Review Report on the PhD thesis ***Effects of confinement on self-assembly in systems with competing interactions*** by Horacio Antonio Serna Serna. Supervisor: prof. dr hab. Wojciech Goźdź, second supervisor: dr. Eva González Noya

Introduction and background

The PhD of Mr Horacio Antonio Serna Serna is devoted to study the systems with competing interactions playing important role in everyday life and industry. Typical examples of such systems are lipids and/or polymers but the PhD of Mr Serna is focused on colloids. The subject of PhD is to check how the self-assembling properties of colloidal systems change under confinement, exactly in the systems of pores with hard walls having different geometry (for example cylindrical elliptical, triangular, hexagonal, wedged-cylindrical). This subject is interesting not only from theoretical but also from practical point of view due to wide application of colloids.

General short description of the thesis (with some remarks)

The author applied Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) simulations methods as a tool for his study. In both cases colloidal systems are assumed as spheres. Interactions are modelled by short - range attraction and long-range repulsion (SALR) potential in GCMC, and due to limitations of SALR (forces must be calculated in MD) the combination of Lennard - Jones attraction and Yukawa repulsion. The effect of confinement is studied by modelling of solids as hard walls.

In Chapter I the Author starts from Introduction showing the basic concepts and definitions as well as the aims of the Thesis. Next, the colloidal systems with competing interactions are described considering mainly the origin and basic properties of the SALR potential, the origin of self-assembly and the universality of the phase diagram topology of systems with competing interactions. Next the literature review is given to show other approaches beyond SALR and experimental study on colloidal systems with competing interactions in bulk.

Very important here is the summary, where the Author put forward 3 major hypotheses trying to understand why the ordered microphases remain undiscovered in experimental studies (dynamical arrest, polydispersity of colloids and unaccounted interactions). It is important that a young researcher is able to critically approach the research methodology he uses.

Next the literature review on the study of interaction between colloids and different surfaces is given and the discussion about the origin of similarity and universality in the phase behaviour of systems with competing interactions.

In Chapter 1.3 the fundamentals of simulation techniques (GCMC, MD) are shown. This chapter is redundant and in my opinion could be omitted and the reader should be referred back to the basic textbooks. Chapter I ends with Scope and thesis plan directing the reader very well to the further content of the dissertation.

In Part I the results of the GCMC simulation are presented. The structure of bulk is simulated, and the conditions representing hexagonal phase according to the phase diagram are chosen. The results (Chapter 2) are divided into confinement in channels with different geometries: in cylindrical channels (Chapter 2.2) and confinement under different cross-sectioned channels (Chapter 2.3). Next the

results for confinement in spherical and ellipsoidal shells (Chapter 3) and confinement in bicontinuous porous materials (Chapter 4) are collected and summarized. It is very important in this, and in the following parts of the dissertation that the results are presented perfectly in terms of graphics (see for example Figures 2.2 and/or 3.3).

The most important achievements of this part of PhD are: the hexagonal bulk structure undergoes modifications under confinement in cylindrical pores, and the formation of helical (clockwise and anticlockwise, single and double) structures is observed. It is important that obtained structures are new and significantly different than previously reported, and the similarities to the results reported for copolymers was observed. Very important is the conclusion that pores with regions of high curvature, or pores with narrow edges, can stabilize straight cylindrical clusters. Confinement into spherical shells promotes the formation of curved cylindrical clusters with similar energy.

The studies of confinement in porous materials modelled as primitive cubic, diamond and gyroid bicontinuous phases showed the formation of various crystals with properties modulated by the properties of porous systems. Very important for me, who is working simultaneously in theory and in experiment as well, is that the obtained results are guidelines for future experimental work with application of porous materials as templates for synthesis of ordered microphases.

In Part II the results of MD simulations are presented. The most important conclusion is that in bulk, besides the formation of the typically ordered microphases, intra-cluster freezing transitions were observed. The author characterized those transitions taking into account structural, thermodynamic and dynamic properties. Confinement into slit pores induced a change in a phase

diagram of the colloidal system and diffusion of colloidal particles could be enhanced for some pore widths.

Specific Comments

The reviewer has an easier task because the result of PhD were published (after additional at least 3 independent referees) in 4 papers, and in very good journals: *Langmuir* (Q2, IF = 3.88), *J. Phys. Chem. B* (Q3, IF = 2.991) and *Soft Mater* (Q2, IF = 3.68) - 2 papers. However, during the study of dissertation the following questions/suggestions appeared (maybe will inspire future studies?):

Is this possible that in pores the interaction between colloid particles and a solvent can be modified by an external potential? May the energy of those interactions depend on pore diameter? What consequences could this have in terms of the structure of the confined fluid? How to take this into account in simulations?

On page 35 the Author claims that *in systems with competing interactions one can observe two or more structures with the same free energy. To check this hypothesis, extensive calculations of free energy for different radii and lengths of the confining cylinder are required.* Could the Author present the basics of the methods that can be used to solve this problem?

Is the diameter of a colloidal particle constant and does not depend on the diameter of a pore?

The surfaces of real solids are usually heterogeneous (both structurally and energetically). Probably this heterogeneity will modify the structure of confined fluids. Is this possible to take these properties of real solids into account in simulations? How?

Final evaluation statement

This doctoral dissertation provides a significant contribution to knowledge in the field. The results are very well presented and the interpretation is at very high scientific level. Moreover Mr. Serna, who is a young researcher is able to critically approach the research methodology he uses. The results, although theoretical, are not detached from the experiment. Also the quality of presentation of the results in on very high level (especially considering graphics). There are practically no misprints in dissertation (I found few missing spaces, and missing brackets in few equations).

Taking into account that the results were published in very good journals I state that this doctoral dissertation is ready to be defended orally because meets the requirements for the degree of PhD in chemistry following Polish regulations (art. 13 ustawy z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki, Dz. U. Nr 65/2003 poz. 595 wraz z późniejszymi zmianami).

Taking into account all the above-mentioned positives of the dissertation i.e. high scientific level, importance of the results and the publication in very good journals I propose to award the dissertation of Mr Horacio Antonio Serna Serna with distinction.