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Surface-Induced Spatial Ordering in Nematic and Smectic Phases of Gay-Berne Model

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By constant temperature molecular dynamics simulation of Gay-Berne model with walls, the formation of liquid crystalline orders is studied, where typical three types of walls are tested. The wall is shown to work as a symmetry breaking field both for smectic order and nematic short range order of position. In addition to the surface-stabilised smectic A phase, smectic C phases stabilised topologically by the periodic boundary condition are obtained. In case these phases coexist it takes quite long time to achieve a uniform state of thermal equilibrium.

Keywords: Gay-Berne model; alignment at liquid crystal/surface interface; surface-stabilised smectic phase; symmetry breaking field for positional order; periodic boundary condition

INTRODUCTION

An effect of walls on the formation of the liquid crystalline order and an alignment of molecules near the wall are the interesting problem from both fundamental and application point of view[1-5]. Recently a surface-stabilised alignment of smectic A phase was found by Stelzer *et al.*[6,7] in the course of the simulation study of the Gay-Berne model[8]. Our group have clarified that this phase is stabilised by the work of the wall as the symmetry breaking field for the smectic layer, and also shown that a phase transition between such smectic phase and the usual smectic A phase to occur[9].

In this work we study the behaviour of the same system introduced before but with larger system size, where walls at the top and bottom of the box are replaced by an imaged particle and a periodic boundary condition is applied in the lateral directions[9]. The effect of wall as the symmetry breaking field to the positional order is observed not only at the surface-stabilised smectic A phase but also in nematic and crystalline phases, which is predicted in gas phase[10]. We will report some phases stabilised topologically by the periodic boundary condition. The process of formation of such order is also tested.

MODEL AND CONDITIONS OF SIMULATION

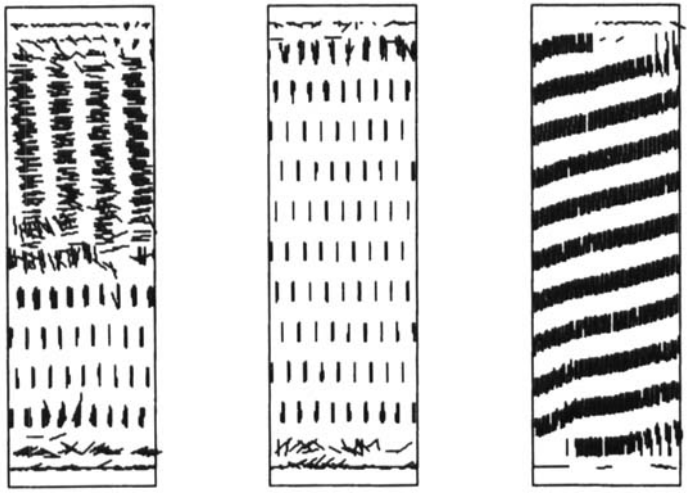
The system is composed of molecules with Gay-Berne potential[8], put into a tetragonal simulation box with walls at the top and bottom in the z-direction. The molecule is three times in length of diameter. The sizes of three types of simulation boxes are 9 (called as L-cell, hereafter), 18 (2L-cell), 27 (3L-cell) in the unit of diameter with some additional space due to the excluded volume effect by the walls in height and 9 in width. The number of molecules is 256 in L-cell, 512 in 2L-cell and 768 in 3L-cell, respectively. The walls are replaced by the imaged particles with which the molecules interact with same Gay-Berne potential. The centre of mass of the imaged particle is put on the wall and the molecular long axis is fixed in respective direction of three types of walls; parallel to the projection of the accompanied molecule onto the wall for isotropic wall, along y-axis for y-anisotropic wall and z-axis for z-anisotropic wall. The former two correspond to the homogeneous anchoring and the latter one the homeotropic anchoring. The periodic boundary condition is applied in both x- and y-directions.

The parameters appearing in the model are determined after the works by Luckhurst *et al.*[11-13] and the anisotropic parameter and that of well-depth are chosen to be same to those used previously[9]. First, molecules are generated randomly in the simulation box at high temperature and then temperature is lowered and equations of motion are solved successively using Verlet algorithm[12] by 20000 time step, during which the system is assumed to reach the thermal equilibrium or similar state at that temperature. By such process of

lowering temperature successively, behaviours of the system are studied at various values of temperature scaled in the unit of a interaction energy appearing in the model. As details of values of parameters and actual process of simulation are abbreviated here, it should be mentioned in order to characterise the conditions and simulation used in this study that under these conditions at L-cell with periodic boundary condition in each direction without walls the results[9] coincide qualitatively with those by Luckhurst *et al.*[12].

RESULTS

We carried out the simulation at systems of 2L-cell and 3L-cell with each wall. First, we report the case of isotropic wall at 3L-cell. Two types of smectic A phases, SmA1 with a layer normal perpendicular to the z-axis and SmA2 with a layer normal parallel to the z-axis[9], are obtained, and a sequence of phases is same to the one reported previously for L-cell[9]; isotropic phase, nematic phase, SmA1, SmA2 and crystalline phase.



(a) $T = 0.2$ (b) $T = 0.1$ (c) $T = 0.1$

FIGURE 1 Snapshot of smectic phase in isotropic wall system.

The snapshot of the configurations projected on the yz-plane is shown in Fig. 1 with $T = 0.2$ (a) and 0.1 (b), where in (a) SmA2 is stable and the area of SmA2 increases gradually with the course of simulation though the coexistence of both smectic phases is observed in the figure. As a movement of domain wall between both phases is quite slow at this temperature, we lowered the temperature to T=0.1 before the ordering of SmA2 governs the whole system. Then, the movement is accelerated and the ordering of SmA2 shown in Fig. 1(b) is obtained easily. We tested this system again and obtained similar results but the behaviour of SmA2 as shown in Fig. 1(c) at T=0.1, where the director tilts from the layer normal and the phase looks like smectic C phase (call SmC, tentatively). Positional distribution of molecules of this phase along an axis z' of director with direction cosine (0.00, -0.02, 0.99) and in the direction z'' of the layer normal with direction cosine (0.00, 0.24, 0.97) are shown in Fig. 2 (a) and (b), respectively, where a degree of a positional order of SmC is quite high though the order is disturbed at the walls.

In the system we are concerned, the periodic boundary condition is applied at each boundary of x- or y-direction. We see that at SmC shown in Fig. 1(c) the layers are dislocated and connected to the neighbouring layers and a tilt angle of the director from the layer normal is determined from a ratio of the width of the layer to the size of the system in the y-direction, corresponding to a component of direction cosine 0.24 quoted in the above. Accordingly the phase SmC stabilised by the periodic boundary condition is reduced to SmA in the limit of large system size. Though the free energy of SmC is assumed to be larger than the one for SmA2, SmC is stable once it appears and no sign of phase change from SmC to SmA2 is observed so long as we have carried out the simulation. In this context the following observation is noteworthy that the domain wall between SmC and SmA1 appearing at T = 0.1 moves rather fast by changing the temperature from T=0.1 to 0.2 though the movement of wall is quite slow at T=0.1. From this process the monodomain of SmC in Fig. 1(c) is achieved.

In Fig. 1 some layers attached to the top and bottom walls are seen for every case. The behaviours of such layers are proved clearly in Fig. 2(a), and also observed in nematic phase and even in isotropic one. These behaviours show

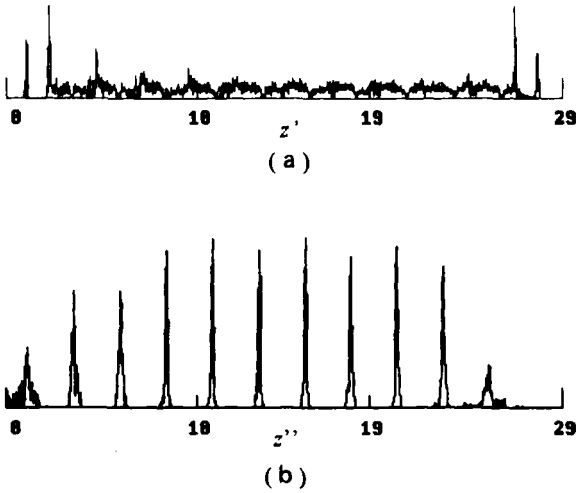


FIGURE 2 Positional distribution of molecules at SmC in isotropic wall system

nothing but the effect of walls as the symmetry breaking field to the formation of the positional order, which stabilises SmA2 in case of smectics[9]. As to a formation of crystalline order we will see such effect in the latter.

Next, we mention observations of system with y-anisotropic wall at 3L-cell. The sequence of phase transitions is same to the one at the system of L-cell[9]. A snapshot of systems projected on yz-plane at T=0.2 is shown in Fig. 3(a), where three ordered domains appear. The domain labelled as A is SmA1 with three layers, where the direction cosine of layer normal is given by (0.01, 0.99, 0.09). On the other hand anther domains look like SmC. To see what happens in this system, the projection of the system onto the plane perpendicular to the smectic layer and containing the direction of director at the part labelled as C of Fig. 3(a) is shown in Fig. 3(b). In the domain labelled as B, four layers are observed clearly in Fig. 3(a), the direction of director is (0.16, 0.96, 0.21) and direction of the layer normal is (0.01, 0.99, -0.09), while in Fig. 3(b) the

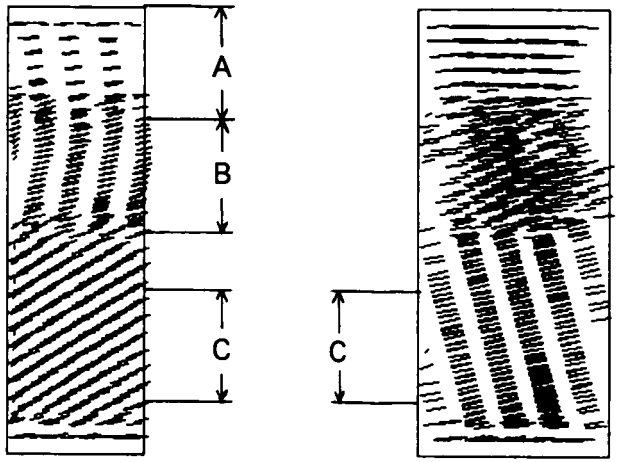
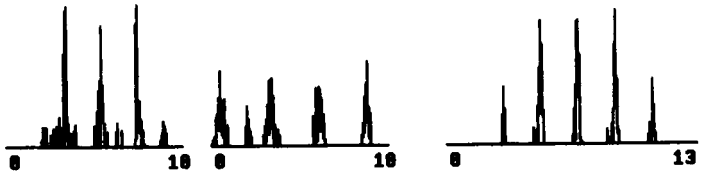


FIGURE 3 Snapshot of y-anisotropic wall system

domain labeled as C is made of five layers with directions of director (0.37, 0.90, 0.23) and of layer normal (0.51, 0.83, 0.20). The distributions of molecules for three domains along each direction of the layer normal are shown in Fig. 4, where the layers are well-ordered in each domain. The latter two orders of SmC are also stabilised by the periodic boundary condition as



(a) Domain A (b) Domain B (c) Domain C

FIGURE 4 Positional distribution of molecules for three domains along each direction of the layer normal

observed in the case of isotropic wall. However it is noticed that in those phases the layers are dislocated in the direction parallel to the xy-plane, while in this phase layers are in the z-direction as shown in Fig. 1(c). The motion of walls separating three domains in Fig. 3 is quite slow and we could not find remarkable tendency even in case the temperature is changed from T=0.2 to 0.5.

From this behaviour the phases stabilised topologically by the periodic boundary condition are sufficiently stable.

The the domain A in Fig. 3(a) looks like almost crystal. It has not been confirmed as yet whether the domain is truly crystal or not, because these three phases coexist and we could not obtain the large size of monodomain of A. Any way, the positional order within a layer is observed to grow from the boundary, showing that the wall works as the symmetry breaking field.

At the systems of z-anisotropic wall the phase stabilised by the periodic boundary condition is not observed in both cases of 2L- and 3L-cells. On the other hand at each system with isotropic wall and y-anisotropic wall, SmC is observed also in case of 2L-cell.

SUMMARY

By constant temperature molecular dynamics simulations of Gay-Berne system the formation of the liquid crystalline orders is studied, in which the effect of the walls as the symmetry breaking field is confirmed in nematic, smectic and crystalline phases. Various types of phases stabilised by the periodic boundary condition imposed to the lateral direction are obtained and the coexistence of these phases are also observed.

In these phases the layers are dislocated and connected with the nearest or next nearest neighbouring ones at the boundary. The director tilts from the smectic layer normal and so the phases look like a smectic C phase. However such phases should be reduced to the smectic A phase in itself as the size of the system is increased. Accordingly the free energies of these phases are considered to be larger slightly than the one at smectic A phase. Nevertheless, once such phases appear, these are stable enough and it takes enormous time step to get a true thermal equilibrium phase. In some cases it is efficient for achieving equilibrium phase to destabilise such ordering by rising the temperature.

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