Report 1

concerning the progress in realization of the tasks: 1.1 (A molecular level modeling of fluid-brush-solid systems) and 1.2 (Application of mesoscale approaches (DPD) to study substrate-brush-fluid systems)

Within the first nine months of the project we have concentrated on the development of theoretical backgrounds and computer codes for density functional theory and simulations of systems involving molecular brushes and fluids. The following computer programs have been developed

1) The program evaluating the structure (local density profiles) and thermodynamic properties (e.g., adsorption isotherms, grand canonical potential and chemical potentials) for a fluid in contact with the surfaces with tethered brush. The program can be applied to the systems with a single wall and to the systems confined between two walls (slits). It also allows to study one, as well as multicomponent fluids. The code is flexible and allows to apply different forms of the intermolecular potentials for the interactions involving fluid, brush and the surface. The programs have been developed for the version of the density functional approach that uses (I) the so-called "white bear"theory for hard-spheres, (ii) the first-order Wertheim's thermodynamic perturbation theory for association, (iii) the mean-field approximation for attractive interactions and (iv) the theory developed by us to describe interactions between ions. The codes, applicable for solving the problems of **Task 1.1** (the package name - BRUSH1) are stored on the server at our Lab and the person responsible for it is S. Sokołowski. This task has been carried out by ICMP, UNAM and UMCS groups. .
2) A new algorithm for dissipative particle dynamics (DPD) simulations of fluids in slit-like pores with non-uniformly distributed brush molecules has been developed **(task 1.2)**. The development was possible owing to collaboration of ICMP and UMCS groups. The novelty of the algorithm is based on appropriate handling of collisions between fluid particles and the walls. The codes (the package name - DPD1) are stored on the server at ICMP lab and the person responsible for it is J. Ilnytskyi.
3) We have developed the programs creating starting configurations and analyzing the outputs for the LAMMPS molecular dynamics package **(tasks 1.1 and 1.2)**. Also, we have developed the scripts appropriate for efficient use of the LAMMPS package. The LAMMPS package is presently used to study the problems associated with the Work Package 1. This part of work has been done by the ICMP and UMCS groups. All programs and scripts are stored on the UMCS cluster.

Taking into account that the above described codes are being used and will also be used in a near future, we do not like the idea of making them accessible to wide scientific community. Of course, these codes can be obtained on a written request.

The above described background work was necessary to study the following problems.

1) The structure and thermodynamics properties (including phase transitions) in the case of a binary mixture in contact with two walls, covered by a brush and at a distance H apart. The walls were permeable for one fluid component. Particular attention was paid to the phase transformations in such systems. We have found that the fluid undergoes capillary condensation between the two walls and wetting and layering transitions at the outer walls. Moreover, we found, for the first time in the literature concerning the behavior of such systems, the transitions connected with the change of symmetry of the distribution of chains and fluid inside the pore. Detailed description of the developed theory and of the obtained results is given in the enclosed paper [1], published in Journal of Chemical Physics. 134 (2011) 044705. This study was carried out within the **task 1.1.**
2) The finding of the possibility of symmetry breaking in the system [1] has stimulated subsequent studies. We were interested in the problem how the presence of chain molecules attached by two their ends paper to the opposing walls of the pore changes the phase behavior of confined one- and two-component fluids. Using density functional approach we found that depending on the amount and length of the chains the topology of the phase diagrams can change completely, as compared to the case of non-modified pores. Performing systematic studies of adsorption of one-component fluids, we determined the scenario of possible phase transformations and possible changes of the phase diagram topology, depending on the parameters of our model. We found "breaking-symmetry" and "re-entrant to symmetry" phase transitions that might be of the first or of the second order. In the case of a binary mixture that exhibits demixing transition in a bulk phase the situation is even more complicated. A competition between layering transitions, symmetry change (breaking and re-entrant) transitions and demixing in the entire pore, or in a paart of the pore (e.g., within the layers formed during layering transition) leads to extremely complicated topology of the phase diagram. The theoretical backgrounds and detailed description of the results obtained is given in the enclosed papers [2,5]. This study was carried out within the **task 1.1.**
3) The next problem considered was the application of the DPD method to study microphase separations in the system involving a binary mixture and a slit-like pore with the walls, "decorated" by a brush in the form of stripes. The first problem we encountered in our study was to develop an appropriate methods for handling the

collisions of fluid particles with the walls of the pore. We have proposed such an algorithm, that was described in details in [3]. Next, we studied how the morphologies of different phases change with the parameters of the model. Apart from different "mixed" phases, we found lamellar phases, pillar phases, and phases that have been already observed during studies of bulk systems. One of interesting phenomena was discovery the "closing" effect by pillars that are formed by the brushes attached at the opposing walls makes possible to form different microphase morphologies inside "closed " parts of the system. Details of the work, together with the proposed phase diagram of morphologies is given in [3]. This work was done within the **task 1.2.**

4) The change of the brush structure cause by adsorption of a single-component, as well as two-component mixture was the next problem studied by us. There exist numerous papers based on application of different theoretical approaches, as well as computer simulations, in which this problem was considered. However, none of earlier works discovered the phenomena observed in our study, namely that for an appropriate surface density of a brush, the dependence of the height of the brush on temperature may exhibit a minimum. The changes in the structure of the brush upon adsorption of fluids was studied in details in the enclosed papers [4] and [S1] (the latter being in press). This study was carried out within **task 1.1.**

The next problems, we considered were connected with the investigations how different interactions (e.g. ionic, and associative) influence the system properties. One of the papers, entitled "Solvation force between tethered polyelectrolyte layers. A density functional approach, by O. Pizio, A. Patrykiejew, S. Sokołowski , J. M. Ilnytskyi, has been already finished and will be submitted for publication. The person responsible for storing the manuscript and all the results of this work is S. Sokolowski. The enclosed pdf files of the papers, named by the numbers of the list of references below are the part of this report.

References

publishes

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S1 M. Borówko, T. Staszewski, A density functional study of the structure of tethered brush in a binary mixture. Condens. Matter Phys., in press.