

Effect of liquid structure on kinetic stability and glassy motifs

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Although atoms in a supercooled liquid appear randomly arranged, local crystal-like structural motifs can emerge. Such motifs are assumed to reduce the kinetic stability of the liquid against crystallization. In this study, the relation between local structure and kinetic stability of a supercooled liquid alloy is investigated through molecular dynamics simulations, using a model alloy that forms Laves phases. To detect subtle structural differences relevant to crystallization, the liquid structure is analyzed using the p_3 code. This method encodes each local environment as a graph with or without species labels. Unexpectedly, our analysis shows that liquids with more crystalline structural units can remain metastable for a longer time before crystallization. This apparent paradox is resolved by showing that kinetic stability increases when crystalline units do not easily connect to form extended clusters. Further analysis shows that clusters with the same Voronoi index can yield distinct graphs that exhibit different correlations with kinetic stability, revealing limitations of the traditional Voronoi index. Even clusters with the same graph can correlate differently due to variations in species labeling, highlighting the importance of chemical ordering. To capture medium-range order undetected by conventional analysis based on crystalline units, the concept of *loose-crystalline* units is introduced. Analysis of loose-crystalline configurations suggests that the previously observed fivefold twin-like motifs in the glassy state are remnants of crystal seeds frozen before they could fully develop. Our approach applies to various systems that form Laves phases.

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I. INTRODUCTION

A supercooled liquid is a substance that remains in the liquid state even when cooled below its freezing point [1,2]. Although thermodynamically unstable, it can persist in a metastable equilibrium state for a finite time before eventually transitioning into a stable crystal. Understanding the behavior of supercooled liquids is essential for investigating the complex and still elusive nature of the glass transition, which fundamentally involves avoiding crystallization in the supercooled liquid state [3–5].

At first glance, the atomic arrangement of supercooled liquids appears random [6]. However, atoms in this state can form locally ordered structures [2], known as short-range order (SRO). These SRO motifs can aggregate into larger configurations called medium-range order (MRO) [7]. Both SRO and MRO can resemble crystalline arrangements, often referred to as *crystal-like* order. Such crystal-like local structures are thought to facilitate crystallization [8,9].

Lennard-Jones models have been extensively studied to gain a fundamental understanding of the supercooled liquid state [7,10–13]. One representative system is the Wahnström

model alloy [14], which consists of two types of atoms: large (L) and small (S). Previous studies showed that a supercooled liquid of this alloy can crystallize into LS_2 Laves phases such as C14 and C15 [15–17]. These crystals can be regarded as an aggregate of hexagonal bipyramidal clusters, each consisting of a pair of bonded L atoms and six S atoms that are neighbors to both L atoms [18,19]. Hereafter, these clusters are referred to as *crystalline bipyramids*. Interestingly, crystalline bipyramids were also observed in the supercooled liquid state [20]. Their presence was associated with a slowdown in structural relaxation [19]. However, it remains unclear how these crystalline bipyramids influence the kinetic stability of the supercooled liquid state against crystallization. Furthermore, in the glassy state, crystalline bipyramids were shown to form structures with MRO resembling the core of a fivefold twin [21]. However, the origin of these MRO structures is not well understood.

Laves phases contain atom-centered clusters such as icosahedral and Frank-Kasper Z16 clusters [18,22]. These clusters are also found in liquid alloys and metallic glasses [17,22–24]. We call a cluster a Z16* cluster if it has the same topology as the Z16 cluster. Here, topology refers to the connectivity of atoms, or equivalently, the atomic graph structure of the cluster. A Z16* cluster can be chemically different from the Z16 cluster, with chemistry referring to the species identity of each atom. The Voronoi index $\langle 0, 0, 12, 4 \rangle$ has been used to identify Z16* clusters [17,22,23]. However, not every cluster with this index is a Z16* cluster [24]. In contrast, all Z16* clusters possess the $\langle 0, 0, 12, 4 \rangle$ index. Moreover, clusters in liquids and glasses exhibit chemical variations that the Voronoi index

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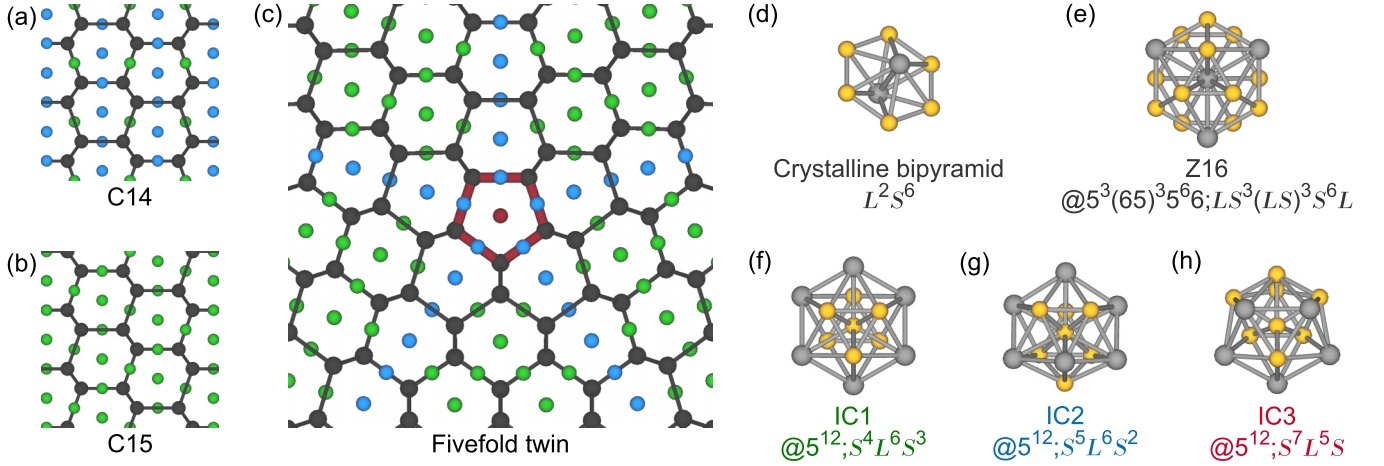


FIG. 1. Structure of Laves crystals. (a) C14 phase. (b) C15 phase. (c) Fivefold twinned crystal. (d) Crystalline bipyramid. (e) Z16 cluster. (f) IC1 cluster. (g) IC2 cluster. (h) IC3 cluster. In panels (a)–(c), dark gray spheres indicate the central L atoms of Z16 clusters; green, blue, and red spheres indicate the central S atoms of IC1, IC2, and IC3 clusters, respectively. Sticks indicate bonds connecting L atoms. IC3 clusters lie along the fivefold axis of the twin. Their L - L bonds, colored red, form pentagonal rings stacked at the center. Since the fivefold twin is shown as a projection, only a single pentagonal ring is visible. In panels (d)–(h), light gray spheres indicate L atoms, orange spheres indicate S atoms, and sticks indicate bonds connecting adjacent atoms.

does not capture. These structurally disordered systems also contain numerous bipyramidal clusters with diverse topologies and chemical arrangements (i.e., how atomic species are distributed within a given topology). For these bipyramids, no reliable characterization method was available. To address these limitations, we developed the p_3 code in our previous studies [25–28].

In this work, using the Wahnström alloy as a representative model, we examine the structure-stability relationship of a supercooled liquid alloy and elucidate the structural origin of fivefold twin-like motifs in the glassy state. To this end, we use molecular dynamics (MD) simulations and the p_3 code [25–28]. The remainder of this paper is organized as follows. Section II describes the methodology. Because this study examines structural similarities between liquids and crystals, Sec. II A details the structure of the relevant Laves crystals, namely C14, C15, and fivefold twinned crystals [18,19,21]. Section II B outlines the p_3 code, a method for analyzing local structures. This method characterizes clusters based on either topology alone or chemi-topology, where chemi-topology refers to both atomic connectivity and species identity. The Wahnström model and the MD scheme used in this study are described in Secs. II C and II D, respectively. Section II E describes the meaning of *kinetic stability* as used in this work. Section III describes MD simulation results showing that a liquid with more crystalline bipyramids can remain metastable for a longer time before crystallization—a result that challenges the natural intuition that crystal-like local structures facilitate crystallization. To resolve this apparent paradox, Sec. IV analyzes the connectivity of crystalline bipyramids. Our results show that kinetic stability is governed by the tendency of crystalline bipyramids to connect to form large superclusters, rather than simply by their total number. Section V examines how the number of clusters of various topological and chemi-topological types correlates with the kinetic stability of the supercooled liquid state against crystallization. Notably, icosahedral clusters generally show little

correlation with kinetic stability, whereas icosahedral clusters chemically identical to those at the fivefold twin core exhibit a clear correlation. This observation suggests a possible role of fivefold twinning in the onset of crystallization. To examine this possibility, Sec. VI introduces the *loose-crystalline* bipyramid, the structural unit being defined under more relaxed criteria than the conventional crystalline bipyramid. Section VII analyzes MRO using loose-crystalline bipyramids as structural units. Our results reveal that pregrowth and growing crystal seeds can exhibit fivefold twin-like motifs. This observation suggests that similar motifs previously observed in the glassy state [21] are remnants of crystal seeds whose growth was kinetically arrested during cooling, rather than structures intrinsically stabilized in the glassy state. Finally, Sec. VIII provides concluding remarks.

II. METHODOLOGY

A. Structure of LS_2 crystals

Three different types of LS_2 crystals—namely, the C14, C15, and fivefold twin—are illustrated, respectively, in Figs. 1(a)–1(c). The structure shown in Fig. 1(d) is a crystalline bipyramid that serves as a structural unit of these crystals. A crystalline bipyramid consists of two apex L atoms and six base S atoms that are neighbors to both L atoms. In Laves crystals, crystalline bipyramids connect through shared apex atoms. We refer to an aggregate of such connected bipyramids as a *crystalline supercluster*. Laves crystals can be viewed as extended crystalline superclusters. The C14, C15, and fivefold twin share the same building blocks, but their connectivity differs. In the C14 structure, the L - L bonds form a tetrahedral network that is isostructural with the hexagonal diamond lattice, whereas in the C15 structure, the corresponding bond network is isostructural with the cubic diamond lattice. The fivefold twin is constructed by joining five crystalline units with C15 symmetry [21]. The C14 structure contains Z16, IC1, and IC2 clusters [Figs. 1(e)–1(g),

respectively]. The Z16 cluster consists of a central L atom surrounded by four L atoms and 12 S atoms. Because it is composed of four crystalline bipyramids connected via a shared apex atom, a Z16 cluster can be regarded as a crystalline supercluster. The C15 structure contains Z16 and IC1 clusters. In addition to Z16, IC1, and IC2, the fivefold twin contains IC3 clusters [Fig. 1(h)], which lie along the twin's fivefold axis. The L atoms in the IC3 clusters form pentagonal rings stacked at the center of the fivefold twin. We point out that glasses of the Wahnström alloy and $\text{Zr}_{35}\text{Cu}_{65}$ metallic glasses can contain MRO structures resembling the core of the fivefold twin [21].

In this work, Z16, IC1, IC2, and IC3 denote cluster structures defined by chemi-topology (i.e., atomic connectivity and species identity). The IC1, IC2, and IC3 clusters are icosahedral clusters that share the same topology (i.e., atomic connectivity) but differ in chemistry (i.e., species identity). We introduce the term IC* to denote clusters with this topology. IC* clusters include IC1, IC2, and IC3, as well as other clusters with the same topology. Similarly, Z16* denotes clusters with the topology of Z16.

B. Chemi-topological structural analysis using the p_3 code

We study the local structure of supercooled liquids through p_3 analysis, a method that combines Voronoi tessellation and the p_3 code [25,26,28]. The computations were performed using the VOROTIS software [27]. For reference, we note that, using a single core of a 13th Gen Intel(R) Core(TM) i7-1370P, the p_3 analysis of one configuration containing 10 000 atoms, representative of the configurations analyzed in this work, takes approximately 60 seconds.

In Voronoi tessellation, space is divided into regions called Voronoi polyhedra. Each polyhedron contains a single atom. Two atoms are considered to be bonded when their polyhedra share a face. A structure consisting of two bonded atoms and their common neighbors is referred to as a bipyramidal cluster. The two bonded atoms form the apices of the bipyramid and are referred to as apex atoms. The common neighbors form the base of the bipyramid and are referred to as base atoms. When the base consists of n atoms, the bipyramid is referred to as an n -gonal bipyramid. Using the p_3 code, the crystalline hexagonal bipyramid shown in Fig. 1(d) is encoded as $LLSSSSSS$ [21,28]. The order of the letters (two L s followed by six S s) reflects the spatial arrangement of the species: the two L atoms occupy the bipyramid's apices, while the base consists of six S atoms. For compact representation and to indicate repeated patterns, the codeword can be abbreviated as L^2S^6 . We note that the same structure is represented by 1551 in the Honeycutt-Anderson index [29], which ignores chemical arrangement.

Figure 2(a) shows an L^2S^6 bipyramid found in a supercooled liquid. By a single modification of this structure, five derivatives can be generated:

- (1) Replace one S atom with an L atom to obtain L^3S^5 [Fig. 2(b)].
- (2) Replace one L atom with an S atom to obtain SLS^6 [Fig. 2(c)].
- (3) Add one L atom to obtain L^3S^6 [Fig. 2(d)].
- (4) Add one S atom to obtain L^2S^7 [Fig. 2(e)].
- (5) Remove one S atom to obtain L^2S^5 [Fig. 2(f)].

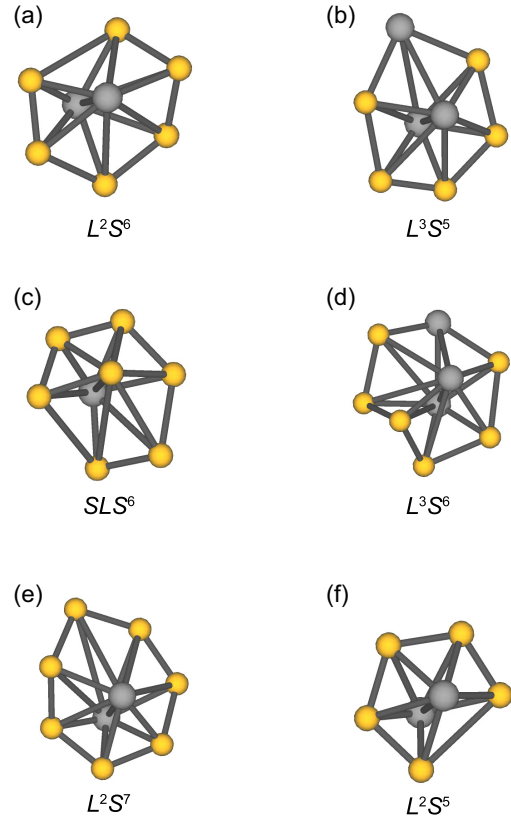


FIG. 2. Crystalline bipyramid and its derivatives found in a supercooled liquid. Large gray spheres represent L atoms, while small orange spheres represent S atoms.

We refer to the bond connecting the two apex atoms of a bipyramid as an apex bond. The apex bond of a p_3 bipyramid is referred to as a p_3 bond. For example, an L^2S^6 bond represents the apex bond of an L^2S^6 bipyramid. In Ref. [19], the same bond is referred to as an FK bond. Although the crystalline bipyramid is represented by the codeword L^2S^6 , we will simply refer to it as the crystalline bipyramid unless the code notation is specifically needed, such as when discussing its derivatives.

A structure consisting of a central atom and its neighbors is referred to as an atom-centered cluster. When there is no risk of confusion with bipyramidal clusters, an atom-centered cluster is simply referred to as a cluster. There is a one-to-one correspondence between a cluster and the Voronoi polyhedron of its central atom. Therefore, the cluster's topology can be characterized by that of the corresponding Voronoi polyhedron. The Voronoi index $\langle 0, 0, 12, 4 \rangle$ has been used to identify Z16* clusters in metallic glasses [17,22,23]. However, O16* clusters [24], which have a different topology from Z16*, exhibit the same Voronoi index (Fig. 3). This is because the Voronoi index counts only the number of faces of the Voronoi polyhedron (12 pentagons and 4 hexagons) and ignores their spatial arrangement. In contrast, the p_3 code includes this spatial information. Figure 3 shows the graph representations of the Voronoi polyhedra of a Z16* cluster and an O16* cluster. These polyhedra share the same Voronoi index but differ in their p_3 codes: 5556565655555556 and 5555565665655555,

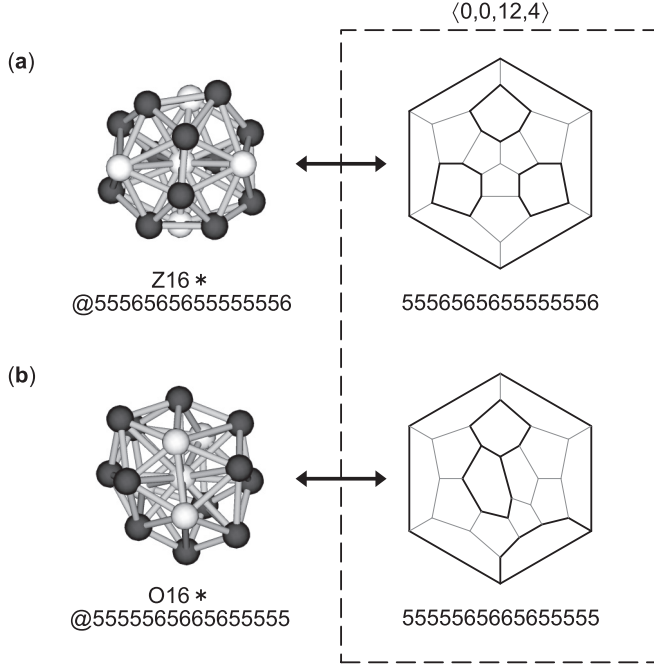


FIG. 3. Representation of (a) Z16* and (b) O16* clusters.

respectively [24]. In these codes, the numbers ‘5’ and ‘6’ represent a pentagon and a hexagon, respectively, and the sequence specifies their arrangement. The codewords can be abbreviated as $5^3(65)^35^66$ for 5556565655555556, and $5^5(656)^25^5$ for 5555565665555555. Using the one-to-one correspondence between a cluster and its Voronoi polyhedron, the topologies of the Z16* and O16* clusters are represented by $@5^3(65)^35^66$ and $@5^5(656)^25^5$, respectively. Therefore, the p_3 code enables definitive identification of Z16* clusters. This capability is essential for examining the influence of Z16* clusters on the kinetic stability of the supercooled liquid state.

Initially, the p_3 code captured only topological features [25], but it was later extended to incorporate chemical identities [26,27]. In this generalized framework, the chemi-topological structure of the Z16 cluster is encoded as $@5^3(65)^35^66; LS^3(LS)^3S^6L$. The first part, $@5^3(65)^35^66$, represents the atomic connectivity, while the second part, $LS^3(LS)^3S^6L$, specifies the chemical identity of each atom (L or S). Similarly, the IC1, IC2, and IC3 clusters are encoded as $@5^{12}; S^4L^6S^3$, $@5^{12}; S^5L^6S^2$, and $@5^{12}; S^7L^5S$, respectively. By applying this approach, we identified Z16, IC1, IC2, and IC3 clusters in supercooled liquids, which provides a basis for analyzing how these structural motifs contribute to kinetic stability.

C. Wahnström model alloy

We examine the Wahnström model as a representative system that forms a Laves phase. Since Laves phases are observed in a wide range of materials, including Cr-, Cu-, Fe-, Mg-, Nb-, Ni-, Ti-, and Zr-based alloys [30], as well as in colloidal mixtures [31], we believe that the results based on this model provide a useful reference and a starting point for comparative studies on the kinetic stability of supercooled

liquids and glass formation in other Laves-phase-forming systems.

The Wahnström model consists of L and S atoms interacting via the cut-and-shifted Lennard-Jones potential,

$$\Phi_{\alpha_i\alpha_j}(r_{ij}) = \begin{cases} \phi_{\alpha_i\alpha_j}(r_{ij}) - \phi_{\alpha_i\alpha_j}(r_{\alpha_i\alpha_j}^c) & (r_{ij} < r_{\alpha_i\alpha_j}^c) \\ 0 & (r_{\alpha_i\alpha_j}^c \leq r_{ij}) \end{cases}, \quad (1)$$

where

$$\phi_{\alpha_i\alpha_j}(r_{ij}) = 4\epsilon_{\alpha_i\alpha_j} \left(\left(\frac{\sigma_{\alpha_i\alpha_j}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\alpha_i\alpha_j}}{r_{ij}} \right)^6 \right). \quad (2)$$

Here, α_i represents the chemical identity of atom i (L or S), and r_{ij} is the distance between atoms i and j . $r_{\alpha_i\alpha_j}^c = 2.5\sigma_{\alpha_i\alpha_j}$ is the cutoff distance. $\sigma_{SS} = \sigma_{SL}/1.1 = \sigma_{LL}/1.2$, $\epsilon_{SS} = \epsilon_{SL} = \epsilon_{LL}$, and $m_S = m_L/2$ [14]. Hereafter, we use the L -atom Lennard-Jones reduced units: length σ_{LL} , energy ϵ_{LL} , temperature ϵ_{LL}/k_B , pressure $\epsilon_{LL}/\sigma_{LL}^3$, and time $\sqrt{m_L\sigma_{LL}^2/\epsilon_{LL}}$.

We examine supercooled liquids composed of a total of 10 000 atoms. In one system, 3333 L atoms and 6667 S atoms are present, yielding an L -atom fraction of $x_L = 0.333$. Although this composition is not strictly stoichiometric, the deviation is small. Therefore, we refer to it as stoichiometric. Two other systems have $x_L = 0.224$ (2240 L atoms and 7760 S atoms) and $x_L = 0.520$ (5200 L atoms and 4800 S atoms). The system with $x_L = 0.224$ corresponds to the eutectic composition between the S -atom fcc phase and the C14 LS_2 phase [32], while the system with $x_L = 0.520$ corresponds to the eutectic composition between the L -atom fcc phase and the C14 LS_2 phase.

D. Molecular dynamics simulations

We performed molecular dynamics simulations using LAMMPS [33], with temperature and pressure controlled by the Nosé–Hoover thermostat and Parrinello–Rahman barostat, respectively [34–36]. Following Ref. [7], the pressure was kept at 10. After equilibrating the system at the liquidus temperature, the temperature was instantaneously changed to the target value to simulate the supercooled liquid state.

E. Kinetic stability

Kinetic stability, in this work, refers to the ability of a supercooled liquid to remain in a metastable state without crystallization. In principle, kinetic stability should be quantified by the lifetime over which the metastable state persists. However, because statistically reliable lifetime values could not be obtained from the present simulations, kinetic stability is operationally quantified by whether crystallization occurs within a time interval of 40.0×10^6 time units. Kinetic stability is inversely related to crystallization: lower crystallizability corresponds to higher kinetic stability. Accordingly, depending on the context, crystallizability is used as a practical indicator to discuss kinetic stability.

III. STABILITY PARADOX

In this section, we present a paradoxical finding: a liquid with more crystalline bipyramids can be kinetically more stable against crystallization. To this end, we first

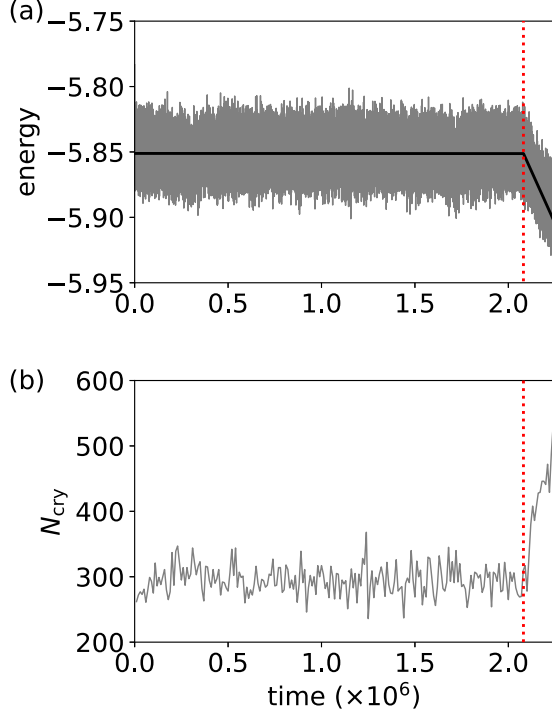


FIG. 4. Time evolution of (a) the potential energy per atom and (b) the number of crystalline bipyramids per 10 000 atoms in the supercooled stoichiometric liquid at $T = 0.705$. In panel (a), the black broken line represents the piecewise linear function $E(t)$. The vertical dashed lines indicate the lifetime of the supercooled liquid state: $t_l = 2.08 \times 10^6$.

determine the lifetime of the stoichiometric liquid ($x_L = 0.333$) at a temperature of $T = 0.705$. This temperature corresponds to approximately 80% supercooling (i.e., $0.705/0.886 \approx 0.80$ [32]). The time evolution of the potential energy is shown in Fig. 4(a). A visual inspection reveals that thermal fluctuations continue until around 2.0×10^6 time units, after which a sharp drop is observed. These fluctuations are indicative of a metastable equilibrium state, and the sharp drop marks the termination of this state, triggered by the onset of crystallization. To identify when the supercooled state ends without relying on visual inspection, the time evolution of the potential energy was fitted to a piecewise linear function $E(t)$ defined as

$$E(t) = \begin{cases} E_0 & t \leq t_l, \\ E_0 + \alpha(t - t_l) & t_l < t. \end{cases} \quad (3)$$

Note that α is negative. We regard the obtained value of $t_l = 2.08 \times 10^6$ as the lifetime of the supercooled liquid state.

The number of crystalline bipyramids (N_{cry}) in this system was computed every 0.01×10^6 time units, and its time evolution is shown in Fig. 4(b). After exhibiting thermal fluctuations, N_{cry} increases sharply. This behavior is consistent with the time evolution of the potential energy. Based on the values of N_{cry} obtained in the metastable equilibrium state, the time-averaged value ($\overline{N_{\text{cry}}}$) was computed to be 294.71 (per 10 000 atoms). The same procedure was repeated for three additional MD simulations. The t_l and $\overline{N_{\text{cry}}}$ for each of the four trajectories are summarized in Table I. From these data,

TABLE I. Lifetimes (t_l) and time-averaged numbers of crystalline bipyramids per 10 000 atoms ($\overline{N_{\text{cry}}}$) for the stoichiometric supercooled liquid at $T = 0.705$, obtained from four independent MD trajectories (Nos. 1–4).

No.	$t_l/10^6$	$\overline{N_{\text{cry}}}$
1	2.08	294.71
2	3.60	294.33
3	2.03	294.70
4	0.62	294.52

the lifetime-weighted average ($\langle \overline{N_{\text{cry}}} \rangle$) was computed to be 294.53 ± 0.18 . Here, the average and uncertainty represent the weighted mean (μ) and its standard deviation (σ), respectively. The weighted mean was calculated as follows. First, the weight $w(i)$ of the i -th trajectory was defined as

$$w(i) = \frac{t_l(i)}{\sum_{j=1}^4 t_l(j)}, \quad (4)$$

where $t_l(i)$ denotes the lifetime of the supercooled liquid state for the i -th trajectory. Since each weight was set proportional to the lifetime of the supercooled liquid state, simulations with longer lifetimes contribute more strongly. The weights are normalized such that

$$\sum_{i=1}^4 w(i) = 1. \quad (5)$$

Each value of $\overline{N_{\text{cry}}}$ was multiplied by its corresponding weight. The weighted mean was then obtained by summing these weighted values:

$$\mu = \sum_{i=1}^4 w(i) \cdot \overline{N_{\text{cry}}}(i), \quad (6)$$

where $\overline{N_{\text{cry}}}(i)$ denotes the time-averaged number of crystalline bipyramids for the i -th trajectory. The standard deviation was evaluated as the weighted variance around the weighted mean:

$$\sigma = \sqrt{\sum_{i=1}^4 w(i) (\overline{N_{\text{cry}}}(i) - \mu)^2}. \quad (7)$$

Next, we examine a nonstoichiometric liquid with $x_L = 0.224$ at $T = 0.705$, the same temperature as in the stoichiometric system. For this nonstoichiometric liquid, $T = 0.705$ corresponds to approximately 81% supercooling (i.e., $0.705/0.873 \approx 0.81$). Four MD simulations of 40.0×10^6 time units were performed, and structures were analyzed every 0.1×10^6 time units. Since the stoichiometric composition represents the ideal composition for the crystal, we initially expected that the nonstoichiometric system would contain fewer crystalline bipyramids, which would lead to higher stability compared with the stoichiometric one. Contrary to this expectation, the nonstoichiometric liquid contained a larger number of crystalline bipyramids, $\langle \overline{N_{\text{cry}}} \rangle = 320.37 \pm 1.07$. Despite this increased presence of crystalline bipyramids, no crystallization was observed during the 40.0×10^6 time units—more than 10 times longer than the longest

TABLE II. Distribution of crystalline bipyramids by connectivity c , where the c of a crystalline bipyramid represents the number of crystalline bipyramids that are connected to it. To explain how to interpret the data: at $T = 0.705$, in the supercooled liquid with $x_L = 0.333$, the average number of crystalline bipyramids with connectivity six is 0.77 ± 0.30 per 10 000 atoms.

c	$T = 0.705$ $x_L = 0.224$	0.705 0.333	0.705 0.520	0.670 0.224	0.690 0.520
6	0.01 ± 0.00	0.77 ± 0.30	0.07 ± 0.04	0.13 ± 0.02	0.20 ± 0.03
5	0.07 ± 0.01	0.76 ± 0.16	0.05 ± 0.02	0.41 ± 0.04	0.14 ± 0.02
4	0.60 ± 0.05	2.37 ± 0.28	0.22 ± 0.06	1.97 ± 0.07	0.67 ± 0.04
3	5.11 ± 0.09	8.48 ± 0.44	1.32 ± 0.18	9.58 ± 0.25	3.21 ± 0.12
2	29.86 ± 0.24	25.03 ± 0.46	2.34 ± 0.09	40.39 ± 0.29	3.63 ± 0.12
1	105.87 ± 0.41	81.74 ± 0.39	12.38 ± 0.12	121.24 ± 1.04	16.05 ± 0.20
0	178.86 ± 0.59	175.38 ± 1.06	64.26 ± 0.23	184.45 ± 0.68	69.80 ± 0.12
sum	320.37 ± 1.07	294.53 ± 0.18	80.65 ± 0.40	358.18 ± 0.67	93.71 ± 0.28

observed lifetime of the stoichiometric liquid. Although the nonstoichiometric liquid is kinetically more stable as expected, it is paradoxical that the liquid containing more crystalline bipyramids (hereafter called the L^2S^6 -rich liquid) exhibits higher kinetic stability than the liquid containing fewer crystalline bipyramids (the L^2S^6 -poor liquid). We recall that L^2S^6 represents the crystalline bipyramid.

IV. THE ORIGIN OF THE STABILITY PARADOX

To resolve the stability paradox, we examine the connectivity of crystalline bipyramids. Here, the connectivity c of a crystalline bipyramid is defined as the number of neighboring crystalline bipyramids connected via either of its two apex atoms. For example, each crystalline bipyramid in Laves crystals has a connectivity of six, while an isolated crystalline bipyramid has a connectivity of zero. Table II summarizes the classification of crystalline bipyramids by c in the L^2S^6 -rich liquid (nonstoichiometric with $x_L = 0.224$) and the L^2S^6 -poor liquid (stoichiometric with $x_L = 0.333$). The results show that the L^2S^6 -rich liquid contains more crystalline bipyramids with low connectivity ($c = 0, 1, 2$) but fewer with high connectivity ($c = 3, 4, 5, 6$) compared to the L^2S^6 -poor liquid. This means that crystalline bipyramids in the L^2S^6 -rich liquid exhibit a weaker tendency to connect. This tendency hinders the formation of large crystalline superclusters that act as seeds for crystal growth. The unexpected result—the longer lifetime of the L^2S^6 -rich liquid, despite the larger number of crystalline bipyramids—can be explained by the difficulty in growing crystalline superclusters. This finding suggests a general principle: the kinetic stability of supercooled liquids may depend on how readily crystalline structural units connect rather than on their mere abundance. Nevertheless, this connectivity alone does not determine crystallization. For instance, liquid SiO_2 exhibits extensive connectivity of SiO_4 tetrahedra [37], the building blocks of its crystal, yet it is well known for its resistance to crystallization.

To clarify the mechanism underlying the difficulty in growing crystalline superclusters, we examine the connectivity dependence of the energy of crystalline bipyramids. The energy of each bipyramid is defined as the sum of the energies of its constituent atoms:

$$E = \sum_i \delta_i e_i, \quad (8)$$

where $\delta_i = 1$ if atom i belongs to the bipyramid, and $\delta_i = 0$ otherwise. e_i is the energy of atom i , defined as

$$e_i = \frac{1}{2} \sum_j \Phi_{\alpha_i \alpha_j}(r_{ij}). \quad (9)$$

For each trajectory, we computed the average energy of crystalline bipyramids with connectivity c , denoted by $\bar{E}_c$. From the four trajectories, we calculated the weighted average $\langle \bar{E}_c \rangle$ using weights defined as

$$w_c(i) = \frac{N_c(i)}{\sum_{j=1}^4 N_c(j)}, \quad (10)$$

where $N_c(i)$ is the total number of crystalline bipyramids with connectivity c observed in the i -th trajectory during the metastable equilibrium supercooled liquid state.

Figure 5 shows that crystalline bipyramids with higher connectivity are energetically more favorable in both L^2S^6 -poor and L^2S^6 -rich liquids. However, the energy difference $\langle \bar{E}_0 \rangle - \langle \bar{E}_6 \rangle$ is smaller in the L^2S^6 -rich liquid than in the L^2S^6 -poor liquid. This result indicates that, compared to the L^2S^6 -poor liquid, the L^2S^6 -rich liquid has a weaker energetic driving force for connecting bipyramids. This weaker driving force hinders the growth of crystalline superclusters, thereby enhancing the kinetic stability of the L^2S^6 -rich liquid.

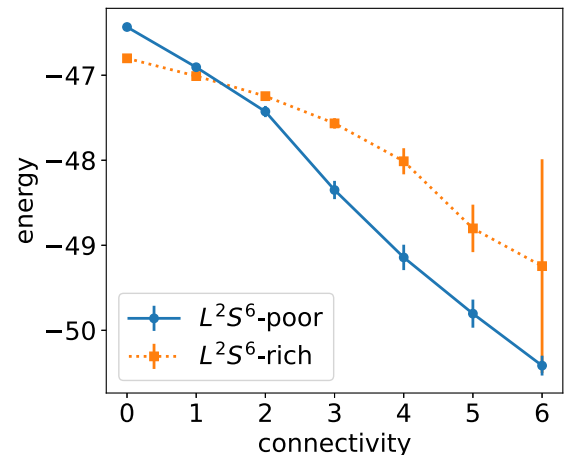


FIG. 5. Energy of crystalline bipyramids ($\langle \bar{E}_c \rangle$) as a function of connectivity (c).

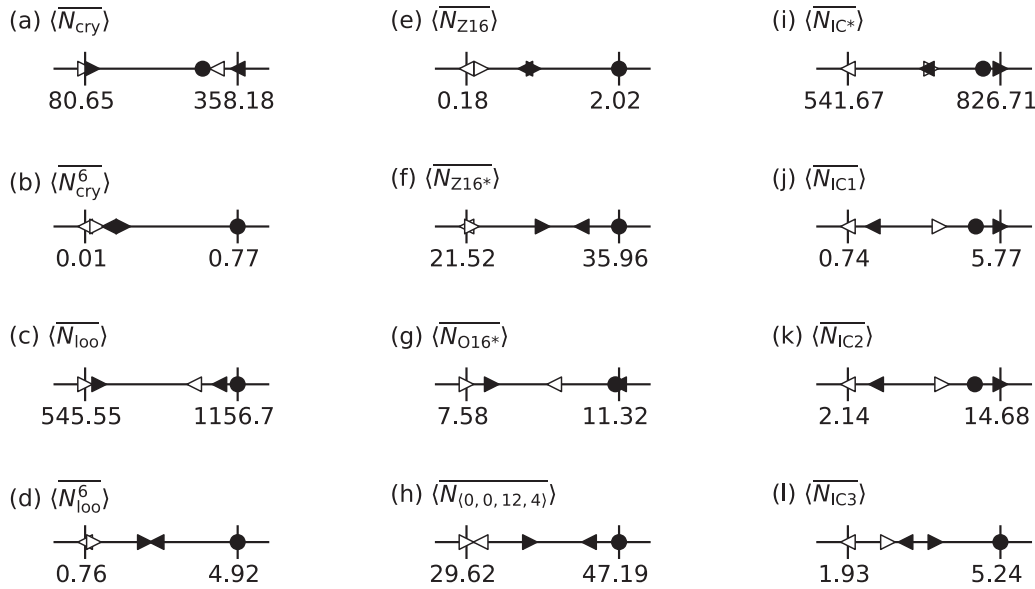


FIG. 6. Relation between the number of clusters and crystallization behavior for different cluster types. Panels (a)–(d) present results for bipyramidal clusters: (a) crystalline, (b) crystalline with connectivity six, (c) loose-crystalline, and (d) loose-crystalline with connectivity six. Panels (e)–(l) present results for atom-centered clusters: (e) Z16, (f) Z16*, (g) O16*, (h) clusters corresponding to the Voronoi polyhedron with (0, 0, 12, 4), (i) IC*, (j) IC1, (k) IC2, and (l) IC3. Symbols denote different state points (x_L , T): $\triangleleft$ denotes (0.224, 0.705), $\blacktriangleleft$ denotes (0.224, 0.670), $\bullet$ denotes (0.333, 0.705), $\triangleright$ denotes (0.520, 0.705), and $\blacktriangleright$ denotes (0.520, 0.690); white indicates no crystallization; black indicates crystallization. Horizontal position corresponds to the number of clusters.

The variation in connectivity can be understood in terms of a competition between energetic and entropic effects in the presence of thermal fluctuations. Bipyramids with higher connectivity tend to exhibit lower potential energy and are therefore energetically favorable. However, their formation is entropically unfavored because it requires a collective and relatively ordered arrangement of multiple neighboring bipyramids, which reduces the number of accessible configurations. As a result, although highly connected bipyramids can form under thermal fluctuations, such connections tend to break down, leading to a variation in connectivity.

V. SYSTEMATIC ANALYSIS OF THE STRUCTURE-STABILITY RELATIONSHIP

To further examine the kinetic stability of the supercooled liquid state against crystallization, we performed MD simulations at three additional state points: (x_L , T) = (0.520, 0.705), (0.520, 0.690), and (0.224, 0.670). In the following discussion, kinetic stability is discussed in terms of crystallizability; higher crystallizability corresponds to lower kinetic stability. The classification of crystalline bipyramids for these liquids is summarized in Table II. We begin by presenting the results for the state point (0.520, 0.705). For the liquid with $x_L = 0.520$, $T = 0.705$ corresponds to approximately 83% supercooling (i.e., $0.705/0.847 \approx 0.83$). Four MD simulations of 40.0×10^6 time units were performed, with structural analysis conducted every 0.1×10^6 time units. In these simulations, crystallization was not observed. For all types of connectivity, this liquid contains fewer crystalline bipyramids than the stoichiometric liquid. The scarcity of these structures explains the lower crystallizability of the nonstoichiometric liquid compared with the stoichiometric one.

Four MD simulations of the stoichiometric liquid at $T = 0.705$ yielded the lifetimes (t_l) reported in Table I, listed in ascending order ($\times 10^6$ time units): 0.62, 2.03, 2.08, and 3.60. By contrast, the nonstoichiometric liquids did not crystallize at $T = 0.705$. However, at lower temperatures, crystallization did occur. For the liquid with $x_L = 0.224$, the observed lifetimes at $T = 0.670$ were 0.57, 4.30, 5.59, and 8.72 ($\times 10^6$ time units). For the liquid with $x_L = 0.520$, the observed lifetimes at $T = 0.690$ were 2.71, 3.73, 4.21, and 15.29 ($\times 10^6$ time units). Even though the simulations were performed under identical conditions, the lifetimes varied significantly. Since statistically reliable lifetime values were not available, we cannot quantitatively compare the kinetic stability of the liquid state among the three state points: (x_L , T) = (0.224, 0.670), (0.333, 0.705), and (0.520, 0.690). Nevertheless, a clear distinction emerges: while no crystallization was observed at (0.224, 0.705) and (0.520, 0.705), crystallization occurred at (0.224, 0.670), (0.333, 0.705), and (0.520, 0.690).

Figure 6(a) illustrates the results described above, showing that the number of crystalline bipyramids, $\langle N_{\text{cry}} \rangle$, is not correlated with crystallizability. However, crystallizability can be explained by considering the connectivity of crystalline bipyramids, which reflects how easily crystalline superclusters grow. In fact, Fig. 6(b) shows that the number of bipyramids with connectivity six, $\langle N_{\text{cry}}^6 \rangle$, serves as an indicator of crystallization. Specifically, crystallization occurred when $\langle N_{\text{cry}}^6 \rangle$ was high, whereas no crystallization was observed within 40.0×10^6 time units when it was low. Figure 7 shows an MRO structure composed of two Z16 clusters that share a crystalline bipyramid. The connectivity of this shared bipyramid is six. A bipyramid with connectivity six is not necessarily part of a Z16-Z16 structure;

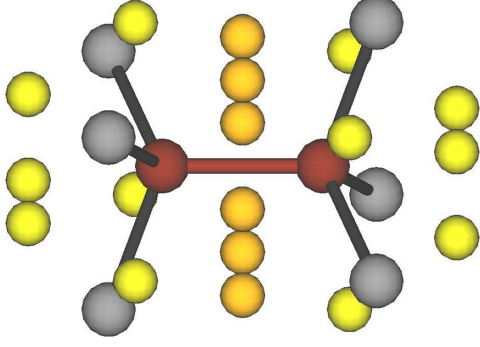


FIG. 7. Z16-Z16 structure. Each red atom represents the L atom located at the center of a Z16 cluster. The two red atoms, together with the six orange atoms, form a connectivity-six bipyrmaid that is shared by the two Z16 clusters. The other L and S atoms are colored gray and yellow, respectively. The sticks indicate L^2S^6 bonds with the red one representing a connectivity-six bond.

however, among the 1016894 bipyramids with connectivity six identified in this study, only one was not part of any Z16-Z16 structure. Consequently, our results indicate that Z16-Z16 MRO structures play a key role in determining crystallizability.

In addition to crystalline bipyramids, we also examined a variant structure referred to as a *loose-crystalline bipyrmaid*. This structure exhibits reduced crystalline order compared to the crystalline bipyrmaid (see Sec. VI for a detailed definition). Our analysis [Table III and Figs. 6(c) and 6(d)] shows that the number of loose-crystalline bipyramids with connectivity six is correlated with crystallizability, whereas the number of loose-crystalline bipyramids does not.

Table IV summarizes the numbers of Z16, Z16*, O16*, IC*, IC1, IC2, and IC3 clusters, as well as clusters for which the Voronoi polyhedron enclosing the central atom is characterized by the Voronoi index $\langle 0, 0, 12, 4 \rangle$. Their relation to crystallizability is illustrated in Figs. 6(e)–6(l). Figure 6(e) shows that the number of Z16 clusters correlates with crystallizability. Given that each Z16 cluster consists of four crystalline bipyramids, this result is consistent with our finding that crystallization is governed by the tendency of crystalline bipyramids to connect. A similar correlation is

observed for Z16* clusters, which have the same topology as Z16 clusters but differ in chemical arrangement in most cases (e.g., only 5.6% of the Z16* clusters are actually Z16 clusters in the liquid with $x_l = 0.333$ at $T = 0.705$; see Table IV). This indicates that the perfect chemical ordering of Z16 is not a determining factor for crystallizability. In contrast, no clear correlation was observed for O16* clusters. These clusters correspond to the same Voronoi index, $\langle 0, 0, 12, 4 \rangle$, as Z16* clusters, but differ in atomic connectivity. This result indicates that topological features not captured by the Voronoi index can play a key role in determining crystallizability. Although clusters corresponding to $\langle 0, 0, 12, 4 \rangle$ correlate clearly, this is not because the Voronoi index itself is important, but because most clusters corresponding to this index are Z16* in the studied liquids. For example, as many as 76.2% of the clusters corresponding to $\langle 0, 0, 12, 4 \rangle$ are Z16 in the liquid with $x_l = 0.333$ at $T = 0.705$ (Table IV).

A previous study reported a linear relationship between the number of IC* clusters (icosahedral clusters) and the number of crystalline bipyramids in Wahnström liquids [20]. As described above, we showed that the number of crystalline bipyramids does not account for crystallizability. These two results imply that the number of IC* clusters is also unlikely to show a correlation. This expectation is confirmed by Fig. 6(i) and Table IV. We point out that IC* clusters have often been regarded as structures that hinder crystallization in supercooled liquids. This view stems from the fact that icosahedra alone cannot tile space. This reasoning does not hold for multicomponent systems. In fact, Laves structures achieve space filling by combining IC* with Z16*. Therefore, in supercooled Wahnström liquids, IC* clusters may not hinder crystallization; they may even facilitate it. Nevertheless, as shown above, no clear correlation is observed between the number of IC* clusters and crystallizability.

For most IC* clusters, their chemical arrangement differs from that in crystalline IC1 and IC2. This difference may explain their lack of correlation with crystallizability. To test this, we examined crystalline IC* clusters, namely IC1 and IC2; however, no correlation was observed for these clusters either [Figs. 6(j) and 6(k)]. In contrast, IC3 clusters correlate with crystallizability [Fig. 6(l)]. Given that IC3 clusters reside at the core of the fivefold twin, this observation suggests a possible involvement of fivefold twinning in the onset of

TABLE III. Distribution of loose-crystalline bipyramids by connectivity c , where the c of a loose-crystalline bipyrmaid represents the number of loose-crystalline bipyramids that are connected to it.

c	$T = 0.705$ $x_L = 0.224$	0.705 0.333	0.705 0.520	0.670 0.224	0.690 0.520
6	0.76 ± 0.04	4.92 ± 0.75	1.00 ± 0.11	2.71 ± 0.05	2.39 ± 0.02
5	4.93 ± 0.09	12.76 ± 0.70	3.09 ± 0.13	10.73 ± 0.09	5.78 ± 0.09
4	34.00 ± 0.18	57.95 ± 1.22	20.20 ± 0.29	53.42 ± 0.45	30.04 ± 0.35
3	155.19 ± 1.07	203.24 ± 2.35	84.53 ± 0.39	197.43 ± 1.07	105.32 ± 0.63
2	383.37 ± 0.84	442.22 ± 0.72	196.29 ± 0.88	415.38 ± 0.79	213.65 ± 0.23
1	404.13 ± 1.26	435.60 ± 0.65	240.43 ± 1.23	403.65 ± 0.67	244.90 ± 0.46
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
sum	982.40 ± 2.73	1156.70 ± 4.96	545.55 ± 2.01	1083.32 ± 1.67	602.08 ± 1.25

TABLE IV. Number of clusters per 10 000 atoms for Z16, Z16*, O16*, clusters corresponding to the Voronoi polyhedron with (0, 0, 12, 4), IC*, IC1, IC2, and IC3 at five state points: $(T, x_L) = (0.705, 0.224)$, $(0.705, 0.333)$, $(0.705, 0.520)$, $(0.670, 0.224)$, and $(0.690, 0.520)$.

type	$T = 0.705$ $x_L = 0.224$	0.705 0.333	0.705 0.520	0.670 0.224	0.690 0.520
Z16	0.18 ± 0.01	2.02 ± 0.33	0.36 ± 0.08	0.89 ± 0.04	0.99 ± 0.06
Z16*	21.52 ± 0.11	35.96 ± 0.96	22.04 ± 0.15	32.42 ± 0.08	28.73 ± 0.21
O16*	9.73 ± 0.06	11.23 ± 0.19	7.58 ± 0.07	11.32 ± 0.09	8.20 ± 0.03
(0, 0, 12, 4)	31.25 ± 0.07	47.19 ± 0.93	29.62 ± 0.19	43.73 ± 0.15	36.93 ± 0.25
IC*	541.67 ± 0.40	794.42 ± 5.60	697.33 ± 2.68	689.19 ± 0.96	826.71 ± 1.28
IC1	0.74 ± 0.02	4.96 ± 0.36	3.76 ± 0.10	1.56 ± 0.05	5.77 ± 0.07
IC2	2.14 ± 0.02	12.58 ± 0.52	9.89 ± 0.23	4.46 ± 0.09	14.68 ± 0.07
IC3	1.93 ± 0.07	5.24 ± 0.15	2.80 ± 0.08	3.18 ± 0.09	3.83 ± 0.07

crystallization. Evidence supporting this hypothesis is provided in the following sections.

Z16-Z16 structures, Z16 clusters, Z16* clusters, and IC3 clusters correlate with crystallizability. However, this study does not determine which of these best explains crystallization behavior. To address this question, more simulations are required to determine the statistically reliable lifetimes of the supercooled liquid state across a wider range of state points. This will be an interesting topic for future research.

VI. LOOSE-CRYSTALLINE ORDER

In this section, we introduce the concept of loose-crystalline bipyramids, which are defined using more relaxed structural criteria compared to the crystalline bipyramid. This concept enables the detection of crystal-like MRO structures that are undetected when focusing exclusively on crystalline bipyramids. In particular, fivefold twin-like structures can be detected in the early stage of crystallization.

In the following discussion, we denote crystalline bipyramids by their code representation, L^2S^6 . Figure 8(a) shows three crystalline superclusters observed in a supercooled liquid prior to crystallization. One supercluster consists of multiple L^2S^6 bipyramids, whereas the other two are each composed of a single L^2S^6 bipyramid. For clarity, the figure shows only the apex atoms and apex bonds of the crystalline bipyramids. The bipyramid whose apex atoms are X and X' is not of the L^2S^6 type, so that these atoms are not connected. The same holds for atoms Y and Y'. Connecting these pairs, together with the existing L^2S^6 bonds, results in a six-membered ring of tetrahedral bonds similar to that found in Laves crystals. This observation suggests that the two bipyramids may be closely related to the L^2S^6 type. Our examination confirmed this by revealing that these bipyramids are of the L^3S^5 type [Fig. 2(b)]. This type derives from the L^2S^6 bipyramid through the replacement of one S atom with an L atom. Thus, the L^2S^6 and L^3S^5 bonds together form a crystal-like tetrahedral bond network. This finding further suggests that L^2S^6 bipyramids and their derivatives (Fig. 2) could form crystal-like configurations that have been overlooked in earlier studies. Therefore, we define a tentative loose-crystalline supercluster as an aggregate of L^2S^6 , L^3S^5 , SLS^6 , L^3S^6 , L^2S^7 , and L^2S^5 bipyramids connected through shared apex atoms. Here, the term ‘tentative’ indicates that the definition will be revised.

In Laves crystals, L^2S^6 bonds form a tetrahedral network. The ideal tetrahedral bond angle is $\theta_i = 180 \times \cos^{-1}(-1/3) \approx 109^\circ$. Bond-angle analysis revealed significant deviations from the ideal bond angle for some apex bonds of tentative loose-crystalline superclusters. Here, the bond angle of two bipyramids means the angle between their apex bonds that share a common apex atom. Because non-tetrahedral bond angles are inconsistent with the notion of crystal-like, we redefine the loose-crystalline supercluster. For this purpose, a bond angle θ is regarded as tetrahedral if $|\theta - \theta_i| < 15^\circ$. This criterion was established based on the observation that 99% of the angles formed by L-L bonds satisfy this condition in a C14 Laves crystal at the liquidus point. Each bipyramid is assigned a state: *on*, *off*, or *pending*. Initially, all bipyramids are in the *off* state. Their states are then updated step by step, and those that eventually reach the *on* state are loose-crystalline bipyramids. A loose-crystalline supercluster is then defined as an aggregate of loose-crystalline bipyramids. The state of each bipyramid is determined according to the procedures described below, where all state updates within a step are applied simultaneously after evaluating all relevant bipyramids, ensuring order independence:

- (1) (a) Initialize all bipyramids to the *off* state.
(b) Change the state of L^2S^6 bipyramids to *on*.
- (2) (a) Change the state of an *off*-state bipyramid to *pending* if its apex atoms are of element L and contained in the same IC3 cluster. Note that the L-L bond forms part of the L-atom pentagonal ring of the IC3 cluster.
(b) (i) Change the state of a *pending*-state bipyramid to *off* if it forms a nontetrahedral bond angle with any of the *on*-state bipyramids. (ii) Change the state of a pair of *pending*-state bipyramids to *off* if their apex bonds form a nontetrahedral angle. (iii) Change the state of the remaining *pending*-state bipyramids to *on*.
- (3) (a) Change the state of the *off*-state hexagonal bipyramids of each Z16* cluster to *pending*.
(b) Repeat Step 2b.
- (4) (a) Change the state of the *off*-state L^3S^5 , SLS^6 , L^3S^6 , L^2S^7 , and L^2S^5 bipyramids to *pending*.
(b) Repeat Step 2b.
- (5) (a) Change the state of an *off*-state bipyramid to *pending* if each of its two apex atoms is shared as an apex atom with at least one *on*-state bipyramid.
(b) Repeat Step 2b.

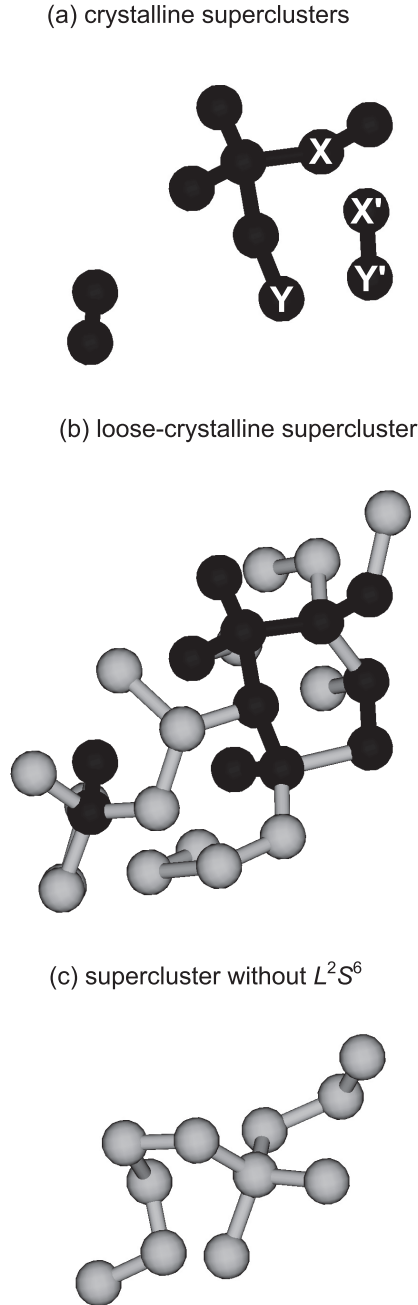


FIG. 8. Superclusters (only apex atoms and bonds are shown). (a) Three crystalline superclusters composed of L^2S^6 bipyramids. (b) Loose-crystalline supercluster incorporating the three superclusters shown in panel (a). (c) Loose-crystalline supercluster that does not contain any L^2S^6 bipyramids. Dark gray spheres represent the apex atoms of L^2S^6 bipyramids, and dark gray bonds represent L^2S^6 bonds.

- (6) Change the state of the isolated *on*-state bipyramids to *off*.
- (7) Repeat Step 5a. Note that this step serves as a preparation for subsequent tasks. Although the *pending*-state bipyramids are not members of loose-crystalline superclusters, they will be used later to identify incomplete pentagonal rings.

Note that the bond angle is not relevant for crystalline bipyramids (i.e., L^2S^6 bipyramids) to become loose-

crystalline (i.e., *on*-state), whereas other types of bipyramids need to form a tetrahedral angle. In Sec. V, we showed that IC3 clusters correlate with crystallizability. This finding is reflected in the definition of the loose-crystalline supercluster (Step 2). It was also shown that Z16* clusters, lacking the perfect chemical ordering of Z16, exhibit a correlation. This insight is incorporated into Step 3. To identify loose-crystalline superclusters in atomic configurations, we developed the LCS software, which is available on Zenodo under the MIT license [38].

We describe the structural features of loose-crystalline superclusters. Figure 8(b) illustrates that the three separate crystalline superclusters shown in Fig. 8(a) are bridged by loose-crystalline bipyramids to form a single loose-crystalline supercluster. We point out that loose-crystalline superclusters can form even in the absence of crystalline bipyramids [Fig. 8(c)]. Figure 9 compares the spatial distributions of crystalline and loose-crystalline bipyramids. Unlike crystalline bipyramids, loose-crystalline bipyramids are densely distributed and frequently share apex atoms. This connectivity results in large loose-crystalline superclusters. In other words, our analysis uncovers crystal-like medium-range order beyond what was previously recognized.

Generalizing beyond the Wahnström system, we can express our findings as follows: Atoms in the supercooled liquid state tend to organize into crystal-like SRO structures. Before the full formation of individual crystalline units, these incomplete units aggregate into crystal-like MRO structures. Here, the term *crystal-like* is used in a qualitative and abstract sense, without a rigorous definition. It simply refers to a structural resemblance to a crystal. The superclusters of loose-crystalline bipyramids observed in the Wahnström system provide a concrete manifestation of this concept of crystal-like MRO. Such a loose-crystalline supercluster is analogous to the medium-range bond-orientational order observed in supercooled colloidal liquids [8], as both involve incomplete crystalline units forming MRO regions.

We compare the structural characteristics of loose-crystalline superclusters in the supercooled liquid state with those of amorphous SiO_2 and amorphous Si. Amorphous SiO_2 shares its structural unit (SiO_4 tetrahedron) with its crystalline phase [39]. In contrast, the superclusters consist of loose-crystalline bipyramids, ranging from crystalline bipyramids identical to the structural units of Laves phases to variants that are similar to but distinct from them. Amorphous SiO_2 is a continuous random network of SiO_4 tetrahedra that extends throughout the bulk. In contrast, the superclusters are localized networks in which loose-crystalline bipyramids are randomly connected. In these superclusters, the apex bonds form finite networks, which can be regarded as localized counterparts of the continuous random network of Si-Si bonds in amorphous Si [40].

VII. FIVEFOLD TWIN-LIKE MOTIF

Loose-crystalline superclusters spontaneously form within supercooled liquids, but tend to dissolve shortly thereafter. The metastable supercooled state is characterized by the repeated cycles of formation and dissolution of loose-crystalline superclusters. When the size of a loose-crystalline

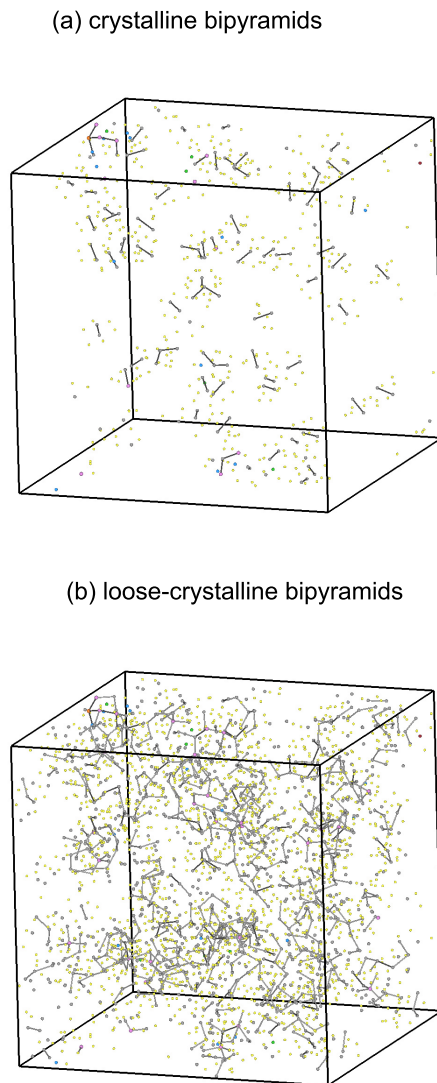


FIG. 9. Spatial distribution of (a) crystalline bipyramids and (b) loose-crystalline bipyramids, illustrating differences in density. This configuration represents the supercooled liquid with $x_L = 0.520$ at $T = 0.690$ prior to crystallization. The atoms at the centers of Z16, Z16* excluding Z16, IC1, IC2, and IC3 clusters are colored orange, pink, green, blue, and red, respectively. The remaining L and S atoms are colored light gray and yellow, respectively. Apex bonds of the L^2S^6 type are colored dark gray, while the remaining apex bonds are colored light gray. Although individual atoms and bonds may be difficult to distinguish, this does not hinder interpretation, as the figures are intended to highlight differences in spatial density—whether sparse or dense—rather than individual structural details.

supercluster happens to exceed a certain threshold, its growth becomes kinetically favored, resulting in a net growth trend. This transition marks the end of the metastable state and the onset of crystallization. In this study, we refer to a loose-crystalline supercluster that begins to grow as a *growing supercluster*.

Figure 10 presents a growing supercluster shortly after the onset of its growth. This supercluster contains pentagonal rings formed by apex bonds, with hexagonal rings attached to some of their edges. This structural motif resembles the core

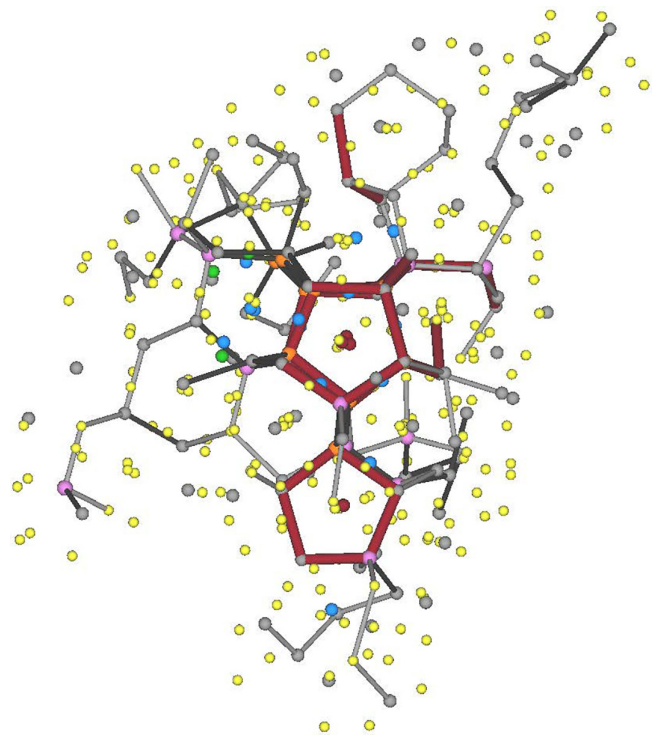


FIG. 10. Growing supercluster shortly after the onset of its growth. This structure is observed in the liquid with $x_L = 0.333$ at $T = 0.705$ (trajectory No. 1), when the time is 0.02×10^6 time units after $t_l = 2.08 \times 10^6$. Complete and incomplete pentagonal rings are highlighted in red. The dark gray sticks represent the remaining L^2S^6 bonds. The light gray sticks represent the remaining apex bonds. The atoms at the centers of Z16, Z16* excluding Z16, IC1, IC2, and IC3 clusters are colored orange, pink, green, blue, and red, respectively. The remaining L and S atoms are colored light gray and yellow, respectively.

of a fivefold twin. To highlight the fivefold twin-like motif, the apex bonds forming complete and incomplete pentagonal rings are colored red. Specifically, when five apex bonds of *on-* or *pending-*state bipyramids form a pentagonal ring consistent with the geometry of the tetrahedral bond network,

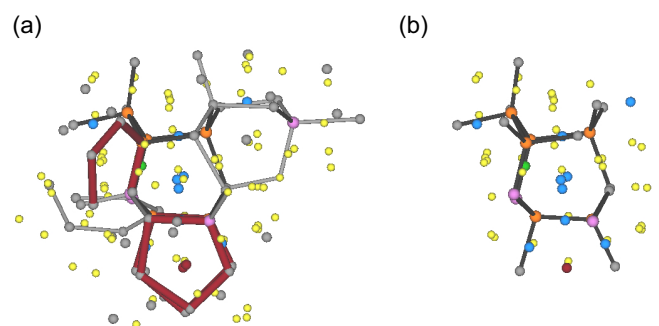


FIG. 11. Comparison of structural features between (a) a growing supercluster shortly after the onset of its growth and (b) the crystalline supercluster within the growing supercluster. These configurations are observed in the liquid with $x_L = 0.520$ at $T = 0.690$ (trajectory No. 3), when the time is 0.10×10^6 time units after $t_l = 3.73 \times 10^6$.

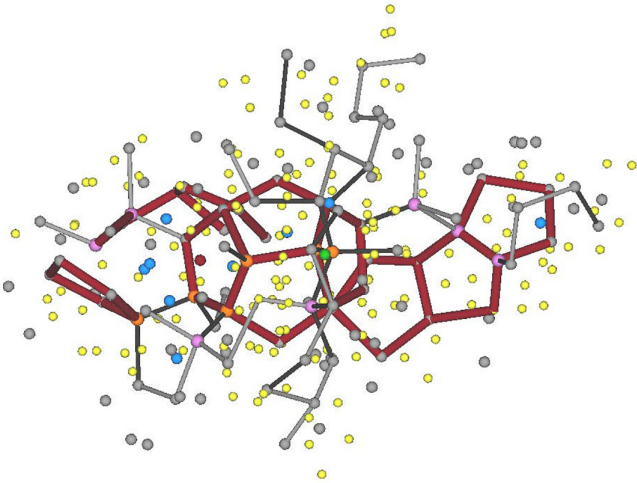


FIG. 12. Growing supercluster containing portions of a dodecahedron. This structure is observed in the liquid with $x_L = 0.520$ at $T = 0.690$ (trajectory No. 4), when the time is 0.35×10^6 time units after $t_l = 4.21 \times 10^6$.

the *on*-state bonds are colored red. Note that the *pending*-state bonds are not shown because they are only used to identify incomplete rings.

Figure 11 illustrates structural differences between a growing supercluster shortly after the onset of its growth and the crystalline supercluster within the growing supercluster. The growing supercluster clearly exhibits pentagonal rings [Fig. 11(a)], whereas such rings are absent in the crystalline supercluster [Fig. 11(b)]. This observation highlights the importance of using less strict structural criteria to reveal the connection between fivefold twin-like motifs and the onset of crystallization.

When 12 fivefold twins are joined such that their fivefold symmetry axes intersect at a single point, an icosahedral

supercluster is formed, with a dodecahedron composed of 12 pentagonal rings at its center [31]. Growing superclusters can have local structural motifs corresponding to portions of a dodecahedron. For example, the growing supercluster shown in Fig. 12 contains an aggregate of four pentagonal rings.

Figure 13 illustrates the growth process of a loose-crystalline supercluster. The pentagonal rings found at $t = 8.77 \times 10^6$ disappear as the supercluster grows, while new ones form elsewhere. As growth proceeds, fivefold twin-like motifs emerge throughout the structure. Rather than forming a single large crystal, the supercluster develops into multiple small crystalline domains, resulting in paracrystallinity. These observations suggest that the tendency to form fivefold twin-like motifs facilitates crystallization and paracrystal formation, which in turn hinders the development of long-range translational order.

Across all 12 trajectories analyzed—spanning different compositions, temperatures, and including independent runs under identical conditions—the growing superclusters observed shortly after the onset of crystallization consistently exhibit fivefold twin-like motifs. All observed growing superclusters, including those shown in Figs. 10–13, are shown in Fig. 14.

Fivefold twin-like motifs can transiently form in the metastable supercooled liquid state prior to crystallization. As an example, Fig. 15 illustrates a transient loose-crystalline supercluster containing such motifs observed in the liquid with $x_L = 0.333$ at $T = 0.705$ (trajectory No. 1) at $t = 0.21 \times 10^6$, well before the onset of crystal growth at $t = 2.08 \times 10^6$. This structure dissolved shortly afterward and was no longer present by $t = 0.22 \times 10^6$.

Our previous work showed that glasses of the Wahnström model alloy formed by melt quenching can exhibit fivefold twin-like motifs (crystalline superclusters) [21]. The present findings suggest that these structures originated as crystal seeds—either transient pregrowth seeds in the equilibrium

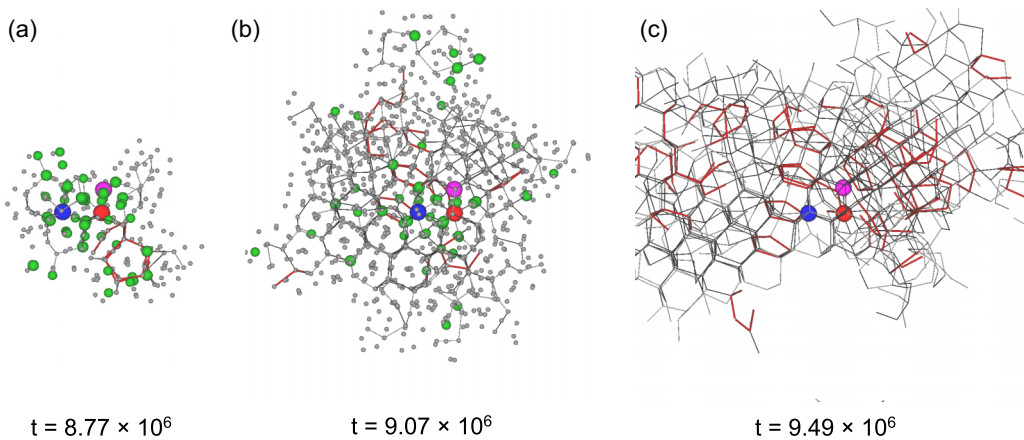


FIG. 13. Growth process of a loose-crystalline supercluster observed in the liquid with $x_L = 0.224$ at $T = 0.670$ (trajectory No. 4). Snapshots at (a) $t = 8.77 \times 10^6$, which is 0.05×10^6 time units after $t_l = 8.72 \times 10^6$, (b) $t = 9.07 \times 10^6$, and (c) $t = 9.49 \times 10^6$. Pentagonal rings are highlighted in red. As time progresses, the number of atoms within the supercluster increases, and the position and orientation of the supercluster change, which complicates the identification of corresponding regions. To aid comparison, three atoms that are present in all snapshots are highlighted as large red, blue, and purple spheres. The orientation of the triangle formed by these atoms is aligned across panels (a)–(c) to provide a reference frame. In panels (a) and (b), atoms common to both snapshots are colored green, while atoms present in only one snapshot are colored gray. In panel (c), only apex bonds are shown, and atoms are omitted to improve clarity.

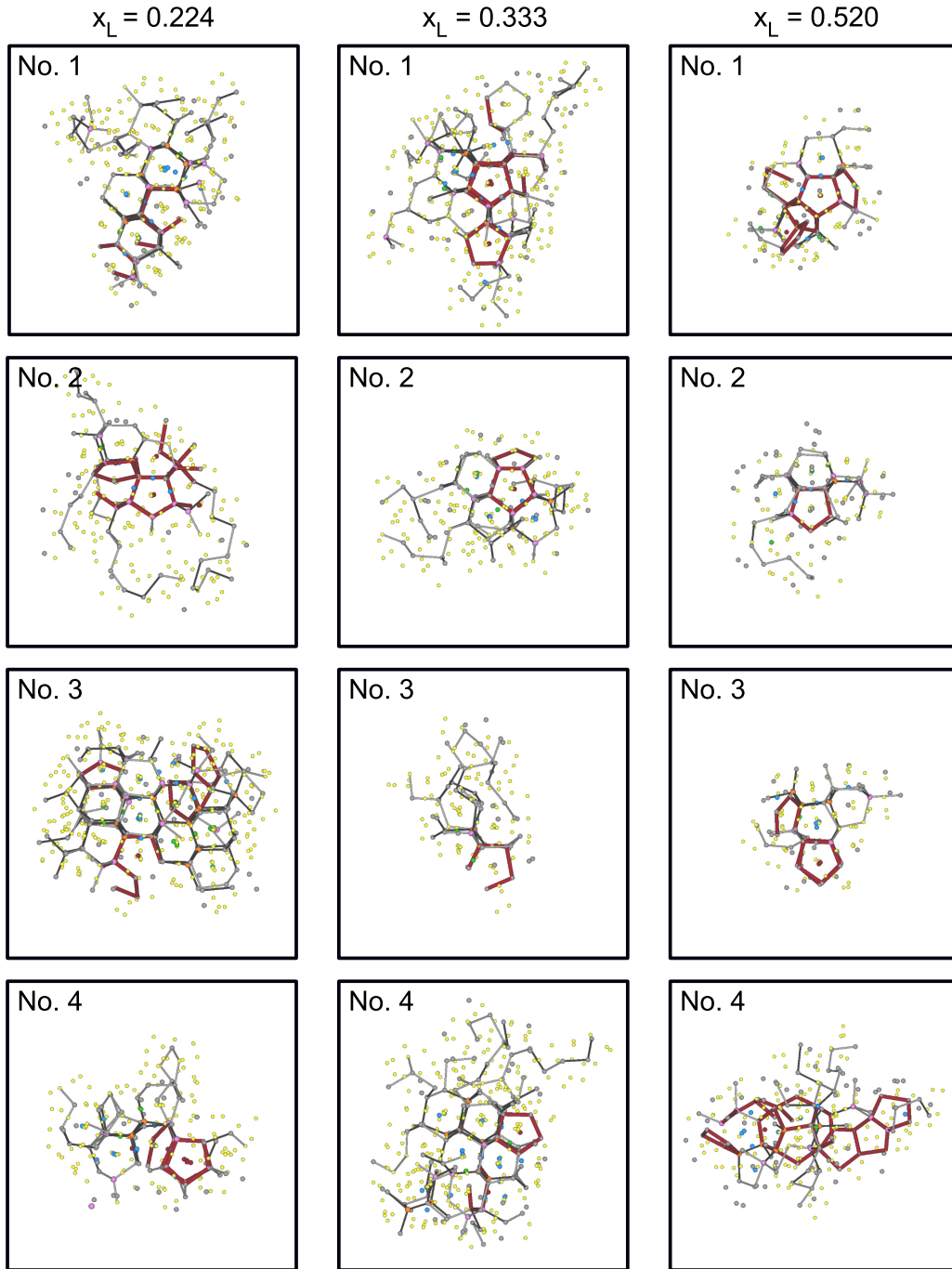


FIG. 14. Growing superclusters observed shortly after the onset of crystallization for the liquids with $x_l = 0.224$ at $T = 0.670$, $x_l = 0.333$ at $T = 0.705$, and $x_l = 0.520$ at $T = 0.690$, obtained from four independent trajectories (Nos. 1–4) for each condition.

supercooled liquid state or growing seeds in the non-equilibrium supercooled liquid state—and were retained within the amorphous matrix once crystal growth was kinetically arrested during cooling. In other words, the fivefold twin-like motifs observed in glasses are not structures intrinsically stabilized in the glassy state, but rather remnants of crystal seeds.

We note that bonds satisfying $|\theta - \theta_i| < \theta_{\text{threshold}}$ are regarded as tetrahedral, and that the value of $\theta_{\text{threshold}}$ affects the structure of loose-crystalline superclusters, i.e., which bipyramids are included and how they are connected (the apex bond

network). In this study, we use $\theta_{\text{threshold}} = 15^\circ$. This criterion was established based on the observation that 99% of the angles formed by L - L bonds satisfy this condition in the C14 Laves crystal at the liquidus point. For reference, Fig. 16 illustrates how the structure of the loose-crystalline supercluster that contains the crystalline supercluster shown in Fig. 11(b) depends on the threshold value. Figure 16(c) illustrates the loose-crystalline supercluster identified at $\theta_{\text{threshold}} = 15.0^\circ$. This structure contains the central S atoms of two linked IC3 clusters (referred to as IC3-A and IC3-B atoms). The L atoms in these clusters are also included, forming pentagonal rings.

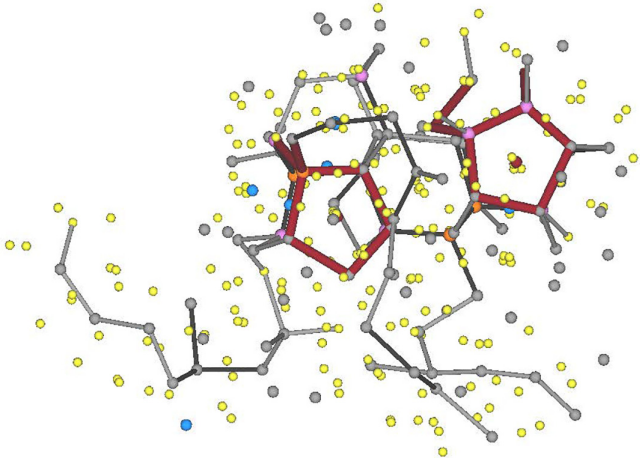


FIG. 15. Transient loose-crystalline supercluster containing five-fold twin-like motifs observed in the liquid with $x_L = 0.333$ at $T = 0.705$ (trajectory No. 1) at $t = 0.21 \times 10^6$. This structure dissolved shortly afterward and was no longer present by $t = 0.22 \times 10^6$.

When $\theta_{\text{threshold}}$ is lowered to 7.5° [Fig. 16(b)], the supercluster still contains the central S atoms of the linked IC3 clusters. However, only part of the L atoms originating from these clusters are included, and the bonds between them are not identified as pentagonal rings. As a result, because the pentagonal rings characteristic of fivefold twin-like motifs are no longer identified, lowering $\theta_{\text{threshold}}$ from 15.0° to 7.5° makes it difficult to reveal their connection to the onset of crystallization. When $\theta_{\text{threshold}}$ is further lowered to 0.0° , revealing the connection between fivefold twin-like motifs and the onset of

crystallization becomes even more difficult. In fact, the IC3-B atom is not contained within the supercluster identified at 0.0° illustrated in Fig. 16(a). When $\theta_{\text{threshold}}$ is increased from 15.0° to 22.5° and further to 30.0° , the pentagonal rings originating from the two linked IC3 clusters remain contained within the supercluster. Upon increasing $\theta_{\text{threshold}}$ from 15.0° to 22.5° , the size of the supercluster increases slightly, as bonds associated with larger bond angles are newly included, extending the structure identified at 15.0° . In contrast, when $\theta_{\text{threshold}}$ is further increased from 22.5° to 30.0° , the size of the supercluster increases abruptly. This sudden growth occurs because multiple superclusters that were separated at 22.5° merge into a single supercluster. Figure 16(f) shows the configuration obtained at 22.5° , where, in addition to the loose-crystalline supercluster containing the crystalline supercluster, three additional distinct loose-crystalline superclusters are observed. These four superclusters merge into a single loose-crystalline supercluster at 30.0° , as shown in Fig. 16(e). Although there is no absolute criterion for the choice of $\theta_{\text{threshold}}$, it is difficult, at least at present, to attribute any clear physical significance to the large supercluster obtained at $\theta_{\text{threshold}} = 30^\circ$. Given that 99% of the apex bond angles observed in the C14 crystal deviate by no more than 15° from the ideal tetrahedral angle, setting $\theta_{\text{threshold}} = 15^\circ$ can be regarded as a reasonable choice, at least as one plausible criterion. Indeed, using this threshold allows the connection between fivefold twin-like motifs and the onset of crystallization to be revealed. In addition, the number of loose-crystalline bipyramids with connectivity six, $\langle N_{\text{loo}}^6 \rangle$, evaluated based on this criterion, correlates with the kinetic stability of the supercooled liquid [Fig. 6(d)]. These findings support the use of $\theta_{\text{threshold}} = 15^\circ$.

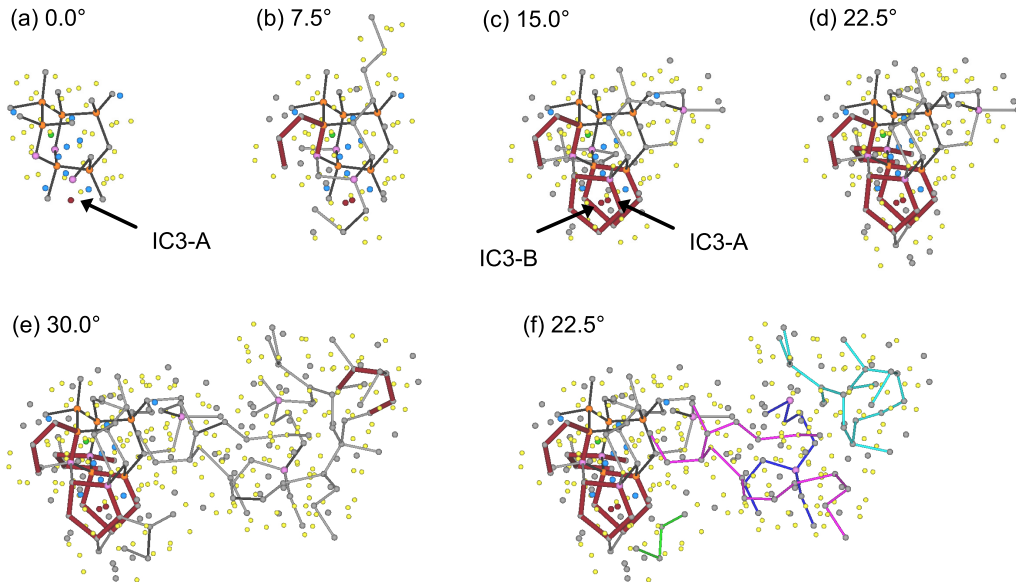


FIG. 16. Dependence of the structure of the loose-crystalline supercluster containing the crystalline supercluster shown in Fig. 11(b) on $\theta_{\text{threshold}}$. Loose-crystalline superclusters at (a) $\theta_{\text{threshold}} = 0.0^\circ$, (b) 7.5° , (c) 15.0° , (d) 22.5° , and (e) 30.0° . The central S atoms of two IC3 clusters observed in panel (c) are referred to as IC3-A and IC3-B. The IC3-B atom is not contained in the loose-crystalline supercluster shown in panel (a). Panel (f) shows the configuration obtained at 22.5° , where, in addition to the loose-crystalline supercluster shown in panel (d), three additional distinct loose-crystalline superclusters (with the apex bonds shown in different colors) are observed. These four superclusters merge into a single loose-crystalline supercluster at 30.0° , as shown in panel (e). The structures shown in panels (a) and (c) are identical to the superclusters shown in Figs. 11(b) and 11(a), respectively, although they are viewed from different angles.

VIII. CONCLUSION

We have examined the structure-stability relationship of a supercooled liquid alloy and elucidated the structural origin of medium-range order (MRO) in the glassy state, using a model alloy that forms Laves phases. To this end, we performed MD simulations of supercooled liquids and analyzed the liquid structure using the p_3 code, which characterizes each local environment in terms of chemi-topology—that is, topology (atomic connectivity) and chemistry (species identity). Our main findings are summarized as follows:

- (1) The connectivity of crystalline bipyramids, rather than their mere number, correlates with the kinetic stability of the supercooled liquid state against crystallization.
- (2) The limitations of the conventional Voronoi index are revealed.
- (3) The importance of chemi-topological analysis is demonstrated.
- (4) The concept of loose-crystalline bipyramids—defined using more relaxed structural criteria than the conventional crystalline bipyramid—uncovers crystal-like medium-range order beyond previous recognition.
- (5) Fivefold twin-like motifs previously observed in the glassy state are remnants of crystal seeds whose growth was

kinetically arrested during cooling, rather than structures intrinsically stabilized in the glassy state.

These results demonstrate that structural connectivity, chemi-topology, and loose-crystalline order are key to understanding the kinetic stability of supercooled liquids and the structural origin of MRO in amorphous materials. Our approach applies to various systems that form Laves phases, indicating the general significance of our findings.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [41].

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