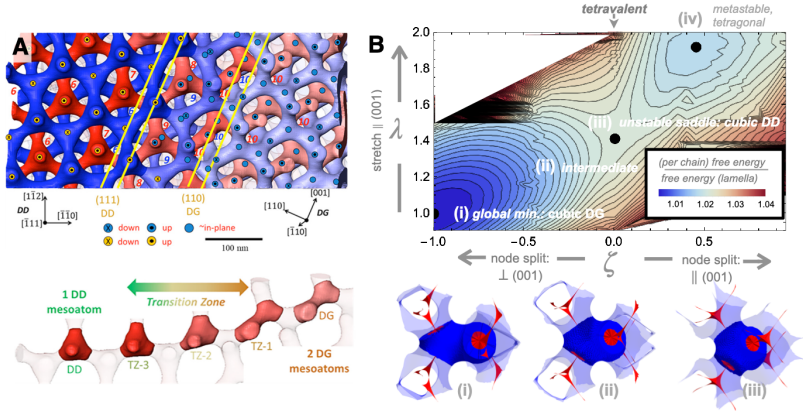

Figure 1 (A) "Slice & view" SEM tomography of continuous inter-phase transformation between DD and DG phase in polydimethylsiloxane-b-polystyrene block copolymers [7]. (B) Free energy landscape of tetragonal transformation pathway between DD and DG in strongly segregated diblocks.

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