# THE DYNAMICS OF 5CB MESOGENE MOLECULES BETWEEN GRAPHITE WALLS - AN MD STUDY

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**Abstract.** Classical molecular dynamics simulations were performed for a thin layer of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) molecules confined between two parallel graphite sheets. Liquid crystal (LC) molecules were treated as rigid bodies interacting via the van der Waals potential with the applied two-dimensional periodic boundary condition. The distance between graphite plains was adjusted in the range from 2.2 to 3.0 nm. The dynamics of the thin layer of 5CB molecules at room temperatures was investigated by calculating the translational and angular velocity autocorrelation functions and their Fourier transforms. The dielectric properties of the liquid crystal molecules were studied by calculating the dipole moment autocorrelation function and its cosine Fourier transform. The simulations were done at wide range of temperatures, from $T = 100K$ to $T = 400K$. We have found a strong dependence of the dynamics of mesogenic molecules on the temperature. Moreover, the more space between the graphite walls, the higher is the dielectric loss of the mesogenic layer.

## 1. INTRODUCTION

The liquid crystal (LC) is a new phase of state (mesophase) with many interesting properties [1]. The nematic LC molecules show up the same orientation in space, but not necessary any spatial ordering. This orientation is defined by vector $\vec{n}$, called director. The research of liquid crystals helps to understand the biological systems and nucleic acids [3]. The electro-optic anisotropy of nematic liquid crystals is widely used in liquid crystalline displays (LCD). The alignment of mesogenes near a solid surface is of high interest in this context. The switching speed of LC molecules is also an important parameter for constructing an LCD. The layers of atoms or molecules covering carbon allotropes are the subject of very intensive studies [4-10]. The interaction of an ultrathin mesogene layer with crystal or amorphous surfaces attracts research attention because of potential technological applications [11-18]. In this paper we study the molecular dynamics and dielectric relaxation in a very specific ensemble – an ultrathin film composed of a small group of mesogene (5CB) molecules embedded between graphite walls.

## 2. COMPUTATIONAL PROCEDURE

A 5CB molecule is modeled as rigid without any internal degrees of freedom. The 5CB shape (Fig. 1) has been optimized by *ab initio* calculations with the DFT/B3LYP method and a 6-31G* basis set. The charge distribution over 5CB molecule has been calculated with the same method and basis set. All the quantum-mechanical calculations have been made using the GAMES code [19]. The graphite has been modeled with two graphene sheets with a constant bond length and a fixed position in space. In our model we have assumed that there is no charge distribution over the graphite sheet. We have used the Lennard-Jones (LJ) and Coulomb site-to-site pair potential to describe the interactions be-

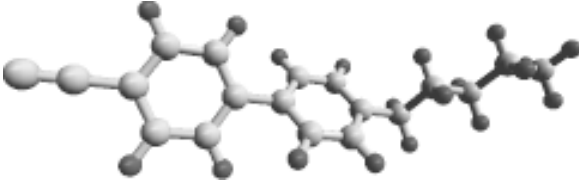Corresponding author: A. Dawid, e-mail: dawid@us.edu.pl
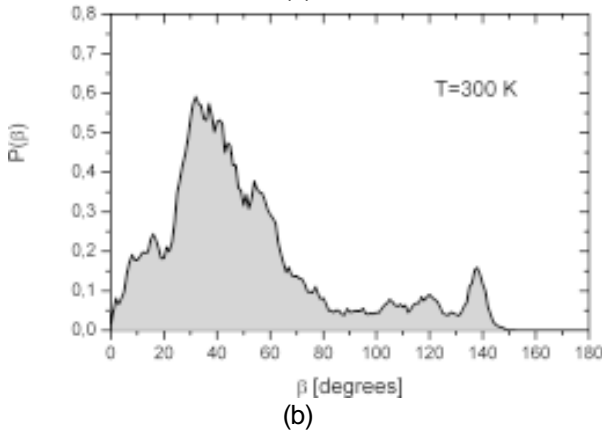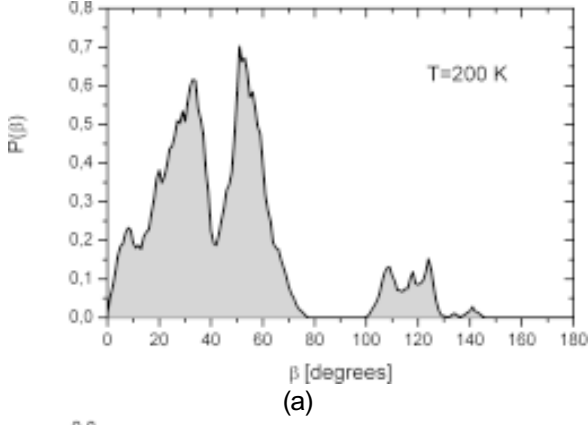
**Fig. 1.** 5CB molecule model.



(a)



(b)

**Fig. 2.** The orientational distribution function of 5CB molecules at (a) $T = 200K$ and (b) $T = 300K$.



**Fig. 3.** A snapshot of 5CB molecules between graphite walls at $T = 300K$.

tween each site in 5CB molecules and graphite walls sites

$$V\left(r_{ij}\right) = 4\varepsilon_{ij}\left[\left(\sigma_{ij}/r_{ij}\right)^{12} - \left(\sigma_{ij}/r_{ij}\right)^{6}\right] +$$

$$Z_i Z_j e^2 / 4\pi\varepsilon_0 r_{ij},$$

where $r_{ij}$ is the distance between the $i$-th and $j$-th atoms of the pair of different molecules or a 5CB molecule and one of the graphite plane, $Z_n$ is the electric charge of the $n$-th site. The Lennard-Jones potential parameters between two different atoms have been calculated using the Lorentz-Berthelot rule, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ , where the indices $i$ and $j$ denote a pair of different atoms. We have ap-
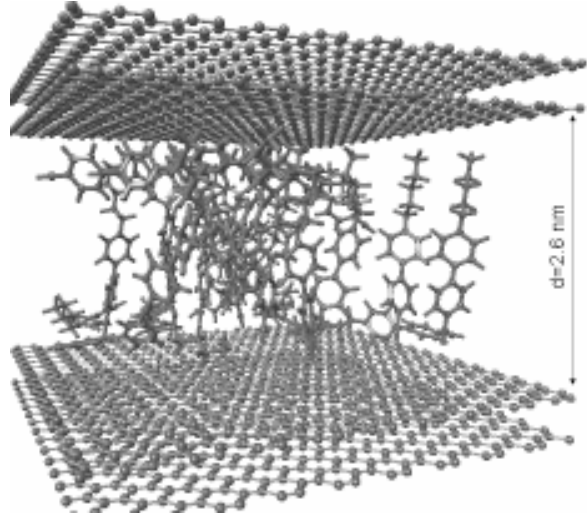
plied a 2-dimensional periodic boundary condition inside the graphite walls.

In our simulation we used 25 5CB mesogenes. Initially, the mesogenes were aligned perpendicular to the graphite sheets forming a simple square 2D lattice (Fig. 2). The distance between the graphite planes was set at 2.6 nm. The classical equations of motion were solved by the Adams-Moulton predictor-corrector algorithm [20]. The integration time step was 1 fs, which ensured total energy conservation within 0.02%. The simulation was carried out in an NVT ensemble. The temperature was adjusted using a Berendsen thermostat [20] with the coupling constant equal to 0.1. The system was equilibrated to the desired temperature during $10^5$ MD steps. The simulation data were collected under a constant temperature, the thermostat was switched on during this process. The temperature in our simulation was calculated from the energy equipartition principle $T = 2\bar{E}_k /(f_d k_B)$, where $k_B$ was the Boltzmann constant, $\bar{E}_k$ was the average kinetic energy, the coefficient $f_d = 6N$ was the total number of translational (3$N$) and rotational (3$N$) degrees of freedom, $N$ was the total number of molecules. The total momentum of molecules was conserved within 0.05%. The autocorrelation function of the 5CB molecule angular velocity $\bar{\omega}$ was calculated by averaging the angular velocity autocorrelation function $G_\omega(t) = \langle \bar{\omega}(0)\cdot \bar{\omega}(t)\rangle / \langle \bar{\omega}(0)\cdot \bar{\omega}(0)\rangle$ over $10^5$ time origins. The origins were separated by a time interval equal to 50 integration time steps which guaranteed no correlation between time origins. The cal-
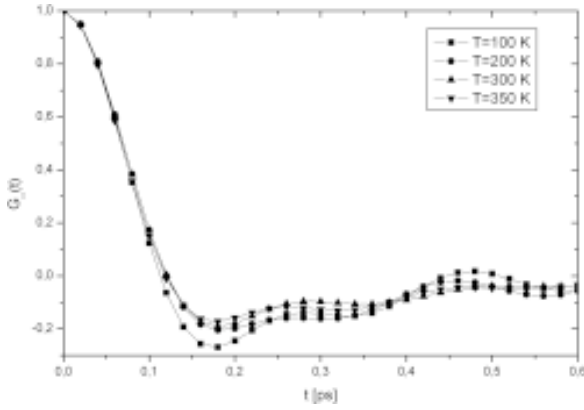
**Fig. 4.** The angular velocity autocorrelation function of 5CB molecules at four temperatures.



(a)



(b)

**Fig. 5.** The cosine Fourier transform of the angular velocity autocorrelation function of 5CB molecules at (a) $T = 200K$ and (b) $T = 300K$.

culations of a classical molecular dynamics simulation were carried out using our self designed MD simulation program.

## 3. RESULTS AND DISCUSSIONS

The molecular order in the layer has been checked by calculating the orientational distribution function $P(\beta)$ as a histogram of angle between the long axis of a molecule and the eigenvector $\vec{n}$ (the sample director) of the order tensor $Q_{\alpha\beta} = \langle 3\cos\Theta_{\alpha}\cos\Theta_{\beta} - \delta_{\alpha\beta}\rangle/2$ corresponding to the maximum eigenvalue of $Q_{\alpha\beta}$ [5]. A broad distribution of orientation of 5CB molecules (long axis) can be observed at higher temperatures, see Fig. 2b. Some molecules are oriented parallel to the graphite planes, which have been visualized on instantaneous snapshot of MD simulation (Fig. 3). The $P(\beta)$ function integral between 0 and 180 degrees gives the total number of molecules. The angular velocity autocorrelation function $G_{\omega}(t)$ shows that the first dip is deeper at low temperatures than at higher temperatures (Fig. 4). The function $G_{\omega}(t)$ decays to zero within 0.6 ps. The cosine Fourier transform of $G_{\omega}(t)$ function reveals a wide band of frequencies of 0 - 200 cm$^{-1}$ at $T$=300$K$, see Fig. 5b and the same band with a little split in the middle at $T$ = 200K, see Fig. 5a. In a typical dielectric experiment the frequency dependence of the dielectric loss $\varepsilon''(\nu)$ is measured which is the imaginary part of complex dielectric permittivity $\varepsilon^*(\nu)$ = $\varepsilon'(\varepsilon) - i\varepsilon''(\nu)$, $i = \sqrt{-1}$. In case of pure dipolar absorption and in the classical limit ($\hbar\eta \rightarrow 0$), $\varepsilon''(\nu)$is related to the cosine Fourier transform of the total dipole moment $\vec{M}(t)$ autocorrelation function $\hat{C}(t) = \langle \vec{M}(0) \cdot \vec{M}(t) \rangle / \langle \vec{M}^2(0) \rangle$ of the form
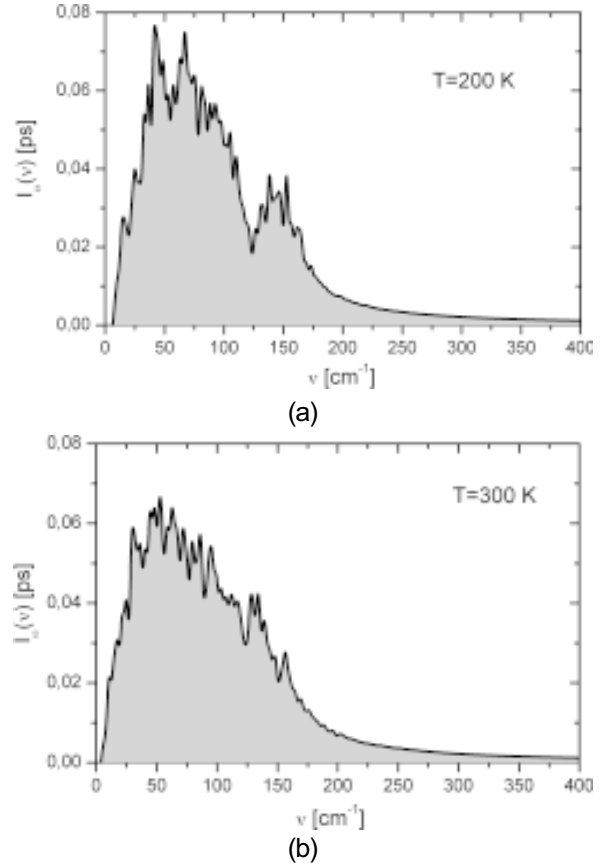
**Table 1.** The Lennard-Jones potential parameters used in simulations.

| Atom | $\varepsilon$ [$10^{-21}$ J] | $\sigma$ [$10^{-10}$ m] | m [$10^{-26}$ kg] |
|------|------|------|------|
| Carbon | 0.387 | 3.4 | 1.99 |
| Nitrogen | 0.386 | 3.1 | 2.325 |
| Hydrogen | 0.171 | 2.81 | 0.17 |

$$\varepsilon''(\nu) = \nu \int_0^{\infty} \hat{C}(t)\cos(2\pi\nu t)\,dt,$$

where $\vec{M} = \sum_{i=1}^{N} \vec{\mu}_i$, $\vec{\mu}_i$ is the electric dipole moment of the $i$-th molecule. The normalized $\hat{C}(t)$ function is shown in Fig. 6. The higher the 5CB layer temperature, the faster is the dipolar relaxation because of a more vigorous motion of molecules. This situation is also visible in a dielectric loss plot (Fig. 7). The dielectric loss maximum in $T$ = 100K is 15% of the dielectric loss maximum in $T$ = 400K. Our simulation did not cover the very low frequency band. $10^{12}$ MD time steps would be required, compared to
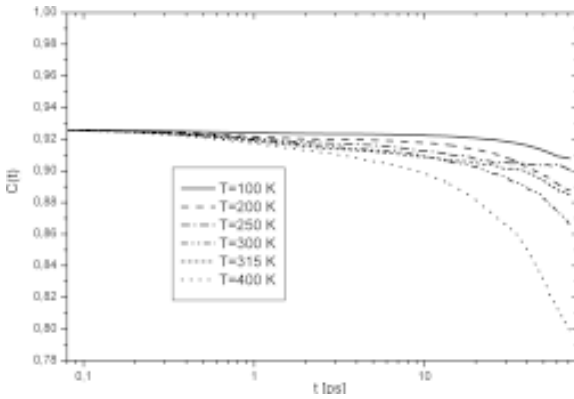
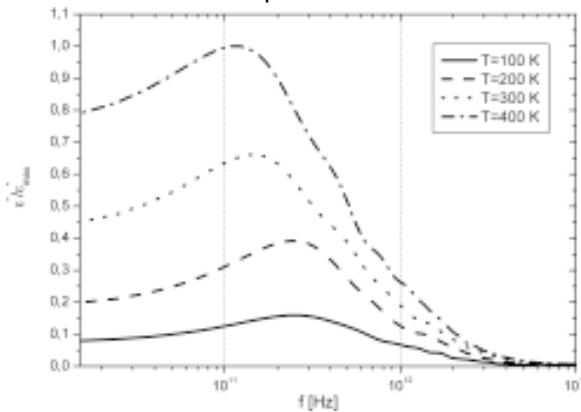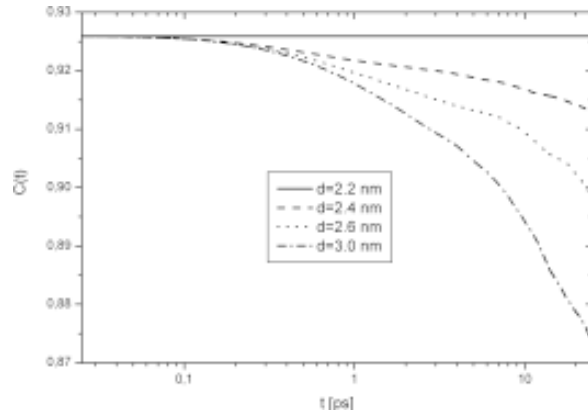**Fig. 6**. The 5CB dipole moment autocorrelation function at several temperatures.



**Fig. 8.** The 5CB dipole moment autocorrelation function at several distances between graphite planes.



**Fig. 7.** The dielectric susceptibility normalized by the maximum loss at each temperature. Note that the frequency is in a log scale.
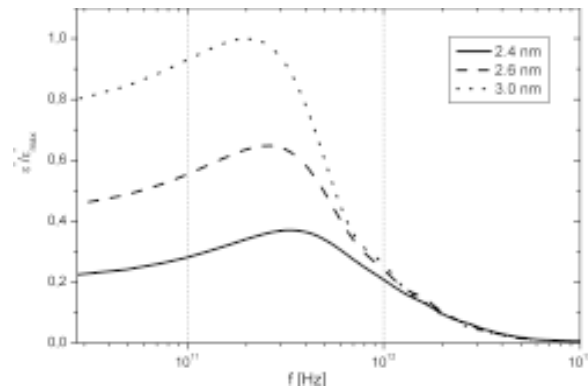


**Fig. 9.** The dielectric susceptibility normalized by the maximum loss at each distance between graphite planes at $T = 300$K. Note that the frequency is in a log scale.

the $5 \cdot 10^6$ steps that we had, to obtain a whole low frequency part of $\varepsilon''(\nu)$. We were also interested in how the separation distance between the graphite planes influenced the dielectric property of the system. We varied the distance $d$ from 2.2 nm to 3.0 nm and observed the $\hat{C}(t)$ function (Fig. 8). The system was equilibrated after each change of the separation distance and then the data were collected. When the planes are close to each other ($d = 2.2$ nm), the function $\hat{C}(t)$ decays very slowly. The more the $d$ increases (more space, more complicated dynamics), the faster the dipolar relaxation is ($d = 3.0$ nm). The maximum dielectric loss at $d = 2.4$ nm is 35 % of the maximum dielectric loss at $d = 3.0$ nm, see Fig. 9. Moreover, the position of the maximum of $\varepsilon''(\nu)$ shifts towards lower frequencies when 5CB molecules have more space. The physical foundation of the observed phenomena comes from the very complicated dynamics of 5CB molecules confined between graphite walls. The given 5CB molecule is not only pushed and swirled by

the neighboring mesogenes, but also bounces (collides) with the carbon atoms of the graphite.

## 4. CONCLUSIONS

Our MD simulation shows that the dynamics of 5CB between graphite walls depends not only on the temperature but also on the distance between the graphite planes. The maximum dielectric loss lies between 120 - 260 GHz in the temperature range of 100 - 400K. We have also found the dielectric relaxation sensitivity of a 5CB molecular layer to a change of the separation distance $d$ between the graphite planes. The position $\nu_{max}$ of the maximum dielectric loss $\varepsilon''(\nu)$ varies from 200 to 350 GHz for constant temperature $T = 300$K. We have also observed that some molecules lie on the graphite wall. This report may serve as guidance for future calculations and experiments with ultra-thin liquid crystal layers embedded between graphite or graphene walls.

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