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Symmetry Breaking in Block Copolymer Thin Films ERIC COCHRAN, Iowa State University, GILA STEIN, KIRILL KATSOV, ED KRAMER, GLENN FREDRICKSON, University of California, Santa Barbara —
This contribution is concerned with the packing of spherical domain block copolymer mesophases in the thin film geometry as a function of the number of layers n. In a single layer, $n = 1$, the spheres pack on a hexagonal lattice; in the bulk, $n = \infty$, the *bcc* ($Im\bar{3}m$) packing is preferred. These symmetries minimize packing frustration in 2- and 3- dimensions, respectively. We find that intermediately segregated films of sphere-forming poly(styrene-*b*-vinylpyridine) pack on a hexagonal lattice ($P6_3/mmc$) for n = 1–3, and then abrupty transform to a $Fmmm$ orthorhombic packing for $n \geq 4$. Beyond the $P6_3/mmc$-$Fmmm$ transition, the unit cell deforms to asymptotically approach the bulk *bcc* packing. These results are interpreted in terms of the competition between the excess surface energy imposed by the interfaces and the free energy of the bulk system. We construct a simple theory, parameterized using high-resolution SCFT calculations, that successfully accounts for the experimentally observed symmetry breaking. From these calculations we conclude that character of the transition from thin-film to bulk behavior may be either continuous or discontinuous, depending on the degree of the block copolymer segregation.

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