Clusters of Local Bond-Orientational Order in Liquid Gallium: Studies of \textit{ab initio} and Classical MD Simulations

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Abstract. The structure of liquid Ga at ambient pressure (AP) were generated separately via \textit{ab initio} and classical molecular dynamics simulations, and analysed with a cluster approach developed in terms of the local bond-orientational order (LBOO) parameters. Two types of cluster structures were found in both simulated liquids, one typified by sixfold orientational symmetry and the other showing fourfold orientational symmetry: The static structure factors (SSF) of the former are akin to that of the hard-sphere (HS) fluid; however, the SSFs of the latter display either an asymmetric first peak with a shape different from that of the HS fluid or even a shoulder on the high-q side of the first peak, similar as the anomalous SSF of liquid Ga at AP.

1. Introduction

Gallium has a complex phase diagram, which contains multiple stable and metastable solid phases [1]. Besides the polymorphism of solid, Ga at AP has a liquid phase characterized with a low melting temperature, a high boiling point, and a density higher than its stable solid phase (\(\alpha\)-Ga). Supercooled liquid Ga exists in a broad temperature range and crystallizes in several metastable solid states at different temperatures, among which \(\beta\)-Ga is the first one and occurs at 257 K. Just above the melting temperature (\(T_m = 302\) K), liquid Ga is well known for its anomalous SSF, which has a highly asymmetric first peak by displaying a shoulder on its high-q side [2,3]. Because of its non HS-like SSF, Waseda categorized liquid Ga as the third type of liquid structures, which have the Q2/Q1 ratios significantly higher than that of the HS fluid [2], where Q1 and Q2 are the first- and second-peak positions of a SSF, respectively. The anomalous SSF of liquid Ga has been explained by several scenarios, including the ledge-shape repulsive core in an early study [4], the interplay of two characteristic lengths determined by the effective HS diameter and the Friedel wavelength [3,5], the partial-covalency dimers such as in \(\alpha\)-Ga [6,7], and clusters primarily composed of special four-atom units [8]. Hence, the physical cause for the high-q shoulder in the SSF of liquid Ga has been a long-standing debating issue, since its early observation in experiments [9,10].

The SSF of liquid Ga at 323K and AP, including the high-q shoulder, can be reproduced by performing classical molecular dynamics (CMD) simulations with an interatomic pair potential \(\phi(r)\) derived from a first-principles pseudopotential theory [11]. The pair potential \(\phi(r)\) consists of a ledge-shape repulsive core \(\phi_0(r)\), which is much softer than the Lennard-Jones potential, and the long-range Friedel oscillations, decaying in distance with \(r^{-3}\), induced by conduction electrons [12]. However, as performing CMD simulation with the soft-core \(\phi_0(r)\) potential only at the same temperature and number density, no high-q shoulder was found in the SSF of this soft-core fluid [13]. Thus, it was concluded that the high-q shoulder in the SSF of the \(\phi(r)\) liquid was resulted from a modulation caused...
by the Friedel oscillations on the structure determined by the soft-core potential $\phi_0(r)$. In real space, a comparison of the radial distribution functions of the liquids with and without the Friedel oscillations manifested that the high-q shoulder was associated with the medium range order beyond the first shell of the radial distribution function. On the other hand, also based on the $\phi(r)$ model, the high-q shoulder in its SSF was attributed to clusters containing special units of four atoms [8]. As quenching the system into supercooled and glassy states, the amounts of the special four-atom units increased considerably, whereas the SSF changed to that of $\beta$-Ga [14]. However, the algorithm for systematically searching these particular clusters in a liquid is complicated, because the clusters were estimated to involve more than 20 atoms.

Recently, an algorithm for searching clusters of LBOO in simple liquids was developed [15]. A LBOO cluster in a liquid is defined as the neighboring seeds and their neighbors, where a seed is an atom having at least $n_b$ local-orientational bonds and the neighbors of a seed are atoms within a cutoff distance $r_c$ from the seed. This cluster approach has been applied to study liquid structures generated via ab initio molecular dynamics (AIMD) simulations by using the VASP code [16,17] for 1331 Ga atoms at 323 K and AP, where the electronic structures were calculated with a projector augmented wave potential in the local-density approximation. The simulation results indicated that liquid Ga at AP contained two types of cluster structures, one characterized by sixfold orientational symmetry and the other showing fourfold orientational symmetry. In simulated liquids, the clusters with sixfold orientational symmetry were dominated and their SSFs behaved similarly as that of a HS-fluid, whereas the SSFs of clusters with fourfold orientational symmetry exhibited an asymmetric first peak, which is different in shape from that of a HS fluid, or even displayed a shoulder on the high-q side of the first peak as the clusters were in high LBOO.

The CMD simulation with the $\phi(r)$ potential and the AIMD simulation for liquid Ga were performed at the same temperature and pressure; their details have been described in Refs. [13] and [15], respectively. It is interesting to compare the characters of the liquid structures generated by the two MD simulations, especially the LBOO clusters. This paper is organized as follows: In Sec. II, the definition of a LBOO cluster is introduced and the cluster SSF is also defined. In Sec. III, the structures of the two simulated liquids are compared, and so are the SSFs of the LBOO clusters found in the two simulated liquids. Our conclusions are given in Sec. IV.

2. LBOO Cluster

In a simple liquid, the neighbors of an atom are defined as those atoms within a cutoff distance $r_c$ from the central one, where $r_c$ is usually set at the first minimum of the radial distribution function of the liquid. The structure of the neighbors around atom $i$ can be characterized by a set of $(2l+1)$ order parameters $q_{lm}(i)$, with $l$ a positive integer and $m$ an integer subject to $-l \leq m \leq l$, which is defined as [18,19]

$$q_{lm}(i) = \frac{1}{N_h(i)} \sum_{j=1}^{N_h(i)} Y_{lm}(\hat{r}_{ij}),$$

(1)

where the sum runs over all neighbors $N_h(i)$ of the atom, $Y_{lm}(\hat{r}_{ij})$ is the spherical harmonics, and $\hat{r}_{ij}$ is a unit vector in the direction from atom $i$ to its neighbor $j$. The LBOO parameter $q_l(i)$ of atom $i$ is given as

$$q_l(i) = \left( \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{1/2},$$

(2)

where $q_l(i)$ measures the degree of $l$-fold orientational symmetry among the atom’s neighbors. Thus, associated with the local structure of each atom, one can define a normalized complex vector $\hat{q}_l(i)$ with
The correlation between the local structures of two neighboring atoms \( i \) and \( j \) can be quantified by the dot product \( \bar{q}_l(i) \cdot \bar{q}_l(j) \) of their normalized complex vectors, where the dot product is defined in Ref. [19]. As usual, if the dot product \( \bar{q}_l(i) \cdot \bar{q}_l(j) \geq 0.5 \), the two neighboring atoms are considered to connect through a local-orientational bond. By our definition, if the local-orientational bond number of an atom exceeds a threshold value \( n_b \), this atom is identified as a seed. Hence, a LBOO cluster is defined as a composition of the adjacent seeds and all their neighbors; the cluster is specified with two integers: the LBOO \( n_b \) and the number of seeds \( n_s \) in the cluster. In a liquid, a cluster ensemble is a collection of all LBOO clusters specified with the two integers of \( n_b \) and \( n_s \), and is, therefore, indexed with \( \{n_b, n_s\} \).

The structure of a LBOO cluster ensemble indexed with \( \{n_b, n_s\} \) can be described with the average cluster SSF, which is defined with the equation [8]

\[
S_{cl}(q) = 1 + \left\{ \frac{1}{M} \sum_{i \neq j} \sum_{j=1}^{M} \sin(qr_{ij}) \right\}_{c},
\]

where \( M \) is the atom number of a cluster and the brackets with a subscript \( c \) denote an average for all LBOO clusters in the ensemble. As a reference, the SSF of a HS fluid displays a symmetric first peak and has the \( Q_2/Q_1 \) ratio close to 1.86 [3]. Two quantities used for examining the deviation of \( S_{cl}(q) \) of a LBOO cluster ensemble from that of a HS fluid were the \( Q_2/Q_1 \) and the \( q_R/q_L \) ratios [15], where \( q_R \) and \( q_L \) are, respectively, the right-half and left-half widths of the first peak at an altitude of one half between the first maximum and first minimum of \( S_{cl}(q) \). Thus, the \( q_R/q_L \) ratio measures the asymmetry of the first peak in \( S_{cl}(q) \).

### 3. Results of AIMD and CMD Simulations

The SSFs and the radial distribution functions of the liquids generated separately via AIMD and CMD simulations are presented in Fig. 1, where the simulated SSFs are also compared with the experimental results of liquid Ga [2]. For each simulated liquid, the SSF exhibits a shoulder on the high-q side of its first peak, and the \( Q_2/Q_1 \) ratio is approximately 1.94, close to the value of liquid Ga. The \( q_R/q_L \) ratios of the SSFs of the classical and the \textit{ab initio} liquids are near 1.61 and 2.60, respectively, while the \( q_R/q_L \) ratio estimated for the SSF of liquid Ga is 2.20, which is referred to the experimental value. These indicate that the SSF of the \textit{ab initio} liquid has a stronger high-q shoulder than that of the classical liquid.
Figure 2 (a) The coordination-number distributions and (b) the bond-angle distributions of simulated liquids at 323 K and AP. The distributions were calculated with \( r_c = 4.65 \, \text{Å} \). The black-solid line and triangles were obtained via AIMD simulation; the red-dash line and circles were via CMD simulation. All distributions are normalized.

According to the definitions given in Ref. [20], the coordination-number distribution \( P(n, r_c) \) and the bond-angle distribution \( g_3(\theta, r_c) \) of the \textit{ab initio} and the classical liquids were calculated, and the results evaluated with \( r_c = 3.61 \, \text{Å} \), which is set at the first minima of the radial distribution functions of the two liquids, have been shown in Fig. 3 of Ref. [15]. Here, we present in Fig. 2 the \( P(n, r_c) \) and \( g_3(\theta, r_c) \) distributions of the two simulated liquids calculated with \( r_c = 4.65 \, \text{Å} \), which includes the first attractive well of \( \phi(r) \). The coordination numbers of atoms in the classical liquid fall in a range between 14 and 24, with the most probable one occurred at 19, whereas the coordination-number distribution of the \textit{ab initio} liquid shifts toward one more atom, with the most probable coordination number at 20, because the number density of the \textit{ab initio} liquid (\( \rho = 0.0525 \, \text{Å}^{-3} \)) is slightly higher than that of the classical liquid (\( \rho = 0.05 \, \text{Å}^{-3} \)).

With \( r_c = 4.65 \, \text{Å} \), the bond-angle distributions of the two simulated liquids are almost identical and display two peaks, which are near 40° and 90°, and a shoulder around 50°, with the heights of the two peaks almost equal and the magnitudes of the shoulder somewhat smaller. Thus, the bond-angle distribution of \( r_c = 4.65 \, \text{Å} \) is quite different in feature from that of \( r_c = 3.61 \, \text{Å} \). The 90° peak in the bond-angle distribution shown in Fig. 2(b) provides a strong indication for the present of local structures with fourfold orientational symmetry in each simulated liquid.

Figure 3 2-D map for the \( q_4-q_6 \) distribution of each simulated liquid at 323 K and AP: (a) the classical liquid and (b) the \textit{ab initio} liquid. The distributions were calculated with \( r_c = 3.61 \, \text{Å} \). The symbols indicate the \((q_4,q_6)\) points of several crystals: bcc (▲), fcc (■), \( \alpha \)-Ga (●), \( \beta \)-Ga (▼), Ga III (◆), and Ga II (★) [15].
Figure 4 The dependences of $q_4$ and $q_6$ on coordination number $n$ of an atom in a liquid. The symbols are the results of simulated liquids. The dash lines serve to guide the eye.

With $r_c = 3.61$ Å, the LBOO parameters $q_6(i)$ and $q_4(i)$ of atoms in the ab initio and the classical liquids were calculated, and the 2-D map for the $q_4$-$q_6$ distribution of each liquid is presented in Fig. 3. The 2-D maps of the two liquids are similar in position and shape, except for higher resolution for the classical liquid due to more atoms involved in CMD simulation. In each 2-D map, we also indicate the $(q_4, q_6)$ points of several crystals, including $\alpha$-Ga, $\beta$-Ga, Ga II and Ga III, with different symbols. Intriguingly, the points of Ga solids lie on the rim of the $q_4$-$q_6$ distribution of each simulated liquid but are located at different directions from the centre of the distribution. Particularly, because of its complicated structure, Ga II [21] has 14 points of $(q_4, q_6)$, which are distributed within a region of lower $q_6$ in the 2-D map. According to the 2-D maps in Fig. 3, it is speculated that the local structure of liquid Ga at AP is constrained by the structures of its crystalline counterparts.

Relative to the Lennard-Jones liquid [22], the $q_4$-$q_6$ distribution of each simulated liquid has a centre shifting toward higher $q_4$ value, causing a broader $q_4$-distribution. The higher $q_4$ values come from atoms with lower coordination numbers. This can be verified by examining the averages of $q_6(i)$ and $q_4(i)$ for atoms having the same coordination number, which are denoted as $\bar{q}_6$ and $\bar{q}_4$, respectively [15]. As shown in Fig. 4, the dependences of $\bar{q}_4$ and $\bar{q}_6$ on coordination number $n$ of an atom are almost identical for the two simulated liquids. For each liquid, both $\bar{q}_6$ and $\bar{q}_4$ increase with decreasing coordination number $n$, and the increase of $\bar{q}_4$ is more significant.

Figure 5 SSFs of cluster ensembles in medium LBOO ($n_b = 5$) in the classical liquid: (a) $q_4$-clusters and (b) $q_6$-clusters. In each panel, the main plot presents the variation of the cluster SSF with the number of seeds $n_s$ up to 6. The black and blue dot lines indicate the first-peak position of the cluster SSF of $n_s = 1$ and $n_s = 6$, respectively. The insert shows the variations of the $Q_2/Q_1$ (circles) and $q_R/q_L$ (squares) ratios of the cluster SSF with $n_s$, and their values are referred to the left and right vertical axes, respectively.
Figure 6  SSFs of cluster ensembles in high LBOO ($n_b = 8$) in the classical liquid: (a) $q^4$-clusters and (b) $q^6$-clusters. The plots are similar as Fig. 5 except that the results in (a) are presented only up to $n_s = 4$ and the red dot line indicates the first-peak position of the cluster SSF with $n_s = 4$.

The SSFs of LBOO cluster ensembles found in the ab initio liquid have been displayed and discussed in Ref. [15]. Here, we present the results of the classical liquid and compare their characters with those of the ab initio liquid. In Fig. 5, the SSFs of the $q^4$- and $q^6$-cluster ensembles of $n_b = 5$ defined with $r_c = 3.61\,\text{Å}$ are displayed, where $n_b = 5$ is about one half of the most probable coordination number of atoms in the liquid. The first-peak position of the SSF of $q^4$-clusters shifts toward a smaller $q$-value as increasing the number of seeds $n_s$ in a cluster, but that of the $q^6$-clusters is insensitive to $n_b$. Further, for the $q^4$-clusters, both $Q_2/Q_1$ and $q_R/q_L$ ratios of the cluster SSF, after a proper rescale, increase with $n_s$ in a similar manner, and as $n_s = 6$ the $Q_2/Q_1$ ratio reaches the value (1.94) of liquid Ga. In general, the behaviours of the cluster SSF of the $q^4$-cluster ensembles in the classical liquid are consistent with those in the ab initio liquid [15]. For the $q^6$-clusters, as more seeds are added to the clusters, the $Q_2/Q_1$ ratio of the cluster SSF keeps at a constant near 1.875 up to $n_s = 6$, whereas the $q_R/q_L$ ratio decreases monotonically with increasing $n_s$. Thus, the SSFs of the $q^6$-clusters in the classical liquid behave somewhat differently from those found in the ab initio liquid and are even more HS-like, which indicates that the extent of $q^6$-cluster structures in the classical liquid mixing with other $l$-fold orientational symmetries is less than that of the $q^6$-clusters in the ab initio liquid.

Fig. 6 presents the SSFs of the $q^4$- and $q^6$-cluster ensembles with $n_b = 8$ in the classical liquid. The SSF of the $q^4$-cluster ensemble was found to deviate even more from that of a HS fluid: The $Q_2/Q_1$ ratio at $n_s = 4$ is near 1.97, and the first peak of the cluster SSF becomes asymmetric as $n_s$ increases. As searching in the classical liquid, no high-$q$ shoulder was found in the SSF of $q^4$-clusters. However, in the ab initio liquid a high-$q$ shoulder was observed in the SSF of $q^4$-clusters involving three seeds [15]. In Fig. 6(b), as $n_s$ increases up to 6, the $Q_2/Q_1$ ratio of the cluster SSF of the $q^6$-cluster ensemble keeps within a range between 1.88 and 1.84, and may have a value less than the HS one (1.86), whereas the $q_R/q_L$ ratio exhibits a small fluctuation between 1.3 and 1.1. The fluctuations of $Q_2/Q_1$ and $q_R/q_L$ are possibly resulted from the rare occurrence of $q^6$-clusters with $n_b = 8$ in the classical liquid. Thus, the SSFs of the $q^4$-cluster ensembles in high LBOO behave quite differently from those of the $q^6$-cluster ensembles; however, their differences found in the classical liquid are not so much as those appearing in the ab initio liquid. This explains why the high-$q$ shoulder observed in the SSF of the ab initio liquid is stronger than that in the SSF of the classical liquid.

It is interesting to investigate further the structure of highly LBOO $q^4$-cluster, which SSF displays a high-$q$ shoulder. Found in the ab initio liquid [15], the cluster is composed of three seeds, indicated with $A$, $B$, and $C$ in Fig. 7(a), where the three seeds form two bonds at nearly $90^\circ$ and the bond length between seed $B$ and $C$ is $2.715\,\text{Å}$ and that between seed $B$ and $A$ is $3.105\,\text{Å}$. By referring to the pair potential $\phi(r)$, the two bond lengths are within the soft repulsive core, whereas the length between seed $A$ and $C$ is $4.125\,\text{Å}$, which is within the region of the first attractive well of $\phi(r)$. The geometry of the right triangle formed by the three seeds provides an insight into the bond-angle distribution shown in Fig.
2(b). On the other hand, obtained via the AIMD simulation, the charge density around the cluster in the \textit{ab initio} liquid is presented in Fig. 7(b), where the 2-D map is plotted in the plane of the three seeds. Clearly, there is no pile up of charge in the center between any two seeds of \textit{A}, \textit{B}, and \textit{C}, which indicates that the bonding among the three seeds is not covalent-like as the dimers in \textit{\alpha}-Ga [23].

\textbf{Figure 7} (a) Structure of \textit{\vartheta}_4-cluster with \textit{n}_b = 8 and containing three seeds. The cluster was found in the \textit{ab initio} liquid. The red and blue circles indicate the seeds and their neighbors of the cluster, respectively. (b) Contours for the charge density (in the unit of \textit{e}\text{\AA}^{-3}) around the cluster in the \textit{ab initio} liquid. The 2-D map of charge density is plotted in the plane of the three seeds, indicated with \textit{A}, \textit{B}, and \textit{C}, of the cluster.

\section{4. Conclusions}

In this paper, we have investigated cluster structures in liquid Ga via AIMD and CMD simulations at the same temperature and pressure. The liquid generated by each of the two simulations can produce a SSF that behaves similarly as the anomalous SSF of liquid Ga at AP, including the shoulder on the high-\textit{q} side of its first peak, whereas the shoulder in the SSF of the \textit{ab initio} liquid is somewhat stronger. Both simulated liquids exhibit similar behaviours in the radial distribution function, the bond-angle distribution, and loose pack structure with low coordination number. Analysed with the \textit{q}_4 and \textit{q}_6 LBOO parameters, both simulated liquids contained cluster structures with fourfold orientational symmetry and with sixfold orientational symmetry, where the two types of cluster structure display different features in their cluster SSFs. The SSFs of cluster structures with sixfold orientational symmetry are akin to that of a HS fluid by showing a symmetric first peak. However, the SSFs of clusters with fourfold orientational symmetry displays an asymmetric first peak or even a shoulder on the high-\textit{q} side of the first peak as the clusters are in high LBOO. Thus, the two types of cluster structure play contrasting roles in the appearance of the high-\textit{q} shoulder in the SSF of the simulated liquid: the clusters with fourfold orientational symmetry favour its appearance but the clusters with sixfold orientational symmetry suppress it.

According to our experiences, the CMD simulation with the \textit{\phi}(\textit{r}) potential is efficient in time and can be performed with larger system sizes; however, the calculated results depend on the force field of the \textit{\phi}(\textit{r}) model. On the contrary, the AIMD simulation does not need any force field model and the results are more close to realistic liquid Ga, but it is drawback in limited system sizes and long computational time due to its demanding on computer resource. Through both AIMD and CMD simulations capture the anomalous structure of liquid Ga at AP, there are still minor differences between the radial distribution functions generated by the two simulations. Produced by the CMD simulation, a small hump showed up in the region between the first minimum and the second maximum of the radial distribution function, where this region is associated with the first attractive well of the \textit{\phi}(\textit{r}) potential. But, there was no hump observed in the corresponding region of the radial distribution function generated by the AIMD simulation, which is agree with the experimental results [15]. The results of the classical liquids indicate that this small hump in the radial distribution function was influenced by the
Friedal oscillations in the $\phi(r)$ potential [13]. Probably, some modification in the first attractive well of the $\phi(r)$ potential will make the structure of the classical liquid more close to realistic liquid Ga. If so, the CMD simulation would provide a useful method to study this peculiar metallic liquid.

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