Effect of boundary conditions on self-assembly

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Nanoscale self-assembly is a process in which initially disordered particles spontaneously organize into thermodynamically stable patterns. In the bulk, structure and symmetries of the patterns are determined only by the interaction potential between the components, while in the case of confined systems the impact of the system size and component-wall interaction play an important role. In the thesis we study these effects of boundary conditions on the self-assembly at nanoscale.

We start the study with comparison between two classes of self-assembling systems in the bulk. The first class consists of systems with spherically symmetric particles which interact *via* an isotropic potential with competing short range attraction and long range repulsion (SALR). Such interactions can be observed in e. g. colloidal suspensions, protein solutions or between quantum dots. The second class is characterized by amphiphilic interactions, that is anisotropic interactions present between e. g. lipids which have hydrophilic heads and hydrophobic tails, or block copolymers with building blocks of different chemical properties. We solve the two models exactly by the transfer matrix method in one dimension, perform Monte Carlo simulations and numerical calculations of the mean-field type. The comparison made between the equations of state, correlation functions, heat capacities and the ground states indicates striking similarities between these systems and significant differences between them and simple fluids. Thus, further studies in a two dimensional (2d) space were carried out only for the model with the SALR potential. In 2d we have obtained the first complete phase diagram for the system with SALR type of potential. In particular, we have discovered the ``molten lamella'' phase which was not previously included in the phase diagrams of systems with the SALR potential.

Knowing the bulk properties of the SALR system, we have focused further studies on the effects of confinement. We have assumed that the system has geometry of a slit and considered one- and two-dimensional models. In the case of 1d model with permeable walls we have found exact solutions for the density profiles and the effective interactions between the walls, i. e. the solvation potential. In the case of impervious walls we have studied density profiles and equation of state by Monte Carlo simulations. In both cases rigid and elastic walls were considered. In the case of rigid walls the impact of the system size which is not favorable for the bulk ground state structures has been analyzed. In particular, we have discovered anomalies which do not occur in simple fluids, and qualitative differences between cluster distributions in canonical and grand canonical ensembles for the same thermodynamic conditions. The study of elastic confinement led us to discovery of a new way in which a complex system may spontaneously change its size. Namely, we have found that if the system self-assembles into periodic structures, then the fluid induced force between the walls may compete with the elastic force of the confinement in such a way, that two system sizes can be equally probable. Moreover, the two stable sizes may differ by as much as a period of the ground state pattern.

The 2d model with slit geometry revealed the ordering effects of the confinement. In contrast to the bulk, in which the ground state is strongly degenerated, in the case of confined system the ground state patterns are unique. We have found that the presence of walls may induce defects in the bulk patterns either locally (in the close neighborhood of the walls in the cluster phase), or globally (across the whole slit in the lamellar phase). Interestingly, the defects appear in an organized manner not only at zero temperature, but also at low temperatures.