

## Origin of tilted-phase generation in systems of ellipsoidal molecules with dipolar interactions

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We report Monte Carlo simulation studies of tilted smectic liquid crystal phases exhibited by systems of rodlike molecules having permanent dipole moments. For a theoretical understanding of the microscopic origin of the tilted smectic phases, different systems consisting of prolate ellipsoidal molecules of three different lengths, embedded with two symmetrically placed terminal antiparallel dipoles, are investigated. We find that the presence of a stable tilted phase depends crucially on the molecular elongation, which effectively makes the dipolar separation longer. We observe that in the case of molecules with transverse dipoles the tilt angle in the smectic phase gradually increases from zero to a large magnitude as we increase the molecular length, whereas systems with longitudinal dipoles show small tilts over different elongations. In this work we determine the combined contribution of dipolar separation and transverse orientations in generating biaxial liquid crystal phases with large tilt angles.

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Liquid crystals exhibit a rich variety of tilted layered mesophases arising from the diversity in both the in-layer positional arrangements of the molecules and in the average molecular tilt orientations with respect to the layer normal [1,2]. The simplest example of a tilted smectic phase is the smectic *C* (SmC) phase, where the centers of mass of the tilted molecules are randomly distributed in two-dimensional fluidlike layers along with a long range orientational ordering of molecules over the bulk system. The microscopic origin of tilted-phase generation in liquid crystals has been a much discussed problem. However, the topic remains unsolved in certain aspects. The origin of the tilted smectic phases is much more complex than that of the orthogonal smectic phases since the existence of a tilted phase is not a favored one because the packing of tilted rodlike molecules in a layer plane needs more area than untilted molecules. This phase can be achieved only if there exist additional specific interactions giving the requisite tilt. It is essential to understand the structure-property relationship to find the basic interactions giving rise to tilt in a smectic phase. In experimental studies, the occurrence of SmC phase has been mostly found in the presence of a lateral component of the permanent dipole moment in the organic molecules [1,2]. As the number of such dipoles increases on a molecule, the tendency to form a SmC phase also increases [3]. McMillan gave the mean field theory on the formation of the SmC phase based on the presence of at least two outboard terminal transverse dipoles [4]. However, a freezing of rotation of the molecules was considered during such a SmA to SmC phase transition that contradicted NMR [5] and neutron scattering experiments [6] which have shown the free rotation of molecules in tilted smectic phases. Wulf attempted to relate the formation of a SmC phase to the packing requirements of the zigzag shaped molecules based on purely steric interactions [7]. However, the lowering of free energy was associated with a freezing of rotations. A zigzag model made of seven soft repulsive spherical particles with two terminal ones at an angle  $45^\circ$  from the five in the line core

showed a tilted phase but the tilt orientation was random and the equilibration process was elaborate [8]. A model based on three rigidly linked hard spherocylinders arranged in a zigzag fashion have shown the presence of a SmC phase [9]. However, the simple model particles built by assembling ellipsoidal Gay-Berne (GB) particles in a zigzag way was unable to show tilted phases [10]. Simulations of rodlike GB molecules with a single dipole at various positions and orientations have not convincingly shown tilted phases. Indeed, earlier claims of tilted smectics, being observed in systems of transversal [11] and axial [12] monodipole GB molecules, are probably due to small and fixed size samples and to the too limited duration of the simulations [12,13]. On the other hand, simulation studies of GB molecules with multiple dipoles have only shown limited success. In the computer simulation study by Zannoni *et al.* [14], the longitudinal components rather than the lateral components of dipole moments were found to be generating a tilted phase for GB molecules having two antiparallel dipoles. In their study, weak nonzero tilts were found for the system of molecules with dipole moments making an angle  $\phi = 0^\circ$  or  $60^\circ$  with the long axis. Similar results were found by Saha *et al.* [15] for a large dipolar orientation  $\phi = 120^\circ$ . As the compounds exhibiting tilted smectic phases generally have lateral dipole moments, the absence of a tilted phase in these conventional molecular models, in the case of a transverse dipolar orientation  $\phi = 90^\circ$ , remains an interesting problem. Our aim in the present Rapid Communication is to explore the role of dipolar interactions as the molecular level origin of tilt generation. We have investigated systems of dipolar GB mesogens where two terminal antiparallel dipoles are placed symmetrically on the long axis of each molecule and our study reveals that the separation between the two dipoles could be an important factor controlling the tilt angle. The tilt angle increases with dipolar separation from zero to a significant magnitude for transverse dipoles. On the contrary, longitudinal dipoles produce a weak effect. It is worth mentioning that our study shows the tilted-phase generation due to the contribution of transverse dipolar interactions. The nonelectrostatic part of the pair interaction is represented by the GB potential, which is a modified form of the Lennard-Jones potential, considering the anisotropy in shape and interaction of the molecules.

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The interaction between two GB ellipsoids  $i$  and  $j$  is given by  $U_{ij}^{\text{GB}}(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) = 4\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)(\rho_{ij}^{-12} - \rho_{ij}^{-6})$ , where  $\rho_{ij} = [r_{ij} - \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) + \sigma_0]/\sigma_0$ . Here  $\mathbf{r}_{ij}$  is the separation vector between the centers of mass of the molecules. The unit vectors  $\hat{u}_i$  and  $\hat{u}_j$  represent the orientations of the molecules.  $\sigma_0$  is the minimum separation for a side-by-side pair of molecules determining the breadth of the molecules. The minimum separation for an end-to-end pair of molecules  $\sigma_e$  is a measure of the length of the molecules. The anisotropic contact distance  $\sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)$  and the depth of the interaction well  $\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)$  depend on the the shape anisotropy parameter  $\kappa = \sigma_e/\sigma_0$  and the energy depth anisotropy parameter  $\kappa' = \epsilon_e/\epsilon_s$ , which are defined as the ratios of the contact distances and energy well depths in the end-to-end and side-by-side configurations. The anisotropy of the well depth  $\epsilon$  is also controlled by two additional parameters  $\mu$  and  $\nu$ . An explicit description of the GB interaction can be found in the original paper [16]. The well depth in the cross configuration is written as  $\epsilon_0$ .  $\sigma_0$  and  $\epsilon_0$  define the length and energy scales. We have used reduced units (\*) in our calculations by expressing lengths and interaction energies in units of  $\sigma_0$  and  $\epsilon_0$ , respectively. Rodlike GB ellipsoids exhibit isotropic, nematic, untilted SmA, SmB, and crystal phases in general at different parts of the phase diagram [17]. In the present work, we put two terminal point dipole moments on the symmetry axis of each GB molecule, separated by a distance  $d^* = (\kappa - 1)$  along the axis. We have studied the bulk phase behavior for three different values of  $\kappa$  (3, 4, and 5), keeping the other parameters fixed to their original values  $\kappa' = 5$ ,  $\mu = 2$ ,  $\nu = 1$  in order to investigate the effects of varying the dipolar separation to higher values. The electrostatic interaction energy between two such dipolar ellipsoids is given by  $U_{ij}^{d^*} = \sum_{\alpha, \beta=1}^2 \frac{\mu_{i\alpha}^* \mu_{j\beta}^*}{r_{\alpha\beta}^{*3}} [(\hat{\mu}_{i\alpha} \cdot \hat{\mu}_{j\beta}) - 3(\hat{\mu}_{i\alpha} \cdot \hat{r}_{\alpha\beta})(\hat{\mu}_{j\beta} \cdot \hat{r}_{\alpha\beta})]$ , where  $\mathbf{r}_{\alpha\beta}^* (= \mathbf{r}_{j\beta}^* - \mathbf{r}_{i\alpha}^*)$  are the vectors joining the two point dipoles  $\boldsymbol{\mu}_{i\alpha}^*$  and  $\boldsymbol{\mu}_{j\beta}^*$  on the molecules  $i$  and  $j$  at the positions  $\mathbf{r}_{i\alpha}^* = \mathbf{r}_i^* \pm \frac{d^*}{2} \hat{u}_i$  and  $\mathbf{r}_{j\beta}^* = \mathbf{r}_j^* \pm \frac{d^*}{2} \hat{u}_j$ . Here we have used a reduced dipole moment  $\mu^* \equiv \sqrt{\mu^2/\epsilon_0\sigma_0^3}=1.0$  which for a molecular diameter of  $\sigma_0 = 5 \text{ \AA}$  and an energy term  $\epsilon_0 = 1.4 \times 10^{-14} \text{ erg}$  corresponds to a value  $\mu \approx 1.32 \text{ D}$ , plausible for real molecules. The long range nature of the dipolar interaction is taken into account with the reaction field method [18], where the reduced radius of the reaction field cutoff sphere was in the range  $5.0 \leq R_c^* \leq 6.0$  and  $\epsilon_{\text{RF}} = \infty$  was the dielectric constant of the medium outside the cutoff sphere. The total interaction between two dipolar molecules is the sum of the GB pair potential and the dipole-dipole interaction terms with long range correction.

We have performed Monte Carlo (MC) simulations in the isothermal-isobaric (constant  $NPT$ ) ensemble with periodic boundary conditions imposed on a system of  $N = 1372$  dipolar molecules. We have used an orthogonal simulation box where the box dimensions were varied independently during simulation of smectic phases so that the system may fit itself to its most suitable configuration at each state point ( $P^* \equiv P\sigma_0^3/\epsilon_0$ ,  $T^* \equiv K_B T/\epsilon_0$ ). This type of volume sampling is preferred, rather than imposing cubic symmetry upon the simulation box, to minimize anisotropic stresses when the smectic phases are formed. All the systems were prepared initially in a completely disordered isotropic phase in a cubic

box by melting a crystal structure at sufficiently low pressure. We then increased the pressure successively by steps of  $\Delta P^* = 0.10$  or less (near a transition). In each case, at a given pressure, the final equilibrated configuration obtained from the previous lower pressure was used as the initial configuration. At each state point, the system was equilibrated for  $3 \times 10^5$  MC cycles and  $3 \times 10^6$  MC cycles were used near a transition. During each MC cycle, each molecule was randomly displaced and reoriented using metropolis criteria, where the reorientation moves were performed using the Barker-Watts technique [18]. One of the three box sides was attempted to change during each MC cycle. The acceptance rates of the rototranslational moves of molecules and volume moves were adjusted to 40%.

In order to fully characterize different phases of the system, various order parameters were computed. The average orientational ordering is determined from the second-rank tensorial order parameter  $Q_{\alpha\beta}$  defined as  $Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N (\frac{3}{2} u_{i\alpha} u_{i\beta} - \frac{1}{2} \delta_{\alpha\beta})$ , where  $\alpha, \beta = x, y, z$  and  $\hat{u}_i$  is the molecular end-to-end unit vector of molecule  $i$ . The nematic order parameter  $S$  is given by the largest eigenvalue of the ordering tensor  $Q_{\alpha\beta}$  and the corresponding eigenvector defines the phase director. The value of  $S$  is close to zero in the isotropic phase and tends to 1 in the highly ordered phase.

We have investigated the smectic structures over various elongations  $\kappa = 3, 4$ , and 5, respectively, at fixed temperatures  $T^* = 1.00, 1.25$ , and 1.50. At these low temperatures we observed a jump in  $S$  directly from  $S \sim 0.10$  to  $S \sim 0.95$  during a direct isotropic to tilted smectic transition with no nematic phase in between. Here the smectic order predominantly results from strong dipolar interactions. Pairing of terminal dipoles stabilizes the layered smectic phase over the nematic phase which might be obtained in this model for other combinations of temperature and pressure not studied here. To measure the average tilt angle  $\langle \theta \rangle$  of the phase director about the layer normal, we have used the method described in Ref. [14], i.e., in smectic phases we first find the sets of particles for which the first neighbor distance is  $\leq 1.3\sigma_0$ . Each such set forms a different layer. Then we find the normal to each such layer by a least squares method. The average normal is obtained by averaging the components over all the layers of a single MC configuration. The angle  $\theta$  between the phase director and the layer normal determines the tilt. Then we measure its average value over a number of configurations. Since all the tilted phases are expected to be biaxial, we have measured the biaxial order parameter  $\langle R_{2,2}^2 \rangle = \langle \frac{1}{2}(1 + \cos^2 \beta) \cos 2\alpha \cos 2\gamma - \cos \beta \sin 2\alpha \sin 2\gamma \rangle$  as described in Ref. [19], where  $\alpha, \beta, \gamma$  are the Euler angles giving the orientation of the molecular body set of axes with respect to the laboratory set of axes. To understand the structure of the phases we also calculate the radial distribution function,  $g(r) = \frac{1}{4\pi r^2 \rho} \langle \delta(r - r_{ij}) \rangle_{ij}$ , where the average is taken over all the molecular pairs. The bond orientational order parameter (BOOP) is used to distinguish between a SmC and tilted SmB phase. The local BOOP for a molecule at the position  $\mathbf{r}_i$  with  $m$  nearest neighbors is given by  $\psi_6(r_i) = \frac{1}{m} \sum_{j=1}^m e^{i6\theta_{ij}}$ , where  $\theta_{ij}$  is the angle between the bond  $\mathbf{r}_{ij}$  and a fixed reference axis. We consider the neighbor molecules such that  $r_{ij}^* \leq 1.5$ . The average value is given by  $\psi_6 = \frac{1}{N} \sum_{j=1}^N \psi_6(r_j)$ . We have generated well equilibrated tilted smectic phases for three different elongations  $\kappa = 3, 4, 5$  with two different dipolar

orientations  $\phi = 0^\circ$  and  $90^\circ$  in order to explore separately the roles of two terminal longitudinal dipoles and two terminal transverse dipoles in producing tilted phases over various dipolar separations. The structure of the phases were changed significantly over different elongations. The snapshots of the phases are shown in Figs. 1 and 2 and the resultant variation of tilt is shown in Fig. 3(d). In case of mesogens having longitudinal dipoles, hexagonal in-layer positional ordering is found in systems of longer molecules, characterized by the values  $\psi_6 \approx 0.6$  and  $0.8$ , respectively for  $\kappa = 4$  and  $5$ . From the plots of  $g(r)$ , shown in Fig. 3(a), we see that longer molecules exhibit short range positional ordering. Hence we identify these phases as the weakly tilted analogs of the SmB phase. The shortest molecules generated a smectic phase with in-layer tetragonal ordering of molecules. Sharp peaks in  $g(r)$  at higher separations indicate the crystalline nature of the phase. Again the energy distribution in tilted phases show an interesting behavior over different elongations. For the shortest molecules, the dipolar energy remains slightly stronger ( $U^{d*} \approx 51\%$  of  $U^{\text{total}*}$ , where  $U^{d*}$  is the average dipolar energy per particle and  $U^{\text{total}*}$  is the average total energy per particle) but the GB interaction wins over the dipolar interactions for higher elongations ( $U^{\text{GB}*} \approx 51\%$ ,  $53\%$  of  $U^{\text{total}*}$  for  $\kappa = 4, 5$  where  $U^{\text{GB}*}$  is the average GB interaction energy per particle). The amount of tilt for the shortest molecules  $\langle \theta \rangle = 1.6^\circ$  decreases to  $\langle \theta \rangle = 0.6^\circ$  in the  $\kappa = 4$  system. The longest ( $\kappa = 5$ ) mesogens show  $\langle \theta \rangle = 1.6^\circ$ . We see that the amount of interdigitation in the smectic phase for  $\kappa = 3$  decreases for higher elongations. The results show that the GB molecules having two terminal longitudinal dipoles do not generate a significant tilt and the tilt angle becomes minimum at an intermediate elongation. We now discuss the tilted structures obtained due to the effects of two transverse dipoles. In this case, the biaxiality comes exclusively from the presence of the dipoles. Biaxial smectic phases are found for all the three elongations. The phases exhibit in-layer hexagonal ordering of the molecules, which is evident from the values of  $\psi_6 \approx 0.7, 0.8, \text{ and } 0.8$ , respectively, for  $\kappa = 3, 4, 5$ . The molecules in the tilted smectic phases for  $\kappa = 4, 5$  exhibit short range positional ordering as seen from the plots of  $g(r)$

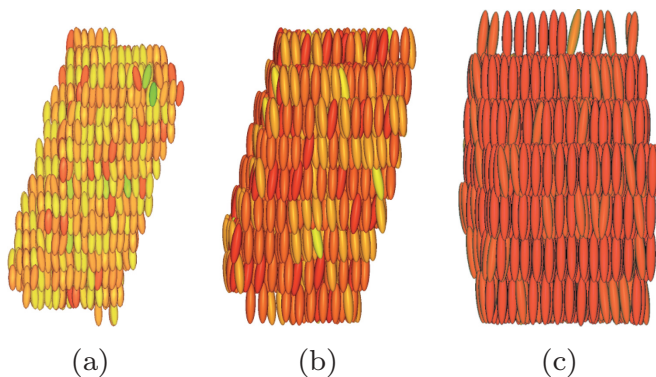


FIG. 1. (Color online) Snapshots of the final configurations from MC simulations of a system of 1372 GB molecules with two terminal longitudinal dipoles for various elongations  $\kappa$ : (a) Smectic at ( $\kappa = 3$ ,  $T^* = 1.00$ ,  $P^* = 2.75$ ) with  $\langle \theta \rangle = 1.6^\circ$ . (b) Smectic at ( $\kappa = 4$ ,  $T^* = 1.25$ ,  $P^* = 1.50$ ) with  $\langle \theta \rangle = 0.6^\circ$ . (c) Smectic at ( $\kappa = 5$ ,  $T^* = 1.5$ ,  $P^* = 1.10$ ) with  $\langle \theta \rangle = 1.6^\circ$ .

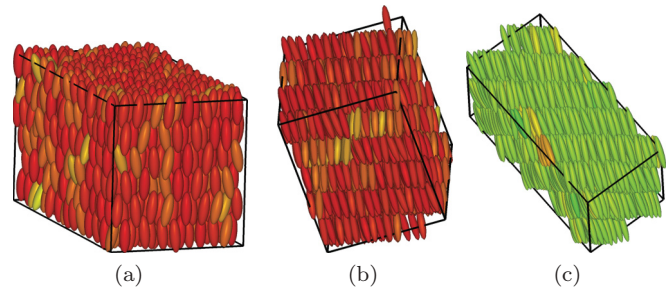


FIG. 2. (Color online) Snapshots of the final configurations generated by MC simulations of a system of 1372 GB molecules with two terminal transverse dipoles for various elongations  $\kappa$ : (a) Smectic at ( $\kappa = 3$ ,  $T^* = 1.00$ ,  $P^* = 1.35$ ) with  $\langle \theta \rangle = 0.25^\circ$ . (b) Tilted smectic at ( $\kappa = 4$ ,  $T^* = 1.25$ ,  $P^* = 1.05$ ) with  $\langle \theta \rangle = 6.6^\circ$ . (c) Tilted smectic at ( $\kappa = 5$ ,  $T^* = 1.5$ ,  $P^* = 1.5$ ) with  $\langle \theta \rangle = 17^\circ$ . The snapshots in Figs. 1 and 2 were generated using QMGA [20].

given in Fig. 3(b). Hence we identify these tilted structures as the tilted analogs of the SmB phase. However,  $g(r)$  for  $\kappa = 3$  shows sharp peaks, which indicates the crystalline nature of the untilted biaxial phase. The values of the biaxial order parameter in the smectic phases are  $\langle R_{2,2}^2 \rangle = 0.87, 0.83$ , and  $0.79$ , respectively, for  $\kappa = 3, 4$ , and  $5$  systems. The contribution to the total energy is always dominated by the dipolar interaction in these phases ( $U^{d*} \approx 75\%$  of  $U^{\text{total}*}$ ) and the dipolar interaction increases significantly with elongation ( $U^{d*} \approx -10.9, -15.1, -19.4$  for  $\kappa = 3, 4, 5$ ). The average tilt order parameter as measured gives  $\langle \theta \rangle \approx 0^\circ$  for  $\kappa = 3$  and, more interestingly,  $\langle \theta \rangle \approx 6.6^\circ$  and  $17^\circ$  for systems with  $\kappa = 4$  and  $5$ , respectively. In the smectic phases, the point dipoles

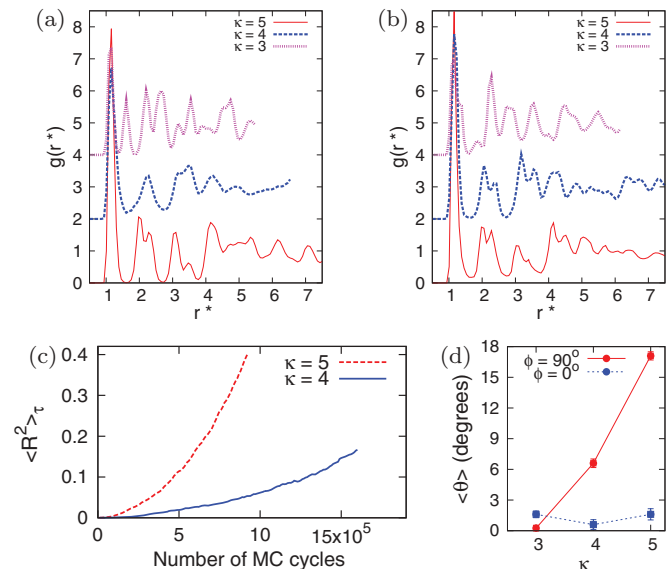


FIG. 3. (Color online) (a) Radial distribution functions for systems of molecules with two terminal longitudinal dipoles. (b) Radial distribution functions for systems of molecules with two terminal transverse dipoles [the zero of  $g(r^*)$  on the vertical scales have been shifted for clarity]. (c) Evolution of mean squared displacements in the tilted smectic phases at ( $\kappa = 5$ ,  $T^* = 1.5$ ,  $P^* = 0.45$ ) with  $\langle \theta \rangle \approx 11^\circ$  (red dotted line) and at ( $\kappa = 4$ ,  $T^* = 1.25$ ,  $P^* = 0.60$ ) with  $\langle \theta \rangle \approx 6.6^\circ$  (blue solid line). (d) Schematic evolution of the average tilt angle  $\langle \theta \rangle$  as a function of elongation  $\kappa$ .

form some distinct dipolar layers. The separation between two such dipolar layers increases here with molecular elongation. Hence local dipole-dipole interactions within these dipolar layers dominate the dipolar contribution to the interaction energy. It is the collective interaction among the dipoles which minimizes the total interaction energy and effectively produces a tilted structure in the smectic phase. The attractive interaction between dipoles belonging to two different dipolar layers within a single molecular layer decreases with an increase in elongation. Thus one molecule slides along the other, increasing the distance between the molecular centers, which brings the requisite tilt and minimizes the total effective interaction energy. This relative shift of the molecules is equivalent to the tilting of molecules inside molecular layers. In order to verify the fluidity of these tilted phases, we calculated the mean square displacement as follows:  $\langle R^2 \rangle_\tau = \frac{1}{N} \sum_{i=1}^N [\mathbf{r}_i(\tau) - \mathbf{r}_i(0)]^2$ , where  $\mathbf{r}_i(\tau)$  is the position vector of the  $i$ th particle after the completion of  $\tau$  MC cycles. In the tilted phases, the mean square displacement steadily increased with increasing  $\tau$ , indicating fluid behavior, as shown in Fig. 3(c). All the tilted phases showed a very small variation in the tilt angle over the variation of pressure except in the case of the longest ( $\kappa = 5$ ) mesogens, where the tilt angle increases from  $\langle \theta \rangle \approx 11^\circ$  to  $17^\circ$  as we increase the pressure from  $P^* = 0.45$  to  $P^* = 1.5$ . To verify the stability of the phases against the system size effect, we performed some simulation studies with a smaller system size ( $N = 500$  for  $\kappa = 3, 4$  and  $N = 900$  for  $\kappa = 5$ ) at some state points ( $P^*, T^*$ ) reported above for the larger system. The structural characteristics of the smectic phases were found to be similar for different system sizes. For the shortest molecules ( $\kappa = 3$ ) with longitudinal dipoles, the smaller system shows  $\langle \theta \rangle \approx 5^\circ$  and for transverse dipoles the smaller system shows  $\langle \theta \rangle \approx 2.2^\circ$ . This difference in tilt

in the case of the shortest molecules might be a system size effect. However, no significant change in the tilt angle was found for elongated molecules ( $\kappa = 4, 5$ ). We have measured the angular correlation function, associated with the spinning motion around the molecular long axis  $C_x(\tau) = \langle \vec{X}(0) \cdot \vec{X}(\tau) \rangle$ , where  $\vec{X}$  is a transversal molecular axis and  $\tau$  is the number of elapsed MC cycles. We have found that the spinning motion is possible in the tilted phases of molecules with longitudinal dipoles, but the motion becomes partially frozen in the tilted phases of molecules with two transverse dipoles. However, here we did not apply any restriction to hinder the free rotation of molecules in our constant  $NPT$  MC simulation study. It is worth mentioning that this two transverse dipolar model does not restrict the spinning motion of the parts of the molecules that are not connected to the dipole moments.

Our  $NPT$  simulation studies show that the increasing dipolar separation as a result of molecular elongation can effectively give rise to a large tilt in layered liquid crystalline phases generated by GB molecules with two terminal transverse antiparallel dipole moments, whereas it has a less significant role in the case of molecules with two longitudinal dipoles. Experimental evidence for tilted smectic phases were reported earlier for compounds with lateral components of dipole moments [1,2]. Our study is successful in gaining insights into the molecular origin of tilted phases by showing that terminal dipoles having a longer separation length coupled with a suitable orientation can bring large tilt to the liquid crystal phases.

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