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# A relationship between non-exponential stress relaxation and delayed elasticity in the viscoelastic process in amorphous solids: illustration on a chalcogenide glass

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## Abstract

Inorganic glasses are viscoelastic materials since they exhibit, below as well as above their glass transition temperature, a viscoelastic deformation under stress, which can be decomposed into a sum of an elastic part, an inelastic (or viscous) part and a delayed elastic part. The delayed elastic part is responsible for the non-linear primary creep stage observed during creep tests. During a stress relaxation test, the strain, imposed, is initially fully elastic, but is transformed, as the stress relaxes, into an inelastic and a delayed elastic strains. For linear viscoelastic materials, if the stress relaxation function can be fitted by a stretched exponential function, the evolution of each part of the strain can be predicted using the Boltzmann superposition principle. We develop here the equations of these evolutions, and we illustrate their accuracy by comparing them with experimental evolutions measured on GeSe<sub>9</sub> glass fibers. We illustrate also, by simple equations, the relationship between any kind of relaxation function based on additive contribution of different relaxation processes and the delayed elastic contribution to stress relaxation: the delayed elasticity is directly correlated to the dispersion of relaxations times of the processes involved during relaxation.

## Keywords:

delayed elasticity, anelasticity, stretch exponent, linear viscoelasticity, chalcogenide glasses

## 1. Introduction

Many models (please see (Phillips, 1996) and references therein) have been proposed to explain the non-exponential relaxation in amorphous solids, and to give an "unified" theory, valid for any kind of relaxation, including stress relaxation. Nevertheless, the "delayed elasticity", that inevitably emerges when the stress relaxation is not exponential, is not often discussed (see (Goldstein, 1969) where this problem is detailed) despite its preponderance during the first stages of relaxation. It is known, since more than a century and a half (Weber, 1835), that the primary or transient creep stage of almost all kind of materials is due to delayed elasticity. It is not only due to a possible non-equilibrium viscosity, as astonishingly suggested by the ASTM standard for viscosity measurements (ASTM C1350-96, 1996), since glasses under equilibrium also exhibit primary creep stage. Delayed elasticity is also named "anelasticity" (mainly for metals (Zener, 1948)), or "retarded elasticity" (Goldstein, 1969) and was originally named "elastic aftereffect" ("*elastische nachwirkung*" (Boltzmann, 1876)). The delayed elastic deformation is a reversible deformation ("elastic") which does not recover instantaneously ("delayed" or "retarded") when the stress is released. The history of the investigation of the "aftereffect", taking its origins in Göttingen with Weber and Kohlrausch, has been nicely summarized by Bendler (1984). The primary creep stage is supposed to occur in any kind of material, including ceramics, crystalline metallic

materials, polymers, inorganic glasses, metallic glasses, as well as biomaterials. Thus, any kind of material is supposed to exhibit, during creep flow, delayed elasticity. Since nowadays a lot of commercial machines are available for measuring the steady state viscosity from the creep rate, it is sometimes forgotten that the creep rate is not solely controlled by the viscosity. During the primary creep stage, the creep rate is mainly controlled by the delayed elasticity, and the viscosity parameter can be measured only when the stationary creep stage is reached. This, for inorganic glasses, below their glass transition temperature, can take hours to days. Consequently, a "continuous viscosity measurement", in the glass transition range, below or just above (down to a viscosity of, let say, 10<sup>9-10</sup> Pa.s), based on the continuous creep rate measurement, using continuous heating or cooling (no matter how slow it is), does not even make sense, and will obviously tend to give an "anomalous" apparent viscosity. In other words, non-isothermal viscosity measurements are necessarily wrong, because of the delayed elasticity. It underlines the necessity of a better knowledge of this delayed elastic deformation.

If it is quite straightforward to measure the delayed elasticity during a creep-recovery test, it becomes more delicate to evaluate it during a relaxation test. Wiechert (1893) is probably the first who has suggested that the delayed elasticity takes its origin in the non-exponentiality of the stress relaxation. A non-exponential relaxation can be modelled by a gen-

54 eralized Maxwell model (Maxwell, 1868) (or more precisely 102  
 55 a "Maxwell-Wiechert model" (Wiechert, 1893)), where the re-103  
 56 laxation modulus is decomposed into a Prony series. The equa-104  
 57 tions, depicting the correlation between a non-exponential re-105  
 58 laxation corresponding to a Maxwell-Wiechert model and the-106  
 59 primary creep stage (including the delayed elasticity), have-107  
 60 been set by Bennewitz and Rötger (see (Simha, 1942)). The-108  
 61 Maxwell-Wiechert model is efficient to describe the viscoelas-  
 62 tic behavior of silica glasses (Duffrène, Gy, Burlet, and Piques,  
 63 1997), but it requires a large number of parameters as com-109  
 64 pared to the well-known stretched exponential or "KWW"  
 65 (Kohlrausch-Williams-Watts) function (Kohlrausch, 1854):

$$66 \quad \varphi(t) = \frac{Q(t) - Q_\infty}{Q(0) - Q_\infty} = \exp\left(-\left(\frac{t}{\tau_0}\right)^\beta\right) \quad (1)_{113}$$

67 where  $\varphi$  is the relaxation function, describing the normalized<sup>115</sup>  
 68 relaxation of a quantity  $Q$  (here the shear stress),  $Q_\infty$  being its  
 69 asymptotic value at  $t \rightarrow +\infty$ .  $\beta$  is the stretch exponent, and  $\tau_0$ <sup>116</sup>  
 70 is a characteristic time, related to the average (or "Maxwell's")  
 71 relaxation time  $\tau_a$  by the following relation: <sup>117</sup>

$$72 \quad \tau_a = \int_0^{+\infty} \varphi(t) dt = \frac{\Gamma(1/\beta)}{\beta} \tau_0 \quad (2)_{119}$$

73 where  $\Gamma$  is the Gamma function:  $\Gamma(x, y) = \int_y^\infty s^{x-1} e^{-s} ds$ <sup>121</sup>  
 74 and  $\Gamma(x) = \Gamma(x, 0)$ . The average relaxation time corre-  
 75 sponds to the average lifetime of an atom/molecule or group of<sup>122</sup>  
 76 atoms/molecules in their equilibrium position (here when they<sup>123</sup>  
 77 are shifted by the stress) (Frenkel, 1926). The stretched expo-  
 78 nential function (SEF) has various advantages. The main one<sup>124</sup>  
 79 is that it has only two parameters to describe the full relaxation  
 80 spectrum. The second one is that the "departure" from the ex-<sup>125</sup>  
 81ponentiality is directly signed by the stretch exponent  $\beta$ . So,<sup>126</sup>  
 82 according to the idea of Wiechert, the delayed elasticity is di-  
 83 rectly signed by  $\beta$ . The SEF has been widely used to describe<sup>127</sup>  
 84 various kind of relaxation processes (see for example (Phillips,  
 85 1996)), but this function is not physically sound, first because<sup>128</sup>  
 86 regarding its time derivation: <sup>129</sup>

$$87 \quad \frac{d\varphi(t)}{dt} = -\varphi(t) \left(\frac{t}{\tau_0}\right)^\beta \beta t^{-1} \quad (3)_{131}$$

88 the relaxation rate tends to  $-\infty$  when  $t \rightarrow 0^+$ , for  $0 < \beta < 1$ .<sup>133</sup>  
 89 Duffrène et al. (1997) have also pointed out the inadequacy<sup>134</sup>  
 90 of the SEF to describe the viscoelastic behavior of soda-lime-<sup>135</sup>  
 91 silica glasses. Additionally, they have shown that if we assume<sup>136</sup>  
 92 that the shear relaxation function corresponds to a SEF, the<sup>137</sup>  
 93 primary creep stage can not be fitted by another SEF, as it is<sup>138</sup>  
 94 often done. <sup>139</sup>

95  
 96 In spite of the weaknesses of the SEF, we will show here,<sup>140</sup>  
 97 experimentally, how much the idea of Wiechert is correct: the  
 98 delayed elasticity is only connected to the stretch exponent. The<sup>141</sup>  
 99 SEF is largely used in the literature mainly in order to describe  
 100 the relaxation kinetic, but what is not often considered is its  
 101 ability to describe the detailed mechanisms of relaxation, such<sup>142</sup>

as, for stress relaxation, the delayed elasticity and the inelas-  
 ticity. We will illustrate, through relaxation-recovery tests on  
 a viscoelastic material, how much efficient is the SEF to pre-  
 dict the evolution of the delayed elasticity. Then, we will show  
 how we can interpret the relationship between any kind of relax-  
 ation function decomposable into a sum of exponential function  
 (such as the SEF) and the delayed elasticity.

## 2. Theory

### 2.1. Linear viscoelasticity

111 Let us consider a linear viscoelastic body, undergoing a shear  
 112 distortion, evolving over time:  $\gamma(t)$ , in the framework of the  
 113 small strain assumption. According to the Boltzmann superpo-  
 114 sition principle (Boltzmann, 1876), the resulting shear stress is  
 115  $\sigma$ :

$$116 \quad \sigma(t) = \int_{-\infty}^t G(t-s) \frac{d\gamma(s)}{ds} ds \quad (4)$$

117  $G$  is the shear relaxation modulus of the viscoelastic body. Of  
 118 course, considering the distortion as something imposed is just  
 119 a point of view, and consequently, if we consider instead the  
 120 stress as imposed, the resulting shear distortion is:

$$121 \quad \gamma(t) = \int_{-\infty}^t J(t-s) \frac{d\sigma(s)}{ds} ds \quad (5)$$

122  $J$  is the shear creep compliance.  $J$  and  $G$  are correlated by a  
 123 Duhamel convolution equation (Ferry, 1980):

$$124 \quad t = \int_0^t G(t-s) \times J(s) ds = \int_0^t G(s) \times J(t-s) ds \quad (6)$$

125 Or, considering the well-known Lee (1955)-Mandel correspon-  
 126 dence principle, the equations, for linear elasticity being:

$$127 \quad \gamma = \mu^{-1} \sigma \text{ and } \sigma = \mu \gamma \text{ so that: } \mu^{-1} \mu = 1 \quad (7)$$

128 where  $\mu$  is the elastic shear modulus, we obtain for linear vis-  
 129 coelasticity, considering  $G$  and  $J$  as the viscoelastic counter-  
 130 parts of  $\mu$  and  $\mu^{-1}$  respectively:

$$131 \quad \gamma^* = J^* \sigma^* \text{ and } \sigma^* = G^* \gamma^* \text{ so that: } J^* G^* = 1 \quad (8)$$

132 where  $f^*$  is the Laplace-Carson transform of  $f$ :  $f^* = s \times \mathcal{L}(f)$ ,  
 133  $\mathcal{L}(f)$  being the Laplace transform of  $f$  and  $s$  the variable in the  
 134 Laplace  $s$ -domain.

135 The shear creep compliance  $J$  is often explicitly divided into  
 136 a sum of three components: elastic  $J_e$  time-independent, de-  
 137 layed elastic  $J_d(t)$  which converges to a time-independent value  
 138 when  $t \rightarrow +\infty$  and inelastic  $J_\eta$  a linear function of time:

$$139 \quad J_e = \frac{1}{\mu} \text{ and } J_\eta(t) = \frac{t}{\eta} \quad (9)$$

140 where  $\eta$  is the shear viscosity. Using Eq.(6), we also obtain:

$$141 \quad J_d(t) = \mathcal{L}^{-1}\left(\frac{1}{s^2 \mathcal{L}(G(t))}\right) - \frac{t}{\eta} - \frac{1}{\mu} \quad (10)$$

This decomposition of  $J$  is clearly assumed for various well-known models. This is the case for the Burger's model, the generalized Burger's model, and for any kind of model or function describing  $J$  with a retardation function (a function corresponding to  $\phi(t) = 1 - J_d(t)/J_d(0)$ ). Other models, describing the shear relaxation modulus, such as the Maxwell-Wiechert model, implicitly assume this division of  $J$ , since the Burger's model is equivalent to a Maxwell-Wiechert model with two cells. Accordingly, the shear distortion, itself, can be divided into three components, associated with  $J_e$ ,  $J_d$  and  $J_\eta$ : an elastic distortion  $\gamma_e$ , reversible, a delayed elastic distortion  $\gamma_d$ , reversible but with delay, and an inelastic distortion  $\gamma_\eta$ , irreversible. We can write, using the Boltzmann superposition principle (Boltzmann, 1876) or the Lee-Mandel correspondence principle:

$$\gamma_c(t) = \int_{-\infty}^t J_c(t-s) \frac{d\sigma(s)}{ds} ds \text{ or } \gamma_c^*(s) = J_c^*(s) \sigma^*(s) \quad (11)$$

where  $c = e, d$  or  $\eta$ . With:

$$\gamma(t) = \gamma_e(t) + \gamma_d(t) + \gamma_\eta(t) \text{ \& } J(t) = J_e(t) + J_d(t) + J_\eta(t) \quad (12)$$

So, we can also write:

$$\begin{aligned} \gamma_e(t) &= \frac{\sigma(t)}{\mu} \\ \gamma_\eta(t) &= \int_{-\infty}^t \frac{\sigma(s)}{\eta} ds \\ \gamma_d(t) &= \gamma(t) - \gamma_e(t) - \gamma_\eta(t) \end{aligned} \quad (13)$$

Regarding these equations, and assuming  $\gamma_\eta(t) = 0$  if  $t < 0$ , we can deduce that:

$$\eta = \frac{\sigma(t)}{\dot{\gamma}_\eta(t)} \quad (14)$$

This is the conventional "newtonian viscosity". But, using Eq.(6) we also have the following relation, known as the "Ferry's relation" (Ferry, 1980):

$$\eta = \int_0^{+\infty} G(t) dt \quad (15)$$

## 2.2. Delayed elasticity

Using Eq.(10) and (11), we can see that there is no delayed elasticity, for any kind of stress history, only if  $J_d(t) = 0$ . It leads to (Eq.(6) & (9)):

$$J(t) = \frac{1}{\mu} + \frac{t}{\eta} \text{ and } G(t) = \mu \exp\left(-\frac{t}{\eta}\right) \quad (16)$$

The average shear relaxation time  $\tau_a$ , according to the Maxwell's relation (Maxwell, 1868) corresponds to:  $\tau_a = \eta/\mu$ . In other words, the only possibility to observe no delayed elasticity is to have an exponential relaxation. It clearly illustrates the assertion of Wiechert (1893) that the delayed elasticity comes from a non-exponential relaxation. The equation of Simha (1942), giving the relationship between a creep curve and the distribution of relaxation times leads to the same conclusion. As a matter of fact, if the shear relaxation modulus

of a linear viscoelastic body is described by a SEF, for any  $0 < \beta < 1$ , when this body deforms non-elastically (whatever if the stress is constant or not), a part of the deformation is or has been delayed elastic.

## 2.3. Stretched exponential relaxation

Let us now assume that the shear relaxation modulus can be fitted by a SEF:

$$G(t) = \mu \varphi(t) \text{ where } \varphi(t) = \exp\left(-\left(\frac{t}{\tau_0}\right)^\beta\right) \quad (17)$$

where  $0 < \beta < 1$ . Using a SEF, it is not possible to obtain an analytic form of  $J_d$  in Eq.(10), since the SEF has no Laplace-transform (Duffrène et al., 1997). But, we can assume:

$$J_d(t) = \frac{1}{\mu_d} (1 - \phi(t)) \quad (18)$$

where  $\phi$  is a retardation function ( $\phi(0) = 1$  and  $\lim_{t \rightarrow +\infty} \phi(t) = 0$ ), and  $\mu_d^{-1}$  corresponds to the asymptotic value of  $J_d(t)$  (when  $t \rightarrow +\infty$ ). According to Duffrène et al. (1997):

$$\frac{1}{\mu_d} = \frac{1}{\mu} \left( \frac{\Gamma(1 + 2/\beta)}{(\Gamma(1 + 1/\beta))^2} - 1 \right) \quad (19)$$

Thus, if we perform a creep test (constant stress  $\sigma_0$ ), the delayed elastic distortion continuously increases over time, and depends on  $\sigma_0$ ,  $\mu$ ,  $\beta$ . According to (Eq.(11)):

$$\gamma_{d\infty} = \lim_{t \rightarrow +\infty} \gamma_d(t) = \frac{\sigma_0}{\mu_d} = \gamma_0 \left( \frac{\Gamma(1 + 2/\beta)}{(\Gamma(1 + 1/\beta))^2} - 1 \right) \quad (20)$$

where  $\gamma_0 = \sigma_0/\mu$ , is the initial shear distortion, fully elastic. Considering a constant  $\gamma_0$ , this equation illustrates that  $\gamma_{d\infty}$  is maximum if  $\beta \rightarrow 0$  and minimum if  $\beta \rightarrow 1$ . This is illustrated on Figure 1. The equation of Duffrène et al. (1997) illustrates that the stretch exponent is an indicator of the delayed elasticity level.

Now, if instead of performing a creep test, we perform a shear relaxation test on a linear viscoelastic body, so that:

$$\gamma(t) = \gamma_0 \mathcal{H}(t) \quad (21)$$

$\mathcal{H}$  being the Heaviside function. Assuming that the relaxation function is a SEF, we have, using Eq.(4) and (17), for  $t \geq 0$ :

$$\gamma_e(t) = \gamma_0 \varphi(t) = \gamma_0 \exp\left(-\left(\frac{t}{\tau_0}\right)^\beta\right) \quad (22)$$

And according to the Hooke's law:  $\sigma(t) = \mu \gamma_e(t)$ . Using Eq.(13), we have:

$$\gamma_\eta(t) = \frac{\int_0^t \sigma(s) ds}{\eta} = \frac{\mu \gamma_0 \int_0^t \varphi(s) ds}{\eta} \quad (23)$$

Using the symbolic computation Mathematica software (from Wolfram Research, Inc., Champaign, Illinois, version 5.2 edition, 2005),

$$\int_0^t \varphi(s) ds = \frac{\tau}{\beta} \left( \Gamma\left(\frac{1}{\beta}\right) - \Gamma\left(\frac{1}{\beta}, \left(\frac{t}{\tau_0}\right)^\beta\right) \right) \quad (24)$$

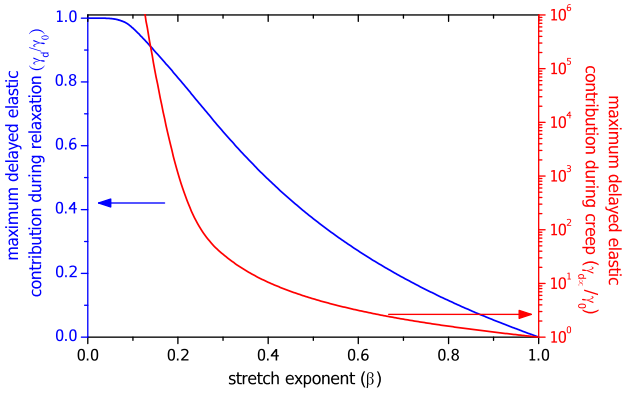


Figure 1: Evolution of the maximum relative (normalized by the initial distortion  $\gamma_0$ ) delayed elastic distortion during conventional mechanical tests for viscoelastic materials, as a function of the stretch exponent ( $\beta$ ) of stress relaxation. On the left axis, during a relaxation test ( $\gamma_d/\gamma_0$ , blue) and on the right axis during a creep test ( $\gamma_{d\infty}/\gamma_0$ , red).

Since  $G(t) = \mu \varphi(t)$ , using Eq.(2) & (15), we have  $\eta = \mu \tau_a$  (well known "Maxwell's relationship"). Substituting, in Eq.(23),  $\eta$  by this latter expression and  $\int_0^t \varphi(s)ds$  by the expression found in Eq.(24), we have:

$$\gamma_\eta(t) = \gamma_0 \left( 1 - \frac{\Gamma\left(1/\beta, \left(\frac{t}{\tau_0}\right)^\beta\right)}{\Gamma(1/\beta)} \right) \quad (25)$$

Finally, using Eq.(13):

$$\gamma_d(t) = \gamma_0 \left( \frac{\Gamma\left(1/\beta, \left(\frac{t}{\tau_0}\right)^\beta\right)}{\Gamma(1/\beta)} - \varphi(t) \right) \quad (26)$$

In order to eliminate  $\tau_0$  in these latter equations, to highlight the role of the exponent  $\beta$ , let us introduce:

$$\Lambda = \frac{\sigma(0) - \sigma(t)}{\sigma(0)} = 1 - \varphi(t) \quad (27)$$

$\Lambda$  is the relative fraction of stress relaxed. The total shear distortion is  $\gamma = \gamma_0$  for  $t \geq 0$ , so that the relative fraction of each distortion component is:

$$\frac{\gamma_e(\Lambda)}{\gamma_0} = 1 - \Lambda \quad (28)$$

$$\frac{\gamma_\eta(\Lambda)}{\gamma_0} = 1 - \frac{\Gamma(1/\beta, -\ln(1 - \Lambda))}{\Gamma(1/\beta)} \quad (29)$$

$$\frac{\gamma_d(\Lambda)}{\gamma_0} = \Lambda - 1 + \frac{\Gamma(1/\beta, -\ln(1 - \Lambda))}{\Gamma(1/\beta)} \quad (30)$$

We can calculate when the delayed elasticity will reach its maximum, when  $\varphi$  is a SEF, by solving  $d\gamma_d/d\Lambda = 0$ . The maximum is obtained, if  $0 < \beta < 1$  when:

$$\Lambda_M = 1 - \exp\left(-\left(\Gamma(1/\beta)\right)^{\frac{\beta}{1-\beta}}\right) \quad (31)$$

Inserting Eq.(31) in Eq.(30), we obtain the maximum delayed elastic distortion during shear relaxation ( $\gamma_d(\Lambda_M)/\gamma_0$ ):

$$\frac{\gamma_d(\Lambda_M)}{\gamma_0} = \frac{\Gamma(1/\beta, \Gamma(1/\beta)^{\frac{\beta}{1-\beta}})}{\Gamma(1/\beta)} - \exp\left(-\Gamma(1/\beta)^{\frac{\beta}{1-\beta}}\right) \quad (32)$$

This maximum is only a function of  $\beta$ : neither  $\tau_0$  nor  $\mu$  appears in this equation. The stretch exponent is the only indicator of the maximum delayed elastic contribution to shear stress relaxation. Therefore, as for creep, we will see that the delayed elasticity is maximum if  $\beta \rightarrow 0$  and minimum (null) if  $\beta \rightarrow 1$ .

### 3. Experiments

In order to challenge all the equations we have developed in the previous section, we have performed shear relaxation and strain recovery tests on GeSe<sub>9</sub> glass fibers by a torsional method. The glass and fibers synthesis is described in (Gueguen, King, Keryvin, Sangleboeuf, Rouxel, Bureau, and Lucas, 2013). The fibers were 300  $\mu\text{m}$  in diameter, 130 mm in length. The glass transition temperature of the GeSe<sub>9</sub> glass, measured by DSC at 10°C/min, is 92°C (Gueguen et al., 2013). The shear relaxation and recovery tests allow for the measurements of all the distortion components during relaxation. This test is described in details in (Gueguen et al., 2013) and in references therein. The shear distortion  $\gamma_0$  is imposed to the fiber by imposing a rotation to one of its ends (the other is fixed) with an angle  $\alpha_0$  (here  $\alpha_0 = 200 \pm 2^\circ$ ). The rotation angle is measured thanks to a thin needle fixed on the fiber, with a uncertainty of  $\pm 2^\circ$ . Each experimental point corresponds to a given fiber, the fibers being all tested under exactly the same conditions. The angle is imposed during a given period, up to a time "t" (only t varies from a fiber to another). At the time t the fiber is released, the elastic distortion instantaneously recovers, and the corresponding recovered angle ( $\alpha_e$ ) is measured. Then, the delayed elastic distortion recovers over time and the corresponding additional recovered angle, evolving over time, is measured until it reaches an equilibrium value ( $\alpha_d$ ). The remaining angle ( $\alpha_\eta$ ) is due to the inelastic distortion ( $\alpha_0 = \alpha_e + \alpha_d + \alpha_\eta$ ). It takes usually few seconds to measure an angle with the naked eye. The relationship between the distortion and the corresponding angle is (classical beam theory):

$$\gamma_0 = r \alpha_0/L \text{ \& } \gamma_c = r \alpha_c/L \quad (33)$$

where  $c = e, d$  or  $\eta$  again,  $L$  the fiber length and  $r$  the distance from the neutral axis of the fiber. All the distortion components are normalized by  $\gamma_0$ , so that  $r$  and  $L$  have no impact on the results and their uncertainty. The error bars on normalized distortions are estimated taking into account the "worst" situation:  $\alpha_c$  is measured with an error of  $+2^\circ$  and  $\alpha_0$  with an error of  $-2^\circ$  (upper limit of the error bar), and conversely (lower limit). The relaxation function corresponds to the normalized shear elastic distortion (Gueguen et al., 2013). These relaxation recovery tests have been performed at room temperature (20°C).

292 Glasses are, by definition, non-equilibrium materials. The<sup>348</sup>  
 293 equations tested here are only valid at equilibrium or, more  
 294 precisely, if the material does not undergo aging during the<sup>349</sup>  
 295 mechanical tests. As an example, the Ferry's relation (Eq.(15))<sup>350</sup>  
 296 makes sense only if no aging occurs: the viscosity is not<sup>351</sup>  
 297 time-dependent in this equation. But the viscosity, being very  
 298 sensitive to the aging of the material, is actually time-dependent,<sup>352</sup>  
 299 in glasses, below their glass transition temperature, until they  
 300 reach their equilibrium, thanks to structural relaxation. In  
 301 order to be sure that the glass is under equilibrium, we have  
 302 used a specific property of some chalcogenide glasses: their  
 303 photosensitivity. The glass fibers have been irradiated during  
 304 two months by two light bulbs (Philips MASTER TL-D  
 305 36W/840) that are separated from fibers by almost 1.20 m, and  
 306 the relaxation-recovery tests have been also performed under  
 307 permanent irradiation. Because of a specific photoinduced  
 308 process, called "photorelaxation" (Gueguen et al., 2013), the  
 309 glass relaxes faster and tends to equilibrate in a photoinduced  
 310 equilibrium which is not its natural configurational equilibrium  
 311 (Gueguen et al., 2013). Thus, after two months, its viscosity  
 312 becomes constant (Gueguen et al., 2013). It can be illustrated  
 313 by the fact that the shear relaxation function remains unchanged  
 314 if the test is done after two months under irradiation, and after  
 315 four months under irradiation (see (Gueguen et al., 2013) and  
 316 references therein). Without irradiation, at room temperature,  
 317 the glass would not reach equilibrium before, at least, a decade  
 318 (Gueguen et al., 2013).  
 319

320 These experimental conditions are chosen for the following  
 321 reasons. Firstly, below the glass transition, the characteristic<sup>353</sup>  
 322 time for stress relaxation is large (here, it corresponds to<sup>354</sup>  
 323 weeks) as compared to the time required (a few seconds, so<sup>355</sup>  
 324 at least 5 orders of magnitude lower) for loading (to apply<sup>356</sup>  
 325 the constant strain) and unloading (to measure the elastic<sup>357</sup>  
 326 part of strain), so that we can consider that the loading and<sup>358</sup>  
 327 unloading periods do not impact on the measurements. This<sup>359</sup>  
 328 is in sharp contrast to the situation above the glass transition.<sup>360</sup>  
 329 Moreover, the full experimental setup is not instrumented<sup>361</sup>  
 330 (there are no displacement sensors or load cells) since there<sup>362</sup>  
 331 are no fast dynamics to measure; therefore it has the advantage<sup>363</sup>  
 332 of preventing any drift of sensors that could impact on<sup>364</sup>  
 333 the measurements. Finally, at low temperatures the delayed<sup>365</sup>  
 334 elasticity is to be more exacerbated (i.e.: the stretch exponent<sup>366</sup>  
 335 is usually lower).<sup>367</sup>  
 336

337 We have also performed various mechanical tests on these<sup>370</sup>  
 338 glass fibers to assess the linearity of the viscoelastic behavior<sup>371</sup>  
 339 in the stress range investigated here (see (Gueguen et al., 2013))<sup>372</sup>  
 340 and references therein). No non-linear viscoelastic behavior is<sup>373</sup>  
 341 detectable below, at least, 55 MPa. Because the shear relax-<sup>374</sup>  
 342 ation test is a torsional test, the imposed distortion linearly in-<sup>375</sup>  
 343 creases with  $r$ , the distance from the neutral axis of the fiber.<sup>376</sup>  
 344 The maximum imposed distortion, at the surface of the fiber,<sup>377</sup>  
 345 was  $\gamma_0 = 4 \pm 0.05 \cdot 10^{-3}$ . The shear elastic modulus being<sup>378</sup>  
 346  $\mu = 4.6$  GPa (see (Gueguen et al., 2013) and references therein),<sup>379</sup>  
 347 it corresponds to an initial stress of  $\sigma(0) = 18.4$  MPa.<sup>380</sup>

#### 4. Results

The relaxation function of the GeSe<sub>9</sub> fibers is plotted in Figure 2. The relaxation function  $\varphi$  is plotted as  $\ln[-\ln[\varphi(t)]]$  vs.  $\ln(t)$ , since:

$$\ln \left[ -\ln \left[ \exp \left( -\left( \frac{t}{\tau_0} \right)^\beta \right) \right] \right] = \beta \ln(t) - \beta \ln(\tau_0) \quad (34)$$

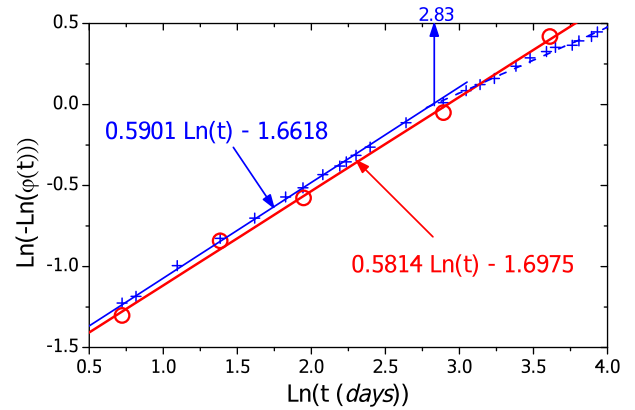


Figure 2: Experimental relaxation function obtained here (open red circle), plotted as  $\ln(-\ln(\varphi(t)))$  vs.  $\ln(t)$  ( $t$  is time), compared with a previous measurement (blue cross) (see (Gueguen et al., 2013) and references therein).

We obtain here, by least square fitting:  $\beta = 0.581$  and  $\tau_0 = 18.5$  days ( $\tau_a = 29.1$  days, according to Eq.(2)), for the five points of Figure 2. The relaxation function obtained here is compared with another one, previously obtained in the same conditions (see (Gueguen et al., 2013) and references therein). It illustrates the reproducibility of this measurement. The stretch exponent previously found was  $\beta = 0.59$ , in very good agreement with that found here. The average relaxation time previously found was somewhat lower ( $\tau_a = 25.9$  days, Eq.(2), with  $\tau_0 = 16.8$  days), but Figure 2 illustrates that this small discrepancy corresponds to the experimental uncertainty. The shear relaxation function previously measured was bimodal (see (Gueguen et al., 2013) and references therein): for  $t < 17$  days, we have a first SEF, corresponding to the data plotted on Figure 2, but at  $t > 17$  days, the relaxation function deviates with a slower stretch exponent ( $\beta = 0.35$ ). We can distinguish this deviation in Figure 2 ( $\ln(17) \sim 2.83$ ). The new measurements performed here do not confirm the bimodality. We do not know exactly why, and we will leave here this issue as unsolved.

The evolution of the inelastic and delayed elastic distortion, obtained from recovery tests are plotted in Figure 3. As expected from Eq.(14), the inelastic distortion continuously increases with time (the stress and the viscosity being strictly positive,  $\dot{\gamma}_\eta$  is strictly positive). The delayed elastic distortion, instead, first increases, reaches a maximum, at  $t \sim 13$  days, and then slowly decreases. It must be underlined here that the values of the inelastic and delayed elastic distortion at a time "t" are obtained by starting a recovery test at this time  $t$  and by

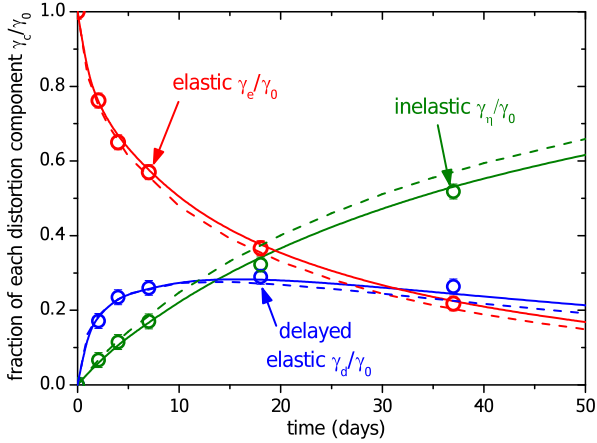


Figure 3: Evolution of each distortion contribution. The red, blue and green open circles correspond to  $\gamma_c = \gamma_e$ ,  $\gamma_d$  and  $\gamma_\eta$ , respectively. The size of the circles corresponds to the error bar. The red, green and blue lines correspond to Eq.(22), (25) and (26), respectively, with  $\beta = 0.58$  and  $\tau_0 = 18.5$  days for the full lines, and  $\beta = 0.59$  and  $\tau_0 = 16.8$  for the dashed lines.

waiting for the delayed elastic to fully recover (see details in (Gueguen et al., 2013)). For the last data plotted in Figure 3, this recovery part took more than one year. This is the reason why we do not have data at very long times.

In Figure 3, we have also plotted the theoretical evolutions of the delayed elastic and inelastic distortions, using Eq.(25) and (26) and the values of  $\beta = 0.581$  and  $\tau_0 = 18.5$  identified from the experiments. As we can see, the theoretical evolutions match the experimental ones, according to the measurement uncertainty. It illustrates the validity of the equations (25) and (26). We have also plotted the theoretical evolutions with the following values, identified from the previous experiments:  $\beta = 0.59$  and  $\tau_0 = 16.8$  days. We can see that it slightly deviates from the experimental data after  $\sim 10 - 18$  days. Indeed, this parameter set does not allow to fit  $\gamma_d$  and  $\gamma_\eta$  when they also does not fit the relaxation function, since the relaxation function deviates from a single SEF after 17 days.

## 5. Discussion

### 5.1. Delayed elasticity vs. stretch exponent

The equations developed here illustrate the robustness of the SEF. Using only three parameters ( $\beta$ ,  $\tau_0$  and  $\mu$ ), it is possible to evaluate, with a very good accuracy, the three components of the viscoelastic deformation, namely: the elasticity, the delayed elasticity and the inelasticity. In Figure 4, we have plotted the distortion contributions vs. the fraction of stress relaxed  $\Lambda$ , in order to illustrate the theoretical evolution of delayed elastic and inelastic distortions as a function of the stretch exponent  $\beta$ . In this Figure, we can observe that  $\Lambda_M$ , the position of the maximum delayed elastic distortion, is shifted to larger values as  $\beta$  decreases. Since  $\Lambda_M \in \mathbb{R}^+$  when  $0 < \beta < 1$ , the delayed

elastic distortion first increases over time, reaches a maximum, and then decreases and tends to 0 when  $t \rightarrow +\infty$ . The inelastic distortion, instead, increases monotonically starting from 0 to tend to  $\gamma_0$  when  $t \rightarrow +\infty$ . We can notice in Figure 4 that, if  $\beta$  is low, the delayed elasticity will be the major contribution to stress relaxation, until the stress relaxes down to a very low level. The maximum relative fraction of delayed elastic distortion is  $\gamma_d(\Lambda_M)/\gamma_0$ . It is plotted vs.  $\beta$  in Figure 1. We have shown (Eq.(32)) that this maximum delayed elastic distortion is not a function of  $\tau_0$ : it is only defined by the stretch exponent  $\beta$ . So, we clearly highlight here that the stretch exponent in a shear relaxation modulus is just the indicator of the delayed elastic contribution to viscoelasticity, and it is self sufficient. More precisely, the time-parameter,  $\tau_0$ , only indicates the kinetics of the relaxation, and the stretch exponent,  $\beta$ , only indicates the amplitude of the delayed elastic contribution to this relaxation.

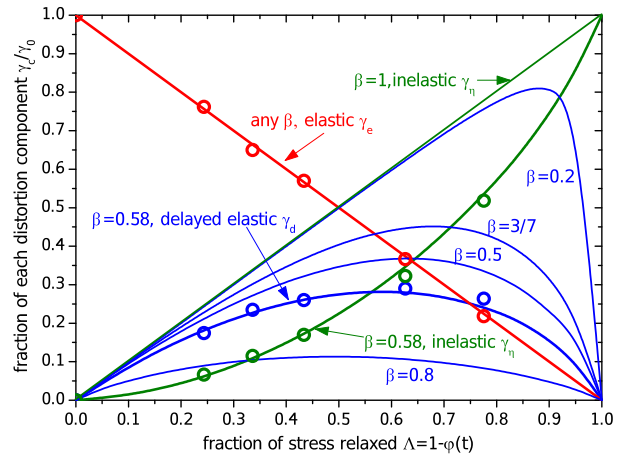


Figure 4: Theoretical evolutions (Eq.(28), (29) and (30)) of each distortion contribution ( $\gamma_c = \gamma_e$ ,  $\gamma_d$  or  $\gamma_\eta$ ) as a function of  $\Lambda$ , the fraction of stress relaxed, for various  $\beta$  values. The open circles correspond to experimental data. The theoretical evolutions are also plotted for  $\beta = 0.59$ , but they are practically indiscernible from those plotted using  $\beta = 0.58$ .

We can note that if  $\beta \rightarrow 0$ , the delayed elasticity increases. Nevertheless, if  $\beta = 0$ , there is no relaxation anymore ( $\varphi(t) = 1$ ), but the delayed elastic contribution predicted is 100%. According to Eq.(6), we also observe that if  $\beta \rightarrow 0$ , so if  $G(t) \rightarrow \mu$ , there is no creep anymore, since  $J(t) \rightarrow 1/\mu$ . It is a clear illustration that the delayed elasticity is not itself able to produce a full stress relaxation.

### 5.2. Origin of the delayed elasticity

Originally, the non-exponential relaxation, and so the existence of various mechanisms of stress relaxation, and corresponding energy barriers, was attributed to the inhomogeneity of glasses. There are various energy barriers first because there are various structural units (in Ge-Se glasses,

443 there is  $\text{GeSe}_{4/2}$  tetrahedra, connected in different ways,  $\text{Se}_{500}$   
444 chains, probably Se-rings... (see (Yang, Gueguen, Sangleboeuf,<sup>501</sup>  
445 Rouxel, Boussard-Pledel, Troles, Lucas, and Bureau, 2013) and<sup>502</sup>  
446 references therein). But the energy barrier for a specific type of<sup>503</sup>  
447 local relaxation event (LRE) varies from one site to another, at<sup>504</sup>  
448 least because of the inherent disorder of glasses (Simha, 1942).<sup>505</sup>  
449 An atom or a structural unit can also contribute to different<sup>506</sup>  
450 types of LRE, with different energy barriers. <sup>507</sup>

451 At a given temperature, under no stress, the LRE will occur<sup>508</sup>  
452 in random directions, producing, macroscopically, no net strain.<sup>509</sup>  
453 Under relatively low stress, the energy barrier is slightly biased<sup>510</sup>  
454 (not enough biased to induce non-linear viscoelasticity) favor<sup>511</sup>  
455 ing the relaxation events in a specific direction. These events,<sup>512</sup>  
456 do not necessarily correspond to global atomic displacements;<sup>513</sup>  
457 it can correspond to a transformation or a configuration change,<sup>514</sup>  
458 as described by Argon and Kuo (1980). Indeed, during a re<sup>515</sup>  
459 laxation test, the strain is constant, so that there is, macroscop<sup>516</sup>  
460 ically, no displacement, but just a "conversion" of the initial,<sup>517</sup>  
461 elastic displacement into delayed elastic and inelastic displac<sup>518</sup>  
462 ements. During a relaxation test all the atoms move initially only<sup>519</sup>  
463 "elastically" and are able to go back to their initial position. As<sup>520</sup>  
464 soon as even a single atom (or more generally speaking a "re<sup>521</sup>  
465 laxing unit", a "cooperatively rearranging subsystem" or a "co<sup>522</sup>  
466 operatively rearranging region" (Dyre, 1998)) has overcome its<sup>523</sup>  
467 energy barrier to reach a new stable position/configuration the<sup>524</sup>  
468 delayed elasticity can emerge. If the stress is released, all the<sup>525</sup>  
469 others atoms will try to go back to their initial position, while<sup>526</sup>  
470 this atom will not be able anymore, without overcoming again<sup>527</sup>  
471 an energy barrier and will disturb the return of the other atoms.<sup>528</sup>  
472 Macroscopically, the material is not able anymore to recover<sup>529</sup>  
473 instantaneously its initial shape. This atom is stressed by all<sup>530</sup>  
474 other (and by reaction, stressed itself the other atoms), so that<sup>531</sup>  
475 a driving force exists to induce its forward motion to its initial<sup>532</sup>  
476 configuration. But since there is an energy barrier to overcome,<sup>533</sup>  
477 this motion is delayed: this is the delayed elasticity. <sup>534</sup>

478 Consequently, each initial LRE only produce delayed elastic<sup>535</sup>  
479 ity, it will be turn into inelasticity (it will be irreversible) only  
480 when its initial configuration will be not reachable anymore:  
481 when the surrounding network will have produced their own  
482 LRE to erase the memory of this initial configuration. This idea  
483 has been developed by Orowan (1952) and nicely discussed lat<sup>536</sup>  
484 ter by Goldstein (1969). We can go deeper into this idea by<sup>537</sup>  
485 using a concept discussed by Argon (1968). Considering one<sup>538</sup>  
486 specific subsystem and its corresponding LRE, with its spe<sup>539</sup>  
487 cific energy barrier (*i.e.*: its specific relaxation time), we un<sup>540</sup>  
488 derstand that if the subsystem wants to move or to change its<sup>541</sup>  
489 configuration, it has no reason to have exactly the free space it<sup>542</sup>  
490 needs to do so: it will "shove" the surrounding network (Tra<sup>543</sup>  
491 chenko, 2007), at it is nicely depicted by the shoving-model<sup>544</sup>  
492 of Dyre (1998), to reach a new state. The difference between<sup>545</sup>  
493 the new and the initial states will let the surrounding network<sup>546</sup>  
494 partially "shoved", if it can not synchronously re-arrange. In<sup>547</sup>  
495 other words, the subsystem will occupy a new site by elasti<sup>548</sup>  
496 cally distorting it and stressing it or, at least will modify its<sup>549</sup>  
497 configuration by stressing the surrounding network (let us name<sup>550</sup>  
498 it the "shoving-stress", ShS). The delayed elasticity is driven<sup>551</sup>  
499 by the modification of the stress of the surrounding network<sup>552</sup>

of the subsystem (Argon, 1968). The shoving-stress (ShS) in-  
duced in the network surrounding the moving subsystems is  
macroscopically self-equilibrated (just like for an Eshelby's in-  
clusion, the LRE corresponding to an eigenstrain): it does not  
increase the macroscopic external stress. When the strain re-  
covery starts, this macroscopic stress becomes null, but at the  
microscopic scale, the ShS will slowly relax, by allowing back-  
ward motions: this is the delayed elasticity recovery. The con-  
cepts of Orowan/Goldstein or Argon have the same basis: all  
LRE contribute initially only to delayed elasticity, they con-  
tribute to inelasticity only because they tend to make the posi-  
tion/configuration changes of the previous LRE irreversible.

During a relaxation test, the macroscopic stress applied re-  
laxes, the elastic energy initially stored being dissipated during  
LRE (Maxwell, 1868). Each event induces a local ShS, increas-  
ing the amount of delayed elasticity. Nevertheless, since this  
ShS can also relax, there is a competition between a creation  
and a relaxation of the ShS. Accordingly, the delayed elastic-  
ity, during a relaxation test, increases and reaches a maximum  
before decreasing. This is illustrated here on Figure 3. Dur-  
ing a creep test, the delayed elasticity created saturates when  
the rate of creation of ShS equilibrates with its rate of relax-  
ation (Argon, 1968). During a relaxation test, each LRE decays  
the stress, that is not fully redistributed to the surrounding net-  
work. During a creep test, a subsystem bears less stress after a  
LRE, but all the stress it does not bear anymore is fully redis-  
tributed on the surrounding network Just imagine a truss made  
of various beams, and break a beam of this truss (by analogy  
to a LRE): if the truss is bearing a constant load, all the other  
beams will support more load to exactly compensate the load  
the broken beam was bearing, and will deform more (this is  
the creep test). If a constant distortion is imposed to the truss,  
once a beam is broken, the truss is less rigid, the load needed  
to impose the same distortion will globally decrease (this is the  
relaxation test).

### 5.3. Generalization to any kind of relaxation functions

There are two standard ways to model a linear viscoelastic  
body by using cells made of springs and dashpots. The first  
one is to use "parallel" models, such as the Maxwell-Wiechert  
model, where there is no individual cell that induces delayed  
elasticity. The second one is to use "serial" models, such as  
the Burgers's model, where the delayed elasticity is usually due  
to Kelvin-Voigt cells. For this latter solution, we have cells to  
model the delayed elasticity, but without clear microscopical  
explanation for it: we could assume that some LRE (associated  
with Kelvin-Voigt cells) induce exclusively delayed elasticity  
and some others induce exclusively viscous flow, without inter-  
acting with each other. But serial models can just be considered  
as other kind of representations of parallel models. For the par-  
allel models, we can assume that a relaxation function can be  
decomposed as a weighted sum of exponential processes, each  
of these processes having its own relaxation time. Let us as-  
sume a finite number ( $N$ ) of relaxation processes (a discontinu-



ous relaxation spectrum) having an additive contribution:

$$\varphi(t) = \sum_{i=1}^N \rho_i \exp\left(-\frac{t}{\tau_i}\right) \quad (35)$$

$\rho_i$  is the weight of the  $i^{\text{th}}$  process having a relaxation time  $\tau_i$ , verifying  $\sum_{i=1}^N \rho_i = 1$  (this is the Maxwell-Wiechert model (Wiechert, 1893)).

Let  $n(t)$  be the numbers of LRE that have already occurred at  $t$  and  $n_T$  is the total number of LRE that will occur until the stress becomes null. The LRE producing the stress relaxation, according to the definition of the relaxation function, we have:

$$\frac{n(t)}{n_T} = 1 - \varphi(t) = \sum_{i=1}^N \rho_i \left(1 - \exp\left(-\frac{t}{\tau_i}\right)\right) \quad (36)$$

Among the  $n$  LRE, a part of them have induced motions that have let some subsystems in configurations where they can produce delayed elasticity. These LRE can be considered as "reversible", since the corresponding backward events occur when the macroscopic stress is removed. Let  $n_r$  be the number of such LRE. It is proportional to the delayed elastic strain. The other part of the LRE produces viscous flow, they have let subsystems in stable configurations, they are "irreversible", since no backward motion is possible. Their number is  $n_i$ , proportional to the viscous strain. So, we have:

$$n(t) = n_r(t) + n_i(t) \quad (37)$$

We first derive this expression, using Eq.(23),  $n_i/n_T$  being equivalent to  $\gamma_\eta/\gamma_0$ , according to Eq.(36):

$$\dot{n}_i(t) = n_T \frac{\dot{\gamma}_\eta}{\gamma_0} = n_T \frac{\gamma_0 \mu \varphi(t)}{\gamma_0 \eta} = \frac{n_T - n(t)}{\tau_a} \quad (38)$$

Then we directly obtain  $n_r(t)$ . After integration, and assuming that  $n_r(0) = 0$ , it leads to the fraction of "reversible LRE":

$$\frac{n_r(t)}{n_T} = \sum_{i=1}^N \left(1 - \frac{\tau_i}{\tau_a}\right) \rho_i \left(1 - \exp\left(-\frac{t}{\tau_i}\right)\right) \quad (39)$$

Now, if we assume a continuous relaxation spectrum:

$$\varphi(t) = \int_0^{+\infty} \rho(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (40)$$

Here, the weight  $\rho$  is per time unit ( $d(\tau) = \rho(\tau)\tau$  is the distribution function of relaxation times), and  $\rho \geq 0$ . According to Eq.(2), we have:  $\tau_a = \int_0^{+\infty} \rho(\tau)\tau d\tau$ . Note that for a SEF,  $\beta$  is a monotonous function of the logarithmic full width at half maximum of  $d(\tau)$  (Johnston, 2006), the distribution function of relaxation times. And we obtain, by analogy with the Maxwell-Wiechert model:

$$\frac{n_r(t)}{n_T} = \int_0^{+\infty} \left(1 - \frac{\tau}{\tau_a}\right) \rho(\tau) \left(1 - \exp\left(-\frac{t}{\tau}\right)\right) d\tau \quad (41)$$

And the fraction of "irreversible LRE":

$$\frac{n_i(t)}{n_T} = \int_0^{+\infty} \frac{\tau}{\tau_a} \rho(\tau) \left(1 - \exp\left(-\frac{t}{\tau}\right)\right) d\tau \quad (42)$$

These two latter equations explicitly show that the delayed elasticity (the reversible LRE) directly comes from the difference between the relaxation time  $\tau$  (or  $\tau_i$  if the spectrum is discontinuous) of a specific LRE and the average relaxation time  $\tau_a$ . The relative proportion of reversible events produced by a process having relaxation times between  $\tau$  and  $\tau + d\tau$  is:  $\left(1 - \frac{\tau}{\tau_a}\right)\rho(\tau)d\tau$ . Obviously, if all the LRE have exactly the same relaxation time ( $\tau = \tau_a$ ), we obtain  $n_r(t) = 0$  and  $n_i(t) = n(t)$ . None of the LRE produces reversible LRE, all are irreversible. So whatever the relaxation function based on a given distribution  $d(\tau)$  used, the delayed elasticity comes from a "dispersion" of the relaxation times. Conversely, some viscoelastic bodies can exhibit delayed elasticity without viscous flow, they are called "viscoelastic solids" (as oppose to viscoelastic liquid (Lakes, 1998)). For such bodies, we may assume that some slow processes have very large relaxation times as compare to fast ones, enough large to consider that, at the human scale, they can be set as infinite (relative Deborah number  $\gg 1$ ). Thus, if at least the  $j^{\text{th}}$  relaxation time ( $\tau_j$ ) in Eq.(35), is set as infinite, then  $\varphi(t) = \rho_j$  when  $t \rightarrow +\infty$ . Additionally, according to Eq.(42),  $n_i \rightarrow 0$ , at any time, since  $\tau_a \rightarrow +\infty$ . In other words, bodies with infinitely dispersed relaxation times, but at least with one finite relaxation time, exhibit only delayed elasticity.

The equations (41) and (42) are in perfect agreement with the concepts proposed by Orowan (1952), Goldstein (1969) and Argon (1968). All initial and "fast" LRE, with small relaxation times ( $\tau \leq \tau_a$ ), first mainly induce delayed elasticity (they induce reversible events:  $n_r > 0$ ): their initial position/configuration/state are still reachable. Then, the "slow" LRE, with large relaxation times ( $\tau \geq \tau_a$ ), occur and tend to make, by their own configuration/position changes, the initial states of fast LRE unattainable (they annihilate the reversibility of the first LRE:  $n_r < 0$ ). It is easy to see that "slow" LRE only annihilate the reversibility of the events produced by "fast" LRE, since their respective contributions to  $n_r$  exactly compensate each other. Indeed, the term  $\left(1 - \frac{\tau}{\tau_a}\right)\rho(\tau)$  satisfies:

$$\int_0^{+\infty} \left(1 - \frac{\tau}{\tau_a}\right) \rho(\tau) d\tau = 0 \quad (43)$$

We can provide an illustration of these equations using a simple  $\rho(\tau)$ , for which we will have only analytical solutions (Johnston, 2006):

$$\rho(\tau) = \frac{\exp\left(-\frac{\tau}{4\tau_0}\right)}{2\sqrt{\pi\tau\tau_0}} \rightarrow \varphi(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{1/2}\right] \quad (44)$$

With this  $\rho(\tau)$ , we have  $\tau_a = 2\tau_0$ . We set  $n_T = 1$  in order to normalize the functions. Then we obtain the contribution ( $n_r^+$ ) of the fast processes ( $\tau \leq \tau_a$ ) to  $n_r$ , by replacing "+" in the integral of Eq.(41) by  $\tau_a$ , and the contribution ( $n_r^-$ ) of the

640 slow processes ( $\tau \geq \tau_a$ ) to  $n_r$  by replacing "0" in the integral  
 641 of of Eq.(41) by  $\tau_a$ .  $n_r^+$  and  $n_r^-$  are plotted on Figure 5 with the  
 642 total amount of  $n_r$ . Note that  $n_r$  is directly found using Eq.(41)  
 643 but also using Eq.(26), these two equations being analytically  
 644 strictly equivalent. We clearly see on this Figure that the total  
 645 amount of  $n_r = n_r^+ + n_r^-$  (and thus the delayed elasticity) is only  
 646 due to the difference between the rate of creation of  $n_r$  by the  
 647 fast processes and the rate of annihilation of these  $n_r$  by the  
 648 slow one.

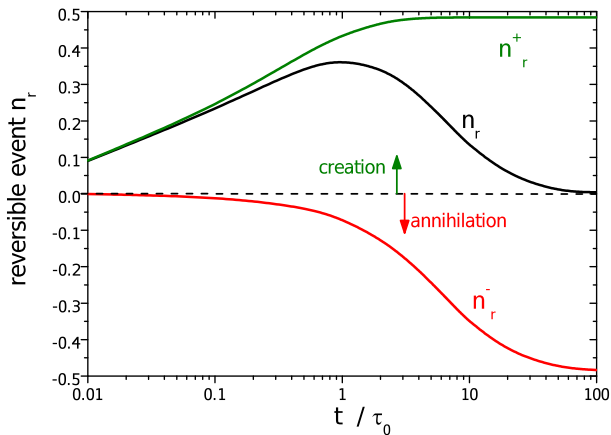


Figure 5: Illustration of the total number of reversible LRE ( $n_r$ , black line) vs. time (normalized by  $\tau_0$ ) for a SEF with  $\beta = 1/2$ , of the amount of reversible LRE ( $n_r^+$ ) produced by all the processes having relaxation times lower than  $\tau_a$  (green line) and of the amount of reversible LRE ( $n_r^-$ ) annihilated by all the processes having relaxation times larger than  $\tau_a$  (red line).

#### 5.4. Models without initial distribution of relaxation times

649 **Trachenko (2007)** is, to our knowledge, the only one propos-  
 650 ing a model corresponding to a SEF, where no pre-set distri-  
 651 bution of relaxation time ( $\rho(\tau)$ ) exists. In this model, since  
 652 a relaxing unit "support less stress after relaxation, later LRE  
 653 should support more stress in order to counterbalance" (**Trachenko, 2007**), thus increasing their energy barrier (actually, since the macroscopic stress relaxes, the later LRE will rather support less stress, they should instead support a new stress field, self equilibrated). Consequently, the relaxation time of the LRE increases with the number of LRE that have already  
 654 occurred, leading to a stretched exponential decay of the macro-  
 655 scopic stress. One consequence of the model is that the stretch  
 656 exponent is inversely proportional to the stress decay ( $\Delta p_0$ )  
 657 due to a LRE (**Trachenko, 2007**) and thus to the initial ap-  
 658 plied stress ( $\sigma(t = 0) = \sigma_0$ ). Indeed, the model assumes  
 659 that all LRE induce the same  $\Delta p_0$  (**Trachenko, 2007**), so that:  
 660  $\sigma(t) = (n_T - n(t))\Delta p_0$  and  $\Delta p_0 = \sigma_0/n_T$ , the final number of  
 661 LRE ( $n_T$ ) at the end of the relaxation being stress independent  
 662 (**Trachenko, 2007**). Thus, this model can clearly not be applied  
 663 as a relaxation function for linear viscoelastic materials, such  
 664 as the glass investigated here, since the relaxation function is  
 665 stress dependent. Since we do not know other models of stress

relaxation in the framework of linear viscoelasticity, without pre-set distribution of relaxation times, we can assume that, in that framework, the delayed elasticity can just be seen as a consequence of the broadness of the distribution.

## 6. Conclusion

677 According the idea of Wiechert, the delayed elasticity takes  
 678 its origins in the non-exponentiality of the stress relaxation, and  
 679 thus, is due to a dispersion of relaxation times of all the pro-  
 680 cesses involved during relaxation. In spite of the fact that the  
 681 SEF is not physically sound and can not be used alone (with-  
 682 out an other model at  $t \rightarrow 0^+$ ) as a phenomenological model  
 683 (**Duffrène et al., 1997**), the experimental investigation done here  
 684 highlights that this function can be perfectly suitable to describe  
 685 the detailed viscoelastic deformation of a linear viscoelastic  
 686 material. The equations developed here highlight the role of de-  
 687 layed elasticity during relaxation and shows that the maximum  
 688 delayed elasticity reached during relaxation is only correlated to  
 689 the stretch exponent ( $\beta$ ). This maximum continuously increases  
 690 as  $\beta$  decreases. Actually, the delayed elasticity is the result of  
 691 the broadness (connected to  $\beta$  for a SEF) of the distribution  
 692 function of relaxation times, whatever this function. For a dis-  
 693 tribution function  $d(\tau)$ , the relative delayed elasticity induced  
 694 ( $> 0$ ) or annihilated ( $< 0$ ) by the process having a relaxation  
 695 time  $\tau$  is:  $(1 - \tau/\tau_a)d(\tau)$ , where  $\tau_a$  is the average relaxation  
 696 time of the whole system. At short time, the subsystems having  
 697 low relaxation times induce large amount of delayed elastic-  
 698 ity by moving in a network of slow subsystems that can only  
 699 accommodate the motions elastically. At long time, these slow  
 700 subsystems, by moving, accommodate inelastically the motions  
 701 of the fast subsystems and annihilate the delayed elasticity by  
 702 turning it into inelasticity.

Additionally, since, to our knowledge, no inorganic glasses exhibits or even approach a Maxwell-Debye stress relaxation ( $\beta \rightarrow 1$ ) until they are far above their glass transition temperature ( $T_g$ ), all of them exhibit delayed elasticity below and above  $T_g$ . Accordingly, viscosity measurements in this range must be isothermal, to reach the stationary creep stage, or they will be just absolutely wrong. Viscosity measurements made during a continuous heating, just give almost something close to the initial delayed elastic strain rate.

## References

- Argon, A., Kuo, H., 1980. Free energy spectra for inelastic deformation of five metallic glass alloys. *J. Non-Cryst. Solids* 37 (2), 241 – 266.
- Argon, A. S., 1968. Delayed elasticity in inorganic glasses. *J. Appl. Phys.* 39 (9), 4080–4086.
- ASTM C1350-96, 1996. Standard test method for measurement of viscosity of glass between softening point and annealing range (approximately  $10^8$  Pa - s to approximately  $10^{13}$  Pa - s) by beam bending (metric). It says : "the method also may be used in experimental programs that focus on nonequilibrium conditions", whereas only the measurement of the delayed elasticity allow such investigation.
- Bendler, J. T., 1984. Levy (stable) probability densities and mechanical relaxation in solid polymers. *Journal of Statistical Physics* 36 (5-6), 625–637.
- Boltzmann, L., 1876. On the theory of the elastic aftereffect. *Pogg. Ann. Erg. Bd.* 7, 624–645.

727 Duffrène, L., Gy, R., Burlet, H., Piques, R., 1997. Viscoelastic behavior of  
728 a soda-lime-silica glass: inadequacy of the KWW function. *J. Non-Cryst.*  
729 *Solids* 215 (2-3), 208–217.

730 Dyre, J. C., 1998. Source of non-arrhenius average relaxation time in glass-  
731 forming liquids. *J. Non-Cryst. Solids* 235-237, 142–149.

732 Ferry, J. D., 1980. *Viscoelastic properties of polymers*. Vol. 3. Wiley New York.

733 Frenkel, J., 1926. Über die wärmebewegung in festen und flüssigen körpern.  
734 *Zeitschrift für Physik* 37 (7-8), 572–609.

735 Goldstein, M., 1969. Viscous liquids and the glass transition: a potential energy  
736 barrier picture. *J. Chem. Phys.* 51, 3728–3739.

737 Gueguen, Y., King, E. A., Keryvin, V., Sangleboeuf, J.-C., Rouxel, T., Bureau,  
738 B., Lucas, P., 2013. Photoinduced aging and viscosity evolution in se-rich  
739 Ge-Se glasses. *J. Appl. Phys.* 114, 074901.

740 Johnston, D. C., Nov 2006. Stretched exponential relaxation arising from a  
741 continuous sum of exponential decays. *Phys. Rev. B* 74, 184430.

742 Kohlrausch, R., 1854. *Pogg. Ann. Phys.* 91, 198.

743 Lakes, R. S., 1998. *Viscoelastic solids*. CRC press.

744 Lee, E. H., 1955. Stress analysis in viscoelastic bodies. *Quarterly Applied*  
745 *Mathematics* 13, 183–190.

746 Maxwell, J., 1868. On the dynamical theory of gases. *Phil. Mag.* 35, 134.

747 Orowan, E., 1952. "Creep in metallic and non-metallic materials". *Proceedings*  
748 *of the First National Congress of Applied Mechanics (American Society of*  
749 *Mechanical Engineers, New York)*, 453.

750 Phillips, J. C., 1996. Stretched exponential relaxation in molecular and elec-  
751 tronic glasses. *Reports on Progress in Physics* 59 (9), 1133.

752 Simha, R., 1942. On relaxation effects in amorphous media. *J. Appl. Phys.*  
753 13 (3), 201–207.

754 Trachenko, K., Jun 2007. Slow dynamics and stress relaxation in a liquid as an  
755 elastic medium. *Phys. Rev. B* 75, 212201.

756 Weber, W., 1835. Über die elastizität der seidenfäden. *Ann. Phys.* 34, 247–257.

757 Wiechert, E., 1893. Gesetze der elastischen nachwirkung für constante temper-  
758 atur. *Annalen der Physik* 286 (11 & 10), 335–348 & 546–570.

759 Yang, G., Gueguen, Y., Sangleboeuf, J., Rouxel, T., Boussard-Pledel, C.,  
760 Troles, J., Lucas, P., Bureau, B., 2013. Physical properties of the  $\text{Ge}_x\text{Se}_{1-x}$   
761 glasses in the  $0 < x < 0.42$  range in correlation with their structure. *J. Non-*  
762 *Cryst. Solids* 377, 54–59.

763 Zener, C., 1948. *Elasticity and Anelasticity of Metals*. University of Chicago  
764 Press, Chicago.