Perspective on structural evolution and relations with thermophysical properties of metallic liquids

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The relationship between the structural evolution and properties of metallic liquids has been a long-standing hot issue in condensed-matter physics and materials science. In this paper, we review recent progress only in several fundamental aspects of metallic liquids, including the methods to study their atomic structures, the liquid-liquid transition, physical properties, the fragility and their correlations with local structures, together with potential applications of liquid metals at room temperature. Involved with more experimentally and theoretically advanced techniques, these studies provide more in-depth understanding of the structure-property relationship of metallic liquids and promote the design of new metallic materials with superior properties.

1. Introduction

Metallic liquids mean the metals in the liquid state, either above the melting point or in the supercooled liquid region. They are major substances of industrial manufacturing and fundamental scientific research in the fields of casting, metallurgy, welding, crystal growth and metallic glass formation, etc. Tracking their internal structural evolution can deepen the understanding of their unique properties and thermal behaviors. For example, a recent study found that some of gallium (Ga)-based liquid metals can act as a self-driven motor by swallowing small pieces of Aluminum (Al), which can operate autonomously without external power supply.^[1] Such liquid metal-particle eating behavior is likely due to the intermetallic wetting between two metallic phases.^[2] When the metal is in a liquid state, it has fluidity with the shear modulus of about zero, but after solidification, it has high strength and hardness. For some metallic liquids, the resultant properties are poor when forming crystalline phases under slow cooling. However, the performance can be significantly improved when forming metallic glasses upon rapid quenching. It implies that the glass transition is important in the formation of new glassy materials. Since the early of the 1990s, metallic glasses have become one of the most active research fields of advanced metallic materials, which can be referred to the landmark overviews given by Johnson and Inoue, and some by others later.^[3-7] These advanced materials have a variety of excellent properties, such as high strength, high elastic limit (~2%), high corrosion and wear resistance, and excellent magnetic properties.^[8,9] They are usually formed by rapid quenching the liquid melts, in which the crystal nucleation is avoided and atomic configurations of liquids are frozen into the solid state. Therefore, they are sometimes also called as “supercooled” liquid metals. A connection between metallic glasses and liquids is that they both do not have the long-range translational (or orientational) ordering but only have the short and/or medium range ordering.^[10] On the other hand, they indeed have structural differences, for example, metallic liquids have high atomic mobility, causing the internal atomic configurations not only different in space but also in time.^[11,12] The structural heredity between metallic liquids and glasses directly affects (1) the ability to form metallic glasses and (2) their final properties. As P.W. Anderson (a Nobel laureate) pointed out that the nature of the glass transition is one of the most important and challenging issues in the field of condensed matter physics.^[13] From materials point of view, metallic

liquids can be regarded as the parent phase of crystalline and amorphous phases in the process of solidification. By understanding the structure-property relationship of metallic liquids, people could design and optimize new materials on the atomic level and finally to improve the quality and performance of the products. Therefore, great efforts have been recently made to study the atomic structure and properties of metallic liquids by applying the advanced experimental techniques and the latest theoretical simulation methods. Many novel results have been reported in last decades. In this review, we briefly summarize the recent developments in studying the structure and properties of metallic liquids by using advanced synchrotron radiation techniques, containerless levitation and theoretical simulations.

2. Methods to study the structure of metallic liquids

The third generation synchrotron radiation source, as a mega scientific facility, has been rapidly developed in recent years, which undergoes in the direction of more brilliant, finer spatial and energy resolution and faster time resolution, providing a powerful tool to detect the micro-, nano-, and even atomic-scale structures in materials. With setting up different material environments and combining with one or two synchrotron x-ray techniques, one can *in situ* measure the structural evolution either static or dynamic in materials changing with temperature, pressure and time. As such, the roles that the advanced x-rays play in studying the structure of materials become more irreplaceable. Synchrotron radiation-based x-ray diffraction (XRD) and x-ray absorption fine structure (XAFS) are often used to characterize the structure of metallic liquids and yield many high quality experimental data.^[14,15] In contrast, small angle x-ray scattering (SAXS) and x-ray photon correlation spectroscopy (XPCS) are not so popular but still indispensable to probe the heterogeneity and atomic dynamics in metallic liquids, respectively.^[16,17]

Compared with crystalline materials, the research on the structure and properties of metallic liquids is far lagging behind. The metallic liquids usually exist around or above the melting point, having high chemical activity. They can be easily oxidized or react with the vessel wall if without special protections. The containerless technique has some merits of microgravity condition and can avoid contacting with the vessel wall to eliminate the heterogeneous nucleation, consequently resulting in a larger undercooling. Thus, it becomes

more convenient for measuring physical properties of metallic liquids and also their atomic structures by combining with other experimental and theoretical techniques.^[18-21] The theoretical simulations make it possible to study the liquid structure on the atomic level when calculated results can well capture main features of the experimental data. It can effectively predict the structural evolution on the atomic level in metallic liquids and phase preferential precipitation during solidification, e.g., the three-dimensional atomic distribution and the liquid-liquid transition.^[22-24]

Due to the lack of periodic atomic packing, the conventional methods for describing the crystalline structures cannot be simply used to describe the structure of metallic liquids. In contrast, the atomic radial distribution function (RDF) is usually adopted for disordered materials, in which one atom is randomly set as the center and how many other atoms locating in the spherical shell around it from r to $r+dr$ are counted. Then taking each atom as the center, the coordination number in each shell is averaged among all the atoms, which can be written as $4\pi r^2 \rho(r) + rG(r)$, $\rho(r)$ is the atomic distribution density, $G(r)$ is the pair distribution function. With the aid of advanced third generation synchrotron radiation sources, high quality and large q range, XRD patterns for metallic liquids up to a few mm thick in the transmission mode can be accurately recorded by using two-dimensional detectors. Scattering intensity $I(q)$ is integrated under the software package FIT2D,^[25] and then normalized to get the total structure factor $S(q)$ with a large q range after standard corrections by removing effects of self-absorption, polarization, fluorescence absorption and Compton scattering, etc. The final $S(q)$ can be simply expressed as Equation (1), where c_i is the concentration and $f_i(q)$ is the atomic scattering factor for x-rays of each component, respectively. By Fourier transform of $S(q)$, $G(r)$ can be obtained by using Equation (2), which can characterize the average structural information from the short to medium range of liquids in real space.

$$S(q) = 1 + \frac{I(q) - \left[\sum_{i=1}^n c_i f_i^2(q) \right]}{\left[\sum_{i=1}^n c_i f_i(q) \right]^2} \quad (1)$$

$$G(r) = \frac{2}{\pi} \int_0^\infty [S(q) - 1] \sin(qr) q dq \quad (2)$$

In combination with the radial atomic distribution function (RDF), the local bond-orientational order (BOO) of atomic packing in disordered materials using the spherical

harmonics analysis was firstly introduced by Steinhardt *et al.*^[26] and the coarse-grained form was adopted by Lechner.^[27] The $(2l+1)$ dimensional complex vector (q_l) can be defined for each atom i as presented in Equation (3),

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{r}_{ij}) \quad (3)$$

where l is the free integer parameter, m is an integer that runs from $-l$ to l , Y_{lm} are the spherical harmonics, $\hat{r}_{ij}$ is the vector from atom i to atom j , and the sum goes over all neighboring atoms $N_b(i)$ of the atom i . One could average the spatially local bond order parameters

according to the equation: $\hat{q}_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} q_{lm}(k)$, and construct the rotationally invariant quantities, as demonstrated in Equation (4).

$$Q_l(i) = \sqrt{4\pi / (2l+1)} |\hat{q}_{lm}(i)| \quad (4)$$

It should be noted that Mickel *et al.* pointed out two flaws of Steinhardt order parameters: one is the definition of the nearest neighboring spheres around a given center atom, the other is the discontinuous function of the atomic coordinates, which can be overcome by weighting each bond by its corresponding Voronoi facet area.^[28] In addition, in the modified version by Lechner, such shortcomings were also reduced by averaging the first neighbor shell of a given atom. The averaged BOO parameters are sensitive to the different bond-orientational symmetries and can be used to characterize the variation of local atomic packing.

X-ray absorption spectrum, including the near edge and extended edge spectra, is composed of some small oscillations after the edge, sensitive to the nearest neighbors around the absorption atom. It has a wide range of applications, especially in the structural characterization of metallic liquids and glasses. The critical problem to measure XAFS for metallic liquids is how to control the sample thickness and prevent it from leakage and oxidation at high temperatures. Using above mentioned techniques together with molecular dynamics (MD) simulations, the liquid structures of Al, Zn, Sn, In, Cu, Ni, Ag, Au, Cd, Ga, Mg, Nb single elements and Ga-In, Ga-Sn, Cd-Sn, Zn-Sn, Ag-Ga, Ag-Ge and Al-Cu binary alloys were thoroughly studied.^[29-31] An abnormal phenomenon in metallic liquids was

reported, namely, the distance between the center atom and atoms in the first nearest-neighbor shell shrinks rather than expands during heating process. The experimental and theoretical simulation results showed that it is mainly ascribed to the redistribution of polyhedra in metallic liquids, evolving from the high-coordinated to the low-coordinated ones, thus resulting in the decrease of average distance between the center atom and atoms in the first nearest-neighbor shell, as shown in **Figure 1**.^[29]

It is commonly believed that metallic liquids are homogeneous on the nanometer scale if no phase separation or crystallization happens. SAXS provides an effective way to detect the phase separation in liquids. For example, a recent *in situ* SAXS results have demonstrated that unlike the former idea there is almost no phase separation occurring above the glass transition (T_g) and prior to the crystallization in a Pd-Ni-P metallic glass.^[32] At the beamline of sector 1, APS, SAXS and XRD have been successfully incorporated together with the energy of 70 keV, which can be used to measure nanometer-scaled heterogeneity and atomic structural change simultaneously in bulk metallic samples. On the other hand, XPCS, like beamline ID 10 at ESRF or P10 at Petra III, is a relatively new technique that needs high quality coherent x-ray beam and high photon flux to detect the atomic dynamics in materials by tracking the diffraction pattern changing with time at fixed q values.^[17] The time scale of XPCS so far is from about 1s to 10^4 s and can be adopted to measure the dynamics in metallic glasses and supercooled liquids. Using this technique, Ruta *et al.* observed different relaxation behaviors in an Mg-Cu-Y glass and the supercooled liquid.^[33] However, for the fast dynamics (from ns to ps) in the liquid state, it is totally beyond the resolution of XPCS now and needs neutron scattering, as discussed below.

Recently, the containerless levitation techniques have been rapidly developed.^[34-36] Equipped with a variety of auxiliary devices, the levitation has been more powerful and widely used for the characterization of metallic liquids. Various levitation techniques, including electromagnetic levitation, electrostatic levitation, aerodynamic levitation, and acoustic levitation, have been developed. The electromagnetic levitation is composed of high frequency power supply and levitation coil, in which there exists a symmetrical levitation force field. Due to the easy coil design and operation, the electromagnetic levitation has been widely used, such as the melting and supercooling of metals. However, as the levitation coil

acts both roles: levitating and heating, it is difficult to ensure that the sample is in a stable position. To overcome this problem, the electrostatic levitation (ESL) was developed, in which the heating and levitation become independent control. It has a high vacuum chamber and a feedback system to stabilize the sample, which can be suspended after surface-charged. **Figure 2a** is a schematic diagram of electrostatic levitation, and **Figure 2b** is a typical temperature profile of a suspended $\text{Al}_{75}\text{Cu}_{25}$ sample upon heating and cooling. Xiong *et al.*^[37] measured the specific heat of $\text{Al}_{75}\text{Cu}_{25}$ liquid alloy by ESL. They found that it increases monotonically with decreasing temperature from 1600 K to 800 K but never observed a liquid-liquid phase transition as theoretically predicted by using 55-atom clusters,^[38] indicating that when the size of $\text{Al}_{75}\text{Cu}_{25}$ liquid is at the nanometer scale, the short and medium range order could be modified due to the high proportion of atoms on the surface. However, in the bulk liquid sample the number of surface atoms is largely reduced so that it is difficult to induce the same transition. Using the ESL technique, Kang *et al.* measured the undercoolability of different Cu-Zr liquids and found that the liquid with higher glass forming ability (GFA) shows deeper undercoolability and longer persistence at a supercooled temperature than other neighboring compositions.^[18] Also, Bendert *et al.* determined the temperature dependence of the specific volume, thermal expansion coefficient, and specific heat in the equilibrium, supercooled liquids, and glasses of bulk metallic glass formers by using ESL, which have not been possible before because of rapid crystallization of the supercooled metastable liquids.^[19] By combining ESL with synchrotron radiation-based XRD, Kim *et al.* did not observe the coordination number change in the supercooled Silicon and question the claims of structural evidence for the existence of a liquid-liquid phase transition.^[20] By application of the isotopic substitution, the partial structure factors were determined for Ni-Nb melts using ESL and neutron diffraction, demonstrating that the liquid $\text{Ni}_{59.5}\text{Nb}_{40.5}$ exhibits a pronounced chemical short range order by the formation of heterogeneous Ni-Nb nearest neighbor pairs.^[39] Thus, ESL provides an advanced technique for the users to measure the structure and properties of metallic liquids that could not be realized previously. However, nowadays people come to recognize the disadvantages of ESL, i.e., (1) the whole equipment is too complicated to control (2) lots of metals are still difficult to levitate in ESL. In contrast, the aerodynamic levitation that is widely used for oxides is

technically simple and can levitate nearly all the metals.^[40] It has potential applications for metallic liquids if the oxidation could be completely overcome. Recent reports showed that the upgraded aerodynamic levitation has been available to combine with synchrotron radiation and neutron sources for studying the structure and dynamics of metallic liquids.^[41] By using this equipment, Georgarkais *et al.* could experimentally trace the atomic rearrangements in a Cu-Zr-Al metallic liquids during *in situ* vitrification.^[42] Such experiments will be extended to other alloy systems that are difficult to levitate by ESL.

MD simulations can produce the three-dimensional atomic structure and explain the evolution of microstructure and dynamic characteristics of metallic liquids on the atomic level, which is difficult to achieve by experiments. By using *ab initio* MD method to simulate the liquid Vanadium (V) in the temperature range of 3000 K to 1500 K during solidification,^[43] Debela *et al.* found that a large number of icosahedra appear in the liquid and supercooled liquid region and the existence of various precursor phases in the liquid melt at low temperatures, especially one kind of body centered cubic (bcc) structure. They also observed that the bond orientational order becomes dominant and occurs prior to density fluctuations during solidification. **Figure 3** shows the structural evolution in the liquid Niobium (Nb) during nucleation and solidification.^[44,45] Note that the structure of icosahedra is also dominant and the bond orientation caused by energy fluctuation happens immediately at the beginning of nucleation prior to density fluctuations. Most of local orderings are bcc-like structures and few are hexagonal-like ones. During the crystallization, the bcc structures spread rapidly in the liquid. In the simulation of liquid Magnesium (Mg) solidification, the phase selection is related to the temperature. When the temperature is slightly lower than the melting point, the pioneering phase with bcc structure is precipitated, which plays a dominant role in the nucleation process, and finally transforms into a hexagonal-close-packed (hcp) phase.^[46] Xiong *et al.* simulated the structural evolution in the liquid Al₂Au and found that the dominant structure is not icosahedron-like but similar to the local structure of crystalline phase, indicating that the liquid phase could inherit its structure to the crystalline phase in the solidification.^[47] Using neutron scattering, XRD, XAFS and *ab initio* MD simulations, icosahedral short-range ordering was early demonstrated to exist in stable and deeply undercooled melts of pure metallic elements Ti, Fe, Zr, Cu, and Ti-Zr-Ni ternary

liquids.^[48-50,14] Later, some results showed that the icosahedral ordering was not so dominant in liquid melts and most could be distorted icosahedra.^[51,52] Although the full icosahedra may be not dominant in metallic liquids, the five-fold short range order was often more pronounced in liquid metals and could act as an indicator of dynamic arrest in metallic glass-forming liquids.^[53,54] Recently, Pasturel and Jakse systemically studied the relationship between dynamic and structural properties of liquid Al-Ni, -Cu and -Zn alloys by *ab initio* MD simulations.^[55-57] They found that the competition between the local icosahedral ordering and the local chemical ordering (composition-dependent) may cause the breakdown of the Stokes-Einstein relation in the liquid phase, which could be understood in terms of the partial excess entropy approximated by the two-body contribution. In addition, complementary to the Honeycutt-Andersen (HA) index and Voronoi tessellation,^[58,59] the atomic cluster alignment method has been recently developed by a group at Ames to visualize the atomic packing configurations in the short and medium range of metallic liquids and glasses,^[60] by which an icosahedron-based Bergman medium range order in the $\text{Cu}_{64.5}\text{Zr}_{35.5}$ glass was proposed.^[61]

3. Liquid-liquid transition in metallic liquids

The phase transition is mainly to study the structural change in materials and accordingly accompanied with the modification of mechanical, electrical, magnetic and other properties, being the basis for the application of structural and functional materials. The understanding of solid state phase transition in crystalline materials is relatively comprehensive. Recent results demonstrated that an intermediate liquid phase seems often to appear during the solid-solid phase transition, acting as a precursor to induce the nucleation of the second solid phase in colloidal systems and a bulk metallic glass.^[62,63] The same phenomenon was also observed in a high pressure crystalline phase of Bismuth (Bi), which can melt into a metastable liquid phase below the melting line during the decompression process.^[64] The metastable liquid can be kept for several hours at static condition and transform into crystalline phases under external perturbations such as heating or cooling. Generally, the structure feature of metallic liquids has an important effect on the atomic structure and phase selection in the subsequent solidification. Due to the lack of advanced probes, the study on the structure and properties of metallic liquids was retarded formerly whereas has recently become the cutting edge in

condensed matter physics and materials science.

Phase transition is common in crystalline materials. This polymorphism may happen between two kinds of liquids with different entropies or/and atomic packing. It has been reported that the liquid-liquid transition (LLT) happens in H_2O , P, Si, Al_2O_3 - Y_2O_3 and other network glasses.^[65-68] For liquid metallic materials, Li *et al.* reported the evidence for a liquid-liquid phase transition by detecting volume changes in several strong glass forming liquids using ESL.^[69] However, it was not observed by Bendert *et al.* later.^[19] Wei *et al.* also found a temperature-induced weak first order LLT in the undercooled region for a bulk metallic glass former of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ liquid (**Figure 4a**).^[70] The process was accompanied by drastic changes in local atomic structure and viscosity but without a detectable density anomaly, providing a support for the hypothesis that the strong-to-fragile transition may occur at higher temperatures above the glass transition. Xu *et al.* observed a LLT in a glass-forming $\text{La}_{50}\text{Al}_{35}\text{Ni}_{15}$ liquid above its liquidus temperature by ^{27}Al nuclear magnetic resonance including the dependence of cage volume fluctuation and atomic diffusion (**Figure 4b**).^[71] The dependence of the incubation time on the degree of undercooling was consistent with the characteristics of a first-order phase transition. Xiong *et al.* carried out synchrotron radiation-based XRD experiments and *ab initio* MD simulations on the structural change in liquid Ga and found that it is likely to have a LLT at about 1000 K (**Figure 4c**).^[72] Below and above 1000 K, the atomic diffusivity, specific heat, bond orientational parameter Q_6 , fraction of Ga-Ga dimers and coordination number of the nearest neighbors exhibit distinct different behaviors. In addition, the reported density,^[73] viscosity,^[74] electrical resistivity^[75] and thermoelectric properties^[76] of liquid Ga also implied a turning point at around 1000 K. Pressure and temperature are two physical parameters to alter the structure of materials. By changing the temperature and pressure, the LLT may be induced, usually accompanied by a change of liquid density with the same composition. Cadien *et al.* studied the behavior of liquid Cerium (Ce) under high temperature and high pressure by *in situ* XRD and reported a liquid-liquid phase transition from a high density liquid (HDL) to a low density liquid (LDL) under the pressure of 13 GPa and the temperature from 1550 to 1900 K,^[77] as shown in **Figure 4d**. The density change between HDL and LDL liquids is up to 14%. The 4f electron delocalization may lead to the occurrence of this first-order phase

transition using the first-principles calculations. In addition, the liquid-liquid crossover or transition was also reported in liquid Rubidium (Rb),^[78] Al^[79] and bulk metallic glass formers etc.^[80] More recently, an anomalous exothermal peak locating in the supercooled liquid region of a Pd-Ni-P glass upon heating has been proposed to relate with the happening of LLT,^[32] which was previously studied in this metallic glass and others, but mainly ascribed to the formation of chemical short range ordering and phase separation, etc.^[81-83] However, limited to the extreme conditions of high temperature and high pressure, or too complexity of the multi-component alloy systems, it is still challenging to monitor the changes in local liquid compositions and structure. Many issues are still in debate, e.g., are the reported LLTs indeed repeatable? What is the nature of the liquid-liquid phase transition in metallic liquids? Is it universal? More detailed works are strongly needed.

4. Physical properties of metallic liquids

Ga, Indium (In), Tin (Sn) and other elements with low melting points, good corrosion resistance, more polymorphic phase transitions, are often used to study the crystallization process and mechanism.^[84-86] Similar to water, the density of liquid Ga at the melting point is about 3% larger than the solid state at ambient pressure, which can often be supercooled to lower temperatures upon cooling. Similarly, the density of Germanium (Ge) can increase about 4.7% after melting, the coordination number increases from 4 of the solid to 6.8 of the liquid. Also, the conductivity increases one order of magnitude, inducing a transition from semiconductor to metal.^[87] The surface structures of liquid Ga, In and Sn are complex and often have the ordered region of 2-3 atomic layers thick. In addition, a shoulder peak often appears at the high q side of the main peak in their structure factors.^[88-90] From industrial application point of view, it is important to know the physical properties of liquid melts (especially alloys), but few data are available. The experimental results showed that in Cu-Zr alloy system, the good glass former has the smallest density difference between the amorphous phase and the competing crystalline phase.^[91] However, Bendert *et al.*^[92] suggested that Cu-Zr system can be grouped to fragile liquids and found that the best glass-forming Cu-Zr liquids exhibit the largest shrinkage to make the system quickly reach a high density state. Zhang *et al.* studied the expansion behavior of La-based liquid alloys and

found that the behavior is opposite to Cu-Zr liquids.^[93] Choosing La-based alloys is just because they have relatively low melting points and significant changes in critical sizes of glasses, i.e., only 4 mm in diameter for La₆₂Al₁₄Cu₂₄ (S-1) and greater than 20 mm of La₆₂Al₁₄(Cu_{5/6}Ag_{1/6})₁₄Ni₅Co₅ (S-2), and fragility parameters of about 17 and 20, respectively, indicating that they are relatively strong glass formers.^[94] The self-made alumina sample holder consists of a sleeve and two pistons (**Figure 5a**). The tolerance between them should be less than 10 microns (otherwise the liquid sample may leak out). The results showed that the expansion coefficient of sample S-1 is always greater than that of sample S-2 while their densities are just vice versa, indicating that in La-based liquids the smaller the expansion coefficient and the larger the liquid density (**Figure 5b**), the higher the GFA.

In recent years, self diffusion coefficients of atoms in metallic liquids have been *in situ* measured by combining the containerless levitation techniques and quasi-elastic neutron scattering (QENS),^[95-97] which can probe the dynamics on the atomic length and picosecond time scales, being available at the beamlines of BASIS and SNS-NSE at Oak Ridge National Laboratory (ORNL), TOFTOF of the Forschung-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Munich and D20 of the Institute Laue-Langevin (ILL), Grenoble, etc. The QENS signal in the small q range is mainly contributed to the incoherent scattering. The self correlation function shows how particles move as a function of time, just corresponding to the incoherent signal. **Figure 6a** shows the intensity of the scattered neutrons of liquid Zr₆₄Ni₃₆ at 1116 K and of the empty instrument was given as a function of time-of-flight (tof) normalized to the flight path distance.^[98] From the scattering intensity $I(q,t)$, the scattering law $S(q,\omega)$ can be calculated by Fourier transform, which describes the self motion of atoms, as shown in **Figure 6b**. In the small q range ($< 1.2 \text{ \AA}^{-1}$), the incoherent dynamic structure factor mainly comes from the contribution of those atoms with large incoherent scattering cross sections and can be expressed by a single central Lorentzian function as Equation (5), in which D is the self-diffusion coefficient of atoms, q the scattering vector and ω the frequency. The full width at half maximum of the Lorentzian Γ is almost linearly correlated with q^2 at small q . Thus, the self diffusion coefficient D can be estimated by Equation (6) and plotted in **Figure 6c**.

$$S_{inc}(q,\omega) = \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2} \quad (5)$$

$$D = \frac{\Gamma(q)}{2\hbar q^2} \quad (6)$$

Using QENS methods, Chathoth *et al.* measured the self diffusivity D of Ni atoms in several metallic liquids, and found that the diffusive motion is governed by the packing fraction of atoms.^[99] In a $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$ melt, a decoupling of more than 4 orders of magnitude was observed between the diffusivity D of Pd and of the smaller atoms at T_g temperature, which almost started from a critical temperature T_c of mode coupling theory.^[100] The Stokes-Einstein relation was held in the whole range of more than 14 orders of magnitude for the diffusivity of Pd atoms, suggesting the formation of a slow subsystem. In a $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vit 4) glass forming liquid, a similar phenomenon was observed for the large Zr atoms. The appearance of some solid-like clusters in the stable liquid state more than 300 K above the T_c temperature could be due to the formation of directed bonds between Zr atoms and others.^[101] In studying the composition dependent Zr-Cu glass forming liquids, it was found that no much difference in self diffusion coefficients of Cu atoms was observed although they have obvious different GFA. After Cu was replaced by Ni, the diffusivity of Ni atoms is much lower in Zr-Ni liquids although they have even worse GFA.^[102] These results indicate that the dynamics may not be the dominant factor determining the GFA in both Zr-Cu and Zr-Ni alloy systems.

Electric resistances of metallic liquids have been intensely studied, which can *in situ* be used to monitor the structural change in melts upon heating. It was reported that an anomalous structure change with temperatures appears in Bi-In^[103] and In-Pb^[104] liquids by using electrical resistance measurements, which was ascribed to the onset of the LLT. However, Khalouk *et al.*^[105] did the same measurements and found that the observed “anomalies” usually occur in the first scan, and would be attributed to the release of gas or vapor bubbles in liquids at the first heating rather than a phase transition. Their work strongly suggests that it is quite necessary to combine several kinds of techniques, either experiments or simulations, to improve the credibility of the observations on metallic liquids.

5. Fragility and glass transition of metallic liquids

Based on the relationship between viscosity and temperature ($\log \eta \sim T_g/T$), where T_g is

the glass transition temperature, Angell classified liquids into two groups - strong and fragile,^[106] in which the viscosity of strong liquids (SiO₂, GeO₂, etc.) basically follows the Arrhenius behavior but for fragile liquids (e.g. o-Terphenyl) their behaviors far deviate from the Arrhenius relationship. While, the reported data showed that the viscosity variation of good metallic glass forming liquids just locates in between. The slope of the curve at $T = T_g$ was defined as fragility index m , $m = d\log(\eta)/d(T_g/T)|_{T=T_g}$. In contrast, for those T_g unpronounced glass forming liquids, such as Al-based glasses, the fragility index could be evaluated using the value at $T = T_l$, T_l the liquidus temperature.^[107] It is generally believed that the larger the m index, the higher the structural heterogeneity of the liquid phase and the lower the GFA. Novikov and Sokolov^[108] found a linear relationship between the fragility index m and K/G of some supercooled liquids, $m = 29(K/G - 0.41)$, K , G the bulk modulus and shear modulus, respectively, indicating a close relationship between m and Poisson's ratio. However, Yannopoulos and Johari^[109] subsequently raised a doubt on the linear relationship between m and K/G when considering more glass systems. In La-based^[94] and Zr-Cu based^[110] metallic glasses, the good glass formers have large m values. For high glass forming Pd₄₃Ni₁₀Cu₂₇P₂₀ alloy, the reported m index is also as high as 65.^[111] Busch *et al.* found that the Zr-Ti-Cu-Ni-Be (Vit1) tends to be a strong liquid, the density difference between the liquid and solid phase is small for the existence of less free volume in the overheated and supercooled liquids.^[112] From the Vit1 amorphous phase to the liquid, the melting enthalpy is relatively small, indicating the existence of chemical short-range order in the melt, leading to the formation of clusters or phase separation. Mukherjee *et al.*^[113] found that the little change of free volume at the melting temperature is the key to its high GFA. They also found that the strong liquid behavior of Vit1 may be due to the icosahedral short range order in a wide temperature range, which decreases the interfacial energy between liquid and solid phase, thus reducing the free volume difference.^[114] These studies show some limitation of the m index, and also implicate the importance of studying the atomic structure and properties of metallic liquids. Combined synchrotron radiation-based XRD with ESL technique, Kelton *et al.* studied the temperature evolution of the height of the first peak in $S(q)$ of Ni-Nb and Vit106 supercooled liquids and defined a structural fragility index.^[115] It was found that the structural fragility index is large, the viscosity of the supercooled liquid at the temperature of $T_g/T =$

0.55 is small and so is the activation energy for the shear viscosity, as shown in **Figures 7a-b**. The larger structural fragility index indicates that the tendency of forming structural ordering in the fragile liquid is greater than that of the strong liquid at the glass transition, thereby leading to the weak GFA. The simulation results suggested that a certain short-range ordering (e.g. icosahedra in Cu-Zr) could accelerate with decreasing temperature upon undercooling, leading to a steeply rising excess specific heat (ΔC_p) and higher fragility, whereas local motifs only responsible for the densification of the liquids could cause a weak T -dependent ΔC_p .^[116] More recently, Krausser *et al.*^[117] connected the fragility and viscoelasticity of metallic liquids to the atomic connectivity, controlled by the steepness of the repulsive short-range interatomic interaction, leading to fragile behavior with steep interatomic repulsion and to a strong glass when the repulsion is softer.

About 65 years ago, Turnbull achieved the undercooling of metals by increasing the purity and cooling rate to suppress the heterogeneous nucleation.^[118] Later he pointed out that all liquids would form glasses when sufficiently undercooled and put forth a famous glass forming criterion, i.e., the reduced glass transition temperature ($T_{rg} = T_g/T_l$), to judge the GFA of metallic liquids.^[119] Since the discovery of the first Au-Si metallic glass,^[120] the liquid-to-glass transition has been intensely studied. The free volume model,^[121] energy landscape^[122] and mode coupling theory,^[123] etc., have been proposed to describe the nature of the glass transition. More details can be found in references.^[124-127] It is generally believed that the formation of a glass is the result of compromise between thermodynamics and kinetics. However, in the process of rapid quenching, the kinetic factors may play a more important role in the formation of a glass. Viscosity is an important parameter to characterize the atomic dynamics of liquids. At the vicinity of T_g temperature, the viscosity change of the supercooled liquid is usually more than 14 orders of magnitude. Based on the position shift of the first principle peaks in static structure factor $S(q)$ and $G(r)$, the appearance of a discontinuity suggested that the short and medium range order could be formed during the glass transition.^[128] In MD simulations, it was demonstrated that the fraction of icosahedral clusters increases rapidly during the glass transition of Cu_{rich}-Zr supercooled liquids upon quenching.^[129,130] Moreover, the bond orientational parameters also showed the topological ordering of local clusters appears during the glass transition and the LLT.^[131,132,70] At high

temperatures, the experimental results showed that the variation of liquid viscosity and diffusivity with temperatures usually follows the Arrhenius relation and Stocks-Einstein relation, respectively. However, with decreasing temperature, the deviation often occurs due to the increase of the dynamic heterogeneity.^[57,100,133] Recently, Iwashita *et al.* found that the macroscopic viscosity (or relaxation time) of metallic liquids deviates from the Arrhenius relation by MD simulations, likely related to the formation of local atomic connectivity network at a crossover temperature T_A , above which the Arrhenius behavior is observed.^[134] Below T_A , the Stokes-Einstein relation begins to break down due to a decoupling of the diffusive and relaxation dynamics for all the components that exhibit different dynamics at lower temperatures. For metallic liquids, the $T_A \approx 2T_g$, as shown in **Figure 8**, locating in the liquid state but for fragile molecular liquids, this crossover appears about $1.4T_g$ and usually in the supercooled liquid state.^[135,136] The theoretical simulation results of Yu *et al.* showed that when the atomic displacements of most atoms reach a critical value ($\sim 20\%$ of the average interatomic distance), whether induced by temperature or by mechanical strain, the α -relaxation always occurs.^[137] The theoretical simulations of Tanaka *et al.* indicated that the slowing-down of atoms in glass-forming liquids is related to the formation of local structural heterogeneity. The density of the supercooled liquid changing with temperatures is small, which leads to the tiny change of the static structure factor. However, the glass transition can be mainly reflected by the structural ordering parameters.^[138] The results showed that the presence of preferential structure (locally-preferred structure) in metallic liquids may play an important role in the dynamics.^[139] For example, in $\text{Cu}_{\text{rich}}\text{-Zr}$ liquids, icosahedral clusters and icosahedrons-stacked medium range order could be formed with decreasing temperature, corresponding to the macroscopic viscosity and diffusivity deviation from the Arrhenius relationship.^[140]

6. Surface structure and properties of liquid metals

In above sections, we mainly discuss the structure and properties of bulk metallic liquids. However, how does the surface structure change in liquids is also promising. By using x-ray reflectivity measurements, Shpyrko *et al.* demonstrated that the free surface of liquid Sn, like other liquid metals (Mercury(Hg), Ga and In), is layered, but forming a high-density surface

layer.^[90] In contrast, there is no observable surface-induced layering in water at 298 K,^[141] thus showing fundamental difference between metallic and dielectric liquids. The x-ray scattering results revealed that the oxidation kinetics of liquid Sn is different from the solid and crystalline Sn, forming a formerly unreported face-centered cubic (fcc) phase of SnO when the molecular oxygen beyond a threshold pressure of about 5.0×10^{-6} Torr.^[142] They also observed the surface crystallization by forming crystalline monolayer phase in the eutectic liquid Au₈₂Si₁₈ at temperatures above the alloy's melting point,^[143] and in the bulk metallic glass forming alloy Au₄₉Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3} when the temperature up to about 50 K above its eutectic temperature.^[144] The MD simulation illustrated direct computational evidence of surface-induced nucleation in supercooled liquid Si and Ge, and implied that the surface-induced crystallization could exist in other tetrahedrally coordinated systems, including water.^[145]

In all metals, Hg, Ga, Rubidium (Ru), Cesium (Cs), Francium (Fr) and some of their alloys are metallic liquids below or near room temperature. If excluding high toxicity and high reactivity, only Ga and its alloys have potentially wide practical applications in the liquid state. Like Al, Ga easily forms a thin oxide layer (~0.7 nm thick) on its surface when exposed to air, which is often considered as a nuisance to restrain its applications. However, by using the solid oxide layer on the surface, Dickey *et al.* found that Ga and its alloys can be used as soft electrodes and sensors, microfluidic devices, self-healing circuits, shape-reconfigurable conductors, and stretchable antennas, wires and interconnects.^[146] For example, they could inject the eutectic GaIn (EGaIn) liquid alloy into microfluidic channels to form stable microstructures when a critical surface stress (~0.5 N/m) is reached to induce EGaIn to flow.^[147] It is mainly controlled by the surface oxide skin since this ability was lost when the oxide layer was removed by chemical etching. Furthermore, they also demonstrated that it is possible to direct-write EGaIn liquid metal at room temperature into a variety of stable free-standing microstructures by 3D printing.^[148] Recently, a technique has been established to deposit and pattern wafer-scale two-dimensional semiconducting GaS of unit cell thickness of about 1.5 nm by using the wettability of the oxide skin of Ga on the oxygen-terminated substrates.^[149] Liquid metal marbles that are droplets of liquid metal galinstan (GaInSn) coated with micro or nanoparticles of insulators and semiconductors, including Teflon, silica,

WO₃, TiO₂, MoO₃, In₂O₃ and carbon nanotubes, were also reported.^[150] The marble coating can operate as an active electronic junction and the nanomaterial coated liquid metal marbles can act as diodes and transistors that could be considered for applications in soft electronics. Thus, whether the self-driven motor or soft electronic circuits,^[1,150] liquid metals at room temperature is a newly developing field, full of novelty and exciting, enabling more opportunities and challenges to us in both scientific research and technological applications.

7. Conclusions and outlook

Advanced synchrotron radiation and neutron scattering techniques, ESL and MD simulations have become effective ways to study the structure and properties of metallic liquids. In the past ten years, with joint efforts of different research groups, some innovative results concerning the dependence of atomic configurations in metallic liquids and their properties (such as viscosity, diffusivity, density and electric resistance etc.) changing with temperatures have been achieved in various metallic systems and briefly reviewed here, which could further promote in-depth understanding of metallic liquids. The results indicated the existence of atomic cluster ordering in many metallic liquids. It changes from high to low coordinated with increasing temperature, likely resulting in a negative expansion of the distance between the center atom and atoms in the first nearest-neighbor shell. Contrary to Cu-Zr fragile liquids, the atoms connect closely in La-based liquids, resulting in that the stronger the glass former, the smaller the liquid volume contracts upon cooling. The structure heredity, i.e., the liquid structure locally resided in the competing crystals, was detected in some metallic liquids, e.g., the Au-Al system. In the Al-Cu system, the so-called LLT phenomenon was not found in bulk liquids. However, in the liquid Ga, a liquid structure crossover was observed at about 1000 K. Similar LLTs were reported in Ce, La₅₀Al₃₅Ni₁₅, Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} liquids. The fragility index and the change of atomic dynamics of metallic liquids could be related to the local structural evolution in the liquids. The glass transition, the structure evolution in the bulk and on the surface of liquids, the GFA, and temperature dependent properties of metallic liquids will continue to be the focuses of disordered glasses and liquids in the near future. In concluding this review, several research issues that are important for the understanding of metallic liquids from our point of views, are

suggested.

(1) One critical question is the nature of the glass transition in different metallic liquids that have different atomic packing. It is worth noting that the glass transition is really under the polyhedron control or still needs other dynamic parameters to characterize. Compared to the chalcogenide, colloidal and molecular liquids, what are the unique features of the glass transition in disordered metallic systems and what are the universal mechanisms on the glass transition among various disordered materials?

(2) The liquid-liquid transition has been reported only in a few metallic liquids. However, the metallic liquid structure is still difficult to be characterized effectively. How to monitor the liquid structural evolution and confirm the existence of liquid-liquid phase transition is still one of fundamental issues? What is the nature of the liquid-liquid phase transition in metallic liquids? Is it only the strong-to-fragile transition or just similar to the polymorphism in crystalline materials?

(3) Although Angell has grouped the liquids into strong and fragile, why the fragility indices of fragile liquids are so large in comparison to strong liquids remains elusive. What are the intrinsic factors that really control the fragility of different metallic liquids? Does the fragility index relate with the GFA and liquid mechanical parameters? More studies of the fragility, esp. the origin of the fragility, can deepen our understanding of the structure and properties of metallic liquids.

(4) The atomic dynamics is another important issue of metallic liquids and glasses. What is the relationship between the β -relaxation and the α -relaxation (the glass transition) in the liquid state? What is the nature of the model coupling temperature T_c , at which the α -relaxation separates from the β -relaxation? And what are the structural origins of the β -relaxation and α -relaxation? Why does the crossover temperature T_A in most metallic liquids roughly equal to 2 times of T_g ?

(5) Different metallic liquids usually exhibit various temperature dependences of properties, such as viscosity, diffusivity, electrical resistance and thermal expansion coefficient, and so on. It is still valuable to collect more precise temperature dependent data of them for metallic liquids. Moreover, how to understand their different variation trends with temperatures from the atomic structure perspective is also a fundamental issue. To construct the

structure-property relationship of metallic liquids will be useful for optimizing their properties by tuning the composition, microstructure and solidification process upon cooling.

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Figure Captions

Figure 1. a) Pair correlation function $g(r)$ curves for Al, indicating the melting point at a temperature between 900 and 1000 K, very close to the experimental value of 933.5 K. From 1000 K to 2000 K, the first maximum in $g(r)$ shifts to low r values. b) The average bond length of high-coordinated polyhedra is larger than that of low-coordinated one. c) Voronoi tessellation shows the fractions of polyhedra at different temperatures. Upon heating, the number of high-coordinated polyhedra (CN = 11 and 12) is reduced with uprising number of low-coordinated ones (CN = 9 and 10). d) Schematically shows the structural evolution from high-coordinated polyhedra to the low-coordinated with increasing temperature. Reproduced with permission.^[29] Copyright 2013, PNAS.

Figure 2. a) Schematic drawing of the vertical cut levitation chamber. TE—Top electrode, GE—ground electrode, SE—side electrode, S—sample, BE—beam expander for laser, M3—mirror, PSD—position sensitive detector, HV—high voltage feed through, TMP—turbo molecular pump, UV—UV lamp, NW—neutron window in vacuum chamber. Reproduced with permission.^[98] Copyright 2011, APS. b) The temperature profile for $\text{Al}_{75}\text{Cu}_{25}$ sample upon heating and cooling by electrostatic levitation. Inset is the snapshot of a levitating ball after melting.

Figure 3. Structural evolution of liquid Nb during solidification: a) Probability distribution of bond orientational order parameter Q_6 at different annealing times. b) Bond orientational order parameter Q_6 of all the atoms changing with annealing time. The average value is shown by the red line. c) Snapshots of atomic configurations according to Q_6 at different annealing times. Atoms with $Q_6 < 0.2$ are colored maroon, $0.2 \leq Q_6 < 0.3$ are colored blue, those with $0.3 \leq Q_6 < 0.4$ are colored yellow, whereas those with $Q_6 \geq 0.4$ are colored red. d) Atomic density of each atom (all atoms are plotted) changing with annealing time. The average value is shown by red line. Reproduced with permission.^[45] Copyright 2014, APS.

Figure 4. a) Temperature dependence of $1/Q_1^3$ on cooling (blue diamonds and squares) and heating (red dots). Filled yellow triangles are isothermal measurements on stepwise heating. The

arrow points out a clear discontinuity of $1/Q_1^3$ upon cooling at around 830 K, Reproduced with permission.^[70] Copyright 2013, NPG. b) A series of isothermal NMR measurements with decreasing temperatures to 973 K followed by isothermal measurements with increasing temperatures up to 1143 K. A crossover temperature occurs at the intersection of 1033 K. Three typical ^{27}Al NMR spectra taken at different temperatures are also shown, Reproduced with permission.^[71] Copyright 2015, NPG. c) The positions of the first main peak and its shoulder in $S(q)$ shift with increasing temperature, deviating from the linear mode at about 1000 K. d) Pressure P - temperature T phase diagram of Ce, showing the LDL-HDL phase boundary and the LLPT highlighted by a thick gray line and ends at a liquid-liquid critical point (LLCP) near 21.3 GPa and 2100 K, Reproduced with permission.^[77] Copyright 2013, APS.

Figure 5. a) Thermal expansion of crystalline La-based S-1 and S-2 samples in the solid and liquid states as a function of temperature. Inset shows the sample shape change in the sample holder before and after melting. b) Liquid density of S-1 and S-2 samples as a function of temperature from 850 to 1273 K evaluated from the expansion data measured by a dilatometer, Reproduced with permission.^[93] Copyright 2014, AIP.

Figure 6. a) Time-of-flight spectrum of a liquid $\text{Zr}_{64}\text{Ni}_{36}$ sample (mass 0.6 g) 167 K below melting temperature and the spectrum of the empty ESL recorded by quasielastic neutron scattering. b) Scattering law $S(q, \omega)$ of $\text{Zr}_{64}\text{Ni}_{36}$ at 1460 K for $q = 0.5 \text{ \AA}^{-1}$ and $q = 1.1 \text{ \AA}^{-1}$ fitted with Lorentzian function. c) Temperature dependence of the Ni self-diffusion coefficient in liquid $\text{Zr}_{64}\text{Ni}_{36}$ processed by the EML and the ESL technique and the average Ni and Ti self-diffusion coefficient in the bulk metallic glass forming Vit1 alloy, Reproduced with permission.^[98] Copyright 2011, APS.

Figure 7. a) Correlation between structural fragility and the activation energy of the shear viscosity at $T_g/T \approx 0.55$. b) The correlation between the activation energy and the viscosity at a reduced temperature of $T_g/T \approx 0.55$. A strong correlation emerges at all reduced temperatures for which data are available, Reproduced with permission.^[115] Copyright 2014, NPG.

Figure 8. Dependence of measured crossover temperature T_A from the high temperature viscosity

data and the glass transition temperature T_g for the glass forming liquids, showing $T_A \approx 2T_g$.
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Figure 1

Figure 2

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Figure 6

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Figure 8