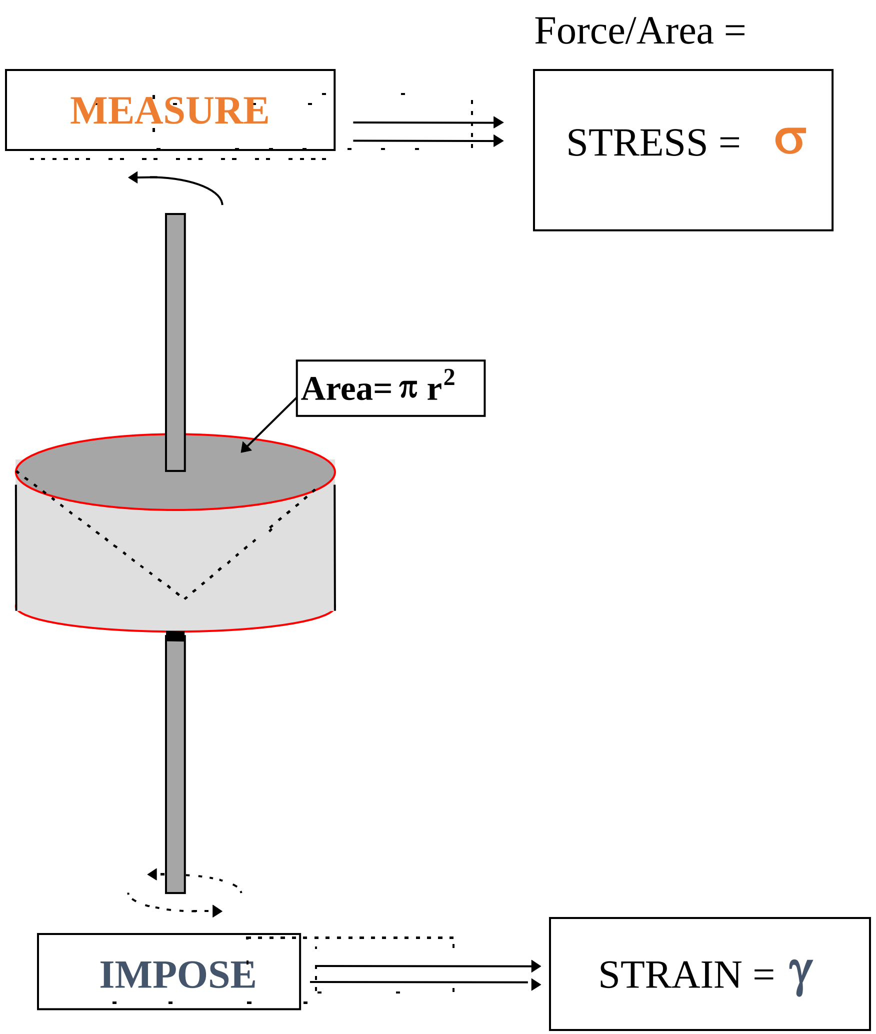
Relaxation Modulus

and

the relaxation spectrum

Relaxation modulus and the material´s response to a sudden strain



MODULUS = STRESS / STRAIN

Relaxation modulus

$$G = \sigma / \gamma$$

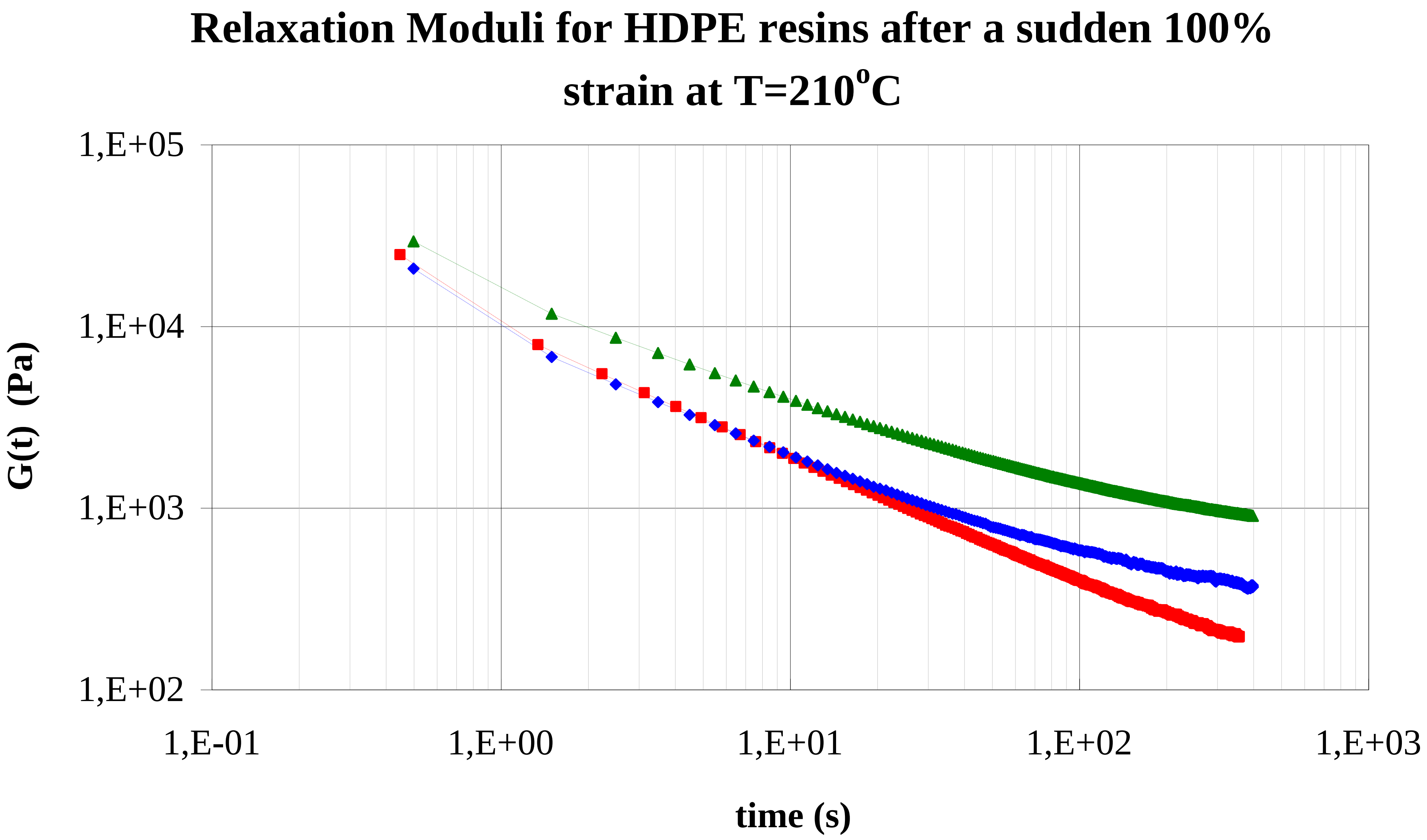
$$\gamma = (L - Lo)/ Lo$$

σ in Pa

then

G en unidades de Pa

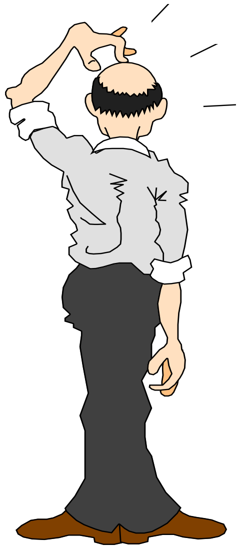
Typical Relaxation Moduli



Viscoelastic Models

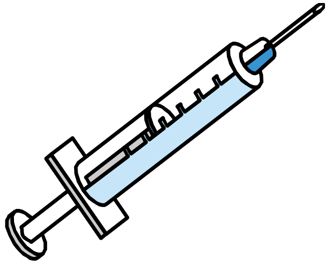
What is a viscoelastic model?

- It is a model that considers the **viscous** and **elastic** properties of a given material and typically uses **mechanical analogs** as a way to represent such properties.

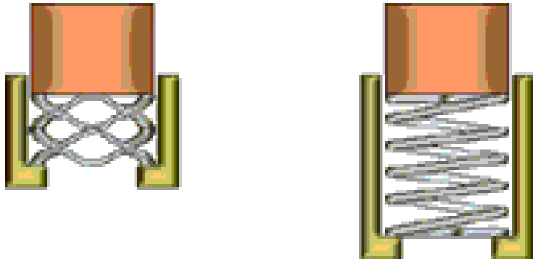


How a viscoelastic model can be represented?

- A conventional way to represent the linear behavior of the viscosity and elasticity is by using dashpots and springs:

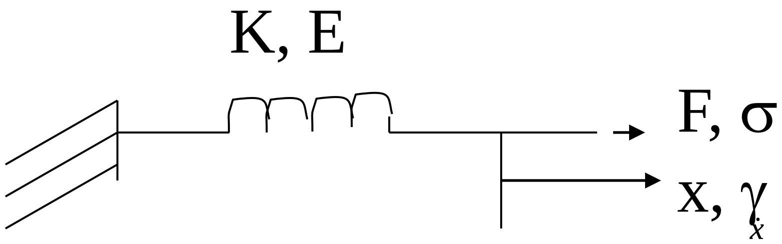


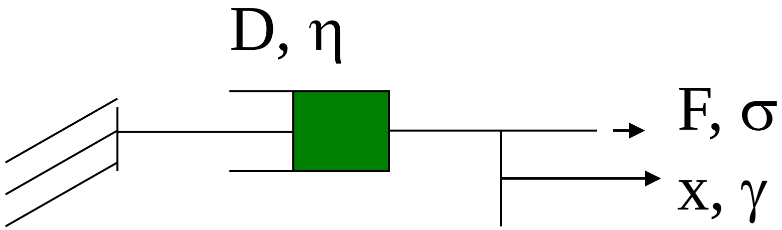
Syringe (dashpot)



Spring

Mechanical Elements





$F = Kx$

$\sigma = E\gamma$

Linear Elastic Element

Hooke´s Law

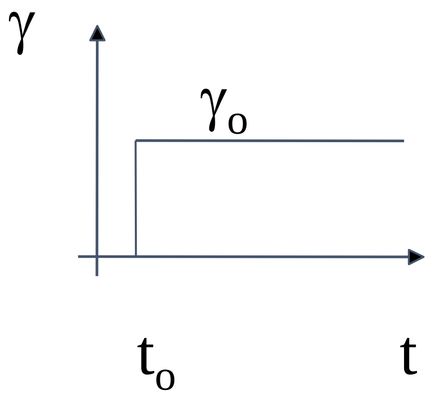
$F = D\, dx/dt = D\dot{x}$

$\sigma = \mu d\gamma/dt = \mu\,\dot{\gamma}$

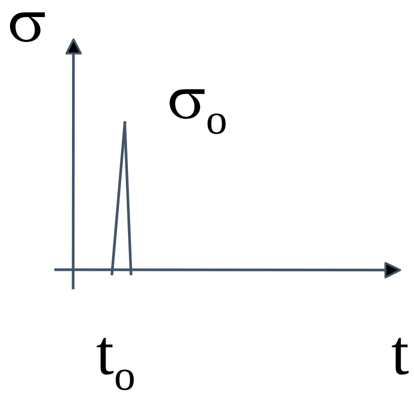
Linear viscous element

Newton´s Law

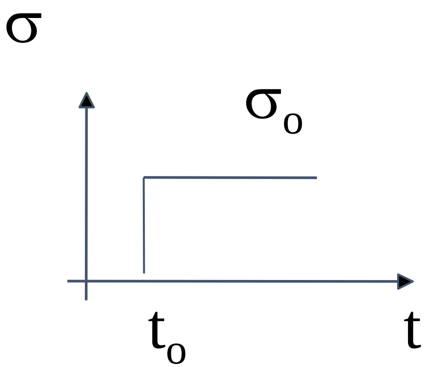
Response to a sudden deformation for different types of materials. Darby (1976)



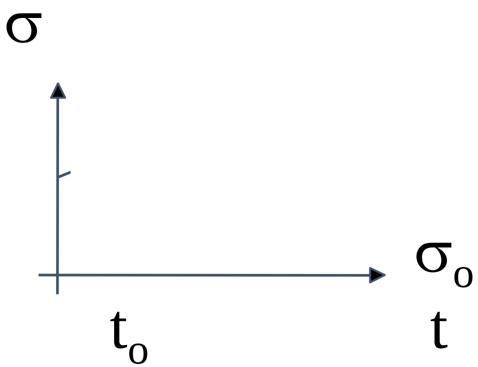
Imposed strain



Newtonian fluid response



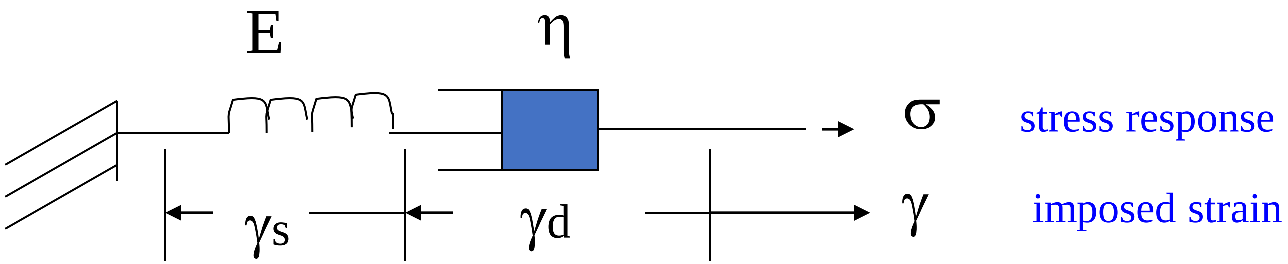
Hookean fluid response



Viscoelastic fluid response???

Maxwell Fluid

- It is a combination of a **spring** and a **dashpot** in serie.



$$\gamma = \gamma s + \gamma d \quad = \text{Total deformation} \qquad (1.1)$$

Differentiation of equation 1.1, with respect to time :

$$\dot{\gamma} = \dot{\gamma}_s + \dot{\gamma}_d = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\eta} = \dot{\gamma} \qquad (1.2)$$

Defining λ as:

$$\lambda = \eta/E, \qquad (1.3)$$

and multiplying equation 1.2 by η, then:

$$\lambda\,\dot{\sigma} + \sigma = \eta\,\dot{\gamma} \qquad (1.4)$$

Equation.1.4, relates the stress to the shear rate for a Maxwell fluid

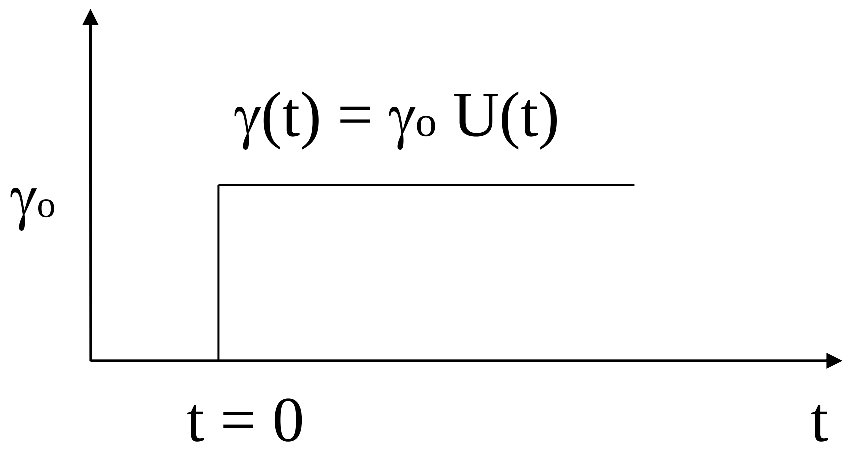
Observe that in equation 1.4,

If $E = \infty$, then $\lambda \rightarrow 0$ and the model is known as **NEWTON´S Viscosity Law**

$$\sigma = \eta\,\dot{\gamma}$$

A stress relaxation test for a Maxwell fluid:

The test consists in applying a unit step deformation, γ_o, at time t=0 . The deformation remains constant throught the test:



(1.5)

where U(t) is a step function, defined as:

$$U(t) = \begin{cases} 0, & t \leq 0 \\ 1, & t > 0 \end{cases}$$

The way the resulting stress behaves as a function of time due to the imposed deformation can be determined from solving equations 1.4 y 1.5. This can be done by applying the Laplace Transform to each equation:

$$\sigma + \lambda\,\dot{\sigma} = \eta\,\dot{\gamma} \longleftarrow \text{Eqn. 1.4}$$

$$L\{\sigma\} + \lambda[sL\{\sigma\} - \sigma\{0\}] = \eta[sL\{\gamma\} - \gamma\{0\}]$$

$$\bar{\sigma}(s) + \lambda[s\bar{\sigma}(s) - \sigma\{0\}] = \eta[s\bar{\gamma}(s) - \gamma\{0\}] \qquad (1.6)$$

From equation 1.6, $\sigma\{0\}$ y $\gamma\{0\}$ are the initial values at time = 0,

(It is convenient to define t=0 when no deformation has occurred)

therefore:

$$\bar{\sigma}(s)\,[1+\lambda s] - \cancel{\lambda\,\sigma\{0\}} = \eta s\bar{\gamma}(s) - \cancel{\eta\,\gamma\{0\}}\,] \qquad (1.7)$$

$$\bar{\sigma}(s)\,[1+\lambda s] = \eta s\bar{\gamma}(s) \qquad (1.8)$$

Rearranging equation 1.8 :

$$\bar{\sigma}(s) = \frac{\eta s \bar{\gamma}(s)}{[1 + \lambda s]} \qquad (1.9)$$

And by applying also the Laplace transform to equation 1.5:

$\gamma(t) = \gamma_o \, U(t)$ ⟵ Ecn. 1.5 (step deformation)

$$\bar{\gamma}(s) = \gamma_o / s \qquad (1.10)$$

Substitution of equation 1.10 into 1.9 and rearranging:

$$\bar{\sigma}(s) = \frac{\eta \gamma_0}{[1 + \lambda s]} \xrightarrow{\lambda = \eta/E} \bar{\sigma}(s) = \frac{E \gamma_0}{\left[\frac{1}{\lambda} + s\right]} \qquad (1.11)$$

And by taking the inverse of the Laplace transform, equation 1.11:

$$\sigma(t) = E\gamma_o \exp^{(-t/\lambda)} = \sigma_o \exp^{(-t/\lambda)}$$

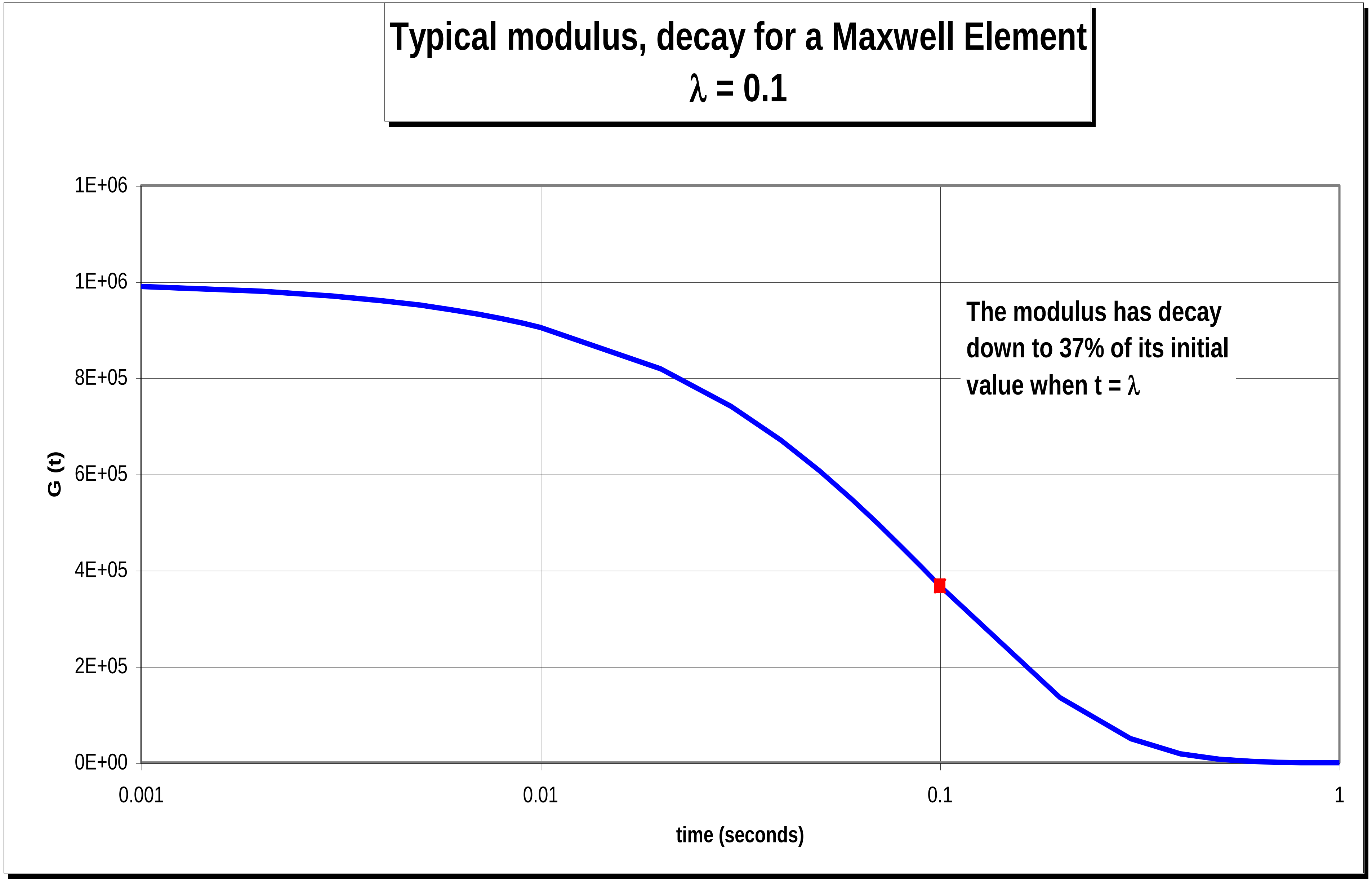
Let us analyze this equation:

Example

If $t \to 0$, then $\sigma(0) = E\,\gamma_o$, therefore we have a pure elastic response.

At $t = \lambda$, the shear stress will decrease, reaching 37% of its initial value.

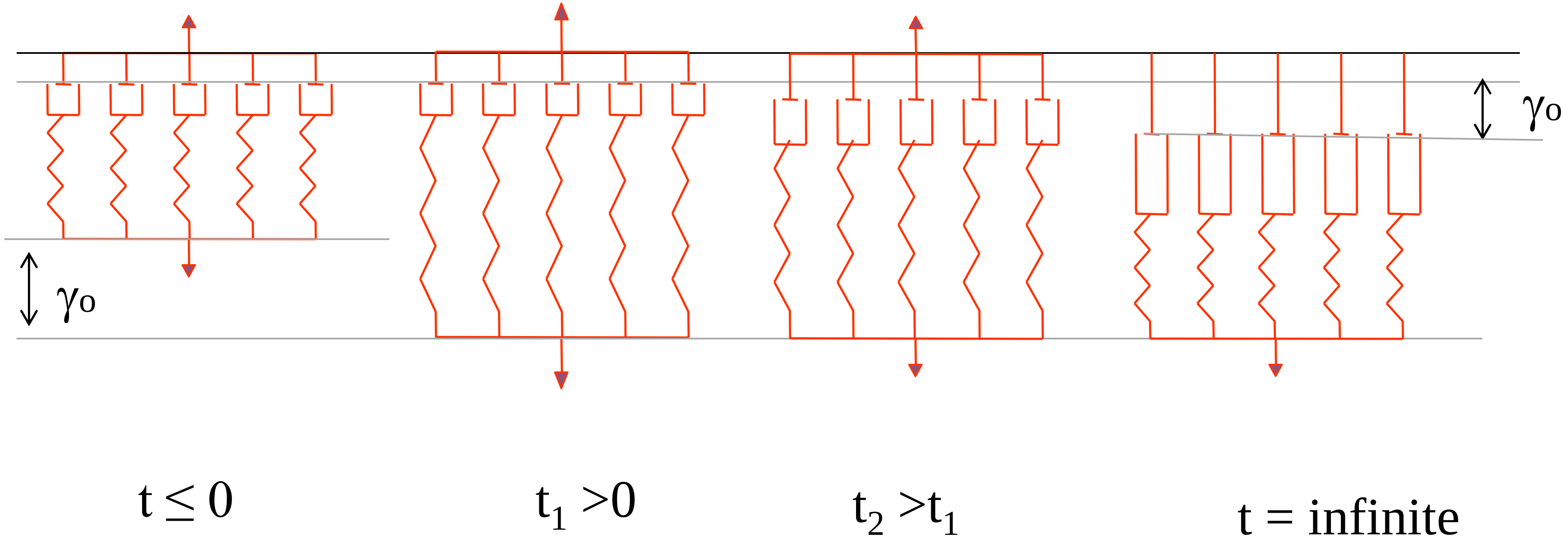
The λ value is called ***a characteristic time*** and is a <u>material constant</u> known as a ***relaxation time*** of the material.



Typical modulus, decay for a Maxwell Element
λ = 0.1
1E+06
1E+06
8E+05
6E+05
4E+05
2E+05
0E+00
G (t)
0.001
0.01
0.1
1
time (seconds)
The modulus has decay
down to 37% of its initial
value when t = λ

But...

for polymers the stress behavior of polymers under the influence of an imposed strain cannot be explained by one Maxwell element, it needs to be approximated by a set of j Maxwell elements in parallel:



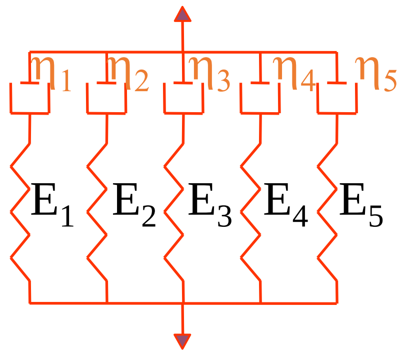
But…

When we have j Maxwell elements in parallel the equation to represent those elements is obtained as follows:

$$\sigma(t) = \gamma_o \, \Sigma \, E_j \exp(-t / \lambda_j)$$

or

$$\sigma(t) / \gamma_o = G(t) = \Sigma \, E_j \exp(-t / \lambda_j)$$



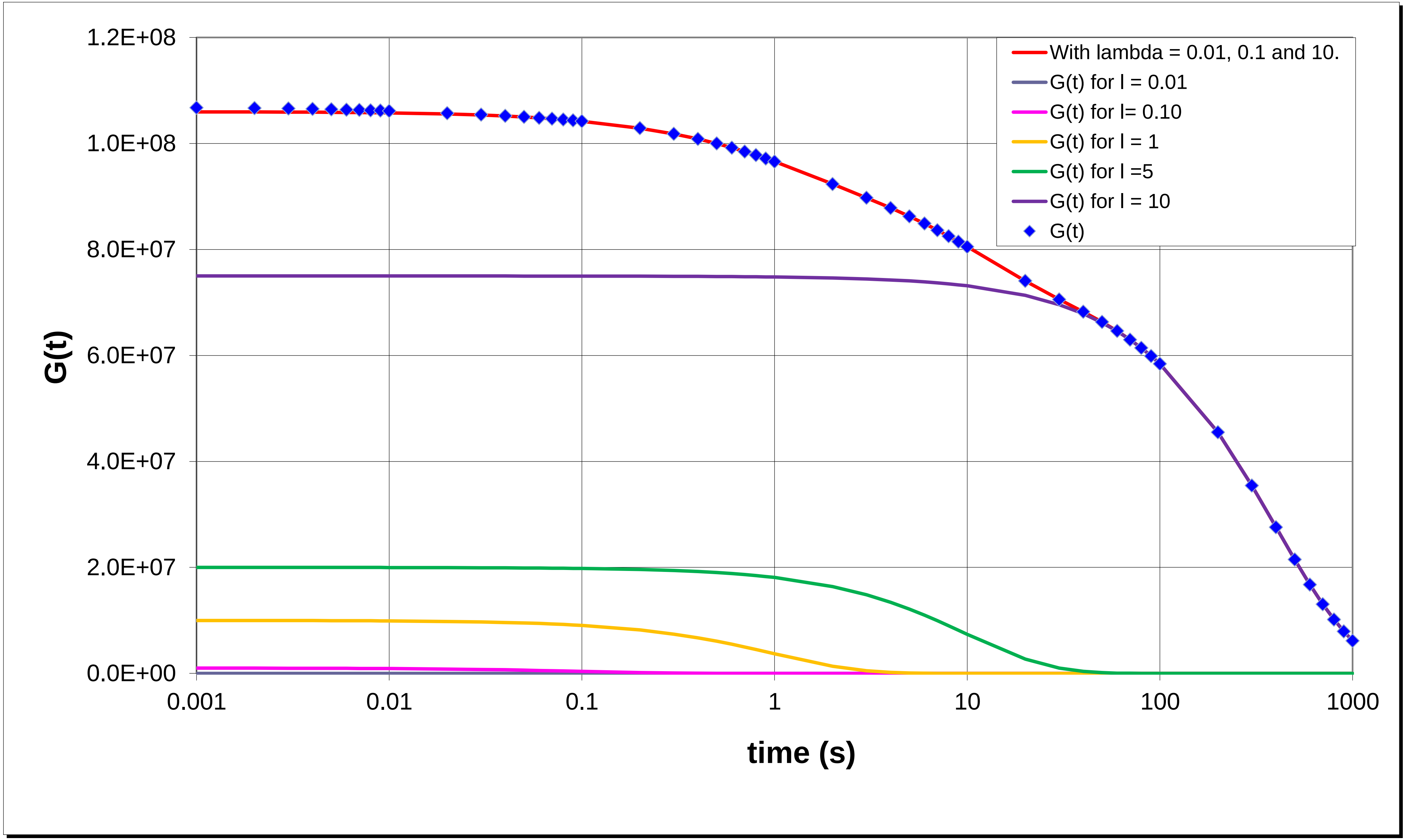
Remember that $\lambda_j = \eta_j / E_j$, then

$$\sigma(t) / \gamma_o = G(t) = \Sigma \, (\eta_j / \lambda_j) \exp(-t / \lambda_j)$$

or

$$\sigma(t) / \gamma_o = G(t) = \Sigma \, E_j \exp(-t \, E_j / \eta_j)$$

j Maxwell elements



1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
G(t)
0.001
0.01
0.1
1
10
100
1000
time (s)
With lambda = 0.01, 0.1 and 10.
G(t) for l = 0.01
G(t) for l= 0.10
G(t) for l = 1
G(t) for l =5
G(t) for l = 10
G(t)

Definition of the relaxation spectrum

since $$G(t) = \Sigma E_j \exp(-t / \lambda_j),$$

the summation can be presented as an integral, if the number of Maxwell analogs (*that is j*) tends to infinite. Such infinite number of analogs reults in a set of relaxation times, $\{\lambda_j\}$, whose magnitudes are material dependent.

The set $\{\lambda_j\}$ is known as the distribution of relaxation times (DRT) or the distribution of the ratios η_j / E_j.

Therefore, a subset of relaxation times between a given λ and $\lambda + d\lambda$, contributes to the total relaxation modulus through the E_j's involved in the subset. A way to extract such contribution from the DRT is to assume the existence of a continuos function, $F(\lambda)$, such that $F(\lambda)d\lambda$ is equal to the G_j's in the range of relaxation times between λ and $\lambda + d\lambda$. The relaxation modulus is therefore defined as:

$$G(t) = \int_{-\infty}^{\infty} F(\lambda)\exp(-t / \lambda_j)d\lambda,$$

Definition of the relaxation spectrum

since $G(t) = \Sigma E_j \exp(-t / \lambda_j),$

$$\Big\Downarrow$$

$$G(t) = \int_{-\infty}^{\infty} F(\lambda)\exp(-t / \lambda_j)d\lambda,$$

but , since the viscoelastic response spans several decades of time and of relaxation times, it is typical to describe the information in a logarithmic fashion, and this is accomplished by multiplying and dividing the integrand by λ:

$$G(t) = \int_{-\infty}^{\infty} \lambda F(\lambda) \exp(-t / \lambda_j)\, (d\lambda / \lambda),$$

where $(d\lambda / \lambda) = d \ln \lambda,$ and

$$\lambda F(\lambda) = H(\lambda),$$

$$G(t) = \int_{-\infty}^{\infty} H(\lambda) \exp(-t / \lambda_j)\, d\ln\lambda.$$

This equation gives the definition for $H(\lambda)$ which is known as the relaxation spectrum and represents a distribution of moduli for the generalized Maxwell model. Conversely, $\lambda H(\lambda)$ is a distribution of viscosities which is known as viscosity density function (VDF).

Getting a discrete relaxation spectra

1. Remember that

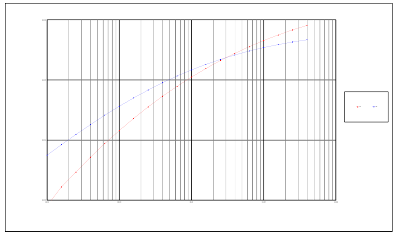
   η_i is the viscous modulus of the ith Maxwell analog

   g_i is the elastic modulus of the ith Maxwell analog

$$\eta_i = g_i \lambda_i \qquad (1)$$

2. and that you need the Dynamic Mechanical Data to get the loss and the elastic modulus:

$$G'(\omega) = \sum_{i=1}^{N} g_i \frac{\omega^2 \lambda_i^2}{1 + \lambda_i^2 \omega^2} \qquad (2)$$



$$G''(\omega) = \sum_{i=1}^{N} g_i \frac{\omega \lambda_i}{1 + \lambda_i^2 \omega^2} \qquad (3)$$

3. The you need to fit the data with the following equations

The continuous function can be obtained (see paper)

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A dynamic nonlinear regression method for the determination of the discrete relaxation spectrum

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Abstract. The relaxation spectrum is an important tool for studying the behaviour of viscoelastic materials. The most popular procedure is to use data from a small-amplitude oscillatory shear experiment to determine the parameters in a multi-mode Maxwell model. However, the discrete relaxation times appear nonlinearly in the mathematical model for the relaxation modulus. The indirect calculation of the relaxation times is an ill-posed problem and its numerical solution is fraught with difficulties. The ill-posedness of the linear regression approach, in which the relaxation times are specified *a priori* and the minimization is performed with respect to the elastic moduli, is well documented. A nonlinear regression technique is described in this paper in which the minimization is performed with respect to both the discrete relaxation times and the elastic moduli. In this technique the number of discrete modes is increased dynamically and the procedure is terminated when the calculated values of the model parameters are dominated by a measure of their expected values. The sequence of nonlinear least-squares problems, solved using the Marquardt–Levenberg procedure, is shown to be robust and efficient. Numerical calculations on model and experimental data are presented and discussed.

Some material parameters as a function of H(λ)

- zero shear viscosity

$$\eta_0 = \int_{-\infty}^{\infty} H(\lambda)\lambda \cdot d\ln\lambda$$

- instantaneous modulus

$$Gg = \int_{-\infty}^{\infty} H(\lambda) d\ln\lambda$$

- steady state recoverable compliance

$$Je^0 = \frac{\int_{-\infty}^{\infty} H(\lambda)\cdot\lambda^2 \cdot d\ln\lambda}{\left(\int_{-\infty}^{\infty} H(\lambda)\lambda \cdot d\ln\lambda\right)^2}$$