

ON THE ORDERING OF n -CYANOBIIPHENYL MESOGENE MOLECULES ON GRAPHENE – A COMPUTER SIMULATION STUDY

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Abstract: We studied ultrathin layers of n -cyanobiphenyl ($n = 5, 6, 7, 8$) mesogene molecules forming thin films on a graphene plane using molecular dynamics simulations in a wide temperature range (220–420 K). Each modeled ensemble was heated to the maximum temperature and then cooled (reverse procedure). We calculated the second rank order parameter as a measure of the molecular order of mesogene molecules and we discuss the distribution of angles between them and the global sample director.

Keywords: order parameter, liquid crystals, graphene, ultrathin layer

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1. Introduction

Liquid crystalline (LC) materials have been known and studied for many years. This mesophase was discovered in 1888 by the Austrian botanist, Friedrich Reinitzer. Nevertheless, interest in liquid crystals is still not diminishing. Liquid crystals are anisotropic substances [1] – they exhibit different physical properties in different directions. This is due to the fact that liquid crystalline materials are made of molecules of an anisotropic rod-like or disk-like shape. This work focuses on the ordering of the nematic rod-like mesogens of the n -cyanobiphenyl (n CB) family, where $n = 5, 6, 7, 8$ [2].

It is well known that the ordering of liquid crystals is sensitive to an electric field. This fact enables their application in displays and other optoelectronic devices. The essential physical property for optimization of liquid crystal compounds for application in liquid crystal devices is their optical anisotropy. The velocity of the light wave propagation in the medium is no longer uniform but depends on the direction and polarization of the light waves traversing the material and the material has different refractive indices in different directions. Aligned liquid crystals allow the control of the polarization of light which has resulted in the use of liquid crystals in displays [3].

Nowadays, very popular and promising materials used in many experimental and theoretical studies are carbon allotropes. Certainly, graphene [4] is one of these materials that deserve special attention. It is not only intensively studied [5–7] but also manufactured for the needs of modern electronics. Current research methods not only allow gaining knowledge about physical properties of such nanomaterials like graphene or fullerenes. It is also possible to place other molecules or atoms on the carbon nanostructure surface. Graphene seems to be a suitable material for a very good base in production of molecular structures and nanodevices. We decided to locate a thin layer consisting of LC molecules near the graphene plane. Such a computer model is the basis of all systems simulated in this work and enables the study of the dynamics of 2D nematic liquid ultrathin films. They can be potentially used as components of modern electronic or optoelectronic devices.

2. Materials and methods

All molecular dynamics simulations were performed using the NAMD 2.9 simulation package [8]. The systems were visualized using VMD 1.9.3 [9]. The equations of motions were integrated using the Brunger–Brooks–Karplus algorithm implemented in NAMD [10] with the timestep set to 1.0 fs to ensure sufficient energy conservation. The 15 ns production runs were preceded by 5 ns equilibration runs for each temperature.

The systems were composed of a graphene sheet ($\approx 71 \times 69 \text{ \AA}$) and 58 nematic molecules in the case of 5CB, 55 molecules in the case of 6CB, 52 molecules in the case of 7CB and 50 molecules in the case of 8CB. The $n\text{CB}$ mesogens were treated as flexible and modeled by the CHARMM like force field adapted from [11], which includes intramolecular harmonic stretching, harmonic bending, torsional, van der Waals and Coulombic terms. The form of the potential energy function is given by the following equation:

$$V_{\text{total}} = V_{\text{stretch}} + V_{\text{bend}} + V_{\text{torsional}} + V_{\text{vdW}} + V_{\text{coulombic}} \quad (1)$$

where

$$V_{\text{stretch}} = \sum_{\text{bonds}} K_r (r - r_0)^2$$

$$V_{\text{bend}} = \sum_{\text{angles}} K_{\Theta} (\theta - \theta_0)^2$$

$$V_{\text{torsional}} = \sum_{\text{dihedral}} \sum_{n=0}^6 \{ K_{\Phi} (1 + \cos(n\phi - \gamma)), n \neq 0 \text{ or } K_{\Phi} (\phi - \gamma)^2, n = 0 \}$$

$$V_{\text{vdW}} = \sum_{\text{atoms}}^{i < j} 4\sqrt{\varepsilon_i \varepsilon_j} \left[\left(\frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^{12} - \left(\frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^6 \right]$$

$$V_{\text{coulombic}} = \sum_{\text{atoms}}^{i < j} \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}}$$

The use of full atomistic potentials which include all hydrogen atoms is very demanding in terms of computer resources. Therefore, we adopted the model proposed by Tiberio *et al.* [11], which is the united-atom (UA) approximation [12] in which CH, CH₂ and CH₃ groups are treated as suitably parameterized spherical interaction sites. Graphene sheet was modeled as a rigid surface. Interactions between the carbon material and the *n*CB molecules were described by the Lennard-Jones 12–6 potential with the Lorentz-Berthelot mixing rules $\sigma_{A-B} = (\sigma_A + \sigma_B)/2$ and $\varepsilon_{A-B} = \sqrt{\varepsilon_A \varepsilon_B}$ [12]. The CHARMM aromatic carbon type CA was used to describe the carbon atoms forming the graphene plane.

3. Calculation of molecular order parameters

In the crystalline solid state, molecules usually exhibit a near-perfect orientational order. In the mesophase this degree of order is partially lost, as the molecules show highly dynamic behavior. The average direction of the molecules is described by the sample director (Figure 1). The most common liquid crystalline phase (nematic) has lower symmetry than the high-temperature isotropic liquid which means that the nematic phase is „more ordered”. The degree of order is described by the order parameter (P), which is a measure of the average angle θ between the director and the long axes of the mesogene molecules. It is essential to define an order parameter that is non-zero in the nematic phase but vanishes in the isotropic phase. $P = 0$ for an isotropic sample, whereas $P = 1$ for a perfectly aligned crystal. For a typical liquid crystal, the value of P is between 0.3 to 0.8 and this value generally decreases with the increasing temperature, due to a higher mobility and disorder (thermotropic mesogens) [13].

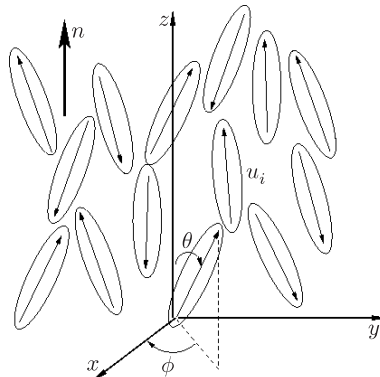


Figure 1. A unit vector u_i along the axis of *i*th molecule describes its orientation; the director n shows the average alignment

As we know, the characterization of a liquid crystalline phase inevitably deals with the investigation of its orientational order and, more generally, with the anisotropy of its physical properties. In the case of a rigid molecule, this is determined by a non-isotropic distribution of molecular orientations $f(\alpha, \beta, \gamma)$. If we take the director frame as the laboratory frame, the distribution becomes independent of the Euler angle α [14]. As in the case of uniaxial molecules this distribution does not depend on γ either, we obtain $f = f(\beta)$. To calculate $f(\beta)$ we need to determine the director at each successive time frame t of the MD trajectory [15]. This can be done by setting up and diagonalizing an ordering matrix Q defined as

$$Q(t) = \sum_{l=1}^N [3u_l(t) \otimes u_l(t) - I] / 2N \quad (2)$$

where $u_l(t)$ is the chosen molecular reference axis, I is the identity matrix and the sum runs over all the N molecules of the sample. The instantaneous order parameter $P_2(t)$ can be obtained from the eigenvalues $\lambda_{\min} < \lambda_0 < \lambda_{\max}$ of the Cartesian ordering matrix $Q(t)$ and this is a suitable observable for describing the nematic–isotropic phase transition. This is normally done by using the largest eigenvalue and identifying it as the order parameter $P_2(t) = \lambda_{\max}(t)$. Another way of calculating the order parameter uses the eigenvectors of $Q(t)$ that provide the instantaneous director frame for the configuration at time t for calculating the Euler angle β between the phase director and the reference axis of the i th molecule. This approach allows computing the overall average of any function of β and the second and fourth rank Legendre polynomials [11], yielding the corresponding order parameters given by the formulas

$$\langle P_2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N (3 \cos^2 \beta - 1) / 2 \right\rangle \quad (3)$$

We have decided to choose the eigenvector of the molecule inertia tensor that corresponds to the highest symmetry, as the molecular reference axis. It is shown in [16] that the order parameter calculated using the inertia axis is slightly higher than in the case of choosing the CN bond as the reference axis.

4. Results and Discussion

As we have already noted, all the simulated systems were initially heated and then cooled. The temperature dependence of average values of the order parameter $\langle P_2 \rangle$ during the heating process is presented in Figure 2.

The nature of each curve is similar, especially for higher temperatures (340–420 K). It is worth noting that the nematic–isotropic temperature for the n CB series bulk sample ($n = 5–8$) is in the range (300–320 K). The thin mesogene layer on the graphene surface retains the liquid crystalline characteristic ($P_2 > 0.3$) in a wider temperature range.

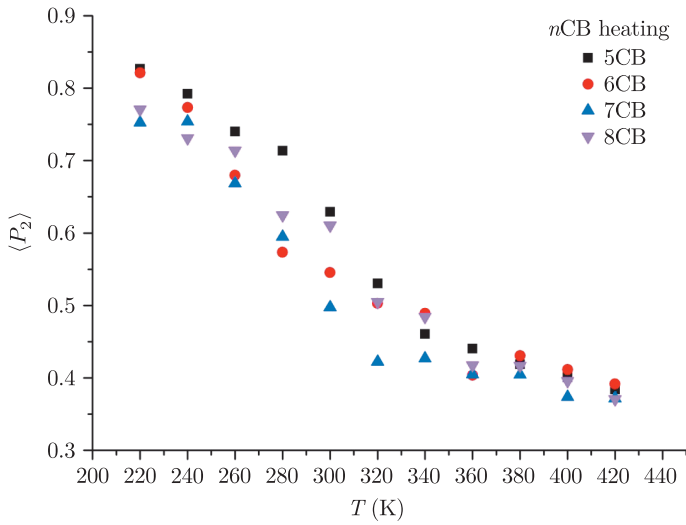


Figure 2. Average value of second rank order parameter as a function of temperature during the heating process

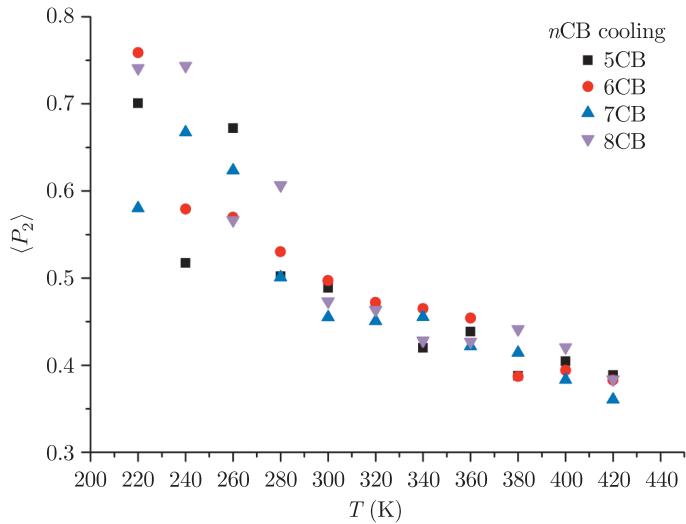


Figure 3. Average value of second rank order parameter as a function of temperature during the cooling process

It turns out that the cooling of the system has some influence on the obtained results, which can be seen in Figure 3. For temperatures above $T = 300$ K, the fluctuation of the order parameter is rather small.

The colder ($T \leq 280$ K) the ensemble, the less stable it becomes. This result suggests that the *n*CB mesogenes that formed the 2D layer on the graphene plane went into a supercooled liquid state. It should be noted that the bulk sample of the examined *n*CB series at the lower temperatures is a crystal.

As one can see the lowest mean value of parameter $\langle P_2 \rangle$ is greater than 0.35. The higher ordering of liquid crystals near carbon nanostructures has been reported earlier [17, 18]. Each point on the presented charts above is the average order value of a liquid crystal layer for a given temperature. The fluctuations of this parameter with time during a computer simulation are shown in Figure 4.

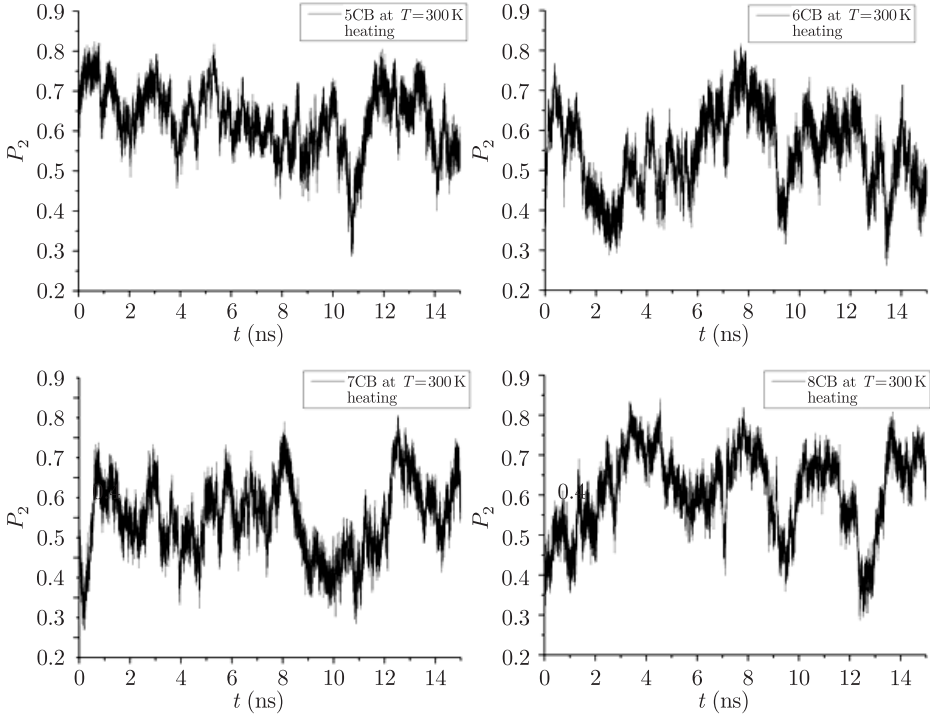


Figure 4. Time evolution of P_2 for n CB series (thin layers on graphene, heating process) at $T = 300$ K

As we can see, every computer experiment lasted 15 ns. This time is long enough to examine how the calculated second rank order parameter changes. This observable belongs to a class of functions that characterize the local structure of a nanomaterial. However, the time dependence represents the order parameter dynamics.

A number of the mesogenic properties, such as the odd-even-effect [19], the nematic-isotropic transition temperature and the entropy of transition are influenced by the presence of the alkyl chain [20]. Zannoni *et al.* showed that the odd-even effect in these kinds of systems can be well reproduced using an MD simulation with the adequately adopted force field [11]. The analysis of the results that we obtained shows that the effect mentioned above does not occur in the case of the n CB ultrathin mesogene films on a graphene substrate.

5. Conclusion

We have shown that *n*-cyanobiphenyl mesogene molecules located on a graphene plane form a layer which exhibits some degree of order. This property depends on the temperature and the length of the alkyl chain as well as on the direction of the process (heating or cooling). We did not observe any significant odd-even effect in this system. Our numerical calculations were carried out in a considerably wide temperature range (220–420 K). Nevertheless, the lowest calculated mean value of the second rank order parameter indicates quite high molecular ordering of the liquid crystal thin film ($\langle P_2 \rangle = 0.35$ for $T = 420$ K).

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