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Lublin, July 6, 2021

The review of doctoral dissertation of Horacio Antonio Serna Serna, entitled Effects of confinement on self-assembly in systems with competing interaction

The dissertation is devoted to the theoretical modeling of self-assembly and is in the mainstream of physicochemical research. This topic is interesting both from a technological and purely cognitive point of view.

The Author explored the behavior of systems with competing interactions under various confinement conditions. Colloidal suspensions, amphiphiles, copolymers, or mixtures of lipids are representative examples of such systems. The behavior of bulk systems with competing interactions is well understood. No matter the origin of the interactions, the bulk fluids exhibit a universal phase behavior. They present similar phase diagram topology and the same ordered structures are observed in considerably different bulk systems (cluster-crystal, cylindrical, bicontinuous, and lamellar, etc).

In confinement, fluids with competing interactions behave differently, exhibiting new thermodynamic and dynamic properties. The effect of the type of confinement on the ordered structures present in these systems is much less studied. The Author focused on this issue.

The thesis presents the results of computer simulations of fluids with competing interactions in channels and pores of different morphology. The considered colloidal fluid consists of spherical particles interacting via an isotropic short-range attraction and long-range repulsion (SALR) potential.

In all simulations, repulsive interactions between the colloid particles and the walls of the confining channels and pores are assumed. Thus, "purely" geometrical effects of the confinement are studied.

Two simulation methods were used, namely Monte Carlo method and molecular dynamics. The standard Monte Carlo simulations in grand canonical ensemble (NVT) were carried out. The MD simulations were performed using LAMMPS package with the Nose-Hoover thermostat and barostat in NVT and NpT ensembles.

The dissertation is organized in a typical way, contains the introductory Chapter 1, the results are discussed later in the thesis and summarized in Chapter 6.

In Chapter 1, the results of the research conducted so far are briefly summarized. The phenomenology and phase behavior of colloidal systems with competing interactions are described and compared with the behavior of copolymers. Then, the fundamentals of simulation techniques used are presented. Finally, the scope and thesis plan are clearly formulated.

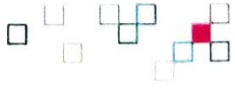
The main part of the thesis in which the results are discussed is divided into two parts. Part I presents the results obtained by means of MC simulations, while Part II is devoted to MD simulations. In Part I, the behavior of particles interacting via the square-well-linear (SWL) potential, consisting of a hard core, an attractive square-well, and a repulsive ramp, is discussed for different confinement conditions. The particles are confined into channels with different cross-section geometries (Chapter 2), into spherical and ellipsoidal shells (Chapter 3), and into bicontinuous porous networks (Chapter 4). The discussion is limited to the thermodynamic and structural properties of the fluid. In Part II (Chapter 5), the results for the systems with interactions modeled through the combination of Lennard-Jones and Yukawa potentials (LJY) are presented. The assembly of the particles is discussed both in bulk (section 5.2) and under confinement (section 5.3) in infinite slit pores. In this case, dynamic properties of the colloidal fluid are also analyzed.

It should be pointed out that the simulations were performed for a very large number of various model systems. I will mention the most important ones here and summarize the results briefly.

In Chapter 2 the morphology of fluids confined in channels with different cross-sections is studied, namely in cylindrical, elliptical, triangular, hexagonal, and wedged-cylindrical channels. Two types of cylinders are considered, axially-periodical cylinders and finite cylinders closed by planar walls at their ends. Most of the simulations were performed at conditions at which the hexagonal phase is stable in bulk, however, the results for other phases (cluster-crystal, and lamellar) are also presented. It is shown how the length of channels and the parameters characterizing their cross-sections affect the self-assembly. For many combinations of these parameters, the average densities and energies were calculated and very carefully analyzed. Numerous detailed conclusions about the structure of the confined fluid are formulated. In general, it is proved that the confinement into cylindrical pores promotes the formation of helical structures. Furthermore, the geometry of the cross-section of the confining pore can either promote novel structures or favor the bulk ordered phases. Depending on the degree of incommensurability between the geometry of the confining pore and the symmetry of the bulk ordered phases, different structures are promoted.

Chapter 3 is devoted to the behavior of the colloidal system under confinement into curved quasi-bidimensional space (spherical and ellipsoidal narrow shells). In the case of spherical shells, the coiled cylindrical clusters are found. They resembled geometrical solutions of the problem of the longest rope filling the surface of a sphere. The confinement into prolate and oblate ellipsoidal shells favored the formation of helical and toroidal structures, respectively.

Next (Chapter 4), the particles confined into ordered bicontinuous porous materials are discussed. Three different models for porous materials are investigated: cubic primitive, diamond, and gyroid. The study revealed that, depending on the morphology and the size of the porous materials, the particles assemble into new ordered phases composed of spherical and cylindrical clusters.



The last part of the thesis (Chapter 5) presents the results of molecular dynamics simulations performed for the colloids with competing interactions (LJY) in bulk and under confinement into slit pores. These systems are characterized not only from structural and thermodynamic points of view but their dynamic behavior is also analyzed. In bulk, besides the formation of the typically ordered microphases, intra-cluster freezing transitions are observed. It has been also shown that the confinement into slit pores induced a change in the phase diagram of the colloidal system.

To characterize the dynamics of the system, different properties were used, such as the mean-squared displacement (MSD) and the coherent and incoherent scattering functions. The dynamics characteristics are discussed for different model parameters. It has been noted that for the chosen parameters, the ordered microphases were kinetically accessible from the fluid phase. In general, the confinement into slit pores can favor, both thermodynamically and kinetically, the formation of the ordered microphases. Moreover, the diffusion of the colloidal particles could be enhanced for some pore widths.

In the thesis, the Author shows the relations between the colloidal fluid properties (structural, thermodynamic, and dynamic) and the morphologies of the confining pores. He clearly proves that the universal phase behavior of systems with competing interactions extends to confined systems and that the confinement not only favors the formation of new ordered structures but also helps in the nucleation of ordered cluster crystals.

The results obtained are new, meaningful, and very interesting. I highly appreciate the substantive value of the work. The following facts deserve the emphasis:

- The problem under study is in the mainstream of world research.
- The research was systematic and well-planned.
- A great number of different model systems was studied for many sets of parameters characterizing their geometry.
- Two different simulation techniques were professionally applied in the research
- Advanced research tools were successfully used to interpret the results.
- Many of the detailed conclusions on the relationship between the structure of the fluid and the system geometry are clearly formulated and well-justified.
- The results have been already published in very good scientific journals.

In addition, the thesis is clearly written and carefully edited.

Among the many important results, those obtained for the wedged-cylindrical pores seem to be particularly inspiring and set the direction for further research. The narrow pores of concave geometry are rather rarely investigated. The presence of wedges creates important nucleation sites and influences the assembly.

I have one comment. The Author uses the term "one-dimensional channels" in the sentence "In section 2.3, we explored the behavior of the system, ..., under confinement in one-dimensional channels with different cross-sections" (page 55). I am not sure if the term "one-dimensional" is adequate for these systems. In particular, for the systems presented in Figure 2. 5 or Figure 2. 8 b, where the system sizes in all directions are of the same order of magnitude ($R=4.5\sigma$ and $Lz/= 16\sigma$). This remark does not detract from my high evaluation of the work.

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Summing up, I state that the evaluated doctoral dissertation meets all requirements set out in the Act on academic degrees and title, and degrees and title in the field of art (Dz. U. No 65/2003, item 595, as amended). I ask for Horacio Antonio Serna Serna to be admitted to the next stages of the doctorate procedure.

In light of the above-mentioned advantages of this dissertation, I request that it be distinguished. At this point, I will repeat the most important arguments behind my decision. The study deals with issues of importance to the mainstream of science. The research was conducted at the highest substantive level. The thesis summarize the results of extensive simulations carried out for an exceptionally large number of different systems. It is based on four articles co-authored by Horacio Serna. These works have been published in the best journals in the field of physical chemistry and condensed matter physics (Langmuir, Soft Matter, Journal of Physical Chemistry B).

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