How to design models for diblock copolymer materials?

Diblock copolymer network morphology

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In Short

- Frequency-dependent Onsager coefficient – Is dynamic Self-Consistent Field Theory (SCFT) valid on short time and length scales?
- Evaporation – How does solvent evaporation influence the structure formation of mesoporous nanostructures?
- Diblock copolymer nanofibrils – Explore the morphology and transport properties of diblock copolymer nanofibrils.
- Delivering copolymers to an interface to fabricate a microemulsion – Explore the free-energy barrier of fusing a copolymer micelle with homopolymer interfaces

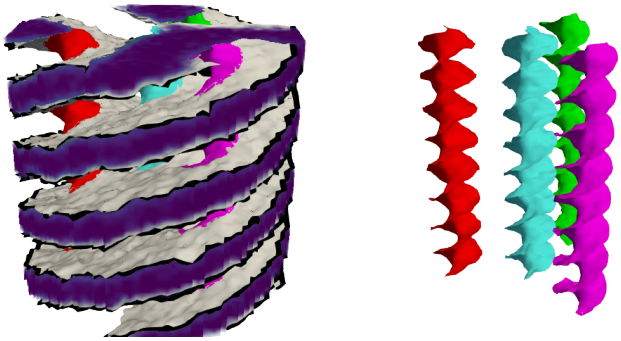

Figure 1: *Spiral-like screw dislocation defects of a lamellar diblock-copolymer material in a cylindrical confinement. This morphology forms spontaneously on the nano-meter scale if the dimensions of cylinder are appropriately chosen. The presence of these long-lived defects mechanically stabilize the materials and enhance its conductivity for applications like battery electrolytes or molecular sieves.*

Scientific background – Diblock copolymers are linear, flexible macromolecules that contain two chemically distinct building blocks. Thermodynamically, the two distinct segment species tend to phase separate but the connectivity of the blocks along the macromolecular backbone prevents the formation of macroscopic domains. Instead, the different segment species arrange into a fascinating variety of spatially modulated microphases with characteristic sizes of 5-100 nanometers. These have attracted abiding technological interest because their geometry and length scale can be tailored by the macromolecular architecture. On large length scales and within a judiciously selected parameter range, copolymer materials microphase-separate into distinct network mesostructures. Applications of these materials range from battery electrolytes over selective membranes to micro-electronics.

The overarching goal of our project consists in exploring strategies for fabricating diblock copolymer materials via computer modeling. The results will promote the understanding and application of the diblock copolymer in modern technologies. Our project is organized into different sub-tasks, each of which focuses on a specific scientific question. **As an example** Figure 1 visualizes a lamellar diblock-copolymer material in a cylindrical confinement – as realized in nano-fibrils. Diblock copolymer materials are interesting here because one block provides mechanical stability while the other block allows the transport of ions or small molecules. With the appropriate dimensions of the cylinder, in the order of 50 nanometers, the lamellae form a spiral morphology. The interesting aspect of this morphology is that it allows mechanical stresses (in one block) as well as small molecules (in the other block) to propagate along the cylinder axis. The formation of this spiral morphology is kinetically driven and long-lived but meta-stable. The corresponding equilibrium morphology, stacked lamellae, does not offer these possibilities. Forming spiral out of incompressible lamellae requires screw dislocations that appear like small spirals: we extracted them in Figure 1 in the right panel. We were able to observe the kinetic pathway leading to their formation with our soft, coarse-grained simulations.

All sub-tasks will use highly coarse-grained models that are characterized by a small number of experimentally measurable parameters – like (i) the molecular size, quantified by the end-to-end distance, R_e, of the flexible, chain molecule, (ii) the incompatibility between building blocks, χN, and (iii) the invariant degree of polymerization, $\bar{N}$ that measures the number of interacting molecules. This top-down modeling allows for a direct comparison with experiments.

The development of meaningful coarse-grained models in conjunction with the application of advanced computational techniques, including the Single-Chain-in-Mean-Field (SCMF) simulation algorithm, numerical Self-Consistent Field Theory (SCFT), and parallel computing allows us to address timely and ambitious research topics that involve ex-

traordinarily big systems and long time scales. In all our projects, the systems contain in general a few million or more soft interaction centers. The preparation, simulation, and analysis of these systems pose 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. We constantly develop our software tools and algorithms, like advanced sampling methods, to be able to address more demanding challenges.

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. We use a spectrum of computational techniques including SCMF simulations of soft, coarse-grained particle-based models, and numerical SCFT.

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. We also advanced the simulations tools to apply SCMF via the string method. An advanced sampling technique that allows us to study the mean-free-energy pathway to determine and quantify free-energy barriers.

Our SCMF code is written in c99 utilizing OpenMP (shared memory), MPI (distributed memory of multiple nodes), and the HDF5 library (parallel MPI/IO for initialization and analysis) for different layers of parallelism. Each MPI-rank handles many independent polymers, which are propagated in time with OpenMP acceleration. If the MPI-rank in heterogeneous configurations computes 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. 2 presents the strong scaling performance of large-size systems on the HPC cluster at HLRN IV. The scaling of the string SCMF implementation is almost perfect up to the maximum number of available nodes in the SKL medium40 partition. This scaling performance enables us to investigate the large system sizes of this project in tractable times.

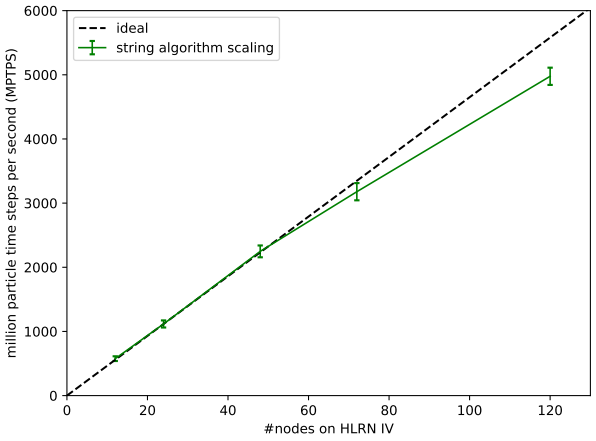

Figure 2: *Strong scaling performance of our implementation string-method SCMF on the HLRN IV with max 128 nodes. We measure performance in Million Particle monte-carlo Time-steps Per Second (MPTPS).*

WWW

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

More Information

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Project Partners

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