Report on visit of J.Ilnytskyi, Institute for Condensed Matter Physics, ICMP
(March 2012) to TUB
Scope of work: Development of simulation and analyzing tools for coarse-grained simulations of liquid crystal dendrimers confined in a pore.

During the stay the simulation code was developed which enables a coarse-grained molecular dynamics study of macromolecules confined in a pore. It utilizes the leap-frog integration scheme for various thermodynamics ensembles, *NVT*, *NPT* and $NP_{xx}P_{yy}P_{zz}T$. To speed-up the simulations 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, the so-called, 9-3 potential with modified attraction by an anisotropic term. This issue was discussed in detail with M. Schoen, M. Mazza and M. Miele from the host institution (TUB). However, this approach was found to be impractical for coarse-grained models with no attractive part in the potential. Instead we considered several options. These include: (i) the set of virtual soft repulsive spherical particles on the wall plus step-like anchoring, (ii) the same but with exponentially decaying anchoring, (iii) ordinary periodic boundary conditions with the step-like anchoring applied within the layer of a given depth near the wall, (iv) frozen layers of perfectly aligned particles outside each wall, (v) frozen periodic boundary conditions, in which the layer of particles located at the other side of the box is replicated but with perfectly aligned orientations.

The test runs being conducted during the visit revealed that the option (iii) is mostly economic and leads to none of density and orientation anomalies near the walls. The following test example was used: 200 macromolecules of a coarse-grained model for liquid crystalline dendrimer near the wall. Each macromolecule consisted of 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 ranging 30-60 Angstroms from both walls in Z direction towards the interior of the simulation box. The important part of the test was the ability for a melt of 200 macromolecules to self-assemble into the smectic phase when the external aligning field is applied (the effect studied in the former simulations of smaller system of 100 molecules in the bulk). This was, indeed, reproduced (see, figure below at external aligning field strength of $2\ 10^{-20}$J, range 60A and temperature T=480K.

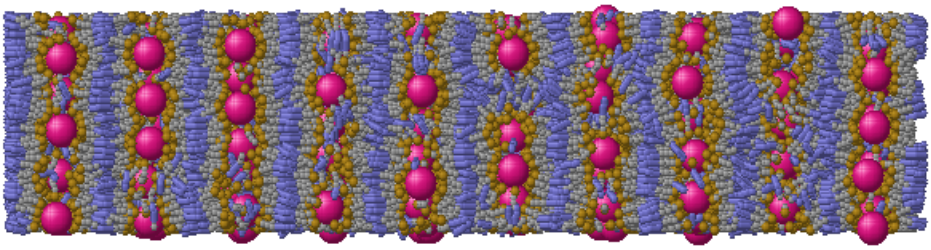

Fig.1 Self-assembled smectic phase of 200 coarse-grained dendrimers under wall anchoring.

We also paid much attention to the stability of the integration scheme. To this end, the runs were conducted with various time-steps of simulations ranging from 10 to 40 fs and the drift of the extended Hamiltonian was analyzed. We found that for typical simulation runs of 10^6 steps, the acceptable drift is not exceeding 5-7% when the timestep is equal or less that 20 fs. This value is chosen for the following simulations.

We started the study of the phase transition from field-aided smectic into isotropic phase for the system of 200 macromolecules in terms of the behavior of nematic and smectic order

parameters, molecules asphericity and order clusters dissolvent. More detailed numerical studied of this transition will be conducted during the following visit to TUB in August 2012.

During the visit intensive discussion and transfer of knowledge were conducted, in particular with M.Schoen, M.Mazza and M.Miele. The algorithm for evaluation of the smectic order parameter was used that was previously developed by M.Mazza for soft spherocylinders. M.Mazza was introduced to the algorithms for molecular dynamics simulations for constant-pressure ensemble, evaluation of forces and potentials for various types of rotational bodies. The details of coarse-grained potentials used by M. Miele for studying colloid immersed in liquid crystal were discussed and used for shaping up the interaction of the central dendritic core with liquid crystal particles. The general discussion leaded by Prof. M.Schoen was made on the role of the surface in self-assembly of anisotropic particles, based on the recent research in the TUB group.