Homogeneous alignment of liquid crystalline dendrimers confined in a slit-pore. A simulation study

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Abstract
In this work we present results from isobaric-isothermal (NPT) Monte Carlo simulation studies of model liquid crystalline dendrimer (LCDr) systems confined in a slit-pore made of two parallel flat walls. The dendrimers are modelled as a collection of spherical and ellipsoidal particles corresponding to the junction points of the dendritic core and to the mesogenic units respectively. Assuming planar uniform (unidirectional) soft anchoring of the mesogenic units on the substrates we investigate the conformational and alignment properties of the LCDr system at different thermodynamic state points. Tractable coarse grained force fields have been used from our previous work. At low pressures the interior of the pore is almost empty, since almost all LCDrs are anchored to the substrates forming two-dimensional smectic-like structures with the mesogens aligned along the aligning direction of the substrates. As the pressure grows the LCDrs occupy the whole pore. However, even at low temperatures, the smectic organization does not transmit in the interior of the pore and is preserved for distances of 2–3 mesogenic diameters from the walls. For this reason, the global orientational order decreases with increasing pressure (density). In the vicinity (2–3 mesogenic diameters) of the pore walls, mesogenic units preserve the smectic structure whose layers are separated by layers of spherical beads. In this region individual LCDrs possess a rod like shape.

Keywords: liquid crystalline dendrimers, homogeneous alignment, Monte Carlo simulation

(Some figures may appear in colour only in the online journal)

1. Introduction

Liquid crystalline dendrimers (LCDrs) are part of dendrimers which usually are derived through functionalization of common dendrimers with low molar mass liquid crystal molecules (Percec and Kawasumi 1992, Donnio et al 2007, Marcos et al 2007). Self-assembly and phase behavior of the combined supermolecules significantly depend on the type of LC-dendrimer combination (Donnio et al 2007, Rosen et al 2009, Nhu et al 2011, Nagy et al 2012). Inclusion of anisotropic molecules into nearly spherical dendritic scaffolds enables multifunctional anisotropic macromolecules to be obtained. This opens up the possibility of achieving a wide variety of physical properties with tailor-made potential applications. Consequently, rigorous research has been conducted in the last few years on the synthesis and characterization (Percec and Kawasumi 1992, Donnio et al 2007, Marcos et al 2007, Rosen et al 2009, Castela et al 2013, Kim et al 2013) as well as theory (Terzis et al 2000, Vanakaras and Photinos 2001, Peroukidis et al 2005), modeling and computational simulation (Hughes et al 2005, Vanakaras and Photinos 2005, Illytskyi et al 2010, Richardson et al 2011, Ostrovskii et al 2013) of these materials.

The interplay between the tendency of maintaining spherically symmetric conformation due to flexible core segments and tending towards anisotropic conformation as the result of peripheral mesogenic units determines the overall structural and dynamic properties of bulk LCDr systems. Strong competition between these two factors could be influenced by the kind
of pair interaction potential energies of dendritic segments and thermodynamic conditions on which the system is imposed. The phase behavior of bulk or confined LCDr system could also be highly affected by these two factors (Nhu et al 2011, Nagy et al 2012). Wilson and coworkers have proved that a bulk LCDr system exhibits isotropic, nematic and smectic phases depending on the length of mesogenic units and the temperature (Hughes et al 2005, Ilnytskyi et al 2010). According to their findings, as the system goes from isotropic to anisotropic state, single LCDr molecules could be changed from spherical shape to either rod-like or disc-like shapes depending on the kind of dendrimer–LC connectivity (side-on or end-on).

The study of ordered stable structures for a system of particles interacting through a specific kind of interaction is an interesting problem both from the scientific and technological points of view. This problem is still an active research curiosity. The search for its comprehensive and satisfactory solution poses a formidable challenge of academical and technological interests. Looking for these ordered equilibrium structures becomes more intricate when their system is under certain geometric constraints due to external confinements (Pineiro et al 2007).

The problem becomes more complicated when it comes to liquid crystalline dendrimer systems under external factors imposed by the mean field or by a confining geometry. Confinement of molecular phases in a porous medium usually modifies their overall properties, in terms of structure, phase behavior and molecular dynamics (Alcoutlabi and McKenna 2005, Alba-Simionesco et al 2006). The main reason behind these changes of properties arises from delicate energetic balance between adhesive (LCDr–surface interaction) and cohesive(inter/intra-dendritic interaction) forces, in addition to thermodynamic conditions. The global and local structural and alignment properties of confined LCDr system can be enormously affected by the strength of surface anchoring potential.

A confining surface with weaker adhesive force could affect positions and orientations of only a few molecules which are in the first vicinity. On the other hand, those with strong adhesive force can induce long ranged effect on the system.

Liquid crystals (LCs) are elastically soft materials with long range translational and orientational orders that may directly couple to the surface of the porous medium (Bellini et al 2001, Ghoufi 2014). The various possible arrangements adopted by LC systems of micro or macro scales with different shapes of confining pores and surface interactions have been widely investigated experimentally and quite well understood in the frame of continuum elastic theories, including the occurrence of director distortions or topological defects (Teixeira and Sluckin 1992). Through controlling the surface–LC interactions, usually by means of chemical and/or mechanical treatment of the substrate, a variety of alignments (homeotropic, planar, tilted, etc) of the LC medium with respect to the substrate are possible. However, in the case of LCDrs, the mechanism behind surface anchoring and alignment do not involve only the translational and orientational restrictions imposed by the substrate to its vicinal beads/mesogens but also the positional/orientational correlations among the dendritic segments. The stability of ordered mesophases could be enhanced or reduced by the presence of confining pores and it strongly affects the nature of the phase transitions (Iannacchione et al 1993, Guégan et al 2006, Kityk et al 2008, Lefort et al 2008). Computer simulation methods are quite unique tools to investigate the structure of nanoconfined LC/LCDr molecules (Care and Cleaver 2005, Ji et al 2009, Moradi and Hashemi 2011, Caneda-Guzmán et al 2014). They provide direct insight into the interfacial properties and the inhomogeneous nature of the confined phases.

Managing the macroscopic alignment of these anisotropic materials in confinement is a key factor for many of their potential applications. Thus, in a system of confined liquid crystals, the first aligned layer in the vicinity of the substrate would be used as the template to induce the next layer so that alignment could propagate throughout the range of the confined film depending on the temperature and the density of the system. However, in LCDrs, that seems unlikely due to the fact that the first layer of mesogenic units in the neighbourhood may be shielded by the core spherical beads under bead-wall repulsive potential circumstances. In this case, for the reason of chemical incompatibility, mesogens will avoid to get closer to the layer of beads above the first layer of mesogens. This breaks alignment correlations between the first and the next layers of mesogens. However, this might be resolved by making the confining wall attractive to both mesogens and beads. In this case, bead layer and mesogen layer would be formed in the first neighbourhood, not one over the other but in parallel. Thus, these first layers of each type could be templates to induce further layers. This situation is different for different anchoring conditions. The extent of layer propagation from the wall surface to the bulk region depends not only on the kind of anchoring conditions, it also depends on anchoring strength, monomer–monomer interaction potential and the thermodynamic conditions.

Several different models for common dendrimers (isolated and confined) (Wallace et al 2001, Gotze and Likos 2003, Klos and Sommer 2009, Lenz et al 2009) liquid crystal dendrimers (Hughes et al 2005, Vanakaras and Photinos 2005, Ilnytskyi et al 2010, Richardson et al 2011, Ostrovskii et al 2013) and dendronized polymers (Christopoulos et al 2003, 2006, Córdova-Mateo et al 2014) have been proposed and used for computer simulation studies of their properties. These models range from detailed atomistic to coarse grained ones. In atomistic models, detailed interaction potentials between individual atoms (molecules) should be considered rendering them as computationally expensive models. Alternatively, in coarse grained models groups of atoms are represented as united interacting sites, preserving at the same time the architectural characteristics of the dendrimer.

The main purpose of this work is to demonstrate Monte Carlo computational simulation results of a model LCDr system confined in a slit pore made of two parallel walls whose inner surfaces induce homogeneous planar alignment to the mesogens based on our previous work (Workineh and Vanakaras 2014). Mainly, structural and alignment properties of the target system have been reported. To our knowledge, no study results of LCDrs under confinement have been reported so far. The rest of the paper is organized as follows. In section 2 models and details of our simulation are presented and simulation results
and their discussions are presented in section 3. Finally, we wrap up our work with conclusions and remarks in section 4.

2. Simulation model and details

In this study, we consider a system of generation two, core functionality three and branch functionality two model LCDr (denoted as $G_2D_3$) confined in a slab geometry. The model single LCDr, its intra-dendritic interaction potential energy and LCDr–substrate interaction potential energy have been reported in our previous work (Workineh and Vanakaras 2014). Our current study is mainly based on the models developed in this reference. According to this model, the junction units are united atoms which represent collectively the atoms around each branching points. The junctions are connected with virtual bonds with variable length which preserve the architectural connectivity of the dendrimer allowing at the same time the junction units to sample available free volume in the interior of the dendrimer. With this assumption the dendrimer is composed of two different spherically symmetric sites (denoted with b) representing the junction points and one representing the core of the dendrimer. The mesogenic units (denoted with m) are assumed to be cylindrically symmetric and are connected by one of their ends to the G – 1 generation junction beads with virtual bonds (see figure 1(left)). As a result, a dendritic conformation is fully described with the positions of the junction sites $r_j$ and the positions and orientations of the mesogenic units $u_i$ and $\hat{u}_i$, respectively.

To model homogeneous anchoring conditions of the LCDr system confined in a slit pore made of two parallel impenetrable walls, $N = 108$ equilibrated $G_2D_3$ LCDrs have been duplicated throughout the volume of the slit according to cubic lattice arrangement. Duplication is made in such a way that the distance between any two LCDrs is far enough to consider the inter-LCDr potential energy to be zero, initially. The two confining parallel walls are placed at $z = 0$ (bottom wall) and $z = L_z$ (top wall). Initially, any LCDr is placed well above the bottom wall and below the top wall in order to avoid initial segment-surface overlap.

In the level of structural resolution described above, the total intra/inter-molecular potential energy of LCDr system is the sum of the bonded (B) and non-bonded (NB) pair interactions,

$$ U = U^B + U^{NB} = \sum_{k,n} U^B(l_{kn}) + \sum_{i,j} U^{NB}_{pq}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j). $$

(1)

Here $l_{kn}$ is the length of the virtual bond connecting the bonded junctions $k, n$. The indexes $p, q$ in $U^{NB}_{pq}$ may be either $b$ or $m$ denoting junction beads and mesogenic segments, respectively. $\mathbf{r}_{ij}$ is the vector that connects the centres of the non-bonded sites $i, j$ and the unit vector $\hat{u}_i$ denotes the orientation of the $i$th mesogenic unit.

For the bonded potential we have adopted a simple pair potential which corresponds to a freely fluctuating bond;

$$ U^B(l) = \begin{cases} 0, & l_{\text{min}} < l < l_{\text{max}} \\ \infty, & \text{otherwise,} \end{cases} $$

(2)

where $l_{\text{min}}$ and $l_{\text{max}}$ are the minimum and maximum allowed center to center separation distances between two bonded segments. The interaction potential of two non-bonded sites of type $p$ and $q$ is given by

$$ U^{NB}_{pq}(r_{ij}, p = q = b) = \begin{cases} U^{NB}_{bb}(r_{ij}), & p = q = b \\ U^{NB}_{mb}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j), & p = b, q = m \\ U^{NB}_{mm}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j), & p = m, q = b. \end{cases} $$

(3)

The spherical junction segments are modeled as Lennard–Jones spheres interacting through $(b\text{-}b)$ interaction as,

$$ U^{LB}_{bb}(r_{ij}) = 4\epsilon_{b\text{bb}} \left[ \left( \frac{\sigma_{b\text{bb}}}{\epsilon_{b\text{bb}}} \right)^{12} \left( \frac{\sigma_{b\text{bb}}}{\epsilon_{b\text{bb}}} \right)^{6} \right], $$

(4)

and the mesogens are modelled as cylindrically symmetric soft ellipsoids interacting with the widely used Gay–Berne interaction potential (Gay and Berne 1981),

$$ U^{NB}_{mm} = 4\epsilon_{m\text{mm}} \left( \frac{\sigma_{m\text{mm}}}{\epsilon_{m\text{mm}}} \right)^{12} - \left( \frac{\sigma_{m\text{mm}}}{\epsilon_{m\text{mm}}} \right)^{6}, $$

(5)

with $r = (r_{ij} - \sigma_{m\text{mm}}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) + \sigma_{b\text{mm}})$. Mathematical descriptions of relative orientation dependent quantities, $\sigma_{b\text{mm}}$ and $\sigma_{m\text{mm}}$ and some associated parameters can be refereed from our previous work (Workineh and Vanakaras 2014).

The bead–mesogen interaction potential is modelled by the Gay–Berne potential of equation (5), where either $\mathbf{u}_i$ or $\mathbf{u}_j$ is considered zero and based on the parametrization shown in the table 1.

Interactions of a Gay–Berne particle with solid surfaces have been described in several ways (Gruhn and Schoen 1997, Gruhn and Schoen 1998, de Miguel and Vega 2002, Mima and Yasuoka 2008, Workineh and Vanakaras 2014). In this study we use the interaction model introduced in reference (Workineh and Vanakaras 2014) and references therein.

According to this model, each dendritic segments (beads or mesogenic units) of an LCDr with coordinates $(x, y, z)$ interacts with one of the two phantom mesogens centred at either $(x, y, z)$ and $(x, y, 0)$ in the bottom wall or $(x, y, 0)$ in the bottom wall. The orientation of the phantom mesogens with respect to the surface determines the anchoring conditions the substrate imposes to the LCDrs. In this study only uniform (unidirectional) planar anchoring condition is considered therein assuming that the phantom mesogens point along a given direction on the surface which is chosen to be the $x$-axis.

The mesogen–surface interaction effective potential is given by the anisotropic $9 - 3$ Lennard–Jones potential;

$$ U^{mvw} = \frac{2\pi}{3} \frac{1}{3} \epsilon_{mvw}(\mathbf{r}_{vw}, \mathbf{u}_v, \mathbf{u}_w) \left[ \frac{1}{15} \left( \frac{\sigma_{mvw}}{\epsilon_{mvw}} \right)^{12} \left( \frac{\sigma_{mvw}}{\epsilon_{mvw}} \right)^{6} \right]^3. $$

(6)

where $r_{\text{eff}} = r_{ij} - \sigma_{m\text{mm}}(\mathbf{r}_{ij}, \mathbf{u}_i, \mathbf{u}_j) + \sigma_{b\text{mm}}$, $\mathbf{u}_v$, and $\mathbf{u}_w$ are unit vectors along the long axes of mesogenic unit $i$ and phantom mesogen $j$. $\mathbf{r}_{ij}$ is the intermolecular vector which connects the center of mass of a mesogenic unit with its phantom counterpart which is located at less distant point of the surface to the actual mesogen. For unidirectional planar anchoring conditions, $\mathbf{u}_i = \hat{x}$. Exactly the same equation as equation (6) is...
used to model bead–wall interaction potential energy except that $u_i = 0$ in this case. Mathematical descriptions for $\sigma_{0\text{mm}}$ and $\epsilon_{0\text{mm}}$ are similar to those of $\sigma_{\text{mb}}$ and $\epsilon_{\text{mb}}$, respectively, which can be given as:

$$\sigma_{0\text{mm}} = \sigma_{\text{mb}} \times \left[ 1 - \frac{\lambda}{2} \left( \frac{\mathbf{r}_{i}(\mathbf{u}_i, \mathbf{u}_j)}{1 + \lambda \mathbf{u}_i(\mathbf{u}_i, \mathbf{u}_j)} + \frac{\mathbf{r}_{j}(\mathbf{u}_i, \mathbf{u}_j)}{1 - \lambda \mathbf{u}_i(\mathbf{u}_i, \mathbf{u}_j)} \right) \right] \frac{1}{2}$$

(7)

and

$$\epsilon_{0\text{mm}} = \epsilon_{\text{mb}} [\epsilon_1(\mathbf{u}_i, \mathbf{u}_j)]^{2\nu} \times [\epsilon_2(\mathbf{r}_i, \mathbf{u}_i, \mathbf{u}_j)]^{2\nu},$$

(8)

with

$$\epsilon_1 = \left[ 1 - \chi_w^2(\mathbf{u}_i, \mathbf{u}_j) \right]^{1/2}$$

(9)

and

$$\epsilon_2 = 1 - \frac{\chi_w}{2} \times \left[ \frac{(\mathbf{r}_{i}(\mathbf{u}_i, \mathbf{r}_j, \mathbf{u}_j))^2}{1 + \lambda \mathbf{u}_i(\mathbf{u}_i, \mathbf{r}_j, \mathbf{u}_j)} + \frac{(\mathbf{r}_{j}(\mathbf{u}_i, \mathbf{r}_j, \mathbf{u}_j))^2}{1 - \lambda \mathbf{u}_i(\mathbf{u}_i, \mathbf{r}_j, \mathbf{u}_j)} \right].$$

(10)

where $\chi_w = \frac{k^2 - 1}{k^2 + 1}$ with $k = L/D = 3$ (length to diameter ratio), the shape anisotropy of the ellipsoidal particle, $\chi'_w = \frac{k^2 - 1}{k^2 + 1}$ with $k' = E_{\text{ee}}/E_{\text{ee}}$ (ratio of side–side to end–end configuration energy), a measure of the anisotropy of the soft interactions and tuning parameters, $\nu_w = 1$ and $\mu_w = 2$. All the constants associated with LCDr–surface interaction potential energy are included in table 1.

Plots of the mesogen–surface interaction potential as a function of the distance $r$ of the mesogenic unit from the surface for unidirectional planar alignments are shown in figure 2 for chosen mesogen–surface configurations at $\phi = 0$ and $\pi/4$. According to this plot, azimuthally parallel configurations of real mesogens and phantom mesogens are energetically favoured in comparison to perpendicular arrangements at higher polar angles. Nevertheless, at lower polar angles, variation in azimuthal angle hardly affects surface–mesogen interaction potential. Controlling parameters, $\nu_w = 1$, $\mu_w = 2$, $\chi_w = 0.8$ and $\chi' = 0.382$ are used to produce figure 2 and are used throughout this work.

Analysis was performed by dividing stored system configurations into $L_z/\delta L$ equidistant slices ($L_z$ is the slit gap and $\delta L$ is slice width) and calculating averages of relevant observables in each slice. This yielded profiles of quantities such as number density, $\rho^0(z)$ (w refers to either bead or mesogen), from which structural changes could be assessed. Number density profile along surface normal ($z$–axis) direction could be calculated as,

$$\rho^0(z) = \frac{1}{N^w} \left\{ \sum_i \delta(z - r_i \cdot \hat{z}) \right\},$$

(11)

where $r_i$ is the position vector of center of mass of site $i$ and, $N^w$ is the total number of beads ($N^b$) or mesogens ($N^m$). Orientational order profiles were also calculated, particularly from orientational order tensor as;

$$S_{\alpha\beta}(z) = \frac{\langle Q_{\alpha\beta}(z) \rangle}{\langle N^m(z) \rangle},$$

(12)

where $Q_{\alpha\beta}(z) = \frac{1}{2} \sum_i (3(u_{i\alpha} u_{i\beta} - \delta_{\alpha\beta}))$, is a traceless symmetric $3 \times 3$ orientational order tensor and $N^m(z)$ is the instantaneous number of mesogens occupying the relevant slice of volume, $V_z = L^2 \delta L$ with constant slice width of $\delta L$. $S_{\alpha\beta}(z)$
measures orientational order variation across the confined films with respect to the substrate normal.

Standard metropolis Monte Carlo (MC) computer simulation has been used to investigate structural behaviour and the possibility of alignment transmission from the surface to the bulk in a system of LCDrs confined in a slit pore. MC simulations have been performed in isobaric-isothermal (NPT) statistical ensemble. The confining box has dimensions $L_x = L_y = L_0$ and $L_z = 20\sigma_{0,\text{nn}}$. The periodic boundary conditions along the $x$- and $y$-directions give an infinite slit pore. Three systems were initially prepared at reduced pressure, $P^* = P_{0,\text{nn}}/\epsilon_{0,\text{nn}} = 0.0$ and reduced temperatures, $T^* = T_{k_B}/\epsilon_{0,\text{nn}} = 1.0$, 1.5 and 2.0. Then, each systems are compressed with pressure increment of 0.05 up to $P^* = \tilde{P}_{\text{max}}$ at constant respective temperatures. The volume compression is made along the $x$- and $y$-directions keeping the slit gap constant. At each pressure/temperature MC simulations with $10^6$ equilibration and $10^6$ production cycles have been performed. In an MC cycle one random displacement on average is attempted for each molecular segment in addition to one random reorientation for the mesogenic units. Finally, we allow the volume of the box to change ($\Delta V = V_o - V_n$) according to isobaric-isothermal distribution function $f_{\text{NPT}} \propto e^{-\left(U_{\text{new}} + P\Delta V\right)/k_B T}$ with the acceptance probability,

$$P_{\text{acc}} = \min\left[1, e^{-\beta \left[P_{\text{new}}(L_n^2 - L_o^2) + (U_{\text{new}} - U_o) - 2K(\frac{\Delta V}{T})\right]}\right],$$

(13)

where $L_n$ and $L_o$ are new and old lengths, respectively, of the box along $x$- and $y$-directions, $\beta$ is Boltzmann constant, $P$ is pressure, $U_n$ and $U_o$ are new and old, respectively, potential energies. The range of random translations/reorientations and volume change are tuned to give an overall acceptance ratio of about 33%.

3. Simulation results

The pressure–density phase diagram of model LCDr system confined in a slit-pore under uniform planar anchoring condition is shown in figure 3. The density was simply calculated as: Density = (Number of beads + Number of mesogens)/(Volume of the slit-pore). It seems at $T^* = 1.0$ the volume of the slit has suddenly compressed at $P^* = 0.5$ changing the density abruptly. For $P^* \geq 0.5$, change in volume/density is too slow showing that the box was almost filled at $P^* = 0.5$. For the other systems, $T^* = 1.5$ and $T^* = 2.0$ the transition looks smoother compared to that of $T^* = 1.0$ system.

The global orientational order parameters along each directions, derived from orientational order tensor shown in equation (12), are also depicted in figure 4. As the density grows the orientational order parameter along the aligning direction decreases unlike bulk LC/LCDr system whose global orientational order parameter increases with density (Steuer et al 2003, Hughes et al 2005). This happens due to the fact that at lower pressures (lower density) the surface effect is dominant so that almost all the mesogenic units are anchored to the surface and oriented in the aligning direction. In these same points, the system is dictated by the external fields imposed by the walls. As the pressure increases some mesogens and beads leave the surfaces of the walls and form successive layers over the first layer. This phenomenon continues until
the space in the box fills. The growth of mesogenic layers along the direction normal to the surface do not guaranty the transmission of mesogenic alignment along the aligning direction. The alignment transmission rate decays with the perpendicular distance from both surfaces of the walls. For instance, the first 2–3 perpendicular layers are almost perfectly aligned with the field (aligning direction) depending on the temperature. Beyond this distance from both upper and
lower walls the alignment of mesogens along the field significantly decreases.

The temperature has an adverse effect on global orientational order parameters along each coordinate axis. As the temperature grows, most mesogens, except those in the immediate neighbourhood of the walls, receive adequate thermal energy to get out of surface trap. As the result, their conformation (position and orientation) is governed by the thermodynamic effect enabling them to align randomly in space. A system of randomly oriented mesogenic units ends up with an isotropic value of orientational order parameters. That is clearly evident from the right panel of figure 4.

In addition, the outcomes of homogeneous surface-LCDr system simulations are summarized by the snapshots shown in figures 5–9. The effect of substrate on the configuration of beads and mesogens is readily apparent from all these, with ordered layers of planarly aligned monomers residing nearby the surface of the wall region. Clear micro-segregation between beads and mesogens is revealed in the snapshots. This separation could be dictated by either the wall or thermodynamic effect. In the vicinity of the walls, the wall effect is dominant over thermodynamic effect so that mesogens are favoured to align in the aligning

**Figure 7.** Snapshots of systems of model LCDr confined in a slit-pore under uniform planar anchoring conditions at $P^* = 1.5$ (a) at $T^* = 1.0$, (b) at $T^* = 1.5$ and (c) at $T^* = 2.0$.

**Figure 8.** Top or bottom view of a layered structures of LCDrs on the wall (remove the wall for clear vision) in increasing order of pressure $P^* = 0.1, 0.5$ and 1.0, respectively from left to right at fixed $T^* = 1.0$.

**Figure 9.** Single LCDrs are changed from globular (spherical) shape to rod like shape, most importantly in the vicinity of the confining walls.
Figure 10. Mass distribution of beads (left column) and mesogenic units (right column) along the surface normal direction, z-axis, as the function of distance from the surface at different pressures and temperatures. The rows from top to bottom refer to $P^*=0.1$, 0.5 and 1.0, respectively.

Figure 11. Average local orientational order parameter along the aligning direction as the function of perpendicular distance $z$ from the surface at $P^*=0.5$ (a) and $P^*=1.0$ (b).
direction. However, in the regions far from the walls, typical thermodynamic effect is dominant over the wall effect. In this region, hexagonal like self-organization of LCDrs are noticed as it is noted by Ilnytski et al. (2010). The range of this bulk region depends on both the temperature and pressure. At lower pressures a mono-/bilayers of mesogens and beads along the surface normal direction and several layers along the aligning direction have been formed. The orientation of most mesogenic units at these pressures is along the aligning direction. At this state, mesogens form well defined 2D smectic A like structure with layers of beads in between successive mesogenic layers (see figure 8). As the result, single LCDrs are changed from their non-confined shape, ‘spherical’ to ‘rod’ like shapes in the vicinity of the walls where their mesogens are aggregated at the two ends of the rod as shown in figure 9.

As the pressure grows the number of plane-parallel layer increases at the expense of perpendicular layers as shown sequentially in figures 5–8. Further compression of simulation box results in making some mesogens and beads to leave the previous layers and form the next ones. This phenomena continues until the system is no more compressible. However, the pace of layer transmission is not uniform. As we get far from the surface perpendicular layer formation decays therein creating isotropic state regions around the middle of the slit.

In order to quantitatively describe the observations revealed in the snapshots, additional averaged quantities have been calculated. These quantities are number density and local orientational order parameters (see equations (11) and (12)) of mesogens along the aligning direction. The density profiles depicted in figure 10 show the adsorption characteristics for the film confined between the homogeneous planar surface regions as the functions of distance along surface normal direction. It is immediately apparent from this figure that layer propagation is highly damped when the distance from the surface increases, specially, in lower pressure cases. In addition, different peak values at the surfaces of the walls at different pressures tells us that some of the monomers have left the surface as the result of increase in pressure. This justifies what has been seen in figure 8 where clear decrease in in-plane number of layers is realized. Increasing pressure leads to formation of layers one over the other with a periodicity of $\sigma_{\theta \theta}$ (for beads) and $\sigma_{\varphi \varphi}$ (for mesogens) in the direction normal to the surface. Surface induced mesogenic layers can traverse the whole region of the slit at higher pressures and lower temperature ($T^* = 1.0$) with dumped like oscillation going from the surface to the middle region (see figure 10(f)). Considerable change in the distribution of beads as the function of distance from the surface with the pressure has also been seen for $T^* = 1.0$. For other systems, $T^* = 1.5$ and $T^* = 2.0$, the change is not that significant.

A more complete understanding of the orientational aspects of the substrate-induced ordering in this system can be obtained from the local components of orientational order tensor; $S_{zz}(z)$ or $S_{xx}(z)$ (diagonal components of the order tensor). For perfect homogeneous planar alignment, $S_{xx}(z)$ should tend to 1 and $S_{zz}(z)$ should tend to $-0.5$. Figure 11 shows $S_{zz}(z)$ profiles as the function of perpendicular distance from the surfaces of the walls. As predicted, the value of $S_{zz}(z)$ is nearly 1 in the first two local maxima from both top and bottom walls for all pressure and temperature values. After these layers, it decreases even up to negative value highly depending on the pressure and temperature. At lower temperature and higher pressure there looks a better alignment transmission from the surface to the bulk but still not uniform. Even much lower temperature ($T^* = 0.5$) simulation has been performed to test if there is any other better alignment transmission but we end up with no significant difference from that of $T^* = 1.0$. Consequently, achieving a uniform perpendicular layer of mesogens of LCDrs oriented in the aligning direction looks challenging task at any surface–LCDr coupling or thermodynamic conditions.

4. Conclusions

A coarse-grained computational simulation study of a $G_2D_1$ model LCDr system confined in a slit-pore of two parallel impenetrable walls under uniform planar anchoring condition has been carried out. The simulation results show significant conformational and structural changes driven by the effect of the substrate at each state points. Substrate induced smectic-A like layers of mesogenic units separated by layers of dendritic core (beads) have been observed along the aligning direction. In the direction normal to the plane of the surface, the development of mesogen layer formation is pressure dependent. At lower pressure, there was only single layers of mesogens and beads in the vicinity of the substrates. As the pressure grows, the number of perpendicular mesogenic layers grows. This transmission of layer formation or alignment of mesogens in the direction perpendicular to the surface is not uniform, but decays as it goes from the vicinity to the middle of the slit. In the regions where smectic-A like structures of mesogenic units are apparent, mesogens from a single LCDr contribute to smectic layers in the left and right side of dendrimer core (beads). According to simulation results strong coupling between internal molecular structure and molecular environment is identified. This leads to mesogenic groups becoming aggregated at the two ends of LCDrs in the regions where the effect of the walls is dominant. Consequently, individual LCDr molecules change their shapes from ‘spherical’ in to ‘rod’ shape.

The LCDr studied here could represent a wider range of polyphilic mesomorphic materials in which separate building blocks with different types of interaction sites are combined. Substrate induced micro-phase separation and alignment transmission in these materials opens up the opportunity to self-assemble in to well-defined nanostructures for different potential applications. Potential applications could be molecular electronics, opto-electronics, photonics, nanotechnology, etc. The CG-simulation method presented here can be used as an inspiration towards further simulation and experimental studies on these systems. As a result, it could be a useful tool in helping design confined nanoscale structures for future applications.
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