Project A3: Nucleation and phase ordering of switchable molecules at surfaces

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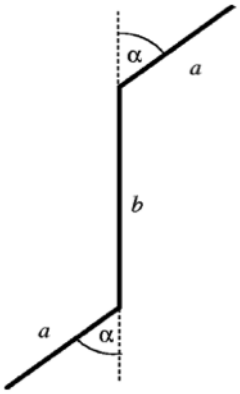

Switchable zigzag molecule.

Outline. Certain chemical groups in organic compounds absorb light and undergo an optically induced trans-cis transition that changes the molecular shape. The two different conformations can then lead to different ordered phase behavior. The main goal of the project is to study the 2D phase behavior of such switchable molecules bound to a surface. Most importantly, we will investigate how the transition from one phase to another occurs if the conformation of the molecule is suddenly switched. To address this problem, we employ a simple model system that can switch between a linear rod and a zigzag shape (see figure). In the zigzag conformation we allow for some elastic distortions in the bend angle α. Recent theoretical investigations show that these zigzag molecules exhibit a smectic phase while needles only show a nematic phase. The interesting aspect of this work is to study how, for example, the nematic phase of the straight rod configuration develops a smectic ordering when the molecule is suddenly switched into the zigzag conformation. How does the system react on this sudden "shape quench"? Does the smectic phase develop in analogy to classical nucleation during an equilibrium phase transition? Or does the system remain in some metastable, potentially jammed or glassy state? These are some of the open questions to be studied. From their answers we anticipate a wealth of new phenomena.

Research within the German group. We start by defining the switchable model molecule. The needle and zigzag shapes have terminal tails of length a, for a molecular total length L=2a+b, as well as a bend angle α. A bending cost for deviating from the prescribed α allows to control the molecular flexibility. For the interaction of the molecules we rely on the Kihara model. We will map out the phase diagram for the zigzag molecule in terms of density and the parameters a and α. We will then concentrate on non-nematic order, such as smectics, of the zigzag molecule and study by Brownian dynamics simulations the ordering from the nematic phase of needles into the non-nematic phase of zigzag molecules upon a sudden molecular shape quench. The friction term in the Brownian dynamics captures the interaction with the surface. Smectic order parameters will be used to monitor the time evolution of the smectic phase after the shape quench. An appropriate order parameter will be developed to identify possible nucleation sites for the smectic phase. A plateau in the recorded mean-square displacement of the molecules will indicate a jammed or glassy state.

Longer-term perspective. Once the basic features of the form quench are known, we will extend our investigations to more realistic model molecules, restrict the shape quench to local regions, and implement a reaction dynamics of the shape quench after initiation. We will also study how the system reacts to a sequence of switching events, which is important for applications.

Complementary work in US partner group. Charbonneau is an expert in soft matter and glass physics. His expertise in simulating systems with complex dynamics and thermodynamics, and in developing methodologies adapted to these systems, will be particularly useful in describing the behavior of our schematic model. Once the first simulation results are available, we will decide on the specific tasks to be performed during the stay at the US partner's group.

Status of the project. The project bears a strong relation to projects A1 (Schoen) where switching of liquid-crystal phases by solid surfaces will be studied in computer simulations and to project A4 (Riegler) which focuses on surface-induced nucleation. Moreover, changes in molecular conformation are an issue in other project areas as well. Examples are project B3 (Grafmüller) and project C1 (Rabe). Therefore, the present project is well integrated into the overall research program. The response to external fields is also a central issue in project C5 (Klapp).