

Effects of confinement on self-assembly in systems with competing interactions

Author: Horacio Antonio Serna Serna

Supervisor: Prof. dr hab. Wojciech Goźdź

Second supervisor: Dr. Eva González Noya

May 20th 2021

Summary

Systems with competing interactions, such as colloidal suspensions, block copolymers and lipids mixtures, have shown interesting self-assembling properties that can be exploited in technological applications. It has been demonstrated that despite the type and nature of the interactions, systems with competing interactions exhibit a universal phase behaviour in bulk. Ordered microphases such as cluster-crystals, hexagonal, cubic bicontinuous and lamellar phases are often observed in this kind of systems.

When confined, systems with competing interactions behave differently, showing new structural, thermodynamic, and dynamic properties. In the thesis, we investigate colloidal fluids with competing interactions under confinement into channels and pores with different morphology. The colloidal fluid consists of spherical particles interacting via an isotropic short-range attraction and long-range repulsion (SALR) potential. We consider repulsive interactions between the colloidal particles and the walls of the confining channels and pores.

We start the study by confining the colloidal fluid into channels with different cross-section geometries. Using Grand Canonical Monte Carlo (GCMC) simulations, we found that the structure of the ordered microphases can be tuned by confinement. We observed the formation of helical structures inside cylindrical and elliptical pores. We also found that triangular, hexagonal and wedged-cylindrical channels promoted the nucleation of ordered microphases with the same structure of the bulk hexagonal phase.

We continue the research by investigating the behaviour of the colloidal system under confinement into curved quasi-bidimensional space. Using GCMC simulations again, we study the colloidal fluid confined into spherical and ellipsoidal narrow shells. We observed that in conditions at which the hexagonal phase is stable in bulk, the system self-assembled into coiled cylindrical clusters that resembled geometrical solutions of the problem of the longest rope filling the surface of a sphere. On the other hand, the confinement into prolate and oblate ellipsoidal shells favoured the formation of helical and toroidal structures, respectively.

Additionally, we investigated the colloidal system when adsorbed into ordered bicontinuous porous materials. A GCMC simulation study revealed that, depending on the morphology and the size of the porous materials, the colloidal system could form a set of new cluster crystals formed from cylindrical and spherical clusters that are not stable in bulk. Interestingly, we observed that some pore sizes and morphologies promoted the formation of ordered microphases with the same structure of the cluster-crystal and hexagonal phases in bulk.

In the last part of the research, we performed Molecular Dynamics (MD) simulations, in bulk and under confinement into slit pores, of a colloidal system with competing interactions modelled with a SALR potential. In bulk, besides the formation of the typically ordered microphases, we observed intra-cluster freezing transitions. Such transitions were characterised from structural, thermodynamic and dynamic points of view. We found that the confinement into slit pores induced a change in the phase diagram of the colloidal system. Moreover, we observed that the diffusion of the colloidal particles could be enhanced for some pore widths.

In the thesis, we presented evidence that the universal phase behaviour of systems with competing interactions extends to confined systems. Moreover, we showed that confinement not only favours the formation of new ordered structures that can be exploited in nanotechnology but also helps in the nucleation of ordered cluster crystals. Thus, the confinement can be used to obtain the ordered microphases in colloidal systems, which have been elusive in experiments so far.