Special Topics in Relaxation in Glass and Polymers

Lecture 5: Viscoelasticity I Shear

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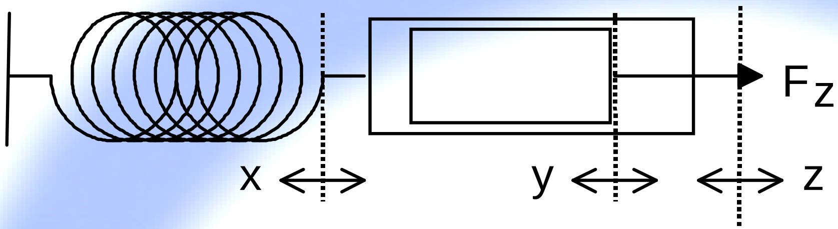
glass made of ideas

Basic viscoelastic models I: Maxwell Model

Mechanical model consisting of a spring and a dash-pot in a series.



$$F_x = F_y = F_z$$

Viscoelastic behaviour according to the Maxwell-model means that the material considered responds like an elastic body on short time scales and like a viscous fluid on long time scales.

$$F_x = D \cdot x \qquad F_y = \eta \cdot \frac{A}{d} \cdot \frac{dy}{dt}$$

$$x + y = z$$

Continuous strain: $$z = \frac{F_z}{D} + \frac{F_z}{\eta \cdot \frac{A}{d}} \cdot t$$

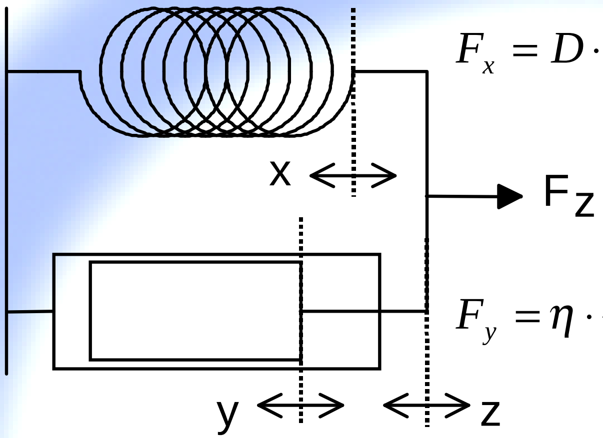
Constant elongation: $$F_z(t) = const \cdot e^{-t \cdot (D \cdot d)/(\eta \cdot A)}$$

derived from: $$\frac{dx}{dt} + \frac{dy}{dt} = 0 \qquad \frac{1}{D} \cdot \frac{dF_z}{dt} + \frac{d}{A} \cdot \frac{F_z}{\eta} = 0$$

The time constant τ=(A×η)/(D×d) is called relaxation time (force response to elongation).

Basic viscoelastic models II: Kelvin-Voigt Model

Mechanical model consisting of a spring and a dash-pot in parallel.



$$F_x = D \cdot x$$

$$F_z = F_x + F_y$$

$$F_y = \eta \cdot \frac{A}{d} \cdot \frac{dy}{dt}$$

$$x = y = z$$

Viscoelastic behaviour according to the Kelvin-Voigt-model means that the material responds like a rigid body on short time-scales and like an elastic body on long time-scales.

Both the Maxwell and the Kelvin-Voigt model are necessary to describe glass.

The case of an instantaneous, fixed elongation may not be realised with a Voigt-model.

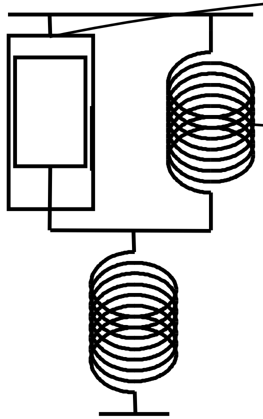
Continuous strain: $$z = \frac{F_z}{D} \cdot \left(1 - e^{-t \cdot (d \cdot D)/(A \cdot \eta)}\right)$$

derived from: $$D \cdot z + \eta \cdot \frac{A}{d} \cdot \frac{dz}{dt} = F_z$$

The time constant τ=(A×η)/(D×d) is called retardation time (elongation response to force).

Some exercises:

1. Consider “Basic viscoelastic models II: Kelvin-Voigt Model”. A Kelvin-Voigt Model acting together with the tyre as additional spring is what you find as damper in cars.



Introduce numbers: $\eta \cdot \frac{A}{d} = 2000\ N \cdot s / m$

Spring: $D = 20\ N / mm$

Calculate τ of the Kelvin-Voigt Model.

2. Consider again “Basic viscoelastic models I: Maxwell Model”. At the bottom, it is said that the formula

$$F_z(t) = const \cdot e^{-t \cdot (D \cdot d)/(\eta \cdot A)}$$

giving $F_z(T)$ for constant elongation follows from the homogeneous linear differential equation

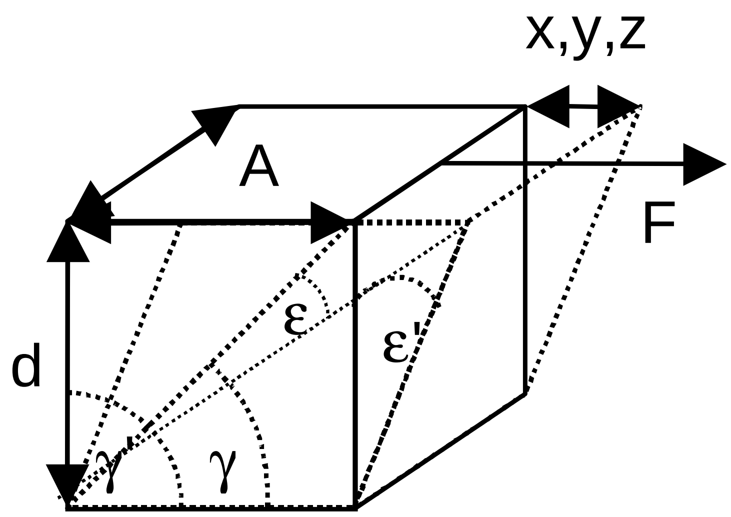
$$\frac{1}{D} \cdot \frac{dF_z}{dt} + \frac{d}{A} \cdot \frac{F_z}{\eta} = 0$$

Find the solution via Laplace-Transform. Write down the subsidiary equation.

Shear Viscoelasticity and Bulk Viscoelasticity

Combining Maxwell- and Kelvin-Voigt-elements, one may describe the viscoelastic behaviour of inorganic glasses and polymers. However, one has to distinguish between shear on one side and dilatation/compression on the other.

Shear



$$F_x = D \cdot x \rightarrow \sigma_x = G \cdot \varepsilon'_x$$

$$F_y = \eta \cdot \frac{A}{d} \cdot \frac{dy}{dt} \rightarrow \sigma_y = \eta \cdot \frac{d\varepsilon'_y}{dt}$$

Mostly not the angle ε' describing the change of γ' is referred to but the angle ε describing the change of γ. One has to introduce a factor of 2 for compensation.

$$F_X = D \cdot x \rightarrow \sigma_X = G \cdot 2 \cdot \varepsilon_X \qquad F_y = \eta \cdot \frac{A}{d} \cdot \frac{dy}{dt} \rightarrow \sigma_y = \eta \cdot 2 \cdot \frac{d\varepsilon_y}{dt}$$

Next step: drop the distinction between “x” and “y”. It is all in one.

Relations for Maxwell- and Kelvin-Voigt-model in case of shear

For the simple Maxwell-model and constant shear stress this leads to:

$$\varepsilon = \frac{\sigma_0}{2G} + \frac{\sigma_0}{2\eta} \cdot t = \left(\frac{1}{2G} + \frac{t}{2\eta} \right) \cdot \sigma_0 =: J(t) \cdot \sigma_0$$

J(t) is called compliance (describes strain response to stress).

For the simple Maxwell-model and constant shear strain this leads to:

$$\sigma(t) = 2 \cdot G \cdot \varepsilon_0 \cdot e^{-t \cdot (G/\eta)} = (2 \cdot G \cdot e^{-t \cdot (G/\eta)}) \cdot \varepsilon_0 =: 2 \cdot G(t) \cdot \varepsilon_0$$

G(t) is the thus defined time-dependent shear modulus (stress response to strain).

For the simple Kelvin-Voigt-model and constant shear stress this leads to:

$$\varepsilon = \frac{\sigma_0}{2G} \cdot \left(1 - e^{-t \cdot (G/\eta)}\right) = \left(\frac{1}{2G} \cdot \left(1 - e^{-t \cdot (G/\eta)}\right) \right) \cdot \sigma_0 =: J(t) \cdot \sigma_0$$

The combination of simple Kelvin-Voigt-model and constant shear strain does not exist.

Shear relaxation experiments from Clemson University I

Kadali et al. have built a spring relaxometer as introduced by S. Rekhson et al.

Visco-Elastic Characterization of Glass

Pyrex® and BK7

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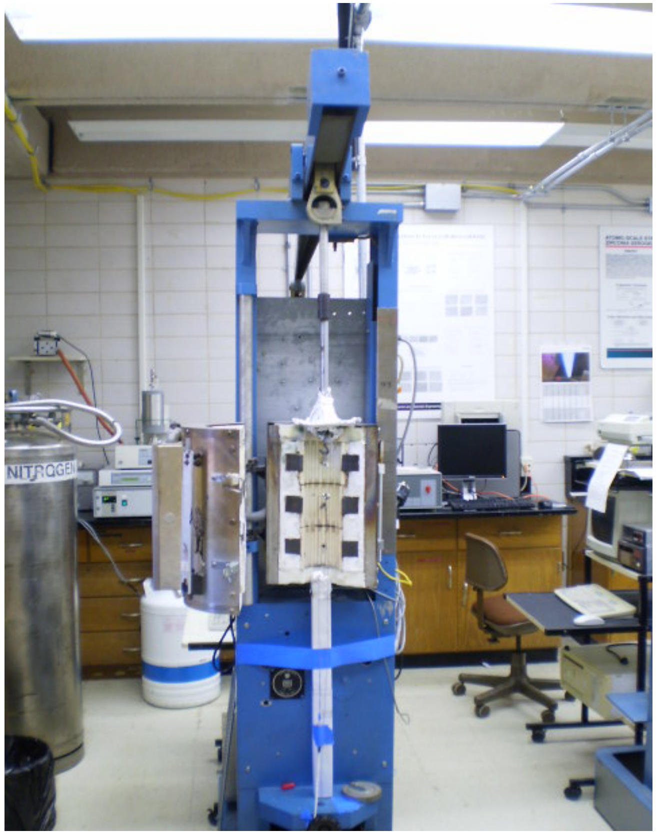
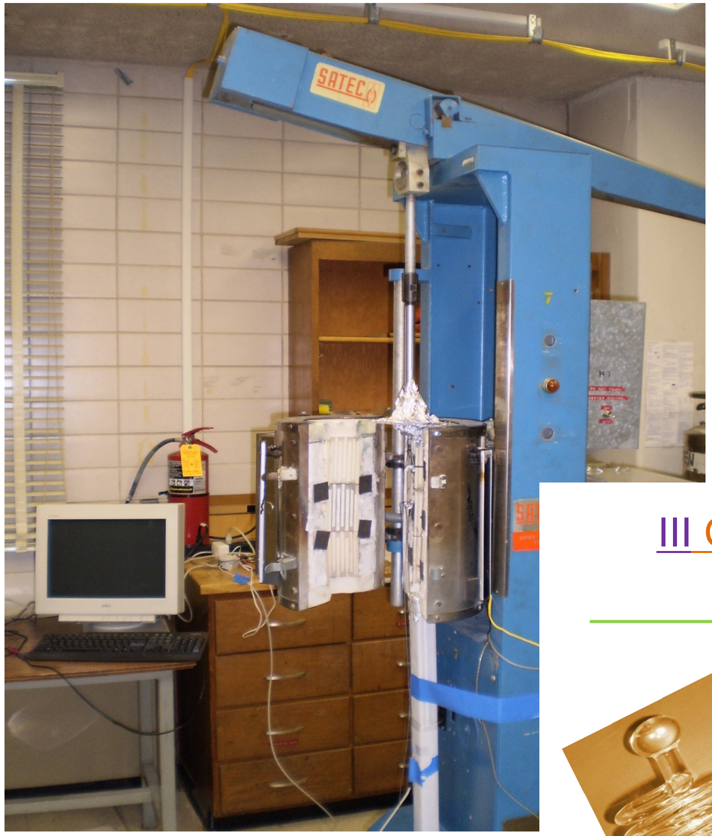
Shear relaxation experiments from Clemson University II

II Creep Recovery Setup



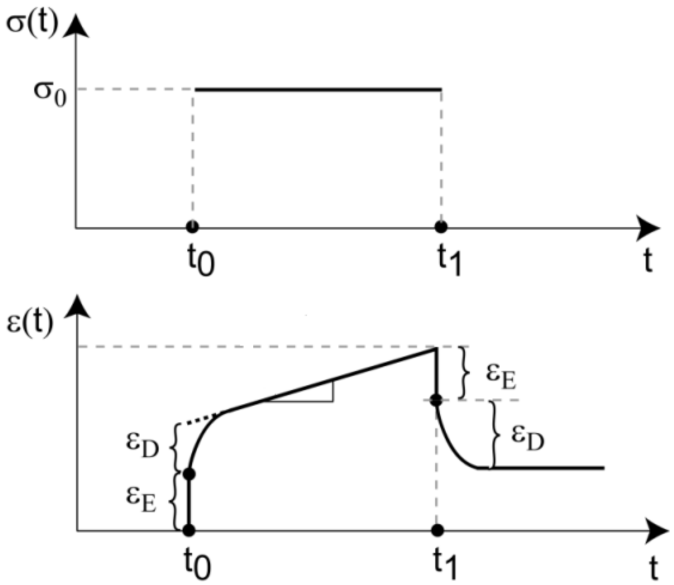


To impose pure shear on a sample, torsion is an appropriate way. The elongation of a helical spring implies torsion of every cross-section => spring elongation means shear.

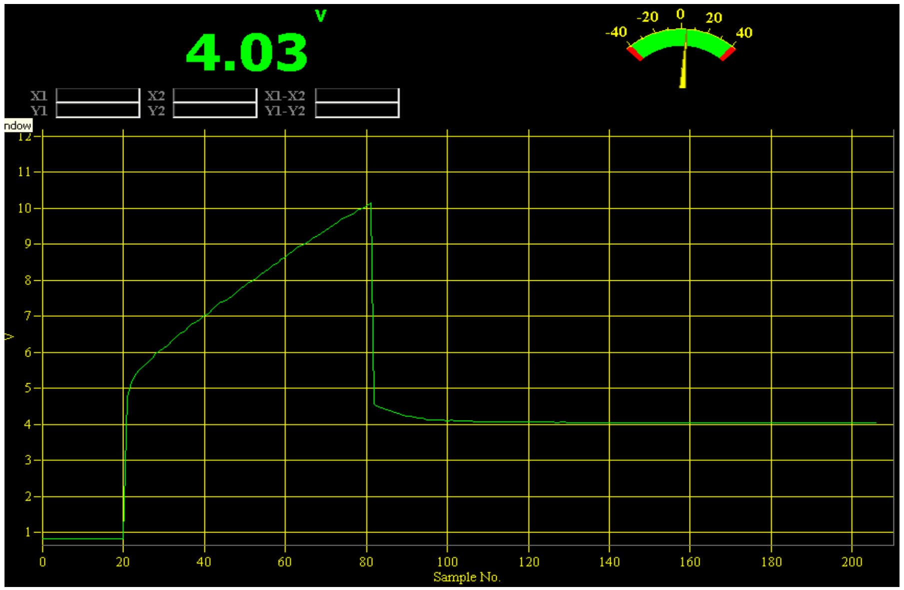
III Creep Testing on Helical Spring sample

Shear relaxation experiments from Clemson University III

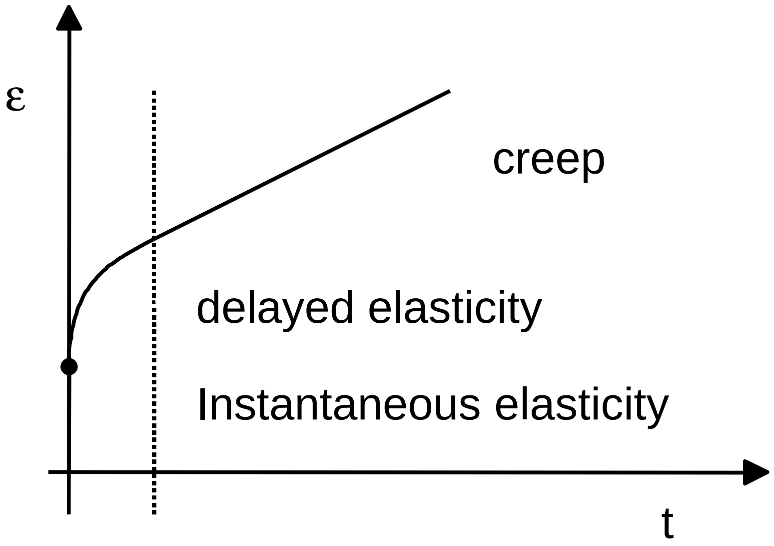
II Creep testing



An Example of an LVDT Result

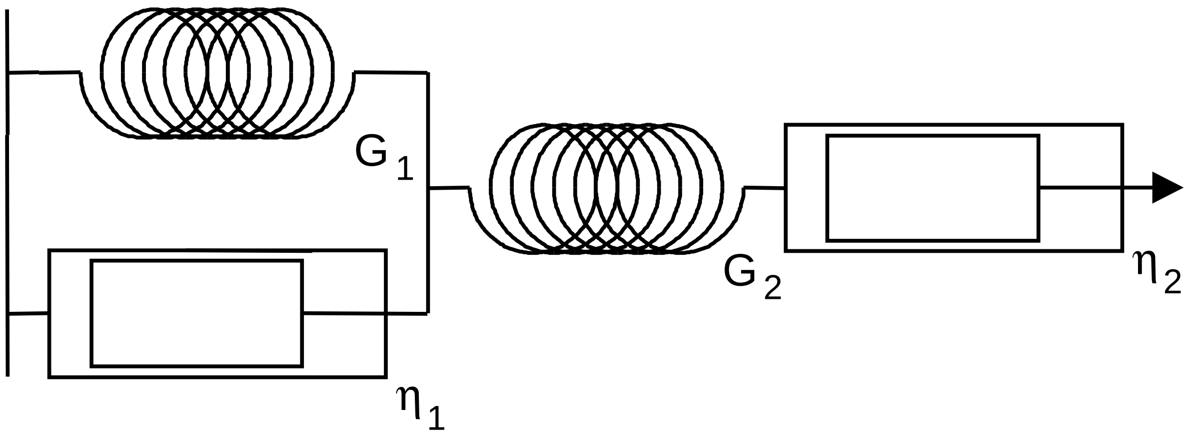


1st Realistic Picture of Shear Relaxation: Burger-Model



As we have seen, the behaviour of inorganic glasses is more complicated and cannot be described with either the Maxwell- or the Voigt-model alone.

The simplest representation is by a Burger-model:



Burger-Model (continued)

In case of constant stress one gets:

$$\varepsilon = \left[\left(\frac{1}{2G_2} + \frac{t}{2\eta_2}\right) + \left(\frac{1}{2G_1}\cdot\left(1 - e^{t\cdot(G_1/\eta_1)}\right)\right)\right]\cdot\sigma_0 =: J_{Burger}(t)\cdot\sigma_0$$

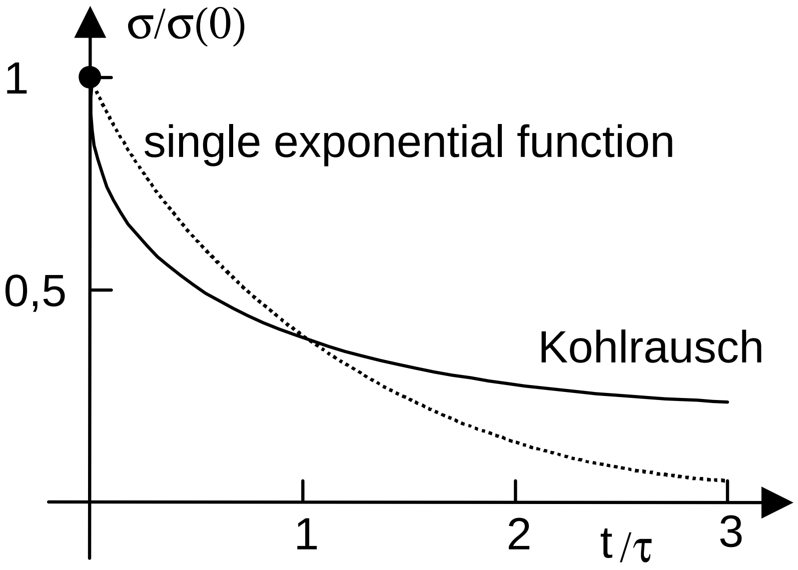
The case of constant strain is more complicated and requires a careful derivation:

$$\sigma = \frac{2\cdot G_2\cdot\varepsilon_0}{(\lambda_+ - \lambda_-)}\cdot\left[\left(\lambda_+ + \frac{G_1}{\eta_1}\right)\cdot e^{\lambda_+\cdot t} - \left(\lambda_- + \frac{G_1}{\eta_1}\right)\cdot e^{\lambda_-\cdot t}\right]$$

λ_+, λ_- are the roots of the equation $G_1\times G_2+(G_2\times\eta_2+G_1\times\eta_2+G_2\times\eta_1)\times\lambda+\eta_1\times\eta_2\times\lambda^2=0$.

$$\lambda_\pm = \frac{-(G_2\eta_2 + G_1\eta_2 + G_2\eta_1) \pm \sqrt{G_2\eta_2(G_2\eta_2 + 2G_1\eta_2 + 2G_2\eta_1) + (G_1\eta - G_2\eta_1)^2}}{2\eta_1\eta_2}$$

Kohlrausch-Kinetics for Shear Relaxation



An even better coincidence of theoretical and experimental data than with the Burger model is obtained, if the single exponential function from above is replaced with a stretched exponential or Kohlrausch(-Williams-Watts)-function.

$$e^{-(t/\tau)^b} \quad , \quad 0<b<1$$

For constant stress one gets:

$$\varepsilon = \left[\frac{1}{2G_0} + \frac{t}{2\eta} + \left(\frac{1}{2G_\infty} - \frac{1}{2G_0} \right) \cdot \left(1 - e^{-(t/\tau_d)^{bd}} \right) \right] \cdot \sigma_0 =: J(t) \cdot \sigma_0$$

J(t) is the time-dependent compliance; τ_d and b_d are retardation parameters.

For constant strain one gets

$$\sigma(t) = 2 \cdot G_0 \cdot \varepsilon_0 \cdot e^{-(t/\tau_x)^{bx}} =: G(t) \cdot \varepsilon_0$$

G(t) is the time-dependent shear modulus; τ_x and b_x are relaxation parameters.

Boltzmann´s superposition principle, relaxation retardation

In general (not only for shear) it is assumed that the stress effects arising from strain contributions imposed at different times overlay without interfering and vice versa:

$$\sigma(t)=2\cdot G_0\cdot\sum\Delta\varepsilon_{(at\ the\ time\ t')}\cdot e^{-((t-t')/\tau_x)^{b_x}}\approx 2\cdot G_0\cdot\int_0^t e^{-((t-t')/\tau_x)^{b_x}}\cdot\frac{d\varepsilon(t')}{dt'}\cdot dt'$$

One may write introducing relaxation function Ψ

$$\sigma(t)=2\cdot G_0\cdot\int_0^t \Psi\left(\frac{t-t'}{\tau_x}\right)\cdot\frac{d\varepsilon(t')}{dt'}\cdot dt'$$

and retardation function Φ

$$\varepsilon(t)=\int_0^t\left[\frac{1}{2G_0}+\frac{t-t'}{2\eta}+\left(\frac{1}{2G_\infty}-\frac{1}{2G_0}\right)\cdot\left(1-\Phi\left(\frac{t-t'}{\tau_d}\right)\right)\right]\cdot\frac{d\sigma(t')}{dt'}\cdot dt'$$

Laplace-Transform yields:

$$L(\sigma)=2\cdot G_0\cdot L(\Psi)\cdot s\cdot L(\varepsilon)$$ **and** $$L(\varepsilon)=\left[\frac{1}{2G_\infty}+\frac{1}{2\eta s}-\left(\frac{1}{2G_\infty}-\frac{1}{2G_0}\right)\cdot s\cdot L(\Phi)\right]\cdot L(\sigma)$$

This allows the mutual conversion of relaxation and retardation parameters.

Relaxation and Viscosity

Consider the special case of constant stress in the long-time limit. According to the nature of the Laplace-Transform

$$L(f)=\int_0^t f(t')\cdot e^{-st'}\cdot dt'$$

only the L-values belonging to small s-values are sensitive to things happening on a broad time scale. This means for the retardation formula:

$$L(\varepsilon)=\left[\frac{1}{2G_\infty}+\frac{1}{2\eta s}-\left(\frac{1}{2G_\infty}-\frac{1}{2G_0}\right)\cdot s\cdot L(\Phi)\right]\cdot L(\sigma)\Rightarrow \lim_{s\to 0,t\to\infty} L(\varepsilon)=\frac{1}{2\eta k}\cdot \lim_{s\to 0,t\to\infty} L(\sigma)$$

Replacing the low s, high t – limit of L(σ)/L(ε) with the expression that follows from the relaxation formula gives:

$$2\cdot G_0\cdot \lim_{s\to 0,t\to\infty} L(\Psi)\cdot k=2\cdot\eta\cdot s$$

$$\Rightarrow \quad \frac{\eta}{G_0}=\lim_{s\to 0,t\to\infty} L(\Psi)=\lim_{s\to 0,t\to\infty}\int_0^t \Psi(t')\cdot e^{-st'}\cdot dt'=\int_0^\infty \Psi(t')\cdot dt'$$

Addenda

Prony Series

For computational purposes, the Kohlrausch-function may be represented by a number of single exponentials (Prony-series):

$$e^{-(t/\tau)^b} = \sum_i v_i \cdot e^{-t/\tau_i} \quad , \quad v_i > 0 \ \forall i \quad , \quad \sum_i v_i = 1$$

In order to allow for the comparatively fast relaxation for t < τ and the comparatively slow relaxation for t > τ, the Prony-series must comprehend both $\tau_i < \tau$ and $\tau_i > \tau$.

Temperature dependence of the relaxation times

As known, the temperature dependence of shear viscosity is well described by the Arrhenius law for a limited temperature range such as the one of glass transition:

$$\eta = \eta_0 e^{\frac{H}{R \cdot T}}$$

Consequently, it is also used for shear relaxation and retardation times:

$$\tau = \tau_0 e^{\frac{H}{R \cdot T}}$$

Some exercises:

1. Consider the correspondence of the Maxwell model with spring and dashpot and the behaviour of a viscoelastic material. It has been said that $F=D \cdot x$ translates into $\sigma=G \cdot \varepsilon' = 2 \cdot G \cdot \varepsilon$. Check dimensions in both cases (Newtons, Pascals etc.). Compare the dimensions of the right sides of both equations.

2. Consider the Burger model. What is $\varepsilon(0)$ in case of constant stress and $\sigma(0)$ in case of constant strain?

3. Compare single-exponential and stretched-exponential (Kohlrausch) behaviour. If b=0.5, what is the amount of $\mathrm{Exp}(-t/\tau)$ and $\mathrm{Exp}(-(t/\tau)^b)$ after $t=0.1 \cdot \tau$, $t=\tau$, $t=10 \cdot \tau$?

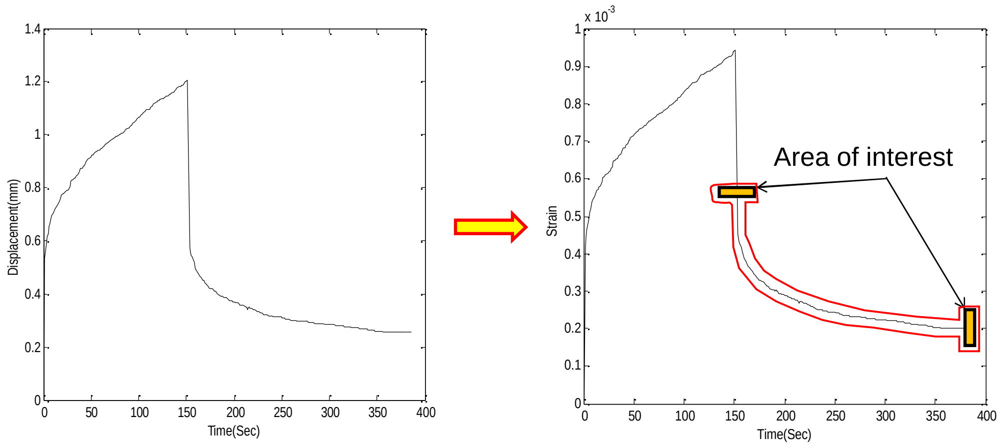
4. Which are the three time domains of a constant stress experiment?

5. How is η/G_0 related to the Kohlrausch-function $\mathrm{Exp}(-(t/\tau_x)^b)$?

Shear relaxation experiments from Clemson University IV

III Characterization of glass in transition region

I. Obtain Strain-time curve through creep recovery experiment



$$\varepsilon(t) = \left[\frac{8*k*D}{\Pi*d^3} + \frac{4*k}{\Pi*d^2}\right]*\delta(t)$$

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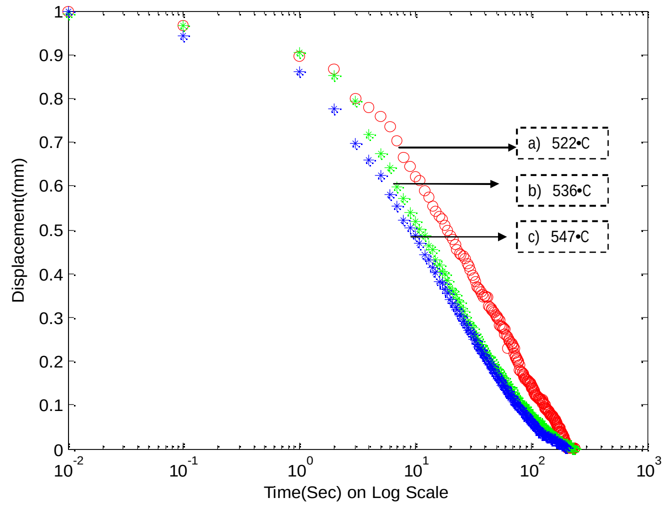
preliminary results

Retardation Spectrum on log time scale at different temperatures



Shear relaxation experiments from Clemson University V

Retardation Parameters

III. Carryout curve fitting for the resultant retardation curve to determine retardation parameters i.e. retardation times and retardation weights.

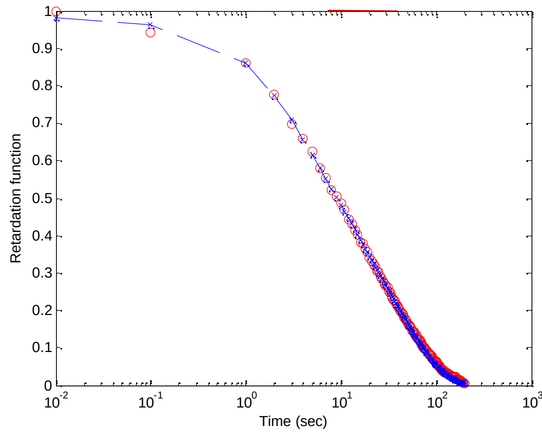
- Retardation function (Prony Series) (m_1 = 5 is the best fit)

$$\Phi(t) = \sum_{j=1}^{m1} \upsilon_{ij} \exp\left(\frac{-t}{\lambda_{ij}}\right)$$

- Determine Retardation weights •$_{1j}$ (j=1 to 5) & Retardation weights •$_{1j}$ (j=1 to 5) such that the resultant curve overlaps experimental curve
- A total of 10 parameters are obtained in this process

preliminary results

Calculated and Experimental Spectrum (Curve Fitting)



- - - :Simulated curve

o : Experimental curve

Shear relaxation experiments from Clemson University VI

Shear Retardation Parameters

$$\Phi(t) = \sum_{j=1}^{m1} \upsilon_{ij} \exp\left(\frac{-t}{\lambda_{ij}}\right)$$

$\bullet_{1j}$	$\bullet_{1j}$
[redacted]	[redacted]
0.0124	1.9944
[redacted]	[redacted]
0.2532	8.6257
[redacted]	[redacted]

preliminary results

Shear Relaxation Parameters for Pyrex®

w_{1j}	$\bullet_{1j}$
[redacted]	[redacted]
0.052928	1.7626990852
[redacted]	[redacted]
0.186358	6.930635274
[redacted]	[redacted]
0.39312	220.6745301