

# RODS AND FILAMENTS

## Fractionation and Low-Density-Structures in Systems of Colloidal Rods



Rigid rods of mesoscopic size can nowadays be synthesized in large amounts. Examples are carbon nanotubes, boehmite needles, cylindrical dendrimers, and metallo-supramolecular polyelectrolytes (see references in [1]). Colloidal rods are of great relevance for the creation of mesoscopic structures. In solution they can self-organize and induce long-range spatial and orientational order.

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Typical examples are liquid-crystalline mesophases, known from systems of small liquid crystal molecules. There are, however, important differences between traditional liquid crystals and systems of mesoscopic rods. While systems of small liquid crystal molecules are typically monodisperse or consist of a small number of components, most systems of synthesized colloidal rods have a polydisperse length distribution, due to the production method. Furthermore, the alignment of small rods is mainly caused by a coupling of the molecules' polarization axes, while orientational order of mesoscopic rods is typically based on steric interactions. Therefore, in many cases colloidal rods can be successfully approximated as hard spherocylinders. However, if van-der-Waals forces between the colloidal rods cannot be neglected or if the solvent generates strong depletion forces between adjacent rods, attractive interactions must be considered.

### Fractionation in Systems of Chemically Homogenous Rods

Polydisperse systems of spherocylindrical rods have a pressure range in which an isotropic phase with no orientational order coexists with a phase which is (at least) orientationally ordered. In this case, long rods are preferentially found in the ordered phase while the majority of small rods is located in the isotropic phase. With the help of Monte Carlo simulations we have investigated the influence of attractive interactions on fractionation effects in a polydisperse system of spherocylinders [2]. A spherocylinder consists of a cylinder of diameter  $D$  and length  $L=\lambda D$ , which is capped by two hemispheres with diameter  $D$ . We analyzed a polydisperse system of rods with cylinder lengths between  $\lambda=1$  and  $\lambda=8$  for various reduced pressures  $P^*=P v_{av}/T$ , where  $v_{av}$  is the average rod volume and  $T$  is the thermal energy including the Boltzmann factor  $k_B$ . At large pressures long rods are strongly aligned while the orientational order for short rods is low. The discrepancy between the order of short and long rods is strongly enhanced by attractive interactions (Fig. 1).

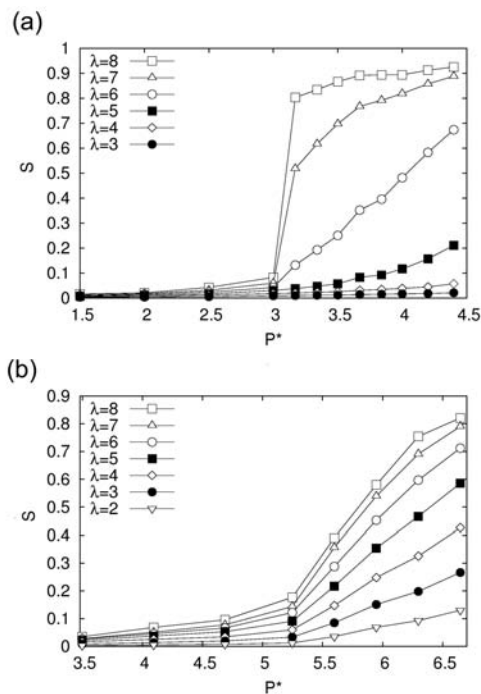


Fig. 1: Orientational order parameter  $S$  of components with cylinder length  $\lambda$  in a polydisperse rod system at reduced pressure  $P^*$ . (a) In a system of attractive rods, long rods are strongly aligned at pressures  $P^*>3$ , while short rods are almost isotropic. (b) For hard rods, the orientational order decreases gradually with the rod length.

An analysis of the local structure reveals that, at high pressures, long attractive rods form a smectic monolayer with hexatic in-plane order, while hard rods form a less ordered nematic droplet which consists of preferentially long rods (cmp. Fig. 2).

This corresponds to experimental results for fd-viruses in a polymer solution which form strongly ordered mono-layers in the presence of strong depletion forces and less ordered domains if depletion forces are weak [3].

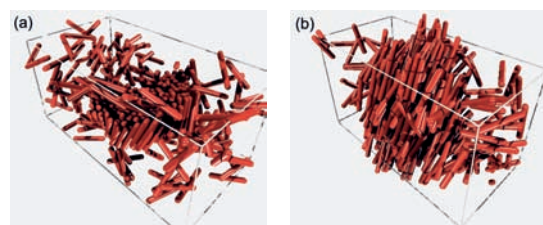
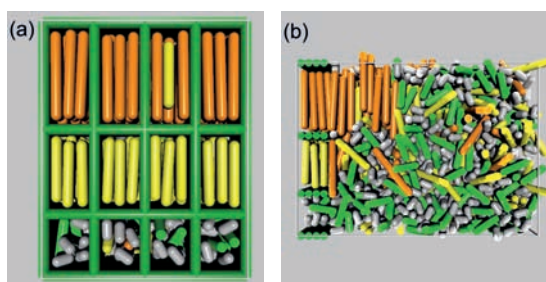


Fig. 2: Typical configurations for polydisperse systems of (a) attractive and (b) hard rods. For clarity reasons short rods ( $\lambda<5$ ) are omitted. In (a) long rods aggregate to a smectic monolayer, in (b) a nematic droplet forms.

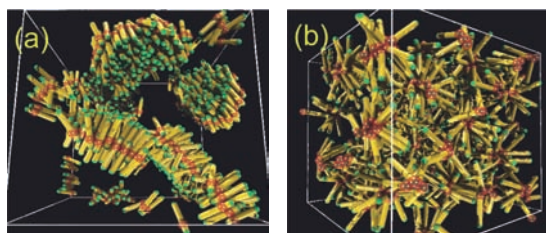
Spatial fractionation can also be induced by an adjacent, structured substrate. For this purpose, substrates with rectangular cavities turned out to be particularly suited. **Fig. 3** shows configurations of an equilibrated rod system with four different lengths in contact with a substrate with cavities of different sizes. Starting from a random configuration, the different rods aggregate inside the corresponding cavities. Long rods form a smectic monolayer which grows out of the substrate cavities.



*Fig. 3: Typical configurations for a system of rods with four different lengths in contact with a structured substrate with rectangular cavities of different sizes. Molecules demix and aggregate in the corresponding cavities as shown in (a) from the planar substrate (not shown) behind the cavities and (b) in a side view.*

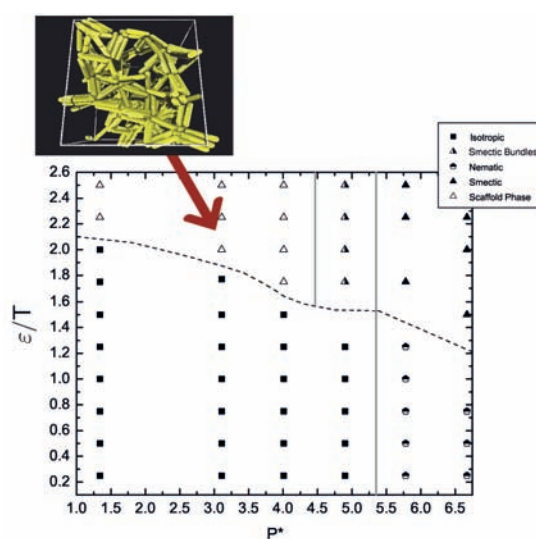
### Low-Density Structures in Systems of Chemically Heterogenous Rods

Additional types of structures can form in systems of chemically heterogenous rods. We have studied rods with one or two short-range adhesive sites along the molecule axis which can adhere to sites of other rods [4]. Typical examples are stiff block-copolymers where the hydrophobic parts aggregate to screen themselves from the surrounding water. The chemically heterogenous rods form complex structures at rather low densities. Hard rods with one adhesive segment located halfway between the center and the end of the rod may form membrane-like clusters (Fig. 4a). For entropic reasons half of the rods point up and half point downward, resulting in a membrane of width  $w \approx 3L/2$ . If the adhesive segment is located at the end of the rods, micellar structures are formed (Fig. 4b).



*Fig. 4: Snapshots of hard rods with one adhesive segment (a) half way between the center and the end of the rod and (b) at the end of the rod.*

The system behaves completely different if adhesive sites are located on both ends. For this type of rods with length  $\lambda=5$ , we have estimated a phase diagram as a function of the reduced pressure  $P^*$  and the adhesive strength  $\epsilon$  (Fig. 5). For small  $\epsilon$ , the system shows an isotropic and a nematic state, just like a system of hard rods. For sufficiently large  $\epsilon$  and low pressure a novel scaffold-like state is found with a flexible network of rods. The scaffold state is characterized by triangular structures formed by three mutually adhering rods. At higher pressures, small smectic-like bundles occur, before at even higher pressure a long-range smectic order sets in.



*Fig. 5: Phase diagram of a system of hard rods with adhesive ends. For sufficiently high adhesion strength  $\epsilon$  and low reduced pressure  $P^*$  the system forms a scaffold-like structure as shown in the snapshot on top.*

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### References:

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