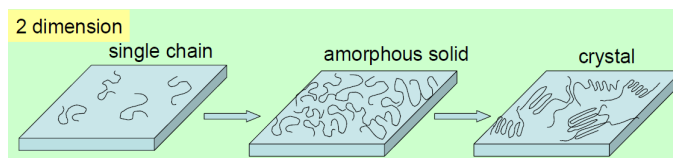


Project C4: Ordering and crystallisation of polymers in quasi-2 dimensions

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Current state of the research. Polymer monolayers on a liquid surface (e.g. on water) represent ideal model systems for studying chain conformations in (quasi) two dimensions (2D). In addition, temperature or density can be used to modify the chain conformations (e.g., density-crossover from dilute to concentrated solutions, temperature- or density-induced polymer crystallization). Such



2D polymer systems are expected to display deviations from three-dimensional (3D) bulk behavior. Here, one can distinguish two cases: strictly 2D self-avoiding chains and quasi 2D polymers where excursions in the third dimension allow the chains to overlap. In the first case, the chains are expected to adopt compact and segregated conformations with a highly irregular (fractal) boundary. The chains can only partially “interpenetrate” at the boundary, which also affects the polymer dynamics (no chain entanglements). On the other hand, chain overlap is possible for the second case of quasi 2D chains. However, this overlap is much reduced relative to the 3D bulk. This implies corrections to chain ideality for the static properties and should also affect the polymer dynamics (e.g., by a change of the entanglement length).

Direct experimental visualization of (quasi) 2D polymer chains is very challenging, but techniques are emerging (e.g., for DNA by fluorescence microscopy or brush-like polymers by atomic force microscopy (AFM)). Inspiring work was performed in the group of J. Kumaki (Yamagata University, Japan) who combined sample preparation on a Langmuir trough with observation on a nanometer scale by AFM. To assure segmental mobility and an initially dispersed state, long chain polymers are embedded in a 2D monolayer of high mobility and compatible short molecules. In this way, it was possible to observe clear images of chains and of their molecular packing in Langmuir monolayers after deposition on a substrate.

Contributions of the principal investigators. The Strasbourg group has recently explored by molecular simulations and scaling arguments static and thermodynamic properties of strictly 2D polymer melts. Extension of this work to thin (quasi-2D) films as well as studies of the polymer dynamics are under way (for the strictly 2D case, the polymer dynamics has also been discussed). The Reiter group has long-standing expertise in preparation of ultrathin polymer films, their imaging and analysis by AFM, and polymer crystallization.

Research project and collaborations. The goal of this project is to measure in direct space chain conformations as a function of polymer concentration (and temperature), controlled by the lateral surface pressure established on a Langmuir trough. These experimental results will be analyzed in the light of the ongoing simulation work in Strasbourg. In addition, viscoelastic properties of the monolayers will be probed by the capillary wave spectrum. A similar analysis will also be attempted for simulation data and compared to the viscoelastic spectra obtained by complementary techniques (e.g., time-correlation function of the stress tensor). Moreover, for crystallisable polymers, questions of nucleation and growth of ordered regions will be addressed experimentally. Corresponding simulations are envisaged.

Work plan. Experiments will be performed by the doctoral researcher in Freiburg. Mutual visits of the involved researchers and extended stays of the doctoral researcher in Strasbourg will aim at linking and exploiting simulation and experimental results in order to develop a detailed understanding of fundamental properties of 2D polymer systems.