

How to stabilize the diblock copolymer networks and tailor their percolation properties?

Diblock copolymer network morphology

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In Short

- Network stabilization – How to fabricate and stabilize the network mesostructures via a step-shear deformation
- Cross-linking – How does the quenched disordered topology interfere with the structure formation of diblock copolymer networks?
- Large-scale percolation – Strategies to enhance the domain connectivity and percolation properties of confined diblock copolymer thin films.

Scientific background – Diblock copolymers are linear, flexible macromolecules that are comprised of two chemically distinct building blocks. Thermodynamically, the two distinct segment species tend to phase separate but the connectivity along the macromolecular backbone prevents the formation of macroscopic domains. Instead, the building blocks form a fascinating variety of periodic, spatially modulated microphases with characteristic sizes of 5–100 nanometers that have attracted abiding technological interest because their geometry and length scale can be tailored by the macromolecular architecture. On large length scales and within the selected parameter range, copolymer materials microphase-separate into distinct network mesostructures, showing interesting application properties such as the enhanced electrical transport in copolymer morphologies that percolate. However, for linear diblock copolymer melts, except the cubic gyroid (GYR) and orthorhombic $Fddd$ networks, most of the other *network* morphologies (e.g., the cubic double-diamond (DD) and plumber’s nightmare (P) structures), are metastable states. Stabilization of these metastable networks will promote the application of micro-phase separated domains formed by self-assembled diblock copolymers. Recent experiments demonstrated that the long-range connectivity and percolation of lamellar nanostructures formed in bulk samples of diblock copolymer melts are suppressed in confined geometry (e.g., thin films), which limits its practical applications.

The overarching goal of our new project consists in the stabilization of metastable diblock copolymer

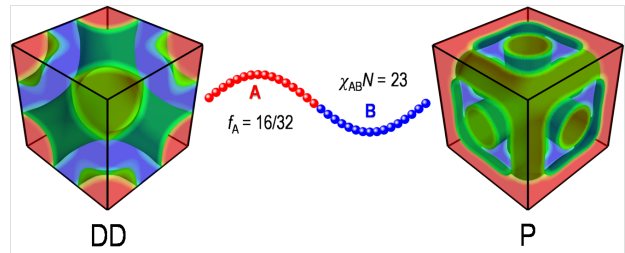


Figure 1: Metastable double-diamond (DD) and cubic plumber’s nightmare (P) mesostructures in the melt of linear AB diblock copolymers with $\chi_{AB}N = 23$ and $f_A = 0.5$. After blending linear A homopolymer, these metastable states can become thermodynamically stable.

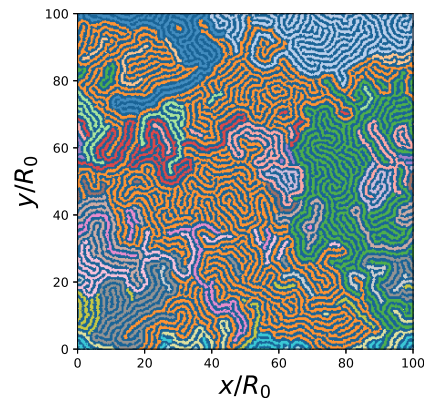


Figure 2: Percolation analysis of the morphology of a confined diblock copolymer melt in a thin film on a neutral surface. The different lamellar clusters are differently colored.

network morphologies via a step-shear deformation or cross-linking, and improving the suppressed domain connectivity observed in recent experiments within geometrically confined regions. Figure 2 shows the percolation analysis of a fingerprint-like morphology formed by diblock copolymer thin films, from which one can see that only the orange domain is percolated in the horizontal x orientation. The results of our simulations will promote the understanding and application of the diblock copolymer network morphologies. Our project is organized into different sub-tasks, each of which focuses on a specific scientific question cf. **In Short**.

All sub-tasks will use highly coarse-grained models that characterize copolymer materials by a small number of experimentally measurable parameters – like the molecular size R_e , the incompatibilities between building blocks, χN , and the invariant degree of polymerization, N . This top-down modeling

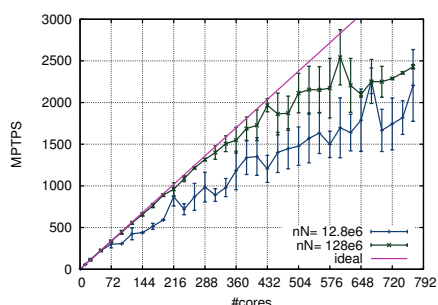


Figure 3: Strong scaling performance of our implementation measured in Million Particle monte-carlo Time-steps Per Second (MPTPS). Error bars have been obtained from multiple runs.

allows for a direct comparison with experiments.

The development of meaningful coarse-grained models and the application of advanced computational techniques, including the Single-Chain-in-Mean-Field (SCMF) simulations, numerical Self-Consistent Field Theory (SCFT), parallel computing, allow us to address timely and ambitious research topics that involve big systems and long time scales. In all our projects, the systems contain, in general, a few millions or more soft particles (or interaction centers). The preparation, simulation, and analysis of these systems poses extreme, computational challenges. Although a careful choice of coarse-grained models and an efficient implementation of algorithms can mitigate some of the high computational cost, the use of parallel computers is crucial for our research projects.

Computational aspects – Although our computational studies employ soft, highly coarse-grained models and advanced analysis techniques, the widespread time and length scales ranging from a highly coarse-grained segment (microsecond and nanometer) to grains of microphase-separated domains or the large distances between defects (hours and micrometers) as well as the stochastic nature of the self-assembly process or the quenched, disordered topology of polymer networks require significant computational resources. Thus the development of advanced simulation and analysis techniques as well as an efficient implementation on modern computer architectures is important. We use a spectrum of computational techniques including Single-Chain-in-Mean-Field (SCMF) simulations of soft, coarse-grained particle based models and numerical self-consistent field theory.

Here, we highlight our recent progress in SCMF simulations that exploit the scale separation between the strong, bonded forces and the weak but computationally expensive, non-bonded forces by approximating the latter ones with quasi-instantaneous fields. This results in an intrinsic, high parallelism of the simulation technique.

Our SCMF code is written in c99 utilizing OpenMP (shared memory), MPI (multiple-nodes) and the HDF5 library (parallel MPI/IO for initialization and analysis) for different layers of parallelism. Each MPI-rank handles a number of independent polymers, which are propagated in time with OpenMP acceleration. If the MPI-rank in heterogeneous configurations compute at different computation speeds, our implementation automatically balances the number of molecules per rank for optimal load-balance. The source code is released as open-source and can be accessed at <https://gitlab.com/InnocentBug/SOMA>.

Fig. 3 presents the strong scaling performance of intermediate-size systems (containing $n = 10^5$ and $n = 10^6$ linear polymers with $N = 128$ monomers each) on the HPC cluster at HLRN (mpp1q queue of Gottfried). Even for the smallest system, the performance of 700 cores is approximately 70% of the ideal performance compared to a full 24-core node. The slight deviation from ideal scaling stems from required all-to-all MPI communications. 700 cores, however, are sufficient to simulate all our systems of interest in a tractable amount of time.

WWW

<http://www.theorie.physik.uni-goettingen.de/forschung/mm/>

More Information

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Project Partners

Soft Matter/Biophysics, University of Göttingen

Funding

DFG-SFB 803: B03; DFG-SFB 937: A4, A5, A7; DFG-SFB 1073: A3; DFG: Mu 1674/15-1, Mu 1674/16-1, Goodyear Luxembourg