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Yann Gueguen, Vincent Keryvin, Tanguy Rouxel, Mickaël Le Fur, Hervé Orain, et al.. A relationship between non-exponential stress relaxation and delayed elasticity in the viscoelastic process in amorphous solids: Illustration on a chalcogenide glass. *Mechanics of Materials*, 2015, 85, pp.47-56. 10.1016/j.mechmat.2015.02.013 . hal-01153240

HAL Id: hal-01153240

<https://univ-rennes.hal.science/hal-01153240>

Submitted on 19 May 2015

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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 GeSe₉ 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, 10⁹⁻¹⁰ 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 Bennowitz 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 φ is the relaxation function, describing the normalized¹¹⁵
 68 relaxation of a quantity Q (here the shear stress), Q_∞ being its
 69 asymptotic value at $t \rightarrow +\infty$. β is the stretch exponent, and τ_0 ¹¹⁶
 70 is a characteristic time, related to the average (or "Maxwell's")
 71 relaxation time τ_a by the following relation:

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

73 where Γ is the Gamma function: $\Gamma(x, y) = \int_y^\infty s^{x-1} e^{-s} ds$ ¹²¹
 74 and $\Gamma(x) = \Gamma(x, 0)$. The average relaxation time corre-
 75 sponds to the average lifetime of an atom/molecule or group of¹²²
 76 atoms/molecules in their equilibrium position (here when they¹²³
 77 are shifted by the stress) (Frenkel, 1926). The stretched expo-
 78 nential function (SEF) has various advantages. The main one¹²⁴
 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-¹²⁵
 81ponentiality is directly signed by the stretch exponent β . So,¹²⁶
 82 according to the idea of Wiechert, the delayed elasticity is di-
 83 rectly signed by β . The SEF has been widely used to describe¹²⁷
 84 various kind of relaxation processes (see for example (Phillips,
 85 1996)), but this function is not physically sound, first because¹²⁸
 86 regarding its time derivation:

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

88 the relaxation rate tends to $-\infty$ when $t \rightarrow 0^+$, for $0 < \beta < 1$.¹³³
 89 Duffrène et al. (1997) have also pointed out the inadequacy¹³⁴
 90 of the SEF to describe the viscoelastic behavior of soda-lime-¹³⁵
 91 silica glasses. Additionally, they have shown that if we assume¹³⁶
 92 that the shear relaxation function corresponds to a SEF, the¹³⁷
 93 primary creep stage can not be fitted by another SEF, as it is¹³⁸
 94 often done.

95
 96 In spite of the weaknesses of the SEF, we will show here,¹⁴⁰
 97 experimentally, how much the idea of Wiechert is correct: the
 98 delayed elasticity is only connected to the stretch exponent. The¹⁴¹
 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, such¹⁴²

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 σ :

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

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 μ is the elastic shear modulus, we obtain for linear vis-
 129 coelasticity, considering G and J as the viscoelastic counter-
 130 parts of μ and μ^{-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_η a linear function of time:

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

where η is the shear viscosity. Using Eq.(6), we also obtain:

$$140 \quad J_d(t) = \mathcal{L}^{-1}\left(\frac{1}{s^2 \mathcal{L}(G(t))}\right) - \frac{t}{\eta} - \frac{1}{\mu} \quad (10)$$

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_η : an elastic distortion γ_e , reversible, a delayed elastic distortion γ_d , reversible but with delay, and an inelastic distortion γ_η , 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 η . 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)):

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

The average shear relaxation time τ_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 ϕ is a retardation function ($\phi(0) = 1$ and $\lim_{t \rightarrow +\infty} \phi(t) = 0$), and μ_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 σ_0), the delayed elastic distortion continuously increases over time, and depends on σ_0 , μ , β . 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 γ_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),

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

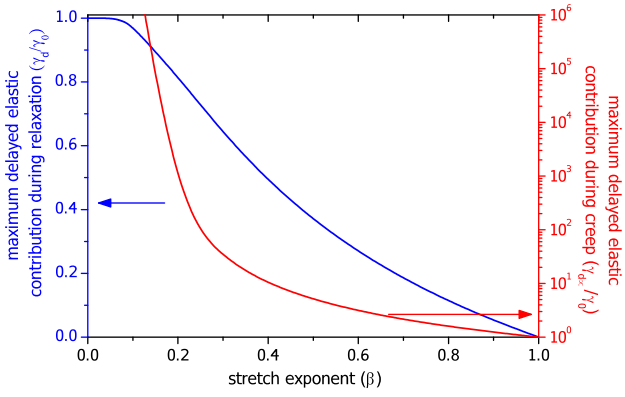


Figure 1: Evolution of the maximum relative (normalized by the initial distortion γ_0) delayed elastic distortion during conventional mechanical tests for viscoelastic materials, as a function of the stretch exponent (β) of stress relaxation. On the left axis, during a relaxation test (γ_d/γ_0 , blue) 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), η 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 τ_0 in these latter equations, to highlight the role of the exponent β , let us introduce:

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

Λ 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 φ 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 β : neither τ_0 nor μ 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 GeSe₉ 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 μm in diameter, 130 mm in length. The glass transition temperature of the GeSe₉ 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 γ_0 is imposed to the fiber by imposing a rotation to one of its ends (the other is fixed) with an angle α_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 (α_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 (α_d). The remaining angle (α_η) 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 η again, L the fiber length and r the distance from the neutral axis of the fiber. All the distortion components are normalized by γ_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: α_c is measured with an error of $+2^\circ$ and α_0 with an error of -2° (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. The³⁴⁸
 293 equations tested here are only valid at equilibrium or, more
 294 precisely, if the material does not undergo aging during the³⁴⁹
 295 mechanical tests. As an example, the Ferry's relation (Eq.(15))³⁵⁰
 296 makes sense only if no aging occurs: the viscosity is not³⁵¹
 297 time-dependent in this equation. But the viscosity, being very
 298 sensitive to the aging of the material, is actually time-dependent,³⁵²
 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 characteristic³⁵³
 322 time for stress relaxation is large (here, it corresponds to³⁵⁴
 323 weeks) as compared to the time required (a few seconds, so³⁵⁵
 324 at least 5 orders of magnitude lower) for loading (to apply³⁵⁶
 325 the constant strain) and unloading (to measure the elastic³⁵⁷
 326 part of strain), so that we can consider that the loading and³⁵⁸
 327 unloading periods do not impact on the measurements. This³⁵⁹
 328 is in sharp contrast to the situation above the glass transition.³⁶⁰
 329 Moreover, the full experimental setup is not instrumented³⁶¹
 330 (there are no displacement sensors or load cells) since there³⁶²
 331 are no fast dynamics to measure; therefore it has the advantage³⁶³
 332 of preventing any drift of sensors that could can impact on³⁶⁴
 333 the measurements. Finally, at low temperatures the delayed³⁶⁵
 334 elasticity is to be more exacerbated (i.e.: the stretch exponent³⁶⁶
 335 is usually lower).³⁶⁷
 336

337 We have also performed various mechanical tests on these³⁷⁰
 338 glass fibers to assess the linearity of the viscoelastic behavior³⁷¹
 339 in the stress range investigated here (see (Gueguen et al., 2013))³⁷²
 340 and references therein). No non-linear viscoelastic behavior is³⁷³
 341 detectable below, at least, 55 MPa. Because the shear relax-³⁷⁴
 342 ation test is a torsional test, the imposed distortion linearly in-³⁷⁵
 343 creases with r , the distance from the neutral axis of the fiber.³⁷⁶
 344 The maximum imposed distortion, at the surface of the fiber,³⁷⁷
 345 was $\gamma_0 = 4 \pm 0.05 \cdot 10^{-3}$. The shear elastic modulus being³⁷⁸
 346 $\mu = 4.6$ GPa (see (Gueguen et al., 2013) and references therein),³⁷⁹
 347 it corresponds to an initial stress of $\sigma(0) = 18.4$ MPa.³⁸⁰

4. Results

The relaxation function of the GeSe₉ fibers is plotted in Figure 2. The relaxation function φ is plotted as $\ln[-\ln[\varphi(t)]]$ vs. $\ln(t)$, since:

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

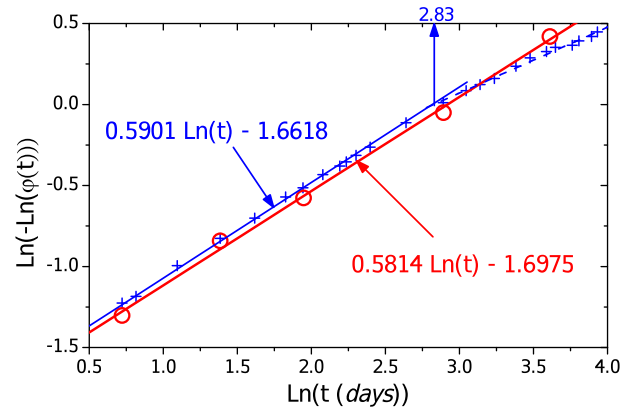


Figure 2: Experimental relaxation function obtained here (open red circle), plotted as $\ln(-\ln(\varphi(t)))$ vs. $\ln(t)$ (t is time), compared with a previous measurement (blue cross) (see (Gueguen et al., 2013) and references therein).

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

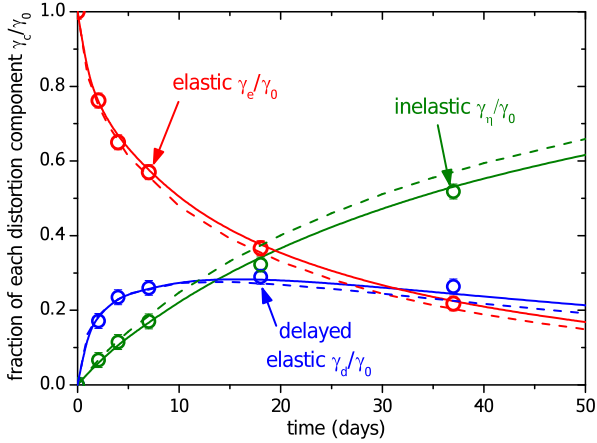


Figure 3: Evolution of each distortion contribution. The red, blue and green open circles correspond to $\gamma_c = \gamma_e$, γ_d and γ_η , respectively. The size of the circles corresponds to the error bar. The red, green and blue lines correspond to Eq.(22), (25) and (26), respectively, with $\beta = 0.58$ 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 γ_d and γ_η 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 (β , τ_0 and μ), 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 Λ , in order to illustrate the theoretical evolution of delayed elastic and inelastic distortions as a function of the stretch exponent β . In this Figure, we can observe that Λ_M , the position of the maximum delayed elastic distortion, is shifted to larger values as β 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 γ_0 when $t \rightarrow +\infty$. We can notice in Figure 4 that, if β 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. β in Figure 1. We have shown (Eq.(32)) that this maximum delayed elastic distortion is not a function of τ_0 : it is only defined by the stretch exponent β . 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, τ_0 , only indicates the kinetics of the relaxation, and the stretch exponent, β , only indicates the amplitude of the delayed elastic contribution to this relaxation.

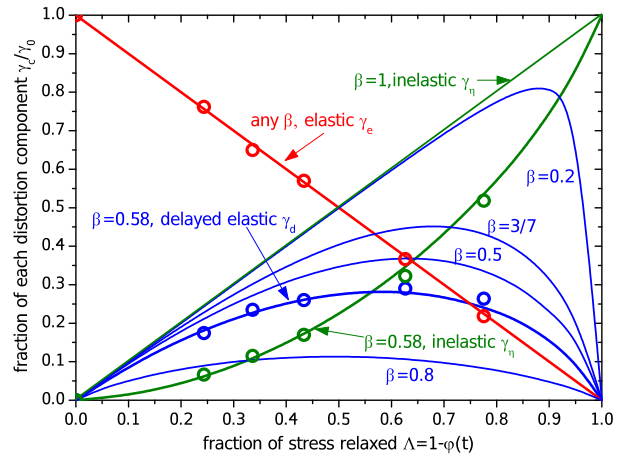


Figure 4: Theoretical evolutions (Eq.(28), (29) and (30)) of each distortion contribution ($\gamma_c = \gamma_e$, γ_d or γ_η) as a function of Λ , the fraction of stress relaxed, for various β values. The open circles correspond to experimental data. The theoretical evolutions are also plotted for $\beta = 0.59$, 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, Se_{500}
444 chains, probably Se-rings... (see (Yang, Gueguen, Sangleboeuf,⁵⁰¹
445 Rouxel, Boussard-Pledel, Troles, Lucas, and Bureau, 2013) and⁵⁰²
446 references therein). But the energy barrier for a specific type of⁵⁰³
447 local relaxation event (LRE) varies from one site to another, at⁵⁰⁴
448 least because of the inherent disorder of glasses (Simha, 1942).⁵⁰⁵
449 An atom or a structural unit can also contribute to different⁵⁰⁶
450 types of LRE, with different energy barriers. ⁵⁰⁷

451 At a given temperature, under no stress, the LRE will occur⁵⁰⁸
452 in random directions, producing, macroscopically, no net strain.⁵⁰⁹
453 Under relatively low stress, the energy barrier is slightly biased⁵¹⁰
454 (not enough biased to induce non-linear viscoelasticity) favor⁵¹¹
455 ing the relaxation events in a specific direction. These events,⁵¹²
456 do not necessarily correspond to global atomic displacements;⁵¹³
457 it can correspond to a transformation or a configuration change,⁵¹⁴
458 as described by Argon and Kuo (1980). Indeed, during a re⁵¹⁵
459 laxation test, the strain is constant, so that there is, macroscop⁵¹⁶
460 ically, no displacement, but just a "conversion" of the initial,⁵¹⁷
461 elastic displacement into delayed elastic and inelastic displac⁵¹⁸
462 ements. During a relaxation test all the atoms move initially only⁵¹⁹
463 "elastically" and are able to go back to their initial position. As⁵²⁰
464 soon as even a single atom (or more generally speaking a "re⁵²¹
465 laxing unit", a "cooperatively rearranging subsystem" or a "co⁵²²
466 operatively rearranging region" (Dyre, 1998)) has overcome its⁵²³
467 energy barrier to reach a new stable position/configuration the⁵²⁴
468 delayed elasticity can emerge. If the stress is released, all the⁵²⁵
469 others atoms will try to go back to their initial position, while⁵²⁶
470 this atom will not be able anymore, without overcoming again⁵²⁷
471 an energy barrier and will disturb the return of the other atoms.⁵²⁸
472 Macroscopically, the material is not able anymore to recover⁵²⁹
473 instantaneously its initial shape. This atom is stressed by all⁵³⁰
474 other (and by reaction, stressed itself the other atoms), so that⁵³¹
475 a driving force exists to induce its forward motion to its initial⁵³²
476 configuration. But since there is an energy barrier to overcome,⁵³³
477 this motion is delayed: this is the delayed elasticity. ⁵³⁴

478 Consequently, each initial LRE only produce delayed elastic⁵³⁵
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 lat⁵³⁶
484 ter by Goldstein (1969). We can go deeper into this idea by⁵³⁷
485 using a concept discussed by Argon (1968). Considering one⁵³⁸
486 specific subsystem and its corresponding LRE, with its spe⁵³⁹
487 cific energy barrier (*i.e.*: its specific relaxation time), we un⁵⁴⁰
488 derstand that if the subsystem wants to move or to change its⁵⁴¹
489 configuration, it has no reason to have exactly the free space it⁵⁴²
490 needs to do so: it will "shove" the surrounding network (Tra⁵⁴³
491 chenko, 2007), at it is nicely depicted by the shoving-model⁵⁴⁴
492 of Dyre (1998), to reach a new state. The difference between⁵⁴⁵
493 the new and the initial states will let the surrounding network⁵⁴⁶
494 partially "shoved", if it can not synchronously re-arrange. In⁵⁴⁷
495 other words, the subsystem will occupy a new site by elasti⁵⁴⁸
496 cally distorting it and stressing it or, at least will modify its⁵⁴⁹
497 configuration by stressing the surrounding network (let us name⁵⁵⁰
498 it the "shoving-stress", ShS). The delayed elasticity is driven⁵⁵¹
499 by the modification of the stress of the surrounding network⁵⁵²

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:

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

ρ_i is the weight of the i^{th} process having a relaxation time τ_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 γ_η/γ_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 ρ 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, β 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 τ (or τ_i if the spectrum is discontinuous) of a specific LRE and the average relaxation time τ_a . The relative proportion of reversible events produced by a process having relaxation times between τ 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^{th} relaxation time (τ_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 τ_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 τ_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.

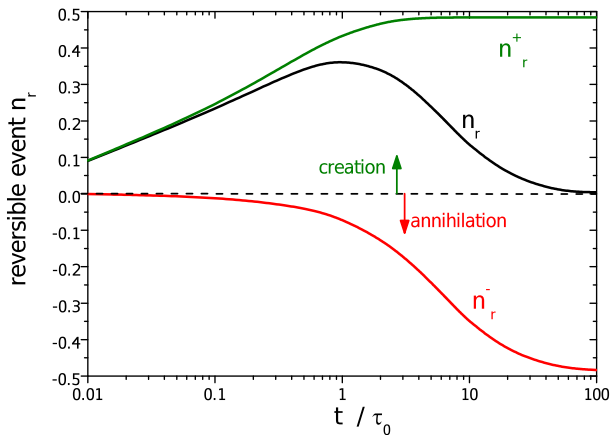


Figure 5: Illustration of the total number of reversible LRE (n_r , black line) vs. time (normalized by τ_0) for a SEF with $\beta = 1/2$, of the amount of reversible LRE (n_r^+) produced by all the processes having relaxation times lower than τ_a (green line) and of the amount of reversible LRE (n_r^-) annihilated by all the processes having relaxation times larger than τ_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 (Δp_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 Δp_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 (β). This maximum continuously increases
 690 as β decreases. Actually, the delayed elasticity is the result of
 691 the broadness (connected to β 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 τ is: $(1 - \tau/\tau_a)d(\tau)$, where τ_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.