

## FINAL REPORT

The project has consisted of three work packages:

WP1: fluids in contact with tethered layers formed on surfaces and in pores,

WP2: substrate driven self-assembly of supramolecular structures formed by complex organic molecules, and

WP3: substrate induced self-assembly of nanoparticles with chemical dichotomy.

The first work package involved research of thermodynamic properties and microscopic structures of fluids in contact with a single surface and in pores with walls modified by tethered brushes. We studied how these properties depend on the molecular parameters of the model, and on thermodynamic variables. Different levels of modelling of tethered brushes (from molecular to coarse-grained models) and different theoretical tools (density functional theories and computer simulations) were employed.

The goal of the second work package was to study the surface-induced self-assembling, in particular self-assembling of liquid crystals in the bulk as well as in the surface phases. We developed effective potentials, due to the presence of surfaces. We also studied the surface driven self-assembly in monolayer and thin films and investigated the surface induced assembling.

The third work package involved studies of the behavior of Janus particles in the bulk and at surfaces. In particular, we determined the structure and phase behavior of self-assembled phases of simple Janus molecules. Then, we investigated transport phenomena in self assembled fluid nanostructures formed by dichotomic molecules and developed realistic models of self-assembled phases formed by complex organic fluids.

The studies involved in the work packages WP1, WP2 and WP3 are strongly correlated. Therefore several attached publications contain the discussion of problems relevant to different work packages. For example the papers [12] addressing the problem of Janus particles at modified surfaces may be considered as carried out within the WP1, as well as within WP3. Similarly, the results on the formation of ordered lamellar phases may be included into the WP1, WP2 and even into the WP3. Another example involves the evaluation of effective potentials, which can be considered as belonging to WP1 or WP2. For the above reason, the results presented in several publications are invoked in parts of this report, related to different work packages.

This report summarizes the objectives of the project achieved and stresses the most important results. It has to be emphasized that all basic objectives of the project (included into WP1, WP2 and WP3) have been reached. The copied of already published and submitted for publication papers are attached to this report. Moreover, detailed information concerning the activities of all researchers involved is given on the project web page:

Below, we present the basic achievements of the research carried out within the work packages WP1, WP2 and WP3.

The planned objectives of WP1 were as follows:

1. Extension and modification of theoretical (scaling law approximation, self-consistent field theories and density functional approaches) and computer simulation (Monte Carlo, molecular, Langevin and dissipative particles dynamics) approaches to be able to handle the case of tethered and patterned tethered surfaces.
2. A study of homogeneous tethered surface emphasizing both the properties of the polymer brush and the behavior of the confined fluid depending on the grafting density, miscibility of the fluid with the polymer and number of components of a fluid.
3. Generalization of the study to the case of inhomogeneous surfaces, in particular, the nanopatterned structures (similar to those fabricated using lithography processes) with various shape, size and spatial distribution of different homogeneous domains.
4. Investigation of the effects of tethered brushes on the structure and thermodynamic properties of confined multicomponent fluid, in particular, selective adsorption, surface phase transitions, surface-induced phase separation, formation of long-ranged fluid structures.

### Ad. 1.

The objectives listed at the point 1 concern the development of new theoretical approaches and computer codes that are next used in our studies. After performing several preliminary investigations we

have decided to concentrate on the density functional (DF) theories (self-consistent field approaches also belong to this class) and on Monte Carlo, Molecular Dynamics, and Dissipative Particle Dynamics simulations. Initially, we also planned to employ the approaches based on the application of the PRISM/RISM integral equations, but those methods have appeared to be much less accurate in predicting thermodynamic and structural properties than the DF approaches. Moreover, they fail to describe phase transitions in the systems under study. Another approach that has been probed by us was based on a lattice model. We tried to develop a new self-consistent type theory for the system involving brushes and solvents of different type. Although this approach bodes some hopes, we have decided to postpone these research for future studies.

Our new theoretical approaches summarizes the list below (the numbers in square brackets refer to the publications, the numbers without brackets – to the conference contributions):

**a)** A new version of DF theory for fluids in contact with semi-permeable walls (membranes). This approach describes the system of real membranes that are built of a bilayer of tethered chains. The particles of a one of the components of a binary fluid can “cross” the membrane, while the particles of the second component cannot [1].

**b)** Development of a new DF theory for fluids in contact with brushes of polyampholytes. Evaluation of solvation forces [9,10]. Two versions of the theory have been proposed. The first one follows the so-called energy route, while the second – the compressibility route and a special weighting density procedure to evaluate the electrostatic contribution to the system free energy.

**c)** Development of new theories for ionic fluids in contact with brushes, including brushes of polyampholytes. Calculations of the electric properties [10,14]. The latter approach has been based on the compressibility route and a special weighting of the local density.

**d)** Development of DF approach to describe the experimental results of Atomic Forces Microscopy. This approach allows for the evaluation of the force acting of a particular segment, as well as an average force perceived by the tip of an AFM apparatus. [13] (also WP2)

**e)** A new DF theory for Janus particles in contact with surfaces modified by bushes. This theory combines of all the ingredients that have been used to describe brushes in contact with spherically with an appropriate approach to describe orientationally dependent interactions. [12] (also in WP3).

To obtain publishable results from new theoretical approaches a)-e) the development of new computer codes was necessary. The new computer programs we have developed have already been described in the periodic reports 1 and 2. The summary of our developments is as follows.

**f)** The development of the computer programs based on the theories a)-e) The results of the calculations were presented in [1,3,9,10,12,14] and 1-13.

**g)** The development of the computer programs based on already established theories in order to investigate new phenomena. The results of all our theoretical works, except for one ([1], in preparation, that uses LAMMPS Molecular Dynamics package), have been obtained using our own computer programs.

**h)** The Monte Carlo simulation program for the evaluation of the force.

**i)** The Dissipative Particle Dynamics simulation programs for fluid mixtures in pores with modified walls.

**j)** Auxiliary programs for the description of starting configurations for simulations and for the analysis of the generated configurations and the results.

#### **Ad. 2 and 4.**

The objectives 2 and 4 concern investigations of similar properties of the systems which involve single (the objective 2) and multicomponent (the objective 4) fluids. Using density functional theory the following results were obtained.

**a)** We studied how the structure of tethered layers changes under the influence of several factors, such as the length of the chains, the grafting density, the strength of the interactions between segments and between segments and fluid molecules. For a one-component fluid immersing the brush we found several power-law type relations describing the changes of the brush height. However, in some cases a quite unusual behavior

of the brush height with the grafting density was found. For low grafting densities the height remained almost constant, then with increasing density the height decreased, passed through a minimum and finally increased. The studies were carried out for a single component fluid [4] and a binary mixture [6] (this paper is an invited article). In the latter case we also studied how the height of the brush depends on the mixture composition. Th conference contributions: 2,9,11,12,13

**b)** We investigated adsorption of single component fluids and binary mixtures on surfaces modified by tethered brushes. In [7] a version of density functional approach, developed by us, was used to study adsorption of spherical molecules on surfaces modified with tethered chains, while in [8,18] we considered adsorption from a mixture containing spherical particles and oligomers. The tethered chains were modeled as tangentially jointed spheres. All species interact via the Lennard-Jones (12-6) potential. Depending on the parameters of the model, different shapes of the relative excess adsorption isotherms were found. The density profiles of all components were analyzed. It was shown that the surface region was highly inhomogeneous. The influence of the grafting density, the length of grafted chains, the nature of the solution, and its composition on the adsorption mechanism and the structure of the bonded-phase were investigated. The theoretical predictions were consistent with the results of computer simulations and experimental data. The most complete DF research on the adsorption from single and two-component fluids was presented in [18]. We attempted to resolve a few of the lingering questions about the layers of tethered chains. First, we dealt with the bonded layers immersed in one-component solvents and the impact of selected parameters on the structure of the surface layer was systematically analyzed. In particular we found that when mobile chains become longer than the grafted chains, the thickness of the bonded phase was almost constant. We also discovered that the variation of the fluid-fluid interactions may lead to interesting effects. When interactions between fluid molecules are much more energetically profitable than grafted chain-fluid and fluid-substrate interactions, the height of the bonded layer increases, while for unprofitable fluid-fluid interactions an increase of their strength causes shrinking of the bonded layer. Next, we examined the behavior of grafted chains in oligomer–monomer solutions. We focused on the problem how the solvent composition affects the bonded layer thickness. The thickness of the bonded phase can be either an increasing or decreasing function of the oligomer volume fraction. For certain values of the energy parameters and oligomer lengths this function can possess a minimum or a maximum. Conference contributions: 5,11,13,17.

**c)** We applied density functional approach to study the phase behavior of one-component fluids and binary mixtures in pores with the walls modified by brushes attached by their both ends to opposing walls [2,5]. Our focus was in the evaluation of the first-order phase transitions in adsorbed phases and, in the case of fluid mixtures, lines delimiting mixed and demixed adsorbed phases. It was found that the scenario of phase changes was sensitive to the pore width, to the energy of fluid-solid interaction, the amount, and the length of the polymer chains. Quantitative trends and qualitative changes of the phase diagrams topology were examined depending on the values of these parameters. The presence of chain particles provided additional excluded volume effects, besides the confinement due to the pore walls. The effects of attraction between fluid species and chains counteracted this additional confinement. We observed that both the increasing surface density of attached chains and the augmenting strength of fluid-solid interactions can qualitatively change the phase diagrams topology. In the case of single component fluids we found additional phase transitions of the first and second order, due to the symmetry breaking of the distribution of chain segments and fluid species with respect to the slit-like pore center. Re-entrant symmetry changes and additional critical, critical end points and tricritical points then were observed. In the case of confined binary mixtures exhibiting strong trends for demixing in a bulk phase we also observed additional phase transitions of the first and second order due to the symmetry breaking of the distribution of chain segments and fluid species with respect to the slit-like pore center. These results are particularly interesting, because they demonstrate that the presence of chains can completely change the topology of the phase transformations inside the pore. Conference contributions: 4,6,7.

**d)** We also investigated the phase behavior of a two-component fluid in the walls (or between “palettes”) modified by tethered chains [1],4. The walls were completely permeable for one component of the fluid and completely impenetrable for the second component. The fluid was perfectly mixed in a bulk phase. We found that depending on the details of the model the fluid undergoes capillary condensation inside the pore and wetting and layering transitions at the outer walls. Moreover, we found transitions connected with the change of symmetry of the distribution of chains and fluid inside the pore. The last finding is very interesting, because it indicates that the behavior of the system depends very much on the ability of the chains to change the character of “outer” and “inner” wall of the surface (palette).

**e)** We also studied a special case of brushes built of polyampholytes [10,14]. Polyampholytes containing blocks of differently charged segments can be also considered as molecules exhibiting chemical dichotomy and the results of our studies can be also considered as carried out within WP3. Particularly interesting results were obtained in [14], 15, where we applied a density functional approach to describe properties of an

ionic fluid in slit-like pores modified by grafted chains. We studied the influence of modification of the pore walls on the structure, adsorption, ion selectivity, and the electric double layer capacitance of ionic fluid. The brush built of uncharged segments acts as a collection of obstacles. Consequently, separation of charges requires higher voltages, in comparison to the models without brushes. At high grafting densities the formation of crowding-type structure is inhibited. The double layer structure becomes more complex, if the brushes are built of charged segments. The evolution of the brush height with the bulk fluid density and with the charge on the walls depends on the length of the blocks of charged segments and on the distribution of charged species along chains. We also investigated how the dependence of the double layer capacitance on the electrostatic potential changes with grafting density, the chain length, distribution of charges along the chain, the bulk fluid density, and, finally, with the pore width. The shape of the curve: electric double layer capacitance vs. voltage changes from a camel-like to bell-like shape, if the bulk fluid density changes from low to moderate and high.

**f)** Two papers remain still unpublished. The paper [S4] (submitted for publication) discusses how the adsorption on modified surfaces and the characteristics of tethered layer depend on the temperature. We found that our model predicts an interesting thermo-responsive behavior of the bonded chain layer in a supercritical fluid. It was shown that the influence of temperature on the configurations of the grafted chains depended considerably on the fluid density. In low density fluids an increase of temperature caused expansion of the chains, whereas in dense fluids an opposite effect was observed. One could find a certain fluid density for which the average thickness of the bonded layer is almost independent of temperature. This density changes with the grafting density and the length of chains. The changes of the brush height with the fluid density depend on the assumed type and strength of interactions and our findings could be useful to control the structure of the bonded phase by changing temperature. In the paper [I] that is still under preparation we employed Molecular Dynamics simulations to study fluids in contact with a wall modified by tethered linear and Y-shaped polymers forming a brush. We determined distributions of polymer particles composing the brush as well as solvent density profiles under different conditions: temperature, amount of a solvent, strength of interaction between solvent and polymer particles. A series of molecular dynamics simulations were performed and the corresponding structural characteristics for polymer and solvent species were obtained and analyzed. These were really long-lasting simulations and after obtaining a set of the results we found that some additional simulations are necessary to explain better the observed changes. This work should be finished during the next three-four months.

### **Ad. 3.**

**a)** In paper [3] we used the DPD simulation technique to study the structure of a binary mixture inside pores modified by stripes of tethered polymer brushes. The solvent was composed of two types of beads. The beads A were identical to the beads of chain particles, while the beads B were selected in such a way that the bulk A-B mixture exhibited partial mixing. All the calculations were carried out assuming that the ratio of the total number of A beads to the number of B beads was equal to one. The main aim of our calculations was to investigate the morphologies that appear inside the pore, depending on the pore size  $d$  and the width of the stripes,  $w$ . We constructed a sketch of the diagram of the morphologies and found that they are governed by (i) the characteristic lengthscale  $L$  that is the length of the chains, and by (ii) the fraction of the A-type molecules in the polymer-free regions. For the values of  $w$  close to  $L/2$  and for  $d > L/2$  lamellar morphology was found, while for  $w > L/4$  and  $L/2 < d < L$ , we observed the formation of pillars. Beyond the above regions either droplets or droplets plus bulk-type morphologies were observed. The self-aggregation within polymer free stripes seems to be governed by the size of the stripes and by the fraction of A beads within these regions. When this fraction was close to  $1/3$ , cylinders inside polymer-free regions were formed, while for the fraction close to  $1/2$  lamellae developed. In order to characterize the observed morphologies we calculated several parameters, as the radii of gyration, local densities and histograms of the minimum distances between polymers located in different (within the same plane, as well as at opposing walls) stripes. Conference contributions: 1,8,10.

**b)** The studies of [3] were continued in [11]. Compared to previous study, a number of extensions were made. In particular, two options of in- and out-of-phase arrangement of polymer stripes were considered. Apart from that, we examined in detail the effect that the composition of A and B beads on the formation of the morphologies in a broad range of pore geometries. At last, for some characteristic cases we undertook supplementary simulations with the one-component solvent of variable quality which replaces the mixture to serve as a reference. Our conclusions from the performed simulations were as follows. (i) The change of the composition of the fluid inside the pores has a great impact on the developing structures. For pore geometries with narrow stripes, the problem of the description of microphase separation inside the pore reduces to quasi two-dimensional; in the case of moderately wide stripes and narrow pore, one faces quasi one-dimensional demixing; whereas for very wide stripes, the system is split into quasi two-dimensional and bulk regions. (ii) The most interesting effects that demonstrate solvent mediated changes in the

nanostructures occur for the geometries with weakly separated stripes of polymer chains. With an increase of A component, the latter dissolves the polymer chains and causes their swelling. As a result, the system acquires a bistability in terms of either bridging the adjacent stripes along the wall or bridging the opposite stripes across the pore. Stable morphology is formed due to the competition between segregation of A and B beads and the deformation of chains. In our simulations we observed morphology switching due to subtle changes in pore geometry and/or in the composition of a mixture. (iii) We found the following solvent mediated morphologies: in-lined cylinders (made of one component), meander structure and wave-shaped modulated internal channels. The suggested applications of such structures (possibly, after making the structure permanent via cross-linking) involve nanopatterning for manufacturing of nanochannels, nanorods and similarly sized objects. Conference contributions: 1.8,10,20.

c) The results reported above were based on the equilibrium DPD simulations. However, it is of interest to check how the morphologies change if the fluid undergoes a pressure-driven flow along the pore axis. The development of an appropriate technique is of importance also for the studies of flows of liquid crystals in nanochannels. Therefore, a part of the results (concerning simulation methodology) of the submitted for publication work [S3] can be considered as carried out within the WP3. We have developed the DPD simulation technique to describe the Poiseuille flow of simple and complex fluids at different flow rates. The method was applied to study the flow of a binary separating mixture in nanochannels decorated with polymer brushes. The simulation of flow using mesoscale DPD simulation method required the introduction of appropriate (non-slippery) boundary conditions in order to ensure the slow down of the flow close to the walls. This problem was solved using structureless fluid-like walls made of fluid particles confined in slabs adjacent to the walls and applying elastic reflections on both sides of the boundary. The second problem involved the overheating resulting from the presence of body force. To solve the problem of thermostating the system we used the method involving the reverse Poiseuille flow. The method assumes that the entire simulation cell contains two sub-flows driven oppositely, keeping the total force equal to zero and using the non-slippery boundary conditions. We considered the flow of simple and oligomeric particles. In the case of simple fluids, it was found that some of the equilibrium morphologies are sensitive to the flow rate. In particular, at higher flow rates the steady state was found to consist of lamellar morphology with the flow occurring mainly at the center of the channel. When, however, the flow rate exceeds a certain threshold value the flow may induce the mixing in the central part of the channel. In general, the flow of oligomeric fluid is qualitatively very similar to the case of a simple fluid. Upon the increase of the flow rate the oligomeric particles are preferentially oriented parallel to the walls. The degree of ordering of oligomeric fluid (parallel alignment) was found to increase with the oligomer length. We also studied the changes of viscosity in systems consisting of oligomers of different length with the flow rate.

Finally, we have also published a review article [17], in which we have summarized a great majority of our findings for fluids in contact with surfaces modified by tethered chains. The above results were obtained by the researcher from UMCS, ICMP and UNAM groups.

#### **The principal objectives of WP2 were as follows:**

- 1) Extension of the multiscale approach developed for computer simulation study of the bulk phases in liquid crystalline dendrimers to the case of their surface-induced self-assembly.
- 2) Development of a range of surface potentials for liquid crystalline dendrimers and study of their surface driven self-assembly in monolayers, thin films and in the cases of the surface anchoring frustration.

#### **Ad.1.**

To perform this research the following numerical methods were developed (2) 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 three liquid crystalline dendrimers and next a coarse-grained molecular dynamics was employed; (3) Analysis of the configurations generated during simulations. The aim of the analysis is to get an insight into smectic-isotropic transition; (4) The program in Fortran-90 for formation of a the spherocylinder colloid particle with mesogen-modified surface to study the defect around such colloid when the latter is placed into a nematic host. The options for surface anchoring include homeotropic and various planar patterns; (5) The code for evaluation of coherence length in nematic phase; (6) The Monte Carlo simulation program of rigid and flexible chain molecules on square lattices and the programs analyzing the obtained results.

a) We developed programs for generating initial configuration and algorithms for solving equations of motion

in coarse-grained molecular dynamics approach. This program is based on a coarse-grained model for Liquid Crystal (LC) dendrimer or LC gold metaparticle. According to this model a large central sphere represents a coarse-grained core of a macromolecule with its internal degrees of freedom being neglected. Four smaller spheres (each being a fragment of a polymer chain of a few hydrocarbons) form a spacer. The latter is terminated by a spherocylinder representing a coarse-grained mesogenic (LC) group. The first bead of each chain can be attached to the surface of a central sphere in a number of ways, in particular: (i) quenched-like grafting to a particular point on a surface; (ii) semi-quenched-like grafting with the employment of an angular elastic spring with respect to a particular point; (iii) annealed-like grafting, when the end bead is capable of sliding freely on the surface. In all cases, radial elastic spring can be used to ensure that the first bead is always located on the surface of a large sphere. It is evident that option (i) would be the best suited to model the LC gold metaparticle, whereas option (ii) would represent the LC dendrimer. Option (iii) can be seen as some limit case representing the infinite generation LC dendrimer or the metamacromolecule with an additional symmetry of chains interexchange. The algorithm of the numerical program and the details of auxiliary calculations are given in [15]. Also, this work gives description of all the potentials used to describe the interactions in the system.

**b)** We also developed several auxiliary programs to analyze the results of simulations a).

**c)** Computer simulations program and the model described in a) was used to study bulk macro-molecular self-assembly of liquid crystal colloids [15]. The focus of this study was on the role played by the mesogens density of chains and on phase behavior of the system. Simple geometry estimates based on space-filling of macromolecule into a rod-like, disc-like and spherulitic shape provided some reasonable starting point for the relation between the number of mesogens and equilibrium conformation. Molecular dynamics simulations using soft interaction models repeat the experimental evidence for the lamellar-columnar-cubic sequence of phases with an increase of surface density. We found the model being conformationally bistable at a wide range of surface density with the possibility to form either lamellar smectic or columnar phase. Conformational analysis was performed by introducing “roddicity” and “discoticity” of their shape and, therefore, sorting the molecules at each time instance into rods and discs. The fraction of molecules in each subsystem provided some preliminary information on the distribution of their conformations. More details were provided by the histograms of their asphericity, these also shed some light on a process of macromolecular self-assembly. In this respect, the main obstacle in efficient self-assembly into a monodomain phases was seen in a lack of control over the molecular conformations. In virtually all the cases considered, the rod- and disc-like conformations coexist and have relatively broad distribution of their asphericity. The problem can be partially remedied by an aided self-assembly used in this study. It implies the use of an external field of certain symmetry (uniaxial, planar, etc.) which acts on the mesogens orientations to promote specific conformations (rod-, disc-like, etc.). When the bulk phase is formed, the field is removed and the system is equilibrated at a desired temperature to check for the stability of thus formed phase and to evaluate its properties. The problem of this approach is a limited choice for the symmetry of the field and a bias towards specific phase which should be known a priori. Another possible reason for, in general, poor self-assembly of this particular model could be connected with the fact that grafted chains are freely sliding on the large sphere resulting in broad distributions for molecular asphericity and, as observed in some cases, an enhanced microphase separation between large and small spheres. Detailed description of the obtained results is given in [15]; they were also presented during the conferences 16 and 18.

## **Ad.2.**

**a)** In the submitted for publication paper [S6], we have used hyper-parallel tempering Monte Carlo simulation, multiple histogram reweighing method and finite size scaling to carry out systematic studies of adsorption of chains, the rigidity of which ranged from fully flexible to rod-coil chains. The simulations were carried out using lattice model with the square lattice. A special computer program was written for this purpose. During the course of a simulation several quantities were monitored. We also evaluated the distribution of the order parameter, its ensemble average, as well as the susceptibility. We also calculated the fourth Binder's cumulant. Additional information was obtained by applying integral geometry analysis. A morphology in a D-dimensional space can be completely characterized using  $D + 1$  Minkowski measures. Specializing for two dimensions there are three Minkowski measures: surface, length and Euler characteristic. The evaluation of the Minkowski's measures required the development of a special algorithm. The above described computer programs were employed to study the phase transitions in the system. We have found that the phase behavior changes with the chain length and its flexibility. For homonuclear rod-coil chains the phase diagram consists of only gas-disorder liquid critical point and the topology of the phase diagram is quite similar to that of fully flexible homonuclear chains. Weakening the interaction energy between the segments belonging to two different subunits gives rise to an order-disorder transition. The topology of the resulting phase diagram depends on the chain length and its flexibility. For short chains both fully flexible and rod-coil diblock copolymers form lamellar ordered phase with fully stretched chains and the

order-disorder transition is of the first order. The phase diagrams are similar for both chain architectures and consist of two binodals which meet in the triple point. When the chain length increases the order-disorder transition becomes second-order and the difference in the phase behavior between the fully flexible and rod-coil diblock copolymers becomes more pronounced. While for the former chain architecture the topology of the phase diagram involves a  $\lambda$ -line which meets the gas-disorder liquid binodal in the critical endpoint, in the latter case the  $\lambda$ -line meets the gas-disorder liquid critical point and forms the tricritical point. We trace back these changes to the change in the morphology of the ordered phase. While for the fully flexible diblock copolymers the ordered phase consists of lamellar type but with chains that are not fully stretched, for the rod-coil diblock copolymers the chains form the so-called the hockey-puck phase. For both chain architectures the order-disorder transition is non-universal. Our study demonstrated that the chemical structure of polyatomic molecules strongly affects the phase behavior of the adsorbed monolayers. However in our study only the square lattice symmetry has been considered. Moreover we have restricted ourselves to chains with equal number of segments in each of the subunits. These features inhibit the formation of some ordered phases of the spherical symmetry. It is expected that for other lattice symmetries (or indeed for the continuous models), and for non-equal number of segments in each of the subunits the global phase diagrams of diblock copolymers adsorbed on solid surfaces will be further enriched. The results of this work will be presented during the 9th Liquid Matter Conference and this conference contribution 30 has been already accepted.

**b)** In the submitted for publication work [S5] work we employed for the first time in literature a coarse-grained models to study defect topologies that emerge if a spherical colloidal particle is immersed in the nematic liquid crystal host phase. The study was based upon molecular dynamics simulation in the canonical ensemble. On account of the coarse-grained nature of the models, we determined the length and energy scale of a host fluid first. Assuming that the host fluid corresponded to para-Azoxyanisole (PAA), we established the energy scale by computing the ratios of the elastic constants corresponding to the usual splay, twist and bend deformation of the director field and relating them to the experimentally known values for PAA. To establish the length scale characteristic of the model we considered mesogen-mesogen pair orientation correlation function and determined the coherence length from its large-distance decay. Our main focus was on the impact of colloidal particles immersed in a nematic host phase, two different model colloids were considered, namely, a so-called soft colloid and a decorated one. The soft colloid, which represented, for example, a main-chain liquid crystal dendrimer, consisted of a spherical region of variable thickness in which bulk mesogens were exposed to an orienting field of variable strength. Hence, during simulation, these mesogens were essentially free to enter or leave the soft colloid. This model was similar in spirit to that used by Tanaka and Araki. However, in their case, only translational viscosity was affected. In a similar spirit, we set up the soft colloids as a region in space in which an orienting field acts upon the mesogens. This not only affected the translational viscosity, as in Tanaka and Araki case, but also the rotational viscosity. If the orienting field had radial symmetry we observed the well known Saturn ring defect topology outside of the soft colloid. In addition, we also found another ring defect located inside the soft colloid.

By tuning the strength of the external field or the thickness of the shell in which it acts, we showed that the radius of the inner and outer defect ring can be shifted with respect to the respective surface of the soft colloid. At the same time, the coherence length of the mesogen-colloid pair correlation function remained unchanged. These results are consistent if one concludes that the anchoring strength remains constant but the effective size of the soft colloid changes if the strength of the external field and the shell thickness are varied.

If the external field induced planar anchoring, the defect topology could be understood as a combination of two separate ones. Outside the colloid we observed the well-known boojum defect topology consisting of regions of low nematic order centered on the colloid's north and south pole, respectively. In addition, an extended region of low nematic order inside a colloid existed, connecting the regions of low nematic order on its outside. Everywhere inside the colloid the local planar orientation of the mesogens was preserved.

The second model assumed that of a colloid consists of a repulsive core, which is decorated with immobilized mesogens attached to the outer surface of the colloid. As before for the soft colloid, local homeotropic and planar alignment of the grafted mesogens were considered. In both cases the interaction strength between the decorated colloid and bulk mesogen was controlled by the grafting density. In the case of homeotropic anchoring of the grafted mesogens we found that at low grafting density bulk mesogens could penetrate in between the shell of grafted mesogens. The higher the grafting density the less capable were bulk mesogens to move into this shell. We found that the coherence length of the mesogen-colloid pair correlation function varied significantly with grafting density, indicating that at higher grafting density the anchoring strength was higher than at lower grafting.

The research initiated in [S5] is continued and we plan to carry out simulations aiming at the determination how the defects discovered by us will change under flow conditions.

The research within WP2 was mainly carried out by TUM and ICMP groups. However, in some studies the

researchers from UMCS were also involved.

**The planned objectives of WP3 can be summarized as follows:**

1. Development of the molecular dynamics code suitable for the simulation of simple dichotomic molecules.
2. Phase behavior of the self-assembled simple dichotomic molecules and the structure of the ordered phases.
3. Dynamics and transport coefficients in ordered nanostructures of dichotomic molecules.
4. Development of macromolecular models for dichotomic molecules

**Ad. 1 and 4.**

We joined the objectives 1 and 4 into one task, since the development of computer codes must be preceded by the construction of appropriate models.

Originally, we planned to employ Molecular Dynamics simulations for simple models of Janus particles (similar to that used in [12], [16] and [19]). We developed the Molecular Dynamics programs, but they appeared to be much less effective than the corresponding Monte Carlo programs, especially for simulating phase transitions. In addition, during realization of the project several works on the application of Molecular Dynamics to study Janus fluids were published (e.g., by S. Klapp and co-workers. Gubbins, (19) J. Chem. Phys. (2012), 136, 174901; Int. J. Mol. Sci. (2012), 13, 9431), so we decided to employ Monte Carlo simulation method. The following computer simulation programs were developed and used in subsequent studies:

**a)** the two-dimensional lattice model program for simulating phase transitions in a monolayer of Janus fluid. This program uses a special model of Janus-like molecules with restricted orientational degrees of freedom, hiperparallel Grand Canonical Monte Carlo and reweighting of histograms methods. This special modelling of orientations allowed us for developing a very effective simulation code and the results obtained with the help of this program were submitted for publication [S2].

**b)** The on-lattice/off-lattice simulation program for Janus molecules confined in slit like pores. The results of this program will be presented in [I1]

**c)** We have also proposed a new model to study dichotomic particles. According to this model each particle possesses two off-center sites of the type A and B and chemical dichotomy results from different associative interactions between the sites. In addition to single A-A and B-B bonds formation of the double A-B-A and B-A-B bonds is allowed. This model was used in [S1] and presented during the conference 24.

**d)** We have also studied an effective force between two plates, modified by polyampholytes. Polyampholytic molecules build of blocks of segments that bear positive and negative charges can be considered as a kind of chemically dichotomic molecules. Our original aim was to obtain the dependence of the force on the plate-plate separation for different parameters characterizing the model. Then, a coarse-grained model that would neglect all the "molecular" details could be constructed and used in a coarse-grained simulations. At the moment we realized only a part of our plans, namely in paper [9] we studied effective force between two plates modified with a tethered layer of polyampholytes. The plates were immersed in an electrolyte solution that involves cations, anions and solvent molecules. We studied the dependence of the force and the structure of polyampholytes and of solute molecules on the grafting density, length of chains, architecture of the chains and on concentration of the solute. Another important problem that was undertaken in our study was the development of a new theoretical approach that allows for the evaluation of a force that acts on the tethered layer of ordered chain molecules. In contrast to previous approaches, our approach takes into account the presence of a solvent in which the system is immersed. Theoretical results have been tested against computer simulation data [13]. The description of an effective force acting between two walls of different type with Janus-like particles between them was discussed in [16]. We considered the cases of "symmetric" walls, "antisymmetric" (Janus-like) walls, as well as neutral walls and showed that the competition between fluid-wall and fluid-fluid interactions can result in important differences in the effective force. The latter results were also presented during the conference 22. However, the second part of our research, i.e., the development of an appropriate coarse grained model for plate-plate (or colloidal particle-colloidal particle) interactions is still under study. We plan to continue this project in a future.

**e)** We have also developed Dissipative Particle Dynamics computer simulation programs for chemically dichotomic molecules in liquid crystalline environment [S3]. However, this research also belongs to WP2.

**f)** Dissipative Particle Dynamics program for the studies of flows of complex molecules through the pores



with modified walls. The main problem with the developing that code was the invention of a method of thermostating the system.

**g)** All simple models of Janus particles proposed in the literature so far were based on the assumption of the existence of a hard-core part of the interaction potentials. However, some of important systems involving colloidal or amphiphilic molecules and ions should be rather characterized by “core-softened” models. Therefore, we attempted to develop a new class of simple models involving soft-core potentials. The soft-core potentials are of interest on their own, since such system exhibit several thermodynamic and structural anomalies. In order to propose models with soft-core, orientationally dependent interactions it is necessary to check how simplified models, without orientation-dependent forces work. Then, the approach could be generalized for to a more complex situation. In [A2] we studied a simple model mixture consisting of ions and soft-core solvent fluid by using Monte Carlo computer simulations in the canonical ensemble. Some results were obtained in the framework of integral equations method of the theory of liquids. The solvent model in question was characterized by a set of anomalies. Namely, a peculiar change of microscopic structure upon increasing density at certain values of temperature was observed. Changes of structure are described in quantitative terms by the pair contribution to excess entropy. On the other hand, the dependencies of solvent pressure on temperature calculated at several fixed densities may exhibit minima straightforwardly related to the temperature of maximum density line. Energetic aspects of anomalous behavior were described in terms of internal energy and its fluctuations. Unfortunately, the lack of time and necessity to perform other studies caused that a generalization of this research to the case of orientation-dependent forces was postponed to future studies.

## **Ad. 2.**

**a)** In the accepted for publication paper [19] and the conferences 21,25 we have introduced new model and a new theory to describe the structure, thermodynamic and electric properties of a fluid containing amphiphilic (Janus-like) molecules and ions. The theory comprises the fundamental measure theory for hard-sphere free energy functional, the approach due to Wang et al. for the free energy functional resulting from coupling between hard-sphere and electrostatic forces and the mean-field approximation for anisotropic interactions. The theory is simple, but captures principal effects due to interactions between species of the mixture and resulting correlations of different range. Studying the systems with different affinity of anions and cations to each of two hemispheres of amphiphilic molecules, we have found that for the models in which both types of

ions are attracted by the repulsive hemispheres (the systems of RR type) a long-range translational and orientational ordering can develop. The ordering of the molecules begins at the surface and then it propagates into the system interior. The ordered structure is built of layers of amphiphilic molecules. The “basic unit” in the RR model comprises three layers. In the first of two possible cases the first (contact) layer molecules expose their repulsive parts towards the surface. The first and the second layer molecules form a bilayer that is built of molecules with their attractive hemispheres facing each other. This bilayer is stabilized by a direct attraction between amphiphilic molecules. The third layer following the bilayer involves the molecules that expose their repulsive hemispheres towards the second layer. Due to attraction between ions and repulsive hemispheres the latter structure is stabilized by a layer of ions located between the amphiphilic layers. An analogous structure is developed in the case when the contact layer molecules expose their attractive hemispheres towards the wall. Moreover, we have also observed in RR systems that when an ordered structure of amphiphilic molecules develops, the oscillations of the charge profile of ions vanish and is almost zero, even at the distances not far from the wall. The development of a long-range order is also possible in the systems with different affinity of ions to two hemispheres of amphiphiles, either in the case when cations are attracted by the attractive parts of molecules while the anions by their repulsive parts, or vice versa. In those cases the bilayer of amphiphiles in each layer with the repulsive parts facing each other is stabilized by a layer of cations or anions between them. In such systems the charge profiles exhibit long-range oscillations and the potential of zero surface charge is different from zero. We also observed interesting changes of the electric properties as, for example, differential capacity of the double layer due to changes the interactions of ions with Janus particles.

**b)** We have already mentioned above about a new model for colloidal particles with chemical dichotomy that results from the presence of different associative sites. The theoretical approach proposed by us [S1] relies on the treatment of colloidal Janus-like particles in the framework of the so-called “patchy colloids model”. The results obtained in [S1] have also been presented during the conferences 24. The details of our research are as follows. We studied the phase behavior of the system confined in slit-like pores of different width with hard walls and at different values of the association energy for bonding between particular sites. Similarly as for bulk system, there exist a range of association energy values where the system exhibits a re-entrant type phase behavior, with lower and upper critical temperatures. The phase transitions in confined systems take place at chemical potentials higher than the bulk chemical potential at the transition point.

Thus, the observed phenomenon can be identified as the capillary evaporation. Within the presented approach the values of lower and upper critical temperatures do not depend on the pore width and are the same as in the bulk system. We attribute this behavior to the fact that the particles with two associative sites can form either multiply connected network or chains with particles located almost in a plane in both cases. Therefore, geometrical constraints imposed by the walls do not almost influence the critical temperatures. The approach outlined in [19], 24 opens new perspectives of research. In particular, it would be of interest to check for a possibility of the occurrence of surface phase transitions like wetting and layering transitions in the systems involving two-site hard-sphere colloids in contact with a single, attractive wall. Next, as we know the presence of additional van der Waals type of attraction between colloidal particles modifies the phase behavior in bulk systems. Attractive van der Waals interactions will also modify the phase diagrams of confined fluids and their dependence on the width of pores. All these problems are currently under study.

**c)** We developed a new theory to describe adsorption of Janus particles on surfaces modified by tethered chain molecules. Such a model that takes into account the anisotropic interactions between fluid particles, well as between fluid particles or segments of chains and the wall has not been presented in the literature so far. According to the proposed approach the Janus molecules were modeled as spheres composed of a hydrophilic and hydrophobic part. The pinned chains were treated as tangentially jointed spheres that can interact with Janus molecules via orientation-dependent forces. Our density functional approach involved fundamental measure theory, thermodynamic perturbation theory for chains, and a mean-field approximation for describing the anisotropic interactions. Using this theory we investigated the structure and adsorption of amphiphilic molecules, focusing on the competition between the external field (due to the surface and due to attached chain molecules) and the interaction-induced ordering phenomena. Particularly interesting finding connected with the occurrence of a transition from the disordered to membrane-like phase. We found that the presence of strong fluid-wall interactions can enforce first-order character of this transition. The developments outlined above were described in the publication [12] and presented during scientific conference 19.

**d)** Investigations of phase transitions. In the submitted paper [S2] we studied phase behavior of Janus discs in two-dimensions by Monte Carlo method. Each Janus particle is composed of two different parts, A and B. Four orientations of a particle on each lattice site have been considered. Interactions between neighboring particles depend on their orientations. To control the strength of the interactions we have used only three energy parameters that characterized AA, BB and AB contacts. It was shown that under condition of a fully filled lattice two ordered phases can be formed, superantiferromagnetic (SAF) and antiferromagnetic (AF). For selected model systems the phase diagrams were estimated. Two kinds of phase transitions were found, first order transition and a continuous order-disorder transition. The influence of energy parameters on the phase diagram topology and critical parameters were discussed. In special model systems we have not found a first order condensation while a strong tendency to self-organization has been observed. The variety of ordered structures can occur in the system, depending on relations between energy parameters and on fluid density. The results obtained in [S2] were also presented during the conference 27. The model used in the second simulation work (the manuscript [II] is still under preparation) is more general. Similarly as in [S2] we use a lattice model, but the system is three-dimensional. Moreover, the Janus particles may assume arbitrary orientations. We studied only the first-order transitions for Janus fluids confined in slit-like pores, and depending on the pore and on the interactions of the particles with the pore wall we observed a rich variety of phase transitions leading to the formation of differently ordered phases. This work has been already accepted for the presentation during the 9th Liblice Conference on Statistical Thermodynamics of Fluids 23.

**e)** In the submitted for publication paper [S6] We used hyper-parallel tempering Monte Carlo simulation, multiple histogram reweighting method and finite size scaling we have carried out systematic studies of adsorption of fully flexible and rod-coil chains on square lattice. The rigid molecules can form liquid-crystalline ordering. It is of interest to investigate the crossover in the behavior of the system when rigidity of the molecules changes from fully flexible to completely rigid. Since the segments of the molecules exhibit different properties we can consider the work [S6] and the conference contribution 30 as belonging also to the WP2 and for this reason more details on the results obtained are outlined within WP2.

**f)** In the submitted for publication paper [S7] we studied the „impurity” driven commensurate-incommensurate transitions in one- and two-dimensional finite systems at zero temperature. The existence of „impurities” (i.e. segments of different chemical kind than the other segments) can be considered as a kind of chemical dichotomy. In the case of one-dimensional finite chains, we investigated the situations in which the impurity was located at one and two ends of the chain. It was shown that in both situations the commensurate-incommensurate transition occurs when the amplitude of the external field experienced by the impurity atoms falls into the region between the lower and upper threshold values. These limiting values depend upon the parameters characterizing the interaction between the atoms in the main chain, the

amplitude of external field acting on the main chain atoms and the interaction between the main chain and the impurities. The number of solitons (domain walls) in the incommensurate structure was different for the chains with one and two ends.

### **Ad. 3.**

In order to study the dynamics and transport coefficients in ordered nanostructures of dichotomic molecules one has to start with the investigation of equilibrium and the dynamics and transport behavior of simple systems. Such studies were performed for single fluids and mixtures using DPD simulation method. The results have been already described in the part of this report referring to WP1. Then we have developed the programs which calculate the orientational order parameters and describe the shape anisotropy of complex particles, the velocity profiles and viscosity profiles for complex fluids flowing through nanochannels. At present we completed the codes suitable for simulation of dynamics in ordered structures of dichotomic molecules. However, finalizing the publication still requires rather extensive and time consuming calculations and we are not able to describe the results and present the conclusions yet.

Summing up our scientific activities within WP1, WP2 and WP3 we can state that all principal scientific aims of the project have been achieved. We published 21 scientific papers, the next 6 papers were submitted for publication and two are under preparation. We also attended 31 conferences, during which the results of this project were presented. All the results obtained within WP3 resulted from a close collaboration between the ICMP, UMCS and UNAM groups. The group from TUB was also involved.

### **The list of TOK activities**

1. A. Patrykiewicz presented at ICMP, Lviv the lecture, entitled "Monte Carlo simulations of complex systems: the melting and low temperature structures of mixed monolayers" (July 9, 2011). He also attended several discussions on the following topics: mechanism of melting transition in two- and three-dimensional systems, the free volume problem in statistical mechanics and the implementation of dissipative particle dynamics method to nonuniform systems involving polymers.
2. M. Borowko presented at ICMP, Lviv the lecture, entitled "Adsorption on surfaces modified with end-grafted polymers" (May 26, 2011). She attended workshop organized by the ICMP for young scientists from the Ukraine and discussed several problems connected with the project with the members of the ICMP. In particular the discussions were devoted to the following topics: theory and applications of chromatography with chemically bonded phases, the implementation of dissipative particle dynamics method to nonuniform systems involving polymers.
3. A. Trokhymchuk presented at UMCS the lecture "Excluded volume and physics of phase transitions in soft matter" (June 10, 2011) and the lecture "PRISM/RISM integral equations for polymers" (July 18, 2011).
4. J. Ilnytskyi presented at UMCS the lecture "Mixing/demixing of a binary mixture in a pore" (July 18, 2011) and attended at UMCS round table discussions on chromatography, investigations of nanostructured morphologies within a pore and on molecular dynamics algorithms for non-spherical particles and on application of dissipative particle dynamics to study Poiseuille flows.
5. In July 2011 S. Sokolowski at ICMP took part of round table discussions on the problems connected with the development of efficient Molecular Dynamics, as well as Dissipative Particle Dynamics algorithms to the simulations of systems involving tethered polymers. Together with T. Pasathan and J. Ilnytskyi, P. Bryk (in Lublin) and S. Sokolowski performed installation of the LAMMPS package on the computer clusters at ICMP and UMCS. (August 2011).
6. O. Pizio delivered the at UMCS the lecture, entitled "Amphiphilic brushes: their properties and modelling" (September 20, 2011).
7. In October M. Schoen gave a talk in the physics department of UNAM. The title was "Finite-size scaling analysis of isotropic-polar phase transitions in an amphiphilic model fluid".
8. W. Rzyzko attended at ICMP a round table discussion on "Novel applications of Monte Carlo methods" (November 15, 2011).
9. O. Pizio delivered at UMCS the lecture entitled "How to model/describe electrolytes in a core-

softened solvents”,(Lublin, January 12, 2012).

10. On February 7, 2012, J. Ilnytskyi presented the lecture "Computer simulations of the self-assembly of liquid crystalline dendrimers" in the Laboratory of Physicochemistry of Dielectrics and Magnetics, Faculty of Chemistry, University of Warsaw. In this laboratory composite materials are synthesized, namely gold nanoparticles with attached liquid crystalline groups. The object can be modeled by basically the same model as coarse-grained dendrimers and both experimental studies in WU and simulations performed in TUB bear much similarities in the dependence of the self-assembly on: mono/polydispersity of chains, ratio of sizes between central core particle and polymer sites, grafting density of chains, etc. The visit is aimed on establishing scientific link between experiment and simulations.
11. In January 2012 J. Ilnytskyi and T. Patsahan organized a series of discussions on prepared paper: "Dissipative particle dynamics study of solvent mediated transitions in pores decorated with tethered polymer brushes in the form of stripes". The problem discussed was how to model different types of flows through pores with chemically modified walls.
12. P. Bryk, during his stay in ICMP (8.02-7.03 2012) I gave a series of three lectures on classical density functional theory for simple and polymeric fluids. In addition, he carried out several scientific discussions with Prof. J. Ilnytskij regarding implementation of the dissipative particle dynamics program under non-equilibrium condition. With Dr. T. Patsahan he discussed the problem of methods of effective implementation of parallelization of molecular-dynamics algorithms for distributed memory model multiprocessor systems.
13. J. Ilnytskyi during his visit to TUB (march, 2012) , Berlin had several intensive discussion and transfer of knowledge were conducted, in particular with M. Schoen, M. Mazza and M. Miele. The problems discussed (and then solved) concerned development of algorithms for evaluation of the smectic order parameter. A final, general discussion was organized by Prof. M. Schoen and concerned the role of surfaces in self-assembly of anisotropic particles.
14. W. Rzyzko during his stay in UNAM gave the seminar "Computer simulations of rod-coil copolymers" (April 23, 2012).
15. T. Patsahan, during his visit to Lublin, (May, 2012) had a number of round table discussions on the use of LAMMPS package to model Lennard-Jones fluids in slit-like pores with walls modified by polymer brush. He developed a number of scripts and auxiliary programs. T. Patsahan taught younger fellows from UMCS (T. Staszewski and students) how to used the scripts and the programs developed by him.
16. A. Trokhymchuk and J. Ilnytskyi during their visit to TUB, (August 2012) had meetings and seminars on computer simulation of Janus particles using coarse-grained molecular dynamics simulations.
17. O. Farenjuk, during his stay in Lublin (September 2012), together with the members of UMCS group, was involved in writing and testing computer codes for extensive analysis of coarse-grained molecular dynamics simulations of colloid particles in a nematic solvent, and for the Janus particles immersed into a nematic solvent. Due to his experience in programing, common work with O. Farenjuk was very instructive for the members of UMCS group.
18. J. Ilnytskyi, together with P. Bryk (UMCS) organized seminar, devoted to modeling of Janus particles in the nematic solvent with the use of coarse grained potentials, modeling of a Poiseuille flow in a micro-channel with polymer-modified walls (UMCS, September 14, 2012).
19. O. Pizio presented the seminar, entitled "Grafted layers of polyampholytes: a density functional approach" (October 16, 2012) at the Department for the Modelling Physico-Chemical Processes, UMCS. O. Pizio attended several scientific discussions in the Department for the Modelling Physico-Chemical Processes and in the Institute of Astrophysics, Polish Academy of Sciences, Lublin.
20. S. Sokolowski and M. Borowko attended the international Conference „4th Meeting on Molecular Simulations”, that was organized by Universidad Autonoma Metropolitana, Mexico City (Dec. 5-7, 2012). They also provided a seminar on the properties of grafted layers for graduate students of O. Pizio (UNAM)
21. J. Ilnytskyi gave a seminar at the Department of Modelling of Physico-Chemical Processes UMCS on methods of DPD simulations of flows in nanochannels (March 6, 2013).

22. P. Bryk and W. Rzyśko during their visit to ICMP (05.04-05.05.2013) gave two seminars on computer simulations of simple and complex fluids. In addition, they carried out several scientific discussions with Prof. Taras Bryk about ab-initio molecular dynamics simulations and his research activities, which involve simulations of high-pressure electronic properties of metals. With prof. A. Trokhymchuk they discussed the problem of the nature of crystallization in 2D systems and possible theoretical solutions to this problem. With Dr Ivan Kravtsov and T. Patsahan they discussed the field-theoretical approach to the problem of adsorption of Yukawa fluid at a hard wall.
23. S. Sokolowski and M. Borowko visited ICMP in the periods of time 01.05-31.05.2013 and 20.05-19.06.2013, respectively. On May 23 S. Sokolowski provided the lecture „Electric double-layers in slit-like pores: a DFT approach” for the entire Institute of Condensed Matter Physics, UAS, Lviv.
24. S. Sokolowski and M. Borowko had discussions with Yu Kalyuzhnyi on similarities and differences between systems involving Janus particles and some selected systems of associating particles that can form structures (clusters) of a given symmetry. They also discussed phase behavior of both the above systems.
25. During his stay in Lublin. (29.04-29.05.2013) T. Pasathan delivered a seminar “Structure of linear and Y-shaped polymer brushes in a solvent of different quality: molecular dynamics study” for the staff and students of the Department for the Modelling of Physico-Chemical Processes, UMCS.
26. During his stay in Lublin (7.10-07.11.2013) O. Pizio delivered a seminar for members of the Department for the Modelling of Physico-Chemical Processes, entitled „Molecular dynamics simulations of mixtures involving water and organic molecules”. He also had several discussions with A. Patrykiewicz, W. Rzyśko, P. Bryk and T. Staszewski on Monte Carlo simulations of different ordered phases adsorbed on solid surfaces. O. Pizio also visited the Institute of Agrophysics, Polish Academy of Sciences, Lublin, where he discussed some problems connected with the behavior of water near particles of soil organic matter and near surfaces of organo-mineral complexes.
27. S. Sokolowski during his visit to UNAM (06.11-03.12.2013) had three meetings with undergraduate and graduate students of O. Pizio and discussed the problems connected with modelling and computer simulations of confined complex fluids. He also discussed several scientific, as well as technical problems connected with different applications of Molecular Dynamics with Dr. Hector Dominguez.
28. During visit of P. Bryk to Lviv (23.11-23.12.2013) he had various scientific as well as teaching/learning activities with members of the group of Prof. A. Trokhymchuk and Dr. T. Patsahan.
29. During stay in Berlin (1.11.2013-30.11.2013), A. Trokhymchuk, O. Farenjuk and J. Ilnytskyi attended (November 11, 2013) two lectures, delivered by Slobodan Zumer (University of Ljubljana) and by Anupam Sengupta (Massachusetts Institute of Technology) in the framework of the International Research Training Group 1524 Colloquium (Technische Universität Berlin). On November 12, 2013 they attended a round table discussion with Prof. Slobodan Zumer on the problems of computer modeling of nematic colloidal dispersions. O. Farenjuk obtained software for bulk and Janus particles properties analysis and, together with the members of M. Schoen group developed automatic shell scripts for effective usage of that software. Thanks to numerous discussions with M. Schoen and his students J. Ilnytskyi developed code for evaluation of coherence length in nematic phase, solved several problems connected with thermostatting for “nematic nanodroplet” model at large values of orientation field constant and developed algorithms for generating of initial configuration for Janus particle and algorithms and for solving equations of motion in coarse-grained molecular dynamics approach.
30. During the visit to Lublin (01.12-31.12.2013) J. Ilnytskyi had numerous discussions with P. Bryk, A. Patrykiewicz and other members of the Department on: (i) generalization of simulation of Poiseuille flows for the case of the mixture of oligomeric solvents, (ii) an extension of viscosity coefficient evaluation for the case of wall bounded mixture of flowing fluid, and (iii) how some properties are affected by molecular weight of the solvent. Moreover, he had discussions with S. Sokolowski and W. Rzyśko on: (I) phase transitions in lattice gas of Janus particles, (ii) introducing of the set of order parameters related to the phase transitions from low-density to high density (lamellar) 2D phase in near-surface layers of Janus particles fluid.
31. M. Borowko visited ICMP in January 15 – March 14. 2014. She I took part in seminars for doctoral

students of Institute of Condensed Matter of Ukrainian Academy of Sciences and in the seminar by S. Sokolowski 'Confined Janus particles' (2014.02.10). She had also discussions with J. Ilnytskyi, A. Trokhymchuk and other research workers of the host Institute.

32. S. Sokolowski visited ICMP in the period of time from 22.01 to 21.02.2014. On February 10, 2014, he provided a seminar, entitled "Confined Janus particles" for the scientific staff of ICMP. He also had numerous discussions with all the members of the group of J. Ilnytskyi and with Yu. Kalyuzhnyi.
33. During the visit in Lviv 22.02-21.03.2014 A. Patrykiewicz has continued the discussions with J. Ilnytskyi and his collaborators on the problem of the flow of oligomeric fluids through slit-like pores decorated with polymeric brushes. A. Patrykiewicz has also been involved in the continuation of collaboration with A. Trokhymchuk on the behavior of fluids of particles interacting via complex potentials. He presented a seminar on the impurity driven commensurate-incommensurate transitions in two-dimensional nanoscopic systems.
34. J. Ilnytskyi and O. Farenjuk visited TUB in the period of time from 1.03.2014 to 31.03.2014. They carried out several discussions with M. Schoen and with the members of theoretical chemistry group. The discussions were concerned with the description and modelling of Janus particles and defects around these. Consultations and experience exchange have been conducted on coarse-grained molecular dynamics and Monte Carlo simulations.

Summing up: The collaboration between all the groups resulted in a significant increase of scientific potential of all institutions involved. This is particularly seen in the case of the groups from UMCS and ICMP. We plan to continue collaboration in a future. Also, the group from UMCS plans to continue collaboration with UNAM and at the moment several new scientific projects are ongoing. The people from UMCS established new scientific contacts with the researchers from ICMP (Yu. Kalyuzhnyi, Z. Usatenko), who were not involved in this project, as well as with other scientists (e.g., with prof. T. Poeschel from Erlangen, Germany, who is interested in a future collaboration aiming at the description of Janus-like particles). Similarly, the scientists from ICMP established new contacts. For example in April 2014 Prof. J. Ilnytskyi was invited by the vice-director of the Institute of Agrophysics Polish Academy of Sciences, Prof. G. Jozefaciuk, to deliver a series of lectures on modern computer simulations and their possible applications in investigations of systems involving organo-mineral components. Prof. J. Ilnytskyi also undertook collaboration with people from Leibniz-Institut fuer Polymerforschung, Dresden. In the results of the works of this project Dr. T. Patsahan was invited by prof. O. Pizio to spend one month (May 2014) in Mexico.