Dynamic heterogeneity of glassy ionics: Results from nuclear magnetic resonance and low-frequency spectral hole burning

Roland Böhmer

Video Module 1: Introduction

1. Introduction
2. Ion dynamics studied by NMR
3. Nonresonant spectral hole burning in CKN
4. Conclusions

Glass Lecture Series: prepared for and produced by the
International Material Institute for New Functionality in Glass
An NSF sponsored program – material herein not for sale
Available at www.lehigh.edu/imi
Delivered at Lehigh University Dec. 7, 2006

Univ. Dortmund

Experimentelle
Physik III

S. Berndt
R. Küchler
F. Qi
C. Rier

Ag **K. R. Jeffrey**
Guelph / Canada

CKN **R. Richert**
Arizona State Univ.

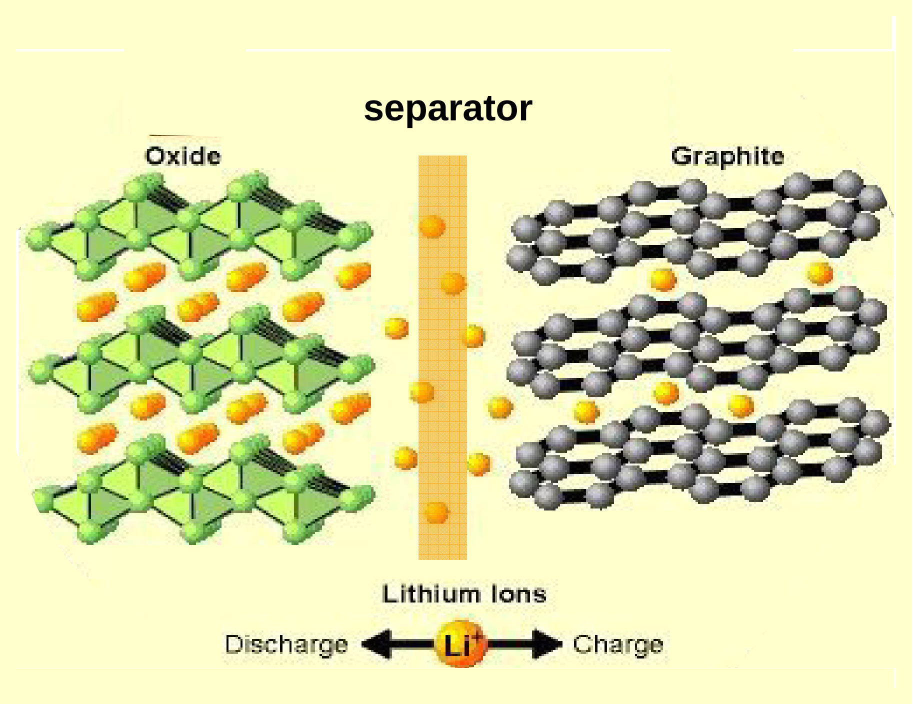
DFG

Struktur-Dynamik-Beziehungen in mikrostrukturierten Systemen

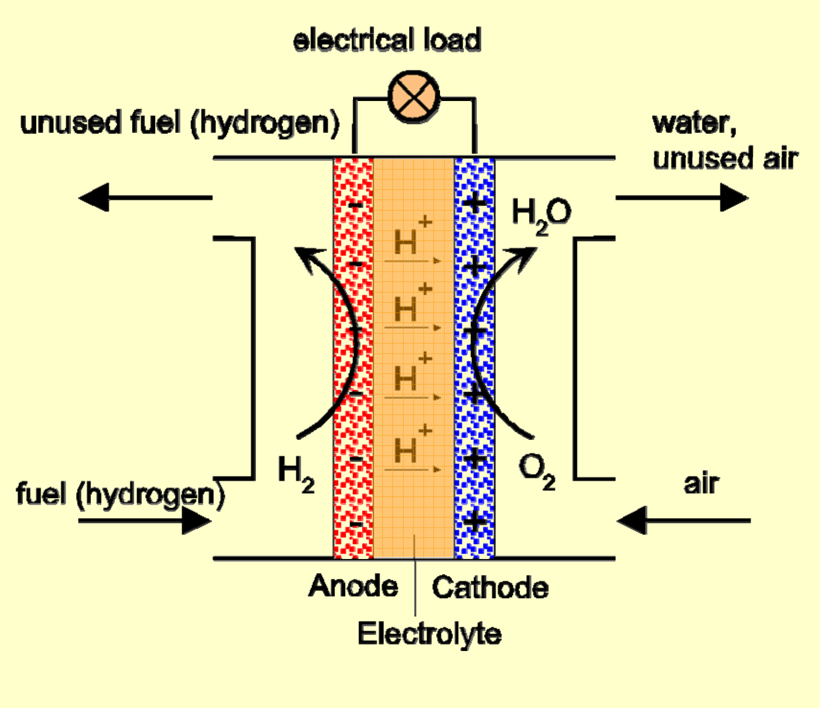
Graduierten-
kolleg 298

Transport in solid electrolytes

Li ion battery

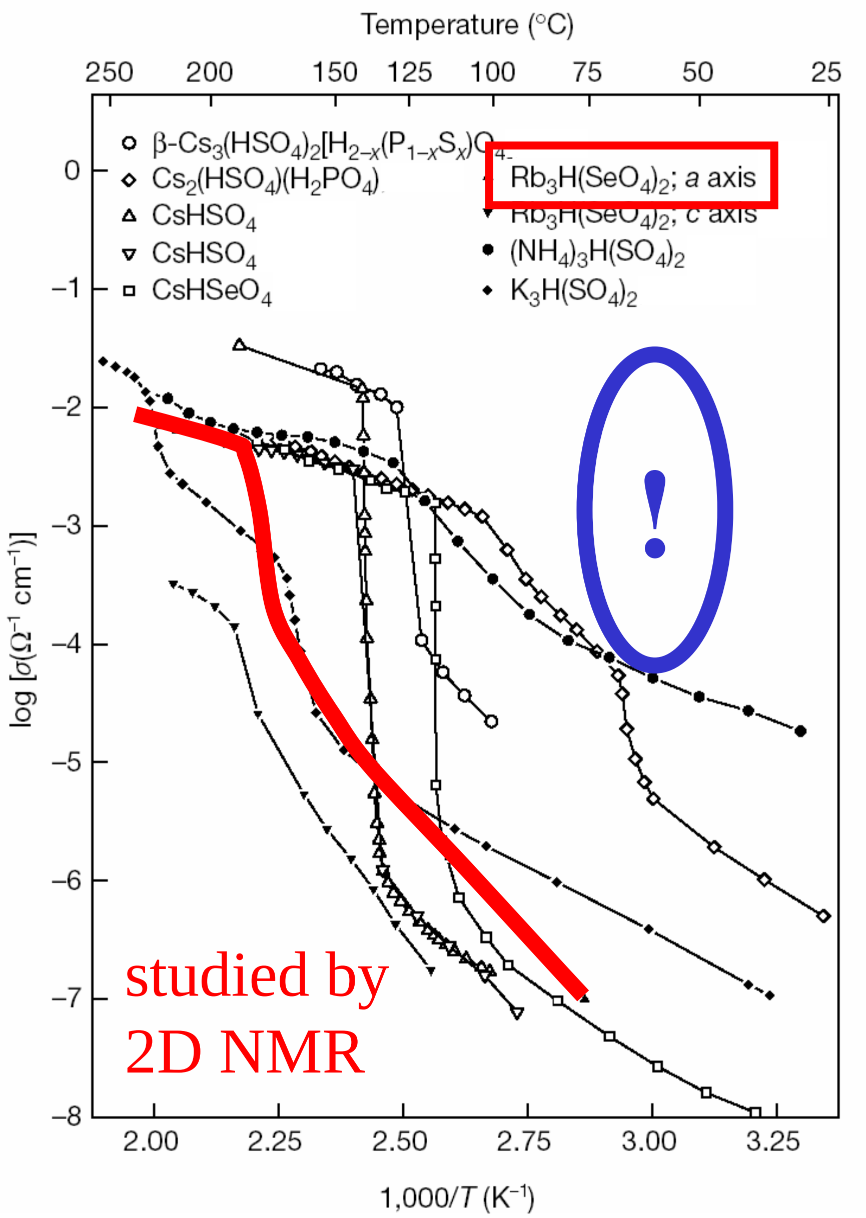


"fuel" cell



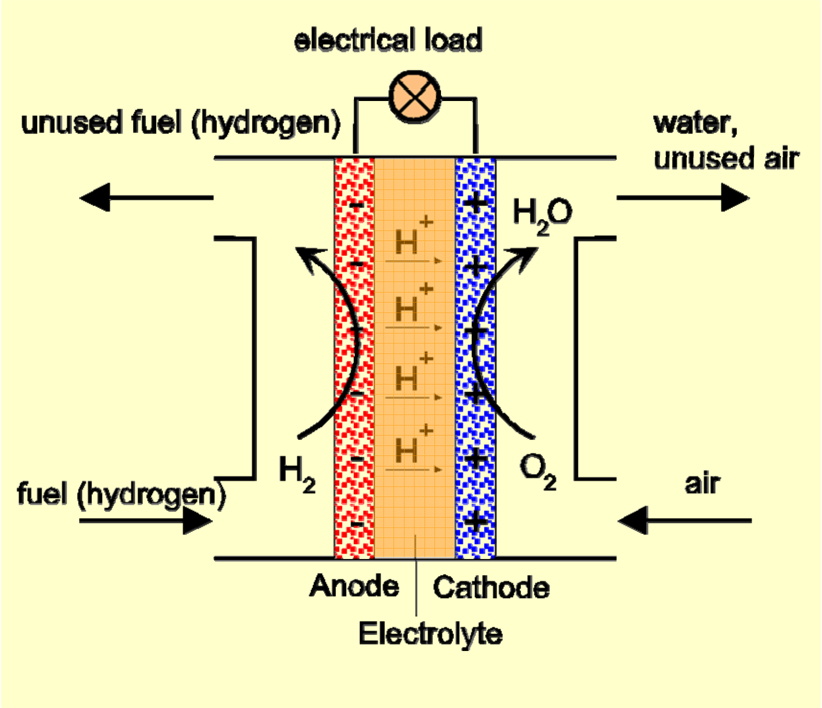
Membranes with high <u>ionic</u> conductivities required

electrical conducitivty of solid electrolytes



studied by 2D NMR

Haile et al., Nature **410**, 910 (2001)



"superionic" anhydrous fuel cell

Insight into transport mechanisms?

applications

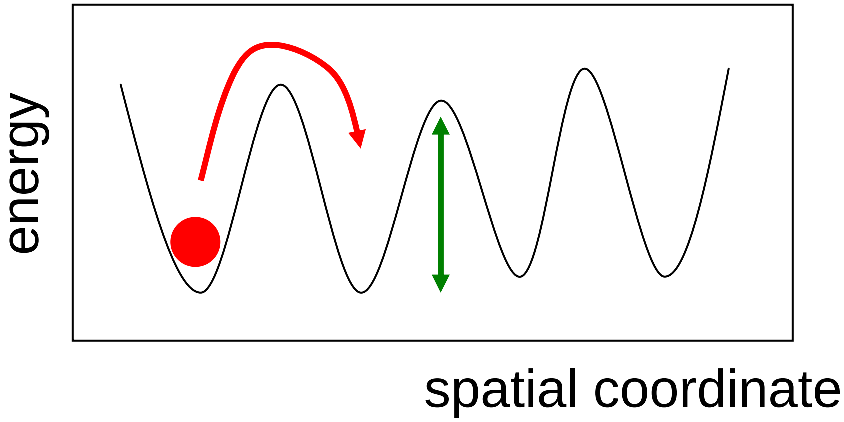
sensors, fuel cells,
rechargeable batteries, ...

requirements

stable, light, solid, inexpensive,
high ionic & low electronic conductivity,
suitable operating temperature, ...

goal of group at Dortmund U

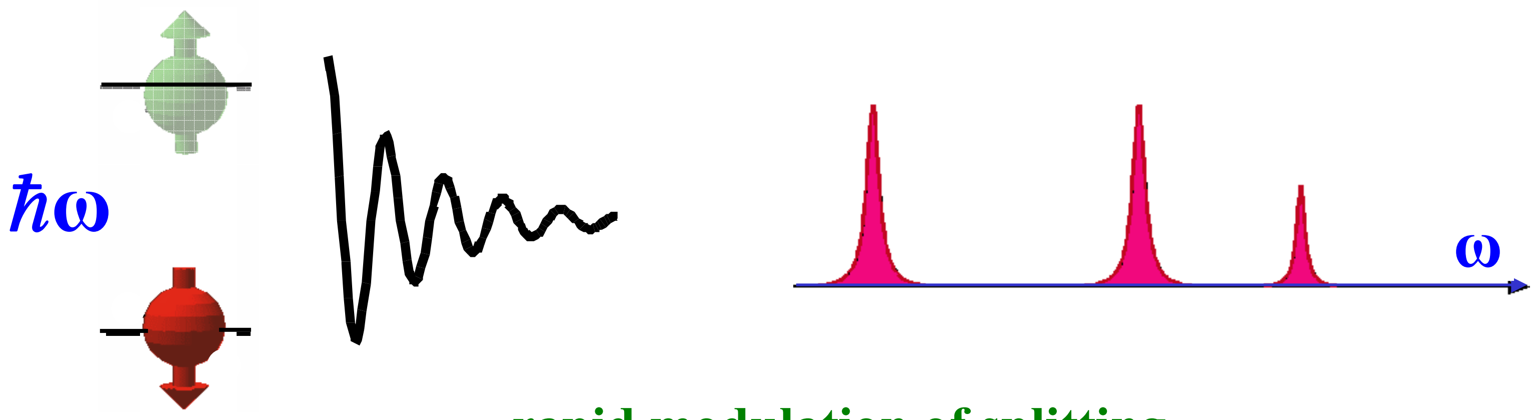
new experimental methods
for better understanding
of transport mechanisms
in solid ion conductors

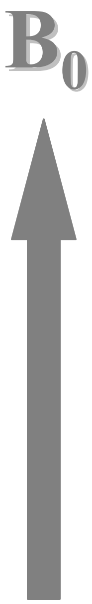


Principle of magnetic resonance

element specific
quantitative
locally selective
non-destructive
experimentally versatile

Principle of magnetic resonance





rapid modulation of splitting
facilitates re-equlilibration
→ spin-lattice relaxation time T_1

frequency perturbation $\Delta\omega$ encoded by

spatial coordinate	imaging
electronic environment	chemical analysis
distances and angles	structural elucidation
orientation	fiber texture testing

element specific
quantitative
locally selective
non-destructive
experimentally versatile

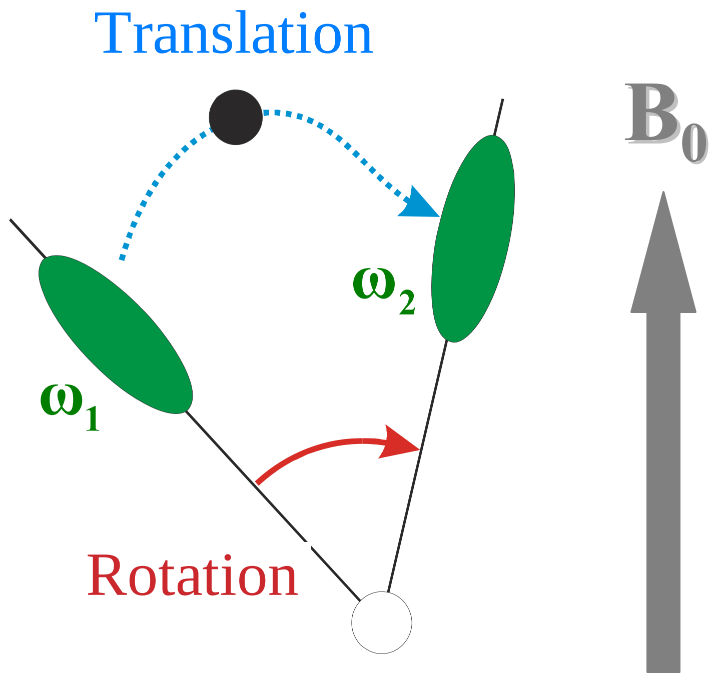
Motional processes

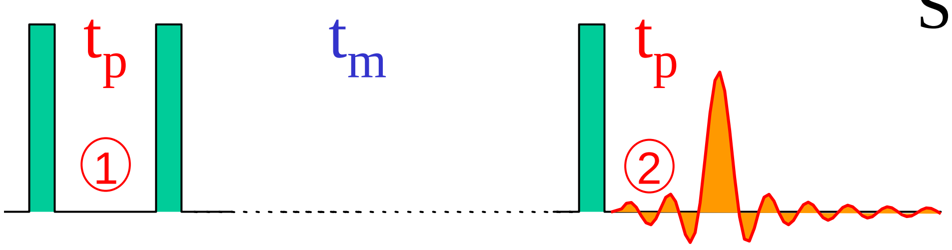
detection of NMR frequencies and their time evolution

⇓

NMR frequency encoded by

spatial coordinate	diffusion, flow
chemical environment	exchange, **translation**
orientation	reorientational motion
. . .	





$$S_2(t_p,t_m) = \langle \exp[i t_p \omega(0)] \exp[-i t_p \omega(t_m)] \rangle$$

$$S(\vec{q},t) \propto \langle \exp[i \vec{q}\vec{r}(0)] \exp[-i \vec{q}\vec{r}(t)] \rangle$$

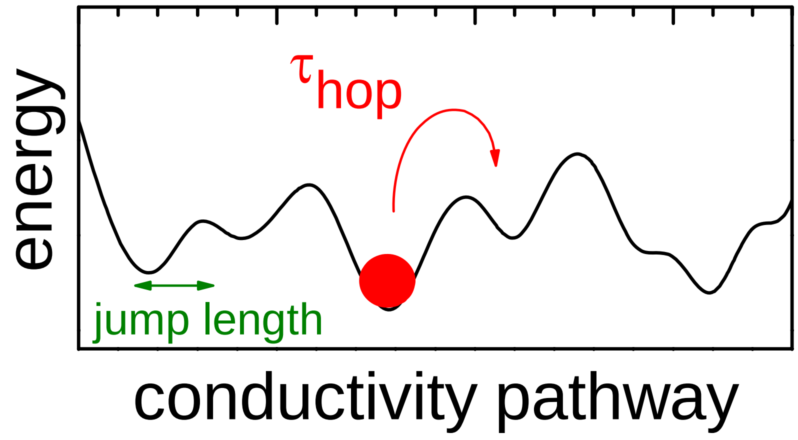
t_p evolution time
t_m mixing time

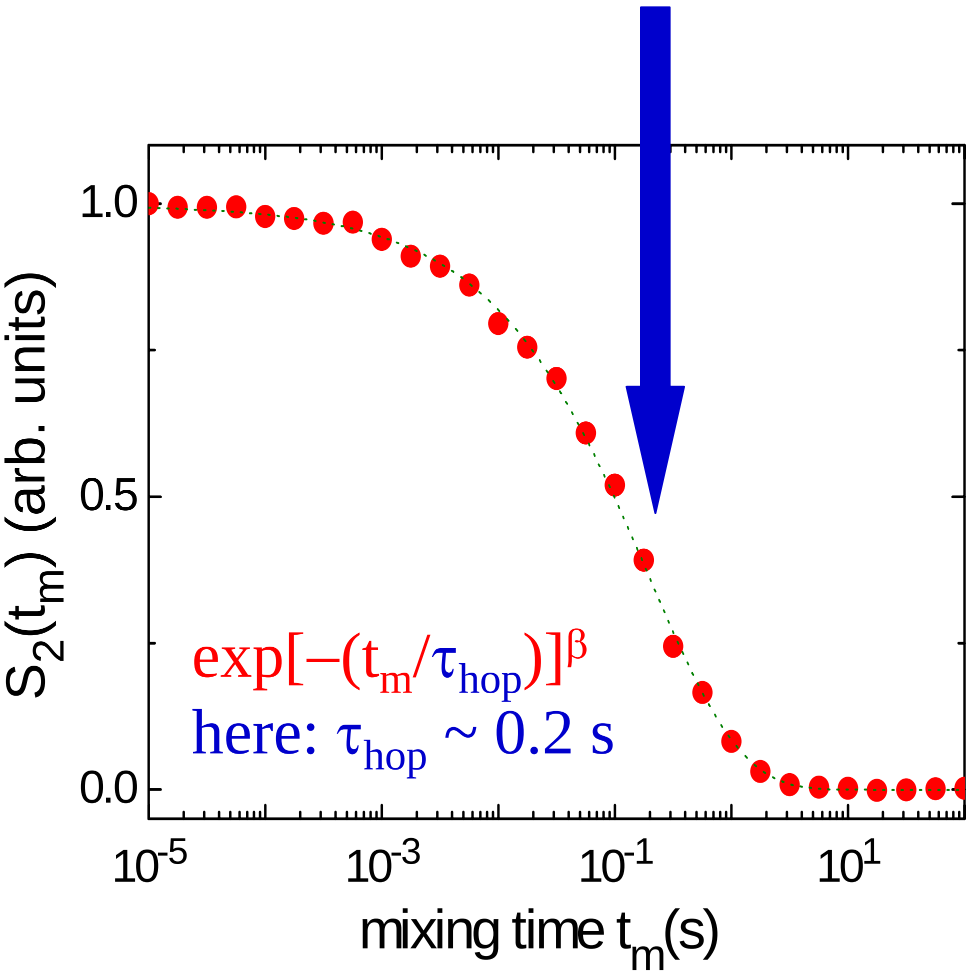
correlation of ω at
2, 3, 4 ... points in time

Echo height measures the fraction of ions which did NOT hop during t_m

Direct determination of correlation time on which an ion hops

Scattering „vector“ q, i.e. spatial sensitivity is determined by the inverse mean jump length





This lecture continues on a 2nd module -

Video Module 2 : Ion Dynamics by NMR (Part 2)

Dynamic heterogeneity of glassy ionics: Results from nuclear magnetic resonance and low-frequency spectral hole burning

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Video Module 2: Ion Dynamics by NMR

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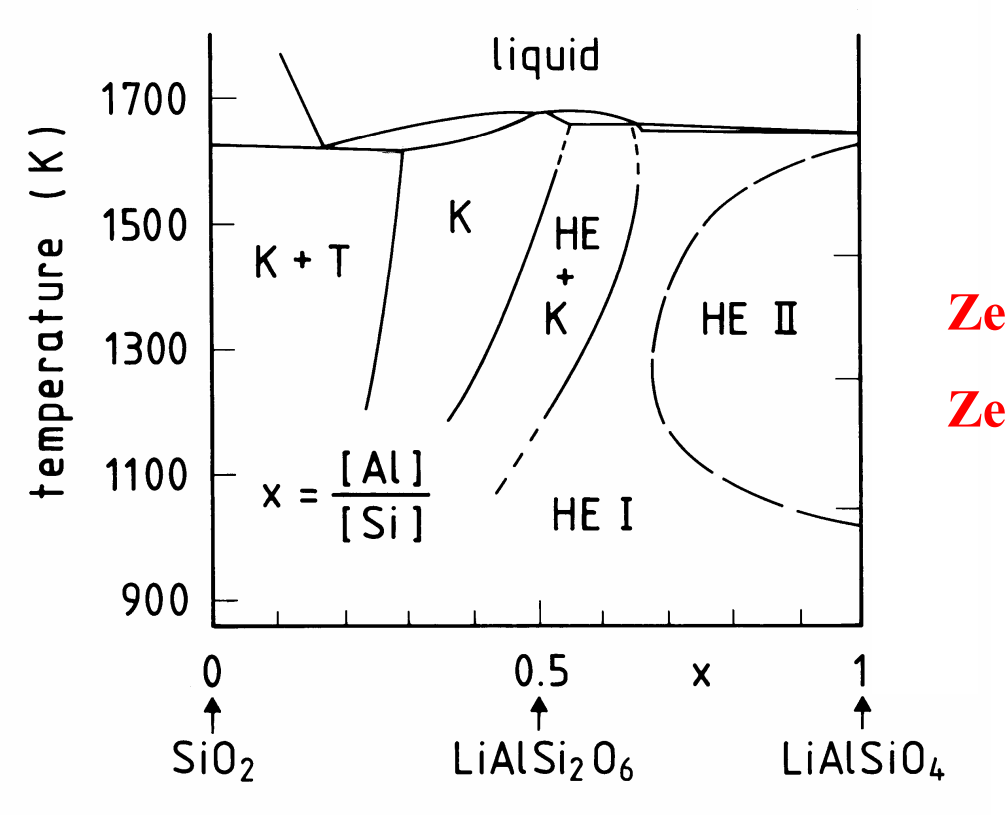
Lithium aluminosilicates

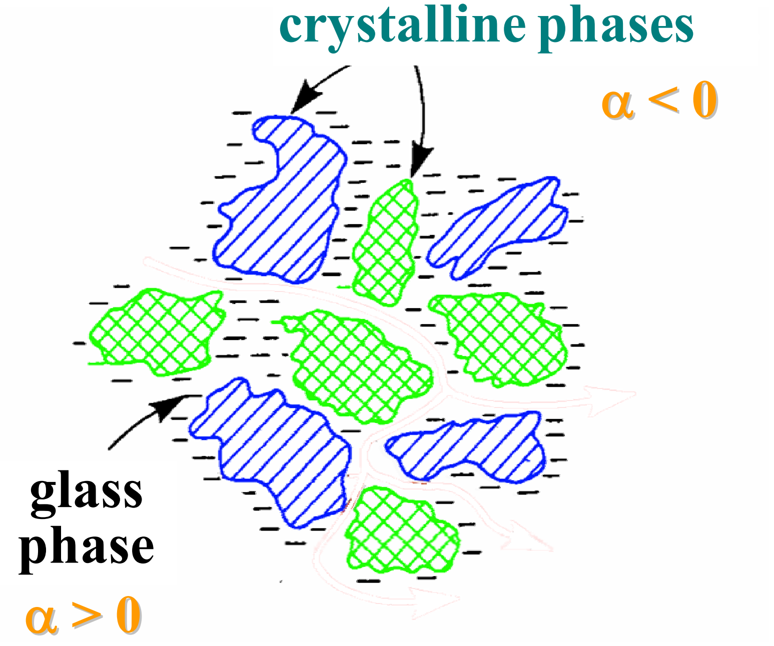


Mesocrystalline texture

(Schott, Mainz)

Zerodur®	**$x = 0.52$**	**70%**	**62 nm**
Zerodur M®	**$x = 0.44$**	**50%**	**45 nm**

crystalline model systems		**$x = [Al]/[Si]$**
β-spodumene	**$LiAlSi_2O_6$**	**0.5**
β-eucryptite	**$LiAlSiO_4$**	**1**



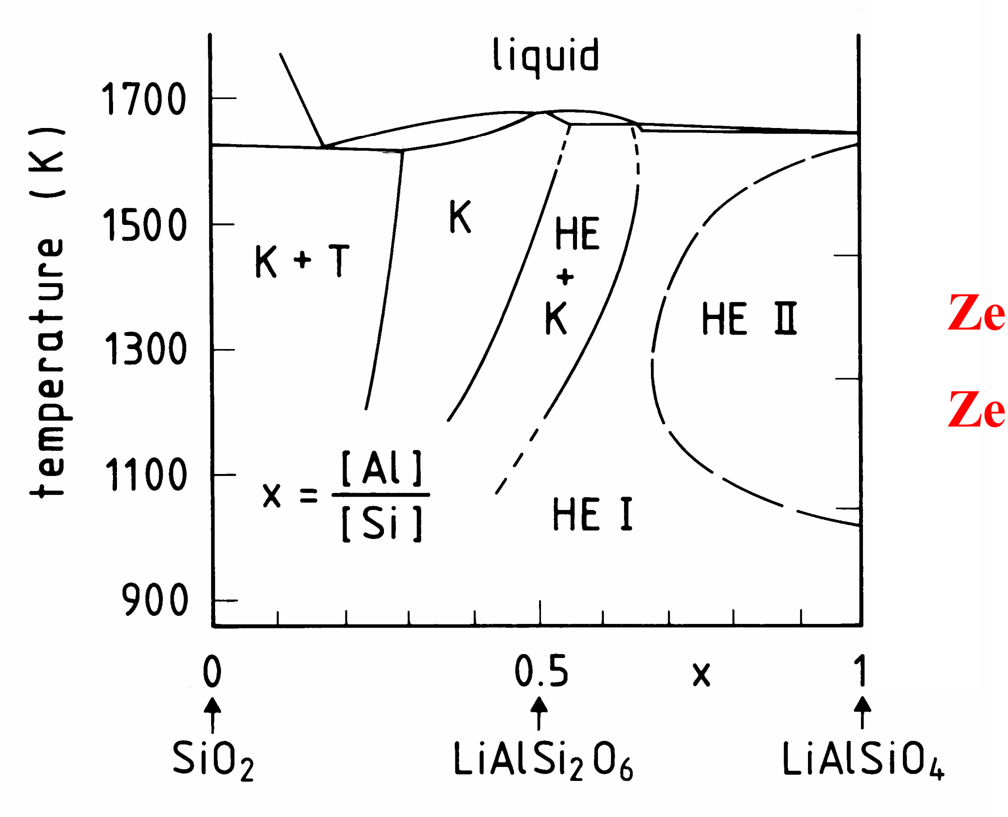
crystalline phases

$\alpha < 0$

glass phase

$\alpha > 0$

Lithium aluminosilicates



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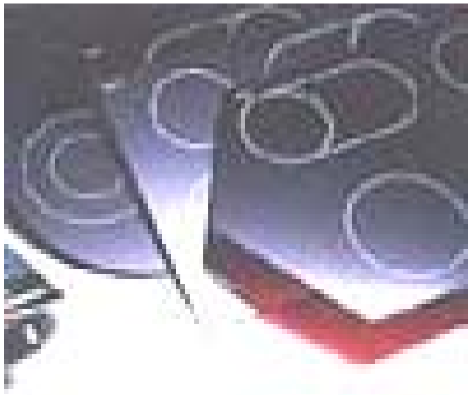
precision optics,
ceramic cooking ware



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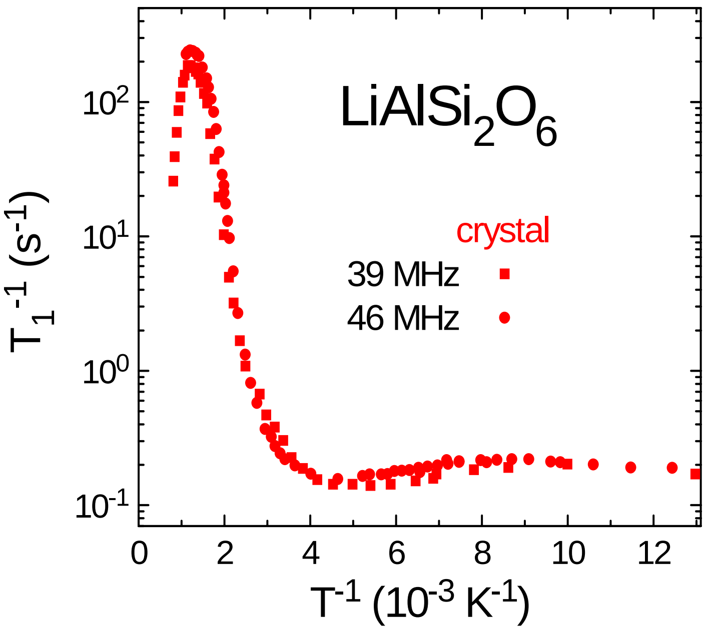
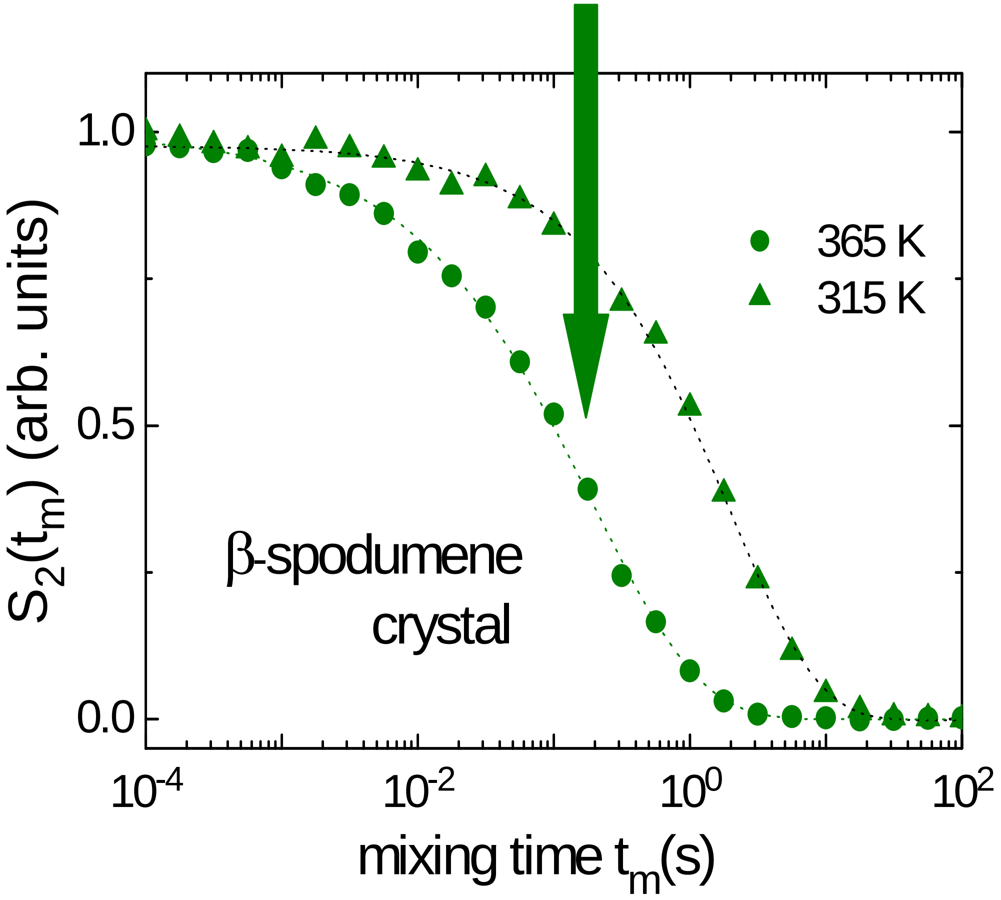
^{7}Li ion conductor β-spodumene

Spin-lattice relaxation indirect information on fast motion

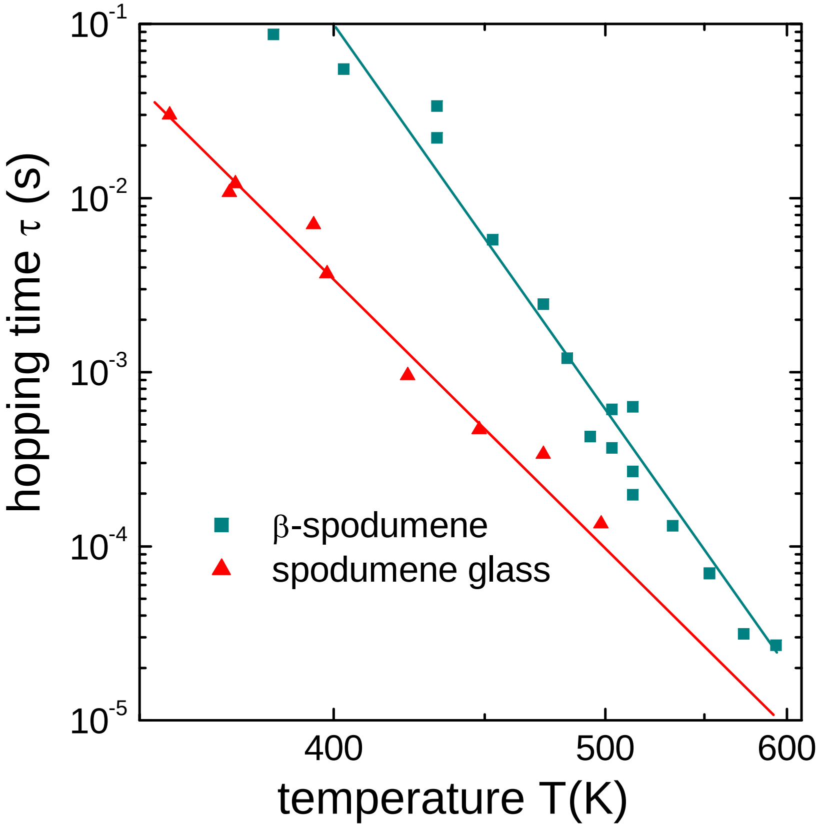


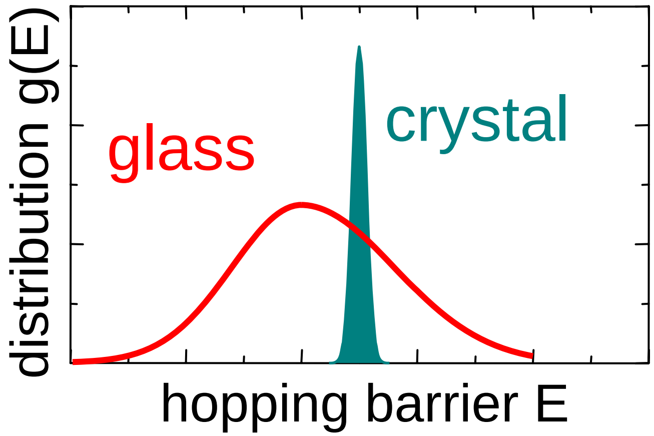
rate maxima for ωτ ~ 0.61

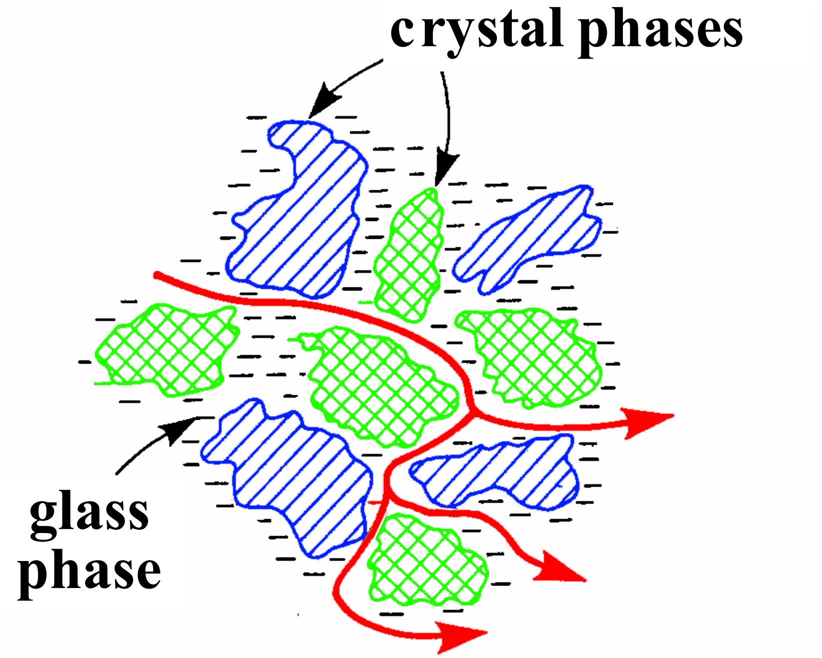
T-dependent time scale and non-exponentiality of ion hopping



Motion of Li$^+$ in crystalline and in glassy environments







Qi, Rier, Böhmer, Franke, Heitjans, *Phys. Rev.* B **72**, 104301 (2005)

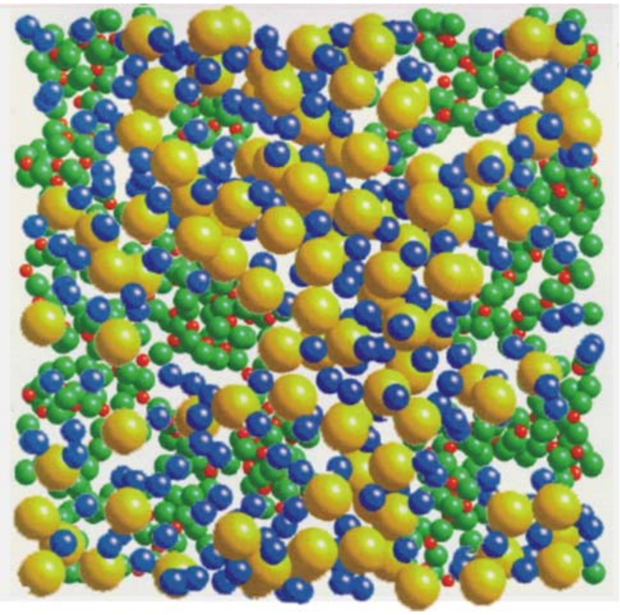
1. **Introduction**
    - Ion conductors
    - Nuclear magnetic resonance

2. **Ion dynamics studied by NMR**
    - Li hopping in alumino silicates
    - Heterogeneity in silver borate glasses

3. **Nonresonant spectral hole burning**
    - Material and method
    - Experiments on Ca-K-NO_3 glass

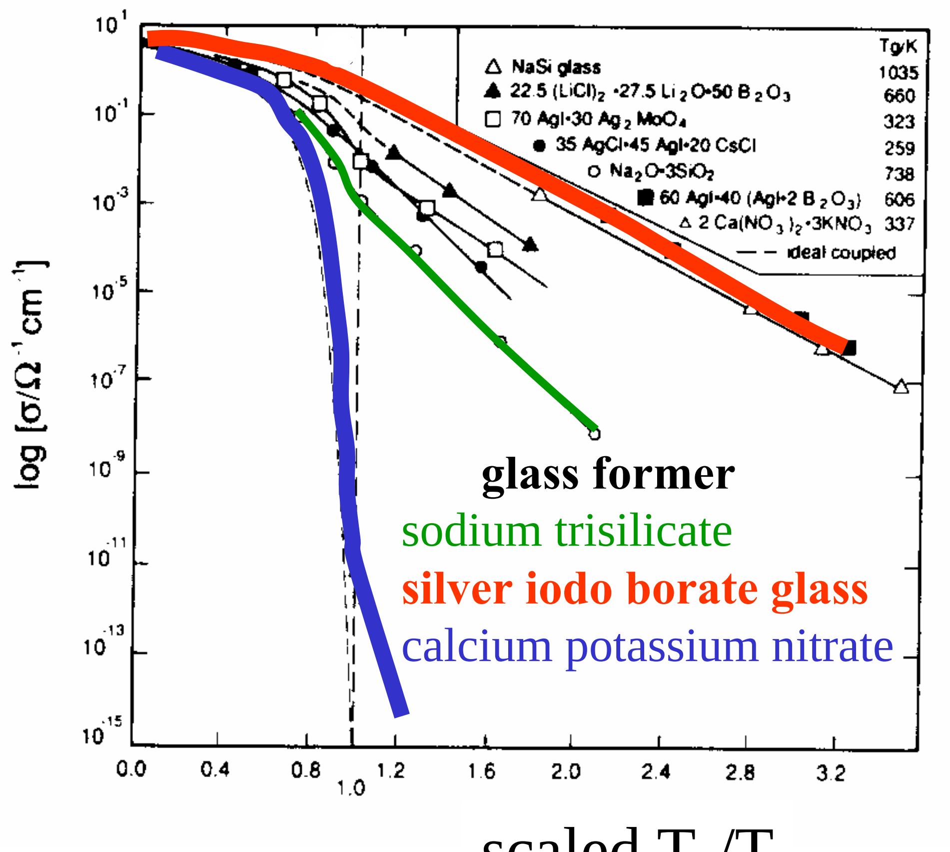
4. **Conclusions**

Conductivity of glassy ionics



Ag: 1.0 I: 1.8 B: 0.5 O: 0.9 Å

Howells et al., JP-CM **11**, 9275 (1999)



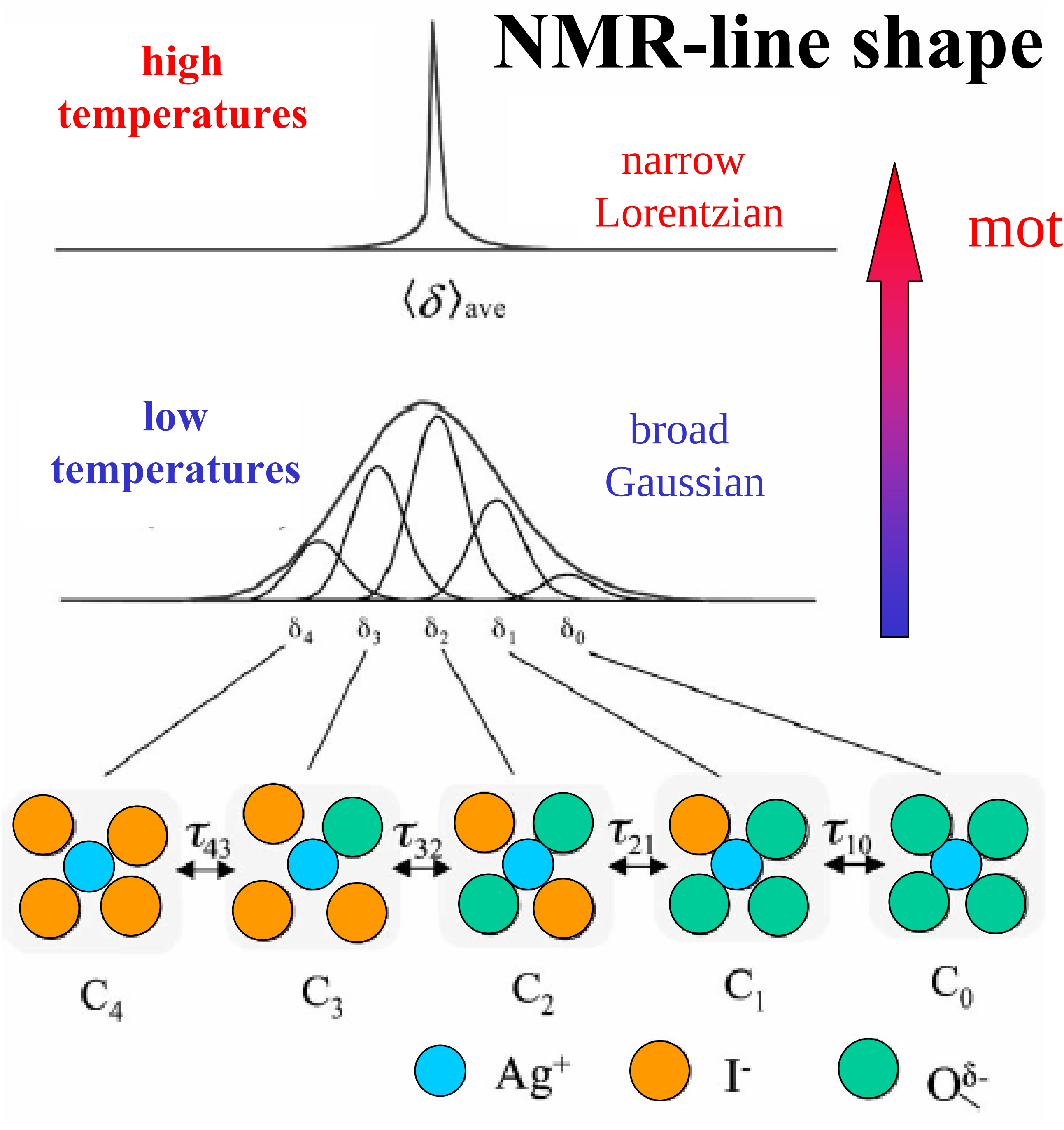
scaled T_g/T

glass former	T_g
sodium trisilicate	738 K
silver iodo borate glass	**610 K**
calcium potassium nitrate	333 K

Angell, Chem. Rev. **90**, 523 (1990)

large decoupling <u>and</u> $T \sim T_g$ are prerequisites for battery application

NMR-line shape of AgI-glasses



high temperatures

narrow Lorentzian

low temperatures

broad Gaussian

motional narrowing

intermediate temperatures

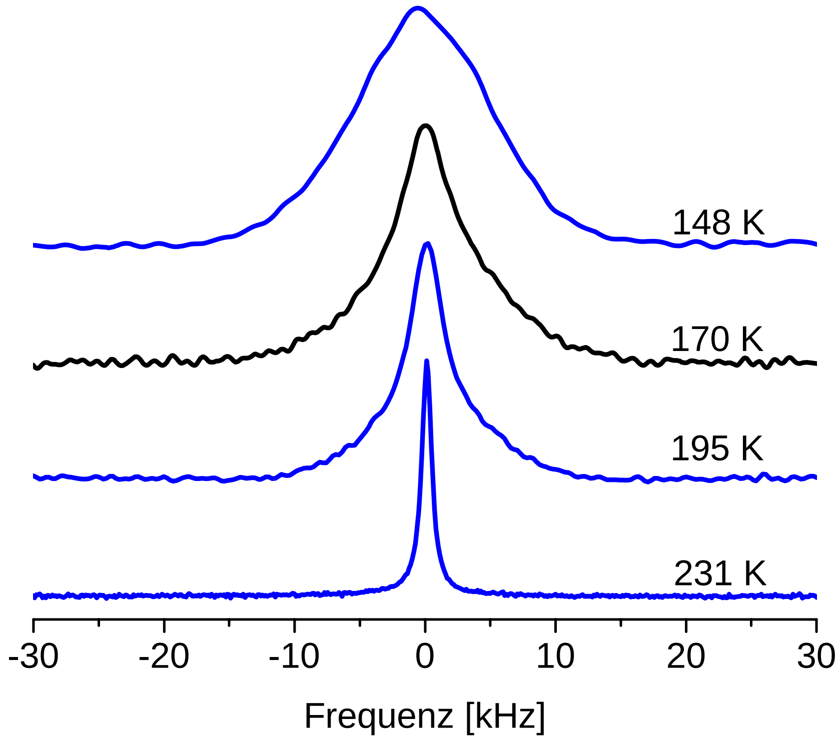
?

hopping rate τ

?

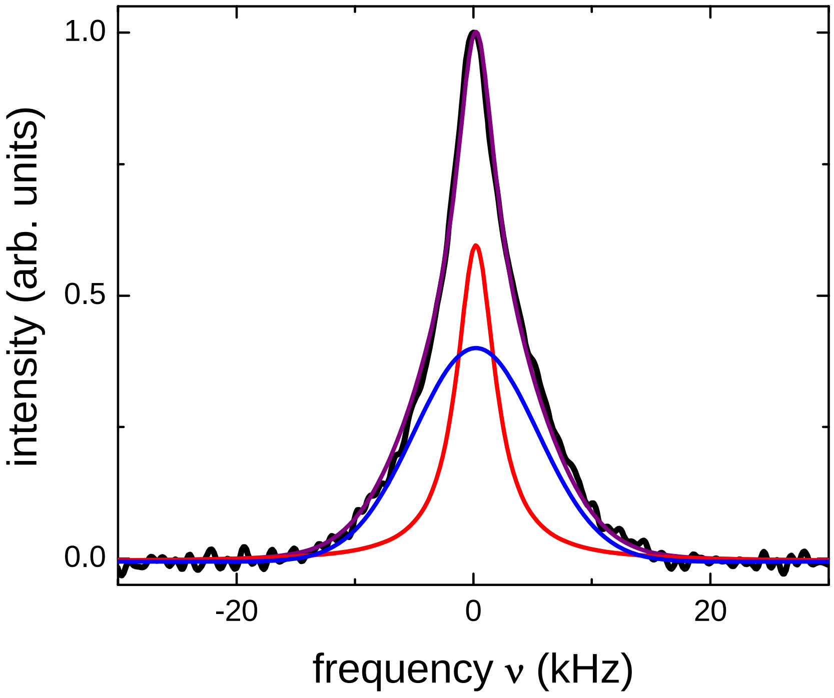
Kawamura et al.,
Solid State Ionics
154-155, 183 (2002)

Line shape of $({}^{109}\mathrm{AgI})_x$-$(\mathrm{Ag_2O\text{-}B_2O_3})_{1-x}$



broadening due to distribution of isotropic chemical shifts

superposition of sub-spectra



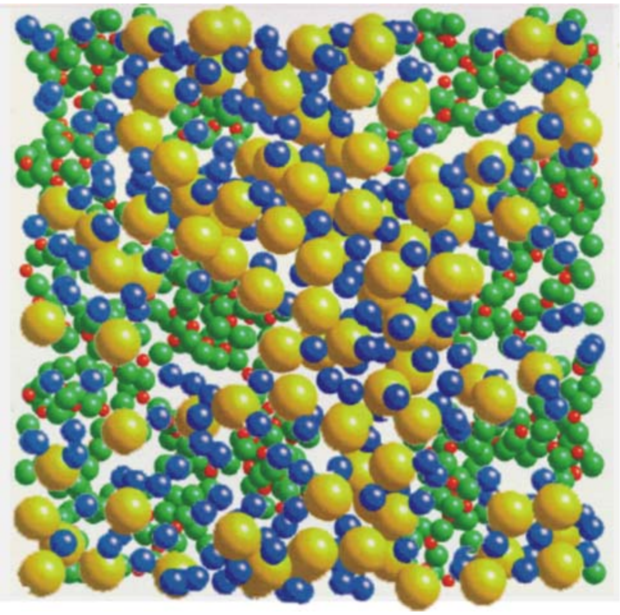
hint: **slow and fast**

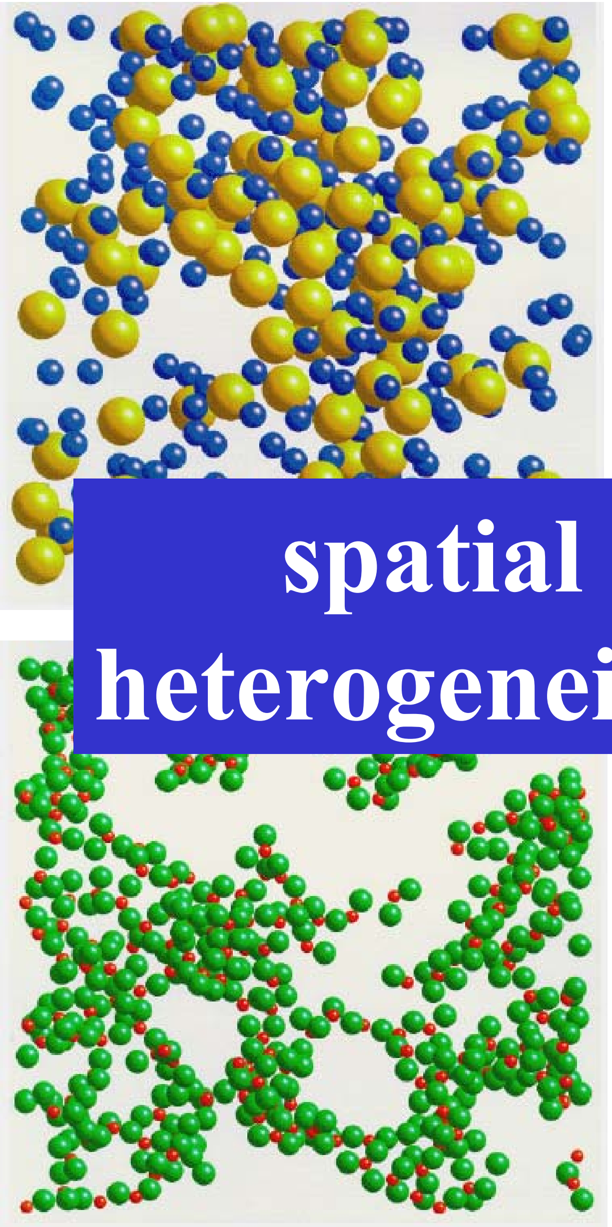
Ag^+ ions could **coexist**

Berndt, Jeffrey, Küchler, Böhmer, *Solid State Nucl. Magn. Reson.* **27**, 122 (2005)

Heterogeneity of ion conductors

$(\mathrm{AgI})_{0.6}\text{-}(\mathrm{Ag_2O}\text{-}\mathrm{B_2O_3})_{0.4}$





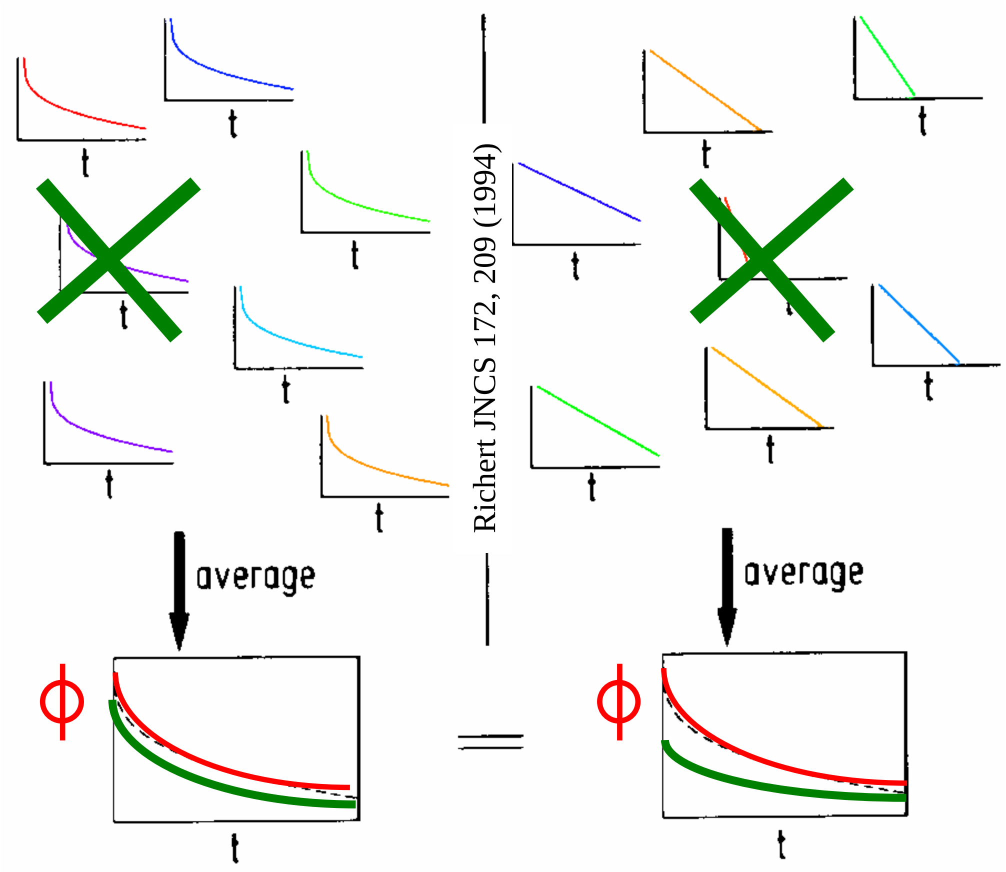
spatial heterogeneity !

Ag: 1.0 I: 1.8 B: 0.5 O: 0.9 Å

Howells et al., JP-CM **11**, 9275 (1999)

Nature of the non-exponential relaxation ?

homogeneous **heterogeneous**



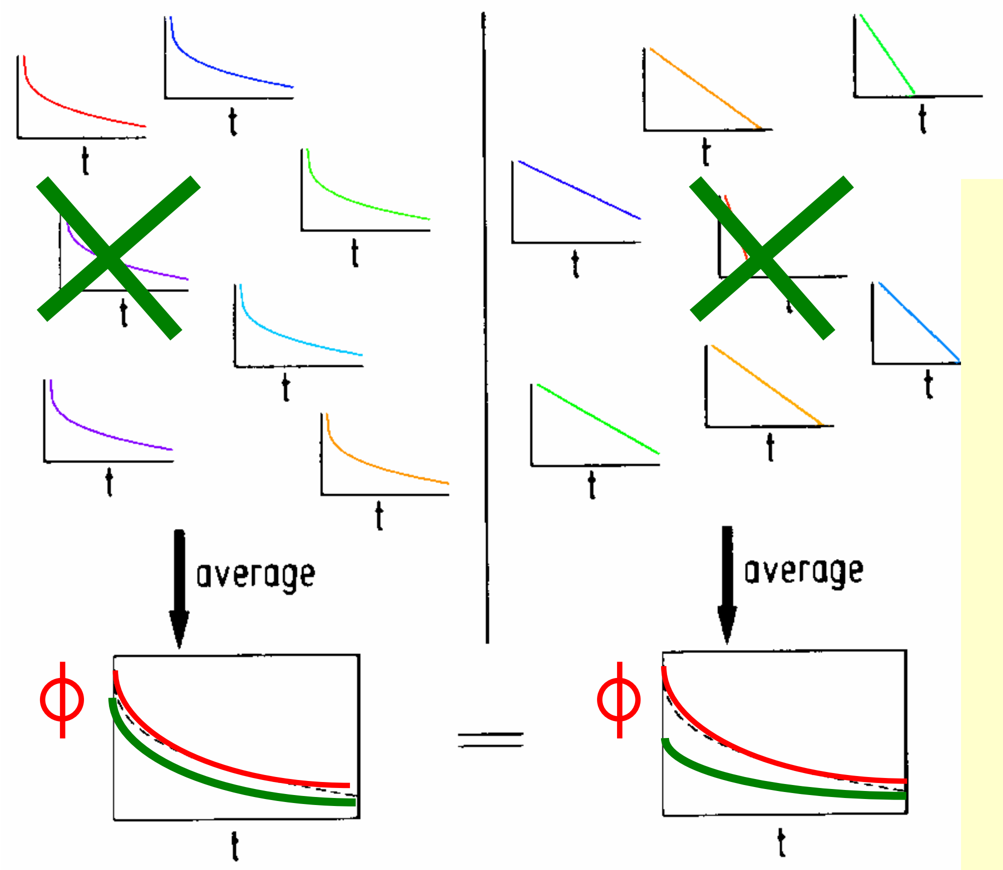
amplitude modification

line shape modification

dynamic heterogeneity ?

Nature of the non-exponential relaxation

homogeneous **heterogeneous**



amplitude modification

line shape modification

experimentally distinguishable via sub-ensemble selection

multi-dimensional NMR
single-molecule detection
nonresonant hole burning
optical probe spectroscopy
computer simulation

resonance frequencies:

^{1}H: 43 MHz/Tesla

^{109}Ag: 2 MHz/Tesla !!

Interdisziplinäres Zentrum für magnetische Resonanz (IZMR)
Universität Dortmund

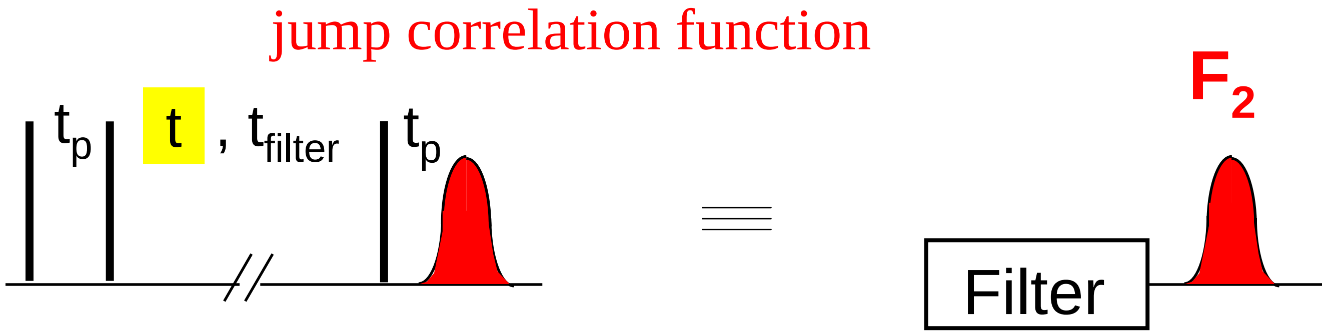
problem:

Ag: very low sensitivity

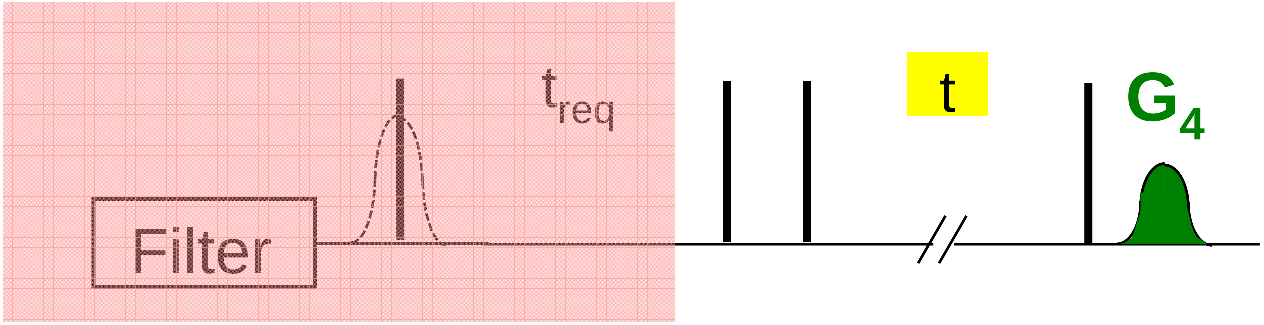
solution:

availability of very high magnetic fields

four-time NMR



measure for the probability that no jump occured during t_{filter}



jump correlation function of the selected subensemble

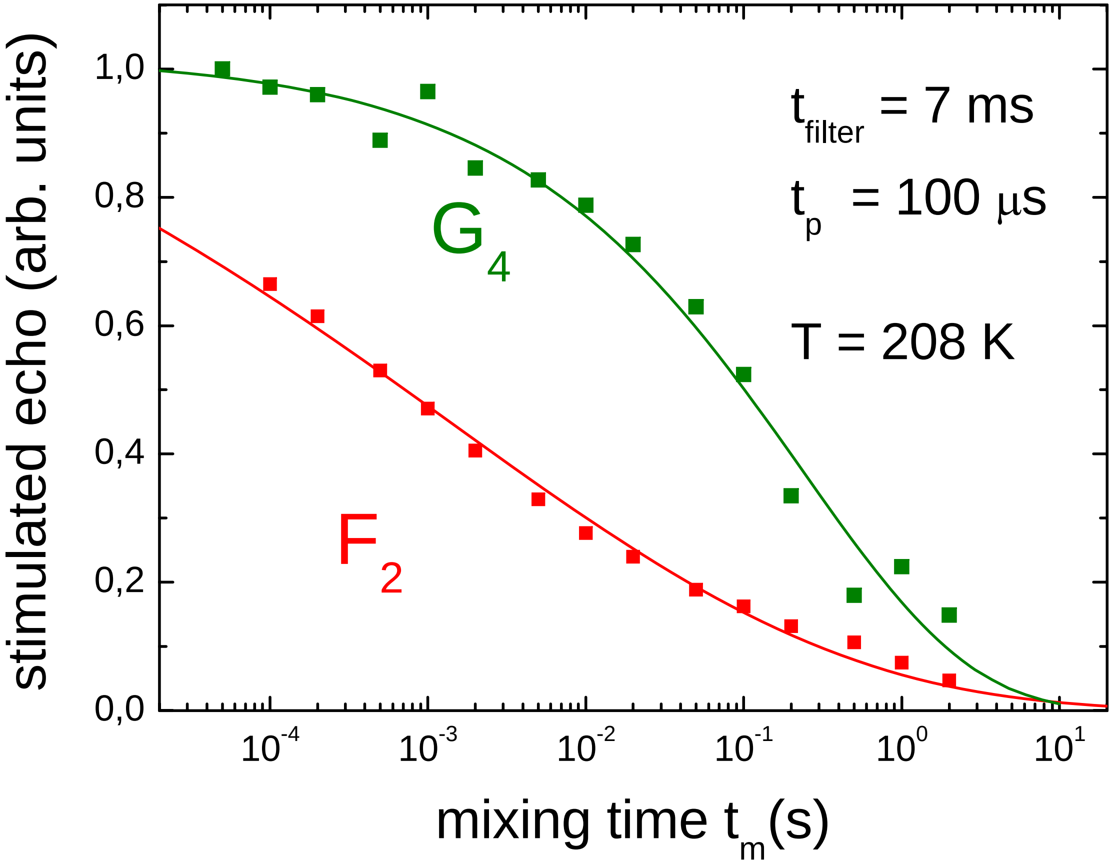
extensively used for polymers and supercooled <u>organic</u> liquids:

Schmidt-Rohr, Spiess, Phys. Rev. Lett. 66, 3020 (1991)

Böhmer, Diezemann, Hinze, Rössler, Prog. NMR Spectrosc. 39, 191 (2001)

Ag-phosphates: Vogel, Brinkmann, Eckert, Heuer, PRB 69, 094302 (2004)

$(AgI)_{0.5}$-$(Ag_2O$-$B_2O_3)_{0.5}$



successful low-pass filtering

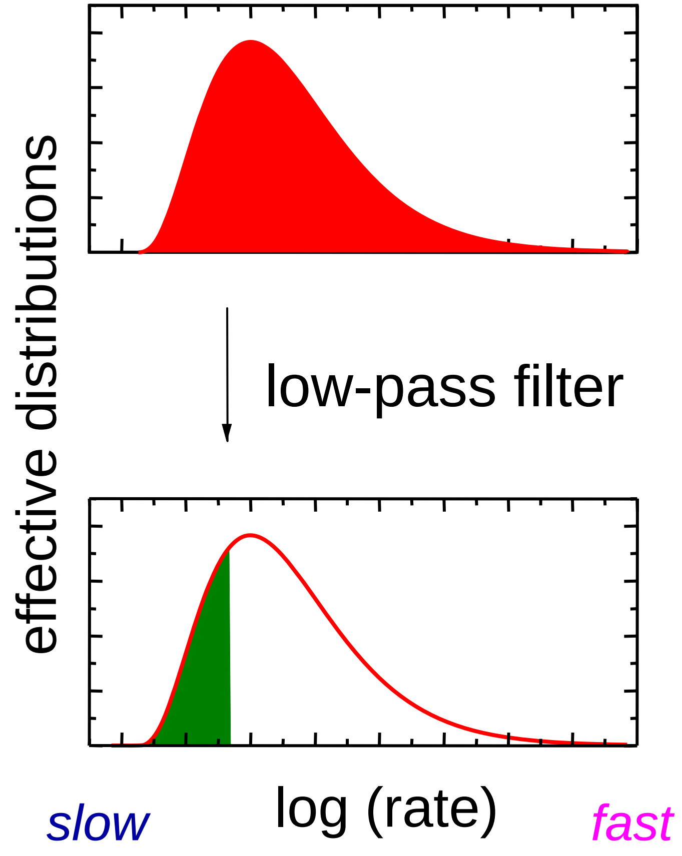
confirms

dynamic heterogeneity

in AgI-borate glasses

$\tau_4 > \tau_2$

$\beta_4 > \beta_2$



This lecture continues on a 3rd module -

Video Module 3 : Nonresonant spectral hole burning

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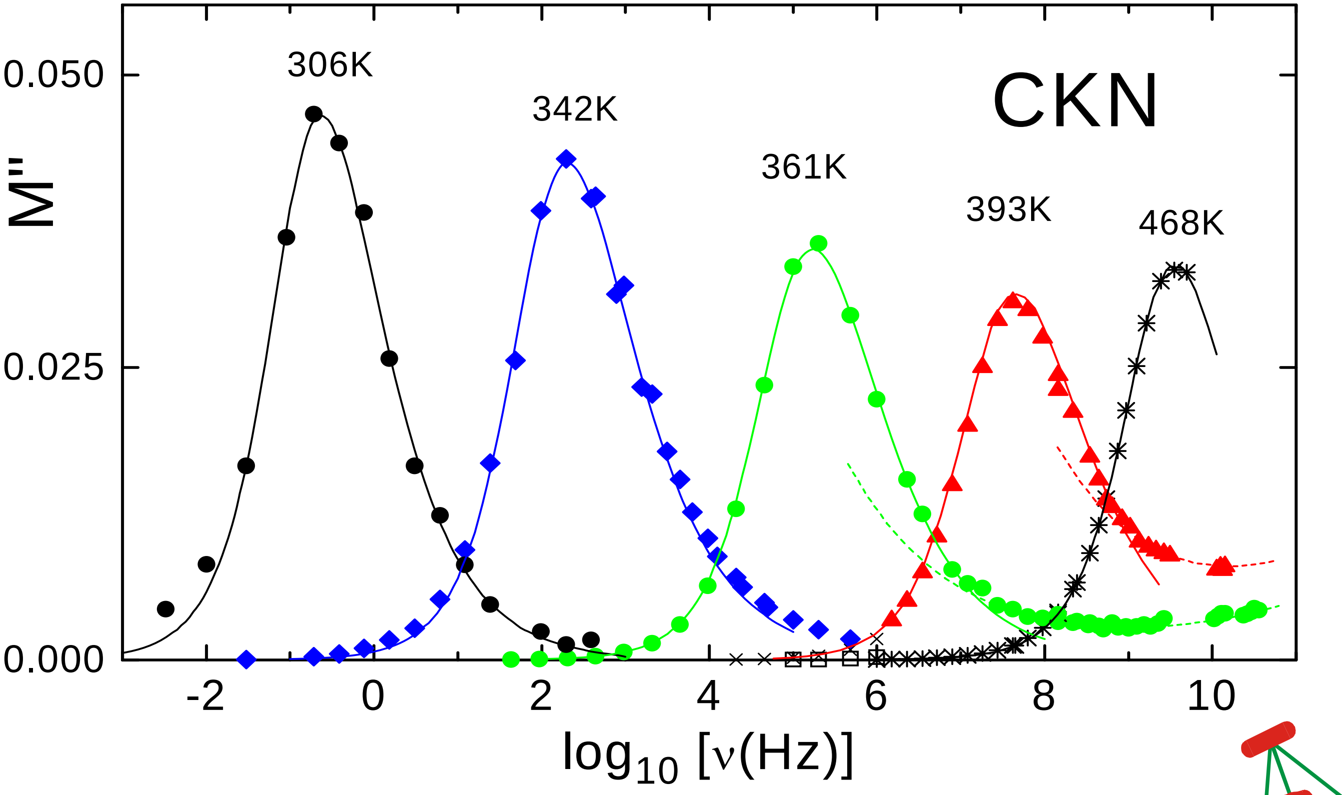
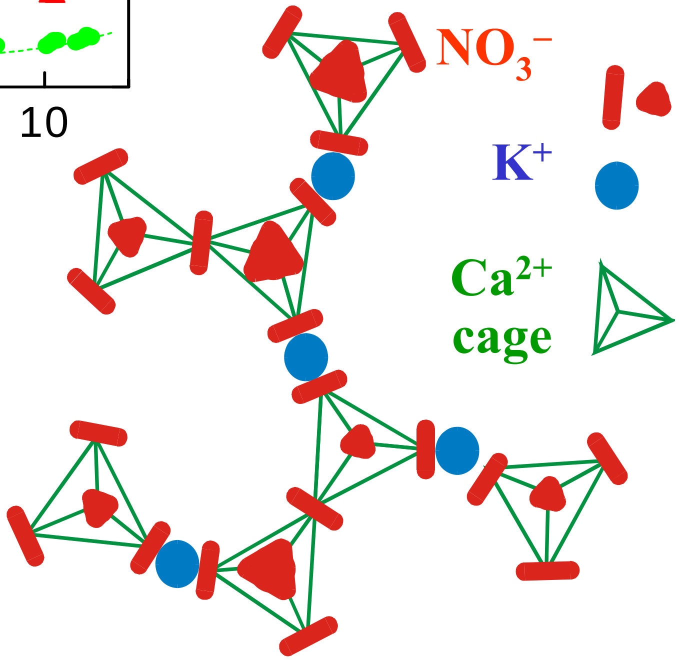
Non-exponential conductivity and structural relaxation



$$M = i\omega\varepsilon_0/\sigma$$

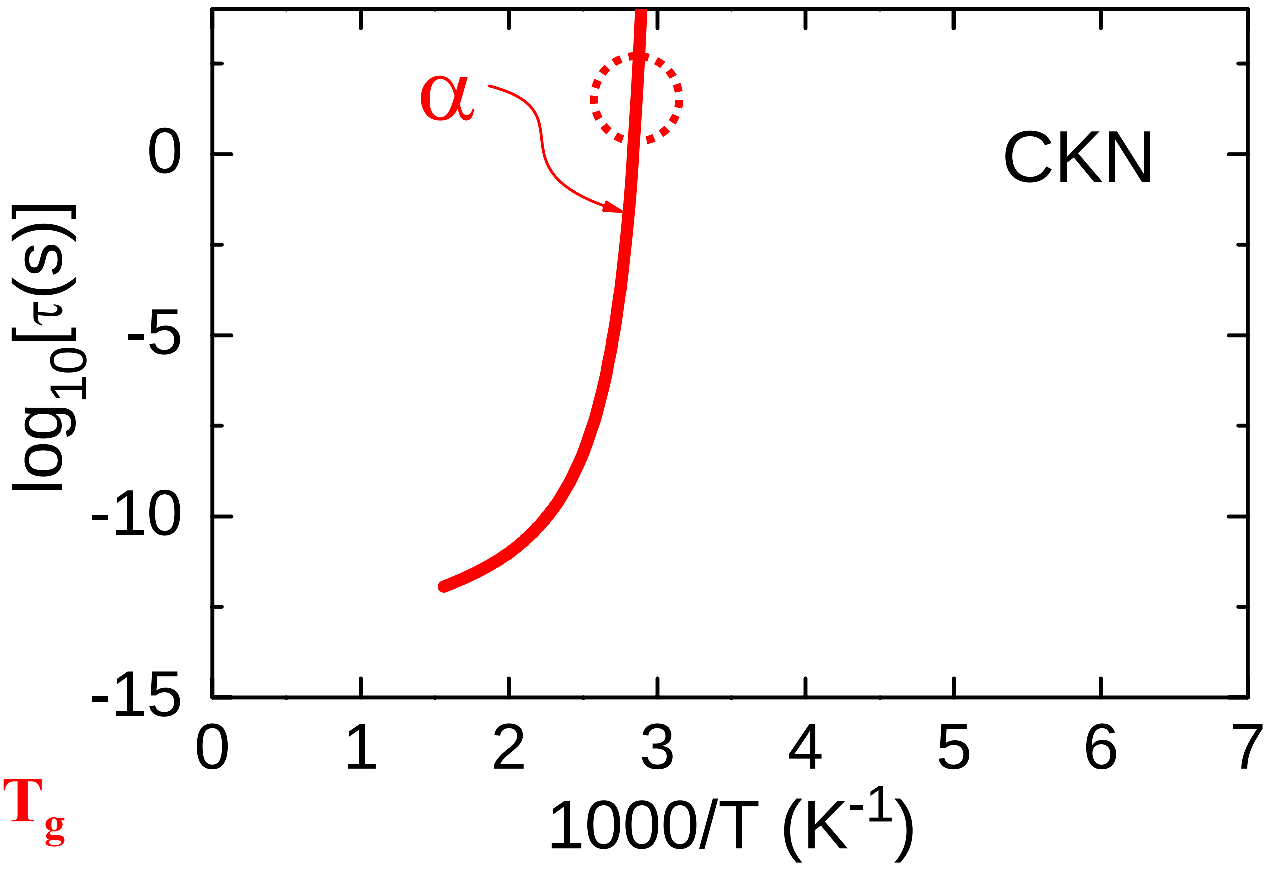
$$T_g = 333\ \mathrm{K}$$



2 $Ca(NO_3)_2 \cdot 3\ KNO_3$ (CKN)

Pimenov, Lunkenheimer, Rall, Kohlhaas, Loidl,
Böhmer, Phys. Rev. E **54**, 676 (1996)

Structural relaxation



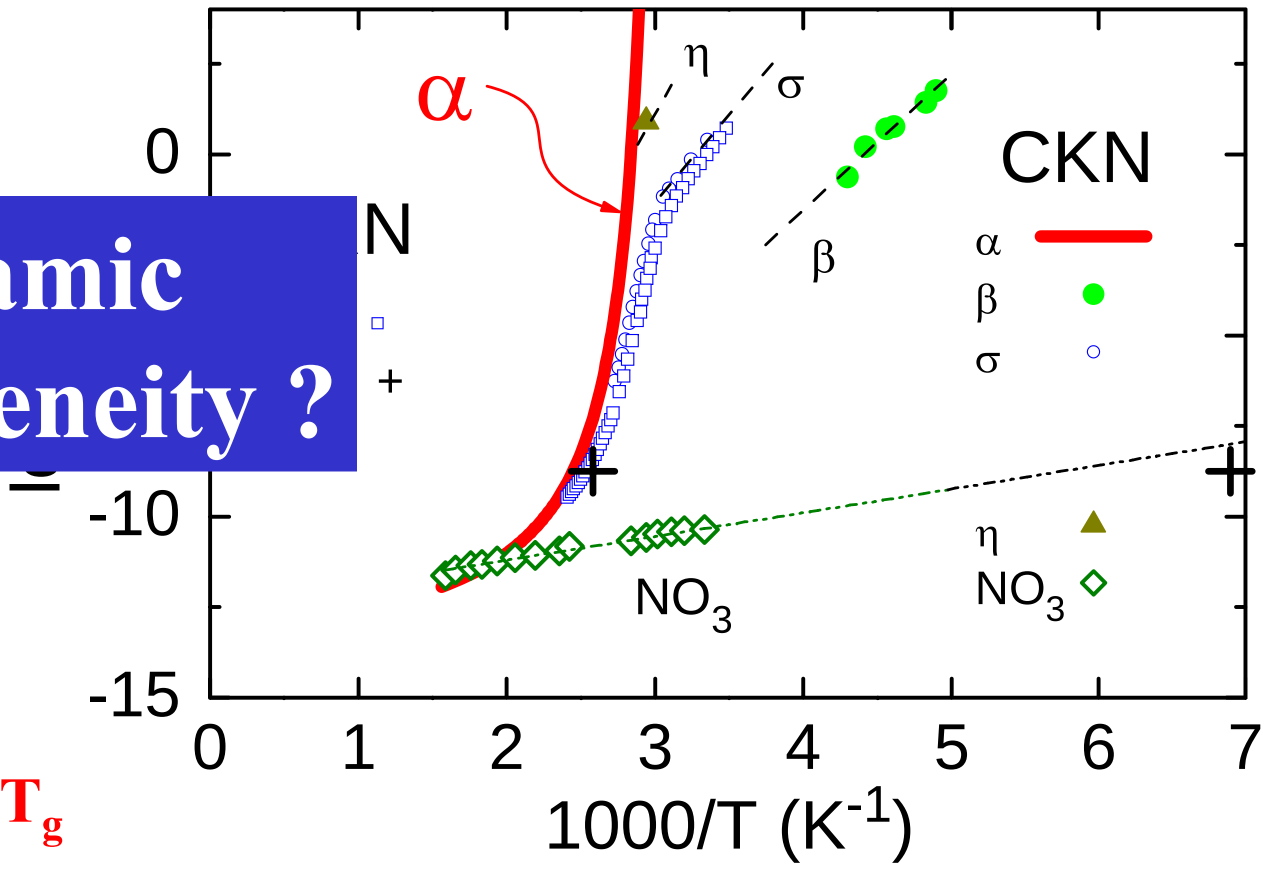
$T \geq T_g$

large slope in Angell plot

fragility $$m = \left.\frac{d(\log_{10}\tau/s)}{d(T_g/T)}\right|_{T=T_g}$$

Böhmer, Ngai, Angell, Plazek, JCP 99, 4201 (1993)

Structural and decoupled relaxations



dynamic heterogeneity ?

$T \geq T_g$

large slope in Angell plot

fragility $$m = \left.\frac{d(\log_{10}\tau/s)}{d(T_g/T)}\right|_{T=T_g}$$

$T < T_g$

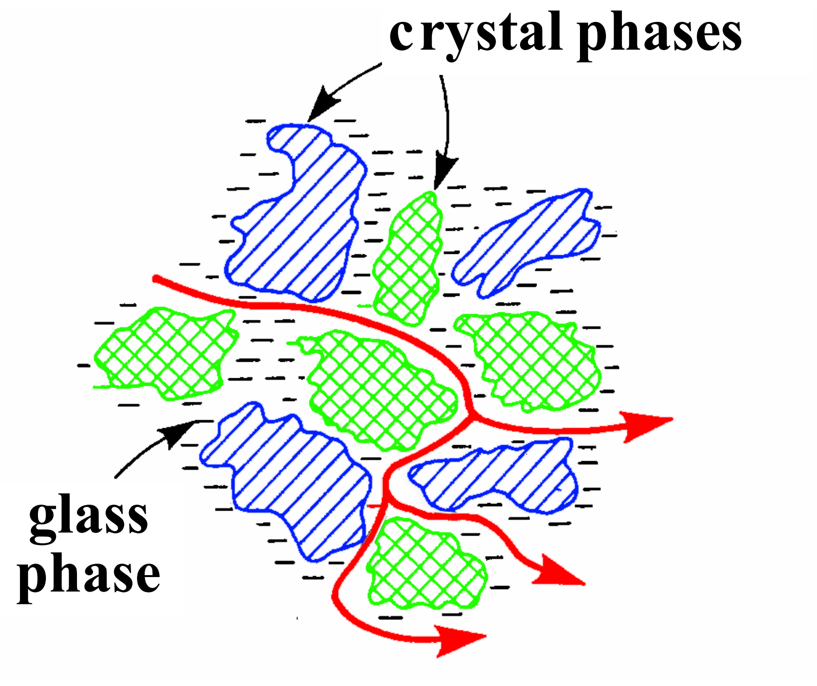
thermally activated processes

Böhmer, Ngai, Angell, Plazek, JCP 99, 4201 (1993)

Origin of non-exponentiality

Nanoscopic heterogeneity in ionic conductors ?

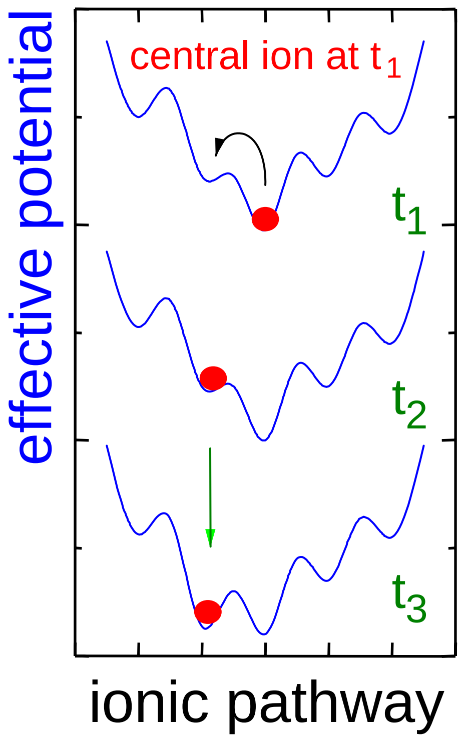
heterogeneous cluster model:



glass ceramics, nanocrystals, ion conductors in general ??

or correlation effects ?

homogeneous jump-relaxation-model:
Coulomb interactions



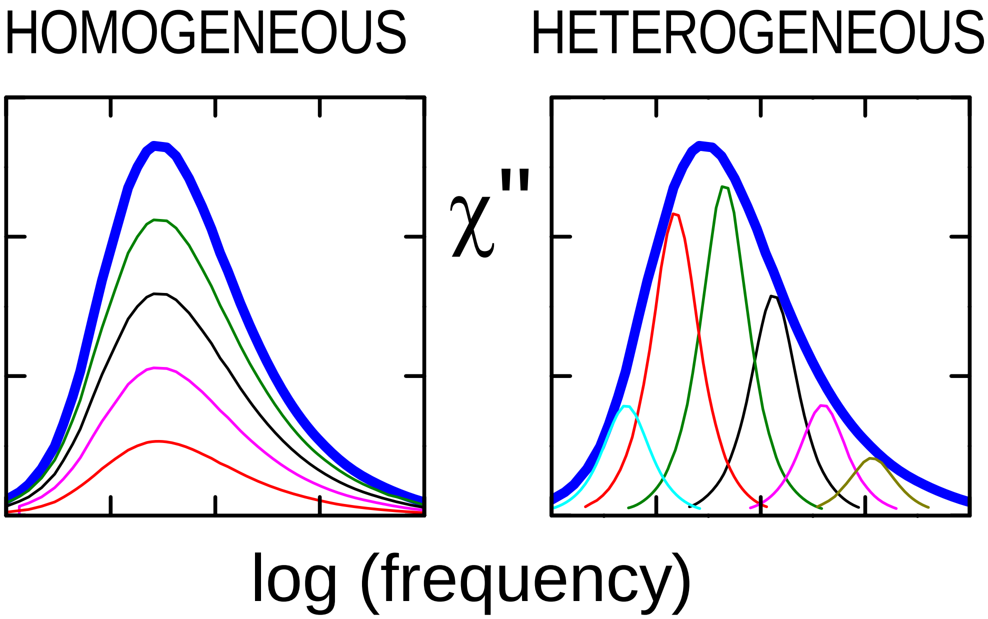
effectively time dependent rates $W(t)$

⇓

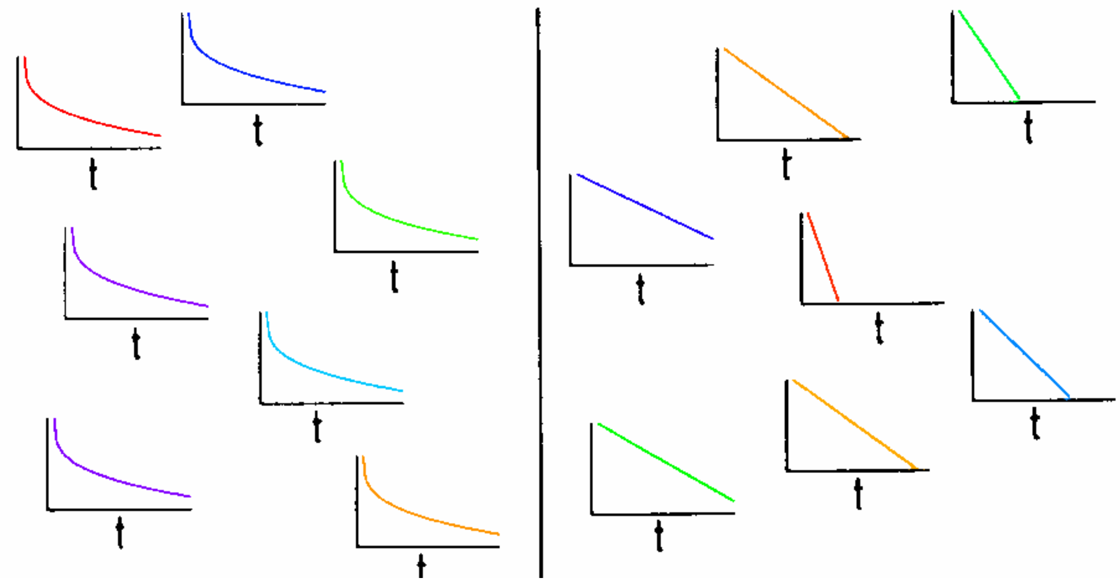
time evolution
$\exp[-t\,W(t)]$
$\propto \exp[-(t/\tau)^\beta]$

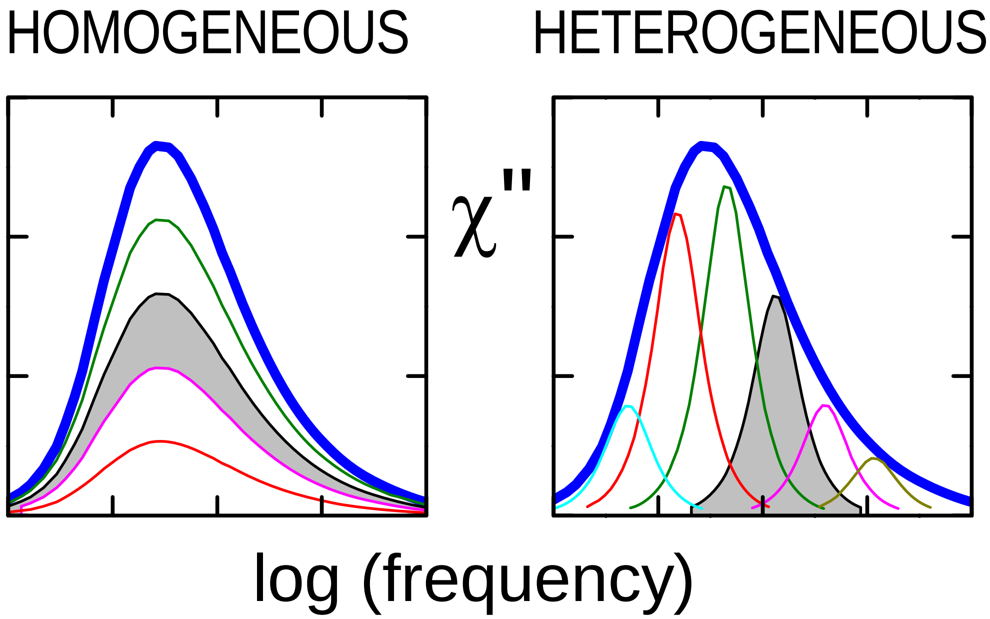
Funke, SSI **40**, 200 (1990)

frequency domain



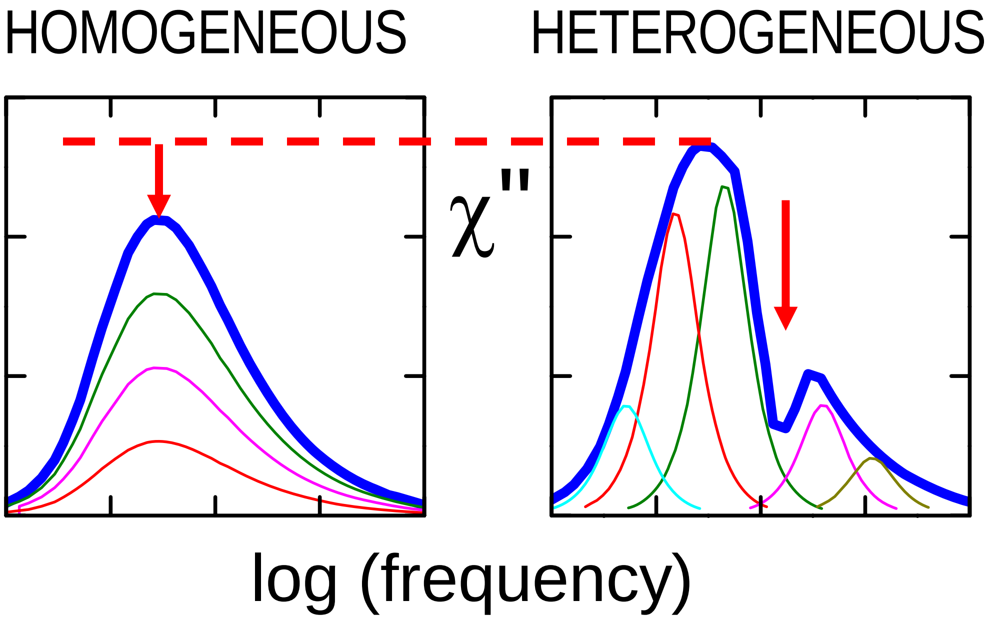
time domain





mark a subensemble

amplitude modification



line shape modification

Selection experiments

1.
spectral or spatial selection or excitation of sub-ensemble

2.
detection of sub-ensemble

Nonresonant hole burning

supercooled liquids : Schiener, Loidl, Böhmer, Chamberlin, Science 274, 752 (1996)

Nonresonant hole burning

supercooled liquids	**α:**	**Schiener, Loidl, Böhmer, Chamberlin, Science 274, 752 (1996)**	
	β:	**Richert, EPL 54, 767 (2001)**	
	wing:	**Jeffrey, Richert, Duvvuri, JCP 119, 6150 (2003)**	
relaxor ferroelectrics		**Kircher, Schiener, Böhmer, PRL 81, 4520 (1998)**	**solids**
plastic crystal		**Wirsch, Kircher, Böhmer (1998, unpublished,*)**	
magnetic (spin glasses)		**Chamberlin, PRL 83, 5134 (1999)**	
ion conductor CKN		**Richert, Böhmer, PRL 83, 4337 (1999)**	
quantum paraelectrics		**Kleemann et al., Ferroelectrics 261, 43 (2001)**	
stochastic models		**Diezemann, EPL 53, 604 (2001)**	
electrical circuit analog		**Richert, Physica A 322, 143 (2003)**	
binary glass-formers		**Blochowicz, Rössler, JCP 122, 224511 (2005)**	
mechanical (polymers)		**Shi, McKenna, PRL 94, 157801 (2005)**	
*review		Böhmer, Diezemann, in: Broadband Dielectric Spectroscopy edited by Kremer, Schönhals (Springer, 2002), p. 523-569	

Nonresonant hole burning

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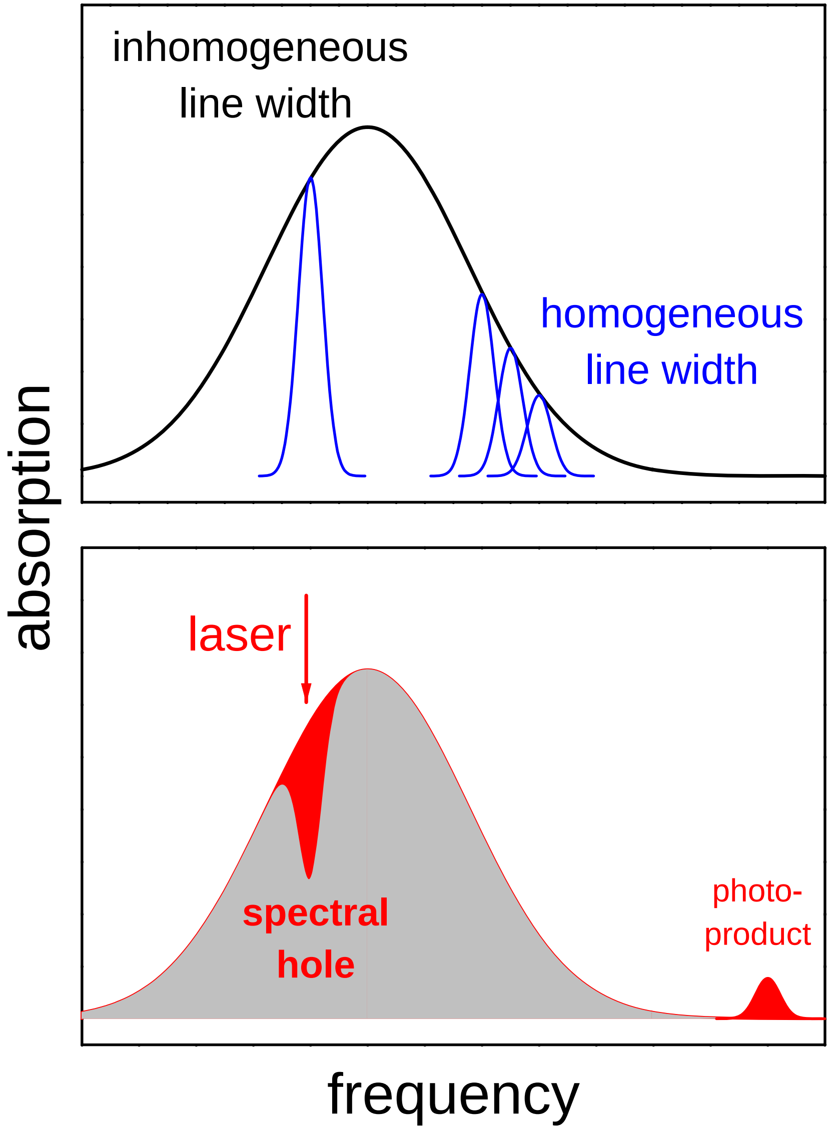
	wing:	**Jeffrey, Richert, Duvvuri, JC[illegible] 1[illegible]9, [illegible]150 (2003)**
relaxor ferroelectrics		**Kircher, Schiener, Böhmer, PRL 81, 4520 (1998)**
plastic crystal		**W[illegible]rsc[illegible], Kircher, Böhmer (1998, unpublished)**
magnetic (spin glasses)		**Chamberlin, PRL 83, 5134 (1999)**
ion conductor C[illegible]		**Richert, Böhmer, PRL 8[illegible] [illegible] (1999)**
quantum paraelectrics		**Kleemann et al., Ferroelectrics 261, 43 (2001)**
stochastic models		**Diezemann, EPL 53, 604 (2001)**
electrical circuit analog		**Richert, Physica A 322, 143 (2003)**
binary glass-former		**Blochowicz, Rössler, JCP 122, 224511 (2005)**
mechanical (polymers)		**Shi, McKenna, PRL 94, 157801 (2005)**
review		Böhmer, Diezemann, in: Broadband Dielectric Spectroscopy edited by Kremer, Schönhals (Springer, 2002), p. 523-569

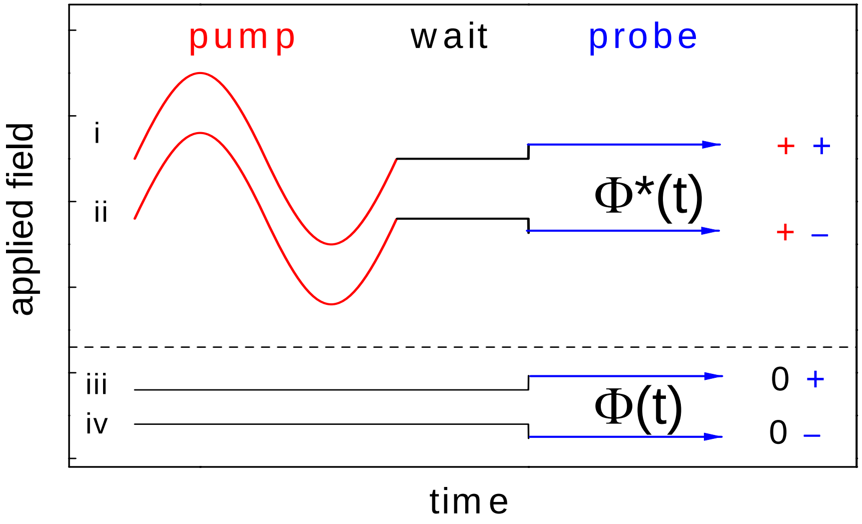
evidence for heterogeneity

conventional SHB

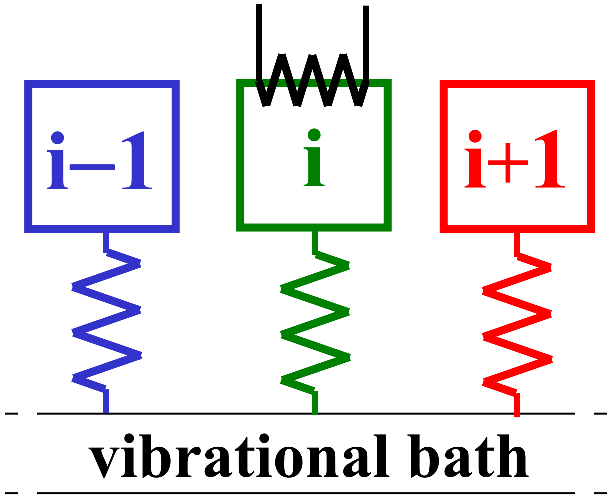


NMR (optical) spectroscopy

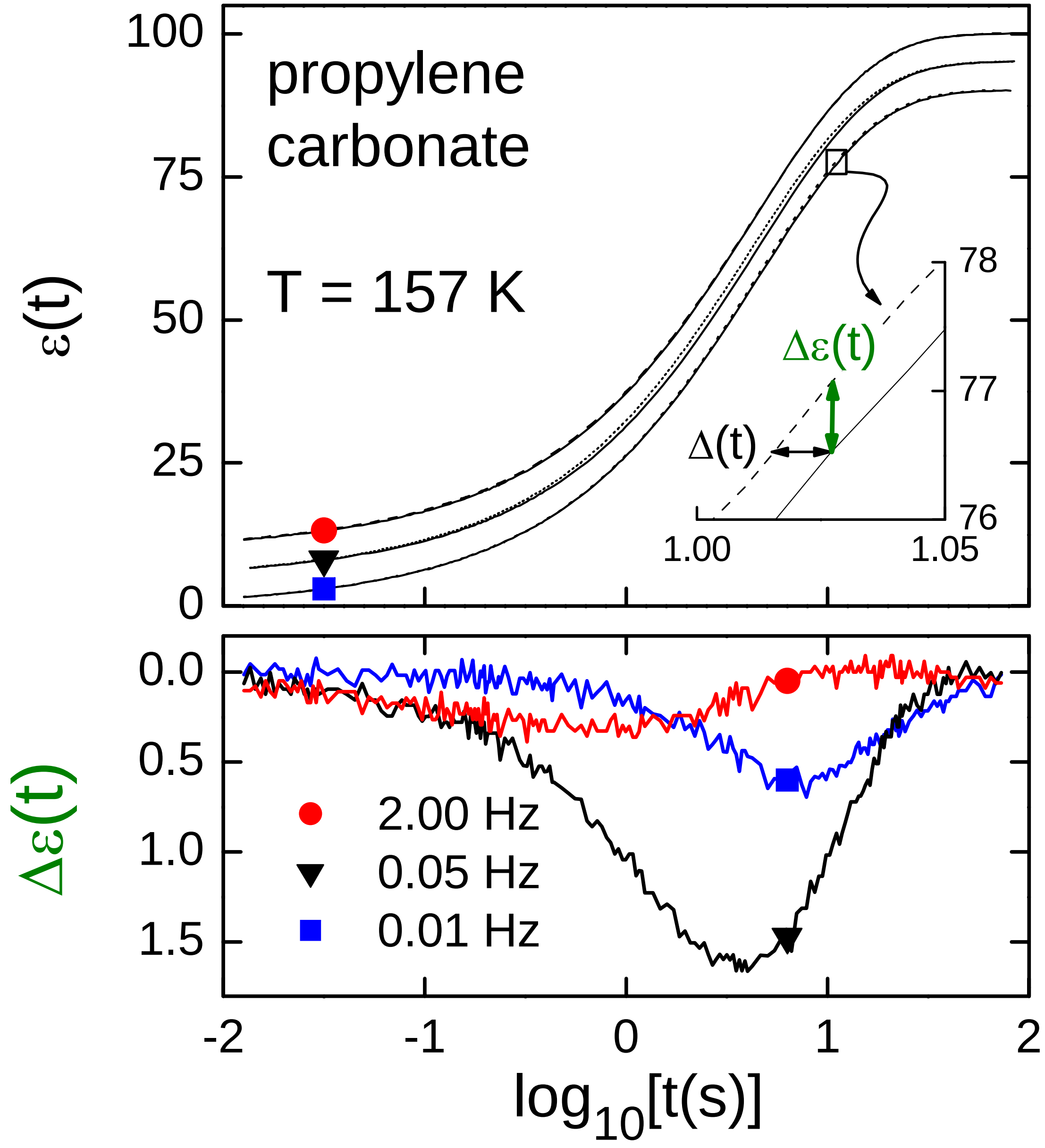
nonresonant (NHB)



phase cycle: $\Delta\Phi(t) = \Phi^*(t) - \Phi(t)$



10 years ago: First results on a viscous liquid



high-frequency pump:
short-time modifications

low-frequency pump:
long-time modifications

⇓

selection of different
sub-ensembles possible:
dynamic heterogeneity

Schiener, Loidl, Böhmer,
Chamberlin, Science 274,
752 (1996)

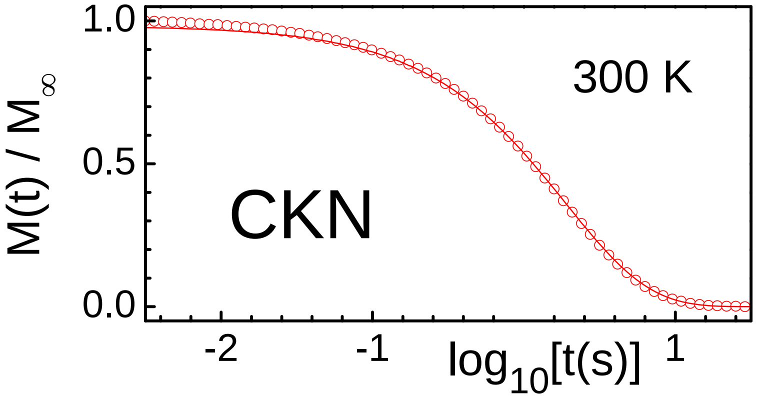
1. **Introduction**
    - Ion conductors
    - Nuclear magnetic resonance

2. **Ion dynamics studied by NMR**
    - Li hopping in alumino silicates
    - Heterogeneity in silver borate glasses

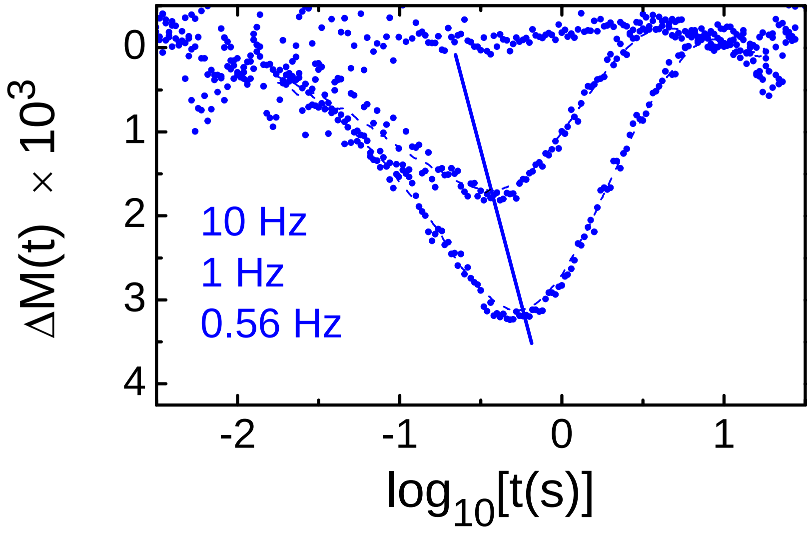
3. **Nonresonant spectral hole burning**
    - Material and method
    - Experiments on Ca-K-NO_3 glass

4. **Conclusions**

high pump frequencies

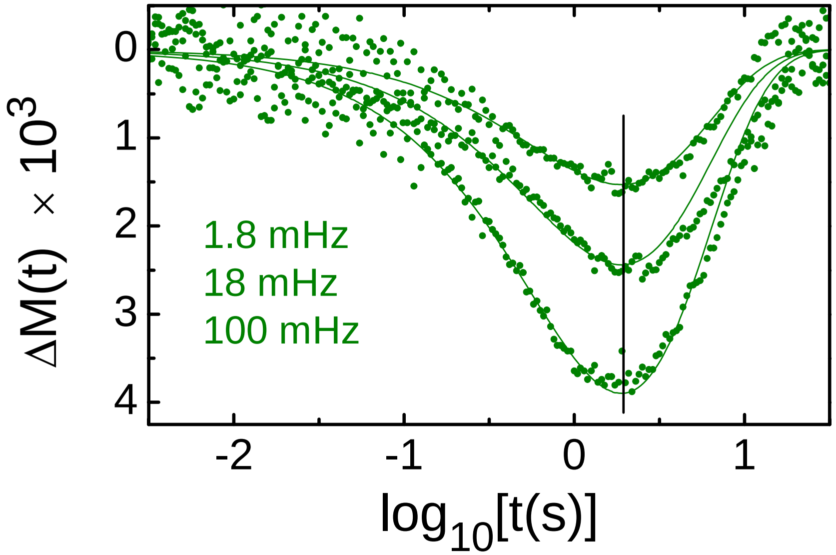


low pump frequencies



→ frequency selectivity

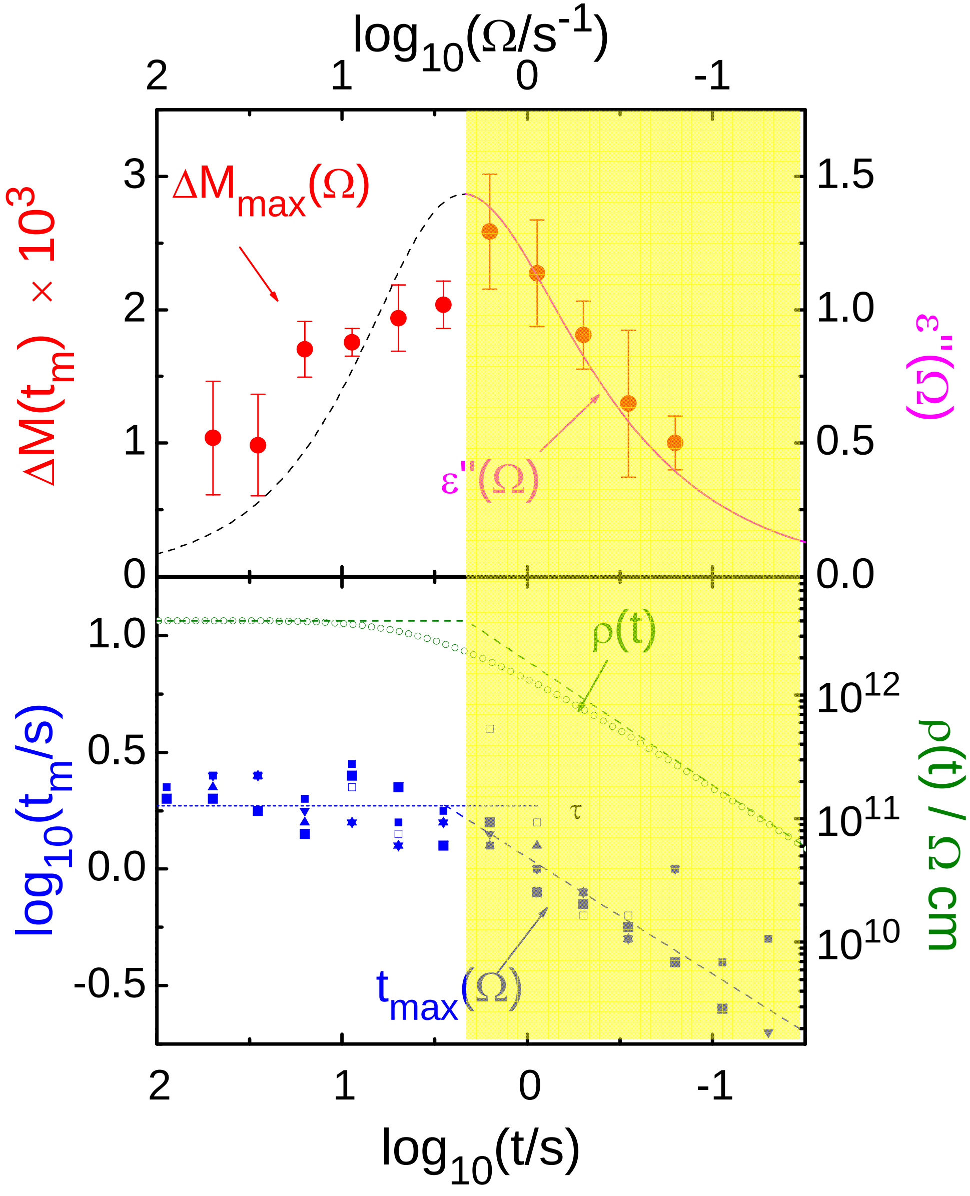
dynamic heterogeneity



→ no frequency selectivity

homogeneous for $\Omega_C/2\pi < 0.1$ Hz

CKN – pump frequency dependence



heterogeneous regime:

hole depths ∝ dielectric loss

frequency selective
energy absorption

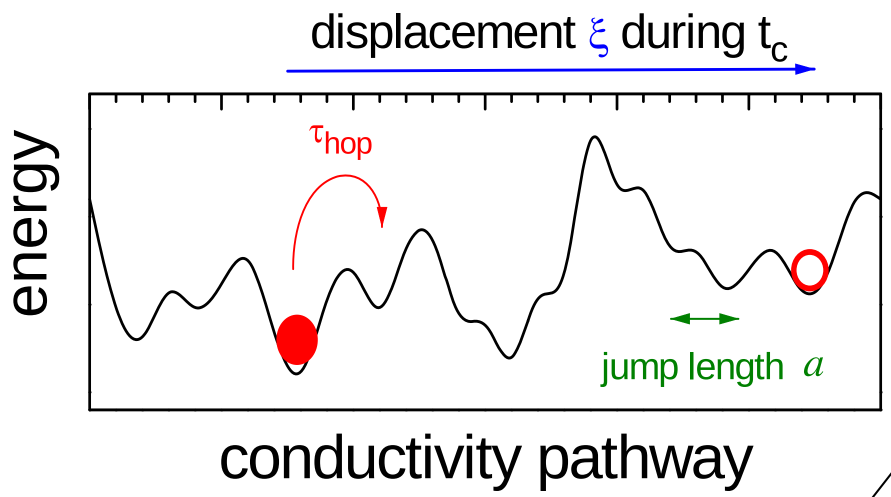
OBSERVATION:

t_C corresponds to transition from
dc to ac resistivity ρ (or σ)

↓

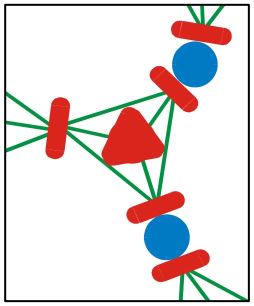
ion needs $t_C \sim 1/\Omega_C$
to average over heterogeneity

heterogeneity length ξ ?



$$\left.\begin{aligned}\langle\xi^2\rangle &= 6\,D\,t_C\\ D &= a^2/(6\,\tau_{hop})\end{aligned}\right\}\ \langle\xi^2\rangle = \boldsymbol{a}^2\,t_C\,/\,\tau_{hop}$$

a hopping length ≈
mean separation of
sites for mobile ions



nonresonant
hole burning spectroscopy
at low frequencies

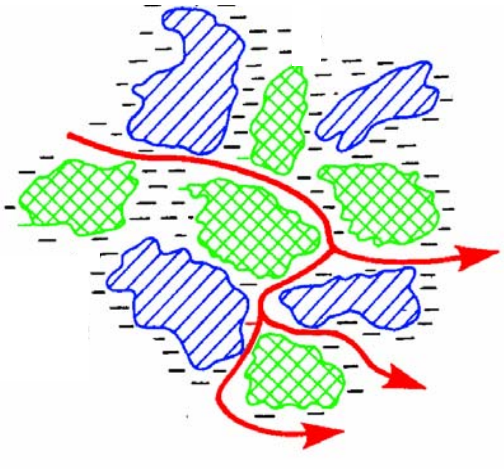
⇓

dynamic and spatial
heterogeneity in CKN

τ_{hop} hopping time necessary
to estimate ξ but
not known for CKN

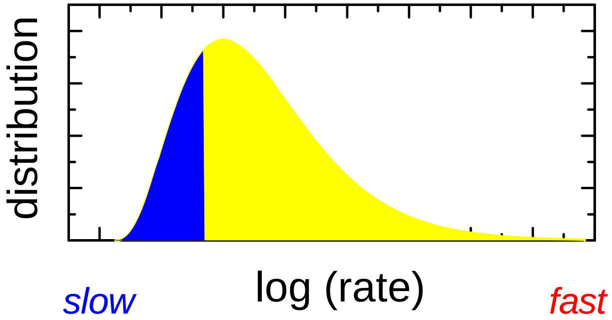
requires direct measurement
of τ_{hop} in the slow domain !

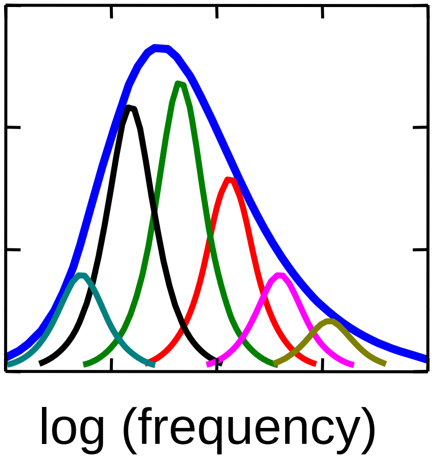
Conclusions



Structure dynamic relationship in crystalline and glassy lithium aluminosilicates

High magnetic fields facilitate investigations of dynamic heterogenities in ion conductors also with less favorable nuclear probes (Ag)





Nonresonant spectral hole burning is a useful tool for different classes of materials.

Direct observation of transition from heterogeneous to homogeneous behavior in CKN