Size-Dependent Viscosity in the Super-Cooled Liquid State of a Bulk Metallic Glass

Zhen Shao[1,2], Manesh Gopinadhan[1,2], Golden Kumar[3], Sundeep Mukherjee[7], Yanhui Liu[2,4], Corey S. O'Hern[2,4,5,6], Jan Schroers[2,4] and Chinedum O. Osuji [1,2]

[1]Dept. of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520, USA

[2]Center for Research on Interface Structures and Phenomena, Yale University, New Haven, CT 06520, USA

[3]Dept. Mechanical Engineering, Texas Tech University, Lubbock, TX 79409, USA

[4]Dept. of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06520, USA

[5] Dept. of Physics, Yale University, New Haven, CT 06520, USA

[6]Dept. of Applied Physics, Yale University, New Haven, CT 06520, USA

[7]Dept. Of Materials Science and Engineering, University of North Texas, Denton, TX 76203

Abstract

We experimentally investigate the role of sample size on the viscosity of a bulk metallic glass by examining pressure driven flows in nm-scale confinement. A $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ metallic glass in the super-cooled liquid state is extruded into isolated cylindrical pores of varying nano-scale dimensions, down to 40 nm. The apparent viscosity of the liquid as a function of sample size is determined from the filling depth by appropriate corrections to the Hagen-Poiseuille equation. We observe a striking, sudden increase of the apparent viscosity for dimensions below approximately 100 nm. Results are discussed in the framework of confinement of collective shear events.

The unusually high viscosity of bulk metallic glass (BMG) -forming liquids is generally believed to be the main origin for their high resistance against crystallization, hence their extraordinary glass forming ability.[1] By comparison with pure metals, at the liquidus temperature the viscosity of BMG forming liquids (~ 1 Pa.s) is considerably higher, by about 2 orders of magnitude, and increases faster with decreasing temperature.[2] Due to its crucial contribution to glass formation, tremendous efforts have been made to determine and understand the viscosity of BMG-forming liquids.[2-5] Viscosity also plays a crucial role in thermoplastic forming (TPF) of BMGs.[6] TPF is based on the rapid yet continuous softening of BMGs when heated above their glass transition temperature. For some BMGs, viscosities as low as 10^6 Pa.s can be accessed on experimentally practical time scales (seconds to minutes) before they crystallize.[4,7-9] Access to such viscosities allows forming or molding of these BMGs using only moderate pressures, very similar to thermoplastic forming of engineering polymers.[10] TPF-based processing has been demonstrated over a wide range of length scales, from Angstroms to meters. [11-16] Due to the ease and versatility of TPF based molding and the absence of size limitations imposed by the

grain size as in crystalline metals or chain length as in polymers, TPF based forming has created broad interests, particularly on the nano scale, from nano imprint lithography,[11] to data storage,[17] catalysts, and fuel cells [18,19].

The large viscosity in BMG-forming liquids is envisioned to originate from a high packing efficiency. Such efficient packing hinders affine displacement during mechanical deformation which requires one to invoke alternate descriptions for the microscopic stress response that gives rise to macroscopic flow. In this context, shear transformation zones (STZs) have been postulated as the carriers of plastic deformation in dense amorphous solids such as metallic glasses. In this framework, flow in such materials is accommodated by intermittent, irreversible and short-lived collective displacements of the constituent grains (atoms, molecules, or particles) in deformable regions of a characteristic size [20,21]. The above described deformation mechanisms have been observed *in silico* [22] and experimentally in model colloidal[23] and granular systems. Although these mechanisms are broadly used to discuss experimental results,[24] no direct experimental evidence in BMGs of the existence of STZs has been put forward. The lack of experimental evidence is due in part to the transient nature of STZs - they are envisioned as short-lived and spatially dilute transition states which exist only during the actual shear event. Furthermore, their size, which is suggested from computational work to range from ca. 1-3 nm,[25] makes direct experimental observation challenging. Nonetheless, they are a subject of great interest. A particularly compelling and as yet unanswered question is their role in determining size-dependent dynamics in glassy systems as the system size approaches more closely the presumed characteristic dimensions of these deformable zones.

In this letter, we report on measurements of the size dependent viscosity of a bulk metallic glass, $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5,}$ in previously un-accessed sub-micron regimes down to 40 nm. We leverage our ability to thermoplastically form this system by pressure driven extrusion into cylindrical cavities with nm-scale diameters. This allows us to study the flow behavior of BMGs on length scales that steadily approach the postulated characteristic size of the STZs.

The apparent viscosity is determined experimentally from the length of TPF-formed BMG nano-rods produced by application of a fixed pressure ramp of constant duration and amplitude. We used $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ BMG due to its high thermoplastic formability.[6] Nanorods of this BMG were produced by extrusion into anodic aluminum oxide (AAO) templates (Fig. 1). The AAO templates (Synkera Inc.) are available in various pore size diameters ranging from 40 to 200 nm with ~15% porosity. A selected template is placed between two hot flat platens that are maintained at a constant temperature of 270 ^{o}C (Fig. 1a). For $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$, this temperature is in the supercooled liquid regime, which is bounded by the glass transition temperature, T_g = 235 ^{o}C, and the crystallization temperature, T_x = 305 ^{o}C. In the supercooled state, the alloy behaves as a highly viscous liquid with a "bulk" viscosity on the order of 10^6 Pa.s. A spherical bead of material was placed on the AAO template and subjected by the platens to a 3 minute load profile with a constant loading rate of 1500 N/min. This results in flow extrusion of

the alloy into the cylindrical nanopores of the AAO template (Fig. 1b). In order to release the BMG rods from the AAO template, a 20 wt% NaOH solution is used to etch the alumina at 80 ^{o}C for 2 days (Fig. 1c). This reveals a "nano-forest" film of BMG nanorods protruding from a flat disc remnant of the starting material. (Fig. 2a). Precise determination of the nanorod height and thus the fill depth during the extrusion step requires cross-sectional imaging and thus fracture of the sample. This was facilitated by crystallization of the alloy by heating to 330 ^{o}C (Fig. 1d) which embrittles the material leading to easy fracture. SEM images taken across the centerline of a representative sample are shown in Figs. 2c and 2d.

The fill depth is a parabolic function of the radial position measured from the contact point of the spherical bead of BMG starting material. Only rods within a radius of *ca*. 20 rod lengths from the center are considered for the viscosity calculation. This provides an internally consistent and robust measure of the material's flow behavior that is not affected by the parabolic profile, where we note that this radial distance is small compared to the final diameter of the sample, $R_{imaged}/R_{final} \sim 10^{-4}$-$10^{-3}$. The viscosity of the supercooled liquid during the confined flow extrusion of the nanorod is determined from a modified Hagen-Poiseuille equation (Eq. 1) using the SEM-measured average nanorod lengths L and diameters d, the final applied pressure P, the filling time t and the fill velocity $v=(L/t)$.

$$P = \frac{32(\eta_{app} v L)}{d^2} - \frac{4\gamma \cos\theta}{d} \tag{1}$$

The Hagen-Poiseuille expression is modified by a correction that accounts for the capillary pressure associated with the surface tension γ of the supercooled liquid and its contact angle θ with the alumina of the template[11]. This pressure resists the filling of the liquid into the nanopores due to the unfavorable contact angle between the liquid and the alumina. This term scales inversely with the pore size is non-negligible below 1 micron for our system. A secondary effect here is that the effective filling time is smaller than the actual duration of the process as no entry of liquid into the pores can occur until the applied pressure exceeds the capillary pressure. This effect is taken into account by appropriate correction of the filling time. For clarity, we refer to the viscosity calculated from Eq. (1) as the apparent viscosity (Eq. 2).

$$\eta_{app} = \frac{t}{32}\left(P + \frac{4\gamma \cos\theta}{d}\right)\left(\frac{d}{L}\right)^2 \tag{2}$$

For the experiments conducted here, $P \cong 10^8$ Pa is the final applied forming pressure, which is calculated based on applied force and final size of the disc. The contact angle of the BMG liquid against alumina is 120^{o} [26] and the surface tension of the liquid is 1N/m[11]. Both quantities should be independent of the pore size, and we use them as such for the calculation of the

apparent viscosity. As discussed later, we also explicitly consider an alternative situation in which these terms exhibit pore size dependence. The potential effect of uncertainty in the numerical values of the contact angle and surface tension were assessed by considering apparent viscosities calculated using a product of surface tension and contact angle, $\gamma\cos\theta$, that ranged from from -0.34 to -0.8. In all cases, we observed no substantive change in the dependence of the apparent viscosity on confinement size.

Experiments were conducted over a range of nanorod diameters down to 40 nm by using AAO templates with a corresponding range of pore sizes. The length and diameter of the rods were determined by averaging over at least 20 rods in the film center for each of three independent extrusion experiments conducted with templates of a given pore size. In all cases, the uncertainty in the apparent viscosity was less than 5%, indicating that the method is robust and that it yields statistically meaningful data.

The measured length of the nanorods for different pore sizes is summarized in Fig. 3a. Assuming a size independent viscosity, Eq. 2 can be used to calculate L as shown in Eq. 3.

$$L = d\sqrt{\frac{t\cdot\left(P+\frac{4\gamma\cos\theta}{d}\right)}{32\eta_{app}}} \qquad \text{Eq. (3)}$$

The measured length of rods increasingly deviates from the theoretical prediction (Eq. 3) with decreasing rod size (Fig. 3a), where the theoretical prediction assumes a size-independent viscosity equal to the viscosity of $9\text{x}10^6$ Pa.s at 200 nm and the value of pressure P is calculated based on applied force and final disc area in each extrusion. Fig. 3b shows the apparent viscosity calculated from Eq. 2 as a function of the rod size. The error bar for each data point is less than 5%. The apparent viscosity is approximately independent of size until about 100 nm. Below 100 nm, the viscosity increases rapidly, by approximately a factor of 5 at the smallest rod diameter considered, 40 nm.

Our results reveal a significant size dependence of the viscosity when the sample size or the flow is confined below 100 nm. Similar findings have been reported for sub-nanometer thin films of non-polar organic liquids, with thicknesses typically within ten molecular diameters, where increases in the viscous resistance relative to flows in the bulk have been reported.[27-30] Size dependence of the viscosity has also been reported for polymers. Here, the viscosity has been reported in some cases to increase[31], in others to decrease[32] or be constant,[33] with decreasing confinement size. The particular effects observed show strong dependence on variations of polymer chemistry, surface chemistry of confining walls and polymer molecular weight. By comparison, size dependent viscosity has not been reported in any metallic liquid to date. Typical metallic liquids exhibit viscosities of 10^{-2} Pa.s or lower whereas the BMG-forming liquids exhibit a viscosity in the supercooled liquid state of 10^6 Pa·s or larger. The 8 orders of

magnitude higher viscosity is generally believed to originate from the dense atomic packing and local order in the super-cooled state of BMG-formers by comparison with non-BMG forming liquids.[34]

In order to rule out contributions that originate from flow induced effects rather than directly from the confinement size, we calculated the average shear rate during the filling of the nano pores, $\dot{\gamma} = 2\mathrm{L}/(\mathrm{td})$. For all considered pore sizes the shear rate is below 0.1 s^{-1}. On this basis we can estimate the Péclet number for the flow $Pe = \eta\dot{\gamma}\pi a^3/(6kT) = 0.002$, where the size (diameter) of the flowing unit, *a*, is *ca.* 0.28 nm, corresponding to the size of a Pt atom, and the viscosity is taken as the asymptotic limiting value at large nanorod diameters, $9\text{x}10^6$ Pa.s. This suggests that there should be no substantial flow-induced distortion of the structure of the liquid during flow and that the system exhibits a shear rate independent viscosity during filling. Indeed, such a Newtonian response is expected for this system based on prior work.[35] [36] Wall roughness within the pores is ruled out as a possible source of error based on the small value of the RMS roughness normalized by the pore size (~10^{-2}-10^{-3}) and the absence of any discernable features on the nanorod surfaces.

Our calculations of apparent viscosity have implicitly assumed that the surface tension and contact angle are independent of pore size. We can indirectly examine the validity of this assumption by determining the dependence of the capillary pressure term that would be required to give a size independent apparent viscosity. In Fig. 4a, capillary pressure P_s is calculated as a function of pore size assuming a constant viscosity using Equation 4.

$$P_S = \frac{32\eta_{app}}{t}\left(\frac{L}{d}\right)^2 - P \qquad \text{Eq. (4)}$$

The results indicate that a constant viscosity implies that the capillary pressure must increase by a factor of *ca*. 20X on decreasing the rod size from 200 to 40 nm. As $P_s = 4\,\gamma\cos\theta/d$, the pore size dependence of the wetting term $\gamma\cos\theta$ can be extracted. We find that the resulting values of $\gamma\cos\theta$ range from -1 to -6. The cosine term has an absolute maximum value at $\theta = 180^o$. As a result, to match this range, the surface tension γ must be as large as 6 N/m, which is 6 times the expected value of 1 N/m. Moreover, the implied dependence of surface tension with pore size is non-monotonic, with a pronounced minimum near 100 nm. Individually these represent quite unusual scenarios and so taken together, it is considered highly unlikely that a size-dependent capillary pressure is the origin of the observed dependence of the apparent viscosity on sample size.

We have ruled out effects associated with large Péclet number flow, surface roughness and pore-size dependent capillary pressure. This suggests that the size dependence observed here is a reflection of an intrinsic property of the system at the temperature of interest. One possibility is that the increase in apparent viscosity is due to a breakdown of continuum flow under strong confinement. The validity of the continuum assumption can be assessed *via* the Knudsen number,

which compares the length scale of the intrinsic flow unit λ to the dimension of the system that confines the flow, d, $Kn = \lambda/d$. Recent studies suggest that for liquids the validity of the continuum assumptions inherent in the Navier–Stokes equation breaks down for Knudsen numbers larger than *ca.* 0.003-0.01. [28,37] On this basis, the onset of size dependence around 100 nm suggests that the characteristic size of the intrinsic flow unit is *ca.* 0.3-1 nm. This range of length scales encompasses both the atomic dimensions as well as the putative size of STZs[25,38,39]. At the smallest pore sizes, the system is flowing in a cavity that accommodates roughly 100 atoms along it diameter. This convergence of the atomic scale and the system size could lead to the observed increases in viscosity as witnessed in some other fluids. [27-30] STZs could also play a role, perhaps simultaneously, if their dynamics are likewise affected by confinement. It is conceivable that the collective motion within STZs that is involved in the flow of the highly dense super-cooled liquid is considerably restricted by the proximity of confining walls, resulting in an increase in the flow resistance.

In summary, we have conducted a series of pressure driven confined flows of super-cooled liquids of a Pt-based bulk metallic glass. We observe a dramatic increase in the apparent viscosity of the system when flow is confined below *ca.* 100 nm. In the context of a departure from continuum behavior, our data suggests that intrinsic structures on the 0.3-1 nm length scale may be responsible for the observed effects. The possibility exists that these effects are associated with the confinement of STZs as well as the atomic constituents of the liquid. While the precise origins of the size dependence are unclear at this point, the data are unambiguous and firmly indicate the existence of finite size effects in these materials, and further studies are clearly warranted.

This work was supported by NSF MRSEC DMR-1119826. Facilities use was supported by YINQE. C.O. acknowledges financial support by NSF through DMR-0847534.

1 J. Schroers, Phys. Today **66** (2), 32 (2013).
2 A. Masuhr, T. A. Waniuk, R. Busch, and W. L. Johnson, Phys. Rev. Lett. **82** (11), 2290 (1999).
3 X. P. Tang, U. Geyer, R. Busch, W. L. Johnson, and Y. Wu, Nature **402** (6758), 160 (1999).
4 N. Nishiyama and A. Inoue, Acta Mater. **47** (5), 1487 (1999).
5 L. Shadowspeaker and R. Busch, Appl. Phys. Lett. **85** (13), 2508 (2004).
6 J. Schroers, Acta Mater. **56** (3), 471 (2008).
7 T. Waniuk, J. Schroers, and W. L. Johnson, Phys. Rev. B **67** (18), 184203 (2003).
8 G. Duan, A. Wiest, M. L. Lind, J. Li, W. K. Rhim, and W. L. Johnson, Adv. Mater. **19** (23), 4272 (2007).
9 Y. Saotome, K. Itoh, T. Zhang, and A. Inoue, Scripta Mater. **44** (8-9), 1541 (2001).
10 J. Schroers, Adv. Mater. **22** (14), 1566 (2010).
11 G. Kumar, H. X. Tang, and J. Schroers, Nature **457** (7231), 868 (2009).
12 P. Sharma, N. Kaushik, H. Kimura, Y. Saotome, and A. Inoue, Nanotechnology **18** (3) (2007).
13 C. T. Pan, T. T. Wu, Y. C. Chang, and J. C. Huang, J. Micromech. Microeng. **18** (2) (2008).
14 D. L. Henann, V. Srivastava, H. K. Taylor, M. R. Hale, D. E. Hardt, and L. Anand, J. Micromech.

Microeng. **19** (11) (2009).
[15] J. P. Chu, H. Wijaya, C. W. Wu, T. R. Tsai, C. S. Wei, T. G. Nieh, and J. Wadsworth, Appl. Phys. Lett. **90** (3) (2007).
[16] J. Schroers, T. M. Hodges, G. Kumar, H. Raman, A. J. Barnes, P. Quoc, and T. A. Waniuk, Mater. Today **14** (1-2), 14 (2011).
[17] N. Nishiyama, K. Takenaka, N. Togashi, H. Miura, N. Saidoh, and A. Inoue, Intermetallics **18** (10), 1983 (2010).
[18] M. Carmo, R. C. Sekol, S. Y. Ding, G. Kumar, J. Schroers, and A. D. Taylor, ACS Nano **5** (4), 2979 (2011).
[19] S. Mukherjee, M. Carmo, G. Kumar, R. C. Sekol, A. D. Taylor, and J. Schroers, Electrochim. Acta **74**, 145 (2012).
[20] A. S. Argon, Acta Metall. **27** (1), 47 (1979).
[21] M. L. Falk, J. S. Langer, and L. Pechenik, Phys. Rev. E **70** (1), 011507 (2004).
[22] M. L. Manning, E. G. Daub, J. S. Langer, and J. M. Carlson, Phys. Rev. E **79** (1), 016110 (2009).
[23] Ke Chen, M. L. Manning, Peter J. Yunker, Wouter G. Ellenbroek, Zexin Zhang, Andrea J. Liu, and A. G. Yodh, Phys. Rev. Lett. **107** (10), 108301 (2011).
[24] Dongchan Jang and Julia R. Greer, Nat. Mater. **9** (3), 215 (2010).
[25] S. G. Mayr, Phys. Rev. Lett. **97** (19), 195501 (2006).
[26] Shiyan Ding, Jian Kong, and Jan Schroers, J. Appl. Phys. **110** (4), 043508 (2011).
[27] Michelle L. Gee, Patricia M. McGuiggan, Jacob N. Israelachvili, and Andrew M. Homola, J. Chem. Phys. **93** (3), 1895 (1990).
[28] Jacob Klein and Eugenia Kumacheva, J. Chem. Phys. **108** (16), 6996 (1998).
[29] John Van Alsten and Steve Granick, Phys. Rev. Lett. **61** (22), 2570 (1988).
[30] Hsuan-Wei Hu, George A. Carson, and Steve Granick, Phys. Rev. Lett. **66** (21), 2758 (1991).
[31] S. A. Gupta, H. D. Cochran, and P. T. Cummings, J. Chem. Phys. **107** (23), 10335 (1997).
[32] Zhaohui Yang, Chi-Hang Lam, Elaine DiMasi, Nathalie Bouet, Jean Jordan-Sweet, and Ophelia K. C. Tsui, Appl. Phys. Lett. **94** (25), 251906 (2009).
[33] R. G. Horn and J. N. Israelachvili, Macromolecules **21** (9), 2836 (1988).
[34] Jun Ding, Yong-Qiang Cheng, Hongwei Sheng, and Evan Ma, Phys. Rev. B **85** (6), 060201 (2012).
[35] H. Kato, Y. Kawamura, A. Inoue, and H. S. Chen, Appl. Phys. Lett. **73** (25), 3665 (1998).
[36] J. Lu, G. Ravichandran, and W. L. Johnson, Acta Mater. **51** (12), 3429 (2003).
[37] M. Gad-El-Hak, B. Pol. Acad. Sci-Te. **53** (4), 16 (2005).
[38] Y. H. Liu, D. Wang, K. Nakajima, W. Zhang, A. Hirata, T. Nishi, A. Inoue, and M. W. Chen, Phys. Rev. Lett. **106** (12), 125504 (2011).
[39] D. Pan, A. Inoue, T. Sakurai, and M. W. Chen, Proc. Natl. Acad. Sci. U.S.A. **105** (39), 14769 (2008).

Figure Captions

Fig. 1. Experimental determination of the filling depth of BMG-forming liquids. (a) Anodic aluminum oxide is used as a mold material and is heated together with the BMG to the processing temperature of 270 ^{o}C, which provides effective thermoplastic molding. (b) The BMG is pressed into the template under an applied force F. (c) The nano rods are released after soaking the partially filled template in a NaOH solution. (d) Crystallized rods after heating to 330 ^{o}C enables controlled breaking through the centerline. The lengths of rods before and after crystallization are compared and no measurable difference is found.

Fig. 2. SEM images of BMG rods. (a) Top-view image of amorphous rods of 200 nm in diameter; (b) Top-view image of amorphous rods of 40 nm in diameter; (c) Cross-sectional image of crystallized rods with size of 200 nm in diameter (d) Cross-sectional images of crystallized rods with 40 nm in diameter.

Fig. 3. (a) Comparison between the experimentally determined length of the rods and the theoretical prediction (Eq. 3). The red bullets represent theoretically predicted length, assuming $\partial\eta/\partial d = 0$ and the black squares represent the experimentally determined lengths. The red and black dashed lines are given as guides to the eye. With decreasing diameter, the experimentally determined lengths increasingly deviate from the theoretical prediction. (b) Confinement size dependent viscosity. The black line is given as guide to the eye. A rapid increase in the viscosity sets in at approximately 100 nm.

Fig. 4. (a) The dependence of predicted surface tension on confinement size. Assuming viscosity is a constant, which is obtained with 200 nm rods, the surface pressure is calculated using Equation 4. (b) Confinement size dependent surface tension. Above 100 nm, the surface tension increases significantly when size decreases because the calculated surface pressure is increased. However, below 100 nm, the size of rods decreases significantly, which overwhelms the effect of surface pressure increase, resulting in a decrease of predicted surface tension.