TOPICAL REVIEW — Amorphous physics and materials

Five-fold local symmetry in metallic liquids and glasses*

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The structure of metallic glasses has been a long-standing mystery. Owing to the disordered nature of atomic structures in metallic glasses, it is a great challenge to find a simple structural description, such as periodicity for crystals, for establishing the structure–property relationship in amorphous materials. In this paper, we briefly review the recent developments of the five-fold local symmetry in metallic liquids and glasses and the understanding of the structure–property relationship based on this parameter. Experimental evidence demonstrates that five-fold local symmetry is found to be general in metallic liquids and glasses. Comprehensive molecular dynamics simulations show that the temperature evolution of five-fold local symmetry reflects the structural evolution in glass transition in cooling process, and the structure–property relationship such as relaxation dynamics, dynamic crossover phenomena, glass transition, and mechanical deformation in metallic liquids and glasses can be well understood base on the simple and general structure parameter of five-fold local symmetry.

Keywords: metallic glass, structure–property relation, five-fold local symmetry

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1. Introduction

Establishing the structure–property relationship is a great challenge for amorphous materials, such as metallic liquids and glasses, because of the disordered nature of atomic structures.[1] Unlike the well-defined long-range order in crystalline metals, the atomic arrangements in metallic glasses remain mysterious.[1] Finding a simple structural description of liquids, such as periodicity for crystals, is a persistent challenge in condensed-matter science and materials science. In 1950's, it was revealed that many simple liquids could be supercooled far below their freezing points without crystallization occurring,[2] which made people conjecture that amorphous materials might contain non-crystallographic highly ordered low-energy atomic clusters. Subsequently, Frank proposed that simple liquids may be composed of icosahedral short-range order (ISRO) building blocks.[3] Icosahedral atomic arrangement has 12 atoms around a central atom, same as face-centered cubic (FCC) and hexagonal close-packed (HCP) atomic clusters. However, it was found that icosahedral atomic configuration has lower energy than FCC or HCP configuration based on the Lennard–Jones pair interatomic interaction.[3] Therefore, it was argued that supercooling of the simple liquids could be due to the prevalence of these icosahedral motifs.

Following Frank's hypothesis, much effort has been devoted to characterizing ISROs in metallic liquids and glasses via experiments and theoretical simulations.[1] Some structure analysis methods, such as Voronoi tessellation,[4,5] bond-orientational order parameter,[6,7] Honeycutt–Andersen (HA) index,[8] and common-neighbor analysis[9] were developed and have been widely applied to characterize the local atomic structures in metallic liquids and glasses.[1] Thus, ISROs were successfully identified in metallic liquids and glasses generated in computer simulations [1,8,10,11]. Moreover, combined with reverse Monte Carlo simulations and the above structure analysis methods, x-ray absorption experiments also reveal the development of ISROs in metallic liquids and glasses to a very high degree.[12–15] On the other hand, plenty of studies have been done to try to establish the relationship between ISROs and properties in metallic liquids and glasses.[1] It has been found that ISRO is closely correlated with dynamical, mechanical properties, glass-forming ability, glass transition, and stability in metallic liquids and glasses.[1,16–21] These results indicate that ISRO is a key atomic structure motif in characterizing the atomic structure feature and understanding the structure–property relationship in metallic liquids and glasses.

Extensive structure analyses based on computer simulations have also revealed that apart from ISRO, metallic liquids and glasses involve a large number of types of atomic clus-

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ters, too.[1,10,11] Such diversity in atomic clusters has been reported in previous classical molecular dynamics simulations for model systems.[22,23] These findings indicate that the local arrangements cannot be simply described by a unique stereochemical structure.[10] It is also found that some atomic clusters with non-icosahedral arrangement such as Zr-centered clusters in CuZr metallic glasses play a key role in slowing down the dynamics and determining the stability of metallic glasses.[24,25] This finding indicates that apart from ISRO, some other types of atomic clusters may also be important in determining the structure–property relationship in metallic liquids and glasses and have to be taken into account. Furthermore, some simulation studies have demonstrated that in some metallic glasses ISRO is not dominant structure motif, and even absent.[1,26–28] This indicates that although ISRO is important in characterizing the structure feature in some metallic liquids and glasses, it may not be important in some other metallic liquids and glasses. Thus, the key issue is whether there is a simple or general structure parameter in metallic liquids and glasses to characterize the structure feature and establish the structure–property relationship.

In Frank's hypothesis, the most significant feature in ISRO is the five-fold local symmetry, which is abhorrent to crystal symmetry.[3] Five-fold symmetry is incompatible with long-range periodicity, so the polytetrahedral short-range order favors the disordered or amorphous structures.[3,29] In this sense, the most difference between liquids/glasses and crystalline solids is the five-fold local symmetry, so that five-fold local symmetry may be general in metallic liquids and glasses.[30,31] The local atomic symmetry of the short-range order in simple liquids has been attracted some attentions for understanding atomic structure in metallic liquids and glasses. In 2000, direct experimental evidence for the existence of five-fold symmetry has been obtained in liquid Pb adjacent to a silicon wall and revealed an experimental portrait of the icosahedral fragment, indicating that liquids contain the atomic configurations with five-fold local symmetry.[32] Furthermore, by means of angstrom-beam electron diffraction of single icosahedra, local icosahedral order was observed experimentally in metallic glasses and found to be distorted, composed of a partial five-fold local symmetry and a partial fcc symmetry.[33] It is also revealed that other prevailing atomic clusters in metallic glasses also contain both icosahedral- and fcc-like structural features, similar to the distorted icosahedral clusters.[33] Therefore, the local symmetry of the atomic clusters is generic in metallic liquids and glasses, and the five-fold local symmetry could be general and suitable for providing a simple structure description of metallic liquids and glasses and their structure–property relationship. Actually, nuclear magnetic resonance (NMR) experiments have demonstrated that local atomic symmetry plays an important role in glass-forming ability (GFA) and anelastic deformation in metallic glasses.[34,35] Computer simulations for some realistic metallic glasses have demonstrated that the evolution of the fraction of pentagons with temperature or shear stress is totally different from that of other type faces, implying the competition and transformation between five-fold local symmetry and local crystalline symmetry in local structures during glass formation or deformation process.[36,37]

As matter of fact, five-fold rotational symmetry is ubiquitous in nature. For example, the armor of pineapples, cross sections of apples, flowers, leaf, starfish, and architectures all exhibit five-fold rotational symmetry. Many plants display five-fold symmetry in arranging petals to get maximum sunlight without shading each other, showing the significance of five-fold symmetry in evolution of nature species.[38] In crystallography, five-fold symmetry is incompatible with translational periodicity, and its discovery once caused confusion until the discovery of quasicrystals.[38–41] About 400 years ago, Kepler had ever found the symmetry of the five Platonic polyhedra in the structure of the solar system, which was associated with the arrangements of plane pentagons.[41] It is also found that most spherical viruses have icosahedral arrangement, containing five-fold rotational symmetry. For example, adenovirus contains 252 capsomeres with icosahedral arrangements.[42] Moreover, five-fold local symmetry has been also observed in colloids, granular particles, and hard-sphere glasses. Due to the incompatibility with translational symmetry, the five-fold symmetry results in severe frustration and hinders crystallization in colloids.[33,34] It is also verified that five-fold local symmetry plays a crucial role in dynamical arrest in colloidal and granular systems[43–54] and closely correlated with some properties such as fragility and boson peak.[46,47] Therefore, it is anticipated that local atomic symmetry could be a simple and general structural parameter in metallic liquids and glasses for better understanding the structure–property relationship in amorphous alloys. In this work, we briefly review recent research progress on the five-fold local symmetry in metallic liquids and glasses. It has been demonstrated that this structure parameter can provide a universal physical picture for atomic evolution, relaxation and dynamical behavior, mechanical deformation, and even liquid–liquid transition in metallic liquids.[28,30,31,55,56]

2. Five-fold local symmetry in metallic liquids and glasses

2.1. Definition of five-fold local symmetry

As mentioned above, the prevailing atomic clusters in metallic glasses contain both icosahedral- and fcc-like structural features.[33] However, different atomic clusters may contain different degree of five-fold local symmetry (FFLS). The

question is how to quantify FFLS in an atomic cluster. A simple way is to evaluate the fraction of pentagons in the polyhedron of this atomic cluster, which can be constructed by the Voronoi tessellation method by bisecting the lines connecting the central atom and all nearest neighbors with a set of planes.[5] The constructed polyhedron type i can be identified in terms of the Voronoi index $\langle n_i^3, n_i^4, n_i^5, n_i^6 \rangle$, where n_i^k $(k = 3,4,5,6)$ denotes the number of k-edged polygon in Voronoi polyhedron type i. Thus, the degree of k-fold local symmetry in an atomic cluster can be defined as $f_i^k = n_i^k \Big/ \sum_{k=3,4,5,6} n_i^k$, and the average degree of k-fold local symmetry can be defined as $\sum_i f_i^k \times P_i$, where P_i is the fraction of polyhedron type i.[28,30,31] The degree of FFLS in a polyhedron type i can be expressed as[28,30,31]

$$f_i^5 = n_i^5 \Big/ \sum_{k=3,4,5,6} n_i^k, \tag{1}$$

and the average degree of FFLS can be expressed as

$$W = \sum_i f_i^k \times P_i. \tag{2}$$

According to the above definition, one can explore the five-fold local symmetry in metallic liquids and glasses and explore the structure–property relationship.

2.2. Temperature evolution of FFLS in metallic glass-forming liquids

Figure 1 shows the temperature dependence of the average degree of FFLS W in various metallic glass-forming liquids obtained in molecular dynamics simulations.[28] With decreasing temperature to glass transition temperature T_g, W increases rapidly. As temperature is below T_g, W reaches constant values. As shown in Fig. 1, in all the simulated systems W exhibits similar temperature dependent behavior. The temperature dependence of W is coincidence with the glass transition, representing the structural evolution of metallic glass-forming liquids during glass transition. In contrast to FFLS, 3-, 4-, and 6-fold local symmetry decrease as temperature is approaching T_g, indicating the critical role of FFLS played in glass transition.[28] Below T_g, W values in different metallic glasses are different, which indicates that FFLS is a material-dependent parameter.

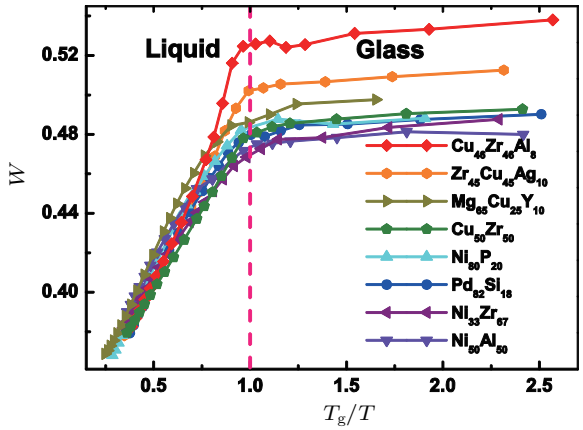


Fig. 1. (color online) The evolution of five-fold local symmetry during quenching. The temperature dependence of W in different metallic alloy systems shows similar trend but different values after glass transition (reproduced from Ref. [28]).

3. Correlation between relaxation dynamics and FFLS in metallic glass-forming liquids

3.1. Relationship between viscosity and FFLS in metallic glass-forming liquids

The increase of FFLS with decreasing temperature indicates that FFLS is closely correlated with dynamical slowdown in glass transition. It has been revealed that the temperature dependence of W in metallic glass-forming liquids follows power-law behavior of $1 - W \sim (T - T_1)^{\alpha}$,[28] and the temperature evolution of viscosity η can be well described by Vogel–Fulcher–Tammann (VFT) equation of $\eta \sim \exp[B/(T - T_0)]$.[48] In addition, it is found that T_1 is approximately equal to the ideal glass transition temperature T_0 ($T_1 \approx T_0 \approx 0.85 T_g$[48]). Therefore, by substituting T_0 in VFT equation with T_1, a direct relationship between W and η can be derived,

$$\eta = \eta_0 \exp \frac{D}{(1-W)^{\delta}}, \tag{3}$$

where η_0 is the viscosity at infinite liquidus temperature, D and δ are fitting parameters.[28] It has been revealed that Eq. (3) describes the behavior of viscosity as a function of W very well, as shown in Fig. 2.

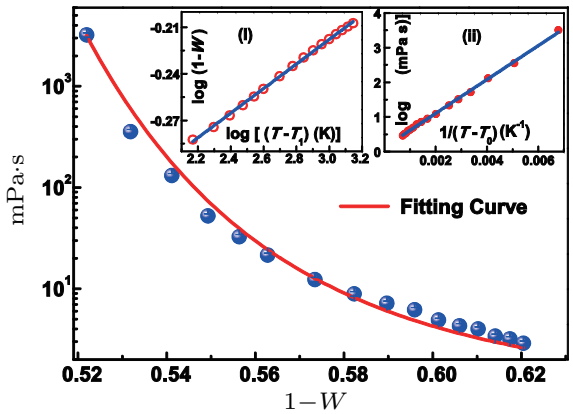


Fig. 2. (color online) Relationship between viscosity η and the average five-fold local symmetry W. The dotted curves are obtained from simulations and the solid line is the fitting by Eq. (3); in the insets (i) and (ii), the open and solid circles show the temperature dependence of W and η, respectively, and the solid lines are fitting of the power-law and VFT functions, respectively (reproduced from Ref. [28]).

Similar relation also exists between structural relaxation time τ_α and W, since τ_α is proportional to shear viscosity η and its temperature dependent behavior can be well fitted by

the VFT equation, too.[49] Therefore, the following equation between τ_α and W can be also obtained,

$$\tau_\alpha = \tau_0 \exp \frac{D}{(1-W)^\delta}, \tag{4}$$

where τ_0 is the relaxation time at infinite liquidus temperature, and δ and D are fitting parameters. τ_α can often be measured by the self-intermediate scattering function $F_s(q,t) = N^{-1}\sum_{i=1}^{N} \exp\{i\boldsymbol{q}\cdot[\boldsymbol{r}_i(t)-\boldsymbol{r}_i(0)]\}$, as it decays to e^{-1} of its initial value,[50] where N is the number of atoms, $\boldsymbol{r}_i$ is the atomic position of atom i, and $\boldsymbol{q}$ is the wave vector often fixed at $q_{\max} = |\boldsymbol{q}|$ corresponding to the first peak position of structure factor.[50] It has been demonstrated that Eq. (4) can well describe the relationship between structural relaxation time and the five-fold local symmetry in metallic glass-forming liquids, as shown in Fig. 3, indicating that the dynamics is closely correlated with the atomic structures in metallic glass-forming liquids.[28]

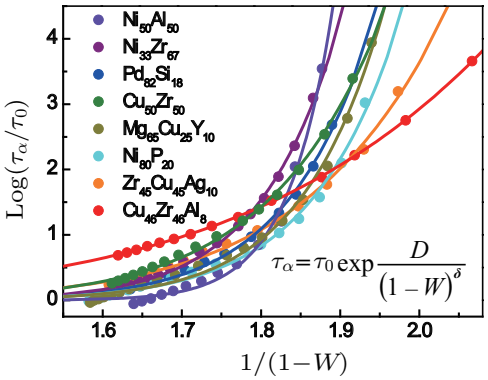


Fig. 3. (color online) Relation between structure parameter W and α-relaxation time τ_α. The dotted and solid curves are the simulation data and the fitting curves with Eq. (4), respectively (reproduced from Ref. [28]).

In Eq. (3) or Eq. (4), there are two fitting parameters, δ and D. By fitting the simulated data of 8 metallic glass-forming liquids, it is found that the fitting parameter D is very small and has similar values $\sim 10^{-5}$ in different systems. However, δ is quite different in different systems. It was fitted to be about 6.78, 13.58, 11.52, 17.65, 17.95, 18.92, 18.94, and 32.74 for $Cu_{46}Zr_{46}Al_8$, $Zr_{45}Cu_{45}Ag_{10}$, $Cu_{50}Zr_{50}$, $Ni_{80}P_{20}$, $Pd_{82}Si_{18}$, $Mg_{65}Cu_{25}Y_{10}$, $Ni_{33}Zr_{67}$, and $Ni_{50}Al_{50}$ metallic glass-forming liquids, respectively. According to Eq. (4), due to the different δ values, the structural relaxation time or viscosity in different systems is different for the same W value. This implies that the influence of the atomic structure on the dynamics is different in different metallic glass-forming liquids, and δ just reflects the sensitivity of the relaxation dynamics to the atomic structure evolution. The larger the δ value is, the more sensitive the dynamics in a metallic glass-forming liquid is to the atomic structure. Figure 4 shows the correlation between δ and W. It is clearly seen that as W increases, δ decreases, clearly illustrating the influence of the atomic structures on dynamics in metallic glass-forming liquids. This finding shows that there exists a universal underlying structural evolution in metallic glass-forming liquids, and the structural parameter FFLS just reflects the structural evolution and is responsible for the drastic dynamic slowdown.

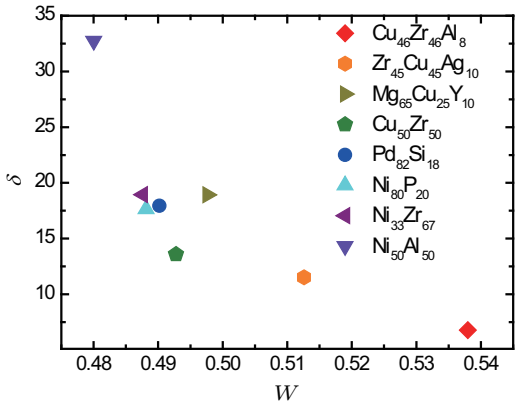


Fig. 4. (color online) Correlation between δ and W.

As mentioned above, given the same W, larger δ value means more drastic change of the viscosity or structural relaxation time, which reflects the sensitivity of the dynamics to the atomic structure evolution in metallic glass-forming liquids. Therefore, δ in Eqs. (3) and (4) can be regarded as 'structural fragility'. Larger δ means that the atomic structure of a metallic liquid is more fragile. This is analogous to the dynamic fragility defined as $m = \left[\mathrm{d}\left(\log\eta\right)/\mathrm{d}\left(T_\mathrm{g}/T\right)\right]_{T=T_\mathrm{g}}$ and describes the sensitivity of the dynamics change to the temperature as temperature is approaching T_g.[51]

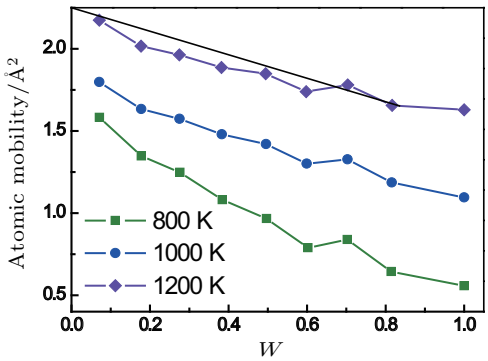


Fig. 5. (color online) Correlation between atomic mobility and W at different temperatures in a model system $Cu_{46}Zr_{46}Al_8$ at 800 K, 1000 K, and 1200 K, respectively (reproduced from Ref. [28]).

The underlying physics of Eqs. (3) and (4) can be understood in terms of the correlation between five-fold local symmetry and atomic mobility in metallic glass-forming liquids. The atomic mobility decreases with increasing W, as shown in Fig. 5.[28] That is, the more the five-fold symmetry in atomic packing around atoms, the more immobile the atoms are. Such correlation has also been observed in other MD simulations.[52] This tendency becomes more remarkable as

temperature decreases (see Fig. 5). This may be because FFLS favors the dense packing, slowing down the dynamics. Thus, five-fold local symmetry in atomic arrangements has great impact on the mobility of the involved atoms and dynamics in metallic glass-forming liquids.

3.2. Link between configurational entropy and FFLS in metallic glass-forming liquids

Both experiments and simulations have observed that the temperature dependence of constant-pressure specific heat c_p in metallic glass-forming liquids shows a jump, an excess specific heat during glass transition[53,54,57–60] (also see Fig. 6(a)). In fast quenching process, c_p increases and reaches a maximum above T_g, then decreases. However, the underlying structure evolution is not clear.[61] The c_p curves in different supercooled metallic liquids ($Mg_{65}Cu_{25}Y_{10}$ and $Cu_{64}Zr_{36}$) were attributed to the temperature dependence of different atomic ordering, tricapped trigonal prisms (TTP, $\langle 0,3,6,0\rangle$) and bicapped square antiprisms (BASP, $\langle 0,2,8,0\rangle$) in $Mg_{65}Cu_{25}Y_{10}$, but full icosahedra ($\langle 0,0,12,0\rangle$) in $Cu_{64}Zr_{36}$ metallic liquids.[60]

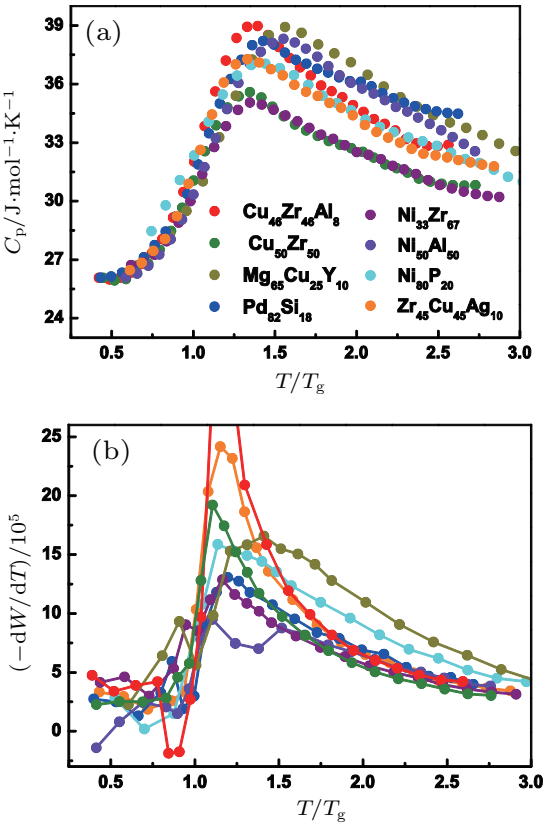


Fig. 6. (color online) (a) Temperature dependence of the specific heat C_p for various metallic alloy systems. (b) The structural change rate during quenching reflected by dW/dT with a jump during glass transition. The coincidence of the excess specific heat and the jump in dW/dT illustrates the structural basis of the thermodynamics (reproduced from Ref. [28]).

According to thermodynamics, c_p is related to the entropy by $c_p(T) = T(\partial S/\partial T)_p$. If the entropy in this equation is just the configurational part S_c, $(\partial S_c/\partial T)_p$ should be related to the structural evolution in metallic glass-forming liquids during glass transition. Therefore, c_p is determined by the reduction rate of S_c as a liquid is quenched. On the other hand, in 1965, Adam and Gibbs derived a theoretical model for liquid dynamics and established a relationship between shear viscosity and configurational entropy as[62]

$$\eta = A\exp(B/TS_c). \tag{5}$$

Although the specific heat and viscosity can be well described in terms of configurational entropy in liquids, the underlying structure basis for configurational entropy is not clear, because of the lacking of a simple description of liquid structures. In addition, in the derivation of Adam–Gibbs theory, an important concept of cooperatively rearranging region (CRR) was invoked in this theory. The size of CRR was related to configurational entropy and thus the size variation with temperature was found to explain the temperature dependence of relaxation in glass-forming liquids.[62] However, there is no clear structure picture for CRR, although much efforts have been devoted to these issues.[1,51,63,64] The structure parameter of five-fold local symmetry can provide an atomic structure picture for temperature dependent behavior of specific heat and configurational entropy.

Comparing Eq. (5) with Eq. (3), a relation between S_c and W can be derived as $S_c \sim (1-W)^{\delta}/T$, so that S_c is closely related to the W parameter and can be quantitatively evaluated in terms of the five-fold local symmetry in metallic glass-forming liquids. According to the relation of $S_c \sim (1-W)^{\delta}/T$, it can be seen that as $W \to 1$, configurational entropy S_c will be zero.[28] As $W \to 1$, T is approaching the ideal glass transition temperature, since $1-W \sim (T-T_1)^{\alpha}$. This indicates the formation of ideal glass. This provides an implication of the atomic structure feature in ideal glass with full five-fold local symmetry and zero configurational entropy. CRR in Adam–Gibbs theory can be also well understood based on the spatial distribution of FFLS in metallic glass-forming liquid (see Section 4).

According to $S_c \sim (1-W)^{\delta}/T$, c_p is then related to the derivative of W, dW/dT. Figure 6(b) shows that the change rate of the W parameter dW/dT exhibits a jump behavior around T_g in various metallic glass-forming liquids.[28] The change rate of W is different in different metallic liquids, reflecting the different influence of the FFLS evolution on the configurational entropy. In addition, it is also found that the specific heat jump during glass transition is coincident with the jump of dW/dT.[28] This suggests that the temperature behavior of the specific heat is intimately related to the evolution of the five-fold local symmetry in metallic glass-forming liquids.

4. Structure correlation length associated with FFLS and link to dynamic crossover phenomena

4.1. Spatial distribution of FFLS and structure correlation length

Spatial distribution of five-fold local symmetry may provide deep insight into the underlying physics of the structure-dynamics correlation in metallic glass-forming liquids. It is found that atoms with different five-fold local symmetry exhibit various spatial correlations. Atoms with $f^5 \geq 0.6$ or $f^5 \leq 0.4$ show strong spatial correlation and thereby tend to form clusters, while the atoms with $f^5 \geq 0.6$ and $f^5 \leq 0.4$ tend to avoid each other.[28] Therefore, the distribution of the five-fold local symmetry in metallic glass-forming liquids is not random, but spatially correlated. Such similar spatial correlation of five-fold local symmetry was also observed in different metallic glass-forming liquids and at different temperatures.[28] This indicates that the structural parameter W is generic in describing the structure properties and spatial structure correlations in metallic glass-forming liquids.

Figure 7 shows the temperature evolution of the average cluster size formed by the atoms with different five-fold local symmetry.[28] The clusters can be defined if the atoms with the same threshold of five-fold local symmetry are nearest neighbors, and the cluster size is defined as the number of atoms in this cluster. Therefore, the average cluster size can be derived by $S = \sum n^2 P(n) / \sum nP(n)$, where n is the individual cluster size and $P(n)$ is its probability.[65] It is found that the clusters of $f^5 \geq 0.5$, 0.6, and 0.7 are growing in quenching process, respectively, while the cluster size of $f^5 \leq 0.2$ is decreasing.[28] This is because that the five-fold local symmetry is increasing with decreasing temperature.

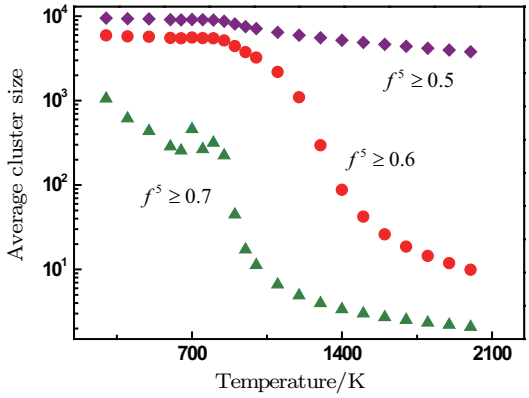


Fig. 7. (color online) The average cluster size formed by atoms with different thresholds of W in $Cu_{46}Zr_{46}Al_8$ metallic glass-forming liquid, indicating that the selection of $f^5 \geq 0.6$ is physically reasonable (reproduced from Ref. [28]).

As shown in Fig. 7, in the case of $f^5 \geq 0.5$, the average cluster size formed by the atoms of $f^5 \geq 0.5$ is too large (> 1000 atoms) in high temperature range. This is unphysical. However, the average cluster size formed by the atoms of $f^5 \geq 0.7$ is relatively small below T_g. Furthermore, the average cluster size in the case of $f^5 \geq 0.7$ increases too slowly with decreasing temperature and still varies below T_g. This is unphysical, either. For $f^5 \geq 0.6$, the average cluster size exhibits reasonable temperature dependent behavior: relatively small (~ 10 atoms) at high temperature, increasing drastically as temperature approaches T_g, and reaching a constant value below T_g. In various metallic-glass forming liquids, the temperature dependence of the average cluster size with $f^5 \geq 0.6$ shows similar behavior.[28] Furthermore, the largest cluster formed by the atoms of $f^5 \geq 0.6$ in a metallic glass-forming liquid is very small at high temperatures, growing rapidly with decreasing temperature, forming a network-like structure and percolating with temperature approaching T_g.[28] Thus, the choice of the threshold of $f^5 \geq 0.6$ is reasonable for cluster analysis. More detailed rationality of the choice of $f^5 \geq 0.6$ can be found in Ref. [28].

The spatial correlation of five-fold local symmetry and cluster formation indicates that the atoms with similar atomic environments in metallic liquids are spatially correlated as liquids are supercooled, reflecting the structural evolution in metallic liquids in glass transition. According to the above cluster analysis, a structure correlation length ξ_s in the liquids can be defined as $\xi_s = \sqrt[3]{\sum_i^n N_i^2 / \sum_i^n N_i}\,\langle d \rangle$, so that the temperature evolution of the structure correlation can be evaluated. Here $\langle d \rangle$ is the average diameter of the atoms determined by the first peak position of the pair correlation functions,[66,67] N_i represents the number of atoms of $f^5 \geq 0.6$ in the i-th cluster and n is the number of clusters. Figure 8 shows the evolution of the structure correlation length ξ_s as metallic liquids are cooled from high temperature to supercooled regions.[55] In various metallic glass-forming liquids, ξ_s exhibits similar temperature evolution behavior. The structure correlation length ξ_s is about $2\langle d \rangle$ in high temperature range, comparable to the nearest-neighbor distance. With decreasing temperature, ξ_s increases abruptly and reaches about $15\langle d \rangle$ below 800 K. If one takes the derivative of ξ_s against temperature, ξ_s changes qualitatively with temperature at two temperature points: T_A and T_S. It is clearly seen that ξ_s starts to increase rapidly at T_A, and the increase rate almost reaches its maximum at T_S.[55] The increase of ξ_s at T_A indicates that the structural correlation in the length scale starts to go beyond the nearest neighbors, corresponding to the cooperative motion of atoms as liquids are cooled down to T_A. At T_S, the response of the atomic structures in metallic liquids to temperature decrease reaches the maximum. Thus, the five-fold local symmetry reveals the characteristics of atomic structural evolution as the metallic glass-forming liquids are cooled from high temperature to supercooled regions. Such a structure correlation represented by five-fold local symmetry may provide the underlying structure basis for the dynamic crossover phenomena in liquids during

quenching, such as breakdown of Stokes–Einstein relation and dynamical heterogeneity.

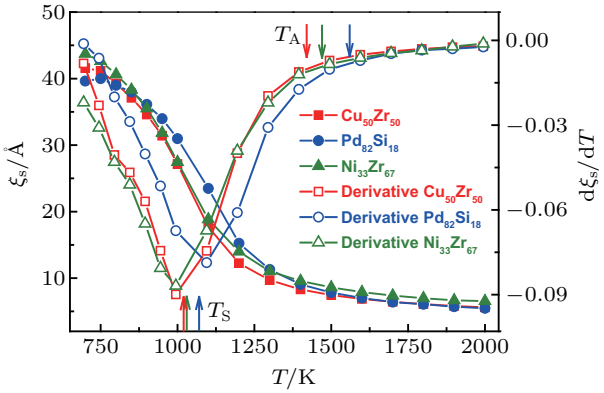


Fig. 8. (color online) Temperature evolution of the structure correlation length ξ_s of atoms with $f^5 \geq 0.6$ and its first derivatives against temperature in $Cu_{50}Zr_{50}$, $Ni_{33}Zr_{67}$, and $Pd_{82}Si_{18}$ metallic glass-forming liquids, respectively. Two characteristic temperature points T_A and T_S are marked, respectively (reproduced from Ref. [55]).

4.2. Correlation between FFLS and dynamic crossover phenomena

As a liquid is quenched from high temperature above melting point T_m toward glass transition temperature T_g, it becomes progressively viscous and the dynamics changes significantly, exhibiting dynamic crossover and some intriguing dynamic phenomena.[64,68–77] During quenching, shear viscosity or structural relaxation time in liquids shows Arrhenius to non-Arrhenius temperature dependent behavior.[64,68–75] In addition, diffusion coefficient D and structural relaxation time τ_α follow the Stokes–Einstein (SE) relation $D \propto (\tau_\alpha/T)^{-1}$ as T is above a temperature point, but deviate and follow a fractional SE relation $D \propto (\tau_\alpha/T)^{\kappa}$ with $-1 < \kappa < 0$ as temperature further decreases.[68,71,75–77] Upon quenching, the local dynamics in liquids becomes increasingly spatially heterogeneous, leading to the so-called dynamical heterogeneity.[68,78–80] Despite numerous efforts, the underlying structure origin as well as the relationship among these dynamic crossover phenomena is still elusive or even controversial. The structural correlation length characterized by the five-fold local symmetry provides a universal structure picture for better understanding these dynamic crossover phenomena in metallic glass-forming liquids.

It is found that during cooling, the dynamics of the metallic melts slows down dramatically and the structural relaxation time transfers from Arrhenius to non-Arrhenius behavior at T_A.[55] Meanwhile, D as a function of τ_α/T obeys SE relation above T_A. Below T_A, however, the behavior of $D \sim \tau_\alpha/T$ deviates from the SE relation, and follows the so-called fractional SE relation as temperature decreases below T_S.[55] It is further revealed that in cooling process, the metallic glass-forming liquids keep the homogenous feature in dynamics until temperature decreases to T_S. Below T_S, the dynamics in metallic liquids becomes spatially heterogeneous.[55] Therefore, at T_S, the dynamics in the liquids experiences a crossover from homogeneous to heterogeneous feature. The two crossover temperatures T_A and T_S ($T_A > T_S$) illustrate the dynamic crossover metallic liquids experience as they are quenched. Moreover, T_A and T_S are coincident with the characteristic temperature points of the structural correlation length as a function of temperature, as shown in Fig. 8.[55] Thus, these intriguing dynamic crossover phenomena can be well understood based on the structure correlation length associated with five-fold local symmetry in metallic glass-forming liquids.

Above T_A, the structural fluctuation in liquids is instantaneous, due to the flat potential energy landscape in high-temperature liquids, so that the size and lifetime of the clusters formed by the atoms with high FFLS are very small and short, resulting in Brownian-like dynamics and the Arrhenius relaxation behavior. As temperature decreases below T_A, due to the appearance of some local shallow minima in the potential energy landscape,[69,81] the lifetime of the clusters gets longer, and the structure correlation becomes significant. The motion of atoms tends to be cooperative, leading to the breakdown of SE relation. With further decreasing temperature, the clusters grow and the structure correlation increases. The development of the structure correlation provides a precondition for the corresponding dynamic evolution in liquids. At T_S, in potential energy landscape, and the structures in liquids reach a critical state and different deep local minima are developed, which results in the emergence of dynamic heterogeneity and fractional SE relation. Thus, the structural heterogeneity associated with the strong spatial correlation of FFLS correlates remarkably with dynamic crossover and plays a role of a structure precursor for the occurrence of dynamic heterogeneity.

5. The role of FFLS in liquid–liquid transition in metallic glass-forming liquids

Recently, a liquid–liquid transition (LLT) has been observed in glass-forming $La_{50}Al_{35}Ni_{15}$ melt above its liquidus temperature using ^{27}Al nuclear magnetic resonance which is very sensitive to the changes of atomic structures and dynamics of liquids.[56] It is found that the liquid exhibits a sudden change in the temperature dependence of dynamics characterized by a sharp change in the temperature dependence of Knight shift and quadrupolar spin-lattice relaxation rate, respectively.[56] In *ab initio* molecular dynamics simulations for $La_{50}Al_{35}Ni_{15}$ melt, the atomic diffusion coefficient was calculated and an abnormal temperature dependent behavior of diffusion was revealed in the temperature range of LLT, in good agreement with experimental observations.[56] However, it is found that the change in density is insignificant in the temperature range of LLT. Similar LLT was also reported in glass-forming liquid of ZrTiCuNiBe[82] in the undercooled regime below the liquidus temperature, and no substantial change of

volume related to LLT was detected, either. Such LLT observed in metallic glass-forming liquids is totally different from that observed in Ce and P where density exhibit drastic change under pressure, due to the unique electronic structures in Ce and P atoms.[83,84] For instance, Ce atom contains either a trivalent $4f^1(5d6s)$ or a tetravalent $4f^0(5d6s)$ electronic structure,[83,85] the latter having smaller ionic size under high pressure, so that a LLT in liquid Ce was observed with a 14% change in density at 13 GPa. In the case of $La_{50}Al_{35}Ni_{15}$ melt, however, density is not the dominant order parameter for describing the observed LLT. The question is what structure parameter is responsible for the LLT observed in metallic glass-forming liquids.

The agreement of the temperature dependent behavior of atomic diffusion between experiments and *ab initio* MD simulations provides an opportunity to elucidate the nature of atomic structural changes associated with the LLT.[56] Further structural analysis based on *ab initio* MD simulations reveals that while the change in density is insignificant, the bond-orientational order (BOO) parameter, a sensitive measure to the change of local structures,[6,7] exhibits a drop in the temperature range of LLT.[56] Figure 9 shows the temperature dependence of the averaged $\hat{W}_6$ which is sensitive to the appearance of five-fold symmetry in $La_{50}Al_{35}Ni_{15}$ melt. It is clear that the values of the average $\hat{W}_6$ change slightly between -0.018 and -0.019 in the temperature range above 1050 K, but drops to -0.021 below 1000 K, indicating that $La_{50}Al_{35}Ni_{15}$ melt changes its state from one with lower fraction of five-fold symmetry above the transition region to one with higher fraction of five-fold symmetry below the transition region. This indicates that local atomic symmetry may be an order parameter which is responsible for the underlying structure basis of the LLT observed in $La_{50}Al_{35}Ni_{15}$ melt.

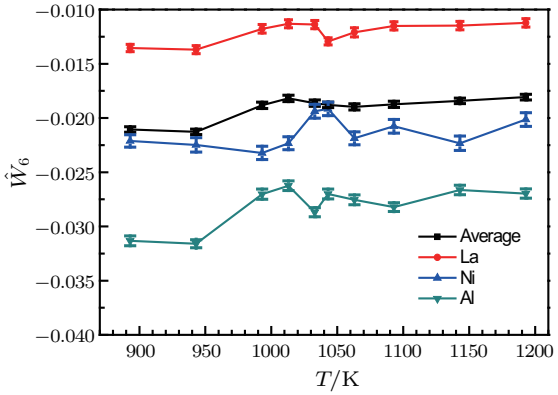


Fig. 9. (color online) Temperature dependence of the averaged $\hat{W}_6$ (squared). The abrupt change of the averaged $\hat{W}_6$ indicates $La_{50}Al_{35}Ni_{15}$ melt changes its state in LLT. The evolution of $\hat{W}_6$ of individual elements La, Ni, and Al with temperature are also shown, respectively. The temperature-induced variations of $\hat{W}_6$ of individual elements are coupled and influence each other. The preference of icosahedral order for one element could be at the cost of others (reproduced from Ref. [56]).

According to the above findings, apart from the order parameter of density, there exists another order parameter of local atomic symmetry represented by the local favored structures in describing the dynamics in metallic melts. This is consistent with the two-order-parameter theory proposed by Tanaka for understanding the critical problems associated with liquid state, such as liquid–liquid transition, liquid–glass transition, crystallization, in a unified manner.[86] In this two-order parameter theory, two order parameters, density ρ and local bond order parameter S characterized by BOO, are invoked in describing LLT. It is proposed that there exist distinct locally favored structures that are energetically more favorable and its population is defined as the order parameter S. With this local bond order parameter S, the phenomenological liquid-state free-energy functional associated with locally favored structures is given by[86,87]

$$f(S) = \int \mathrm{d}\boldsymbol{r}\big[-\Delta G S(\boldsymbol{r}) + JS(\boldsymbol{r})(1-S(\boldsymbol{r})) + k_{\mathrm{B}}T\left(S(\boldsymbol{r})\ln S(\boldsymbol{r}) + (1-S(\boldsymbol{r}))\ln(1-S(\boldsymbol{r}))\right)\big],$$

where $\Delta G = \Delta E - T\Delta\sigma - \Delta vP$ is the free energy change associated with the formation of a locally favored structure, and J is the cooperativity strength. These locally favored structures interact with the surrounding environment represented by a term $JS(\boldsymbol{r})(1-S(\boldsymbol{r}))$ in the free energy, leading to the cooperativity. Thus, a thermodynamic phase transition in liquid could occur between two free energy valleys, which are determined by two distinct values of the order parameter S. Therefore, a LLT could correspond to a sudden change of S associated with a change of BOO. In the case of $La_{50}Al_{35}Ni_{15}$ melt, a sudden change of BOO represented by the averaged $\hat{W}_6$ indeed occurs before and after the LLT,[56] indicating a substantial increase of locally favored structures with enhanced five-fold local symmetry below the LLT point. The above findings demonstrate that the five-fold local symmetry, as an order parameter, plays a key role in LLT observed in metallic liquids.

6. Correlation between five-fold local symmetry and deformation in MGs

Five-fold local symmetry was also found to be able to characterize irreversible atomic rearrangements in the plastic deformation of metallic glasses. It is observed in MD simulations that the degree of the irreversible atomic rearrangements increases as FFLS in local atomic structures decreases,[30] so that the local atomic symmetry in local structures may have significant impact on their response to deformation in metallic glasses. Here the irreversible atomic rearrangements can be characterized by the non-affine displacements.[30,88–90] Figure 10 clearly illustrates that the irreversible atomic rearrangements in deformation tend to avoid the local structures having higher degree of FFLS, but prefer to occur in regions with

less degree of FFLS.[21] It is also found that in the early stage of deformation, the irreversible atomic rearrangements tend to occur in those regions with less FFLS. Meanwhile, the local structures response to the deformation accordingly, lowering FFLS in them. As metallic glasses are deformed to some extent, the local structures reach a saturated situation in which LFFS cannot be reduced anymore. Further deformation will be transformed into the less deformed regions where the degree of LFFS should be relatively higher. This indicates that the plastic deformation is initiated in the regions with less FFLS. As strain increases, the plastic deformation is propagating to the regions with more FFLS in metallic glasses. Therefore, FFLS in metallic glasses can simply capture the local structural features responding to the plastic deformation.

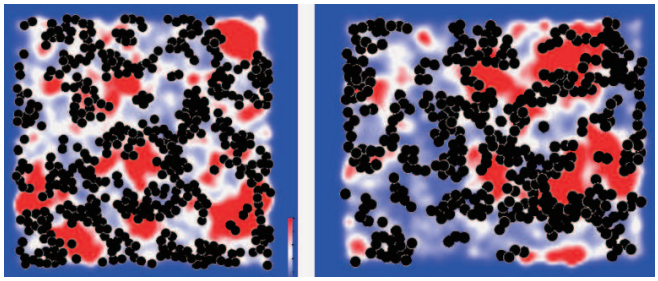


Fig. 10. (color online) Correlation between local structures with more degree of LFFS and the irreversible atomic rearrangement during deformation. A slice in the middle of the samples along Z direction with a thickness of the first minimum of the pair correlation function is taken for the illustration. Black points represent the atoms having more degree of LFFS ($f^5 \geq 0.5$) at the strain of 5% (a) and 10% (b). The red and blue areas are the mostly deformed regions emerged in the time interval of 40 ps and the less deformed regions, respectively (reproduced from Ref. [30]).

7. Conclusion and perspectives

So far, both experiments and theoretical simulations show the evidence that metallic liquids and glasses contain both five-fold local symmetry and partially crystalline symmetry. As liquids are quenched to form glassy states, the population of five-fold local symmetry increases, and the temperature dependent behavior coincides with the glass transition, indicating that five-fold local symmetry may be a simple and general structure parameter for the understanding of atomic structure feature and structure–property relationship in metallic liquids and glasses. Recent studies have clearly shown that five-fold local symmetry is able to provide a general description for the structure evolution, relaxation dynamics, and dynamic crossover phenomena in glass transition. The atoms with larger five-fold local symmetry exhibit strong spatial correlation, and tend to form clusters which are percolating in glass transition. This structure parameter can also provide deep understanding for plastic deformation mechanism in metallic glasses. Furthermore, the local bond order parameter associated with five-fold local symmetry is also found to be responsible for LLT in metallic glass-forming liquids. All these findings show the importance of five-fold local symmetry in metallic liquids and glasses.

Although five-fold local symmetry has been observed in metallic liquids and glasses, it is quite difficult to quantitatively measure the population. The experimental measurement of five-fold local symmetry could definitely boost the research on the fundamental issues related to liquid structure and dynamics and glass transition, and promote the application of metallic glasses in industry and engineering. A simple but rough definition was proposed for five-fold local symmetry in theoretical simulations. A more accurate definition is desirable. To realize that, some new structure analysis methods for disordered materials have to be developed in future.

References

[1] Cheng Y Q and Ma E 2011 *Prog. Mater. Sci.* **56** 379
[2] Turnbull D 1952 *J. Chem. Phys.* **20** 411
[3] Frank F C 1952 *Proc.R. Soc. Lond. A* **215** 43
[4] Voronoi G 1908 *J. Reine Angew Math.* **134** 198
[5] Borodin V A 1999 *Phil. Mag. A* **79** 1887
[6] Steinhardt P J, Nelson D R and Ronchetti M 1981 *Phys. Rev. Lett.* **47** 1297
[7] Steinhardt P J, Nelson D R and Ronchetti M 1983 *Phys. Rev. B* **28** 784
[8] Honeycutt J D and Andersen H C 1987 *J. Phys. Chem.* **91** 4950
[9] Clarke A S and Jonsson H 1993 *Phys. Rev. E* **47** 3975
[10] Sheng H W, Luo W K, Alamgir F M, Bai J M and Ma E 2006 *Nature* **439** 419
[11] Li M Z, Wang C Z, Hao S G, Kramer M J and Ho K M 2009 *Phys. Rev. B* **80** 184201
[12] Cicco A D, Trapananti A and Faggioni S 2003 *Phys. Rev. Lett.* **91** 135505
[13] Saksl K, Franz H, Jovari P, Klementiev K, Welter E, Ehnes A, Saida J, Inoue A and Jiang J Z 2003 *Appl. Phys. Lett.* **83** 3924
[14] Luo W K, Sheng H W, Alamgir F M, Bai J M, He J H and Ma E 2004 *Phys. Rev. Lett.* **92** 145502
[15] Shen Y T, Kim T H, Gangopadhyay A K and Kelton K F 2009 *Phys. Rev. Lett.* **102** 057801
[16] Cheng Y Q, Sheng H W and Ma E 2008 *Phys. Rev. B* **78** 014207
[17] Wang S Y, Wang C Z, Li M Z, Huang L, Ott R T, Kramer M J, Sordelet D J and Ho K M 2008 *Phys. Rev. B* **78** 184204
[18] Hao S G, Wang C Z, Li M Z, Napolitano R E and Ho K M 2011 *Phys. Rev. B* **84** 064203
[19] Wang Q, Liu C T, Yang Y, Dong Y D and Lu J 2011 *Phys. Rev. Lett.* **106** 215505
[20] Soklaski R, Nussinov Z, Markow Z, Kelton K F and Yang L 2013 *Phys. Rev. B* **87** 184203
[21] Wu Z W, Li M Z, Wang W H and Liu K X 2013 *Phys. Rev. B* **88** 054202
[22] Finney J L 1977 *Nature* **266** 309
[23] Qi D W and Wang S 1991 *Phys. Rev. B* **44** 884
[24] Sha Z D, Wu R Q, Lu Y H, Shen L, Yang M, Cai Y Q, Feng Y P and Li Y 2009 *J. Appl. Phys.* **105** 043521
[25] Peng H L, Li M Z, Wang W H, Wang C Z and Ho K M 2010 *Appl. Phys. Lett.* **96** 021901
[26] Huang L, Wang C Z, Hao S G, Kramer M J and Ho K M 2010 *Phys. Rev. B* **81** 014108
[27] Senkov O N, Cheng Y Q, Miracle D B, Barney E R, Hannon A C and Woodward C F 2012 *J. Appl. Phys.* **111** 123515
[28] Hu Y C, Li F X, Li M Z, Bai H Y and Wang W H 2015 *Nat. Commun.* **6** 8310
[29] Spaepen F 2000 *Nature* **408** 781
[30] Peng H L, Li M Z and Wang W H 2011 *Phys. Rev. Lett.* **106** 135503
[31] Li M Z 2014 *J. Mater. Sci. Technol.* **30** 551
[32] Reichert H, Klein O, Dosch H, Denk M, Honkimaki V, Lippmann T and Reiter G 2000 *Nature* **408** 839
[33] Hirata A, Kang L J, Fujita T, Klumov B, Matsue K, Kotani M, Yavari A R and Chen M W 2013 *Science* **341** 376

[34] Xi X K, Li L L, Zhang B, Wang W H and Wu Y 2007 *Phys. Rev. Lett.* **99** 095501
[35] Sandor M T, Ke H B, Wang W H and Wu Y 2013 *J. Phys.: Condens. Matter* **25** 165701
[36] Wakeda M, Shibutani Y, Ogata S and Park J 2007 *Intermetallics* **15** 139
[37] Cheng Y Q, Cao A J and Sheng H W 2008 *Acta Mater.* **56** 5263
[38] Hargittai I 1999 *Fivefold Symmetry* (Singapore: World Scientific)
[39] Bagley B G 1965 *Nature* **208** 674
[40] Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
[41] Caspar D L and Fontano E 1996 *Proc. Natl. Acad. Sci. USA* **93** 14721
[42] Van Raaij M J, Mitraki A, Lavigne G and Cusack S 1999 *Nature* **401** 935
[43] Royall C P, Williams S R, Ohtsuka T and Tanaka H 2008 *Nat. Mater.* **7** 556
[44] Wochner P, Gutt C, Autenrieth T, Demmer T, Bugaev V, Ortiz A D, Duri A, Zontone, Grubel G and Dosch H 2009 *Proc. Natl. Acad. Sci. USA* **106** 11511
[45] Li J D, Cao Y X, Xia C J, Kou B Q, Xiao X H, Fezzaa K and Wang Y J 2014 *Nature Commun.* **5** 5014.
[46] Shintani H and Tanaka H 2008 *Nat. Mater.* **7** 870
[47] Shintani H and Tanaka H 2006 *Nat. Phys.* **2** 200
[48] Starr F W, Sastry S, Douglas J F and Glotzer S C 2002 *Phys. Rev. Lett.* **89** 125501
[49] Jackle J 1986 *Rep. Prog. Phys.* **49** 171
[50] Kob W and Andersen H C 1995 *Phys. Rev. E* **52** 4134
[51] Angell C A 1995 *Science* **267** 1924
[52] Gao W, Feng S D, Qi L, Zhang S L and Liu R P 2015 *Chin. Phys. Lett.* **32** 116101
[53] Wessels V, Gangopadhyay A K, Sahu K K, Hyers R W, Canepari S M, Rogers J R, Kramer M J, Goldman A I, Robinson D, Lee J W, Morris J R and Kelton K F 2011 *Phys. Rev. B* **83** 094116
[54] Lu I R, Wilde G, Gorler G P and Willnecker R 1999 *J. Non-Cryst. Solids* **250–252** 577
[55] Hu Y C, Li F X, Li M Z, Bai H Y and Wang W H 2016 *J. Appl. Phys.* **119** 205108
[56] Xu W, Sandor M T, Yu Y, Ke H B, Zhang H P, Li M Z, Wang W H, Liu L and Wu Y 2015 *Nat. Commun.* **6** 7696
[57] Li Y, Bai H Y, Wang W H and Samwer K 2006 *Phys. Rev. B* **74** 052201
[58] Ke H B, Wen P, Zhao D Q and Wang W H 2010 *Appl. Phys. Lett.* **96** 251902
[59] Ding J, Cheng Y Q, Sheng H W and Ma E 2012 *Phys. Rev. B* **85** 060201
[60] Ding J, Cheng Y Q and Ma E 2013 *Acta Mater.* **61** 3130
[61] Trachenko K and Brazhkin V V 2011 *Phys. Rev. B* **83** 014201
[62] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
[63] Angell C A 1995 *Science* **267** 1924
[64] Royall C P and Williams S R 2015 *Phys. Rep.* **560** 1
[65] Donati C, Glotzer S C, Poole P H, Kob W and Plimpton S J 1999 *Phys. Rev. E* **60** 3107
[66] Kawasaki T and Tanaka H 2010 *Proc. Natl. Acad. Sci. USA* **107** 14036
[67] Heussinger C, Berthier L and Barrat J L 2010 *Eruophys. Lett.* **90** 20005
[68] Ediger M D 2000 *Annu. Rev. Phys. Chem.* **51** 99
[69] Andersen H C 2005 *Proc. Natl. Acad. Sci. USA* **102** 6686
[70] Roland C M 2008 *Soft Matter* **4** 2316
[71] Mallamace F, Branca C, Corsaro C, Leone N, Spooren J, Chen S H and Stanley H E 2010 *Proc. Natl. Acad. Sci. USA* **107** 22457
[72] Iwashita T, Nicholson D M and Egami T 2013 *Phys. Rev. Lett.* **110** 205504
[73] Ngai K 2011 *Relaxation and Diffusion in Complex Systems* (New York: Springer)
[74] Debenedetti P G and Stillinger F H 2001 *Nature* **410** 259
[75] Tarjus G and Kivelson D 1995 *J. Chem. Phys.* **103** 3071
[76] Becker S R, Poole P H and Starr F W 2006 *Phys. Rev. Lett.* **97** 055901
[77] Xu L, Mallamace F, Yan Z, Starr F W, Buldyrev S V and Stanley H E 2009 *Nat. Phys.* **5** 565
[78] Kob W, Donati C, Plimpton S J, Poole P H and Glotzer S C 1997 *Phys. Rev. Lett.* **79** 2827
[79] Widmer-Cooper A, Harrowell P and Fynewever H 2004 *Phys. Rev. Lett.* **93** 135701
[80] Royall C P, Williams S R, Ohtsuka T and Tanaka H 2007 *Nat. Mater.* **7** 556
[81] Tanaka H 2005 *J. Non-Cryst. Solids* **351** 3385
[82] Wei S, Yang F, Bednarcik J, Kaban I, Shuleshova O, Meyer A and Busch R 2013 *Nat. Commun.* **4** 2083
[83] Cadien A, Hu Q Y, Cheng Y Q, Chen M W, Shu J F, Mao H K and Sheng H W 2013 *Phys. Rev. Lett.* **110** 125503
[84] Katayama Y, Mizutani T, Utsumi W, Shimomura O, Yamakata M and Funakoshi K 2000 *Nature* **403** 170
[85] Poole P H 1997 *Science* **275** 322
[86] Tanaka H 2012 *Eur. Phys. J. E* **35** 113
[87] Tanaka H 2000 *Europhys. Lett.* **50** 340
[88] Falk M L and Langer J S 1998 *Phys. Rev. E* **57** 7192
[89] Shang B S, Li M Z, Yao Y G, Lu Y J and Wang W H 2014 *Phys. Rev. E* **90** 042303
[90] Ding J, Cheng Y Q and Ma E 2012 *Appl. Phys. Lett.* **101** 121917