Glass Formation of \(n\)-Butanol: Coarse-grained Molecular Dynamics Simulations Using Gay-Berne Potential Model

Gui-long Xie\textsuperscript{a}, Yong-hong Zhang\textsuperscript{b}, Shi-ping Huang\textsuperscript{a}∗

\textsuperscript{a} Division of Molecule and Materials Simulation, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
\textsuperscript{b} Department of Applied Physics, Tianjin Polytechnic University, Tianjin 300160, China

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Using coarse-grained molecular dynamics simulations based on Gay-Berne potential model, we have simulated the cooling process of liquid \(n\)-butanol. A new set of GB parameters are obtained by fitting the results of density functional theory calculations. The simulations are carried out in the range of 290−50 K with temperature decrements of 10 K. The cooling characteristics are determined on the basis of the variations of the density, the potential energy and orientational order parameter with temperature, whose slopes all show discontinuity. Both the radial distribution function curves and the second-rank orientational correlation function curves exhibit splitting in the second peak. Using the discontinuous change of these thermodynamic and structure properties, we obtain the glass transition at an estimate of temperature \(T_g=120\pm10\) K, which is in good agreement with experimental results \(110\pm1\) K.

Key words: Gay-Berne potential, Coarse-grained molecular dynamics simulations, Glass formation

I. INTRODUCTION

The glass formation is often considered as the transition from a liquid to a surviving non-crystalline phase when all crystallizations fail, which has attracted widespread interest in recent years [1−3]. Besides practical engineering reasons, understanding the glass formation is of great importance to any explanation of the real nature of the glass phase. Molecular dynamics (MD) simulations have become a powerful tool for studying the structure and dynamic properties of condensed phases [4−7]. Many potential models are now available for molecular simulations, for example, the classical non-bonded potential, Lennard-Jones (LJ) potential model [8−12]. It is well known that choosing the appropriate potential model is a key factor to simulate the particular property. The Gay-Berne (GB) potential model is proposed for an anisotropic coarse-grained (CG) model to describe the interaction between molecules whose repulsive cores are basically ellipsoids of revolution [12]. In an anisotropic CG model, the anisotropic part of a molecule or the whole molecule is treated like a rigid ellipsoidal GB bead. Neglecting the atomic details, each molecule or the anisotropic part of each molecule is characterized by an ellipsoidal bead with a center separation \(\vec{r}\) and a long axis vector \(\vec{u}\) describing its orientation.

The GB potential model has been proven to be particularly effective to study the phase behavior of liquid crystal (LC) molecules [13−20]. The LC molecules, i.e., 4′-methoxy-benzyliden-aniline, are often aromatic compounds containing benzene rings which can be treated as anisotropic cores. Nevertheless, there are a few research works dealing with non-aromatic molecules using the GB potential model. Orsi \textit{et al.} have put forward a quantitative CG model for a lipid containing 115 atoms which is simplified by 10 CG beads [21]. N-butyl group or a segment of four consecutive methylene groups in the lipid is treated as an ellipsoidal GB bead. Sun and Gezelter have proposed a larger scale model for a lipid which is represented as a head-body ellipsoidal CG model [22]. Since \(n\)-butyl group in macro-molecules can be simplified as GB beads, can this kind of group or segment in small anisotropic molecules also be done? In the current study, we try to define a small anisotropic molecule, \(n\)-butanol molecule, as an ellipsoidal GB bead. Recently, experimental works on organic liquids have indicated that \(n\)-butanol is a relatively good glass-former [23−26]. Therefore, if we use MD simulations based on the GB potential model and verify the glass formation, the answer will be affirmative.

Some attempts have been made to parameterize the GB potential to real anisotropic molecules. Luckhurst \textit{et al.} have discussed the well depth and intermolecular separation for special orientational configurations [27]. They considered the exponents \(\nu\) and \(\mu\) as adjustable parameters, and used a resultant uniaxial model to ob-
tain the GB parameters [28]. Cleaver et al. have written a generalized form of the GB potential which is suitable for computing the interaction between dissimilar uniaxial or biaxial particles [29]. Golubkov et al. have determined the GB parameters by comparing to the van der Waals' (vdW) interactions given by all-atom AMOEBA forced field [30]. However, GB parameters in these works are generally related from real LC systems. In comparison with LC molecules, \( n \)-butanol molecule is quite short with small molecular length/breadth ratio which has been proven to have strong effect on phase behavior of systems [31, 32]. Consequently, a new set of GB parameters need be developed for \( n \)-butanol. Prampolini have derived the parameterization of the CG potentials from \textit{ab initio} calculations [33]. In our work, density functional theory (DFT) calculations have been employed to compute the intermolecular interactions in four particular orientational configurations which are adequate to determine the parameters of the GB potential [34, 35].

To study whether or not glass formation of GB bead is feasible, we have chosen the liquid \( n \)-butanol with a density of 810.1 kg/m\(^3\) as a model system to mimic experimental conditions. Characterization of glass formation by MD simulations can be typically done on the basis of the variations of thermodynamic and structure properties. Both the slopes of specific volume and potential energy versus temperature show a sensible discontinuity in the glass transition zone [6, 36–38]. Additionally, liquids exhibit a mean squared displacement that is linear in time, while glassy materials deviate significantly from this linear behavior at intermediate times, entering a sublinear regime with a return to linear behavior in the infinite time limit [39, 40]. In particular, recent molecular simulations have reported that glassy materials exhibit strong ordering among nearest neighbors, and hence the orientational order parameter can also be used to characterize the glass formation [40–42].

In this work, a CG model is employed to describe the shape of an \( n \)-butanol molecule, and the GB potential used for MD simulation is parameterized by DFT calculations. We presents the results for MD simulations. Thermodynamic and structure properties in the glass transition process are mainly discussed.

### II. COMPUTATION MODEL AND SIMULATION METHODS

#### A. Definition for the shape of an \( n \)-butanol molecule

CG methods are developed to simplify the representation of a system possibly. These methods generally involve grouping together entire clusters of atoms into single macro-sites [43]. Due to the reduction (in contrast with atom-level methods) in the degrees of freedom and the elimination of interactions calculated, the simulation of a CG system goes faster than that for the same system in an atom-level description. As a result, the simulated time and length scales can be increased by several orders of magnitude so that the molecular simulation can be bridged with experimental techniques more reasonably.

However, it is not straightforward to construct a proper CG model to approximate the shape of a molecule because many atomistic interactions need be coarse-grained when we group a cluster of atoms together to form a CG bead [44]. Fortunately, \( n \)-butanol molecule with fifteen atoms is pretty small compared with macromolecules. Therefore, the shape of an \( n \)-butanol molecule can be modeled with a few CG beads, even only one bead. The glass and crystalline phases of \( n \)-butanol detected by experimental techniques indicate that \( n \)-butanol molecule is anisotropic [23–26]. As a result, we try to define the shape of \( n \)-butanol molecule as an ellipsoidal bead to study its anisotropy. In this work, an \( n \)-butanol molecule is optimized by DFT calculations with the DMol3 software (the calculation details are shown in the Supplementary material) [34, 35]. The barycentre of the CG ellipsoidal model is decided by the centroid of the optimized molecule. The vector \( \vec{u} \) along the long axis of this model is derived from the positions and masses of atoms in a hemi-ellipsoid and defined as

\[
\vec{u} = \frac{\sum_{i=1}^{N_h} m_i \vec{r}_i}{\sum_{i=1}^{N_h} m_i}
\]

where \( N_h \) is the total number of atoms in a hemi-ellipsoid which is also symmetry around the long axis. As is shown in Fig.1, a schematic drawing is made for an \( n \)-butanol molecule. The ellipsoid represents the CG bead for this molecule. There are two arrows in the drawing. The long arrow denotes the major axis vector of the model and the short arrow is an arbitrary vector perpendicular to the major axis vector.

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**FIG. 1** A CG model for a single optimized \( n \)-butanol molecular structure. This ellipsoidal model can be seen as a Gay-Berne bead which has only one major or long axis exhibited as a long arrow in the sketch. The hemi-ellipsoid used for calculating long axis vector is marked with several red dash lines. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

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TABLE I The well depth, corresponding distance \( d \), and intermolecular separation for four particular orientational configurations deduced from the GB potential.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \sigma(\hat{u}_i, \hat{u}<em>j, \hat{r}</em>{ij}) )</th>
<th>( d )</th>
<th>( \varepsilon(\hat{u}_i, \hat{u}<em>j, \hat{r}</em>{ij}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-to-end</td>
<td>( \sigma_0 \sigma / \sigma_s )</td>
<td>( (2^{1/6} - 1 + \sigma / \sigma_s) \sigma_0 )</td>
<td>( \varepsilon_0 (\varepsilon_s / \varepsilon_0) (1 - \chi^2)^{-\nu/2} )</td>
</tr>
<tr>
<td>Side-by-side</td>
<td>( \sigma_0 )</td>
<td>( 2^{1/6} \sigma_0 )</td>
<td>( \varepsilon_0 (1 - \chi^2)^{-\nu/2} )</td>
</tr>
<tr>
<td>Cross</td>
<td>( \sigma_0 \sqrt{\left(\frac{\sigma_0 / \sigma_s}{2}\right)^2 + 1} )</td>
<td>( 2^{1/6} - 1 + \sqrt{1 + (\sigma_s / \sigma_s)^{1/\mu}} )</td>
<td>( \varepsilon_0 )</td>
</tr>
<tr>
<td>Tee</td>
<td>( \sigma_0 )</td>
<td>( 2^{1/6} - 1 + \sqrt{1 + (\sigma_s / \sigma_s)^{1/\mu}} )</td>
<td>( \varepsilon_0 )</td>
</tr>
</tbody>
</table>

B. Interaction potential for two CG particles

Given that \( \text{n-butanol} \) molecule is modeled as only one anisotropic ellipsoidal bead, we just introduce the interaction potential used for pairs of anisotropic particles. As mentioned in the introduction, the GB potential is a standard model to study interaction between pairs of anisotropic sites or ellipsoid sites. This potential is related to LJ potential with orientation-dependent regulation [12],

\[
U = 4 \varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) \left\{ \frac{\sigma_0}{r_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) + \sigma_0} \right\}^{12} - \frac{\sigma_0}{r_{ij} - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) + \sigma_0} \tag{2}
\]

where \( \hat{u}_i \) is a unit vector along particle \( i \)’s long axes, representing \( i \)’s orientation. \( \hat{r}_{ij} = \hat{r}_{ij} \) is the intermolecular vector. \( r_{ij} \) is the distance between the particles. \( \sigma_0 \) is a constant.

As for the standard GB potential, \( \sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) \) is the intermolecular separation at which the intermolecular potential is zero and defined as

\[
\sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) = \sigma_0 \left\{ 1 - \frac{\chi}{2} \left[ \frac{\hat{r}_{ij}}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} \right]^{1/2} + \frac{\hat{u}_i \cdot \hat{r}_{ij} - \hat{u}_j \cdot \hat{r}_{ij}}{1 - \chi(\hat{u}_i \cdot \hat{u}_j)} \right\}^{-1/2} \tag{3}
\]

with the shape anisotropy parameter \( \chi \) given by

\[
\chi = \frac{(\sigma_s / \sigma_s^2 - 1)}{(\sigma_s / \sigma_s^2 + 1)} \tag{4}
\]

where \( \sigma_s \) and \( \sigma_s \) are the separation when the molecules are end-to-end and side-by-side, respectively. \( \sigma_s / \sigma_s \) is often called molecular length/breadth ratio.

The well depth for GB potential \( \varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) \) is defined as

\[
\varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) = \varepsilon_0 \left[ \varepsilon(\hat{u}_i, \hat{u}_j) \right]^{\nu} \tag{5}
\]

where \( \nu \) and \( \mu \) are adjustable exponents and \( \varepsilon_0 \) is a constant. The first component of \( \varepsilon(\hat{u}_i, \hat{u}_j) \) is given by

\[
\varepsilon(\hat{u}_i, \hat{u}_j) = [1 - \chi^2(\hat{u}_i \cdot \hat{u}_j)]^{-1/2} \tag{6}
\]

and the second by

\[
\varepsilon'(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) = 1 - \frac{\chi}{2} \left[ \frac{(\hat{u}_i \cdot \hat{r}_{ij} + \hat{u}_j \cdot \hat{r}_{ij})^2}{1 + \chi(\hat{u}_i \cdot \hat{u}_j)} \right]^{1/2} + \frac{(\hat{u}_i \cdot \hat{r}_{ij} - \hat{u}_j \cdot \hat{r}_{ij})^2}{1 - \chi(\hat{u}_i \cdot \hat{u}_j)} \tag{7}
\]

where \( \chi' \) is related to the anisotropy in the well depth and given by

\[
\chi' = 1 - \left( \frac{\varepsilon_s / \varepsilon_s^{1/\mu}}{(\varepsilon_s / \varepsilon_s^{1/\mu}) + 1} \right) \tag{8}
\]

where \( \varepsilon_s \) and \( \varepsilon_s \) are the well depth when the molecules are end-to-end and that when they are side-by-side, respectively.

C. Parameterization of interaction potential

In most works referring to the GB potential, values of the parameters, \( \nu=1, \mu=2, \sigma_s / \sigma_s = 3, \varepsilon_0 / \varepsilon_s = 0.2 \), are used, which are related from real LC systems and have been proven to be effective to study the LC phases [12–20]. Whereas \( \text{n-butanol} \) molecule is too short with small molecular length/breadth ratio to show an LC phase, we need to develop a new set of GB parameters for \( \text{n-butanol} \). Luckhurst et al. have discussed the well depth and intermolecular separation for four special orientational configurations: the end-to-end, side-by-side, cross, and tee configurations respectively [27]. The values of \( \sigma(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) \) and \( \varepsilon(\hat{u}_i, \hat{u}_j, \hat{r}_{ij}) \) for these particular orientational configurations are adequate to determine the parameters of the GB potential, i.e. \( \sigma_0 \) and \( \varepsilon_0 \) are the well depth and intermolecular separation of the cross configuration, respectively. The well depth, corresponding distance \( d \) (the intermolecular distance at which the intermolecular potential is minimal) and intermolecular separation for the four particular configurations deduced from the GB potential are exhibited in Table I. Apparently, the parameters of the GB potential \( \sigma_0, \varepsilon_0, \sigma_s / \sigma_s, \varepsilon_s / \varepsilon_s, \nu, \mu \) for \( \text{n-butanol} \) can be estimated by calculating the intermolecular interactions for the four orientational configurations. We still employ DFT with the Dmol3 software to compute the binding energy of an optimized \( \text{n-butanol} \) molecule [34, 35].

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In order to calculate the intermolecular interactions, we put two optimized n-butanol molecules into end-to-end, side-by-side, cross, and tee positions, respectively, which can be seen in Fig. 2. Then we change the intermolecular distance in position and also use DFT calculations the corresponding total binding energy. The intermolecular interaction energy can be approximately obtained by subtracting double the binding energy of an interaction energy can be approximately obtained by subtracting double the binding energy of an n-butanol molecule from the total binding energy.

As it is mentioned in Section II A, the ellipsoidal model is derived from the positions and masses of atoms in n-butanol molecule. The optimized n-butanol molecule as a whole can rotate along its long axis or turn back without change of its long axis. Taken the asymmetry of n-butanol molecule into account, we can find the O–H bond in n-butanol molecule is placed at one end with specific position in our model, which may lead to the large dipole moment of n-butanol. As a result, when computing the binding energy of the two molecules placed in a particular orientational configuration such as side-by-side, we must rotate or turn back one of them to adjust the position of the O–H bond in this molecule (Fig. S1–S5 in the Supplementary material). Interestingly, the binding energies of the two molecules placed in a particular orientational configuration with the different positions of the two O–H bonds have the different values, indicating the effect of O–H bond on intermolecular interaction (Fig. S6 in the Supplementary material). The detailed calculation results and discussion for intermolecular interaction are illustrated in the Supplementary material. However, by comparing the binding energies of the two molecules placed in particular orientational configurations, we generally consider the effect of O–H bond on intermolecular interaction can be ignored by averaging the values of some typical binding energies of the two molecules with particular arrangements. Therefore, the computed intermolecular interaction energies for the four particular orientational configurations are average values. The calculation results for the four configurations show the relationship between the intermolecular interaction and the intermolecular distance. Here the intermolecular interaction is regarded as the potential energy. Table II exhibits the calculated well depth, corresponding distance \(d\), and intermolecular separation for four particular orientational configurations deduced from the GB potential.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(\sigma/\text{Å})</th>
<th>(d/\text{Å})</th>
<th>(\varepsilon/(\text{kJ/mol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>End-to-end</td>
<td>8.29</td>
<td>8.66</td>
<td>0.53</td>
</tr>
<tr>
<td>Side-by-side</td>
<td>4.54</td>
<td>5.02</td>
<td>2.34</td>
</tr>
<tr>
<td>Cross</td>
<td>4.59</td>
<td>5.05</td>
<td>1.96</td>
</tr>
<tr>
<td>Tee</td>
<td>6.25</td>
<td>6.76</td>
<td>1.82</td>
</tr>
</tbody>
</table>

D. MD algorithm and simulation details

Initial MD simulations are carried out in the canonical ensemble (\(NVT\)) for the systems of \(N=1000\) GB molecules at the temperature \(T^*\)=290 K (with the reduced value \(T^*=1.23\)) and the Anderson thermostats are used to control temperature of the system. The density for the starting system is set \(\rho=810.1 \text{ kg/m}^3\) (with the reduced value \(\rho^*=0.6087\)) to meet experimental conditions. The simulation box is cubic and
the usual periodic boundary conditions are used. The potential is cut and shifted at $r_c=4\sigma_0$, and a neighbor list is used to save computing time. All the GB molecules are arranged at the points of a body-centered cubic lattice with the same long axis vector (0, 1, 1) to generate initial configuration. The initial velocities are taken from a Maxwell-Boltzmann distribution. The equations of motions are integrated using a form of the leap-frog algorithm suitable for anisotropic systems [45, 46]. The integration time-step is 2.78 fs and the system is allowed to equilibrate over $8.5 \times 10^5$ time-steps, and $1.5 \times 10^5$ additional time-steps are carried out to calculate equilibrium properties. Initial MD simulations in NVT ensemble is intended to get a stable relaxed configuration with the density near the value 810.1 kg/m$^3$ that is the density of $n$-butanol at standard state.

Later MD simulations employ the isothermal isobaric ensemble (NPT) using the Anderson thermostats to control temperature and pressure of the system. The starting configuration is a stable relaxed configuration from initial MD simulations to ensure that the density of $n$-butanol liquid is matched with experimental value. In order to study the glass formation in the cooling process, we carry out MD simulations along twenty-five isotherms, namely from 290 K to 50 K with temperature decrements of 10 K. At each isotherm, a total of 2.4 ns are run for equilibration and a production time of 0.4 ns is used for obtaining the average structural properties, and hence the cooling rate is 3.6 K/ns.

III. RESULTS AND DISCUSSION

A. Thermodynamic properties

During the simulations, the density and potential energy of $n$-butanol are monitored. The two quantities have been used to examine the characteristics of glass formation in many works [6, 36–38]. Figure 4 shows the temperature dependence of the specific volume of $n$-butanol. At both high and low temperatures, the specific volume decreases linearly with the temperature reducing, indicting the phase condensation of $n$-butanol. To further measure the variations of specific volume versus temperature curve, we also plot graphical derivation of this curve, namely the slope of the specific volume versus temperature.

Interestingly, the slope reaches the maximum value at 120 K, which is in good agreement with the slope of specific volume versus temperature. More importantly, the derivation of potential versus temperature reflects the heat capacity of $n$-butanol and the variation trend of the derivation of potential versus temperature in our MD simulations is similar with experimental work [25]. All these observations demonstrate that our MD simulations can capture the experimental trends in liquid-glass transition behavior.

B. Structural properties

To better understand the phase transition in the cooling process, we have computed several structural properties including the orientational order parameter, $P_2$; the radial distribution function $g(r)$, and the second-rank orientational correlation function $q_2(r)$. The orientational order parameter has been extensively used for determining orientational symmetry in condensed phase. Steinhart et al. first proposed an orientational bond order parameter to characterize glass formation [41]. Although the GB model for $n$-butanol molecule is molecular level without any bond order, each molecule still has a long axis vector representing its orientation, which can be used to define an orientational order param-
In this study, the ordering tensor $Q_{\alpha\beta}$ in terms of the orientation vectors of each molecule $i$ is defined as

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} 3\hat{u}_i^\alpha\hat{u}_i^\beta - \delta_{\alpha\beta}, \quad \alpha, \beta = x, y, z$$

where $\hat{u}_i^\alpha$ is the $\alpha$-component of the unit vector along particle $i$'s long axes. $\delta_{\alpha\beta}$ is the Kronecker delta. Then, $\bar{P}_2$ is obtained by calculating the largest eigenvalue of $Q$ for a particular configuration and averaging over the simulation.

Figure 6 shows the calculation results of the orientational order parameter in relation to the temperature. As the temperature decreases, the orientational order parameter rises from about 0.05 to 0.65 with a jump process. This verifies the presence of two distinctly different phases during the cooling process: liquid and the glass phase. We can observe the jump starts at 140 K and ends at 100 K and therefore also estimate $T_g = 120 \pm 10$ K. In addition, the orientational order parameter of the glass phase (about 0.65) is smaller than that of more ordered LC phases (smectic phase $\bar{P}_2 > 0.7$) in $NPT$ ensemble [16–20]. As a result, the glass phase formed in the cooling process is different from more ordered LC phases.

$g(r)$ describes how the particles in a system are radially packed around each other. It has been proven to be effective to study the average structure of molecular systems and given by

$$g(r) = \frac{\text{d}N}{V} \frac{V}{N^2} \left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \delta(r - r_{ij}) \right\rangle$$

where $r_{ij}$ is the distance between the centroids of GB particles $i$ and $j$. The behavior of the radial distribution function in the transition region is presented in Fig. 7. Several peaks can be found in each $g(r)$ curve. As the temperature decreases, the first peak of $g(r)$ becomes sharper, indicating an enhancement of short-range pair correlation; and other peaks also increases apparently, demonstrating a growth of the correlations. These features are also observed in the $g(r)$ functions found from previous computer simulations of anisotropic molecules [16]. More interestingly, the second peak begins to split when the temperature is reduced to 120 K, and splits obviously at 110 K. In Fig. 7, a dotted line is drawn for monitoring this change and we can find that the second-peak splitting of the $g(r)$ curves occurs at $r \approx 9$ Å. This phenomenon reflects the apparent different arrangements of pair molecules at $r \approx 9$ Å, which may be caused by the fluidity of the liquid phase in glass and further confirms the existence of a glass phase [47, 48].

The molecular level model for n-butanol is nonspherical or ellipsoidal and has a long axis vector representing its orientation. For this special property, it is necessary to discuss pair orientation correlations. We calculate the second-rank orientational correlation functions, $g_2(r)$, which is given by:

$$g_2(r) = \langle P_2(\hat{u}_1 \cdot \hat{u}_2) \rangle$$

where $P_2$ is a second-order Legendre polynomial. $\hat{u}_i$ is a unit vector along particle $i$'s long axes, representing $i$'s orientation. A plot of $g_2(r)$ in the transition region is given in Fig. 8. As the temperature decreasing, the first
FIG. 7 Radial distribution functions $g(r)$ with the temperature range from 140 K to 80 K in NPT ensemble. The dotted line is drawn for showing the change of $g(r)$ curves. The splitting of second peak occurs at $r \approx 9$ Å, which is of great importance to determine the liquid-glass phase transition.

The splitting of second peak occurs at $r \approx 9$ Å when the temperature below 130 K. This characteristic is consistent with the discussion for $g(r)$, and hence can be used to characterize the glass formation. In liquid above 120 K $g_2(r)$ decays to zero at large molecular distance $r$, while in glass phase below 120 K $g_2(r)$ tends to the square of orientational order parameter $\langle \vec{P}^2 \rangle$ at large $r$. Moreover, the $g_2(r)$ curves are almost completely overlapped when the temperature is lower than 100 K. This indicates that $n$-butanol would tend to favor glassy state over more condensed phases, such as crystalline phase. Using the splitting of second peak and the overlapping of $g_2(r)$ curve, we estimate the glass transition temperature $120 \pm 10$ K.

C. Snapshots in transition region

We also plot molecular configurations in the transition region in Fig.9. Visualization of simulation snapshots from MD simulations confirms the change of molecular order provided by $\langle \vec{P}_2 \rangle$, $g(r)$, and $g_2(r)$. At high temperatures in isotropic liquid there is no evidence for strong correlation between GB molecules. However, close to glass transition region, there is clear evidence for local ordering. The observed anisotropic condensed phase is nematic-like, which also have been found by Smondyrev et al. [49]. In order to find the difference between this nematic-like glass phase and the standard LC phases, we carry out MD simulations of standard LC molecules in several isotherms (values of the parameters, $\nu=1$, $\mu=2$, $\sigma_e/\sigma_s=3$, $\epsilon_e/\epsilon_s=0.2$) [12–20], which are enough to get standard LC phases. The snapshots of three different phases for LC system are shown in Fig.10 with the pair correlation functions $g(r)$, which agree with previous work [18]. Apparently, the similarity of snapshots can be observed between the glass phase and nematic LC phase, but for LC system, $g(r)$ does not show the second-peak splitting in nematic phase. Therefore, the nematic-like glass phase of $n$-butanol is different from LC phases.
IV. CONCLUSION

We have molecular level resolution of glass formation of liquid n-butanol. A CG model is constructed to represent the shape of n-butanol molecule. The GB potential is employed to describe the intermolecular interaction energy. A method using DFT calculations is put forward to parameterize the GB potential for n-butanol. To study the glass formation in the cooling process, MD simulations are carried out in NPT ensembles and the isotherms varied in the range of 290 K to 50 K with temperature decrements of 10 K.

During the simulations, thermodynamic and structure properties are monitored, together with visualization of simulation snapshots. Using the discontinuity in variations of density, potential energy, orientational order parameter versus temperature, and the splitting of pair correlation functions, we observe the glass transition phenomenon and arrive at an estimate of the glass transition temperature $T_g = 120\pm10$ K, which is in good agreement with experimental results $110\pm1$ K.

It is to be remarked that the potential model we used is a standard model for the study of thermotropic LC molecules. Little research has been conducted in applying the GB potential model to other types of molecules. We should assess whether or not the stable anisotropic phase formed in the cooling process for n-butanol GB bead is an LC phase, so as to determine the feasibility of using this potential model. Interestingly, we find at low temperatures, the orientational order parameter of the anisotropic phase is smaller than that of smectic LC phase, indicating GB beads for n-butanol molecules would tend to favor glass phase over more ordered phase, such as smectic LC phases. We also have found the difference of pair correlation functions between the nematic-like glass phase and the nematic LC phase. Therefore, it would be possible to use the parameterized GB potential to study the glass formation of n-butanol.

Supplementary material: A table of coordinates of atoms in an optimized n-butanol molecule is listed. Figures of side-by-side, end-to-end configurations and the intermolecular interaction energies are given.

V. ACKNOWLEDGMENTS

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