Universal short-range order and material dependent glass-forming ability of metallic liquids and glasses

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Although the crystal structures of pure metals are material dependent, we theoretically find that entropy-driven docosahedral local structures are the most frequent in their melts and glasses, independent of their crystal structures. In terms of the docosahedral short-range order, we explain why body-centered-cubic metals have higher glass-forming ability than face-centered-cubic ones.

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When a liquid is so rapidly cooled that crystal growth is prevented, a glass is formed. The glass-forming ability (GFA), which is the potential for forming a glass or suppressing crystallization, varies from one material to another. Understanding the factors that determine the GFA of materials has been a long-standing challenge in materials science [1–5]. It is known that the atomic size ratio is an important factor for understanding the GFAs of oxides and alloys [1,2]. By contrast, what determines the GFAs of monatomic metals remains mysterious. One of the reasons is that they are poor glass formers [3,4] and it was not until quite recently that monatomic metallic glasses were experimentally obtained [5].

Recently, liquids of Ta, V, W, and Mo, which adopt the body-centered-cubic (bcc) structure in the crystalline solid phase, have been experimentally vitrified into glasses by using nanobridge cooling devices that make it possible to achieve an extremely high cooling rate of 10^{14} K/s [5]. However, the same approach fails to suppress crystallization for face-centered-cubic (fcc) metals such as Au, Ag, Cu, Pd, Al, Rh, and Ir. Those liquid metals belong to a class of liquids called simple liquids, which consist of identical spherical atoms. Despite the simplicity, the GFA of a metal depends on the element. In the nanobridge cooling device, a liquid metal is bounded by two crystalline substrates of the same metal element. Since crystals grow from the substrates, nucleation is not required for the crystallization of the bounded liquid [4]. The successful vitrification of the bcc metals and unsuccessful vitrification of the fcc ones means that crystal growth rates are slower for the bcc crystals than for the fcc ones. These results not only pose the question of what determines the crystal growth rate [6], or GFA of metals, but also provide an opportunity to deepen our understanding of the atomic structure of liquid metals.

Although the atoms in a liquid seem to be arranged randomly, the atomic arrangement shows short-range order [7]. The short-range order of a liquid is believed to be related to its GFA [8]. In general, the atomic structure of materials is determined by the competition between entropy and energy. For simple liquids including liquid metals, it has been believed for a long time that the energetic effects dominate the local structure [9–19]. However, this widely accepted energetic picture has been disproven recently [7]. In fact, it has been shown that entropy-driven docosahedral local structures are the most favored in a system composed of atoms interacting via a Lennard-Jones (LJ) potential, from which the energetic picture originates. The most stable crystal structure of the LJ system is the hexagonal-close-packed (hcp) structure. However, depending on the element, a metal may adopt the loosely packed bcc structure. As discussed later, the energetic effects play a central role for stabilization of the bcc crystals. The question that then arises naturally is whether the docosahedral structures found in the LJ system are also dominant in liquid metals. If so, the entropy-driven docosahedral short-range order would be the universal structural feature of simple liquids. Answering this question is an important milestone for understanding the GFA of simple liquids.

In this Rapid Communication, by combining molecular dynamics (MD) simulations and a recently developed structure descriptor [7,20–22], we explain the experimental observation that bcc metals have higher GFA than fcc ones. To this end, we first study the short-range order of liquid bcc metals (Ta and V) and liquid fcc metals (Cu and Al) by *ab initio* MD simulation. We also study that of liquid hcp metals (Hf and Zr). We find that entropy-driven docosahedral local structures are dominant in the liquid metals independent of their crystal structures. This suggests that the entropy-driven docosahedral short-range order is the universal structural feature of simple liquids and glasses. We then study crystal growth of Ta (as a representative model of bcc metals) and Cu (as a representative model of fcc metals) by classical MD simulation and uncover the fundamental difference that differentiates the GFA of bcc metals from that of fcc ones.

Ab initio MD simulations are performed using the OPENMX code [23–33]. Details in the *ab initio* MD simulations are provided in the Supplemental Material [33]. We study the

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FIG. 1. Distributions of the five most frequent local structures in *ab initio* liquid models. (a) Ta, (b) V, (c) Cu, (d) Al, (e) Hf, and (f) Zr. All the local structures are the docosahedral structure [$@4(56)^25^8$] and its derivatives. The frequencies of occurrence of the docosahedral structure are colored violet. Red is for structures obtained by adding an atom to the docosahedral structure. Blue is for structures obtained by locally rearranging atoms of the docosahedral structure. Green is for structures obtained by removing an atom from the docosahedral structure. Gray is for structures obtained by combining local atomic rearrangement and addition of an atom.

short-range order of the liquid metals by Voronoi tessellation. Although the Voronoi index has traditionally been used to classify the Voronoi polyhedra of liquids and glasses, it has been shown recently that this analysis fails to characterize properly the short-range order of the LJ liquid since different types of polyhedra may have the same index [7]. We therefore classify the Voronoi polyhedra according to their p_3 code-words [20–22]. A polyhedron represented by p_3 is called a p_3 polyhedron. Each Voronoi polyhedron contains exactly one atom. When the Voronoi polyhedron associated with an atom is a p_3 polyhedron, the atoms surrounding the central atom are placed at the vertices of a $\star p_3$ polyhedron. Here, $\star p_3$ represents the dual of a p_3 polyhedron. The local structure composed of the central atom and its neighbors is represented by $@p_3$. By classifying the local structures according to their $@p_3$ codewords, we can identify the dominant local structure.

Figure 1 lists the five most frequent local structures in liquid bcc metals (Ta and V), liquid fcc metals (Cu and Al), and liquid hcp metals (Hf and Zr) at the experimental melting point [27–31]. The most frequent type of local structure

is the docosahedral structure ($@4(56)^25^8$), independent of the metal element. As an example, a docosahedral structure found in liquid Ta is illustrated in Fig. 2. It consists of a central atom and its 13 neighbors placed at the vertices of a docosahedron ($\star 4(56)^25^8$) [7]. Note that a docosahedral

FIG. 2. Docosahedral local structure found in liquid Ta.

TABLE I. Five most frequent local structures in the *ab initio* models of fcc Cu and Al. r_{fcc} (r_{liq}) denotes the rank in the fcc crystal (liquid). f_{fcc} (f_{liq}) denotes the frequency of occurrence in the fcc crystal (liquid).

r_{fcc}	Cu				Al			
	Local structure	f_{fcc} (%)	r_{liq}	f_{liq} (%)	Local structure	f_{fcc} (%)	r_{liq}	f_{liq} (%)
1	@45 ² 6 ⁵ 4645 ² 46	10.81 ± 0.11	97	0.14 ± 0.01	@45 ² 6 ⁵ 4645 ² 46	10.69 ± 0.13	100	0.11 ± 0.01
2	@45 ² 6 ² 56 ² 45 ³ 46	7.97 ± 0.33	6	1.17 ± 0.07	@45 ² 6 ² 56 ² 45 ³ 46	8.16 ± 0.25	5	0.90 ± 0.07
3	@4(56) ³ 465(64) ²	5.52 ± 0.22	26	0.39 ± 0.08	@45 ² 6 ² 565 ² 4645	5.71 ± 0.12	2	1.53 ± 0.11
4	@456 ³ 5645 ² (46) ²	5.46 ± 0.24	30	0.34 ± 0.04	@456 ³ 5645 ² (46) ²	5.44 ± 0.21	36	0.24 ± 0.03
5	@45 ² 6 ² 565 ² 4645	5.46 ± 0.17	2	1.91 ± 0.12	@4(56) ³ 465(64) ²	5.20 ± 0.13	29	0.29 ± 0.01

structure corresponds to a Voronoi index of $\langle 0, 1, 10, 2 \rangle$ and has often been called a distorted icosahedral structure. However, referring to a dicosahedron as a distorted icosahedron is a category error because the dicosahedron is a polyhedron with 22 faces and cannot be any type of icosahedron. The dicosahedral short-range order is entropy driven, for it is also dominant in the dense-random packing of hard spheres. In other words, efficient atomic packing is favored in the liquid metals. Although the density assigned to a local structure is maximized for a regular icosahedral structure (@5¹²), there are gaps between the atoms. Therefore, icosahedral structures are not favored. When some gaps are narrowed by rearranging the atoms, the other gaps are inevitably enlarged. As a result, an additional 14th atom fits in one of the enlarged gaps of a 13-atom local structure (such as @5¹² and @45²6²54⁴45²) to form a dicosahedral structure. Thus, our findings disprove the generally accepted picture that the energetic effects dominate the local structure of liquid metals. Since it is due to the packing efficiency maximization, we propose that dicosahedral short-range order is universally found in simple liquids. In addition to the dicosahedral structure, five different types of local structures appear in the list of the five most frequent local structures. All of them are derivatives of the dicosahedral structure [7]. Specifically, @45²6²565² and @456³5³465² are obtained by adding an atom to the dicosahedral structure. @45²6²565²4645 is obtained by locally rearranging atoms of the dicosahedral structure. @45²6²54⁴45² is obtained by removing an atom from the dicosahedral structure. @45²6²56²45³46 is obtained from the dicosahedral structure by combining local atomic rearrangement and addition of an atom.

It is interesting to note that the local structure of liquid fcc metals has similarities to that of the fcc crystal. For example, Table I shows that @45²6²565²4645, which ranks second in the liquid Cu (Al) with a frequency of 1.91% (1.53%), ranks fifth (third) in the fcc crystal of Cu (Al) with a frequency of 5.46% (5.71%). In contrast, in the bcc crystals of Ta and V, all the local structures are @46⁴(46)⁴4. This structure is rarely found in their melts. Specifically, it ranks 228th (287th) in liquid Ta (V) with a frequency of 0.05% (0.05%).

To explain the experimentally observed differences in GFA of metallic glasses, we study crystal growth of Ta and Cu by classical MD simulation [33–39]. Details of the classical MD simulations are provided in the Supplemental Material [33]. We first construct a liquid/crystal/liquid structure, in which the liquids contact with (100) surfaces of the crystal, at a temperature slightly above the melting point, and cool down

the system to 300 K at a cooling rate of 10¹⁴ K/s. Not only for Ta but also for Cu, liquids vitrify without crystallization and glass/crystal/glass structures are formed. However, the Ta and Cu glasses differ in resistance to crystallization. To show this, we illustrate the temperature dependence of the crystal growth rate $v(T)$ in Fig. 3. The growth rates of both metals are well described by the Arrhenius equation, $v(T) = v_0 \exp(-\epsilon/k_B T)$, where v_0 is the pre-exponential factor and ϵ is the activation energy. The pre-exponential factors of both metals are similar in magnitude: 200 and 95 m/s for Ta and Cu, respectively. Thus, these terms are not relevant to the difference in GFA. In contrast, the activation energy of Ta (637 K) is significantly higher than that of Cu (0.32 K). Because of its negligibly small activation energy, it is nearly impossible to avoid growth of fcc Cu at any finite temperature. In fact, even if the system is cooled, $v(T)$ decreases little above 5 K. Even at 1 K, fcc Cu grows at a rapid rate of 70 m/s. By contrast, since Ta has a substantial activation energy of 637 K, $v(T)$ decreases rapidly with decreasing temperature. Note that the model Ta glass is stable in the experimental timescale at 17 K, for the estimated crystal growth rate is 0.9 nm/day. Since the experimental Ta glass was stable at 300 K, our simulations overestimate $v(T)$ of Ta but qualitatively reproduce the higher GFA of Ta than of Cu.

Although it has been proposed that the magnitude of activation energy for crystal growth determines the thermal stability of metallic glasses [5], it remains mysterious why bcc metals have a significantly higher activation energy than fcc ones [40]. We explain it in terms of the dicosahedral

FIG. 3. Temperature dependence of the crystal growth rate. Filled and open circles are the simulation results for Cu and Ta, respectively. The solid curves are fits to the Arrhenius equation.

short-range order. Since the glass of a simple liquid is a frozen liquid [7], icosahedral short-range order is expected to be dominant in metallic glasses. In fact, our classical MD simulations show that Ta and Cu glasses are dominated by icosahedral short-range order [33]. We then discuss the negligibly small activation energy of Cu as a representative example of fcc metals. We first point out that the Cu glass has a structural similarity to the dense random packing of hard spheres. Specifically, both structures are dominated by icosahedral short-range order. We also point out that when a hard-sphere glass and a hard-sphere fcc crystal are in contact, the crystal region grows at the expense of the glass one [33]. We stress that the growth of the hard-sphere fcc crystal occurs due to purely entropic effects and there is no energy barrier between the glass and the crystal. Because of the structural similarity and the absence of the energy barrier in the hard-sphere system, the energy barrier between glassy Cu and fcc Cu is negligible.

Next, we discuss the substantial activation energy of Ta as a representative example of bcc metals. We first point out that the bcc structure is not the most stable crystal structure of the hard-sphere system, for its packing fraction (0.68) is smaller than that of the fcc crystal (0.74). This means that energetic effects are essential to stabilize bcc Ta. Since fcc Ta is a metastable phase [41], there is an energy barrier between fcc

Ta and bcc Ta. For the same reason as Cu, the energy barrier between glassy Ta and fcc Ta is negligible. Thus, there exists an energy barrier between glassy Ta and bcc Ta.

In conclusion, we have theoretically demonstrated that entropy-driven icosahedral local structures are dominant in monatomic metallic liquids and glasses independent of their crystal structures. As a result, it turns out that different GFAs of bcc and fcc metals do not originate from their liquid and glass structures themselves. We have shown that the difference between the mechanisms governing the glass structure and the corresponding ground-state crystal structure is a key factor for the crystal growth rate of a metal and thus its GFA. Crystallization of bcc metallic glasses is a process of transforming the entropy-driven glass structure into the energy-driven bcc structure, while that of fcc metallic glasses is transformation from the entropy-driven glass structure into the entropy-driven fcc structure. Therefore, bcc metals have a significantly larger activation energy for crystallization than fcc ones. In other words, bcc metals have higher GFA than fcc ones. By discovering the universal entropy-driven icosahedral short-range order, we have identified what governs the glass-forming ability of simple liquids and glasses. Thus, establishing an accurate picture of the liquid and glass structure is essential to deepen our understanding of glass transition and crystallization.

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