Broad Band Dielectric Spectroscopy

A Powerful Method for the Study of Molecular Motions in Solids

by

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Molecular dynamics of Organic Solids.

Molecular motions may be studied by

Relaxation Dielectric, NMR, dynamic mechanical

Scattering Quasi-elastic light scattering, neutron scattering

Spectroscopic
Time-resolved fluorescence depolarization (Monnerie, Ediger)
'solvation dynamics' (Richert)

frequency range $10^{-4} \ldots 10^{+10}\, Hz$

time range $10^{4} \ldots 10^{-11}\, \mathrm{sec}$

Measurement Techniques

$10^{-4}...10^{6}\,Hz$

Frequency-response impedance analysers
(HP, Solartron, Novocontrol)

Time-domain spectroscopy

$10^{6}...10^{10}\,Hz$

HP impedance analyser, transmission lines, network analysers
Time-domain reflectometry

Measured Dielectric Properties

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$ Complex dielectric permittivity

Y(ω) Complex Admittance

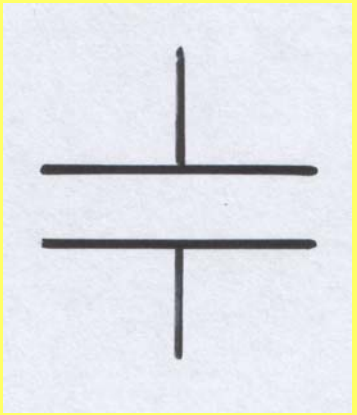
Z(ω) Complex Impedance

M(ω) Complex Modulus

σ(ω) Complex conductivity

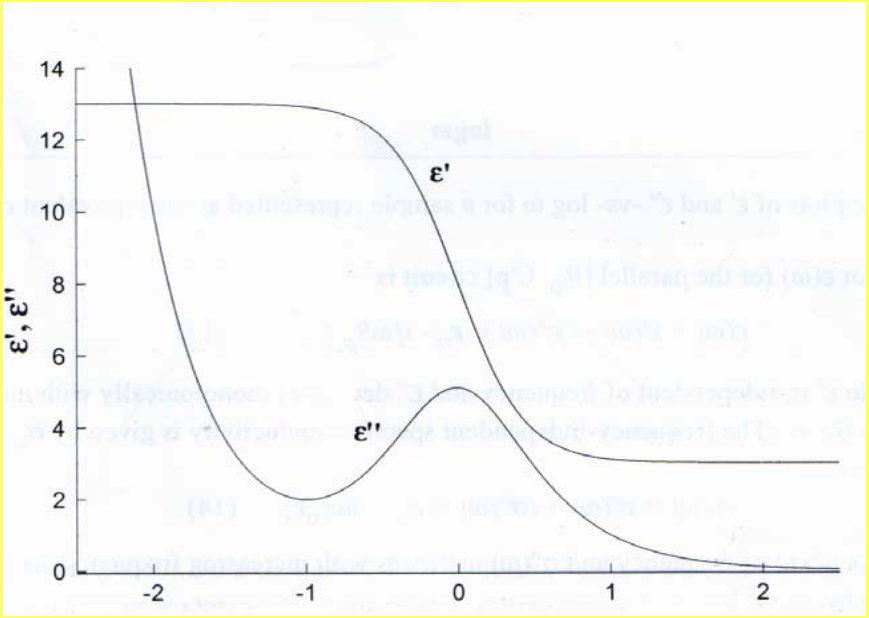
$$\varepsilon(\omega) = \frac{Y(\omega)}{i\omega C_0} = \frac{1}{i\omega C_0 Z(\omega)}$$

$$\varepsilon(\omega) = \frac{1}{M(\omega)} = \frac{\sigma(\omega)}{i\omega\varepsilon_v}$$



C_0

Broadband Dielectric Spectroscopy



Complex Permittivity

$$\varepsilon = \varepsilon' - i\varepsilon''$$

$$\varepsilon' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+\omega^2\tau^2}$$

$$\varepsilon'' = \frac{\Delta\varepsilon.\omega\tau}{1+\omega^2\tau^2}$$

1. Relaxation Strength $\Delta\varepsilon$
2. Relaxation time $\tau(T,P)$
3. Shape of process

Low frequencies $\varepsilon'' = \dfrac{\sigma}{\omega\varepsilon_0}$ σ is dc conductivity

Recommended Texts

Anelastic & Dielectric Effects in Polymeric Solids
NG McCrum, BE Read & G Williams, Wiley 1967, Dover 1991

Dielectric Spectroscopy of Polymeric Materials
JP Runt & JJ Fitzgerald (Eds), Amer Chem Soc 1997

Broadband Dielectric Spectroscopy
F Kremer & A Schonhals (Eds), Springer Verlag 2003

Electrical Properties of Polymers
E Riande & R Diaz-Calleja, Marcel Dekker 2004

Introductory Review
G Williams & DK Thomas, Novocontrol Application Notes, No.3, 1998.

Polymer Systems studied using BBDS

Time-invariant materials

Amorphous Glassy, elastomeric, copolymers,
blends & composites, photosets, thermosets, gels

Partially Crystalline Bulk materials, oriented films & fibres

Liquid Crystalline (LC)
Thermotropic main-chain & side chain materials
Lyotropic solutions of rod-like polymers

Time-varying Systems

Thermosetting Epoxide-amine
Photo-setting dimethacrylates
Crystallizing isothermal or quench-anneal
Phase-separating, volume relaxing & ageing

Organic Solids

Rotator Phase Solids eg Ice, cyclohexanol

Glass-formers eg 0rtho-terphenyl

Liquid-Crystal-Forming Materials

Organic Semiconductors and Photoconductors

Solid Electrolytes and Poly-electrolytes

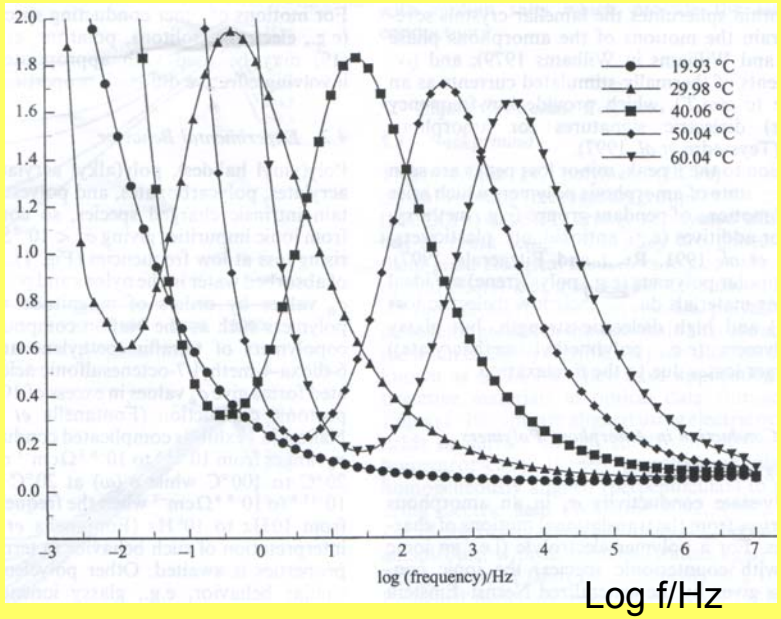
Amorphous Polymers

‘’The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition This could be the next breakthrough in the coming decade’’

P.W. Anderson, Nobel Laureate, in SCIENCE 1995, 267, March, p.1616

Polyvinyl Acetate: α–process

ε''



Log f/Hz

Data of Schaumburg, Novocontrol GMBH

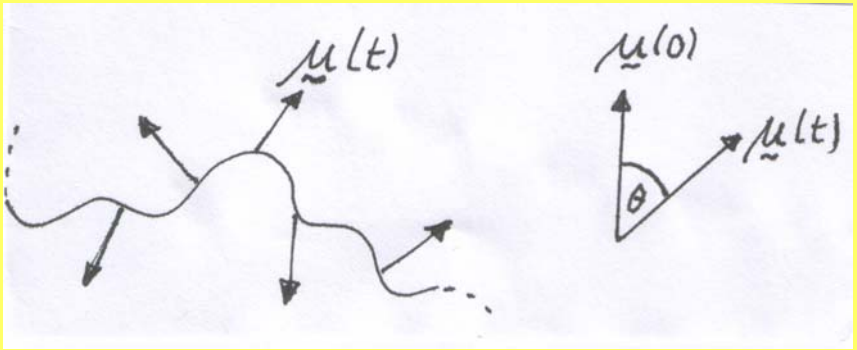
$$-[CH_2CH(OCOCH_3)]_n-$$

Motions of chain dipole groups

$$<\tau_\alpha>=[2\pi f_{\max}{}^{-1}]$$

1. The loss peak moves to ultra-low frequencies as Tg is approached
2. Vogel-Fulcher function $<\tau>=A\exp B/(T-T_0)$ fits data
3. Broad loss curves; KWW function $C(t)=\exp-(t/<\tau>)^{\beta}$ fits data

Amorphous polymers: theory of dielectric relaxation



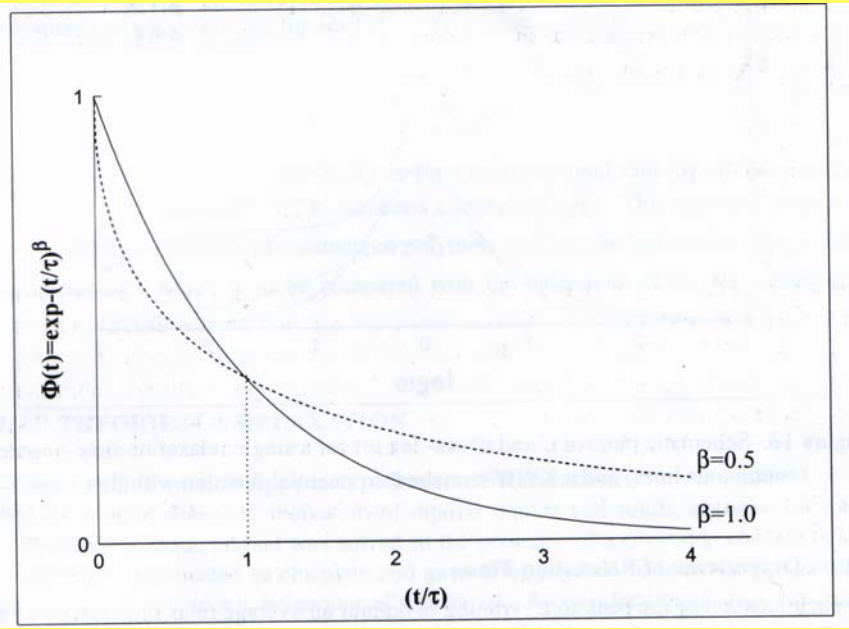
Dipole correlation function $C_\mu(t) = \dfrac{<\mu(0).\mu(t)>}{<\mu^2>}$

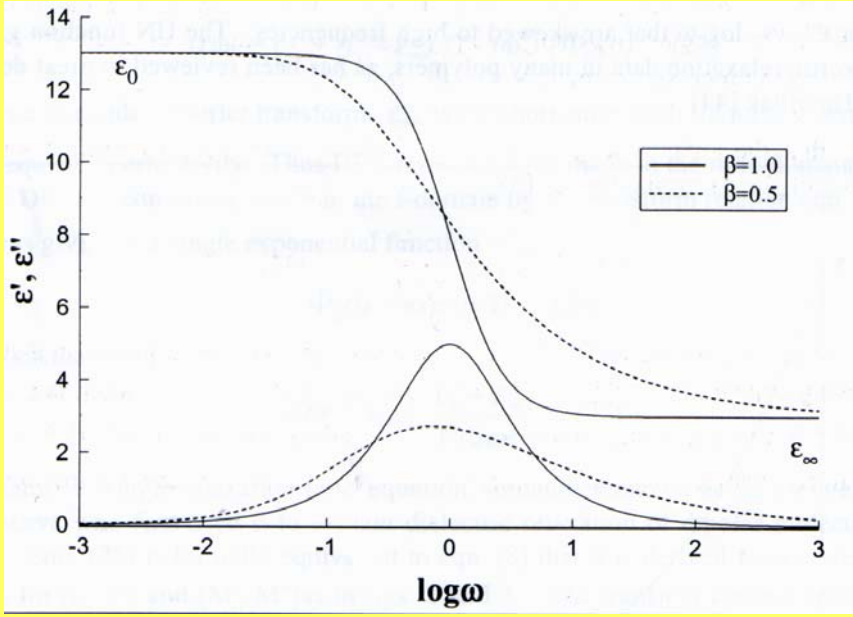
$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty}.p(i\omega)=1-i\omega\Im[C_\mu(t)]$$

The α-loss curves are broad so C(t) is a stretched exponential

The Kohlrausch-Williams-Watts function 1854, 1971

$$C(t) = \exp[-(t/\tau)]^{\beta}$$

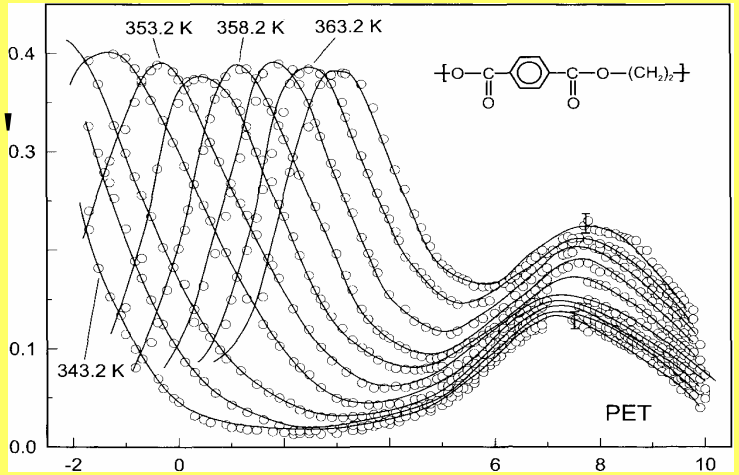




Amorphous Polymers the α, β and αβ relaxations

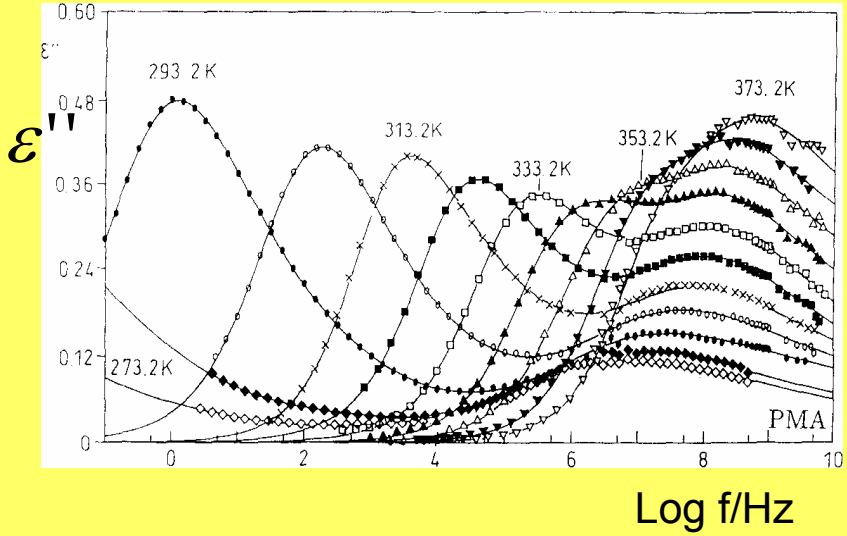
Amorphous PET

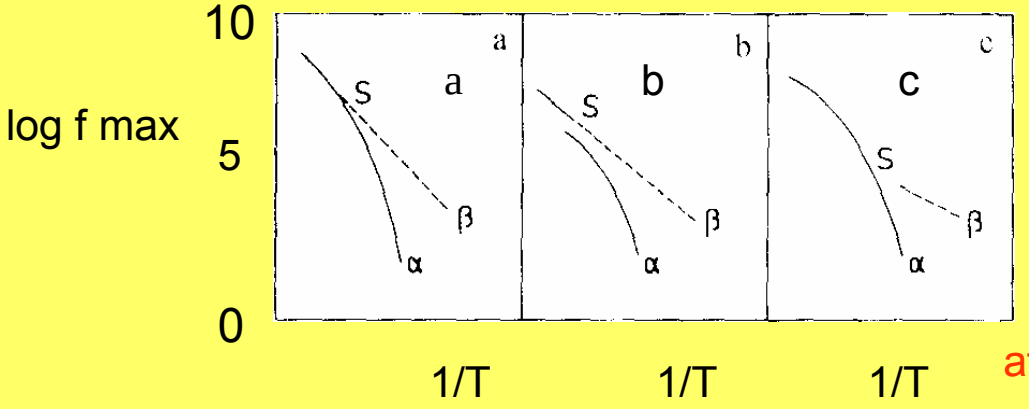
Hofmann, Kremer et al 1994



PMA $-[CH_2CH(COOCH_3)]_n-$

Kremer et al 1992





PET is a or b

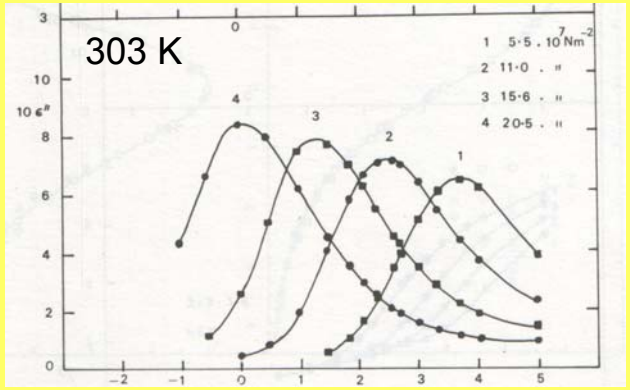
PMA is c

after Schonhals 1997

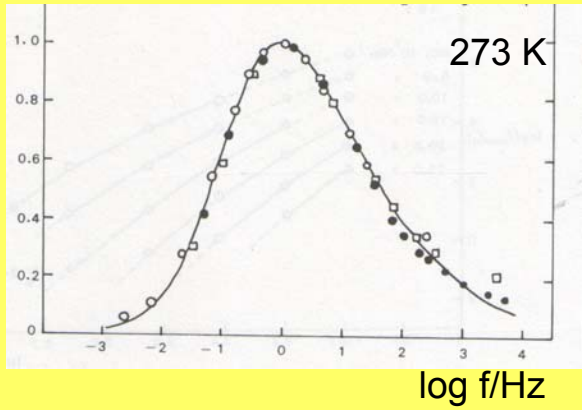
The effect of pressure on the α process in PEA

Williams and Watts 1971

ε''

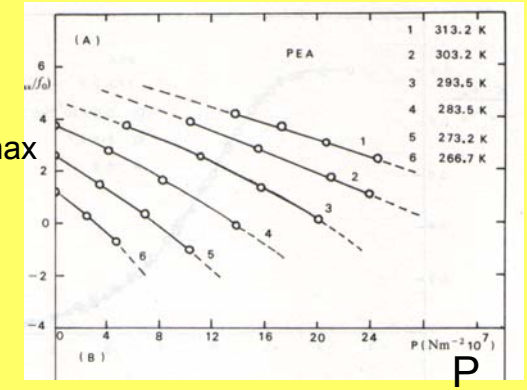


ε''



Process moves to low frequencies with P, shape unchanged, β(KWW) = 0.38

log f max



$$Q_V(T,P) = Q_P(T,V) - RT^2(\partial P/\partial T)_V(\partial \ln <\tau> / \partial P)_T$$

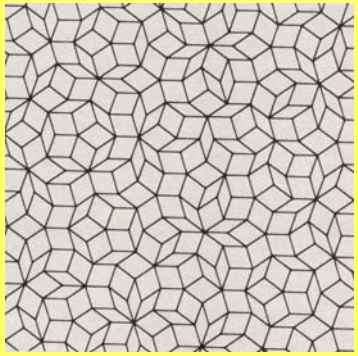
Data of Williams 1964 for PMA
show that Qv/Qp ≥ 0.65

$$(\partial \log <\tau> / \partial P)_T = 1 - 3kb^{-1}$$

This rules out free volume theories
Favours thermal activation of the process

DYNAMIC HETEROGENEITY.

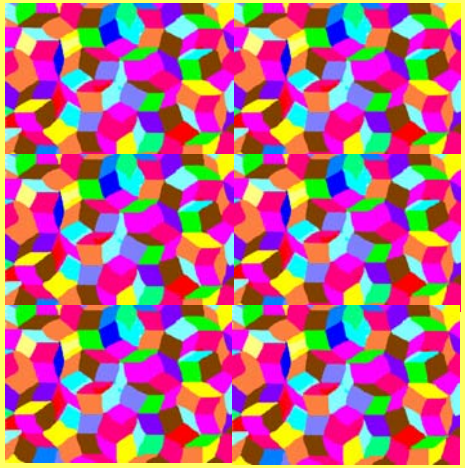
At the mesoscopic level amorphous polymer is heterogeneous



2-D Cartoon: Penrose Tiling of a mesoscopic region

No symmetry, so it is a disordered system

Paint in the energies of the small regions at t = 0



Snapshot of an ensemble at time t = 0

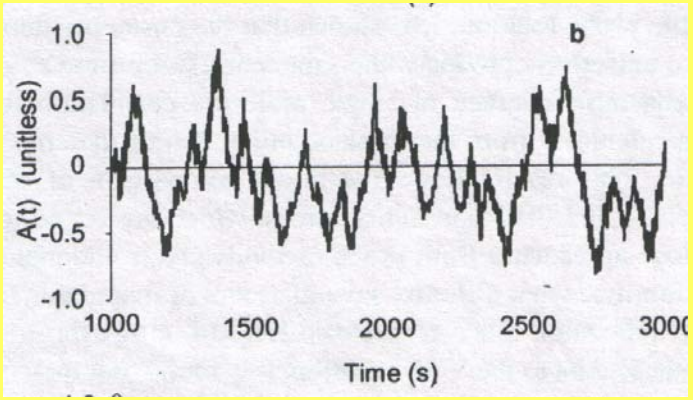
The local regions span the range of dynamical behaviour - giving **slow to fast relaxations**

Motions occur in the local regions; continual exchange of energies between the regions changes their dynamics continually

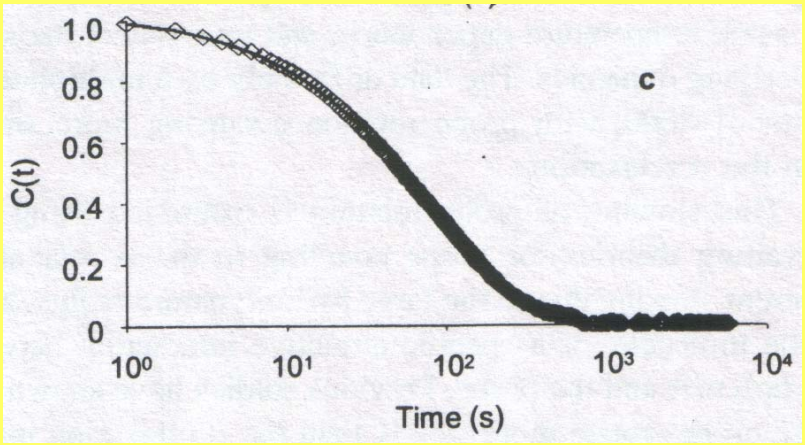
Single Molecule Motions: Rhodamine G in Polymethyl Acrylate

Deschenes & Vanden Bout, J Chem Phys 2002, 116, *5850*

Real-time polarized fluorescence anisotropy
probes rotational motions of single dye molecules in PMA above Tg



Optical signal vs. time at 291 K



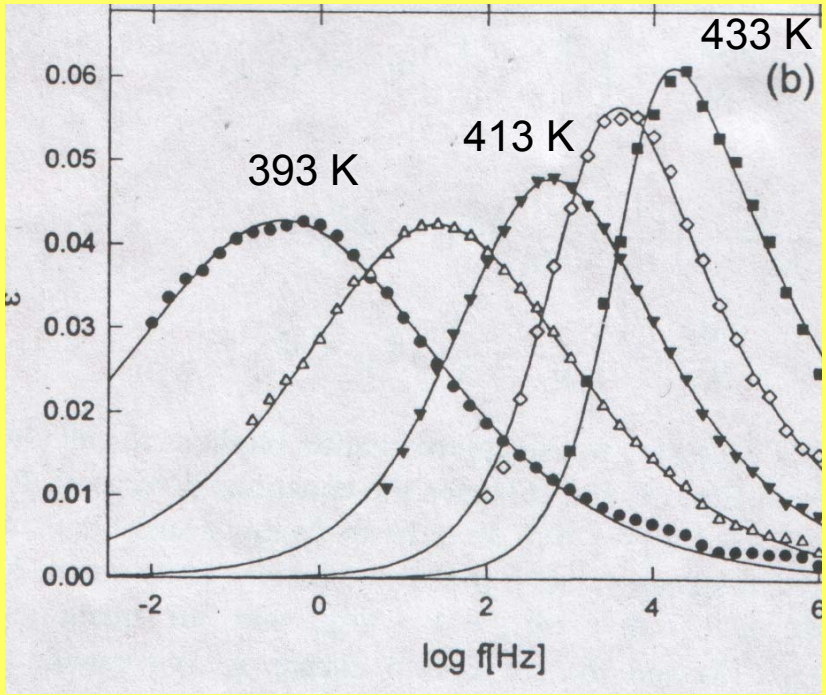
Time-correlation function C(t)

C(t) obeys KWW function with $\tau_{KWW} = 99\,\mathrm{sec}$ $\beta = 0.73$

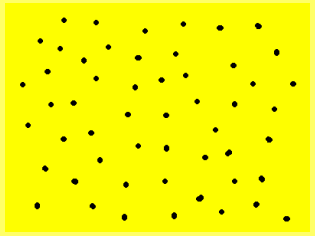
Miscible Blends of PStyrene / P-ortho-chlorostyrene

Miura, MacKnight, Matsuoka & Karasz Polymer 2001

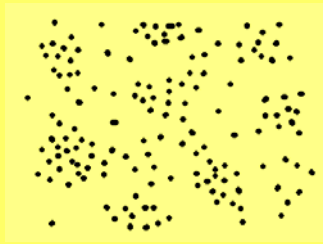
Loss curves broaden as T is reduced due to '**concentration fluctuations**'



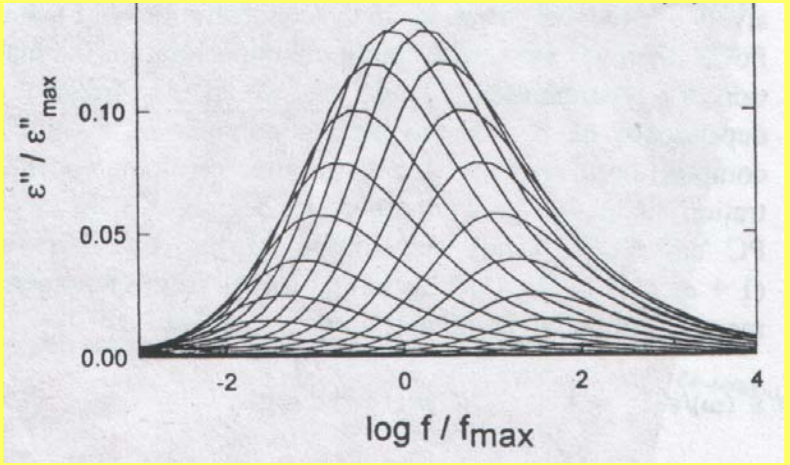
50 mol % PStyrene/Po-Chlorostyrene



High temperature

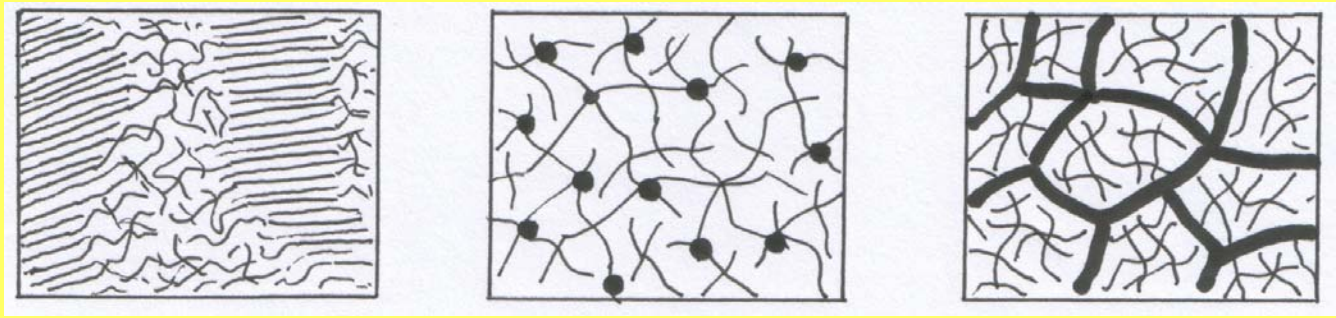


Low temperature

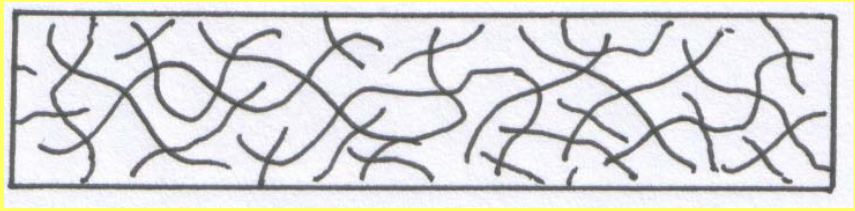


Simulated Loss curve at 413 K

Constrained Motions in Polymers



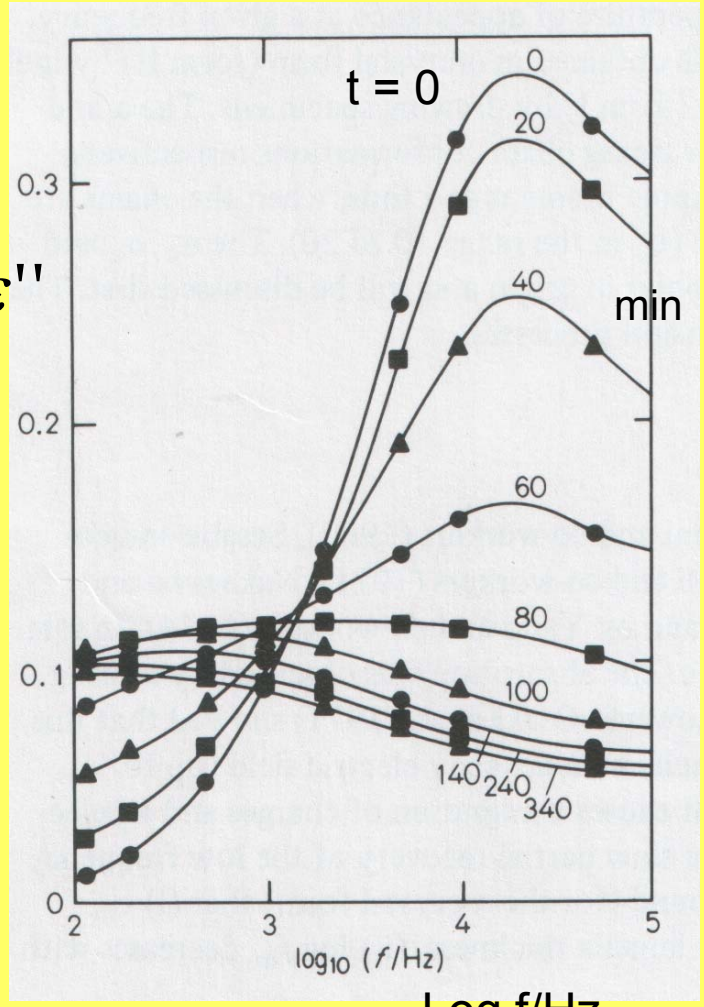
Crystalline Networks Gels, Zeolites



Ultra-thin films < 20 nm

Real-time crystallization of amorphous PET

Tidy & Williams Adv Polym Sci. 1979



ε''

Log f/Hz

Quenched (amorphous) PET is isothermally crystallized at 106.7 K

Normal amorphous phase is replaced by Abnormal amorphous phase as Spherulitic crystalline material is formed

But only 50% crystalline !

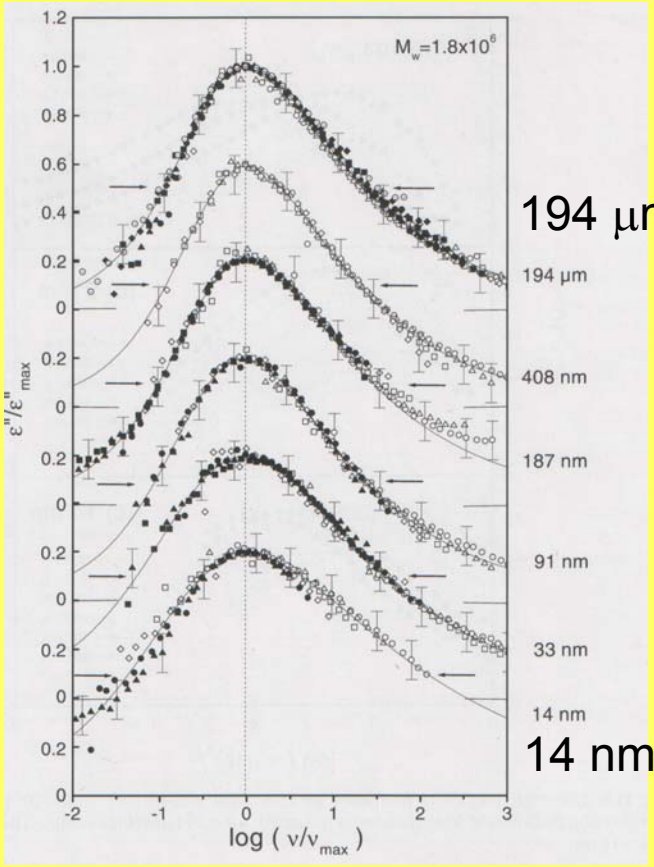
Many recent papers by

Ezquerra & Balta-Calleja, Floudas

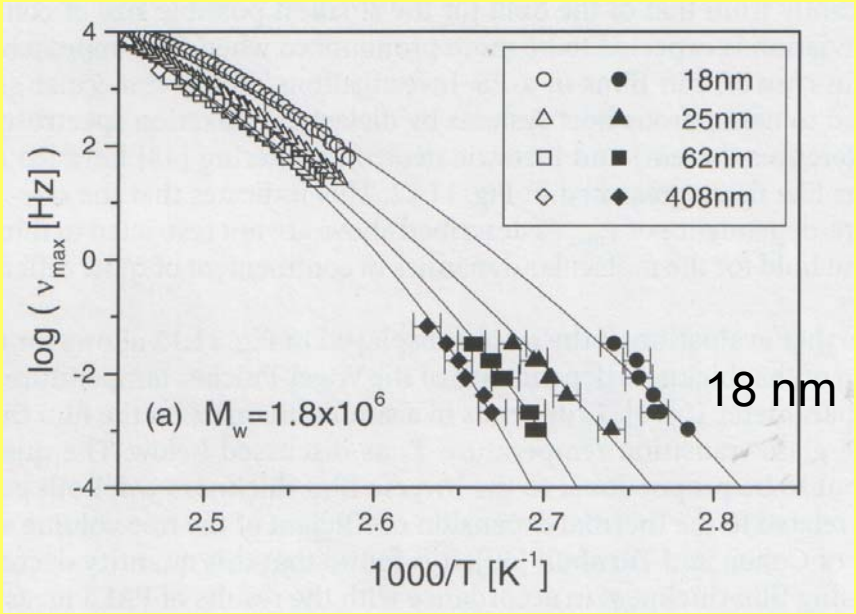
for different crystallizable polymers

α-relaxation in Ultra-thin films of Polystyrene

shown by Hartmann, Fukao & Kremer in Kremer & Schonhals 2003



KWW behaviour



Fmax increases as **d** decreases

Tg decreases as **d** decreases

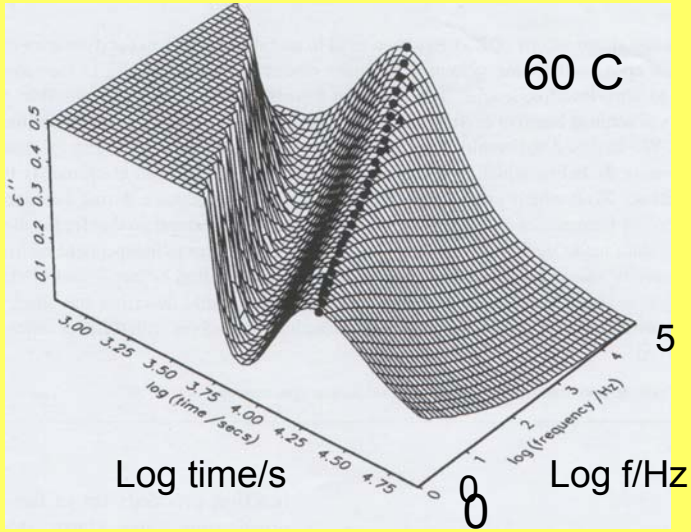
ΔTg = 20 K from bulk to 18 nm

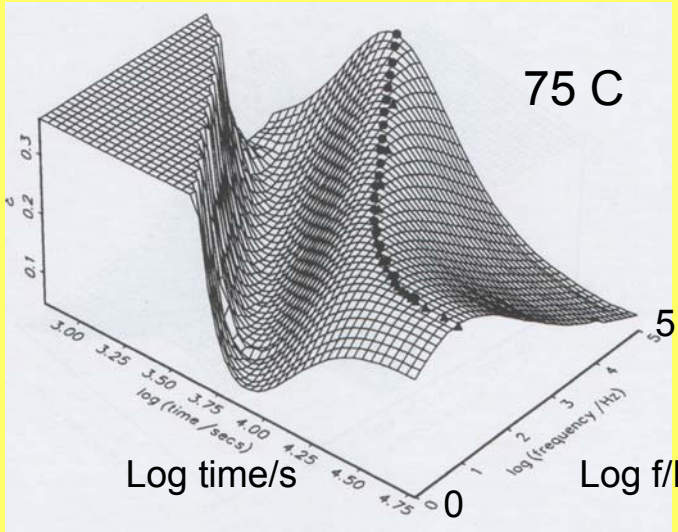
Real-time bulk polymerization of an epoxide/boroxine mixture

Williams, Smith et al Polymer 2001, 42, 3533

α–process goes to ultra low frequencies at 60 C so glass formed

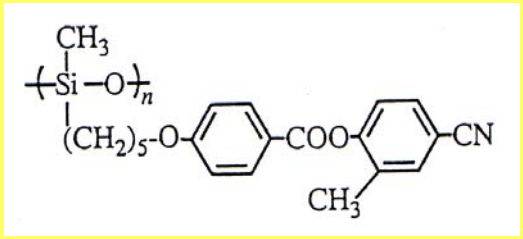
settles at ~ 300 Hz at 75 C so elastomer formed





Floor Temperature for reaction = 72 C

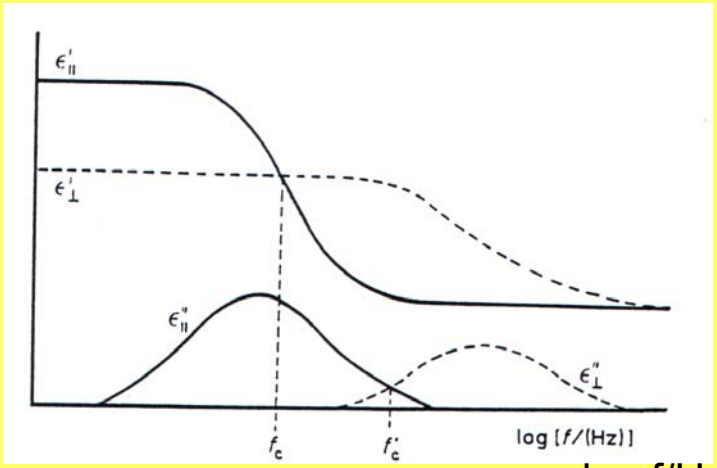
Side-chain LC Polymers: Anisotropic dielectric properties.



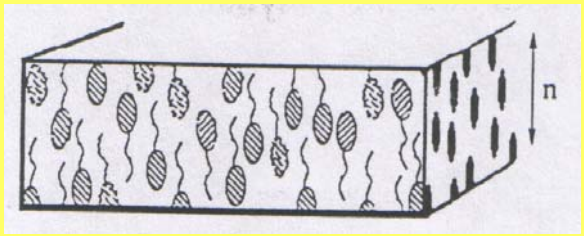
Nematic siloxane LCP

Araki and Attard, Liq. Cryst. 1988

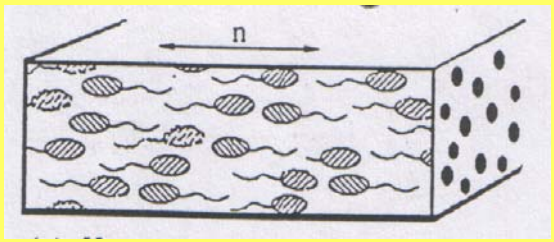
$\varepsilon(\omega)$



log f/Hz



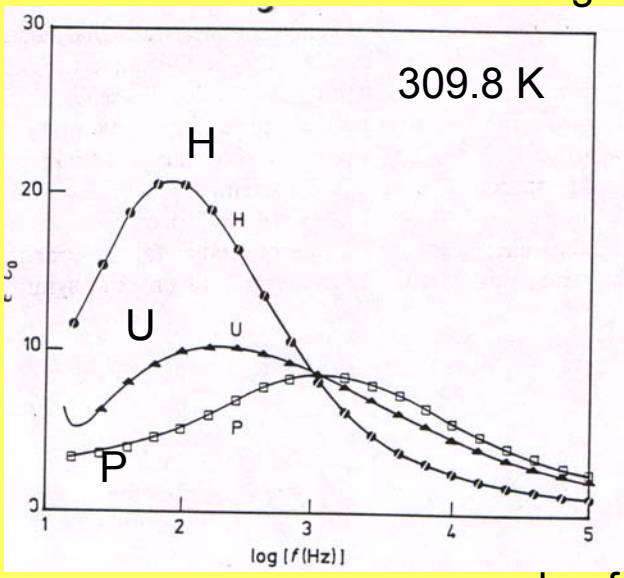
a



b

a Homeotropic; b Planar

$\varepsilon'' C_0$



log f/Hz

Complex Systems: Challenges for BDS

Confined Systems

Molecules in Zeolites, Nano-Porous Glasses, in Mesoporous Membranes

How does confinement affect molecular mobility ?

Ultra-thin Polymer Films

Does Tg change remarkably as d decreases???

Liquid Crystal Systems

Polymer Dispersed Liquid Crystals, Low Molar Mass Liquid Crystal Gels

Alignment in E-fields seen in BDS experiments

Crystalline Polymers

The abnormal amorphous phase between crystallites revealed and studied in real time as material crystallises

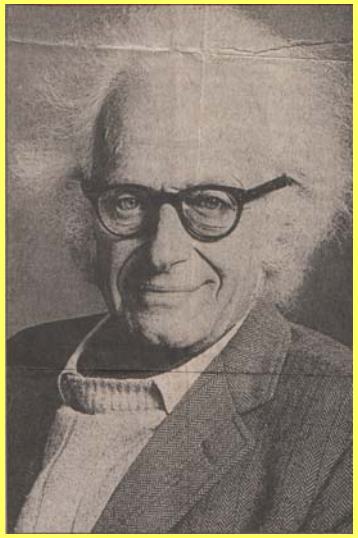
Systems undergoing CHEMICAL CHANGE

Monitoring photochemical transformations in real time at microwave frequencies

‘’If I (we) have seen further it is by standing on ye shoulders of Giants’’ **Isaac Newton**

C.P. Smyth

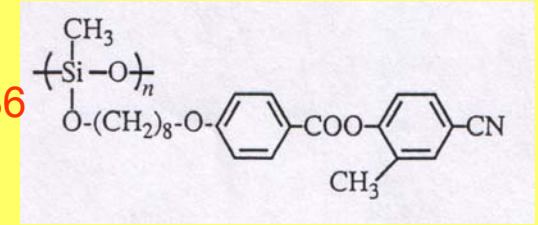
R.H. Cole



H. Frohlich

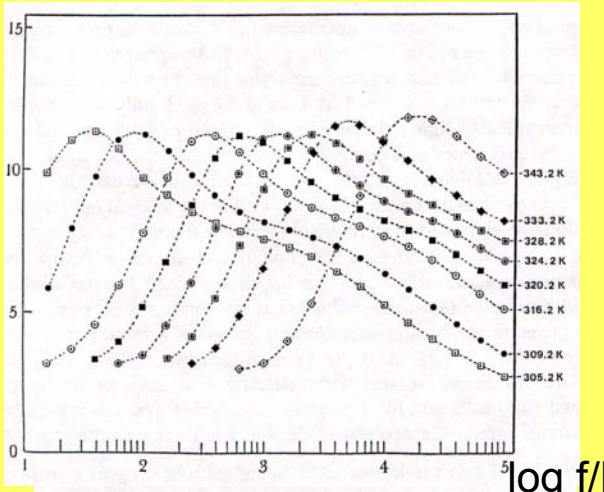
Smectic siloxane LC Polymer

Attard & Williams Liquid Cryst. & Brit. Polym.J 1986



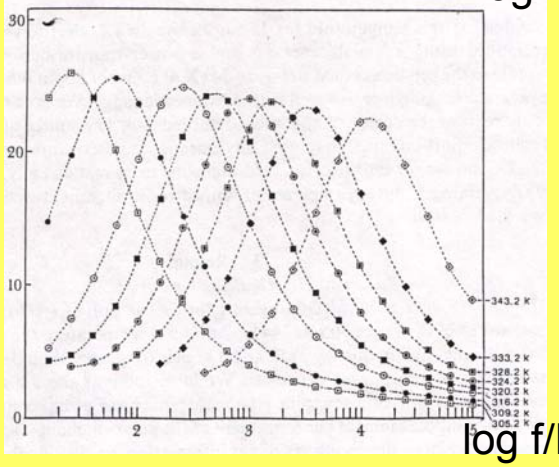
Unaligned material

Shows two relaxation regions
δ–process at low frequencies
α–process as a h.f. shoulder



Homeotropic material

Shows one process, δ–process



$$\varepsilon'' = \frac{(1+2S_d)}{3}\varepsilon''_{//} + \frac{2(1-S_d)}{3}\varepsilon''_{\perp}$$

Sd is the DIRECTOR ORDER PARAMETER

Theoretical approaches to the α-process to predict Super Arrhennius and KWW behaviour

Simulations
Molecular Dynamics Roe 1987, Boyd and Smith 1990's -
Monte Carlo Binder, K Kremer & Paul 1990's -, Pakula 1990's –

Configurational Entropy Adam & Gibbs 1965

Defect diffusion Glarum 1960, Shlesinger & Montroll 1984

Fluctuations Anderson & Ullman 1967, Williams 1975

Ising chains Glauber 1963, JE Anderson 1970, Skinner & Wolynes 1980

Rotational Isomeric models Jernigan,1972, Beevers & Williams 1974,
Monnerie, 1970, Helfand 1971

Theoretical approaches contd

Based on KWW function Ngai 1987-

Mode Coupling theory Gotze 1988-,

Energy Landscapes Angell, Sillescu, Diezemann 1998-, Schweizer 2003-

Tiling Models Stillinger, Weber & Fredricksen 1985

Mosaics, frustrated domains, dynamic heterogeneity
Kivelson 1995-, Wolynes 2001

Problem. Most of these theories, with their adjustable parameters can be fitted to data for α-process, so new criteria needed !

Answer. Study selected sub-ensembles within materials