

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

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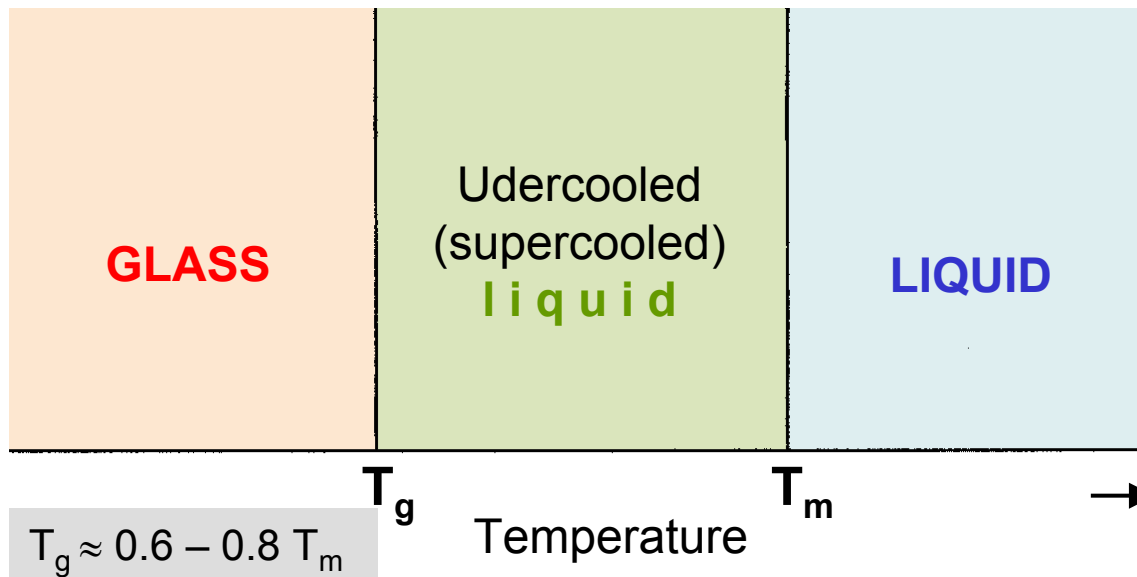
Polymers, glasses and amorphous solids are similar to the crystalline solids:

- 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**



Glass transition T_g :

- when **viscosity** is higher than **10^{13} Poise**
- when **thermal fluctuations** in undercooled liquid become too slow to be measured in experimental time 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**

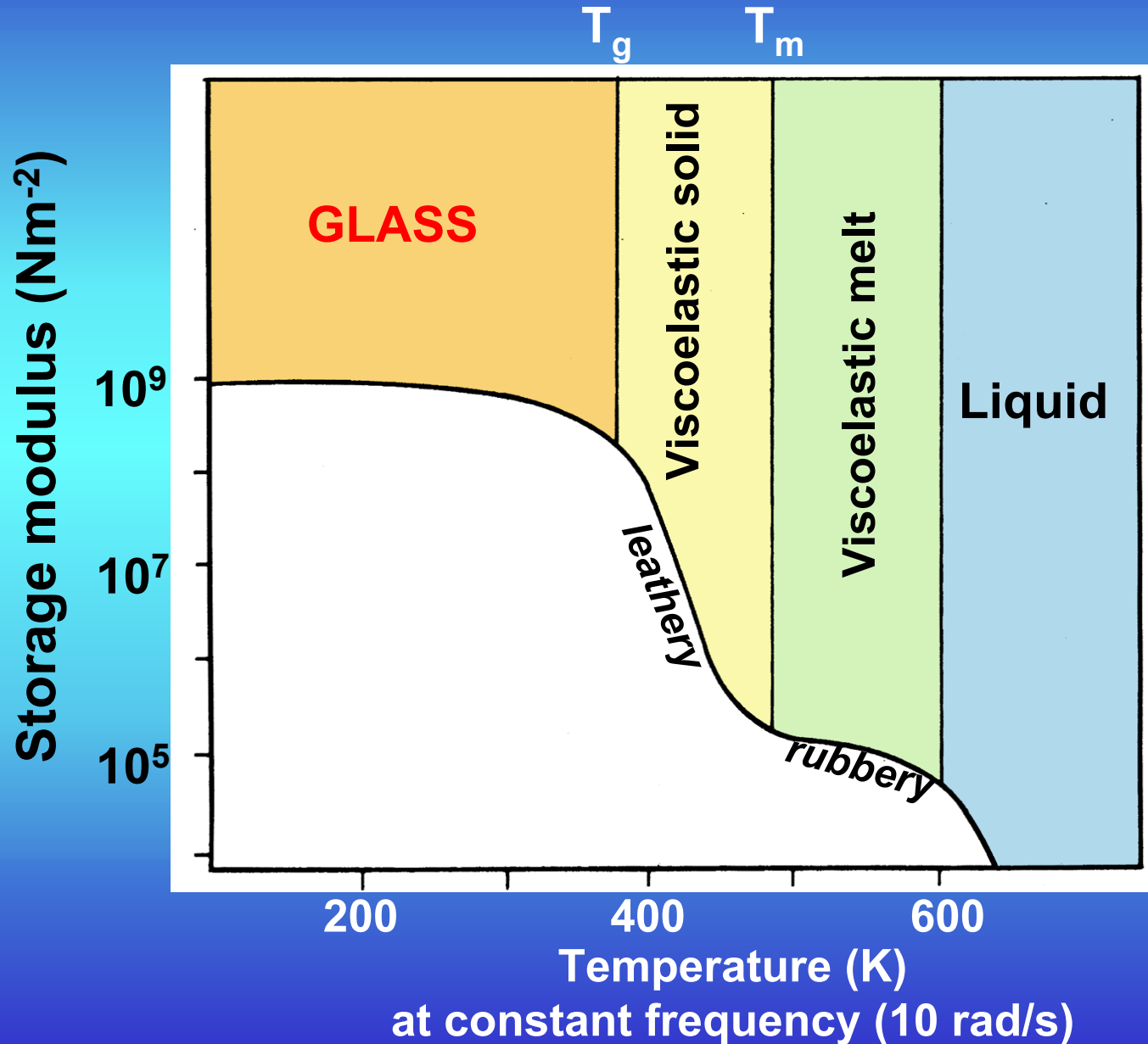
What is structure of a glass?

„True” glass → after a rapid quenching ?

Macroscopic structure:

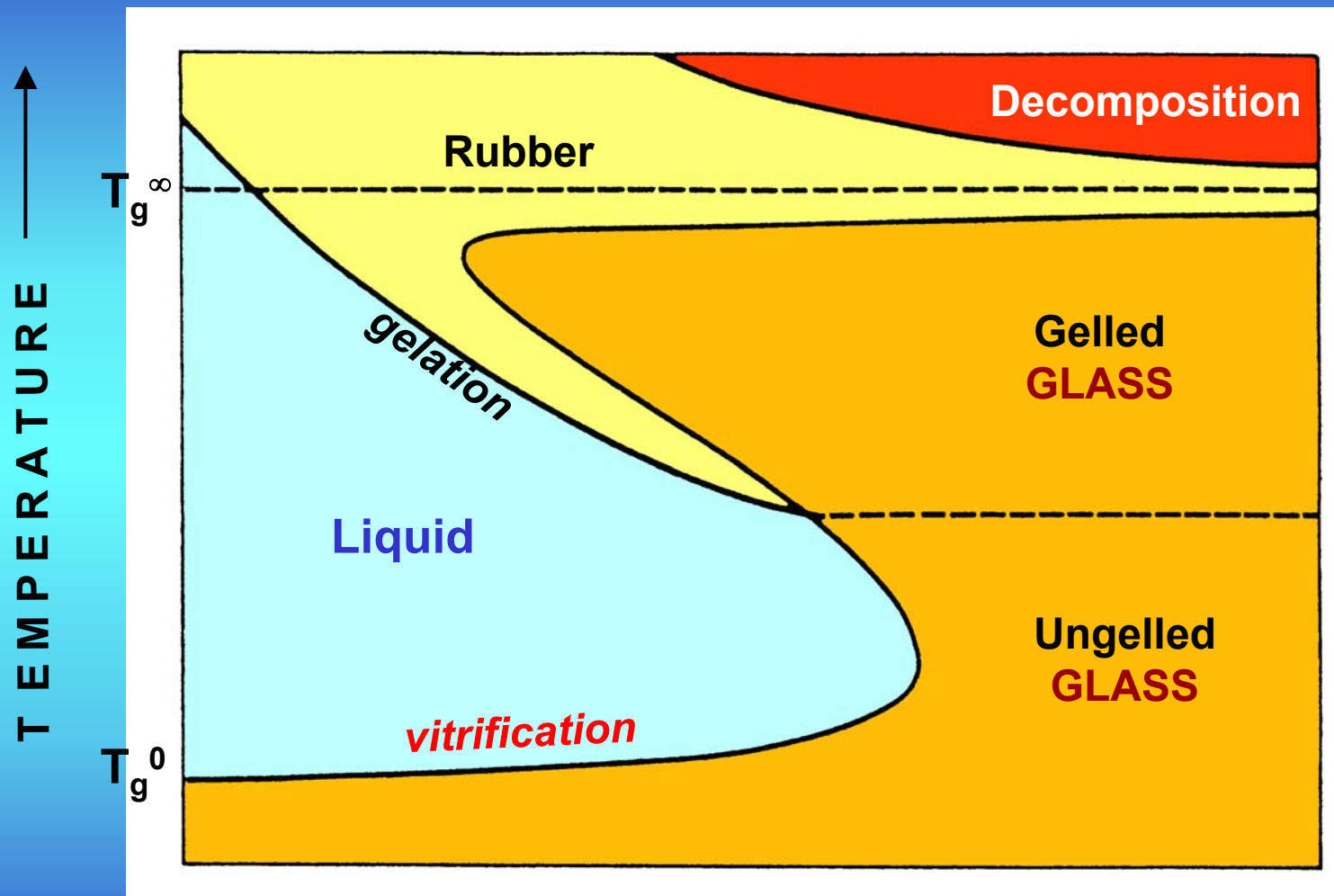
- more „phases” or intermediate states than in the simple phase diagram
- a) in **thermoplastic (linear) polymers**
depending on the temperature (and measured frequency)
- b) in **thermosetting polymers (resins)**
depending on the temperature and time

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



Generalized time-temperature-transformation (TTT) for the curing of a thermosetting polymer (resin)

Gillham's diagram, 1986

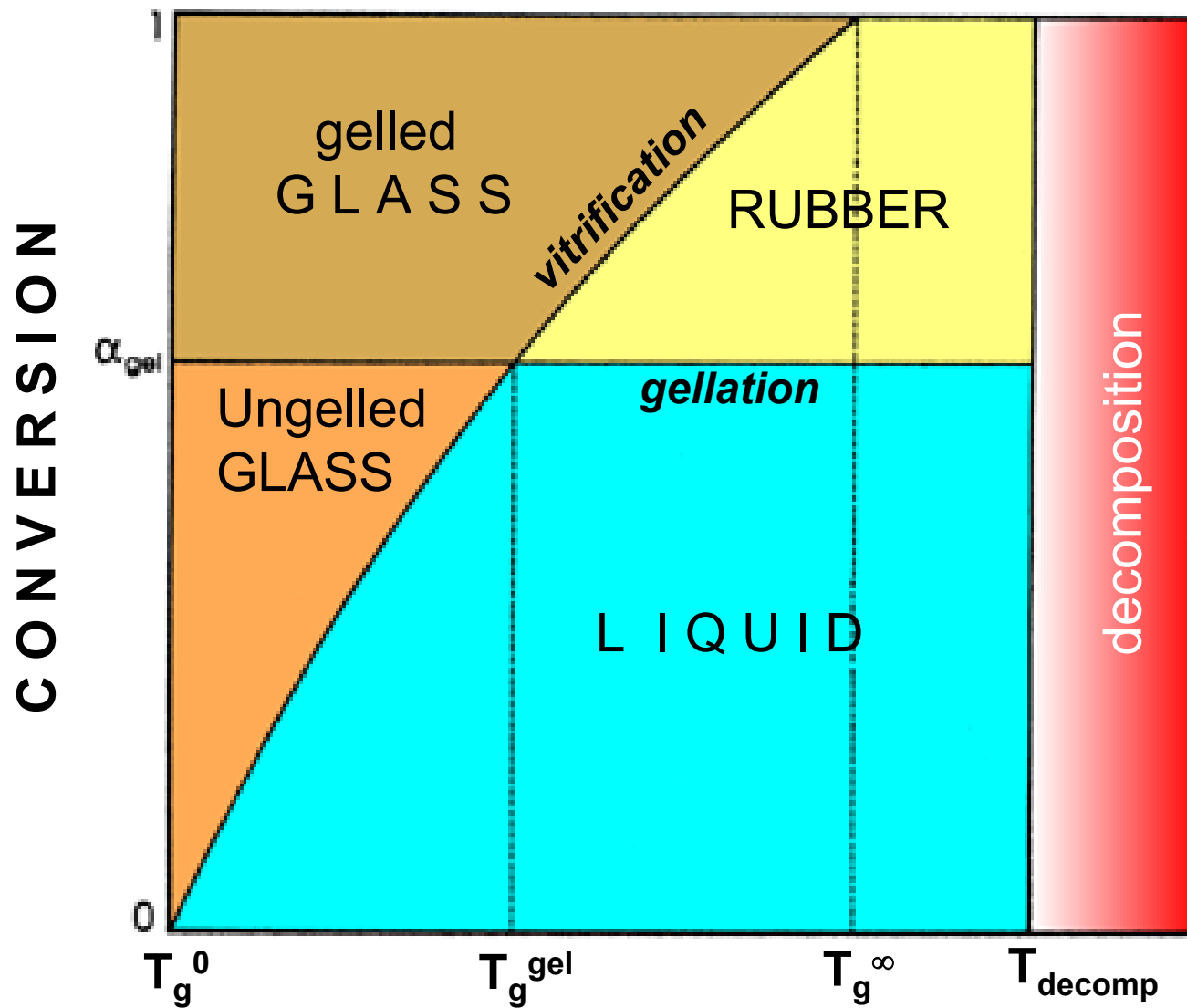


T_g^0 - thermal glass transition
 T_g^∞ - maximum possible T_g
(minimum cure temperature)

TIME →

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 length scale 5 - 10 nm
decides on its properties and stability**

(E. Courten....., 2001)

Dynamics of polymers and amorphous solids is

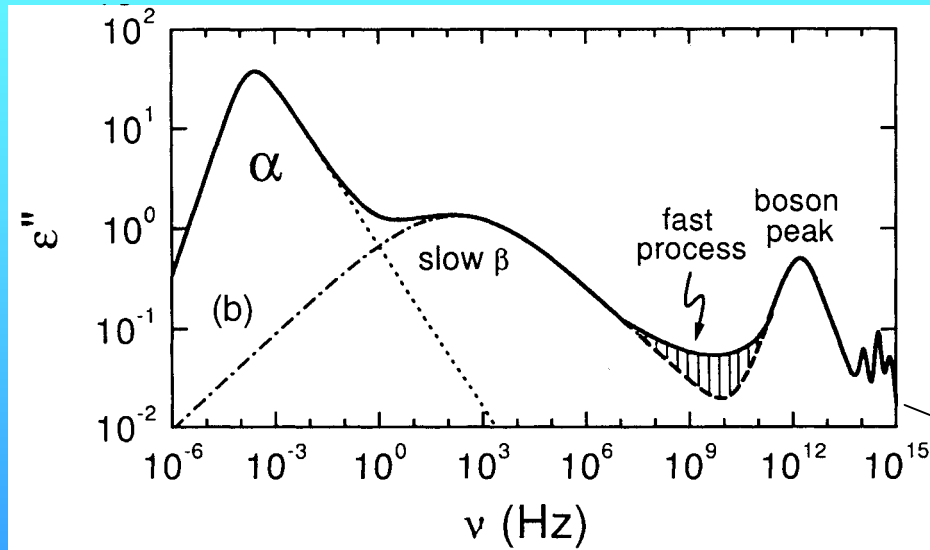
- more complex than that in crystalline materials
- affected by intrinsic disorder

and is observed as:

- **relaxation phenomena** (aperiodic fluctuations)
mainly by dielectric spectroscopy
 - **harmonic or quasi-harmonic excitations** (vibrations)
-

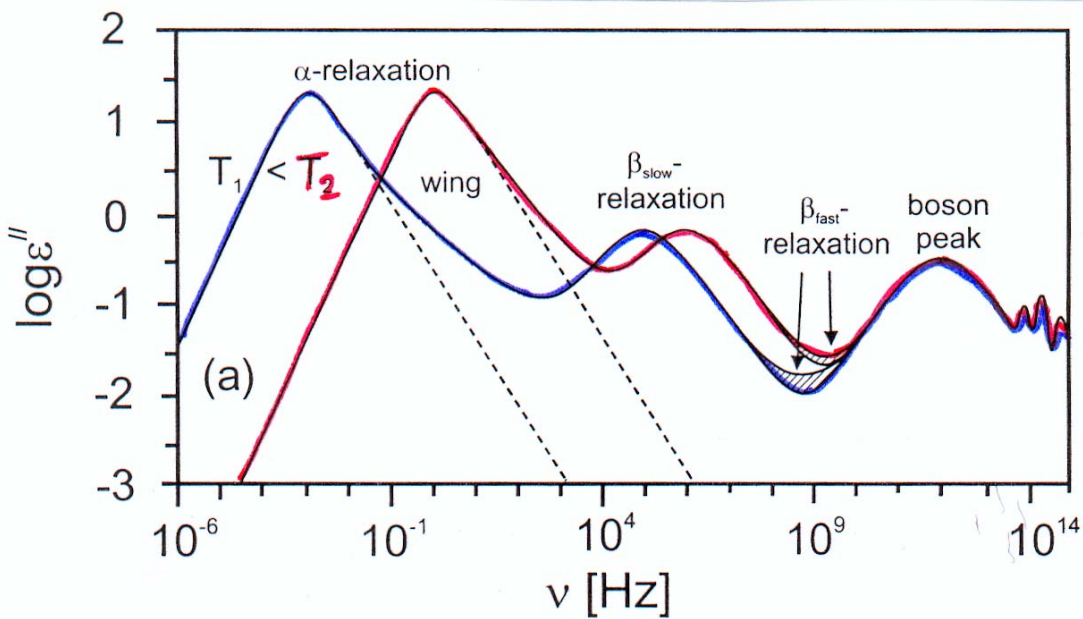
Central and most important dynamical phenomenon in glassy-forming polymers is

α - relaxation



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

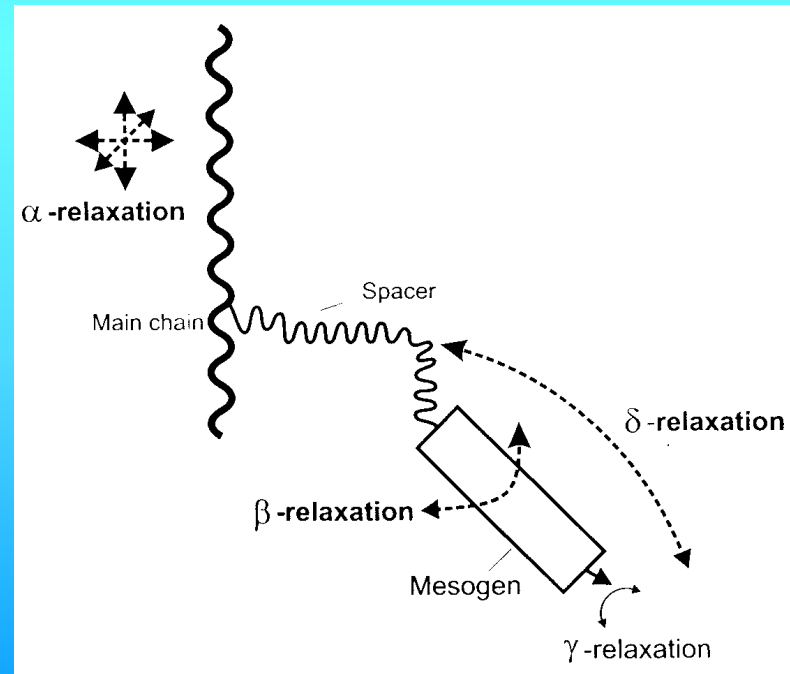
F. Kremer, A. Schönhal's (Eds)
Broadband Dielectric Spectroscopy
Springer, Berlin 2003, p. 134



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, σrelaxations**
- **boson peak** (harmonic excitations)



α and β relaxations reflect **slow dynamics**

α - relaxation (primary response)

≡ **structural relaxation** ≡ **dynamic glass transition**

- micro-Brownian motion of chain segments
- molecule fluctuates in **a cage** of its neighbours. (Fluctuations of the molecules forming the cage cannot be independent from each other thus α -relaxation is to some extent **cooperative**)
- forming and decay of the cage

Characteristic features:

1. **Non-exponentiality**

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

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

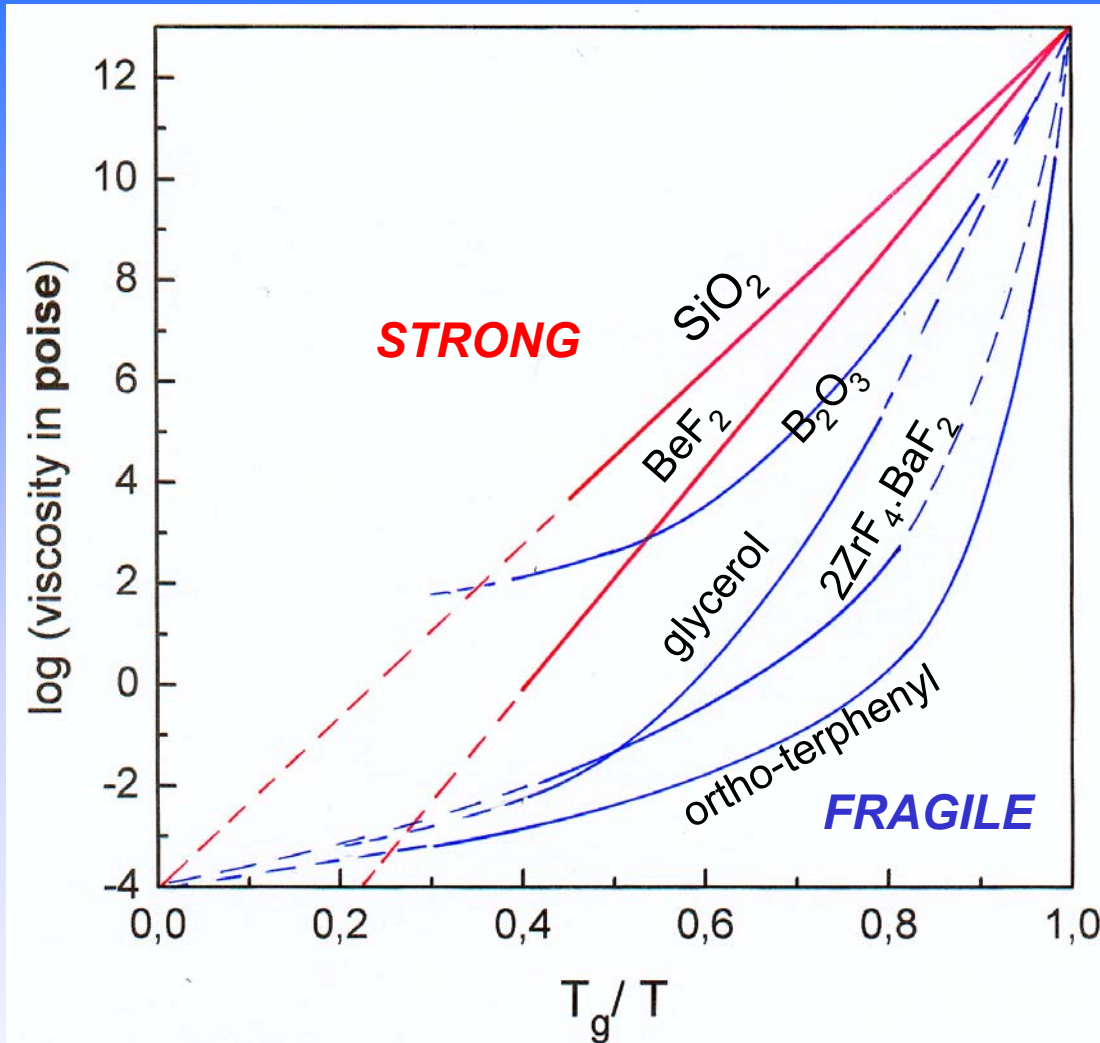
A **distribution of the relaxation time τ** exists

$\beta = 0.5 - 1$, decreases on cooling

2. **Non-Arrhenius behaviour**

Angel plot :

strong and fragile glass-formers



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

Maxwell mechanical equation

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

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

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

T_g - thermal glass transition

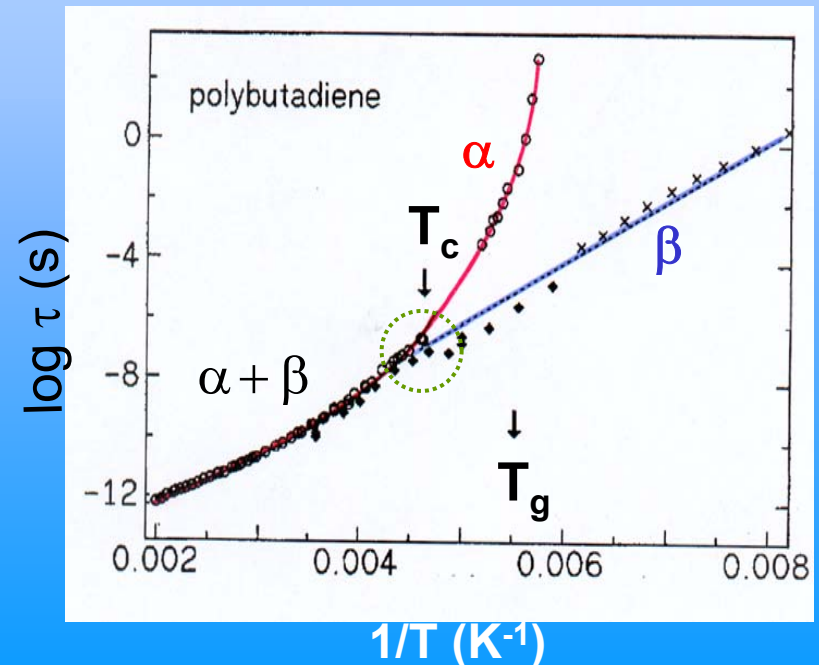
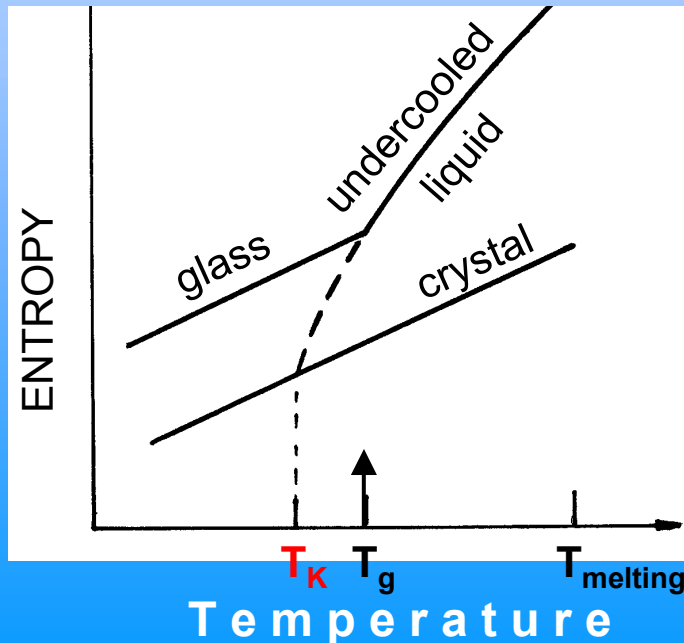
T_0 - Vogel temperature = ideal glass transition temperature
(τ and η diverge) typically 30 – 50 K below T_g

T_K - Kauzmann temperature
At that temperature **entropy** of the undercooled liquid extrapolated to temperatures below T_g "reaches" entropy of a crystal. **Close to T_0 .**

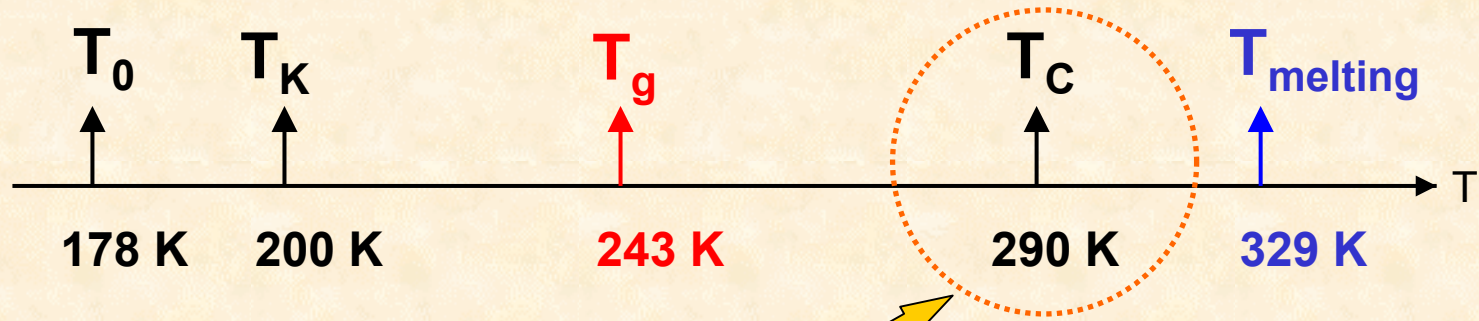
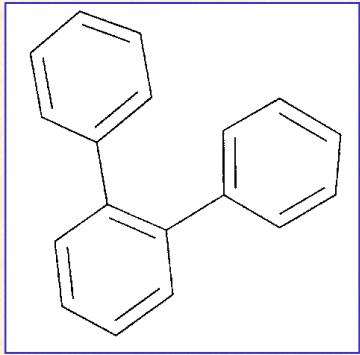
T_c - cross-over temperature

Cross-over to cooperative relaxation.
Structural arrest in the cage.

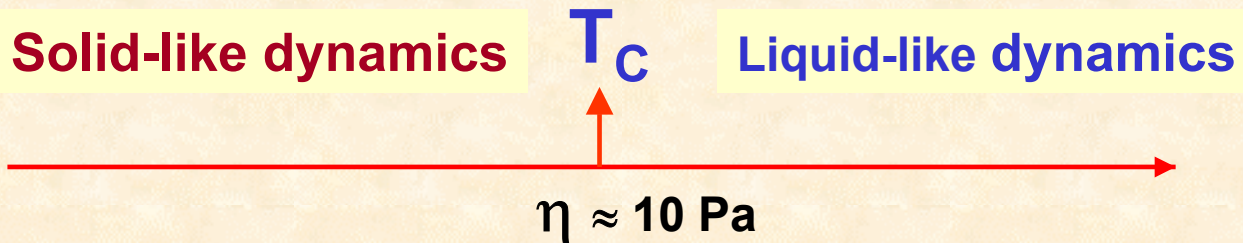
Typically $\approx 1.2 T_g$



Characteristic temperatures for **ortho-terphenyl**



$\alpha + \beta$ merging region



- 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

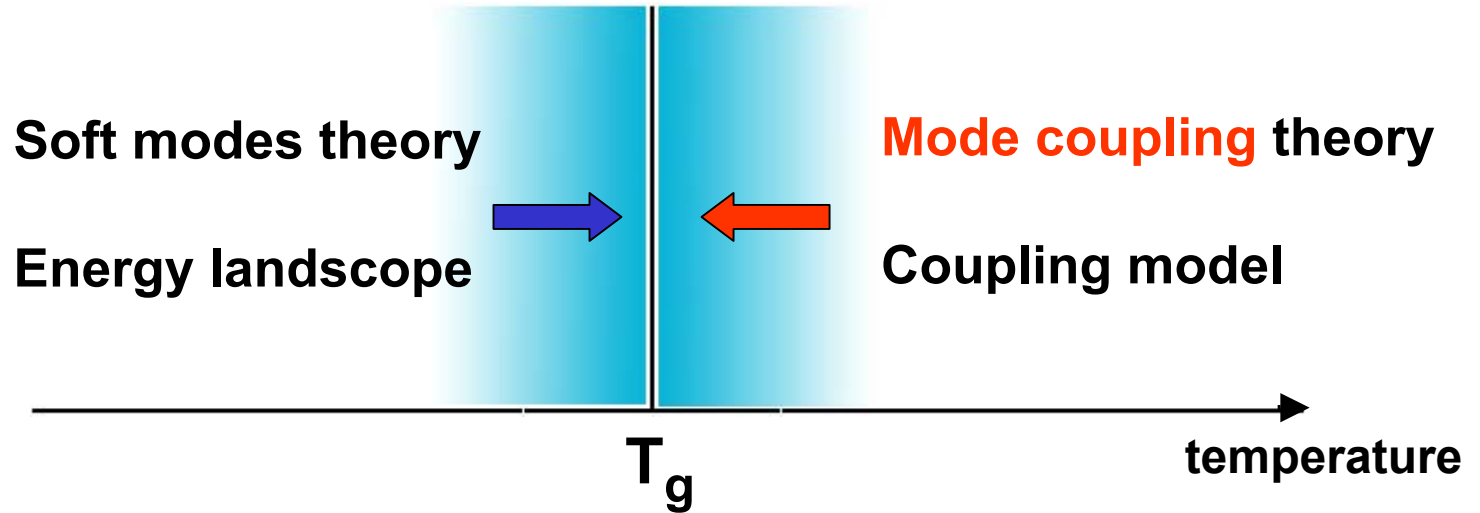
$$E_a = 20 - 50 \text{ kJ/mol,}$$

$$\tau_{\infty} \sim 10^{-13} \text{ s} \quad \leftarrow \text{ often smaller, indicating a contribution from}$$

activation entropy

- **Local relaxation.** Takes place on a local length scale not larger than a monomer unit (1.5 Å jumps, 60-90° rotations around the center of mass)
- **Fluctuations of localized part of the main chain.**
- **Rotational fluctuations of side groups or part of them.**

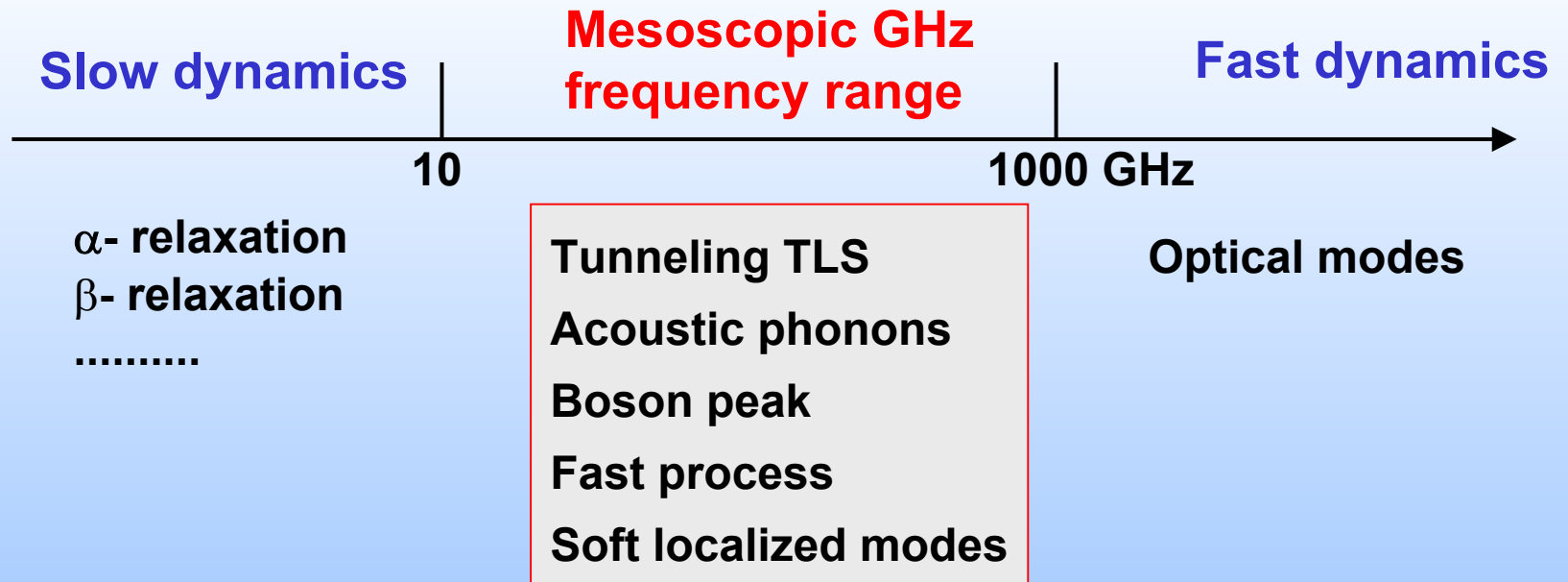
THEORY



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.



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

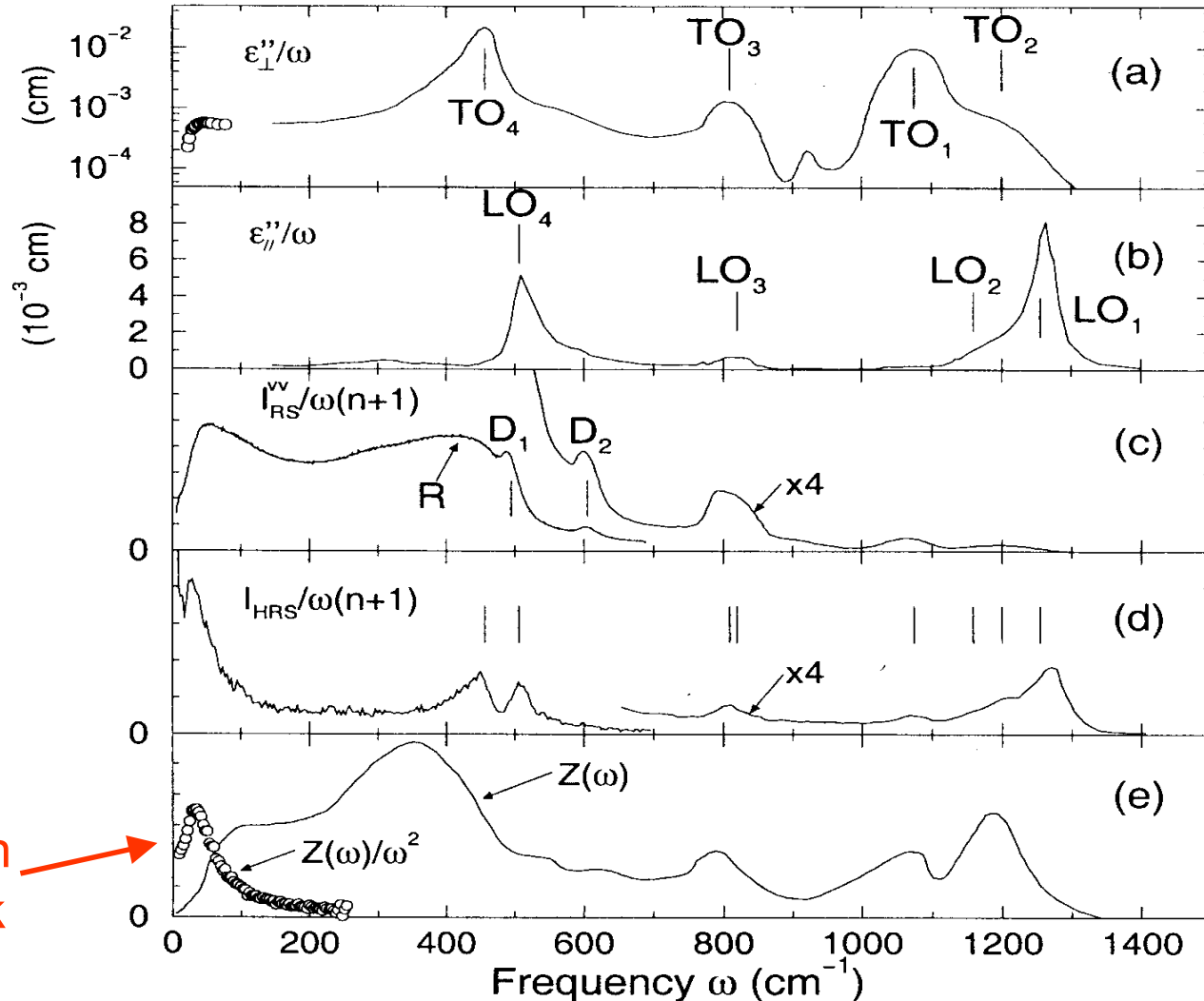
(Sokolov, 1997)

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



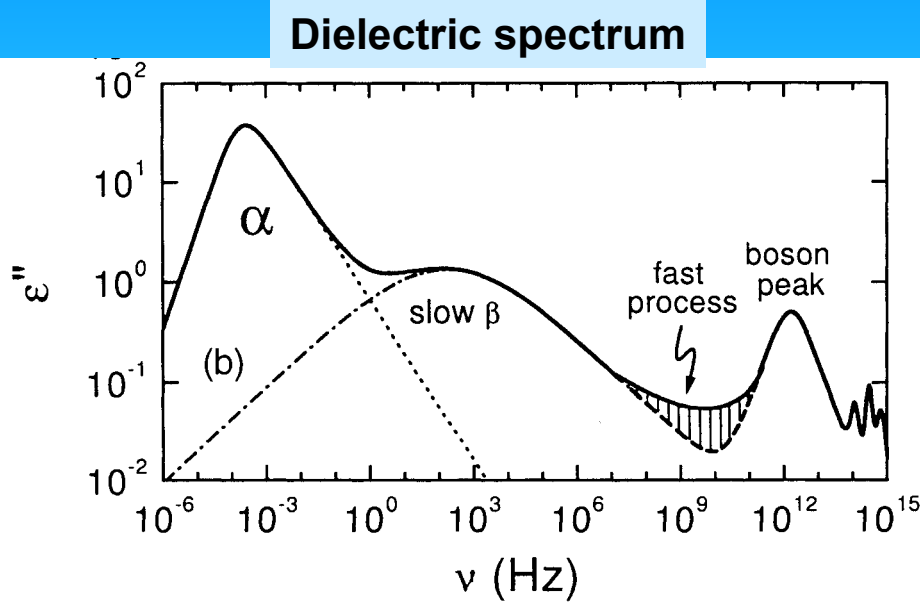
IR

Raman

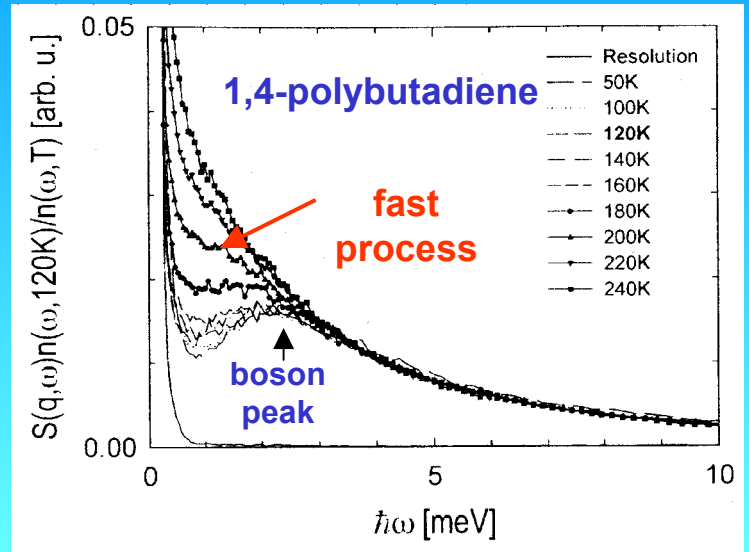
Theory

Boson peak →

FAST PROCESS (β_{fast} – relaxation)



Incoherent inelastic neutron scattering spectra



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

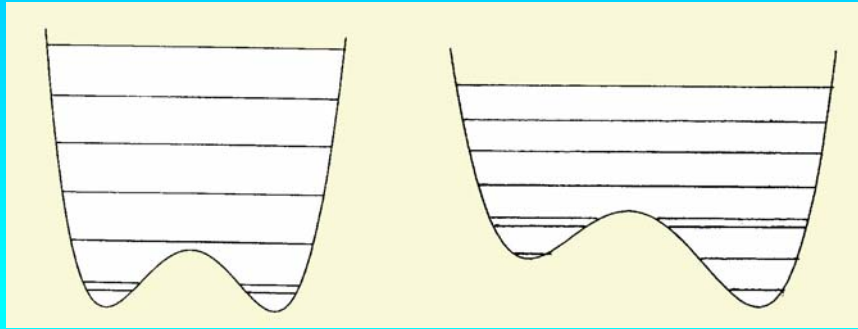
- Above T_x the mean square displacement of atoms begins to increase more strongly than linear dependence $\langle u^2 \rangle \propto T$ predicted for harmonic vibrations (Ngai coupling model)

- 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 of 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 considered as a collection of asymmetrical double-wells (TLS):

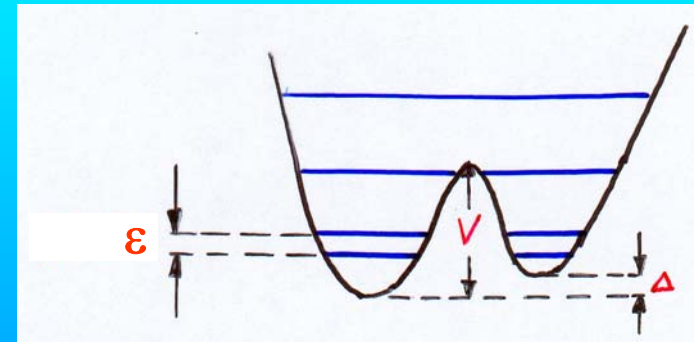


Thermally activated reorientations between the potential minima can be produced by **1. Phonon assisted tunneling** (one-phonon process) - **dominates**

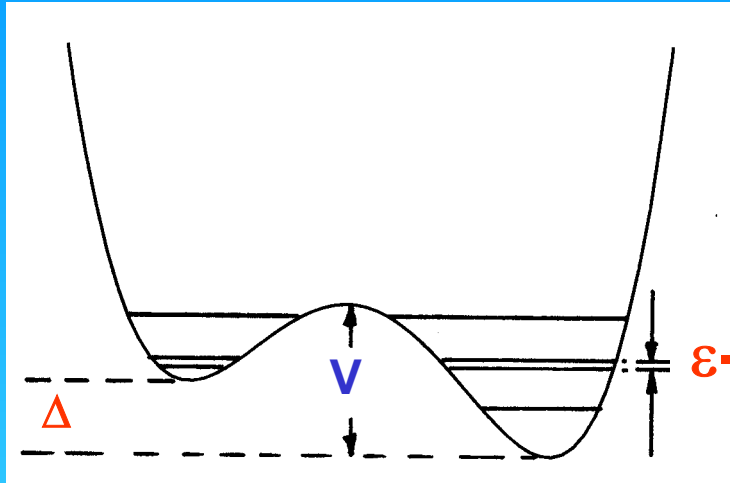
$$\frac{1}{\tau} = A \cdot \Delta^2 \varepsilon \coth\left(\frac{\varepsilon}{2kT}\right) \quad \varepsilon = \text{tunneling splitting}$$

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



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

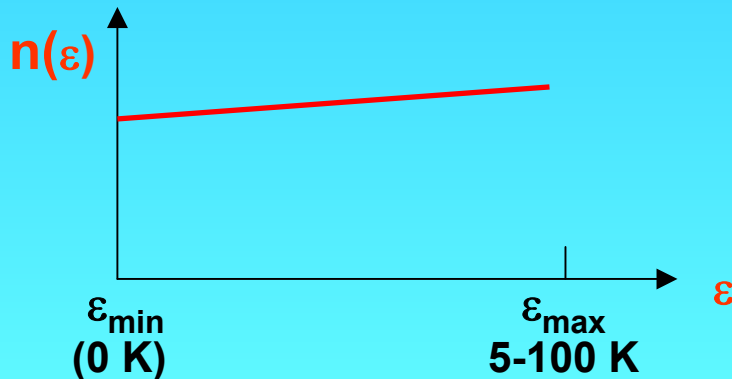
$$\varepsilon = \sqrt{\Delta^2 + \Delta_0^2}$$

Δ_0 = overlap energy = coupling energy in symmetrical state

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

$$\lambda = \sqrt{2mV} \frac{d}{\hbar}$$

Density $n(\varepsilon)$ 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:

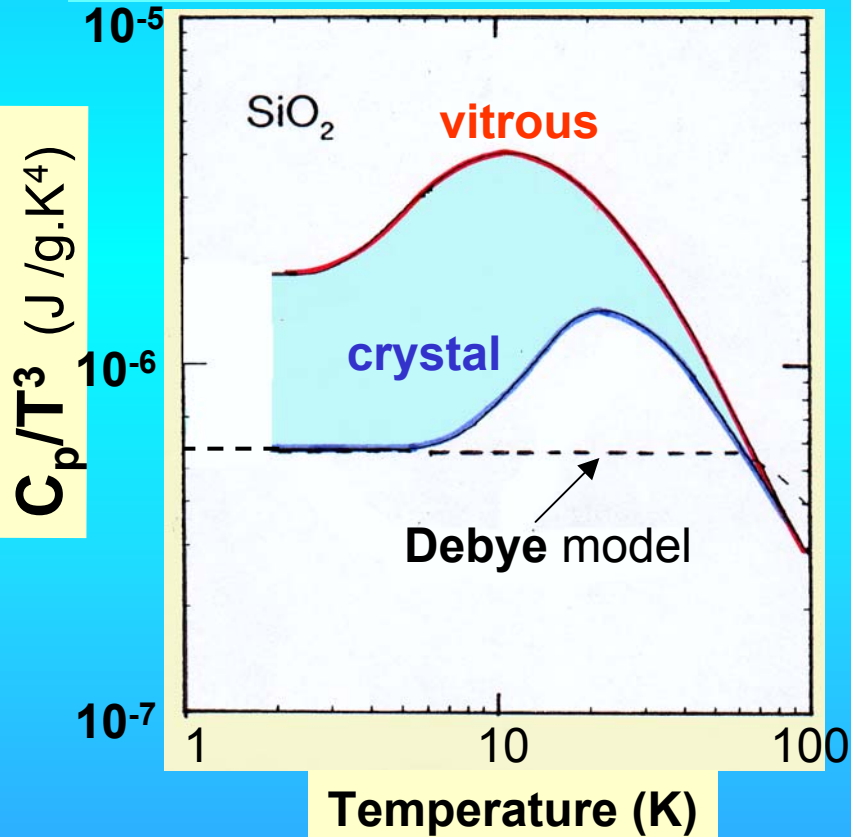
specific heat

$$C_p \propto T^3$$

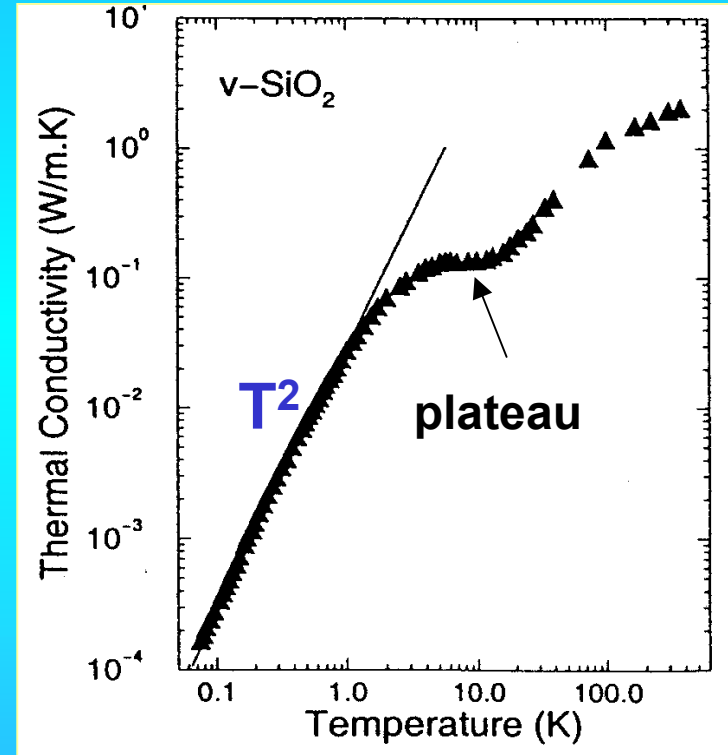
thermal conductivity

$$\kappa \propto T^3$$

In vitreous silica - **v-SiO₂**



Excess of vibrational modes



1. TLS do not conduct heat ($\rightarrow T^2$)
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** .

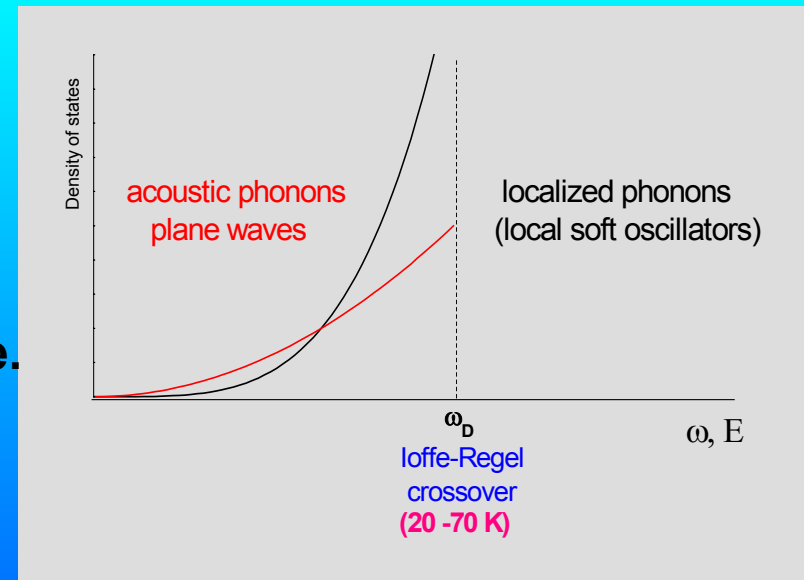
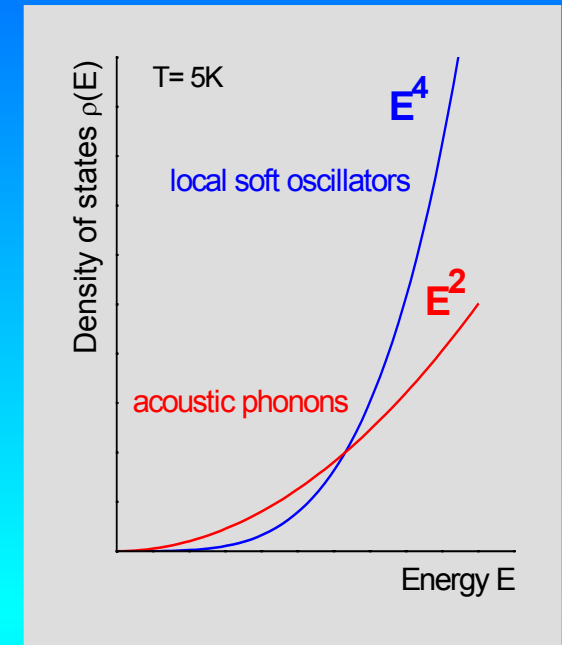
As the results at some frequency, so called **loffe-Regel crossover frequency ω_d** :

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

phonon wavelength = phonon free path

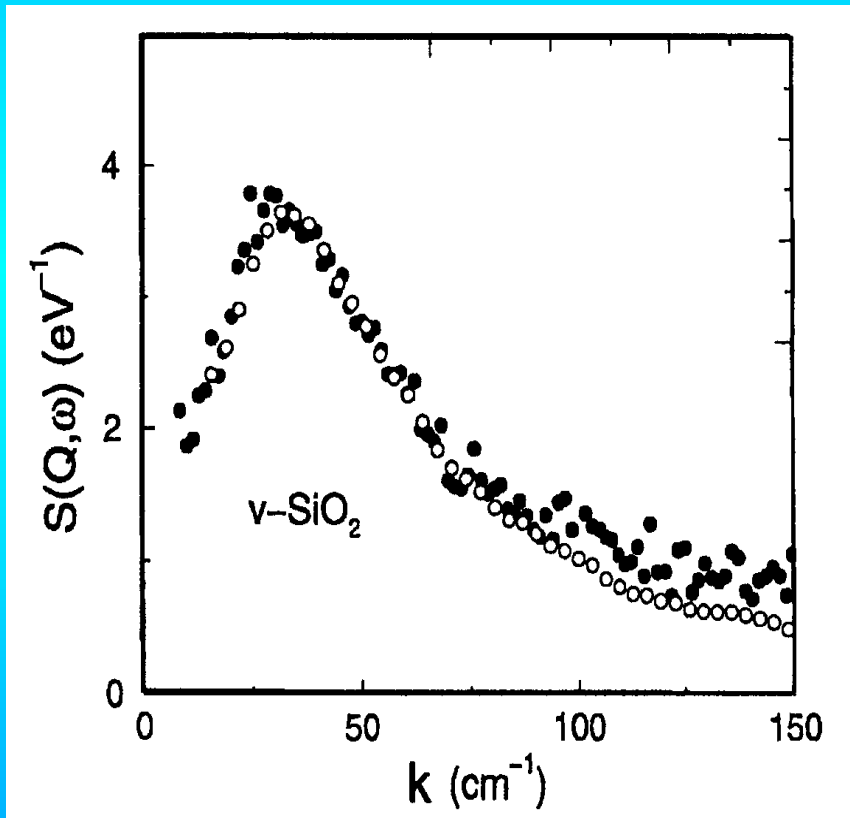
and concept of phonons has further no sense.

Above the crossover frequency ω_d only **localized excitations** exist



Boson peak

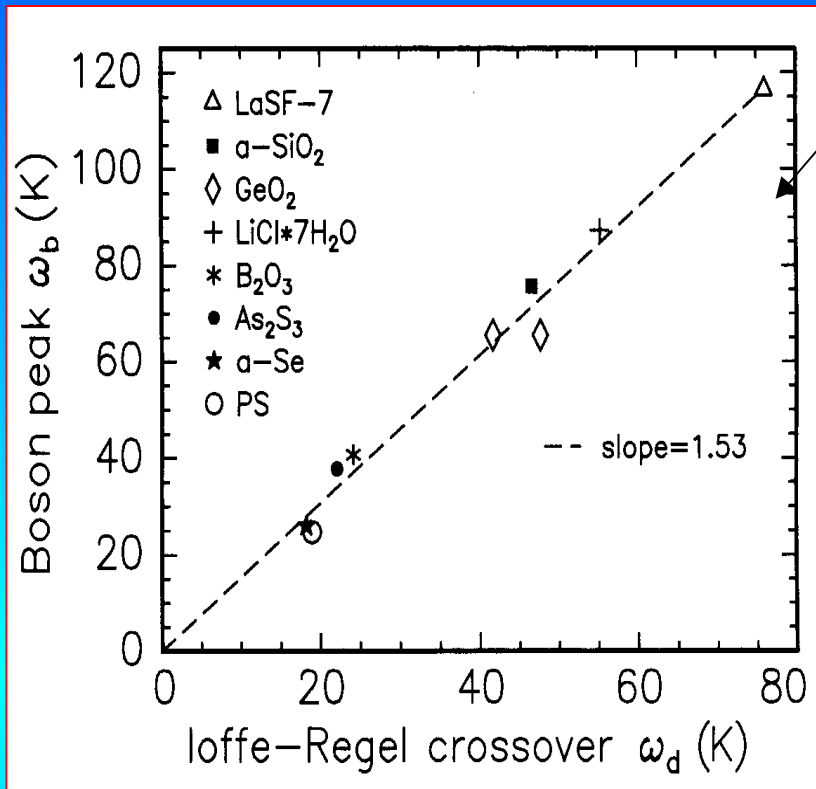
Boson peak it is a broad band of low frequency **harmonic excitations** (optical type) centered about **1 THz** frequency (**$30 \text{ cm}^{-1} = 43 \text{ K}$**) appearing in **disordered solids, glasses and polymers**.



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.

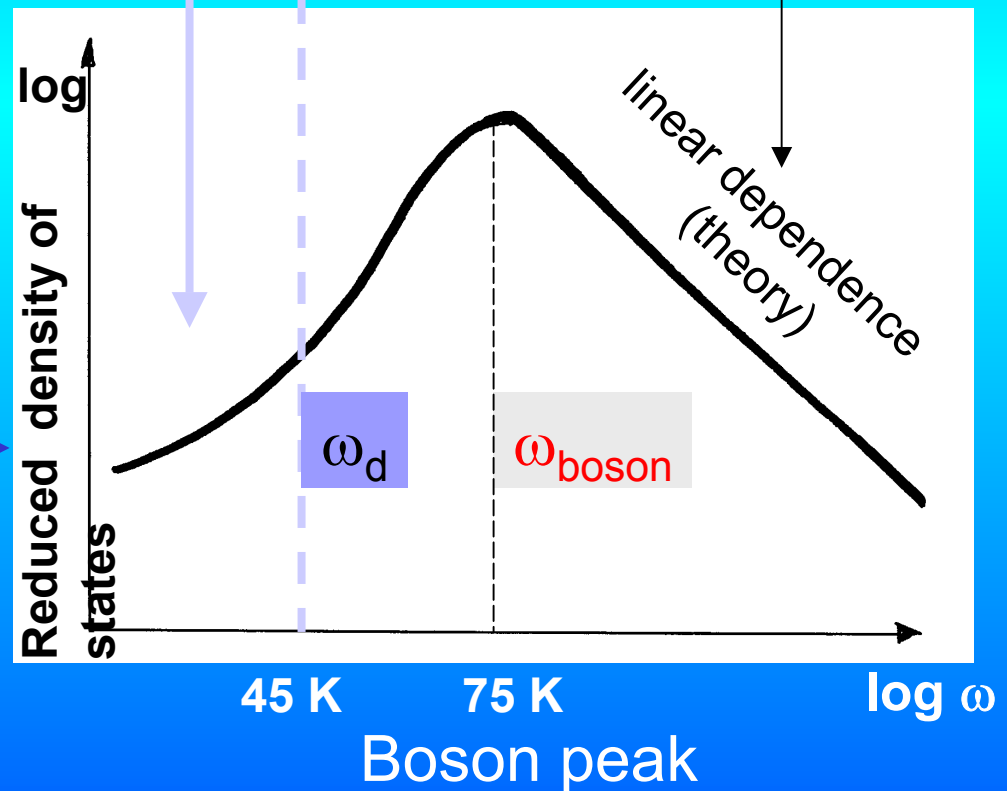
Boson peak is observed in **low-frequency Raman** spectra and in **inelastic neutron** scattering experiments



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

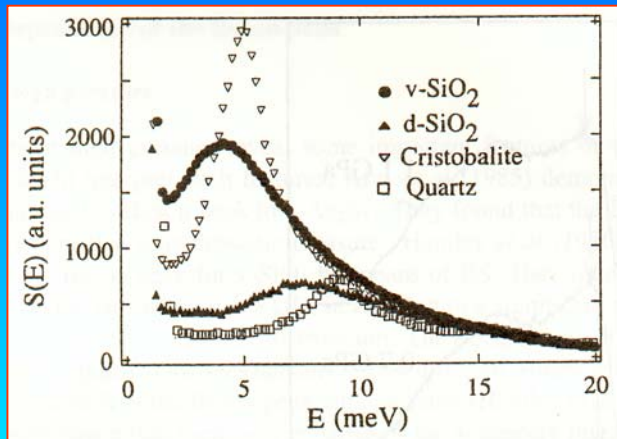


α -SiO₂

$\omega_d = 45$ K (Ioffe-Regel)

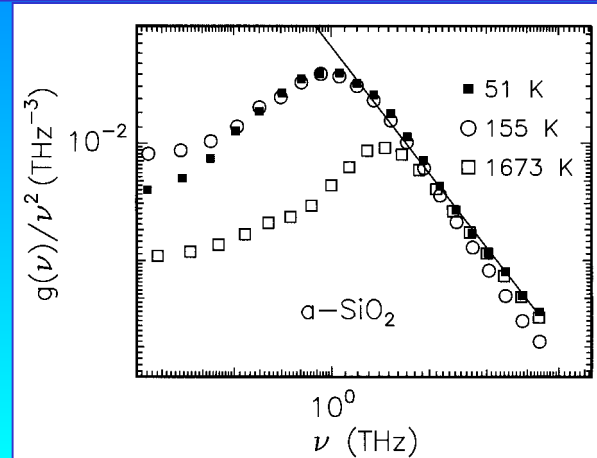
$\omega_{\text{boson}} = 75$ K

Boson peak exists in various amorphous materials,

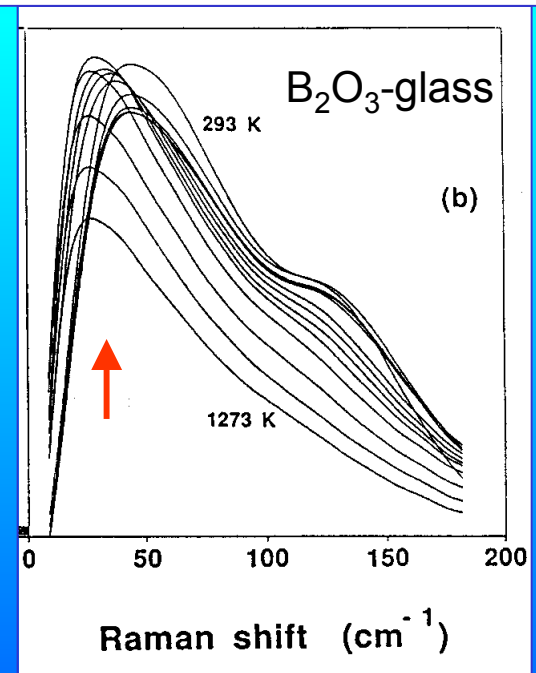
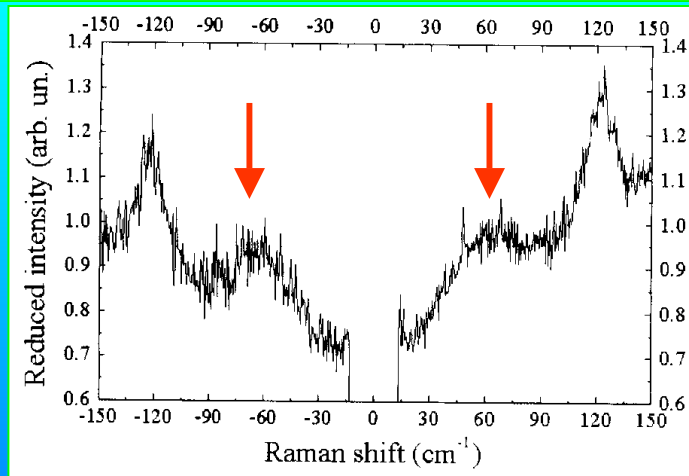


persists over broad range of temperature,

in polycrystals (cristobalite, quartz)



In neutron irradiated quartz single crystal



EPR:

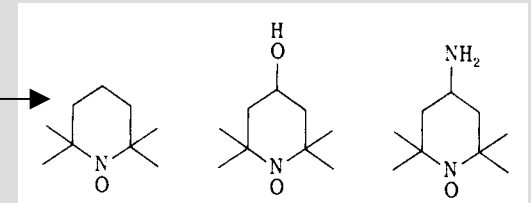
- at **microwave frequencies** where the most complex dynamics
- **high sensitivity** - 10^{14} spins/gram
- pulsed EPR (**electron spin echo = ESE**) very sensitive to dynamics

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

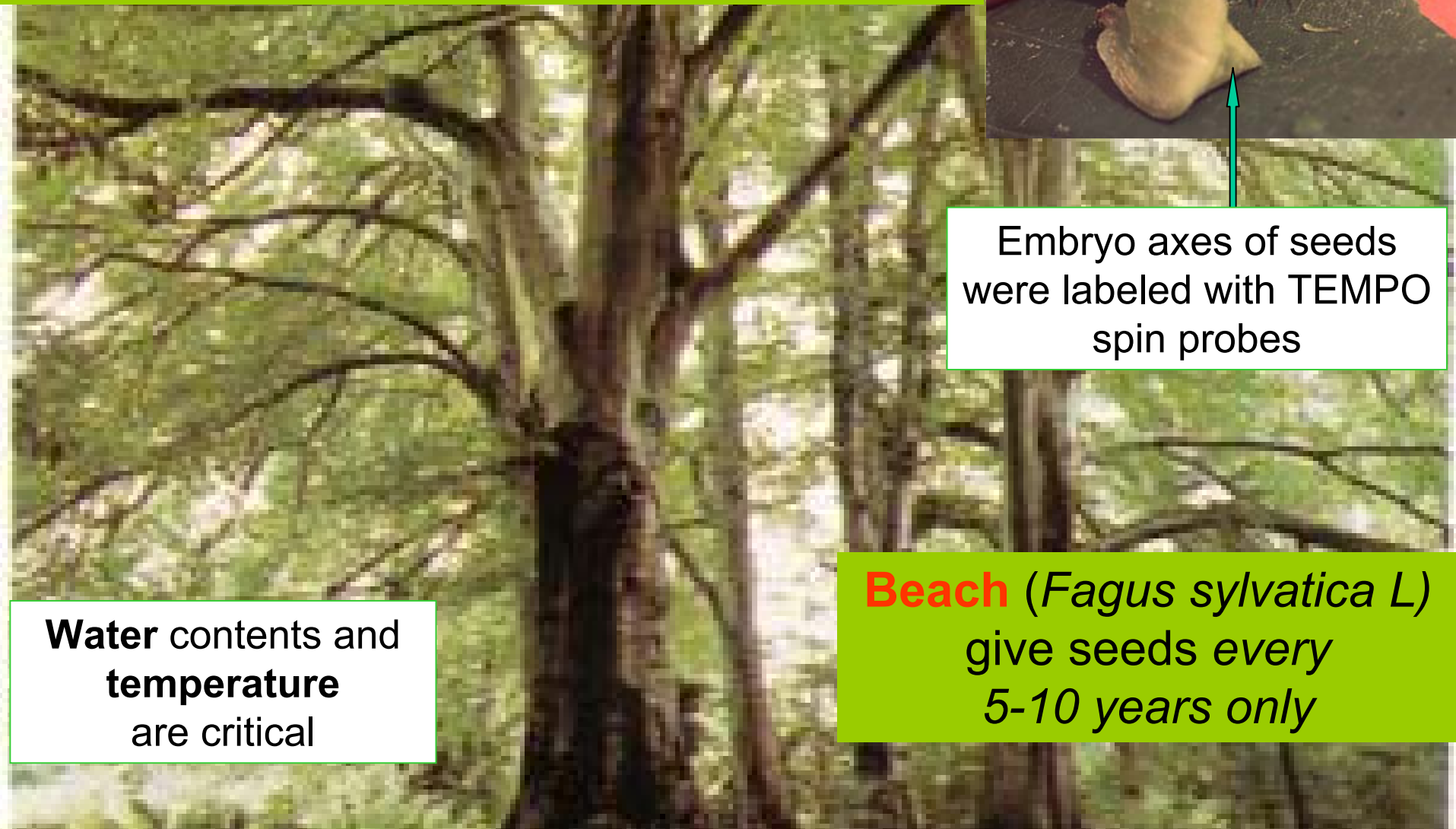
S. Pukacka, S. K. Hoffmann, J. Goslar, P. M. Pukacki
E. Wojkiewicz, *Biochim. Biophys. Acta* 1621, 48 (2003)



Embryo axes of seeds
were labeled with TEMPO
spin probes

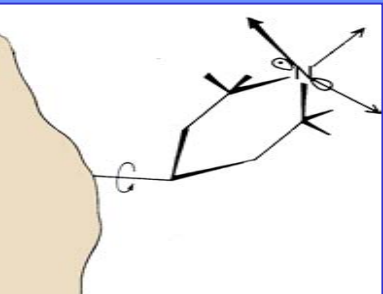
**Water contents and
temperature**
are critical

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

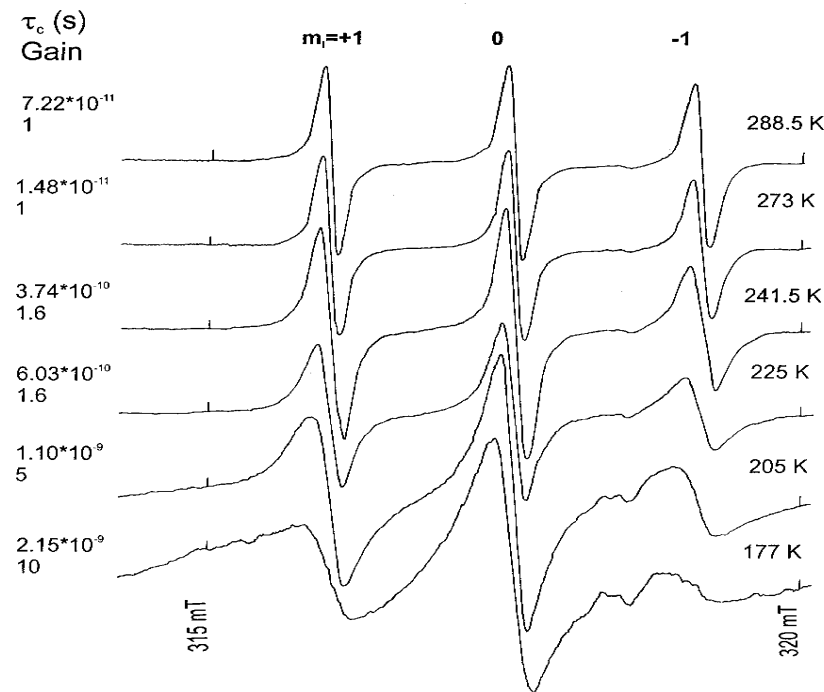


Nitroxide TEMPO molecules

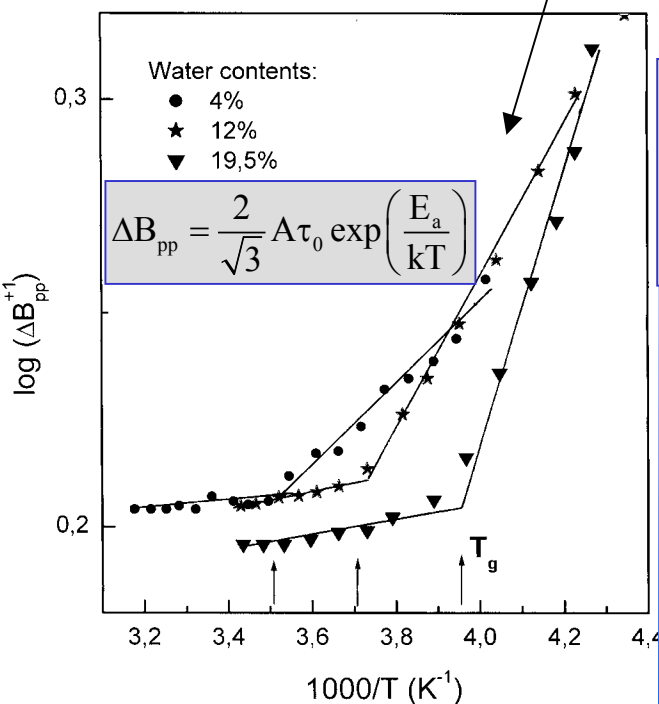
label the lipid fraction of cell membrane and are also located in cytoplasm interior



EPR spectra at 8.915 GHz (for 12% H₂O sample)

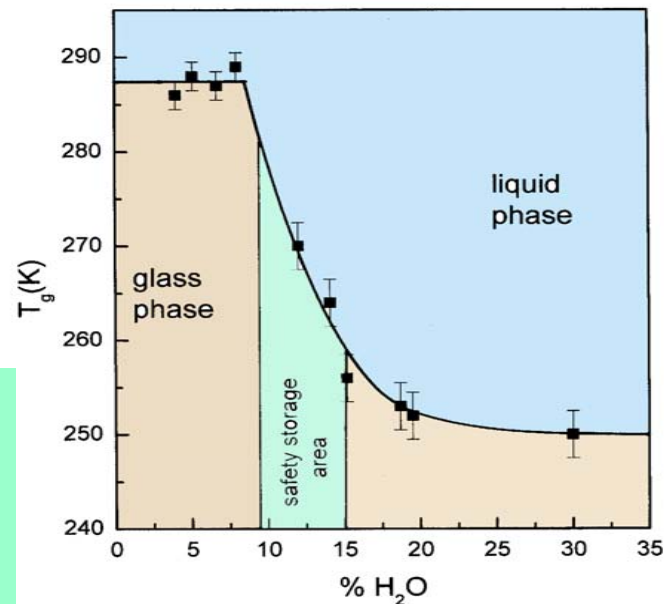


Spectra indicate **thermally activated reorientations** visible as line broadening (for the low field line):



$E_a \approx 3 \text{ kJ/mol}$
(depends on H₂O contents)
 $\tau_0 \approx 10^{-12} \text{ s}$

Glass transition vs water contents for embryo axes of beech seeds

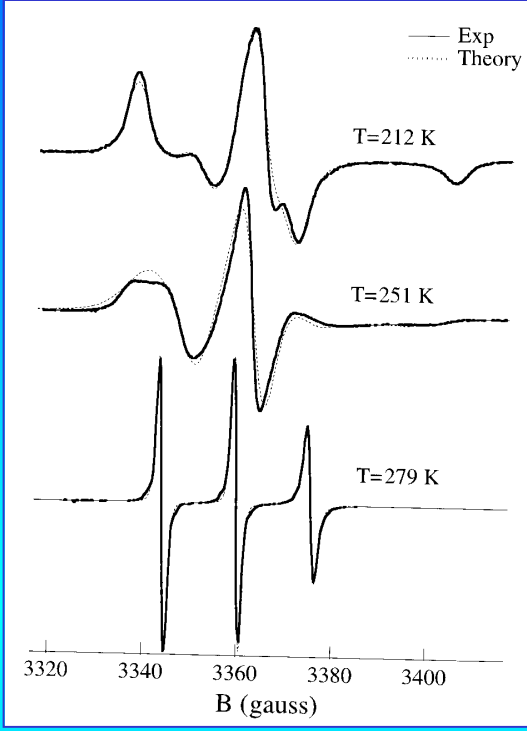
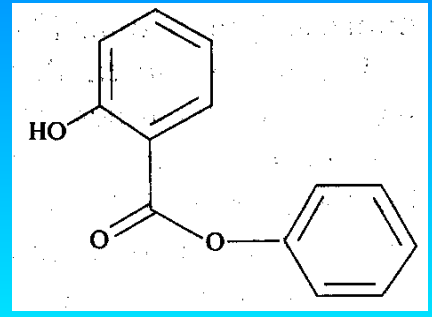
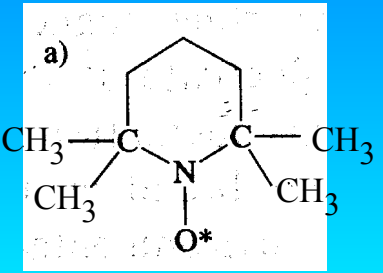


Dynamics of SALOL observed by spin-probe EPR

Isotropic jump reorientations with τ

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

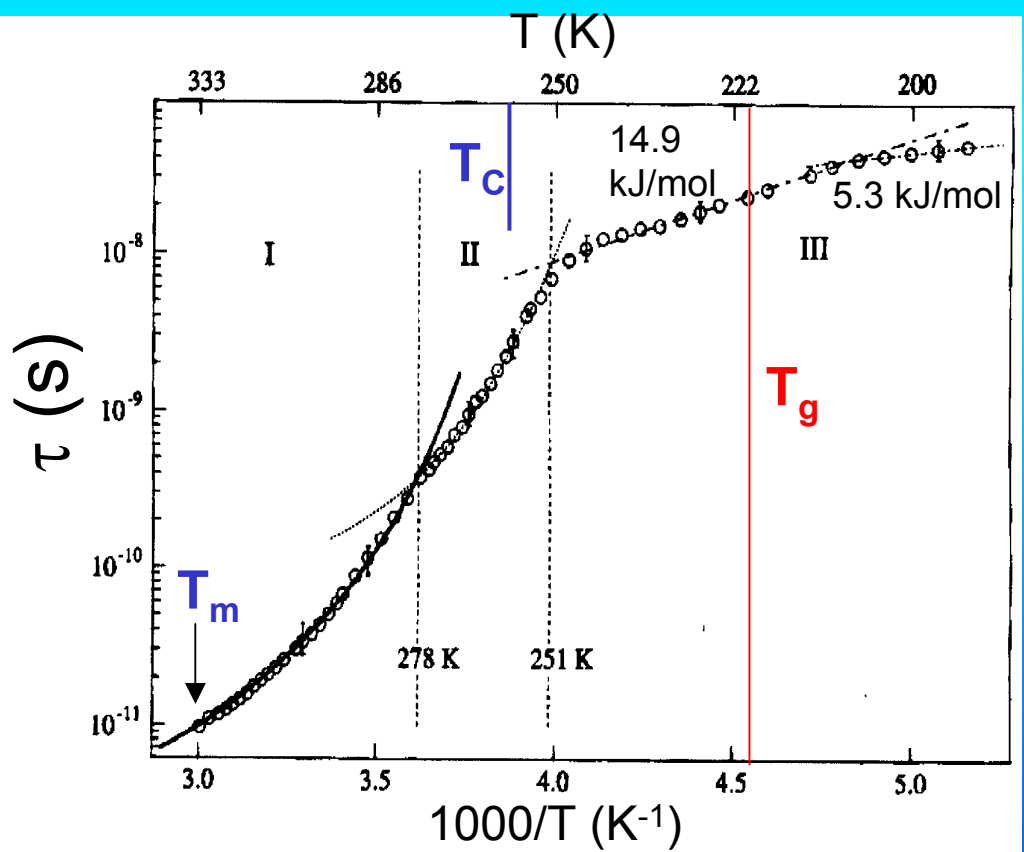
SALOL
Phenyl-salicylato



3.2×10^{-8} s

6.9×10^{-9} s

2.8×10^{-10} s



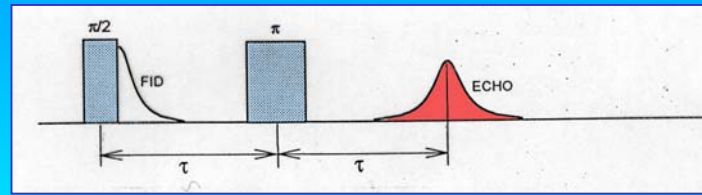
$T_m = 315$ K, $T_c = 260$ K, $T_g = 220$ K

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 frequency generate **electron spin echo** signal. In EPR microwave pulses are order of **ns**



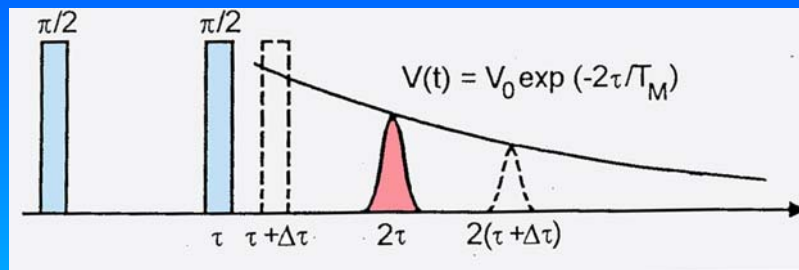
ESEEM Spectroscopy
(FT-ESE Spectroscopy)
ENDOR-type spectra

ESE dephasing
(Electron phase relaxation)
(ns - μ s)

Electron spin-lattice
relaxation
(μ s - s)

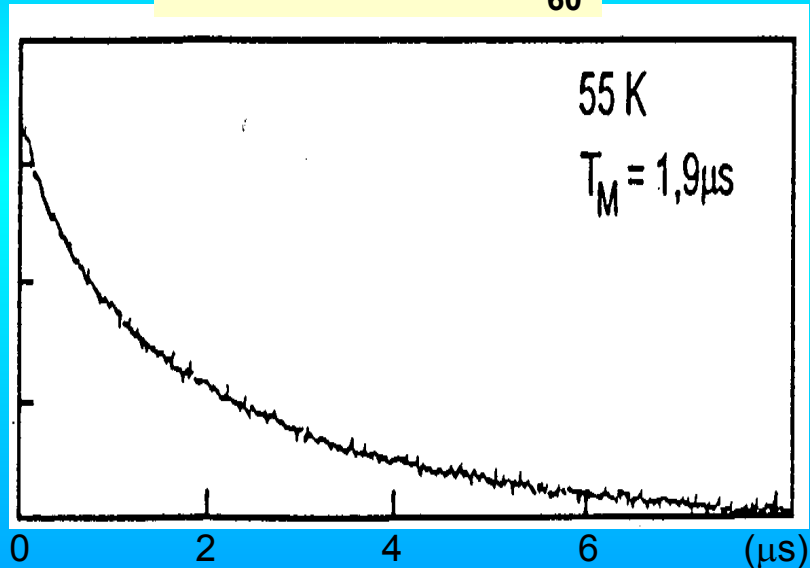
ESE = Electron Spin Echo

ESEEM = Electron Spin Echo Envelope Modulations



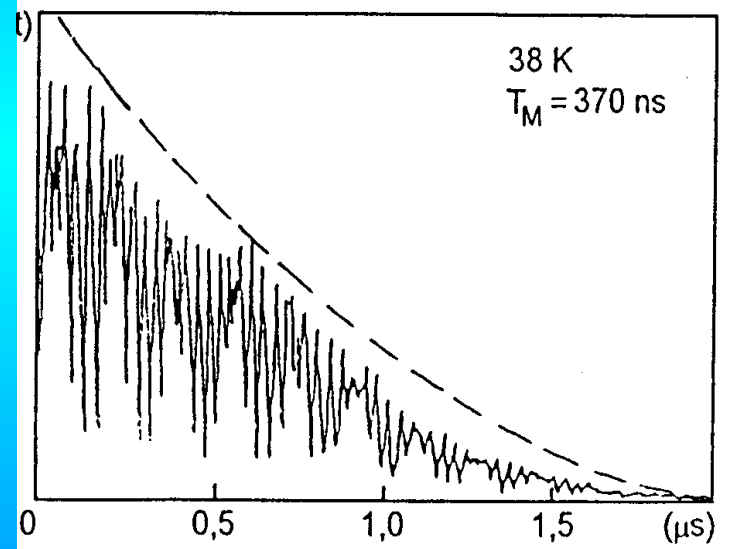
ESE signal amplitude decays with time after excitation with characteristic time called phase memory time T_M

Free radical in C_{60}



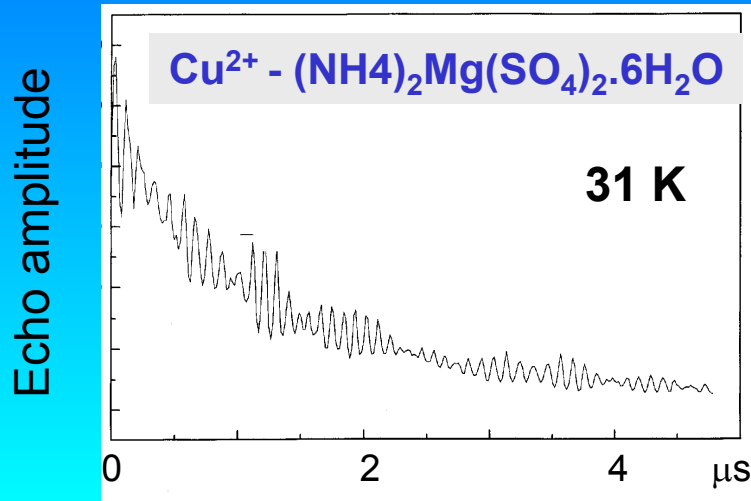
Phase memory time is very sensitive to molecular motions (varies with temperature)

Cu^{2+} ions in triglycine selenate crystal



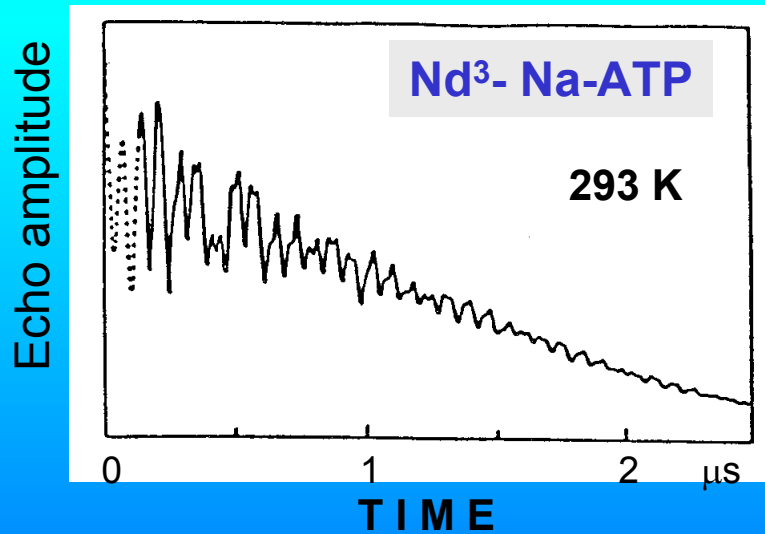
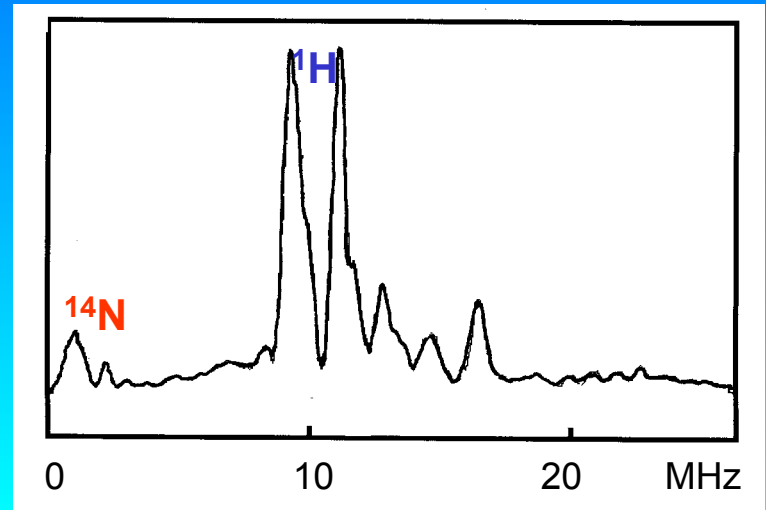
Modulations of the decay = **ESEEM = Electron Spin Echo Envelope Modulations**

Modulations of the Electron Spin Echo decay and Fourier Transform (ESEEM) spectra



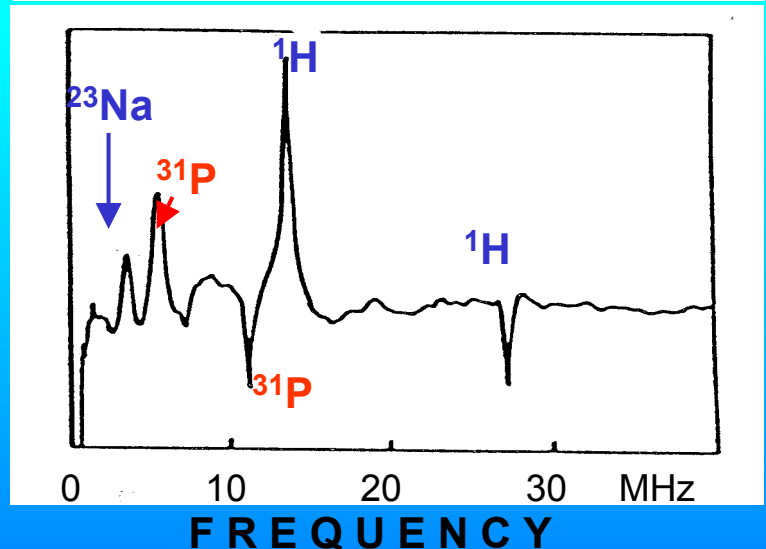
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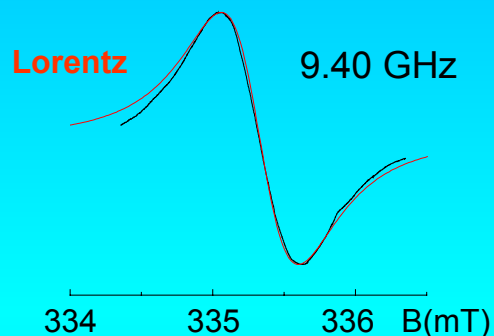
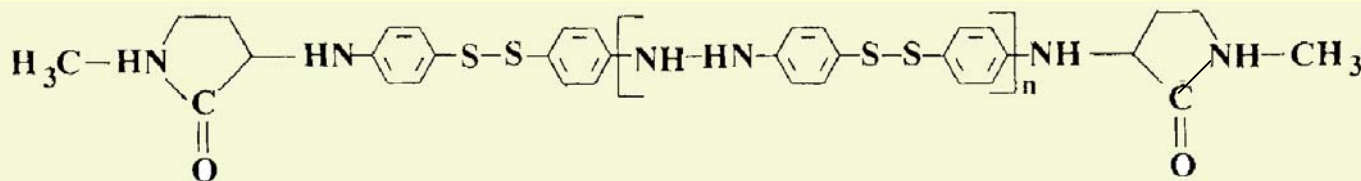
\rightarrow

F



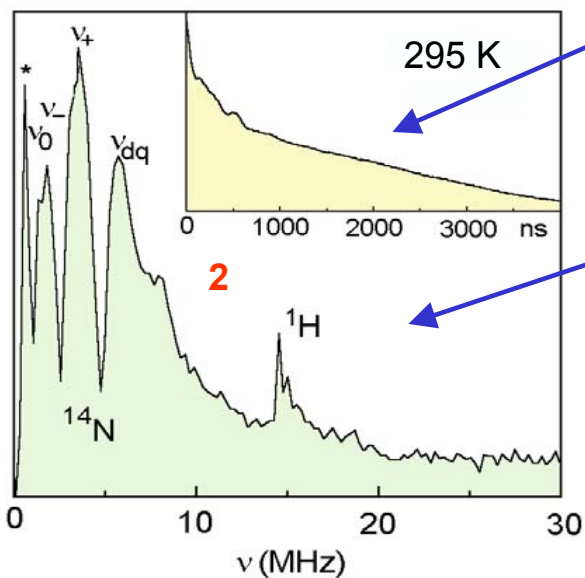
Number of peaks in ESEEM spectrum and modulation depth allow to determine :
magnetic nuclei, their number and often a distance from paramagnetic center
(up to about 5Å)

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

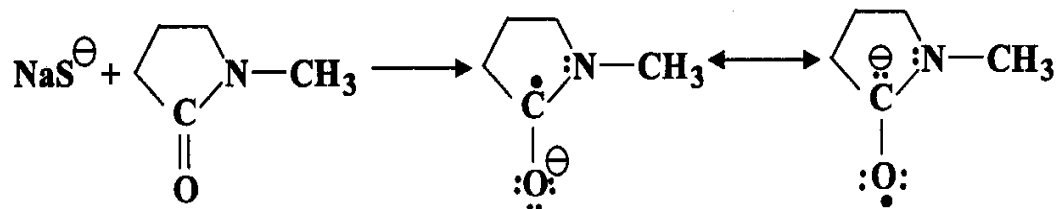


Electron spin echo (three pulse) amplitude decay is weakly modulated

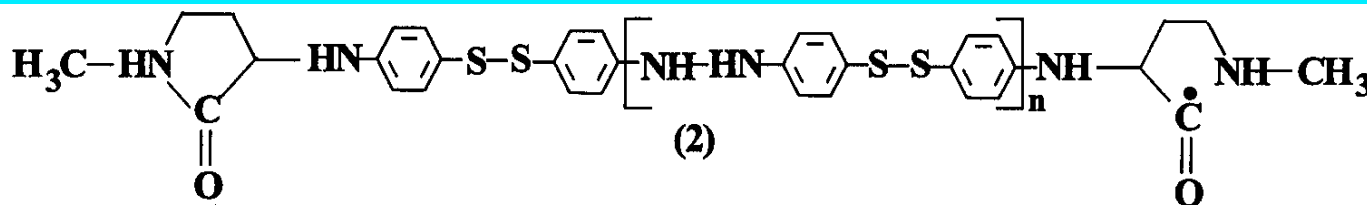
Fourier Transform (ESEEM) spectrum indicate:

1. Weak peak from **distant hydrogens**
2. Reach quadrupole structure v_0, v_+, v_-, v_{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)

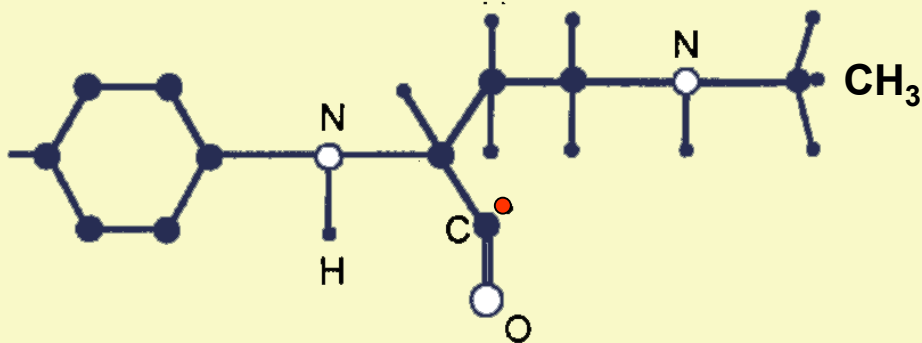
On a one of the stages of the reaction a transfer of electron from NaS^\ominus to N-methyl-2-pyrrolidone appears allowing a reaction with terminal amine group of polymerizing 4-hydrazo-diphenylenedisulfide chain



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



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

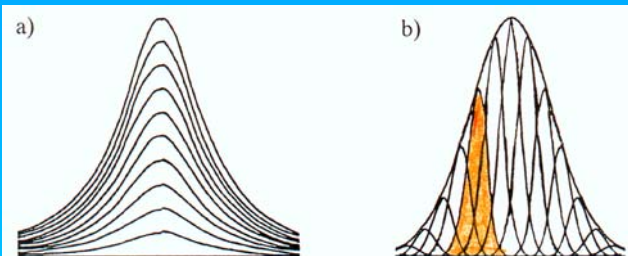


Free radical should be sensitive to:

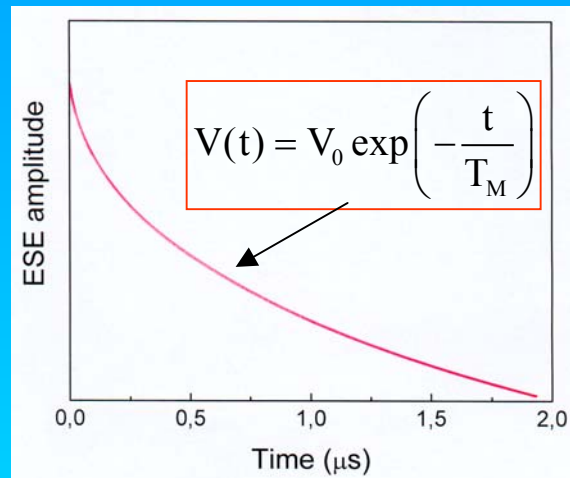
- CH_3 reorientations
- chain-end dynamics

Electron Spin Echo (ESE) dephasing

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



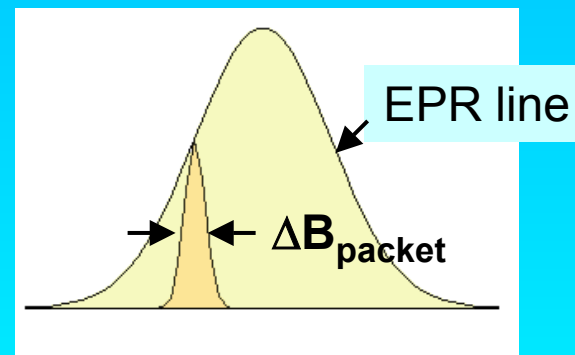
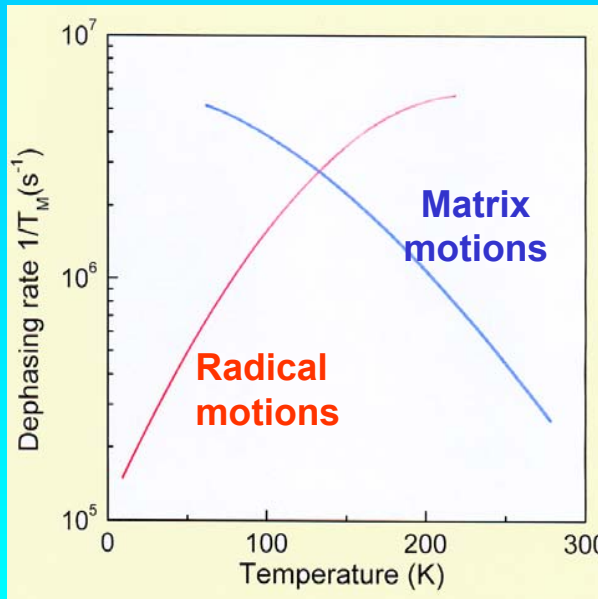
ESE amplitude decay with time, with characteristic time T_M



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

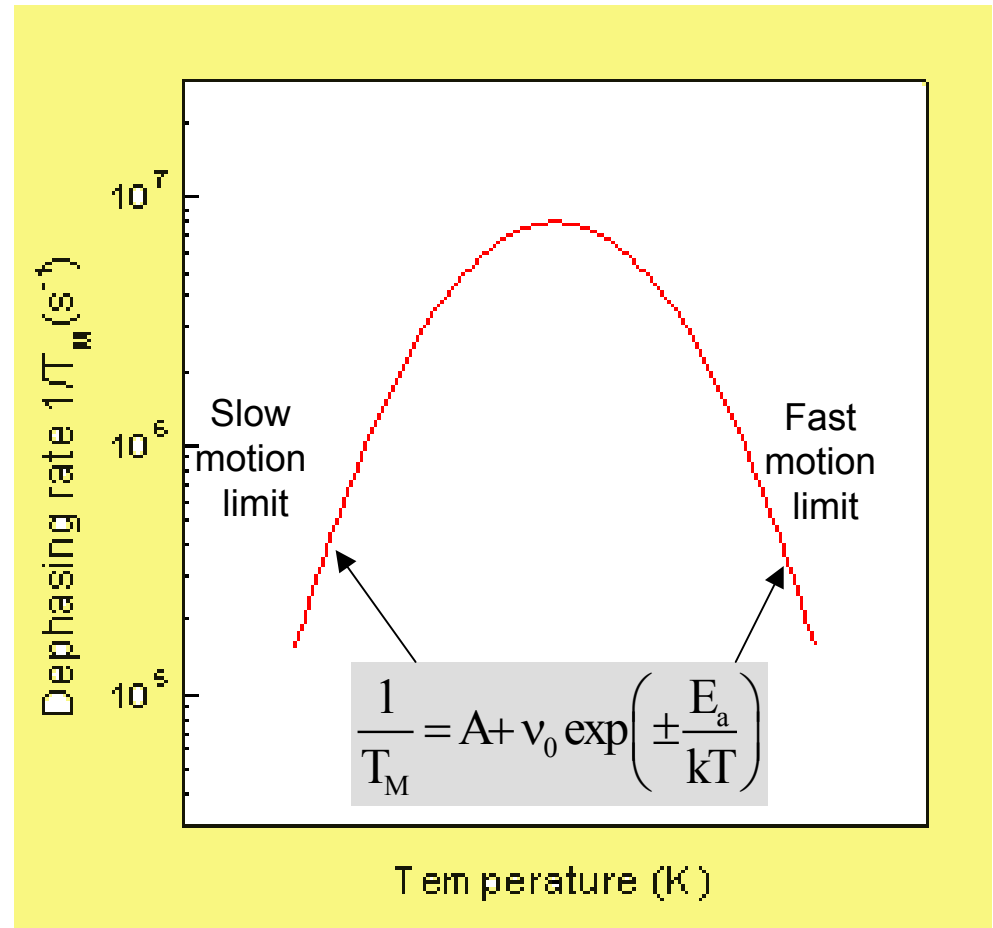
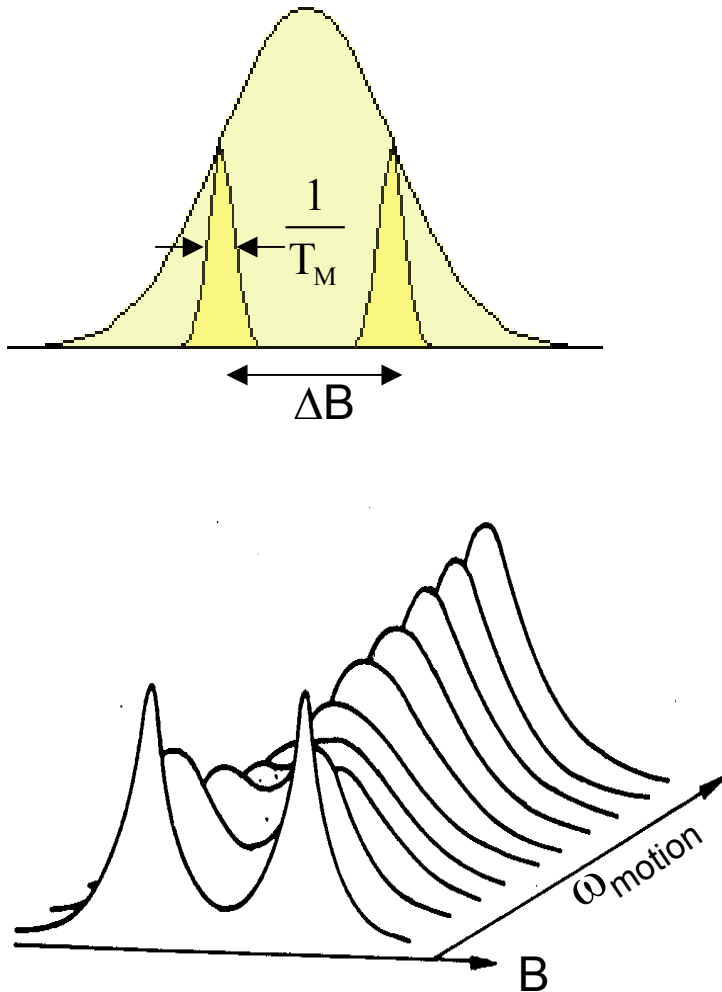
ΔB_{packet} is 0.01 – 1G, is very sensitive to dynamical processes:

- radical motions produce spin packet broadening
- matrix molecule motions produce spin packet narrowing

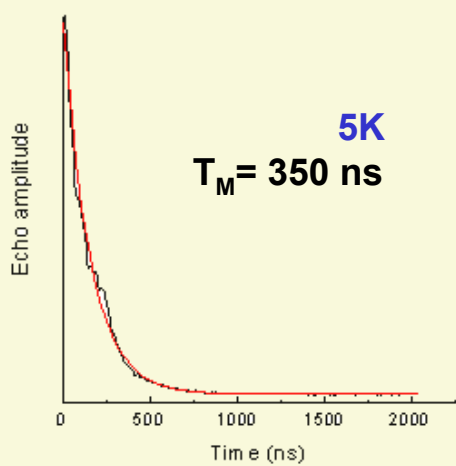


$$\frac{1}{T_M} = \Delta B_{\text{packet}}$$

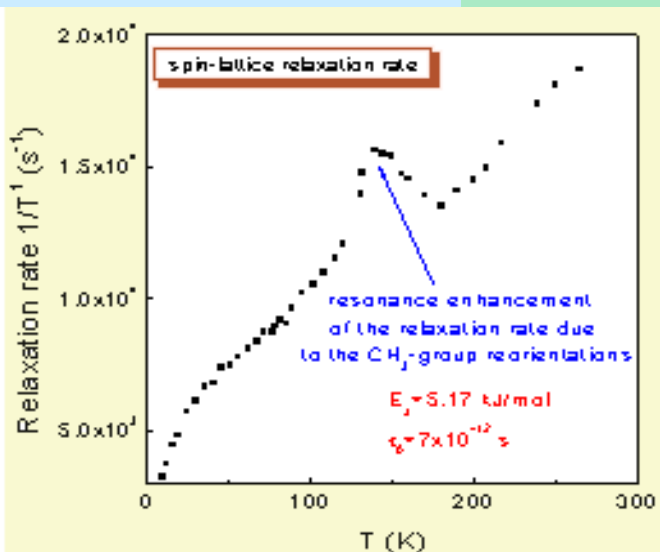
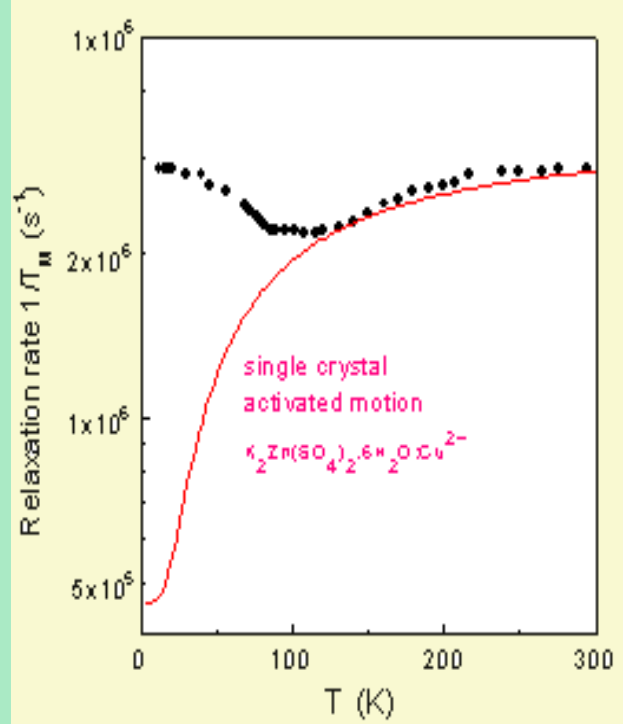
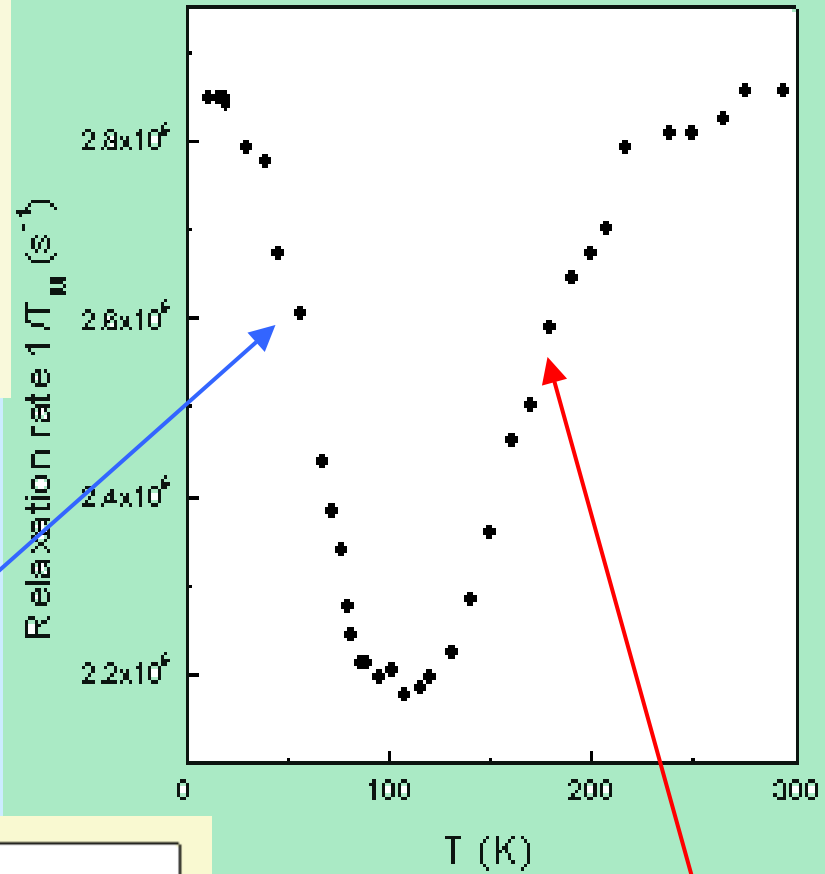
Merging effect between spin packets (unresolved hyperfine structure lines) produces **resonance-type enhancement** of the dephasing rate (**maximum in temperature dependence of $1/T_M$**)



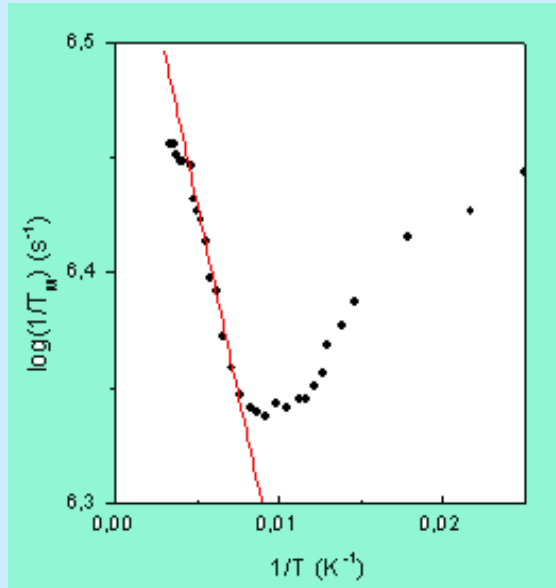
v_0 is order of $10^6 - 10^8 \text{ s}^{-1}$



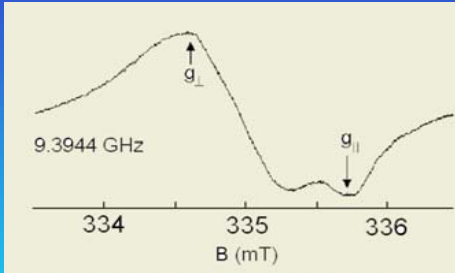
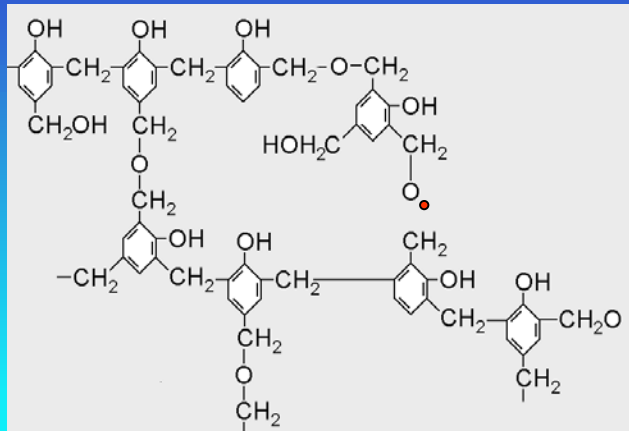
CH₃-tunneling rotation
 $\tau_0 = 7 \times 10^{-12}$ s
 $E_a = 5.17$ kJ/mol



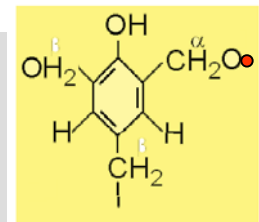
Slow molecular motion
 $\tau_0 = 2.6 \times 10^{-7}$ s
 $E_a = 49$ cm⁻¹ = 6.1 meV
= 0.6 kJ/mol



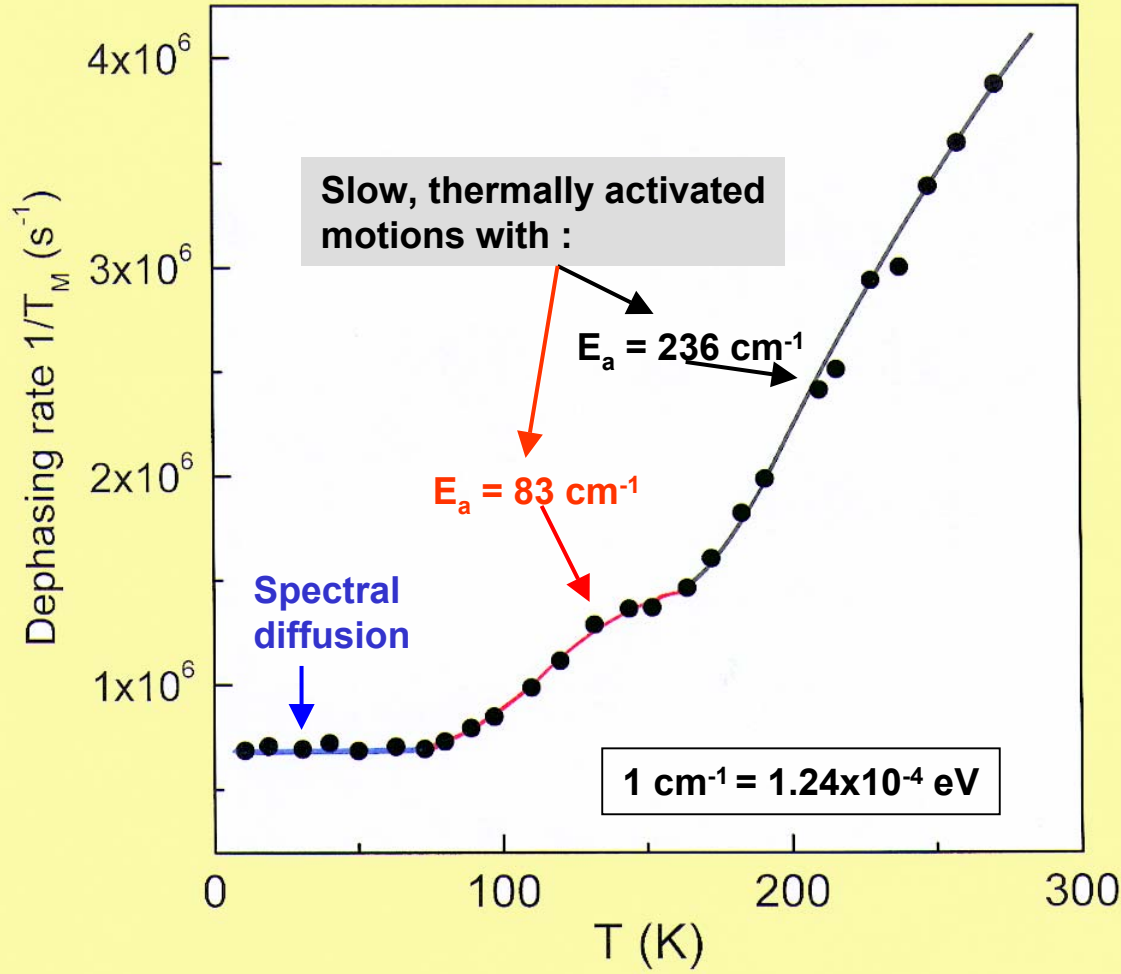
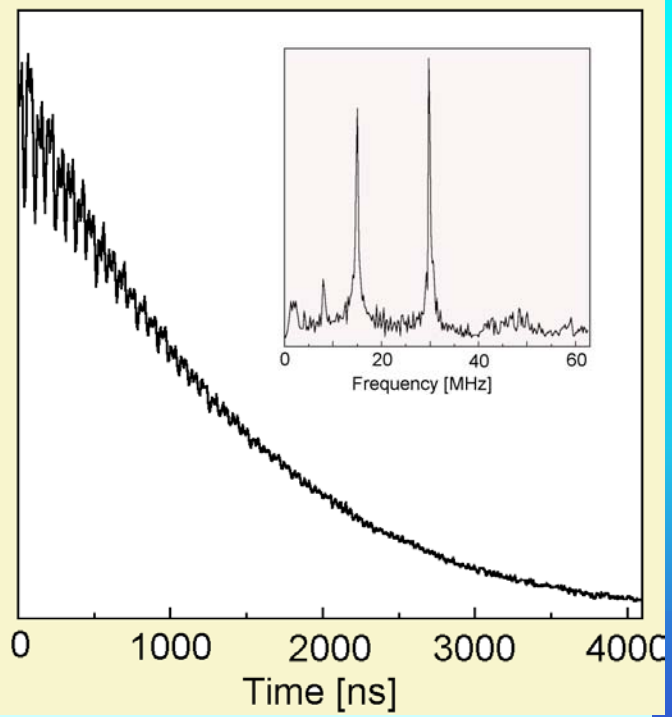
Phenol-formaldehyde resin



EPR spectrum with $g_{\parallel}=1.9994$
 $g_{\perp}=2.0058$ suggests
 localization on an oxygen

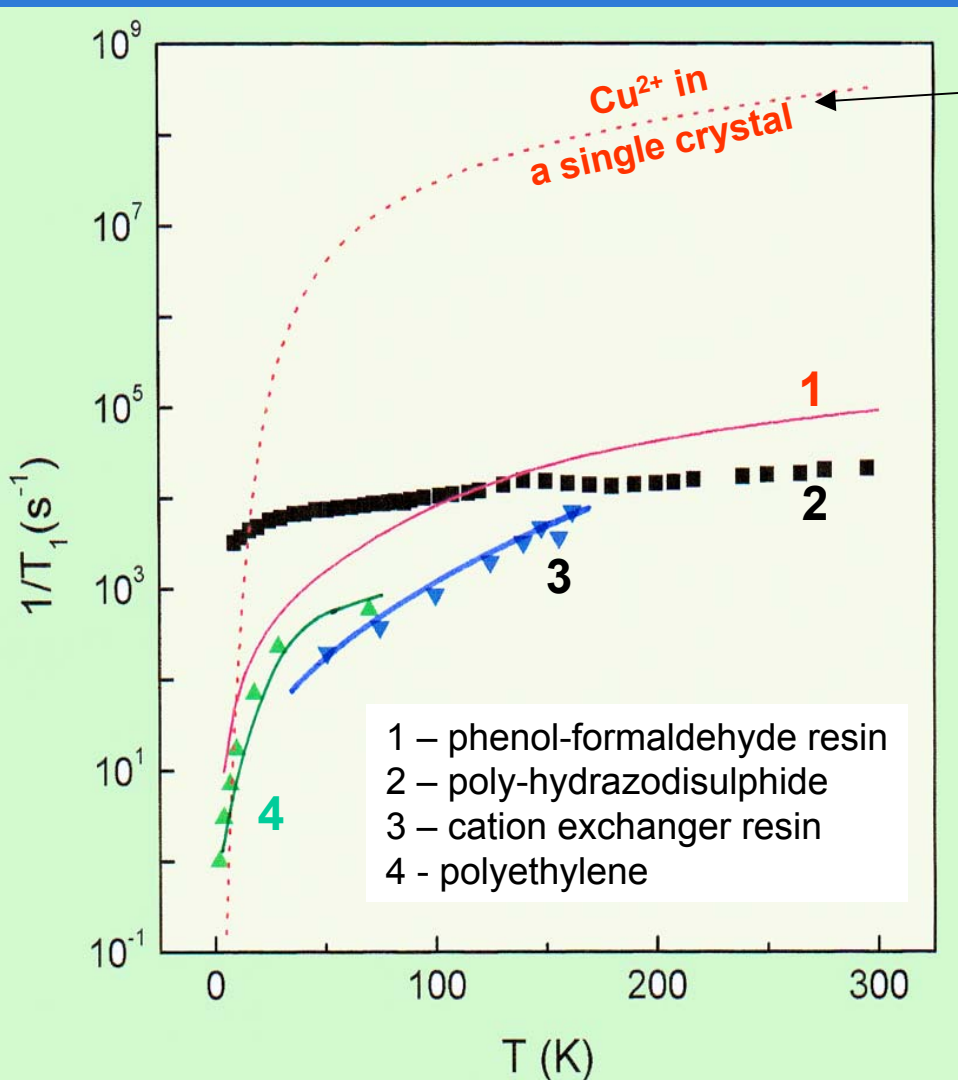


Electron spin echo decay



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

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 paramagnetic centers:

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

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

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 **CH₃**, **NH₃** 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