Nanocolloids at Block Copolymer Interfaces: Mesoscale Modelling of Self-Assembly and Morphology Control

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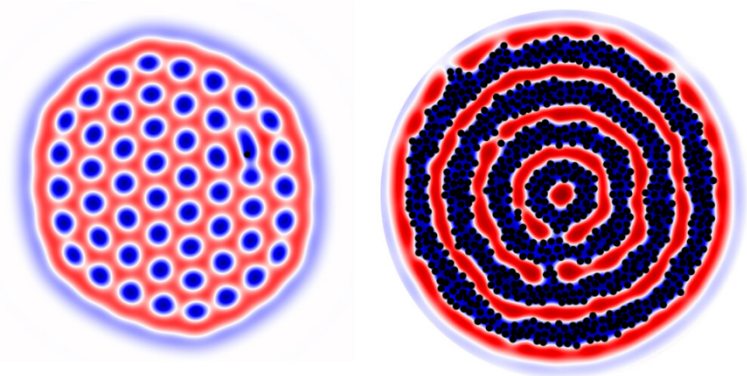
Block copolymer (BCP) systems provide a versatile platform for directing the spatial organisation of nanocolloids through their ability to self-assemble into ordered nanostructures. Under confinement, such as in droplets and thin films, additional constraints and surface selectivity introduce frustration, enabling complex morphologies and enhanced control over nanoparticle localisation. In this work, we employ a mesoscale phase-field computational framework, combining a time-dependent Ginzburg–Landau description of the BCP with Brownian dynamics for nanocolloids, to investigate self-assembly and morphology control in BCP nanocomposites.
Simulations reveal that nanocolloids preferentially localise at specific regions of the BCP morphology, including internal interfaces and domain boundaries, depending on their interactions, size, shape, and aspect ratio. In confined droplets, increasing nanocolloid loading induces morphological transitions driven by changes in effective composition and solubility, leading to Janus-like and onion-like structures. In thin films, nanocolloids modify phase behaviour and orientation, and can alleviate confinement-induced frustration, promoting transitions away from metastable states such as perforated lamellae.
Anisotropic nanocolloids introduce additional mechanisms of morphology control. Particles with large aspect ratios break local symmetry and induce sphere-to-cylinder transitions, while their orientational (nematic) ordering, guided by BCP domains, enhances lamellar alignment. In circular-forming morphologies, competition between nematic ordering and hexagonal packing leads to deformation of the mesophase at higher concentrations. More generally, particle shape plays a key role in interfacial assembly: square and rectangular nanocolloids can form ordered structures within domains or align along interfaces, with aspect ratio governing aggregation and co-assembly behaviour. These findings are supported by comparison with experimental observations, demonstrating the ability of the phase-field framework to capture key features of nanoparticle–BCP co-assembly.
These results demonstrate that nanocolloids actively control BCP morphology across different confinement geometries and particle characteristics. The computational approach provides a flexible and scalable framework for exploring structure formation in complex nanocomposite systems, offering insights for the design of hierarchical materials.

Keywords:
Nanocolloid, Block Copolymer, Computational Modelling, Self-Assembly, Phase Behaviour, Nanostructure



Block copolymer droplet morphology transformation with increasing nanocolloid loading [1].

References:

[1] Javier Diaz, Marco Pinna, Andrei Zvelindovsky, Ignacio Pagonabarraga, Macromolecules 2025 , 58 , 10 , 5240–5253.