Chapter 7

Summary

We performed viscosity measurements on $Pd_{43}Ni_{10}Cu_{27}P_{20}$ and isoconfigurational shear modulus experiments on $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ and $Pd_{43}Ni_{10}Cu_{27}P_{20}$. Furthermore, we presented a rheological law based on the concept of cooperatively sheared flow zones, in which the effective thermodynamic variable governing flow is identified to be the isoconfigurational shear modulus of the liquid. We found the law capable of explaining the equilibrium as well as the non-equilibrium flow of metallic-glass-forming liquids.

We applied this model to alloys over a range of fragilities. This included the $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$, $Pd_{40}Ni_{40}P_{20}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pd_{77.5}Cu_6Si_{16.5}$, $La_{55}Al_{25}Ni_{20}$, and $Mg_{65}Cu_{25}Y_{10}$ alloys. In all cases the fits worked equally well in the high- and low-temperature regimes. Additionally, the fit is found to be as good as the three parameter Cohen-Grest Law.

Furthermore, shear moduli obtained by experiment were compared to shear moduli calculated from viscosity data for different strain rates. It was shown that there was a good correlation between the measured and calculated shear moduli. The model was also found to fit Newtonian data over a wide range of temperatures. This suggests that the assumption of a unique function of shear modulus with temperature is valid. This demonstrates that variations in viscosity with both temperature and strain rate can be uniquely correlated to variations in isoconfigurational shear modulus, and hence verifies

that viscosity has a unique functional relationship and a one-to-one correspondence with shear modulus.

Continuous-strain-rate compression experiments and ultrasonic measurements were used to evaluate the equilibrium and non-equilibrium viscosity of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$. Ultrasonic measurements were utilized to determine the isoconfigurational shear modulus of $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$. The cooperative shear model was applied to the viscosity data. Furthermore, we correlated the variations in viscosity due to temperature and strain rate with the variations in isoconfigurational shear modulus. This correlation led to an accurate prediction of the liquid fragility and to a good description of the liquid strain rate sensitivity.

Viscosity and isoconfigurational shear modulus data from the literature and current experiments were analyzed. This study utilized fragile to strong liquids and included organic, metallic, and silicate glasses. The cooperative shear model was utilized to fit the viscosity of the different glasses. The elastic and cooperative volume fragility indices were used to describe the softening of the shear flow barrier. Furthermore, the elastic fragility index was determined by fitting the isoconfigurational shear modulus behavior versus temperature.

By looking at the combined fragility indices and the elastic fragility index, determined from the isoconfigurational shear modulus, it was possible to correlate the relative influence of the separate indices on the flow softening of the material. It was determined empirically that the elastic and cooperative volume fragility indices are equivalent. Due to this equivalence a factor of $\sim G^2$ may be attributed to the softening of the shear flow barrier used in the cooperative shear model. New viscosity fits were

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calculated using the ~ G^2 dependence in the shear flow barrier. These fits were compared to the original fits obtained from the cooperative shear model. The best agreement between the two fits was observed in the metallic glasses. While the fits for the other glasses were adequate there was some deviation between the two methods. This is very likely due to the more complex interactions inherent in the different glasses presented. The bonding in the metallic glasses will be the closest to that expected for centrosymmetric atomic pair interactions. The organic glasses and SiO_2 will have more complex interactions due to their molecular structures and covalent/directional bonding. This difference in bonding gives rise to differences in the relative influence of the elastic and cooperative volume fragilities.

From deformation experiments we found that the isoconfigurational shear modulus decreases with increasing configurational enthalpy in an approximately linear trend. This trend is in agreement with recent molecular dynamics simulations. By recognizing that an equivalent dependence of shear modulus on configurational enthalpy arises via a thermal softening path, we have established that this dependence of shear modulus on configurational enthalpy is essentially a unique functional relation.

Furthermore, since there are two independent processes that result in the same dependence of shear modulus on configurational enthalpy it is evident that it does not matter how a particular configurational state is reached. A final state may be reached by deformation, thermal excitation, radiation, or any other means of raising the mean energy of the system. All that is relevant for predicting the properties of the material is the amount of energy that has been stored in it. Since there is a unique functional relation between the configurational energy of the system and the isoconfigurational shear

modulus, we can predict the properties of the material by simply measuring the isoconfigurational shear modulus.

The transient deformation regime was investigated by measuring the configurational enthalpy, isoconfigurational shear modulus, and the anelastic recovery through steady state. The results from these tests identified an efficient conversion of input mechanical work into stored configurational enthalpy through steady-state deformation. In steady-state deformation the system transitioned to a completely dissipative process. The isoconfigurational shear modulus decreased with increasing configurational enthalpy. The anelastic response accounted for the complete inelastic deformation of the system prior to the transient peak stress. Once the transient peak stress was reached a mixture of plastic and anelastic deformation was observed. As the amount of total deformation increased, the percentage of anelastic deformation decreased.

The cooperative shear model and the concept of mechanically polarized regions were used in an attempt to explain the observed behavior [1-5]. In conventional glasses there is an anelastic β response that is completely recoverable and an irreversible α relaxation. These are the processes that have been identified to govern the storage and dissipation of energy in conventional glasses. In the current thesis the β response is described in terms of a β buckle up that is a mechanically polarized region within the glass. Furthermore, the mechanically polarized regions will be subject to an Eshelby stress, and it is that Eshelby stress that gives rise to the anelastic behavior of the material. In this description, as the β buckle up density increases, select β buckle ups will cooperatively deform to relieve the associated Eshelby stresses in a dissipative α process that is responsible for the observed plastic deformation.

By looking at the responses of the system to different strain rates approaching the shear localization strain rate it was possible to probe the criteria for forming a shear band and the barrier controlling flow. At a constant deformation temperature and an increasing strain rate both the steady-state flow stress and the steady-state configurational enthalpy appear to go to constant values. When the rate at which energy is input into the system exceeds the dissipative ability of the material at a given temperature, the glass will shear localize in an attempt to lower the energy of the system. The amount of energy stored in β buckle ups at strain rates just prior to shear localization will be related to half the barrier height controlling flow. β buckle ups are areas of increased stress and will be involved in determining the absolute value of the flow stress. Furthermore, the stress and the energy stored in individual β buckle ups will be related to the Eshelby stress field. Therefore, it should be possible to relate the density of β buckle ups and the value of the Eshelby stress to the barrier controlling the flow of the system and the flow stress prior to shear localization.

From the entirety of the experiments presented in this thesis a self-consistent law for determining the flow of metallic glasses has been developed. It has also been experimentally validated, and the assumptions made in developing it were verified. This thesis has also given insight into the physical properties related to flow, and has presented experiments that probed the transient responses of metallic glasses.

References

[1]   A. S. Argon, Acta Metall. 27, 47 (1979).

[2]   A. S. Argon, and H. Y. Kuo, J. Non-Crystalline Solids 37, 241 (1980).

[3]   A S Argon, and L T Shi, Acta Metall. 31, 499 (1983).

[4]   W. L. Johnson, and K. Samwer, Phys Rev. Lett. 95, 195501 (2005).

[5]   M D Demetriou, J S Harmon, M Tao, G Duan, K Samwer, and W L Johnson, Phys. Rev. Lett. 97, 065502 (2006).