Chapter 3

STRONG CONFIGURATIONAL DEPENDENCE OF ELASTIC PROPERTIES OF A CU-ZR BINARY MODEL METALLIC GLASS

We report the strong dependence of elastic properties on configurational changes in a Cu-Zr binary metallic glass assessed by molecular dynamics simulations. By directly evaluating the temperature dependence and configurational potential energy dependence of elastic constants, we show that the shear modulus dependence on the specific configurational inherent state of metallic glasses is much stronger than the dependence on Debye-Grüneisen thermal expansion.

3.1. Introduction

Bulk metallic glasses (BMGs) have acquired considerable attention from scientific and technological viewpoints in the last two decades [1-9]. BMGs have very high yield strength, at least double that of ordinary commercially used crystalline materials, and high

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elastic strain limit, roughly 2 % in tension or compression, due to their disordered atomic structure [1-4]. Upon yielding, BMGs tend to form highly localized shear bands, where one observes large local plastic strains [10-12]. To describe the yielding in metallic glasses, a Cooperative Shear Model [13] has been developed for the glassy state based on Potential Energy Landscape (PEL) / Inherent State (IS) theory [14-16]. A scaling relationship among the shear flow barrier, a universal critical yield strain, and the isoconfigurational shear modulus G was constructed. The model reveals that for a fixed glass configuration, the barrier height for shear flow is proportional to the isoconfigurational shear modulus G, which makes the elastic properties of great importance in fully understanding the mechanical behaviors of BMGs. A wide variety of experimental work has been performed to measure the elastic properties of BMGs [4, 17-18]. Molecular Dynamics (MD) simulations have been extensively utilized to calculate the elastic stiffness coefficients in crystals [19, 20]. In this work we present the Debye-Grüneisen thermal expansion effect, as well as the strong configurational inherent state dependence of the elastic properties for a model binary metallic glass.

3.2. MD Simulations

In order to obtain numerical results for the elastic stiffness coefficients, we perform MD simulations using an interatomic many-body Rosato-Guillope-Legrand (RGL)-type potential model developed for the Cu-Zr binary alloy system [21]. The original simulation cell contains N = 2000 atoms, arranged in a random bcc structure with periodic boundary conditions. At the beginning, the system was heated to 2400 K and the structure of the liquid phase was allowed to equilibrate. The system was then cooled to 50 K under zero pressure using a range of quenching rates from 1 to 10 K/ps (1 ps = 10^{-12} seconds) to generate glass configurations. This yielded the reference shapes and size matrices, h_0, in Parrinello-Rahman formalism [22] to calculate elastic stiffness coefficients by constant-temperature and constant-volume (NVT) simulations. The glass transition temperature occurs at 700 K under the cooling rate of 5 K/ps, and there is a slight difference among the glass-transition temperatures when varying the cooling rates.

Upon determining elastic stiffness coefficients, NVT simulations for each state point were carried out. After equilibration of 20,000 steps (20 ps with a time step of 1 fs; 1 fs = 10^{-15} seconds), we calculated the elastic stiffness coefficients at different temperatures and at different potential energies, after collecting statistics over 100,000 steps for the convergence of the fluctuation terms. The elastic stiffness coefficients were evaluated using the following statistical fluctuation formula [23]:

$$C_{ijkl}^{T} = -\frac{\Omega_0}{k_B T}\left(\langle P_{ij} P_{kl} \rangle - \langle P_{ij} \rangle \langle P_{kl} \rangle\right) + \frac{2Nk_B T(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})}{\Omega_0} + \langle \chi_{ijkl} \rangle \qquad (1)$$

where <> denotes the averaging over time, and $\Omega_0 = \det h_0$ is the reference volume for the model system. The first term represents the contribution from the fluctuation of the microscopic stress tensor, the second term represents the kinetic energy contribution, and the third term is the Born term. The thermal relaxation effect on the elastic stiffness constants were simulated to guarantee that the calculations performed in this work reached the steady states. For instance, at the highest temperature 500 K, the shear moduli for the samples obtained by the cooling rate of 10 K/ps are respectively 9.5 GPa, 8.0 GPa, and 8.2 GPa when collecting statistics by 50000 steps (50 ps), 80000 steps (80 ps), and 100000 steps (100 ps) for the convergence of the fluctuation terms.

3.3. Debye-Grüneisen Thermal Expansion Effect

We first analyzed the Debye-Grüneisen thermal expansion effect on the elastic stiffness coefficients for the model glass under the same configuration. The calculations were carried out under zero pressure at different temperatures below the glass-transition temperature T_g to ensure no configurational changes happen. Figure 3.1 and Figure 3.2 present the temperature dependence of the shear modulus G and the bulk modulus B for the binary $Cu_{46}Zr_{54}$ metallic glass prepared at two different cooling rates, 5.0 K/ps and 2.5 K/ps. The shear modulus Debye-Grüneisen slope was measured to be $[dG/dT] = -18 \sim 20$ MPa/K and the bulk modulus Debye-Grüneisen slope $[dB/dT] = -37$ MPa/K. The MD glass samples quenched using different cooling rates have different but fixed configuration states; the linear fits to the low-temperature modulus data have essentially the same slope, which demonstrates that the low-temperature modulus dependence (both G and B) is intrinsically independent of the configurational states. This is truly the expected Debye-Grüneisen effect of thermal expansion on elastic constants for an isolated configuration state.

In order to verify the temperature dependence of the elastic properties of the binary Cu-Zr metallic glass, the following procedure was adopted: Starting with the cell volume V set at the equilibrium value V_0 (corresponding to zero pressure and minimum potential energy) at 300 K, we equilibrated the system at incrementally larger and smaller values while strictly maintaining constant temperatures by velocity rescaling after each time step. During the calculations, we limited the volume change within ±2% to make sure that the simulation system remained in the elastic regime and no configurational change occured. Another issue of concern was that the pressure would show up at different scaled volumes. The above fluctuation formula is for the systems at zero pressure only. An additional pressure-dependent term was added to get the correct elastic stiffness constants. Figure 3.3 presents the volume dependence of the elastic constants, G and B, for the $Cu_{46}Zr_{54}$ binary model glass at a cooling rate of 2.5 K/ps, in which 1.0 represents the equilibrium volume for the x axis. Both G and B drop linearly with increasing volume. The volume slope of shear modulus is measured to be $[dG/dv] = -17.5$ MPa, and the volume slope of bulk modulus, $[dB/dv] = -41$ MPa, where v stands for V/V_0. This suggests that the temperature dependence of shear modulus G and bulk modulus B can be primarily attributed to the Debye-Grueneisen thermal expansion effect if we take the thermal expansion coefficient ($\sim 1\times10^{-4}$ 1/K) into account for this binary alloy. Wang et al. measured the hydrostatic pressure effect on the elastic properties of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass by acoustic methods and found that both G and B increase monotonically and linearly with increasing pressure, which strongly supports our MD-simulation results.

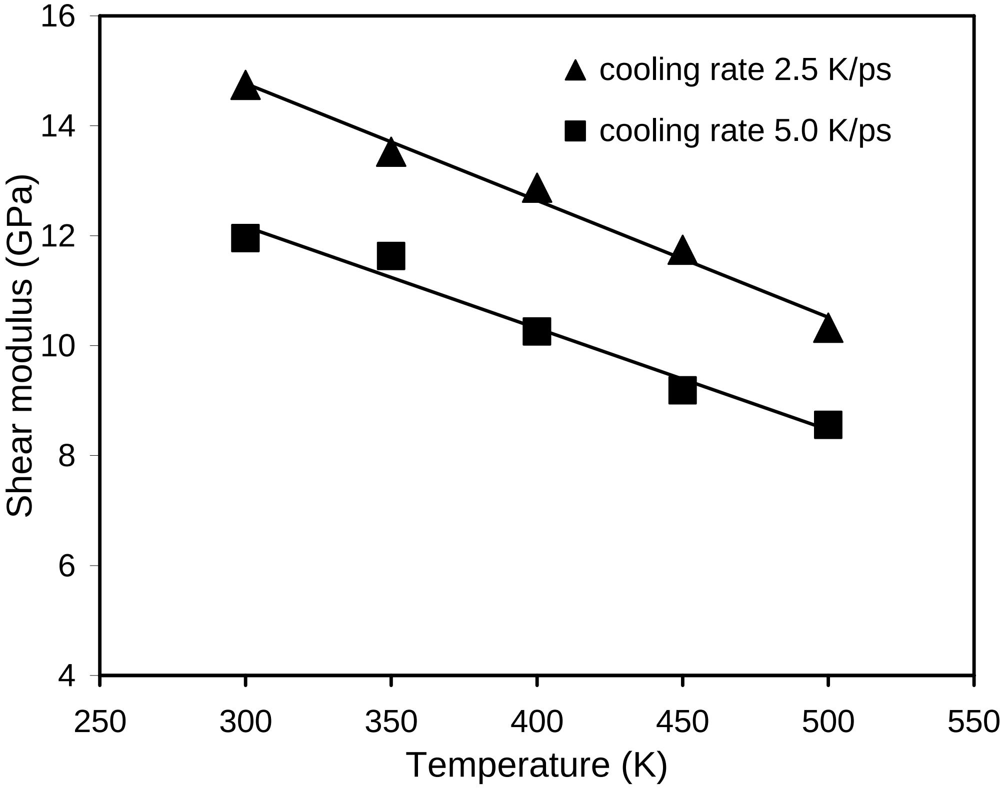

Figure 3.1. Temperature dependence of shear modulus G for the $Cu_{46}Zr_{54}$ metallic glass prepared at two different cooling rates (2.5 K/ps and 5 K/ps). The MD glass samples quenched using different cooling rates have different but fixed configuration states; the linear fits to the low temperature modulus data have essentially the same slope, showing that the low temperature G dependence is intrinsically independent of the configurational states.

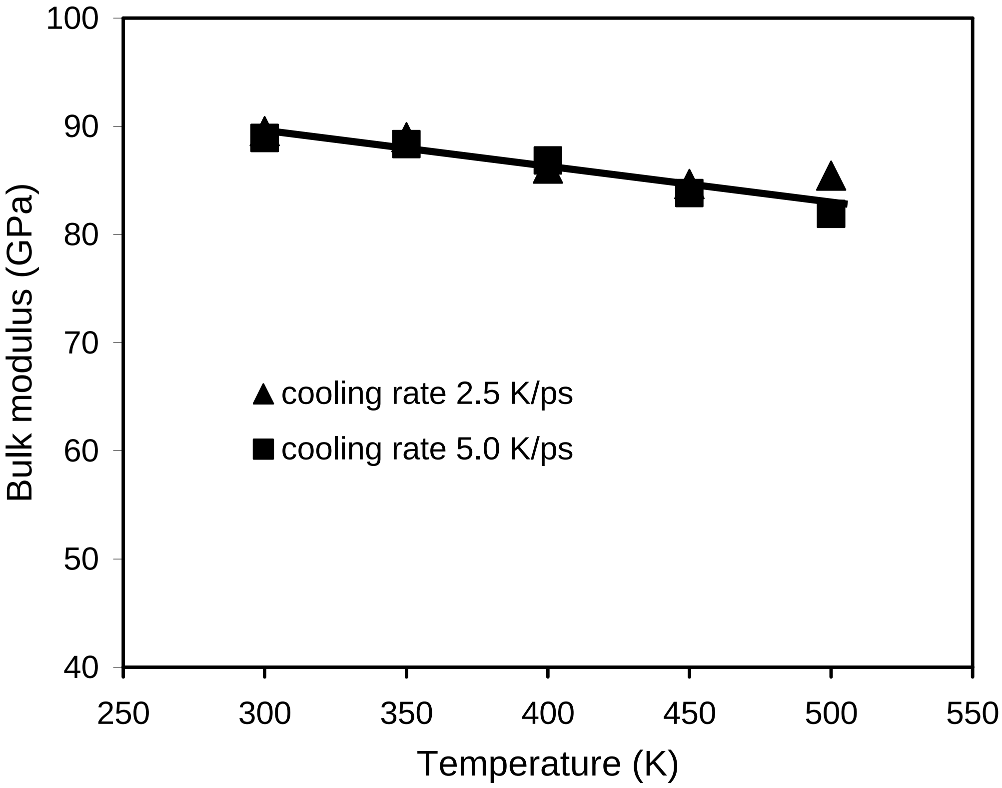

Figure 3.2. Temperature dependence of bulk modulus B for the $Cu_{46}Zr_{54}$ metallic glass prepared at two different cooling rates (2.5 K/ps and 5 K/ps). The two different configurational states are indistinguishable, demonstrating that B is not as sensitive as G to the configurational inherent state changes.

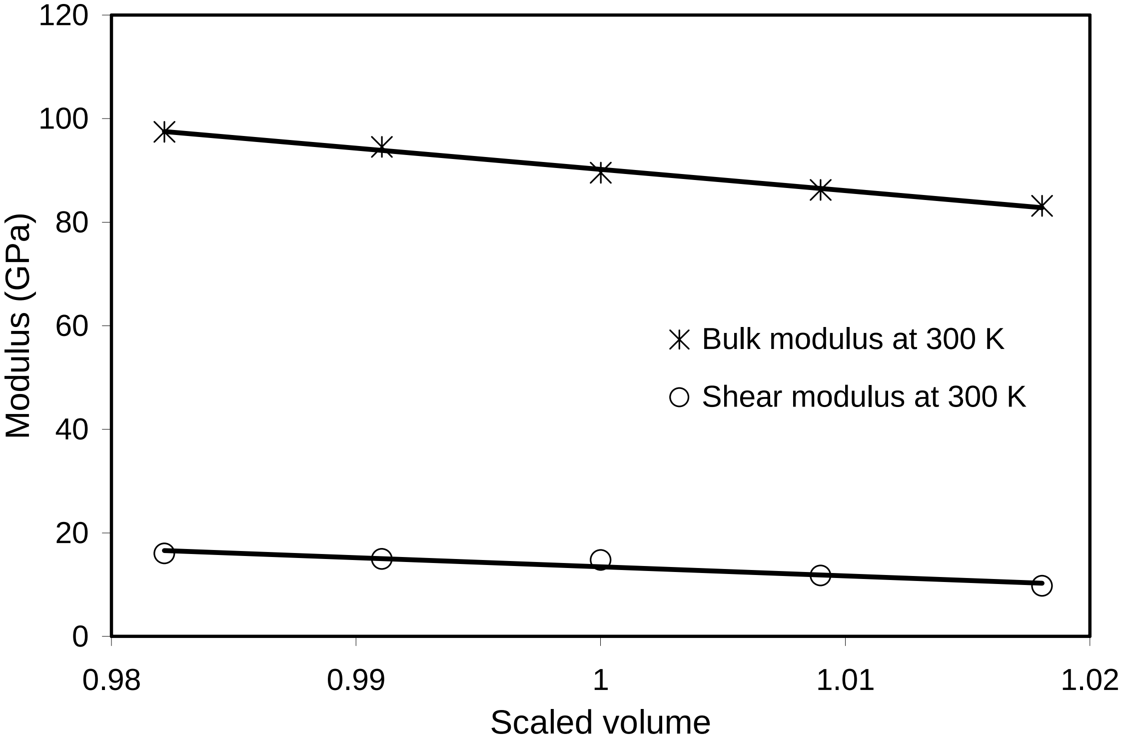

Figure 3.3. Volume dependence of bulk modulus B and shear modulus G for the $Cu_{46}Zr_{54}$ metallic glass prepared at a cooling rate of 2.5 K/ps. This suggests that the temperature dependence of shear modulus G and bulk modulus B can be primarily attributed to the Debye-Grueneisen thermal expansion effect.

3.4. Configurational Dependence

The configurational inherent state dependence of the elastic constants was further considered. By means of the same MD simulation model we calculated the elastic stiffness coefficients at five temperatures for different configurations (with different potential energies) obtained by quenching the system at different rates from the same liquid state under no pressure. It is found that at five temperatures (300 K, 350 K, 400 K, 450 K, and 500 K) the slope of shear modulus G with respect to the total potential energy is nearly the same: ~750 GPa/(eV/atom) (approximately three times larger than the Debye-Grüneisen effect). The volume change at each temperature due to different cooling rates is negligible. It is noted that the volume difference at all five temperatures between the highest cooling rate 10 K/ps and the lowest cooling rate 1 K/ps is less than 0.15 %, which means that the Debye-Grüneisen thermal expansion effect here is negligibly small.

According to PEL/IS theory, the liquid enthalpy could be separated as the vibrational and configurational contributions, $h_L = h_V + h_C$. The glass transition can be identified with the freezing of configurational inherent states. The vibrational contribution to the enthalpy is $3k_BT/2$. Therefore, to the first approximation, the configurational enthalpy can be directly obtained from the total enthalpy, which is the total potential energy in this work (considering the fact that the calculations were made under no pressure). After subtracting the vibrational enthalpy from the total enthalpy, we plotted all the shear modulus data with respect to the configurational potential energy. As indicated in Figure 3.3, a dramatically strong configurational dependence of shear modulus G can be observed, and the configurational energy slope of G is noted to be ~720 GPa/(eV/atom). This direct evaluation of configurational inherent state dependence of shear modulus G from MD simulations shows that G strongly depends on the specific configurational changes of the glassy states, while it weakly depends on the Debye-Grüneisen thermal expansion effect.

Recently Lind, Duan, and Johnson experimentally measured the isoconfigurational elastic constants of the $Zr_{46.25}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit-4) samples using the pulse-echo overlap technique [24]. The samples were isothermally annealed and quenched near the glass transition temperature. It is found that the shear modulus G has a strong dependence on annealing temperatures and, thus, on the specific configurational potential energy of the equilibrium liquid, although the low temperature dependence of G of the configurationally frozen glasses shows linear temperature dependence. Our simulation results presented in this work are consistent with the experimental progress obtained from Vit-4 (see Figure 3.5).

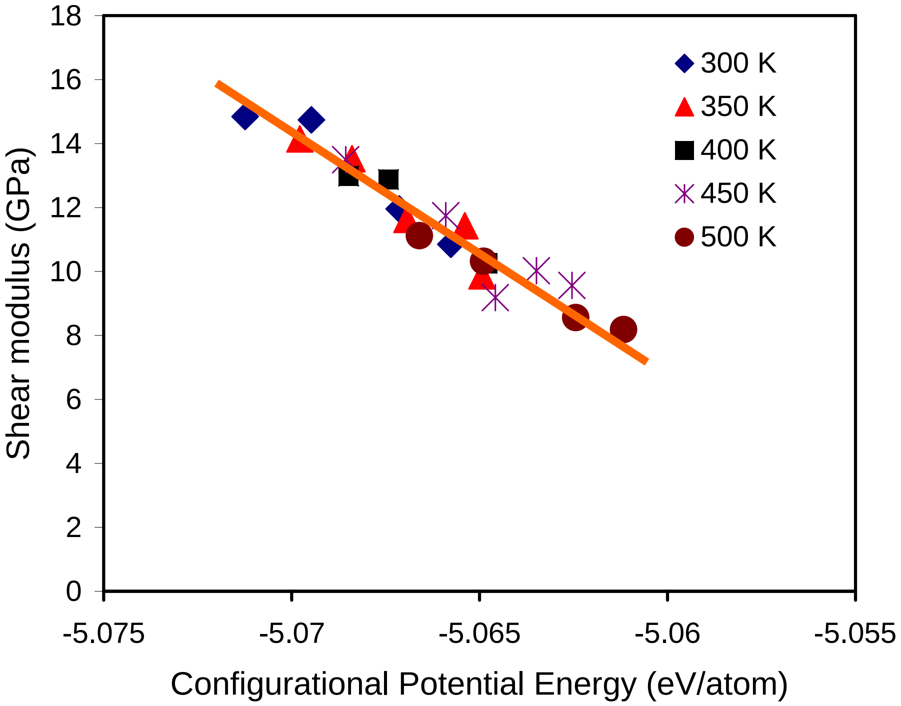

Figure 3.4. Strong configurational potential energy dependence of shear modulus G for the $Cu_{46}Zr_{54}$ metallic glass when varying the cooling rates to obtain different configurations. This direct evaluation of the configurational inherent state dependence of shear modulus shows that G strongly depends on the specific configurational changes of the glassy states, while weakly depending on the Debye-Grüneisen thermal expansion effect.

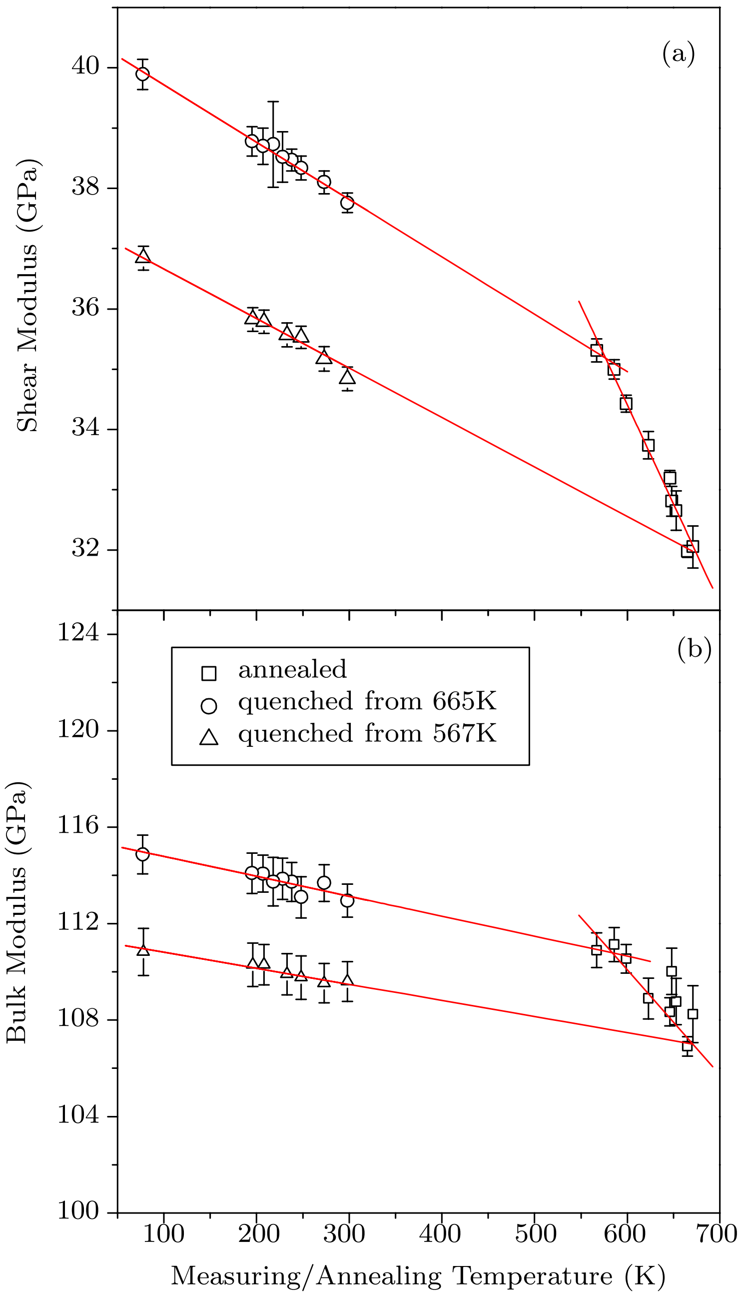

Figure. 3.5. The shear and bulk modulii of Vit-4 as measured in-situ from -78 to 298 K and measured from samples quenched from the equilibrium liquid around T_g. (Reproduced from Ref. 24. Copyright 2006 American Physical Society.)

3.5. Chapter Concluding Remarks

In summary, the temperature and configurational dependence of elastic properties for a binary model metallic glass have been obtained from MD simulations. It is shown that the shear modulus dependence on the specific configurational inherent state of metallic glasses is much stronger than the dependence on Debye-Grüneisen thermal expansion.

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