Molecular dynamics simulation of a nematic liquid crystal under an applied electric field

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A reorientational behavior for a nematic liquid crystal under an electric field has been investigated by molecular dynamics simulations of isothermal-isobaric ensemble. The behavior of the relaxation for the director and field strength dependence of the relaxation time were studied together with a change in the structure during the process. These results were compared with a continuum theory for a nematic phase as well as experimental results, and found to be comparable with the theoretical prediction qualitatively.

Key words: liquid crystal, nematic, molecular dynamics simulation, electric field

1. INTRODUCTION

The understanding for a reorientation behavior of liquid crystals in an external field, such as magnetic and electric, is one of the most interesting significances for application of an electro-optical device. [1] The response time of the switching process is a key parameter when the liquid crystal is subjected to new torque. [2] Thus, knowing a relationship between intermolecular interaction and the response time is essentially important. For the sake of the task, molecular simulation techniques such as molecular dynamics and Monte Carlo simulation using mesogenic models would be expected to give us useful insight for the field-induced alignment process at molecular level. The molecular dynamics simulation has an advantage because a time-dependent property can be obtained not only for equilibrium state but also for non-equilibrium one. By advances of computer modeling methodology in liquid crystals, a computer-aided molecular modeling would be powerful tool for materials design of liquid crystals.

The experimental studies by a deuterium NMR for the field-induced alignment of a nematic phase [3, 4] and smectic A phase have been reported. [3, 5] Especially, the behavior has been found to be complicated for the smectic A phase. [5] On the other hand, the behavior for the nematic phase was much simpler than that for the smectic phase. [3, 4] Therefore, in order to check the validity of the mesogenic model system, it is important how molecules reorient in an external field for a nematic phase firstly since the molecular motion and structure during the process have also not cleared yet.

In this study, the simulations for the field-induced alignment process of a nematic liquid crystalline phase have been performed by an isothermal-isobaric molecular dynamics method for the Gay-Berne nematogenic model. We simulated the system in which the molecules reorient in an electric field, and the result was compared with a continuum theory by Ericksen [6] and Leslie. [7] Further, we have attempted to evaluate a rotational viscosity coefficient, which is one of the key properties for the reorientation, from the simulation

directly.

2. COMPUTATIONAL DETAILS

Molecular dynamics simulations have been performed in order to monitor the time dependence of the director as well as the motion of the molecules. The system was simulated under isothermal-isobaric condition (*NPT*) which corresponds to those used in experiments. Since the extend system method developed to simulate a system in a condition of fixed pressure and temperature by Andersen [8] and Nosé [9], some extensions have been done.[10] Hoover has made slightly different set of equations on the base of Nosé's formulation and extended the equations to the isothermal-isobaric case. [11] Moreover, these equations have been written to generate the isothermal-isobaric ensemble correctly as following. [12]

$$\mathbf{r}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\varepsilon}{W}(r_i - r_{c.m.}),$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\varepsilon}{W}\mathbf{p}_i - \frac{p_\xi}{Q}\mathbf{p}_i,$$

$$\dot{\mathbf{L}}_i = \mathbf{T}_i - \frac{p_{\xi(\mathrm{rot})}}{Q}\mathbf{L}_i + \lambda_i \mathbf{u}_i$$

$$\dot{V} = \frac{dVp_\varepsilon}{W},$$

$$\dot{\mathbf{p}}_\varepsilon = dV(P_{\mathrm{inst}} - P_{\mathrm{ext}}) - \frac{p_\varepsilon p_\xi}{Q},$$

$$\dot{\xi} = \frac{p_\xi}{Q},$$

$$\dot{p}_\xi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\varepsilon^2}{W} - (N_f + 1)k_B T,$$

Here, $\mathbf{r}_i$, $\mathbf{p}_i$, $\mathbf{F}_i$, $\mathbf{L}_i$ and $\mathbf{T}_i$ are the position, momentum, Force, angular momentum and

Torque of the ith particle, respectively. λ_i is the Lagrange multiplier setting the length of the molecular orientation vector u_i equal to unity. V is the volume, p_ε is the barostat momentum, W is virtual mass of piston, ξ, p_ξ and $p_{\xi(\text{rot})}$ are the thermostat position, momentum for the translational motion and momentum for rotational motion, respectively. Q is a parameter to control thermostat, m_i and $r_{c.m.}$ are mass of particle i and centre-of-mass position, N_f is degree of freedom for a system with N particles, P_{inst} and P_{ext} are instantaneous pressure and external/applied pressure, k_B is a Boltzmann constant. In this study, the temperature and pressure were controlled by the Nose-Hoover relaxation method. [8-11] The simulation box of cubic shape was used. In practice, we have used the scheme modified by Melchionna *et al.* [12] which has improved on Hoover's equations of motion to generate the correct trajectory for the *NPT* ensemble without the addition of extra degrees of freedom. To solve the equations for the case of the isothermal-isobaric ensemble, the implicit leap-frog scheme was applied. The generic Gay-Berne model, GB(3.0,5.0,2,1) was used. [13] The reduced time step, $\Delta t^*(\equiv\Delta t(\varepsilon_0/m\sigma_0^2)^{1/2})$, was taken to be 0.001, here m is the mass of a particle, σ_0 and ε_0 are parameters for length and energy in the Gay-Berne potential function.

The reduced moment of inertia, $I_\perp^*(\equiv I_\perp/m\sigma_0^2)$, of the particles was set equal to 1.0. The reduced pressure, $P^*(\equiv P\sigma_0^3/\varepsilon_0)$, was set equal to 10.0 at which the system undergoes a transition from the isotropic to the smectic A phase through the nematic phase. We have performed the simulation at the reduced temperature, $T^*(\equiv k_B T/\varepsilon_0)$, of 1.9 at which the nematic phase is stable. The cut-off distance, $r_c^*(\equiv r_c/\sigma_0)$, for the potential energy calculation was set equal to 4.2, and a Verlet neighbor list was used in order to improve the efficiency of the simulation. The second rank orientational order parameter, $<P_2>$, was determined via the Q-tensor

$$Q^n_{\alpha\beta} = N^{-1}\sum_i (3u^i_\alpha u^i_\beta - \delta_{\alpha\beta})/2,$$

where u^i_α is a component, $\alpha=x$, y or z, of the unit vector giving the orientation of the symmetry axis for molecule i and N is the number of molecules. The second-rank orientational order parameter, $<P_2>$, was defined as the maximum eigenvalue obtained by diagonalizing the Q-tensor, its eigenvector is then identified as the director. The effect of the external field is introduced to the potential of mean torque in the orientational partition function [2] via the second-rank orientational term

$$U_{\text{ext}} = -\lambda P_2(\cos\beta),$$

Here β denotes an angle between the applied field and the instantaneous director. Unlike the molecular field contribution the strength of the applied field does
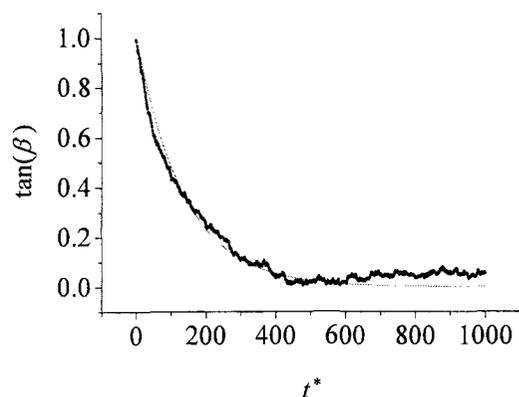

FIG. 1. The relaxation for the director during the field-induced alignment process. The solid line denotes the simulation result, and the dotted line indicates theoretical fitting curve. The field was applied by 45° with respect to the initial director.

not originate from interactions between molecules but simply from the interaction between the field and a single molecule.

$$\lambda = \varepsilon_0 \Delta\alpha E^2/3$$

The field strength parameter λ depends on the nature of the field. In case of an electric field, where $\Delta\alpha$ is the anisotropy in the molecular polarizability and E is the electric field. In case of a molecule with electric dipole moment, the contribution of the first-rank interaction with the electric field must be considered. Thus the nature of the interaction for the system would be more complicated than the system in a magnetic field. However, we ingore the interaction bewteen the field and electric dipole moment to avoid such a complication in this simulation. The reduced strength parameter, $\lambda^*(\equiv \lambda/\varepsilon_0)$, of 0.075 to 1.0 were used. The electric field was applied by 45° with respect to the initial director in order to avoid degenerecy of a rotation. Typically 0.2 to 1.0 x 10^6 time steps were used for equilibration and then 0.6 to 1.0 x 10^6 steps were taken to monitor the field-induced alignment process. A large system with 8,788 particles was used.

3. RESULTS AND DISCUSSION

Figure 1 shows that the relaxation behavior of the director for the system at λ^* of 0.2 together with theoretical curve from the continuum theory by Ericksen-Leslie. [6, 7] As can be seen, the director starts to rotate towards the field applied immediately without induction. In the experimental work by deuterium NMR for 5CB, [4] an induction period has been observed which is different from that in the simulation. However, this is caused by the technical reason in the NMR according the authors. [4] An anchoring effect may also be considered for the induction period in the reorientation process in case of the experiment by NMR. Thus the behavior of the nematic phase in the simulation

was comparable with real system and the theoretical prediction for nematic liquid crystals by Ericksen-Leslie essentially. The simple model system, more or less, could reproduce a nature of the field-induced alignment process of a nematic phase in a bulk system. In this study, the time scale for the relaxation behavior was slightly faster than that for the real nematogens, because of the simple nematogenic model of uniaxial and with no flexible tails such as typical calamitic nematic liquid crystalline molecules. So the orientational behavior by the external field for the Gay-Berne model should behave faster than that for the real systems. However, if the system follows the continuum theory by Ericksen-Leslie as we shall discuss below, the scaled relaxation time should be an order in msec. which is faster but not so unrealistic time scale. Here values of the mass m=258g·mol^{-1}, length σ_0=4.5Å and energy ε_0=2.19kJ·mol^{-1} for p-azoxyanisole (PAA) were used. The relaxation time observed for 5CB-d$_{15}$ is 10-10^2 times longer than that obtained in the simulation. [4] Regardless the qualitative discrepancy, the simulation result gives us a lot of useful information on the dynamics during the field-induced alignment process at molecular levels. Further, it is possible to evaluate flow properties such as elastic [14] or viscosity coefficients [15] from the molecular simulations.

The typical configurational snapshots during the relaxation process are shown in Figure 2. Here the initial director aligns to z-axis in a laboratory frame. After the system was relaxed by the same strength of field as the applied field for a reorientation, and then the field was applied by 45° with respect to the initial director as similar to the experiments. In the initial configuration (see (a)), the second-rank orientational order parameter $<P_2>$ is 0.70. The nematic ordering did not change so much even in the relaxation process as can be seen in the configuration (b). The order parameter is 0.65 at this moment. In the final configuration (see (c)), most molecule finished to reorient to the field direction. As the whole process, therefore, the molecules reoriented smoothly without losing nematic order.

Figure 3 shows that the field strength dependence of the relaxation time for the director with the line fits. Clearly the relaxation times change linearly as the continuum theory by Ericksen-Leslie predicts. The relaxation time of the director for the field-induced alignment process is given

$$\tau_d = \gamma_1 \, / \, \varepsilon_0 \Delta \widetilde{\varepsilon} \, E^2,$$

where γ_1 is the Ericksen-Leslie rotational viscosity coefficient and $\Delta \widetilde{\varepsilon}$ is the dielectric anisotropy. The nematic order parameter was smoothly induced as the field was increased until λ^* of 1.0. Since the relaxation rate depends on the nematic order parameter, the nematic order parameter was considered in the relation. As can been seen in the figure, the relationship between τ^*, and $1/(\lambda^* \cdot <P_2>)$ indicated linear significantly. This means that it is possible to evaluate the Ericksen-Leslie rotational viscosity coefficient, γ_1, from the slope of the relationship. In fact, there are several ways to evaluated rotational viscosity coefficient, [15, 16] thus, it is useful to compare

with the data obtained from other methods. The value evaluated from the slope for the simulation was 87.3. The value is comparable with other evaluated values. [16] However, most of evaluated values from the simulations are smaller than real nematogen for PAA. A possible reason is caused by a simple shape of the Gay-Berne mesogenic model. Therefore, modification for the model would be required for quantitative
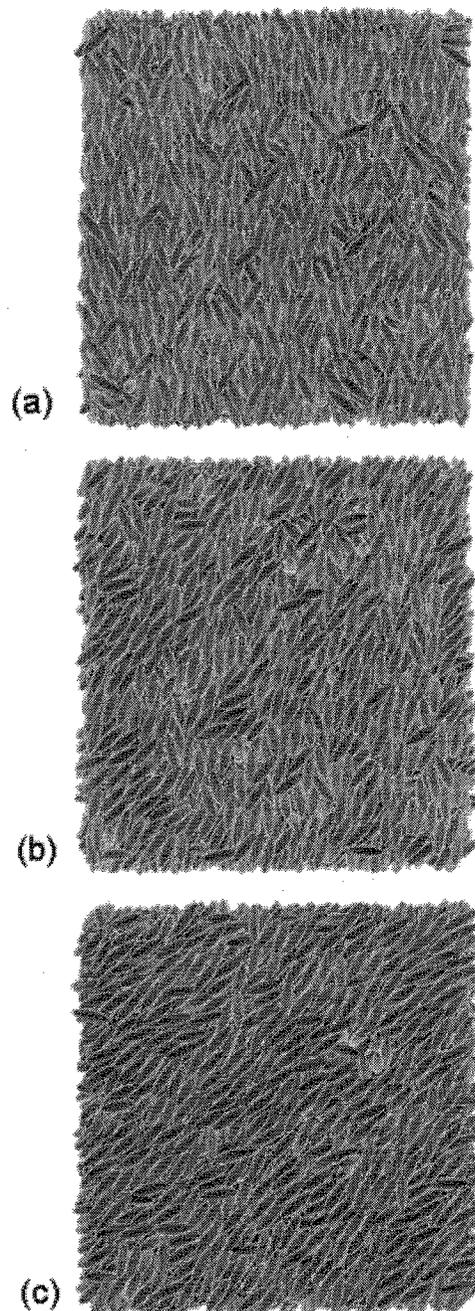

FIG. 2. Typical configurational snapshots for the field-induced alignment of the nematic phase. (a) the initial configuration, just before the field applied, (b) a typical configuration during the reorientation process at t^* of 100 (c) a typical configuration after the reorientation finished.
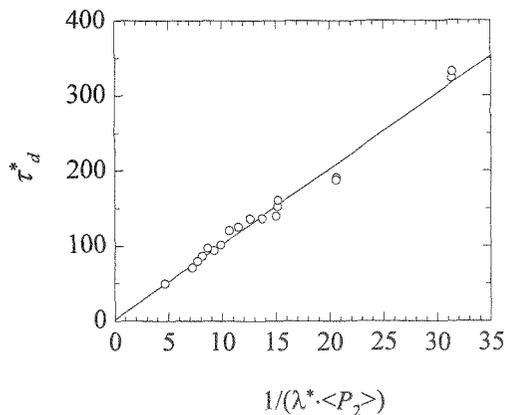
$$1/(\lambda^* \cdot <P_2>)$$

FIG. 3. The field strength dependence of the relaxation time for the director. The straight line shows the least-squares fit.

discussion. Further, the detail analysis on the dynamics at molecular level using the simple model mesogens would be possible. The details on the rotational dynamics for the model nematogens GB(4.4,20.0,1,1) have been discussed on basis of the first- and second-rank orientational time correlation functions. [17]

3. CONCLUDING REMARKS

Molecular dynamics simulation of the Gay-Berne model for the reorientation process of the nematic phase in an electric field has been performed at an isothermal-isobaric condition which is the same as in the experiments. A large system with 8,788 GB(3.0,5.0,2,1) molecules was used in the study. The electric field was applied by 45° with respect to the initial director, and then the molecular motion and structure were monitored until the relaxation process finished. The behavior for the director relaxation was found to be a single-exponential decay which is the same as the Ericksen-Leslie continuum theory predicts. The nematic order parameter did not change so much even in the process. More or less, the nematic order never broke during the switching process. The relaxation time as a function of the field strength increased linearly as the field strength became larger. This is also comparable with the continuum theory. This made it possible to evaluate a rotational viscosity from the linear relation. The evaluated rotational viscosity was comparable with the values which evaluated from another approach in the simulation.

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