Dynamics in $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts: Interplay between packing density and viscosity

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We have investigated microscopic dynamics in the bulk glass-forming $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts using quasielastic neutron scattering (QENS). Self-correlation functions show a fast β and a slow α -relaxation process. α relaxation exhibits stretching and is independent of momentum transfer and temperature. The melt is characterized by low packing density and high viscosity. The dynamics observed and the critical packing density derived from the QENS data are in good agreement with mode-coupling theory predictions for hard-sphere liquids. However, we can show that viscosity dominates over packing density in determining the atomic dynamics and glass-forming ability of the metallic melt. © 2009 American Institute of Physics. [DOI: 10.1063/1.3142389]

Even though there is no direct correlation between density (ρ) and viscosity (η) of liquids, the glass-forming melts are found to be highly dense and viscous. For example, the η of the best glass-forming metallic liquids like $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ (Ref. 1) (PdNiCuP) and $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Ni}_{10}\text{Cu}_{12.5}\text{Be}_{22.5}$ (Ref. 2) is about three to four times larger than that of simple metallic and binary alloy liquids at their melting temperatures³ (T_m). The ρ of metallic liquids can be better represented by packing density (φ), which is about 25%–35% higher than that of simple liquid metals.^{3,4} If we compare the η and φ of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ (Ref. 5) and $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ melts,⁴ the η of the former is greater than that of the latter but the φ is larger for $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$. Both melts are glass forming but the glass-forming ability (GFA) is different.^{6,7} We have studied the microscopic dynamics in $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ previously by QENS.⁴ In this letter, we report on our research in to bulk glass-forming $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts using QENS to understand the influence of the interplay between φ and η in microscopic dynamics and GFA of metallic melts.

Details of experiments as described in Ref. 8. Only Cu atoms possess incoherent scattering cross section in this alloy. So the resulting self-correlation functions $\Phi(q,t)$ represent the mean dynamics of Cu atoms in the melt. The sample was measured at room temperature to obtain the instrument energy resolution function. In the melt, the sample was measured at 1130 K, which was close to the T_m and at four more temperatures up to 1330 K with a step interval of 50 K. The data were collected over a period of 4–5 h at each temperature. The scattering law, $S(q,\omega)$, was determined by normalizing the raw data to a vanadium standard, correcting for self-absorption and container scattering, interpolating to constant q , and symmetrizing with respect to energy with the detailed balance factor. Fourier deconvolution of $S(q,\omega)$ and normalization to 1 for $t=0$ gives the $\Phi(q,t)$. Figure 1 displays the $\Phi(q,t)$ of the liquid $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ at $q = 1.09 \text{ \AA}^{-1}$, which clearly shows a two-step relaxation process. Between 0 and 0.3 ps, phonon leads to a rapid decay of

$\Phi(q,t)$. As time increases, $\Phi(q,t)$ shows almost a constant value or a plateau for f_q . On approaching this plateau, before $\Phi(q,t)$ decays toward zero, a fast relaxation is clearly visible. Since the vibrational part of the spectrum [represented by the first data point in $\Phi(q,t)$] is well separated from the relaxational parts, this gives an advantage for investigating the picosecond dynamics in the vicinity of f_q , the fast β -relaxation process. According to mode-coupling theory (MCT), the time correlation function of the dynamical variable in the β -relaxation regime is expected to follow⁹ as

$$\Phi_q(t) = f_q + h_q g_\lambda(t/t_\sigma), \quad (1)$$

where the time dependent term $g_\lambda(t/t_\sigma)$ is completely determined by a single unique exponent parameter λ . Here, f_q is the Debye–Waller factor, h_q is the amplitude of β relaxation, and t_σ is the crossover time. The theory predicts the temperature variation of t_σ and h_q with the asymptotic scaling functions

$$h_q \propto (T - T_c)^{1/2} \quad \text{and} \quad t_\sigma \propto (T - T_c)^{-1/2a}, \quad (2)$$

where the exponent a is determined by λ . The values of a , g_λ , and γ as a function of λ were obtained from Ref. 9. The

FIG. 1. (Color online) The $\Phi(q,t)$ of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts obtained on the neutron time-of-flight spectrometer, FOCUS. The solid lines are from fits using the MCT β -scaling law [Eq. (1)] with $\lambda=0.77$. The dotted lines are fits with the KWW function with $\beta_q=0.7$ in the α -relaxation regime.

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FIG. 2. (Color online) (a) The ϕ depends on the mean relaxation time of the α -process rescaled using Eq. (3). The dotted lines are the linear fit crossing at zero, $\phi_c = 0.519 \pm 0.002$. (b) The temperature dependence of the amplitude $\langle h_q \rangle$ and time scale $\langle t_\sigma \rangle$ of the β -relaxation process according to Eq. (2). Both lines are extrapolated consistently to obtain the MCT T_c at 840 ± 5 K. The corresponding ϕ_c is 0.517 ± 0.002 .

two-step decay can be fitted with an MCT β -scaling law [Eq. (1)] in the range from 0.3 to 15 ps. Details of fitting iteration are described in Ref. 8. The temperature dependence of the amplitude h_q and the crossover time t_σ strongly indicate the slowing down of the relaxational dynamics upon cooling.

Figure 2(b) displays the temperature variation of h_q and t_σ for the fast β relaxation in liquid $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, given according to Eq. (2). The temperature dependence of h_q and t_σ is in accordance with the MCT predictions with an exponent $a=0.295$, based on $\lambda=0.77$. When h_q and t_σ are extrapolated T_{liq} , a consistent value for the MCT glass-transition temperature, $T_c=840 \pm 10$ K is obtained. In the fluid regime, the T_c derived from idealized MCT shows its universal character, i.e., $T_c \approx 1.2T_g$. The corresponding ϕ of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melt at 840 ± 10 K is 0.517 ± 0.002 . The $\Phi(q, t)$ in the α -relaxation time was fitted with Kohlrausch–Williams–Watts (KWW) function, $\Phi(q, t) = f_q \exp[-(t/\tau_q)^{\beta_q}]$ (Fig. 1). The data points were initially fitted using an arbitrary value for β_q . Over the assessable q range, β_q is found to vary around a value of 0.70 ± 0.04 . Further analysis was carried out by fixing the β_q value to a constant, 0.70. This fitting procedure shows that the data measured at different temperatures can be best described by a temperature and a q independent stretching exponent (β_q). MCT gives a microscopic explanation for stretching in terms of a nonlinear coupling of density fluctuation caused by a feedback effect in the dense liquids. On the other hand, η is characterized by resistance to move the atoms. So at high η and comparatively low ϕ , the feedback effect is negligible as compared to the viscous resistance. This in fact stabilizes the stretching of $\Phi(q, t)$ over wide temperature range. In contrast, $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ and $\text{Ni}_{59.5}\text{Nb}_{40.5}$ melt shows a temperature-dependent stretching. This is due to low η and high ϕ , and the ϕ changes with temperature which in turn reduces the feedback, as a consequence changing the β_q .

The resulting mean relaxation time obtained as $\langle \tau_q \rangle = \int_0^\infty \Phi(q, t) / f_q = \tau_q \beta_q^{-1} \Gamma(\beta_q^{-1})$, where Γ is the gamma function. In glass-forming liquids, $\langle \tau_\alpha \rangle$ of the collective motion of atoms are strongly influenced by the ϕ .¹⁰ The MCT predicts the variation of $\langle \tau_\alpha \rangle$ with ϕ as

FIG. 3. (Color online) q^2 depends on the inverse of $\langle \tau_q \rangle$ observed for five different temperatures. At $q \ll q_0$, which shows a linear dependence. The straight line is the linear fit and the slope gives the D .

$$\langle \tau_\alpha \rangle^{-1/\gamma} \propto [\phi - \phi_c]. \quad (3)$$

Figure 2(a) displays $\langle \tau_\alpha \rangle^{-1/\gamma}$ as a function of the ϕ with $\gamma = 2.7$ for the three different values of q . The variation of $\langle \tau_\alpha \rangle^{-1/\gamma}$ with ϕ is linear, as predicted by the MCT. Linear fits to the data points cross at zero, where the viscous flow arrest and hopping process become the dominant transport mechanism or the ϕ_c . The values of ϕ_c obtained from the above analysis was 0.519 ± 0.001 .

Additionally, $\langle \tau_\alpha \rangle$ is proportional to $1/q^2$ as expected in the hydrodynamic limit for $q \ll q_0$ ¹¹ (Fig. 3). This enables us to determine the average self-diffusivity $D = \frac{1}{q^2 \langle \tau_q \rangle}$. The D obtained at 1130 K is $1.82 \pm 0.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and at the highest measured temperature, i.e., at 1330 K, D obtained was $9.60 \pm 0.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This is comparatively larger than the better metallic glass-forming $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ ($D = 3 \pm 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$),¹² $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, and $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ at their liquidus temperatures.¹³ The temperature dependence of the D is well described by a τ scaling law of MCT, $D \propto [(T - T_c)/T_c]^\gamma$. In Fig. 4, the solid line is the τ -scaling law fit to the measured D with $T_c = 900$ K and $\gamma = 2.7$. The ϕ_c at 900 K is 0.516 ± 0.001 .

The average value for ϕ_c obtained from β relaxation, $\langle \tau_\alpha \rangle$ of the α process, and τ -scaling analysis is 0.517 ± 0.003 . This value is about 6.3% lower than that observed in $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ and $\text{Ni}_{59.5}\text{Nb}_{40.5}$ liquids. However it is close to the MCT calculation for monoatomic hard-sphere liquids. The MCT calculation shows that the ϕ_c for dynamic cross

FIG. 4. (Color online) The D of Cu atoms in the liquid $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ as observed by QENS. The dotted curve is the τ -scaling fit to D with $T_0 = 900$ K and $\gamma = 2.7$. The corresponding ϕ_c is 0.516 ± 0.002 .

over is 0.515 using the Percus–Yevick structure factor as an input.¹⁰ Rather $S(q)$ obtained from simulation as input gives $\varphi_c=0.525$.¹⁰ A binary mixture with size ratio of 0.83 and using $S(q)$ from the simulation as input gives $\varphi_c=0.545$.¹⁰ Theoretical studies indicate a variation of φ_c using $S(q)$ obtained in different ways as an input and mixing of atoms with different size ratio. Generally it is observed that $T_c \approx 1.2T_g$ and this is valid in many polymeric,¹⁴ organic,¹⁵ and metallic¹² glass-forming liquids. The bulk-glass-forming $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts give similar result but the packing density at $1.2T_g$ is only 0.519. In this liquid, the major contribution to the slowing down of atomic motion with decrease in temperature is due to the increase in η but not by increase in φ . Due to its high η , the liquid becomes frozen before it reaches the maximum possible φ . This must be the reason for the comparatively low value of φ_c . Nevertheless, the φ_c derived from the QNS study is within the MCT results for a hard-sphere liquid.

The GFA of metallic glass forming melts can be characterized by their critical-casting thickness. On comparing the GFA of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ and $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$, the former can mold-cast more than 10 mm but $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ can only cast up to 2 mm diameter rods. $\text{Ni}_{60}\text{Nb}_{34.8}\text{Sn}_{5.2}$ melt is the highest packed metallic liquid ever known but the high value of φ did not contribute to its GFA. Similarly, if we compare the φ of $\text{Ni}_{80}\text{P}_{20}$, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and PdNiCuP , it is similar at their T_m .¹⁶ However the viscosities of these liquids are very different at their T_m .^{1,17} PdNiCuP can mold cast more than 10 cm rods but $\text{Ni}_{80}\text{P}_{20}$ can make amorphous only in ribbons. Thus, η is the determining factor of GFA rather than the φ of metallic liquid.

In summary, we used QENS to investigate microscopic dynamics in $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melts. The $\Phi(q,t)$ show fast β and slow α relaxation. α relaxation shows stretching and the β_q value is independent of q and temperature. We believe that stretching of the $\Phi(q,t)$ is stabilized due to the high η and comparatively low φ of the melts. The φ_c obtained from β -scaling analysis, $\langle\tau_q\rangle$ of α -process, and τ -scaling analysis

of D is 0.517 ± 0.003 . This value is comparatively smaller than that observed in other glass-forming metallic melts. The reason for this is believed to be the high viscosity, which dominates over packing density of the melt in determining the atomic dynamics. The value of φ_c obtained for $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ melt is within the range of the MCT prediction for hard-sphere liquids.

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