Electron Paramagnetic Resonance
and
Electron Spin Echo
Evidence
of Molecular Dynamics in Polymers

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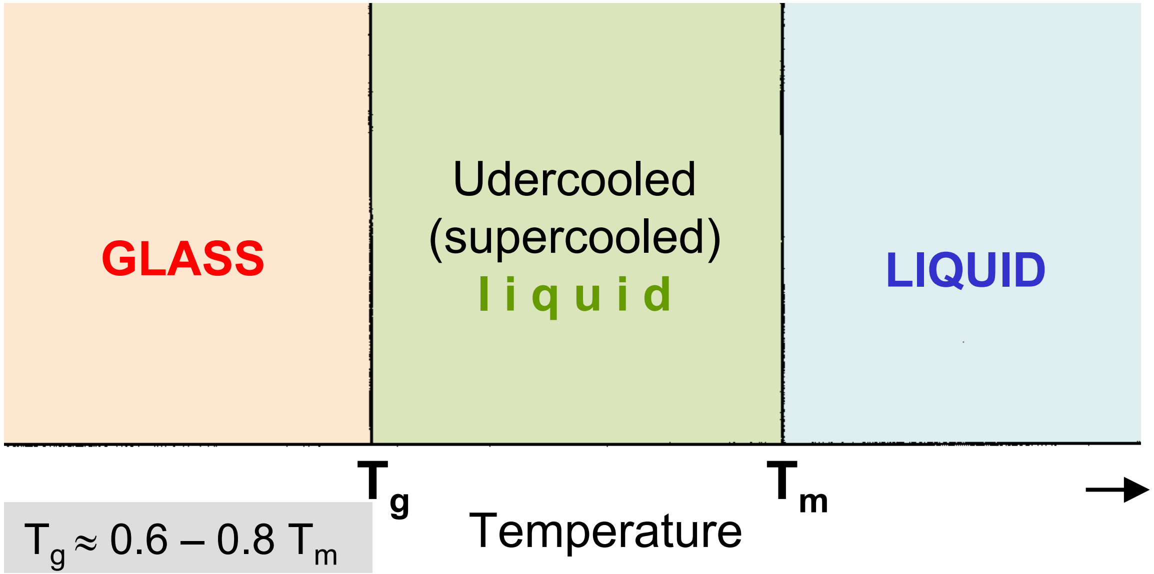
Polymers, glasses and amorphous solids are similar to the crystalline solids:

- similar mechanical properties
- carry sound waves
- carry heat

But they are **isotropic** with **distribution** of microscopic physical parameters.

It is a consequence of a lack of long range order although a considerable **short range order** exists

Central problem: **GLASS TRANSITION**



$T_g \approx 0.6 - 0.8\ T_m$

Glass transition T_g:

a) when **viscosity** is higher than **10^{13} Poise**

b) when **thermal fluctuations** in undercooled liquid become to slow to be measured in experimental time the i.e.

$\tau = 10^2 - 10^3$ second

Any material vitrifies if its liquid is cooled down sufficiently fast

Most of materials can exist in undercooled liquid state. They are called **glass formers:**

- **with strong covalent bonds (*silicate glasses*)**
- **with hydrogen bonds (*glycerol, alcohols*)**
- **with non-directed van der Waals and ionic interactions**
- **polymers**
- **metals**

What is structure of a glass?

„True" glass → after a rapid quenching ?

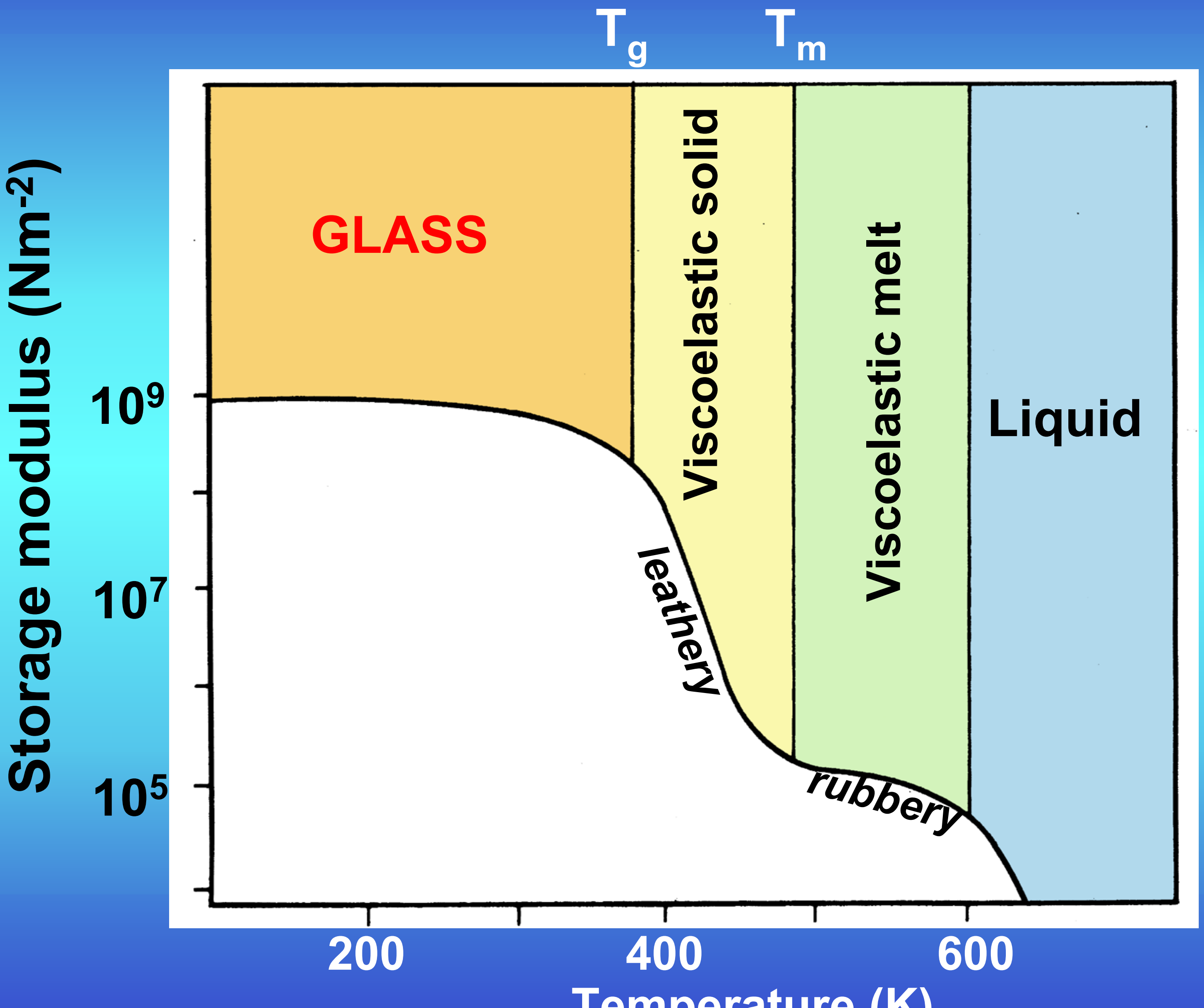
Macroscopic structure:

- more „phases" or intermediate states than in the simple phase diagram

a) in **thermoplastic (linear) polymers**
depending on the temperature (and measured frequency)

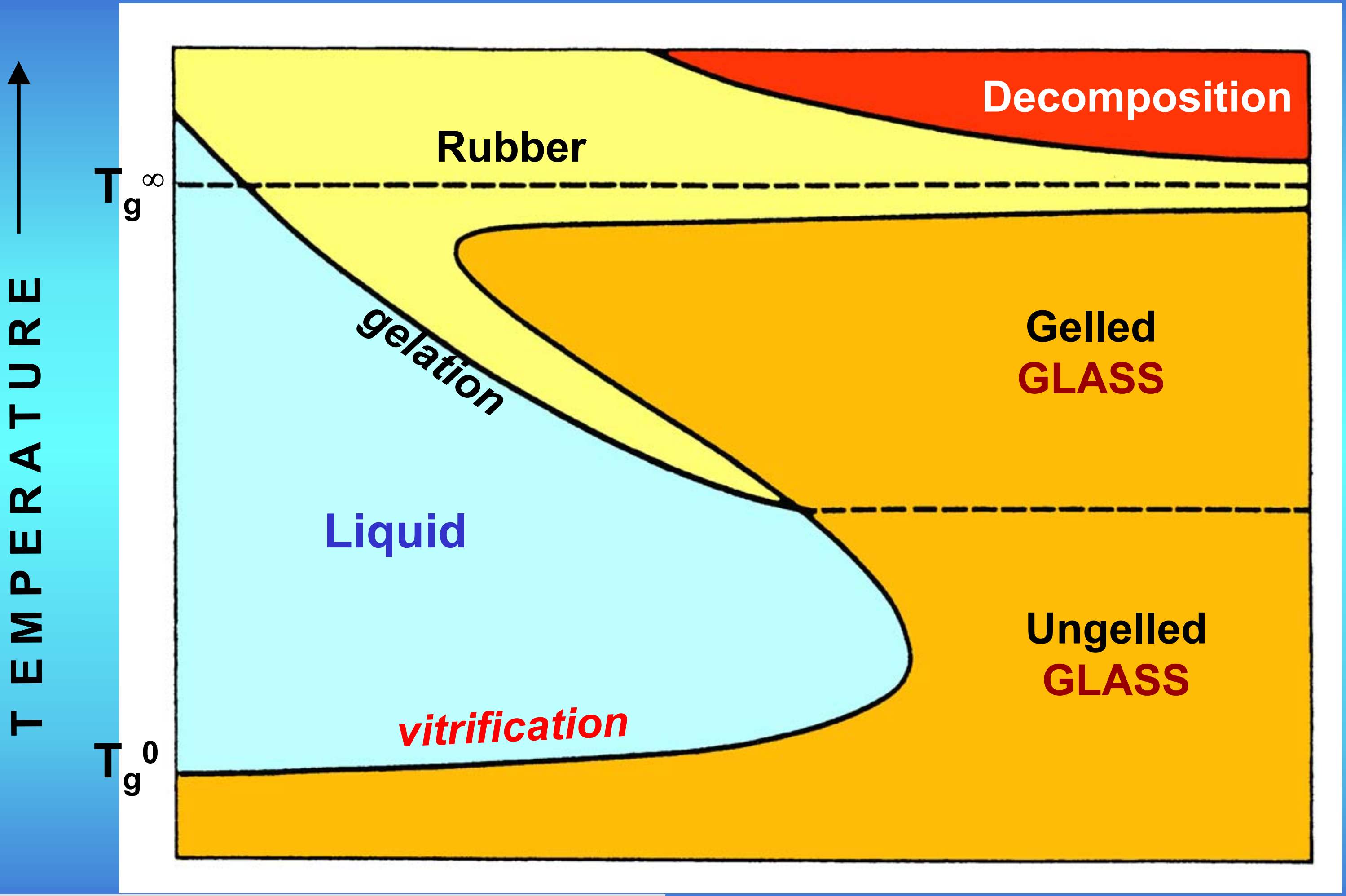
b) in **thermosetting polymers (resins)**
depending on the temperature and time

Four states of thermoplastic amorphous polymer (polystyrene, T_g = 373 K)



Temperature (K)
at constant frequency (10 rad/s)

Generalized time-temperature- transfomation (TTT) for the curring of a thermosetting polymer (resin)

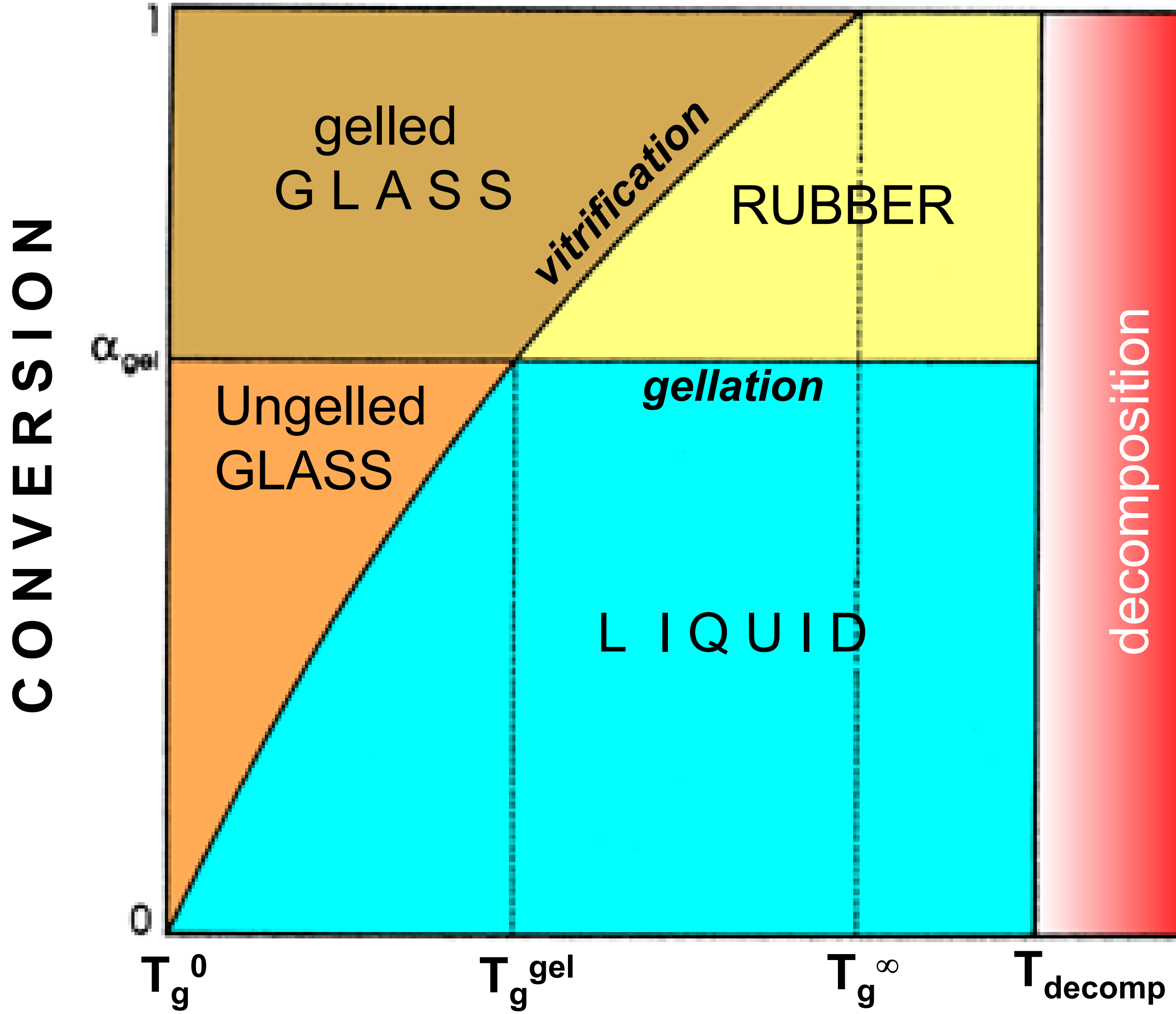


Gillham's diagram, 1986

T_g^0 –thermal glass transition
T_g^{∞} - maximum posssible T_g
(minimum cure temperature)

S-shaped glass transition line

Conversion-temperature-transformation (CTT) diagram for thermosetting polymers (resins)



MICROSCOPIC STRUCTURE:

- short range order vanishes on distance of a few neighbours

- local structure of a glass in the lenght scale 5 - 10 nm

decides on its properties and stability

(E. Courtens....., 2001)

Dynamics of polymers and amorphous solids is

- more complex than that in crystalline metarials
- affected by intrinsic disorder

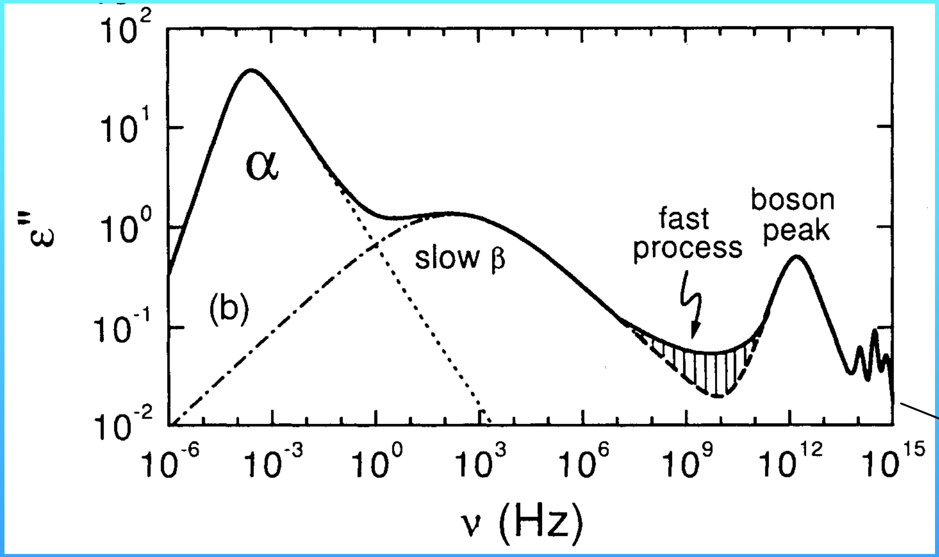
and is observed as:

- **relaxation phenomena** (aperiodic fluctuactions)

  mainly by dielectric spectroscopy
- **harmonic** or quasi-harmonic **excitations** (vibrations)

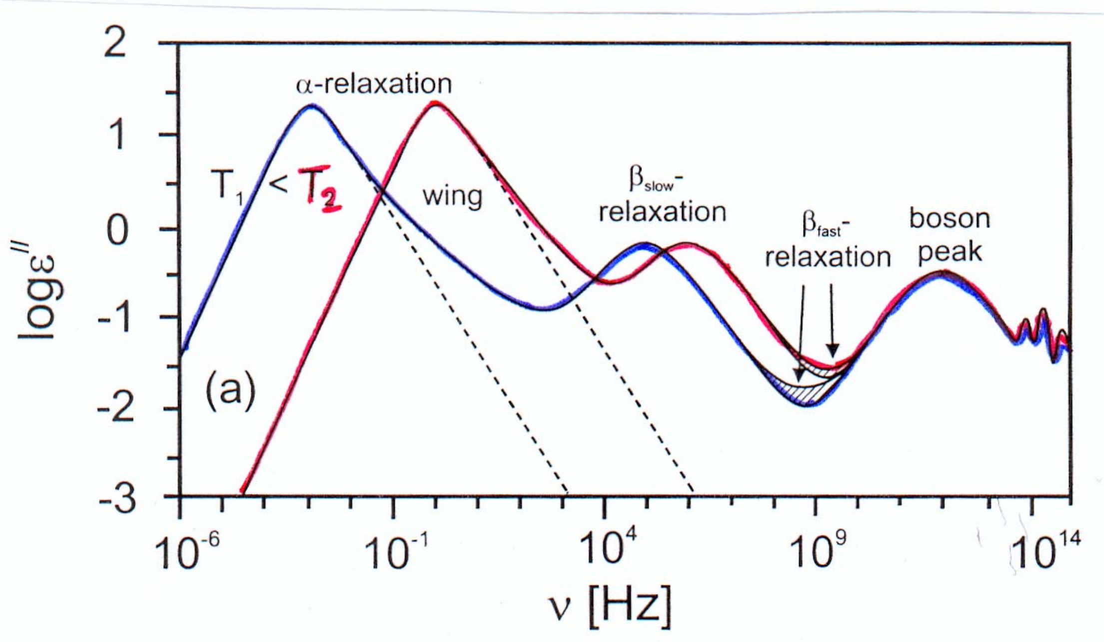
Central and most important dynamical phenomenon in glassy-forming polymers is

α - relaxation



This relaxation and other relaxation phenomena can be observed as **peaks in dielectric losses ε''**

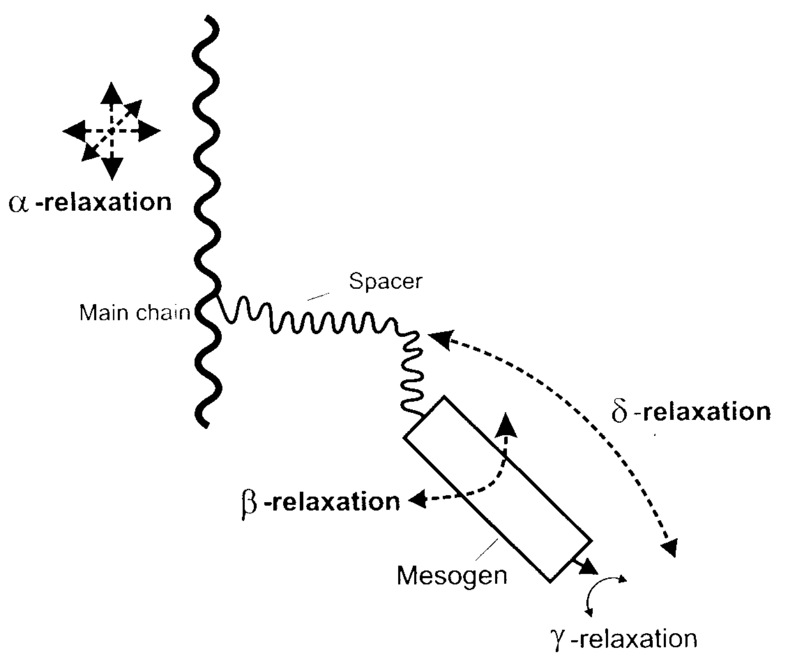
F. Kremer, A. Schönhals (Eds)
Broadband Dielectric Spectroscopy
Springer, Berlin 2003, p. 134



At higher temperatures relaxation peaks shift toward higher frequency range

Except the main α-peak additional relaxation peaks appear:

- **β-relaxation** - slow and fast
- γ, δ, σ.......**relaxations**
- **boson peak** (harmonic excitations)



α and β relaxations reflect slow dynamics

α - relaxation (primery response)

≡ structural relaxation ≡ dynamic glass transition

-**micro-Brownian motion of chain segments**

- **molecule fluctuates in a cage of its neighbours**.(Fluctuactions of the molecules forming the cage cannot be independent from each aother thus α-relaxation is to some extend **cooperative**)
- **forming and decay of the cage**

Characteristic features:

1. **Non-exponentiality**

   correlation function Φ(t) of fluctuations is not single exponential, but **stretched exponential**.

A **distribution of the relaxation time τ** exists

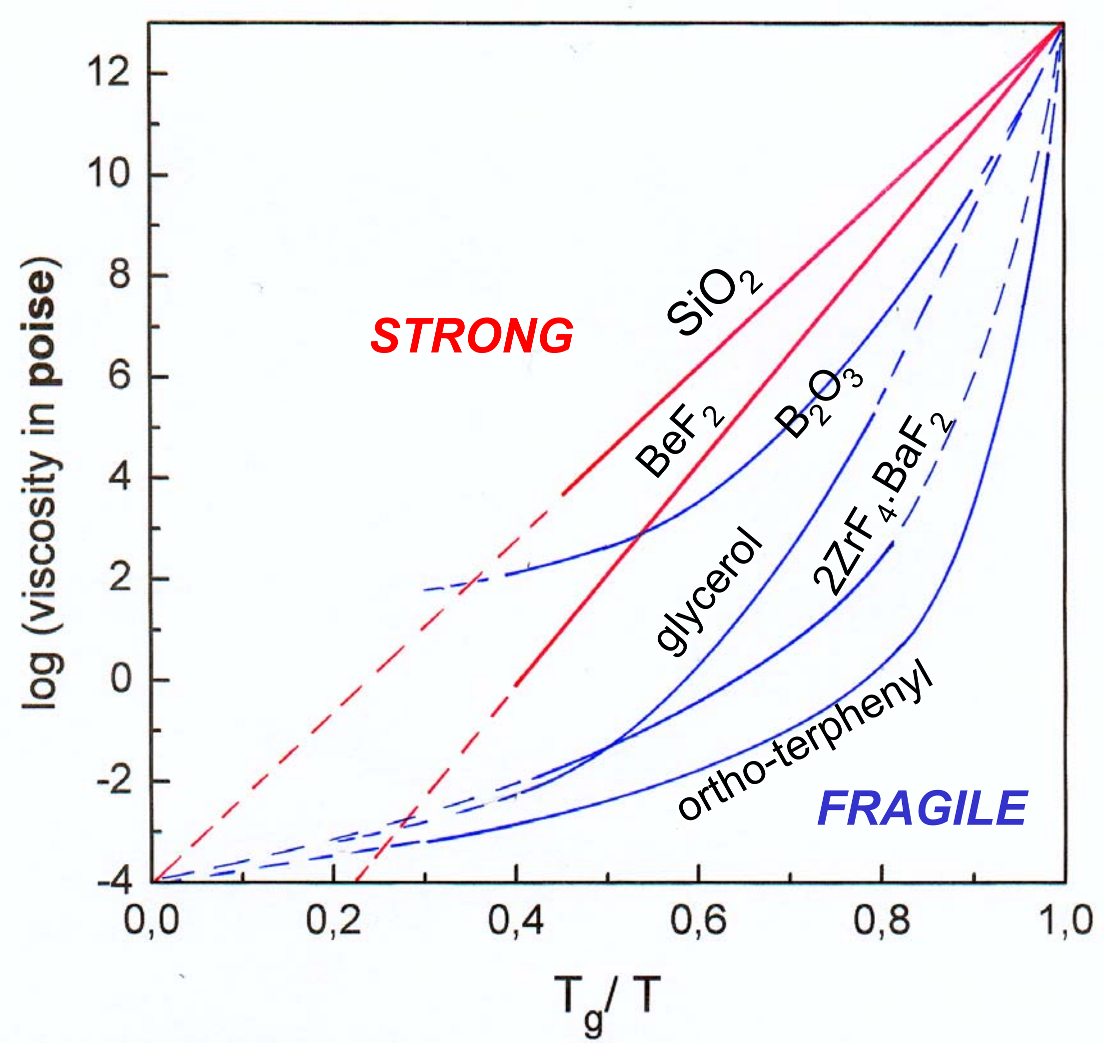
$$\Phi(t) = A \exp\left[-\left(\frac{t}{\tau} \right)^{\beta} \right]$$

β **= 0.5 – 1,** decreases on cooling

2. **Non-Arrhenius behaviour**

Angel plot :

strong and fragile glass-formers



Maxwell mechanical equation

$$\eta \approx G_{glass} \cdot \tau$$

G_{glass} – glass modulus = $10^9 - 10^{10}$ Pa

Strong glasses:

$$\tau(T) = \tau_\infty \exp\left(\frac{E}{k_B T}\right)$$

Arrhenius equation

Fragile glasses

$$\tau(T) = \tau_\infty \exp\left(\frac{D T_0}{T - T_0}\right)$$

Vogel-Fulcher-Tammann equation

T_0 – Vogel temperature
D – fragility parameter

Characteristic temperatures of the dynamic glass transition (α-relaxation)

T_g - thermal glass transition

T_0 - Vogel temperature = ideal glass transition temperature

(τ and η diverge) **typically 30 – 50 K below T_g**

T_K - Kauzmann temperature

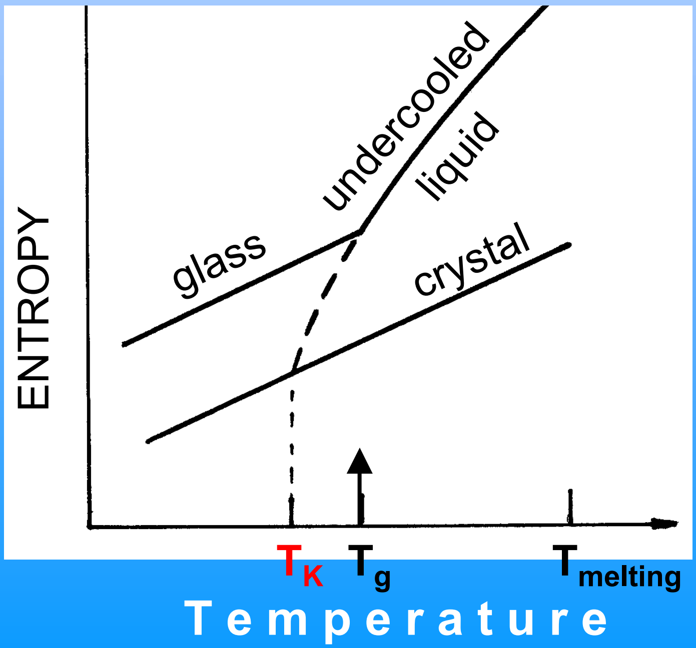
At that temperature **entropy** of the undercooled liquid extrapolated to temperatures below T_g „reaches” entropy o of a crystal. **Close to T_0.**

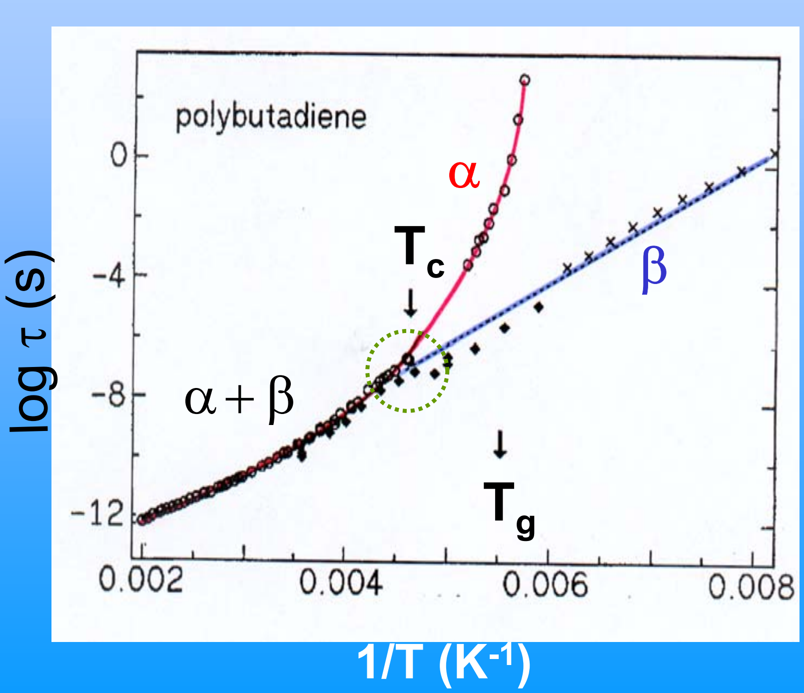
T_C - cross-over temperature

Cross-over to cooperative relaxation.

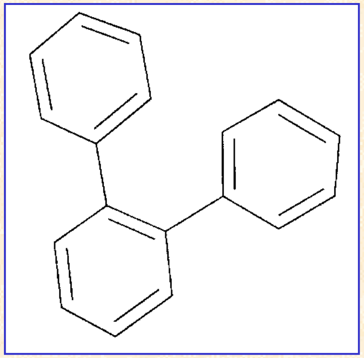
Structural arrest in the cage.

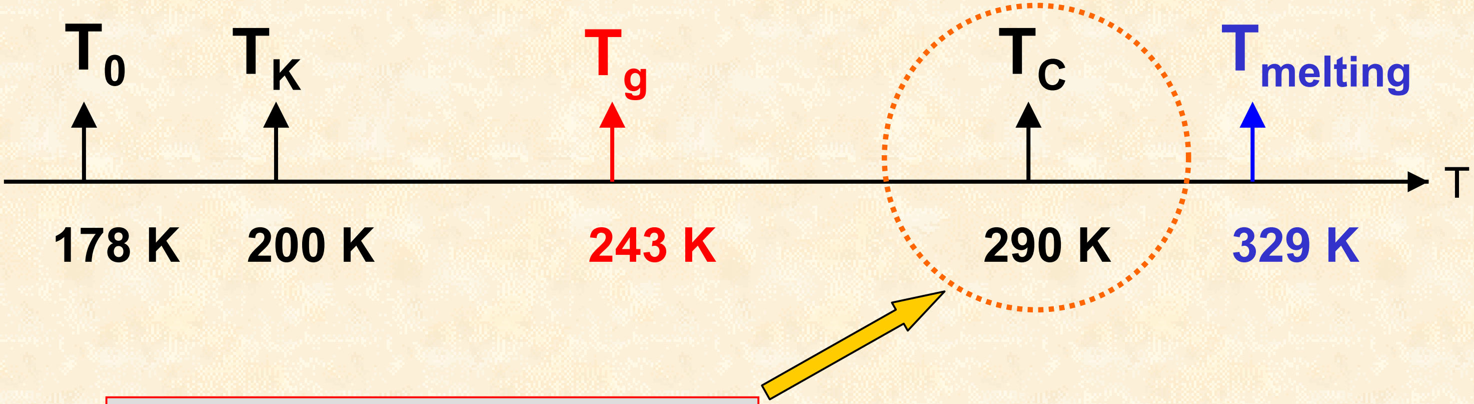
Typically ≈ 1.2 T_g





Characteristic temperatures for **ortho-terphenyl**





T_0 T_K T_g T_C $T_{melting}$

T

178 K 200 K 243 K 290 K 329 K

$\alpha + \beta$ merging region

Solid-like dynamics T_C **Liquid-like dynamics**

$\eta \approx$ **10 Pa**

- non-ergodic – ergodic state transition

- decoupling of translations and rotations

- deconvolution of translations and rotations

β- relaxation (secondary relaxation)

$$\tau(T) = \tau_{\infty} \exp\left(\frac{E}{k_B T}\right)$$

- **Arrhenius**-like temperature dependence of the relaxation time τ with

  E_a = 20 – 50 kJ/mol,

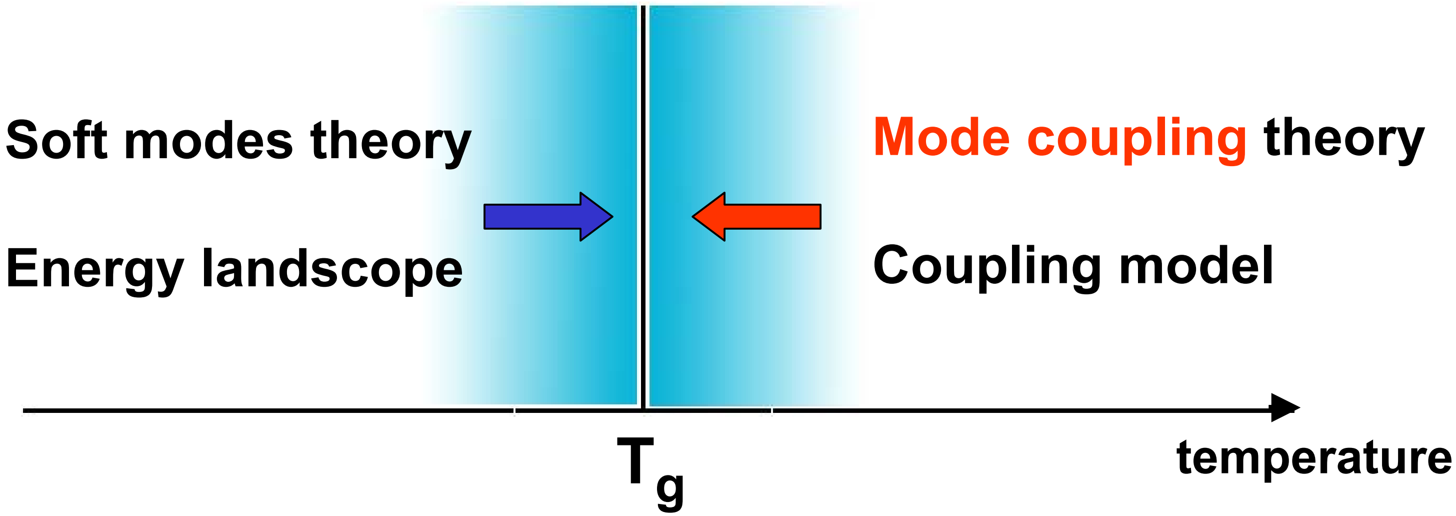
  τ_{∞} **~ 10^{-13} s** ← often smaller, indicating a contribution from **activation entropy**

- **Local relaxation**. Takes place on a local length scale not larger than a monomer unit (1.5 Å jumps, 60-90^0 rotations around the center of mass)

- **Fluctuations of localized part of the main chain.**

- **Rotational fluctuations of side groups or part of them.**

THEORY



Soft modes theory

Energy landscope

Mode coupling theory

Coupling model

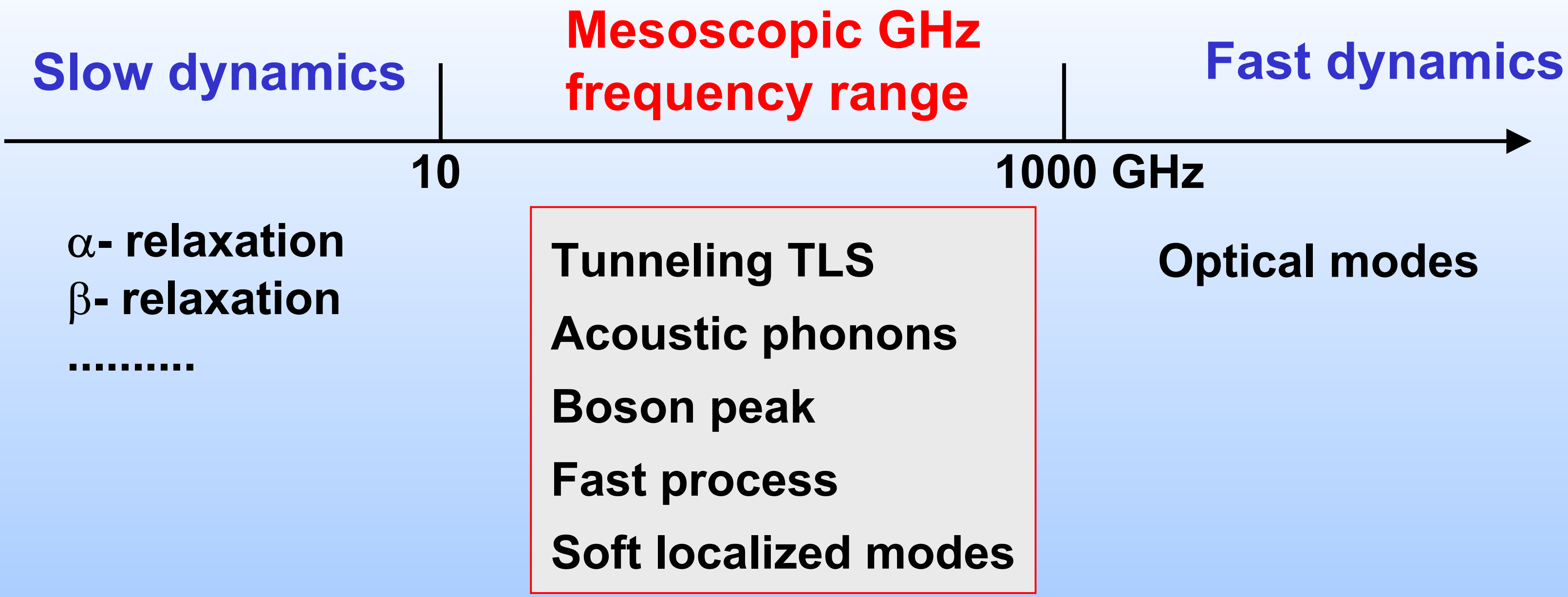
T_g

temperature

Heterogeneity of undercooled liquid close to the glass transition (?)

Can explain non-exponentiality near $T_{g:}$

There exist islands of mobility with its own dynamical parameters. An average over all islands gives broad distribution and nonexponentiality.



Slow dynamics

Mesoscopic GHz frequency range

Fast dynamics

10

1000 GHz

α- relaxation
β- relaxation
……….

Tunneling TLS
Acoustic phonons
Boson peak
Fast process
Soft localized modes

Optical modes

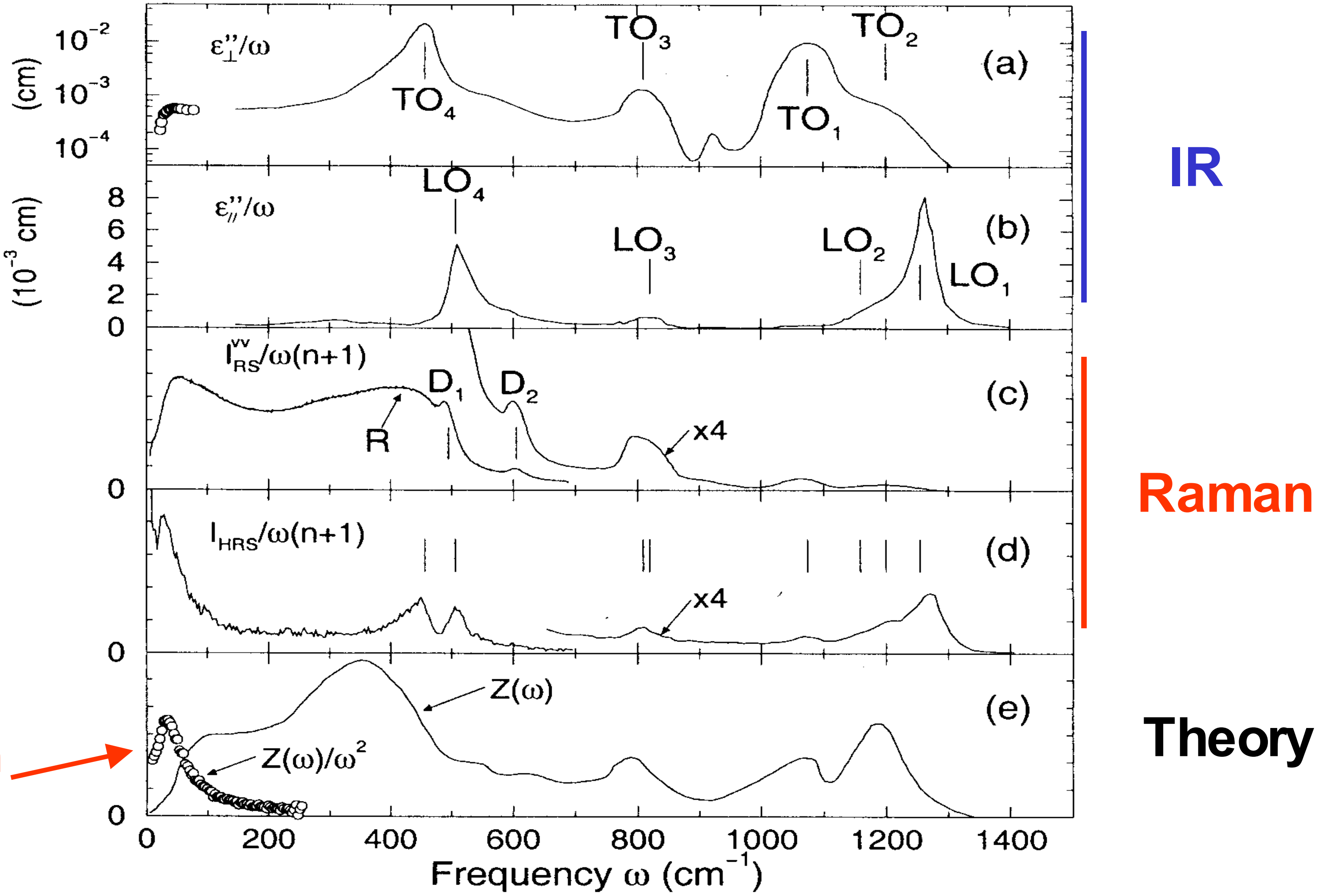
Dynamics in the mesoscopic frequency range drives (or at least strongly influences) the dynamics of the glass transition

(Sokolov, 1997)

Fast dynamics (visible in IR and Raman spectra) is **very similar to that in crystals** but also

- **forbidden transition** can appear
- **localized modes** (on defects) can exist

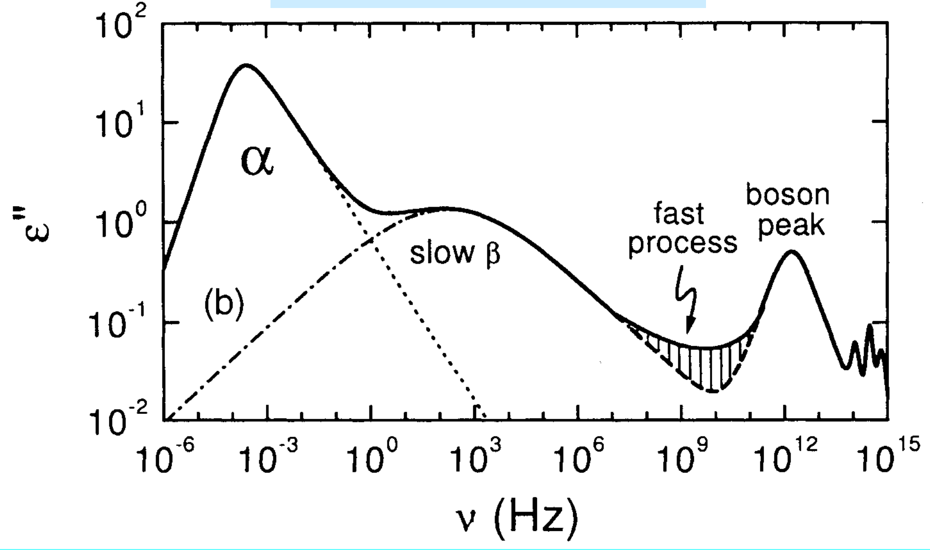
E. Courtens et al. / Solid State Communications 117 (2001) 187–200 195



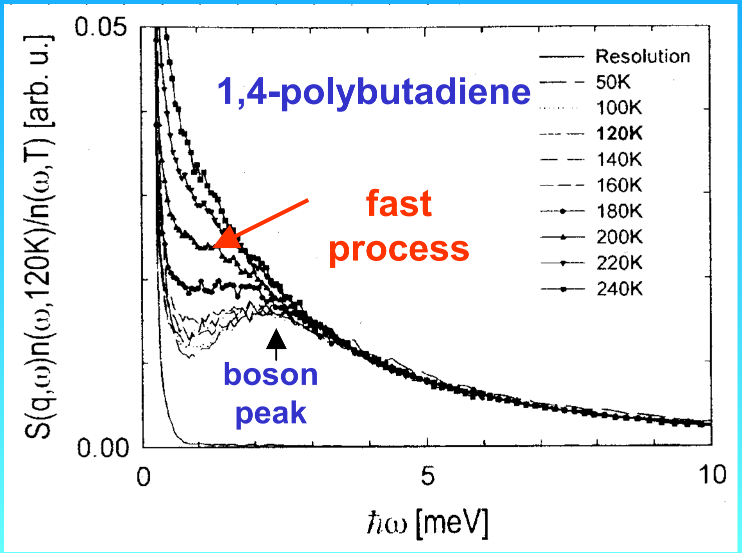
Boson peak

FAST PROCESS (β_{fast} – relaxation)

Dielectric spectrum



Incoherent inelastic neuton scattering spectra



- Appears at some „critical” temperature T_X as decoupling (deconvolution) of rotation and relaxation.

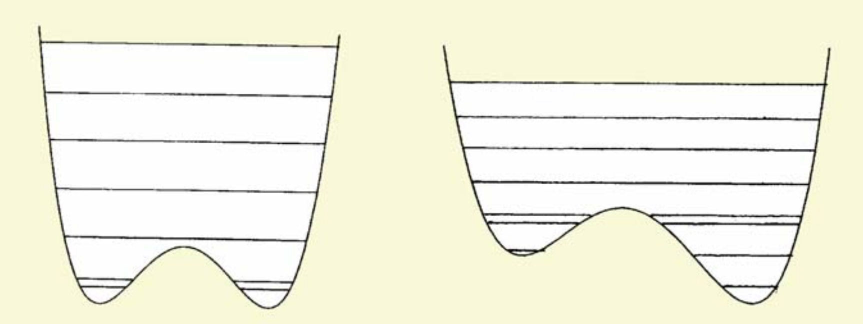
- Above T_x the mean square displacement of atoms begins to increase more strongly than linear dependence $\langle u^2 \rangle \propto T$ predicted for harmonic vibrations (Ngai coupling model)

-Vibrations in a potential well with over-barrier rotations (- C – C – torsional rotations ?)

Tunneling two-level systems (TLS) – below 1K

- asymmetrical double-well potentials, disordered modes

Group od atoms can exist in different configurations with small differences Δ in energy, i.e. potential energy surface can have many shallow minima and can be considred as a collection of asymmetrical double-wells (TLS):

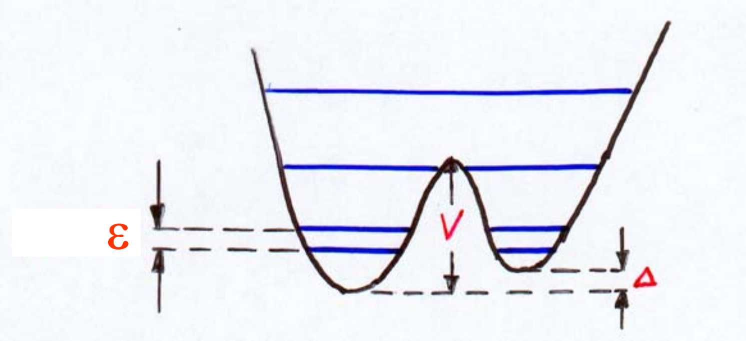


Thermally activated reorientations between the potential minima can be produced by **1. Phonon assisted tunneling** (one-phonon process) - **dominates**

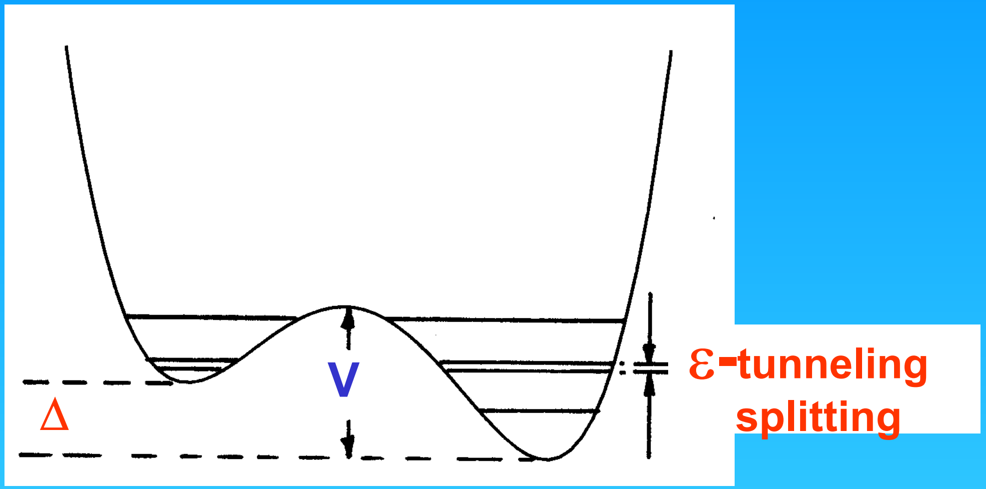
$$\frac{1}{\tau} = A \cdot \Delta^2 \varepsilon \coth\left(\frac{\varepsilon}{2kT}\right) \quad \varepsilon = \text{tunneling splitting}$$

2. Over-barrier jumps

$$\frac{1}{\tau} = \frac{1}{\tau_0} \cosh\left(\frac{\Delta}{2kT}\right) \exp\left(-\frac{V}{kT}\right) \quad v = \text{barrier height}$$



Parameters of the TLS ε, Δ, V are distributed in amorphous systems



$$\varepsilon = \sqrt{\Delta^2 + \Delta_0^2}$$

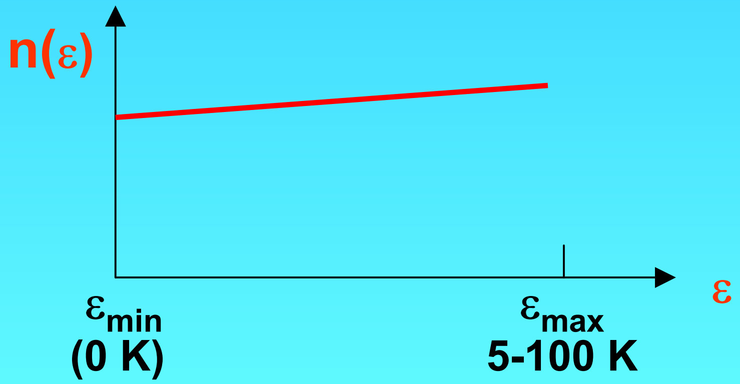
Δ_0 **= overlap energy** = coupling energy in symmetrical state

$$\Delta_0 = \hbar\omega_0 e^{-\lambda},$$

$$\lambda = \sqrt{2mV}\,\tfrac{d}{\hbar}$$

Tunneling levels are broad with the width order of 0.1 cm^{-1}

Density n(ε) of tunneling states:



Nearly constant:

$$n(\varepsilon) = \varepsilon^{\lambda}, \quad \lambda = 0.4 – 2$$

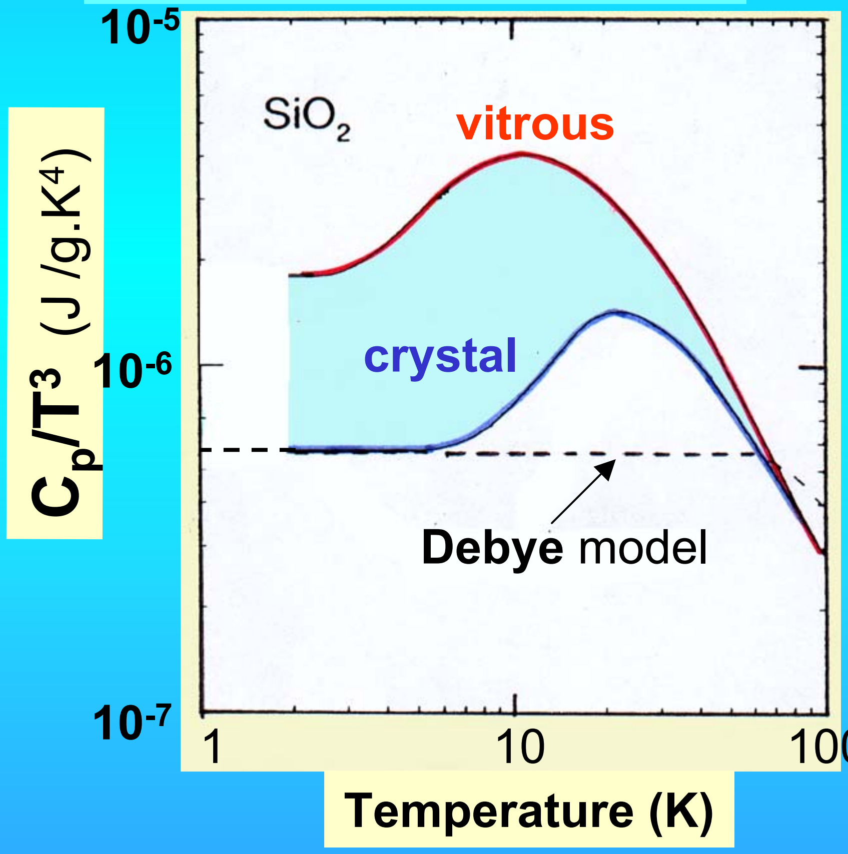
Thermal anomalies in amorphous solids

In crystalline materials the Debye model of phonon dynamics gives:

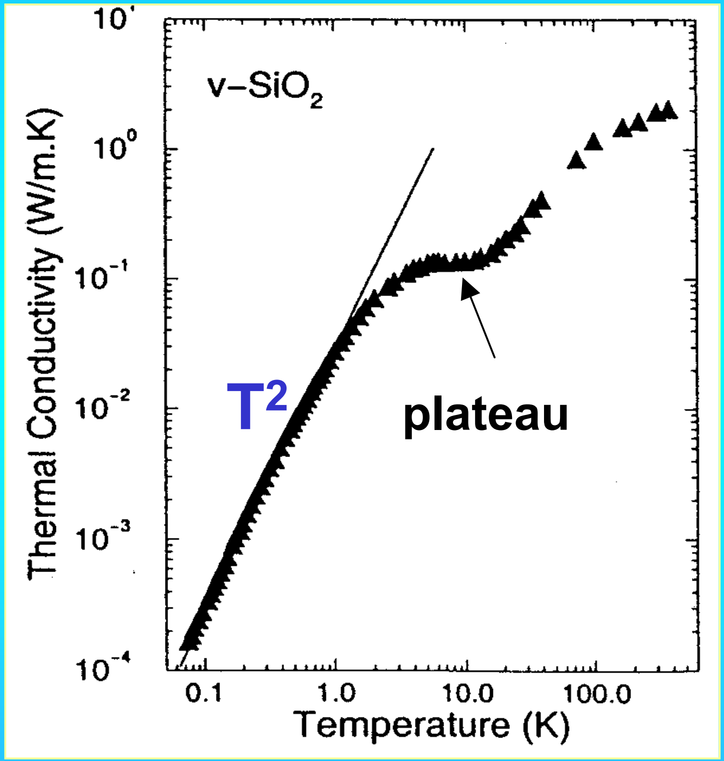
specific heat $c_p \propto T^3$

thermal conductivity $\kappa \propto T^3$

In vitreous silica - v-SiO_2



Excess of vibrational modes

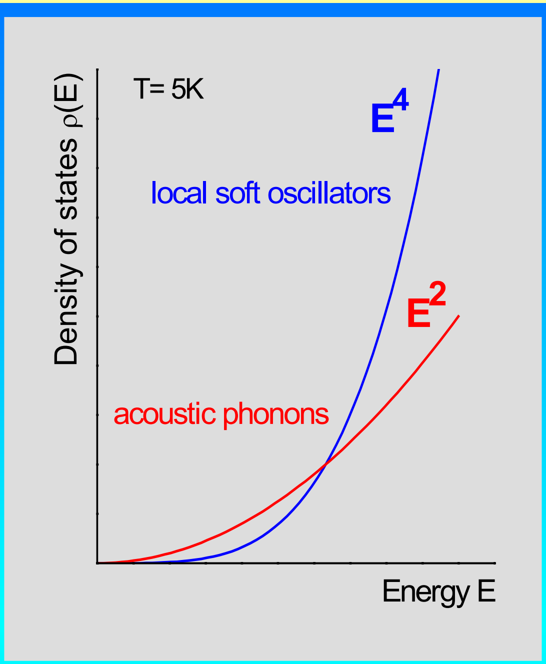


1. TLS do not conduct heat (→T^2)
2. Phonon mean free path tends to zero (**plateau**)

Acoustic phonons and local oscillators in amorphous solids

Acoustic phonons (plane-waves) exist
at **low temperatures** only and have **picosecond lifetime**

They are dominated by **localized excitations**
(**soft local oscillators**) with density of states growing
as **E^4**.



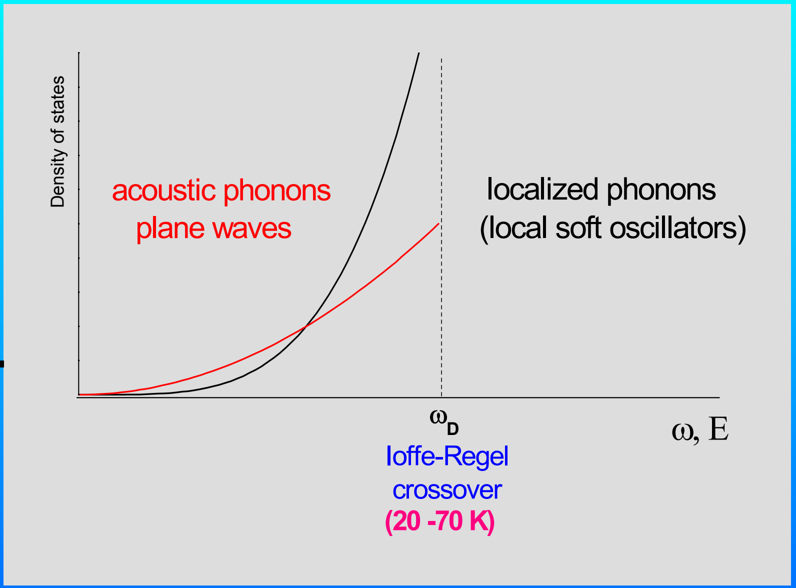
Number of local oscillators grows rapidly with temperature
and phonon scattering on these centers leads
to a shortening of the **phonon free path Λ.**

As the results at some frequency, so called
Ioffe-Regel crossover frequency ω_d :

$$\lambda_{\mathbf{phonon}} = \Lambda_{\mathbf{phonon}}$$

phonon wavelength= phonon free path

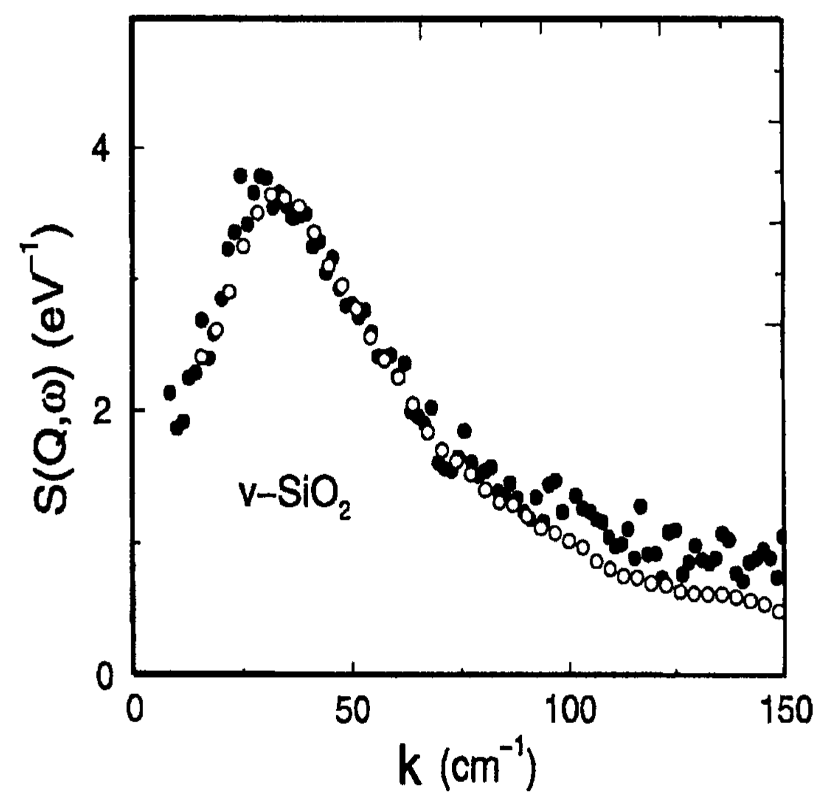
and concept of phonons has further no sense.



Above the crossover frequency ω_d
only localized excitations exist

Boson peak

Boson peak it is a broad band of low frequency **harmonic excitations** (optical type) centered about **1 THz** frequency (**30 cm^{-1}** = 43 K) appearing in **disordered solids, glasses and polymers.**



Inelastic neutron scattering

Its spectrum obeys Bose-Einstein statistics $I(\omega)=C(\omega)[n(\omega)+1]/\omega$, where $n(\omega)$ is the Bose-Einstein occupation factor.

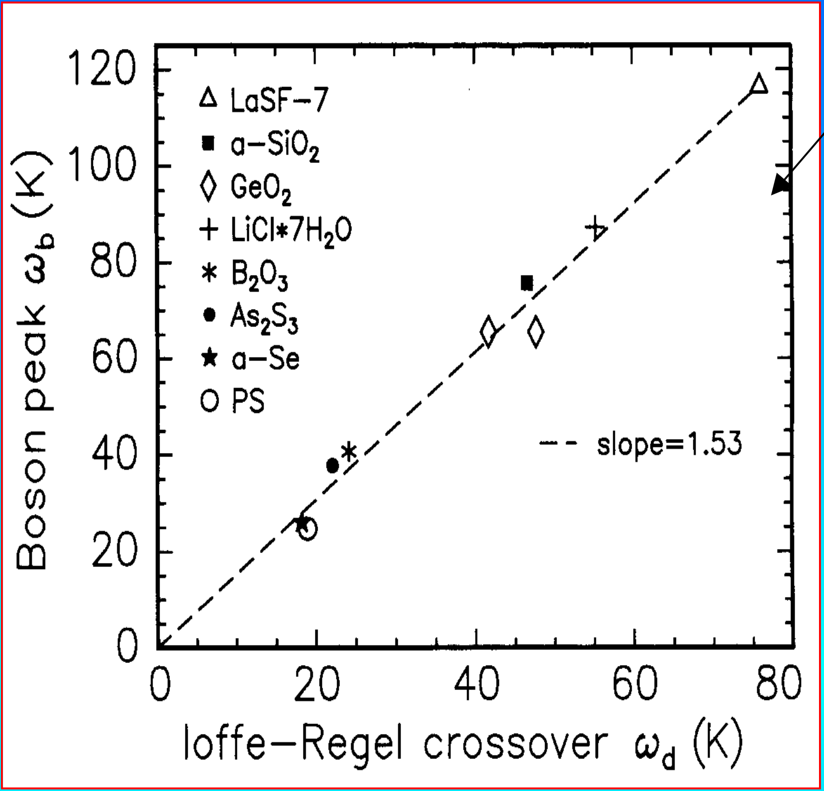
Boson peak is observed in **low-frequency Raman** spectra and in **inelastic neutron** scattering experiments

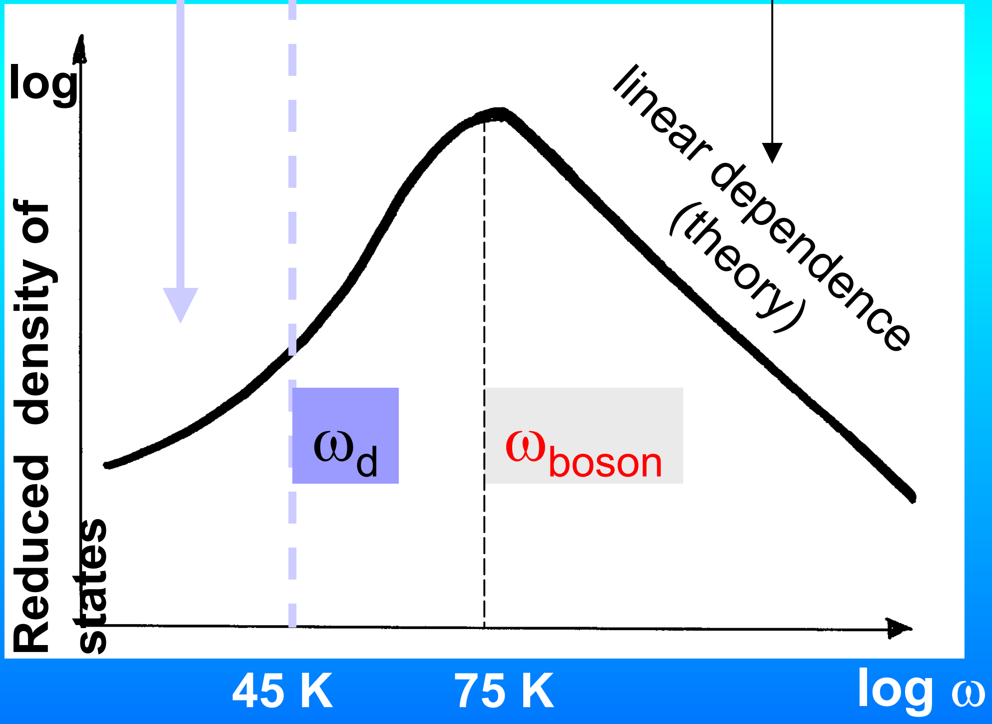
Boson peak position is related to the Ioffe-Regel crossover frequency:

Propagating sound waves =
acoustic phonons
+quasi-local oscillators

Non-propagating

(diffusive)excitations
Coupled local oscillators





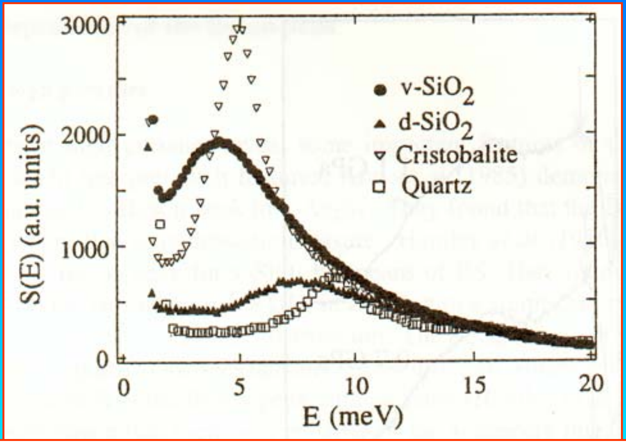
a-SiO_2

ω_d = 45 K (**Ioffe-Regel**)

ω_{boson} = 75 K

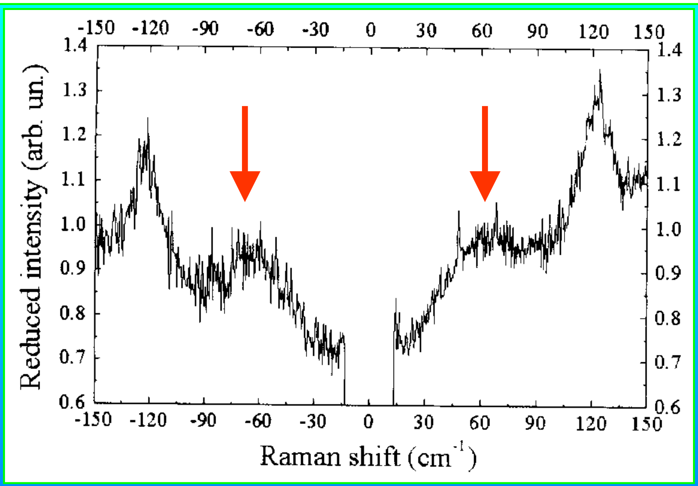
Boson peak

Boson peak exists in various amorphous materials,

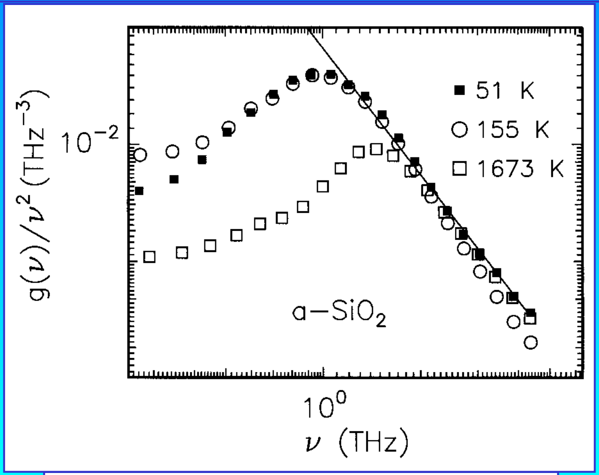


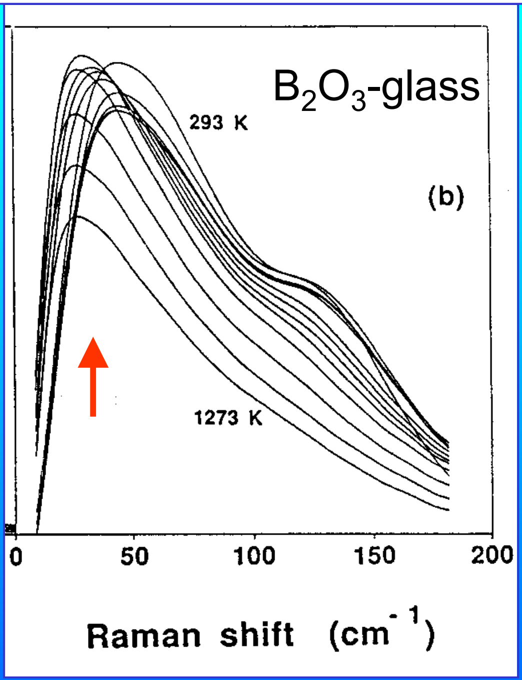
in policrystals (cristobalite, quartz)

In neutron irradiated quartz single crystal



persists over broad range of temperature,





EPR:

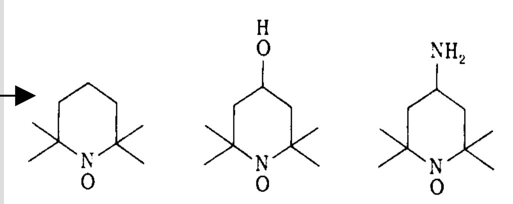
- at microwave frequencies where the most complex dynamics
- high sensitivity - 10^{14} spins/gram
- pulsed EPR (electron spin echo = ESE) very sensitive to dynamics

Paramagnetic centers:

A) Free radicals

- γ, X, UV-Vis irradiation generated
- spontaneously occurring:
  - residuals of polymeric or curing reactions
  - aging processes

B) Spin probes and spin labels (nitroxides) → of various shape and size



C) paramagnetic ions introduced into a material

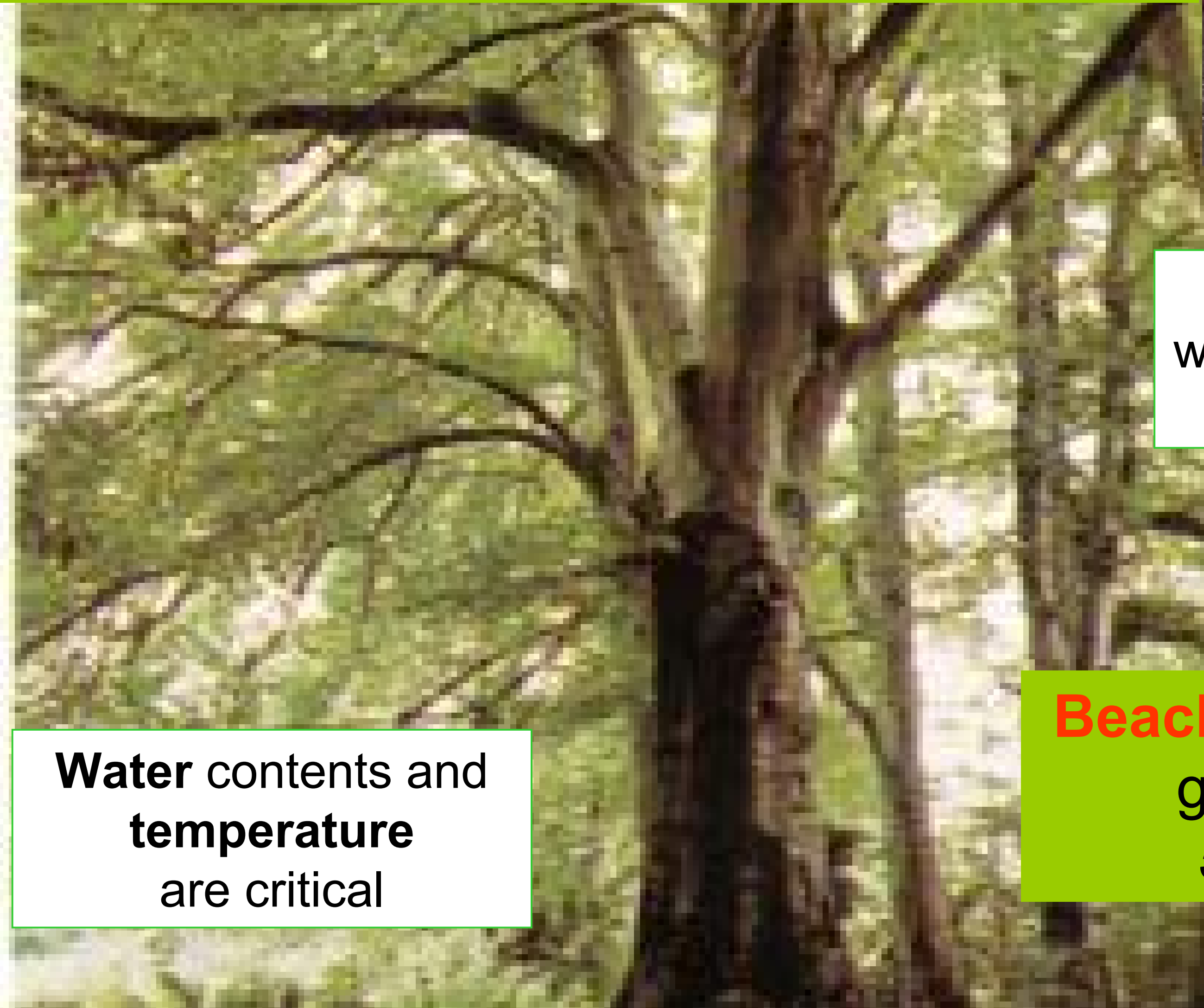
EPR applications in polymers and amorphous systems

- identification and localization of a paramagnetic center
  (EPR spectra and ESEEM spectroscopy)
- detection of the glass transition (by spin label EPR)
- detection of various dynamical regions of a material
  (spin probe EPR)
- determination of slow dynamics
  (dephasing of the electron spin echo)
- determination of dynamics of reorienting molecular groups
  like CH_3, NH_3 (spin-lattice relaxation, phase relaxation)
- localized modes of paramagnetic defects
  (spin-lattice relaxation)

EPR determination of the glass transition In beech seeds to evaluate long-term storage conditions

S. Pukacka, S. K. Hoffmann, J. Goslar, P. M. Pukacki
E. Wojkiewicz, Biochim. Biophys. Acta 1621, 48 (2003)

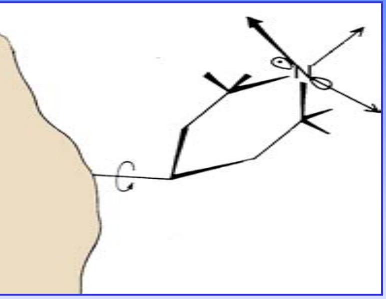
Embryo axes of seeds were labeled with TEMPO spin probes



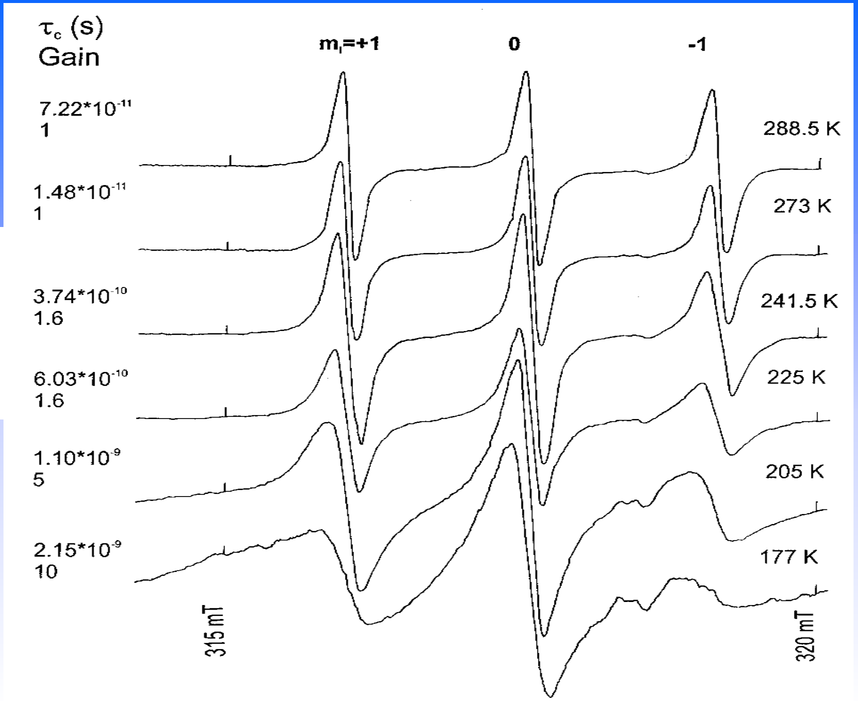
Water contents and **temperature** are critical

Beach (*Fagus sylvatica L)* give seeds *every 5-10 years only*

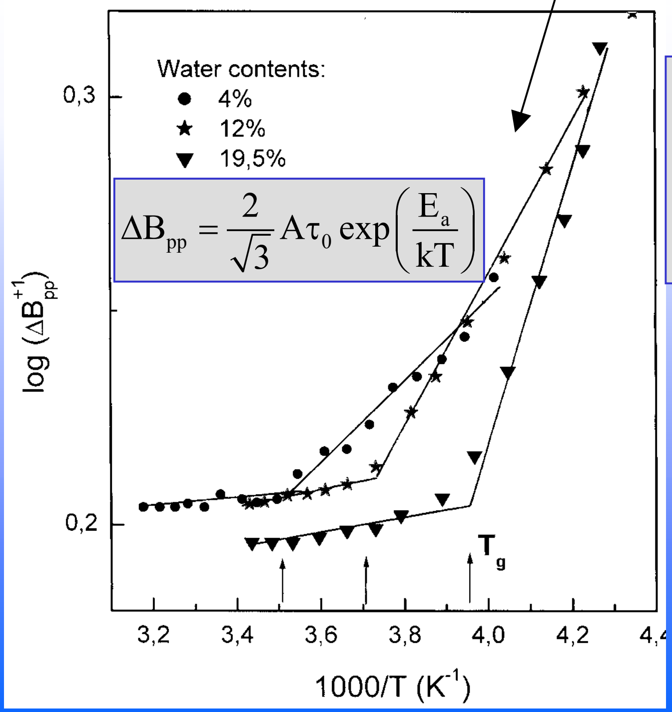
Nitroxide TEMPO molecules
label the lipid fraction of cell membrane
and are also located in cytoplasma interior



EPR spectra
at 8.915 GHz
(for 12% H_2O sample)



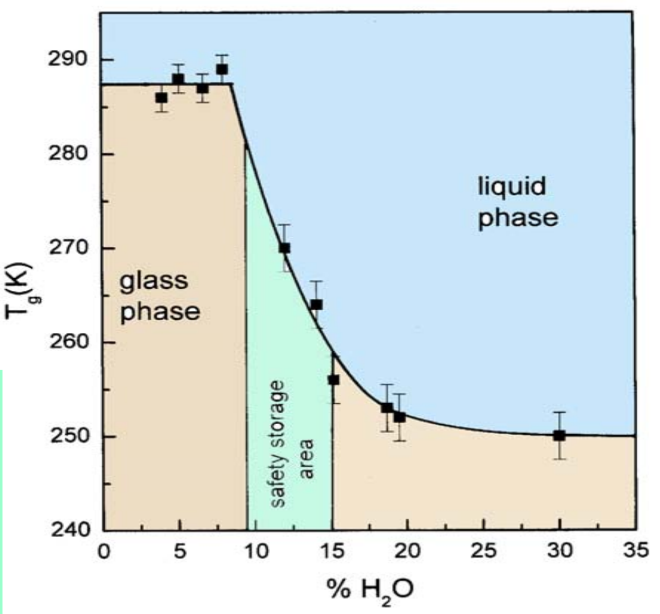
Spectra indicate **thermally activated reorientations** visible as line broadening (for the low field line):



$$\Delta B_{pp} = \frac{2}{\sqrt{3}} A \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

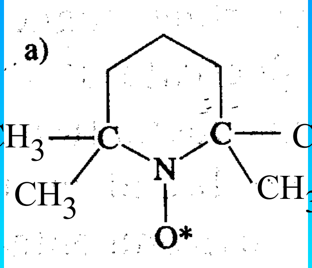
$E_a \approx 3$ kJ/mol
(depends on H_2O contents)
$\tau_0 \approx 10^{-12}$ s

Glass transition *vs* water contents for embryo axes of beech seeds

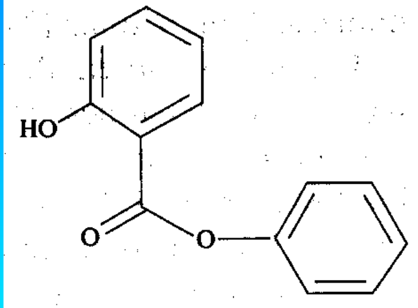


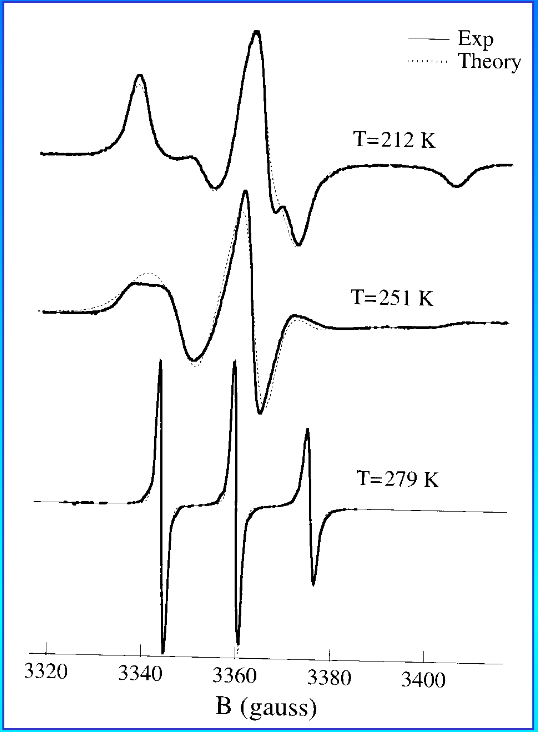
Dynamics of SALOL observed by spin-probe EPR

Spin probe - **TEMPO**
2,2,6,6-tetramethyl
-piperidin-1-oxyl



SALOL
Phenyl-salicylato



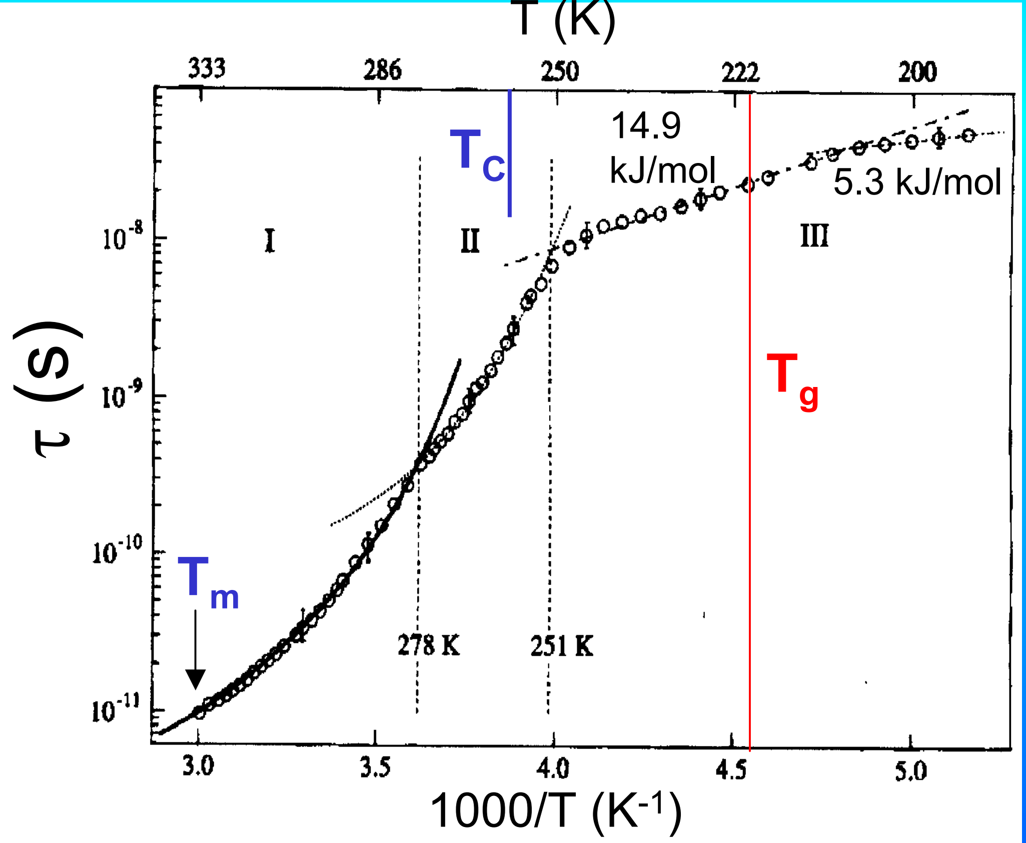


Isotropic jump reorientations with τ

3.2×10^{-8} s

6.9×10^{-9} s

2.8×10^{-10} s



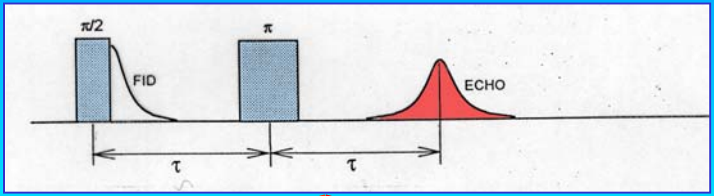
T_m= 315 K, T_C =260 K, T_g= 220 K

Detection of different dynamic regions
New „phase" II (diffusive)

L. Andreozzi, M. Bagnoli, M. Faetti, M. Giordano
J. Non-Cryst. Sol. **303**, 262 (2002)

ELECTRON SPIN ECHO SPECTROSCOPY

Every two pulses of resonance freqency generate electron spin echo signal.
In EPR microwave pulses are order of ns



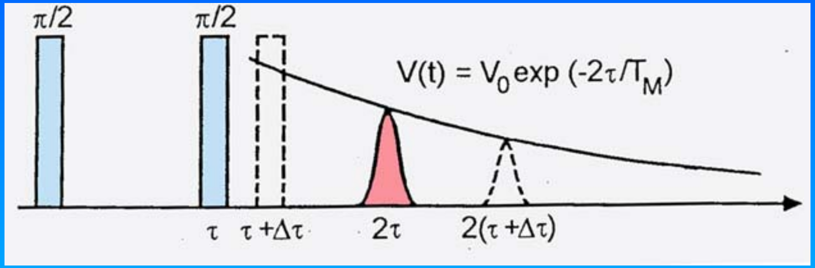
ESEEM Spectroscopy
(FT-ESE Spectroscopy)
ENDOR-type spectra

ESE dephasing
(Electron phase relaxation)
(ns - μs)

Electron spin-lattice
relaxation
(μs –s)

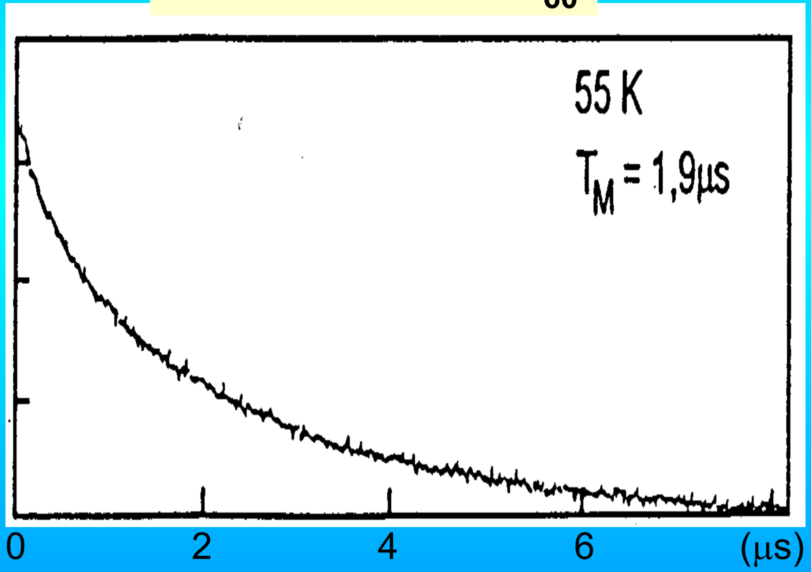
ESE = Electron Spin Echo

ESEEM = Electron Spin Echo Envelope Modulations



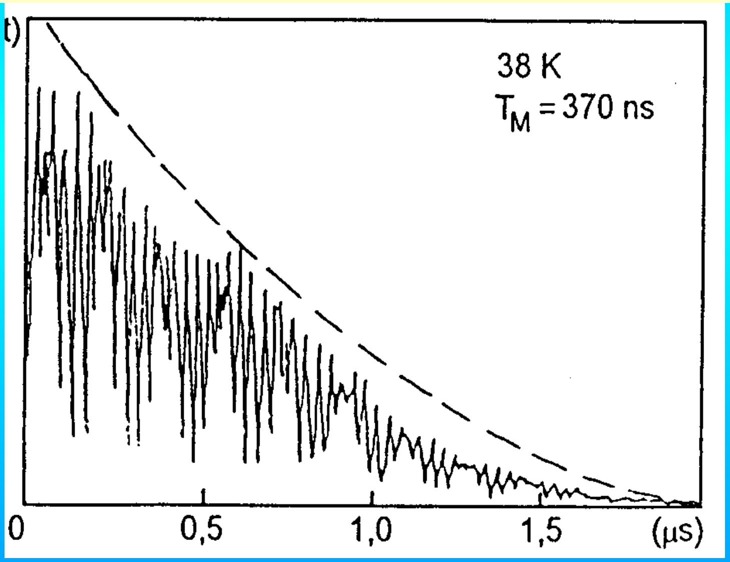
ESE signal amplitude decays with time after excitation with characteristic time called phase memory time T_M

Free radical in C_{60}



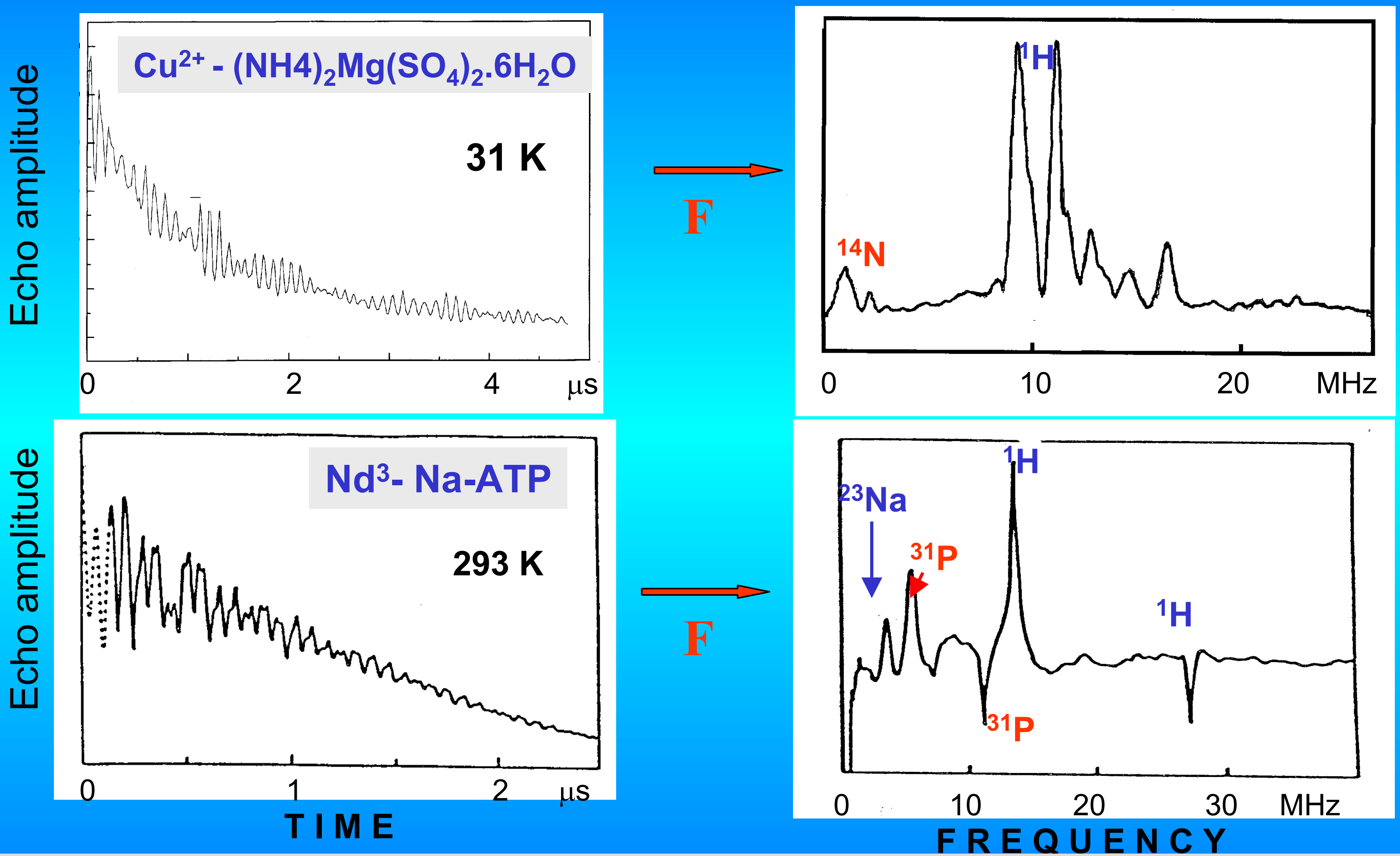
Phase memory time is very sensitive to molecular motions (varies with temperature)

Cu^{2+} ions in triglycine selenate crystal



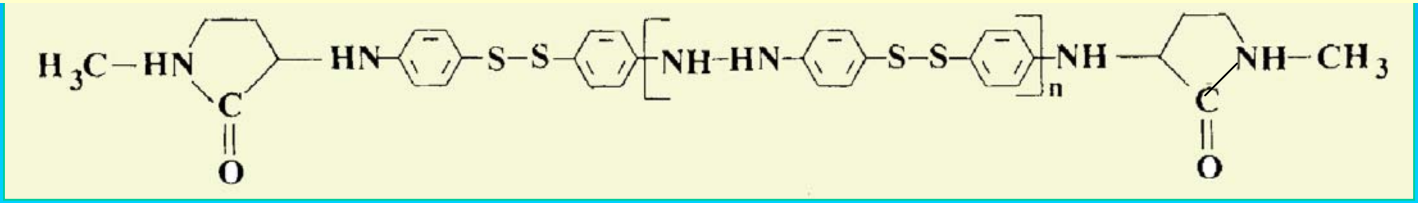
Modulations of the decay = **ESEEM** = **E**lectron **S**pin **E**cho **E**nvelope **M**odulations

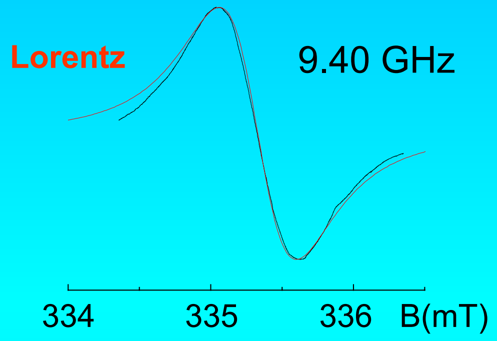
Modulations of the Electron Spin Echo decay and Fourier Transfrorm (ESEEEM) spectra



Number of peaks in ESEEM spectrum and modulation depth allow to determine : magnetic nuclei, their number and often a distance from paramagnetic center (up to about 5Å)

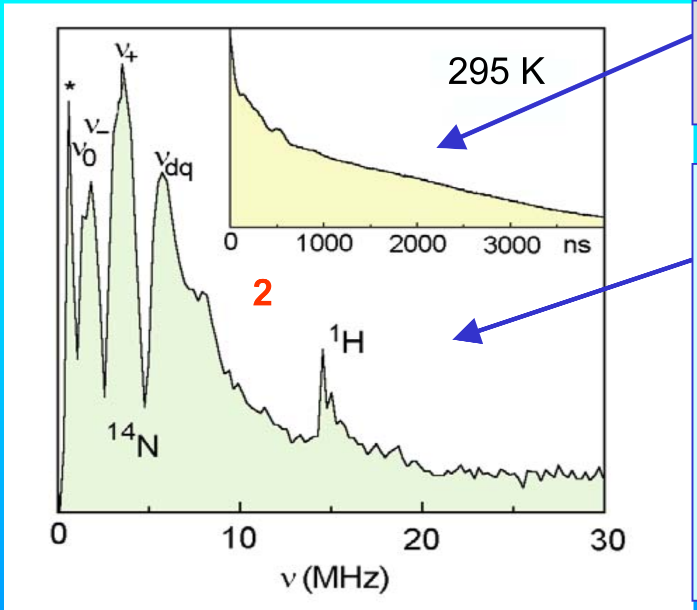
Identification of free radical and dynamics of oligomeric system poly(4-hydrazo-diphenylene disulfide with N-methyl-2-pyrrolidone chain ends





Strong EPR signal (non-informative single line) exists at g=2.0025 with 3.8×10^{18} radicals /gram

g-factor value suggests the unpaired electron is localization on a carbon atom

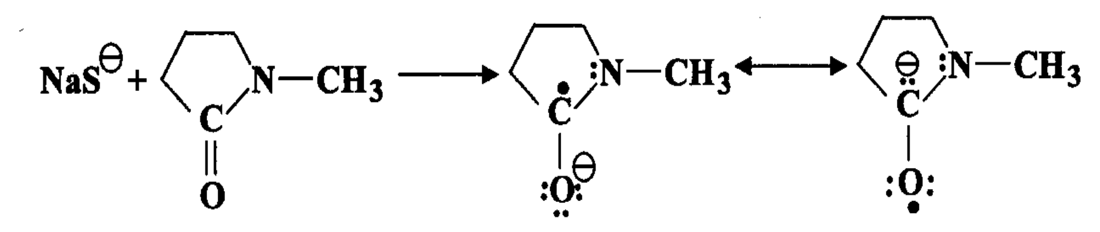


Electron spin echo (three pulse) amplitude decay is weakly modulated

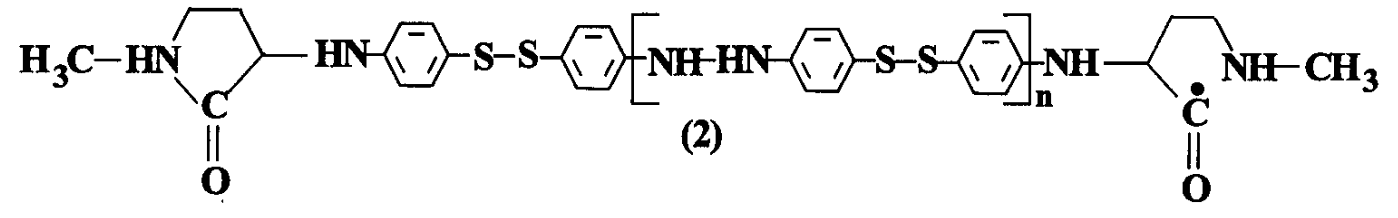
Fourier Transform (ESEEM) spectrum indicate:

1. Weak peak from **distant hydrogens**
2. Reach quadrupole structure $\nu_0,\nu_+,\nu_-,\nu_{dq}$ from closely located **single ^{14}N** (I=1) (about 1.8 Å)
3. Weak peak (marked as **2**) from **more distant nitrogen** atom (about 4.5 Å)

On a one of the stages of the reaction a transfer of electron from NaS^- to N-methyl-2-pyrrolidone appears allowing a reaction with terminal amine group of polymerazing 4-hydrazo-diphenylenedisulfide chain

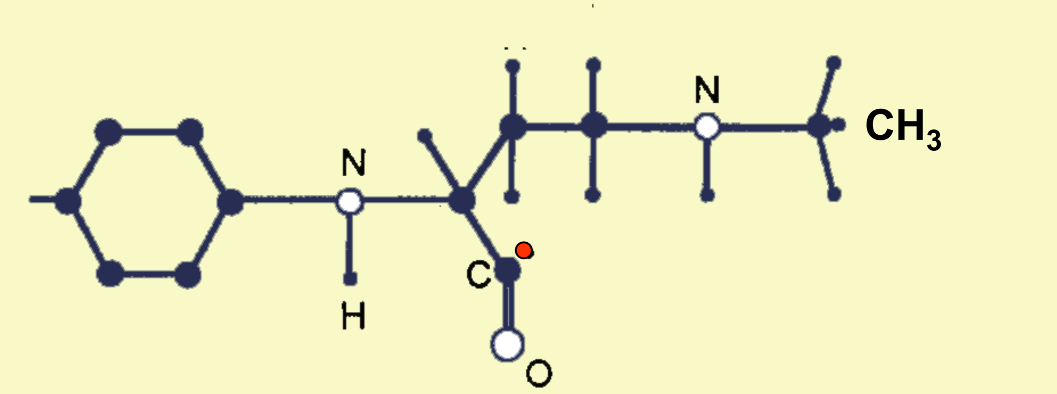


Our results suggest that about 1% of final product contains free radicals localized on the carbon atom as residuals of the last state of the reaction



(2)

However, the molecular structure of the end-chain containing free radical center is proposed as:

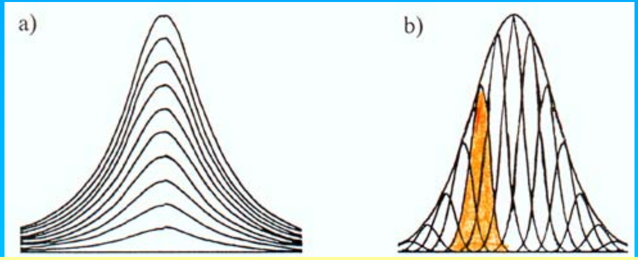


Free radical should be sensitive to:

- **CH_3 reorientations**
- **chain-end dynamics**

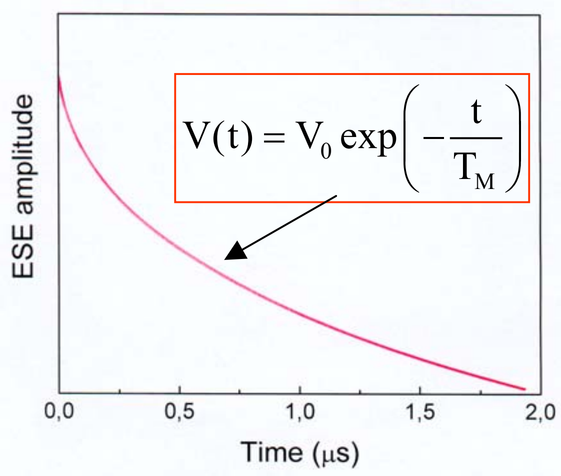
Electron Spin Echo (ESE) dephasing

Temperature dependence of the phase memory (dephasing) time T_M display effects from molecular reorientations



ESE can be generated only for **inhomogeneously** broadened EPR lines formed from spin packets

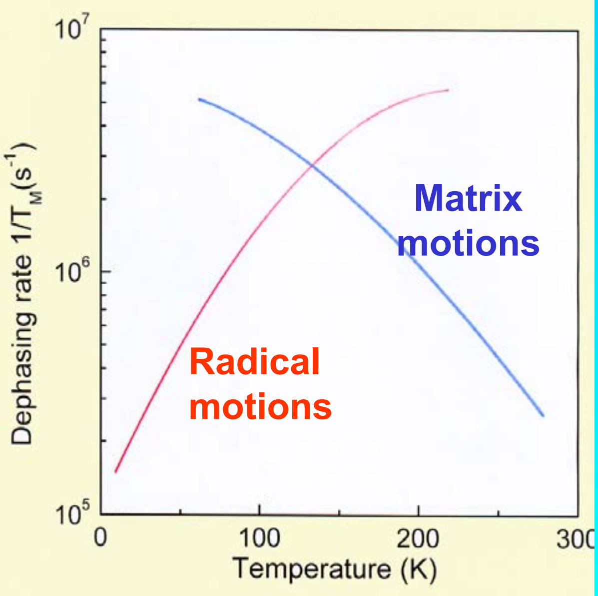
ESE amplitude decay with time, with characteristic time T_M

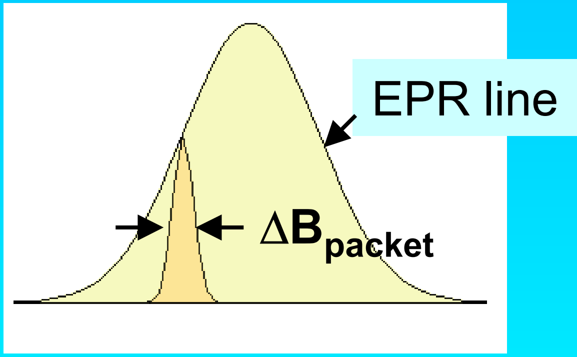


ΔB_{packet} is 0.01 – 1G, is very sensitive to dynamical processes:

-radical motions produce spin packet broadening

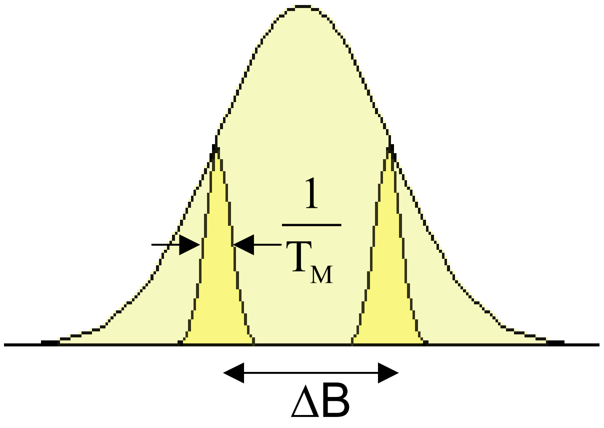
-matrix molecule motions produce spin packet narrowing

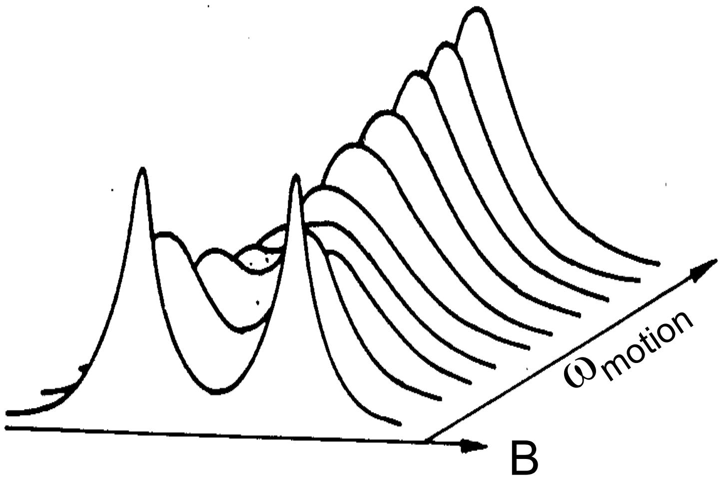


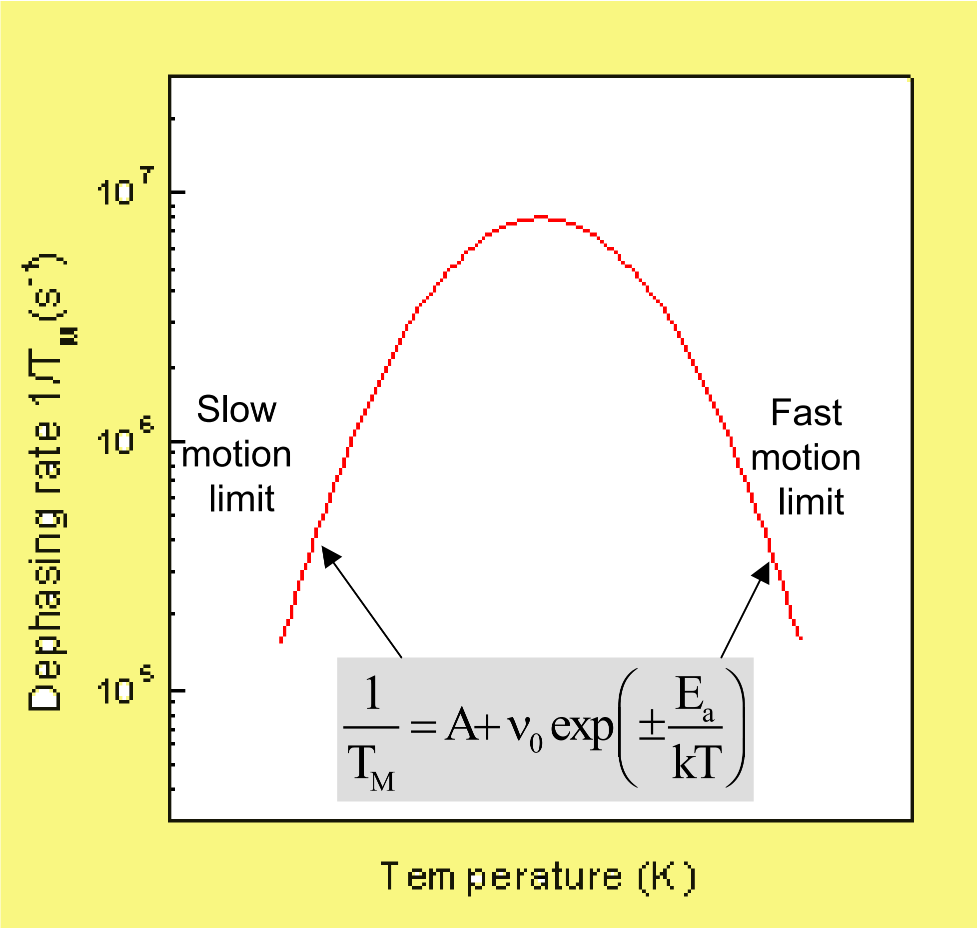


$$\frac{1}{T_M} = \Delta B_{packet}$$

Merging effect between spin packets **(unresolved hyperfine structure lines)** produces **resonance-type enhancement** of the dephasing rate (**maximum in temperature dependence of $1/T_M$**)

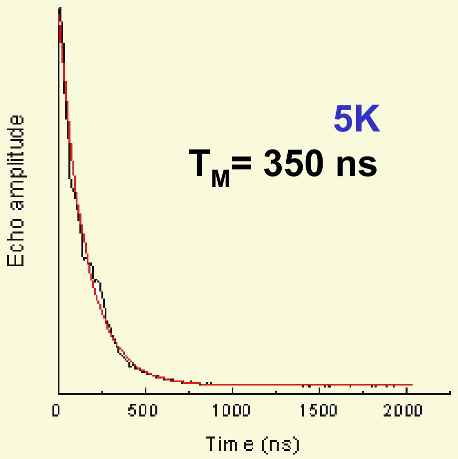






$$\frac{1}{T_M} = A + \nu_0 \exp\left(\pm\frac{E_a}{kT}\right)$$

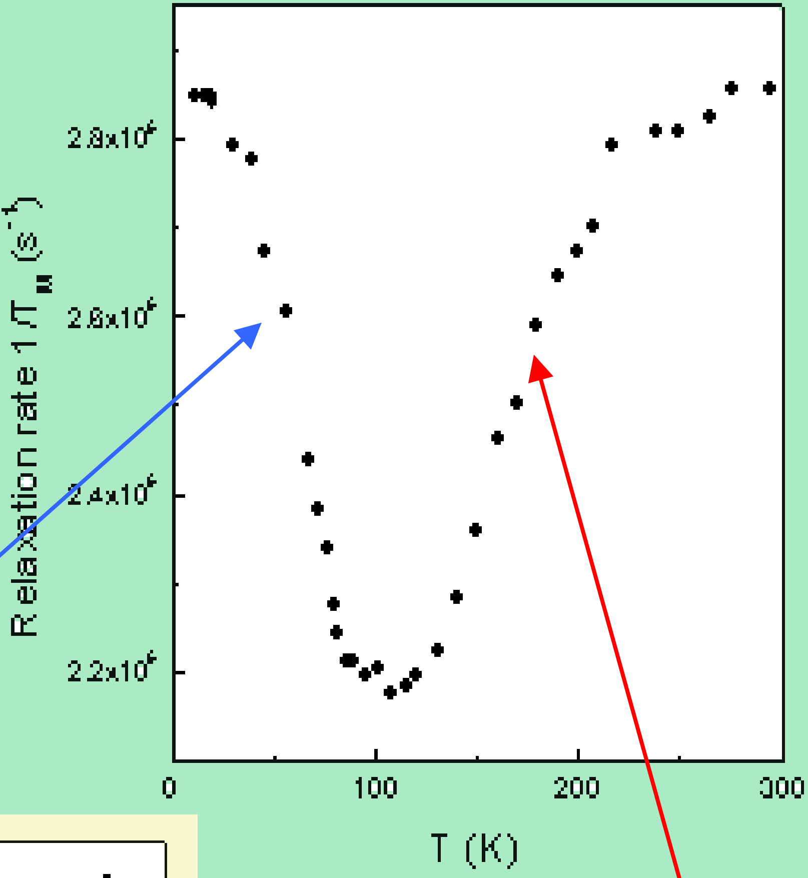
ν_0 is order of $10^6 – 10^8$ s^{-1}

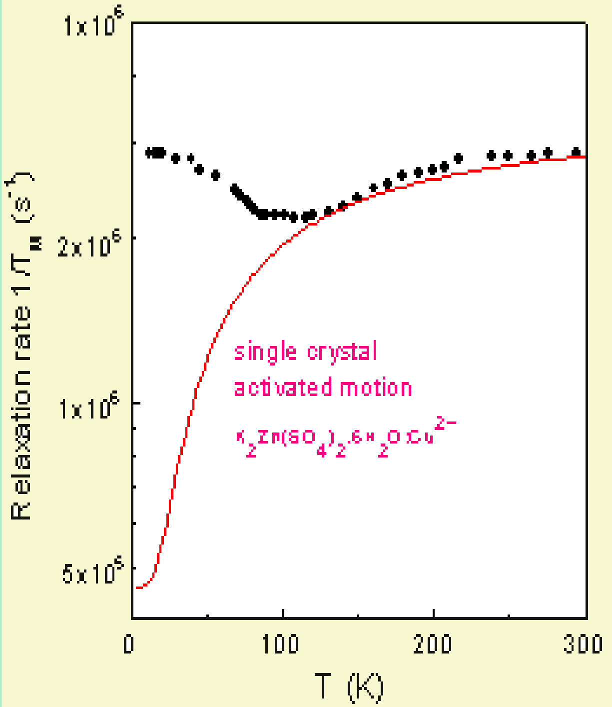


CH_3-tunneling rotation

$\tau_0 = 7\times10^{-12}$ s

E_a = 5.17 kJ/mol



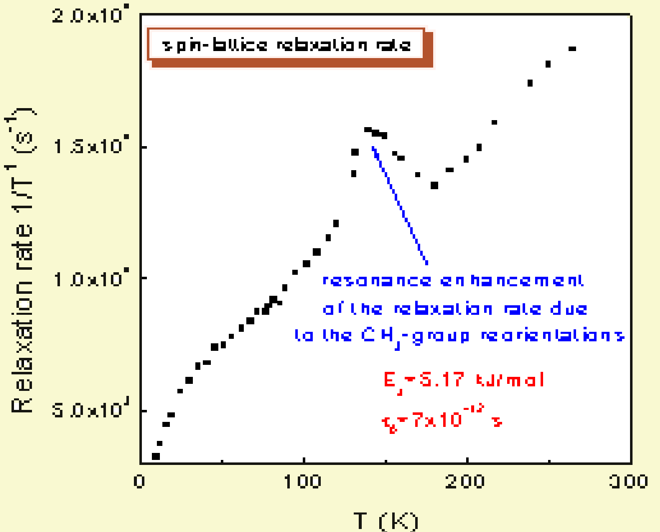


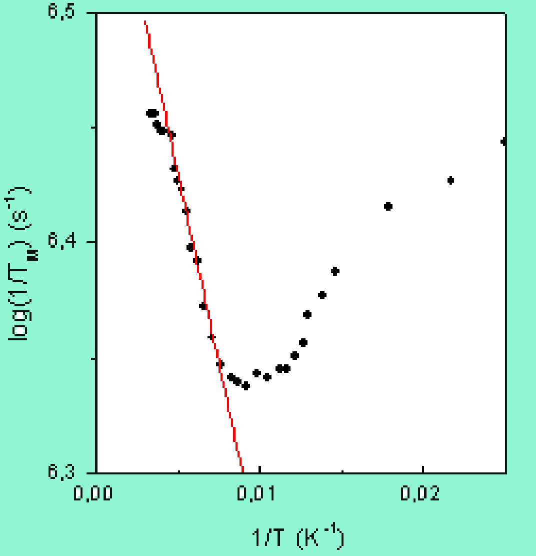
Slow molecular motion

$\tau_0 = 2.6\times10^{-7}$ s

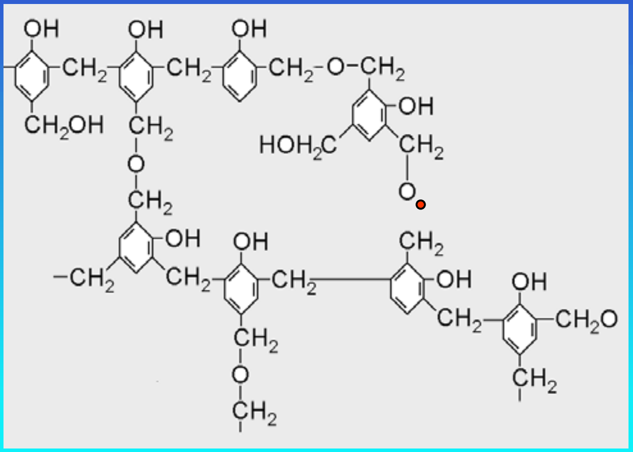
E_a = 49 cm^{-1} = 6.1 meV

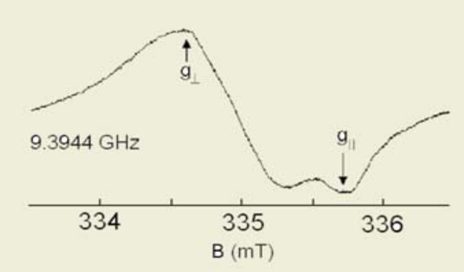
= **0.6 kJ/mol**



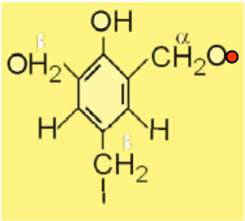


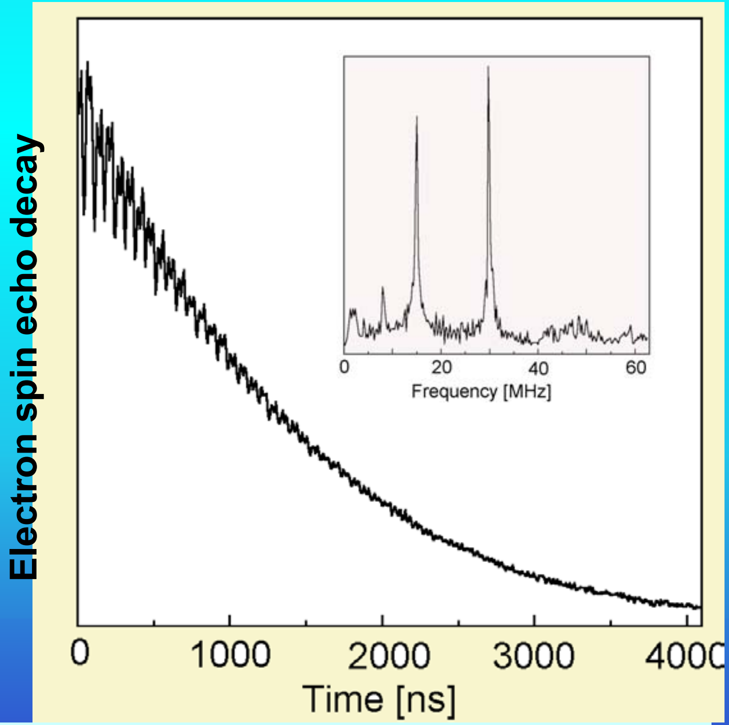
Phenol-formaldehyde resin



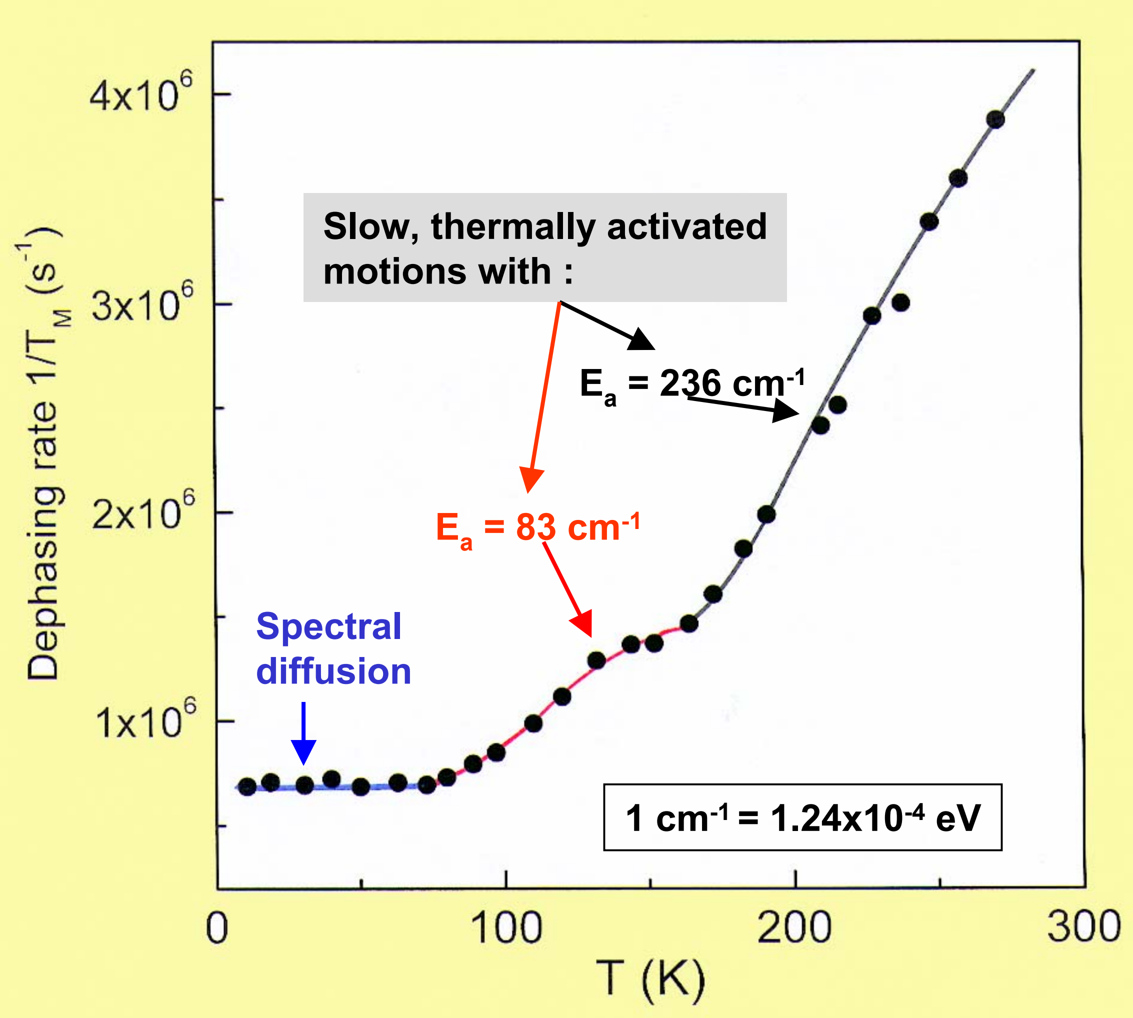


EPR spectrum with g-factors $g_\parallel = 1.9994$ $g_\perp = 2.0058$ suggests localization on an oxygen





S. K. Hoffmann, W. Hilczer
IEEE Trans.Diel.Electr.Ins. **9**, 316 (2002)



Slow, thermally activated motions with :

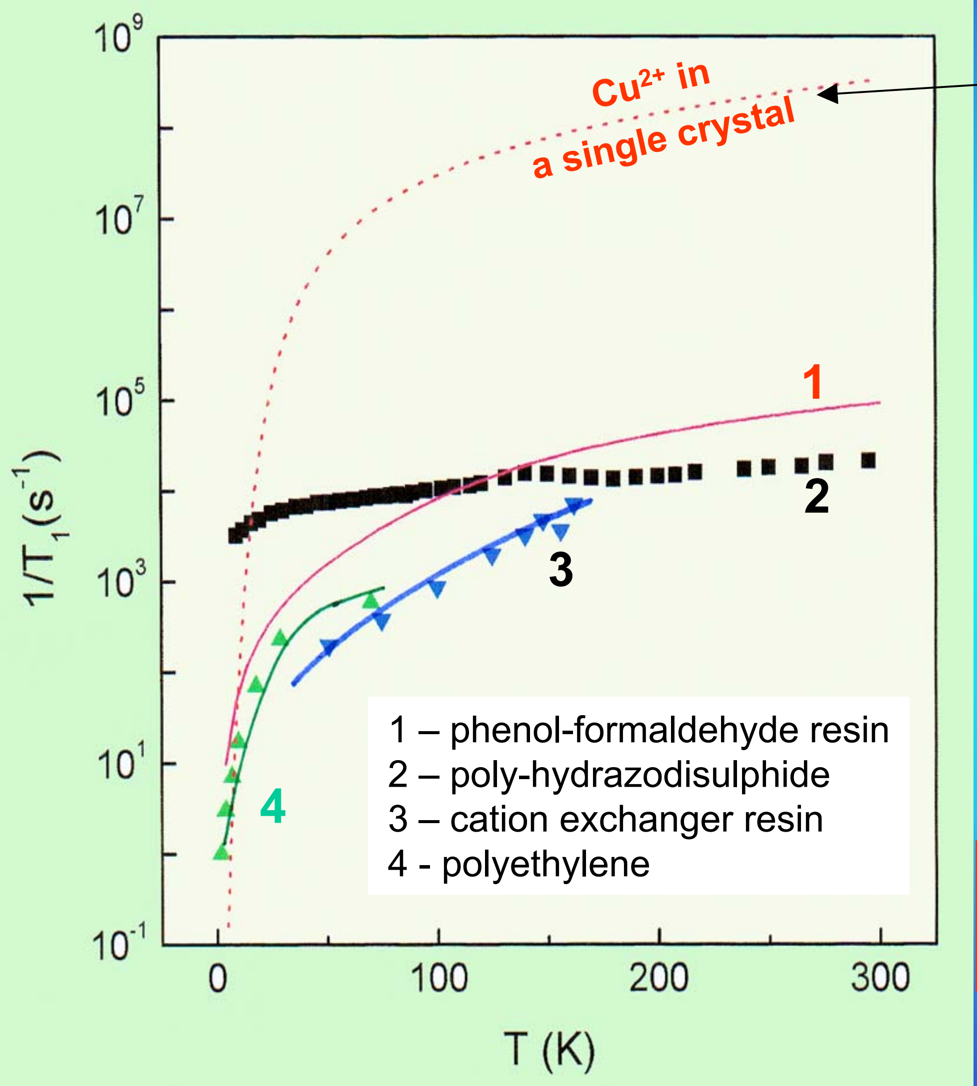
E_a = 236 cm^{-1}

E_a = 83 cm^{-1}

Spectral diffusion

1 cm^{-1} = 1.24x10^{-4} eV

Electron spin-lattice relaxation in polymers



In **single crystals** the relaxation is governed by extended **acoustic phonons**

In **polymers** the relaxation is governed by **local modes** of paramagnteic centers:

$$\frac{1}{T_1} = a \cdot \operatorname{cosech}^2\left(\frac{E_{mode}}{2kT}\right)$$

In phenol-formaldehyde resin (1)
$E_{local} = 296\ cm^{-1}$

CONCLUSIONS

1. **Cw-EPR and ESE spectroscopy can be apply to study free radicals and spin probes or spin labels in polymeric systems**

2. Cw-EPR and ESEEM spectra allow **identification paramagnetic centers** and determination its localization

3. Temperature dependence of EPR spectra allow to determine:
   - **glass transition temperature**
   - **regions of different dynamics** of paramagnetic centers

4. Electron spin dephasing (T_M time) is sensitive to **slow motions** (10^6-10^8 s^{-1}) and allows determination **small activation energies** (order of 0.1 kJ/mol)

5. Electron spin relaxation can detect reorientations of molecular groups like **CH_3, NH_3** and determines its activation energies

6. Spin-lattice relaxation deliver parameters of **local vibration modes**

EPR and pulsed EPR (ESE spectroscopy) can be used as complementary to other techniques in studies of slow motions in polymers and amorphous solids