Relationship between the shear modulus G, activation energy, and shear viscosity η in metallic glasses below and above T_g: Direct *in situ* measurements of G and η

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In situ linear heating measurements of 560 kHz shear modulus G together with the data on the shear viscosity η of bulk glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ both below and slightly above the glass transition temperature T_g have been presented. It has been found that the shear modulus at $T>T_g$ is proportional to $k_BT \ln \eta$ that directly supports the notions implying that the activation energy of elementary relaxation events is controlled by the macroscopic shear modulus. Below T_g, this relationship fails and structural relaxation (which mainly defines η in this temperature range) becomes distributed in activation energies. By extracting the activation energy spectrum from the relaxation of G, it is possible to explain the temperature and heating rate dependence of η.

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The idea that the unrelaxed shear modulus G (i.e., the shear modulus measured at a frequency high enough to suppress any relaxation processes) is the key physical quantity controlling the main thermodynamic and kinetic properties of supercooled liquids and glasses is currently considered to be one of the most promising approaches in the physics of noncrystalline materials.[1–14] It was long ago supposed that the macroscopic G controls the activation energy of elementary flow events in supercooled liquids.[3] Most convincingly this idea was formulated in the "shoving model" by Dyre *et al.*,[2] who argued that since a flow event requires a local volume increase, its activation energy E should be identified as the work done in shoving aside the surrounding liquid, which is proportional to G, i.e.,

$$E(T) = G(T)V_c, \tag{1}$$

where V_c is some characteristic volume estimated to be less than the volume change during shoving.[2] They experimentally confirmed on a number of supercooled organic liquids above the glass transition temperature T_g that the shear viscosity obeys an Arrhenius relationship,

$$\eta(T) = \eta_0 \exp[E(T)/k_BT], \tag{2}$$

where η_0=const and E is dependent on G through Eq. (1). Johnson and Samwer[4] proposed a criterion for plastic yielding of metallic glasses below T_g also based on the proportionality of type (1) and the use of Arrhenius relationship (2) for the viscosity. Relationships (1) and (2) were further used by Johnson and co-workers for the calculation of η above T_g,[5,6] as well as for the explanation of the isothermal transition from Newtonian linear flow to nonlinear behavior with increasing strain rate at $T<T_g$.[5,8]

The joint use of relationships (1) and (2) actually constitutes a hypothesis which has to be experimentally verified by simultaneous *in situ* measurements of G and η. To our knowledge, such verification was done only in the aforementioned work by Dyre *et al.*[2] for temperatures $T>T_g$. The case of metallic glasses at both $T>T_g$ and $T\leq T_g$, therefore, has to be investigated. It is this goal which was accepted in the present Brief Report.

Glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (at. %) produced by melt jet quenching as $62\times5\times2$ mm^3 bars at a rate of $\approx$200 K/s was used for the investigation. The bars were confirmed by x-rays (Thermo Scientific ARL X'TRA diffractometer) to be fully amorphous. The calorimetric glass transition temperature T_g was found to be 559 K at $\dot{T}=5$ K/min.[15] The temperature dependencies of η of this glass at different $\dot{T}$ up to a temperature of $\approx$580 K were reported earlier.[15,16] Some additional viscosity measurements were performed specially for this investigation.

As a rule, high-frequency modulus measurements are being performed *ex situ* at room temperature after heat treatment of samples is finished. Only just a few *in situ* shear modulus measurements are reported in the literature (e.g., Refs. 14 and 17). In the present investigation, high-precision *in situ* shear modulus measurements were performed using the contactless electromagnetic acoustic transformation (EMAT) method.[18] In this method, sample's transverse vibrations occur due to the Lorentz force induced by the interaction of the external magnetic field with the current excitation coil. The primary advantage of this technique consists in the absence of a direct acoustic contact between the sample and current/receiving coils. Transverse vibrations at a frequency $f\approx560$ kHz were continuously monitored with a relative precision of about 1×10^{-5} upon heating up the samples with the dimensions of $5\times5\times2$ mm^3. The shear modulus was then calculated as $G(T)=4\rho(T)f^2(T)h^2$, where h is the sample's thickness and ρ is the density. The latter was extracted from detailed specific volume (V) data presented in Ref. 19 for the same bulk glass at temperatures $T\leq T_g$ and $T>T_g$. For the relative modulus error, one can write $\Delta G/G = \Delta V/V + 2\Delta f/f + 2\Delta h/h$, where $V=1/\rho$. The last summand here is $\approx10^{-3}$. Figure 4 in Ref. 19 implies that $\Delta V/V\approx4\times10^{-3}$ and hence $\Delta G/G\approx5\times10^{-3}$ that is about twice and a half of the size of G data points in Fig. 1.

Temperature dependence of G in the initial state at $\dot{T}=5$ K/min is shown in Fig. 1. A nearly linear decrease of G due to the anharmonicity upon heating up to $\approx$470 K is

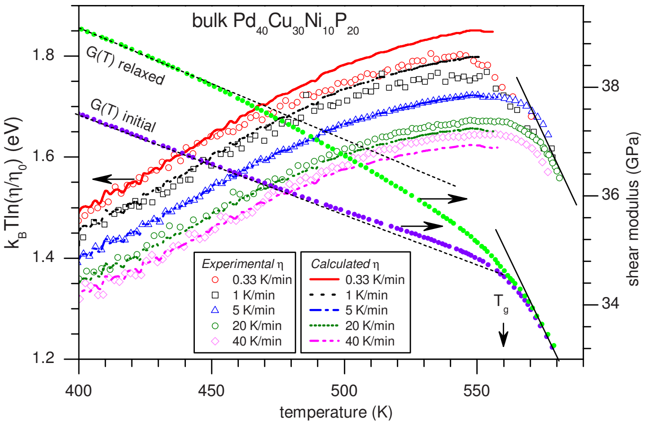

FIG. 1. (Color online) The shear viscosity η of glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at indicated heating rates plotted as temperature dependence of $k_BT\ln(\eta/\eta_0)$ [left axis; the symbols and curves show the experimental results and calculation data obtained using Eq. (5), respectively] together with the shear modulus G (closed circles, right axis) dependencies in the initial and relaxed states at $\dot{T}=5$ K/min. The vertical arrow gives the calorimetric T_g measured at the same $\dot{T}$. The solid lines denoting the approximations of these dependencies at $T>T_g$ have the same slope that means that the activation energy is proportional to G. Below T_g, such a relationship does not exist. The dashed lines represent low-temperature approximations of G.

observed. At higher temperatures, a notable increase in G over the "normal" behavior (i.e., over the dashed line in Fig. 1) due to progressive structural relaxation just in the course of heating is observed. Near T_g, the slope $|dG/dT|$ increases by 4.7 times, from 1.8×10^{-2} GPa/K to 8.4×10^{-2} GPa/K. Because of the rapid increase of the ultrasound attenuation above T_g, the measurements were possible only up to 580 K.

On the same temperature scale, Fig. 1 gives the quantity $k_BT\ln(\eta/\eta_0)$ calculated for different heating rates $0.33\leq\dot{T}\leq40$ K/min with the high-temperature viscosity limit η_0 accepted to be 0.0001 Pa s. Provided Eq. (2) is valid, this quantity corresponds to the temperature dependence of the activation energy. Reflecting the heating rate dependence of the viscosity,[15,16] the quantity $k_BT\ln(\eta/\eta_0)$ significantly depends on $\dot{T}$ at $T<T_g$. The character of its temperature dependence cardinally changes above the glass transition: $k_BT\ln(\eta(T)/\eta_0)$ becomes $\dot{T}$ independent and decreases with T (as usually observed for supercooled liquids[2,3]). The linear approximations of $k_BT\ln(\eta(T)/\eta_0)$ and $G(T)$ above T_g are given by the solid lines in Fig. 1. Although the temperature interval available for measurements of η and G at $T>T_g$ is rather narrow (about 20 K), it is clearly seen that these lines are nearly parallel each other. This means that the activation energy E in Eq. (2) is proportional to G in this temperature range and Eq. (1) is therefore valid. The proportionality constant $V_c\approx8\times10^{-30}$ m^3 that is about a half volume per atom. Our results, therefore, directly support the hypothesis implying that the shear viscosity above T_g obeys Arrhenius relationship (2) with *single* activation energy (1) defined by the *macroscopic* shear modulus.

Figure 1 also demonstrates that in the $T<T_g$ range, which is characterized by a strong structural relaxation, the quantity $k_BT\ln(\eta/\eta_0)$ increases with temperature while G decreases, in contradiction with the above hypothesis (see also Ref. 20). Besides that, η displays a rather strong heating rate dependence (vanishing above T_g), which is in no way captured by Eq. (2). The failure of Arrhenius viscosity law (2) below T_g is not unexpected. In this case, the shear viscosity is mostly controlled by structural relaxation with a distribution of activation energies[15,16,21] and simple exponential law (2), therefore, cannot be applied. However, there are no reasons to abandon the general idea that elementary relaxation events are controlled by the unrelaxed shear modulus as expressed by Eq. (1). In this case, this equation can be interpreted as a proportionality between the *local* activation energy and *local* shear modulus. Different atomic structure of local centers of structural relaxation should result in different local shear moduli (the significance of this idea in the inhomogeneous plasticity of metallic glasses was recently pointed out by Poon *et al.*[22]) and, therefore, in a continuous distribution of activation energies. The corresponding activation energy spectrum (AES) can be determined from structural relaxation-induced change in the *macroscopic* shear modulus and further used for the viscosity calculation. It is shown below that such a scheme with a few reasonable assumptions can explain the temperature dependence of η and its heating rate dependence.

Figure 1 shows temperature dependence of the shear modulus G_{rel} after heating up to a temperature of 580 K $>T_g$ (supercooled liquid region), i.e., after structural relaxation is completed. The difference between the relaxed and initial states, $G_{\text{rel}}-G_{\text{ini}}$, represents the modulus increase due to structural relaxation. A method to derive the AES using this difference was recently proposed in Ref. 14. Assuming that relaxation centers responsible for structural relaxation are similar in properties to dumbbell interstitials in simple crystalline metals and, therefore, their concentration is governed by the *macroscopic* G, the AES (concentration of relaxation centers per unit activation energy) is given by[14]

$$n_0(E_0)=\beta^{-1}\,\partial g(E_0)/\partial E_0, \tag{3}$$

where $g(T)=[G_{\text{ini}}(T)-G_{\text{rel}}(T)]/G_0$ [where $G_0=G_{\text{ini}}(T=293\text{ K})$], a dimensionless relaxation parameter $\beta\approx25$ (which reflects the sensitivity of G to the concentration of dumbbell-like relaxation centers) and E_0 is the characteristic activation energy (which corresponds to the maximal relaxation rate at a given instant) linearly increasing with temperature as

$$E_0=AT, \tag{4}$$

where the proportionality constant $A\approx3.13\times10^{-3}$ eV/K.[14,21] The AES thus calculated is shown in Fig. 2. The spectral density of relaxation centers n_0 first linearly increases with E_0 and then rapidly goes to zero near 1.75 eV, reflecting the approach to the glass transition. A very similar shape of the AES was recently reconstructed from the low-frequency internal friction measurements on the same bulk glass[23] as well as from G measurements on a Zr-based bulk glass.[14] The averaged AES (solid curve in Fig. 2), $\bar{n}_0(E_0)$, can be used to estimate the concentration of relaxation centers

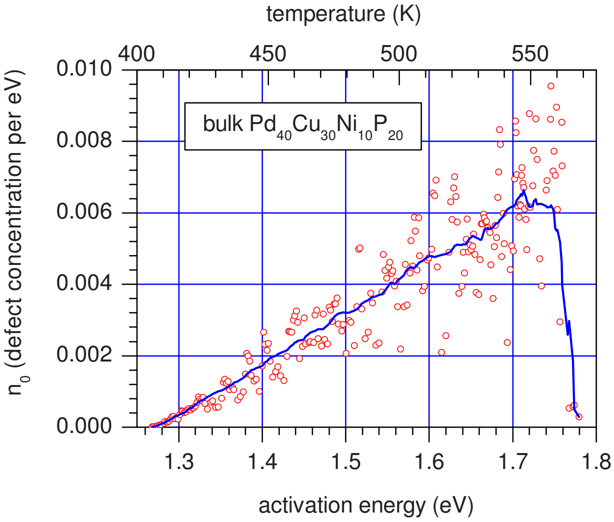

FIG. 2. (Color online) Activation energy spectrum of structural relaxation derived from shear modulus relaxation using Eq. (3). The solid curve is produced by adjacent averaging.

annealed out during structural relaxation, $c=\int_{E_{\min}}^{E_{\max}}\bar{n}_0(E)dE$, with the integration limits $E_{\min}$ and $E_{\max}$ equal to 1.27 and 1.78 eV, respectively (Fig. 2). The calculation gives $c \approx 0.0017$, which is comparable with the concentration of relaxation centers annealing out due to structural relaxation in a Zr-based bulk glass.[14]

The temperature dependencies of η below T_g were calculated within the framework of directional structural relaxation (DSR) model (see Ref. 21, and papers cited therein). According to this model, every elementary flow event occurs as a thermoactivated shear in the direction predetermined by the local atomic structure (first flow stage) and immediate athermal viscous flow in the surrounding volume Ω in strict accordance with the applied stress (second flow stage; the corresponding strain is sometimes named "concordant"). Implying a first-order exponential kinetics for the flow events with a given activation energy, the DSR model gives a simple equation for the macroscopic viscous shear strain rate,[21] $\dot{\varepsilon}=\varepsilon_0 N_0 \Omega \dot{E}_0$, where N_0 is the number of relaxation centers per unit volume and activation energy interval, $\dot{E}_0$ is the time derivative of the characteristic activation energy given by Eq. (4), and ε_0 is the mean local deformation. Due to the orienting impact of the external stress σ on the flow events, $\varepsilon_0=\sigma C$, where C is the corresponding orienting factor. The defect spectral volume density N_0 is connected with the defect spectral concentration n_0 in Eq. (3) through $N_0 = n_0 \rho N_A / m_\mu$, where ρ is the density, N_A is the Avogadro number, and m_μ is the molar mass. The shear viscosity $\eta=\sigma/\dot{\varepsilon}$ then becomes

$$\eta(T)=\frac{m_\mu}{n_0[E_0(T)]\rho N_A \Omega C A \dot{T}}, \qquad (5)$$

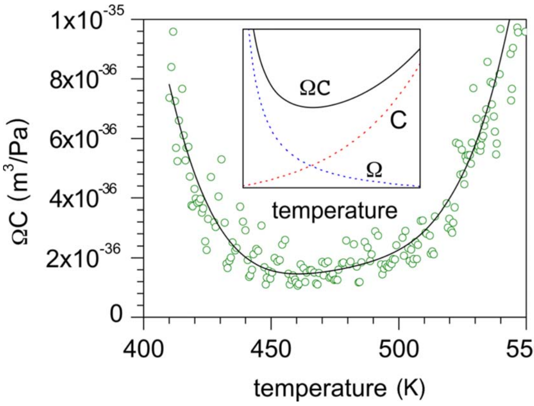

FIG. 3. (Color online) The product ΩC from Eq. (5) as a function of temperature. The solid curve represents a fourth degree polynomial approximation. The inset represents a sketch of assumed temperature dependencies of Ω and C.

where $\dot{T}$ is the heating rate. The unknown product ΩC was calculated using Eq. (5) with the help of reconstructed AES (Fig. 2) and viscosity $\eta(T)$ curve taken at $\dot{T}=5$ K/min (Fig. 1). Figure 3 shows that ΩC is a sharply nonmonotonous function, which has a minimum at around 460 K. Such a form may suggest that one of the multipliers in this product rapidly increases with temperature while the other one quickly decreases. Since η decreases with temperature, one can suppose that elementary shear rearrangements embrace smaller volume Ω. On the other hand, the orienting impact of the applied stress on these rearrangements should increase with temperature, resulting in the rise of the parameter C, which defines the local deformation ε_0. Such temperature behavior of Ω and C can explain temperature behavior of ΩC product, as schematized in the inset of Fig. 3.

The temperature dependencies of η at other heating rates (0.33, 1, 20, and 40 K/min) calculated using Eq. (5) with ΩC product shown in Fig. 3 are given by solid/dashed/dotted curves in Fig. 1. It is seen that Eq. (5) gives quite acceptable description of the viscosity behavior. Other positive tests of this equation were presented earlier in Refs. 15 and 16. These tests together with successful applications of the DSR model for the interpretation of different mechanical relaxations below T_g (for a review, see Ref. 21) make it quite plausible that structural relaxation-induced viscous flow of metallic glasses below T_g occurs as a set of two-stage relaxation events with distributed activation energies. The origin of this distribution could be due to a distribution of local shear moduli. On the other hand, the applicability of modulus relaxation analysis using Eq. (3) implies that the relaxation centers producing flow events are similar in properties to dumbbell interstitials, as discussed above.

It is important to understand why simple Arrhenius viscosity law (2) with single activation energy (1) is valid above T_g whereas at $T<T_g$ exponential relaxations with distributed activation energies leading to specific viscosity relationship (5) must be involved. This difference may be attributed to certain features of the potential-energy landscape.[24] Below T_g, the glass samples potential barriers of different heights between neighboring basins within a certain megabasin that is reflected in distributed relaxation (controlled by a distribution of local shear moduli) of a physical property. At or above T_g, the thermal energy becomes sufficient to sample different megabasins. Since one observes a single E in this

case [for glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$, such behavior is observed up to at least 645 K (Ref. 15)], the heights of these megabasins should be nearly equal leading to a proportionality between E and macroscopic G.

In conclusion, the results of direct *in situ* measurements of 560 kHz shear modulus G and shear viscosity η both well below and slightly above T_g ($400\ \mathrm{K} \leq T \leq T_g + 20\ \mathrm{K}$) have been presented. Above T_g, the shear modulus is found to be proportional to $k_B T \ln \eta$, implying that plastic flow obeys a simple Arrhenius relationship with the activation energy E proportional to G, in line with a number of recent theoretical models.[2–5] Below T_g, this proportionality fails, the Arrhenius flow law cannot be applied, and there appears a strong heating rate dependence of η. The latter obeys relationship (5) derived on the assumption that the origin of viscous flow is due to structural relaxation occurring upon heating through two-stage elementary relaxation events distributed in activation energy E and oriented by the applied stress. It is argued that the general idea on the proportionality between G and E still holds, but the origin of distributed activation energy spectrum (AES) below T_g is determined by a distribution of *local* shear moduli.

Using the obtained data on relaxation of macroscopic shear modulus upon heating, the AES of elementary relaxation events has been reconstructed. The shape of this spectrum together with the measured $\eta(T)$ temperature dependence give the evidence that the volume embracing an elementary shear event of structural relaxation rapidly decreases with temperature at $T < T_g$ while the orienting impact of the applied stress quickly increases.

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