Today's Plan

Linear viscoelasticity III

I. Rheological models

II. Generalised models

III. Time spectra

IV. Equivalency between quasi-static and dynamic data

V. Summary

I. Rheological models

Recall : Differential representation of linear viscoelasticity

- General linear differential equation

$$a_n \frac{\partial^n \sigma}{\partial t^n} + a_{n-1} \frac{\partial^{n-1} \sigma}{\partial t^{n-1}} + \ldots + a_0 \sigma = b_n \frac{\partial^n \varepsilon}{\partial t^n} + b_{n-1} \frac{\partial^{n-1} \varepsilon}{\partial t^{n-1}} + \ldots + b_0 \varepsilon$$

where a_i, b_i are material parameters

This is equivalent to describing the viscoelastic behaviour by rheological models constructed of elastic springs and viscous dashpots.

Laplace-Carson transform properties

Function	Transformed
$f(t)$	$f^+(p)$
$C.f(t)$	$C.f^+(p)$
$\frac{d}{dt}$	p
$H(t)$	1
$H(t-\tau)$	$\exp(-\tau p)$
$f(t-\tau)$	$\exp(-\tau p)\, f^+(p)$
if $f(t) = 0$	for $t \leqslant 0$
$f'(t)$	$p f^+(p)$
$\frac{df}{dt}(t) \otimes g(t)$	$f^+(p)\, g^+(p)$

Function	Transformed
t	$1/p$
t^n	$\frac{n!}{p^n}$
$\exp(-at)$	$\frac{p}{p+a}$
$1-\exp(-at)$	$\frac{a}{p+a}$
$\cos \omega t$	$\frac{p^2}{p^2+\omega^2}$
$\sin \omega t$	$\frac{p\omega}{p^2+\omega^2}$
$f(t)\exp(-at)$	$\frac{p}{p+a} f^+(a+p)$
$(-t)^m f(t)$	$p \frac{d^m}{dp^m}\left(\frac{f^+(p)}{p}\right)$

Emmanuelle CHABERT chabert@lms.polytechnique.fr

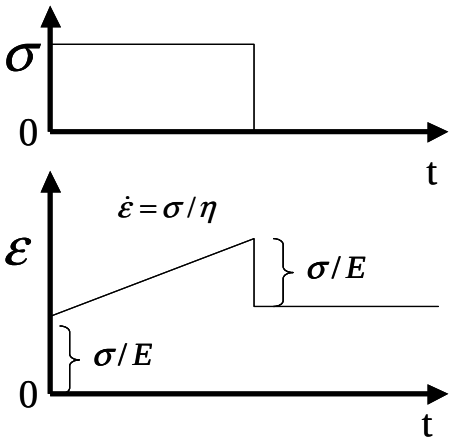
Maxwell model

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\eta}$$

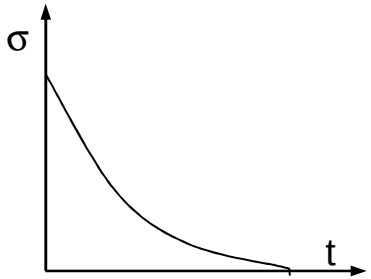
$$p\varepsilon^* = \left(\frac{p}{E} + \frac{1}{\eta}\right)\sigma^*$$

$$\sigma^* = E\frac{p}{p + E/\eta}\varepsilon^*$$

creep response



relaxation response



$$\boxed{E(t) = E\exp(-t/\tau)} \qquad \tau = \eta/E$$ characteristic time

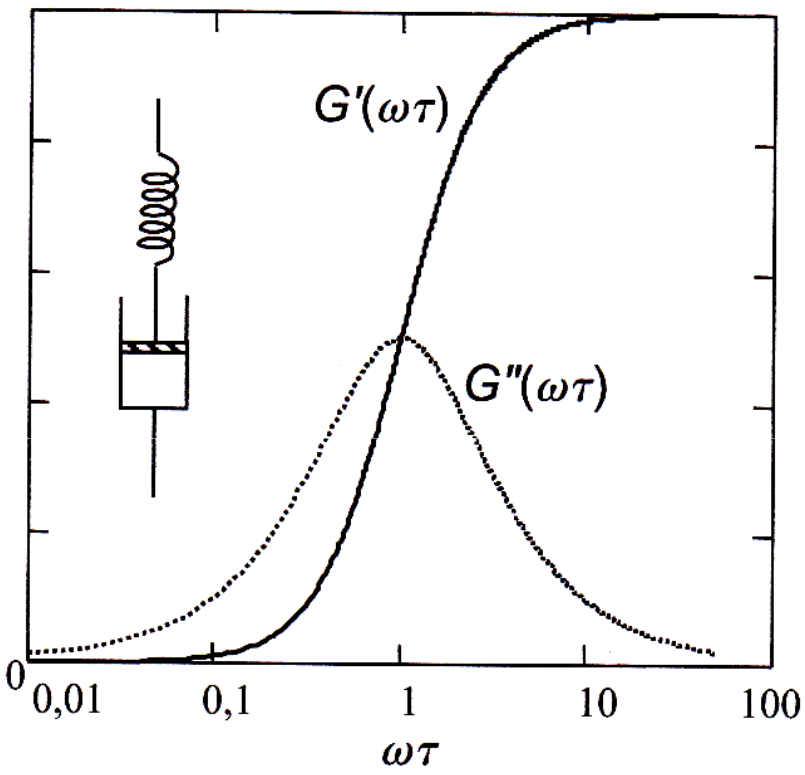
dynamic response

$$\tilde{E}(\omega) = E^*(p = i\omega) = E\frac{iw}{iw + E/\eta}$$

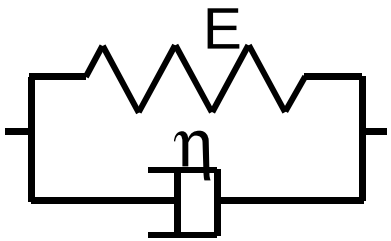
Maxwell model: dynamic response

$$E' + iE'' = E\frac{iw}{iw + E/\eta}$$

$$\frac{E\tau^2\omega^2}{1+\tau^2\omega^2} + i\frac{E\tau\omega}{1+\tau^2\omega^2}$$



Voigt model



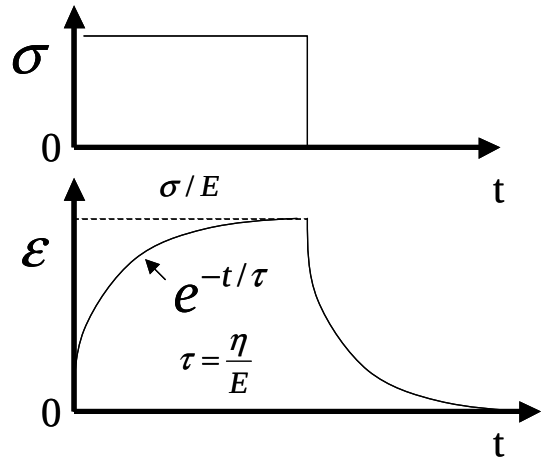
$$\sigma = E\varepsilon + \eta\dot{\varepsilon}$$

$$\sigma^* = E\varepsilon^* + \eta p\varepsilon^* = \left(1/J^*\right)\varepsilon^*$$

$$J^* = \frac{1}{E}\left(\frac{1}{1+p\tau}\right)$$

$$\boxed{J(t) = \frac{1}{E}\left(1-\exp(-t/\tau)\right)} \quad \tau = \eta/E$$

creep response

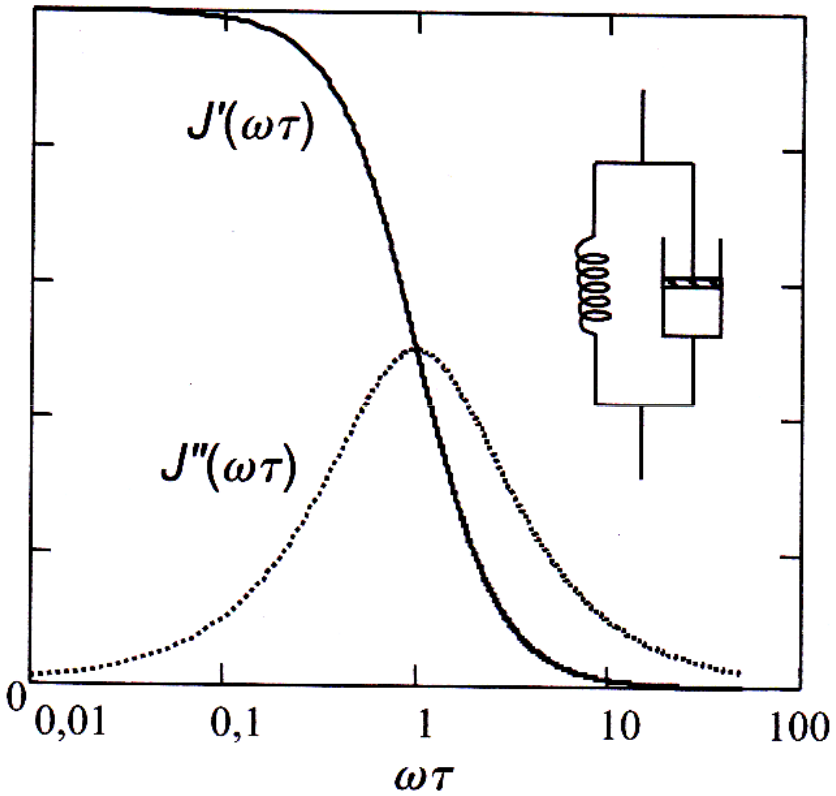


dynamic response $\tilde{J}(w) = J^*(iw)$

$$J(w) = \frac{1}{E}\left(\frac{1}{1+iw\tau}\right)$$

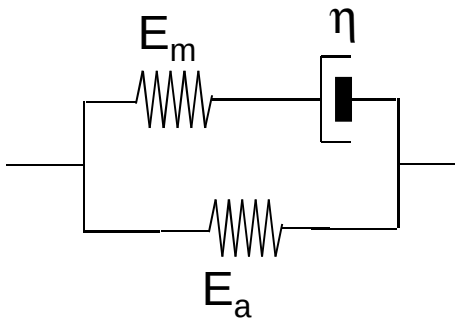
Voigt model: dynamic response

$$J'(\omega) - iJ''(\omega) = \frac{1}{E}\left(\frac{1}{1+i\omega\tau}\right)$$



Standard linear solid (Zener model)

$$a_0\sigma + a_1\frac{d\sigma}{dt} = b_0\varepsilon + b_1\frac{d\varepsilon}{dt}$$



$$\sigma + \tau\frac{d\sigma}{dt} = E_a\varepsilon + (E_m + E_a)\tau\frac{d\varepsilon}{dt}$$

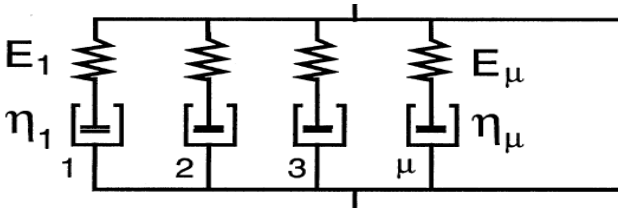
where $\tau = \eta/E_m$

Homework : plot creep and relaxation responses

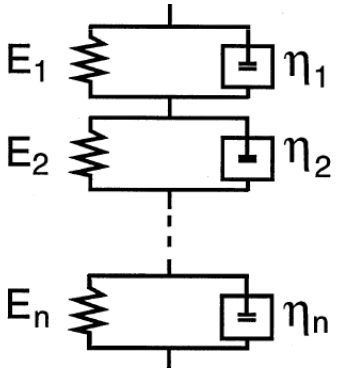
II- Generalised models

The behaviour of a “real” polymer can be approached only if the model incorporates a distribution of relaxation times. For a discrete distribution, each time constant represents a decade from about 0.0001s to perhaps 10000s.

Maxwell

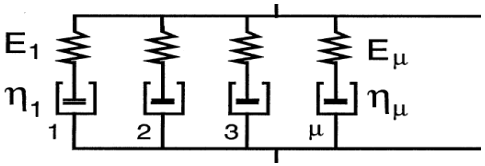


Voigt



Generalised models : Relaxation and retardation time spectra

Maxwell



$$E(t) = \sum_{i=1}^{N} E_i \exp(-t/\tau_i)$$

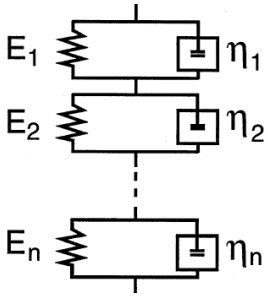
$$E(t) = \int_0^{\infty} P(\tau)\exp(-t/\tau)d\tau$$

$$= \int_{-\infty}^{+\infty} H(\ln(\tau))\exp(-t/\tau)d\ln\tau$$

relaxation time spectrum

H(τ)dLn(τ) gives the contributions to the stress relaxation associated with relaxation times between lnτ and lnτ+d(lnτ)

Voigt

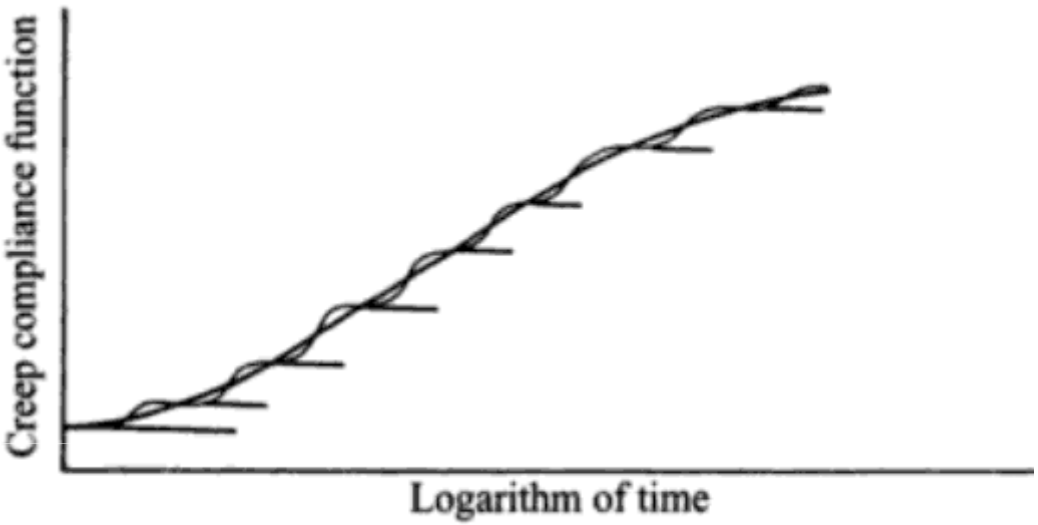


$$J(t) = \sum_{i=1}^{N} J_i(1-\exp(-t/\tau_i))$$

$$J(t) = \int_{-\infty}^{+\infty} L(\ln(\tau))(1-\exp(-t/\tau))d\ln\tau$$

retardation time spectrum

Time spectra



Simulation of creep function through combining Kelvin units in series (schematic)

After [Ward, 1979]

Time spectra are only mathematical descriptions of the macroscopic behavior. They do not have a simple interpretation in molecular terms.

Time spectra : determination

It is often required to combine dynamic mechanical measurements of complex moduli at high frequency (or short times) with stress relaxation modulus measurements at long times (or low frequencies).

We can use approximate methods to determine the relaxation time spectrum

$$E = E_r + \int_{-\infty}^{+\infty} H(\ln(\tau)) \exp(-t/\tau) d\ln\tau$$

Assume that :

« Alfrey approximation »

for $\tau < t$ $\quad \exp(-t/\tau) = 0$

for $\tau > t$ $\quad \exp(-t/\tau) = 1$

Then $$E = E_r + \int_{\ln t}^{+\infty} H(\ln(\tau)) d\ln\tau$$

so $$\boxed{H(\tau) = -\left[\frac{dE(t)}{d\ln\tau}\right]_{t=\tau}}$$

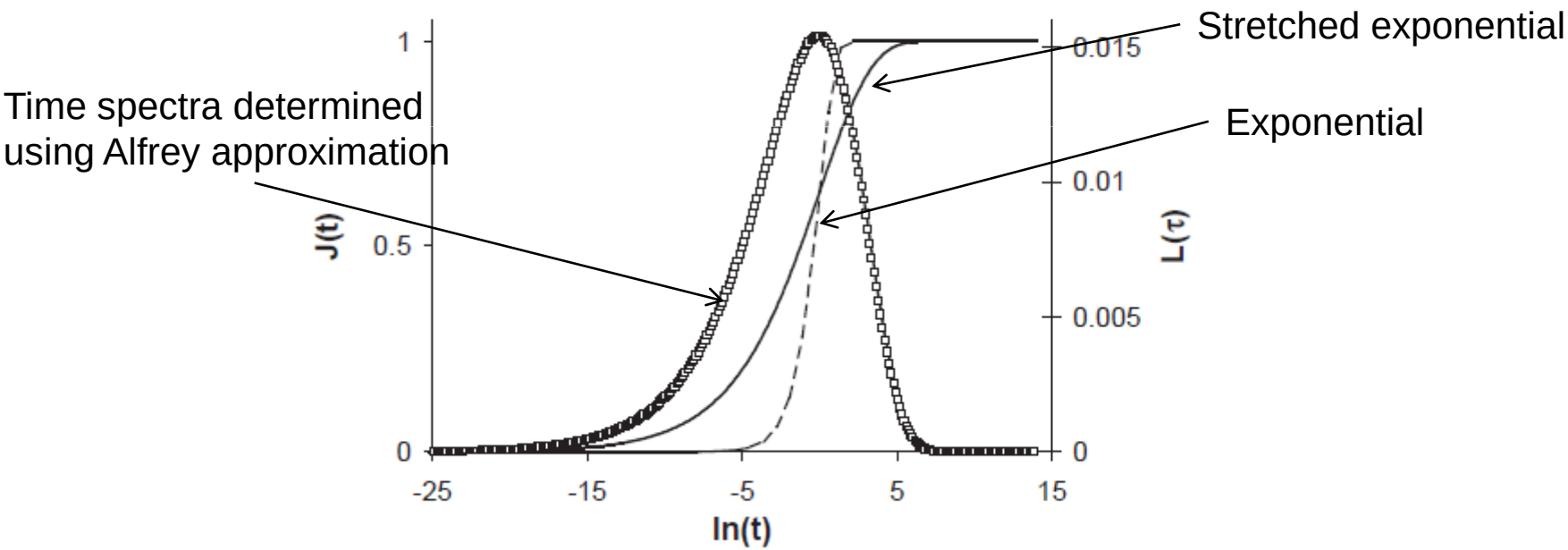
In a similar manner, we have :

$$H(\tau) = -\left[\frac{dE'(\omega)}{d\ln\omega}\right]_{1/\omega=\pi} = \frac{2}{\pi}\left[E''(\omega)\right]_{1/\omega=\pi}$$

Phenomelogical functions

- KWW function (Kohlraush-Williams-Watts), streched exponential

$$J(t) = J_u + (J_r - J_u)\left[1 - \exp\left(-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right)\right]$$ with $0<\beta<1$



Phenomelogical functions

- HN function (Havriliak-Negami)

$$J^*(i\omega) = J_u + \frac{J_r - J_u}{[1 + (i\omega)^\alpha]^\beta}$$

$\alpha \rightarrow$ width

$\beta \rightarrow$ asymetry

- Biparabolic model

$$G^*(i\omega, T) = G_r + \frac{G_u - G_r}{1 + \delta(i\omega\tau)^{-\chi} + (i\omega\tau)^{-\chi'}}$$

Recall : Hereditary constitutive relationships

- Creep integral form :

$$\boxed{\varepsilon(t)=J_u\sigma+\int_{-\infty}^{t} J(t-\tau)\frac{d\sigma(\tau)}{d\tau}d\tau}$$

J(t): creep function

Ju : unrelaxed compliance

$$\varepsilon=J\otimes\frac{D\sigma}{Dt}$$

$\otimes$: convolution product

- Relaxation integral form :

$$\boxed{\sigma(t)=E_r\varepsilon+\int_{-\infty}^{t} E(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau}$$

E(t): relaxation function

Er : relaxed modulus

$$\sigma=E\otimes\frac{D\varepsilon}{Dt}$$

Viscoelastic functions rule entirely the material's response.

Relationship between static and dynamic data

We may obtain the complex modulus E*(iω) from the static modulus E(t) by using the Boltzmann principle:

We have $\sigma(t) = E_r \varepsilon(t) + \int_{-\infty}^{t} E(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau$

If $\varepsilon(t)=\varepsilon_0 \exp(i\omega t)$, then $\sigma(t) = E_r \varepsilon_0 \exp(i\omega t) + \varepsilon_0 i\omega \int_{-\infty}^{t} E(t-\tau) \exp(i\omega\tau) d\tau$

With the change of variables $t-\tau=\eta$, $d\tau = -d\eta$,

we have $\sigma(t) = \left[E_r + i\omega \int_0^{\infty} E(\eta) \exp(-i\omega\eta) d\eta \right] \varepsilon_0 \exp(i\omega t)$

or: $$\sigma(t) = \underbrace{\left[E_r + \omega \int_0^{\infty} E(\eta) \sin(\omega\eta) d\eta + i\omega \int_0^{\infty} E(\eta) \cos(\omega\eta) d\eta \right]}_{E^*(i\omega)} \underbrace{\varepsilon_0 \exp(i\omega t)}_{\varepsilon(t)}$$

And therefore :

$$\boxed{E'(\omega) = E_r + \omega \int_0^{\infty} E(\eta) \sin(\omega\eta) d\eta}$$ and $$\boxed{E''(\omega) = \omega \int_0^{\infty} E(\eta) \cos(\omega\eta) d\eta}$$

Fourier transforms

Emmanuelle CHABERT chabert@lms.polytechnique.fr

Relationship between static and dynamic data …

We can write : $\sigma(t) = E^*(i\omega)\varepsilon_0 \exp(i\omega t)$

$$\sigma(t) = |E^*(i\omega)|\varepsilon_0 \exp(i\omega t + \delta)$$

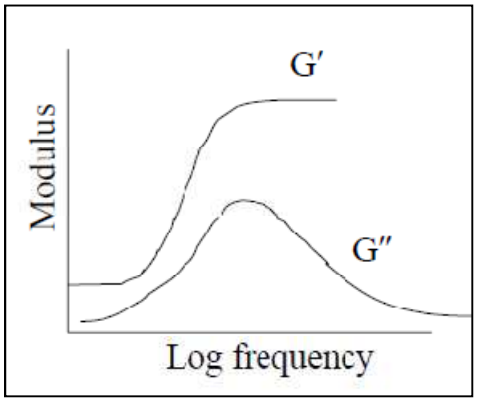
↑ magnitude of E*(iω)

and $\delta = \tan^{-1}\dfrac{E''(\omega)}{E'(\omega)}$

We can invert the Fourier transforms to give :

$$\boxed{E(t) = \frac{2}{\pi}\int_0^\infty \frac{E'(\eta) - Er}{\omega}\sin(\omega t)d\omega}$$

$$\boxed{E(t) = \frac{2}{\pi}\int_0^\infty \frac{E''(\eta)}{\omega}\cos(\omega t)d\omega}$$



The complex modulus as a function of frequency

The real and imaginary parts of the complex modulus are interrelated:

$$E(t) - E_r = \frac{2}{\pi}\int_0^\infty \frac{E''(\lambda)\omega^2}{\lambda(\omega^2 - \lambda^2)}d\lambda$$

For more details, see [Christensen, 1982]

Generalised models : dynamic reponses

Maxwell

$$G'(\omega) = G_r + \int_{-\infty}^{+\infty} H(\ln \tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \, \mathrm{d} \ln \tau$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\ln \tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \, \mathrm{d} \ln \tau$$

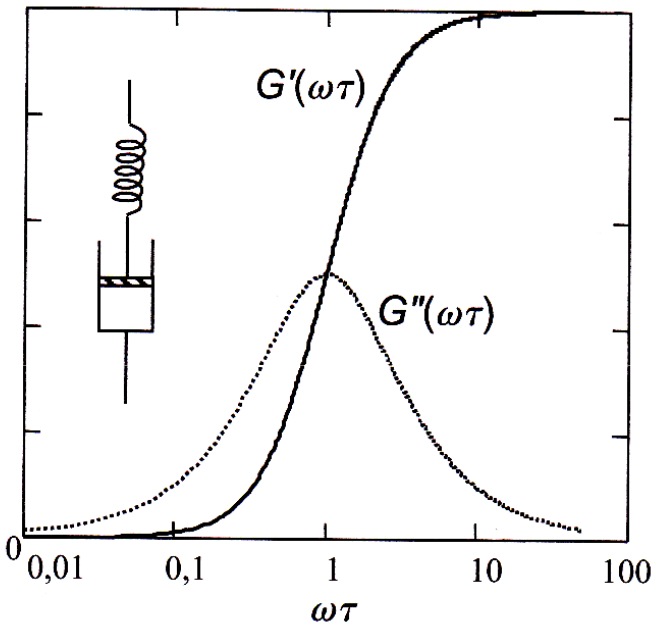
Kelvin Voigt

$$J'(\omega) = J_u + \int_{-\infty}^{+\infty} L(\ln \tau) \frac{1}{1 + \omega^2 \tau^2} \, \mathrm{d} \ln \tau$$

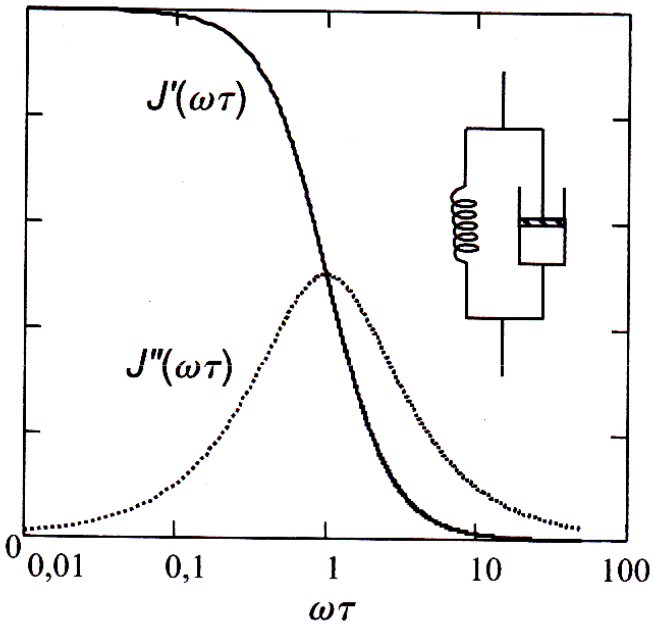
$$J''(\omega) = \frac{1}{\omega \eta} + \int_{-\infty}^{+\infty} L(\ln \tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} \, \mathrm{d} \ln \tau$$

Recall : Molecular motions and peaks

Maxwell



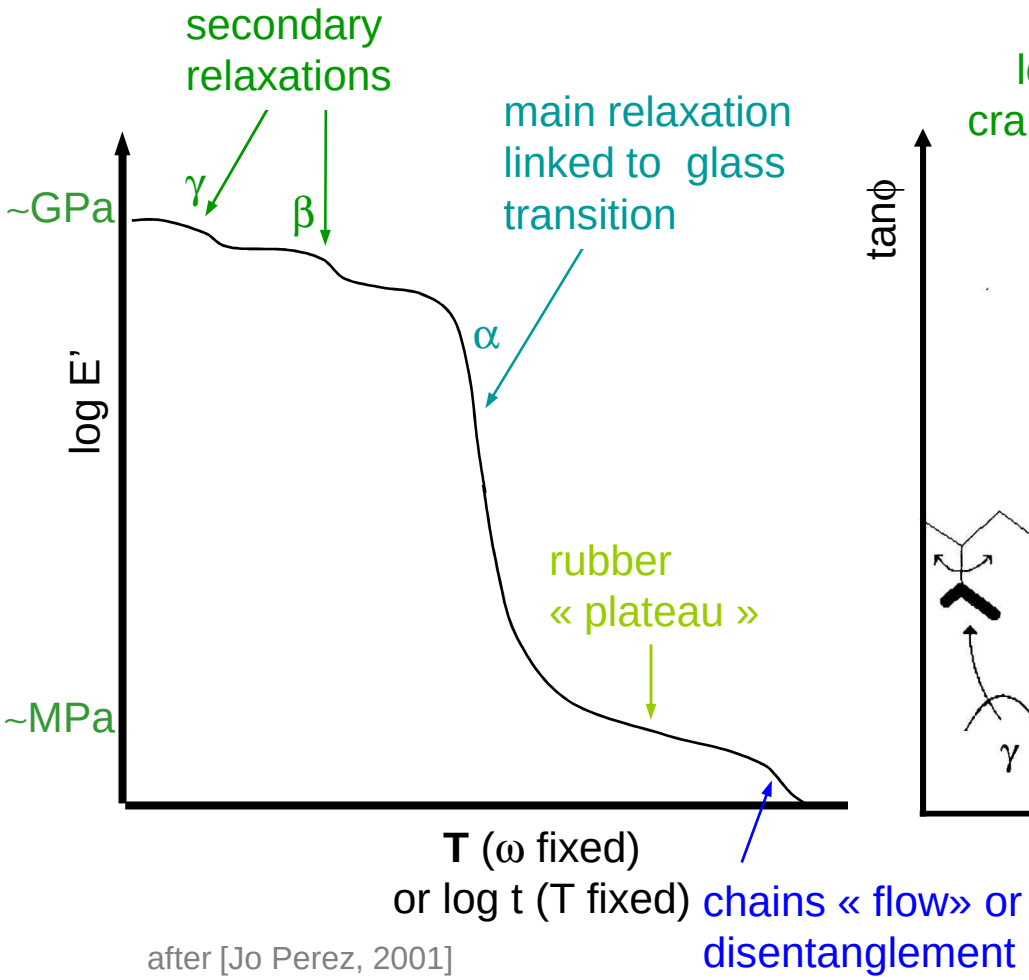
Kelvin-Voigt



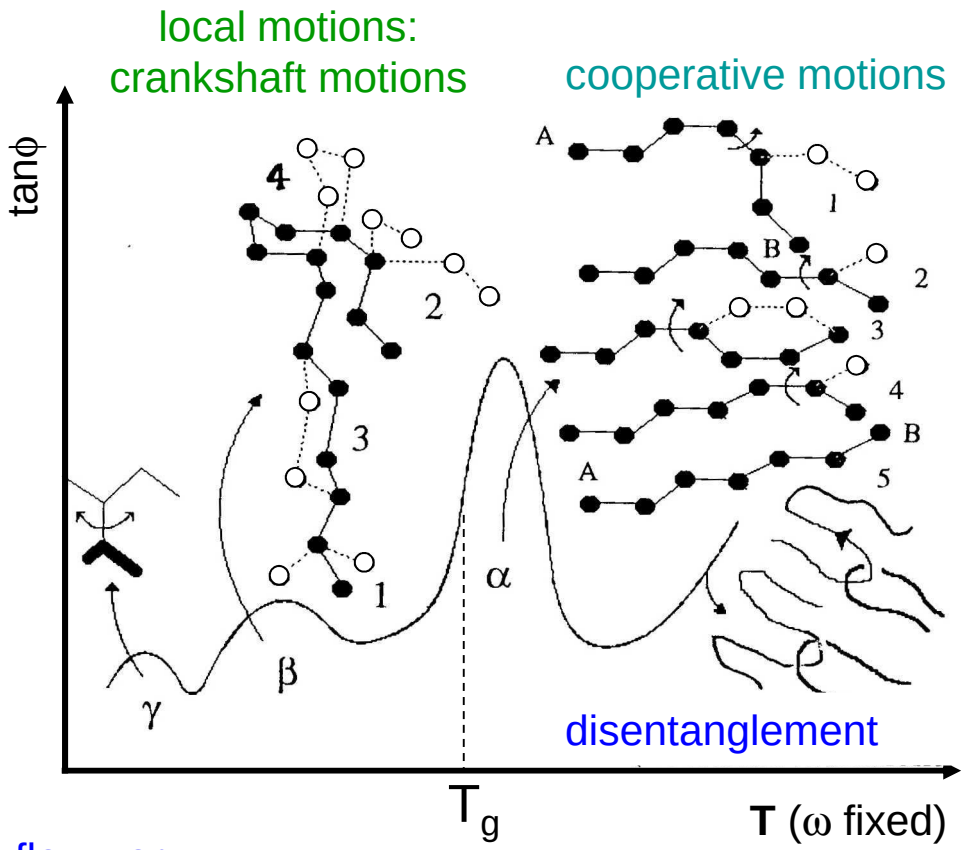
Peaks in G'' occur when the $\omega\tau=1$

The frequency of some molecular motion matches the imposed frequency.

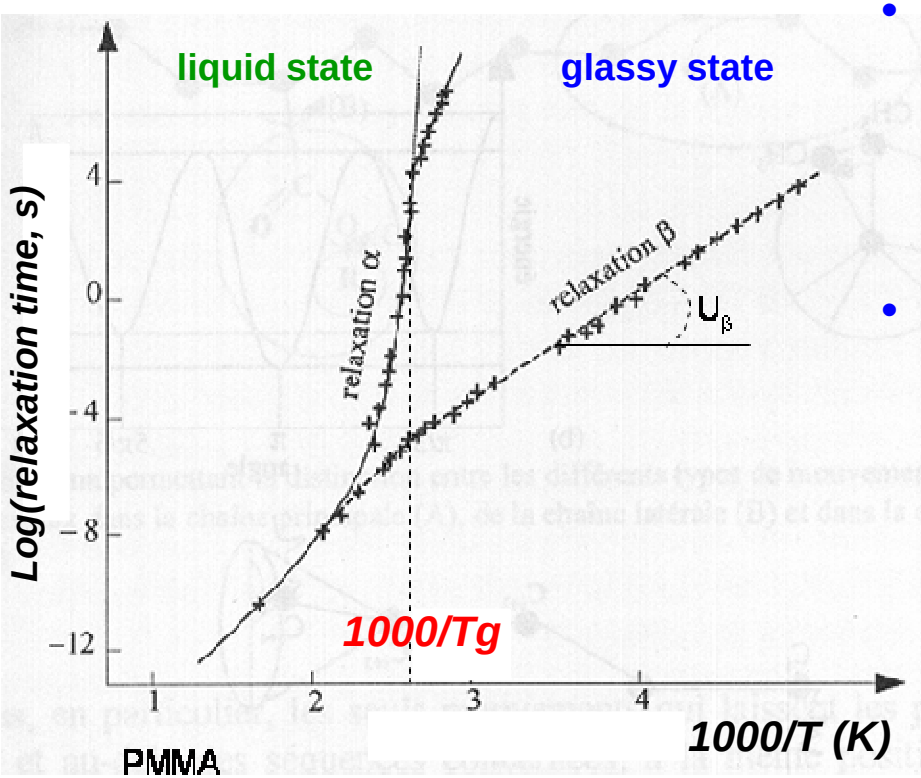
Recall : Typical dynamic mechanical response



after [Jo Perez, 2001]



Characteristic times for molecular mobility



- β relaxation: arrhenien process

$$\tau_\beta = \tau_{\beta 0} \exp \frac{U_\beta}{kT}$$

$U_\beta : 0{,}5 ... 0{,}85 eV$

$\tau_{\beta 0} : 10^{-12} ... 10^{-16} s$

- α relaxation : cooperatives motions

-T<T_g very high apparent activation energy

-T>T_g WLF law

$$\log(a_T) = \log\left(\frac{\tau(T)}{\tau(T_g)}\right) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

where C_1 and C_2 are so called universal constants (17,4 K et 51,6 K)

Linear viscoelasticity #3 : Summary

- Viscoelastic behavior of polymers is time (frequency) and temperature-dependant. Usual tests are: loading tests at various strain rate, relaxation tests, creep tests and DMA.

- Two mathematical descriptions of linear viscoelasticity :
  - *Hereditary integrals*, deriving from *Boltzmann superposition principle*.
  - *Linear differential representation*

    This leads to combinations of elastic springs and viscous dashpots.

-Rheological models may be generalised using time spectra. Determination of time spectra can be done using approximations.

- Relationships and between creep and relaxations functions, and between static and dynamic data has been established.

- Classical laws of linear elasticity can be recovered by replacing quantities by their Laplace Carson transform couterparts.

Thank you for your attention

Lecture# 9 will be given on June 19th