

Report on PIRSES visit of J.Ilnytskyi, ICMP (August 2012 to TUB

Scope of work: Coarse-grained simulations of liquid crystal dendrimers confined in a pore.

The system of 200 macromolecules each representing a coarse-grained model for liquid crystalline dendrimer were considered. Each macromolecule consisted of large central sphere (representing time averaged dendritic scaffold) and 32 chains attached to its surface, each terminated by a mesogen. Both bulk case and the melt of macromolecules confined within the pore with homeotropic anchoring were considered. The box size is of the order of 150x150x600 Angstroms.

The self-assembly into a monodomain smectic phase was aided by an uniaxial field acting on mesogens only (representing e.g. electric or magnetic field). After this, the smectic phase was heated up to study the phase transition into isotropic phase in detail. The study reveals some important details of this transition not observed before. 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. First of all, this duality in the system is analyzed by means of a configurational analysis, by evaluating the fraction  $f_r$  of rod-like and the fraction  $f_d$  of disc-like conformations (identified from the sign of the asphericity of each macromolecule). As follows from Fig.1 (on the left), there is a prominent exchange in  $f_r$  and  $f_d$  values at temperature range  $T=[490K-550K]$ , after that both fractions became equal to 0.5. Both phases coexist at  $T=490K$ , as is clearly indicated by the center-center distribution functions evaluated for each subsystem, see Fig.1 on the right.

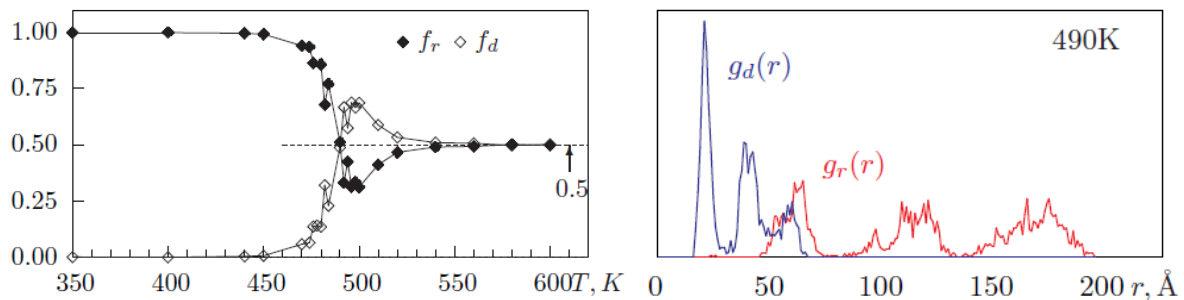


Fig.1. On the left: fractions of rod-like,  $f_r$  and disc-like,  $f_d$  molecules at various temperatures  $T$  from heating up initially monodomain smectic phase. On the right: molecular center-center distribution functions,  $g_r(r)$  and  $g_d(r)$  for rod-like and disc-like subsystems, respectively, along their respective symmetry axes.

Deeper insight into the coexistence of both phases (smectic and columnar) is obtained by finding explicitly the domains of both types. These are identified by the algorithm similar to the Hoshen-Copelman one taking into account the metric properties of both phases in bulk (namely, lamellar and columnar pitches along respective principal axes as well as the 2D order in perpendicular planes). From the data presented in Fig.2 one can see that, indeed, columnar domains prevails at the temperatures  $T=[492K-500K]$  until both smectic and columnar subsystems de-clusterize at  $T=510K$ .

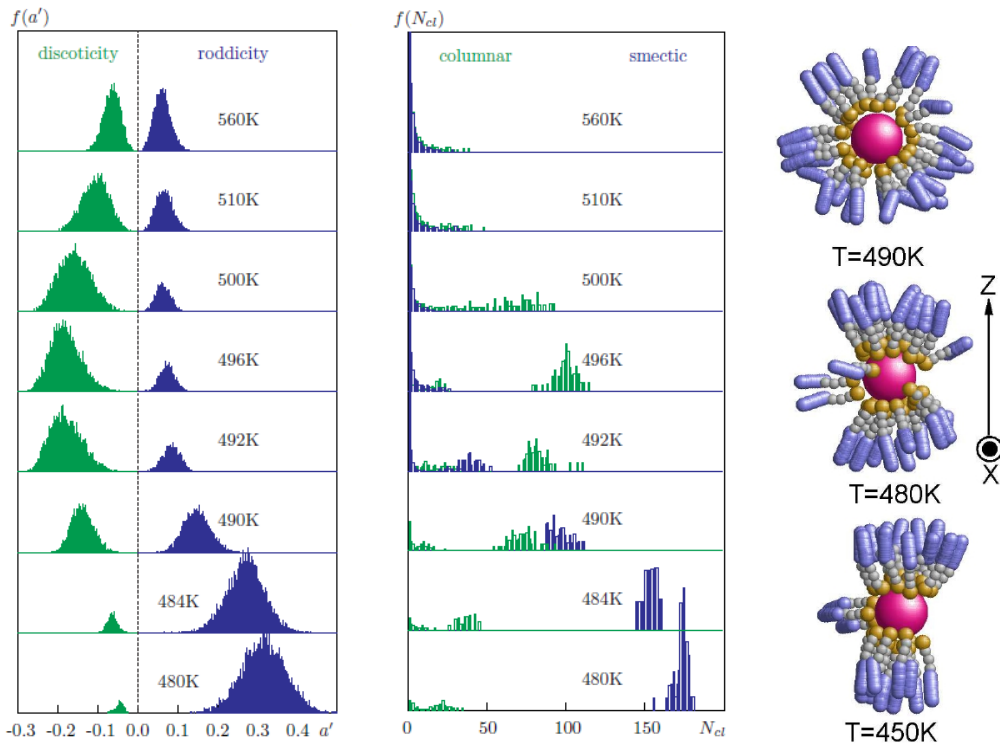


Fig.2. On the left: histograms for the distributions of weighted “discoticity” (in green) and “roddicity” (in blue) for the molecules at various temperatures near the transition. In the middle: histograms for the distributions of smectic and columnar cluster sizes. On the right: gradual transformation of a rod-like molecule ( $T=450K$ ,  $480K$ ) into a disc-like molecule ( $T=490K$ ).

This analysis proves that the smectic order terminates at about  $T = 496K$  and columnar order is dominating at  $T = 496K-510K$ . The director for discotic subsystem (which points normal to the average disc plane) is found always perpendicular to that of the former nematic director of rods. This can be explained by the spatial symmetry of the molecule when it gradually transforms from a rod into a disc with the increase of the temperature (see, Fig. 2). Self-assembly of such conformationally transformed discs involves minimum molecular rearrangement.

The study was extended to the case of the dendrimers constrained inside a pore with homeotropic step-like anchoring potential defined via the extra energy term:  $V_h = -f \cos^2(\theta)$  if  $z < 60\text{\AA}$  or  $z > L_z - 60\text{\AA}$  and  $V_h = 0$  otherwise. Here  $\theta$  is the angle between the mesogen long axis and the normal vector to the surface,  $z$  is the mesogen  $z$  coordinate,  $f$  – is the strength of the anchoring. We used the value  $f = 3.5kT$ . The effective correlation length for the nematic order induced by this anchoring potential is estimated at various temperatures, the results are shown in Fig.3 alongside with the analytical fits. The modulation of curves in  $z$  is the result of a lamellar structure with the layers of mesogens alternating with that of the dendritic cores (in the latter the nematic order is negative). Correlation length is infinite in the smectic phase, it is found to be around  $300\text{\AA}$  within the transition region ( $T=496-498K$ ) and drops down to about  $50\text{\AA}$  at  $T=520-580K$ . The last value is of the order of the distance between the up and down bunches of mesogens (see, Fig.2).

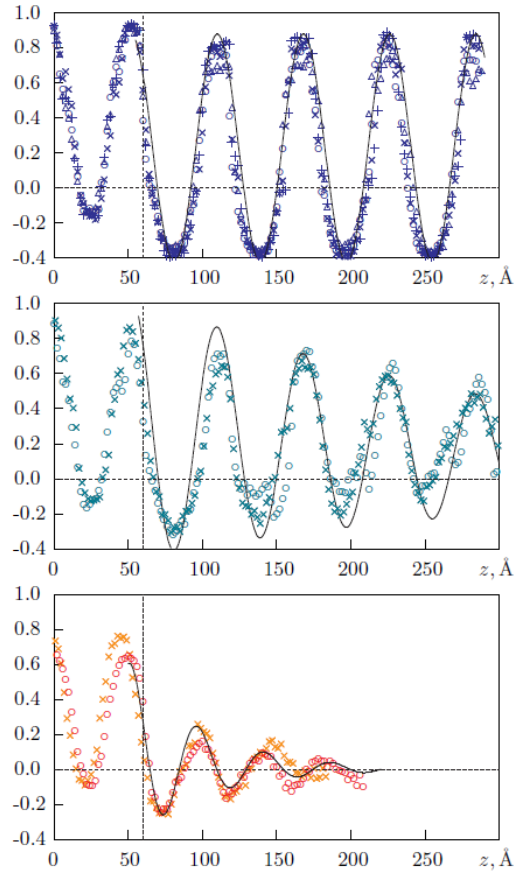


Fig.3. Effective correlation length estimated from the profiles of the nematic order parameter for the mesogens along Z-axis. The external step-like field is applied along Z-axis at distances  $z=0-60\text{\AA}$  from both walls. The results are averaged over the distances from both walls. Top frame:  $T=460\text{K}-490\text{K}$ , analytical fit:  $0.65(\cos(2\pi z_0/58\text{\AA})+0.35)$ ; middle frame:  $T=496\text{K}-498\text{K}$ , fit:  $0.75\exp(-z_0/300\text{\AA})(\cos(2\pi z_0/58\text{\AA})+0.4)$ ; bottom frame:  $T=520\text{K}-580\text{K}$ , fit:  $0.5\exp(-z_0/50\text{\AA})(\cos(2\pi z_0/45\text{\AA})+0.2)$ ,  $z_0=z-52\text{\AA}$ .

The step-like anchoring imposed on both walls is found not to change the properties of the system in the smectic phase, whereas the transition temperature is shifted up for about 10K due to obvious reason of stabilization of the ordered phase. However, the analysis performed in the vicinity of the transition reveals the same behavior as observed with no anchoring being imposed, in terms of splitting the system into smectic and columnar domains and the interchange of their fractions (Fig.1, on the left). Some properties are collected in Fig.4.

The study reveals that a short ranged step-like anchoring has a minimal effect (besides the shift of the transition temperature) on the way the phase transition from the smectic to isotropic phase takes place. It will be continued for the case of more sophisticated anchoring potentials with longer range, for instance those that can be realized via polymer brushes that contain mesogenic groups, or by other means.

The paper with the title “Simulation of a self-assembly of polyphilic liquid crystal dendrimers confined inside the pore with homeotropic anchoring” based on this study is currently under preparation.

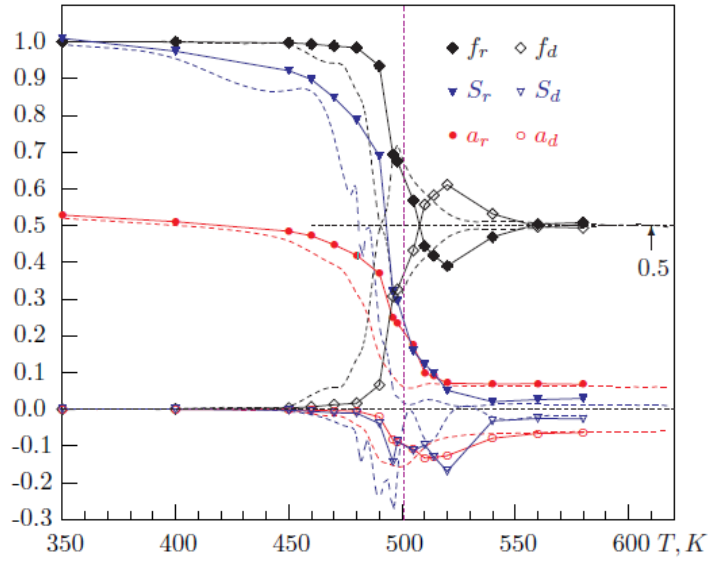


Fig.4. Comparison of the fractions of rod- and disc-like molecules  $f$ , weighted nematic orders,  $S$ , and weighted asphericities,  $a$  (all marked via  $r$  and  $d$ , respectively) for the case of bulk system with no anchoring (dashed lines) and with anchoring applied near both walls. Note basically the same behaviour but shift of the transition up by 10K.