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Molecular dynamics simulations of liquid crystal molecules adsorbed on graphite

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Preliminary results are presented on molecular dynamics simulations of the alignment of 8CB (4-*n*-octyl-4′-cyanobiphenyl) liquid crystal molecules on a graphite surface. Their stable alignment direction was found to be the $\langle 3\bar{1}\bar{2}0\rangle$ direction of the basal plane of graphite. The calculated adsorption energy of an 8CB molecule was $151{\cdot}5\,\mathrm{kJ\,mol^{-1}}$ and its alkyl chain was the main adsorption portion. Molecular dynamics simulation could therefore be an effective probe to the surface-induced alignment mechanism of liquid crystal molecules.

1. Introduction

The alignment mechanism of liquid crystal molecules at the liquid crystal/substrate interface in a liquid crystal device has not yet been clarified. However, it is becoming more and more important to understand this mechanism, because the alignment condition of the interface greatly affects display quality, especially in the latest large area displays. Recently, direct observations of the liquid crystal molecules on inorganic substrates (for example, graphite [1,2], MoS_2 [3]) have become possible using scanning tunnelling microscopy (STM). These observations of a rather simple interface are a good starting point for further investigation of the actual (usually liquid crystal/polymer) interface in a liquid crystal device. A number of STM studies of the former interface has clarified the relationship between the alignment structures and the material characteristics [3–5]. Another approach is to apply molecular dynamics (MD) simulations, which have been used to study the adsorption of mainly simple molecules (butane and decane [6], benzene [7], alkanes [8]) on graphite. A simulation of liquid crystal molecules on graphite was attempted by Ikeda *et al.* [9]. They simulated the dynamics of the liquid crystal 8CB (4-*n*-octyl-4′-cyanobiphenyl) on a basal plane of graphite. Their results were rather discouraging, mainly because the aligned structure similar to the observed STM image was not stable at room temperature in their simulations.

In this study, we did simulations of a similar system to that of Ikeda *et al.*, to verify the effectiveness of MD simulations. By examining the influence of the initial configurations, and aligned structure was realized at room temperature in our simulation. Simulated structures and energetics of adsorbed 8CB molecules were also determined.

2. Methods

2.1. *Simulation model*

We choose a simulation system quite similar to that of Ikeda *et al.* [9], i.e. a monolayer of eight 8CB liquid crystal molecules on a basal plane of graphite with only one surface layer. Except for its side-chain length, our 8CB molecule model was the same as that for 5CB (4-*n*-pentyl-4′-cyanobiphenyl) molecule used by Picken *et al.* [10], i.e. it is a detailed atomic model except for the CH_2 and CH_3 groups, which are regarded as united atoms. The following GROMOS force field [11] was used as inter- and intramolecular interaction potentials.

$$U_{\text{total}} = \sum_{j}\sum_{i<j}\left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right) + \sum_{\text{bonds}}\frac{k_d}{2}(d-d_0)^2 + \sum_{\text{angles}}\frac{k_\theta}{2}(\theta-\theta_0)^2 + \sum_{\text{improper dih.s}}\frac{k_\psi}{2}(\psi-\psi_0)^2 + \sum_{\text{dihedrals}} k_\phi(1+\cos(n\phi-\delta)). \tag{1}$$

The first term represents the non-bonding interaction due to the Lennard-Jones and Coulomb potentials. The remaining terms correspond to bond stretching, bond angle bending, and improper and proper dihedral angle torsioning potentials, respectively. The values of the force field parameters and the partial atomic charge distribution of the 8CB molecules were taken from those of Picken *et al.* [10]. The Lennard-Jones parameters for carbon atoms of graphite were set to the values of bare carbon in the GROMOS force field. The distance between graphite's nearest neighbour atoms was constrained to a fixed length

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(1·42 Å) to model the graphite substrate surface. The basal plane of the graphite was located on the x–y plane, and we applied a two-dimensional periodic boundary condition in this plane to avoid unfavourable edge effects.

We used the MD simulation program developed by our group [12] for the dynamics simulation. Time integration was done with a leap-frog algorithm and the non-iterative matrix method [13] was used to constrain the bond stretching degrees of freedom of the 8CB molecules and the nearest neighbour atomic distance of the graphite carbon atoms. The cut-off length of the non-bonding interactions was set to 15 Å.

2.2. *Simulation procedures*

We built initial configurations by referring to the STM image of 8CB molecules on a graphite substrate taken by Hara *et al.* [3]. Smith *et al.* [2], found by STM studies that the alignment direction of an 8CB alkyl chain is in the $\langle 10\bar{1}0\rangle$ direction of a graphite basal plane. Hara *et al.*, only clarified the aligned structure of the 8CB molecules; the relation between the alignment direction of the 8CB molecules and the surface orientation of the graphite was not determined. To clarify this relation, we calculated the static energy of a system with a graphite surface and one 8CB molecule on it while varying their relative angles. The calculation was done without the two-dimensional periodic boundary condition or any molecular deformation. The average distance between the 8CB molecule and the graphite surface was set to 4·0 Å. Figure 1 shows the resultant dependence of the adsorption interaction energy on the angles between the biphenyl axis of the 8CB molecule and the graphite surface orientation. We see clear adsorption selectivity in the relative angles.

From these results, we selected two initial configurations in which the relative angles were within the strong adsorption region. Figure 2 shows these two initial configurations. The configuration in figure 2 (*a*) roughly corresponds to the adsorbed 8CB model which was obtained by Smith *et al.* [2].

Starting from these configurations, we did 100 steps of energy minimization and then, 400 steps of initial relaxation dynamics with the Boltzmann distributed initial velocities of atoms. Production runs were then done with a time-integration step of 1·0 fs up to 45 ps (corresponding to 45 000 simulation steps). During these runs, the temperature of the system was maintained around 300 K by using weak coupling to a heat bath [14].

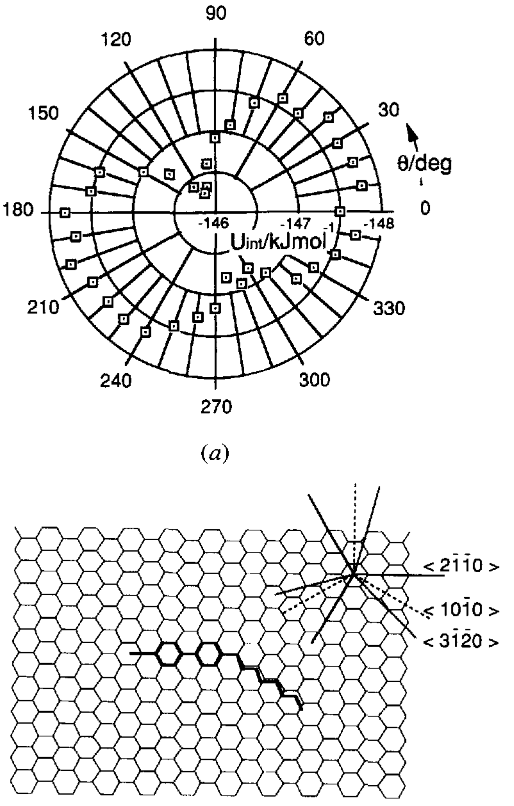

Figure 1. (*a*) Dependence of interaction energy (U_{int}) on the angle (θ) between the biphenyl axis of the 8CB molecule and the surface orientation of the graphite. (*b*) Configuration corresponds to $\theta°$ angle case in (*a*).

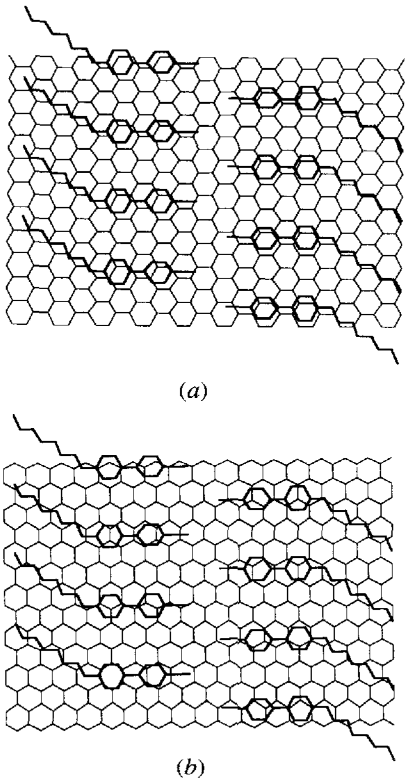

Figure 2. Initial configurations: 8CB biphenyl axes are along (*a*) $\langle 2\bar{1}\bar{1}0\rangle$ and (*b*) $\langle 10\bar{1}0\rangle$ directions of graphite surface.

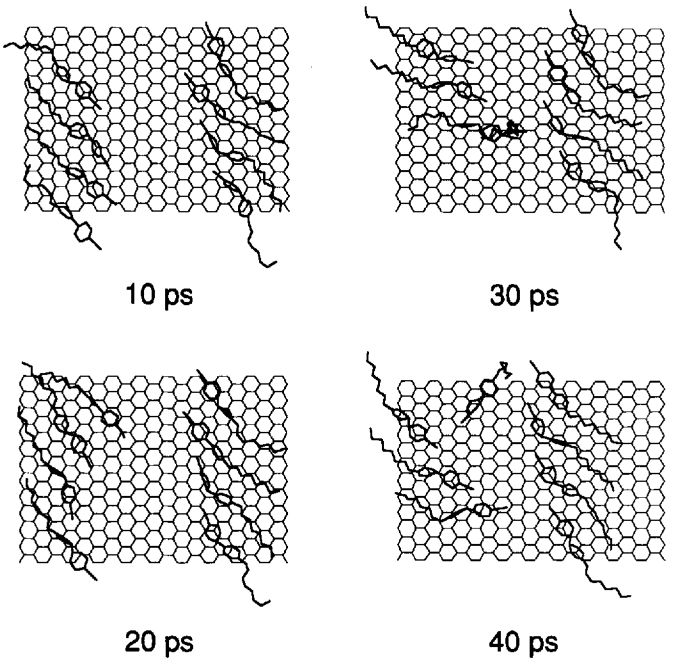

Figure 3. Instantaneous configurations of the simulation starting from the initial configuration in figure 2 (*a*).

3. Results

In figure 3, we show instantaneous configurations of the simulation starting from the initial configuration in figure 2 (*a*). Each 8CB molecule deformed to a straighter shape and, average orientation of these molecules changed from the initially applied direction to the $\langle 3\bar{1}\bar{2}0\rangle$ direction of the basal plane of graphite. To look at this change in the molecular orientation more quantitatively, we calculated the time evolution of the order parameter and corresponding director. We followed the method described in Zannoni [15] in calculation of these values, i.e. calculate the largest positive eigenvalue and eigenvector of the order parameter tensor which is made up of molecular axis vectors. The molecular axis was determined by the principal axis of inertia of the molecule. The calculated values are shown in figure 4 (*a*). They fluctuated a lot after 20 ps and this fluctuation was caused by desorption of a 8CB molecule from graphite surface. This would occur due to a limitation in our simulation model, i.e. the model only takes into account one molecular layer of 8CB. Because of this, such a desorption would be more likely to occur than in the case of a model with many molecular layers on the interface layer. On the other hand, the 8CB molecules in the right hand side low in figure 3 experienced less disturbance due to the desorption. Figure 4 (*b*) shows results corresponding to those of figure 4 (*a*) for only these stably adhered molecules. In this case, we found that the order parameter was kept at high values of more than 0·9, and the director was also kept in almost the same direction after it changed about 30° in the first few pico-seconds. In figure 5, we show the averaged configuration over 10 ps to 11 ps during which the adhesion of 8CB molecules was fairly stable. In contrast to the result above, we found the initial aligned structure was not stable when we started from the initial

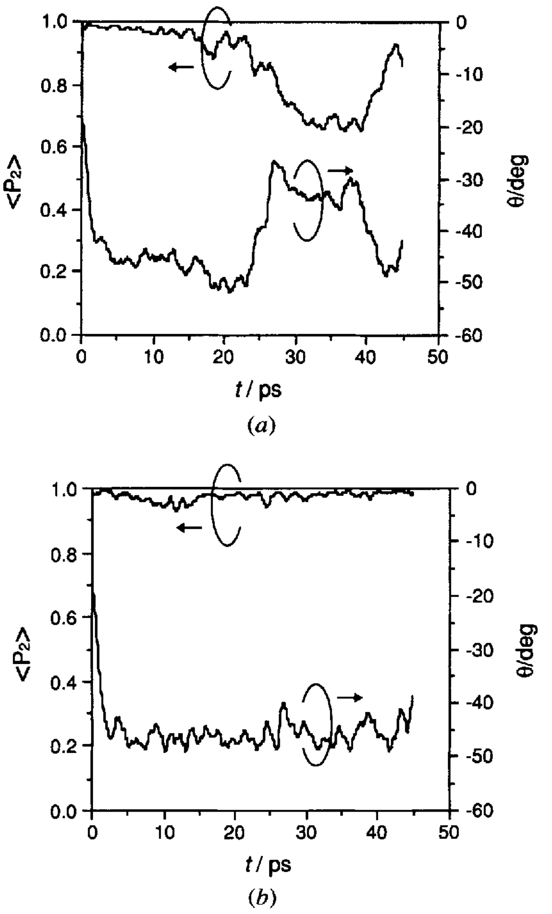

Figure 4. Evolution over time of order parameter ($\langle P_2 \rangle$) and director angle (θ) in x–y plane (measured from $\langle 2\bar{1}\bar{1}0\rangle$ direction of graphite surface) (*a*) calculated with all eight 8CB molecules and (*b*) with only stably adhered molecules.

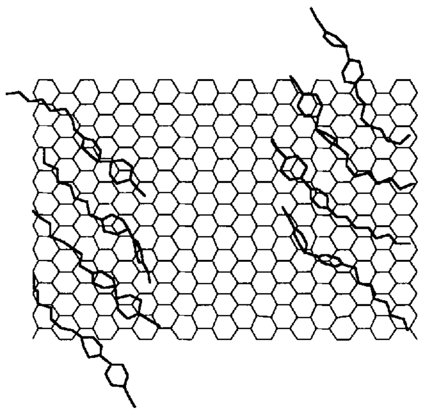

Figure 5. Averaged configuration over 10 ps to 11 ps.

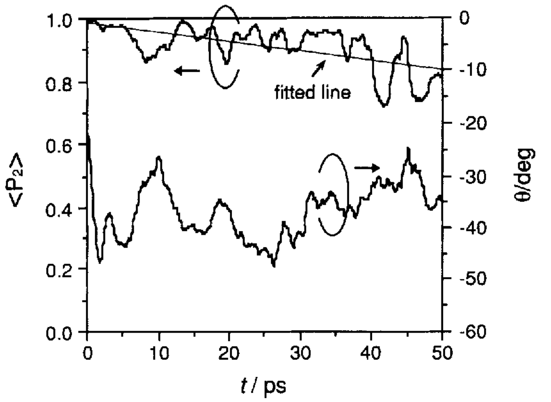

Figure 6. Evolution over time of order parameter ($\langle P_2 \rangle$) and director angle (θ, the same definition as in figure 4) of the simulation starting from the initial configuration in figure 2 (*b*).

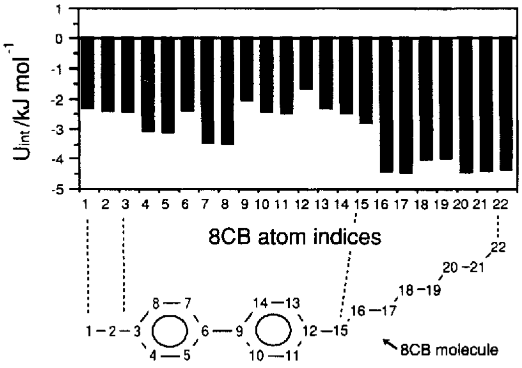

Figure 7. Interaction energies (U_{int}) between 8CB molecular atoms and graphite surface (schematic 8CB molecular structure is also shown with its atom indices).

configuration in figure 2 (*b*). In this case, the orientational order of the 8CB molecules, on average, clearly decreased as illustrated in figure 6.

We estimated the adsorption energy of an 8CB molecule on to graphite using the average energy difference between the adsorbed configuration in figure 5 and the separated system of the 8CB monolayer and graphite. We found an adsorption energy of 151·5 kJ mol^{-1}. We also examined the averaged interaction energies between 8CB molecular atoms and the graphite surface to evaluate which part of an 8CB molecule is the adsorption portion on to the graphite. This result is shown in figure 7. The interaction energies were all negative (stabilizing the adsorbed structure) and among them, alkyl chain part was larger than the other parts, i.e. these parts was considered to be the main adsorption portion.

4. Discussion

As described in the previous section, an initial aligned structure was maintained at room temperature in our simulation when we started from the configuration in figure 2 (*a*). However, the structure was not maintained in the simulation when we started from the configuration in figure 2 (*b*), that was the same as in the simulation of Ikeda *et al.* [9]. These stability differences might be caused by the difference in the relative direction between the 8CB molecular alignment direction and the graphite surface orientation in the initial configurations. Since, the adsorption strength was largely dependent on these relative directions (see figure 1), and moreover, the simulated periods were very short (a few tens of pico seconds) in both Ikeda [9] and our study, the initial configuration dependence was considered to be strong [8].

Using STM studies, Smith *et al.* [2], determined that the alignment direction of an 8CB alkyl chain on graphite is in the graphite basal plane $\langle 10\bar{1}0 \rangle$ direction. They suggested that the aligned structure of 8CB on graphite was primarily formed as a result of alkyl chain fitting into the graphite lattice. This might correspond to our finding that the main adsorption portion was the alkyl chain part of 8CB. They also found that the cyano groups of 8CB aligned along a different direction from that of the alkyl chains, meaning that the total molecular alignment direction was slightly shifted from the $\langle 10\bar{1}0 \rangle$ direction. Our simulated results showed that the (total) 8CB alignment direction was $\langle 3\bar{1}\bar{2}0 \rangle$, so the above shift was 15°. The straightening of adsorbed 8CB molecules observed in our simulation was also reported by them. The calculated adsorption energy of an 8CB molecule with a graphite surface of 151·5 kJ mol^{-1} was in good agreement with the corresponding experimental value ~ 150 kJ mol^{-1} (for the first monolayer 8CB on the highly ordered pyrolytic graphite surface) reported by Patrick and Beebe, Jr. [16].

Our results demonstrate the effectiveness of the MD simulation approach for studying the molecular alignment mechanism on substrates. This approach will be extended in the near future to the study of liquid crystal/polymer interfaces which are of great practical interest.

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