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(I) Building blocks of soft matter crystals: Complex symmetries via frustrated packing of 'mesoatomic' elements in block copolymer melts

Tuesday 7 June 2022 11:45 (30 minutes)

Supramolecular soft crystals are periodic structures formed by the hierarchical assembly of macromolecular constituents and occur in a broad variety "soft matter"systems, from polymers and liquid crystals to biological matter. Often the building blocks consist of groups of molecules, termed "mesoatoms,"such collections are readily reconfigurable individually and collectively at the sub-unit cell scale, strongly coupling to periodic symmetries at supra-unit cell scale. In this talk I describe structure formation of soft crystals deriving from the assembly block copolymer (BCP) melts, a prototype for a broader class of supramolecular materials. While supramolecular crystals are observed to form crystal symmetries whose complex symmetries rival their hard atomic counterparts, rational frameworks for understanding and guiding these complex symmetry based on properties of the molecular constituents lag far behind. I will describe theoretical models that map thermodynamics of soft crystal formation in BCP onto geometric models which encode two competing tendencies. On one end, generically repulsive interactions favors *minimal* area of the inter-material dividing surface (IMDS) between unlike chemistries with mesoatomic domains. At the same time, the entropic cost of extending polymeric blocks to fill space evenly in these domains tends for favor uniformity in domain "thickness". I will describe how assembly thermodynamics maps onto models that integrate generalizations of the *Foam (or 'Kelvin') problem* , and the *Quantizer problems* which seek, respectively, tessellations of space that minimize area and minimize second moments of distance within cells.
I will discuss two applications of this geometric formulation of thermodynamic principles. In the first, I will briefly describe a model of complex crystals of "quasi-spherical"mesoatomic units that describes the thermodynamic competition between complex phases including the Frank-Kasper phases, which have recently been observed in BCP and number of supramolecular systems [1]. Second, I will describe recent attempts to generalize the "mesoatomic picture"to BCP crystals of polycontinuous and inter-catenated network topologies. I will describe a basic framework to deconstructing these more complex domain topologies into elementary units whose non-convex shapes and packing may shed new light on the process of their formation. Additionally, I will describe how complex and non-uniform network domains motivate a generic picture for space filling in arbitrary complex BCP domains, known as the *medial packing* [2]. I will describe a (strong-stretching) theoretical model for medial packing in triply-periodic double network crystals (e.g. the double-gyroid and double-diamond) phases, whose predictions suggests this geometric principle may be the key to resolving a long-standing problem in BCP assembly regarding the their thermodynamic stability [3].

References:
1) A. Reddy, M. B. Buckley, A. Arora, F. S. Bates, K. D. Dorfman and G. M. Grason, "Stable Frank-Kasper phases of self-assembled, soft matter spheres", Proceedings of the National Academy of Sciences USA 115, 10233-10238 (2018).
2) A. Reddy, X. Feng, E. L. Thomas and G. M. Grason, "Block Copolymers Beneath the Surface: Measuring and Modeling Complex Morphology at the Subdomain Scale ", Macromolecules 54, 9223-9257 (2021).
3) A. Reddy, M. S. Dimitriyev and G. M. Grason, "Medial packing and elastic asymmetry stabilize the double-gyroid in block copolymers", submitted, arXiv: 2112.06977 (2022).

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