

The Origin of Tilted Phase Generation in Systems of Ellipsoidal Molecules with Dipolar Interactions

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We report Monte-Carlo simulation studies of some systems consisting of polar rod-like molecules interacting via a pair potential that exhibit liquid crystal phases, attributed with tilt angles of large magnitude. For theoretical understanding of the microscopic origin of the tilted phases, different systems consisting of prolate ellipsoidal molecules of three different lengths, embedded with two symmetrically placed anti-parallel terminal dipoles are considered. We find that the presence of a stable tilted phase crucially depends on the molecular elongation which effectively makes dipolar separation longer. We observe that in case of mesogens with transverse dipoles the tilt in the layered smectic phase gradually increases from zero to a large magnitude as we increase the molecular length. However tilt remains weak with molecular elongation for systems with longitudinal dipoles which shows a small tilt at shorter lengths. This is the first work determining the combined contribution of dipolar separation and orientations in generating biaxial liquid crystal phases with large tilt angles.

Polar liquid crystals exhibit a rich variety of tilted layered mesophases arising out from the diversity in both the inlayer positional arrangements of the molecules and in the average molecular orientations with respect to the layer normal [1, 2]. The most common example of such a tilted Smectic phase is the Smectic C (SmC) phase where the center of mass of the tilted molecules are randomly distributed in two dimensional fluid like layers alongwith a long range orientational ordering of molecules over the bulk system. Tilted phases with the same point symmetry as SmC phase also exist in other orientationally ordered soft matter systems like mesogenic polymers, lamellar L_β phase and in SmC elastomers [3–5]. The tilted phases are important not only from the fundamental scientific viewpoint but recent discoveries of a large variety of ferroelectric, anti-ferroelectric and ferrielectric phase behavior in the tilted phases have made them a topic of huge interest from technological point of view. These phases are used for developing new generation opto-electric devices and various non-display applications [6].

The origin of tilt in liquid crystalline phases has been a topic of much discussion. A large number of theoretical and experimental studies have been done on tilted phases. However the topic remains unsolved in certain aspects till today. It is essential to understand the structure-property relationship to find the basic interactions giving rise to tilt in Sm C phase. The microscopic origin of the tilted smectic phases are much more complex than that of the orthogonal smectic phases since the existence of a tilted phase is not a favored one because packing of tilted rod like molecules in a layer plane needs more area than the untilted molecules. This phase can be achieved only if there exists additional specific interactions giving the requisite tilt.

In the experimental studies, occurrence of the SmC phases has been mostly found in presence of a lateral component of permanent dipole moment in the organic molecules [1, 2]. As the number of such dipoles increases on a molecule, the tendency to form SmC phase also increases [7]. Motivated by the experimental observations, Mcmillan gave the mean field theory on the formation of SmC phase based on the presence of at least two outboard terminal dipoles [8]. However a freezing of rotation of the molecules was resulted during such a SmA to SmC phase transition contradicting NMR [9] and neutron scattering experiments [10] which have shown the free rotation of molecules in a tilted smectic phase. Wulf attempted to relate the formation of SmC phase to the packing requirements of the zig-zag shaped molecules [11]. However lowering of free energy was associated to a freezing of rotations. A zig-zag model made of seven Lennard Jones spheres with two terminal ones at an angle 45° from the five in line core, showed a SmC behavior but the tilt orientation was random and the equilibration process was elaborate [12]. A model based on three rigidly linked hard spherocylinders arranged in a zig-zag fashion have shown the presence of SmC phase [13]. However the simple model particles built by assembling in a zig-zag way ellipsoidal Gay-Berne particles was unable to show tilted phases [14]. In computer simulation studies by Zannoni et.al. [15], the axial component rather than the transverse component of lateral dipole moments were found to be generating a tilted phase for polar GB molecules. In their system, the biaxial order parameters were very small and weak non zero tilt was found for the system of molecules with lateral dipole moments making an angle $\phi = 0^\circ$ or 60° with the long axis. Similar results were found by Saha et.al.[16] for a large dipolar orientation $\phi = 120^\circ$. However absence of tilt in these conventional model of polar molecules with transverse dipoles, contradicting experimental results, remains an open problem.

We explored systems of polar ellipsoidal molecules where each molecule is embedded with two terminal anti parallel permanent dipole moments placed at equal dis-

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tance from the center of the molecules to get considerable tilt in the smectic phases. In our model, the apolar part of the interaction is represented by the Gay-Berne(GB) potential which is a modified form of the Lennard-Jones potential, considering the anisotropy in interaction. The interaction between two such apolar GB ellipsoids i and j is given by

$$U_{ij}^{GB}(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) = 4\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)(\rho_{ij}^{-12} - \rho_{ij}^{-6})$$

where $\rho_{ij} = \frac{[r_{ij} - \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) + \sigma_0]}{\sigma_0}$. Here \mathbf{r}_{ij} is the

separation vector between the center of mass of the molecules. The unit vectors \hat{u}_i and \hat{u}_j represent the orientations of the molecules. σ_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 σ_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 anisotropic contact distance varies with κ as $\sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)$ is given by $\sigma =$

$$\sigma_0 \left[1 - \frac{\chi}{2} \left(\frac{(\hat{r}_{ij} \cdot \hat{u}_i + \hat{r}_{ij} \cdot \hat{u}_j)^2}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} + \frac{(\hat{r}_{ij} \cdot \hat{u}_i - \hat{r}_{ij} \cdot \hat{u}_j)^2}{1 - \chi(\hat{u}_i \cdot \hat{u}_j)} \right) \right]^{-\frac{1}{2}}$$

where $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$. The anisotropy of the well depth ϵ is also controlled by two additional parameters μ and ν . An explicit description of the GB interaction can be found in the original paper [17]. The well depth in the cross configuration is written as ϵ_0 . σ_0 and ϵ_0 define the length and energy scales. We have used reduced units in our calculations by expressing lengths and interaction energies in units of σ_0 and ϵ_0 respectively. In the present work, we put two point dipole moments on each GB molecule at a reduced distance $d^* = (\kappa - 1)/2$ along the symmetry axis from the center of mass of the uniaxial molecules with shape anisotropy κ . We have studied the bulk phase behavior for three different values of κ (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 large 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 $\mathbf{r}_{i\alpha}^* = \mathbf{r}_i^* \pm d^* \hat{u}_i$ and $\mathbf{r}_{j\beta}^* = \mathbf{r}_j^* \pm d^* \hat{u}_j$. The reduced dipole moment $\mu^* \equiv \sqrt{\mu^2/\epsilon_0 \sigma_0^3}$ is chosen $\mu^* = 1.0$. The long range nature of the dipolar interaction is taken into account with the reaction field method [18]. The

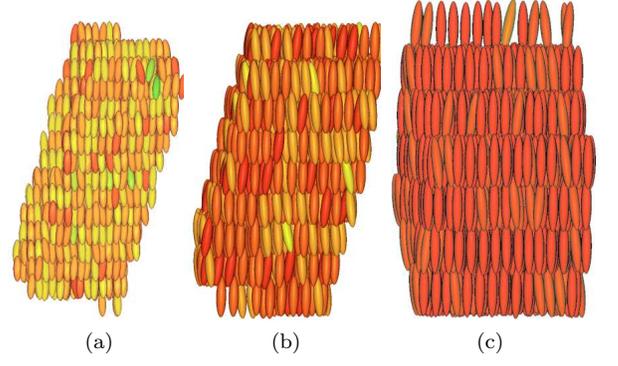


FIG. 1. (color online). Snapshots of the final configurations from MC simulations of a system of 1372 GB molecules with two terminal longitudinal dipoles for various elongations κ : (a) Smectic at ($\kappa = 3, T^* = 1.00, P^* = 2.75$) with $\langle \theta \rangle = 1.6^\circ$, (b) Smectic at ($\kappa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

dipolar part of the total interaction energy including long range correction can then be written as

$$U_{ij}^{d^*} = U_{ij}^{d^*} - \sum_{\alpha, \beta=1}^2 \frac{2(\epsilon_{RF} - 1) \mu_{i\alpha}^* \mu_{j\beta}^*}{2\epsilon_{RF} + 1 R_c^{*3}}$$

Where $R_c^* \equiv R_c/\sigma_0$ is the reduced radius of the RF cut-off sphere and $\epsilon_{RF} = \infty$ is the dielectric constant of the medium. Then the total interaction between two dipolar molecules is given by $U_{ij}^{total^*} = U_{ij}^{GB^*} + U_{ij}^{d^*}$.

We have performed Monte Carlo (MC) simulations in the NPT(isothermal-isobaric) ensemble with periodic boundary conditions imposed on a system of $N=1372$ dipolar molecules. The simulation cell is an orthogonal box of dimensions L_x, L_y, L_z . The dimensions are varied independently during simulation so that the system may fit itself to its most suitable configuration at each state point ($P^* \equiv P\sigma_0^3/\epsilon_0, T^* \equiv K_B T/\epsilon_0$). All the systems are prepared initially in a completely disordered isotropic phase in a cubic box by melting a crystal structure at sufficiently low pressure. We then increase 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 previous lower pressure is used as the initial configuration. At each state point, the system is equilibrated for 3×10^5 MC cycles and 3×10^6 MC cycles are used for equilibration near a transition. During each MC cycle each molecule is randomly displaced and reoriented using metropolis criteria where the reorientation moves were performed using Barker-Watts technique[18]. One of the three box-sides was attempted to change during each MC cycle. The acceptance rates of the roto-translational 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

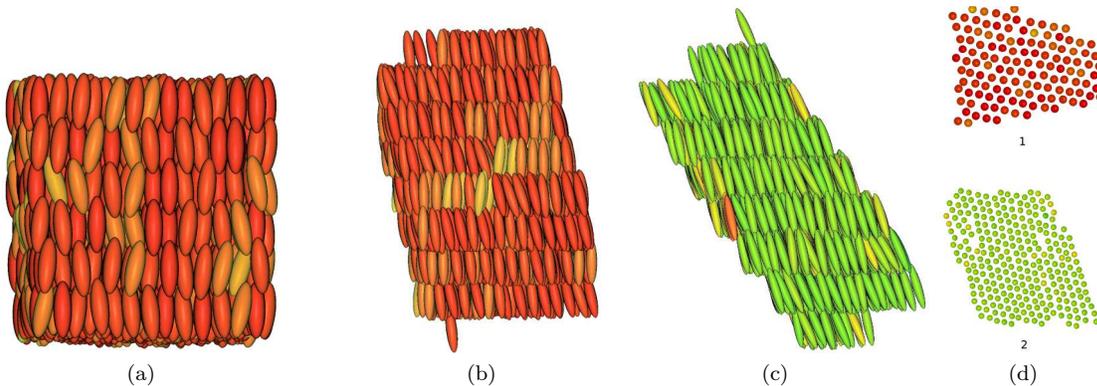


FIG. 2. (color online). Snapshots of the final configurations generated by MC simulations of a system of 1372 GB molecules with two terminal transverse dipoles for various elongations κ : (a) Smectic at ($\kappa = 3, T^* = 1.00, P^* = 1.35$) with $\langle\theta\rangle = 0.25^\circ$, (b) Tilted Smectic 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 $\langle\theta\rangle = 17^\circ$, (d) molecular center of mass positions on a single 2D layer of the tilted phases showing local hexagonal orderings (1)($\kappa = 4, T^* = 1.25, P^* = 1.05$), (2)($\kappa = 5, T^* = 1.5, P^* = 1.5$).

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 such temperatures we observed a jump in S directly from $S \sim 0.10$ to $S \sim 0.95$ indicating a direct isotropic to tilted smectic transition. To measure the average tilt angle $\langle\theta\rangle$ of the phase director about the layer normal, we have used the method described in [16] i.e. in smectic phases we first find the sets of particles for which 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 square method. The average normal is obtained by averaging the components over all the layers of a single MC configuration. The angle θ 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 also measure 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 [19], where α, β, γ are the Euler angles giving the orientation of the molecular body set of axes w.r.t. 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.

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° in order to explore separately the roles of a longitudinal component and a transverse component in producing tilted phases.

From the snapshots and various distributions functions as described, we analyzed the phase structures. The structure of the phases were changed significantly over different elongations.

In case of mesogens having longitudinal dipoles, the GB interaction plays dominant role in the isotropic phases and as we increase the pressure along the isotherms, the dipolar energy makes larger jump than the GB energy in reaching smectic phases. The energy distribution in tilted phases show an interesting behavior over different elongations. For the shortest molecules ($\kappa = 3$), the GB energy remains stronger than the dipolar energy and as we increase elongation they become comparable at $\kappa = 4$ and 5 . The amount of tilt in 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 $\langle\theta\rangle = 1.6^\circ$. The snapshots of the phases are shown in Fig.1 and the corresponding radial distribution functions are shown in Fig.3(a). We see that the amount of interdigitation in the smectic phases decreases with elongation showing an interdigitated phase at $\kappa = 3$.

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. For $\kappa = 3$ we obtained an orthogonal biaxial phase and for other higher elongations we found tilted biaxial phases where the amount of tilt increases with κ as shown in the Fig.2. The contribution to the total energy is always dominated by the dipolar interaction in these phases and the dominance increases with the elongation. 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° for systems with $\kappa = 4$ and 5 respectively. We may infer that longer dipolar separation gives larger torque arising out from larger dipole moments, which is responsible for giving significant change in the magnitude of tilt never found before. The values of

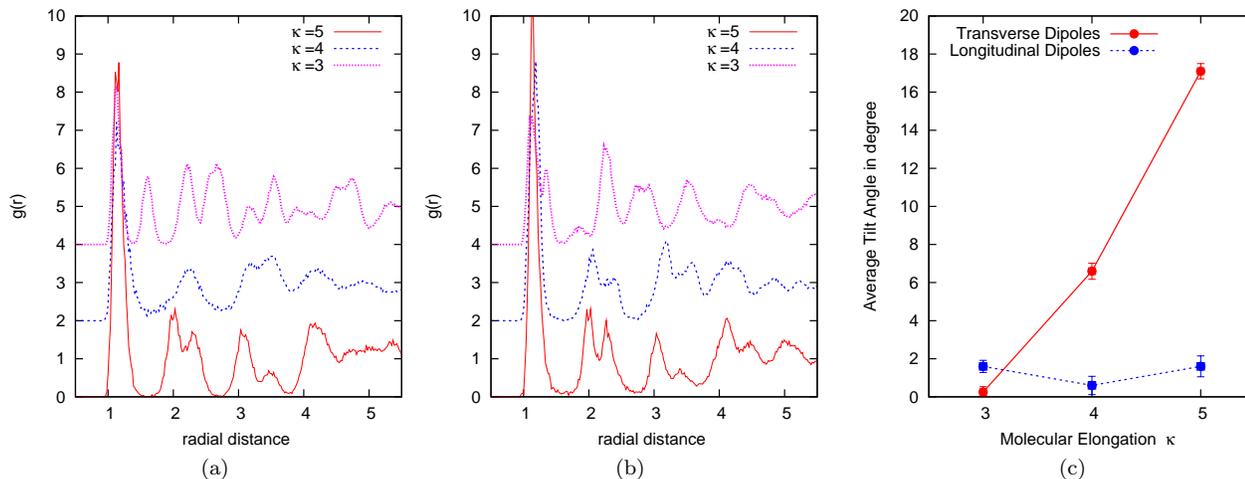


FIG. 3. (color online)(a) radial distribution functions for systems of molecules with two terminal longitudinal dipoles,(b) radial distribution functions for systems of molecules with two terminal transverse dipoles [The zero of $g(r)$ on the vertical scales have been shifted for clarity] (c) Schematic evolution of the average tilt angle $\langle \theta \rangle$ as a function of elongation κ for systems of molecules with two terminal dipoles .

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 radial distribution function shows a crystalline nature in all three elongations at higher pressures as shown in Fig.3(b). In all the tilted phases, the smectic structure were never interdigitated but show some difference in local hexagonal ordering as shown in Fig.2(d). Again the tilt angle increased from $\langle \theta \rangle \approx 11^\circ$ to 17° in smectic phases as we increase the pressure $P^* = 0.45$ to $P^* = 1.5$ in systems of longest ($\kappa = 5$) molecules. We noticed that the attempt to increase dipole moment by increasing μ^* to a value greater than 1.1 fails due to enhanced probability of dimer formation. We have observed the presence of Nematic Phase in these systems at different state points as a part of our ongoing work.

Our NPT simulation studies show that the increasing dipolar separation as a result of molecular elongation

can effectively give rise to large tilt in layered liquid crystalline phases generated by GB molecules with two terminal transverse anti parallel dipole moments whereas it has less significant and reverse role in case of molecules with two longitudinal dipoles. Experimental evidence for tilted smectic phases were earlier reported for compounds with two or more lateral dipole moments [1, 2]. Our study is successful in gaining insights into the molecular origin of tilted phases by showing that terminal dipoles having longer separation length coupled with suitable orientation can bring large tilt to the liquid crystal phases.

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