Structure Formation in Systems of Mesoscopic Rods

Thomas Gruhn 10.06.1969
1995: Diploma, Physics
(Technische Universität Berlin)
Thesis: Monte-Carlo-Untersuchungen der Ausrichtung nematischer Flüssigkristalle (A Monte Carlo study of the alignment in nematic liquid crystals)
1998: PhD, Physics (Institut für Theoretische Physik, TU Berlin)
Thesis: Substrate-induced order in confined molecularly thin liquid-crystalline films
1999: R&D Project
(Siemens AG, Berlin)
2000: Postdoc
(University of Massachusetts, USA)
2001: Group Leader
(Max Planck Institute for Colloids and Interfaces, Potsdam)

Mesoscopic structures are a timely research area since new experimental techniques like atomic force microscopy or optical tweezers allow a detailed investigation and manipulation on this length scale. The controlled production of nanostructures on larger scales facilitates the design of new materials, whose mechanical, optical, and chemical properties can be tailored in completely new ways. Inspirations are given from the rich complexity found in molecular cell biology. The controlled production of mesoscopic devices has a wide range of applications reaching from microsurgery, over nanochemistry to a further minimization of microprocessors.

One building block for the creation of nanostructures are mesoscopic rods, which nowadays can be produced in large amounts **[1, 2]**. With the help of Monte Carlo simulations we investigate how structure formation in systems of mesoscopic rods is influenced by the properties of the molecules and the influence of the environment. The results help to control rod systems in such a way that rodlike macromolecules can be used to build ordered superstructures.

Systems of Chemically Homogenous Rods

Mesoscopic rodlike molecules and molecular assemblies **[3]** are typically the product of a linear growth process. Therefore, these rods have the same diameter along their axes. For a fluid phase the rods have to be in a solvent. The steric interaction of the rods can be well described by hard spherocylindric rods (*hr*).

Further, attractive interactions may arise from van der Waals and depletion forces. A simplified model for the complete interaction is found by integrating a square well potential along both rod axes. The resulting attractive rod (*ar*) potential can only be calculated with a large numerical effort.

Instead we have developed an angular-dependent site-site potential (see **Fig. 1**) that mimics the ar potential very well with a computational effort comparable to the *hr* potential.

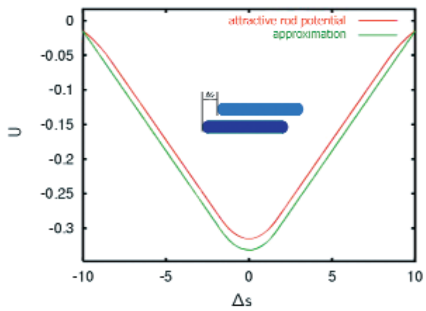

Fig. 1: Attractive rod potential compared with simplified potential.

Caused by the production processes, systems of mesoscopic rods typically have a broad length distribution, while for many applications a narrow length distribution would be favorable. A fractionation of rod lengths occurs in the phase coexistence region of the isotropic and a nematic or smectic phase of the system. For the ar potential the formation of an ordered phase occurs at much lower pressures as for the *hr* potential. In an ongoing project, we compare the nucleation behavior of attractive rods with that for hard rods **[4]**.

A binary 1:1 mixture of rods with lengths L_1=3 and L_2=6 has been investigated in a Gibbs ensemble simulation, in which two simulation boxes are run in parallel **[5]**. The two boxes can exchange rods and volume such that they have the same pressure and chemical potential. In the phase coexistence region the two sorts of particles demix almost completely. **Fig. 2** shows the two boxes before and after the demixing. The plot in **Fig. 3** illustrates the growing number of small rods and the decreasing number of large rods in box (a). In subsequent simulations the behavior of polydisperse mixtures and the influence of adjacent substrates will be investigated.

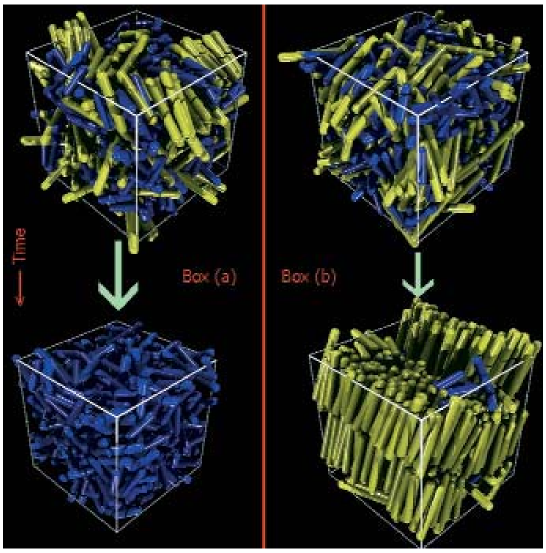

Fig. 2: Demixing of short rods (blue) and long rods (yellow) in a Gibbs ensemble simulation.

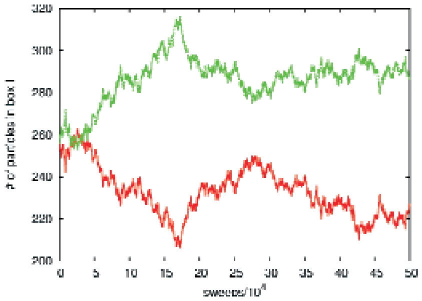

Fig. 3: Time development of long rods (red) and short rods (green) in box (a).

Systems of Chemically Heterogeneous Rods

Mesoscopically large rods can be tailored to have a chemically heterogeneous structure, which provides new types of ordered structures in the rod system. We investigate hard rods with attractive potentials at the end. In large regions of the phase diagram the behavior of such systems is qualitatively similar to that of systems with chemically homogenous rods. At rather low pressure, however, the formation of a three dimensional, scaffold-like network structure is found showing cluster points where the rods meet with a finite angle (see **Fig. 4**). These structures are stabilized by the addition of an angular dependence of the attractive potential. In a next step we will check if a regular scaffold structure, such as the one shown in **Fig. 5** can be thermodynamically stable with an appropriate potential at the rods' ends.

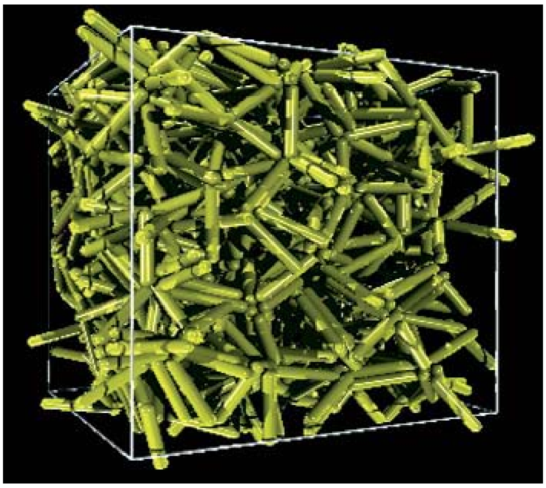

Fig. 4: Ultraporous structure formed by chemically heterogenous rods with attractive endgroups.

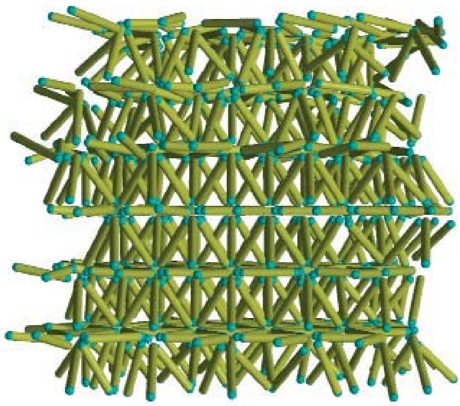

Fig. 5: A scaffold-like fcc-structure is expected to be stable for suitable chemically heterogenous rods.

In another project a system of small rods with attractive ends and long chemically homogenous rods is investigated. This provides a simple model for the cytoskeleton, where the long rods are filaments and the small heterogeneous rods mimic the crosslinkers. Here it will be investigated, how the structure of the filament network depends on the concentration of the crosslinkers.

T. Gruhn, R. Chelakkot, R. Lipowsky, A. Richter
Thomas.Gruhn@mpikg.mpg.de

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