

How to control structure formation in soft and biological materials by molecular processing

Process-directed assembly of soft and biological materials

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In Short

- Membrane deformation in presence of a hydrodynamic flow: How do hydrodynamics lead to vesicle formation by budding from a planar bilayer?
- Onsager coefficient in the ordered phase: Can we estimate the mobility coefficient of a continuum description by comparing self-consistent field theory and particle-based simulations?
- Understanding stability of nonplanar membrane structures: What is the molecular mechanism of “kiss-and-run” fusion in synaptic release?
- How to control the properties of switchable brushes with electric fields?

Scientific background – We study transformation processes in soft and biological materials by particle-based and field-theoretic techniques [1]. Soft and biological materials, such as self-assembled structures of block copolymers, polyelectrolytes, or lipids, are characterized by energy scales of the order of the thermal energy, $k_B T$, and length scales of the order of nanometers. Minuscule free-energy differences dictate the equilibrium structure, and thermal fluctuations of the molecular configurations are important. The free-energy landscape of soft and biological materials often features multiple local minima, i.e., metastable states such as a hemifusion diaphragm that connects two opposing membranes, and there is an intricate interplay

between the dynamics of the individual string-like macromolecules and collective variables such as the density or the position of interfaces.

The overarching goal of our project is to devise and use highly coarse-grained, particle-based or field-theoretic models of lipids or polymers, study their collective response to external fields (e.g., hydrodynamic flow or electric field), and thereby devise processing strategies to control and manipulate the structure and properties on the length scales of tens of nanometers. On the one hand, this requires the prediction of the kinetics of transformation processes including the effect of hydrodynamic flow or the role of entanglements in a microphase-separated block copolymer system. On the other hand, this involves exploring structures that do not have an analog in the equilibrium phase diagram, e.g. nonplanar structures of biological membranes or metastable states of polyelectrolyte brushes in an electric field.

These systems pose exciting fundamental questions of nonequilibrium structure formation [2,3], and they also have significant relevance for practical applications, such as e.g. the formation of integral asymmetric diblock copolymer membranes that are promising materials for the next generation of ultrafiltration and nanofiltration devices [4,5].

As an example Figure 1 illustrates how the composition of a mixed polymer brush influences the structure. These systems self-assemble into spatially modulated phases because the two polymer species thermodynamically repel each other but, since one end-point of each chain molecule is immobilized onto the grafting surface, macroscopic phase separation is prevented [6]. When adding an electric field to such a system, which is the goal of one of our subprojects, new morphologies can be found. The self-consistent field theory (SCFT) code for this project has been optimized to efficiently calculate

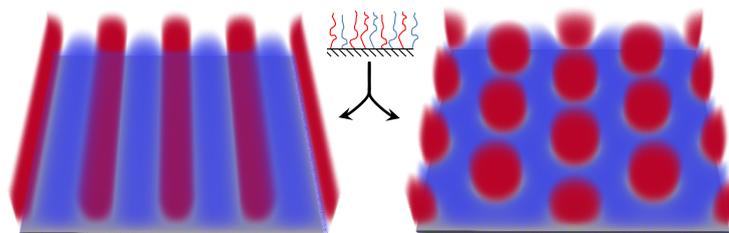


Figure 1: Ordered phases formed by an incompatible mixture of polymers irreversibly grafted onto a surface. Incompatible polymers of equal lengths and densities form lamellae (left), whereas brushes with a minority of one type form hexagonally-packed blobs of the minority type.

such microphase-separated morphologies during the last funding period.

All subtasks use highly coarse-grained models. For most of the subprojects we employ top-down models [7] 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, as well as with the standard Gaussian model of SCFT [8]. Additionally, we use systematically coarse-grained models, such as the MARTINI 3 model [9], for biological systems where more molecular details are required to capture e.g. the local stimuli exerted by conformational changes of proteins (i.e. proteins of the SNARE family).

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), rare-event techniques such as Forward-Flux Sampling, advanced free-energy techniques, and parallel computing allows us to address timely and ambitious research topics that involve extraordinarily big systems and long time scales. 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.

Computational aspects – All our subprojects use highly coarse-grained models in conjunction with the molecular dynamics program HOOMD-BLUE [10] and GROMACS [11]. We also develop own simulation codes such as the Monte-Carlo program SOMA [7], or numerical self-consistent field theory (SCFT) calculations. These efficient codes enable us to access the wide-spread time and length scales ranging from a highly coarse-grained segment (microsecond and nanometer) to the size of vesicles or the grain morphology of block copolymer melts as well as the stochastic nature of the self-assembly processes.

Our code SOMA 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 under GNU Lesser General Public License and can be accessed at <https://gitlab.com/InnocentBug/SOMA>.

WWW

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

More Information

- [1] M. Müller, *Prog. Polym. Sci.* 101, 101198 **2020**
- [2] M. Müller, *J. Chem. Phys.* 156, 124902 **2022**
- [3] N. Blagojevic and M. Müller, *ACS Polymers AU* 3, 96 **2023**
- [4] M. Müller and V. Abetz, *Chem. Rev.* 121, 14189 **2021**
- [5] O. Dreyer, G. Ibbeken, L. Schneider, N. Blagojevic, M. Radjabian, V. Abetz, and M. Müller, *Macromolecules* 55, 7564 **2022**
- [6] M. Müller, *Phys. Rev. E* 65, 030802(R) **2002**
- [7] L. Schneider and M. Müller, *Comp. Phys. Comm.* 235, 463 **2019**
- [8] M.W. Matsen *J. Phys.: Condens. Matter* 14, R21 **2002**
- [9] P.C.T. Souza *et al.*, *Nature Methods* 18, 382 **2021**
- [10] J.A. Anderson, J. Glaser, and S.C. Glotzer, *Comput. Mater. Sci.* 173, 109363 **2020**
- [11] S. Pall, A. Zhmurov, P. Bauer, M. Abraham, M. Lundborg, A. Gray, B. Hess, and E. Lindahl, *J. Chem. Phys.* 153, 134110 **2020**

Project Partners

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