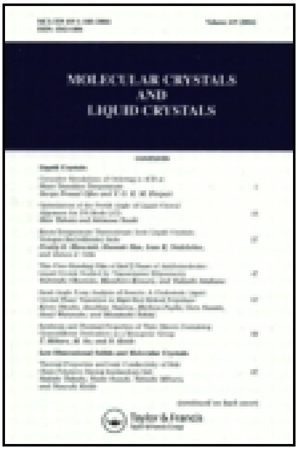

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Microscopic Calculation of Relaxation of Liquid Crystalline Order

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Microscopic Calculation of Relaxation of Liquid Crystalline Order

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In the microscopic point of view, a decay rate of the nematic liquid crystalline order is formulated in a tractable form on the basis of a projection method, which is calculated by a Monte Carlo simulation of the Gay-Berne particle system. Three types of systems with different particle lengths are studied, where at a sampling during early stage of relaxation process, the decay rate is shown to increase as the length of the particle becomes short. At the system of particles of length with 3 times of a diameter, remarkable increase is observed at a transition to a disordered phase. The relaxation process of an order parameter is also simulated simultaneously in place of an experiment, from which the decay rate at the system with 3 times length is tentatively obtained as a macroscopic estimate by fitting the Monte Carlo curve of the order parameter to an exponential function. Both estimates of the decay rate are compared, where the correspondence is qualitatively good.

Keywords: decay rate; Gay-Berne model; molecular theory; Monte Carlo simulation; nematic order; projection method

INTRODUCTION

A study of relaxation of a liquid crystalline order is not only important in a field of display device application but also interesting in a fundamental field to understand a microscopic origin of characteristics of transport coefficients appearing at a thermodynamic stage [1,2]. Especially, the relation between the relaxation of nematic order and a molecular interaction is not clear so far, because much theoretical studies of nematic dynamics are executed in a framework of

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phenomenological theories [3,4]. From the microscopic point of view, the decay rate of nematic order can be formulated on the basis of a fluctuation dissipation theory [1,2]. But, it is not easy to calculate practically molecular theoretic quantities such as a memory function.

In the present study, we formulate the decay rate of nematic order by a projection method [5], which is applied at a coarse-graining procedure of individual molecular motion, and calculate microscopic quantities by Monte Carlo simulation by which all microscopic quantities at any time we can know. The projection method is based on the general prospect that time scales of changes of conserved quantities and/or order parameters and the molecular motion are distinguished distinctly [1,2]. Under the assumption of fast decay of memory function in nematics, the decay rate of nematic order is obtained in a tractable form.

The Monte Carlo simulation is carried out at a Gay-Berne particle system, from which the formalism of decay rate is calculated numerically, where a dependence of the decay rate on the particle length and temperature is studied. Simultaneously, the relaxation process of the order parameter is fitted to an exponential function tentatively to estimate the decay rate from the macroscopic point of view, and a couple of estimates of decay rate derived by both procedures, microscopic and macroscopic, are compared at a representative system of a certain particle length of the constituent Gay-Berne particle.

MICROSCOPIC FORMALISM OF DECAY RATE

Hamiltonian of the system is given by

$$\mathcal{H}(\{\boldsymbol{r}_i,\boldsymbol{u}_i,\boldsymbol{v}_i,\boldsymbol{w}_i\}) = \sum_i \left(\frac{m}{2}\boldsymbol{v}_i^2 + \frac{I}{2}\boldsymbol{w}_i^2\right) + \sum_{i>j} V(\boldsymbol{r}_i,\boldsymbol{u}_i,\boldsymbol{r}_j,\boldsymbol{u}_j), \qquad (1)$$

where m and I are the mass and the moment of inertia of a molecule, respectively, and $\boldsymbol{r}_{\mathrm{i}}$ is the positional vector of centre of mass of molecule i, $\boldsymbol{u}_{\mathrm{i}}$ the unit vector denoting the direction of long axis, $\boldsymbol{v}_{\mathrm{i}}$ $(= \mathrm{d}\boldsymbol{r}_{\mathrm{i}}/\mathrm{d}t)$ the velocity and $\boldsymbol{w}_{\mathrm{i}}$ $(= \mathrm{d}\boldsymbol{u}_{\mathrm{i}}/\mathrm{d}t)$ the rotational velocity vector. A nematic order parameter is given by

$$S = \frac{1}{N}\sum_i \frac{1}{2}(3\cos^2\theta_i - 1), \qquad (2)$$

in which N is a total number of molecules and θ_{i} the angle between $\boldsymbol{u}_{\mathrm{i}}$ and the director vector which is assumed in the direction of z-axis.

Then, an evolution equation of S is given by *Liouville* equation,

$$\frac{dS}{dt} = \sum_i \left(\dot{\boldsymbol{r}}_i \frac{\partial S}{\partial P\boldsymbol{r}_i} + \dot{\boldsymbol{u}}_i \frac{\partial S}{\partial \boldsymbol{u}_i} + \dot{\boldsymbol{v}}_i \frac{\partial S}{\partial \boldsymbol{v}_i} + \dot{\boldsymbol{w}}_i \frac{\partial S}{\partial \boldsymbol{w}_i} \right), \tag{3}$$

in which the dot, e.g., $\boldsymbol{r}_{\mathrm{i},}$ denotes a time derivative of respective quantity.

For the sake of convenience, we define *Liouville* operator as,

$$i\mathcal{L} = \sum_i \left(\dot{\boldsymbol{r}}_i \frac{\partial}{\partial \boldsymbol{r}_i} + \dot{\boldsymbol{u}}_i \frac{\partial}{\partial \boldsymbol{u}_i} + \dot{\boldsymbol{v}}_i \frac{\partial}{\partial \boldsymbol{v}_i} + \dot{\boldsymbol{w}}_i \frac{\partial}{\partial \boldsymbol{w}_i} \right). \tag{4}$$

Then, the *Liouville* Eq. (3) is transformed to the following form as

$$\frac{dS}{dt} = -\int_0^t \mathcal{M}(t-\tau) S(\tau) d\tau + \mathcal{R}(t), \tag{5}$$

where the first term is memory term and the memory function $\mathcal{M}(t)$ is given by

$$\mathcal{M}(t) = \frac{\langle \mathcal{R}(t), \mathcal{R} \rangle}{\langle S, S \rangle}. \tag{6}$$

The random force $\mathcal{R}(t)$ appearing in Eq. (5) and (6) is given by

$$\mathcal{R}(t) = e^{t(1-\mathcal{P})i\mathcal{L}} (1-\mathcal{P}) i\mathcal{L} S, \tag{7}$$

where the projection operator, $\mathcal{P}$, means a projection onto S, which is defined in a concrete form with a variable A by

$$\mathcal{P}A = \frac{\langle A, S \rangle}{\langle S, S \rangle} S. \tag{8}$$

The inner product such as $\langle A, B \rangle$ is defined by

$$\begin{aligned} \langle A, B \rangle = \int \exp\left\{ \frac{-\mathcal{H}(\{\boldsymbol{r}_i, \boldsymbol{u}_i, \boldsymbol{v}_i, \boldsymbol{w}_i\})}{kT} \right\} A(\{\boldsymbol{r}_i, \boldsymbol{u}_i, \boldsymbol{v}_i, \boldsymbol{w}_i\}) \\ \times B(\{\boldsymbol{r}_i, \boldsymbol{u}_i, \boldsymbol{v}_i, \boldsymbol{w}_i\}) \prod_i dr_i d\boldsymbol{u}_i d\boldsymbol{v}_i d\boldsymbol{w}_i, \end{aligned} \tag{9}$$

in which T denotes a temperature, k the Boltzmann constant, and the integral is carried out over the Γ-space. Generally, a term linear to S called the streaming term, $i\Omega S = \langle i\mathcal{L}S, S \rangle S / \langle S, S \rangle$, appears in the right hand side of Eq. (5) in case S is of multi-component [1,2], though it vanishes in the present case because of scalar S.

By taking account of the general assumption that the relaxation of the order parameter S is very slowly than individual molecular motions, Eq. (5) is rewritten as

$$\frac{dS}{dt} = -S(t)\int_0^t \mathcal{M}(t-\tau)d\tau + \mathcal{R}(t), \tag{10}$$

which is nothing but the *Langevin* equation for S and the decay rate γ is given by the coefficient of $S(t)$ as $\int_0^t \mathcal{M}(t-\tau)d\tau$. Because $\mathcal{M}(t)$ is assumed to attenuate rapidly as time increases, γ is approximated as

$$\gamma = \int_0^t \mathcal{M}(t-\tau)d\tau \approx \int_0^\infty \mathcal{M}(t)dt. \tag{11}$$

Equation (11) is the practical expression of a fluctuation-dissipation theorem of the second kind for the decay rate. In general, kinetic coefficients are expressed in terms of correlation functions of random forces like Eq. (11).

To estimate γ, we expand the factor $e^{t(1-\mathcal{P})i\mathcal{L}}$ of $\mathcal{M}(t)$ in power series of t(1-$\mathcal{P}$)$i\mathcal{L}$ up to the 2nd order as

$$\begin{aligned}\mathcal{M}(t) &= \frac{\langle e^{t(1-\mathcal{P})i\mathcal{L}}(1-\mathcal{P})i\mathcal{L}S, (1-\mathcal{P})i\mathcal{L}S\rangle}{\langle S,S\rangle}\\ &= \frac{\langle [1+t(1-\mathcal{P})i\mathcal{L}+1/2\{t(1-\mathcal{P})i\mathcal{L}\}^2](1-\mathcal{P})i\mathcal{L}S, (1-\mathcal{P})i\mathcal{L}S\rangle}{\langle S,S\rangle}.\end{aligned} \tag{12}$$

The term proportional to t vanishes because of the time reversal symmetry. The constant term and the term proportional to t^2 are calculated using Eq. (8), and the memory function is summarized up to the order of t^2 in the following expression as

$$M(t) = \langle \dot{S},\dot{S}\rangle \exp\left[-\frac{1}{2\langle \dot{S},\dot{S}\rangle}\left\{\frac{\langle \ddot{S},\ddot{S}\rangle}{\langle S,S\rangle} + \frac{\langle \dot{S},\dot{S}\rangle\langle \ddot{S},S\rangle}{\langle S,S\rangle^2}\right\}t^2\right]. \tag{13}$$

By the integration of time in Eq. (11), we obtain a tractable form of γ as

$$\gamma = \frac{\langle \dot{S},\dot{S}\rangle}{2}\left[\frac{2\pi\langle \dot{S},\dot{S}\rangle\langle S,S\rangle^2}{\langle \ddot{S},\ddot{S}\rangle\langle S,S\rangle + \langle \dot{S},\dot{S}\rangle\langle \ddot{S},S\rangle}\right]^{1/2}. \tag{14}$$

The averages, $\langle\ldots\rangle$, are calculated here by a Monte Carlo ensemble average.

SYSTEM AND CONDITION OF MONTE CARLO SIMULATION

The system of Monte Carlo simulation consists of 1024 Gay-Berne particles (G-B particles) [6] in a cubic cell with the periodic boundary condition. Three types of constituent G-B particles are studied; the lengths of the particle l are 2, 3 and 4 in the unit of a diameter, and dimensions of cell scale are 13.0, 14.8 and 16.3, respectively, so as that a volume fraction is common. An interaction between particles is a Gay-Berne potential V_{GB}, and parameters appearing therein are chosen to the standard ones used in the precious study [7]. The initial condition of simulation is taken in a completely ordered state where all particles are directed along the z-axis as shown in Figure 1. Then, S, $\dot{S}$ and $\ddot{S}$ are expressed as,

$$S = \frac{1}{N}\sum_i \frac{1}{2}(3u_{iz}^2 - 1), \tag{15}$$

$$\dot{S} = \frac{3}{N}\sum_i u_{iz}w_{iz}, \tag{16}$$

$$\ddot{S} = \frac{3}{N}\sum_i (w_{iz}^2 + \frac{u_{iz}f_{iz}}{I}), \tag{17}$$

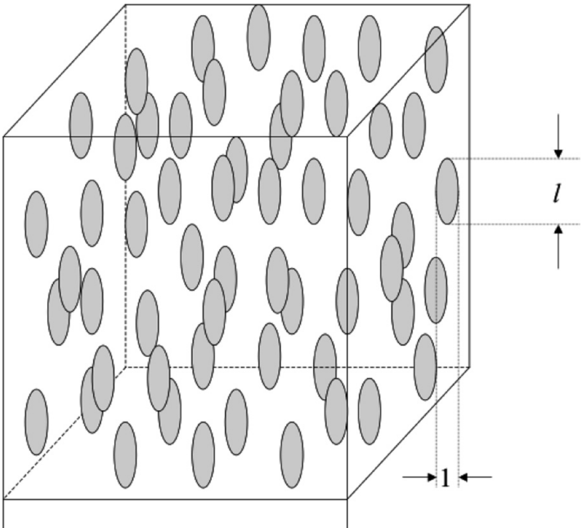

FIGURE 1 Initial state of the system.

where the force f_{iz} is given by

$$f_{iz} = -\frac{\partial V_{\mathrm{GB}}}{\partial u_{iz}}. \tag{18}$$

For the Monte Carlo average of decay rate, a sampling (MC sampling) is taken as follows; at an early stage up to 10^4 Monte Carlo step (MC step), the average is taken during every 10^3 MC step, and at the latter stage after 10^4 MC step up to 10^5, the average is taken during every 10^4 MC step, where 1 MC step is 10^3 MC sampling (not 1024, for simplicity). The relaxation process of the order parameter is obtained simultaneously, from which a macroscopic estimate of the decay rate, γ, is also obtained by fitting the curve to an exponential function.

RESULTS

First, the relaxation of nematic order parameter in the Monte Carlo simulation is shown in Figure 2, where curves are obtained for each G-B particle lengths at various temperatures; circles, squares and triangles are for the systems of $l = 4$, 3, 2, and guide curves of solid

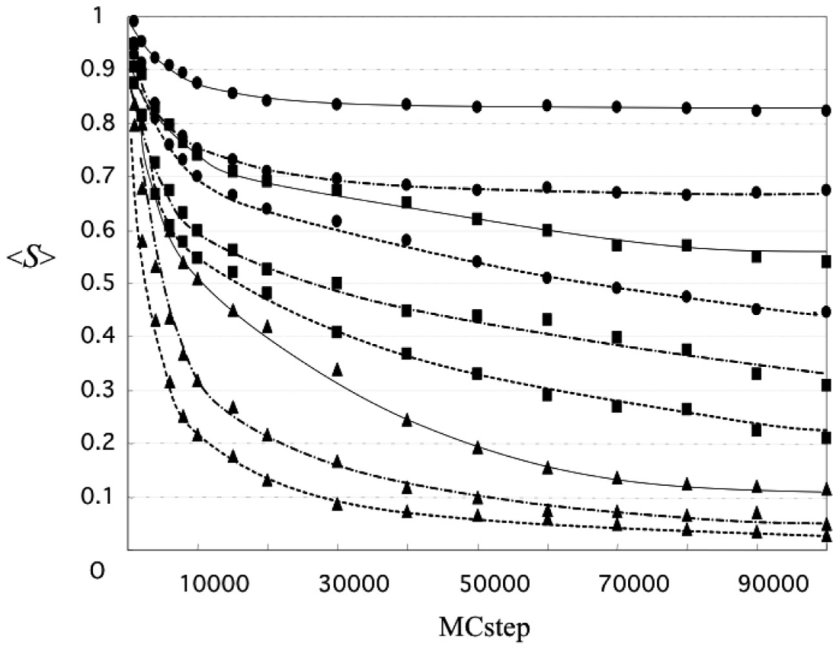

FIGURE 2 Relaxation of the nematic order.

line, dotted chain line and chain line are for $T = 1$, 4 and 10 in a unit of Gay-Berne potential strength ε_0 divided by k, respectively. The system with $l = 4$ at $T = 1$ and 4 and that with $l = 3$ at $T = 1$ are considered to be ordered while others are in a disordered phase, though details of ordering process of each systems are not checked practically. At the molecular dynamic simulation carried out previously the transition temperature of the present system with $l = 3$ is estimated to be 3[7].

The decay rate γ in Eq. (14) is calculated at each system for various values of temperature. Estimates at the latter stage of relaxation are rather dispersed, and in the present stage, we have no concrete statement. On the other hand, the data at the early stage are systematic. In Figure 3 the temperature dependence of γ in the early stage of relaxation is shown. We observe that γ increases as the length of particle becomes short. For the system with $l = 2$, γ has large value, which is considered to come from the disordered phase even at $T = 1$. On the other hand in the system with $l = 3$, a remarkable increase is observed at $T = 4$, where the system is probably in the disordered phase near the phase transition, and for the system with $l = 4$ the small increase is seen at $T = 8$. Thus, it is demonstrated that in the early stage, γ has larger value at the disordered phase than that at the ordered phase and generally increases as the temperature increases, and also has larger value for shorter particles.

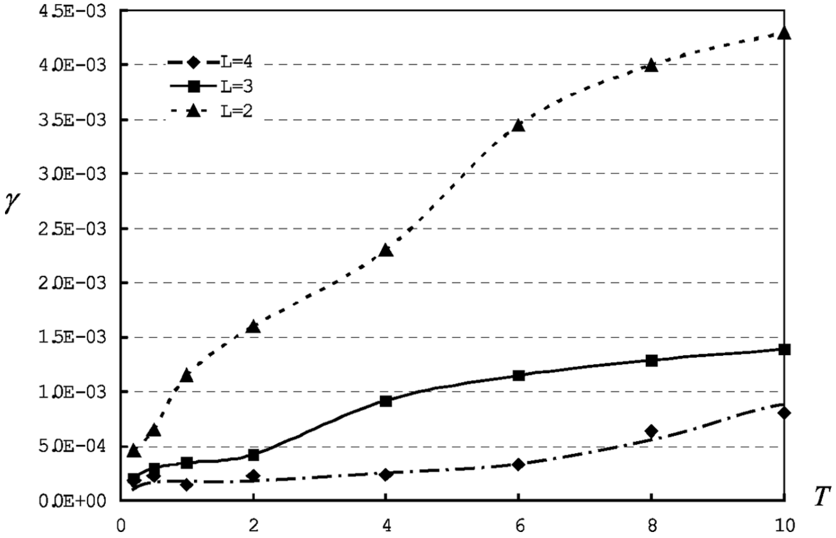

FIGURE 3 Temperature dependence of γ at early stage estimate.

So far, we have not heard any experimental result about γ. Here, we try to obtain a macroscopic estimate of the decay rate by this MC procedure in place of experiment. The MC average is a kind of ensemble average, in which the ensemble consists of systems generated successively by each MC step. On the other hand, we observe in Figure 1 the change of the order parameter as if the decay process occurs in the course of the MC step, in which the MC step looks like a physical time. However, we have no dynamical reason to relate MC step n to the physical time t. We introduce here a stochastic interpretation relating n to t. Let's plot the representative points of the systems generated by the MC procedure successively in one Γ-space. Then, we obtain a locus of the representative point driven not by the Newtonian equation of motion but by the stochastic process ruled by the Metropolis algorism of MC simulation. In practice, the representative point moves only a bit within the volume element ($\{\Delta \boldsymbol{r}_i, \Delta \boldsymbol{u}_i, \Delta \boldsymbol{v}_i, \Delta \boldsymbol{w}_i\}$) in the Γ-space during one MC step. Assume $\Delta t(n)$ an interval of physical time corresponding to one MC step from the (n-1)-th MC step to the n-th MC step. Then, we are led to the probabilistic relation given by

$$v\Delta t(n) = r(n)\bar{a}, \tag{19}$$

where v denotes a velocity of the particle satisfying the principle of equipartition of energy, $mv^2/2 = 3kT/2$, $r(n)$ an acceptance ration during the n-th MC step which is related to an acceptance ratio up to the n-th MC step $R(n)$ as $nR(n) = \Sigma_{n'=1}^{n} r(n')$ and $\bar{a}$ a mean of the

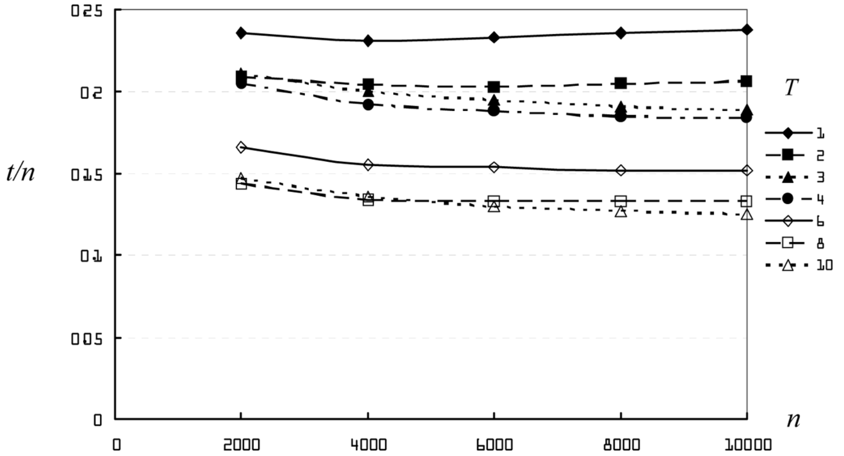

FIGURE 4 Relation between t and n at the early stage of the system with $l = 3$.

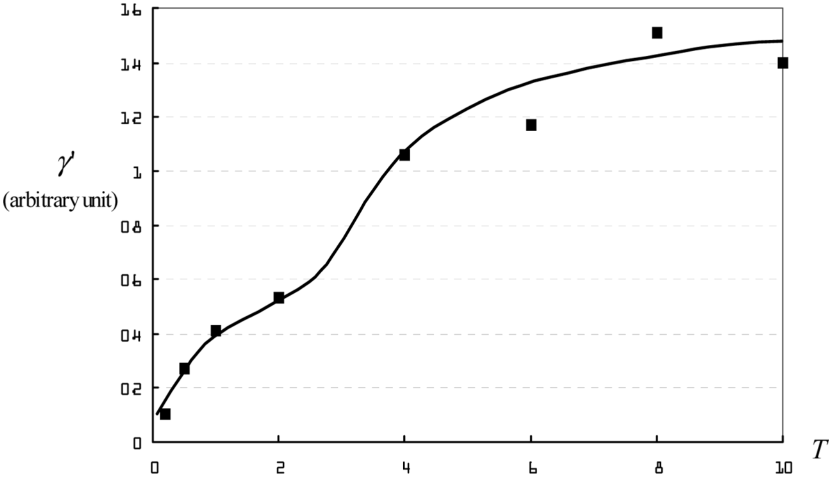

FIGURE 5 Temperature dependence of γ' of early stage estimate.

displacement at one MC step. By summing up $\Delta t(n)$, we obtain the relation between n to t as,

$$t = \sum_{n'=1}^{n} \Delta t(n') = \sqrt{\frac{m\bar{a}^2}{3kT}}\, R(n)n. \tag{20}$$

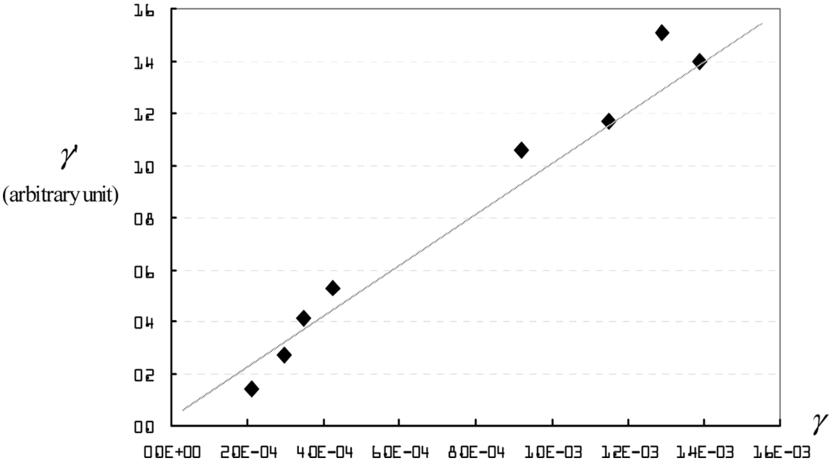

FIGURE 6 Relation between γ and γ'.

Now, we can obtain the S-t relation, which is fitted to an exponential function exp(-γt), where γ is interpreted as a macroscopic estimate of the decay rate.

In Figure 4, the relation between t and n at the early stage is shown for various temperature $T = 1, 2, 3, 4, 6, 8$, and 10 at the system with $l = 3$, where the ratio t/n of the ordinate is depicted in the unit $\sqrt{m/3\varepsilon_0}\bar{a}$. We see rather small deviation from a constant value and monotonous behaviours. The estimates of γ at various temperatures are obtained as shown in Figure 5, which resembles to the curve γ for $l = 3$ in Figure 3. In practice, we seea good correspondence between γ and γ for various values of temperature as shown in Figure 6.

SUMMARY

A new method to calculate the decay rate of nematic liquid crystalline order is proposed in the microscopic point of view. The formalism of the decay rate of nematic order parameter is given in a tractable form by the projection method, which is calculated numerically using the Monte Carlo simulation at Gay-Berne particle systems of different lengths ($l = 2, 3, 4$). The decay rate is shown to increase as the length becomes short, and also the temperature increases. At the system $l = 3$, we see a stepwise increase of the decay rate clearly at the phase transition to the disordered phase, while a gradual increase is observed at the system $l = 2$ in which no transition is assumed to occur in the temperature range where the simulation is carried out. The behaviour of the system with $l = 4$ seems to support the result that the decay rate increases at the transition to the disordered phase, though the data is not so clear as the case of $l = 3$. From the decay process starting at the completely aligned state in the course of Monte Carlo simulation, the decay rate is also obtained for the system with $l = 3$ by fitting the decay curves to an exponential function. Both estimates coincide to each other in the wide range of temperature, which suggests to justify the new calculus of kinetic coefficient based on the projection method and also the stochastic interpretation introduced here to relate the Monte Carlo step to the physical time.

At the first stage of present investigation, we had a plan to calculate only the decay rate microscopically, in which the Monte Carlo method is utilized for simplicity. However, we could not find any experimental data about the decay rate to be compared to the calculated ones, and tried to obtain the decay rate as a macroscopic estimate by fitting the decay process of the order to the exponential function as the Monte Carlo simulation proceeds. In this study, a stochastic interpretation of the relation between the Monte Carlo step and the physical time is introduced. From the point of the real physical time, molecular dynamics simulations are preferred in nature to obtain the macroscopic estimate of the decay rate. Nevertheless, it is quite interesting to certify the reliability of stochastic interpretation of the Monte Carlo step to relate the physical time introduced newly, which will be carried out systematically in a near future.

The analyses of the present systems are restricted mainly in the early stage of the decay process. The phenomena such as the slowing down near the phase transition are considered to be observed remarkably rather in the latter stage. Next, the simulation will be extended to much longer step than 10^5 step to clarify such phenomena.

As for the decay rate of the magnitude of order parameter here studied, we do not know experimental studies at present, though nice studies on the dynamics of director fluctuation have been carried out [8,9]. In this respect, we expect experimental investigations of decay process of the order parameter, especially a systematic study for the homologous series of materials.

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