

Glass physics

- > **Systems**
- > **Structure**
- > **Glass transition**
- > **MCT**
- > **Metallic glasses**
- > **Mechanical properties**
- > **Applications**

Hermann Franz

Master course Modern X-ray Physics

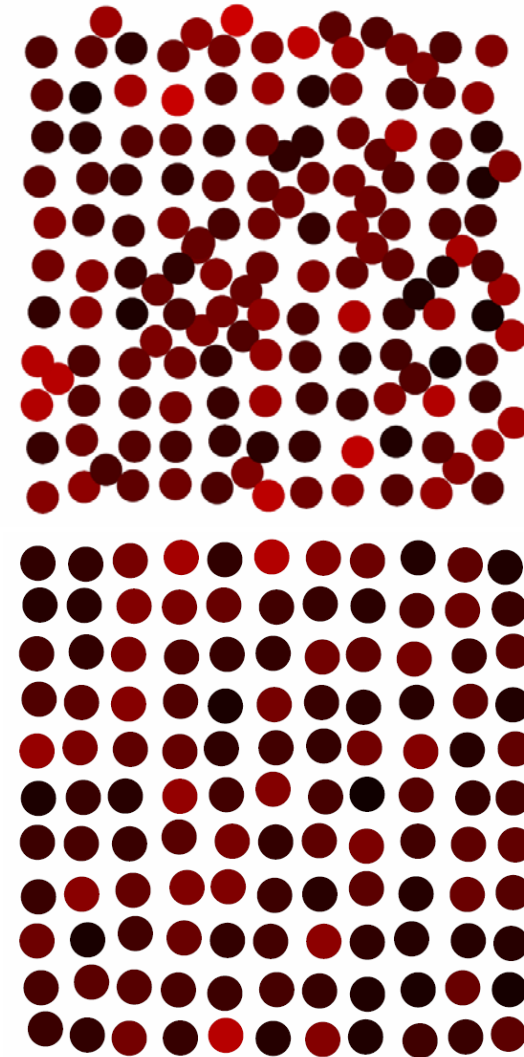
12 May 2009

Introduction

Glasses are materials with
amorphous structure showing
a **gradual transition** from the
liquid to the solid without well
defined melting point

Favorable conditions for forming

Particular mechanical properties



Introduction

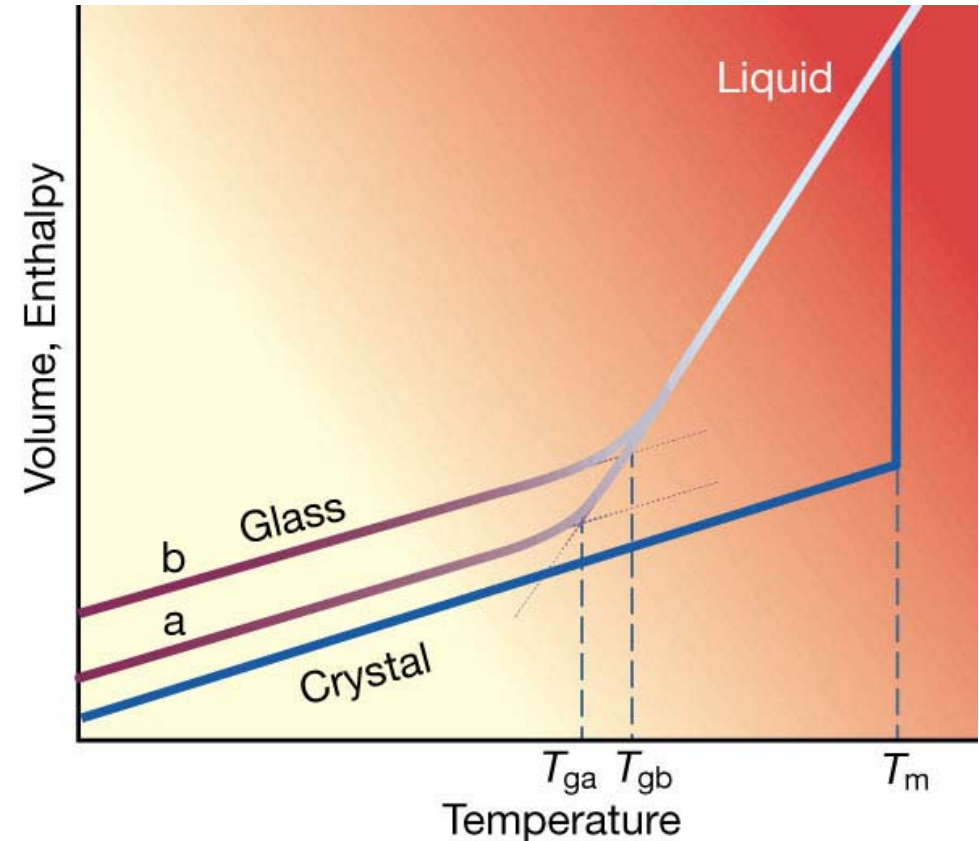
Physical properties change gradually on lowering the temperature

Cross-over depends on cooling/heating rate

i.e. properties depend on thermal history

Glasses are in a frozen in metastable state

►susceptible to crystallisation



Examples for glasses in everyday life

Traditional glasses

SiO_2 , B_2O_3 , P_2O_5 based

Window glass

SiO_2 with sodium or potassium minerals
(soda, potash)

Glasses for art work



doped with variety of
elements

Industrial glasses

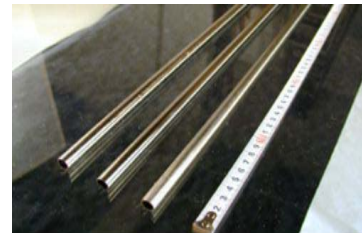
Polymers

Plastic materials: PE, PMMA, PS.....

SMO (small organic molecules)

Glycerol, OTP, salol, squalane,

Metallic glasses

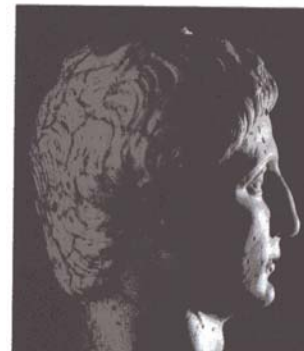


History

Art of glass making known since
ca 3000 b.c.

Earliest records in Egypt and
Mesopotamia, later many
records in Rome

Sacophagus of Tut Ench Amun



Glas 2): Becher aus dem Grab Thutmosis' III.; Höhe 8,5 cm, um 1450 v. Chr. (München, Staatliche Sammlung Ägyptischer Kunst)

Structure by X-rays

Recall:

Scattering amplitude from a crystal

$$F_{\text{crystal}}(Q) = \underbrace{\sum_{r_j} F_j^{\text{mol}}(Q) \exp(i\mathbf{Q}r_j)}_{\text{unit cell structure factor}} \bullet \underbrace{\sum_{R_n} \exp(i\mathbf{Q}R_n)}_{\text{lattice sum}}$$

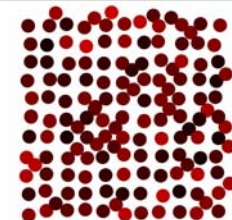
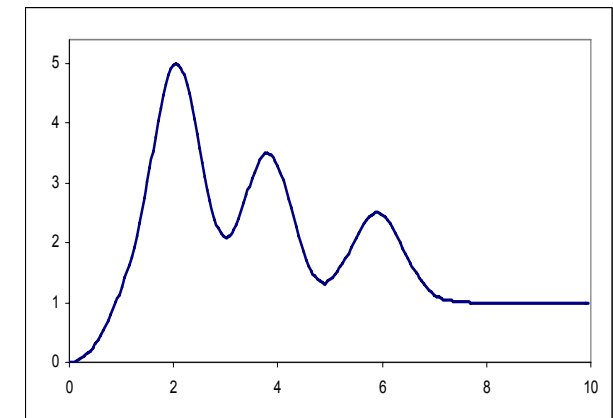
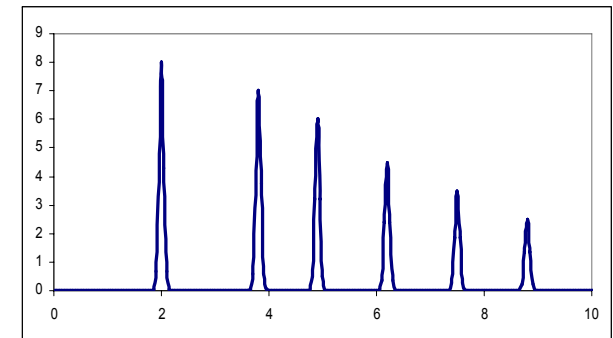
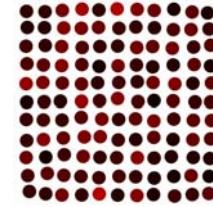
leading to reciprocal lattice

$$\mathbf{G} \bullet \mathbf{R}_n = 2\pi (hn_1 + kn_2 + ln_3)$$

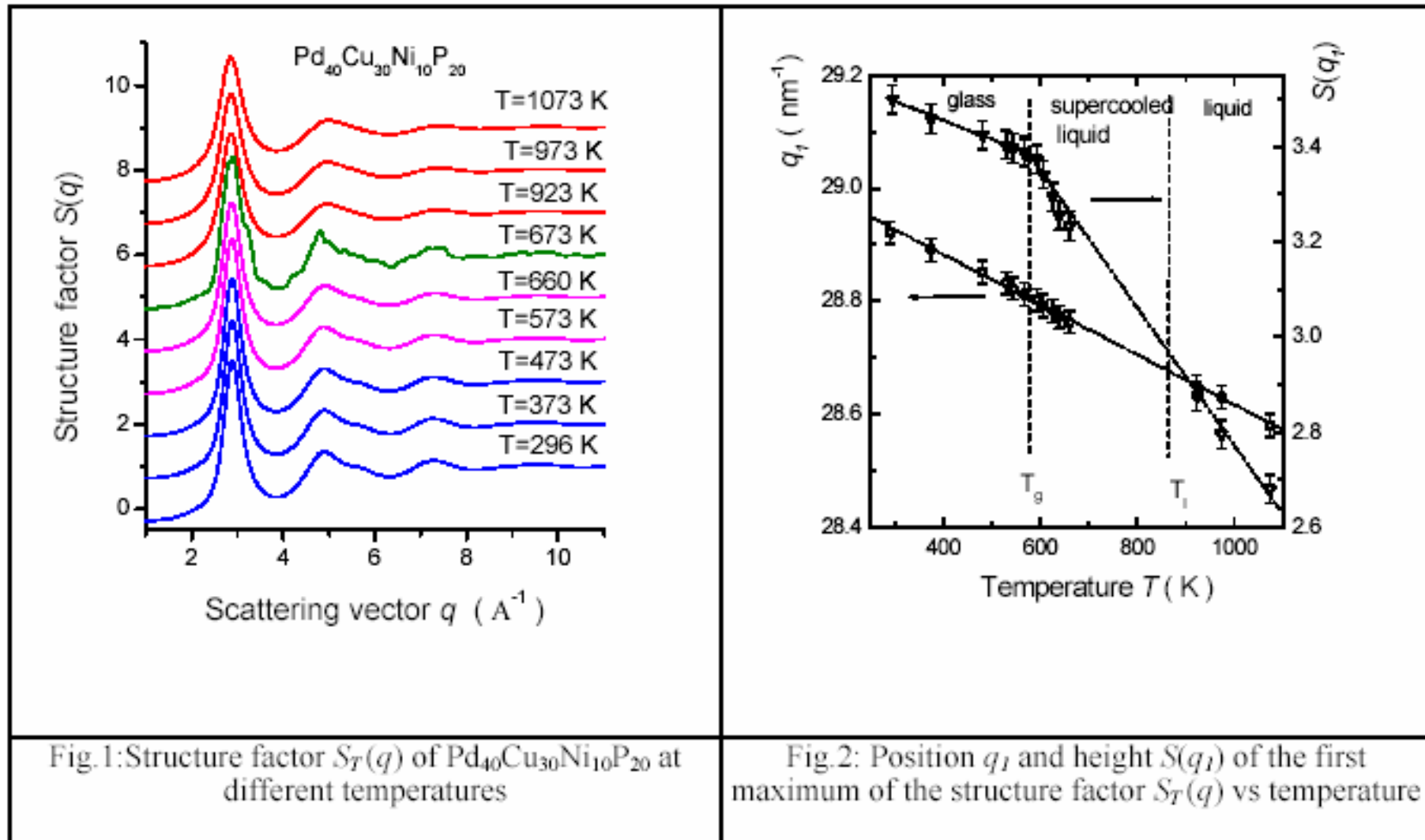
As there is no lattice in amorphous structures we have to treat the whole sample like a molecule

$$F^{\text{mol}}(Q) = \sum_{r_j} f_j(Q) \exp(i\mathbf{Q}r_j)$$

With the sum running over all atoms in the illuminated volume



Structure by X-rays temperature dependence



N. Mattern et al APL 2003



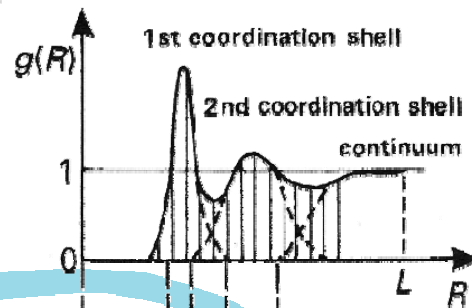
Structure determination of amorphous materials

X-ray diffraction using high energy photons

- + high penetration depths (mm-cm)
- + relatively fast, suitable for in-situ studies
- less sensitive to elements
- ASF depend on Q

Neutron diffraction

- + sensitive to different isotopes
- + ASF do not depend on Q
- + probes magnetic state of matter
- large sample volumes
- relatively slow, not suitable for in-situ studies



Extended X-ray Absorption Spectroscopy

- + highly sensitive to elements
- + reveals local atomic configuration
- + relatively fast, suitable for in-situ studies
- restricted sample size, geometry
- rather difficult to quantitatively analyze data on amorphous samples

However, none of these techniques gives a complete 3D image of amorphous structure ☹️

Reverse Monte Carlo modeling

Diffraction:

The partial $g_{ij}(r)$ functions are calculated from the atomic coordinates and transformed to reciprocal space:

$$S_{ij}(Q) = \frac{4\pi\rho_j}{Q} \int r \sin Qr (g_{ij}(r) - 1) dr$$

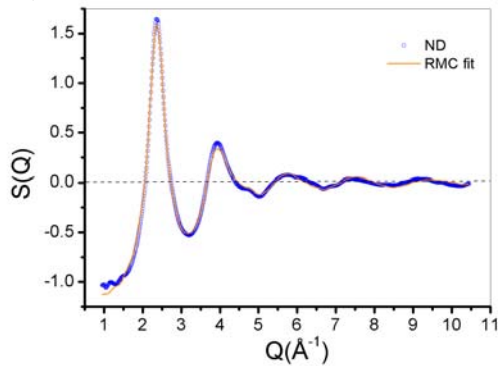
together with a weights (for ND $f(Q)=b$)

$$w_{ij} = \frac{(2 - \delta_{ij})c_i c_j f_i(Q) f_j(Q)}{\sum_{ij} c_i c_j f_i(Q) f_j(Q)}$$

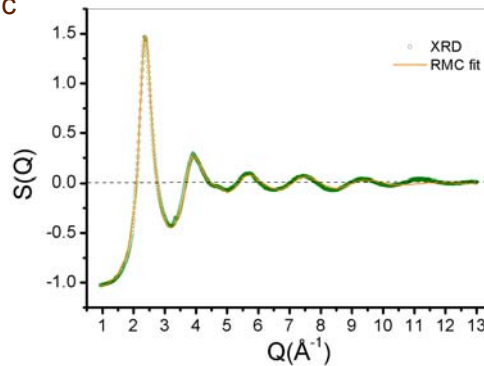
are combined in total structure factor

$$S^{RMC}(Q) = \sum_{ij} w_{ij}(Q) S_{ij}(Q)$$

ND



XRD

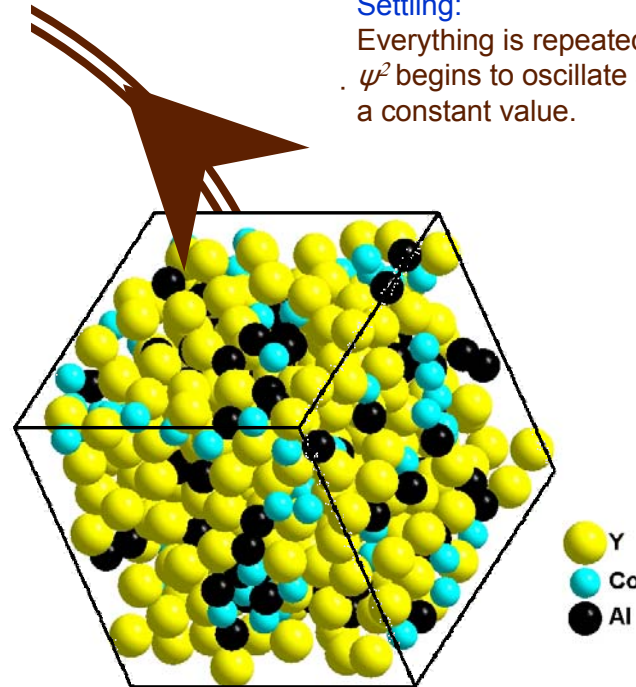


Move:

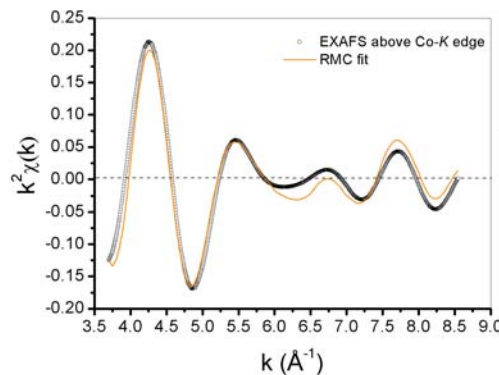
One particle is moved randomly taking into account applied constraints.

Settling:

Everything is repeated until ψ^2 begins to oscillate around a constant value.



EXAFS



EXAFS:

The model of EXAFS signal $\chi_i(k)$, at the absorption edge of i-type atoms can be calculated from the g_{ij} :

$$\chi_i(k) = \sum_j 4\pi c_j \rho \int_0^\infty r^2 \gamma_{ij}(r, k) g_{ij}(r) dr$$

while γ_{ij} is the atomic pair backscattering signal

$$\gamma_{ij}(r, k) = A_{ij}(k, r) \sin(2kr + \Phi_{ij}(kr))$$

Courtesy of Dr. K. Saksl

Acceptance of the move:

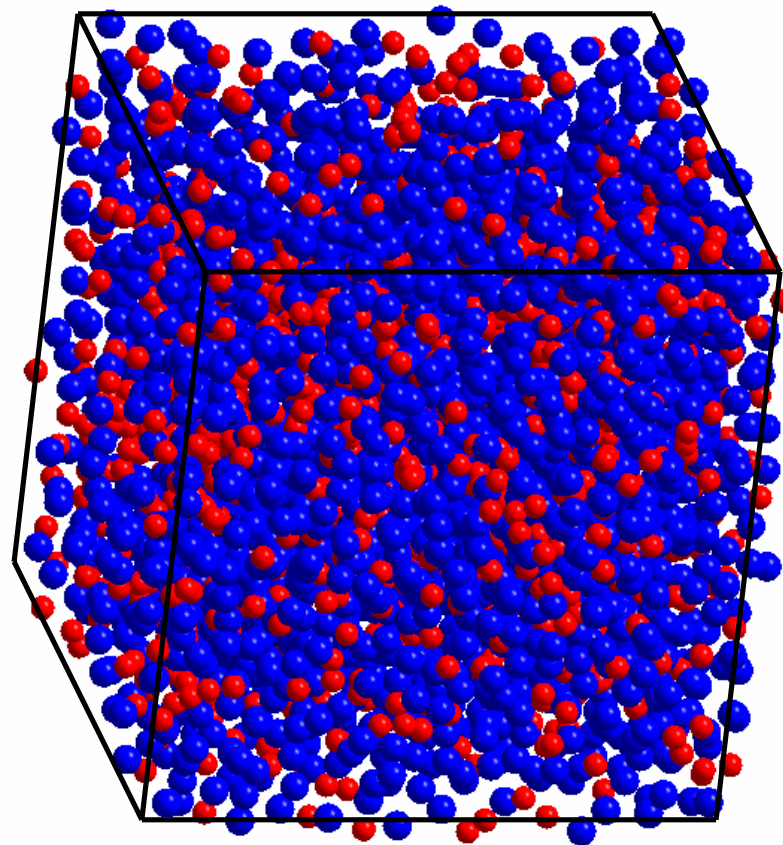
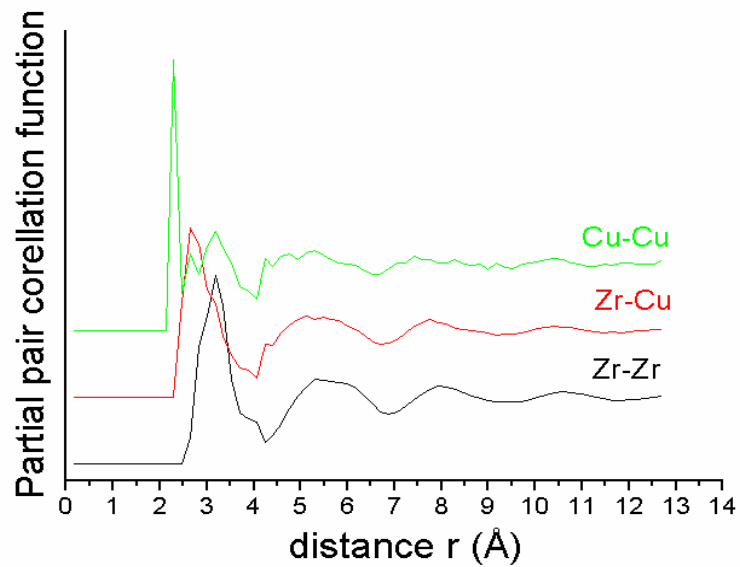
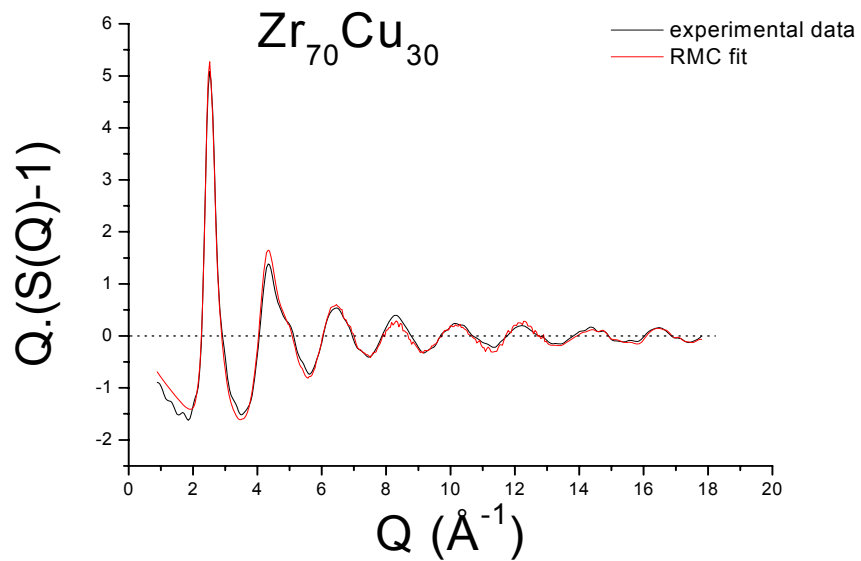
First the experiment-model difference is calculated

$$\psi^2 = \frac{1}{\delta} \sum_{i=1}^m [\zeta^{\text{exp}} - \zeta^{\text{RMC}}]^2$$

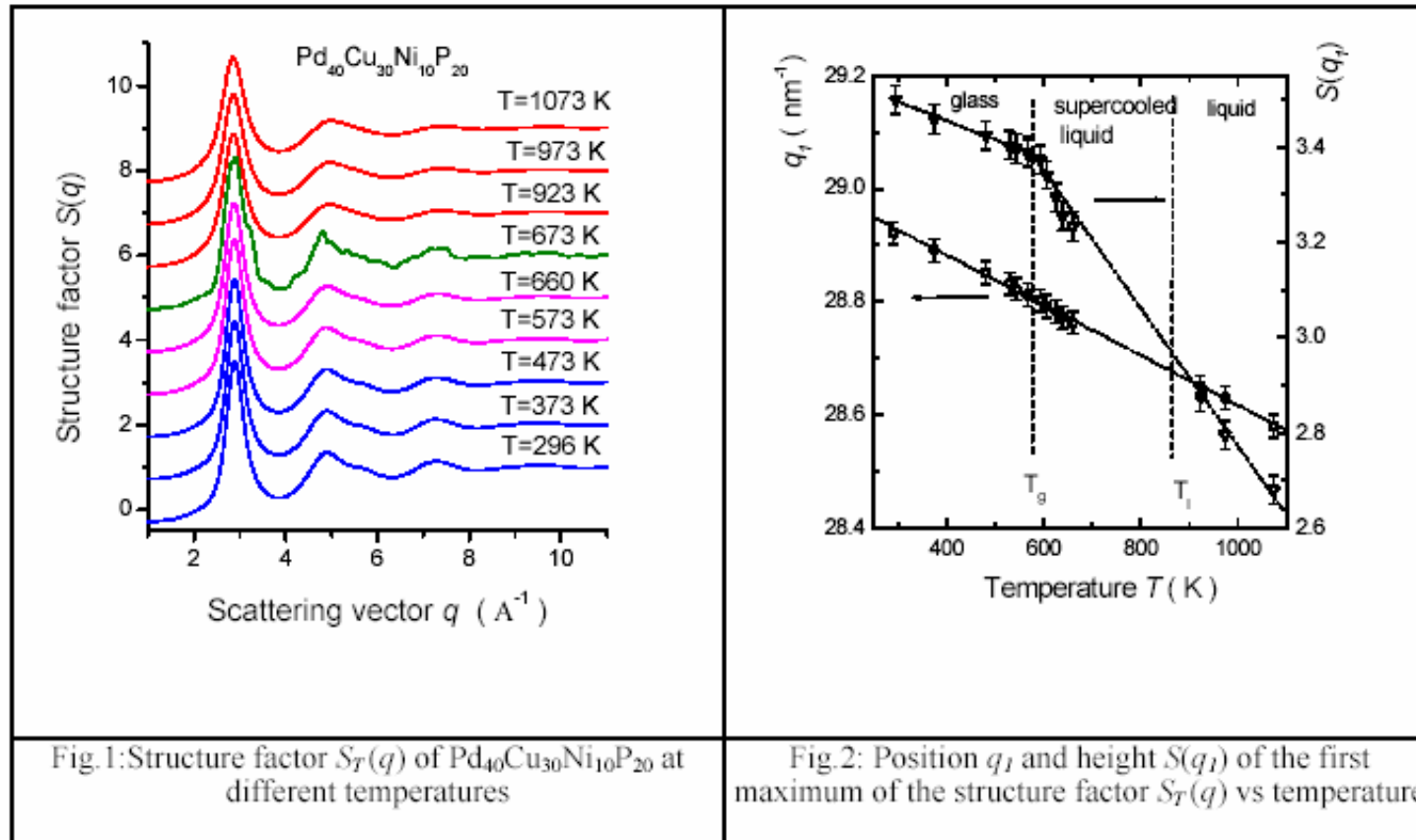
If $\psi^2_{n+1} < \psi^2_n$ the move is always accepted.

If $\psi^2_{n+1} > \psi^2_n$ the move is accepted with the probability $\exp[-(\psi^2_{n+1} - \psi^2_n)/2]$





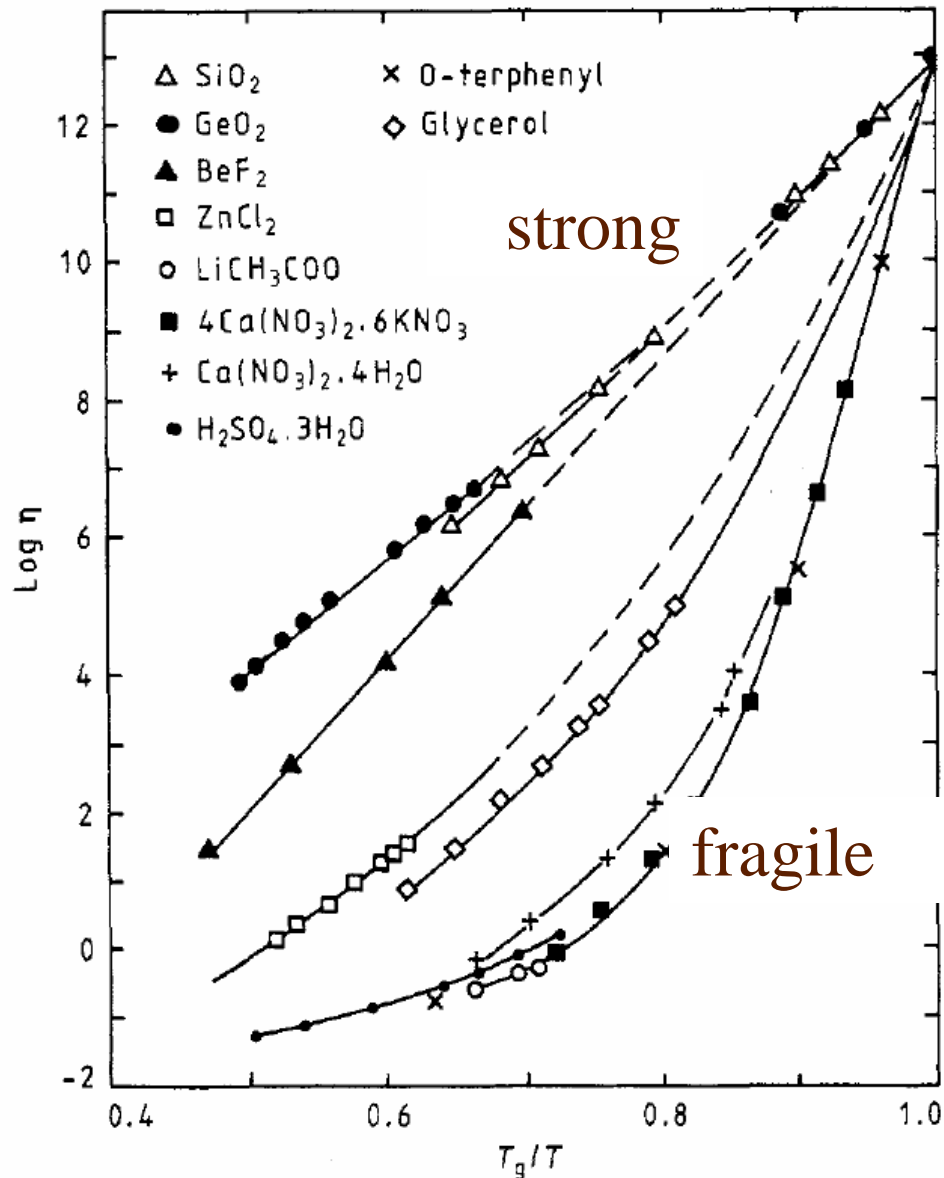
Structure by X-rays temperature dependence



N. Mattern et al
APL 2003

Below T_g : harmonic change, described by Debye behavior
At T_g : Transition to lower Debye-temperature
+ structural changes

The glass transition temperature T_g



$$\eta = \exp\left(-\frac{E_0}{k(T - T_0)}\right)$$

VFT law

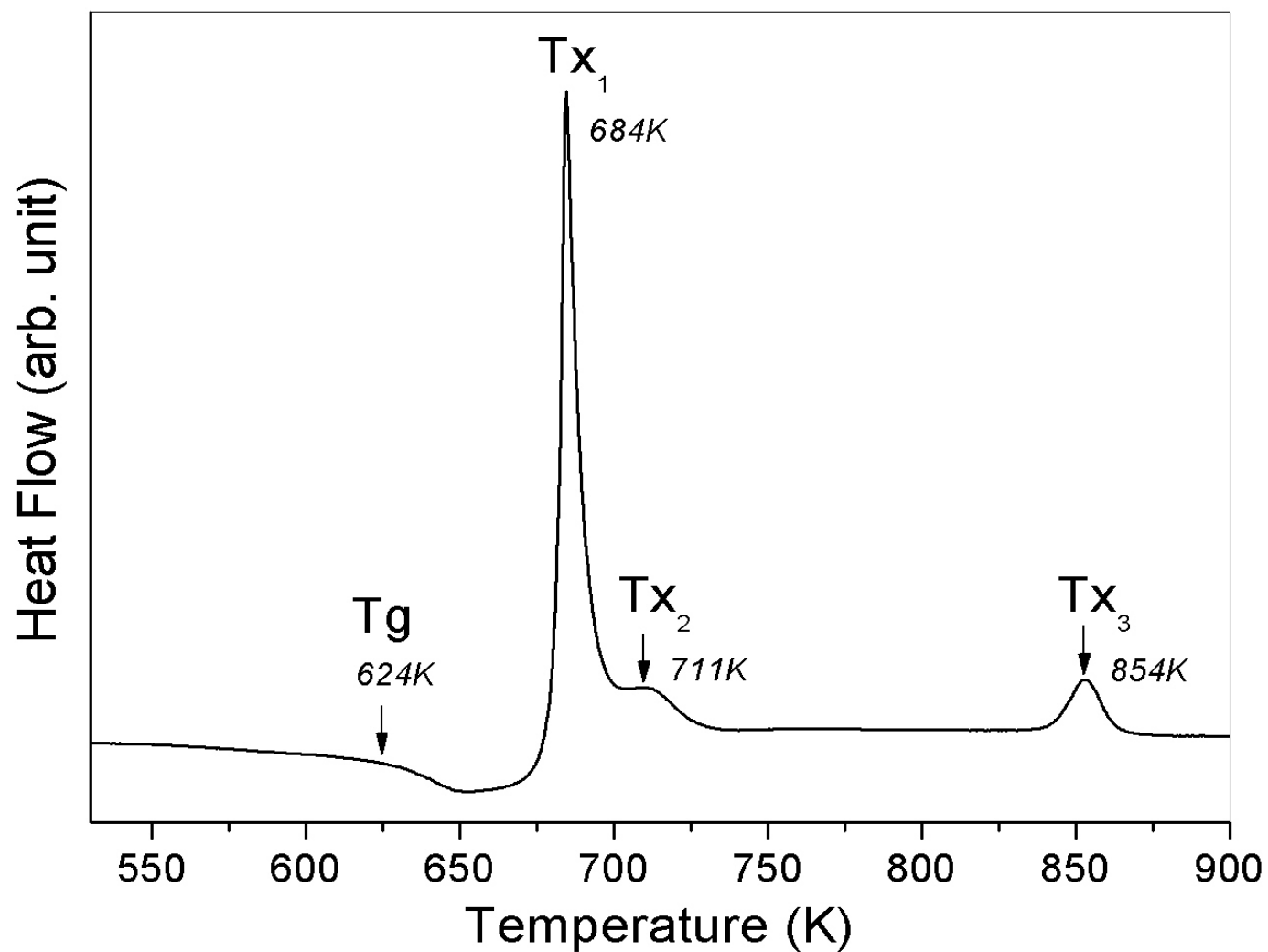
transition
temperature T_0

Very strong
variation of η / τ
with temperature

T_g determined by state of the experimental technique



Differential Scanning Calorimetry (DSC)



Differential Scanning Calorimetry

Supercooled liquid region:

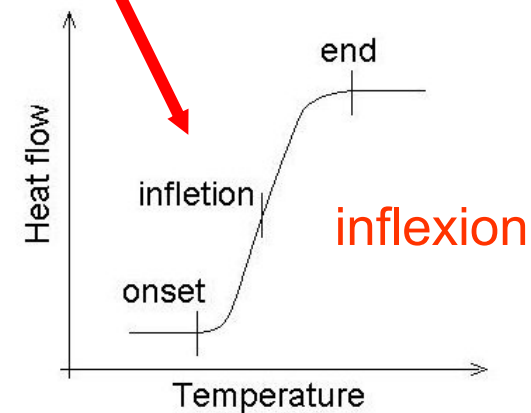
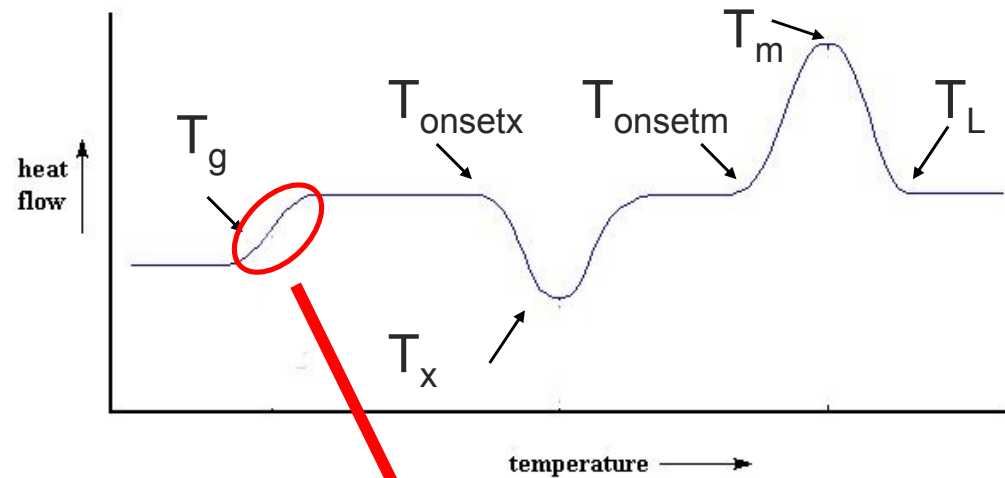
$$\Delta T = T_{\text{onsetx}} - T_g$$

Glass forming ability (GFA)

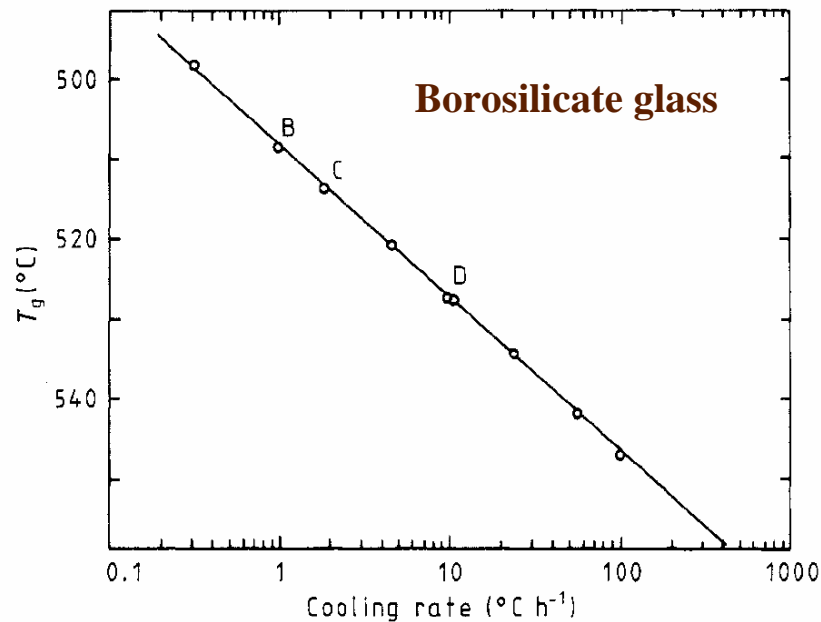
$$\Delta T$$

$$T_{\text{rg}} = T_g / T_m$$

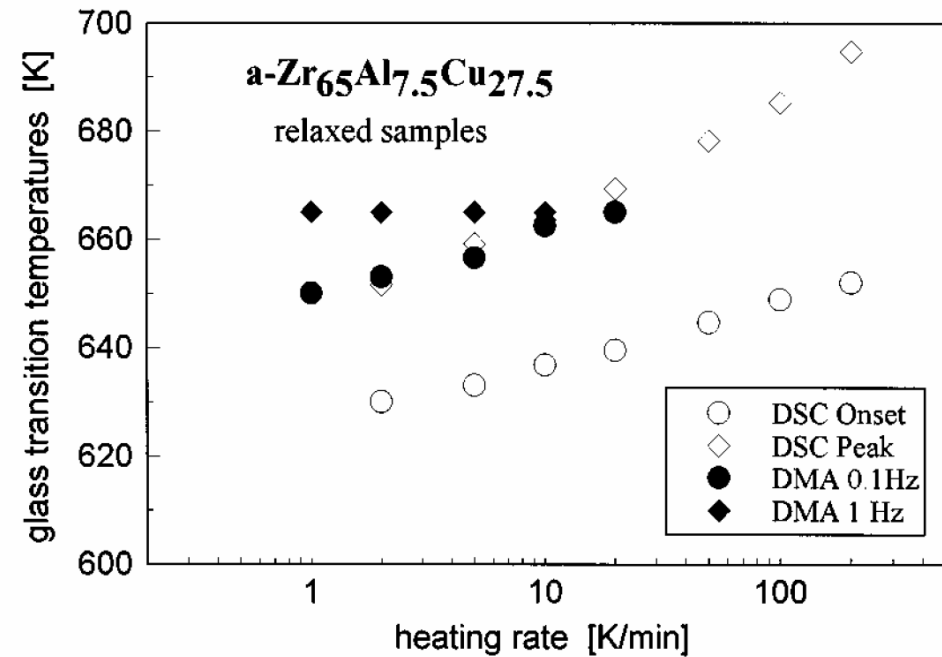
and many others



T_g depends on the experimental parameters



Ritland 1954

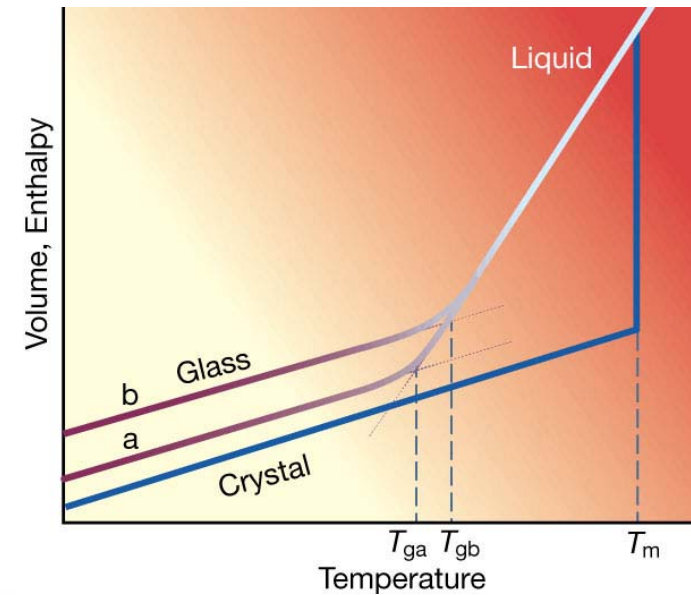


Rambousky 1996

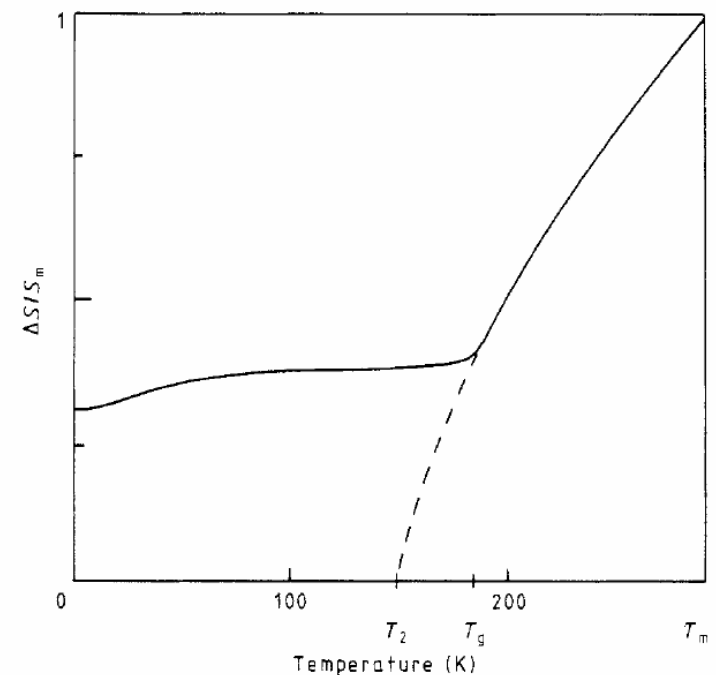


Kautzmann paradoxon

Glass transition at T_K when entropy of the amorphous is lower than in the corresponding crystal

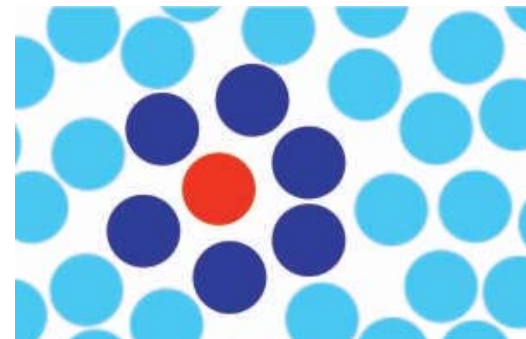


All **real** systems fall out of equilibrium before



Dynamics in real disordered solids

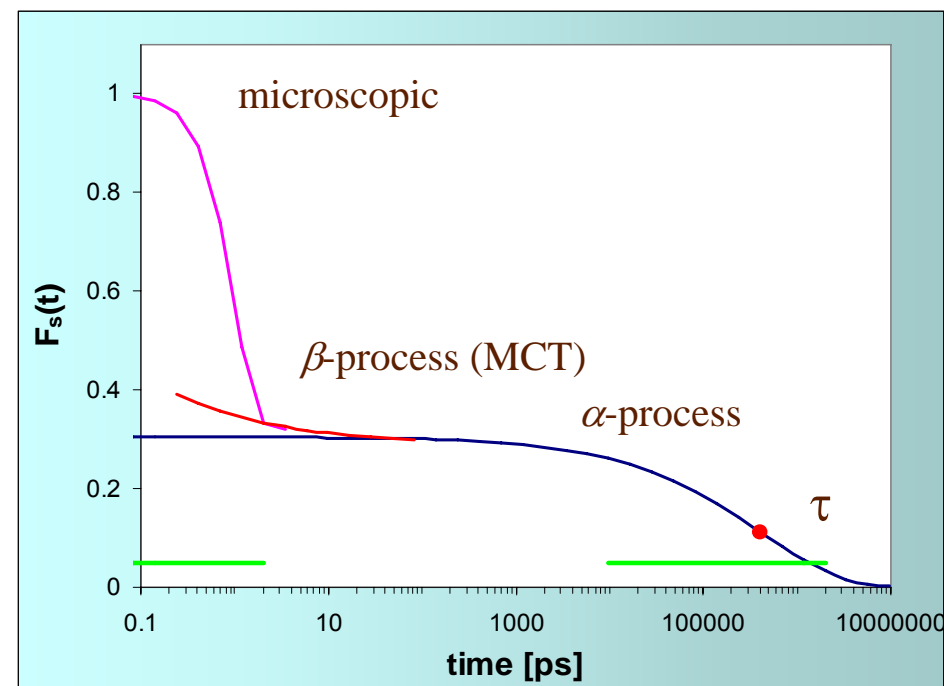
- **microscopic process: rather harmonic in most glasses**



- **cage (β)- process: intermediate times**

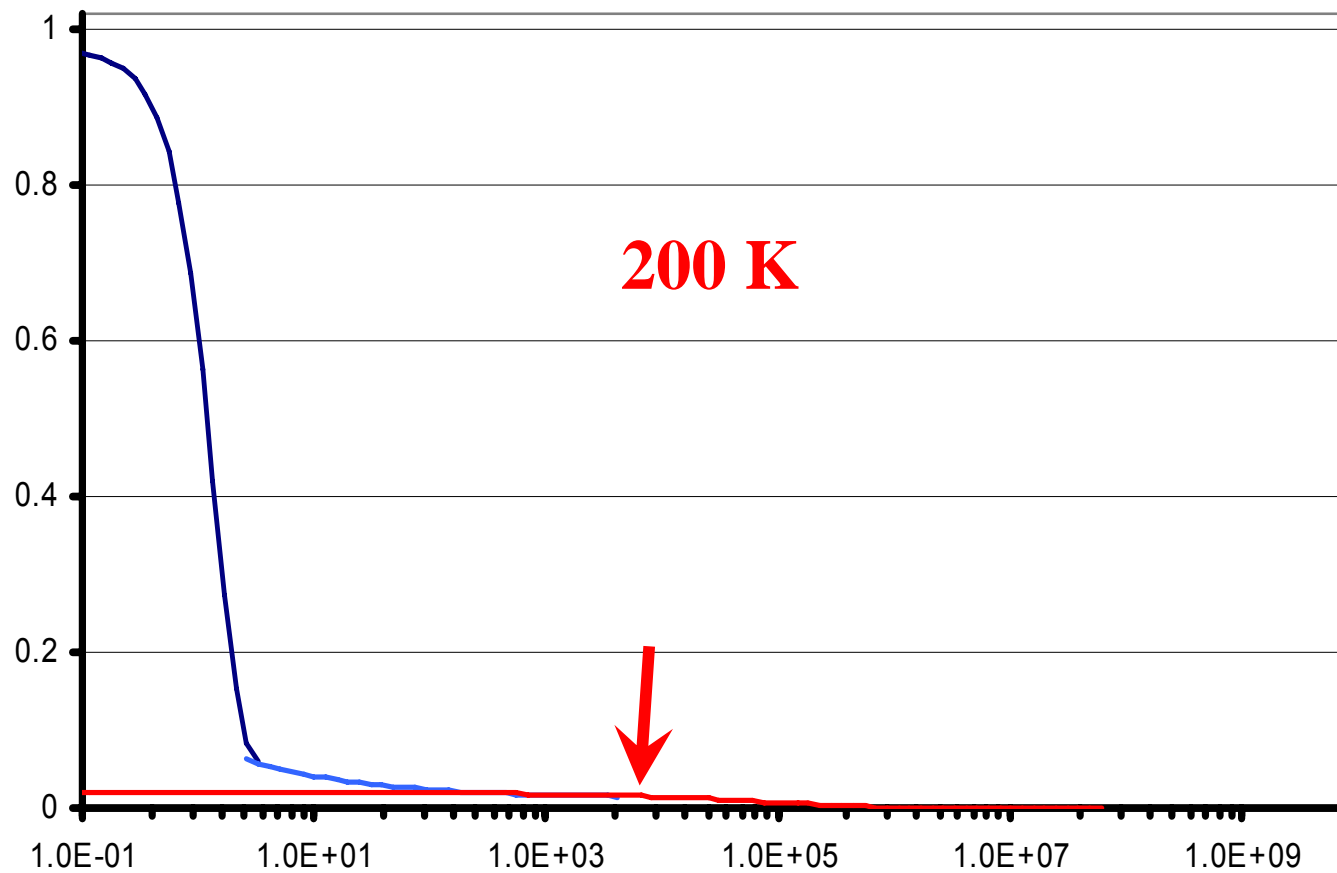
α - process: long range diffusion, very strong T-dependence, stretched exponential $f_q \exp(-(t/\tau)^\beta)$

glass transition T_c : α and β process merge



Glass transition

Correlation functions



Density correlation functions and MCT

$$\phi_q(t) = \langle \rho_q^*(t) \rho_q(0) \rangle / \langle |\rho_q(0)|^2 \rangle$$

$$\ddot{\phi}_q(t) + \Omega_q^2 \phi_q(t) + \Omega_q^2 \int m_q(t-t') \dot{\phi}_q(t') dt' = 0$$

Equation of motion for density correlators including „memory term“

Ergodicity - non-ergodicity transition at T_c

Power laws for correlation functions near T_c

Order parameter is the ergodicity parameter f_q

$$F_q(t) = f_q - h_q (t/\tau)^b + \dots \approx f_q \exp(-t/\tau_K)^\beta \quad \alpha\text{-relaxation}$$

$$F_q(t) = f_q + h_q (t_0/t)^a + \dots \quad \beta\text{-relaxation (cage process)}$$

$$f_q \approx \sqrt{T_c - T} \quad \text{Square-root singularity}$$



$$f_q \approx \sqrt{T_c - T} \quad \text{Square-root singularity}$$

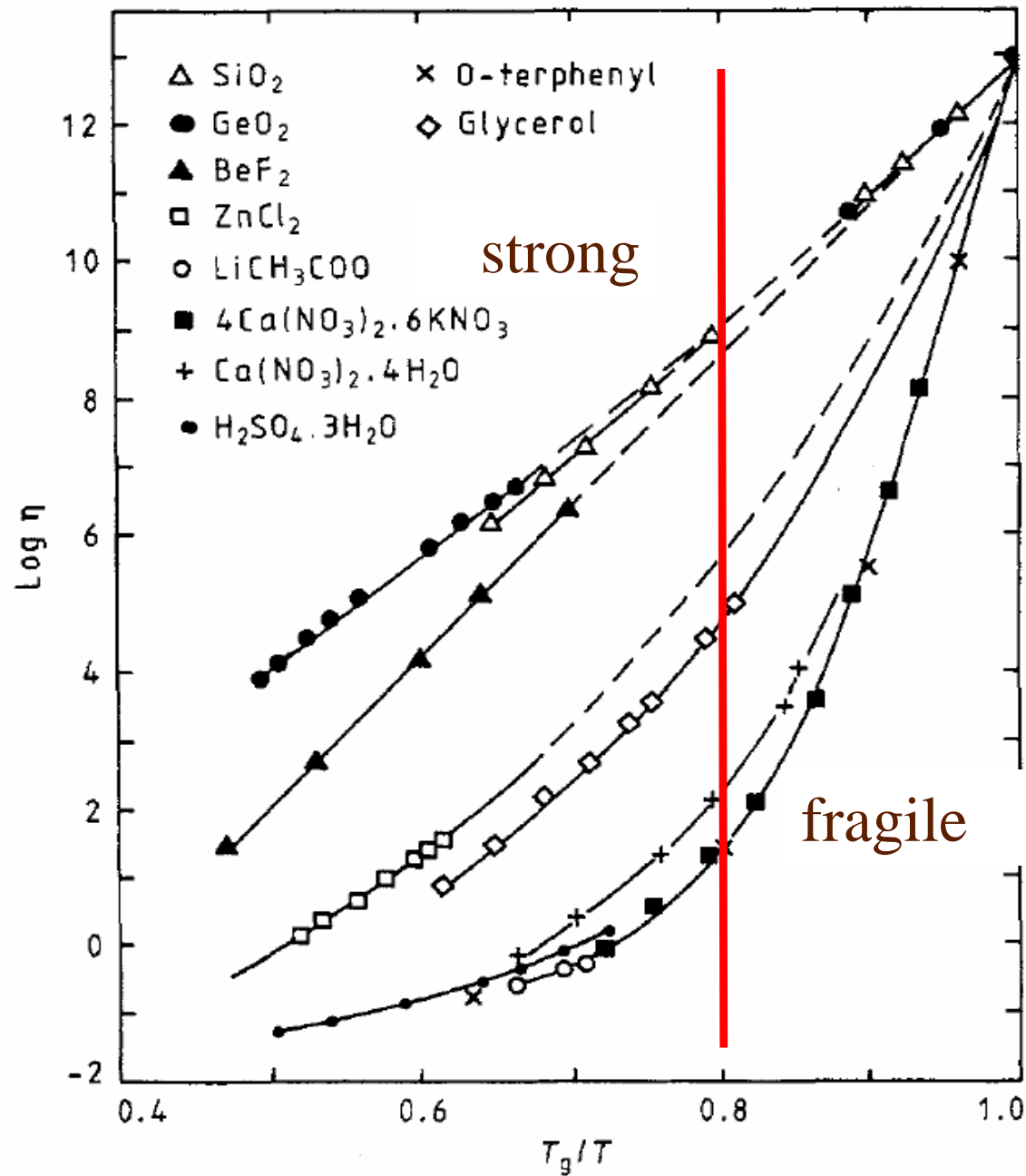
**T_c describes a transition temperature which
in contrast to T_g does not depend on
experimental parameters.**

**The glass transition is an ergodic - non
ergodic cross over**

**In most systems T_c is 20% higher than T_g ,
i.e. the transition is in the “liquid” region**



The glass transition temperature T_g and T_c



Density correlation functions and MCT

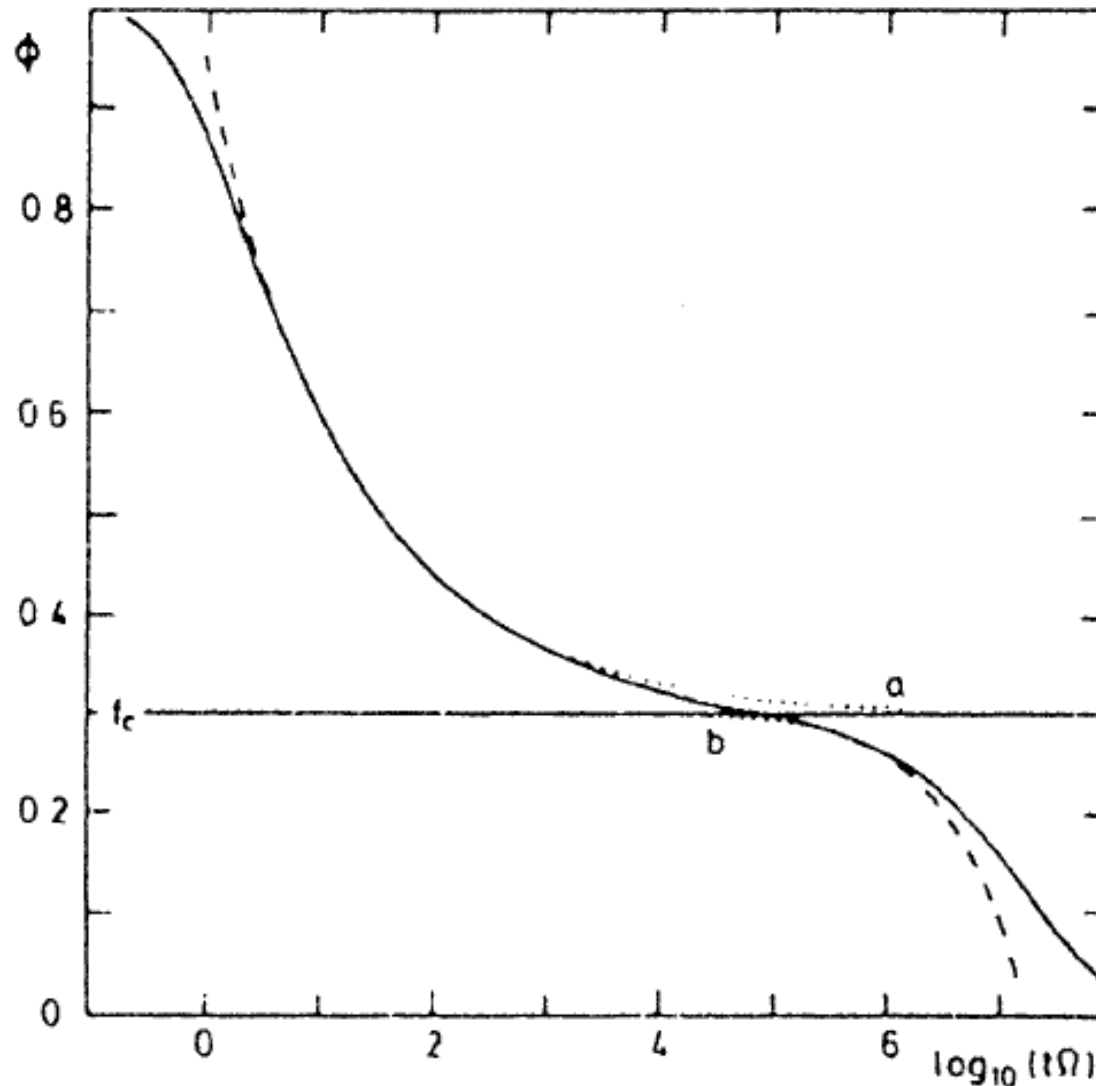
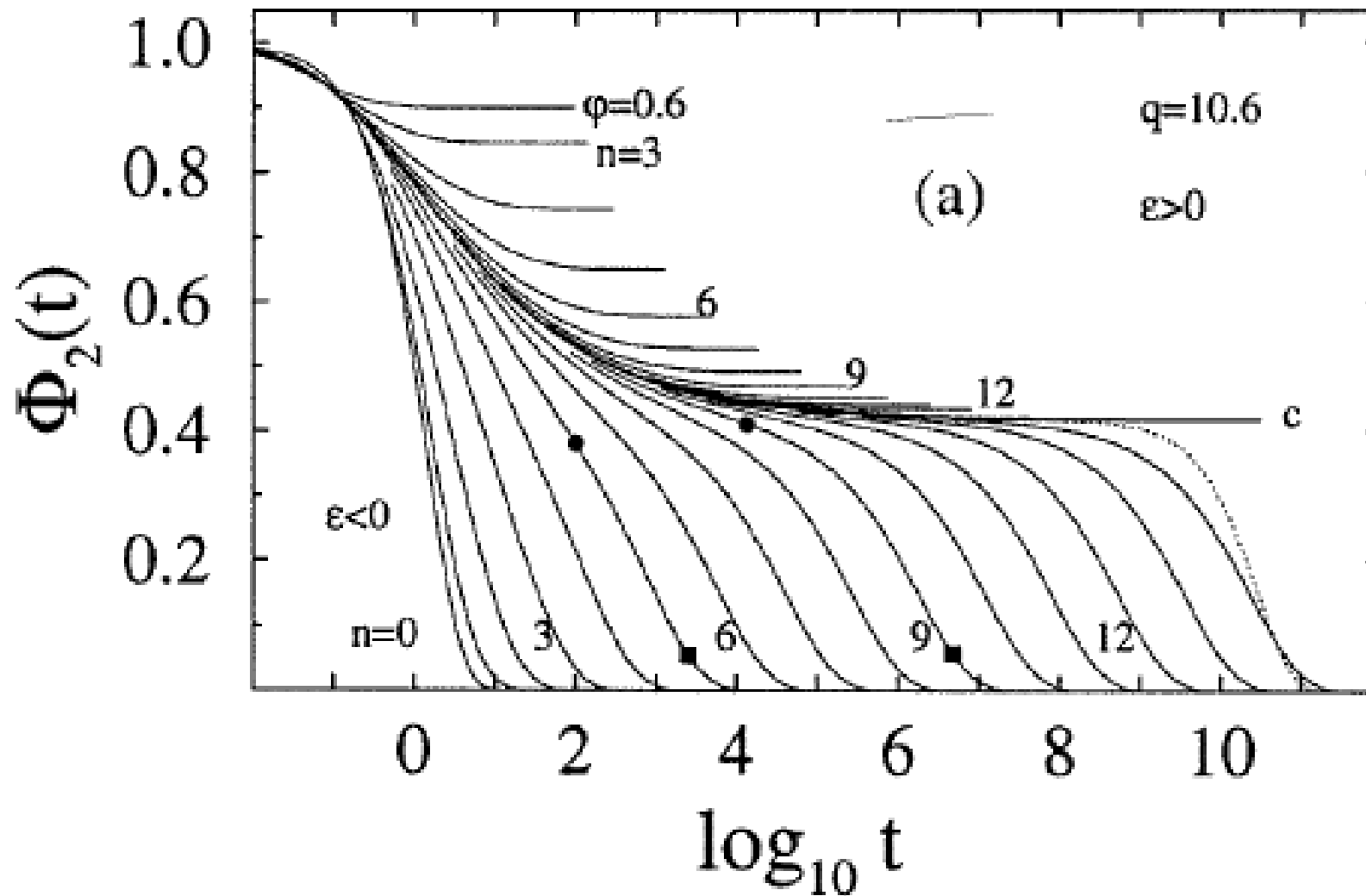


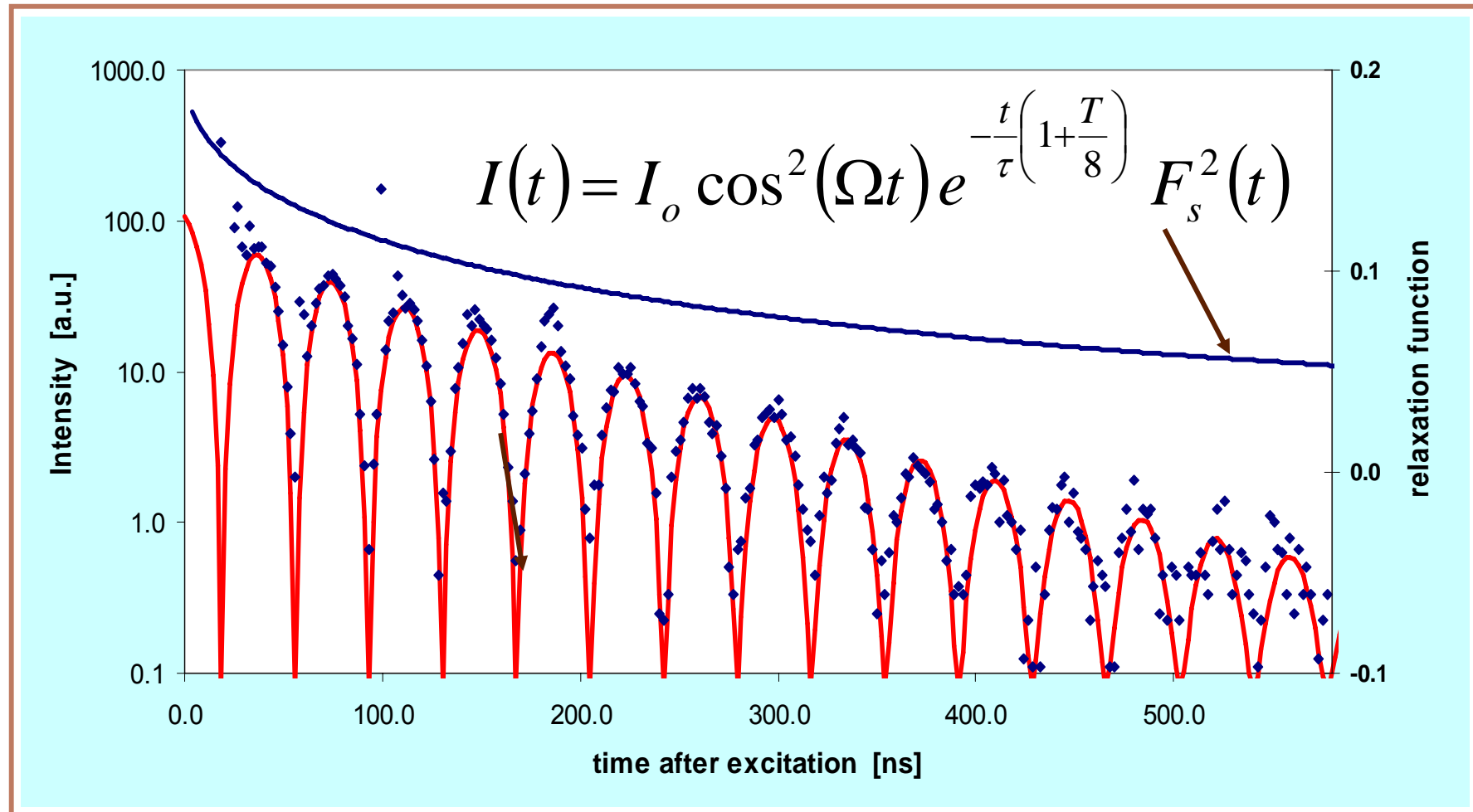
Figure 4. Comparison of the MCT solution for $\phi_q(t)$ (solid curve) with the asymptotic β -relaxation approximation (dashed curve) (equations (25) and (26)). The dotted curves show the two power laws. (From reference [4].)



MCT results for correlation functions at the glass transition



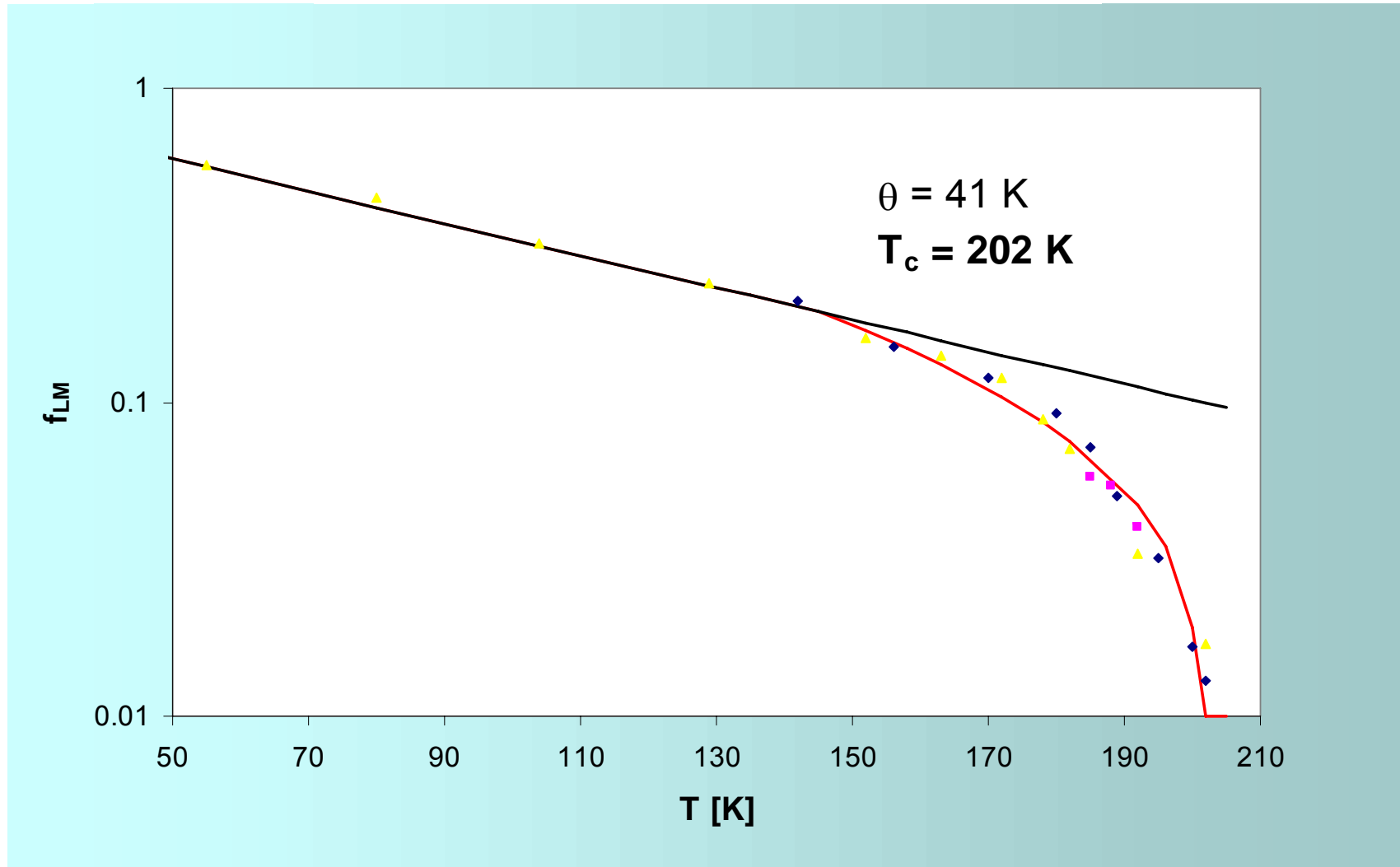
Quasielastic nuclear resonant forward scattering



Butyl phthalate / ferrocene

Exact treatment of QNFS: I. Sergueev, HF,.. PRB 2003

Non ergodicity parameter

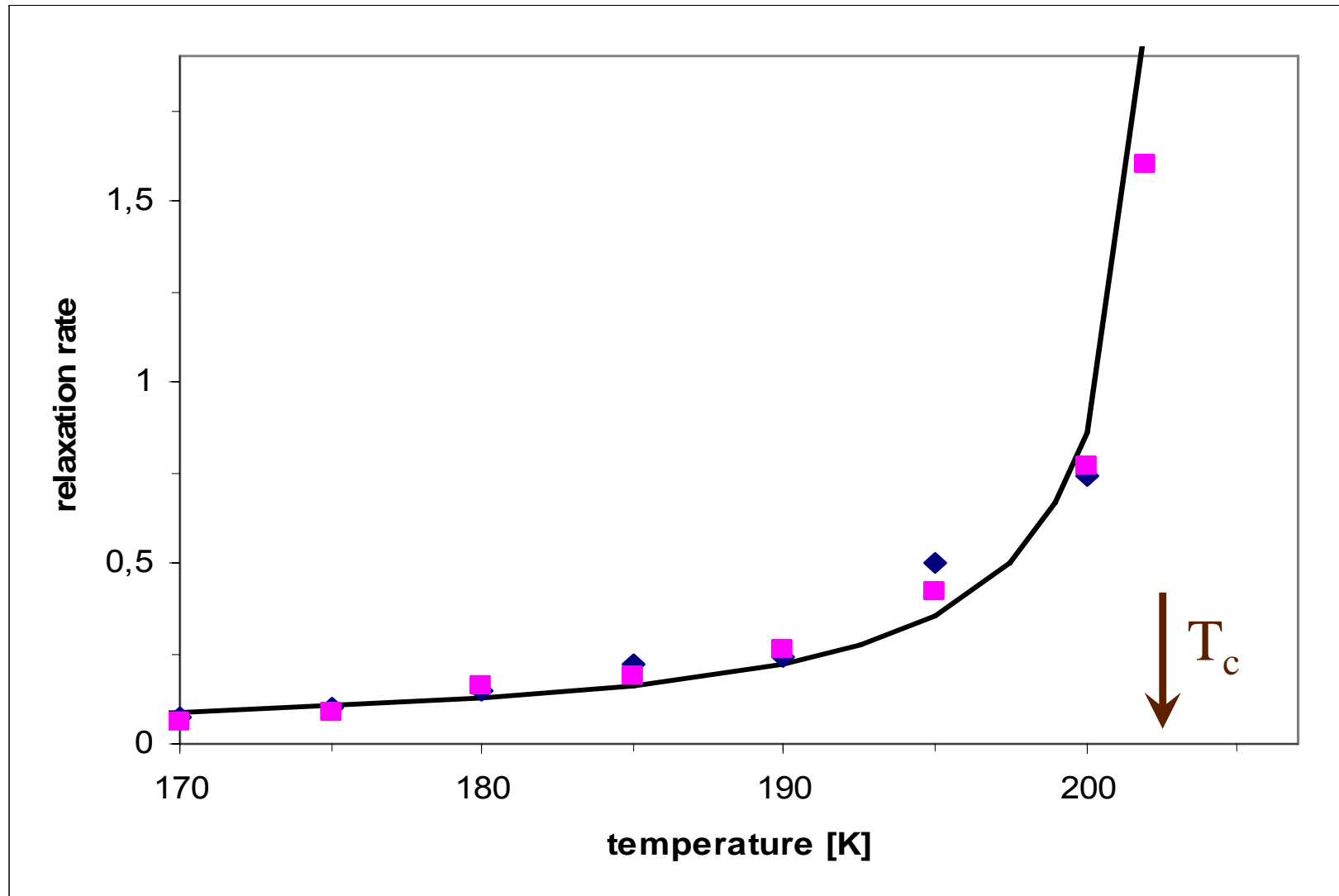


Square-root behaviour as predicted by mode-coupling theory

Stretching exponent $\beta = 0.48$, independent of T



Relaxation rates

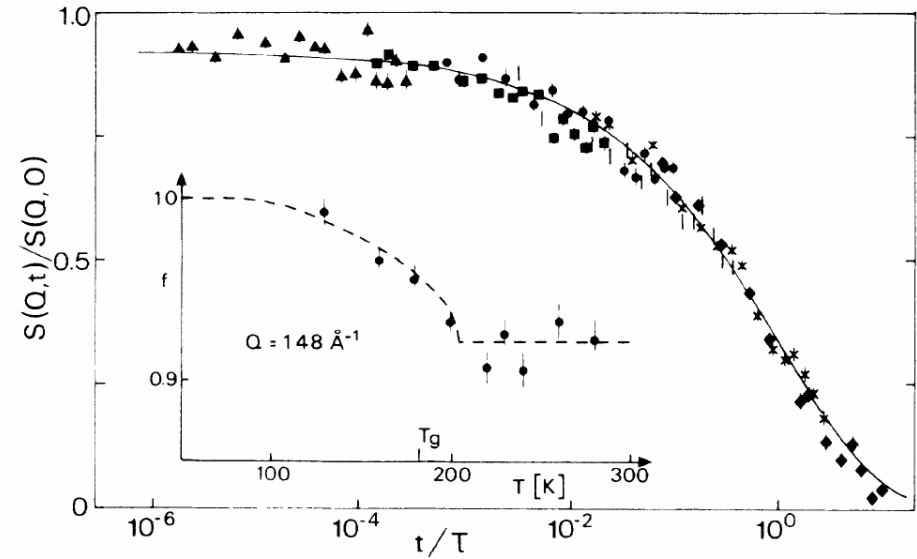
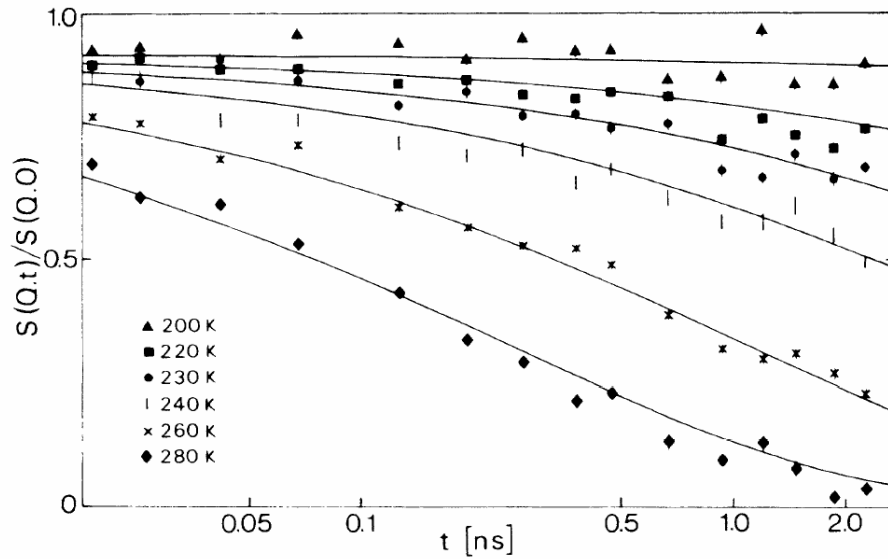


T. Asthalter, I.Sergueev, HF, et al EPJ B (2001)



Neutron scattering results

Masterplot



J. Wuttke et al, Physica B (1997)



Dielectric spectroscopy

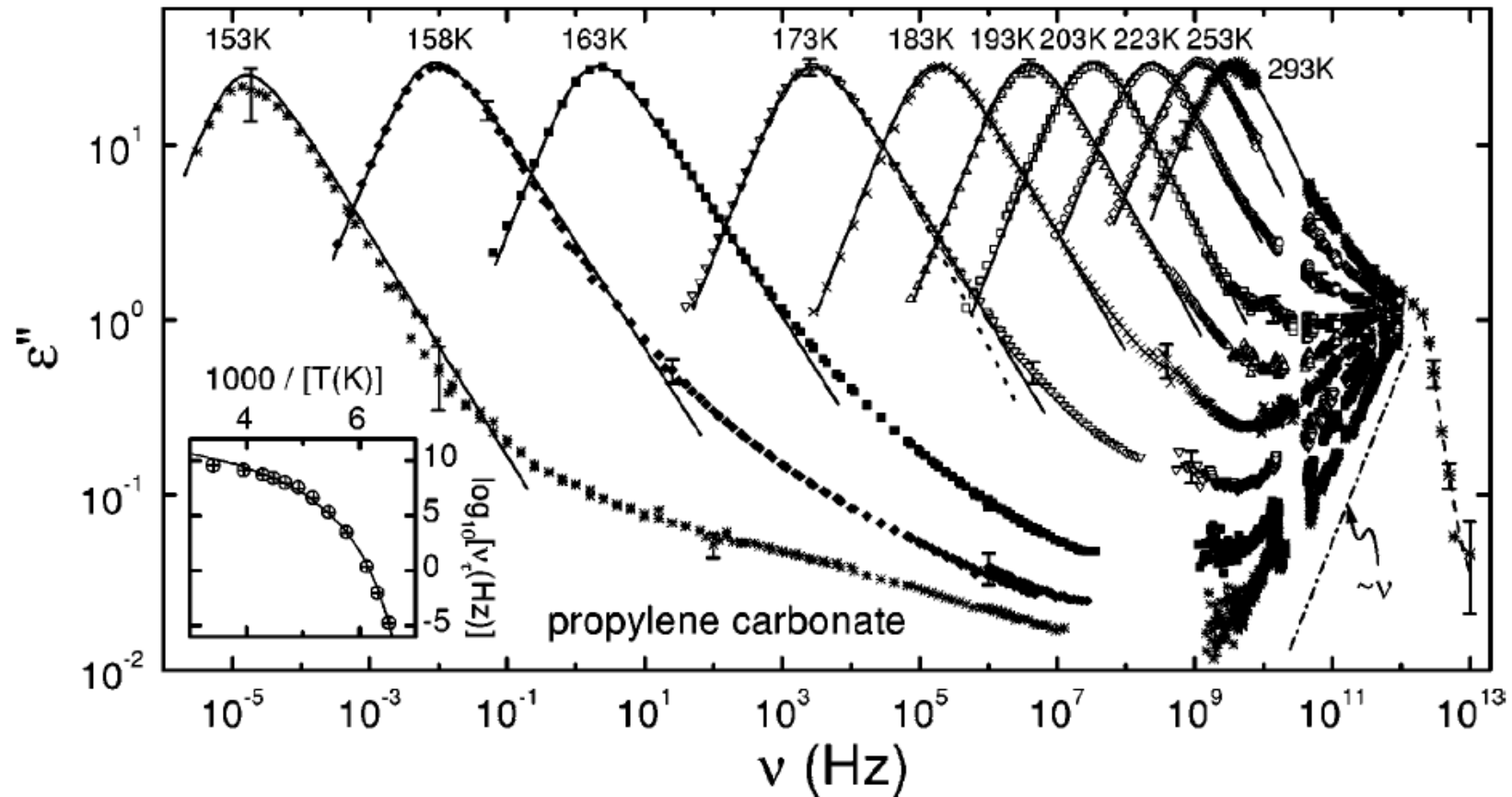


FIG. 2. Frequency dependence of the dielectric loss in propylene carbonate at various temperatures. The solid lines are fits with the CD function, the dotted line is a fit with the Fourier transform of the KWW law, both performed simultaneously on ϵ' . The dash-dotted line indicates a linear increase. The FIR results have been connected by a dashed line to guide the eye. The inset shows $\nu\tau = 1/(2\pi\langle\tau\rangle)$ as resulting from the CD (circles) and KWW fits (pluses) in an Arrhenius representation. The line is a fit using the VFT expression, Eq. (1), with $T_{VF} = 132$ K, $D = 6.6$, and $\nu_0 = 3.2 \times 10^{12}$ Hz.

U. Schneider et al. PRE (1999)

