The role of grain boundaries for the self-assembly of cylinder-forming copolymers into polymer membranes

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JUWELS Booster

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Principal investigator

Prof. Dr. Marcus Müller

Georg-August-Universität Göttingen, Institut für Theoretische Physik, Friedrich-Hund-Platz 1, 37077 Göttingen

Project contributor(s)

N. Blagojevic, G. Ibbeken, L. Pigard, L. Schneider

Georg-August-Universität Göttingen, Institut für Theoretische Physik, Friedrich-Hund-Platz 1, 37077 Göttingen

and

O. Dreyer

Helmholtz-Zentrum Hereon, Institut für Membranforschung, Max-Planck-Straße 1, 21502 Geesthacht, Germany

Abstract: Copolymers self-assemble into spatially modulated phases on the nanoscale, used e.g. as filtration membranes. Long-range order is often not achieved, instead grains with different orientations form. Using a multiscale approach, we study grain-boundary motion (GBM): Particle simulation using the GPU-program SOMA provides insights into elementary, activated transitions during GBM that are correlated in space and time. We obtain the barriers by calculating the minimum free-energy path of the corresponding free-energy functional. The spatiotemporal correlations arise from the environment dependence of the path characteristics. We use this information to parameterize a lattice model and investigate large-scale GBM by kinetic-MC simulation.

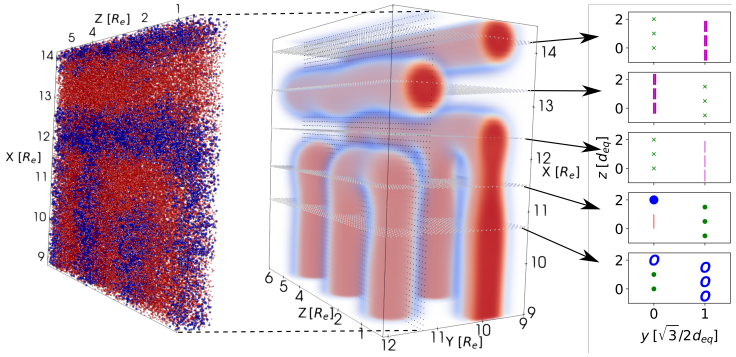

Figure 1: Sketch of the multiscale approach used to study grain-boundary motion (GBM). Left: Snapshot from a particle simulation, depicting the two types of segments of the AB diblock copolymer in red and blue. Middle: Snapshot from a simulation used for the free-energy calculations depicting the averaged minority-block density. Right: Sketch of the lattice model used to study the large-scale behavior of grain-boundary motion. Adapted from [1]

Report: In equilibrium, asymmetric AB diblock copolymers form cylindrical domains of the minority component that uniformly arrange on an hexagonal lattice. In the bulk or a film, however, defects of the morphology typically arise in the course of structure formation, *ie.*, multiple grains are formed. In each grain the cylinders are mutually aligned and registered, whereas different grains are distinguished by their orientation. For many application purposes, *e.g.* polymer membranes for nanofiltration or directed self-assembly in microelectronics, however, long-ranged order is a requirement.
In order to understand and facilitate the coarsening of grains, we need to understand the motion of a grain boundary (GBM). This is a huge computational challenge: A cylindrical domain is comprised of many polymer molecules that, in turn, are each flexible strings of multiple repeating units. Moreover, GBM involves both, local changes of the domain topology on the scale of a fraction of the polymer size and the long-range elastic interactions of the liquid-crystalline structure that greatly exceed the periodicity of the spatially modulated phase. Thus, even on the largest supercomputer, a direct simulation of large-scale GBM with molecular resolution is not feasible.
In our project we employ a triple-scale modeling strategy, as illustrated in Figure 1 to study the GBM between two orthogonally oriented grains of cylindrical domains.

- Kinetic, particle-based simulations using the Single-Chain-in-Mean-Field algorithm [2] implemented in the multi-GPU-accelerated simulation program SOMA [3] were employed to directly observe GBM on the smallest scales, *i.e.*, using $\mathcal{O}(10^8)$ polymer segments (particles). Here, two relevant processes classes were identified that drive grain-boundary motion: (i) the fusion of cylinder ends and (ii) the rupture of junctions between differently oriented cylinders. The direct observation of the relevant processes in kinetic simulations indicated that these thermally activated processes are correlated in space and time and depend on their local environment. Moreover, we

found that the deformation of one grain *via* uni-axial compression results in the directed growth of the undisturbed grain with a velocity proportional to the square of the compression factor.

- For a relevant selection of processes in different local environments, the minimum-free energy pathways and the corresponding free-energy profiles were calculated. For this, the string method [4] was applied, where the transformation pathway – denoted by the string – is discretized into points and each point is represented by a system replica. The configurations at intermediate replicas are constrained to the non-equilibrium configuration *via* field-theoretic umbrella sampling [5, 6]. Each pathway is discretized into 20 points and to achieve a high statistical accuracy of the nonequilibrium chemical potential, a large number of polymer segments, $\mathcal{O}(10^8)$, is employed for each replica. Thus, a large number of particles, $\mathcal{O}(10^9)$, is employed each string calculation, highlighting the need for large-scale supercomputers. The use of the Single-Chain-in-Mean-Field algorithm [2] in conjunction with the string method introduces multiple layers of parallelism that we exploited by the usage of multiple nodes of JUWELS Booster.

  The free-energy calculations quantified the dependency of the processes on the local environment, observed in the kinetic simulations. Here, for example, the free-energy barrier of a fusion of two cylinder heads is decreased if a ruptured junction is present in direct vicinity of the fusing heads.

  An example for the free-energy profile of a fusion process is presented in Figure 2.

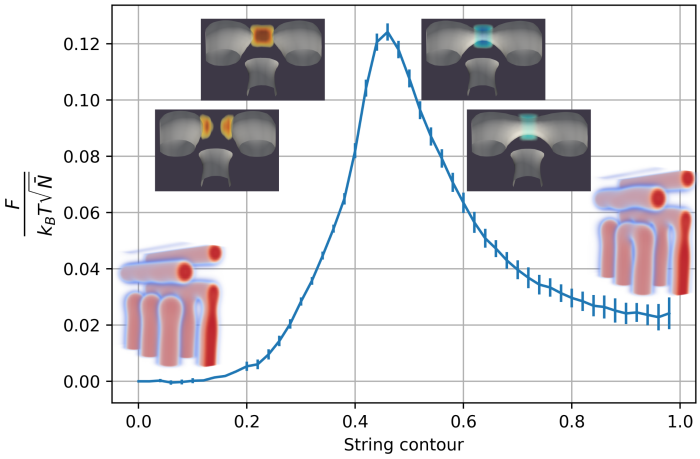

Figure 2: Free-energy profile of the minimum free-energy path (MFEP) for the fusion of perpendicular cylinder heads to a partial parallel cylinder.

- The environment-dependent free-energy profiles for fusion and rupture processes were subsequently employed to parameterized a lattice model for the simulation of grain boundary motion on significantly longer time and length scales. In this model, each lattice point represents a region of the cylindrical morphology. Lattice points adopt different states and perform transitions between the states according to the previously calculated free-energy changes and barriers of the transition paths in the corresponding local environment. Possible states include, for example, a portion of a parallel or perpendicular cylinder, a cylinder-end cap, a junction between cylinders or ruptured junction. We employed kinetic Monte-Carlo simulations [7, 8, 9] for the lattice model to study the kinetics of grain-boundary motion which proved to be consistent with the observations from the particle-based simulations.

The free-energy landscape of grain boundary motion was investigated by Wang-Landau simulations [10] of the lattice model. These reveal that GBM proceeds by nucleating a two-dimensional cluster inside the grain-boundary plane, in which the location of the grain boundary is shifted by a half-layer. The lateral growth of the cluster completes the grain-boundary translation. The line tension, of the cluster exhibits a pronounced anisotropy, giving rise to lens-shaped clusters.

Combining of large-scale particle-based simulations, free-energy calculations, and a complex lattice model of grain-boundary motion, our multiscale modeling provides a rather detailed and rich picture of grain-boundary motion in these soft, self-assembled systems [1]. These result contribute to reduce the grain-boundary friction and accelerate the ordering of multigrain structures on large time and length scale by (i) reducing the free-energy barriers associated with individual fusion and rupture transitions or (ii) tailoring their spatiotemporal correlations, mediated by long-range elastic contributions to the free-energy.

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