INTERNATIONAL
CENTRE for
THEORETICAL
SCIENCES

# School on glasses and glass formers

JNCASR, January 4-20 2010

# Experimental Techniques -I

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Today's Lecture Plan
1) Rheology
2) Dielectric spectroscopy

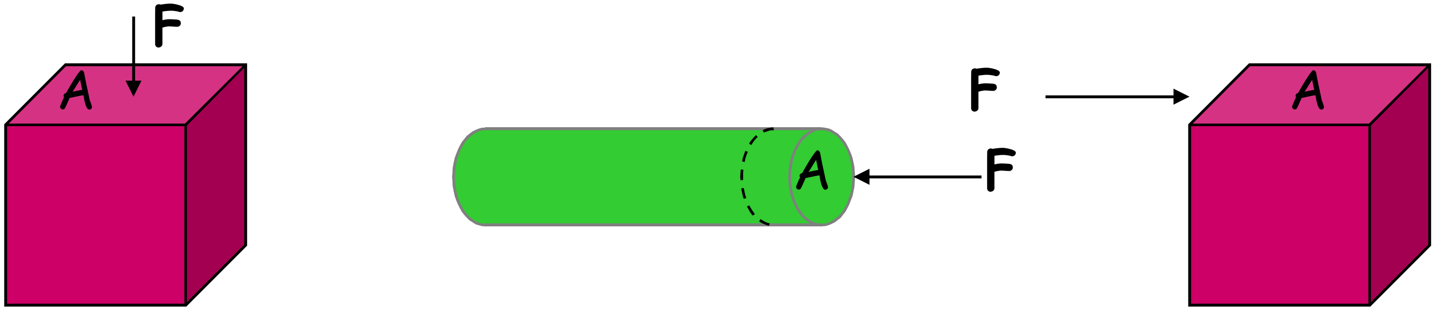
Later
DSC, Scattering techniques,
Imaging, NMR

# Rheology : a brief history

- Rheology, the study of the flow and deformation of matter, started with the invention of synthetic polymers, which were known to exhibit very "odd" flow behaviors.
- Root: Greek verb ρηεο, meaning "to flow" (the term rheology was coined by Bingham to describe his study of the flow properties of paint)
- Historically, rheologists studied mechanical behaviour using very simple deformations (linear rheology) and mechanisists studied the effects of very complex deformations in materials (nonlinear rheology)

# Stress

- Hookes Law : $\tau \sim G\,\gamma$
- Newton's Law of Viscosity: $\tau \sim \eta\dot{\gamma}$



$\tau \sim F/A$
Elastic for small stresses

Normal stress:
acts normal to the surface
Eg. Compression or tension

Shear stress: acts tangentially to the surface: elastic for small stresses

## Stress tensor

$$\mathbf{T} = \begin{bmatrix} \sigma_1 & \tau_{12} & \tau_{13} \\ \tau_{21} & \sigma_2 & \tau_{23} \\ \tau_{31} & \tau_{32} & \sigma_3 \end{bmatrix}$$

Diagonal: normal
Off-diagonal: shear

# In-between materials

- Silly Putty, foams, mayonnaise etc.

+ Weissenberg effect ('the ductless siphon': nonzero Normal stress differences)
+ Shear thinning and thickening
+ time-dependent modulus
+extensional thickening

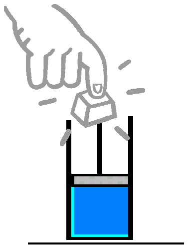
# Newtonian behavior

- The only stresses generated in simple shear flow are the shear stresses, the two normal stress differences being zero.
- The shear viscosity $\eta$ does not vary with shear rate.
- The viscosity is constant w.r.t time of shearing and the stress in the liquid falls to zero immediately after the shear is stopped.
- No rod-climbing, no shear thinning or thickening

# Viscoelasticity: a recap

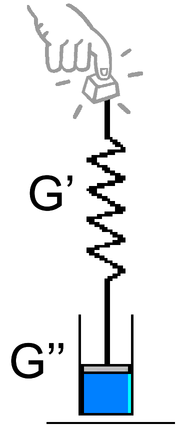
Ideal viscous ← Viscoelastic fluid or solid → Ideal elastic

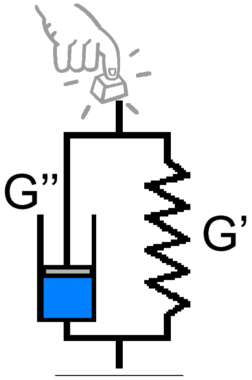
Newton's law



$\sigma = \eta d\gamma/dt$

shear viscosity $\eta$ [Pas]

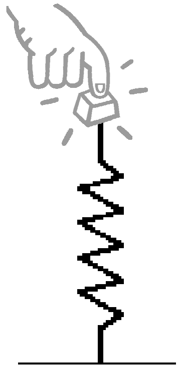




Apparent Yield Point, Thixotropy, …

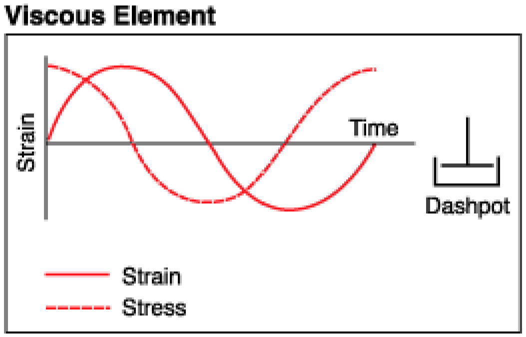
Coatings, Food, Cosmetics, Pharmaceuticals, Polymers

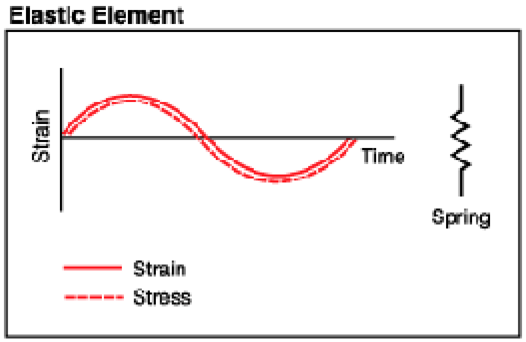
Hooke's law



$\sigma = E\gamma$

shear modulus G [Pa]





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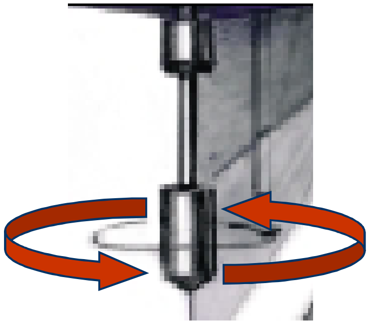
# Rheology measures the deformation behavior of solids and the flow behavior of liquids



Oscillatory linear rheology

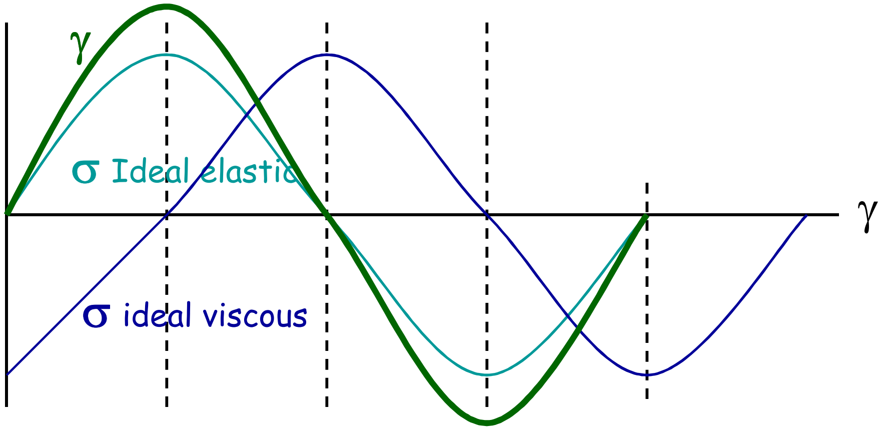
Presetting of

- strain (deflection) with the amplitude $\gamma_o$,
- and the angular frequency $\omega$ in [rad/sec]

→ Two independent measuring quantities: stress $\sigma$ and phase shift $\delta$

$\delta = 0°$ → pure elastic behaviour
$\delta = 90°$ → Pure viscous behaviour

$G^* = \sigma(t)/\gamma(t) = G' + iG''$
$G' = G^* \cos\delta$
$G'' = G^* \sin\delta$
$G'$ : elastic modulus
$G''$ : viscous modulus



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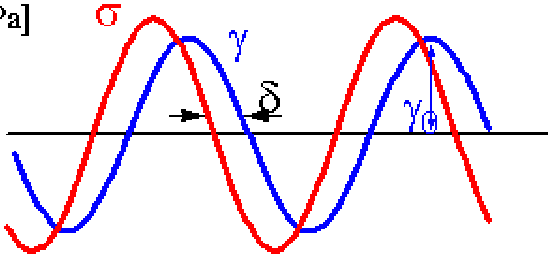
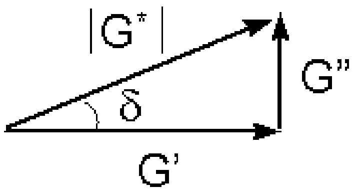
# Viscoelasticity:

G* = complex shear modulus [Pa]
G' = storage modulus [Pa]
G" = loss modulus [Pa]
$\delta$ = phase angle [rad]
$\sigma$ = stress [Pa]
$\gamma$ = strain [-]



$$\gamma = \gamma_0 \sin \omega t$$
$$\omega = 2\pi f$$

$$G^* = \frac{\sigma}{\gamma_0}\cos\delta + j\frac{\sigma}{\gamma_0}\sin\delta$$
$$j^2 = -1$$



$$G^* = G' + jG''$$
$$\tan\delta = \frac{G''}{G'}$$

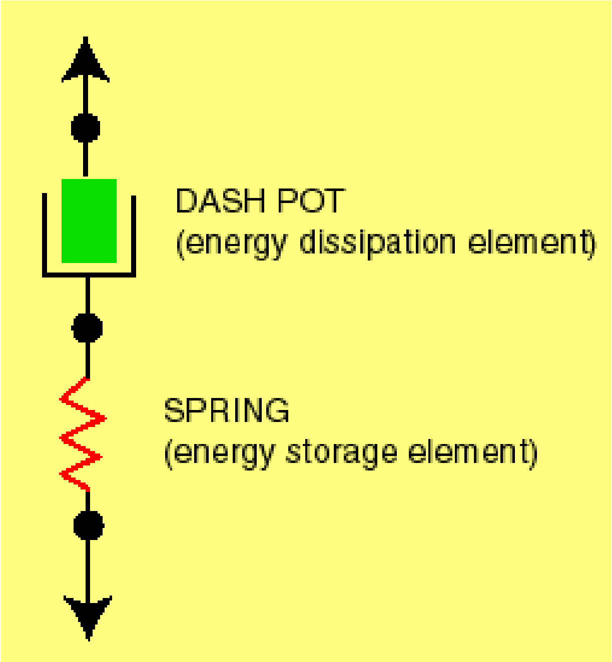
As a result:

- Time dependent G(t)
- Shear thinning/thickening
- Normal stresses in shear
- Extensional thickening viscosity

## Linear viscoelasticity

$d\sigma = G\, d\gamma \Rightarrow$ $\boxed{\sigma = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt'}$

For $G(t) = G_0 e^{-t/\tau}$, $\boxed{\sigma + \tau d\sigma / dt = \eta\dot{\gamma}}$



DASH POT
(energy dissipation element)

SPRING
(energy storage element)

Maxwell
(1867)

# Linear viscoelasticity

The superposition principle holds: response is directly proportional to applied force

General differential equation for linear viscoelasticity:

$(1 + \alpha_1\partial/\partial t + \alpha_2\partial^2/\partial t^2 + \ldots + \alpha_n\partial^n/\partial t^n)\sigma = (\beta_o + \beta_1\partial/\partial t + \beta_2\partial^2/\partial t^2 + \ldots + \beta_n\partial^m/\partial t^m)\gamma$
where n=m or n=m-1_

Properties of linear viscoelasticity equation:

1) Linear differential equation
2) Coefficients of time differentials are time-independent and are material parameters such as rigidity modulus and viscosity.

LVE: Special cases

1) SC-I: $\beta o \neq 0$, everything else = 0, $\sigma = \beta_o \gamma$ (Hookean spring with rigidity modulus $\beta_o$)
2) SC-II:_$\beta_1 \neq 0$, everything else = 0, $\sigma = \beta_1 \partial\gamma/\partial t$ (Newtonian viscous flow with coefficient of viscosity $\beta_1$)

# Linear Viscoelasticity Equation (cont'd)

$(1 + \alpha_1\partial/\partial t + \alpha^2\partial^2/\partial t^2 + \ldots + \alpha_n\partial^n/\partial t^n)\sigma = (\beta_o + \beta_1\partial/\partial t + \beta_2\partial^2/\partial t^2 + \ldots + \beta_n\partial^m/\partial t^m)\gamma$
where n=m or n=m-1_

LVE: Special cases

1) $\beta o \neq 0$, everything else = 0, $\sigma = \beta_o\,\gamma$ (Hookean spring with rigidity modulus $\beta_o$)

2) $\beta_1 \neq 0$, everything else = 0, $\sigma = \beta_1\,\partial\gamma/\partial t$ (Newtonian viscous flow with coefficient of viscosity $\beta_1$)

3) $\beta_o \neq 0$, $\beta_1 \neq 0$, everything else = 0, $\sigma = G\,\gamma + \eta\,\partial\gamma/\partial t$ (Kelvin-Vöigt model)

$\Rightarrow \gamma = [\sigma(t=0)/G][1-\exp(-t/\tau_K)]$ (Hookean at $t \rightarrow \infty$)

4) $\alpha_1 \neq 0$, $\beta_1 \neq 0$, everything else = 0, $\sigma + \tau_M\,\partial\sigma/\partial t = \eta\,\partial\gamma/\partial t$ (Maxwell model)

$\Rightarrow\ \sigma = [\eta\,\partial\gamma/\partial t(t=0)][1-\exp(-t/\tau_M)]$ for t>0 (Ideal viscous fluid at $t \rightarrow \infty$)

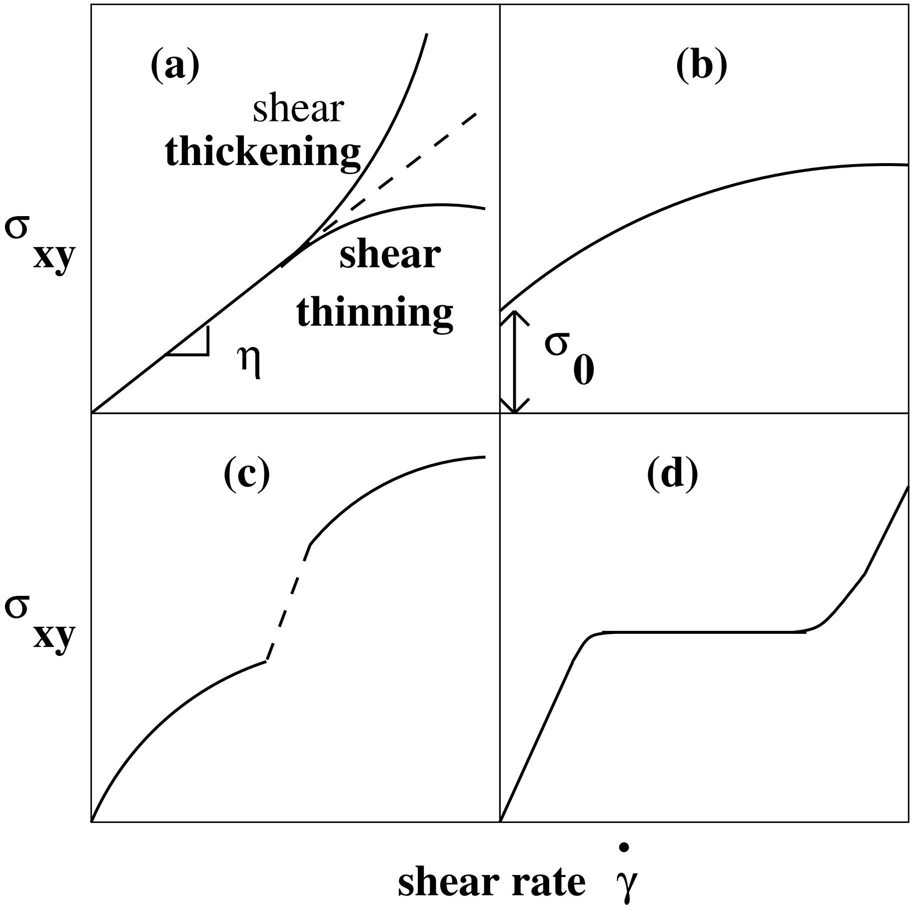
5) And so on….. (Jeffreys model has $\alpha_1$, $\beta_1$ and $\beta_2$ non-zero)

Relaxation spectrum

*A combination of springs and dashpots can give a spectrum of relaxation times*

# Non-Newtonian behavior: nonlinear viscoelasticity

$$\sigma(t) = \gamma_o G_{nl}(t, \gamma_o)$$

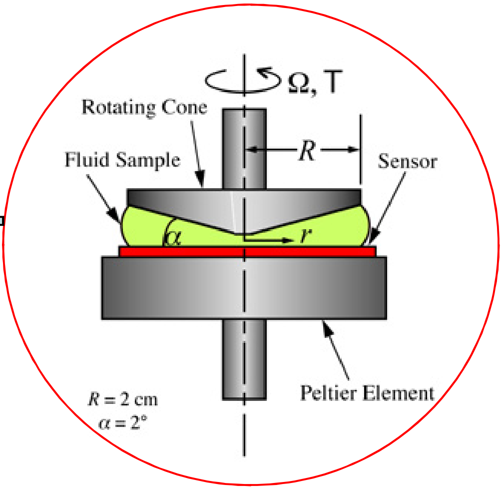


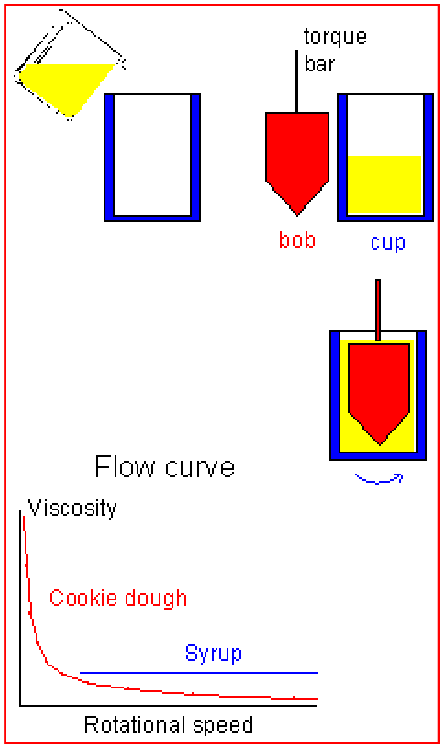
a) shear-thinning/thickening (Cross model, Carreau model, thixotropy)
b) Herschel-Bulkley plastic with $\sigma = \sigma_o + K\dot{\gamma}^p$
c) Flow curve for system undergoing flow-induced phase transition
d) Shear banding instability

# Rheometry: measuring how materials flow & deform

MCR 501 from Anton Paar

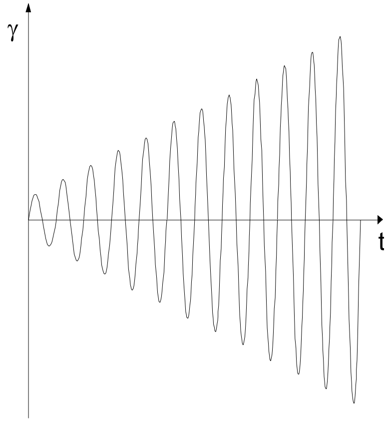
- Measuring drive : Electronic commutated motor drive with air bearing: stresses: 0.01μNm-230mNm
- Air bearing : friction-free motion
- Min resolution of optical encoder : 1μrad
- Stresses and strain rates varying over 10 orders of magnitude can be measured.
- Temperature control: -30°C - 200°C

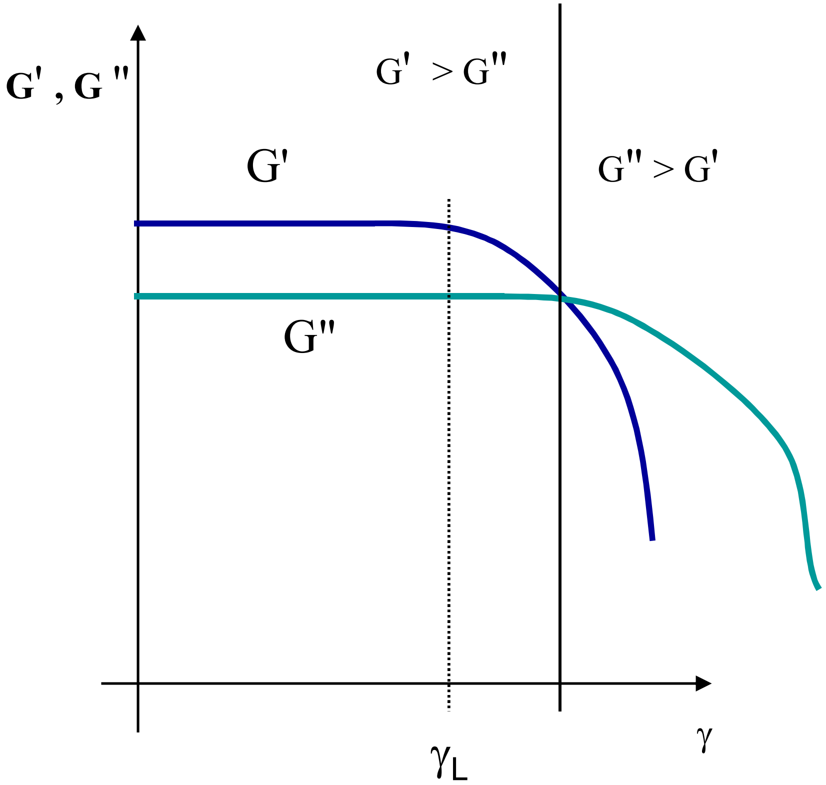




# Measuring Properties: Amplitude Sweep Test

An amplitude sweep is an oscillatory test with variable amplitude and constant frequency values





$\gamma_L$: linear viscoelasticity range

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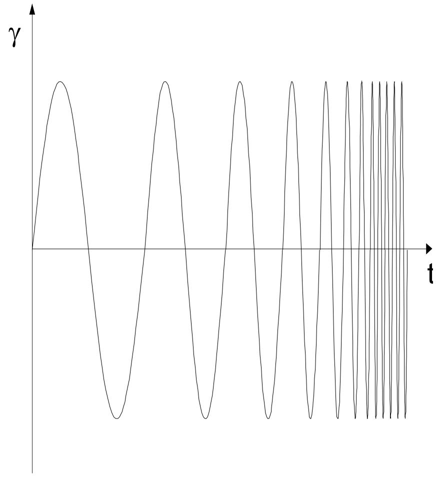
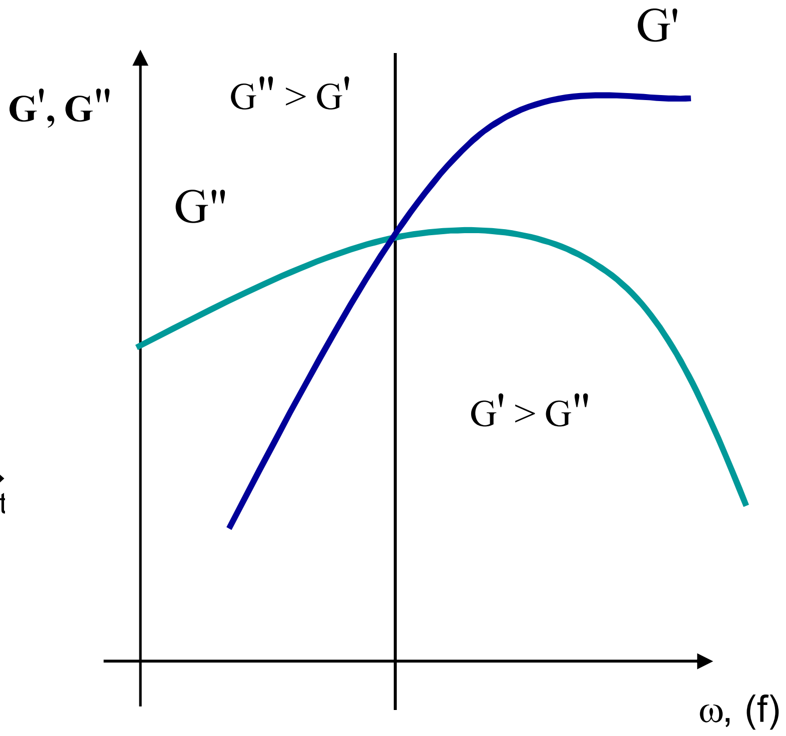
# Measuring Properties: Frequency Sweep Test

A frequency sweep is an oscillatory test with variable frequency and constant amplitude values





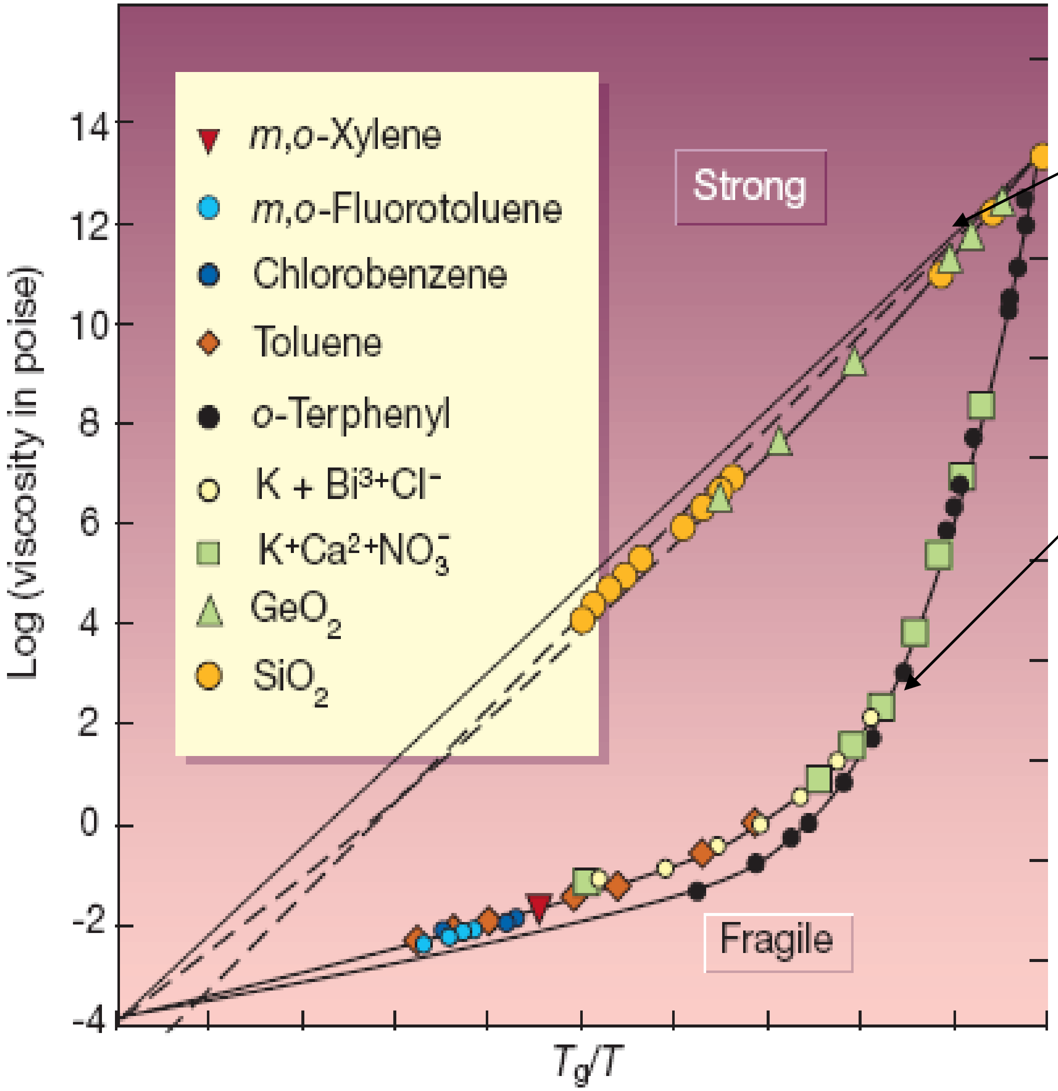
# Rheology: why do we care?

- Very important in the industry : food, polymers, paint, glue, cosmetics etc....
- Soft materials serve as model systems for understanding flow-structure correlations in condensed matter systems.

## Why are soft materials good candidates for rheological measurements?

- Individual constituents are macromolecules $\Rightarrow$ slow dynamics and very nonlinear rheology
- $n_p \sim 10^{13}$ /cm$^3$ (much smaller than in molecular solids), $G \sim n_p \Rightarrow$ soft and therefore viscoelastic.
- $\tau_R \sim$ ms $\Rightarrow$ long lived metastable states.

# Rheology of glassy liquids



Arrhenius: $\eta = \eta_o \exp(-E/RT)$:
Strong

Vogel Tammann Fulcher:
$\eta = \eta_o \exp[-DT_o/(T-T_o)]$:
fragile

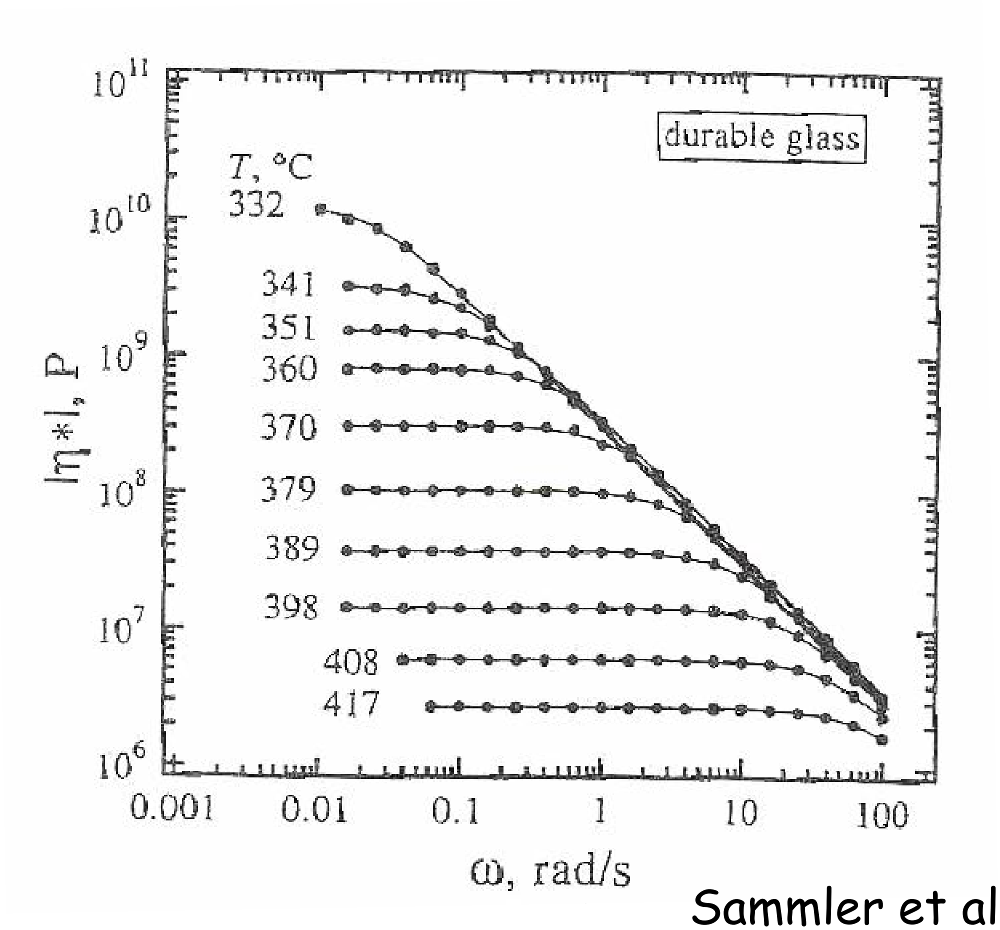
Angell, J Non-Cryst Solids (1988)

# Linear rheology

- Maxwell behavior (inorganic glassy liquids like zinc alkali phosphate)

$$\eta^* = (G'^2+G''^2)^{1/2}/\omega = G_o\tau/(1+i\omega\tau)$$

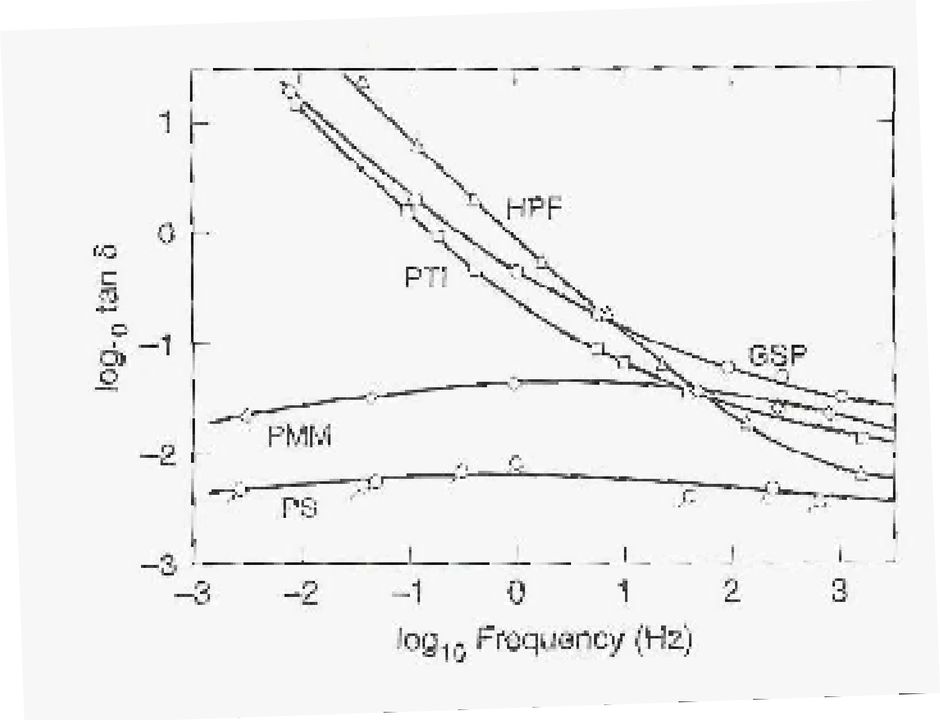
$G_o = \nu k_B T = \rho RT/M$, where $\nu$ is the number density of the relaxing units. Fits are obtained by varying M and $\tau$.



Sammler et al. J. Rheol, 1996

# Linear rheology -II

- Bulky non-polymeric molecules Maxwellian behavior at low frequencies
- And additional relaxation modes (due to internal flexing of individual molecules) at high frequencies.



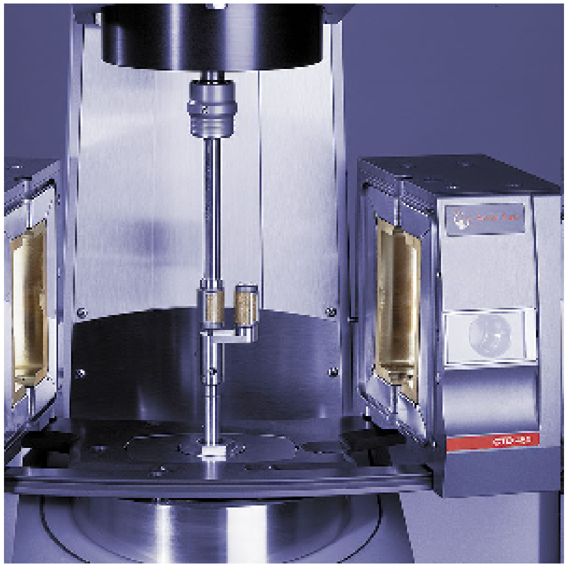
Tan δ measurements of small molecule organic liquids:

Maxwell model: tan δ ~ 1/ω.
HPF, GSP, PTI show this at low frequency but flatten at high frequencies.

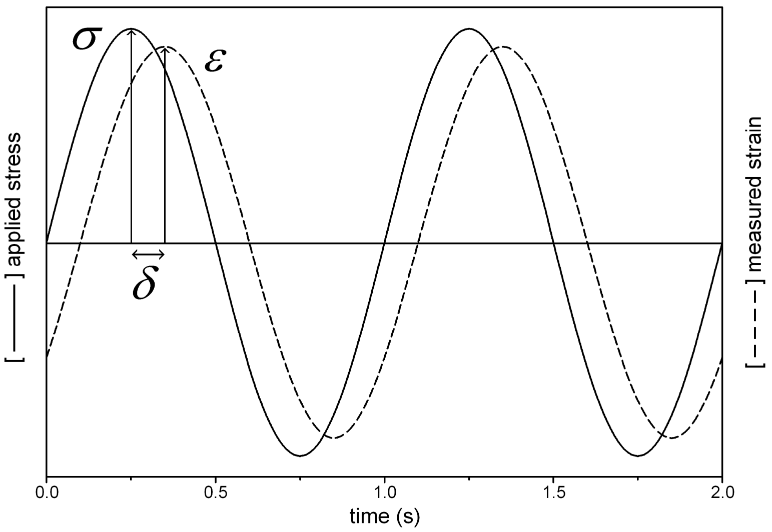
Benbow and Wood,
Trans Faraday Soc (1958)

# Dynamical Mechanical Analysis - I

- Measurement of solids, films and fibres in torsion and extension (not just shear)
- Determination of the glass transition temperature, melting point and other transition temperatures
- Relaxation measurements
- Investigation of material properties as a function of temperature with higher sensitivity than DSC
- Multiwave analysis to measure the frequency dependence of transition processes

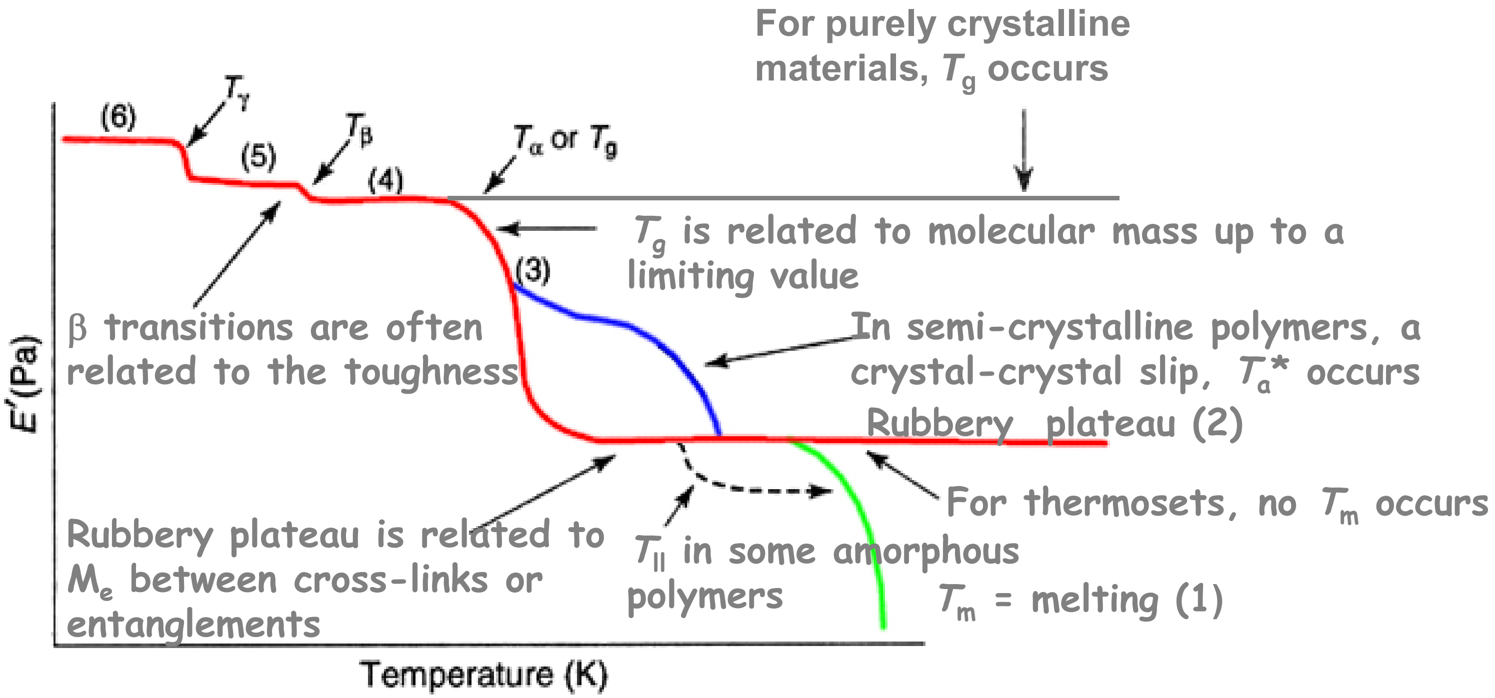


Paar Physica DMTA



# Dynamical Mechanical Analysis - II

- Moduli values change with temperature and transitions in materials can be seen as changes in the E′ or tan delta curves.
- This includes not only the glass transition and the melt, but also other transitions that occur in the glassy or rubbery plateau.
- These transitions indicate subtler changes in the material.



For purely crystalline materials, $T_g$ occurs

$T_g$ is related to molecular mass up to a limiting value

β transitions are often related to the toughness

In semi-crystalline polymers, a crystal-crystal slip, $T_a$* occurs

Rubbery plateau (2)

For thermosets, no $T_m$ occurs

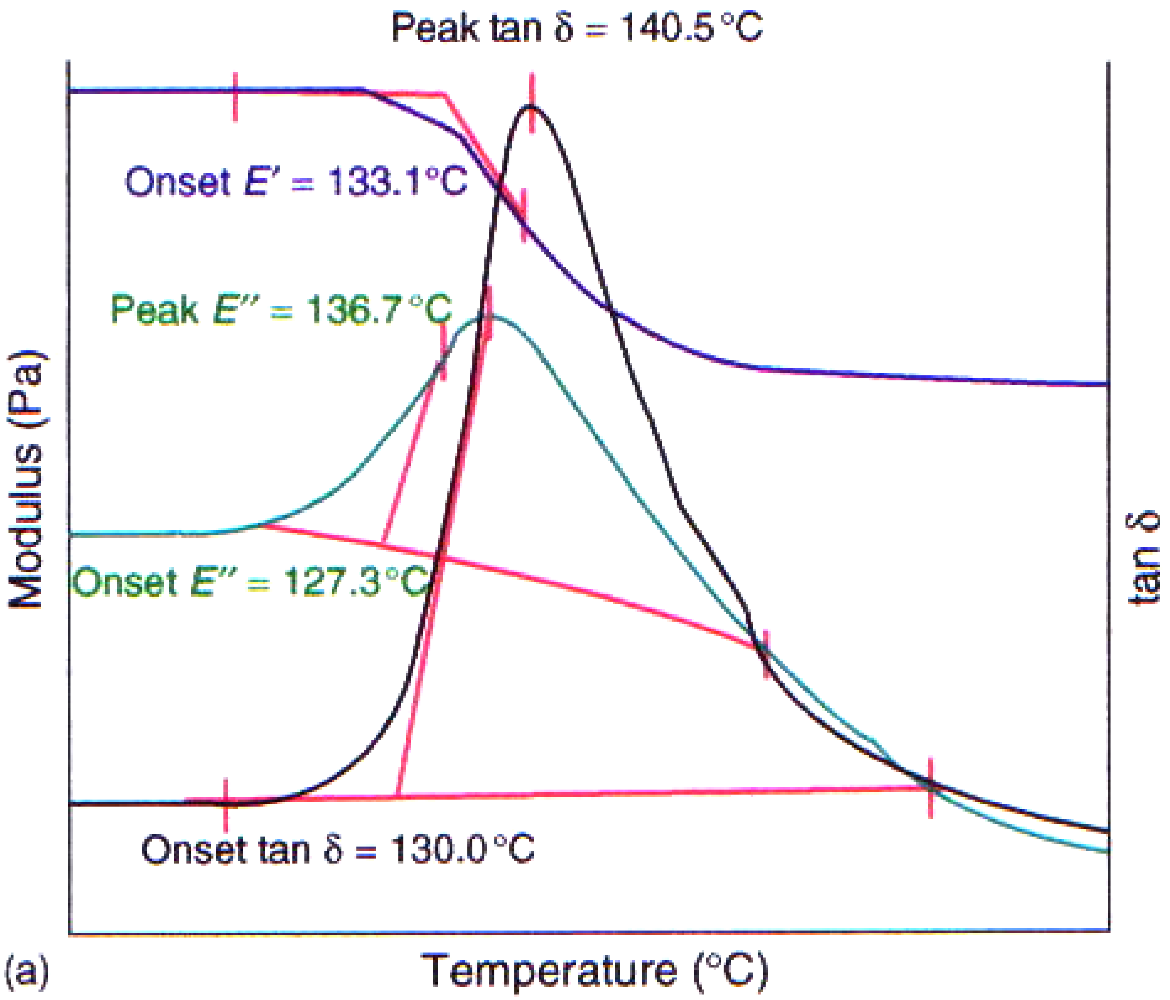
Rubbery plateau is related to $M_e$ between cross-links or entanglements

$T_{ll}$ in some amorphous polymers

$T_m$ = melting (1)

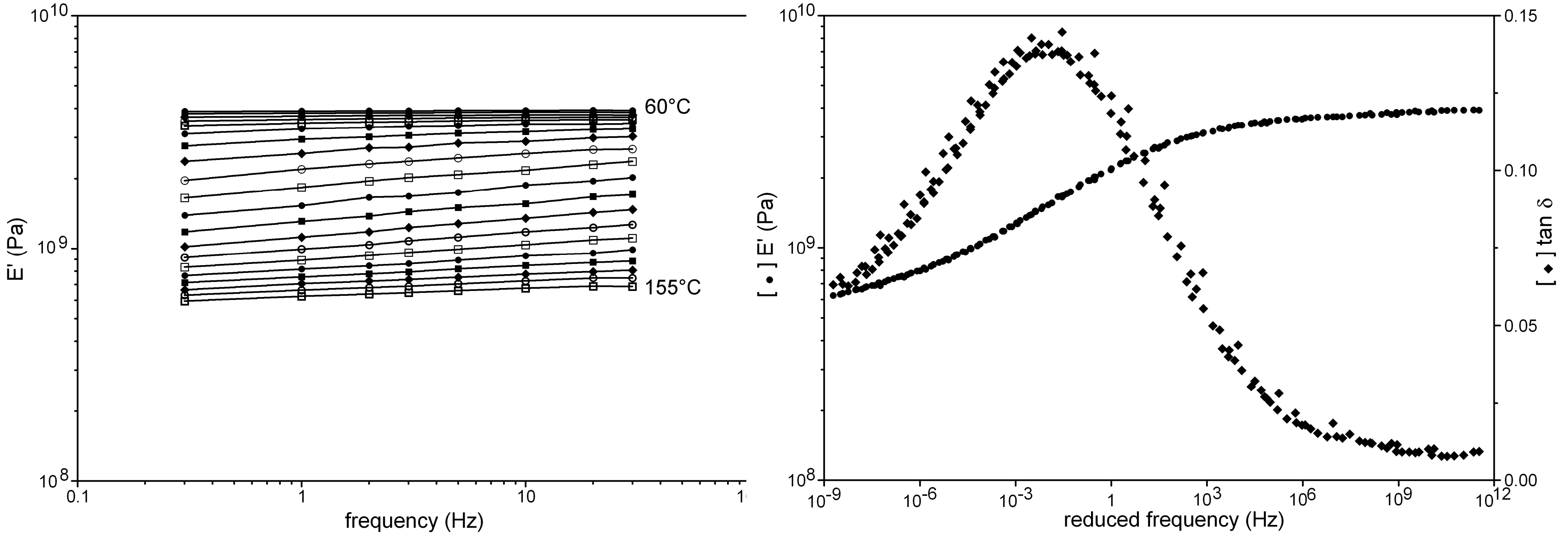
(6) : local motions, (5): bend and stretch, (4): side groups, (3): main chain, (2): large scale chain, (1) chain slippage

# Dynamical Mechanical Analysis - III



# Dynamical Mechanical Analysis - IV

## Time Temperature Superposition

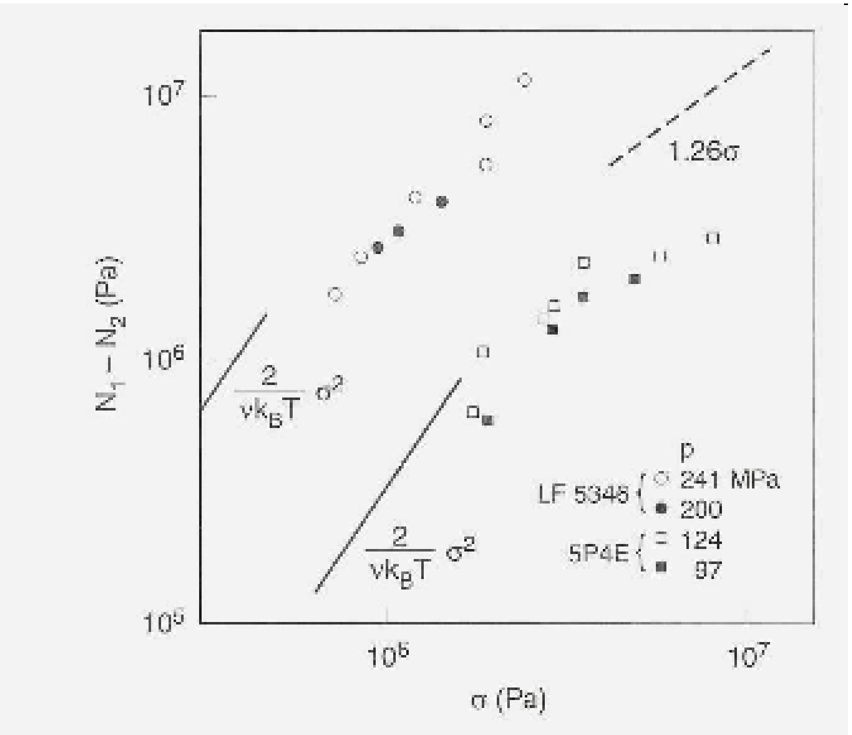


# Non -Linear rheology

- At low shear stress, steady shear viscosity is $\eta(\omega \to 0)$
- At high shear stresses, glasses yield and fracture

} Ambient pressure

- Under high pressures (~ 300 MPa) shear thinning is observed in small-molecule glassy liquids with viscosities between $10^2$ and $10^5$ Pa-s.

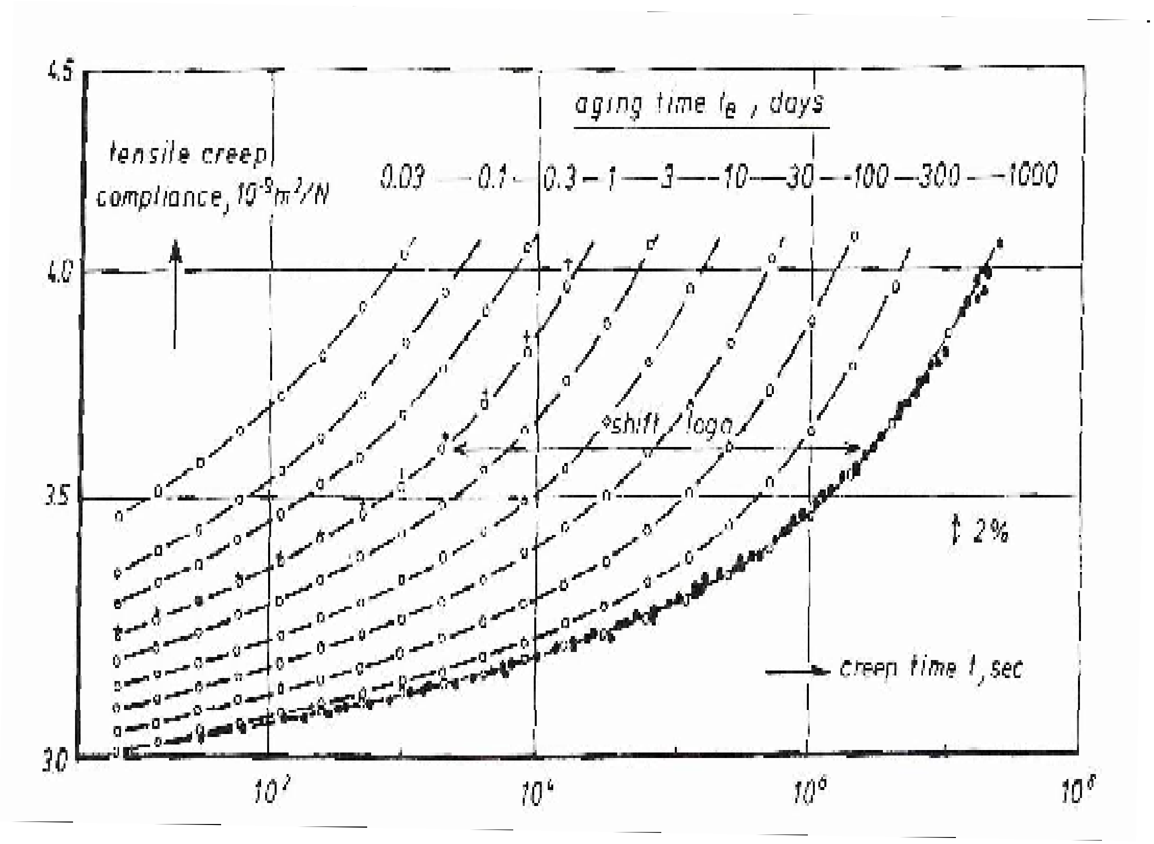


Non-zero normal stress difference for Versus shear stress for polyphenyl ether (5P4E)+ polybutene (LF5346) at high pressure. In 5P4E, shear banding occurs above σ = 20MPa.

Blair, Rheol Acta, 1996

# Creep rheology (Glassy PVC)

1) Eqm PVC is quenched rapidly to a temperature well below $T_g$
2) Aging
3) Relaxation time $\tau$ increases enormously



Struik, Ann NY Acad of Science, (1976)

# Soft glassy rheology

Ref: Sollich et al. PRL (1997)

- For systems showing metastability and disorder
- Some examples: foams, emulsions, slurries etc.

Model describes the deformation and yielding of coupled mesoscopic domains in systems where thermal activation is not enough to achieve complete structural relaxation.

$G'' \sim \omega$ for $2 < x$, $\quad \sim \omega^{x-1}$ for $1 < x < 2$

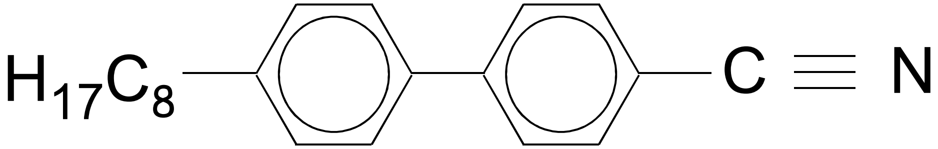
$G' \sim \omega^2$ for $3 < x$, $\quad \sim \omega^{x-1}$ for $1 < x < 3$

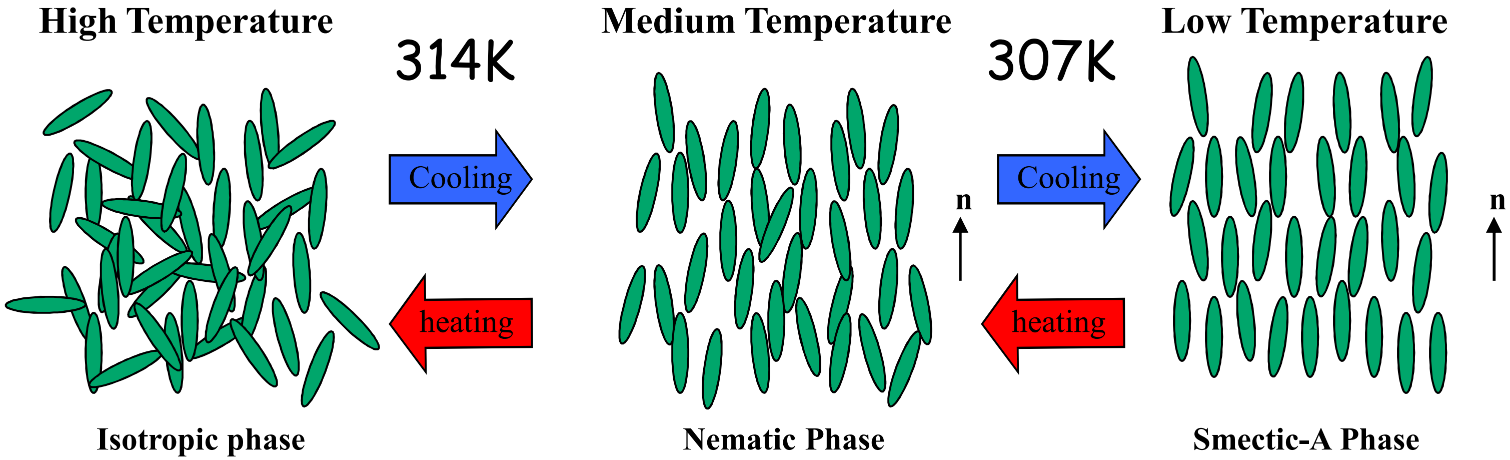
$x$ : mean field/ effective/ “noise” temperature

$x = 1$ is the glass transition temperature

# Experiment 1: Liquid crystal rheology: Octylcyanobiphenyl

**8CB:**




**High Temperature**

314K

Cooling

heating

**Medium Temperature**

307K

Cooling

heating

**Low Temperature**

n

n

**Isotropic phase**

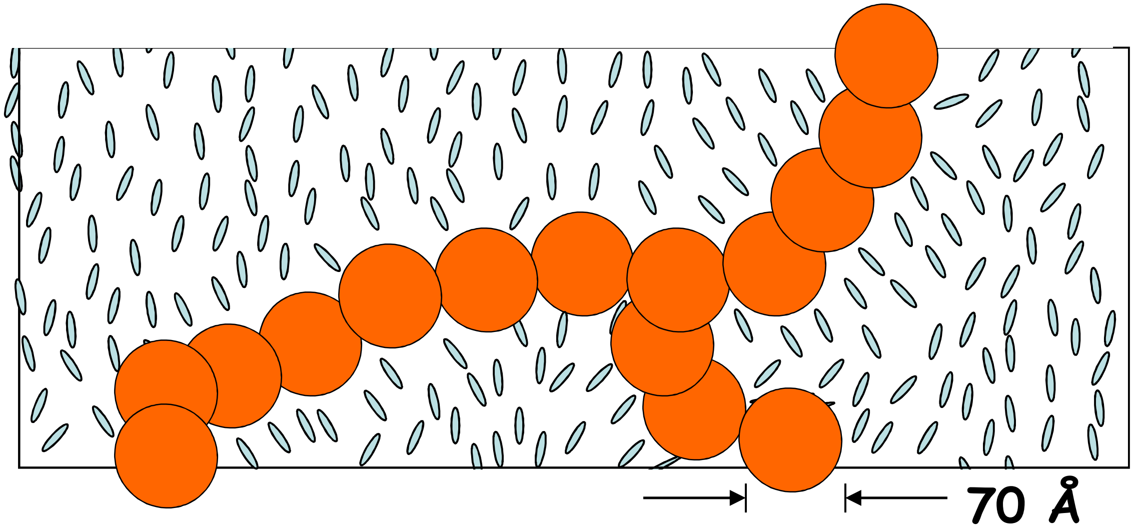
**Nematic Phase**

**Smectic-A Phase**

Rheology of liquid crystals (Larsen, 1993, Colby 1997)

Viscoelastic, weak solids

# The 8CB-aerosil system



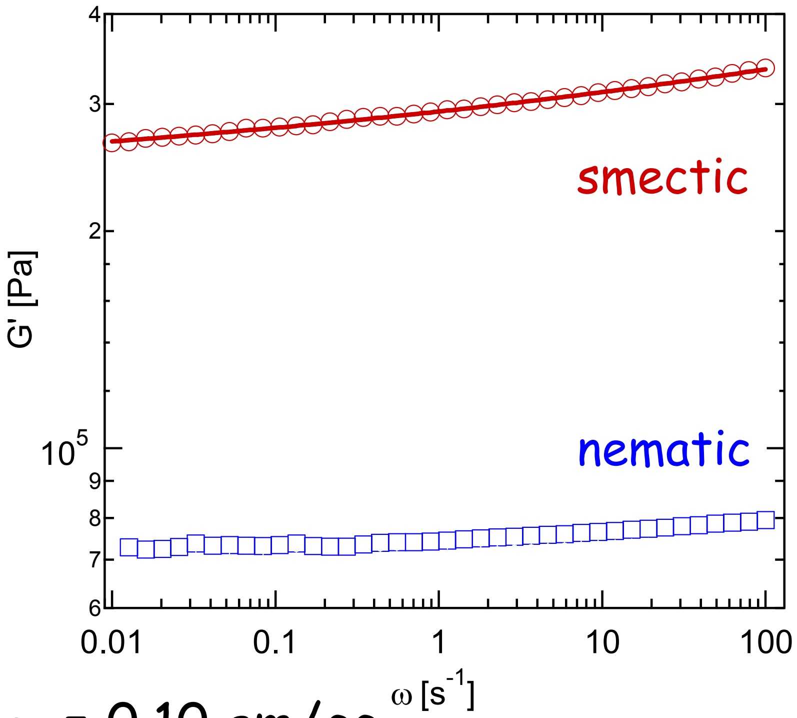
Aerosil gel within 8CB: Aggregation of hydrophilic $SiO_2$ spheres (weakly bonded compliant gel)

- Random field effects
- smectic transition destroyed, only short- range smectic correlations survive

# Effect of quenched disorder on the elasticity of a smectic liquid crystal

Bandyopadhyay et al., PRL (2005)

Frequency dependent elastic modulus measurements



$\rho_s$ = 0.10 gm/cc

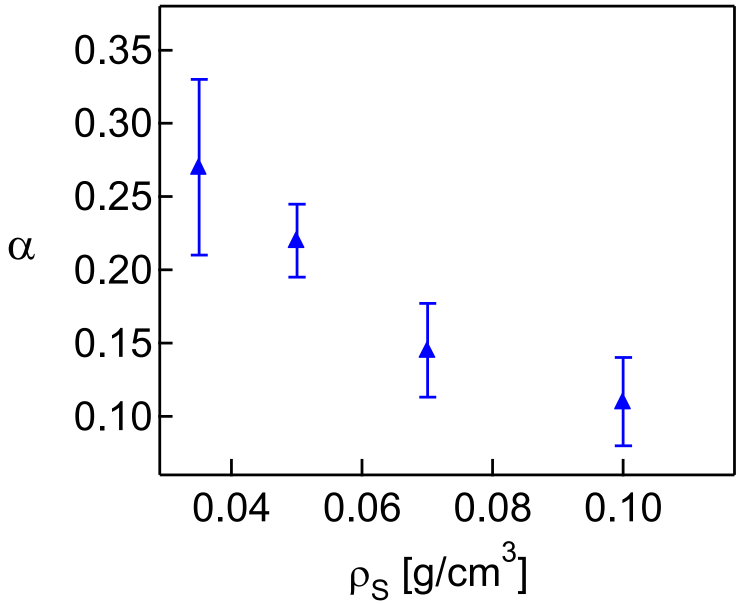
For smectic w/o aerosil,
$G_o = 10^3$ dynes/cm$^2$ (Colby, 1997)

In the smectic phase,
$G'(\omega) = Gg + G_s(T) + \beta_s\, \omega^\alpha$
$\alpha = x - 1$,
x → noise temperature

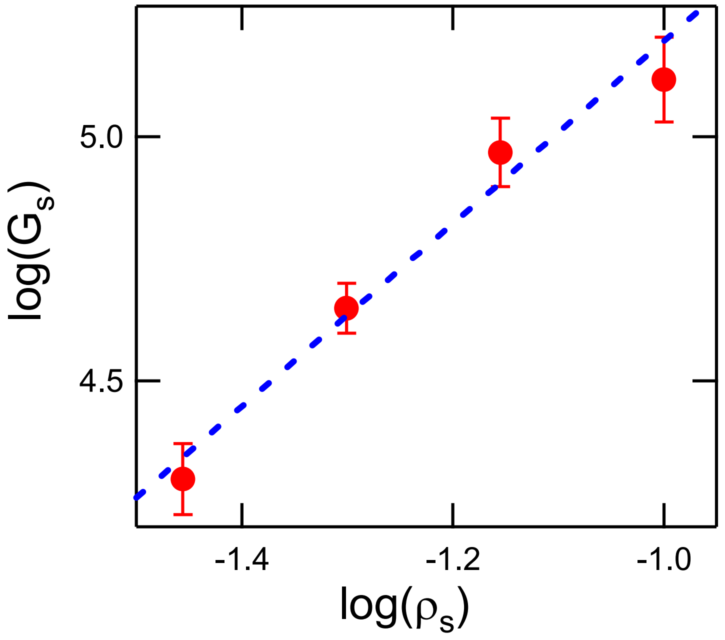
In nematic & isotropic phases,
$G'(\omega) \sim G_g \sim \rho_s^{4.8+/-0.8}$

$\beta_s$ and $G_s$ huge > 2-3 orders of magnitude larger than for pure 8CB

# Rheology of disordered smectics: $G'(\omega) = G_g + G_s + \beta_s\, \omega^{\alpha}$

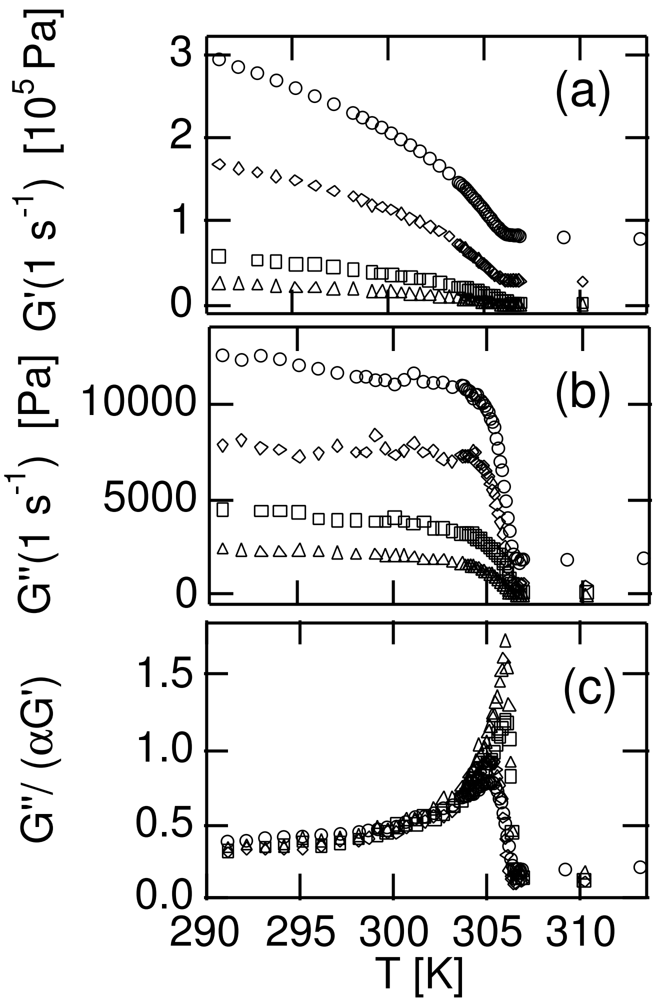


- Dynamics slows with increasing quenched disorder (note: $\alpha = x-1$)
- $\alpha$ shows no temperature dependence
- Glassy rheology connects the our data with light scattering from 8CB and aerogel systems which show glassy behavior [Mertelj et al. Mol. Cryst. Liq Cryst. 331, 1941 (1999)].

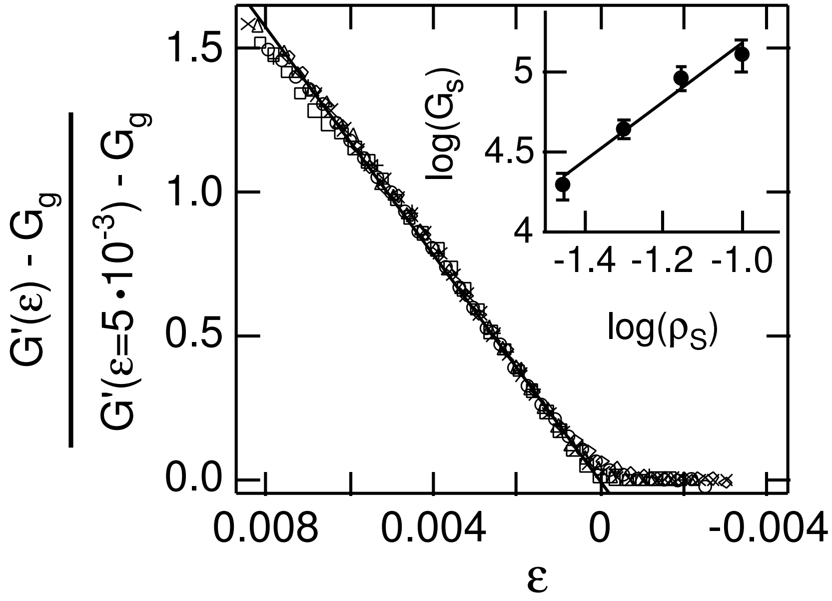


- $G'_s \sim \rho_s^{1.9 +/- 0.2}$: elasticity of defects (in analogy with rubber)

# Temperature dependence



Smectic modulus critical:



$\varepsilon = (T_{NA}-T)/T_{NA}$, $G' \sim \varepsilon^z$, $z \sim 1$

For screw dislocations,
$G' \sim \tau \sim Bb^4/128\pi^3 r_c^2$ [1]
$r_c^{-2} \sim \varepsilon^{0.5}$, $b \sim \varepsilon^{0.4}$ [2] give
$G' \sim \varepsilon^{0.9}$

Collapse in c) ⇒ direct
correspondence between $\rho_s$ and $\alpha$

# Experiment 2: SGR: The triblock copolymer Pluronic

A micelle-forming copolymer (ABA type triblock with A: poly(ethylene) oxide or PEO, B: poly(propylene)oxide or PPO)

## Why is this system so interesting?

PPO hydrophobicity increases on raising the temperature

⇓

They self associate into spherical micelles in selective solvents and in certain ratios of PPO to PEO (with PPO cores and swollen PEO coronas)

⇓

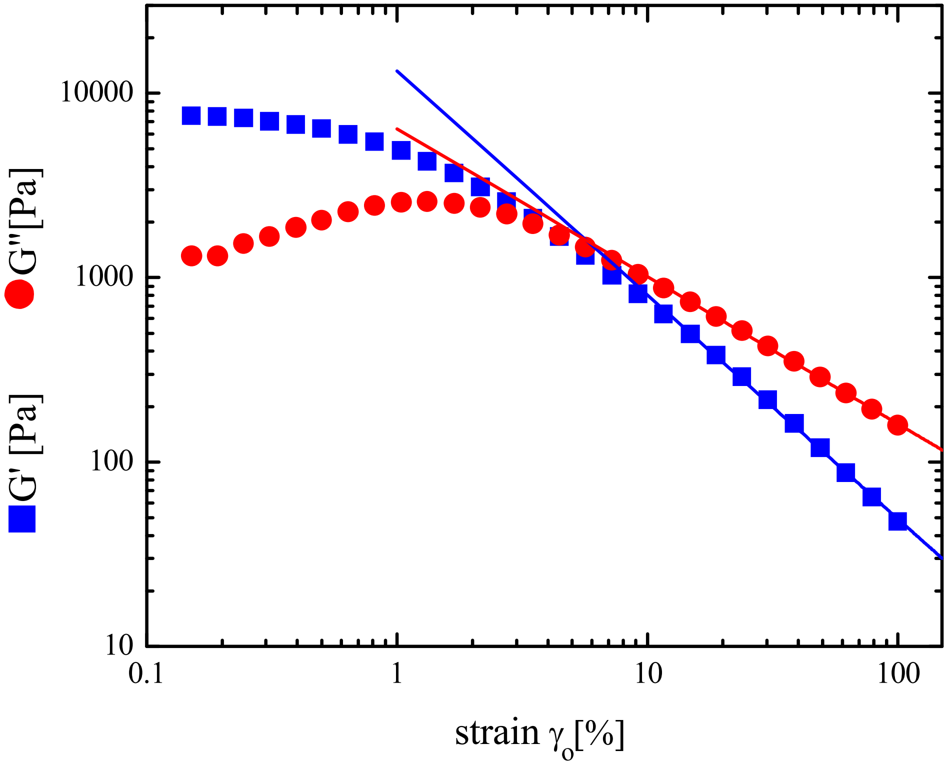
At appropriately high concentrations, Pluronic can undergo crystallisation on *raising temperature* : "inverse crystallisation"

Finds important uses as a nonionic surfactant in industrial/ technical processes (detergency, emulsification, foaming/ defoaming agent) and in drug delivery applications (Pluronic block copolymers as novel polymer therapeutics for drug and gene delivery, J Control Release. 2002 Aug 21;82(2-3):189-212)

Mohan and Bandyopadhyay PRE (2008)

# Large amplitude oscillatory sweep (LAOS)

Pluronic concentration = 0.25 g/cc, T = 59.3° C



- For higher concentrations, not perfectly linear even at the lowest accessible strains!
- At high strains, $G'(\gamma) \propto \gamma_o^{-\nu'}$ , $G''(\gamma) \propto \gamma_o^{-\nu''}$
- Peak in G" typical of soft glassy materials

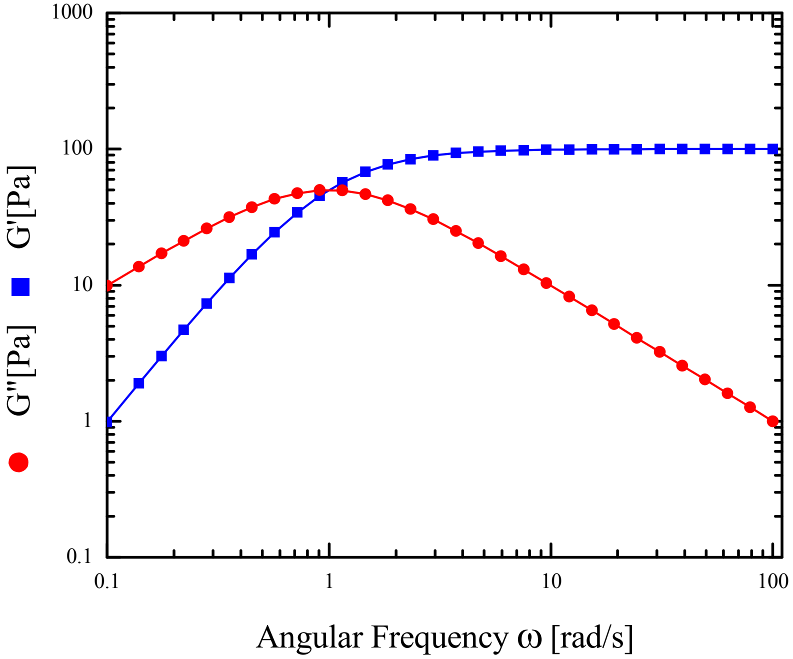
# Notes on the Maxwell model

$$G' = \frac{G_o(\omega\tau_o)^2}{1+(\omega\tau_o)^2} \quad .......(1a)$$

$$G'' = \frac{G_o\omega\tau_o}{1+(\omega\tau_o)^2} \quad .......(1b)$$

G" has a peak at $\omega = 1/\tau_o$

$G_o$=100 Pa and $\tau_o$ =1 sec



- There is a crossover from solid-like to liquid-like behaviour at low frequencies giving rise to a peak in G"
- This peak in G" indicative of a structural relaxation time $\tau_o$

# Notes on the structural relaxation peak

K.Miyazaki *et al.*, EPL, (2006)

$$G' = \frac{G_o(\omega\tau_o)^2}{1+(\omega\tau_o)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1a)$$

$$G'' = \frac{G_o\omega\tau_o}{1+(\omega\tau_o)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1b)$$

$$1/\tau \simeq 1/\tau_o + K|\dot{\gamma}|^{\upsilon}$$

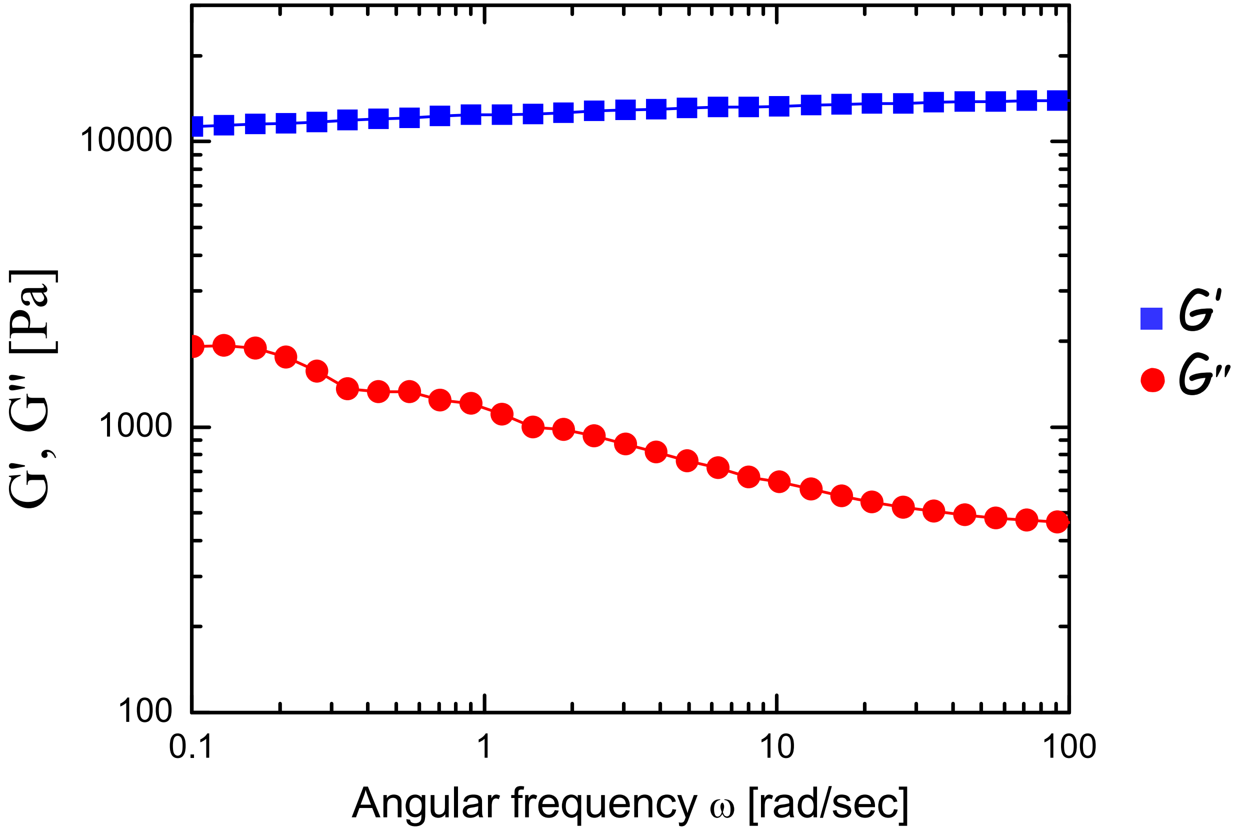
Replacing $\tau_o$ by $\tau$ in equation (1b), maximum of G" is at $\omega \approx 1/\tau \approx K|\dot{\gamma}|^{\nu}$ , when $\tau_o >> \tau$.

Metastable systems with slow dynamics show *K* ~ 1 and $\nu$ ~ 1 with the peak of G″ at $\omega \approx |\gamma|$ $( |\overset{o}{\gamma}| \Rightarrow \approx 1)$

i. Peak is insensitive to frequency
ii. G" peak appears when G' > G"
iii. At large strains, G' $\underset{o}{\approx} |\gamma|^{-2\nu}$ and $G''_o \approx |\gamma|^{-\nu}$

# <u>Frequency response of pluronic polycrystal</u> (0.29 g /cc, 59.3°C)

Mohan and Bandyopadhyay PRE (2008)



- $G' \gg G''$
- $G'$ very weakly frequency dependent
- $G''$ shows weak frequency dependence, but magnitude much larger than that of continuous fluid phase

# Notes on frequency sweep experiments….

- These features of G' and G" characteristic of soft solids

- Possible characteristic time scales: slow dynamics due to coarsening domains, also bridging and looping of PEO chains and micellar rearrangements.

- How do we measure this relaxation process for our soft solid?

- Answer: by doing strain rate frequency sweep experiments (SRFS : Wyss *et al.*, *PRL 2007*)

- SRFS idea: applying nonlinear strain to drive the structural relaxation to a higher, experimentally attainable value (remember: $1/\tau \sim \gamma^{\nu}$, $\nu \sim 1$)

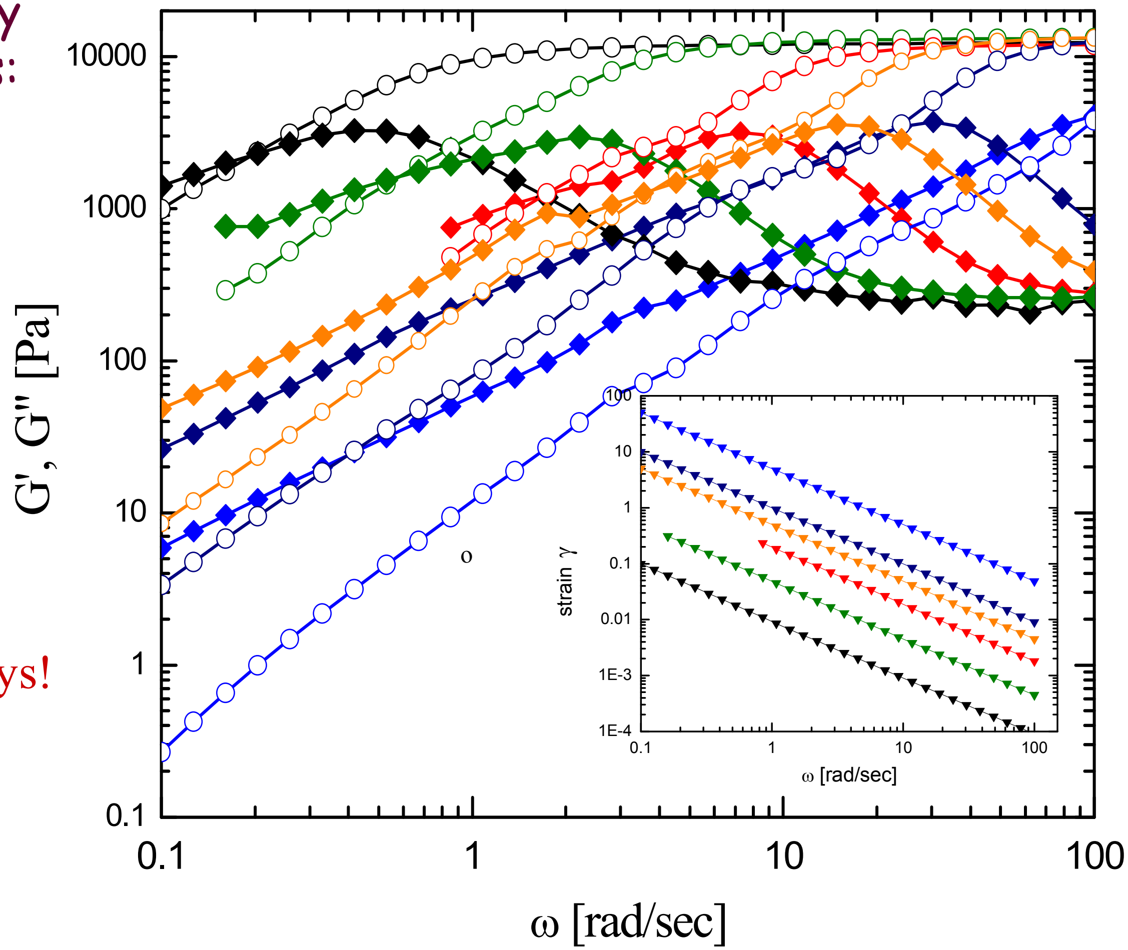
# Strain rate frequency sweep (SRFS), Wyss *et al.*, PRL (2007)

## Accessing very relaxation processes

### Our experiment

Step 1: Drive the slow relaxation processes at the time scale of an imposed shear rate $\dot{\gamma}$: *i.e.* make the dynamics faster by increasing $\dot{\gamma}$ and thus bringing them to experimentally accessible frequencies:

Shear rates
- ● 0.01
- ●0.05
- ● 0.2
- ● 0.5
- ● 1
- ● 5



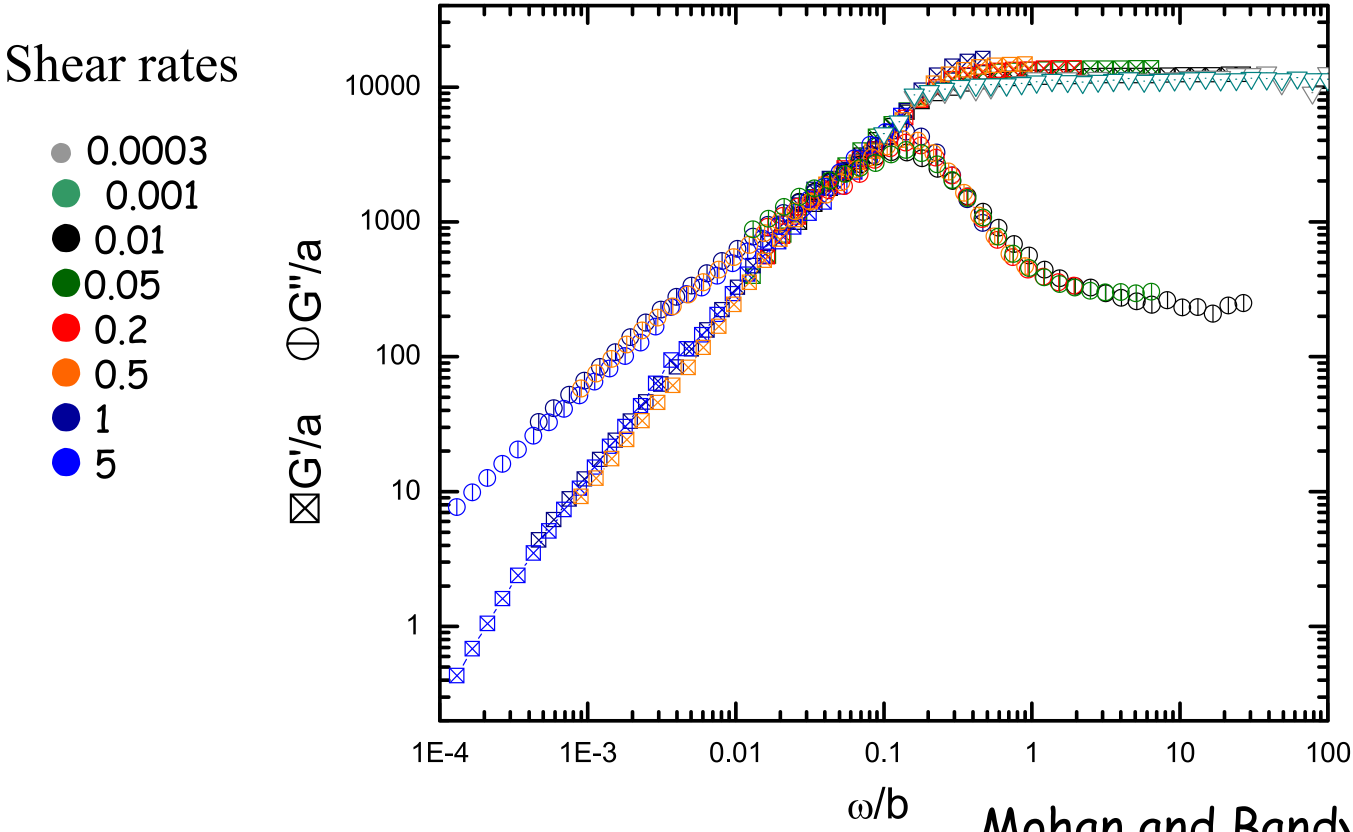
$\gamma_o = \dot{\gamma}\,\omega$ always!

# Strain rate frequency sweep (cont'd), c = 0.28 g/cc

Step 2: Shift the data to collapse onto a single master curve

Recipe for collapse: To highlight the similarities in the shape of the viscoelastic response, we rescale as follows :

$$\boxed{G^*_{\text{scaled}}(\omega) = G^*(\omega/b(\dot{\gamma}))/a(\dot{\gamma})}$$

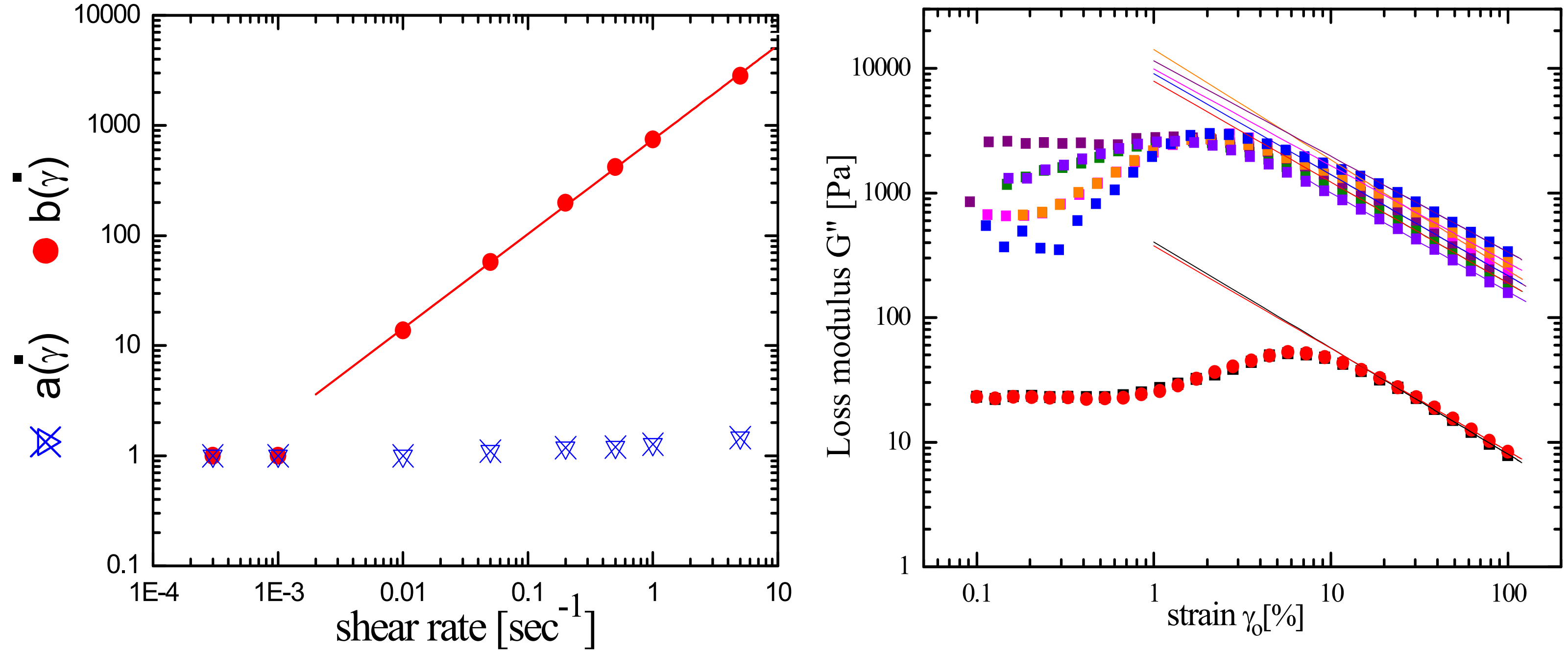


$$\omega \approx 1/\tau \approx K|\dot{\gamma}|^{\nu} \quad ,$$

Mohan and Bandyopadhyay PRE (2008)

# Collapse functions a and b versus shear rate
# c = 0.28 g/cc

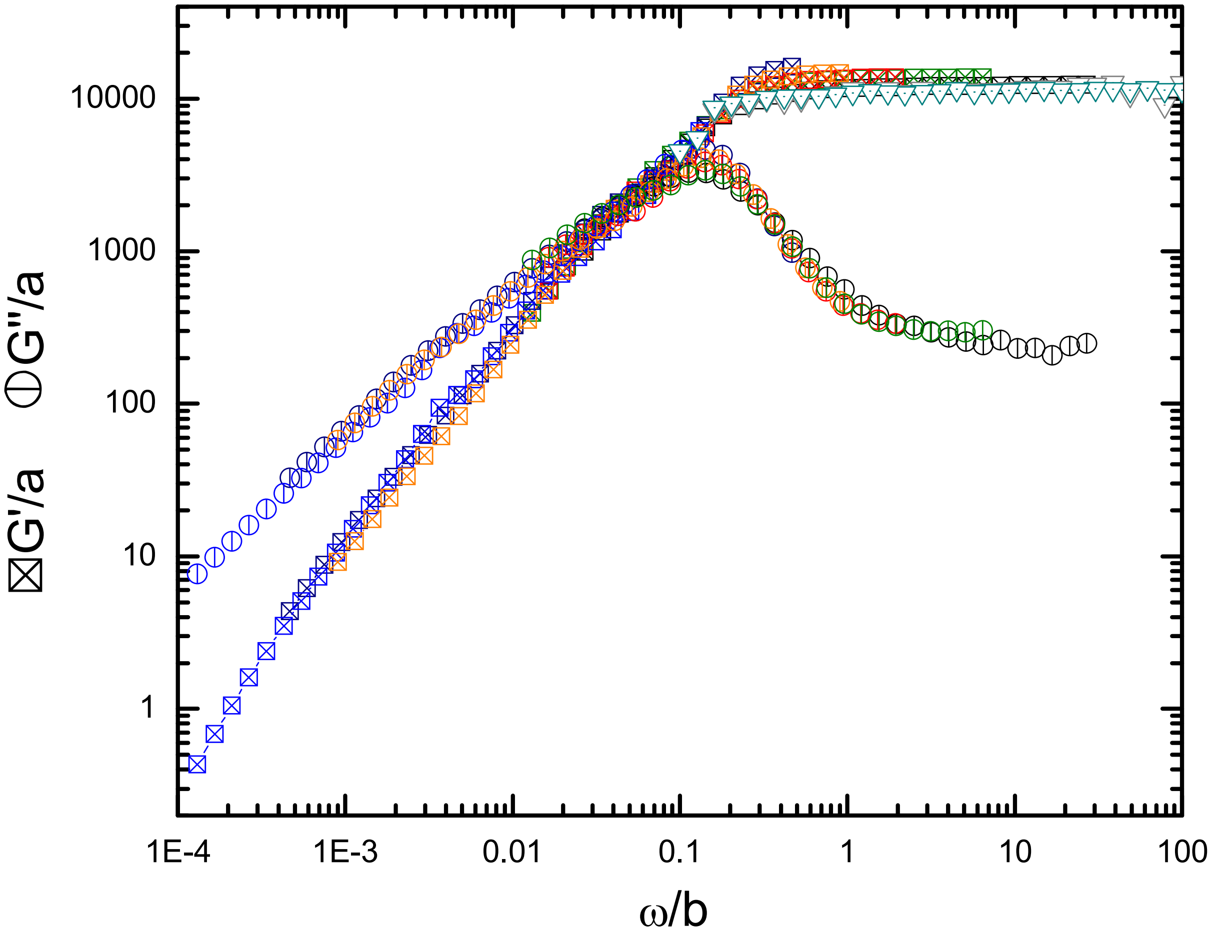
$$G^*_{scaled}(\omega) = G^*(\omega/b(\dot{\gamma}))/a(\dot{\gamma})$$



- a : almost shear rate independent
- $b(\dot{\gamma}) \propto \dot{\gamma}^{0.86}$ at high shear rates, ~ 1 for lowest shear rates
- $G''(\gamma) \propto \gamma_o^{-0.82}$

Mohan and Bandyopadhyay PRE (2008)

# Strain rate frequency sweep (cont'd), c = 0.28 g/cc: scaled data (again)



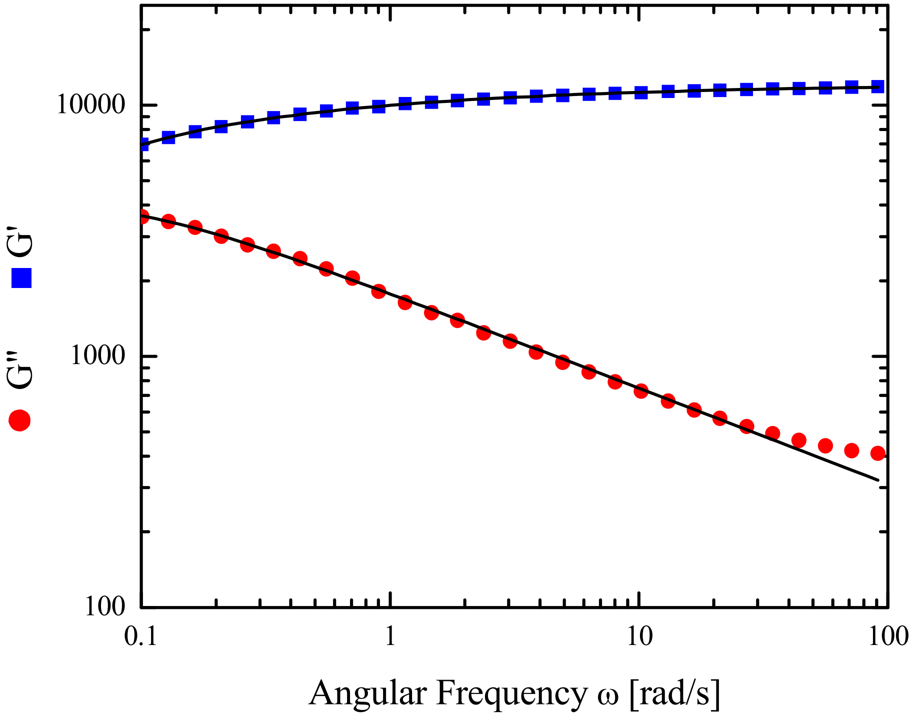
- Collapse of data extends frequency range to lower values
- Note similarities to time-temperature superposition
- peak in scaled G" gives correct relaxation time:

$\tau_o = 2\pi/\omega_{peak} = 45 \pm 5$ sec for our 0.28 g/cc sample

# Fit to Cole-Davidson Model (c = 0.28 g/cc)

$$G^{*} = G_{o}\left[1 - \frac{1}{(1+\mathrm{i}\omega\tau)^{\alpha}}\right]$$

α ≈ 1 for Maxwell model



| | G' | G" |
|---|---|---|
| $G_o$ (Pa) | 12220 | 12586 |
| τ (s) | 69.12 | 36.29 |
| α | 0.36 | 0.38 |

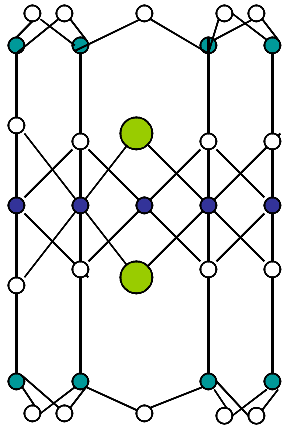
From Cole-Davidson fit:
τ = 52 ± 16 sec
From SRFS:
τ = 45 ± 5 sec

Mohan and Bandyopadhyay PRE (2008)

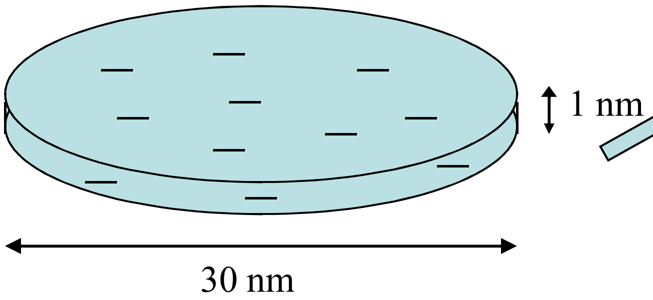
# Experiment 3: KWW relaxation: Aging Laponite clay

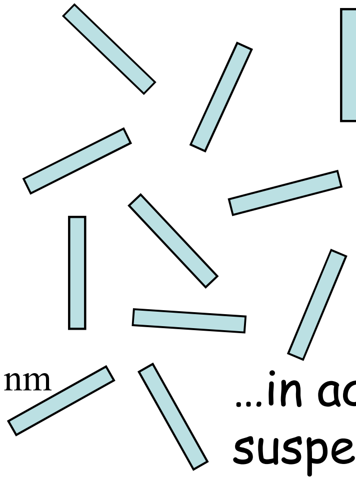
## Laponite RD: a synthetic clay

$Na_{0.7}^{+}[Si_8Mg_{5.5}Li_{0.3}H_4O_{24}]_{0.7}^{-}$

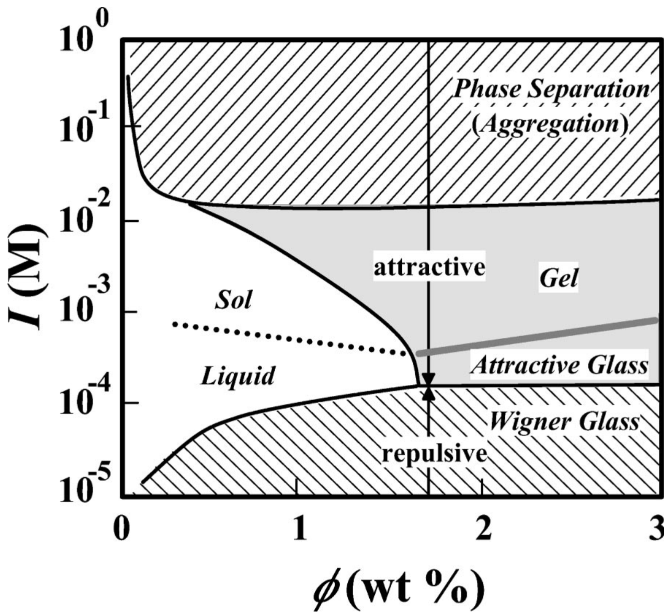


Charged disks…





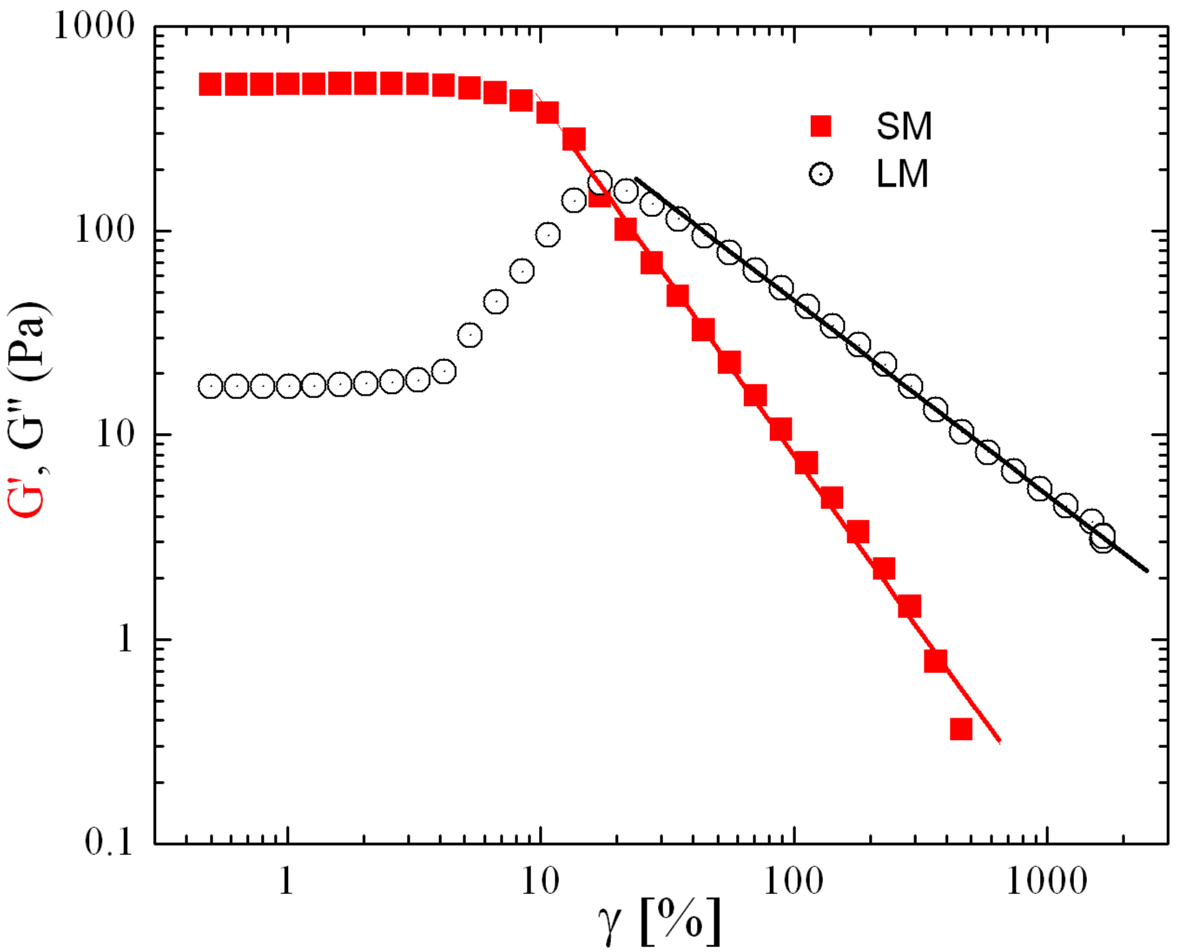
…in aqueous suspensions form soft glasses…



Tanaka et al. *Phys Rev E* 69, 031404 (2004)

# Amplitude Sweep: soft glassy behavior

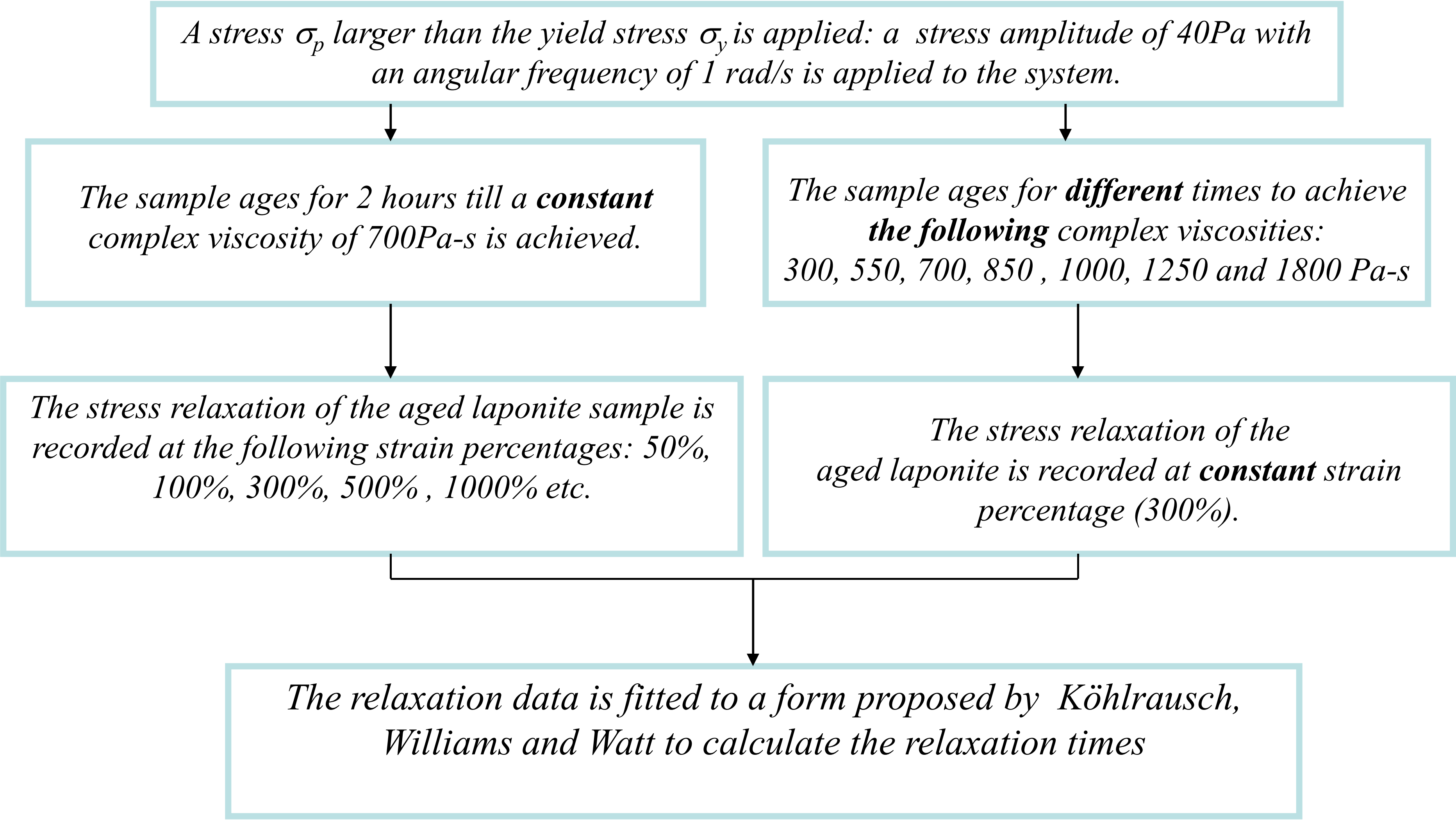
Bandyopadhyay, Mohan and Joshi, Soft Matter (To appear in 2010)



Bump in G", G' ~ $\gamma^{1.8}$, G" ~ $\gamma^{0.9}$

[Miyazaki *et al.* EPL (2006)]

# Our experimental protocol to study the effect of strain deformations on the aging of clay



*A stress $\sigma_p$ larger than the yield stress $\sigma_y$ is applied: a stress amplitude of 40Pa with an angular frequency of 1 rad/s is applied to the system.*

*The sample ages for 2 hours till a* ***constant*** *complex viscosity of 700Pa-s is achieved.*

*The sample ages for* ***different*** *times to achieve* ***the following*** *complex viscosities: 300, 550, 700, 850 , 1000, 1250 and 1800 Pa-s*

*The stress relaxation of the aged laponite sample is recorded at the following strain percentages: 50%, 100%, 300%, 500% , 1000% etc.*

*The stress relaxation of the aged laponite is recorded at* ***constant*** *strain percentage (300%).*

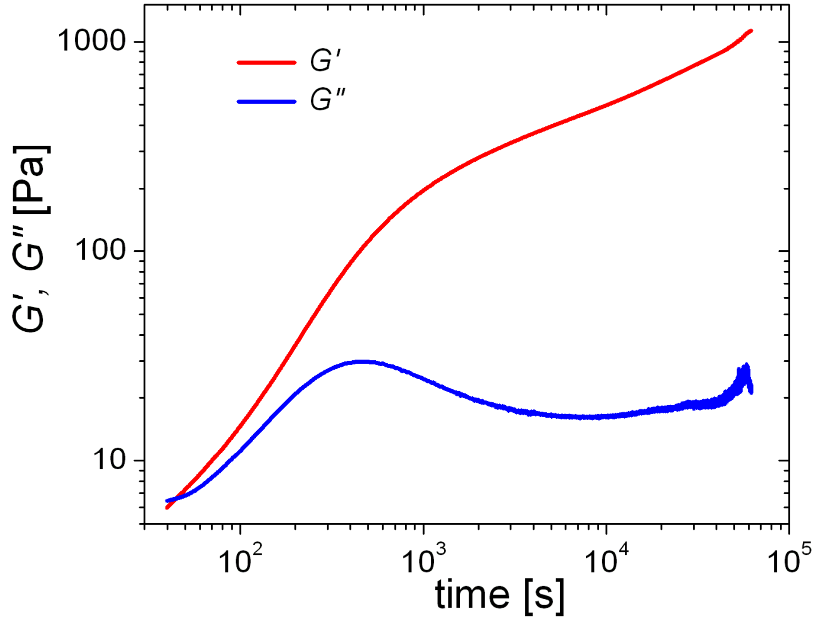
*The relaxation data is fitted to a form proposed by Köhlrausch, Williams and Watt to calculate the relaxation times*

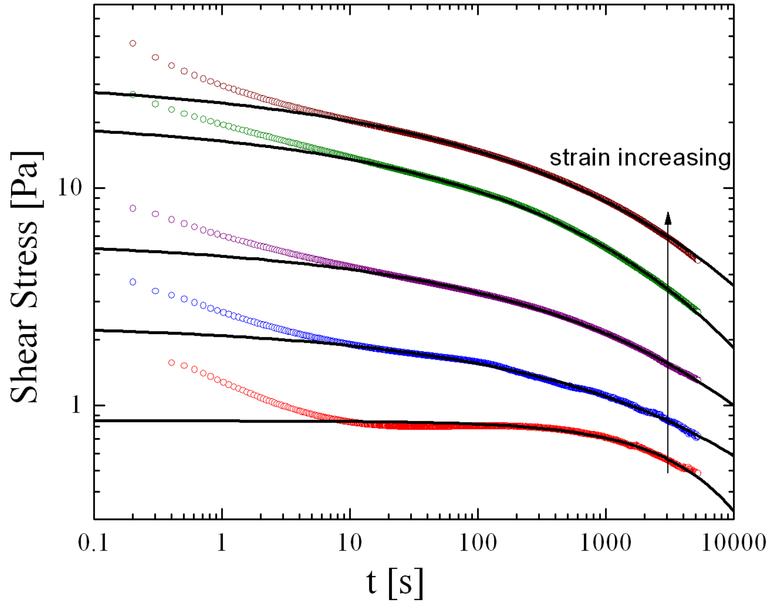
# Data analysis

Relaxation curve has two regimes:

- Short time relaxation regime (cage forming regime)
- Long time relaxation regime (cage-hopping or full aging regime)

300 % strain applied after complex viscosity reaches 1800 Pa.s ( after 62044 sec)





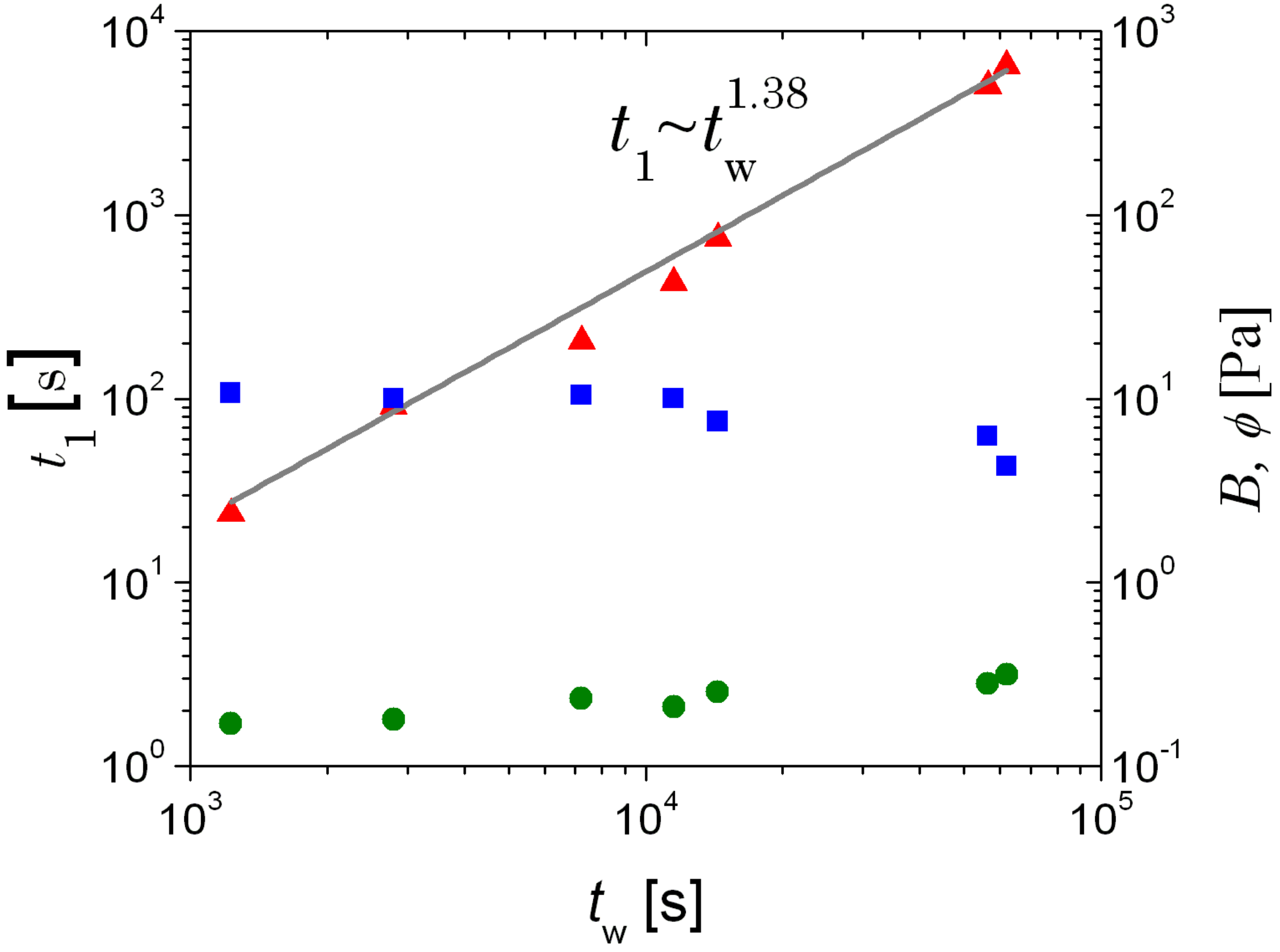
We fit the data to: $\sigma(t) = \phi \exp[-(t/t_1)^{\beta}]$

$\phi$ - Amplitude of long time relaxation function

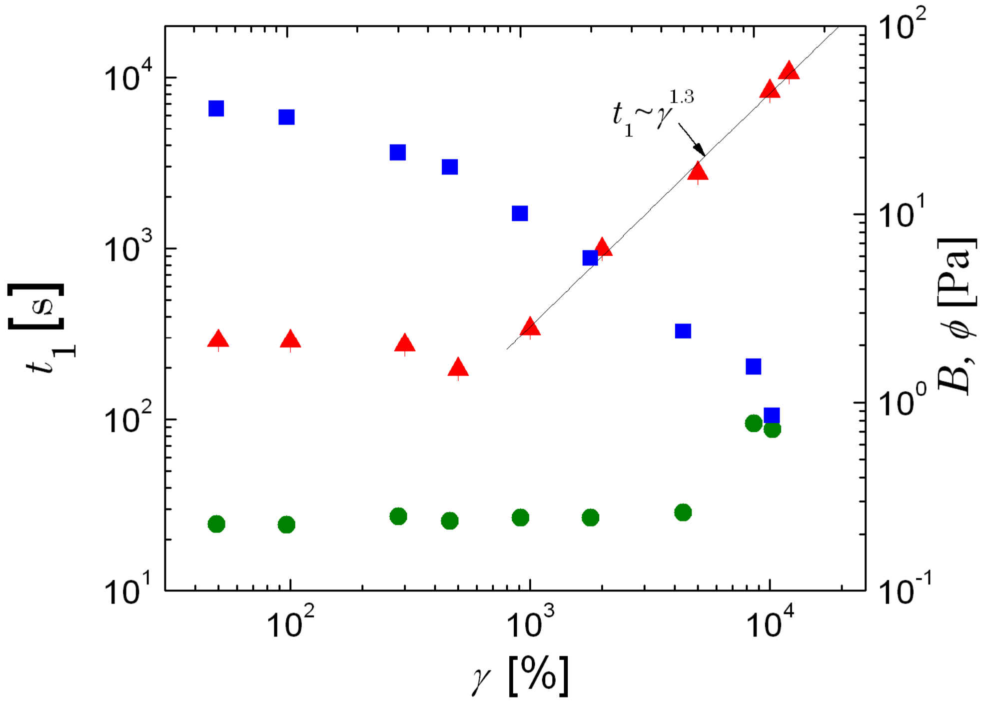
$\beta$ - Stretching exponent

$t_1$ - Long-time relaxation

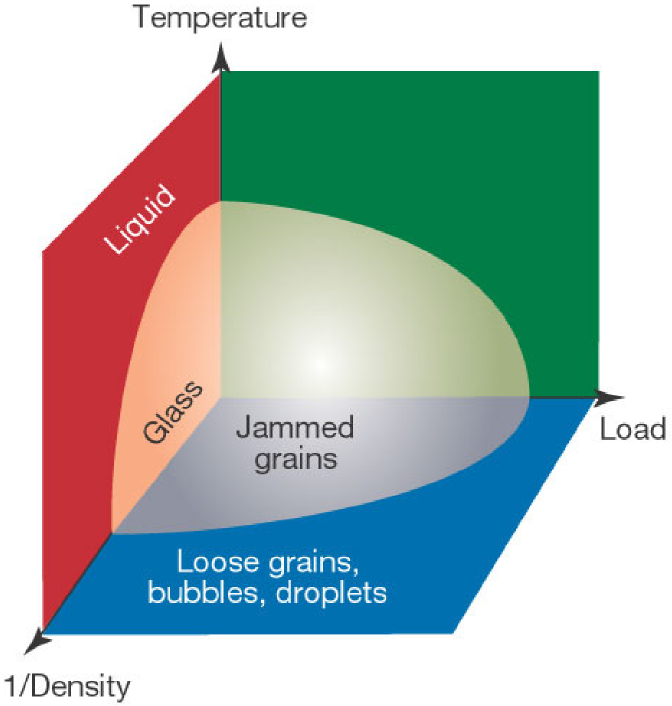
# Stress relaxation results – I : different ages, followed by the same strain deformation (300%)



# Stress relaxation results – II : same ages, followed by different strain deformation (300%)



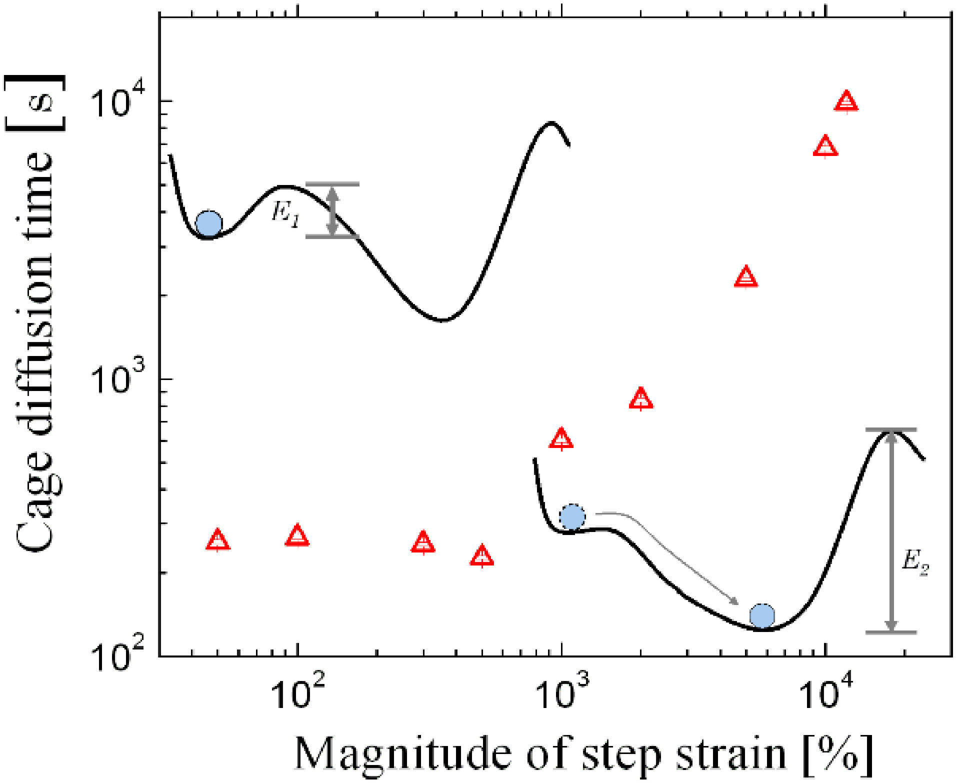
Strain induced jamming!



The Jamming Phase Diagram
[Liu and Nagel, Nature (1998)]

# Conclusions

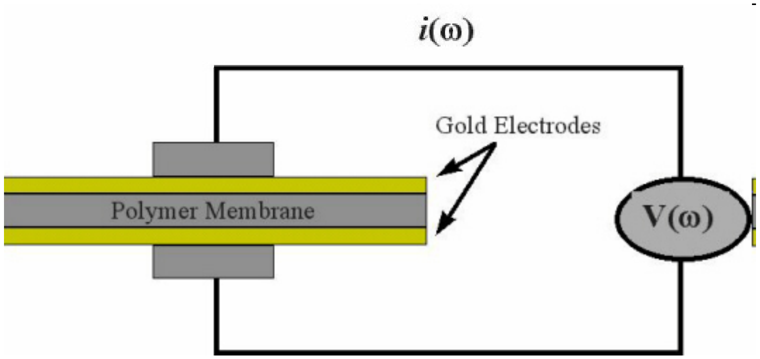
In our case, as deformation increases, aging is *actually facilitated!*

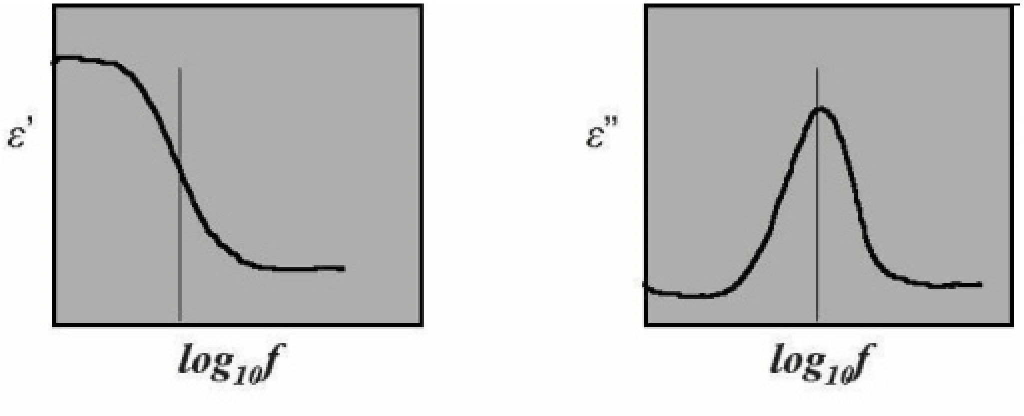


1) Complex energy landscape alters dramatically on application of strains
2) Enhanced sluggishness of dynamics as strain is increased

# Dielectric Spectroscopy

- Dielectric spectroscopy measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed as permittivity.
- Fluctuations in the local electric field are connected to the dynamics on a molecular scale





$P = \varepsilon_o \chi_e E$, $D = \varepsilon_o E + P = \varepsilon_o(1+\chi)E = \varepsilon_o \varepsilon_r E$

$D_o e^{i\omega t} = \varepsilon(\omega)\, E_o e^{\,i\omega t}$,

$\varepsilon = \varepsilon'(\omega) - i\varepsilon'(\omega)$

# Broadband Dielectric spectroscopy

For a capacitor $C^*$ filled with the material under study, the complex dielectric function is given by $\varepsilon = \varepsilon'(\omega) - i\varepsilon'(\omega) = C^*(\omega)/C_o$, $C_o$ is the vacuum capacitance

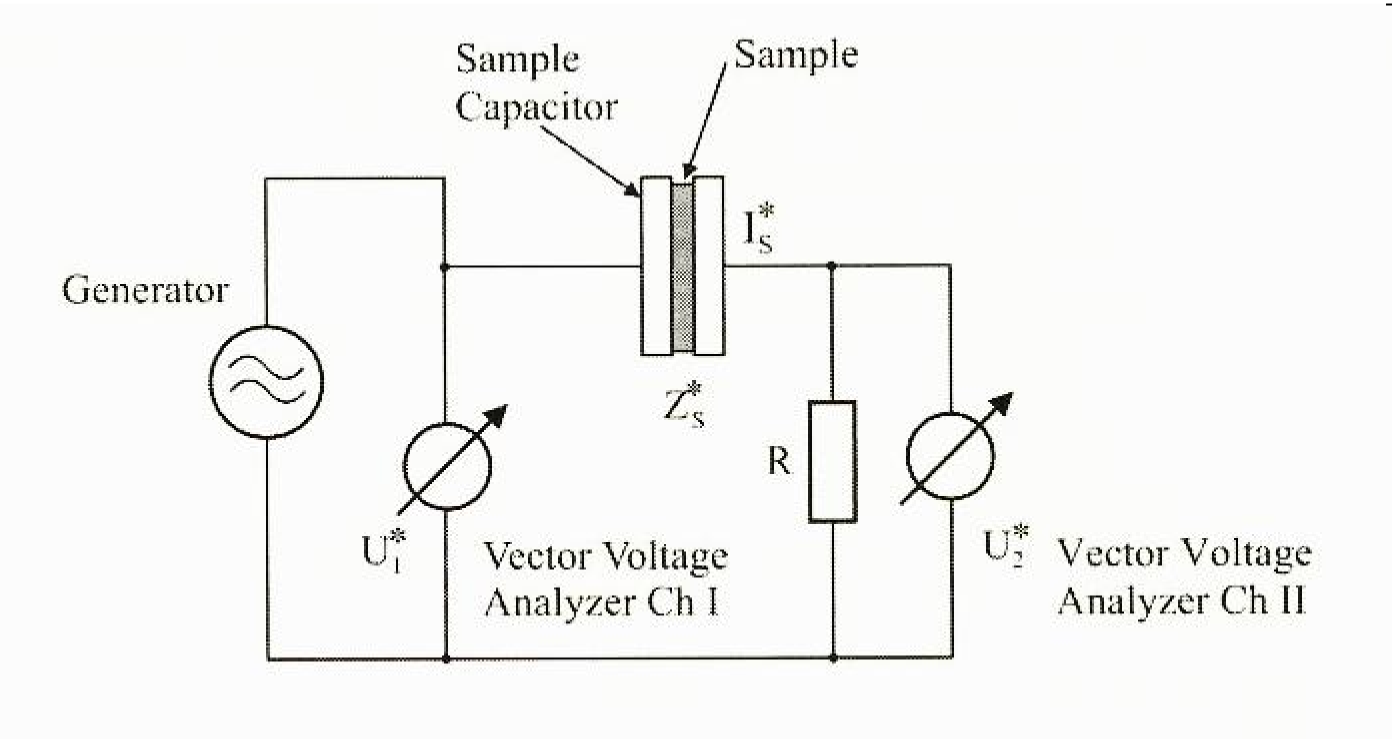
Applied electric field: $E^*(\omega) = E_o e^{i\omega t}$, with $E_o$ small enough to be in the linear response regime:

$$\varepsilon^*(\omega) = J^*(\omega)/i\omega\varepsilon_o E^*(\omega) = 1/\ i\omega\varepsilon_o Z^*(\omega)C_o$$

Different measurement techniques are used depending on the frequency range to be investigated:

1) Fourier correlation analysis in combination with dielectric converters ($10^{-6}$ – $10^{7}$ Hz)
2) Impedance analysis ($10^{1}$-$10^{7}$ Hz)
3) RF Reflectometry ($10^{6}$ Hz – $10^{9}$Hz)
4) Network analysis ( $10^{7}$ Hz – $10^{11}$ Hz)

# Fourier Correlation Analysis

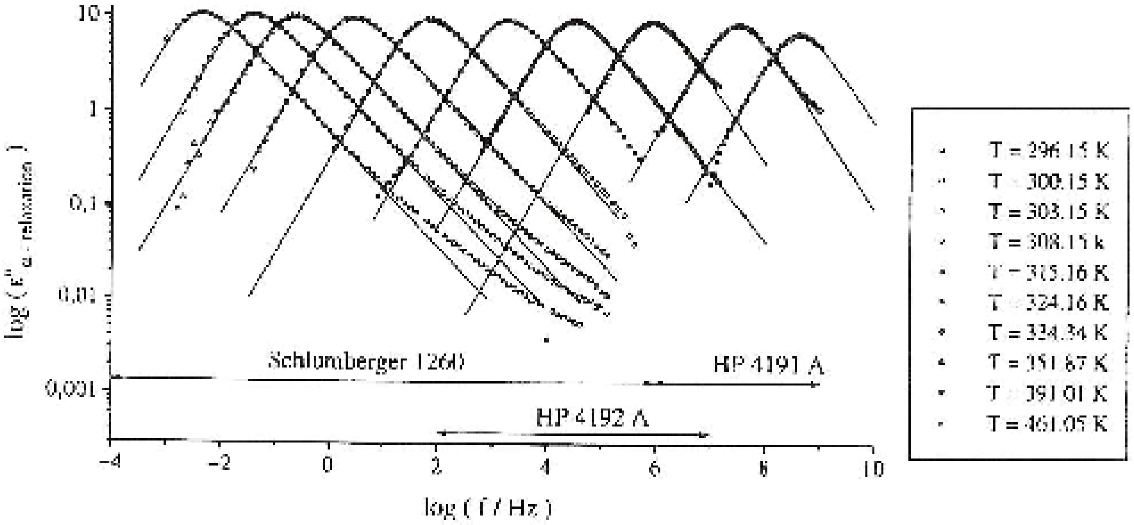


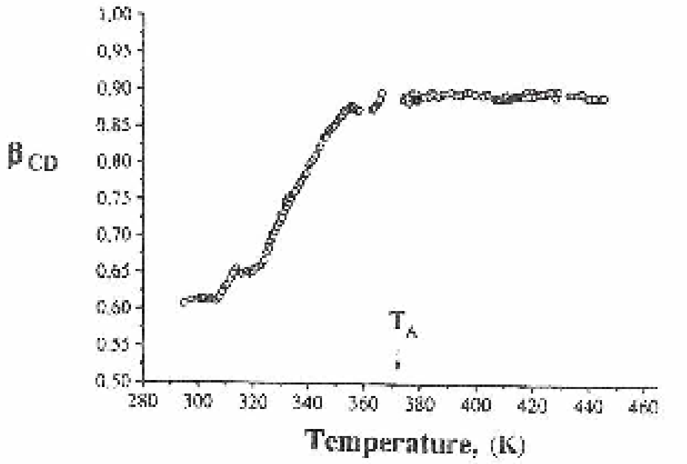
- $U_1(t)$: sine wave voltage with frequency between $10^{-6}$ -$10^7$ Hz
- R converts sample current $I_s(t)$ into a voltage $U_2(t)$
- 2 phase sensitive sine wave correlators analyze $U_1(t)$ and $U_2(t)$ in terms of the phases and amplitudes of the Fourier base waves $U_1^*(\omega)$ and $U_2^*(\omega)$
- Complex impedance $Z_s^*(\omega) = U_s^*(\omega)/I_s^*(\omega) = R[\{U_1^*(\omega)/U_2^*(\omega)\}-1]$

# Relaxation time spectra

- KWW form: $M(t)/M(0) = \exp[(-t/\tau)^{\beta}]$, $M(t)$ ~ any linearly relaxing property, $\beta = 1$ is a mono-exponential relaxation, $0<\beta<1$ implies a distribution of relaxation times.
- Cole Davidson form: $\varepsilon^* - \varepsilon_{\infty} = \Delta\varepsilon/(1+i\omega\tau)^{\beta}$

Phenolphthalein Dimethylether (PDE), a simple organic glass former

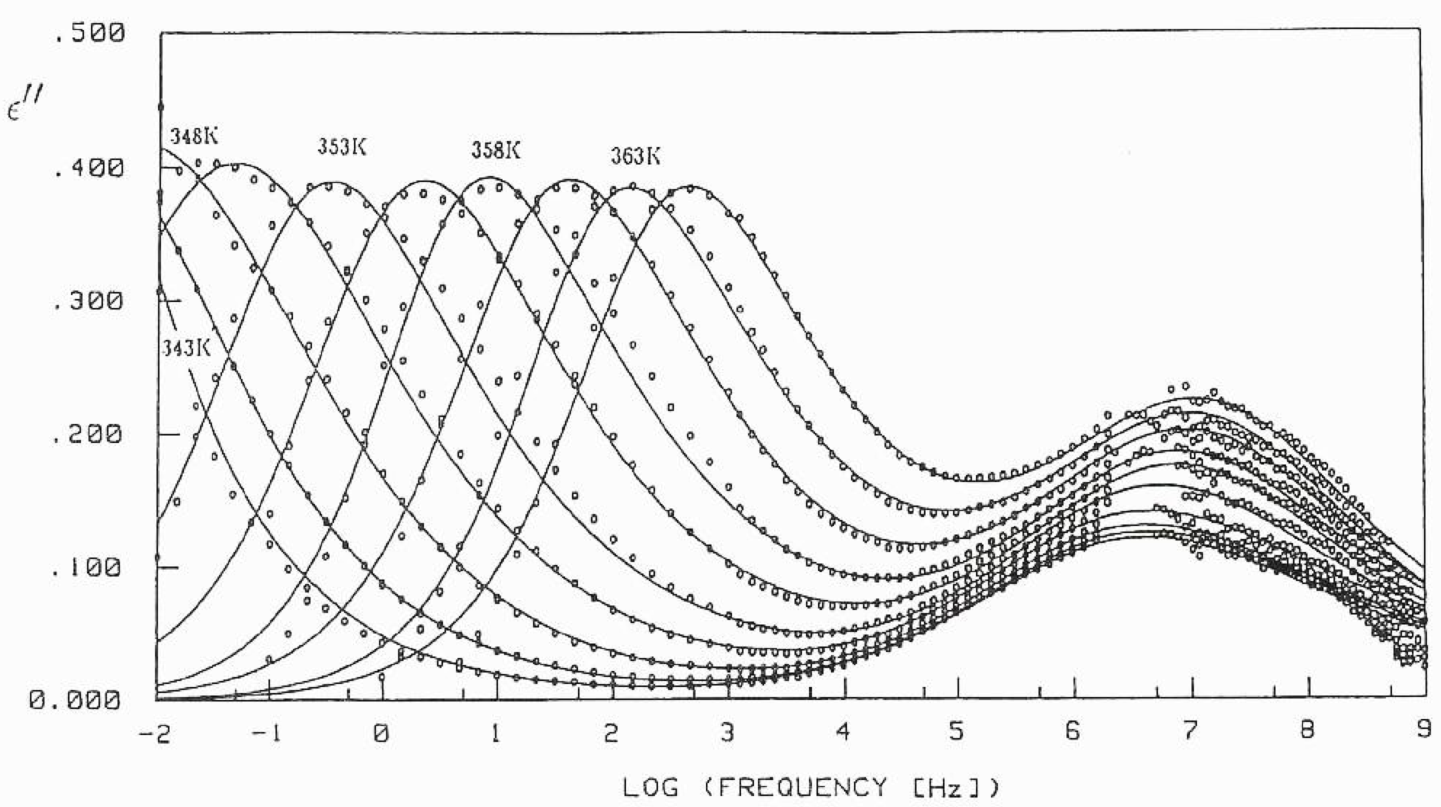




Stickel et al., Physica A (1993)

# Relaxation time spectra

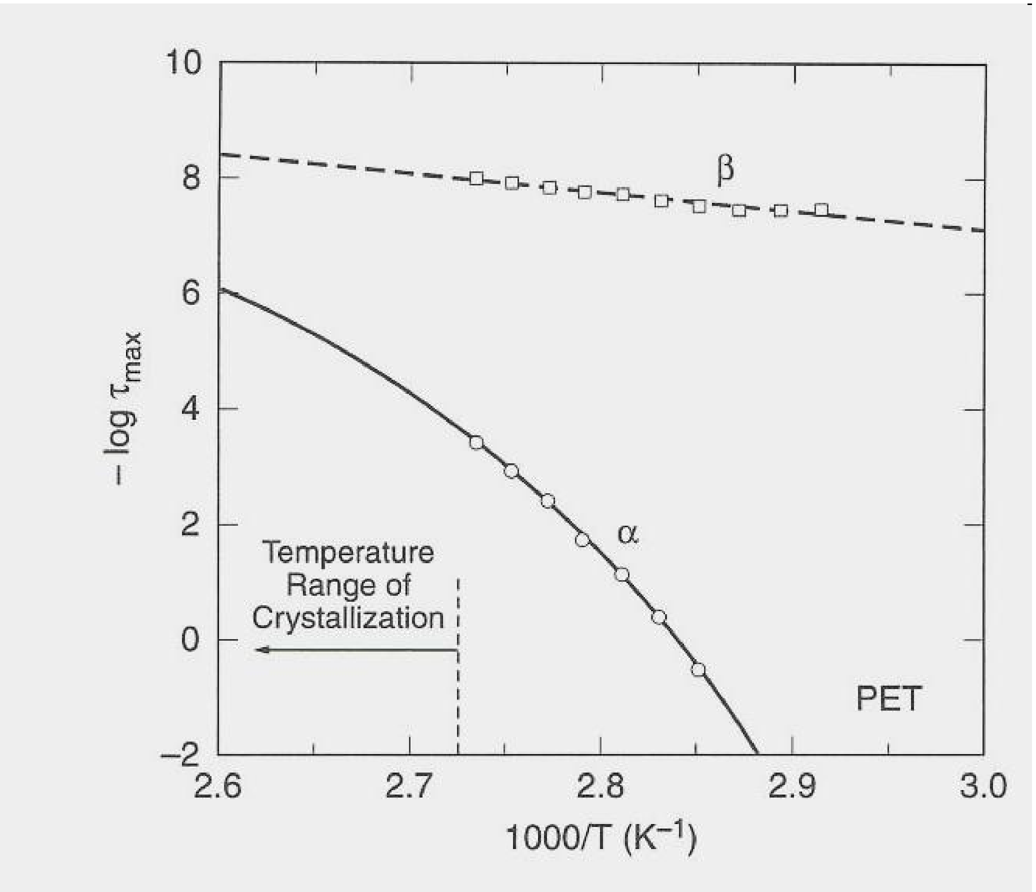
Polyethyleneterephthalate at various T with fits to Havriliak Negami functions



Hofmann et al., Physica A (1993)

# Relaxation time spectra of PET (cont'd)

Relaxation times of Polyethyleneterephthalate at various T
$\beta$ relaxation shows Arrhenius T-dependence, slow $\alpha$ mode slows down as $T_g$ is approached



Hofmann et al., Physica A (1993)