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Fluctuations in Systems of Hexatic Smectic B Liquid Crystals

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Systems of hexatic smectic B liquid crystal are investigated by constant-pressure and constant-temperature molecular dynamics simulations. By using a symplectic integrator designed for soft-matter under a condition where the fluctuation of the system is large, spontaneous transfer among the metastable states is observed. By analyzing the transfer in both directions, distributions of work values corresponding to the forward and reverse processes are obtained.

Keywords hexatic smectic B; molecular dynamics simulation; metastable states; fluctuation theorem

1. Introduction

The solutions of symplectic integrators preserve the structure of the Hamilton's equations of motion. Recent molecular dynamics simulations using the symplectic integrator designed for soft matter [1] has revealed the importance of treating the pressure not as a scalar but as a tensor, especially in metastable states and non-equilibrium systems [1–6]. The anisotropic fluctuation becomes extremely important not only in systems with anisotropy in the constituent molecules, but also in metastable states, such as glass, of systems consisting of isotropic molecules [3, 4]. Thus, to investigate systems under hydrostatic pressure, a simulation method which treat the pressure as a tensor is necessary;it allows the anisotropic fluctuations of the volume.

Using the symplectic integrator designed for soft matter, a phase sequence of crystal-hexatic smectic B(HexB)-smectic A(SmA) is obtained for systems of soft parallel spherocylinders. In addition, dynamical transfer among the metastable states of HexB has been observed under a condition at which thermal fluctuation becomes strong [5]. When the temperature is close to the HexB-SmA transition and the system size sufficiently small,

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the system transfers among different HexB metastable states in a single calculation under constant-pressure and constant-temperature. The occurrence of transfer among the metastable state is spontaneously triggered by fluctuations inside the system. Thus, the life time in each state and the number of transfer among them reflect the topology of the free energy landscape of HexB accurately [6]. Two series of HexB simulation data of N = 1344 soft parallel spherocylinders with rigid core length L = 4 has been obtained and analyzed by network theory. Each series starts from different initial configurations: (A) crystal phase (T = 10) and (B) SmA phase (T = 200), but kept at the same temperature T = 135 and pressure P = 1000. In this paper, we pick up several sets of metastable states and analyze transfers among them to see if Crooks fluctuation theorem [7] holds for them.

Crooks has assumed the system to be Markovian and microscopically reversible, and concluded that

$$\frac{\rho_F\left(+W_{i\to j}\right)}{\rho_R\left(-W_{j\to i}\right)} = \exp\left(+\beta W^{dis}\right) = \exp\left(+\beta\left[W - W^{rev}\right]\right) \tag{1}$$

where $\rho_F(+W_{i\to j})$ and $\rho_R(-W_{j\to i})$ corresponds to the work distribution in forward and reverse process, respectively. The dissipative work W^{dis} is defined as the difference between reversible work and the actual one, *i.e.*, $W^{dis} = W - W^{rev}$. The reversible work W^{rev} is the free energy differences between the initial and final ensembles. The fluctuation theorem in this form holds both in the canonical and in the isothermal-isobaric ensembles [7]. Equation (1) easily leads to the nonequilibrium work theorem of Jarzynski [8].

The symplectic integrator designed for soft matter [1] utilizes the Nosé-Poincaré thermostat. Thus the system is described by Hamiltonian dynamics on the symplectic extended phase space [9]. As discussed by Cuendet, the work directly connected to the work function in Jarzynski's nonequlibrium work theorem and Crooks fluctuation theorem is

$$W = H\left(t\prime\right) - H_0\left(t\prime = 0\right) = \int_0^{t\prime} \frac{\partial \Phi}{\partial \tau} d\tau \tag{2}$$

in the simulation [10]. In many theoretical work, it is assumed that the heat bath can be described additively to the Hamiltonian of the original system [11, 12]. However, in our simulation method the heat bath is not described as an additive term to the original Hamiltonian, but is described as a Poincaré time transformation of the time dependent Hamiltonian of the original system. In our simulation method, the change in total energy

$$\Delta E = \nu\left[\boldsymbol{H}_a\left(t'\right) - \boldsymbol{H}_0\right] = \nu W \tag{3}$$

and work W defines the heat absorbed by the system from the heat bath, *i.e.*,

$$\Delta Q = \Delta E - W. \tag{4}$$

The time scaling factor ν is common to the Poincaré time transformation and for the temperature scaling in $\boldsymbol{H}_a\left(t\prime\right)$ of our method. The whole system including the heat bath in symplectic extended phase space obeys the isothermal reversible process, thus,

$$TdS = -dF^{tot} + \delta W^{rev} = 0 \tag{5}$$

where $dF^{tot} = d\left(E - Q\right) = \nu W - \left(\nu - 1\right)W = W$ and $\delta W^{rev} = W$ since $W^{dis} = 0$ for the total system including the heat bath. Considering this situation in the conventional

symplectic phase space without the heat bath, the heat absorbed by the system

$$\Delta Q = (\nu - 1)\, W = -W^{dis} \tag{6}$$

defines the work of the thermostat, i.e., W^{dis} where

$$W^{dis} = W - W^{rev}. \tag{7}$$

The reversible work W^{rev} is the free energy differences between the two equilibrium ensembles. We will see later on that the situation extends to ensemble averages of two metastable states. Equations (6) and (7) lead to

$$W^{rev} = \nu W \tag{8}$$

in our simulation. In the conventional symplectic phase space, this is the irreversible process

$$T\Delta S = -W^{rev} + W = (1 - \nu)\, W \geq 0. \tag{9}$$

Note that in our simulation, the free energy difference cannot be divided into the internal energy and entropy terms since the heat bath is not additive to the Hamiltonian of the original state; the thermostat includes the Poincaré time transformation. However, it is sufficient to monitor the total work W and the time scaling factor ν in our simulation to observe whether the fluctuation theorem holds.

2. Simulation Model and Method

2.1. Intermolecular Potential

The model particles are parallel soft spherocylinders [2, 5] interacting through purely repulsive pairwise potential expressed by minimum distance between the particles;

$$\phi_{ij} = \begin{cases} \varepsilon \left[\left(\frac{D}{R_{ij}} \right)^{12} - \left(\frac{D}{R_{ij}} \right)^{6} + \frac{1}{4} \right] & \text{if} \quad R_{ij} < r_0 \\ 0 & \text{otherwise,} \end{cases} \tag{10}$$

where $r_0 = 2^{1/6} D$ and R_{ij} is the shortest distance between lines representing the long axis of two spherocylinders i and j:

$$R_{ij}^2 = \begin{cases} x_{ij}^2 + y_{ij}^2 & \text{if} \quad |z_{ij}| \leq L \\ x_{ij}^2 + y_{ij}^2 + \left(|z_{ij}| - L \right)^2 & \text{otherwise,} \end{cases} \tag{11}$$

where (x_{ij}, y_{ij}, z_{ij}) is the relative position of the center of mass the spherocylinders i and j, and L is the length of the line representing the long axis of the spherocylinder which is fixed parallel to the z-axis. Periodic boundary conditions are applied in x, y, and z-directions. Reduced units where length, energy, and mass are measured in D, ε, m (where m is the mass of a spherocylinder), respectively, are used throughout this work. The Boltzmann factor k_B is set to unity in the simulations. Systems with $L = 4$ of system size $N = 1344$ which show crystal–HexB–SmA phase transition is used in this work.

2.2. Symplectic Integrator Designed for Soft Matter

For details of the simulation method refer to [1]. The MD simulation method consists of equations with time reversibility. This ensures that the system is microscopically reversible which is Crook's assumption to obtain the fluctuation theorem. In our simulation, the equilibrium distribution is not necessary preserved. For instance, when the system is under slow equilibration with a large thermostat piston mass [13], the temperature distribution is quite flat at the beginning and evolves toward equilibrium distribution slowly under the deterministic equations.

3. Discussion

3.1. Metastable States of HexB

The metastable states of HexB are clearly distinguished by the sixfold bond orientational order (BOO) C_6 and it's higher harmonics C_{6n}

$$C_{6n} = \left| \left\langle \frac{1}{N_b} \right\rangle \sum_{j}^{N} \sum_{k} \cos\left(6n\theta_{kj}\right) \right| \tag{12}$$

where θ_{kj} is the angle between the fixed x-axis and the projection of the line connecting the center of mass of particles k and j on the xy-plane, and N_b denotes the total number of bonds in the system. The index j runs over all the molecules in the system, and k runs over all the nearest-neighbor molecules of j. The nearest neighbors are defined as molecules with horizontal distance $\leq 1.5r_{1st}$ where r_{1st} is the distance of the first peak of the 2D radial distribution function. The bracket $\langle \cdots \rangle$ denotes the time average. Note that C_6 contains information on all layers in the system. The states are identified by a combination of (C_6, C_{12}, C_{18}). Altogether, thirteen discrete values are identified for C_6, six for C_{12}, and four for C_{18}. Each state i is assigned a number by $S_i = (S_{C_6} - 1) \times 24 + (S_{C_{12}} - 1) \times 4 + S_{C_{18}}$ where $1 \leq S_{C_6} \leq 13$, $1 \leq S_{C_{12}} \leq 6$, $1 \leq S_{C_{18}} \leq 4$. The numbering $S_{C_{6n}}$ starts from lower values for each C_{6n}. The total number of combinations (312) does not appear in this system, because there are correlations among the values of C_{6n}. In the HexB states, there exists a scaling relation $C_{6n} = C_6^{\sigma}$. The value of σ depends on the temperature. The scaling relation is known experimentally [14] and also appears in our simulation [5, 15]. The difference in physical properties and inter- and intra-layer spacing of the molecules of HexB metastable states are discussed in addition to the correlation among the layers [15]. The data analyzed here is common with that used to construct the network on the free energy phase space [6] and consists of two series. Series (A) uses a crystal configuration obtained at $T = 10$ as an initial configuration. Series (B) starts from a SmA LC initial configuration obtained at $T = 200$. The time evolution of both series are conducted under the same temperature ($T = 135$) and same pressure ($P = 1000$). Figures 1(a) and (b) show examples of time sequence of the simulated system fluctuating among different metastable states. As discussed in [6], series (B) which starts from a high-temperature SmA configuration has larger fluctuations than series (A). Series (B) which have larger fluctuations than in (A), have a larger number of transformations among metastable HexB states.

In Figs. 2 (a) and (b), the total work W is shown for the same time sequence as Figs. 1 (a) and (b), respectively. The time sequence of $6n$-fold BOOs C_{6n} shows sharp transformation among the metastable states, while the value of work evolves without any obvious correlation. When the transformation among two states with large value difference

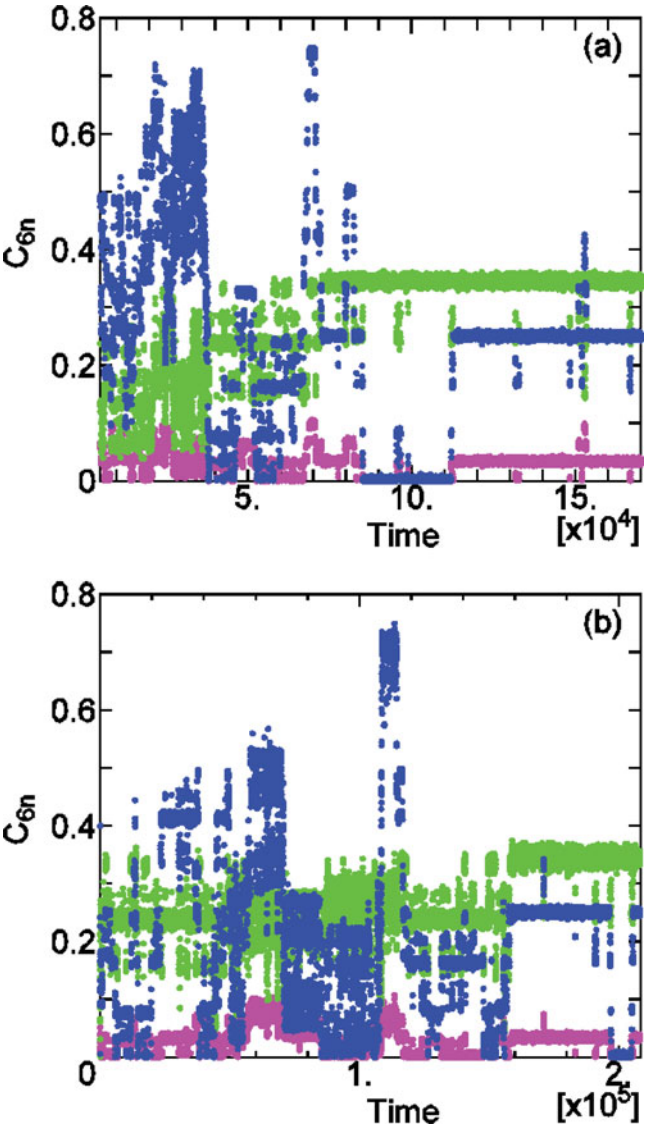

Figure 1. Time evolution of C_6 (●), C_{12} (●), C_{18} (●) in fluctuating states of HexB at $T = 135$ and $P = 1000$ with initial configuration of crystal phase ($T = 10$). The thermostat piston masses K, which determine the response speed to the heat bath, are (a) $K = 1.0 \times 10^3$ and (b) $K = 6.0 \times 10^5$. The mass of the barostat is $M = 0.01$ for both systems. Time is shown in reduced simulation unit.

in physical property, such as volume, occurs, it can also be detected by that physical property. However, such observation is not common as seen in Fig. 2. Note that the fluctuations in the value of W is much smaller than k_BT.

3.2. Work Distribution Functions of Transformation Among Two States i and j

We choose two pairs of i and j states from each series (A) and (B) and analyze the transformations among those pairs. The work distribution functions of the forward process

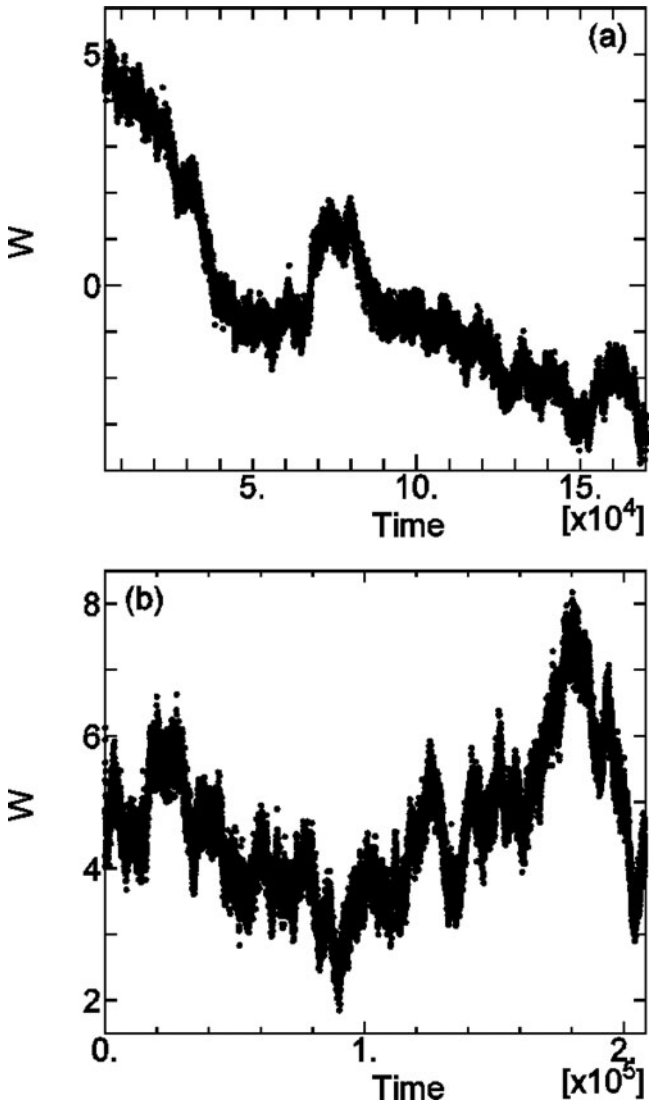

Figure 2. Work W for the same time sequence as Figs. 1 (a) and (b)

$i \rightarrow j$ and the reverse process $j \rightarrow i$ are shown in Fig. 3. For all the data in each series, transformations from i to j state are detected. We calculate the difference in work values between the last time step in state i and the first time step in state j. Thus, the number of data coincides with the number of transformations from i to j state to obtain the work distribution function. Table 1 shows the chosen pair, the number of transfers $N_{i\rightarrow j}$ and $N_{j\rightarrow i}$ among pairs, and the average of the reversible work W^{rev}. Equation (1) means that the crossing point of the work distribution functions $\rho_F(+W_{i\rightarrow j})$ and $\rho_R(-W_{j\rightarrow i})$ is precisely at $W = W^{rev}$, i.e., the free energy differences between i and j states. To compare with the crossing point of the forward and reverse distribution function, W_i^{rev} is calculated for the whole time in each state i, regardless of the previous and next states. The average

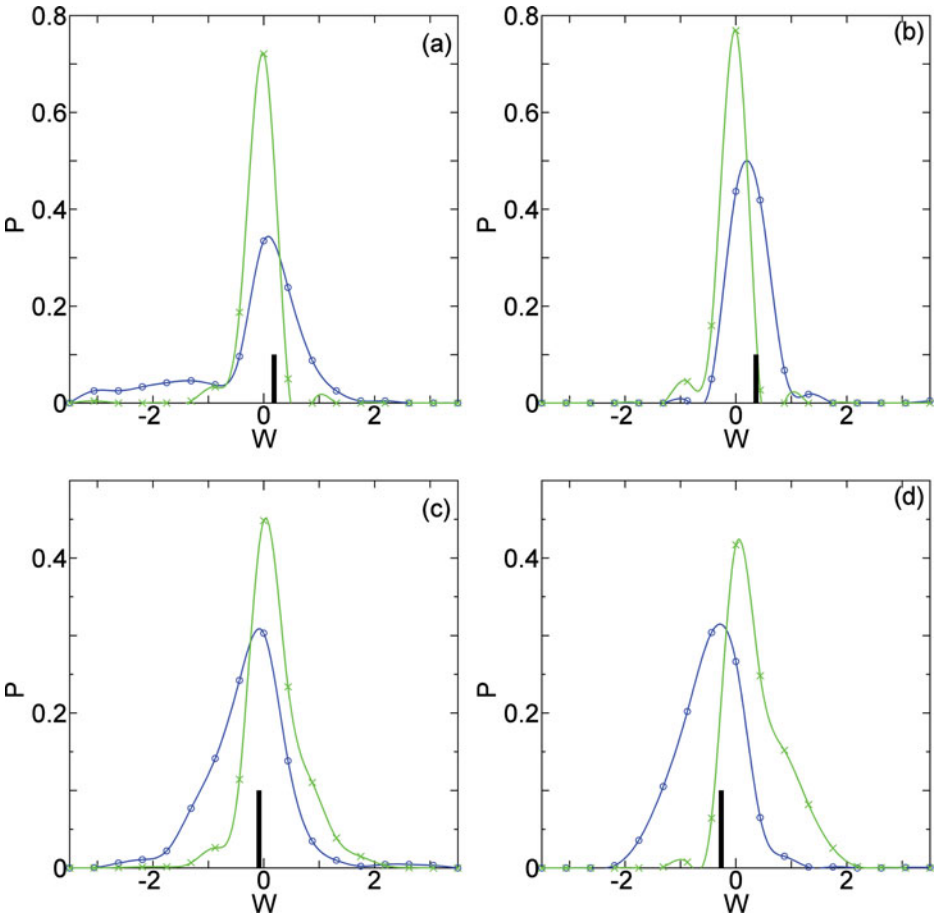

Figure 3. Work distribution functions of the forward process (○) and the reverse process (×) for transformation among pair of states. Details are in Table 1. (a),(b):Series (A) and (c),(d):Series (B).

is taken throughout the lifetime τ_i of state i;$W_i^{rev} = \sum_{\tau_i} \nu W/\tau_i$. Thus, the statistics of W_i^{rev} is larger compared to that of the work distribution functions $\rho_F(+W_{i\to j})$ and $\rho_R(-W_{j\to i})$. The lifetime τ_i of each state is shown in Table 2. The average value of $W^{rev} = W_j^{rev} - W_i^{rev}$ is also depicted in Fig. 3 as a thick bar.

In our simulation, the values of work W are measured from the initial configuration. Since series (B) start from an initial configuration of SmA LC state, the horizontal axis of Figs. 3 (c) and (d) should be reversed (or the values multiplied by minus) to obtain the work distribution in absolute values. The transformations among metastable states are spontaneous in our simulations, so the number of statistics differ for each pair and each direction of the process as shown in Tables 1 and 2.

4. Concluding Remarks

We have analyzed transformations among different metastable states of HexB and obtained work distribution functions. In the present analyzed system, spontaneous fluctuations induce the transformation among different metastable states, thus the statistics to obtain the work

distribution functions are limited. However, at least for the analyzed pairs in this paper, Crook's fluctuation theorem seems to be valid. Such observation is possible due to the high precision symplectic method designed for soft matter. Especially, systems with relatively small numbers of molecules leading properly to large fluctuations can only be simulated by the barostat which accommodates anisotropic fluctuations treating the pressure as a tensor.

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Table 1. Number of transfers and the value of reversible work W^{rev} among selected metastable states of HexB depicted in Figure 3

Series	State i	State j	$N_{i\to j}$	$N_{j\to i}$	W^{rev}	Corresponding Figure
A	139	135	230	133	0.1887	Fig. 3(a)
A	312	283	224	92	0.3646	Fig. 3(b)
B	62	42	2221	1878	−0.0850	Fig. 3(c)
B	111	115	1596	1247	−0.2619	Fig. 3(d)

Table 2. Lifetime τ_i of each selected state i

Series	State i	Lifetime τ_i
A	135	27410
A	139	1880
A	283	10880
A	312	17100
B	42	68610
B	62	161360
B	111	17140
B	115	45140