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Non-exponentiality of structural relaxations in glass forming metallic liquids

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ABSTRACT

The non-exponentiality of structural relaxations in glass forming metallic liquids is studied with an emphasis of a comparison of modulus relaxation and enthalpy relaxation measurements. The non-exponential (stretching or Kohlrausch) parameter β_{KWW} determined from the modulus measurements of metallic liquids does not exhibit appreciable difference, and a definite fragility dependence is lacking. Extensive analyses of modulus relaxation data of molecular (mechanical) and ionic liquids (electrical) repeat the observation in metallic liquids. By contrast, the enthalpy relaxation measurements of metallic glasses gave distinct β_{KWW} values, and the use of the enthalpy relaxation dispersion results largely restores Böhmer's correlation. A discussion is presented with regards to enthalpy, compliance and modulus relaxations.

1. Introduction

As temperature decreases below equilibrium freezing points T_f, some liquids can easily get access to undercooling, even to vitrification. Studies reveal that the dynamics and thermodynamics of undercooled liquids greatly differ from those of *normal* liquids ($T > T_f$). Structural relaxation non-exponentiality is considered as one of the three canonical dynamic characters in supercooled liquids [1], and proves to be a key property in understanding intermolecular associations [2,3]. This property is usually addressed with a stretched exponential function in the time domain [1]:

$$\varphi(t) = \varphi_0 \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right], \tag{1}$$

where β_{KWW} is the non-exponential (stretching or Kohlrausch) parameter, $0 < \beta_{KWW} \le 1$. The non-exponential behavior is also studied in frequency domain, and compliance ($J^* = J' - iJ''$) and modulus ($M^* = 1/J^* = M' + iM''$) relaxations are widely used in various classes of liquids. The frequency domain relaxation data are usually explained with Havriliak–Negami (HN) equation [4]:

$$\begin{aligned} J^*(\omega) &= J'(\omega) - iJ''(\omega) = J_\infty + \Delta J(1 + (i\omega\tau_J)^\alpha)^{-\gamma} \\ M^*(\omega) &= M'(\omega) + iM''(\omega) = M_\infty + \Delta M(1 + (i\omega\tau_M)^\alpha)^{-\gamma}, \end{aligned} \tag{2}$$

where τ is the relaxation time, and α and γ determine the profiles of relaxation spectrum, $0 < \alpha \le 1$, $0 < \gamma \le 1$. The stretching exponent is usually calculated from α and γ in terms of $\beta_{KWW} = (\alpha\gamma)^{1/1.23}$ [5,6].

Metallic liquids are of the simplest structure, and the dynamic studies facilitate to parallel the simulation results. Bulk-metallic-glass (BMG) forming liquids have high thermal stability, which allows the thermodynamic and dynamic studies in deep undercooling region [7–9]. The viscous flow behaviors or temperature dependent kinetics have been widely studied in various BMG liquids in deep undercooling regions near their glass transition temperatures (T_g) [10–13], while the relaxation dispersion was less highlighted [14,15]. Frequency-domain mechanical relaxations are often used for the non-exponential dynamics of metallic liquids with moduli and compliance measurements, and the moduli relaxation proceeds by applying a periodic strain with elastic (E) and shear (G) moduli as measured quantities. However, the reported stretching exponents for liquids and glasses are rather scattered [16–19]. Our recent analyses of the mechanical modulus relaxations in metallic liquids preliminarily presented the structural relaxation non-exponentiality at deep undercooling regions [20]. In this paper, the results of modulus relaxations are further compared with compliance and enthalpy relaxations.

2. Results

The stretching parameters $\beta_{Mech\text{-}Mod}$ determined from mechanical modulus relaxations in glass forming metallic liquids are presented in Fig. 1 as a function of the relaxation frequency, $\nu_0 = (2\pi\tau)^{-1}$ [20]. The systems are $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4, E [21]; G) [22], $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ (Vit1, E) [23,24], $Zr_{55}Cu_{25}Ni_5AL_{10}Nb_5$ (G) [25], $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ (G) [26], $Zr_{55}Al_{10}Ni_5Cu_{30}$ (G) [27], and $Zr_{36}Ti_{24}Be_{40}$ (E) [28], $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (E) [29], $Pd_{40}Ni_{40}P_{20}$ (G) [26], $Ce_{70}Al_{10}Cu_{20}$ (G) [30]. The inset of Fig. 1 shows the frequency dependence of moduli

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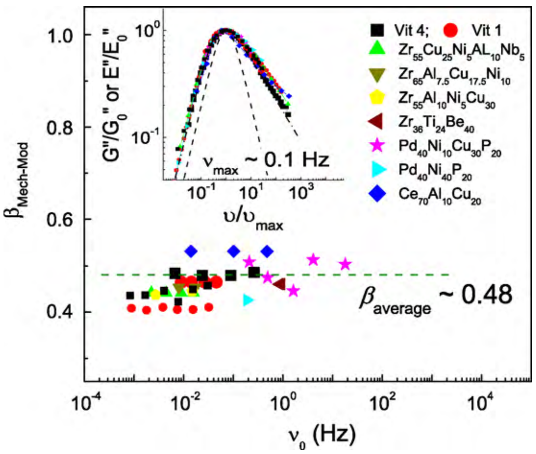

Fig. 1. Stretching exponent $\beta_{Mech\text{-}Mod}$ of the mechanical modulus relaxations in glass forming metallic liquids as a function of relaxation frequency ν_0 ($\nu_0 = 1/2\pi\tau$, τ is the relaxation time). Inset shows the normalized mechanical relaxation profiles of some metallic liquids with relaxation peak frequency ν_{max} near 0.1 Hz. G_0 and E_0 are the shear and elastic moduli at the peak positions. The pure exponential (Debye) relaxation is shown with the dashed line. The fitting to the data of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (E) in terms of Havriliak–Negami equation was shown with a dash–dot line.

in some metallic liquids measured with relaxation frequency near 0.1 Hz. Remarkably, all the metallic glass forming liquids have comparable $\beta_{Mech\text{-}Mod}$ centered around 0.48. This remarkably contrasts with the dielectric compliance measurements in generic molecular liquids, where the relaxation dispersion β_{Die} spans in a broad range at temperature near their glass transition, typically between 0.3 and 0.75 [6,31].

The relaxation dispersions can be determined with various relaxation techniques. Our recent studies showed a consistency of the relaxation dispersions between enthalpy and dielectric compliance relaxations for most of generic (non-Debye type) molecular glass forming liquids [32]. The volume relaxation [33], anelastic relaxation [34], and enthalpy relaxation [35–38] in metallic systems have been studied, but most studies were carried out in glassy states. Note that the Kohlrausch exponents determined in glasses ($T < T_g$) usually differ much from the values obtained from the equilibrium supercooled liquids [19,33]. And thus, the extrapolation of stretching exponents from glass to liquid regions might not give reasonable results. Enthalpy relaxation is of special significance in the recognition of the non-exponential and the non-linear dynamic characters of supercooled liquids [32,39]. The comparison of enthalpy relaxation and modulus relaxation measurements probably assist understanding the unusual relaxation dispersions of metallic liquids, as shown in Fig. 1.

The determination of the non-exponential parameters from enthalpy relaxation is based on Tool–Narayanaswamy–Moynihan–Hodge (TNMH) equations [40]. The use of TNMH equation requires the unambiguous expression of temperature dependence of heat capacity C_p (or equivalent quantity such as thermal expansion coefficient [32]) for the supercooled liquid and glass under well-defined cooling and heating rates. Such C_p data are not much for the alloy systems due to the low stability of the undercooled metallic liquids at temperature above T_g. Fortunately, glass transition C_p curves of two glass forming systems, $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$, are available with cooling/heating rates of −10/+10 K/min [41]. The non-exponential (β_{TNMH}) and the non-linear (x) parameters are calculated with the C_p data. Fig. 2 shows the fit results of TNMH equation to the normalized C_p curves, giving $\beta_{TNMH} = 0.66$ and $\beta_{TNMH} = 0.625$ for $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$, respectively. The insets in Fig. 2 show the original C_p measurements. $\beta_{TNMH} = 0.66$ of $Pd_{40}Ni_{40}P_{20}$ is comparable with the values 0.65–0.74 determined with the dynamic specific heat measurements [42].

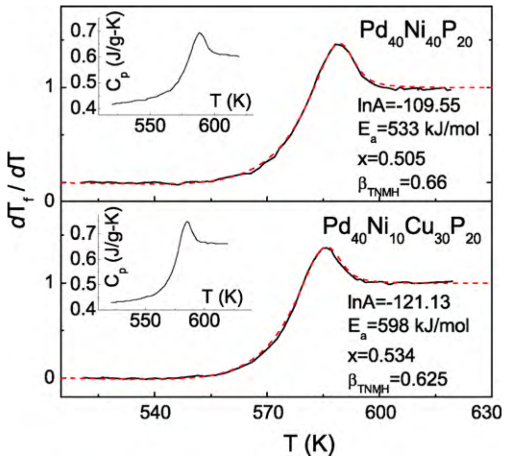

Fig. 2. Normalized heat capacity C_p curves of $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$. Non-exponential ($\beta_{TNMH}$) and non-linear ($x$) parameters are determined with the fit of Tool–Narayanaswamy–Moynihan–Hodge (TNMH) equation to the data. The original C_p curves reported in Ref. [42] with the cooling/heating rates of −10/+10 K/min are shown in insets.

3. Discussion

Structural relaxation non-exponentiality in supercooled liquids is associated with the non-Arrhenius character, which has been explored extensively with the concept of fragility [1,43]. Fragility was usually digitalized by the definition $m = d\log x/d(T_g/T)\big|_{T=T_g}$, where x is structural relaxation time or viscosity. Böhmer et al. proposed an empirical correlation between fragility indexes and stretching exponents on the basis of various relaxation measurements [31], indicating that β_{KWW} basically decreases with fragility. Alloy systems are found to hold marked fragility difference [44,45], and this fails to account for the experimental observation from modulus relaxation (Fig. 1) that $\beta_{Mech\text{-}Mod}$ does not differ much among Zr-, Pd-, and Ce-based metallic liquids with a nearly constant value of ∼0.48. $\beta_{Mech\text{-}Mod}$ is, therefore, somehow independent of fragility in the metallic liquids.

Schröter and Donth's studies of the relaxation dispersions in molecular, metallic and inorganic liquids illustrate that the stretching exponents determined from modulus relaxations distributes in a narrow range near 0.45 while the fragility has a span from 34 to more than 100 [16]. This agrees well with our observation. Recent measurements of mechanical modulus relaxations in molecular liquids indicate that relaxation dispersion profiles do not show a pronounced change with $\beta_{Mech\text{-}Mod}$ being around 0.47, although fragility indexes greatly vary [46]. Similarly, the dielectric modulus analyses of the structural relaxations in ionic liquids also gave $\beta_{Mech\text{-}Mod} \sim 0.5$, while the stretching exponents derived from compliance relaxations (for example, dielectric epsilon) can reach as high as 0.8 [47]. It is therefore obvious that the lacking correlation of $\beta_{Mech\text{-}Mod}$ with fragility is not exclusively limited to the metallic liquids, and the modulus relaxations in inorganic, molecular, ionic and metallic liquids hold similar relaxation dispersions.

Enthalpy relaxation studies in metallic glasses have been reported. However the available relaxation dispersion data obtained on the basis experimental measurements are quite limited. TNMH equation was applied to the enthalpy relaxation of a metallic glass, $Zr_{65}Al_{10}Ni_{10}Cu_{15}$, and gave $\beta_{TNMH} = 0.79$ [48]. Fig. 3 presents a comparison of relaxation dispersions of enthalpy relaxations with modulus and compliance relaxations for metallic and molecular liquids. For the molecular liquids, the dielectric

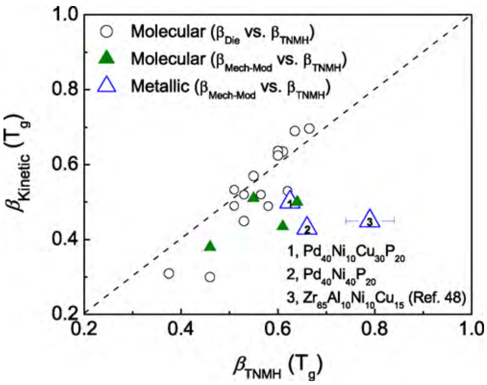

Fig. 3. Comparison of non-exponential parameters determined from dielectric compliance (β_{Die}) and mechanical modulus ($\beta_{Mech\text{-}Mod}$) with those from enthalpy relaxations (β_{TNMH}) for metallic and molecular glass forming liquids. The molecular liquids are decahydroisoquinoline [49], di-*n*-butyl phthalate [46], glycerol [16] and propylene glycol [46] (in the increasing order of β_{TNMH}).

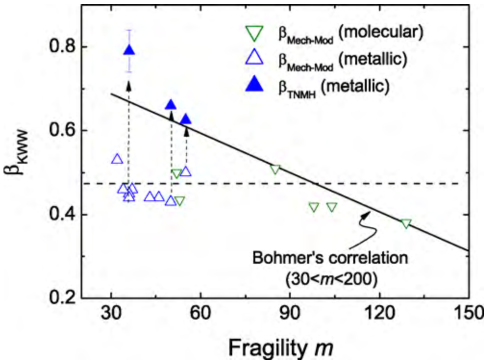

Fig. 4. Fragility (*m*-index) dependence of non-exponential parameter determined from mechanical modulus ($\beta_{Mech\text{-}Mod}$) relaxation in metallic and molecular glass forming liquids. Solid line reads the general dependence reported in Ref. [31], and dash line is a guide for eyes.

compliance data were taken from Ref. [32], and the modulus measurements are from Refs. [16] (glycerol), [49] (decahydroisoquinoline) and [46] (propylene glycol and di-*n*-butyl phthalate). A mismatch of the stretching exponents between $\beta_{Mech\text{-}Mod}$ and β_{TNMH} is immediately visible, in particular, for the metallic systems. By contrast, for the molecular liquids, β_{TNMH} and β_{Die} are comparable.

Although Böhmer's correlation of fragility and stretching exponent is empirically established, it has showed certain success [6]. Based on the dielectric compliance measurements, it was well recorded that less fragile molecular liquids such as glycerol ($m = 53$) have β_{Die} up to ~0.7 at low temperature near glass transitions, while for fragile liquids like decalin ($m = 145$) β_{Die} might be less than 0.4 [6,50,51]. Fig. 4 re-plotted fragility dependence of the exponential exponent by using $\beta_{Mech\text{-}Mod}$ for metallic and molecular liquids, the original correlation is shown as the solid line. It is not a surprise that $\beta_{Mech\text{-}Mod}$ is not subject to Böhmer's correlation. When the modulus relaxation data is substituted by enthalpy relaxation, the correlation is approximately restored, notwithstanding not perfect.

The explanation of the unusual behavior of modulus relaxation dispersion is not straightforward. Parallel studies of the modulus and compliance (dielectric, in particular) relaxations have been done in molecule liquids and polymers [49,52–54], and most of the studies emphasized the correlation of relaxation time. The kinetic decupling of various relaxations has been reviewed [55], while the detailed comparison of the relaxation dispersion profiles is less available [52,56,57]. DiMarzio–Bishop model outlined the correlation of dielectric compliance with shear modulus relaxations [58], however a conversion from mechanical measurements to dielectric ones in terms of the model leads to a marked deviation of relaxation dispersions [59]. Based on this work together with our recent studies [32], two facts are highlighted: the relaxation dispersions from enthalpy relaxations agrees with those from dielectric compliance relaxations in molecular glass forming liquids (Fig. 3), and the use of the enthalpy relaxation stretching exponents favors to reproduce original Böhmer's correlation (Fig. 4). It is therefore emphasized that although a specific correlation of relaxation dispersions among various relaxations is still a challenge, enthalpy relaxation accounts for the substantial stretching exponents, as pointed out early [39]. The unusual modulus relaxation dispersion still requires further studies.

4. Conclusions

The relaxation dispersions of metallic glass forming liquids are discussed with the comparison of the non-exponential relaxation exponents from modulus and enthalpy measurements. A large difference of relaxation dispersions is demonstrated. An extensive survey from modulus relaxations among molecular, metallic and ionic liquids reveals that the non-exponential exponents do not differ much, and a fragility dependence is lacking. The results contrast with the compliance (dielectric) measurements from small molecular liquids, which give comparable non-exponential exponents with enthalpy relaxation.

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