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MECHANICAL RELAXATION IN AMORPHOUS SELENIUM

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ABSTRACT. Literature mechanical relaxation data of amorphous selenium are interpreted in terms of the soft potential model and its extension to higher temperatures, the Gilroy-Phillips model. At the crossover temperature from tunneling states to thermally activated relaxation, one finds a stronger decrease of the barrier density $f(V)$ with increasing barrier height V than in silica. On the high barrier side, $f(V)$ is determined by the Kohlrausch t^{β}-tail of the viscous flow, with $\beta = 0.31$. In longitudinal ultrasound absorption data, one finds weak oscillations of the Kohlrausch barrier density, similar to those found recently in metallic glasses, consistent with an increase of the barrier by $V_1 = S_1 T_g/\beta$ for the addition of one selenium atom to the rearranging domain, where S_1 is the structural entropy per atom at the glass temperature T_g.

From the point of view of elasticity theory, a glass is a very simple solid, elastically isotropic, described by a density ρ, a bulk modulus B and a shear modulus G. Consequently, one has isotropic longitudinal and transverse sound velocities v_l and v_t, respectively. The complications begin when one looks for the absorption of these sound waves as a function of frequency and temperature. Then one realizes that there is a multitude of other excitations coexisting and interacting with the sound waves. The key to the understanding of this multitude lies in the multiminimum concept of the glass; although the disordered structure does not flow any longer, there are still many minima of the potential energy. One has to reckon with low and high barriers between them, and one has to take into account the energy difference between neighbouring minima of the glass. This is the conceptual basis of the tunnelling model (Phillips 1987) and its two extensions, the soft potential model (Parshin 1994; Ramos and Buchenau 1997) and the Gilroy-Phillips model (Gilroy and Phillips 1981).

The Gilroy-Phillips model is the proper choice if one is not especially interested in the low-temperature anomalies of glasses, but wants to study what happens outside the quantum mechanics region and at the glass transition. It describes the classical shear relaxation of the glass in terms of a barrier density function $f(V)$, given by:

$$f(V) = \frac{\gamma_t^2 n(V,0)}{G}\,, \tag{1}$$

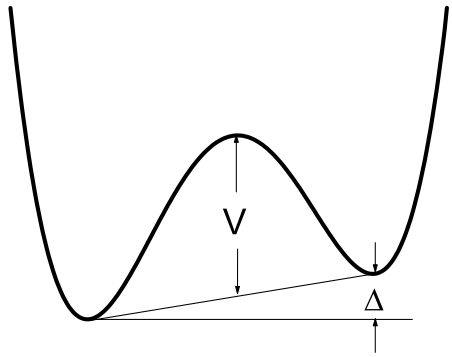

FIGURE 1. Definition of the barrier height V and the asymmetry Δ of an asymmetric double well potential.

where $n(V,\Delta)$ is the number density of relaxing entities with barrier height V and the asymmetry Δ (see Fig. 1) and γ_t is the coupling constant to an external shear distortion (Buchenau 2001). The model assumes that $n(V,\Delta) = n(V,0)$ for all relevant values of Δ, making the integration over Δ straightforward. Note that here the definition

$$\gamma_t = \frac{\partial \Delta}{\partial \varepsilon_t}, \tag{2}$$

where ε_t is the shear angle of the external shear distortion, does not have the factor 1/2 of the corresponding definitions in the tunneling (Phillips 1987) and soft potential model (Parshin 1994; Ramos and Buchenau 1997). If the external distortion ε_l is a uniaxial one, the distortion of longitudinal sound waves, one has to replace γ_t by γ_l and G by the uniaxial modulus $M = B + 4G/3$ in Eq. (1).

In selenium, one finds five measurements of internal friction at low and intermediate temperatures: the longitudinal sound absorption data of Carini Jr. *et al.* (1978), the transverse sound absorption data of Duquesne and Bellessa (1980), the oscillator data of Jacqmin *et al.* (1983) and Keil *et al.* (1993) and the new oscillator data of Liu *et al.* (2018).

Figure 2 shows the tunneling plateau in the sound absorption predicted by the tunneling model (Phillips 1987) for three shear measurements at different frequencies (Jacqmin *et al.* 1983; Keil *et al.* 1993; Liu *et al.* 2018). In principle, the height of this plateau should be frequency-independent, $C_t\pi/2$, where C_t is a parameter combination of the tunneling model. But the three measurements give different C_t-values, probably because the density of tunneling states in selenium depends on the cooling rate through the glass transition. Therefore they were plotted as $Q^{-1}/Q^{-1}_{\text{plateau}}$, demonstrating that all three give the onset of the classical relaxation at the temperature predicted by the soft potential model (Ramos and Buchenau 1997), but with a slope which is markedly smaller than the predicted $T^{3/4}$ (this conclusion was already drawn by Keil *et al.* (1993) and is corroborated here by the two

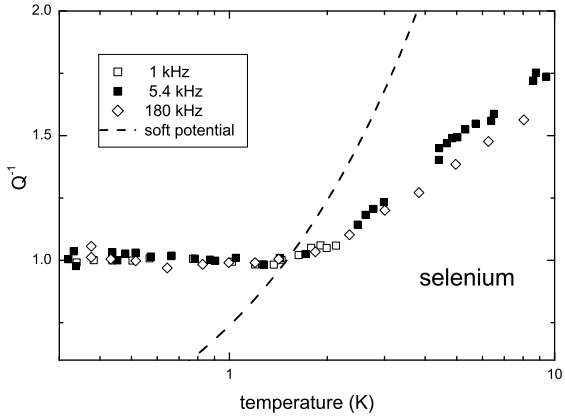

FIGURE 2. Sound absorption in selenium at low temperatures. The data are normalized to the height of the tunneling plateau, $3.5 \cdot 10^{-4}$ in the measurement by Jacqmin *et al.* (1983) at 1 kHz, $4.2 \cdot 10^{-4}$ in the measurement by Liu *et al.* (2018) at 5.4 kHz and $10 \cdot 10^{-4}$ in the measurement by Keil *et al.* (1993) at 180 kHz. The dashed line is the soft potential prediction of Eq. (4).

other measurements). According to the definition of Q^{-1}:

$$Q^{-1} = \tan\delta = \frac{G''}{G'} = \frac{v_t l_{\mathrm{rel,class}}^{-1}}{\omega}\,, \tag{3}$$

where v_t is the transverse sound velocity, $l_{\mathrm{rel,class}}$ is the inverse mean free path of the transverse sound waves under the influence of classical relaxation and ω is the frequency of the sound wave. With Eq. (11) of Ramos and Buchenau (1997), one gets

$$Q_{\mathrm{rel,class}}^{-1} = \pi C_t \left(\frac{k_B T}{W}\right)^{3/4} \ln^{-1/4} \frac{1}{\omega\tau_0}\,, \tag{4}$$

with $\tau_0 = 10^{-13}$ s. The crossover temperature W/k_B lies at about 1.2 K (Ramos and Buchenau 1997). The finding of Fig. 2 is a bit different from Ramos and Buchenau (1997) in silica, germania and B_2O_3, where one does indeed find the predicted soft potential rise, though not to very high temperatures. In selenium, the breakdown of the soft potential assumptions seems to occur earlier, in terms of the soft potential definitions already at a positive restoring force D_2.

Figure 3(a) shows the barrier density $f(V)$ of the Gilroy-Phillips model calculated from the longitudinal sound absorption data (Carini Jr. *et al.* 1978) at 15 and 25 MHz, and from the oscillator data (Liu *et al.* 2018) at 5.4 kHz. The oscillator data supply Q^{-1}, the sound absorption data are given as α_{db} in db/cm, from which one can calculate Q^{-1} via Pohl *et al.* (2002):

$$Q^{-1} = 0.23 \frac{v}{\omega} \alpha_{\mathrm{db}}\,, \tag{5}$$

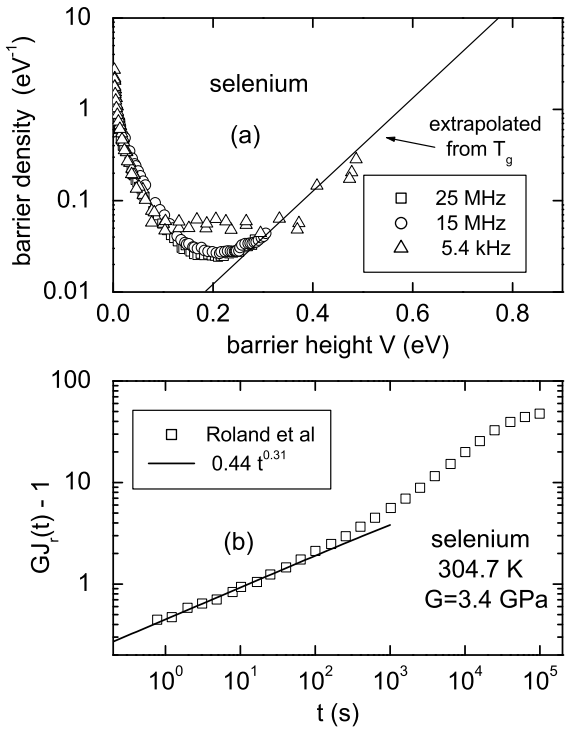

FIGURE 3. (a) Barrier density function $f(V)$ in selenium evaluated from longitudinal sound absorption data (Carini Jr. *et al.* 1978) at 25 and 15 MHz and internal friction data (Liu *et al.* 2018) at 5.4 kHz. The continuous line is the Kohlrausch tail of the viscous flow data in the lower part of the figure (b) Recoverable shear compliance $J_r(t)$ of selenium at the glass temperature $T_g = 304.7$ K, with a Kohlrausch t^β-tail at short times. The G-value of 3.4 GPa stems from ultrasound data (Kozhevnikov *et al.* 2007). The shortest measured time corresponds to a barrier of 0.78 eV in (a).

where v is the respective sound velocity. Having $Q^{-1} = G''/G'$, one makes the approximation $G' \approx G$ and calculates $f(V)$ from another approximation (Buchenau 2001)

$$f(k_B T \ln(1/\omega\tau_0)) = \frac{2G''}{\pi G k_B T}\,. \tag{6}$$

Naturally, for the longitudinal sound absorption data (Carini Jr. *et al.* 1978) one should replace G''/G by M''/M, defining a longitudinal $f(V)$. But Fig. 3(a) shows that the two definitions provide practically the same $f(V)$ in selenium. On the high barrier side, $f(V)$ turns upward and begins to approach the extrapolation

$$f(V) = f_0 \exp(\beta V/k_B T_g)\,, \tag{7}$$

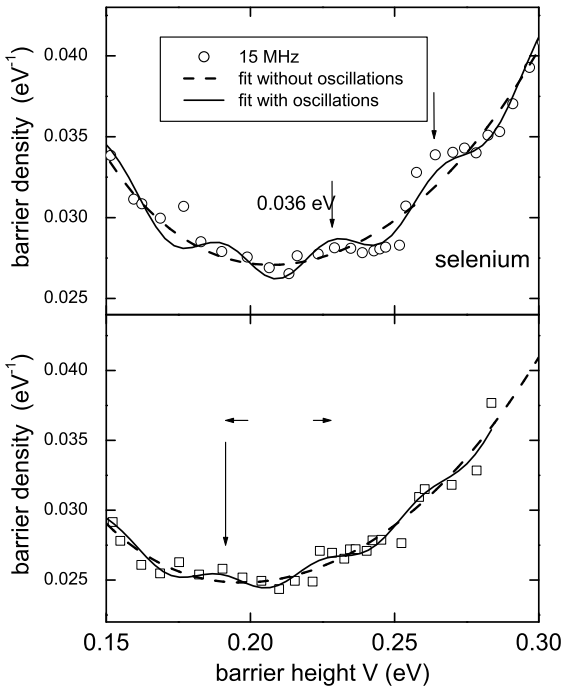

FIGURE 4. Barrier density function in the crossover region from low to high barriers for (a) 15 MHz (b) 25 MHz. Note the weak oscillations of the data with a period of 0.036 eV in both datasets.

with $f_0 = 0.0011$ eV^{-1}, $\beta = 0.31$ and $T_g = 304.7$ K. This is precisely the barrier density needed to explain the measured short-time Kohlrausch part t^β of the viscous flow data (Roland *et al.* 1999) of selenium at $T_g = 304.7$ K, shown in Fig. 3(b), with $\beta = 0.31$. The accuracy of this connection is greatly improved by the knowledge of the shear modulus $G = 3.4$ GPa at T_g, taken from the ultrasound data of Kozhevnikov *et al.* (2007), which in turn corroborate earlier data (Galli *et al.* 1986) (remember that $J_r(t)$ contains also the elastic contribution $1/G$). Obviously, selenium is a glass former which has no secondary relaxation, a glass former where the low-barrier relaxation neighbors of the tunneling states have a continuous crossover to the high Kohlrausch barriers announcing the beginning of the viscous flow.

The longitudinal sound absorption data (Carini Jr. *et al.* 1978) contain an important additional information on these Kohlrausch barriers. This is shown in Fig. 4, which magnifies the results for the barrier density function $f(V)$ obtained for the two frequencies around the minimum. If one fits the minimum with a continuous function (the dashed lines), one sees that the data tend to oscillate around this average with a period of 0.036 eV (the continuous curves), both sets showing maxima and minima at the same places. The finding corroborates an earlier finding of such oscillations in the internal friction of a metallic glass at room temperature (Ju *et al.* 2011). In the case of the metallic glass, the period is 0.05 eV,

about $k_B T_g$ at its glass temperature around 600 K. The interpretation (Ju *et al.* 2011) was that two subsequent maxima stand for cooperatively rearranging regions with N and $N+1$ atoms, respectively. The interpretation implies that the rearrangement barrier V increases linearly with the number of atoms in the rearranging region, an additional atom adding the amount V_1 to the total barrier. For the metallic glass, this would imply that the regions responsible for relaxation times close to the Maxwell time $\tau_M = \eta/G$ (η viscosity) consist out of about forty atoms. The interpretation suggests in turn an interpretation (Buchenau 2018) of the Kohlrausch β:

$$\beta = \frac{S_1 T_g}{V_1}, \tag{8}$$

where S_1 is the structural excess entropy per atom of the glass at T_g. The interpretation is based on the consideration that each additional atom increases the number of possible rearrangements of the region by the factor $\exp(S_1/k_B)$. At the same time, it increases the rearrangement barrier by V_1, pushing the Arrhenius relaxation time up by the factor $exp(V_1/k_B T_g)$. Together, the two tendencies result in a Kohlrausch β given by Eq. (7).

The interpretation fits in the case of the metallic glass; S_1 at T_g is 0.36 k_B per atom in $Pd_{40}Ni_{40}P_{20}$ (Wilde *et al.* 1994) and in vitralloy-1 (Busch *et al.* 2001). This yields the $\beta = 0.4$ usually observed in metallic glasses (Wang *et al.* 2008). Similarly, in selenium, $S_1 = 0.43$ k_B per atom (Chang and Bestul 1974) at T_g, so Eq. (7) supplies indeed the observed value $\beta = 0.31$ with $V_1 = 0.036$ eV. This implies about twenty-five atoms in the regions responsible for the viscous flow in selenium.

To conclude, the available sound absorption and internal friction data of selenium in the literature have been transformed into a reasonably temperature-independent Gilroy-Phillips barrier density function. The function has the strong decrease at low barriers which is seen in all studied cases. No secondary relaxation peak is found. At higher barriers, one starts to see the Kohlrausch tail of the highly viscous flow, frozen in at the glass transition. In this tail, one observes weak oscillations of the barrier density, similar to those observed earlier in a metallic glass and supporting a recent interpretation of the Kohlrausch exponent.

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