Report 3

Part A: the report concerning the progress in the realization of the tasks within the WP2.

The work package WP2, entitled “Substrate driven self-assembly of supramolecular structures formed by complex organic molecules” includes the tasks: 2.1. Development of a range of surface potentials and study of the surface driven self-assembly of liquid crystalline dendrimers into monolayers and thin films and 2.2. Study of the surface induced assembly of liquid crystalline dendrimers into bulk phases in thick slit pores and in the cases of the surface anchoring frustration.

1) The following computer programs have been developed:

a) Computer simulations of a self-assembly of liquid crystalline dendrimers in pores with various anchoring potentials. Coarse-grained model was used to represent generation of the liquid crystalline dendrimers and next a coarse-grained molecular dynamics was employed. We tested the application of different algorithms and methods do speed-up the calculations. The program was developed by the TUB and ICMP groups and the person responsible for storing it is J. Ilnytskyi.

b) Analysis of the configurations generated by the program 1. The aim of the analysis is to get an insight into smectic-isotropic transition. The program was developed by the TUB and ICMP groups and the person responsible for storing it is J. Ilnytskyi.

c) The molecular dynamics simulation program of macromolecules in contact with a colloidal particle. This program is also used to investigate the problems within the WP3 (program a) described below).The program was developed by the ICMP group and the person responsible for storing it is J. Ilnytskyi.

2. The obtained results: published papers and papers that will be submitted for publication in the nearest future.

Two papers are prepared for the publication. They are almost ready and will be submitted to scientific journals very soon. The groups involved: TUB and ICMP. Within this working package we also collaborate with M.R. Wilson from Department of Chemistry, University of Durham, UK.

a) In paper [1] we consider the applicability of coarse-grained molecular dynamics for simulation of defects in nematic liquid crystal around a colloidal particle with various surface anchoring. The potential, introduced by Lintuvuori and Wilson, which contains soft repulsive and anisotropic attractive parts, is used for mesogens interactions. Typical time-scale for the formation of the nematic phase from isotropic one is estimated for several system sizes. The properties of the nematic phase are studied via Frank elastic constants. Two models for the colloid particle are used: the “virtual colloid”, in which colloid is an aggregate of liquid crystal particles subject to soft orientation ansatz; and the “grafted colloid”, which consists of a soft sphere with various number of liquid crystal particles frozen on its surface. The cases of homeotropic and various planar anchoring are considered in both models, as the result the Saturn ring and boojum defects are obtained. For special case of the longitudal planar anchoring the biaxial boojum defect is obtained. The study revels the potential of coarse-grained simulations for studying the defects in liquid crystals.

b) In paper [2] we concentrate on bulk phases formed by liquid crystal macromolecules with various density of mesogens on their external surface. The generic model is considered, which is made of a central sphere covered by polymer chains of given grafting density terminated by mesogenic units. The model resembles (with certain restrictions) the liquid crystal dendrimer or polymer-modified gold nanoparticle. The self-assembly is aided by uniaxial or planar orientation field which acts on mesogens and affects macromolecules conformation. At low grafting density layered smectic phases are observed for fields of both symmetry below the transition to the isotropic phase. At high grafting densities discotic columnar phases are obtained below this transition, and two types of cubic phases - above it. At moderate grafting densities both layered smectic and discotic columnar phases can be made stable via the symmetry of the field, and both coexist at the edge of the transition to the isotropic phase. Detailed study of this coexistence (which has relation to the liquid crystal biaxiality) is performed by splitting system into clusters of tro types and analyzing their size and dynamics.

The results obtained within WP2 were also presented on the international conference [Ilnytskyi, Microphase separation driven transitions in macromolecular liquid crystals by computer simulations, the conference Analytical and Computational Paths from Molecular Foundations to Continuum Descriptions, Oxford, 2013]

3. The problems under study

a) We continued studies concerning the problem of distribution of liquid crystals around a big colloidal particle.

4. Publications (to be submitted)

1) *J.M. Ilnytskyi, M.Schoen, M.R.Wilson, Self-assembly of polyphilic liquid crystal macromolecules with various density of polymer shell: coarse-grained molecular dynamics simulation.*
2) *J. Ilnytskyi, A. Trokhymchuk, M.Schoen, Defects around spherical particle in nematic liquid crystal via coarse-grained molecular dynamics simulations.*

Part B: the report concerning the progress in realization of the tasks within the WP3.

The work package WP3, entitled "Substrate induced self-assembly of nanoparticles with chemical dichotomy" includes three tasks: 3.1.-Towards realistic models of self-assembled phases formed by complex organic fluids; 3.2: Transport phenomena in self-assembled fluid nanostructures formed by dichotomic molecules and 3.3: Towards realistic models of self-assembled phases formed by complex organic fluids.

1) The following computer programs have been developed:

a) Dissipative Particle Dynamics program for simulations of the structure of complex molecules around Janus particles. The program allows for the studies of the following cases (i) non-Janus particle, with the homeotropic anchoring of equal strength on both hemispheres; (ii) asymmetric homeotropic-homeotropic Janus particle, with constant homeotropic anchoring on one hemisphere and reduced homeotropic constant on another hemisphere; (iii) homeotropic-planar Janus particle with the planar anchoring of various strength on one of hemispheres. The person responsible for storing the program is J. Ilnytskyi from ICMP. The groups involved: TUB and ICMP

b) Monte Carlo simulation program to study self-assembly of molecules with chemical dichotomy on solid surfaces. This program is based on a 2D lattice model. The hyperparallel and histogram reweighting simulation techniques have been employed. The obtained configurations are analyzed using RASMOL or VMD graphical programs. The person responsible for storing the program is W. Rzysko from UMCS. The groups involved: UMCS and ICMP.

c) Lattice Monte Carlo simulation program to study simple model of Janus particles confined in slit-like pores. We model the system using lattice representation of the positions of molecules, but the molecular orientations are changed in a continuous space. The model studied by us resembles the so-called Heinsenberg's model for simulating systems of spins. There are two versions of this program. The first one uses "classical" grand canonical ensemble simulations, while the second one – the hyperparallel and histogram reweighting techniques. The aim of the program is to evaluate the phase diagrams for the confined Janus particles. The person responsible for storing the program is S. Sokolowski from UMCS. The groups involved: UMCS, UNAM and ICMP.

d) The program analyzing the formation of clusters during simulations using the program c). This program uses a very sophisticated method of analysis of the clusters of Janus particles and their distribution in the space. The program uses the configurations stored by the program c) as the input. It also calculates the statistics of the cluster sizes and graphical display of the results. The graphics is obtained using RASMOL graphical program. The person responsible for storing the program ins Ilnytskyi from ICMP. The groups involved: UMCS and ICMP.

e) The off-lattice Monte Carlo simulation program for Janus particles in slit like pores. This program is based on grand canonical algorithm and evaluates thermodynamic properties and the structure (local densities and orientational density profiles), as well as the histograms of the number of Janus particles confined in slit-like pores. Finally, from density profiles the solvation force is calculated. The person responsible for storing the program is S. Sokolowski from UMCS. The groups involved: UMCS and ICMP.

f) The mean-field and a "beyond mean-field" density functional calculations of the structure and thermodynamic properties of Janus particles at a single wall and confined in pores. The program is based on the fundamental measure theory and (I) on the mean-field approximation for attractive-repulsive interactions between Janus particles, or (ii) the "exp" approximation. The person responsible for storing the program is S. Sokołowski. The groups involved: UMCS and ICMP.

g) The lattice density functional program for confined Janus particles. This program is still under development by S. Sokołowski from UMCS and O. Pizio from UNAM.

2. The obtained results: published papers and papers that will be submitted for publication in the nearest future.

The developed the computer were applied to study selected systems. Two papers have been already published and reported previously. The next two published papers are outlined below, one paper is just finalized. Also, some auxiliary study concerned with a possibility of application of some simplified models for describing complex systems has been published. These works result from collaboration between ICMP, TUB and UMCS groups. In current investigations the UNAM group is also involved.

a) In paper [1] we developed a version of density functional approach to study structure and thermodynamic properties of Janus particles confined in pores modified with chain molecules. The Janus molecules were modeled as spheres composed of hydrophilic and hydrophobic parts. The pinned chains are treated as tangentially jointed spheres that can interact with fluid molecules via orientation-dependent forces. Our density functional approach involves fundamental measure theory, thermodynamic perturbation theory for chains, and a mean-field approximation for describing the anisotropic interactions. We studied the adsorption of the particles, focusing on the competition between the external field (due to the surface and due to attached chain molecules) and ordering phenomena induced by the interactions between Janus particles. In particular, we have carried out calculations for the nonzero anisotropic part of the fluid−solid potential. Depending on the orientation of fluid molecules enforced by the anisotropic fluid−solid potential, we can expect either enhancement or inhibition of the formation of ordered adlayers in the vicinity of the surface. Moreover, the fluid−solid anisotropic potential can act “in accordance” with or “against” the fluid−segment orientation forces. Also, a change of the grafting density, as well as the change of the length of tethered chains, can alter the volume exclusion effects, which can become more or less important. The structure of the adsorbed fluid depends on an interplay between all those factors, and even a small change of some modeled parameters and in our paper we have explored this problem.

b) In the work [2] we have proposed the application of density functional approach to determine an effective force acting on a selected segment of a tethered chain during its movement in the direction perpendicular to the solid surface. We have also calculated the average force that is experienced by a tip that during its movement meets random encountered segments. The calculations have been carried out for athermal systems, i.e.,for the systems with the chains built of tangentially jointed hard spheres immersed in a solvent of hard spheres. We only considered the case when the interactions of all the segments, but the anchored one, and solvent molecules with the wall were of hard-wall type. The density functional theory allows one to determine the effects due to the presence of other chains and solvent molecules. For high and moderate solvent densities the plot of the force versus the distance of the segment from the surface exhibits oscillatory behavior that has not been predicted by other approaches. One of co-authors of this work is Z. Usatenko. When this study was initiated, Z. Usatenko was employed by ICMP, Lviv, but during finalizing this work she changed her affiliation. We should stress, however, that Z. Usatenko is not a member of the ICMP group; when our study was initiated our intention was to find a new co-workers for a future collaboration.

c) In the paper prepared for publication [3] we employed Monte Carlo simulation technique to study self-assembly of molecules with chemical dichotomy on solid surfaces. The simulated molecules consisted of two chemically different segements connected by a covalent bond. The molecule were either fully flexible or rigid. Rigid coil molecules can self-assemble into various morphologies that greatly affect the optical and physical properties of the system. We determined full topology of the phase diagrams for a series of molecules. We have found three distinct phases, the gas, disordered liquid and the ordered phase. The critical chemical potential and critical density for the gas-disordered liquid increases non-monotonically, whereas the critical temperature increases monotonically with size of the segments. We also determined Minkowski's measures in order to better characterize the structure of the observed phases.

d) As we have previously noted in the periodic report we have also carried out some auxiliary studies, aiming on the investigations of a possibility of introducing some simplified (“core-softened”) models for the description of star polymer particles. One of the previously reported works [c2, in the periodic report] has been already published [4]. In that work the canonical Monte Carlo computer simulations and integral equation theory were applied to examine the structural and thermodynamic properties of a mixture of ions and a core-softened molecules. The positive and negative ions were modeled as charged hard spheres. It was shown that the core-softened molecules exhibited a set of structural, thermodynamic, and dynamic anomalies. The principal objective of this work was to elucidate how the presence of ions alters this behavior. The structural properties of the mixtures are discussed in terms of the pair distribution functions; in addition, the pair contribution to the excess entropy was

calculated. Thermodynamic properties are investigated by using the dependencies of energy and compressibility factor on density, composition of the mixture, and reduced temperature. The heat capacity was also evaluated. Our principal findings concern the description of structural anomalies in the mixture, the dependence of the temperature of maximum density on the ionic concentration, and establishing the regions delimiting the structural and thermodynamic anomalies of the model mixture.

e) The problem of evaluation of effective forces between two “macromolecules” (modeled as planes), with surfaces modified by polyampholytes was already discussed in the periodic report (Report 2)m where we described the results of two papers [papers 9 and 10 from the periodic report, Report 2]

3. The problems under study

a) We continued studies concerning the problem how to build the director distribution around Janus particle. We simulate colloid particles of different sizes immersed in a fluid of complex molecules. We consider the following cases: (i) non-Janus particle, with the homeotropic anchoring of equal strength on both hemispheres used as a reference system; (ii) asymmetric homeotropic-homeotropic Janus particle, with constant homeotropic anchoring on one hemisphere and reduced homeotropic constant on another hemisphere; (iii) homeotropic-planar Janus particle with the planar anchoring of various strength on one of hemispheres. The groups involved: ICMP, TUB and UMCS.
b) We initiated the simulations of Janus particles for (i) two-dimensional systems (ii) the particles confined in slit-like pores, investigations of phase transitions. These studies are carried out by using appropriately defined lattice models. Also, the lattice density functional calculations will be carried out. The groups involved: ICMP, UNAM, UMCS.
c) Off-lattice Monte Carlo simulations of Janus particles between two plates. The aim of this study is to determine how the solvation force is influenced by the formation of different orientational structures in the system. The groups involved: ICMP and UMCS.

4. Publications

1. *M. Borowko, T. Poeschel, S. Sokolowski, T. Staszewski, Janus particles at walls modified with tethered chains. J. Phys. Chem. B 117 (2013) 1166.*
2. *M. Borowko, W. Rzysko, S. Sokolowski, Z. Sokolowska, Z. Usatenko, Stretching tethered polymer chains: Density functional approach. J. Chem. Phys. 138 (2013) 204707.*
3. *D. Przech, W. Rzysko, P. Bryk, Adsorption of short block copolymers on solid surfaces. A Monte Carlo study, to be published.*
4. *M. Luksic, B. Hribar-Lee, V. Vlachy, O. Pizio, Structural and thermodynamic properties of charged hard spheres in a mixture with core softened model solvent, J. Chem. Phys. 137, (2012) 244502.*