

Comment on “Origin of tilted-phase generation in systems of ellipsoidal molecules with dipolar interactions”

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In this Comment, I point out that the physical origin of molecular tilt in the smectic phase, found in the Monte Carlo simulations of systems of rodlike molecules with two terminal antiparallel transverse dipole moments by Bose and Saha [*Phys. Rev. E* **86**, 050701(R) (2012)], is similar to the one proposed by McMillan. In particular, unlike in smectic-*C* liquid crystals, in which the molecules are known to have practically free rotations about their long axes, the molecular rotations are found to be partially frozen in the simulations. Further, I suggest that the attractive interaction between correlated splay fluctuations of the antiparallel polarized sublayers which lie close to each other in adjacent molecular layers give rise to the tilting, rather than a reduced attractive interaction between dipoles belonging to the two dipolar sublayers within one molecular layer, as proposed by the authors.

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Bose and Saha [1] present results of Monte Carlo (MC) simulations of dipolar rodlike Gay-Berne (GB) molecules of three different aspect ratios ($\kappa = \sigma_e/\sigma_0 = 3, 4, \text{ and } 5$) at three reduced temperatures T^* lying between 1 and 1.5, which are rather low. The earlier simulations of Berardi *et al.* [2] on GB molecules with $\kappa = 3$ had shown that two outboard antiparallel point dipoles lying on the molecular axis generate tilted structures only when the angle φ between the dipole and the molecular axis is either 0° or 60° , but not when it is 90° . The simulations of Bose and Saha [1] show that when the aspect ratio κ is increased to 4 and 5, and the reduced temperature is low enough, transverse dipoles (with $\varphi = 90^\circ$) generate a much larger tilt with hexatic order, compared to that found with longitudinal dipoles with $\varphi = 0^\circ$, unlike the results of Berardi *et al.* [2]. Practically all compounds exhibiting the smectic-*C* (Sm-*C*) phase, in which the molecules tilt in the layers, have significant lateral components of the dipoles, and the authors claim that their study is “successful in gaining insights into the molecular origin of tilted phases . . .”

If the rodlike molecules rotate freely about their long axes, the transverse components of dipoles average out, and do not contribute to intermolecular interactions. This is the reason for McMillan [3] to propose that *rotational freezing* of molecules due to interactions between the transverse components of the dipoles is the origin of molecular tilting in the Sm-*C* phase. Indeed, McMillan estimated the temperature at which such a rotational freezing transition would take place, and found that it was far below the temperatures at which the Sm-*C* phase is found in typical compounds. Further, as the authors note in the opening paragraph of their paper, NMR [4] and neutron scattering [5] experiments indicate a free rotation of molecules in the tilted smectic phase. It is for this reason that Cabib and Benguigui [6] proposed that *longitudinal* dipoles at both ends of the molecules, which do not average out in freely rotating molecules, may cause the tilting. The dipolar repulsive interaction between neighboring molecules in a layered structure can be lowered by the tilt, as has been confirmed by the MC simulations of Berardi *et al.* [2], as the dipoles will have significant longitudinal components even when $\varphi = 60^\circ$.

Towards the end of the paper [1], Bose and Saha mention that they have measured the angular correlation function,

associated with the spinning motion around the long molecular axis, defined as $C_x(\tau) = \langle \vec{X}(0) \cdot \vec{X}(\tau) \rangle$. They have stated 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.” By conducting the MC simulations at very low temperatures, the authors have just confirmed McMillan’s physical idea that rotational freezing can cause molecular tilting. The additional hexatic order found by the authors does not depend on the tilt, as the freely rotating molecules with longitudinal dipoles with a low tilt angle, and shorter molecules (with $\kappa = 3$) with transverse dipoles without any molecular tilting, also exhibit the hexatic order. In view of the NMR and neutron scattering experiments quoted by the authors, the claim that the “study is successful in gaining insights into the molecular origin of tilted phases” is not quite correct, as far as the smectic-*C* phase is concerned.

The authors attribute the larger tilt angle found for the longer molecules to a *reduction in the attractive interaction* between dipoles belonging to the two different dipolar layers *within* a single molecular layer, allowing adjacent molecules to slide with respect to each other to generate the tilted structure. If this were the mechanism for tilting, molecules without any dipole moments would be the better candidates for exhibiting tilted layers!

One possibility for the tilted structure found in the simulations is that, at any given low temperature, the rotational motion will be frozen to a larger extent in longer molecules which have higher moments of inertia about their long axes, thus increasing the polarization of both the dipolar layers. If we consider the *upper* dipolar layer of a given molecular layer, the polarized layer which is closest to it will be the *lower* dipolar layer belonging to the molecular layer sitting just above the first one. The separation between the two *oppositely oriented* dipolar layers is of the order σ_0 or even less if there is some average interpenetration of the molecules of one layer to the neighboring layer due to thermal fluctuations. The interaction between two layers with *uniform* polarization (P) is also zero, but as was shown by Bruinsma and Prost [7], correlated splay fluctuations of the polarization vectors in layers can lead to an attractive interaction energy which is $\propto -k_B T P^2 / (Kd)$, where as usual, k_B is the Boltzmann

constant, T the absolute temperature, K the splay elastic constant, and d the separation between the polarized layers. The attractive interaction indicated by the negative sign holds for antiferroelectric order between the polarization layers. If the average orientation direction of the molecular long axis is normal to the layers, $d \leq \sigma_0$. The interaction energy can be lowered by bringing the layers closer. This can be brought about by a tilting of the molecules. As the layers with longer molecules can be expected to have a higher sublayer polarization resulting from a better freezing, the above interaction energy ($\propto P^2$) can lead to a larger tilting when the molecular length is increased.

Returning to the dipolar origin of the tilting in the smectic- C phase, we [8,9] argued some time ago that the molecular

structures of compounds exhibiting that phase are such that the transverse dipoles are *not* located *on* the molecular long axes, but slightly shifted away. In that case, the net dipolar interaction between neighboring *freely rotating molecules* in a smectic- A layer will be repulsive. The repulsive interaction can be reduced by a sliding of neighboring molecules parallel to their long axes, which results in the tilting. We have correlated the observations on smectic- C forming compounds with this picture, and we have extended the highly successful McMillan model of the smectic- A phase [10] to include an interaction arising from this process to develop a mean field theory of smectic- C liquid crystals. The theory [8,9] qualitatively describes most of the phase diagrams found in real compounds.

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