Ideality of liquid structure: A case study for metallic alloy liquids

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Abstract

It is difficult to characterize by experiment the structural features of liquids and glasses which lack long-range translational periodicity in the structure. Here we suggest that the height and shape of the first peak of the structure function, $S(Q)$, carry significant information about the nature of the medium-range order and the coherence of density correlations. It is further proposed that they indicate how ideal the liquid structure is. Here the ideal state is defined by long-range density correlations, not by structural coherence at the atomic level. The analysis is applied to the $S(Q)$ of metallic alloy liquids determined by X-ray diffraction and simulation. The ideality index defined here may provide a common parameter to characterize structural coherence among various disparate groups of liquids and glasses.

The atomic structure of liquids and glasses has long been investigated by scattering experiments with X-rays and neutrons [1,2]. Usually the structure function, $S(Q)$, determined by experiment, is converted to the atomic pair-distribution function (PDF), $g(r)$, to discuss the local and medium-range structures. Interestingly, whereas the first peak of $g(r)$ varies with composition reflecting the differences in atomic sizes and the nature of bonding, the medium-range correlations beyond the first peak often appear similar, regardless of composition. This suggests that there may be features in the medium-range order (MRO) common or nearly universal to many liquids and glasses. In this Rapid Communication, we point out that the medium-range correlations in metallic liquids are characterized by the coherence in the coarse-grained density fluctuations, not by the structural coherence at the atomic level, and propose that the height and shape of the first peak of $S(Q)$ describe the ideality of the liquid structure, toward the ideal state having long-range density correlations.

For simple liquids, such as metallic liquids, the shape of the first peak is usually distinct from that of the higher order peaks for both $S(Q)$ and $g(r)$. The first peak is sharper, whereas the higher order peaks are of the damped sinusoidal form. It should be noted that the first peak of $S(Q)$ mainly reflects the higher order peaks of $g(r)$, thus MRO, whereas conversely the first peak of $g(r)$ chiefly depends on the higher order peaks of $S(Q)$ [2], as shown in Fig. 1 for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ glass at $T_g = 573K$. In the same manner, for complex liquids, such as oxides and polymers, the first sharp diffraction peak (FSDP) in $S(Q)$ describes the MRO [4-9]. Despite the importance, the nature of the first peak of $S(Q)$ are rarely discussed at the level beyond the full-width at half maximum (FWHM) and the values of the peak position Q_1.

The first peak of $g(r)$ describes the distribution of the distances to the near neighbor atoms from the central atom. The number of the near neighbors is called the coordination number, N_C, which is 4 for amorphous silicon and 12 – 14 for closed-packed metallic liquid

and glass. On the other hand, the higher order peaks represent groups of a larger number of atoms. For instance the n-th order peak describes the density of atoms of the order of $N_n \approx n^2 N_C$. Through the study of the time-delayed PDF, the Van Hove function, $G(r, t)$, it was found that the decay time of the higher order peaks is not the same as that of the first peak, but increases linearly with distance [10]. This is because the decay of the higher order peaks represents the dynamics of density fluctuations of many atoms, not diffusion of each atom, and thus it is proportional to $\sqrt{N_n} \propto n \propto r$. In other words, the higher order peaks in $g(r)$ describes coarse-grained density fluctuations, rather than the atomic-level structural fluctuations. This is understandable because the peak width of these peaks is of the order of 1 Å, whereas higher spatial resolution is required to specify the atomic structure. Whereas usually the medium-range order is considered to be a mere consequence of the short-range order, it is possible that the short- and medium-range orders are governed by different mechanisms. Even though microscopically the same forces are involved for both, the many-body nature of the medium-range correlations may add distinct emergent nature to the MRO [11].

Classic work by Ornstein-Zernike [12] predicts that the long-range part of $g(r)$ decays with r as $\exp(-r/\xi_s)/r$, where ξ_s is the structural coherence length. Its Fourier transformation is a Lorentzian function. Thus, the first peak of $S(Q)$ should be Lorentzian, because the primary contributions to the first peak of $S(Q)$ come from the long-range part of $g(r)$ [2]. We examined the shape of the first peak of $S(Q)$ for variety of metallic alloys studied in Ref. 3 and the models of Fe liquids with Yukawa, Lennard-Jones (LJ) and modified Johnson (mJP) potentials [13,14]. Most of the results were obtained by molecular dynamics simulation using the LAMMPS software, whereas the result for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ alloy system was obtained by X-ray diffraction with electrostatic levitation at the 6-ID-D beamline of the Advanced Photon Source

(APS), Argonne National Laboratory. The details of the determination of S(Q) are described in Ref. 3 and the Supplemental Material.

We found that the first peak of $S(Q)$ for Fe (mJP) is fit better by the Lorentzian function than the Gaussian function, whereas that for ZrNi is fit better by the Gaussian function as shown in Fig. 2. In order to assess how the first peak shape deviates from the Lorentzian shape, we employed the Voigt profile, defined as the convolution of a Gaussian and a Lorentzian distribution [15]. The first peaks of $S(Q)$ in the liquid and glass states for twelve alloy systems and pure Fe are fit well by the Voigt profile defined as

$$y = y_0 + A \cdot \frac{2ln2}{\pi^{3/2}} \frac{W_L}{W_G^2} \cdot \int_{-\infty}^{\infty} \frac{e^{-t^2}}{\left(\sqrt{ln2}\frac{W_L}{W_G}\right)^2 + \left(\sqrt{4ln2}\frac{x-x_c}{W_G} - t\right)^2} dt$$

where W_L and W_G are the Lorentzian and Gaussian widths, as shown in Fig. S1 of the Supplemental Material. The peak is more Lorentzian for high values of the W_L/W_G ratio, and more Gaussian for low values of the W_L/W_G ratio. We found that the W_L/W_G ratio is strongly correlated to the height of the first peak, $S(Q_1) - 1$ at the glass transition temperature, T_g, as shown in Fig. 3. Because the height of the first peak scales with the structural coherence length, ξ_s [3], this result indicates that the more coherent is the structure, the more Lorentzian is the peak shape. The W_L/W_G ratio changes only moderately with temperature as shown in Fig. 4. Thus the height of the first peak, $S(Q_1) - 1$, as well as the W_L/W_G ratio at T_g can be considered as "parameters" of the structural coherence.

In Ref. 3 we defined the ideal liquid (glass) structure by extrapolating the coherence length, ξ_s, to infinity. More specifically, the reduced PDF, $G(r) = 4\pi\rho_0 r [g(r)-1]$, where ρ_0 is atomic number density, decays as $G(r) = G_0(r)\exp(-r/\xi_s)$. Therefore, we can obtain $G_0(r)$ by

multiplying $G(r)$ through $\exp(r/\xi_s)$. The structure thus attained has long-range density correlations, without structural periodicity. For this structure the first peak of $S(Q)$ is a δ-function, forming a Bragg sphere in three-dimensional Q space, just as for a crystalline powder. Unlike a crystalline powder, however, there is only one Bragg sphere. Therefore, the higher value of $S(Q_1) - 1$ means the structure closer to the ideal structure. In the same way the higher value of the W_L/W_G ratio also indicates the structure closer to ideality. Thus, both the values of $S(Q_1) - 1$ and the W_L/W_G ratio can be considered as the idealism indices (II).

Here the ideality of the structure does not mean the structural coherence at the atomic scale. The coherence indicated by the first peak is that of coarse-grained density fluctuations, not that of the atomic structure. Actually the model of the ideal glass has extremely diverse local structures with little atomic-level structural coherence [3], totally different from the model of ideal structure dominated by local icosahedral clusters [16-18]. This density coherence supersedes chemistry, and is not much dependent on the nature of the interatomic potential. For instance, the three different potentials for Fe, ranging from the purely repulsive, hard-sphere-like Yukawa potential (Yukawa) to very harmonic Johnson potential (mJP), all result in high values of $S(Q_1) - 1$ and the W_L/W_G ratio.

The wide variety in the values of $S(Q_1) - 1$ at T_g defies the commonly used Hansen-Verlet criterion for glass transition [19]. A possible origin of this variety is the complexity in atomic sizes of the constituent elements. To test this idea, we calculated the average atomic-level volume strain,

$$\varepsilon_v = \left(\sum_\alpha c_\alpha \left(\varepsilon_{v,\alpha} \right)^2 \right)^{1/2}$$

where c_α and $\varepsilon_{v,\alpha}$ are the concentration and volume strain of the element α,

$$\varepsilon_{v,\alpha} = \frac{V_\alpha}{\langle V \rangle} - 1, \qquad V_\alpha = \frac{4\pi}{3} R_\alpha^3, \qquad \langle V \rangle = \sum_\alpha c_\alpha V_\alpha$$

and R_α is the metallic atomic radius of the element α [20]. As shown in Fig. 5 the correlation between the W_L/W_G ratio and ε_v is weak or non-existent, suggesting that the atomic size variation is not the main origin of ideality. Furthermore, a chemically complex alloy, $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, shows excellent coherence. It is possible that the high structural coherence of this alloy, which results in high viscosity [12], is related to the exceptional glass stability of this alloy [21].

The exponential decay of $|G(r)|$ is compared for two liquids, Fe (mJP) which is close to ideal ($W_L/W_G = 2.52$) and $Pd_{82}Si_{18}$ which is far from ideal ($W_L/W_G = 0.35$), in Fig. 6. Whereas the $|G(r)|$ for Fe follows the expected exponential decay quite well with a single sinusoidal oscillation, the $|G(r)|$ for $Pd_{82}Si_{18}$ deviates significantly from the expected line, indicating the presence of multiple components of oscillation. It is possible that the strong short-range order around Si because of covalent Pd-Si bond [22, 23] is biasing the density correlations. The theory by Ornstein and Zernike presumes spherical interatomic potentials [12]. Strongly directional covalent bonds could cause deviations from the exponential decay behavior. These results suggest that there must be deep and multiple causes of ideality, which requires further study.

It is interesting to note that the W_L/W_G ratio can show notable variation above T_g, as shown in Fig. S4. The temperature where the W_L/W_G ratio becomes maximum is very close to the critical temperature T_c for the mode coupling theory (MCT) [24], for $Zr_{64}Ni_{36}$ ($T_c = 927K$ [25]) and $Pd_{43}Ni_{10}Cu_{27}P_{20}$ ($T_c = 710K$ [26]) alloy systems. However, these observations are not universal, and in most cases no anomaly is observed at T_c. The same applies to the viscosity crossover at T_A above which viscosity shows Arrhenius temperature dependence [27]. No

anomaly is seen at T_A, consistent with the idea that the Arrhenius crossover is purely dynamic, and not structural [28].

In conclusion, we found that the height of the first peak of the structure function, $S(Q_1)$ – 1, is closely related to the Lorentzian nature of the peak shape and to the coherence of the coarse-grained local density fluctuations in metallic liquids and glasses. Thus $S(Q_1)$ – 1 and the W_L/W_G ratio, which indicates the closeness of the peak shape to the Lorentzian form, are the ideality indices (II) of the liquid state; the higher are these values the more ideal is the structure. The ideality here does not imply structural coherence at the atomic level, but refers to the coherence in the coarse-grained density fluctuations which depends only weakly on chemistry. These parameters could provide common tools to characterize the structural coherence among various disparate groups of liquids and glasses.

Acknowledgment:

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Figure captions:

Fig. 1 (a) $F(Q) = Q[S(Q) - 1]$ for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ glass at $T_g = 573K$ (solid curve), and the first peak (dotted curve), Fourier-transformed to (b) $G(r) = 4\pi\rho_0 r[g(r) - 1]$ where ρ_0 is atomic number density (solid curve), and the Fourier-transformed first peak of $S(Q)$ (dotted curve). The data for $S(Q)$ and G(r) are from Ref. 3.

Fig. 2 Fit for the first peak of $S(Q)$ determined by molecular dynamics simulation: (a) Fe (mJP) at 1000K (b) $Zr_{50}Ni_{50}$ at 750K. Gaussian fits are shown by navy dash-dots and Lorentzian function fits by orange dots.

Fig. 3 The height of the first peak of the structure function, $S(Q_1) - 1$, at the glass transition temperature, T_g, plotted against the W_L/W_G ratio in logarithmic scale for various alloy liquids by molecular dynamics simulation, and the experimental result for $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$.

Fig. 4 Variation of the W_L/W_G ratio with temperature for various alloy liquids.

Fig. 5 The plot of average atomic-level volume strain, ε_v, against the W_L/W_G ratio for various alloys at T_g.

Fig. 6 The Exponential decay of $|G(r)|$ for (a) Fe (mJP) at 1000K (b) $Pd_{82}Si_{18}$ at 800K. The dotted yellow line is a linear guide to the eye and its slope gives the inverse of the structural coherence length.
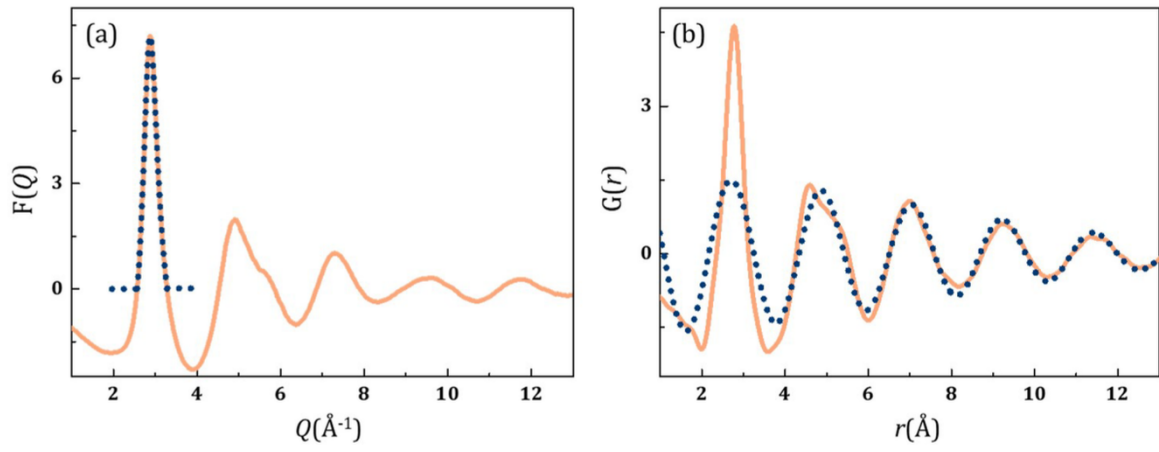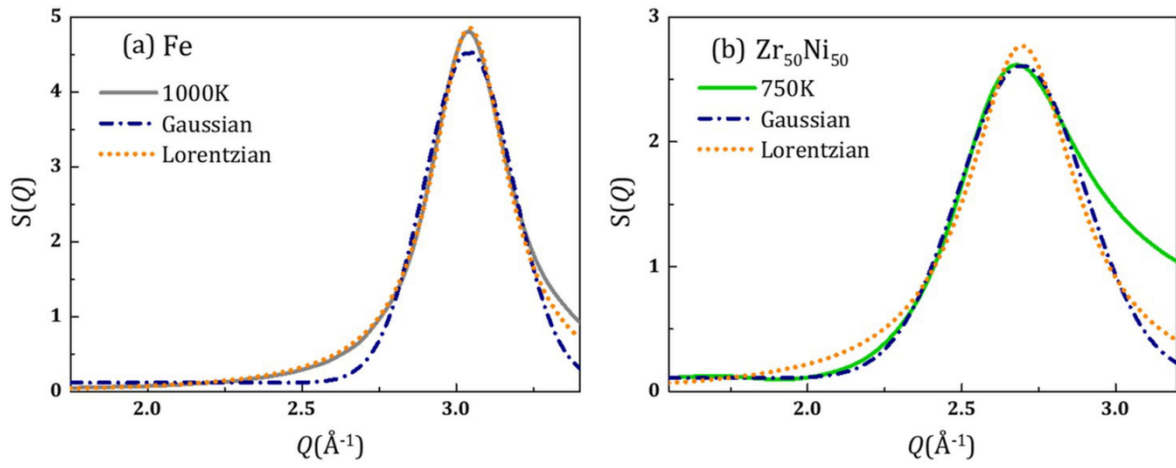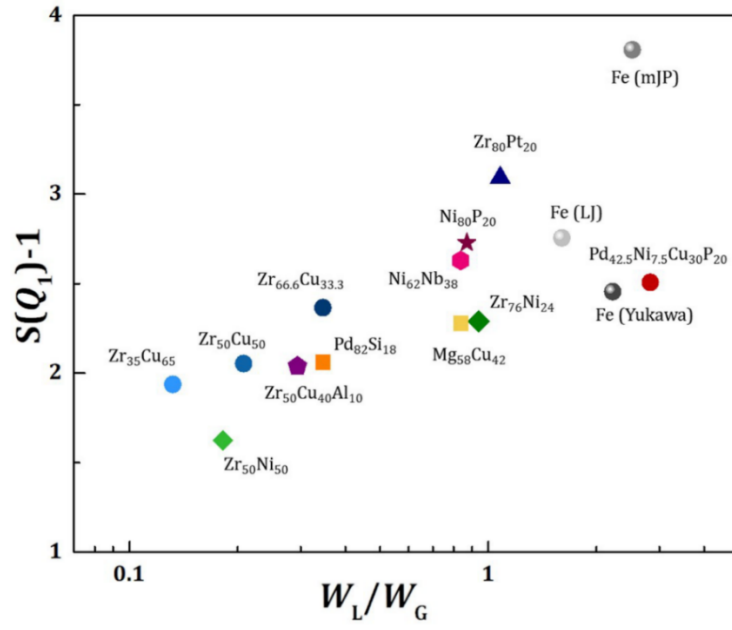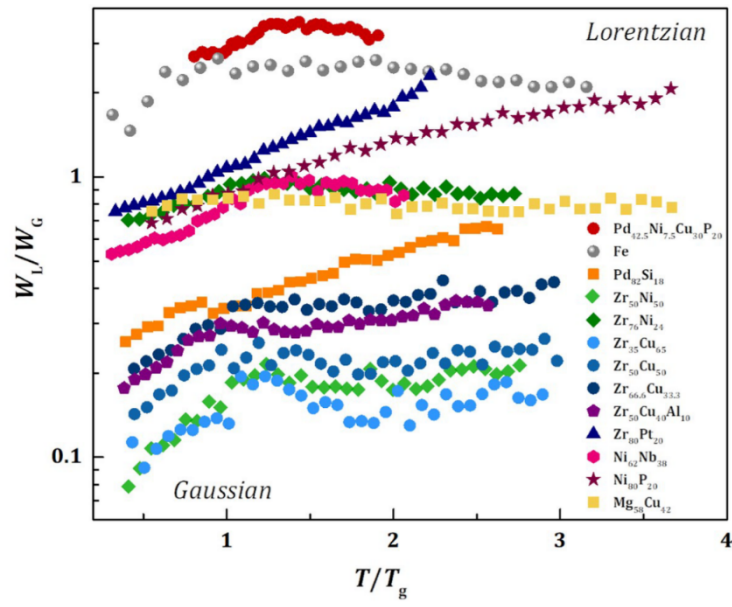
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