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ELASTIC PROPERTIES BEHAVIOUR OF METALLIC GLASSES

Eloi Pineda[1,3] and Daniel Crespo[2,3]

[1]Departament de Física i Enginyeria Nuclear, ESAB, Universitat Politècnica de Catalunya, Avda. Canal Olímpic 15, 08860 Castelldefels, Spain
[2]Departament de Física Aplicada, EPSC, Universitat Politècnica de Catalunya,Avda del Canal Olímpic 15, 08860 Castelldefels, Spain
[3]Centre de Recerca de l'Aeronautica i l'Espai, Universitat Politècnica de Catalunya, Spain

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Abstract. Estimating a fictive temperature of the glasses by means of their values of T_g, the glass elastic properties are interpreted in terms of the elastic behaviour of the equilibrium liquid above the glass transition. A correlation between the Poisson ratio of the glass and the anharmonic properties of the supercooled liquid is proposed.

The application of metallic glasses as structural materials requires improving glass-forming ability and ductility. The brittle-ductile behaviour of amorphous metals seems to be directly related to the values of the elastic moduli [1]. Hence, the relationship between the elastic properties and other glass characteristics is of great interest when considering new compositions for obtaining metallic glasses with good mechanical properties.

The structural state of a glass is described in terms of the fictive temperature T_f associated with a certain liquid/glass physical property; T_f is defined as the temperature at which the glass and the equilibrium liquid have the same value of the associated property [2]. The elastic properties of a glass are described by the bulk (K) and shear (G) moduli or equivalently by the longitudinal ($C_{11}=K+4/3G$) and shear ($C_{44}=G$) stiffness coefficients. As the structural state of a glass is inherited from the equilibrium liquid, the elastic properties of the glass are expected to be also inherited from the infinite-frequency elastic response (K^{∞} and G^{∞}) of the equilibrium liquid at T_f. Different theoretical models predict the dependence on temperature, pressure and density of K^{∞} and G^{∞} for equilibrium liquids [3]. When lowering the temperature, $G^{\infty}(T)$ and $K^{\infty}(T)$ increase while the Poisson's ratio, or equivalently K^{∞}/G^{∞}, decreases. This process continues in the glassy state, the decrease of T_f during structural relaxation increase the stiffness and so the values of the elastic coefficients of metallic glasses [4,5].

In the absence of defects and anharmonicity, the Cauchy relation $C_{11}=3C_{44}$ (or equivalently $K=5/3G$) is expected to hold for an isotropic material. However, this relation is usually not fulfilled. In ideal simple mono-atomic fluids the high-frequency elas-

Corresponding author: Eloi Pineda, e-mail: eloi.pineda@upc.edu

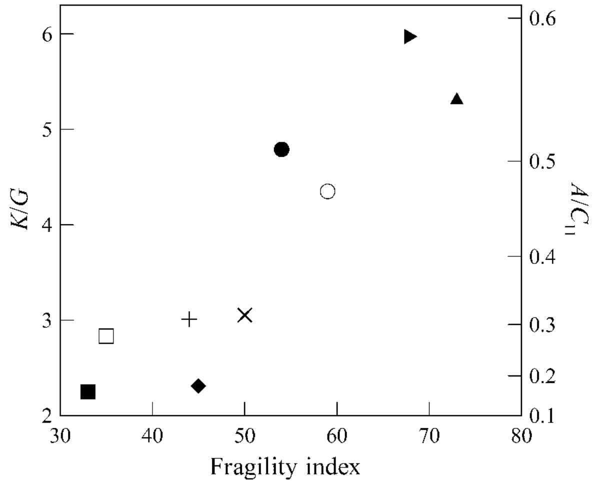

Fig. 1. K/G and the estimated values of A/C_{11} as a function of the kinetic fragility parameter *m* for metallic glasses with available data in the literature: (■)$Nd_{60}Al_{10}Fe_{20}Co_{10}$, (□)$La_{55}Al_{25}Ni_{20}$, (◆)$Mg_{65}Cu_{25}Y_{10}$, (+)$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$, (×)$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, (O)$Pd_{40}Ni_{10}Cu_{30}P_{20}$, (●)$Pd_{40}Ni_{40}P_{20}$, (▲)$Pd_{77.5}Si_{16.5}Cu_{6}$, (▶)$Pt_{60}Ni_{15}P_{25}$. For $La_{55}Al_{25}Ni_{20}$ and $Mg_{65}Cu_{25}Y_{10}$ the elastic constants are estimated from available data of similar compositions.

tic properties are expected to fulfil a generalized Cauchy relation: $K^{\infty}(T)=5/3G^{\infty}(T)+f(T,P)$, which contains and additive term $f(T,P)$ depending on temperature and thermodynamic pressure [3,6]. For an amorphous solid, there are theoretical approximations that allow the calculation of the elastic constants in some simplified cases. The pair distribution function $g(r)$ or equivalently the radial distribution function $RDF(r)=4\pi r^2\rho g(r)$ determines many of the features of the structural state of a liquid and a glass. Using the model of Knuyt *et al.* [7] the relation between K^{∞} and G^{∞} for an amorphous mono-atomic metal with a pair potential interaction $U(r)$ is obtained to be

$$K^{\infty}=\frac{5}{3}G^{\infty}-\frac{\rho}{12}\left\langle r\frac{dU}{dr}\right\rangle, \tag{1}$$

where ρ is the atomic density and

$$\left\langle r\frac{dU}{dr}\right\rangle=\int_0^{\infty} r\frac{dU}{dr}RDF(r)dr. \tag{2}$$

A very similar result is obtained if K^{∞} and G^{∞} are calculated using the expressions for the Born terms given in the classic work of Zwanzig *et al.* [3].

Assuming a first radial distribution peak with a position close to the minimum of the interatomic potential and a relatively small dispersion around this value, which would be the case in a dense supercooled liquid near the glass transition, the value of $\langle rdU/dr\rangle$ is nearly zero for an harmonic potential (or equivalently for a pair potential with a very deep well) and negative for an anharmonic potential [7]. The model used for obtaining Eq. (1) does not allow a quantitative evaluation of the results predicted [4], however, it is interesting to notice that the degree of departure from a Cauchy relation, that is the value of the last term in equation (1), is due to the anharmonicity of the material.

Recently, a generalized Cauchy relation

$$C_{11}(T)=BC_{44}(T)+A \tag{3}$$

or equivalently,

$$K^{\infty}(T)=\left[B-\frac{4}{3}\right]G^{\infty}(T)+A \tag{4}$$

was observed to hold in supercooled liquids near and throughout the glass transition [6], and also during the ageing process of polymerizing liquids and metallic glasses [5,6]. *B* and *A* were obtained to be independent of temperature and pressure within the *T* and *P* range involving the glass transition. Krüger *et al.* [6] found $B\approx 3$ for all the materials they investigated. In the case of metallic glasses, the dependence on temperature of the elastic constants of the equilibrium liquid [8] and the change of the elastic properties during a process of ageing [5] were recently estimated for the Vit4 alloy. The ratio of the dK/dT and dG/dT values obtained gives values of B=2.53 and B=2.87 in Eq. (3). These first results indicate an interesting agreement with the linear relation with $B\approx 3$ obtained for very different glass-forming materials.

In ref. [6], Krüger *et al.* obtained

$$A=2C_{11}(T_g)(\gamma_4-\gamma_1)/(1+2\gamma_4), \tag{5}$$

where γ_1 and γ_4 are the longitudinal and the shear mode Grüneisen parameters of the equilibrium liquid. The Grüneisen parameter

$$\gamma_i=-d\ln\omega_i/d\ln V. \tag{6}$$

where ω_i is the frequency of the *i*-vibrational mode and *V* is the volume, expresses the variation of the acoustic modes frequency because of a density change of the material, and it is related to the anharmonicity of the solid. Hence, similarly to Eq.

(1), Eq. (5) relates the parameter A, and so the degree of departure from the Cauchy relation $K=5/3G$, to the anharmonicity of the material.

The relation between the K/G ratio (or equivalently the Poisson's ratio ν) of the glass and the fragility m of the corresponding liquid has been intensely discussed [9,10]. Novikov *et al.* [9] found a rough correlation between ν and m for a wide set of different glass-forming materials. Some models claim to account for this empirical correlation [11], while some objections to its validity have been also made [10,12]. The K/G ratio of a metallic glass at room temperature is expected to be close to the K^{∞}/G^{∞} ratio of the equilibrium liquid at T_f. For a glass quenched at low cooling rates, or a glass rapidly quenched but structurally relaxed by a posterior annealing, it is expected that $T_f \approx T_g$, and the change of properties between room temperature and T_g is then due to the thermal expansion of the glass but not to a change of the glass structural state. In the case of Vit-4 the change in K and G due to the thermal expansion of the glass is estimated to be 2% and 8% respectively when going from room temperature to glass transition temperature [8], this gives a 6% of change of the K/G ratio.

Considering the values of the elastic properties of the glass at room temperature to be a sufficiently good approximation to the values of the elastic properties of the liquid at T_g and assuming a generalized Cauchy relation with $B=3$ valid for metallic glass-forming liquids, we can estimate the values of A from the K and G values of metallic glasses found in literature. Fig. 1 shows the correlation between the calculated A/C_{11} values and the fragility m of the liquid at T_g. The data used in Fig. 1 are obtained from refs. [13,14]. Only compositions with available data for the kinetic fragility, that is calculated from the shear viscosity behaviour near T_g and not from calorimetric measurements, were considered. The reasons for restricting the study to the kinetic fragility data will be discussed below.

Fig. 1 shows a K/G vs m correlation, in fact, $A/C_{11}=1-3G/(K+4/3G)$ and obviously A/C_{11} increases if K/G increases. However, now the correlation can be interpreted in terms of the vibrational properties of the liquid near the glass transition. From Eqs. (4) and (5), the correlation shown in Fig. 1 means that a more fragile liquid has a bigger difference between shear and longitudinal Grüneisen parameters. This relation seems quite plausible; the shear mode Grüneisen parameter accounts for the variation of the shear vibration frequency with density while the fragility index accounts for the variation of the shear viscosity with density as temperature is reduced.

The validity of the correlation shown in Fig. 1 has to be taken with great precautions, more experimental evidences are needed to confirm it [10,12]. There are more available data for the calorimetric fragility of metallic glasses. However, while the kinetic fragility is calculated at a well defined T_g (the temperature at which the shear viscosity attains a value of 10^{13} Poise), the calorimetric fragility is usually calculated at a higher and not well defined T_g. For this reason, the use of calorimetric fragility data is not considered in this work. In order to clarify the validity of the generalized Cauchy relation and the correlation between the K/G ratio and the fragility of the liquid, measurements of the high-frequency elastic constants of the equilibrium liquid at the same T_g where the glass fragility is calculated should be performed. Unfortunately, there is no such data available in literature for metallic glasses. However, in case a generalized Cauchy relation was certain for metallic liquids above the glass transition, the observed relation between the vibrational properties during the glass transition and the fragility of the liquid would explain the highly debated Poisson's ratio vs fragility correlation. Furthermore, the validity of this hypothesis implies that the anharmonicity of the material is a main factor controlling the relation between the bulk and the shear moduli of the liquid and the glass, this relation being crucial for determining the brittle-ductile behaviour of metallic glasses.

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