Report 2
concerning the progress in realization of the program STCSCMBS 268498.

WP1, 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.

The developed computer programs.

1) The programs evaluating the structure and thermodynamic properties for single or multicomponent fluids in contact with tethered brushes at a single wall or inside a pore. The codes for solving the problems of **task 1.1** (the codes are stored on the UMCS server; the person responsible: S. Sokołowski). This task has been carried out by ER1, ER3, ER4, ER5, ER8, ER11

2) Dissipative particle dynamics (DPD) program for fluids in slit-like pores with non-uniformly distributed brush molecules and several auxiliary programs (evaluation of local properties and graphical presentation of results) have been developed **(task 1.2)**. The are at stored at ICMP; the person responsible: J. Ilnytskyi. This task has been carried by ER2, ER5, ER8 and ER9.

3) The programs and scripts for starting and performing LAMMPS simulations and analyzing the outputs **(tasks 1.1 and 1.2)**. This has been done by the ICMP (ER7,ER8,ER9) and UMCS (ER1,ER5) groups. The programs and scripts are stored on the ICMP and UMCS clusters. The person responsive: T. Pasathan.

4) The Monte Carlo program (**task1.1; also task 3.2**) for simulating oligomers tethered to a surface and for calculating the force acting on the tip of an AFM apparatus. The program was developed in collaboration between ER3, ER4 and ER10 from ICMP. The person responsible: W. Rżysko.

The most important results and published papers (ER1, ER3,ER4,ER5,ER8, ER9 and ER11)***.***

1) The changes of the structure and thermodynamics properties (phase transitions) in the case of a binary mixture in contact with two walls (at a distance H apart), covered by a brush. The walls were permeable for one fluid component. Particular attention was paid to the phase transformations. We found, for the first time, the transitions connected with the change of symmetry of the distribution of chains and fluid inside the pore [1]. **Task 1.1.**

2) Studies of symmetry breaking in the system. Using density functional approach we found that depending on the amount and length of the chains, the topology of the phase diagrams can change. Performing systematic studies, we determined the scenario of possible phase transformations and diagram topologies. We found symmetry breaking and re-entrant to symmetry transitions. In the case of a binary mixture that exhibits demixing in a bulk phase the situation is even more complicated, due to a competition between surface-driven and demixing transitions [2,5]. **Task 1.1.**

3) The investigation of the structure change of the brush caused by changes of the surface density and of the length of tethered chains, solvent and temperature. For some systems we found an unusual dependence (the existence of a minimum)-of the brush height on temperature [4,6]. **Task 1.1.**

4) Studies of adsorption from binary solution involving spherical and/or chain particles. For spherical molecules [7] we analyzed how different parameters affect the relative excess isotherm. The adsorption azeotropy was found for selected systems. In the case of solutions involving oligomers [8], we found that if an attractive interactions between free and grafted chains strengthen, the relative excess adsorption isotherm can change from negative, through S-shaped with an adsorption azeotropic point, to positive in the whole concentration region. **Task 1.1.**

5) We applied DPD method [3,b1] 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. A new method for handling the collisions of fluid particles with the walls of the pore was developed. Next, we studied how the morphologies of different phase changes with the parameters of the model. Apart from different "mixed" phases, we found lamellar phases, pillar phases, and phases that were observed during studies of bulk systems. . **Task 1.2.**

The problems under study

1) There are several problems under study. First, the paper describing DPD simulations of flow through slits with walls modified by tethered brush is prepared for publication by ER2, ER8 and ER9. The simulation setup consists of paralellpiped box with walls covered by polymer brush. The brush is in contact with phase-separating binary mixture. So far we have found that for Poiseuille flow the pillar morphology is quite unstable and tends to change to the lamellar morphology. **Task 1.2.**

2) Investigations of unusual behavior of the electric capacitance in slits with charged walls, covered by charged/uncharged brushes. We found an oscillatory changes of the capacitance with the pore width. The character of oscillations changes with the grafting density, length of chains and with the architecture (e.g., the distribution of charges) of the chains. The paper is prepared for publication by ER5 and ER11 and ER12. **Task 1.1.**

3) We also conducted also some auxiliary studies on a possibility of application of spherically symmetric, core-softened potentials models to study systems involving polymers. The results were published in [c1]; one paper is in press [c2].

4) We initiated Molecular Dynamics simulations to check whether the predictions of the density functional theory [4,6] agree with Molecular Dynamics results. In the case of MD study we also performed calculations for Y-shaped polymers. The relevant paper is in preparation by ER5, ER9 and ER10 (cf. also reports from

visits r5.pdf and r6.pdf) **Task 1.2.**

WP2, 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

The first report on deliverables, connected with the realization of WP2 has to be presented after 27 months. Here we describe the works being under study.

The developed computer programs.

1) The program for simulating and analyzing liquid crystal dendrimers confined in slits. This coarse-grained simulations are based on Molecular Dynamics in various ensembles, NVT, NPT and NPxxPyyPzzT. Linked-cells and neighbor-lists are used for potential and forces evaluation. Several options for repulsive/anchoring wall potentials have been employed and tested. For atomistic and semi-atomistic studies one normally uses spherical 9-3 potential with modified attraction by an anisotropic term. This issue was solved by ER6, ER8, ESR1 and ESR2. T**ask 2.1**

The problems under study

1) The computer program 1) was used for a system comprising 200 macromolecules of a coarse-grained model for liquid crystalline dendrimer near the wall. Each macromolecule consisted of a large central sphere (representing time averaged dendritic scaffold) and 32 chains attached to its surface, each terminated by a mesogen. The anchoring was applied at distances 3-6 nm from both walls towards the interior of the simulation box. We discovered the ability of 200 macromolecules to self-assemble into a smectic phase when the external aligning field is applied (this effect was studied in the former bulk simulations of much smaller system). This work is continued by the ER6, ER8, ESR1, ESR2 (cf. enclosed r1.pdf file). **Task 2.1.**

2) The paper "Simulation of a self-assebmly of polyphilic liquid crystal dendrimers confined inside the pore with homeotropic anchoring" based on this study is under preparation by ER6, ER8, ER10 and ESR1. In this work self-assembly into a monodomain smectic phase has been aided by an uniaxial field acting on mesogens only. After self-assembling, the smectic phase was heated up to study the phase transition into isotropic phase. The study has revealed some important details of this transition. In particular, in the vicinity of the phase transition, instead of expected polydomain smectic phase, one observes the coexistence of both smectic and columnar domains, with the dominance of the latter. This duality in the system can be analyzed by means of a configuration analysis, by evaluating the fraction of rod-like and the fraction of disc-like conformations. The study was extended into the case of dendrimers inside a pore with homeotropic step-like anchoring potential. The step-like anchoring imposed on both walls do not to change the properties of the system in the smectic phase, but the transition temperature is shifted up. (cf. r2.pdf and r3.pdf files).

WP3, tasks: 3.1. Towards realistic models of self-assembled phases formed by complex organic fluids, but also and 3.3: Towards realistic models of self-assembled phases formed by complex organic fluids.

Note that the first report on the progress in realization of the task 3.2 has to be presented after 27 month. The same concerns the task 3.3, but we have already obtained some results within that task

The developed computer programs.

1) The Monte Carlo simulation program for evaluating an effective force, acting on grafted chains that is measured in AFM experiments. This program has been reported in the description of WP1 (point 4)

2) A Density Functional program for evaluating forces acting on the tethered layers (solvation, detachment, compression). This program uses a similar model as the program BRUSH1. The code is at UMCS, the person responsible: S. Sokołowski. The program was develop by ER1 and ER8

3) Density functional program for Janus-like particles in contact with "bare" surfaces and surfaces modified by tethered chains. The orientation forces between Janus particle, Janus particles and the segments of brush and Janus particles and the surface are described by using potentials proposed by Tarazona. The program was developed by ER8 and ER11, in collaboration with prof. T. Poeschel from FAU Erlangen-Nuernberg. The person responsible: S. Sokołowski.

4) Computer codes for an extensive analysis of coarse-grained molecular dynamics simulations of colloid particles in a nematic solvent and for analyzing the defects of the nematic director around colloidal particles. This task was carried out by ER7 (cf. r4.pdf) This program will be used in further investigations of the behavior of Janus particles, in particular the defects arising near surfaces (which affect the symmetry of the director field) and their aggregation in bulk, due to the effective interactions of Janus particles via the deformation of director field, according to the director field around each particle studied during this scientific visit

The most important results and published papers.

The published and submitted papers were written by ER1, ER3, ER5, ER8 and ER11.

1) The description of Janus particles at walls modified with tethered chains is considered in paper [b2]. The molecules were modeled as spheres composed of a hydrophilic and hydrophobic parts. The chains interact with fluid molecules via orientation-dependent forces. We studied the structure and adsorption of Janus particles. For some selected parameters (temperature, bulk fluid density) we found that the formation of a

“membrane-like” structure can occur as a first-order transition. Tethered chains can either enforce or diminish the transition, depending on the character of chain-fluid forces. **Task 3.1.**

2) The problem of evaluation of effective forces between two “macromolecules” (modeled as planes), with surfaces modified by polyampholytes was discussed in [9,10]. The plates were immersed in an electrolyte solution that involves cations, anions and possibly 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, concentration of the solute. and architecture of the chains. By the term “architecture” we mean different distribution of the charges along the chain. It has been shown that the architecture influences very much the effective force. The most pronounced changes of the force with the distance were observed for the cases when the charges are forming bigger “blocks”. Such systems also exhibited the highest selectivity of adsorption of ions of a given sort. **Task 3.2.**

The problems under study

1) Continuation of the studies reported in the papers [9.10]. We have developed a new version of the Density Functional Theory and have performed the relevant calculations of the solvation forces. This paper is under preparation by ER1, ER5 and ER11.

2) The force acting on the tip of an Atomic Force Microscope, while the tip is approaching a tethered brush has been evaluated by using Monte Carlo and Density Functional calculations. This work is under preparation by ER4, ER5, ER10 and ER11.

Finally, we should mention that ER5 and ER11 are finishing a review on the problems from WP1 and WP2 for Wiley-VCH. Moreover, the results obtained were presented during a number of scientific conferences.
List of publications, conference contributions and individual reports is given in the DISSEMINATION file.