Order Parameter Simulation of Liquid Crystal Host Mixture for Blue Phase by Means of GROMACS

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Abstract

Order parameter of a modeled liquid crystal mixture which was selected with reference to the blue phase liquid crystal mixture used in the past literature was calculated with molecular dynamics simulation package, GROMACS. Results of the simulation qualitatively consistent with the classical mean field theory were obtained.

1. Introduction

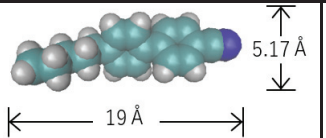
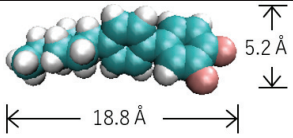
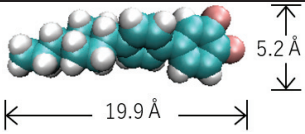
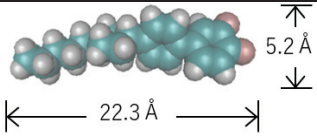
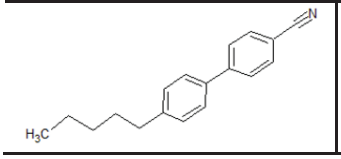
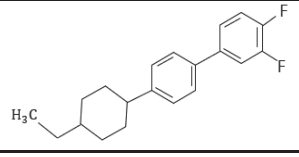
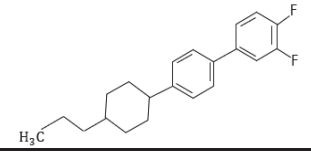
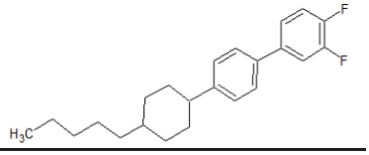
Molecular order and phase behavior of liquid crystals (LCs) is full of mystery and no one may know what is the completion of phenomenological survey on LCs. For the interpretation of the newly found phenomenon, needless to say, theoretical verification is indispensable. Generally, fundamental physical theories based on microscopic or macroscopic viewpoints are principally molecular theory, mean field and continuum theory. Let me allow to take nematic phase as an example [1]. Since the accumulation of various discussions, no one disputes the nematic phase, because the macroscopic characteristics has been well explained by continuum theory and molecular order has been well interpreted by classical molecular theory including steric and inter-molecular interaction, where liquid crystal molecules had been supposed by hard sphero-cylinder. However, actual liquid crystal molecules composed of various functional groups are not simple enough to be represented by a hard sphero-cylinder, and intermolecular interactions including coulomb potential that differ for each functional group should also be considered. Molecular dynamic (MD) simulation is a promising tool that gives more realism to the discussions on molecular theory so far. Cacelli *et al*. demonstrated MD simulation of the phase transition temperature between isotropic and nematic phase and its bulk order parameter of the series of the 4-n-alkyl-4‘-cyanobiphenyls (nCB) with n=6, 7, and 8, where well-known odd−even effect was well reproduced [2]. Recently, layer structured molecular ordering to be seen in smectic phase was replicated [3] by the open source program package for MD simulation (GROMACS) [4]. The next subject of study is the reproduction of the helical structure with using MD simulation. Blue phase (BP) of LCs had experimentally confirmed the three-dimensional spatial periodicity between the high-temperature isotropic phase and the low-temperature cholesteric phase [5–7]. Especially in short-pitch cholesteric phase, expected potential for high-speed response LC devices attracts the researchers’ interest [8,9].

In this study, LC order parameter of the mixture composed of cyanobiphenyl and fluorine-based liquid crystal, which was used for the world first demonstration of polymer-stabilized blue phase [8], was emulated by GROMACS package. Suitable procedure of selecting the thermostat for accelerating the MD calculation was also proposed.

2. MD Procedure

Fully atomistic MD simulation were performed using GROMACS 5.0.7 and the general amber force field (GAFF), where the composition molecules is listed in Table I. Molecules used in the simulation are 5CB (4'-pentyl-4-biphenylcarbonitrile) and fluorine-based molecules, which were selected with reference to the blue phase liquid crystal mixture used in the past literature [8,9]. The simulations were run under the condition of 300 K and 1 fs step calculation, all bonds were constrained to their equilibrium geometries, and periodic boundary conditions were used. The simulation trajectories were sampled every 2 ps. An electrostatic interaction was calculated using the restrained electrostatic potential (RESP) or semi-empirical with bond charge correction (AM1-BCC) models. The temperature of each system was controlled using

Table I LC molecules used in our MD simulation

5CB	C-MIX_A	C-MIX_B	C-MIX_C
$C_{18}H_{19}N$ = 249.342	$C_{20}H_{22}F_2$ = 300.38	$C_{21}H_{24}F_2$ = 314.4	$C_{23}H_{28}F_2$ = 342.45
			
			

a Nosé–Hoover thermostat [10,11], and a pressure of 0.95 bar was maintained using Parrinello–Rahman pressure coupling [12].

3. Results

Figure 1 represents one of a snapshot during the MD calculation (20 ns elapsed), where the number of the molecules of 5CB, C-MIX_A, C-MIX_B, and C-MIX_C were 512, 256, 128, and 128, respectively. In order to insert total number of 1024 molecules into the cubic cell, the length of one side of the cubic cell at the start of calculation was set to 10 nm. First duration of 80 ns was calculated with Parrinello–Rahman pressure coupling, then the length of one side of the cubic cell was stabilized to 7.78 nm and the density was 1.03 g/cm^3.

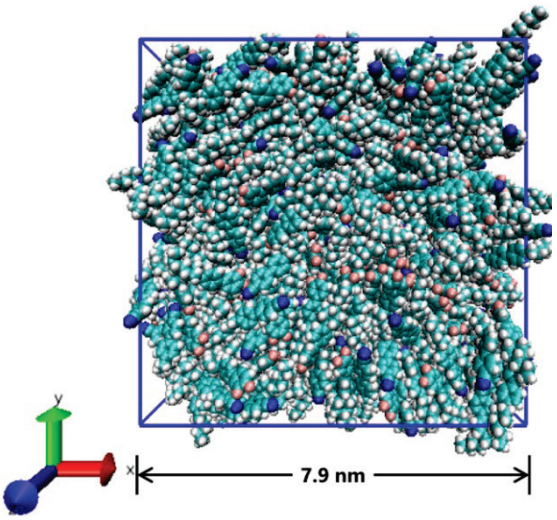


Fig. 1 Snapshot of MD calculation (first 20 ns elapsed).

Then the subsequent MD calculation was switched to the Nosé–Hoover thermostat. The obtained order parameter is shown in Fig. 2. It is found that it takes a considerable amount of MD calculation time for the order parameter to stabilize at a constant value around 0.7. This result also suggests that the longer molecule has a higher order parameter. The same tendency was confirmed when the MD calculation was performed with different molecular number (5CB, C-MIX_A, C-MIX _B and C-MIX _C were 512, 128, 128, and 256).

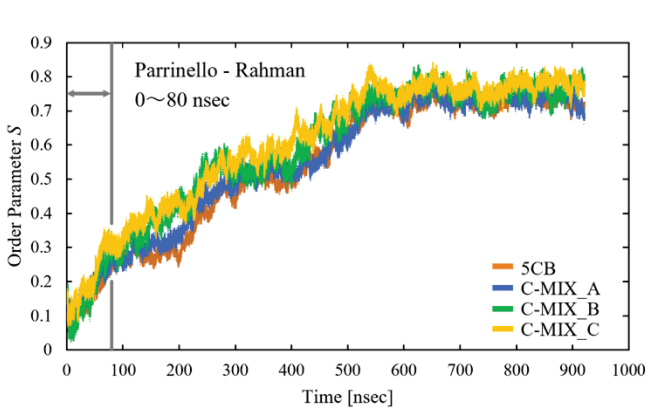


Fig. 2 Obtained order parameter of LC mixture.

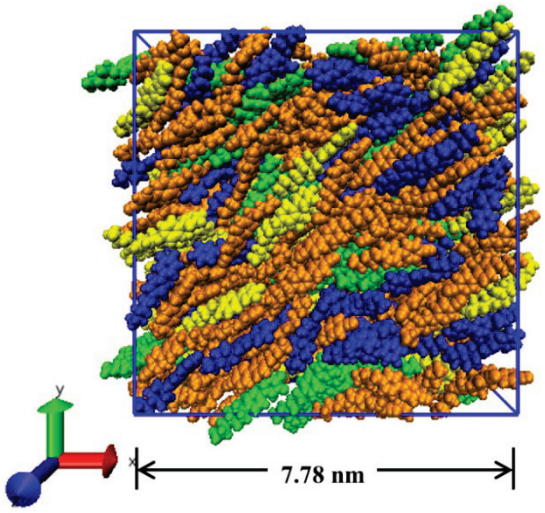


Fig. 3 Snapshot of MD calculation (920 ns elapsed), where the colored molecules represent 5CB (orange), C-MIX_A (blue), C-MIX_B (green) and C-MIX_C (yellow), respectively.

4. Conclusions

Order parameter of the modeled LC mixture was calculated with using GROMACS. Our future goal is to reproduce the double twist structure by adding the chiral molecules whereas the huge computer resource is required.

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