Anisotropy in condensed matter – liquid crystals, glass, and phase coexistence

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Abstract. Molecular dynamics (MD) methods suitable for treating anisotropic fluctuations in condensed matter are discussed. Barostats with two anisotropic factors to control the simulation cell dynamics are introduced in three MD simulation methods; constant pressure, constant surface tension, and canonical hydrostatic. To demonstrate the possibilities of these methods, calculations of two systems, one consisting of anisotropic particles and other consisting of isotropic particles, are presented.

1. Introduction
Liquid crystals (LCs) are the liquid which orientational order among the constituent molecules remains. In addition to the orientational order, a loose layer structure exists in the smectic (Sm) LC phase. There are many variants of the Sm phase. SmA phase consists of liquid like layers. The hexatic smectic B (HexB) phase shows 6-fold symmetry in relative positions inside the layers, characterized by 6-fold bond orientational order. Orientational fluctuations of molecules are fast, while the undulation of the smectic layers are comparatively very slow. Because of the anisotropy in length and time scale, LC phase simulation is generally difficult.

Extended molecular dynamics (MD) methods to obtain states in various statistical ensembles have been introduced to date. Since abundant experimental data are those taken under constant pressure, constant pressure methods \cite{1, 2} and their variants have been explored extensively. Simulations of anisotropic molecules by the Andersen’s method \cite{1} easily lead to non-hydrostatic stress and those by the Parrinello & Rahman method \cite{2} easily lead to collapse the simulation cell because the Virial theorem is not generally satisfied. To properly simulate the anisotropic melting observed in liquid crystals, barostats, \textit{i.e.}, the simulation cell control method to obtain the desired stress tensor, has been developed \cite{3, 4, 5}. An anisotropic factor $\alpha$ is introduced to describe anisotropic fluctuations of the simulation cell. It drastically reduces the artifact, which is caused by non-hydrostatic stress that are easily induced by other methods. We take $\alpha = L_z/L_{xy}$ where $L_z$ and $L_{xy}$ are, respectively, the lengths of the simulation cell in the $z$ (normal) and $L_x = L_y$ (transverse) directions. The volume of the simulation cell is expressed by two variables $V = \alpha Q$, where $\alpha$ and $Q$ are respectively the anisotropic factor and the isotropic volume factor. These barostats can be integrated in symplectic integrators with the explicit algorithm\cite{6}. For temperature control, the Nosé-Poincaré thermostat \cite{7, 8} is added. Because the heat production/absorption can be precisely measured in this method, the thermodynamic
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approach to measure entropy has been proposed [6]. By this approach, the relative entropy change in the phase sequence of crystal-hexatic smectic B (HexB) LC-smectic A (SmA) LC has been measured [9, 10].

In addition to thermodynamic equilibrium states, metastable states can be obtained [6]; supercooled and amorphous solids were observed in systems of isotropic sphere WCA potential [12]. Many metastable states were obtained later on and discussed in relation to inherent structures of glass [13, 14].

We also obtained many metastable states of HexB with different discrete values of the 6-fold bond orientational order [15, 16]. The variation of metastable states appears due to differences in correlation among smectic layers. When relatively small systems \( N = 1344 \) and \( N = 4680 \) are kept near the HexB-SmA transition temperature, fluctuations among different metastable states were clearly discerned. By analyzing the time sequence of these spontaneous fluctuations, the network of states in the free energy landscape of HexB has been constructed [17]. We also obtained the work distribution of the transfer process among different metastable states [18], and investigated whether the Crook’s fluctuation theorem [19] holds.

By analyzing the spontaneous fluctuation of the stress tensor and strain, the elastic moduli normal and transverse to the smectic layers were calculated [20]. Softening of the layer compression modulus near HexB-SmA phase transition was observed. Surface tension enhances this softening and lowers the transition temperature. However, there was only one anisotropic factor in these simulations. The measured elastic modulus in transverse direction is 2 dimensional bulk modulus and is not the shape elastic modulus. In order to investigate the transverse visco-elastic properties of the smectic layers, the shape in transverse direction should be able to fluctuate. Thus, we need two anisotropic factors in the simulation cell.

As a general extension of our barostats, here we add another anisotropic factor in the dynamics of the simulation cell. This should make the method more effective to investigate the visco-elastic properties.

In LCs, the shape of the molecular volume change is dependent on temperature, and it drastically changes around phase transitions. In order to properly investigate these phenomena in canonical ensemble, a method, which allows the shape of the simulation cell to fluctuate under constant volume, is required. We also construct a constant volume method where the cell shape fluctuates in response to the stress tensor.

2. Symplectic MD simulations with two anisotropic factors in the simulation cell dynamics

The symplectic integrators designed for soft matter [6] are extended to include two anisotropic factors in the simulation cell dynamics. In addition to \( \alpha = L_z/L_x \), we introduce \( \theta = L_y/L_x \), where \( L_x \) and \( L_y \) are respectively the lengths of the simulation cell in transverse directions \( x \) and \( y \). The simulation cell lengths in each direction are \( L_x = Q^{1/3} \), \( L_y = \theta Q^{1/3} \), and \( L_z = \alpha Q^{1/3} \). The volume of the simulation cell is \( V = \alpha \theta Q \). The real coordinate \( r_i \), and velocity \( \dot{r}_i \) of particle \( i \) are related to the scaled ones \( s_i \) and \( \dot{s}_i \), respectively, by

\[
\begin{align*}
    r_i &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \theta & 0 \\ 0 & 0 & \alpha \end{pmatrix} Q^{1/3} s_i, \\
    \dot{r}_i &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \theta & 0 \\ 0 & 0 & \alpha \end{pmatrix} Q^{1/3} \dot{s}_i.
\end{align*}
\]

All of the barostats can be explicitly integrated since momentum conjugate pairs do not appear in the same splitted term of the Hamiltonian [6]. The Nosé-Poincaré thermostat is added for temperature control [7, 8]. All the following Hamiltonians can be solved explicitly by the symplectic integrator by utilizing the explicit formula for Nosé-Poincaré thermostat [21].

For the MD methods of extended systems including environmental condition, the definition of the kinetic energy term of the cell parameter \( K_{cell} \) is the key to get physically reasonable
characteristics of the simulated ensemble \([3, 10]\). In Andersen’s method, \(K_{cell} = M \dot{Q}_A^2 / 2\) where \(\dot{Q}_A\) is the rate of change of the coordinate of the piston and has a dimension of velocity \([L/t]\) and \(M\) is the mass of the piston \([1]\). The piston is not of the usual type which expands or contracts the system along one direction; instead, a change in \(Q_A\) whose value is the volume, causes an isotropic expansion or contraction. In the constant surface tension method under constant volume \([5]\), \(K_{cell} = M \dot{A}^2 / 2\) where \(\dot{A}[L/t]\) is the rate of change of the coordinate of the piston which expands or contract the simulated area. In these methods, the degree of freedom concerning the periodic simulation cell is one. The parameters which are used to describe the rate of change of the fluctuating space element (\(\dot{s}, \dot{\theta}, \dot{Q}\)) do not enter the equation of motion of the particles/molecules, but remain as an environment. Note that Eq. (1) does not include the rate of change of space elements (\(\dot{\alpha}, \dot{\theta}, \dot{Q}\)). This comes from a physical requirement. In MD simulations, the kinetic energy which contribute to temperature is the random thermal dynamic motion of the particles. When there is a flow inside the system, the average velocity of the nearby particles should be extracted and only the fluctuations from the average must be considered.

The rate of change of space elements multiplied by the scaled coordinates (\(s_i dQ_i^{1/3}\) in Andersen’s method) corresponds to the flow accompanying the expansion/contraction of the simulation cell. Such term will not contribute to pressure or temperature. In addition, a term dependent on position inside the simulation cell is not desirable considering all particles are equivalent. Each particle should be in the center of the environment, only considering the velocities of each specific motion (\(Q_i^{1/3}\)). The two relations in Eq.(1) can be considered the basic of the constant pressure methods \([11]\). A different choice of \(K_{cell}\) from the original Parrinello & Rahman method \([2]\) will straightforwardly lead to the Virial theorem even in extremely anisotropic simulation cells\([3]\).

### 2.1. Constant hydrostatic pressure MD method

For systems under constant hydrostatic pressure\([4, 6, 10]\), the proper kinetic energy term of the simulation cell is \(K_{cell} = MV^2 / 2\). With

\[
K_{cell} = \frac{M}{2} \left( \dot{\alpha} \theta Q + \alpha \dot{\theta} Q + \alpha \dot{Q} \right)^2 ,
\]

the Lagrangian is

\[
\mathcal{L}(s^N, \dot{s}^N, \alpha, \dot{\alpha}, \theta, \dot{\theta}, Q, \dot{Q}) = \sum_{i=1}^{N} \frac{m}{2} Q^{2/3} \left( s_{ix}^2 + \theta^2 s_{iy}^2 + \alpha^2 s_{iz}^2 \right) - \Phi - P_{ex} \alpha \theta Q + \frac{M}{2} \left( \dot{\alpha} \theta Q + \alpha \dot{\theta} Q + \alpha \dot{Q} \right)^2
\]

where \(P_{ex}\) is the given value of the external hydrostatic pressure which the system stress tensor will balance with. The potential energy \(\Phi\) is the sum of pair-wise interatomic potentials \(\phi_{ij}(r_{ij})\) which is dependent on the real atomic distance \(r_{ij}\). The momentum conjugate to \(s_i\) is

\[
\pi_i = \frac{\partial \mathcal{L}}{\partial \dot{s}_i} = m Q^{2/3} \begin{pmatrix} \dot{s}_{ix} \\ \theta^2 \dot{s}_{iy} \\ \alpha^2 \dot{s}_{iz} \end{pmatrix} .
\]

The momentum conjugate to \(\alpha\) is

\[
\Lambda = \frac{\partial \mathcal{L}}{\partial \dot{\alpha}} = M \theta Q \left( \dot{\alpha} \theta Q + \alpha \dot{\theta} Q + \alpha \dot{Q} \right) .
\]

The momentum conjugate to \(\theta\) is

\[
\Theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = M \alpha Q \left( \dot{\alpha} \theta Q + \alpha \dot{\theta} Q + \alpha \dot{Q} \right) .
\]
The momentum conjugate to \( Q \) is
\[
\Pi = \frac{\partial L}{\partial \dot{Q}} = M \alpha \theta \left( \dot{\alpha} \dot{Q} + \alpha \dot{\theta} Q + \alpha \dot{Q} \right).
\] (7)

The Hamiltonian is
\[
\mathcal{H} \left( s^N, \pi^N, \alpha, \Lambda, \theta, \Theta, Q, \Pi \right) = \sum_{i=1}^{N} s_i \cdot \pi_i + \dot{\alpha} \Lambda + \dot{\theta} \Theta + \ddot{Q} \Pi - \mathcal{L} \left( s^N, \dot{s}^N, \alpha, \dot{\alpha}, \theta, \dot{\theta}, Q, \dot{Q} \right)
\]
\[
= \sum_{i=1}^{N} \frac{1}{2mQ^{2/3}} \left( \frac{\pi_{ix}^2}{\theta^2} + \frac{\pi_{iy}^2}{\alpha^2} + \frac{\pi_{iz}^2}{\alpha^2} \right) + \Phi + P_{ex} \alpha \theta Q + \frac{1}{6M} \left[ \frac{\Lambda}{\theta Q} \right]^2 + \left( \frac{\Theta}{\alpha Q} \right)^2 + \left( \frac{\Pi}{\alpha \theta} \right)^2
\] (8)

In constructing the Hamiltonian, we used the relation
\[
K_{cell} = \frac{1}{2M} \left( \frac{\Lambda}{\theta Q} \right)^2 = \frac{1}{2M} \left( \frac{\Theta}{\alpha Q} \right)^2 = \frac{1}{2M} \left( \frac{\Pi}{\alpha \theta} \right)^2
\] (9)

and added a constraint that \( K_{cell} \) is divided among each term in Eq.(9) equally. It is possible to add other constraints, which determine how to distribute \( K_{cell} \) among the different terms, as discussed in appendix A of [4].

The Hamiltonian for constant hydrostatic pressure and constant temperature is
\[
H_k \left( s^N, \pi^N, \alpha, \Lambda, \theta, \Theta, Q, \Pi, \nu, N \right) = \nu \left\{ \sum_{i=1}^{N} \frac{1}{2mQ^{2/3}} \left( \frac{\pi_{ix}^2}{\theta^2} + \frac{\pi_{iy}^2}{\alpha^2} + \frac{\pi_{iz}^2}{\alpha^2} \right) + \Phi + P_{ex} \alpha \theta Q + \frac{1}{6M} \left[ \frac{\Lambda}{\theta Q} \right]^2 + \left( \frac{\Theta}{\alpha Q} \right)^2 + \left( \frac{\Pi}{\alpha \theta} \right)^2 \right\} + \mathcal{L} = \nu \mathcal{H} + \mathcal{L}
\]
(10)

where \( \nu \) is the time scaling factor common to the Poincaré time transformation [22] and the Nosé thermostat [23, 24] controlling the kinetic energy of the particles through time scaling.

2.2. Constant surface tension MD method

For systems under constant surface tension, the proper kinetic energy term of the simulation cell is \( K_{cell} = M \dot{V}^2 / (2V) \) [5, 6, 10]. To obtain an explicit algorithm for the symplectic integration[6], we introduce variables \( \beta = \alpha^{1/2}, \mu = \theta^{1/2}, \) and \( \chi = Q^{1/2} \). The cell lengths are \( L_x = \chi^{2/3}, L_y = \mu^2 \chi^{2/3}, \) and \( L_z = \beta^2 \chi^{2/3}, \) respectively in x, y, and z directions. The volume of the simulation cell is \( V = \beta^2 \mu^2 \chi^2 \). The kinetic energy term of the simulation cell is
\[
K_{cell} = 2M \left( \dot{\beta} \mu \chi + \dot{\beta} \mu \chi + \beta \mu \chi \right)^2.
\] (11)

The Lagrangian is
\[
\mathcal{L} \left( s^N, \dot{s}^N, \beta, \dot{\beta}, \mu, \dot{\mu}, \chi, \dot{\chi} \right) = \sum_{i=1}^{N} \frac{m}{2} \chi^{4/3} \left( \ddot{s}_{ix}^2 + \mu^4 \ddot{s}_{iy}^2 + \chi^4 \ddot{s}_{iz}^2 \right) - \Phi - P_n \beta^2 \mu^2 \chi^2 + \gamma \mu^2 \chi^{4/3} + 2M \left( \dot{\beta} \mu \chi + \dot{\beta} \mu \chi + \beta \mu \chi \right)^2
\] (12)
where $P_\alpha$ and $\gamma$ are the given values of the external normal pressure and surface tension, respectively. The momentum conjugate to $s_i$ is

$$
\pi_i = \frac{\partial L}{\partial \dot{s}_i} = m_i \chi \frac{4/3}{\beta^4 s_{iz}} \left( \frac{\dot{s}_{ix}}{\mu} + \frac{\dot{s}_{iy}}{\beta^4 s_{iz}} \right).
$$

(13)

The momentum conjugate to $\beta$ is

$$
\mathcal{B} = \frac{\partial L}{\partial \dot{\beta}} = 4M \mu \chi \left( \dot{\beta} \mu \chi + \dot{\beta} \dot{\mu} \chi + \beta \mu \dot{\chi} \right).
$$

(14)

The momentum conjugate to $\mu$ is

$$
\mathcal{M} = \frac{\partial L}{\partial \dot{\mu}} = 4M \beta \mu \left( \dot{\beta} \mu \chi + \dot{\beta} \dot{\mu} \chi + \beta \mu \dot{\chi} \right).
$$

(15)

The momentum conjugate to $\chi$ is

$$
\Xi = \frac{\partial L}{\partial \dot{\chi}} = 4M \beta \mu \left( \dot{\beta} \mu \chi + \dot{\beta} \dot{\mu} \chi + \beta \mu \dot{\chi} \right).
$$

(16)

The Hamiltonian is

$$
\mathcal{H}(s^N, \pi^N, \beta, \mathcal{B}, \mu, \mathcal{M}, \chi, \Xi) = \sum_{i=1}^{N} \pi_i \cdot \dot{s}_i + \mathcal{B} + \mathcal{M} + \chi \Xi - \mathcal{L}(s^N, \dot{s}^N, \beta, \dot{\beta}, \mu, \dot{\mu}, \chi, \dot{\chi}) =
$$

$$
\sum_{i=1}^{N} \frac{1}{2m_i \chi \frac{4/3}{\beta^4}} \left( \frac{\pi_{ix}^2}{\mu^4} + \frac{\pi_{iy}^2}{\beta^4} + \frac{\pi_{iz}^2}{\beta^4} \right) + \Phi + P_n \beta^2 \mu^2 \chi^2 - \gamma \mu^2 \chi^{4/3} + \frac{1}{24M} \left[ \left( \frac{\mathcal{B}}{\mu \chi} \right)^2 + \left( \frac{\mathcal{M}}{\beta \chi} \right)^2 + \left( \frac{\Xi}{\beta \mu} \right)^2 \right].
$$

(17)

In constructing the Hamiltonian, we employed the relation

$$
K_{\text{cell}} = \frac{1}{8M} \left( \frac{\mathcal{B}}{\mu \chi} \right)^2 = \frac{1}{8M} \left( \frac{\mathcal{M}}{\beta \chi} \right)^2 = \frac{1}{8M} \left( \frac{\Xi}{\beta \mu} \right)^2
$$

(18)

and added a constraint that $K_{\text{cell}}$ is divided among each term in Eq.(18) equally.

The Hamiltonian for constant surface tension and constant temperature is

$$
H_s(s^N, \pi^N, \beta, \mathcal{B}, \mu, \mathcal{M}, \chi, \Xi, \nu, \mathcal{N}) =
$$

$$
\nu \left\{ \sum_{i=1}^{N} \frac{1}{2m_i \chi \frac{4/3}{\beta^4}} \left( \frac{\pi_{ix}^2}{\mu^4} + \frac{\pi_{iy}^2}{\beta^4} + \frac{\pi_{iz}^2}{\beta^4} \right) + \Phi + P_n \beta^2 \mu^2 \chi^2 - \gamma \mu^2 \chi^{4/3} + \frac{1}{24M} \left[ \left( \frac{\mathcal{B}}{\mu \chi} \right)^2 + \left( \frac{\mathcal{M}}{\beta \chi} \right)^2 + \left( \frac{\Xi}{\beta \mu} \right)^2 \right] + \frac{\mathcal{N}^2}{2K} + gkT \ln \nu - \mathcal{H}_0 \right\}.
$$

(19)

### 2.3. Canonical hydrostatic MD simulation method with fluctuations in the cell shape

The volume of the simulation cell $V$ is a given constant value in this method, thus the isotropic volume factor $Q$ becomes an unnecessary variable. The simulation cell lengths in each direction are $L_x = \{V/(\alpha \theta)\}^{1/3}$, $L_y = \theta \{V/(\alpha \theta)\}^{1/3}$, and $L_z = \alpha \{V/(\alpha \theta)\}^{1/3}$. With

$$
K_{\text{cell}} = \frac{M}{2} \left( \dot{\alpha} \theta + \alpha \dot{\theta} \right)^2,
$$

the Lagrangian is

$$
\mathcal{L}(s^N, \dot{s}^N, \alpha, \dot{\alpha}, \theta, \dot{\theta}) = \sum_{i=1}^{N} \frac{m_i}{2} \left( \frac{V}{\alpha \theta} \right)^{2/3} \left( \dot{s}_{ix}^2 + \dot{s}_{iy}^2 + \alpha^2 \dot{s}_{iz}^2 \right) - \Phi + \frac{M}{2} \left( \dot{\alpha} \theta + \alpha \dot{\theta} \right)^2.
$$

(20)
The momentum conjugate to $s_i$ is

$$\pi_i = \frac{\partial L}{\partial \dot{s}_i} = m \left( \frac{V}{\alpha \theta} \right)^{2/3} \left( \frac{1}{\theta^2} \right) \dot{s}_i. \tag{21}$$

The momentum conjugate to $\alpha$ is

$$\Lambda = \frac{\partial L}{\partial \dot{\alpha}} = M \left( \dot{\alpha} \theta + \alpha \dot{\theta} \right). \tag{22}$$

The momentum conjugate to $\theta$ is

$$\Theta = \frac{\partial L}{\partial \dot{\theta}} = M \left( \dot{\alpha} \theta + \alpha \dot{\theta} \right). \tag{23}$$

The Hamiltonian is

$$\mathcal{H} (s^N, \pi^N, \alpha, \Lambda, \Theta) = \sum_{i=1}^{N} \frac{1}{2m} \left( \frac{\alpha \theta}{V} \right)^{2/3} \left( \pi^2_{ix} + \pi^2_{iy} + \pi^2_{iz} \right) + \Phi + \frac{1}{4M} \left[ \left( \frac{\Lambda}{\theta} \right)^2 + \left( \frac{\Theta}{\alpha} \right)^2 \right]. \tag{24}$$

In constructing the Hamiltonian, we employed the relation

$$K_{cell} = \frac{1}{2M} \left( \frac{\Lambda}{\theta} \right)^2 = \frac{1}{2M} \left( \frac{\Theta}{\alpha} \right)^2 \tag{25}$$

and added a constraint that $K_{cell}$ is divided among each term in Eq.(25) equally.

The Hamiltonian for constant volume and constant temperature is

$$H (s^N, \pi^N, \alpha, \Lambda, \Theta, \nu, N) = \nu \left\{ \sum_{i=1}^{N} \frac{(\alpha \theta/V)^{2/3}}{2m \nu^2} \left( \pi^2_{ix} + \pi^2_{iy} + \pi^2_{iz} \right) + \Phi + \frac{1}{4M} \left[ \left( \frac{\Lambda}{\theta} \right)^2 + \left( \frac{\Theta}{\alpha} \right)^2 \right] + \frac{N^2 \nu^2}{2K} + gkT \ln \nu - \mathcal{H}_0 \right\} \tag{26}$$

where $\nu$ is the time scaling factor common to the Poincaré time transformation [22] and the Nosé thermostat [23, 24].

3. **Isotropic potential for symplectic integrators with a clean cutoff**

Development of the above MD methods was originally motivated to simulate systems of anisotropic molecules. However, these methods proved to be useful to simulate other condensed matter states such as glass. The variety of metastable states (inherent structures of glass) obtained for systems with isotropic excluded volumes [13, 14] encourages us to employ these methods also for systems with isotropic potentials. To further pursue investigations, I propose the following isotropic pairwise potential with the attractive force. To apply it in a symplectic integrator, the potential must be twice continuously differentiable. At the cutoff distance of the pairwise potential, the potential and it’s derivative must both vanish, i.e $f = f' = 0$. For this goal, we first consider the following function;

$$y(x) = (x-a) \left( x - \frac{b}{2} \right)^2 = x^3 - (a + b) x^2 + \left( ab + \frac{b^2}{4} \right) x - \frac{ab^2}{4}. \tag{27}$$

The value of this function is $y = 0$ at $x = a$ and $x = b/2$ and its differential is $dy/dx = 0$ at $x = (4a + b)/6$ and $x = b/2$. So if we cutoff this function at $x = b/2$, the value and it’s
differential both vanish. In addition, we can choose the coefficient in a manner that the function has a minimum at \( x = (4a + b)/6 \). The function \( g(x) \) in Eq.(27) is used for constructing a pairwise potential. The pairwise potential \( \Phi \) is a function of the distance between molecules \( i \) and \( j \), i.e. \( r_{ij} \). We choose \( x = (D/r_{ij})^4 \), where \( D \) is the diameter of the molecule:

\[
\Phi_{ij} = \epsilon \left[ \left( \frac{D}{r_{ij}} \right)^{12} - (a + b) \left( \frac{D}{r_{ij}} \right)^8 + \left( ab + \frac{b^2}{4} \right) \left( \frac{D}{r_{ij}} \right)^4 - \frac{ab^2}{4} \right].
\]  

The reduced units are defined by taking the units of length, mass, and energy as \( D, m, \) and \( \epsilon' \), respectively. We employ these reduced units throughout this paper. The values of \( a \) and \( b \) can be chosen to give the potential minimum and cutoff at desired intermolecular distances \( r_{ij} \). Here we take the values \( a = 47/32 \) and \( b = 1/8 \) which give \( \Phi \) a minimum at \( r_{ij} = 1 \) and \( \Phi = d\Phi/dr_{ij} = 0 \) at \( r_{ij} = 2 \). This gives a harder core and a more attractive tail than the Lennard-Jones potential. Another potential designed to have both \( \Phi \) and \( \partial \Phi/\partial r \) vanishing at the cutoff, is reported in Ref. [25]; this potential function can be derived from the base function(27) using \( x = (C/r_{ij})^3 \) where the potential minimum and cutoff are at distances \( 0.5C \) and \( C \), respectively.

4. Canonical hydrostatic MD simulation of LC phase transitions

The phase sequence of crystal-hexatic smectic B(HexB) LC-smectic A (SmA)LC has been investigated by constant hydrostatic pressure MD simulations[9, 10, 15]. The crystal-HexB phase transition is the 2nd order, while HexB-SmA phase transition is clearly the 1st order one. Here we investigate the same model system, i.e. parallel spherocylinders with \( L = 4 \), to investigate how the nature of the liquid crystal phase transition changes in canonical ensemble. The phase sequence of this system is crystal-HexB-SmA as observed for the same model simulated with constant hydrostatic pressure[9]. In Fig.1(a), we show diagonal elements of stress tensor, i.e., the pressure in \( x, y, z \)-directions, for two different volumes \( V/N = 2.046 \) and 2.083. The system is under hydrostatic pressure (the symbols overlap and cannot be discerned separately) and the values of pressure change continuously against temperature. This is in contrast to the MD simulations under constant hydrostatic pressure where the phase transition between HexB and SmA is clearly a 1st order one. In Fig.1(b), we show the 6-fold bond orientational order \( C_6 \). More simulations are necessary in the temperature range \( 50 \leq T \leq 90 \) to give a definite conclusion, however it seems that \( C_6 \) continuously decreases in canonical hydrostatic MD simulation. In constant hydrostatic pressure, \( C_6 \) sharply decreases to low values around \( C_6 < 0.1 \).

Above results show that a system with anisotropic constituents can be simulated in canonical hydrostatic ensemble, which is difficult with other methods.

5. Phase coexistence of an isotropic potential systems

Systems of isotropic sphere potential Eq.(28) are simulated with the constant hydrostatic pressure method with two anisotropic factors given in the subsection2.1. Here, we report of the system size \( N = 1344 \) with period boundary conditions in all three directions. When the system is slowly annealed with large masses \( M \) and \( K \) of the barostat and thermostat, phase coexistence is observed.

In Fig.2, a crystal domain appeared in the middle low region at \( T = 900 \), grows inside the liquid. Note that the surface between the crystal and liquid becomes nearly flat.

In Fig.3, the bubble at \( T = 900 \) grows larger at \( T = 900 \) and becomes a vapor slab (c).

By simulating phase coexistence where fluctuations are large, it has been demonstrated that the constant hydrostatic pressure method with two anisotropic factors in subsection 2.1 is also useful in systems of isotropic constituents. An approximately flat surface appears under cell shape fluctuations. In the future, we will try to estimate the surface tension between two phases by measuring the spontaneous surface area change against the energy fluctuation.
Figure 1. (a) Diagonal elements of stress tensor and (b) 6-fold bond orientational order in system of $N = 1344$ parallel sphrocylinders of $L = 4$ with volume $V/N = 2.046$ [(a) upper branch, (b) +] and $V/N = 2.083$ [(a) lower branch, (b) ×].

Figure 2. Crystal-liquid coexistence observed in system of potential Eq.(28) with $N = 1344$ at $P=1.0$ and $T=0.64$ with piston masses $M = K = 1.0 \times 10^5$ at time (a) $T = 500$, (b) 900, (c) 10400.

Figure 3. Liquid-vapor coexistence observed in system of potential Eq.(28) with $N = 1344$ at $P=0.14$ and $T=0.69$ with piston masses $M = K = 1.0 \times 10^2$ at time (a) $T = 900$, (b) 2100 (c) 5200.
6. Concluding remarks
MD methods with the simulation cell control to obtain the desired stress tensor, has been extended to include two anisotropic factors in the cell dynamics. In addition, a constant volume method with simulation cell fluctuation is introduced to enable canonical hydrostatic MD simulation for systems with strong anisotropy. These methods are not only effective in simulating systems with anisotropic constituents, but also give a new perspective for systems with isotropic constituents.

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